

## Th-234 applied to particle removal rates from the surface ocean: a mathematical treatment revisited

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**Abstract.** It has been recognized since the 1950's that radioisotopic disequilibrium between naturally occurring parent-daughter isotope pairs in seawater can provide information on the rate of processes segregating them. In the surface ocean, the U-238: Th-234 parent-daughter pair tends to display measurable disequilibrium that is attributable to the effects of scavenging on particle reactive thorium. A range of approaches has been applied to deriving quantitative information on particle scavenging and sinking rates from U-238:Th-234 measurements. Here, we review the mathematical underpinnings of a very basic conceptual model of the removal process in order to correct a misunderstanding that has arisen in recent literature.

### 1. Introduction

Data collected over the past decade at several locations have shown upper ocean carbon fluxes inferred from Th-234 based particle sinking rates differ from those estimated directly from sediment traps [Buesseler, 1991; Buesseler *et al.*, 1994; Murray *et al.*, 1996]. Understanding the source of this discrepancy has important implications for how we should study carbon fluxes in the oceans. A recent article [Kim *et al.*, 1999] offered hope of clarifying this issue through applying a single continuous box model containing all thorium phases versus several discrete boxes for each of the phases for interpreting Th-234 observations. In response to this publication, Buesseler and Charette [2000] argued that uncertainty in both the Th measurements and trap data preclude definitive comparisons. We believe that a more fundamental error was made regarding the application of Th-234 to quantification of particle removal rates from the surface oceans. The intent of this contribution is to correct that misunderstanding.

### 2. Model Presentation and Discussion

The conceptual model of the removal process developed by previous investigators and at issue here is depicted in Figure 1.

Dissolved Th-234 is produced by the alpha decay of dissolved U-238. Long-lived U-238 ( $t_{1/2} = 4.47 \times 10^9$  yr) behaves essentially as a conservative element, hence the production rate of short-lived Th-234 ( $t_{1/2} = 24.1$  d) is fairly

uniform in ocean waters. Particle reactive Th-234 can then be adsorbed onto particles and removed from the surface either by sinking of particles, by radiodecay or by mixing. If it is assumed that: (1) mixing rates are negligible with respect to radiodecay and the rate at which particles sink from surface waters; (2) adsorption obeys a first order rate law with respect to the dissolved Th-234 concentration; and (3) the loss of particulate Th-234 via sinking also obeys a first order rate law with respect to the concentration of particulate Th-234, then the following equations hold:

$$\frac{\partial A_{Th}^d}{\partial t} = \lambda A_U - \lambda A_{Th}^d - k_d A_{Th}^d \quad (1)$$

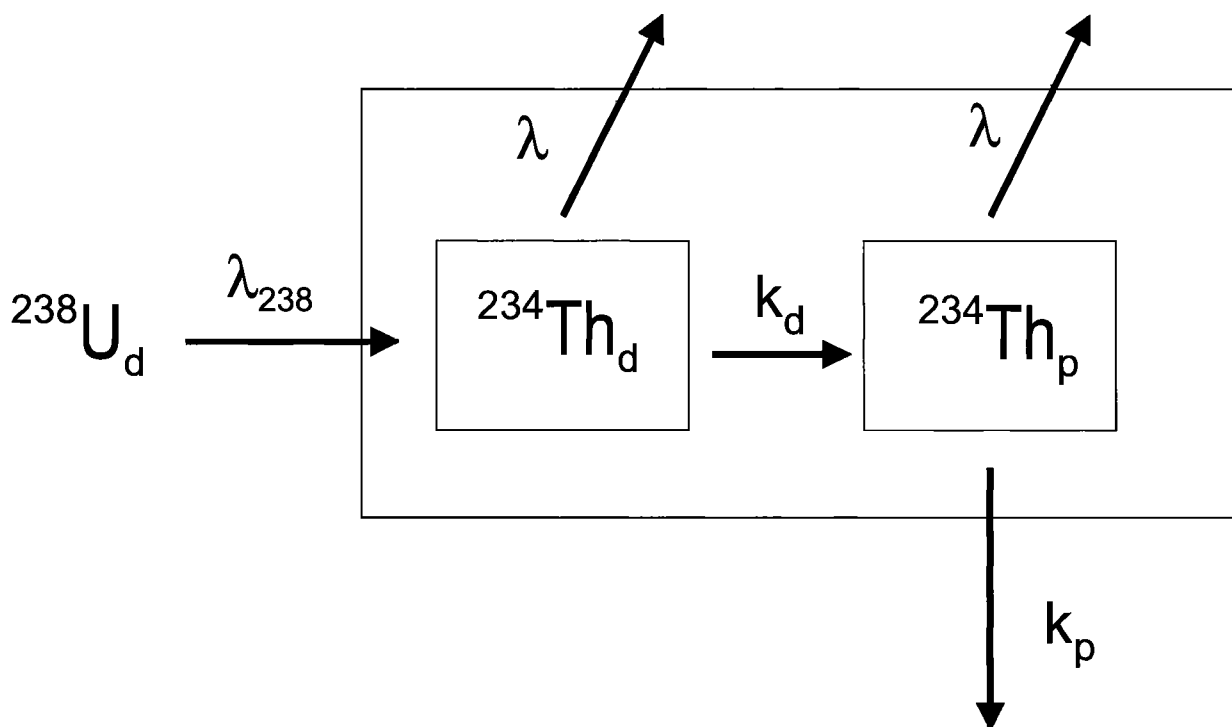
$$\frac{\partial A_{Th}^p}{\partial t} = k_d A_{Th}^d - \lambda A_{Th}^p - k_p A_{Th}^p \quad (2)$$

where  $A_U$ ,  $A_{Th}^d$  and  $A_{Th}^p$  are activities per unit volume of U-238, dissolved Th-234 and particulate Th-234 respectively,  $\lambda$  is the decay constant for Th-234, and  $k_d$  and  $k_p$  are the first order adsorption and particulate Th removal rate coefficients respectively. (We note that if the Th distributions are taken to be spatially homogenous, the equations can be expressed even more simply as a derivative rather than a partial differential.)

If it is further assumed that the system is at steady state (i.e.  $\frac{\partial A_{Th}^d}{\partial t} = \frac{\partial A_{Th}^p}{\partial t} = 0$ ) and the activities per unit volume of U-238 and dissolved and particulate Th-234 are determined, then equations (1) and (2) can be solved for the unknowns  $k_d$  and  $k_p$ . This is of particular interest because  $k_p$  should in principle give some estimate of the rate of particle removal from the surface ocean. This simple model could be expanded to include interactions with a colloidal phase [e.g., Kim *et al.*, 1999 and previous investigators]. Provided a colloidal phase measurement is available and all previous assumptions also hold for this phase, the number of variables and the system of equations are both expanded by one and so can be solved uniquely. More sophisticated models that allow for reversible interactions between the various Th phases, include mixing terms, are time-dependent or a combination of these factors have also been presented in the literature. The additional variables require additional measurements for closure and are beyond the scope of the present discussion.

There has been extensive discussion in the literature about how  $k_p$  determined in accord with Figure 1 relates to carbon flux [i.e. references in Buesseler and Charette, 2000]. Numerous questions can be posed about how well the assumptions underlying these equations hold in a given ocean setting and about how thorium and carbon cycling compare. While such questions are important to the practical application of Th isotopes to the study of particle flux,

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**Figure 1.** Input/output pathways of simple thorium box model. The larger of the boxes represents the surface ocean. See text for definition of terms.

we focus here on an error that arose at a more fundamental level. The problem arises when we consider total Th-234 (the sum of both dissolved and particulate forms). This quantity was of particular interest to earlier investigators who, given the analytical limitations of the time, reported only total measurements.

Because the first derivative is a linear operator (i.e.  $\frac{\partial(x+y)}{\partial t} = \frac{\partial x}{\partial t} + \frac{\partial y}{\partial t}$ ) and the total Th-234 activity  $\Sigma_{\text{Th}}$  is a simple sum of the dissolved and particulate activities ( $\Sigma_{\text{Th}} = A_{\text{Th}}^{\text{d}} + A_{\text{Th}}^{\text{p}}$ ), an expression for  $\Sigma_{\text{Th}}$  can be obtained by addition of equations (1) and (2):

$$\frac{\partial \Sigma_{\text{Th}}}{\partial t} = \lambda A_{\text{U}} - \lambda \Sigma_{\text{Th}} - k_{\text{p}} A_{\text{Th}}^{\text{p}} \quad (3)$$

As the linear combination of two independent equations, this is a dependent equation and, as such, does not reduce the degrees of freedom in the thorium mass balance even though the total thorium concentration can be directly measured. This equation can be compared with another expression for  $\Sigma_{\text{Th}}$  that has appeared in the literature [Coale and Bruland, 1985 and references therein; Kim *et al.*, 1999]:

$$\frac{\partial \Sigma_{\text{Th}}}{\partial t} = \lambda A_{\text{U}} - \lambda \Sigma_{\text{Th}} - k_{\text{t}} \Sigma_{\text{Th}} \quad (4)$$

Equation 4 is consistent with Eq. 3 if and only if the non-decay loss of  $\Sigma_{\text{Th}}$  is equal to the loss of particulate thorium, i.e.:

$$k_{\text{t}} \Sigma_{\text{Th}} = k_{\text{t}} (A_{\text{Th}}^{\text{p}} + A_{\text{Th}}^{\text{d}}) = k_{\text{p}} A_{\text{Th}}^{\text{p}} \quad (5)$$

which requires that

$$k_{\text{t}} = \frac{k_{\text{p}} A_{\text{Th}}^{\text{p}}}{A_{\text{Th}}^{\text{p}} + A_{\text{Th}}^{\text{d}}} \quad (6)$$

If this is the case, Eq. 4 does not further constrain the system and treating it as though it is an independent equation can only lead to erroneous results. If Eq. 4 is taken to be independent, then it is inconsistent with Eq. 3, and with the conceptual model of Figure 1, which provides for thorium removal only by particle export and decay.

Kim *et al.* [1999] encountered this problem in their attempt to reconcile a geochemical meaning for  $k_{\text{t}}$  in Eq. 4. Treating Eqs. 1, 2 and 4 as independent equations, they derived the following quantities (equivalent to Kim *et al.*'s Eqs. 4-6):

$$\frac{1}{k_{\text{d}}} = \tau_{\text{d}} = \frac{A_{\text{Th}}^{\text{d}}}{(A_{\text{U}} - A_{\text{Th}}^{\text{d}})\lambda} \quad (7)$$

$$\frac{1}{k_{\text{p}}} = \tau_{\text{p}} = \frac{A_{\text{Th}}^{\text{p}}}{(A_{\text{U}} - \Sigma_{\text{Th}})\lambda} \quad (8)$$

$$\frac{1}{k_{\text{t}}} = \tau_{\text{t}} = \frac{\Sigma_{\text{Th}}}{(A_{\text{U}} - \Sigma_{\text{Th}})\lambda} \quad (9)$$

The inverse of the specific particle adsorption rate,  $\tau_{\text{d}}$ , and the inverse of the specific particle sinking rate,  $\tau_{\text{p}}$ , can be thought of as measures of the mean-lives or “residence times” of Th-234 with respect to adsorption and particulate sinking, respectively. In the simple conceptual framework shown in Figure 1,  $k_{\text{t}}$  derived in this way has no physical meaning and thus, its inverse ( $\tau_{\text{t}}$ ) does not have a corresponding mean-life with respect to an identifiable “removal” process affecting  $\Sigma_{\text{Th}}$ . As Kim *et al.* [1999] reported, Eq. 9 is not equivalent to the simple sum of Eqs. 7 and 8; rather,

$$\tau_{\text{t}} = \tau_{\text{d}} + \tau_{\text{p}} + \lambda \tau_{\text{d}} \tau_{\text{p}} \quad (10)$$

Note that this result is robust regardless of the dependence

or independence of Eq. 4, and demonstrates that residence times are not simply additive. In a previous publication, Coale and Bruland [1985] indirectly noted this relation in the form of a numerical example (paragraph 1 p. 27). In attempt to explain their numerical results, they stated that "When both dissolved and particulate forms of Th-234 are present, the loss of Th-234 due to radioactive decay on suspended particles in the surface zone leads to  $\tau_d + \tau_p$  being less than  $\tau_t$ ." This assessment is not strictly correct since the middle term of the right hand side of Eq. 4 accounts for radiodecay in the particulate form. Despite this confusion, the conclusions of this and subsequent works of Coale and Bruland were based on the application of equations (1) and (2) only and so are mathematically sound and conceptually consistent with the simple model of Figure 1.

Kim *et al.* [1999] reported that by subtracting  $\tau_d$  via Eq. 7 from  $\tau_t$  via Eq. 9, they obtained "residence times" for Th-234 with respect to removal by sinking particles in accord with direct measures of particulate organic carbon sinking rates. Their "residence time" for Th-234 removal by sinking particles is thus numerically equal to  $(\tau_p + \lambda\tau_d\tau_p)$  rather than to  $\tau_p$ . They report four examples for which this quantity matched particle residence times based on sediment-trap carbon export determinations. Although they offered no conceptual reason why  $(\tau_p + \lambda\tau_d\tau_p)$  should provide a better measure of the particulate organic carbon sinking rates than  $\tau_p$ , they claimed these four examples resolve previous discrepancies between Th-deficiency and trap-based carbon flux determinations.

If Kim *et al.*'s conclusions had been correct, it could have put to rest the longstanding debate about how well thorium serves as a proxy for organic carbon export. Instead it ap-

pears that the few examples of "agreement" between the trap data and their  $\tau_t$  are numerically fortuitous. The situation remains then that the relationship between the sinking of Th-234 and particulate organic carbon tends to be more complicated in the surface ocean than the simple conceptual model depicted in Figure 1 would suggest.

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