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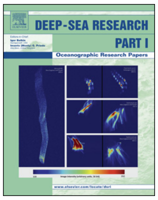

Testing models of thorium and particle cycling in the ocean using data from station GT11-22 of the U.S. GEOTRACES North Atlantic section

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ABSTRACT

Thorium is a highly particle-reactive element that possesses different measurable radio-isotopes in seawater, with well-constrained production rates and very distinct half-lives. As a result, Th has emerged as a key tracer for the cycling of marine particles and of their chemical constituents, including particulate organic carbon.

Here two different versions of a model of Th and particle cycling in the ocean are tested using an unprecedented data set from station GT11-22 of the U.S. GEOTRACES North Atlantic Section: (i) ^{228,230,234}Th activities of dissolved and particulate fractions, (ii) ^{228}Ra activities, (iii) ^{234,238}U activities estimated from salinity data and an assumed ^{234}U/^{238}U ratio, and (iv) particle concentrations, below a depth of 125 m. The two model versions assume a single class of particles but rely on different assumptions about the rate parameters for sorption reactions and particle processes: a first version (V1) assumes vertically uniform parameters (a popular description), whereas the second (V2) does not. Both versions are tested by fitting to the GT11-22 data using generalized nonlinear least squares and by analyzing residuals normalized to the data errors.

We find that model V2 displays a significantly better fit to the data than model V1. Thus, the mere allowance of vertical variations in the rate parameters can lead to a significantly better fit to the data, without the need to modify the structure or add any new processes to the model. To understand how the better fit is achieved we consider two parameters, $K = k_1/(k_{-1} + \beta_{-1})$ and K/P, where k_1 is the adsorption rate constant, k_{-1} the desorption rate constant, β_{-1} the remineralization rate constant, and P the particle concentration. We find that the rate constant ratio K is large ($\geqslant 0.2$) in the upper 1000 m and decreases to a nearly uniform value of ca. 0.12 below 2000 m, implying that the specific rate at which Th attaches to particles relative to that at which it is released from particles is higher in the upper ocean than in the deep ocean. In contrast, K/P increases with depth below 500 m. The parameters K and K/P display significant positive and negative monotonic relationship with P, respectively, which is collectively consistent with a particle concentration effect.

1. Introduction

Roughly 20–25% of carbon fixed photosynthetically by phytoplankton in near surface-waters is estimated to sink as particles to depths below 100 m, with approximately 10% of this sinking material reaching the sediments (Bishop, 2009). The sinking and subsequent remineralization of particulate organic matter strongly influence the vertical concentration gradients of chemical constituents in the ocean, including dissolved inorganic carbon, nutrients, and dissolved oxygen. Therefore, understanding the processes that control the cycling of particles and the exchange of elements between the dissolved and particulate phases is essential in order to understand the distribution of these constituents in the ocean.

The processes that impact marine particles include, e.g., (dis)aggregation, remineralization, dissolution, and gravitational sinking. The

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radioactive isotopes of thorium have for a long time been used to study these processes (for reviews see Savoye et al. (2006); Lam and Marchal (2014)). Thorium is highly particle reactive in seawater, and its isotopes are characterized by widely different half-lives: $t_{1/2} = 24.101 \pm 0.025$ days for ^{234}Th (Knight and Macklin, 1948), $75{,}584 \pm 110$ yr for ^{230}Th (Cheng et al., 2013), and 1.910 ± 0.002 yr for ^{228}Th (Kirby et al., 2002). Additionally, the sources of these thorium isotopes in the ocean are relatively well understood. ^{234}Th, ^{230}Th, and ^{228}Th are produced in situ by radioactive decay of ^{238}U, ^{234}U, and ^{228}Ra, respectively. Since uranium seems to behave quasi-conservatively in the ocean (Ku et al., 1977; Delanghe et al., 2002), the ^{234}U and ^{238}U activities are often estimated from salinity (Chen et al., 1986; Owens et al., 2011), whereas the ^{228}Ra activity is generally measured directly (Henderson et al., 2013). Another potential source of ^{230}Th is the dissolution of lithogenic materials, although this contribution appears negligible except in surface waters close to mineral dust sources (Hayes et al., 2013). The high particle reactivity of Th combined with multiple isotopes that have a wide range of half-lives makes it particularly well suited to study the variety of processes that affect particles. For example, ^{230}Th has found several applications in paleo-oceanography. These include using ^{230}Th to correct for sediment lateral redistribution (e.g., François et al., 2004) and (in concert with ^{231}Pa) to estimate biological productivity (e.g., Kumar et al., 1993, 1995) and aspects of ocean circulation (e.g., Yu et al., 1996).

The concept of scavenging, i.e., the attachment of trace metals to sinking particles and their subsequent removal to the sea floor, was proposed by Goldberg (1954). Subsequently, there has been widespread recognition of the importance of scavenging in controlling the distribution of trace metals in the ocean (Krauskopf, 1956; Turekian, 1977). Bhat et al. (1969) concluded from ^{234}Th data obtained from the Arabian Sea, Java sea, Australian coast, Wharton Sea, and the Tasmania coast, that the distribution of ^{234}Th is controlled by adsorption of thorium onto particles. They considered an irreversible scavenging model for particulate ^{234}Th, which explained the deficit of ^{234}Th relative to ^{238}U in the surface mixed layer. Their model, however, was based on the assumption that all ^{234}Th is adsorbed onto particles. Krishnaswami et al. (1976), using ^{234}Th data from the Pacific GEOSECS expedition, estimated particulate ^{234}Th to be only 10–20% of the total activity of ^{234}Th (dissolved and particulate). They also found ^{230}Th in the particulate phase to increase approximately linearly with depth in the water column. Based on their observations, they proposed a one-dimensional (vertical) scavenging model for particulate thorium, similar to that of Bhat et al. (1969) but with an added scavenging term to account for the existence of both dissolved and particulate phases.

Nozaki et al. (1981), using data from the western North Pacific, and Bacon and Anderson (1982), using data from the Panama and Guatemala Basins, observed that the activities of ^{230}Th in both dissolved and particulate forms increase generally with depth. This observation necessitated a revision of the scavenging model and prompted the authors to develop a reversible exchange model to account for the observed vertical distributions of dissolved and particulate ^{230}Th. The innovation in this model was a term for the loss of thorium from the particles (one particle class) through desorption and (or) remineralization. Since then, the reversible exchange model has become a popular description of thorium isotope cycling in the oceanic water column, and many studies used this model in combination with a "ventilation" term in the interpretation of ^{230}Th and ^{231}Pa data (e.g., Rutgers van der Loeff and Berger, 1993; Scholten et al., 1995, 2008; Vogler et al., 1998; Moran et al., 2002; Hayes et al., 2015a).

Nevertheless, there has been extensive modifications to the reversible exchange model with one particle class. Clegg and Whitfield (1990) modeled thorium and particles in both small and large size classes. Included in their model are terms for the aggregation of small particles and disaggregation of large particles. More recently, Burd et al. (2000) presented a "coupled adsorption-aggregation" model, in which a particle size spectrum (particle size ranging from less than 10^{-2} to 53 μm) is represented in order to interpret field observations of the particulate organic carbon (POC) to ^{234}Th ratio.

Observational estimates of the rate constants of thorium and particle cycling in the ocean display large variations. They range from 0.1 to 1 yr^{-1} for adsorption and 1–10 yr^{-1} for desorption (Nozaki et al., 1987; Bacon and Anderson, 1982; Murnane et al., 1990, 1994; Murnane, 1994), 1–100 yr^{-1} for remineralization (Clegg et al., 1991), 0.1–100 yr^{-1} for aggregation, and 1–2500 yr^{-1} for disaggregation (Nozaki et al., 1987; Murnane et al., 1990; Cochran et al., 1993; Murnane et al., 1996; Cochran et al., 2000). Likewise, estimates of the sinking speed of bulk particles, including all sizes, vary widely, from 300 to 900 m yr^{-1} (Krishnaswami et al., 1976, 1981; Rutgers van der Loeff and Berger, 1993; Scholten et al., 1995; Venchiarutti et al., 2008). For the average sinking speed of particles greater than 45 μm in diameter, McDonnell and Buesseler (2010) found values from 10 to 150 m d^{-1} in waters near the west Antarctic Peninsula. Turner (2002) reported an even larger range, from less than tens to over thousands m d^{-1}, for the sinking velocity of fecal pellets. These large variations are a current impediment to any attempt to develop large-scale models of particle and biogeochemical processes in the ocean.

In a series of studies, R. Murnane and colleagues pioneered the use of inverse methods in order to estimate rate constants of particle and thorium cycling in the ocean (Murnane et al., 1990, 1994, 1996; Murnane, 1994). Using a generalized nonlinear least squares technique (Algorithm of Total Inversion or ATI) (Tarantola and Valette, 1982), Murnane (1994) performed an inversion of Th and particle data from Station P (50°N, 145°W) in the Gulf of Alaska. He compared solutions obtained from the ATI with two other regression techniques: ordinary least squares and a regression procedures by Wolberg (1967). He found that the solution obtained from the ATI was both more realistic and consistent with prior estimates of the rate constants and with data from station P than solutions obtained from the other techniques.

The adequacy of the ATI to infer rate constants of sorption reactions, however, was questioned by Athias et al. (2000a, 2000b). These authors reported that a least squares approach could not recover rate parameters of a model of Al (another relatively insoluble trace metal) cycling from a simulated data set generated by the same model. They concluded that the generalized least squares approach of Tarantola and Valette (1982) could not be applied to their problem. In contrast, Marchal and Lam (2012) succeeded in inferring rate parameters using the ATI from simulated Th and particle data. Their study suggests that field observations could be used to constrain rate parameters of Th and particle processes in the ocean. Furthermore, they concluded that measurements of particle and ^{228,230,234}Th concentrations in different size fractions, such as generated during GEOTRACES, should significantly improve the precision of the rate parameters inferred relative to *a priori* estimates.

The differences between the results of Athias et al. (2000b) and Marchal and Lam (2012) were discussed by Marchal and Lam (2012). These authors found that relatively large prior errors in the rate parameters in combination with the constraint that the model equations be imposed exactly can prevent the ATI from converging to a stable solution. Thus differences in assumptions about the prior errors between these two studies may have led to different results regarding the adequacy of the ATI to infer rate parameters. Besides Murnane (1994), Murnane et al. (1994, 1996), and Marchal and Lam (2012), other studies have successfully applied the ATI to oceanographic problems (e.g., Mercier, 1986, 1989; Mercier et al., 1993; Paillet and Mercier, 1997; Marchal et al., 2007).