

1 **WHAT CAN PAIRED MEASUREMENTS OF Th ISOTOPE**
2 **ACTIVITY AND PARTICLE CONCENTRATION TELL US**
3 **ABOUT PARTICLE CYCLING IN THE OCEAN?**

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Abstract

14

15 The ability of paired measurements of thorium isotope activity and particle concentration
16 to constrain rate constants of sorption reactions and particle dynamics in the ocean is
17 examined. This study is motivated by GEOTRACES and other sampling programs where
18 Th and particle data are gathered in various oceanic environments. Our approach relies
19 on inversions with a model of trace metal and particle cycling in the water column.
20 First, the model is used to simulate vertical profiles of (i) the activity of three Th isotopes
21 ($^{228,230,234}\text{Th}$) in the dissolved phase, small suspended particles, and large sinking particles,
22 and (ii) the concentration of small and large particles. The simulated profiles are then
23 subsampled and corrupted with noise to generate a pseudo data set. These data are
24 combined with the model with arbitrary values of rate constants of Th adsorption, Th
25 desorption, particle sinking, particle remineralization, and particle (dis)aggregation in an
26 effort to recover the actual values used to generate the data. Inversions are performed
27 using a least-squares technique with varying assumptions about data noise, data sampling,
28 and model errors.

29 We find that accurate and precise recovery of rate parameters is possible when all data
30 have a relative error of less than 20%, vertical sampling is dense enough to resolve activity
31 and concentration gradients, and model errors are negligible. Estimating cycling rates
32 from data with larger errors and (or) at locations where model assumptions are not
33 tenable would remain challenging. On the other hand, the paired data set would improve
34 significantly the relative precision of rate parameters compared to that of prior estimates
35 ($\geq 100\%$), even with current data uncertainties and significant model errors. Based
36 on these results, we advocate the joint measurement of all three Th isotopes, ^{228}Ra , and
37 particles collected by in situ filtration within GEOTRACES and other sampling programs
38 targeted at the study of particle processes in the ocean.

1 INTRODUCTION

The production, transport, and destruction of particles in the ocean have profound consequences for the marine biogeochemical cycle of a wide range of constituents. For example, chemical elements such as nitrogen, phosphorous, and carbon are incorporated into the biogenic particles that are produced in the upper layers of the sea. These particles sink by gravity and tend to be decomposed at depth, leading to the release of these elements to the dissolved phase in deep water. This vertical transport of constituents by particle cycling is thought to strongly influence the large-scale distribution of a number of substances in the ocean, such as biological nutrients, dissolved oxygen, and dissolved inorganic carbon.

The exchange of chemical constituents between the dissolved phase and particles in the ocean can take different forms, including adsorption, desorption, (in)organic complexation, and biologically-mediated uptake and remineralization. Besides, ocean particles are subject to a wide variety of processes, such as precipitation, sinking, remineralization or dissolution, (dis)aggregation, and transport by currents. Present-day knowledge about sorption reactions and particle processes in the ocean stems largely from measurements of particle-reactive metals, in particular thorium. Estimates of rate constants of Th and particle cycling have been obtained from such measurements at various locations in the world oceans, e.g., in the North Pacific (*Nozaki et al.*, 1981; *Nozaki et al.*, 1987; *Murnane et al.*, 1990; *Clegg et al.*, 1991), the Equatorial Pacific (*Clegg et al.*, 1991), the Panama Basin (*Bacon and Anderson*, 1982), the Arctic Ocean (*Bacon et al.*, 1989; *Lepore and Moran*, 2007), the North Atlantic (*Cochran et al.*, 1993; *Murnane et al.*, 1994; *Murnane et al.*, 1996), the Ross Sea (*Cochran et al.*, 2000), the Indian Ocean near Kerguelen Islands (*Venchiarutti et al.*, 2008), and the Drake Passage (*Venchiarutti et al.*, 2011). These estimates range over several orders of magnitude and suffer generally from very large uncertainties (Figure 1): point estimates of the cycling rates range from 0.1 to 1 y^{-1} for adsorption, 1 to 10 y^{-1} for desorption, 10 to 100 y^{-1} for remineralization, 0.1 to 100 y^{-1} for aggregation, and 1 to 1000 y^{-1} for disaggregation. Likewise, estimates of the sinking speed of marine particles that have been derived from various methods span a large range and commonly lie between tens to a few hundred m d^{-1} (for a recent short review

68 see *McDonnell and Buesseler* (2010). These very large uncertainties constitute a severe
69 impediment to the description of biogeochemical processes in ocean models.

70 This paper explores the extent to which measurements of the activity of three Th isotopes
71 ($^{228,230,234}\text{Th}$) can, in combination with measurements of particle concentration, constrain
72 aspects of Th and particle cycling in the ocean. It is motivated by the extensive set of
73 measurements obtained during GEOTRACES and other sampling programs concerned
74 with particle-reactive substances. Among the overriding goals of GEOTRACES is the
75 evaluation of sources, sinks, and internal cycling of selected trace elements and isotopes
76 in the ocean (*GEOTRACES*, 2006). A major objective of this paper is to determine
77 the extent to which the types of measurements gathered during GEOTRACES and other
78 programs could provide accurate and precise estimates of the rate constants of Th and
79 particle cycling in the deep sea. In particular, the sensitivity of the derived rate constants
80 to the uncertainties in the Th and particle data is estimated, thereby providing a target
81 for analytical improvements.

82 Our approach to reach the above objective is the following. First, a model that describes
83 the cycling of trace metals and particles in the oceanic column is used to simulate the
84 vertical distributions of $^{228,230,234}\text{Th}$ activity and particle concentration in different size
85 fractions. The distributions of Th isotope activity and particle concentration calculated
86 by the model are then subsampled and contaminated with noise in order to generate an
87 idealized data set. These data are combined with the model with arbitrary values of the
88 rate constants in an effort to recover the original values of the constants that have been
89 used to generate the data. Since the values of the rate parameters used to generate the
90 data are known exactly, the ability of the data to estimate these parameters can be tested.
91 The approach described above is often referred to as ‘twin experiments’ in other contexts
92 and is routinely applied to test data assimilation procedures.

93 An inverse method is used to combine the data of Th isotope activity and particle concen-
94 tration with the model of trace metal and particle cycling. Accordingly, this investigation
95 builds to a large extent upon prior work by R. Murnane and his colleagues, who exten-
96 sively applied such methods to the study of thorium and particles in the ocean (*Murnane*

97 *et al.*, 1990; *Murnane et al.*, 1994; *Murnane*, 1994; *Murnane et al.*, 1996). Our work
98 shows both similarities and differences with these previous applications. The most signif-
99 icant difference is perhaps the absence of measurements of the vertical flux of Th isotopes
100 and particles in the present study, since sediment traps are typically not deployed along
101 transoceanic sections such as completed during GEOTRACES. On the other hand, mea-
102 surements of particle concentration in different size fractions, which are lacking in previous
103 applications, are considered here since such measurements are becoming more commonly
104 available.

105 This paper is organized as follows. The model of trace metal and particle cycling, the
106 idealized data, and the inverse method are described in section 2. In section 3, the ability
107 of the data to recover rate constants in the presence of data errors, model errors, and (or)
108 limited sampling is examined. Emphasis is placed on both the accuracy and the precision
109 of the rate constants estimated by inversion. More specific aspects of the estimation
110 problem and limitations of our approach are discussed in section 4. Conclusions follow in
111 section 5.

112 2 METHODOLOGY

113 The methodology being used comprises three main components: a model that describes
114 the cycling of trace metals and particles in the ocean, a set of idealized measurements,
115 and an inverse method that combines the model with the measurements. The domain of
116 investigation is supposed to represent the water column at a deep ocean station occupied
117 during a large-scale sampling program such as GEOTRACES. It extends from the base
118 of the euphotic zone (taken at $z_e = 110$ m) to the bottom ($z_b = 5000$ m). By restricting
119 the domain to below the euphotic zone, particle production by photosynthesis does not
120 need to be considered and a relatively simple model of particle cycling could be used. By
121 convention, the vertical direction is pointing downwards.

122 2.1 Model of Trace Metal and Particle Cycling

123 2.1.1 Trace metal cycling

124 The model of trace metal cycling is a very simplified description of the behaviour of
125 particle-reactive substances in the ocean (Figure 2). It is analogous to the model proposed
126 by *Bacon et al.* (1985), with the addition of the remineralization of small particles leading
127 to the release of small particulate material to solution (see below). The resulting model
128 is identical to that applied in subsequent analyses of Th and particle measurements on
129 oceanic samples (e.g., *Murnane et al.* (1990); *Cochran et al.* (1993); *Murnane et al.*
130 (1994); *Murnane* (1994); *Murnane et al.* (1996); *Cochran et al.* (2000); *Lepore and Moran*
131 (2007)). The interested reader is invited to consult these references for a discussion of the
132 model assumptions.

133 In the model, the activity of each Th isotope (^{228}Th , ^{230}Th , and ^{234}Th) is divided in
134 three phases: the dissolved phase, the small particles, and the large particles (Figure 2).
135 These phases have the following operational definitions. The dissolved phase designates
136 the material that passes through a conventional filter with a nominal porosity of about
137 $0.5\ \mu\text{m}$. The small particle fraction refers to the material in the size range from about 0.5
138 μm to about $50\ \mu\text{m}$. This fraction can be sampled from water pumped by large volume
139 filtration (LVF) and is assumed here to be suspended, i.e., it does not sink by gravity.
140 Finally, the large particle fraction denotes the material with a size larger than about 50
141 μm . It can also be sampled by LVF and is assumed here to sink.

142 The specific processes being considered in the model include, for each Th isotope, the pro-
143 duction by the radioactive parent, the radioactive decay, the adsorption onto small par-
144 ticles, the release from small particles by desorption and remineralization, the exchange
145 between the small and large particles by particle (dis)aggregation, and the vertical trans-
146 port due to the sinking of large particles. The processes associated with solution-solid
147 exchange are assumed to follow first-order kinetics. Thus, the governing equations for the
148 activity of each isotope in the dissolved phase (A_d , in dpm m^{-3}), the small particles (A_s ,

149 dpm m⁻³), and the large particles (A_l , dpm m⁻³) are

$$T(A_d) = \lambda A_p + (k_{-1} + \beta_{-1}) A_s - (k_1 + \lambda) A_d, \quad (1a)$$

$$T(A_s) = k_1 A_d + \beta_{-2} A_l - (k_{-1} + \beta_{-1} + \beta_2 + \lambda) A_s, \quad (1b)$$

$$T(A_l) = \beta_2 A_s - (\beta_{-2} + \lambda) A_l - w \frac{\partial A_l}{\partial z}. \quad (1c)$$

150 Here A_p is the activity of the radioactive parent, λ the radioactive decay constant, k_1 the
 151 adsorption rate, k_{-1} the desorption rate, β_{-1} the remineralization rate, β_2 the aggregation
 152 rate, β_{-2} the disaggregation rate, and w the particle sinking speed. The term $T(\cdot)$ includes
 153 the temporal rate of change as well as the effects of advection and diffusion, e.g., $T(A_d) =$
 154 $\partial A_d / \partial t + \mathbf{u} \cdot \nabla A_d - \nabla \cdot (\mathbf{K} \nabla A_d)$, where t is time, \mathbf{u} the vector velocity, and \mathbf{K} a diffusion
 155 tensor. Note that the different effects in $T(\cdot)$ are not represented in Figure 2. There is
 156 a system of equations (1a–1c) for each Th isotope, so the model of trace metal cycling
 157 comprises a total of nine equations.

158 The radioactive decay constants and the radioactive parent activities that are assumed in
 159 this work are listed in Table 1. The activity of ²²⁸Ra (half-life of 5.7 y) shows generally
 160 large vertical variations in the ocean, with maxima near the surface and the bottom, and
 161 minima at mid-depth (e.g., *Key et al.* (1992)). Since ²²⁸Ra is supplied from sediments,
 162 highest ²²⁸Ra activities are observed in surface waters near the coasts and in bottom
 163 waters. In order to represent vertical variations of ²²⁸Ra activity in our analysis, the
 164 ²²⁸Ra activity is set to vary with depth according to:

$${}^{228}\text{Ra}(z) = A e^{-(z-z_e)/l_{\text{Ra}}} + B e^{-(z_b-z)/l_{\text{Ra}}}, \quad (2)$$

165 where $A = 30$ dpm m⁻³, $B = 5$ dpm m⁻³, and $l_{\text{Ra}} = 500$ m. The vertical distribution
 166 of ²²⁸Ra described by this equation exhibits an exponential decrease from the base of the
 167 euphotic zone (where ²²⁸Ra = 30 dpm m⁻³) and an exponential decrease from the bottom
 168 (where ²²⁸Ra = 5 dpm m⁻³), with much smaller activities at mid-depth (minimum of
 169 0.2 dpm m⁻³ near $z = 3000$ m). In contrast to ²²⁸Ra, the ²³⁴U and ²³⁸U activities are
 170 thought to exhibit relatively small variations in the ocean where uranium tends to vary
 171 linearly with salinity and hence to behave conservatively (e.g., *Owens et al.* (2011)). Here
 172 these activities are taken as vertically uniform. The ²³⁸U activity is fixed at 2.4×10^3

173 dpm m⁻³ assuming a salinity of 35 (*Owens et al.*, 2011) and the ²³⁴U activity is fixed at
 174 $2.4 \times 1.14 = 2.7 \times 10^3$ dpm m⁻³ assuming a ²³⁴U/²³⁸U ratio of 1.14 for seawater (*Chen*
 175 *et al.*, 1986; *Robinson et al.*, 2004).

176 In order to generate idealized Th data, equations (1a–1c) are solved for the Th isotope
 177 activity in each phase by making the following assumptions. First, the effects of unsteadiness,
 178 advection, and diffusion are assumed to be negligible in the Th isotope balances,
 179 i.e., $T(A_d) = T(A_s) = T(A_l) = 0$. These assumptions are unlikely to be valid for all Th
 180 isotopes and (or) at all oceanic locations. Vertical profiles of ²³⁰Th at several locations in
 181 the North Pacific are consistent with a reversible exchange with settling particles and do
 182 not seem to require a significant influence of ocean circulation (e.g., *Nozaki et al.* (1981);
 183 *Roy-Barman et al.* (1996)). Measurements of ²³⁰Th activity in the North Atlantic, how-
 184 ever, have been suggested to reflect a significant effect of deep circulation (e.g., *Cochran*
 185 *et al.* (1987); *Moran et al.* (1997); *Vogler et al.* (1998); *Moran et al.* (2002); *Marchal*
 186 *et al.* (2007)). Second, the presence of a vertical derivative in (1c) implies that a bound-
 187 ary condition is required to solve the system (1a–1c). The derivative is present in the
 188 equation for large particle activity, so either the large particle activity or the flux of Th in
 189 large particles should be prescribed at a given depth. Here the large particle activity at
 190 depth z_e is fixed to 0.01 dpm m⁻³ for ²²⁸Th, 0.001 dpm m⁻³ for ²³⁰Th, and 2.5 dpm m⁻³
 191 for ²³⁴Th. These values are generally consistent with specific activities (dpm per particle
 192 mass) measured on material collected by sediment traps deployed in the upper 400 m
 193 at different locations in the North Atlantic (*Brewer et al.*, 1980; *Cochran et al.*, 1993;
 194 *Roy-Barman et al.*, 2005), assuming a concentration of large particles of 1×10^{-6} kg m⁻³
 195 (see below). Finally, the rate constants k_1 , k_{-1} , w , β_{-1} , β_2 , and β_{-2} take on the values of
 196 Table 2 (3rd column), which are within the range of published estimates (Figure 1).

197 With the above assumptions, the Th isotope equations (1a–1c) reduce to a system of
 198 ordinary differential equations that can be solved exactly by Laplace transform. Note
 199 that equations (1a–1c) can be solved for the Th isotope activities independently of the
 200 concentrations of particles. This possibility arises from the fact that these activities are
 201 expressed in dpm per volume of water, since measured ^{228,230,234}Th activities, including

202 particle activities derived from in situ filtration, are usually given in dpm per volume
203 or mass of water. If the particle activities were expressed instead in dpm per mass of
204 particles, then particle concentrations would appear explicitly in (1a–1c) and they should
205 be known in order to determine the Th activities (the particle cycling model is described
206 section 2.1.2).

207 The vertical distributions of Th isotope activity, which are obtained by analytical solution
208 of (1a–1c), are displayed in Figure 3 to Figure 5 (solid lines). The activity of ^{228}Th in the
209 dissolved phase and the small particles show maxima near the surface and the bottom,
210 where the radioactive parent ^{228}Ra is relatively abundant (Figure 3). In contrast, the
211 activity of ^{228}Th in the large particles presents a subsurface maximum, which reflects a
212 balance between the effects of particle (dis)aggregation, radioactive decay, and particle
213 sinking (equation 1c). The activity of ^{230}Th increases quasi-linearly with depth in each
214 phase, which arises from the reversible exchange with particles and a relatively long half-
215 life (Figure 4). Finally, the activity of the short-lived ^{234}Th shows, for each phase, a
216 decrease in the upper 1000 m and nearly uniform values in the deeper part of the water
217 column, where secular equilibrium with the progenitor ^{238}U is almost reached (Figure 5).

218 Albeit instructive, the analytical model described above would generally not be appropri-
219 ate for combination with real measurements, as it neglects possible vertical variations of
220 the rate constants. In order to allow for such variations, a numerical model is considered.
221 Equations (1a–1c) are thus approximated with finite differences at grid points extending
222 from the base of the euphotic zone to the bottom. The grid points of the numerical model
223 belong to two subsets. The grid points of a first subset coincide with the fourteen deep-
224 est levels of a sampling scheme adopted at some of the stations occupied during the US
225 GEOTRACES North Atlantic section (completed in 2010–2011): 110, 135, 185, 250, 550,
226 850, 965, 1500, 2100, 3000, 3600, 4300, 4750, and 4900 m. For convenience, stations with
227 this sampling scheme are referred to below as ‘GEOTRACES NA deep stations’. The
228 grid points of the second subset are intermediate points located between the sampling
229 depths. Specifically, two additional points whose depth is found by linear interpolation
230 are included between each pair of adjacent sampling depths. The addition of intermediate

231 points between sampling depths increases the resolution of the numerical model and leads
 232 to accurate results (see below). The two subsets form a total of 40 grid points includ-
 233 ing the boundary point at $z_e = 110$ m where the large particle activities are prescribed.
 234 The sinking term $w\partial A_l/\partial z$ in (1c) is approximated by a central difference scheme at all
 235 points except at the deepest point ($z = 4900$ m) where it is approximated with backward
 236 differencing.

237 The vertical distributions of $^{228,230,234}\text{Th}$, which are obtained numerically, are compared to
 238 those calculated analytically in order to test the accuracy of the numerical model (compare
 239 dashed lines with solid lines in Figure 3 to Figure 5). They rely on the same assumptions
 240 as for the analytical solution. The relative error in the Th isotope activities determined
 241 numerically is ≤ 0.01 on average for each Th isotope and for each phase, indicating that
 242 the numerical solution is accurate.

243 **2.1.2 Particle cycling**

244 The model of particle dynamics is a very crude description of the behaviour of particles
 245 in the ocean (Figure 2). It is similar to the model proposed and applied by *Clegg and*
 246 *Whitfield* (1990), *Clegg and Whitfield* (1991), and *Clegg et al.* (1991), except that the
 247 production of small particles and the remineralization of large particles are disregarded.
 248 It is identical to the model adopted in previous inversions of Th and particle data (*Mur-*
 249 *nane et al.*, 1990; *Murnane et al.*, 1994; *Murnane*, 1994; *Murnane et al.*, 1996). A critical
 250 discussion of the model assumptions was recently provided by *Burd and Jackson* (2009).
 251 For example, whereas the model assumes first-order kinetics for particle processes, aggre-
 252 gation is thought as a second-order process that involves the collision of two particles,
 253 leading to a different interpretation of the rate constant for aggregation in the model.

254 In the model, the concentration of particles is considered only in two size classes: the
 255 small particles and the large particles (Figure 2). The processes being considered are
 256 the aggregation of small particles to form large particles, the remineralization of small
 257 particles, the disaggregation of large particles into small particles, and the sinking of large

258 particles. The governing equations for particle concentration in the small size fraction (P_s ,
 259 in kg m^{-3}) and large size fraction (P_l , kg m^{-3}) are thus

$$T(P_s) = \beta_{-2}P_l - (\beta_{-1} + \beta_2)P_s, \quad (3a)$$

$$T(P_l) = \beta_2P_s - \beta_{-2}P_l - w\frac{\partial P_l}{\partial z}. \quad (3b)$$

260 In order to generate idealized particle data, equations (3a–3b) are solved for the vertical
 261 distributions of P_s and P_l by making assumptions similar to those for the Th isotopes.
 262 First, the effects of unsteadiness, advection, and diffusion are assumed to be negligible
 263 i.e., $T(P_s) = T(P_l) = 0$. Second, the presence of a vertical derivative in (3b) implies
 264 that a boundary condition is required to solve the particle equations (3a–3b), as for the
 265 Th equations. Since the derivative occurs in the equation for large particles, either the
 266 concentration or the flux of large particles should be imposed at a given depth. Here the
 267 concentration of large particles at depth z_e is fixed at $P_l = 1 \times 10^{-6} \text{ kg m}^{-3}$. This value
 268 can be derived, for example, from (i) a vertical particle flux of $100 \text{ mg m}^{-2} \text{ d}^{-1}$ at this
 269 depth, which compares favorably with the particle flux intercepted over most of the year
 270 by a sediment trap at 150 m in the Sargasso Sea (*Lohrenz et al.*, 1992), and (ii) a sinking
 271 velocity of large particles of 100 m d^{-1} . Finally, the rate constants w , β_{-1} , β_2 , and β_{-2}
 272 take on the values that are listed in Table 2 (3rd column).

273 The vertical distributions of P_s and P_l , which are obtained by solving equations (3a–3b)
 274 analytically, show maxima near the surface and an exponential decrease with depth (solid
 275 lines in Figure 6). The length scale characterizing the exponential decrease of particle
 276 concentration is equal to $w(\beta_{-1} + \beta_2)/\beta_{-1}\beta_{-2}$ and is therefore the same for the two particle
 277 fractions. The ratio of small particle concentration to large particle concentration is given
 278 by $\beta_{-2}/(\beta_{-1} + \beta_2)$ and is thus the same at all depths.

279 Note that the decrease with depth of the concentration of particulate organic carbon
 280 (POC) measured on material collected by LVF has been described with a power law, not
 281 with an exponential function (*Lam et al.*, 2011). However, the POC decrease takes place
 282 primarily through the mesopelagic zone (between approximately 100 and 1000 m). In the
 283 abyssal region, which is the focus of this study (section 2.2.1), the difference between a

284 power law and an exponential function to describe the vertical distribution of particle
285 concentrations should be relatively slight.

286 The vertical distributions of P_s and P_l obtained numerically using the same grid and
287 finite-differencing as for the model of trace metal cycling are compared to the analytical
288 solution (compare dashed lines with solid lines in Figure 6). The relative error in the
289 particle concentrations determined numerically averages to less than 0.01, indicating good
290 accuracy of the numerical solution.

291 2.1.3 Model errors

292 The assumption of vanishing model errors when inferring rate parameters from field mea-
293 surements is likely to be generally unrealistic. Indeed, a variety of processes that are
294 poorly or not represented in models of trace metal and particle cycling may significantly
295 influence the Th isotope activities and (or) particle concentrations that are observed in
296 situ (such processes include, for example, mesoscale eddies; *Sweeney et al. (2003)*). When
297 such an influence is suspected, the model equations should not be imposed exactly in
298 the data analysis. Moreover, model errors should include uncertainties in the radioactive
299 sources λA_p (equation 1a), since these are never known perfectly. In particular, ^{228}Ra
300 measurements at mid-depth can suffer from significant uncertainties, implying that the
301 radioactive source and hence the equation for dissolved ^{228}Th should not be imposed too
302 strictly in the analysis.

303 Different approaches to constrain model errors have been adopted in previous inversions of
304 Th and particle measurements on oceanic samples (e.g., *Murnane et al. (1994)*; *Murnane*
305 *et al. (1996)*). In some inversions, model errors were assumed to be proportional to a
306 prior estimate of the sum of the source, sink, and sinking terms (where present) in the Th
307 and particle equations (*Murnane et al., 1994*). In other inversions, based on time-series
308 of data, model errors were taken as proportional to the standard deviation of the trends
309 observed in the data (*Murnane et al., 1996*). In the present analysis, where the data do
310 not occur in the form of time series, the former approach to constrain model errors is

311 adopted (section 2.3.2).

312 2.2 Idealized Data Set

313 The vertical distributions of Th isotope activity and particle concentration, which are
 314 computed from the numerical model (Figures 3–6), are used to produce an idealized data
 315 set from which the ability of Th and particle data to estimate cycling rates could be
 316 tested. This data set includes (i) the activity of ^{228}Th , ^{230}Th , and ^{234}Th in the dissolved
 317 phase, the small particles, and the large particles, and (ii) the particle concentration in the
 318 small and large size fractions. They would represent the types of measurement available
 319 at stations occupied during modern sampling programs, such as at the GEOTRACES
 320 NA deep stations. The types of measurement and the measurements errors, which are
 321 considered here, are specific to the US GEOTRACES North Atlantic plans and investi-
 322 gators, although they may apply to other programs as well. Two limitations need to be
 323 considered: the relatively limited number of samples and the presence of non-negligible
 324 uncertainties in the data.

325 2.2.1 Limited sampling

326 The Th isotope activities and particle concentrations will not be measured on all size
 327 fractions and at all pumping depths at GEOTRACES NA deep stations. The set of
 328 measurements that is considered to be available in this study is consistent with current
 329 expectations for the samples collected at these stations, although it is perhaps too op-
 330 timistic (section 4.2). Specifically, the following data set is assumed to be available: (i)
 331 ^{228}Th for all size fractions and at all depths, (ii) $^{230}\text{Th}_d$ at all depths, (iii) $^{230}\text{Th}_s$ at the
 332 ten deepest levels (in our analysis, at $z \geq 550$ m), (iv) $^{230}\text{Th}_l$ at a single depth (2100 m),
 333 (v) $^{234}\text{Th}_d$ and $^{234}\text{Th}_s$ at all depths, (vi) $^{234}\text{Th}_l$ in the upper 500–1000 m ($z \leq 965$ m),
 334 and (vii) P_s and P_l at the ten deepest levels ($z \geq 550$ m), as for $^{230}\text{Th}_s$. The following
 335 procedure is adopted to assign activity and concentration values at the model grid points,
 336 unless stipulated otherwise. The Th isotope activities and particle concentrations at grid

337 points coinciding with measurement depths are the values derived from the numerical so-
338 lution at these depths. The activities and concentrations at points between measurement
339 depths are obtained by linear interpolation of these values. The activities and concentra-
340 tions at all other points are obtained by extrapolation from the values derived numerically
341 at the closest measurement depth (for example, $^{230}\text{Th}_i$ values above and below 2100 m
342 are set equal to the value at 2100 m).

343 The number of data used in our analysis is further reduced for the following reason.
344 Testing the ability to recover rate parameters from the present approach requires an
345 assumption about their actual vertical distribution in the ocean. Rate parameters of
346 sorptive reactions and particle cycling are likely to vary with depth, in particular in the
347 mesopelagic zone. For example, the concentration of strong organic ligand in particulate
348 matter (PM), as determined from the amount of Th adsorbed onto PM in 0.1 M HCl, was
349 found to decrease with depth between 100 and 1000 m in the South Pacific and South
350 Atlantic (*Hirose et al.*, 2011). Chemical and biological processes modify the physical
351 properties of aggregates as they sink, thereby altering their settling speed (*Burd and*
352 *Jackson*, 2009). The settling speed of particles has been estimated to increase by a factor
353 of two between 100 and 2000 m and by 15–60% between 2000 and 3500 m at two stations
354 in the Equatorial Pacific Ocean and the Arabian Sea (*Berelson*, 2002). Rates of particle
355 sinking have also been inferred to increase with depth off Cape Blanc in the Eastern North
356 Atlantic (*Fischer and Karakaş*, 2009). The rate constant for particle remineralization
357 would decrease with depth as particles would comprise less labile material as they settle
358 (for a review about particle degradation see *Boyd and Trull* (2007)). Likewise, processes
359 responsible for particle (dis)aggregation (*Burd and Jackson*, 2009), such as zooplankton
360 feeding and fecal pellet production, are likely to vary in intensity with depth.

361 For simplicity, our analysis is restricted to the abyssal region at depths ≥ 965 m (the
362 deepest level where $^{234}\text{Th}_i$ might be measured at GEOTRACES NA deep stations). Ac-
363 cordingly, only the data occurring at depths ≥ 965 m are used to recover the rate pa-
364 rameters by inversion. Furthermore, the rate parameters to be recovered from Th and
365 particle data are taken as vertically uniform in the abyssal region, unless stated other-

366 wise. Note that the assumption of uniform cycling rates even at abyssal depths cannot be
367 rigorously defended. It would certainly not be valid at all oceanic locations. For example,
368 the presence of a benthic nepheloid layer can lead to variations in at least some of the
369 rate constants, as discussed in section 4.1. In that section, the estimation of a nonuniform
370 rate parameter from Th and particle data is addressed.

371 2.2.2 Data errors

372 Uncertainties in the measurements of Th isotope activity and particle concentration on
373 oceanic samples arise from various sources, such as inadequate sample volumes, imperfec-
374 tions in sample collection, preservation, and preparation, and instrumental errors. The
375 relative errors for the measurements of Th isotope activity and particle concentration,
376 which are assumed in this work, are listed in Table 3. The relative error of 15% for
377 ^{228}Th measured on the dissolved phase and the small particles is within the expected
378 range of uncertainty (M. Charette, pers. comm.). The relative error of 20% for ^{230}Th
379 measured on these fractions is an assessment by the present authors based on results
380 from an intercalibration coordinated by GEOTRACES (plots kindly provided by R. An-
381 derson). Measurements of ^{228}Th and ^{230}Th on large particles have rarely or never been
382 attempted and are arbitrarily assumed here to have a relative error of 50%. Although
383 samples from multiple depths may need to be combined in order to exceed the detection
384 limits of instruments (M. Charette, pers. comm.), combination of multiple samples is not
385 considered in our analysis. The errors in ^{234}Th measurements are relatively small due to
386 the abundance of ^{234}Th in seawater compared to that of ^{228}Th and ^{230}Th . The relative
387 error of 5% for ^{234}Th measured on each fraction (Table 3) is consistent with published
388 estimates (e.g., *Buesseler et al.* (2008)). Finally, a relative error of 20% is assumed for
389 particle concentrations measured on water samples collected by LVF.

390 In order to account for measurement errors, the Th isotope activities and particle con-
391 centrations obtained from the numerical solution are corrupted with noise. The addition
392 of noise requires an assumption about the underlying probability distributions of the ac-
393 tivities and concentrations. If a normal (gaussian) probability distribution is assumed,

394 the addition of noise can lead to negative values, which is unrealistic. Negative values are
 395 most likely to occur for measurements with the largest relative errors (Table 3). In order
 396 to avoid the occurrence of negative values, the Th isotope activities and the particle con-
 397 centrations are assumed to follow lognormal distributions (*Aitchison and Brown, 1957*).
 398 For example, the ^{228}Th activity in the dissolved phase is, in the presence of measurement
 399 errors, set equal to

$$^{228}\text{Th}'_d = e^{\mu+r\sigma}, \quad (4)$$

400 where

$$\mu = \ln(^{228}\text{Th}_d) \quad \text{and} \quad \sigma = \sqrt{\ln(1 + \epsilon^2[^{228}\text{Th}_d])}. \quad (5)$$

401 Here $^{228}\text{Th}_d$ is the value obtained from the numerical solution and (when applied) subse-
 402 quent interpolation or extrapolation, and $\epsilon[^{228}\text{Th}_d] = 0.15$ is the relative error in $^{228}\text{Th}_d$
 403 measurement (Table 3). The quantity r in (4) is a normal deviate with zero mean and
 404 unit variance, which is generated randomly. If a large number of values of r is generated
 405 for fixed $^{228}\text{Th}_d$ and $\epsilon[^{228}\text{Th}_d]$, the probability distribution of $^{228}\text{Th}'_d$ tends to a lognormal
 406 distribution with median μ and variance σ^2 . A test ensures that the values of $^{228}\text{Th}'_d$
 407 that are derived randomly are within $1 \pm \epsilon[^{228}\text{Th}_d]$ of the value of $^{228}\text{Th}_d$. The above
 408 procedure is applied to the other Th isotope activities and to the particle concentrations
 409 in all fractions. The Th and particle values at sampling depths, which are used to produce
 410 the idealized data for the inversions, are displayed together with their respective errors in
 411 Figure 3 to Figure 6 (open and solid circles, with horizontal bars).

412 2.3 Inverse Method

413 An inverse method is used to combine the model of trace metal and particle cycling
 414 (section 2.1) with the (idealized) measurements of Th isotope activity and particle con-
 415 centration (section 2.2). This combination will inform us about the extent to which these
 416 types of measurement could be used to recover the rate constants k_1 , k_{-1} , w , β_{-1} , β_2 ,
 417 and β_{-2} in the abyssal region (below a depth of 965 m). Since the measurements have
 418 significant errors, they should not be imposed exactly when inferring the rate constants.
 419 Here, the Th isotope activities and particle concentrations are, in addition to the rate

420 constants, considered to be actually part of the solution. This approach allows the val-
 421 ues of Th isotope activity and particle concentration to adjust in the inversions, while
 422 remaining consistent with the observed values. In order to avoid the inference of negative
 423 values, the inverse method aims at estimating, not the actual values, but their natural
 424 logarithm (e.g., *Murnane et al. (1994)*).

425 2.3.1 Algorithm of total inversion

426 The inverse method being used is a generalized least-squares method known as the algo-
 427 rithm of total inversion (*Tarantola and Valette, 1982a; Tarantola and Valette, 1982b*). A
 428 brief description of this method allows us to introduce concepts that are referred to later
 429 in the paper (for details see the above references). Let us first introduce a state vector \mathbf{x} of
 430 dimension n . The components of \mathbf{x} are the natural logarithm of (i) the activity of ^{228}Th ,
 431 ^{230}Th , and ^{234}Th in the dissolved phase, the small particles, and the large particles, (ii) the
 432 particle concentration in the small and large size fractions, and (iii) the rate constants k_1 ,
 433 k_{-1} , w , β_{-1} , β_2 , and β_{-2} , at different depths. The components of \mathbf{x} represent the actual,
 434 true values to be estimated by inversion. If the number of depths where the components
 435 are to be estimated is m , then the dimension of \mathbf{x} is $n = (3 \times 3 + 2 + 6)m = 17m$.

436 Let us then consider an a priori estimate of \mathbf{x} , which is noted \mathbf{x}_o . This prior estimate
 437 of the solution is obtained from the measurements of Th isotope activity and particle
 438 concentration (section 2.2) and from values of rate constants that are consistent with
 439 published estimates (Figure 1). Here the prior values of the rate constants are set equal
 440 to $5 \pm 5 \text{ y}^{-1}$ for both k_1 and k_{-1} , $300 \pm 150 \text{ m d}^{-1}$ for w , $10 \pm 50 \text{ y}^{-1}$ for β_{-1} , $10 \pm 100 \text{ y}^{-1}$
 441 for β_2 , and $500 \pm 5000 \text{ y}^{-1}$ for β_{-2} (Table 2, 4th column). The ranges defined by these
 442 values encompass most of the point estimates of these parameters in the ocean (Figure 1).

443 Let us then define a $n \times n$ error covariance matrix \mathbf{C}_o . The diagonal elements of \mathbf{C}_o are
 444 the variances (standard deviations or errors squared) of the prior estimates in \mathbf{x}_o and the
 445 off-diagonal elements of \mathbf{C}_o are the covariances between these errors. Assuming that the
 446 Th activities, particle concentrations, and rate constants are lognormally distributed, the

447 variances are set equal to $\ln(1 + \epsilon^2[\cdot])$, where $\epsilon[\cdot]$ is the relative error for these variables
 448 (e.g., $\epsilon[k_1] = 5/5 = 1$). On the other hand, the covariances are set to zero, i.e., \mathbf{C}_o is
 449 assumed to be diagonal.

450 Finally, let us consider the equations of the model of Th cycling (1) and particle dynamics
 451 (3), but with the trend and transport terms set equal to zero ($T(\cdot) = 0$). The finite-
 452 difference approximations that result from the discretization of these equations on the
 453 grid are included in a vector $\mathbf{f}(\mathbf{x}) = \mathbf{0}$. Thus, the vector $\mathbf{f}(\mathbf{x})$ includes the finite-difference
 454 forms of the source, sink, and sinking terms in equations (1) and (3). Its dimension is equal
 455 to $(3 \times 3 + 2)m = 11m$. The sinking terms are approximated with central differences at
 456 all interior points. The boundary points where large particle activities and concentrations
 457 are prescribed occur at $z = 965$ m and 4900 m. As for the data, the equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$
 458 should not be imposed exactly when inferring rate constants in the ocean, since these
 459 equations contain uncertainties due to the assumption of steady state, the neglect of the
 460 effect of ocean circulation, the truncation error introduced by the numerical approximation
 461 of the sinking term, etc. Consequently, an error covariance matrix is also introduced for
 462 $\mathbf{f}(\mathbf{x}) = \mathbf{0}$, and noted \mathbf{C}_f . The diagonal elements of \mathbf{C}_f are the square of the errors of
 463 the components of $\mathbf{f}(\mathbf{x})$, i.e., the square of the errors in the difference forms of the model
 464 equations. The off-diagonal elements of \mathbf{C}_f are the covariances between these errors and
 465 are set equal to zero.

466 The problem considered in this paper is to find estimates of Th isotope activity, particle
 467 concentration, and rate constants k_1 , k_{-1} , w , β_{-1} , β_2 , and β_{-2} , which are consistent with
 468 (i) prior estimates of all these quantities and (ii) a model of trace metal and particle
 469 cycling. Equivalently, the problem is to find an estimate of \mathbf{x} that is consistent with
 470 both the prior estimate \mathbf{x}_o and the model equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$, given estimates of their
 471 respective errors. It is solved by determining a minimum of the objective function

$$J = (\mathbf{x} - \mathbf{x}_o)^T \mathbf{C}_o^{-1} (\mathbf{x} - \mathbf{x}_o) + \mathbf{f}(\mathbf{x})^T \mathbf{C}_f^{-1} \mathbf{f}(\mathbf{x}), \quad (6)$$

472 where the superscript T denotes the transpose. The first and second terms on the right-
 473 hand side describe, respectively, the deviation from the prior estimates and the deviation

474 from the model equations. Since \mathbf{C}_o and \mathbf{C}_f are approximated by diagonal matrices, the
 475 objective function is a weighted sum of squares:

$$J = \sum_{i=1}^{17m} \left(\frac{x_i - x_{o,i}}{\sigma_{o,i}} \right)^2 + \sum_{i=1}^{11m} \left(\frac{f_i(\mathbf{x})}{\sigma_{f,i}} \right)^2, \quad (7)$$

476 where $\sigma_{o,i}$ is the standard deviation for the i th component of \mathbf{x}_o and $\sigma_{f,i}$ is the standard
 477 deviation for the i th component of $\mathbf{f}(\mathbf{x}) = \mathbf{0}$. The matrices \mathbf{C}_o and \mathbf{C}_f play therefore
 478 the role of weighting factors, such that prior estimates or model equations with relatively
 479 large uncertainties contribute only modestly to the objective function to be minimized.
 480 For example, the relative errors $\geq 100\%$ for the prior estimates of the rate constants
 481 (Table 2) imply that the posterior estimates of these constants to be found by inversion
 482 may strongly deviate from the prior estimates (indeed, by one order of magnitude or
 483 more).

484 Note that the search for a minimum of J is a nonlinear problem, since the equations
 485 $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ contain products of elements of \mathbf{x} (e.g., $k_1 {}^{228}\text{Th}_d$ in equation (1a)): if the Th
 486 and particle data were to contain no error, then they could be taken as constant values
 487 and moved out of the state vector \mathbf{x} . In this case, the equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ could be written
 488 as $\mathbf{A}\mathbf{x} = \mathbf{b}$, where \mathbf{A} is a matrix of coefficients constrained from the data, \mathbf{x} a vector of
 489 unknowns containing the rate constants, and \mathbf{b} a vector including, e.g., the production
 490 rates from the radioactive parents. The search for a minimum of J would then reduce to
 491 a linear problem. The general validity of this approach, however, is doubtful for real (and
 492 thus uncertain) observations.

493 The method of total inversion is iterative in nature and proceeds by successive lineariza-
 494 tion of the nonlinear equations using their gradient with respect to the state vector.
 495 Accordingly, convergence of the method is only ensured if the nonlinearity is not too
 496 strong (*Tarantola and Valette, 1982a*). Here the algorithm is initialized with the prior
 497 estimate of the state, \mathbf{x}_o , and iteration is stopped when all the elements of the solution
 498 differ by less than 1% from those of the solution at the previous iterative step.

499 When a solution is found, the posterior estimates of the rate constants and their errors are
 500 derived as follows. The posterior estimates are obtained from the antilog of the solution

501 elements (e.g., the posterior estimate of k_1 is obtained from the antilog of $\widehat{\ln k_1}$, where $\widehat{\ln k_1}$
 502 is the estimate of the logarithm of k_1 that is found by inversion). If a solution element is
 503 the mean value of a normal distribution, then its antilog would be the median value of a
 504 lognormal distribution. Alternately, the posterior estimates of the rate constants can be
 505 derived using the formula for the mean of a lognormal random variable. For example, the
 506 posterior estimate of the adsorption rate, $\widehat{k_1}$, can be obtained from $\exp\left(\widehat{\ln k_1} + \sigma_{\widehat{\ln k_1}}^2/2\right)$,
 507 where $\sigma_{\widehat{\ln k_1}}$ is the error in the posterior estimate of $\ln k_1$ (*Aitchison and Brown* (1957);
 508 p. 8, equation 2.7). If nonlinearity is not too strong, the error $\sigma_{\widehat{\ln k_1}}$ can be derived using
 509 the formula for the error covariance matrix of the solution for the linear case (*Tarantola*
 510 *and Valette*, 1982a). The two forms (median and mean) of posterior estimate of the rate
 511 constants are considered here, as in previous inversions of Th and particle data (e.g.,
 512 *Murnane et al.* (1994)).

513 Finally, the errors in the posterior estimate of the rate constants are computed using the
 514 formula for the standard deviation of a lognormal random variable (*Aitchison and Brown*
 515 (1957); p. 8, equation 2.8). For example, for the adsorption rate k_1 ,

$$\sigma_{\widehat{k_1}}^2 = \exp\left(\sigma_{\widehat{\ln k_1}}^2 + 2\widehat{\ln k_1}\right) \left(\exp\left(\sigma_{\widehat{\ln k_1}}^2\right) - 1\right). \quad (8)$$

516 In summary, the number of depths where the rate constants k_1 , k_{-1} , w , β_{-1} , β_2 , and β_{-2}
 517 are to be estimated from the Th and particle data amounts to $m = 20$ (six sampling
 518 depths plus fourteen intermediate depths between $z = 965$ m and 4900 m excluded).
 519 Consequently, the number of unknowns (size of \mathbf{x}) is 340 and the number of equations
 520 (size of \mathbf{f}) is 220. The inference of the rate constants is a formally underdetermined (and
 521 nonlinear) problem.

522 2.3.2 Prescription of model errors

523 Based on some of the concepts of the inverse method, the prescription of model errors in
 524 our analysis can be described precisely. Following a previous approach (*Murnane et al.*,
 525 1994), the model errors are assumed to be proportional to the prior estimate of the sum

526 of the source, sink, and sinking terms in the Th and particle equations:

$$\{\mathbf{C}_f\}_{i,j} = p \delta_{i,j} \{\mathbf{f}(\mathbf{x}_o)\mathbf{f}(\mathbf{x}_o)^T\}_{i,j}, \quad (9)$$

527 where $\{\cdot\}_{i,j}$ is the i, j element of the matrix, p is a proportionality factor, and $\delta_{i,j} = 1$
 528 if $i = j$ and $\delta_{i,j} = 0$ if $i \neq j$. For example, the assumption $p = 1$ is equivalent to the
 529 statement that processes that are not represented explicitly in the model can be on the
 530 same order of magnitude as the prior estimate of the sum of the source, sink, and sinking
 531 terms.

532 3 RESULTS

533 In this section, the Th and particle data are combined with the model of Th and particle
 534 cycling to test the ability of these data to recover the rate parameters of the model.
 535 Emphasis is placed on the accuracy and precision with which the rates of adsorption,
 536 desorption, sinking, remineralization, and (dis)aggregation can be estimated. Results from
 537 a variety of inversions are reported in order to isolate the effects, on parameter recovery, of
 538 data errors, model errors, and limited sampling. Hypothetical cases where data or model
 539 errors are small or even zero and where data are available at all depths are considered
 540 first. We then examine more realistic cases where the uncertainty and availability of data
 541 approach those at stations occupied during modern sampling programs and where the
 542 model contains significant errors.

543 3.1 Effect of Data Errors

544 We first consider two different inversions where the Th and particle data have small
 545 uncertainties, they are available at all depths (no data interpolation or extrapolation is
 546 applied), and model errors are very small ($p = 10^{-5}$). Although these conditions are
 547 unlikely to be met in any real circumstances, the results from these inversions provide
 548 a useful reference as more realistic assumptions about the measurements and the model
 549 will be considered.

550 In a first inversion, the relative error of all data is fixed to 5%, which is comparable
551 to the relative error of ^{234}Th measurements (for convenience this inversion is referred
552 to below as our ‘reference inversion’). It is seen that the rate parameters can all be
553 successfully recovered in this case (solid circles in Figure 7). The posterior estimates
554 of these parameters are close to the actual values used to generate the Th and particle
555 data, and their posterior errors are small. This result indicates that accurate and precise
556 recovery of the kinetic parameters from Th and particle data is a theoretical possibility.
557 The Th and particle data overdetermine effectively the problem, so that all a priori
558 information about the rate constants can be neglected. In this case, the iteration of the
559 linearized problem always leads to the correct solution (*Tarantola and Valette, 1982a*).

560 In the second inversion, the relative error of all data is raised to a maximum of 20%,
561 a value that seems to approximately hold for ^{230}Th measurements on the dissolved and
562 small particle fractions. Thus, all measurements have the relative errors listed in Table 3,
563 except ^{228}Th and ^{230}Th measurements on large particles whose relative error is 20%. As
564 in the previous inversion, the prior estimates of the rate constants are adjusted so as to
565 jointly satisfy the data and the model equations given their respective uncertainties (open
566 circles in Figure 7). As expected, the recovery of the rate constants is generally poorer
567 than in the previous case where data have a relative error of 5%, except for the adsorption
568 rate that is still estimated with high accuracy and precision. The estimated rate constants
569 are generally larger than those derived in this previous case. This pattern is due to the
570 fact that inversions with larger data errors are less strongly influenced by Th and particle
571 data and more strongly influenced by prior estimates of the rate constants (equation 7).
572 Accordingly, since the prior estimates of the rate constants are set to be greater than their
573 actual values, the posterior estimates of the rate constants obtained by inversion increase
574 with the errors in the data. Nonetheless, most of the posterior estimates of the cycling
575 rates are considerably more precise than the prior estimates, while being generally within
576 one standard deviation of the actual values. This result suggests that Th and particle
577 data with a relative error $\leq 20\%$ may still dramatically improve our understanding of
578 solid-solution exchange and particle processes. Of course, this conclusion would hold only
579 at locations where the data are available with good vertical resolution and the model

580 provides an accurate description of Th and particle cycling (the effects of model errors
581 and data resolution are explored later in sections 3.2 and 3.3, respectively).

582 A set of inversions illustrates more comprehensively the effect of varying data errors on
583 the accuracy and precision of the recovered rate parameters (Figures 8–9). All these
584 inversions assume that the data are available at all depths and that model errors are
585 very small ($p = 10^{-5}$). The accuracy of a rate constant is measured by the normalized
586 difference $(\hat{x} - x)/x$, where \hat{x} is the value of the rate constant estimated by inversion
587 (here the mean) and x is its actual value ($x \in \{k_1, k_{-1}, w, \beta_1, \beta_2, \beta_{-2}\}$). The precision
588 is measured by the ratio $\sigma_{\hat{x}}/\hat{x}$, where $\sigma_{\hat{x}}$ is the standard deviation of rate constant x
589 estimated by inversion (equation 8). As expected, both the accuracy and the precision
590 of the recovered rate parameters deteriorate as the Th and particle data contain larger
591 errors (Figures 8–9). Nonetheless, parameter recovery with $|\hat{x} - x|/x < 1$ and $\sigma_{\hat{x}}/\hat{x} < 1$
592 remains generally possible even in the presence of significant data errors (maximum of
593 20%). As already illustrated, not all parameters can be recovered with the same accuracy
594 and precision: in general, the rate of Th adsorption onto small particles (k_1) and the rate
595 of Th desorption from small particles (k_{-1}) are the parameters that are the easiest to
596 infer from Th and particle data.

597 Note that, so far, the relative errors listed in Table 3 have been assigned to some but not
598 all Th and particle data. Specifically, ^{228}Th and ^{230}Th measurements on large particles
599 have been assumed to have a relative error of less than 50%. The case where the relative
600 error in these measurements is equal to this value is examined in section 3.4.

601 **3.2 Effect of Model Errors**

602 As suggested above, the assumption of vanishing model errors when inferring rate con-
603 stants from field data should generally be discouraged. In order to isolate the effect of
604 model errors, inversions are considered where the Th and particle data are assumed to be
605 perfect ($\sigma_o = 0$ for these data) and available at all depths. Note that the situation $\sigma_o = 0$
606 for some variables does not lead to infinite values in the algorithm of total inversion, as

607 equation (7) may suggest. Indeed, the algorithm can rely on either \mathbf{C}_o or its inverse
 608 through the use of a matrix identity (e.g., *Liebelt (1967)*).

609 The rate parameters that are estimated in two inversions with $p = 0.1$ or $p = 1$ are
 610 compared in Figure 10. It is seen that the second, more conservative assumption about
 611 the model ($p = 1$) leads to a significant deterioration of the accuracy and precision of
 612 the rate constants compared to the first assumption. In the second inversion, the rate
 613 constants are adjusted generally to a lesser degree from their prior estimates, which is
 614 consistent with a lower weight given to the model equations and, consequently, to the Th
 615 and particle data. On the other hand, the rate constants estimated by inversion are much
 616 more precise than the prior estimates (except for k_{-1} and w), while being within two
 617 standard deviations of the actual values. This result suggests that important information
 618 about the cycling rates could be extracted from Th and particle data even at locations
 619 where significant model errors should be assumed, provided that these data are accurate
 620 and numerous.

621 **3.3 Effect of Limited Sampling**

622 The above inversions assumed that Th and particle data are available at each depth of
 623 the model grid, i.e., at twenty two depths (8 sampling depths plus 14 intermediate depths
 624 between 965 and 4900 m included). No data interpolation or extrapolation was applied.
 625 In order to explore the effect of limited sampling, two other inversions are considered. In
 626 a first inversion, Th and particle data are assumed to be available at all depths and to
 627 contain no error. In the second inversion, the Th and particle values at levels between
 628 sampling depths are obtained by interpolation or extrapolation of the data at the sampling
 629 depths (section 2.1.1). Thus, for example, the values of ^{230}Th and ^{234}Th activity for large
 630 particles are extrapolated from their values at $z = 2100$ m and 965 m, respectively. The
 631 relative error of the data is fixed to 0% at the sampling and interpolation depths, and to
 632 100% at the extrapolation depths. Both inversions assume that the model provides an
 633 accurate description of Th and particle cycling ($p = 0.01$).

634 We find that the rate parameters can still be recovered even with an incomplete data
635 set, although the accuracy and precision of the posterior estimates vary between the rate
636 constants and between different depths (Figure 11). This result suggests that the sampling
637 scheme considered here (section 2.1.1) should be adequate for a successful estimation of
638 cycling rates, provided that the data and the model are both accurate. This conclusion,
639 however, should be tempered by the fact that the Th isotope activities and particle
640 concentrations could exhibit, at some oceanic locations, much larger vertical gradients
641 than in our synthetic data set (Figures 3–6). Indeed, no successful recovery of rate
642 parameters should be anticipated at locations where sampling is not dense enough to
643 resolve the property gradients.

644 **3.4 Recovery of Cycling Rates at a Deep Ocean Station**

645 The rates of Th and particle cycling are now estimated in the presence of data errors,
646 model errors, and limited sampling. The errors in the Th and particle data that are
647 anticipated for samples collected at GEOTRACES NA deep stations (Table 3) and the
648 set of measurements that may be expected at these stations (section 2.2.1) are considered
649 to provide a realistic example. Specifically, the relative errors at measurement depths are
650 the values listed in Table 3. The relative errors at the interpolation points are given the
651 same values, whereas the relative errors at the extrapolation points are set equal to 100%.
652 The errors in the Th and particle equations are assumed to be on the order of the prior
653 estimate of the sum of the source, sink, and sinking terms in these equations ($p = 1$).
654 Note that whether this assumption would be generally valid when applied to the analysis
655 of real data is unclear. For example, the prior estimate of the source, sink, and sinking
656 terms at a given location may be very poor due to the currently large uncertainties in the
657 rate parameters.

658 As expected from our previous inversions, the presence of significant errors both in the
659 data and in the model decreases considerably the ability to recover the rate constants
660 (Figure 12). Accurate and precise estimation of the cycling rates would remain challeng-
661 ing even with a relatively exhaustive data set, unless data errors are reduced and the

662 assumption of small model errors is justified. Nevertheless, the posterior estimates of the
 663 rate constants would constitute a significant improvement over the prior estimates, in the
 664 sense that they would be generally much more precise (with the exception of k_{-1} and
 665 w), while being within two standard deviations of the actual values (Figure 13). When
 666 averaged over all depths in the abyssal region, the relative precision of the kinetic param-
 667 eters (as measured by $\sigma_{\hat{x}}/\hat{x}$) is improved by about a factor of two for adsorption, four for
 668 remineralization and aggregation, and seven for disaggregation.

669 It is instructive to compare these results with those obtained from simpler approaches to
 670 infer rate constants of Th and particle cycling. Consider first the particle settling speed
 671 that would be inferred solely from ^{230}Th activity in sinking particles (here available only
 672 at $z = 2100$ m; Figure 4). Summing equations (1a-1c) gives a simple equation for total
 673 ^{230}Th ,

$$0 = \lambda A_p - w \frac{\partial A_l}{\partial z}, \quad (10)$$

674 where it has been assumed that $T(\cdot) = 0$ and that the radioactive decay constant is
 675 negligible compared to other rate constants (a good approximation for ^{230}Th). Integrating
 676 this equation from depths z to 2100 m, assuming a vertically uniform w , and solving for
 677 w yield

$$w = (2100 - z)\lambda \frac{A_p}{A_l(2100 \text{ m}) - A_l(z)}. \quad (11)$$

678 With only one measurement of ^{230}Th in sinking particles ($0.0019 \text{ dpm m}^{-3}$ at $z = 2100$
 679 m; Figure 4), w cannot be uniquely determined. If the ^{230}Th activity in particles vanishes
 680 at $z = 0$ m, as assumed in some models (e.g., *Bacon and Anderson (1982)*), the estimated
 681 value of w would be 75 m d^{-1} , which is half the actual value (150 m d^{-1}). Thus, the
 682 assumption of vanishing $^{230}\text{Th}_l$ at $z = 0$ m leads to inaccurate recovery of w . A poor
 683 estimate of w was also obtained in our inversion where the posterior value of w is close
 684 to its prior value of 300 m d^{-1} (Figure 12). Note that the measurement of ^{230}Th in large
 685 particles at just one additional depth would allow w to be accurately estimated (if it is
 686 constant). For example, if the value $^{230}\text{Th}_l = 0.001 \text{ dpm m}^{-3}$ at $z = 110$ is known in
 687 addition to that at 2100 m, then application of (10) predicts a particle sinking speed of
 688 150 m d^{-1} (keeping three significant digits), which is precisely the actual value.

689 Consider then the adsorption rate k_1 and the sum $k_{-1}^* = k_{-1} + \beta_{-1}$. Summing equations
 690 (1b–1c) leads to an equation for Th activity in all particles (small and large). Neglecting
 691 the sinking and radioactive decay of large particle activity compared to other terms in
 692 this equation,

$$\frac{k_1}{k_{-1}^* + \lambda} = \frac{A_s}{A_d}, \quad (12)$$

693 which is equation (13) in *Bacon and Anderson* (1982) (note that these authors did not
 694 explicitly consider particle remineralization, so k_{-1}^* is equivalent to k_{-1} in their equa-
 695 tion). These authors used this equation to derive individual estimates of k_1 and k_{-1}^* from
 696 measurements of ^{230}Th and ^{234}Th activity on dissolved and particle fractions. Here the
 697 average value of A_s/A_d for the eight sampling depths (Figures 4 and 5) amounts to 0.16
 698 for ^{230}Th and 0.037 for ^{234}Th , which lead to an estimate of 0.50 y^{-1} for k_1 and 3.2 y^{-1} for
 699 k_{-1}^* . These values are close to the actual ones (Table 2), in contrast to the results from
 700 our inversion (Figure 12). Given this result, the poor recovery of $k_{-1} + \beta_{-1}$ (Figure 12)
 701 may seem surprising. However, this result is obtained by assuming that the Th data
 702 and the approximate balance $k_1/(k_{-1}^* + \lambda) = A_s/A_d$ are perfectly accurate, whereas our
 703 inversion assumes data and model errors that should be more representative of oceanographic
 704 conditions. Should lower data and model errors be assumed, then the recovery of
 705 $k_{-1} + \beta_{-1}$ (and w) would be more successful and their posterior errors would be smaller,
 706 as illustrated in previous inversions (Figure 7; Figures 10 and 11).

707 4 DISCUSSION

708 In this section, the potential of Th and particle data to estimate rate constants of Th and
 709 particle cycling in the ocean is further explored. Emphasis is placed on (i) the ability to
 710 recover vertical variations in rate parameters, (ii) the contribution of ^{228}Th , ^{228}Ra , and
 711 particle data to parameter recovery, and (iii) the relative importance of $^{228,230}\text{Th}$ data in
 712 different size fractions. Three potential limitations of this study are then discussed. These
 713 are related to (i) the use of additional measurements to constrain the rate constants, (ii)
 714 the adequacy of the algorithm of total inversion as a general method to infer the rate
 715 parameters, and (iii) the interpretation of errors in the least-squares solution.

4.1 Vertical Variations in Rate Parameters

The inversions reported in section 3 are restricted to the case where the rate constants of Th and particle cycling that are to be estimated from Th and particle data are vertically uniform. As already stated it is plausible, however, that these ‘constants’ vary markedly in the deep sea. For example, significant depletion of ^{234}Th compared to secular equilibrium with its parent ^{238}U has been observed in benthic nepheloid layers (e.g., *Bacon and Rutgers van der Loeff* (1989); *Turnewitsch and Springer* (2001); *Rutgers van der Loeff et al.* (2002); *Inthorn et al.* (2006)). The relatively large $^{234}\text{Th}_s/^{234}\text{Th}_d$ ratio that is sometimes observed in these layers would result from a relatively large value of $k_1/(k_{-1}^* + \lambda)$, assuming equilibrium for sorption reactions (equation 12; *Bacon and Rutgers van der Loeff* (1989)).

The inverse method used in this study could also be applied to recover rate constants that vary along the water column. To illustrate this, an inversion is considered with two modifications compared to our reference inversion. First, Th adsorption onto small particles is assumed to be relatively slow except in a deep layer where it is faster. This case would represent a situation where particles suspended in deep water, such as MnO_2 -rich particles in a benthic nepheloid layer (e.g., *Balistrieri and Murray* (1986); *Geibert and Usbeck* (2004)), have a high capacity for attaching Th onto their surfaces compared to particles in overlying water. Specifically, the following vertical profile is assumed for k_1 ,

$$k_1(z) = k_{1o} (1 + \alpha \phi(z)), \quad (13)$$

where $k_{1o} = 0.5 \text{ y}^{-1}$, $\alpha = 0.2$, and $\phi(z) = \arctan((z - z_*)/l_*) + \pi/2$ with $z_* = 4000 \text{ m}$ and $l_* = 200 \text{ m}$. This profile is characterized by quasi uniform values close to 0.5 y^{-1} above 3500 m, a sharp increase from 3500 m to 4500 m, and relatively uniform values below reaching a maximum of about 0.8 y^{-1} (solid line in Figure 14). Second, a source of small particles carrying the long-lived ^{230}Th is invoked near the bottom. The following source terms are added to the right-hand side of, respectively, the $^{230}\text{Th}_s$ equation (1b) and the

742 small particle equation (3a):

$${}^{230}\text{Th}_s(z) = {}^{230}\text{Th}_{s,o} \phi(z) \quad \text{and} \quad \dot{P}_s(z) = \dot{P}_{s,o} \phi(z), \quad (14)$$

743 where ${}^{230}\text{Th}_{s,o} = 10^{-2} \text{ dpm m}^{-3} \text{ y}^{-1}$ and $\dot{P}_{s,o} = 10^{-5} \text{ kg m}^{-3} \text{ y}^{-1}$. The sources described
 744 by (14) are relatively uniform above 3000 m, increase sharply from about 3500 to 4500
 745 m, and are more uniform below (not shown). They would represent the effect of lateral
 746 transport of fine particles near the bottom or the effect of resuspension of fine particles
 747 from the seafloor, two processes that are thought to contribute to the formation and
 748 maintenance of benthic nepheloid layers in the ocean (e.g., *McCave* (1986)).

749 Profiles of ${}^{228,230,234}\text{Th}$ activity and particle concentration in the three size fractions are
 750 obtained by numerical solution of (1–3) with (i) k_1 varying according to (13) and (ii) the
 751 ${}^{230}\text{Th}_s$ and small particle sources (14). The ${}^{228}\text{Th}$ profiles are qualitatively similar to those
 752 obtained with uniform k_1 (Figure 15). On the other hand, the ${}^{230}\text{Th}$ profiles are noticeably
 753 affected by the enhanced adsorption rate and the ${}^{230}\text{Th}_s$ source in deep water (Figure 16).
 754 At depths greater than about 3500 m, the dissolved ${}^{230}\text{Th}$ activity shows lower values and
 755 the particle activities show larger values compared to those obtained with uniform k_1 and
 756 no ${}^{230}\text{Th}_s$ source. The ${}^{234}\text{Th}$ activity in each size fraction is significantly influenced by
 757 enhanced k_1 in deep water (Figure 17): the dissolved activity shows lower values below
 758 3500 m and the particle activities show higher values below 3500–4000 m relatively to the
 759 profiles computed with uniform k_1 . Finally, the small and large particle concentrations
 760 show relative maxima below about 3500–4000 m, consistent with the presence of a particle
 761 source near the bottom (Figure 18).

762 An inversion is conducted in order to determine whether the vertical variations in the rate
 763 constant k_1 could be estimated from Th and particle data. The assumptions regarding the
 764 data and the model are the same as for the reference inversion: the data have a relative
 765 error of 5%, they are available at all depths, and model errors are very small ($p = 10^{-5}$).
 766 It is seen that the rates of Th adsorption estimated by inversion are all close and within
 767 two standard deviations of the actual values (Figure 14). The same result generally holds
 768 for the other rate constants (not shown). This result suggests that vertical variations of k_1

769 at a given oceanic location could be detected with high accuracy and precision, provided
 770 that data errors are reduced compared to their present values (Table 3), measurements are
 771 available with good vertical resolution, the ^{230}Th , and small particle sources are known,
 772 and the model provides an accurate description of Th and particle cycling.

773 4.2 Contribution of ^{228}Th , ^{228}Ra , and Particle Data

774 Since this study is primarily motivated by GEOTRACES, it is probably worth clarifying
 775 further the sampling plans for GEOTRACES cruises. The sampling scheme considered
 776 here (section 2.1.1) corresponds only to one adopted at some of the deep stations occupied
 777 during the US GEOTRACES North Atlantic section. It does not apply to all stations
 778 of GEOTRACES sections but only to specific stations occupied during a specific cruise
 779 of this program. Furthermore, among the Th isotopes, only ^{230}Th is a key parameter to
 780 be measured on all GEOTRACES cruises. Thorium-228 would be measured rarely. The
 781 ^{228}Th activities are typically very low at mid-depth in the ocean, implying that a precise
 782 and accurate measurement of this nuclide would be challenging. A similar difficulty applies
 783 to its radioactive parent ^{228}Ra , also not a key parameter of GEOTRACES. Accordingly,
 784 the availability of ^{228}Th and ^{228}Ra data, which is assumed in this study, may be generally
 785 too optimistic. Thorium-234 will be determined on many but not all GEOTRACES
 786 cruises. Finally, the collection of particulate matter by in situ filtration (for Th analysis)
 787 is part of many GEOTRACES cruises but not all. Particle weights for small and large
 788 particles may not be available for many GEOTRACES expeditions.

789 Given these considerations, the contributions of ^{228}Th activity, ^{228}Ra activity, and particle
 790 concentration data to the estimation of rate constants of Th and particle cycling appear
 791 to deserve some discussion. Consider first the contribution of ^{228}Th data. In order to
 792 isolate this contribution, an inversion similar to our reference inversion (section 3.1) is
 793 performed but with the constraint provided by ^{228}Th dramatically reduced. Specifically,
 794 this new inversion assumes a relative error of 5% for all the data, their availability at all
 795 depths, and very small errors for the model equations ($p = 10^{-5}$) except for the ^{228}Th
 796 equations ($p = 1$). Compared to the reference inversion, the precision of the recovered

797 rate parameters deteriorates noticeably except for k_1 (Figure 19). As the error factor for
 798 the ^{228}Th equations is increased from $p = 10^{-5}$ to $p = 1$, the relative precision ($\sigma_{\hat{x}}/\hat{x}$)
 799 of the posterior estimates changes from 0.06 to 0.07 for k_1 , 0.20 to 0.33 for k_{-1} , 0.20 to
 800 0.36 for w , 0.24 to 0.42 for β_{-1} , and 0.24 to 0.43 for β_2 and β_{-2} (all values are averages
 801 for the estimates at the six different depths displayed in Figure 19). Thus, the constraint
 802 provided by ^{228}Th data leads to a notable improvement in the relative precision of the
 803 rate constants, in particular of the rates of remineralization and (dis)aggregation.

804 Consider then the contribution of ^{228}Ra data. This contribution is illustrated from an
 805 inversion similar to the reference inversion except that (i) ^{228}Ra activity data are re-
 806 placed by a constant value and (ii) the error for the dissolved ^{228}Th equation is increased.
 807 Assumptions (i)–(ii) would mimic those made for a location where an estimate of rate
 808 constants is desired but where ^{228}Ra activity data are not available. The ^{228}Ra activity at
 809 each depth is set equal to 2.4 dpm m^{-3} , which is twice the average value between 965 and
 810 4900 m computed according to (2). Hence, the ^{228}Ra activities assumed in the inversion
 811 differ markedly from those used to generate the Th and particle data, an intentionally un-
 812 favourable situation. The error for the $^{228}\text{Th}_d$ equation is set equal to the constant value of
 813 2.4 dpm m^{-3} times the ^{228}Th radioactive decay constant. This assumption acknowledges
 814 that, given the use of a constant ^{228}Ra in the analysis, the error in the $^{228}\text{Th}_d$ equation
 815 can be on the order of the radioactive source in this equation. It is seen that assump-
 816 tions (i)–(ii) reduce to some extent the precision of most of the recovered rate constants
 817 compared to the reference inversion (Figure 20). The results are broadly comparable to
 818 those obtained for the case where the ^{228}Th constraint is reduced (Figure 19), although
 819 the relative precision of the estimated rate constants is better: when assumptions (i)–(ii)
 820 are made, the $\sigma_{\hat{x}}/\hat{x}$ ratio amounts to 0.07 for k_1 , 0.26 for k_{-1} , 0.25 for w , 0.30 for β_{-1} ,
 821 and 0.32 for β_2 and β_{-2} (all values are again averages for the estimates at the six different
 822 depths displayed in Figure 20).

823 Consider finally the contribution of particle concentration data. The contribution of these
 824 data to the estimation of the rate constants could in principle be isolated using the same
 825 approach as for ^{228}Th . However, our attempts to generate an inversion similar to our

reference inversion but with the particle concentration constraints much reduced ($p = 1$ for the particle equations) have failed. We speculate that the lack of convergence of the objective function that occurs in this case is associated with the fact that estimates of all rate constants cannot be simultaneously obtained if the particle concentration constraints are much reduced or absent. Specifically, the rate constants of desorption and remineralization always appear as a sum in the Th equations (1a–1b), whereas in the particle equations (3a–3b) β_{-1} is present but k_{-1} is not. Accordingly, if only Th data are considered to infer the rate constants, the sum $k_{-1} + \beta_{-1}$ could be determined but not the individual values of k_{-1} and β_{-1} .

4.3 Importance of $^{228,230}\text{Th}$ Data in Different Size Fractions

Whereas the activity of the most abundant Th isotope (^{234}Th) would be measured with high accuracy, the activity of the other Th isotopes, in particular in the large particles, would not (Table 3). This state of affairs raises the question of whether ^{228}Th and ^{230}Th errors in all three size fractions are equally important for the estimation of the rate constants of Th and particle cycling.

To address this question, three inversions are performed, which differ from the reference inversion in the following respects. In a first inversion, the relative error in $^{228,230}\text{Th}$ data for the dissolved phase is raised to, respectively, 15% and 20% (Table 3). In a second inversion, the relative error in $^{228,230}\text{Th}$ data for small particles is fixed to the same values. Finally, in a third inversion, the relative error in $^{228,230}\text{Th}$ data for large particles is set equal to 20%. In each of these three inversions, the error for all the other data, the data availability, and the model errors are the same as those assumed in the reference inversion.

We find that, for each of these three inversions, the estimated rate constants differ generally from their actual values by less than two standard deviations (not shown). More relevant to the above question, the relative precision $\sigma_{\hat{x}}/\hat{x}$ varies by ≤ 0.07 for each rate constant between these inversions and the change in $\sigma_{\hat{x}}/\hat{x}$ is not systematic. That is, the presence of relatively high error for a given size fraction worsens the precision of some

853 of the rate constants but improves the precision of others, compared to results obtained
 854 with relatively high error in another fraction. These results suggest that ^{228}Th and ^{230}Th
 855 should be measured with comparable (and high) accuracy in all size fractions if a precise
 856 estimate of all rate constants is sought.

857 4.4 Use of Additional Data

858 As shown by the present analysis, the extent to which measurements of a given property
 859 can constrain sorption and particle processes depends on the uncertainties in these mea-
 860 surements (data errors) as well as on our understanding of the behaviour of this property
 861 in the ocean (model errors). These processes will be completely unresolved if this prop-
 862 erty does not appear in the equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ and if no correlation is introduced in \mathbf{C}_o
 863 between this property and the other components included in \mathbf{x} . If this is not the case,
 864 then knowledge about sorptive reactions and particle dynamics should be increased com-
 865 pared to that obtained from, say, Th and particle data alone. The errors in the posterior
 866 estimates of the rate constants should be even more reduced compared to those in the
 867 prior estimates (e.g., Figure 1), the amount of reduction depending on the data errors
 868 (\mathbf{C}_o), the model errors (\mathbf{C}_f), and the sensitivity of the model equations to the components
 869 of \mathbf{x} (*Tarantola and Valette, 1982a*).

870 Accordingly, this work is limited by the fact that not all types of measurement that may
 871 be available at stations occupied during modern oceanographic programs have been con-
 872 sidered. Other properties may be available and provide additional information about rate
 873 constants of Th and particle cycling, such as the concentration of particulate organic car-
 874 bon (POC), particulate organic nitrogen (PON), calcium carbonate (CaCO_3), biogenic
 875 silica (bSi), and another particle-reactive radio-isotope (protactinium-231). The concen-
 876 tration of Al, P, Ba, Pb, and transition elements (Ti, V, Mn, Fe, Co, Ni, Cu, Zn, and Cd)
 877 on different size fractions could also be measured and be useful to estimate cycling rates.

878 The motive for not including measurements of POC, PON, CaCO_3 , bSi, and ^{231}Pa in
 879 our analysis is not only simplicity. It seems plausible that measurements of POC, PON,

880 CaCO_3 , and bSi are the most likely to provide additional information about the cycling
881 rates, not in the deep, but in the upper ocean (say, at $z < 1000$ m), where these properties
882 tend to show large vertical gradients (e.g., *Lam et al.* (2011)). Besides, the kinetics of
883 exchange with marine particles is even less constrained for Pa than for Th. Several
884 studies have shown that Pa interacts in general less intensively with particles than Th,
885 with exceptions such as MnO_2 precipitates and biogenic opal (e.g., *Anderson et al.* (1983);
886 *Rutgers van der Loeff and Berger* (1993); *Walter et al.* (1997); *Chase et al.* (2002); *Moran*
887 *et al.* (2002); *Geibert and Usbeck* (2004); *Scholten et al.* (2005); *Kretschmer et al.* (2011)).
888 Consequently, the ability of ^{231}Pa activity data to significantly increase knowledge about
889 processes such as particle coagulation and fragmentation over that already gained from
890 Th and particle data does not seem to be obvious.

891 Still other types of data, however, might be used to further constrain sorption and particle
892 processes at stations occupied along transoceanic sections. Whereas sediment traps are
893 typically not deployed along such sections, sediment trap data from compilations (e.g.,
894 *Honjo et al.* (2008)) and local studies (e.g., *Roy-Barman et al.* (2005)) may provide useful
895 constraints on the vertical flux of components such as POC, CaCO_3 , bSi, and Th isotopes
896 in some of the environments that are sampled along these sections. Particularly valuable
897 would be data that would help better understand the relative importance of the trend and
898 transport terms in the Th and particle equations. Better understanding of these terms
899 would allow one to assume relatively small model errors and hence to better constrain the
900 rate constants of Th and particle cycling. Vertical profiles of water density at adjacent
901 stations might be used to estimate the vertical shear of the geostrophic velocity in the
902 direction normal to the line joining the stations. Estimates of absolute velocity might
903 then be obtained, provided that the velocity at some reference level is known or assumed.
904 The product of absolute velocity times the horizontal gradient of Th isotope activity or
905 particle concentration normal to the line could be derived at crossover stations, which
906 would provide an estimate of the advection of Th or particles by the geostrophic flow
907 along this direction. Moreover, measurements of core parameters such as temperature,
908 salinity, dissolved oxygen, and dissolved nutrients could be consulted to identify whether
909 features in the vertical profiles of Th isotope activities and particle concentrations could

910 be associated with deep water masses of distinct origins. Short-lived isotopes such as
 911 ^{223}Ra (half life of 11.4 d) and ^{224}Ra (3.7 d) could be used to trace water transport from
 912 the margins over time scales of several days to weeks.

913 4.5 Appropriateness of Total Inversion

914 The method of total inversion has been applied in several studies aimed at interpreting
 915 Th and particle measurements on oceanic samples (e.g., *Murnane et al.* (1994); *Murnane*
 916 (1994); *Murnane et al.* (1996)). However, the appropriateness of this method to infer rate
 917 constants of trace metal and particle cycling has more recently been challenged (*Athias*
 918 *et al.*, 2000a; *Athias et al.*, 2000b). In particular, *Athias et al.* (2000b) argued that an
 919 approach based on a linearization around an a priori solution and on a gradient descent
 920 method is not adequate, given the complexity of the objective function and our poor a
 921 priori knowledge of the rate parameters. These authors presented results from twin ex-
 922 periments with a model of Al and particle cycling, which suggest that other minimization
 923 methods, such as genetic algorithms, are superior to the algorithm of total inversion for
 924 inferring the rate constants.

925 As acknowledged by *Tarantola and Valette* (1982a), the total inversion algorithm will only
 926 converge in problems where nonlinearity is not too strong. The source of nonlinearity for
 927 the present problem resides in the quadratic terms (products of variables in \mathbf{x}) that are
 928 present in the model equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$. Consequently, the total inversion algorithm
 929 should fail to converge in situations where Th and (or) particle data have relatively large
 930 errors *and* the model equations are imposed relatively strictly. For example, failure to
 931 converge is observed to occur in an inversion where the maximum relative error in the
 932 data is raised to 50% (so the relative errors take on the values in Table 3 for all data),
 933 the data are assumed to be available at all depths, and the model equations are assumed
 934 to be exact ($\mathbf{C}_f = \mathbf{0}$). On the other hand, this inversion does converge if even modest
 935 model errors are taken into consideration ($p = 0.1$). This example demonstrates that
 936 the performance of the total inversion algorithm depends on the specific data and model
 937 errors that are assumed by the investigator.

938 Accordingly, the total inversion algorithm may not be a generally applicable method to
 939 provide estimates of the cycling rates of trace metals and particles in the ocean. Alterna-
 940 tive methods to provide such estimates, such as explored by *Athias et al.* (2000b), may
 941 be more universally applicable. On the other hand, the algorithm of total inversion has
 942 features that tend to make it attractive compared to other methods used to solve mini-
 943 mization problems, e.g., it can provide a formal estimate of the error in the solution and
 944 it does not require the prescription of parameters besides a criterion for convergence. The
 945 interpretation of posterior errors in the solution, however, is not always straightforward,
 946 as discussed below.

947 4.6 Interpretation of Error Estimates

948 The error estimates for the rate constants that are obtained by generalized least-squares
 949 are only approximate and do not all have a straightforward interpretation. First, the
 950 model equations $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ are always imposed (in the mean square) in our inversions (if
 951 $\mathbf{f}(\mathbf{x}) = \mathbf{0}$ were not imposed, the problem would have the trivial solution $\mathbf{x} = \mathbf{x}_o$). This
 952 implies that nonlinearity is always present and that the error covariance matrix for the
 953 solution, which is obtained using the formula for the linear case, is always approximate
 954 (*Tarantola and Valette*, 1982a). On the other hand, all solutions reported in this paper
 955 are convergent, which suggests that nonlinearity is relatively weak and that the posterior
 956 variances of the rate ‘constants’, which these solutions provide, are useful estimates.

957 Second, the method of total inversion as applied here provides estimates of the standard
 958 deviation of the logarithm of the rate constants, not of their actual values. Although
 959 formula (8) allows posterior errors to be calculated, it assumes that the values obtained
 960 by inversion are the medians of normal distributions, which is not necessarily correct.
 961 Furthermore, the variance of a lognormal distribution determines not only the dispersion
 962 but also higher moments of the distribution such as skewness (*Aitchison and Brown*,
 963 1957), in particular for variables with large spread around the mean (large variance).
 964 Accordingly, the large posterior errors for some of the rate constants that are estimated
 965 by inversion are relatively difficult to interpret. This is particularly the case for the rates

966 of aggregation and disaggregation, which are among the parameters that are the most
967 difficult to constrain from Th and particle data.

968 5 CONCLUSIONS

969 The rates at which particles are decomposed, settle, and (dis)aggregate in the ocean are of
970 paramount importance from a geochemical viewpoint. However, they also are very difficult
971 to estimate. A common approach to estimate these rates relies on measurements of
972 particle-reactive elements, in particular Th radio-isotopes, on samples collected by bottles,
973 in situ pumps, and sediment traps. Ongoing and future programs such as GEOTRACES
974 are providing an unprecedented opportunity to estimate particle processes in a variety of
975 oceanic settings. Whereas sediment traps are typically not deployed during large-scale
976 sampling programs that are section-based, large volumes of water can now be collected
977 over the entire water column during these programs. This sampling permits to document,
978 at the same station, the vertical distribution of the activity of several Th isotopes and
979 the vertical distribution of the concentration of particles, in different size fractions. The
980 extent to which this unique set of observations could constrain the rates of Th and particle
981 cycling in the ocean emerges as a question of preeminent interest.

982 Our study suggests that the data set gathered during modern sampling programs should
983 improve very significantly our present understanding of the rates of Th and particle cy-
984 cling in the deep sea. With current estimates of data uncertainties and plausible estimates
985 of the uncertainty in Th and particle governing equations, the relative precision of rates
986 of particle processes such as aggregation and disaggregation could be largely improved,
987 sometimes by one order of magnitude, over that of prior estimates. On the other hand, es-
988 timates of cycling rates that are both precise and accurate would remain difficult to obtain,
989 unless a significant effort is made to reduce the data uncertainties and the assumption of
990 small model errors is justified. Accurate and precise estimates could be derived when (i)
991 all the data have a relative error of less than 20%, (ii) vertical sampling is dense enough
992 to resolve activity and concentration gradients, and (iii) model errors are negligible. In

993 the favourable situation where (ii)–(iii) would hold, reducing the uncertainties in mea-
994 surements of ^{228}Th and ^{230}Th activities and in particle concentrations from a maximum
995 of 20% to a value of 5% would lead to a dramatic improvement in the estimates of the rate
996 constants, in particular for Th desorption, particle sinking, and particle (dis)aggregation.

997 Overall, our study suggests that (i) analytical improvements should be prioritized on
998 the measurement of ^{228}Th , ^{230}Th , and particle concentrations and (ii) Th and particle
999 cycling rates should be estimated at locations where model assumptions are valid or
1000 where knowledge about temporal variability and transport processes is available. Accurate
1001 measurements of ^{228}Th and ^{230}Th in all size fractions would be needed for a precise
1002 estimation of all rate constants. Accurate measurements of ^{230}Th in large particles at only
1003 two depths should provide an important constraint on the particle sinking speed. Good
1004 candidates for the above locations include crossover stations away from ocean margins
1005 and where time series of oceanographic observations are available.

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References

- 1016
- 1017 Aitchison, J., and J. A. C. Brown. *The lognormal distribution (with special reference to*
1018 *its uses in economics)*. Cambridge University Press, 1957. 176 pp.
- 1019 Anderson, R. F., M. P. Bacon, and P. G. Brewer, Removal of ^{230}Th and ^{231}Pa at ocean
1020 margins, *Earth Planet. Sci. Lett.*, *66*, 73–90, 1983.
- 1021 Athias, V., P. Mazzega, and C. Jeandel. Nonlinear inversions of a model of the oceanic
1022 dissolved-particulate exchanges, P. Kasibhatla, M. Heimann, P. Rayner, N. Mahowald,
1023 R. G. Prinn, and D. E. Hartley (Eds.), *Inverse methods in global biogeochemical cycles*,
1024 Volume 114 of *Geophysical Monograph*, pp. 205–222. Am. Geophys. Union, 2000a.
- 1025 Athias, V., P. Mazzega, and C. Jeandel, Selecting a global optimization method to
1026 estimate the oceanic particle cycling rate constants, *J. Marine Res.*, *58*, 675–707, 2000b.
- 1027 Bacon, M. P., and R. F. Anderson, Distribution of thorium isotopes between dissolved
1028 and particulate forms in the deep sea, *J. Geophys. Res.*, *87*, 2045–2056, 1982.
- 1029 Bacon, M. P., C.-A. Huh, A. P. Fleer, and W. G. Deuser, Seasonality in the flux of
1030 natural radionuclides and plutonium in the deep Sargasso Sea, *Deep Sea Res.*, *32*, 273–
1031 286, 1985.
- 1032 Bacon, M. P., C.-A. Huh, and R. M. Moore, Vertical profiles of some natural radionu-
1033 clides over the Alpha Ridge, Arctic Ocean, *Earth Planet. Sci. Lett.*, *95*, 15–22, 1989.
- 1034 Bacon, M. P., and M. M. Rutgers van der Loeff, Removal of thorium-234 by scavenging
1035 in the bottom nepheloid layer of the ocean, *Earth Planet. Sci. Lett.*, *92*, 157–164, 1989.
- 1036 Balistrieri, L. S., and J. W. Murray, The surface chemistry of sediments from the Panama
1037 Basin: The influence of Mn oxides on metal adsorption, *Geochim. Cosmochim. Acta*, *50*,
1038 2235–2243, 1986.
- 1039 Berelson, W. M., Particle settling rates increase with depth in the ocean, *Deep Sea Res.*
1040 *II*, *49*, 237–251, 2002.

- 1041 Boyd, P. W., and T. W. Trull, Understanding the export of biogenic particles in oceanic
1042 waters: Is there a concensus?, *Prog. Oceanogr.*, *72*, 276–312, 2007.
- 1043 Brewer, P. G., Y. Nozaki, D. W. Spencer, and A. P. Fler, Sediment trap experiments
1044 in the deep North Atlantic: Isotopic and elemental fluxes, *J. Marine Res.*, *38*, 703–728,
1045 1980.
- 1046 Broecker, W. S., and T.-H. Peng. *Tracers in the Sea*. Lamont-Doherty Geological
1047 Observatory, Palisades, NY: Eldigio Press, 1982.
- 1048 Buesseler, K. O., C. Lamborg, P. Cai, R. Escoube, R. Johnson, S. Pike, P. Masque,
1049 D. McGillicuddy, and E. Verdeny, Particle fluxes associated with mesoscale eddies in the
1050 Sargasso Sea, *Deep Sea Res. II*, *55*, 1426–1444, 2008.
- 1051 Burd, A. B., and G. A. Jackson, Particle aggregation, *Annu. Rev. Marine Sci.*, *1*, 65–90,
1052 2009.
- 1053 Chase, Z., R. F. Anderson, M. Q. Fleisher, and P. W. Kubik, The influence of particle
1054 composition and particle flux on the scavenging of Th, Pa and Be in the ocean, *Earth
1055 Planet. Sci. Lett.*, *204*, 215–229, 2002.
- 1056 Chen, J. H., R. L. Edwards, and G. J. Wasserburg, ^{238}U , ^{234}U and ^{232}Th in seawater,
1057 *Earth Planet. Sci. Lett.*, *80*, 241–251, 1986.
- 1058 Cheng, H., R. L. Edwards, J. Hoff, C. D. Gallup, D. A. Richards, and Y. Asmerom, The
1059 half-lives of uranium-234 and thorium-230, *Chem. Geol.*, *169*, 17–33, 2000.
- 1060 Clegg, S. L., M. P. Bacon, and M. Whitfield, Application of a generalized scavenging
1061 model to thorium isotope and particle data at equatorial and high-latitude sites in the
1062 Pacific Ocean, *J. Geophys. Res.*, *96*, 20655–20670, 1991.
- 1063 Clegg, S. L., and M. Whitfield, A generalized model for the scavenging of trace metals
1064 in the open ocean-I. Particle cycling, *Deep Sea Res.*, *37*, 809–832, 1990.
- 1065 Clegg, S. L., and M. Whitfield, A generalized model for the scavenging of trace metals
1066 in the open ocean-II. Thorium scavenging, *Deep Sea Res.*, *38*, 91–120, 1991.

- 1067 Cochran, J. K., K. O. Buesseler, M. P. Bacon, and H. D. Livingston, Thorium isotopes
1068 as indicators of particle dynamics in the upper ocean: Results from the JGOFS North
1069 Atlantic Bloom Experiment, *Deep Sea Res.*, *40*, 1569–1595, 1993.
- 1070 Cochran, J. K., K. O. Buesseler, M. P. Bacon, H. W. Wang, D. J. Hirschberg, L. Ball,
1071 J. Andrews, G. Crossin, and A. P. Fler, Short-lived thorium isotopes (^{234}Th , ^{228}Th) as
1072 indicators of POC export and particle cycling in the Ross Sea, Southern Ocean, *Deep*
1073 *Sea Res.*, *47*, 3451–3490, 2000.
- 1074 Cochran, J. K., H. D. Livingston, D. J. Hirschberg, and L. D. Surprenant, Natural
1075 and anthropogenic radionuclide distributions in the northwestern Atlantic Ocean, *Earth*
1076 *Planet. Sci. Lett.*, *84*, 135–152, 1987.
- 1077 Fischer, G., and G. Karakaş, Sinking rates and ballast composition of particles in the
1078 Atlantic Ocean: Implications for the organic carbon fluxes to the deep ocean, *Biogeo-*
1079 *sciences*, *6*, 85–102, 2009.
- 1080 Geibert, W., and R. Usbeck, Adsorption of thorium and protactinium onto different
1081 particle types: Experimental findings, *Geochim. Cosmochim. Acta*, *68*, 1489–1501, 2004.
- 1082 GEOTRACES, 2006. An international study of the marine biogeochemical cycles of trace
1083 elements and their isotopes. Science plan, Scientific Committee on Oceanic Research,
1084 International Council for Science.
- 1085 Hirose, K., T. Saito, S. H. Lee, and J. Gastaud, Vertical distributions of the strong
1086 organic ligand in the twilight zone of Southern Hemisphere Ocean particulate matter,
1087 *Prog. Oceanogr.*, *89*, 108–119, 2011.
- 1088 Honjo, S., S. J. Manganini, R. A. Krishfield, and R. François, Particulate organic carbon
1089 fluxes to the ocean interior and factors controlling the biological pump: A synthesis of
1090 global sediment trap programs since 1983, *Prog. Oceanogr.*, *76*, 217–285, 2008.
- 1091 Inthorn, M., M. Rutgers van der Loeff, and M. Zabel, A study of particle exchange
1092 at the sediment-water interface in the Bengulea upwelling area based on $^{234}\text{Th}/^{238}\text{U}$
1093 disequilibrium, *Deep Sea Res. I*, *53*, 1742–1761, 2006.

- 1094 Key, R. M., J. L. Sarmiento, and W. S. Moore, 1992. Transient Tracers in the Ocean
1095 North Atlantic Study, Final Data Report for ^{228}Ra and ^{226}Ra . Technical report, 92-2,
1096 Ocean Tracer Lab. Princeton University, Princeton, N. J.
- 1097 Kretschmer, S., W. Geibert, M. M. Rutgers van der Loeff, C. Schnabel, S. Xu, and
1098 G. Mollenhauer, Fractionation of ^{230}Th , ^{231}Pa , and ^{10}Be induced by particle size and
1099 composition within an opal-rich sediment of the Atlantic Southern Ocean, *Geochim.*
1100 *Cosmochim. Acta*, *75*, 6971–6987, 2011.
- 1101 Lam, P. J., S. C. Doney, and J. K. B. Bishop, The dynamic ocean biological pump:
1102 Insights from a global compilation of particulate organic carbon, CaCO_3 , and opal
1103 concentration profiles from the mesopelagic, *Global Biogeochem. Cycles*, *25*, GB3009,
1104 doi:10.1029/2010GB003868, 2011.
- 1105 Lepore, K., and S. B. Moran, Seasonal changes in thorium scavenging and particle
1106 aggregation in the western Arctic Ocean, *Deep Sea Res.*, *54*, 919–938, 2007.
- 1107 Liebelt, P. B. *An introduction to optimal estimation*. Addison-Wesley, Reading, MA,
1108 1967. 273 pp.
- 1109 Lohrenz, S. E., G. A. Knauer, V. L. Asper, M. Tuel, A. F. Michaels, and A. H. Knap,
1110 Seasonal variability in primary production and particle flux in the northwestern Sargasso
1111 Sea: U.S. JGOFS Bermuda Atlantic Time-series Study, *Deep Sea Res.*, *39*, 1373–1391,
1112 1992.
- 1113 Marchal, O., R. François, and J. Scholten, Contribution of ^{230}Th measurements to the
1114 estimation of the abyssal circulation, *Deep Sea Res.*, *54*, 557–585, 2007.
- 1115 McCave, I. N., Local and global aspects of the bottom nepheloid layers in the world
1116 ocean, *Neth. J. Sea Res.*, *20*, 167–181, 1986.
- 1117 McDonnell, A., and K. Buesseler, Variability in the average sinking velocity of marine
1118 particles, *Limnol. Oceanogr.*, *55*, 2085–2096, 2010.

- 1119 Moran, S. B., M. A. Charette, J. A. Hoff, R. L. Edwards, and W. M. Landing, Distri-
1120 bution of ^{230}Th in the Labrador Sea and its relation to ventilation, *Earth Planet. Sci.*
1121 *Lett.*, *150*, 151–160, 1997.
- 1122 Moran, S. B., C.-C. Shen, H. N. Edmonds, S. E. Weinstein, J. N. Smith, and R. L.
1123 Edwards, Dissolved and particulate ^{231}Pa and ^{230}Th in the Atlantic Ocean: Constraints
1124 on intermediate/deep water age, boundary scavenging, and $^{231}\text{Pa}/^{230}\text{Th}$ fractionation,
1125 *Earth Planet. Sci. Lett.*, *203*, 999–1014, 2002.
- 1126 Murnane, R. J., Determination of thorium and particulate matter cycling parameters at
1127 station P: A reanalysis and comparison of least squares techniques, *J. Geophys. Res.*, *99*,
1128 3393–3405, 1994.
- 1129 Murnane, R. J., J. K. Cochran, K. O. Buesseler, and M. P. Bacon, Least-squares esti-
1130 mates of thorium, particle, and nutrient cycling rate constants from the JGOFS North
1131 Atlantic Bloom Experiment, *Deep Sea Res.*, *43*, 239–258, 1996.
- 1132 Murnane, R. J., J. K. Cochran, and J. L. Sarmiento, Estimates of particle- and thorium-
1133 cycling rates in the northwest Atlantic Ocean, *J. Geophys. Res.*, *99*, 3373–3392, 1994.
- 1134 Murnane, R. J., J. L. Sarmiento, and M. P. Bacon, Thorium isotopes, particle cycling
1135 models, and inverse calculations of model rate constants, *J. Geophys. Res.*, *95*, 16,195–
1136 16,206, 1990.
- 1137 Nozaki, Y., Y. Horibe, and H. Tsubota, The water column distributions of thorium
1138 isotopes in the western North Pacific, *Earth Planet. Sci. Lett.*, *54*, 203–216, 1981.
- 1139 Nozaki, Y., H.-S. Yang, and M. Yamada, Scavenging of thorium in the ocean, *J. Geophys.*
1140 *Res.*, *92*, 772–778, 1987.
- 1141 Owens, S. A., K. O. Buesseler, and K. W. W. Sims, Re-evaluating the ^{238}U –salinity
1142 relationship in seawater: Implications for the ^{238}U – ^{234}Th disequilibrium method, *Mar.*
1143 *Chem.*, *127*, 31–39, 2011.

- 1144 Robinson, L. F., N. S. Belshaw, and G. M. Henderson, U and Th concentrations and
1145 isotope ratios in modern carbonates and waters from the Bahamas Bank, *Geochim.*
1146 *Cosmochim. Acta*, *68*, 1777–1789, 2004.
- 1147 Roy-Barman, M., J. H. Chen, and G. J. Wasserburg, ^{230}Th – ^{232}Th systematics in the
1148 central Pacific Ocean: The sources and fates of thorium, *Earth Planet. Sci. Lett.*, *139*,
1149 351–363, 1996.
- 1150 Roy-Barman, M., C. Jeandel, M. Souhaut, M. Rutgers van der Loeff, I. Voege,
1151 N. LeBlond, and R. Freydier, The influence of particle composition on thorium scav-
1152 enging in the NE Atlantic ocean (POMME experiment), *Earth Planet. Sci. Lett.*, *240*,
1153 681–693, 2005.
- 1154 Rutgers van der Loeff, M. M., and G. W. Berger, Scavenging of ^{230}Th and ^{231}Pa near
1155 the Antarctic Polar Front in the South Atlantic, *Deep Sea Res. I*, *40*, 339–357, 1993.
- 1156 Rutgers van der Loeff, M. M., R. Meyer, B. Rudels, and E. Rachor, Resuspension and
1157 particle transport in the benthic nepheloid layer and near Fram Strait in relation to
1158 faunal abundances and ^{234}Th depletion, *Deep Sea Res. I*, *49*, 1941–1958, 2002.
- 1159 Scholten, J. C., J. Fietzke, A. Mangini, P. Stoffers, T. Rixen, B. Gaye-Haake, T. Blanz,
1160 V. Ramaswamy, F. Sirocko, H. Schulz, and V. Ittekkot, Radionuclide fluxes in the Arabian
1161 Sea: The role of particle composition, *Earth Planet. Sci. Lett.*, *230*, 319–337, 2005.
- 1162 Sweeney, E. N., D. J. McGillicuddy, and K. O. Buesseler, Biogeochemical impacts due
1163 to mesoscale eddy activity in the Sargasso Sea as measured at the Bermuda Atlantic
1164 Time-series Study (BATS), *Deep Sea Res. II*, *50*, 3017–3039, 2003.
- 1165 Tarantola, A., and B. Valette, Generalized nonlinear inverse problem solved using the
1166 least squares criterion, *Rev. Geophys. Space Phys.*, *20*, 219–232, 1982a.
- 1167 Tarantola, A., and B. Valette, Inverse problem = quest for information, *J. Geophys.*, *50*,
1168 159–170, 1982b.
- 1169 Turnewitsch, R., and B. M. Springer, Do bottom mixed layers influence ^{234}Th dynamics
1170 in the abyssal near-bottom water column?, *Deep Sea Res.*, *48*, 1279–1307, 2001.

- 1171 Venchiarutti, C., C. Jeandel, and M. Roy-Barman, Particle dynamics study in the wake
1172 of Kerguelen Island using thorium isotopes, *Deep Sea Res. I*, *55*, 1343–1363, 2008.
- 1173 Venchiarutti, C., M. Rutgers van der Loeff, and I. Stimac, Scavenging of ^{231}Pa and
1174 thorium isotopes based on dissolved and size-fractionated particulate distributions at
1175 Drake Passage (ANTXXIV-3), *Deep Sea Res. II*, *58*, 2767–2784, 2011.
- 1176 Vogler, S., J. Scholten, M. Rutgers van der Loeff, and A. Mangini, ^{230}Th in the eastern
1177 North Atlantic: the importance of water mass ventilation in the balance of ^{230}Th , *Earth*
1178 *Planet. Sci. Lett.*, *156*, 61–74, 1998.
- 1179 Walter, H. J., M. M. Rutgers van der Loeff, and H. Hoeltzen, Enhanced scavenging
1180 of ^{231}Pa relative to ^{230}Th in the South Atlantic south of the Polar Front: Implications
1181 for the use of the $^{231}\text{Pa}/^{230}\text{Th}$ ratio as a paleoproductivity proxy, *Earth Planet. Sci.*
1182 *Lett.*, *149*, 85–100, 1997.

Table 1. $^{228,230,234}\text{Th}$ half-lives and parent activities

1183

| | Half-life ^a | Parent | Parent activity ^b |
|-------------------|------------------------|-------------------|---------------------------------------|
| ^{228}Th | 1.91 yr | ^{228}Ra | variable |
| ^{230}Th | 75.69×10^3 yr | ^{234}U | 2.7×10^3 dpm m ⁻³ |
| ^{234}Th | 24.1 d | ^{238}U | 2.4×10^3 dpm m ⁻³ |

1184

^a The ^{228}Th and ^{234}Th half-lives are from *Broecker and Peng* (1982). The ^{230}Th half-life is from *Cheng et al.* (2000)

^b The ^{238}U activity is based on an empirical relationship with salinity (*Owens et al.*, 2011) assuming a salinity of 35. The ^{234}U activity is derived from the resulting ^{238}U activity value and a seawater $^{234}\text{U}/^{238}\text{U}$ ratio of 1.14 (*Chen et al.*, 1986; *Robinson et al.*, 2004).

Table 2. Rate constants of thorium and particle cycling

1190

| Symbol | Definition | Model Value ^a | Prior Estimate ^a | Relative Error ^b |
|--------------|-----------------------|--------------------------|-----------------------------|-----------------------------|
| k_1 | Adsorption rate | 0.5 | 5 | 1 |
| k_{-1} | Desorption rate | 2 | 5 | 1 |
| w | Sinking rate | 150 | 300 | 0.5 |
| β_{-1} | Remineralization rate | 1 | 10 | 5 |
| β_2 | Aggregation rate | 3 | 10 | 10 |
| β_{-2} | Disaggregation rate | 150 | 500 | 10 |

1191

^a All values are in y^{-1} , except for w that is in m d^{-1}

^b The relative error pertains to the prior estimate

1193

Table 3. Relative errors in measurement of $^{228,230,234}\text{Th}$ and particle concentration†

1194

| | Definition | Relative error |
|---------------------|---|----------------|
| $^{228}\text{Th}_d$ | ^{228}Th activity in dissolved phase | ± 0.15 |
| $^{228}\text{Th}_s$ | ^{228}Th activity in small particles | ± 0.15 |
| $^{228}\text{Th}_l$ | ^{228}Th activity in large particles | ± 0.50 |
| $^{230}\text{Th}_d$ | ^{230}Th activity in dissolved phase | ± 0.20 |
| $^{230}\text{Th}_s$ | ^{230}Th activity in small particles | ± 0.20 |
| $^{230}\text{Th}_l$ | ^{230}Th activity in large particles | ± 0.50 |
| $^{234}\text{Th}_d$ | ^{234}Th activity in dissolved phase | ± 0.05 |
| $^{234}\text{Th}_s$ | ^{234}Th activity in small particles | ± 0.05 |
| $^{234}\text{Th}_l$ | ^{234}Th activity in large particles | ± 0.05 |
| P_s | Concentration of small particles | ± 0.20 |
| P_l | Concentration of large particles | ± 0.20 |

1195

1196 †Note our reference inversion assumes a relative error of 5% for all measurements

1197 Figure 1: Published estimates of rate constants of (1) thorium adsorption (k_1) and desorp-
 1198 tion (k_{-1}) and (2) particle remineralization (β_{-1}), aggregation (β_2), and disaggregation
 1199 (β_{-2}). The numbers along the lower horizontal axis are 0 for *Nozaki et al.* (1987), 1
 1200 for *Bacon et al.* (1989), 2 for *Bacon and Anderson* (1982), 3 for *Nozaki et al.* (1981), 4
 1201 for *Clegg et al.* (1991), 5 for *Clegg and Whitfield* (1991), 6 for *Murnane et al.* (1990),
 1202 7 for *Murnane et al.* (1994), 8 for *Murnane* (1994), and 9 for *Murnane et al.* (1996).
 1203 The plotted values are those compiled by *Murnane et al.* (1994) and *Murnane* (1994)
 1204 (cf. Table 1 of these two papers) as well as those obtained in these two studies and by
 1205 *Murnane et al.* (1996). They include (i) point estimates with errors (solid circles with
 1206 vertical bars), (ii) ranges, and (iii) point estimates without error (solid circles alone). The
 1207 error bars in contact with the lower horizontal axis reach negative values and cannot be
 1208 shown on a logarithmic scale. Some of the intervals (ranges) reported in the compilations
 1209 or original publications are open, implying a larger error than it appears on the figure.
 1210 Note that not all published estimates are shown to avoid congestion of the figure.

1211 Figure 2: Schematic diagram of the cycling of trace metals (top) and particles (bottom)
 1212 in the ocean aphotic zone. Metal activity is partitioned between the dissolved phase (A_d),
 1213 the small particles (A_s) and the large particles (A_l). Particle concentration is partitioned
 1214 between the small particles (P_s) and the large particles (P_l). The processes affecting
 1215 metal activity and particle concentration in these different forms are the production by
 1216 the radioactive parent (A_p), the radioactive decay (at a specific rate λ), the adsorption
 1217 onto small particles (k_1), the desorption from small particles (k_{-1}), the remineralization
 1218 of small particles (β_{-1}), the aggregation of small particles (β_2), the disaggregation of large
 1219 particles (β_{-2}), and the sinking of large particles (with velocity w).

1220 Figure 3: Vertical profiles of ^{228}Th activity in the dissolved phase (upper horizontal axis),
 1221 the small particles (middle axis), and the large particles (lower axis). The ^{228}Th activities
 1222 that are obtained from the analytical (numerical) solution of the model are shown by
 1223 solid (dashed) lines. The two lines are barely distinguishable. The ^{228}Th activities at
 1224 sampling depths, which are used to produce the idealized data for the inversions, are
 1225 shown by circles: open circles for the dissolved phase, small solid circles for the small

1226 particles, and large solid circles for the large particles. The horizontal bars show the
1227 errors in these activities. These activities are shown only at some of the pumping depths
1228 at GEOTRACES NA deep stations.

1229 Figure 4: Same as Figure 3 but for ^{230}Th .

1230 Figure 5: Same as Figure 3 but for ^{234}Th .

1231 Figure 6: Same as Figure 3 but for the concentration of particles. The concentration of
1232 small (large) particles is shown by small (large) circles.

1233 Figure 7: Rate constants of Th and particle cycling estimated with varying data errors.
1234 The vertical solid lines indicate the values used to generate Th and particle data. The
1235 vertical dashed lines indicate the prior estimates assumed in the inversions. The solid
1236 circles with horizontal bars show the means with their errors estimated in an inversion
1237 where data have a relative error of 5% (reference inversion). The open circles (crosses)
1238 with horizontal bars show the means (medians) with their errors estimated in an inversion
1239 where data have a relative error of $\leq 20\%$. In both inversions, data are available at all
1240 depths and model errors are assumed to be very small ($p = 10^{-5}$). The rate constants
1241 estimated by inversion are shown at six of the pumping depths at GEOTRACES NA deep
1242 stations.

1243 Figure 8: Effect of maximum data error on the accuracy of the rate constants of Th
1244 and particle cycling estimated by inversion. The accuracy is measured by the difference
1245 between the estimated value and the actual value, divided by the actual value.

1246 Figure 9: Effect of maximum data error on the precision of the rate constants of Th and
1247 particle cycling estimated by inversion. The precision is measured by the ratio between
1248 the standard deviation of the estimated value and the estimated value.

1249 Figure 10: Rate constants of Th and particle cycling estimated with varying model errors.
1250 The vertical solid lines indicate the values used to generate Th and particle data. The
1251 vertical dashed lines indicate the prior estimates assumed in the inversions. The solid
1252 circles with horizontal bars show the means with their errors estimated in an inversion

1253 where $p = 0.1$. The open circles with horizontal bars (crosses) show the means (medians)
1254 with their errors estimated in an inversion where $p = 1$. In both inversions, the data have
1255 no error and are available at all depths. The rate constants estimated by inversion are
1256 shown at six of the pumping depths at GEOTRACES NA deep stations.

1257 Figure 11: Rate constants of Th and particle cycling estimated with varying sampling
1258 schemes. The vertical solid lines indicate the values used to generate Th and particle
1259 data. The vertical dashed lines indicate the prior estimates assumed in the inversions.
1260 The solid circles with horizontal bars show the means with their errors estimated in an
1261 inversion where data are available at all depths. The open circles (crosses) with horizontal
1262 bars show the means (medians) with their errors estimated in an inversion where data are
1263 interpolated or extrapolated. In both inversions, the data have no error (except in the
1264 second inversion where extrapolated values have a relative error of 1) and the factor for
1265 model errors $p = 0.01$. The rate constants estimated by inversion are shown at six of the
1266 pumping depths at GEOTRACES NA deep stations.

1267 Figure 12: Rate constants of Th and particle cycling estimated in the presence of data
1268 errors, model errors, and limited sampling. The vertical solid lines indicate the values
1269 used to generate Th and particle data. The vertical (horizontal) dashed lines indicate
1270 the prior estimates (their errors) assumed in the inversions. The open circles (crosses)
1271 with horizontal bars show the means (medians) and their errors estimated in an inversion
1272 where (i) the errors and depths of the measurements would be those at GEOTRACES
1273 NA deep stations and (ii) the factor for model errors $p = 1$. The rate constants estimated
1274 by inversion are shown at six of the pumping depths at these stations.

1275 Figure 13: Cumulative distribution function (CDF) of the relative precision of the rate
1276 constants of Th and particle cycling, which are estimated in the presence of data errors,
1277 model errors, and limited sampling. The relative precision is the standard deviation of
1278 the rate constant divided by the value of the rate constant. The dashed (solid) line is the
1279 CDF for the prior (posterior) estimates. Also shown is the CDF of the difference between
1280 the estimated and actual value, divided by the standard deviation of the estimated value
1281 (dotted line). Note that the CDFs for the posterior estimates are based on values at all

1282 depths of the model grid.

1283 Figure 14: Recovery of vertical variations in the rate constant of Th adsorption. The
 1284 solid line indicates values used to generate Th and particle data. The solid circles with
 1285 horizontal bars show the means with their errors estimated in an inversion where the data
 1286 have a relative error of 5%, they are available at all depths, and model errors are very
 1287 small ($p = 10^{-5}$). Note that the values estimated by inversion are shown only at some of
 1288 the pumping depths at GEOTRACES NA deep stations.

1289 Figure 15: Vertical profiles of ^{228}Th activity in the dissolved phase (upper horizontal axis),
 1290 the small particles (middle axis), and the large particles (lower axis). The ^{228}Th activities
 1291 that are obtained by numerical solution with uniform (variable) rate of Th adsorption
 1292 are shown by dashed (solid) lines (left most lines for large particles, middle lines for the
 1293 dissolved phase, and right most lines for small particles).

1294 Figure 16: Same as Figure 15 but for ^{230}Th (left most lines for large particles, middle
 1295 lines for small particles, and right most lines for the dissolved phase).

1296 Figure 17: Same as Figure 15 but for ^{234}Th (left most lines for large particles, middle
 1297 lines for small particles, and right most lines for the dissolved phase).

1298 Figure 18: Same as Figure 15 but for the concentration of particles (left lines for large
 1299 particles and right lines for small particles).

1300 Figure 19: Rate constants of Th and particle cycling estimated with varying errors in
 1301 the ^{228}Th equations. The vertical solid lines indicate the values used to generate Th and
 1302 particle data. The vertical dashed lines indicate the prior estimates of the rate constants
 1303 assumed in the inversions. The solid circles with horizontal bars show the means with their
 1304 errors estimated in the reference inversion. The open circles (crosses) with horizontal bars
 1305 show the means (medians) with their errors estimated in an inversion with a relatively
 1306 large error for the ^{228}Th equations ($p = 1$). In both inversions, the data have a relative
 1307 error of 5% and are available at all depths. The rate constants estimated by inversion are
 1308 shown at six of the pumping depths at GEOTRACES NA deep stations.

1309 Figure 20: Rate constants of Th and particle cycling estimated with or without local ^{228}Ra
1310 data. The vertical solid lines indicate the values used to generate Th and particle data.
1311 The vertical dashed lines indicate the prior estimates assumed in the inversions. The solid
1312 circles with horizontal bars show the means with their errors estimated in the reference
1313 inversion. The open circles (crosses) with horizontal bars show the means (medians) with
1314 their errors estimated in an inversion where (i) ^{228}Ra activity is fixed to 2.4 dpm m^{-3} at
1315 all depths and (ii) the error in the $^{228}\text{Th}_d$ equation is set equal to this value times the
1316 ^{228}Th radioactive decay constant. The rate constants estimated by inversion are shown
1317 at six of the pumping depths at GEOTRACES NA deep stations.

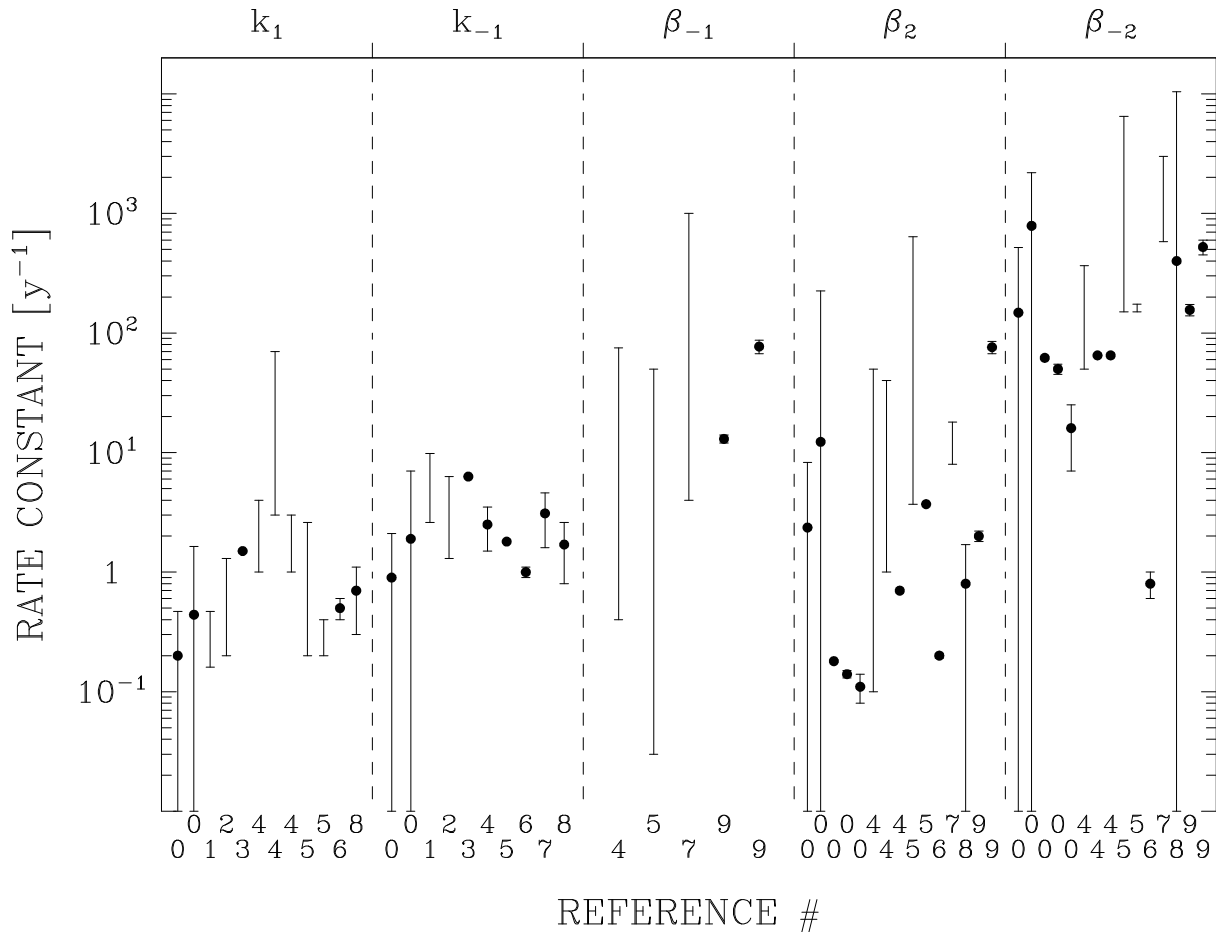


Figure 1: Published estimates of rate constants of (1) thorium adsorption (k_1) and desorption (k_{-1}) and (2) particle remineralization (β_{-1}), aggregation (β_2), and disaggregation (β_{-2}). The numbers along the lower horizontal axis are 0 for *Nozaki et al.* (1987), 1 for *Bacon et al.* (1989), 2 for *Bacon and Anderson* (1982), 3 for *Nozaki et al.* (1981), 4 for *Clegg et al.* (1991), 5 for *Clegg and Whitfield* (1991), 6 for *Murnane et al.* (1990), 7 for *Murnane et al.* (1994), 8 for *Murnane* (1994), and 9 for *Murnane et al.* (1996). The plotted values are those compiled by *Murnane et al.* (1994) and *Murnane* (1994) (cf. Table 1 of these two papers) as well as those obtained in these two studies and by *Murnane et al.* (1996). They include (i) point estimates with errors (solid circles with vertical bars), (ii) ranges, and (iii) point estimates without error (solid circles alone). The error bars in contact with the lower horizontal axis reach negative values and cannot be shown on a logarithmic scale. Some of the intervals (ranges) reported in the compilations or original publications are open, implying a larger error than it appears on the figure. Note that not all published estimates are shown to avoid congestion of the figure.

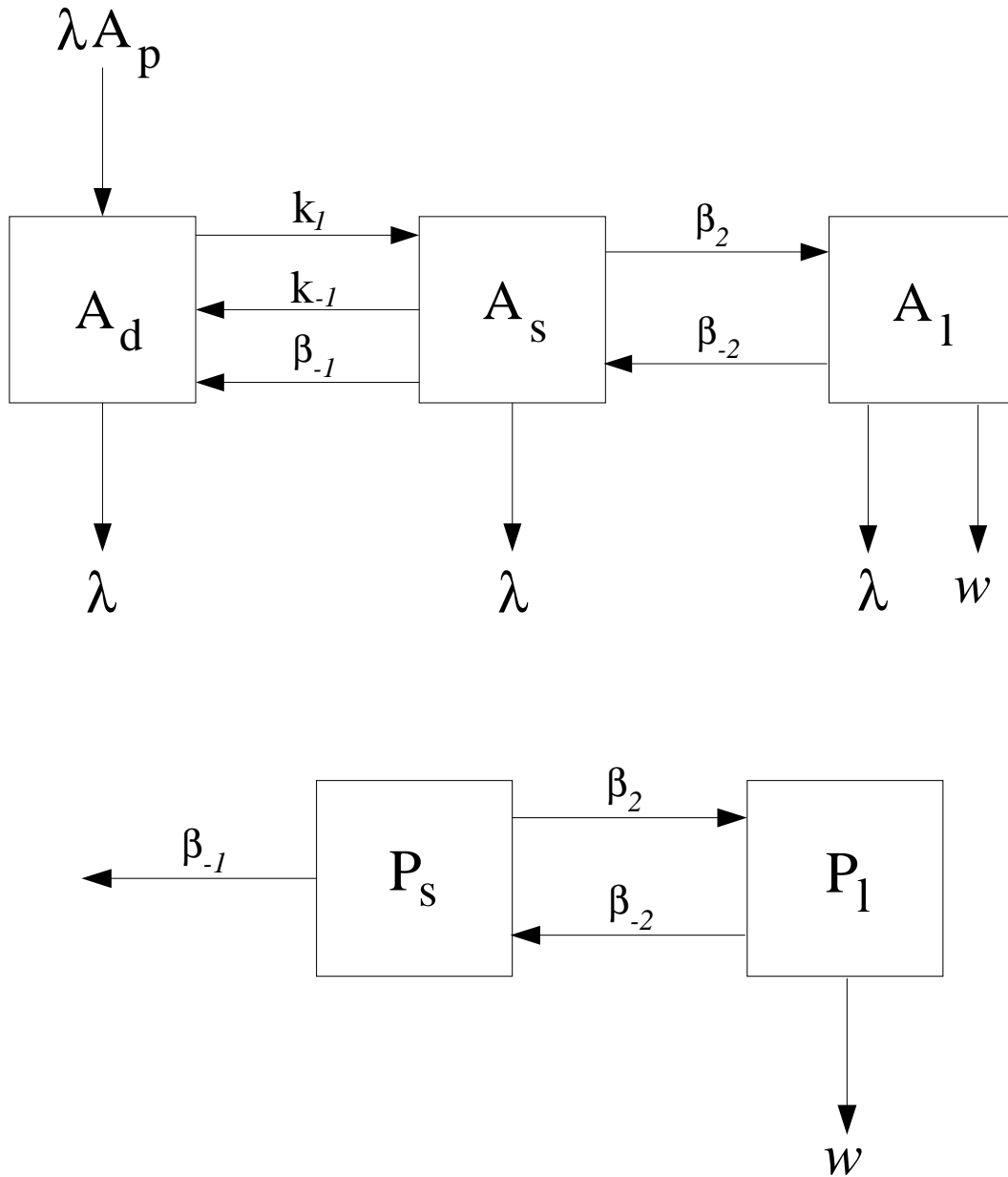


Figure 2: Schematic diagram of the cycling of trace metals (top) and particles (bottom) in the ocean aphotic zone. Metal activity is partitioned between the dissolved phase (A_d), the small particles (A_s) and the large particles (A_l). Particle concentration is partitioned between the small particles (P_s) and the large particles (P_l). The processes affecting metal activity and particle concentration in these different forms are the production by the radioactive parent (A_p), the radioactive decay (at a specific rate λ), the adsorption onto small particles (k_l), the desorption from small particles (k_{-l}), the remineralization of small particles (β_{-1}), the aggregation of small particles (β_2), the disaggregation of large particles (β_{-2}), and the sinking of large particles (with velocity w).

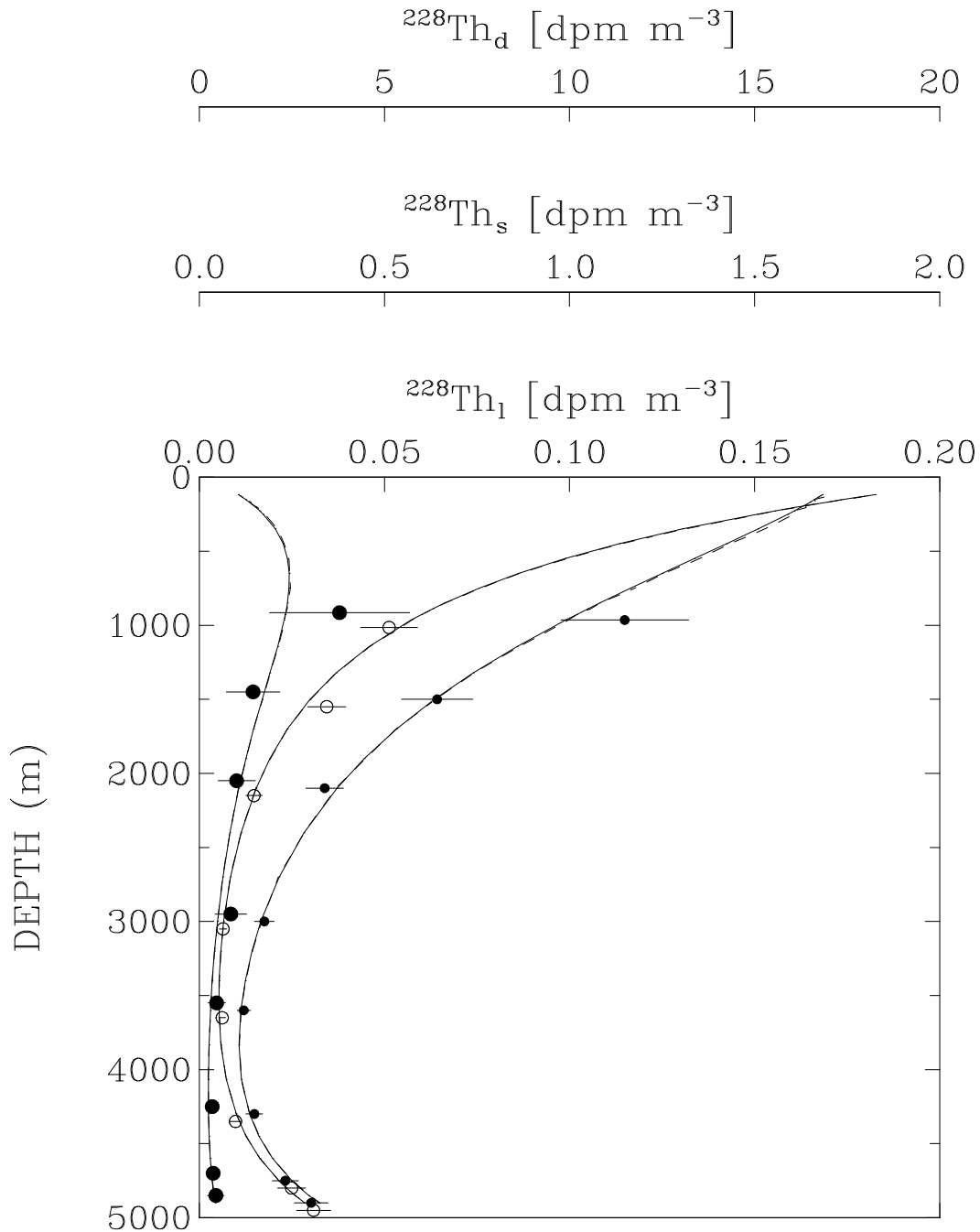


Figure 3: Vertical profiles of ^{228}Th activity in the dissolved phase (upper horizontal axis), the small particles (middle axis), and the large particles (lower axis). The ^{228}Th activities that are obtained from the analytical (numerical) solution of the model are shown by solid (dashed) lines. The two lines are barely distinguishable. The ^{228}Th activities at sampling depths, which are used to produce the idealized data for the inversions, are shown by circles: open circles for the dissolved phase, small solid circles for the small particles, and large solid circles for the large particles. The horizontal bars show the errors in these activities. These activities are shown only at some of the pumping depths at GEOTRACES NA deep stations.

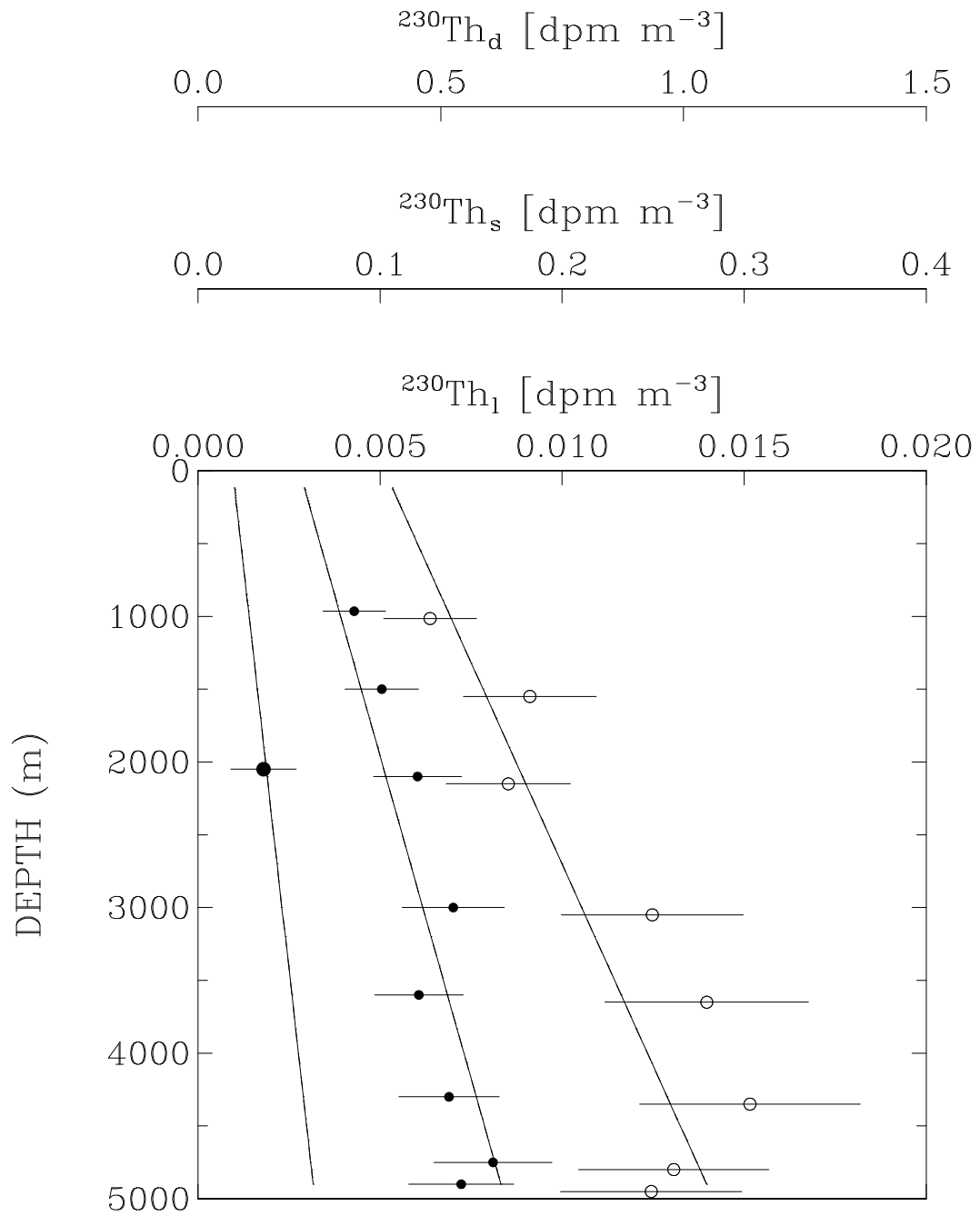


Figure 4: Same as Figure 3 but for ^{230}Th .

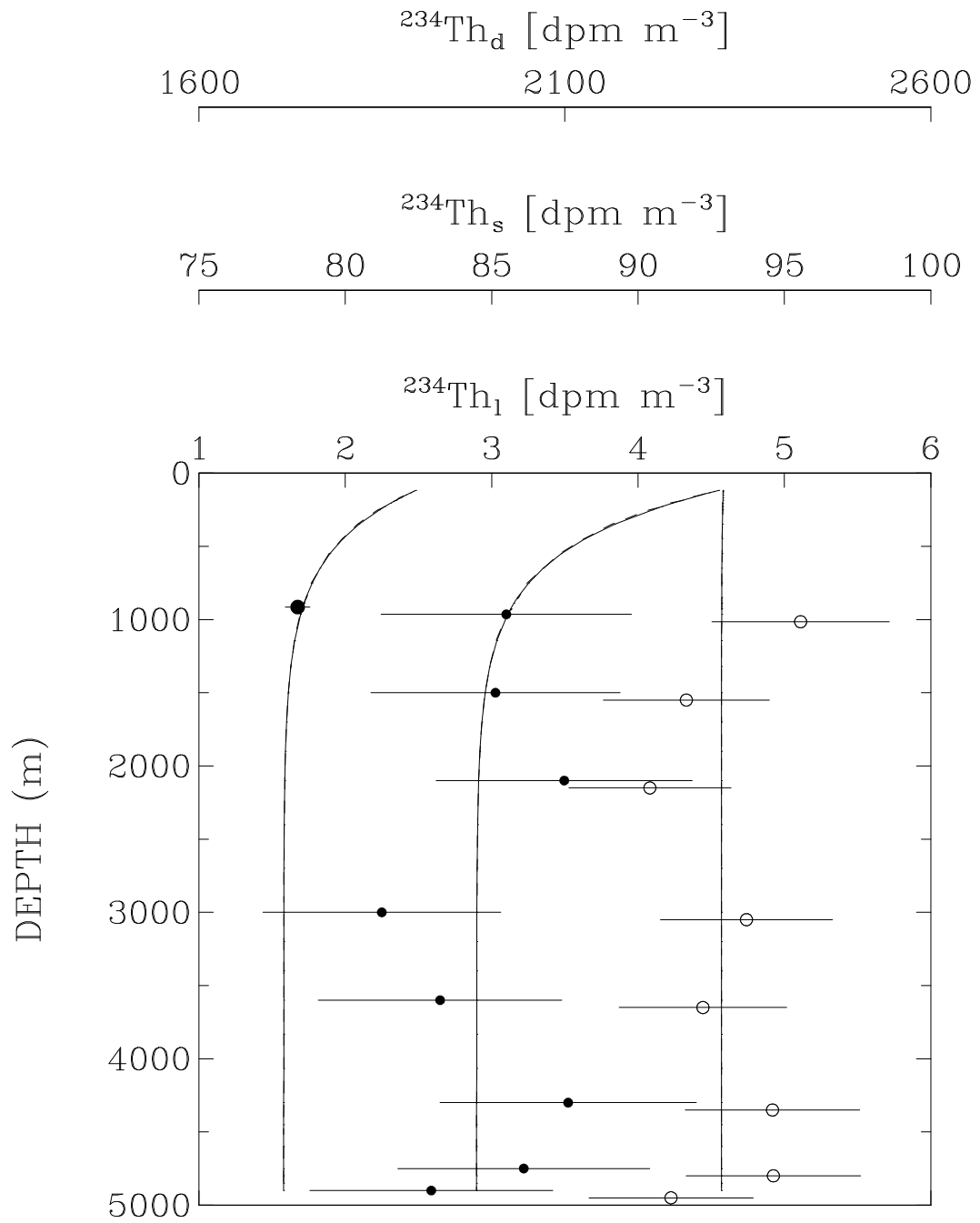


Figure 5: Same as Figure 3 but for ^{234}Th .

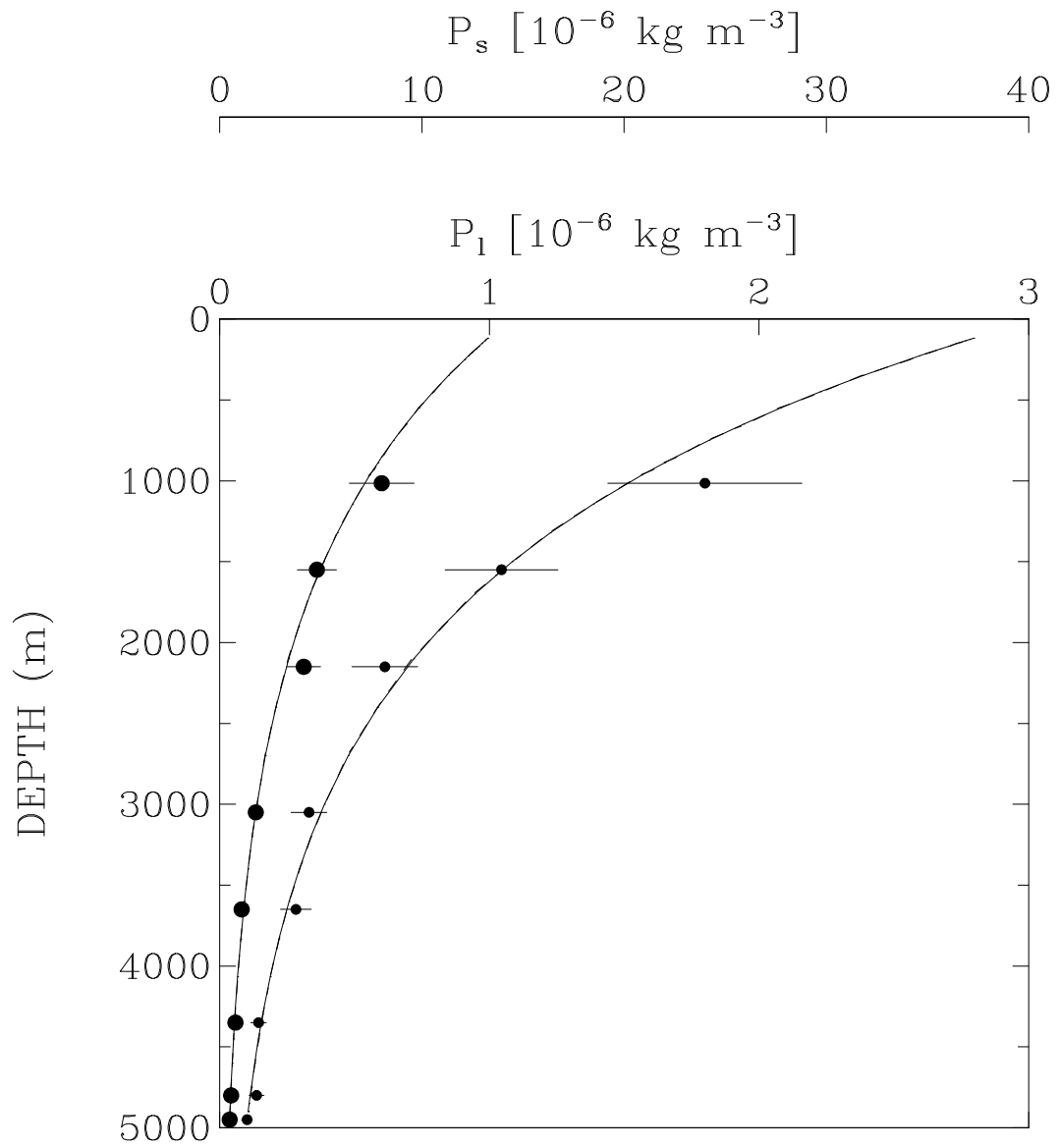


Figure 6: Same as Figure 3 but for the concentration of particles. The concentration of small (large) particles is shown by small (large) circles.

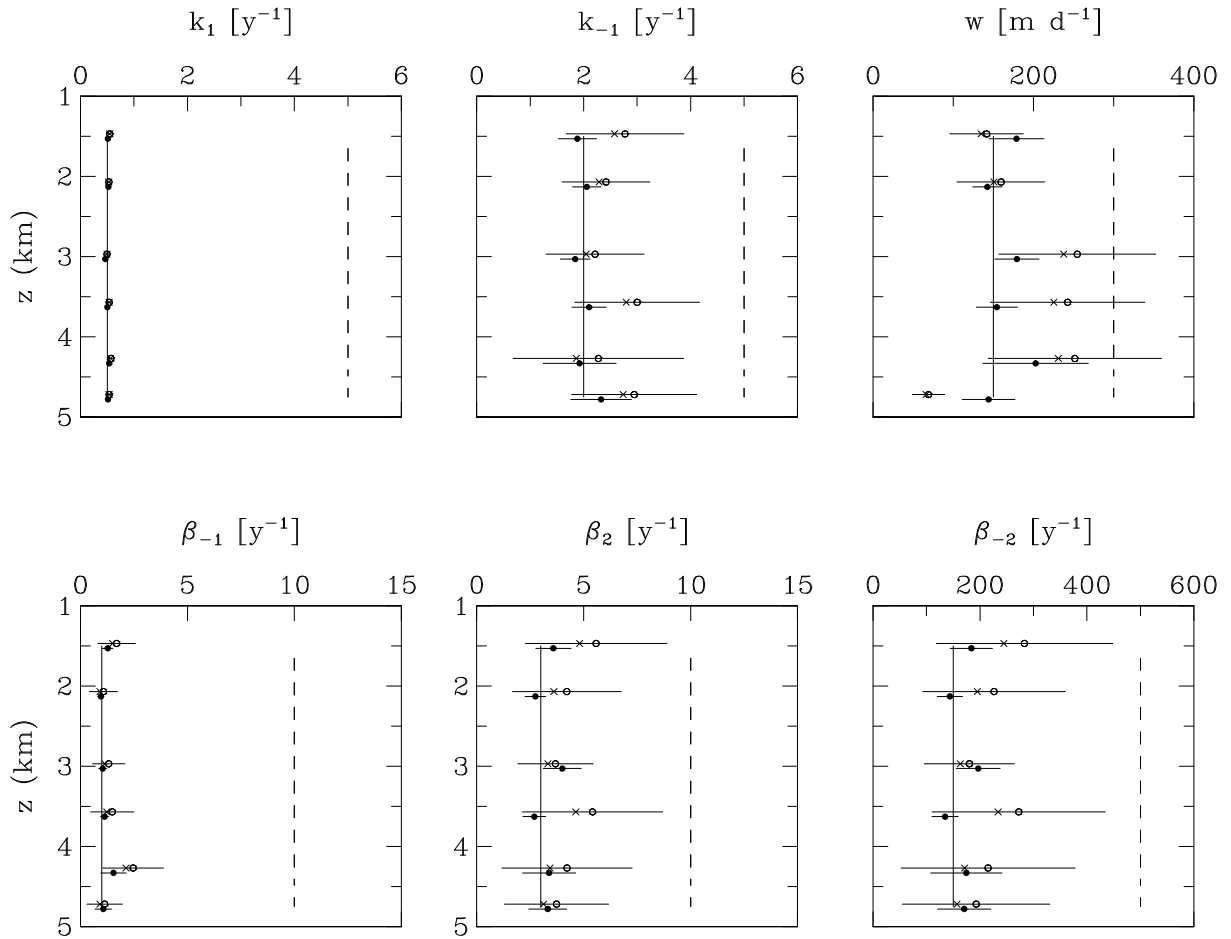


Figure 7: Rate constants of Th and particle cycling estimated with varying data errors. The vertical solid lines indicate the values used to generate Th and particle data. The vertical dashed lines indicate the prior estimates assumed in the inversions. The solid circles with horizontal bars show the means with their errors estimated in an inversion where data have a relative error of 5% (reference inversion). The open circles (crosses) with horizontal bars show the means (medians) with their errors estimated in an inversion where data have a relative error of $\leq 20\%$. In both inversions, data are available at all depths and model errors are assumed to be very small ($p = 10^{-5}$). The rate constants estimated by inversion are shown at six of the pumping depths at GEOTRACES NA deep stations.

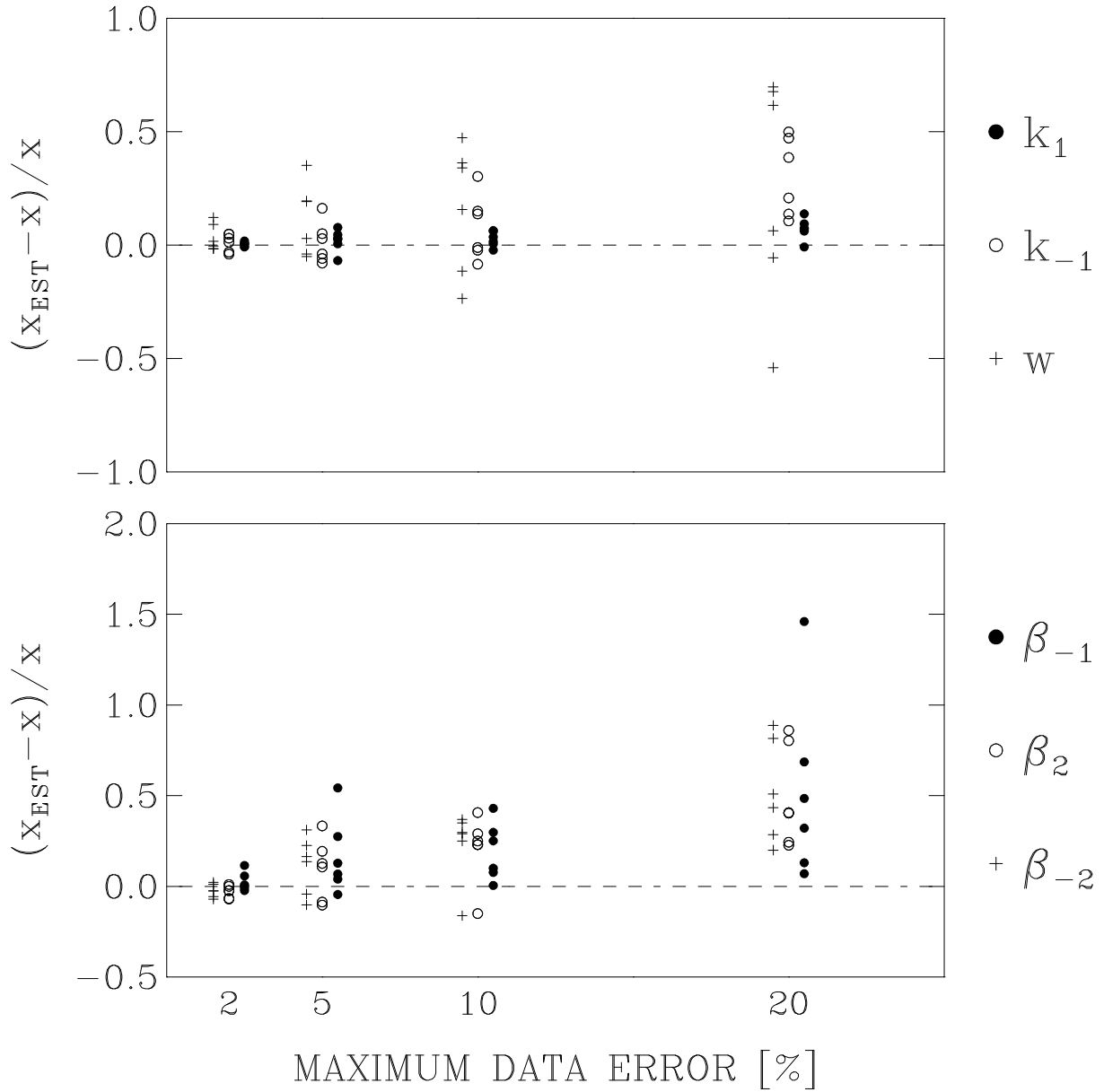


Figure 8: Effect of maximum data error on the accuracy of the rate constants of Th and particle cycling estimated by inversion. The accuracy is measured by the difference between the estimated value and the actual value, divided by the actual value.

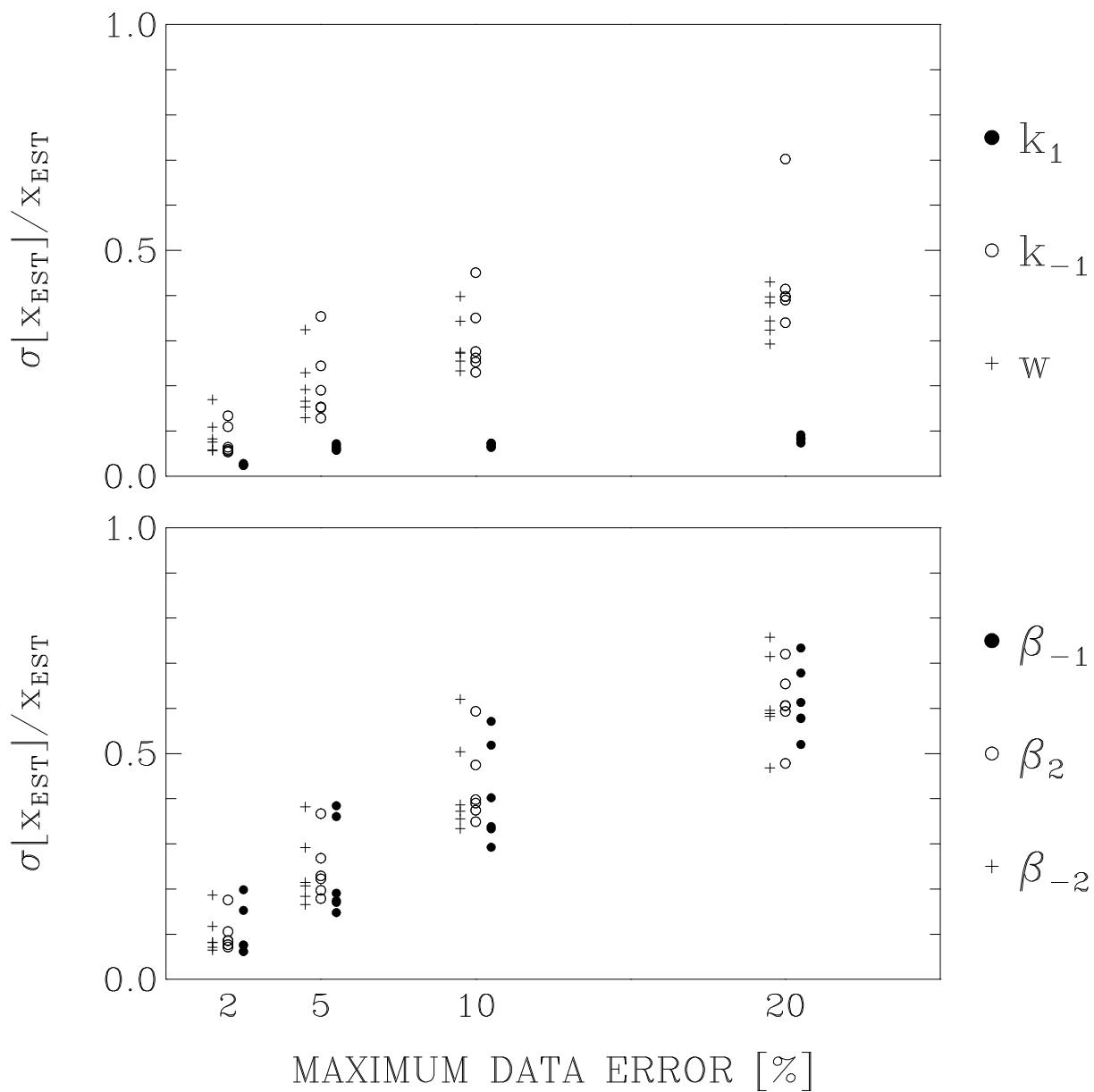


Figure 9: Effect of maximum data error on the precision of the rate constants of Th and particle cycling estimated by inversion. The precision is measured by the ratio between the standard deviation of the estimated value and the estimated value.

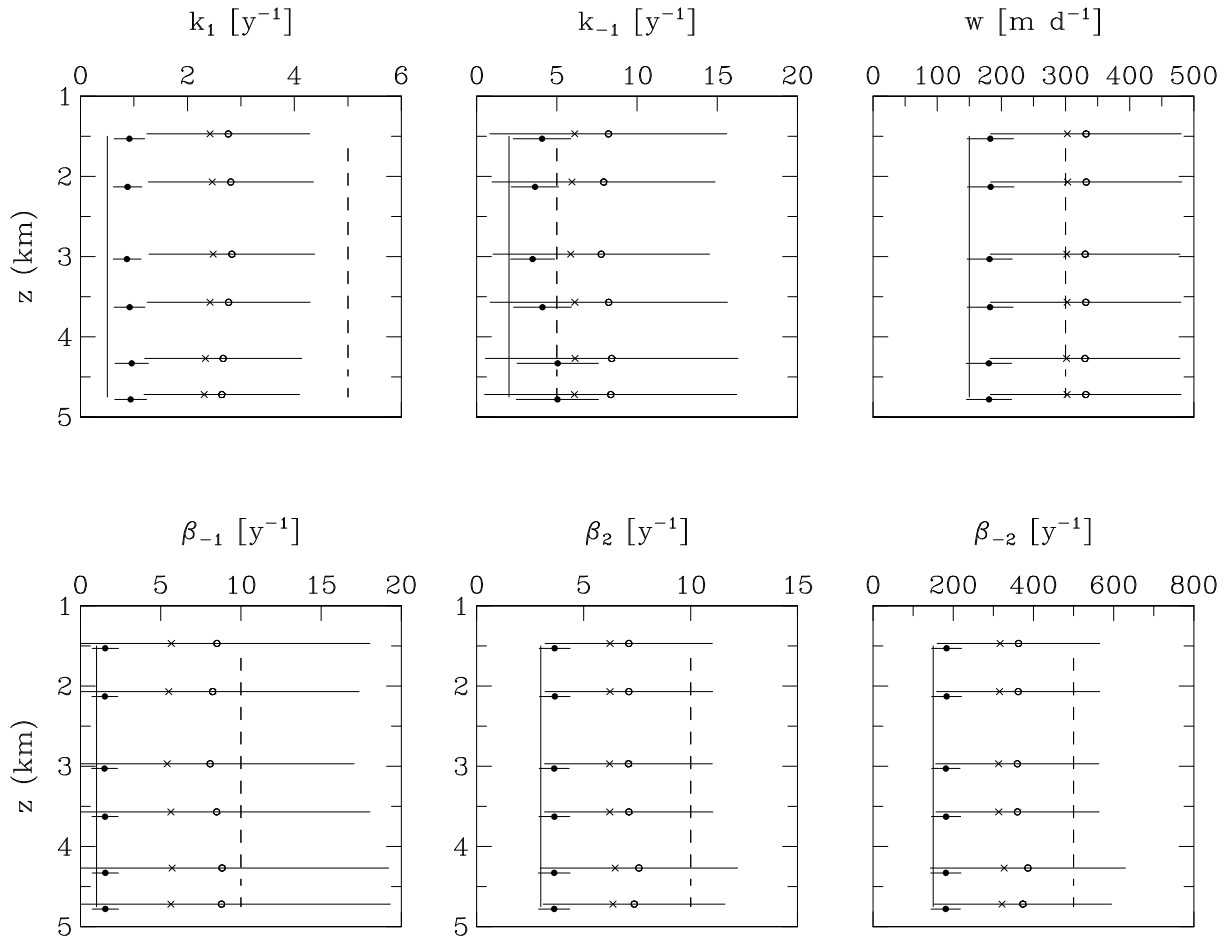


Figure 10: Rate constants of Th and particle cycling estimated with varying model errors. The vertical solid lines indicate the values used to generate Th and particle data. The vertical dashed lines indicate the prior estimates assumed in the inversions. The solid circles with horizontal bars show the means with their errors estimated in an inversion where $p = 0.1$. The open circles with horizontal bars (crosses) show the means (medians) with their errors estimated in an inversion where $p = 1$. In both inversions, the data have no error and are available at all depths. The rate constants estimated by inversion are shown at six of the pumping depths at GEOTRACES NA deep stations.

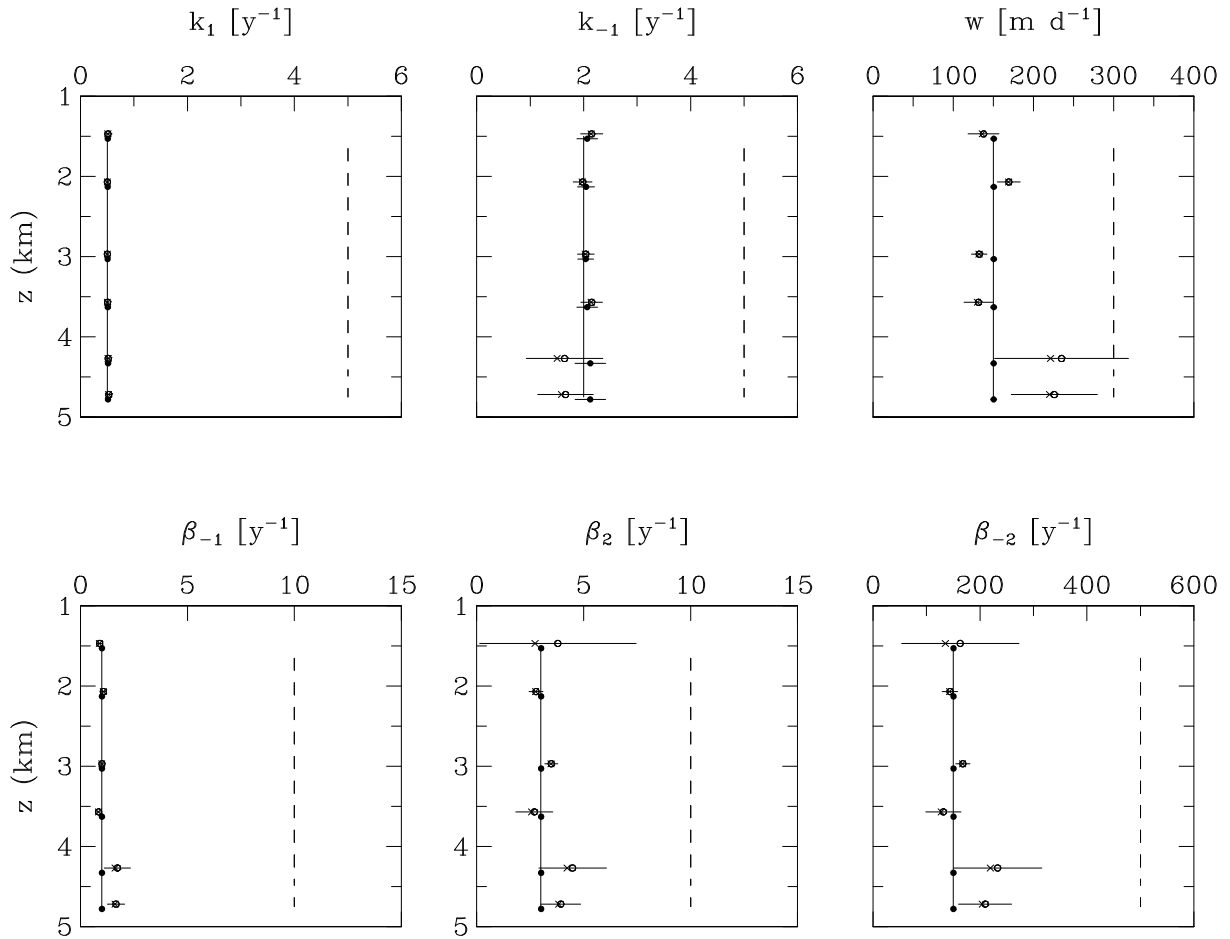


Figure 11: Rate constants of Th and particle cycling estimated with varying sampling schemes. The vertical solid lines indicate the values used to generate Th and particle data. The vertical dashed lines indicate the prior estimates assumed in the inversions. The solid circles with horizontal bars show the means with their errors estimated in an inversion where data are available at all depths. The open circles (crosses) with horizontal bars show the means (medians) with their errors estimated in an inversion where data are interpolated or extrapolated. In both inversions, the data have no error (except in the second inversion where extrapolated values have a relative error of 1) and the factor for model errors $p = 0.01$. The rate constants estimated by inversion are shown at six of the pumping depths at GEOTRACES NA deep stations.

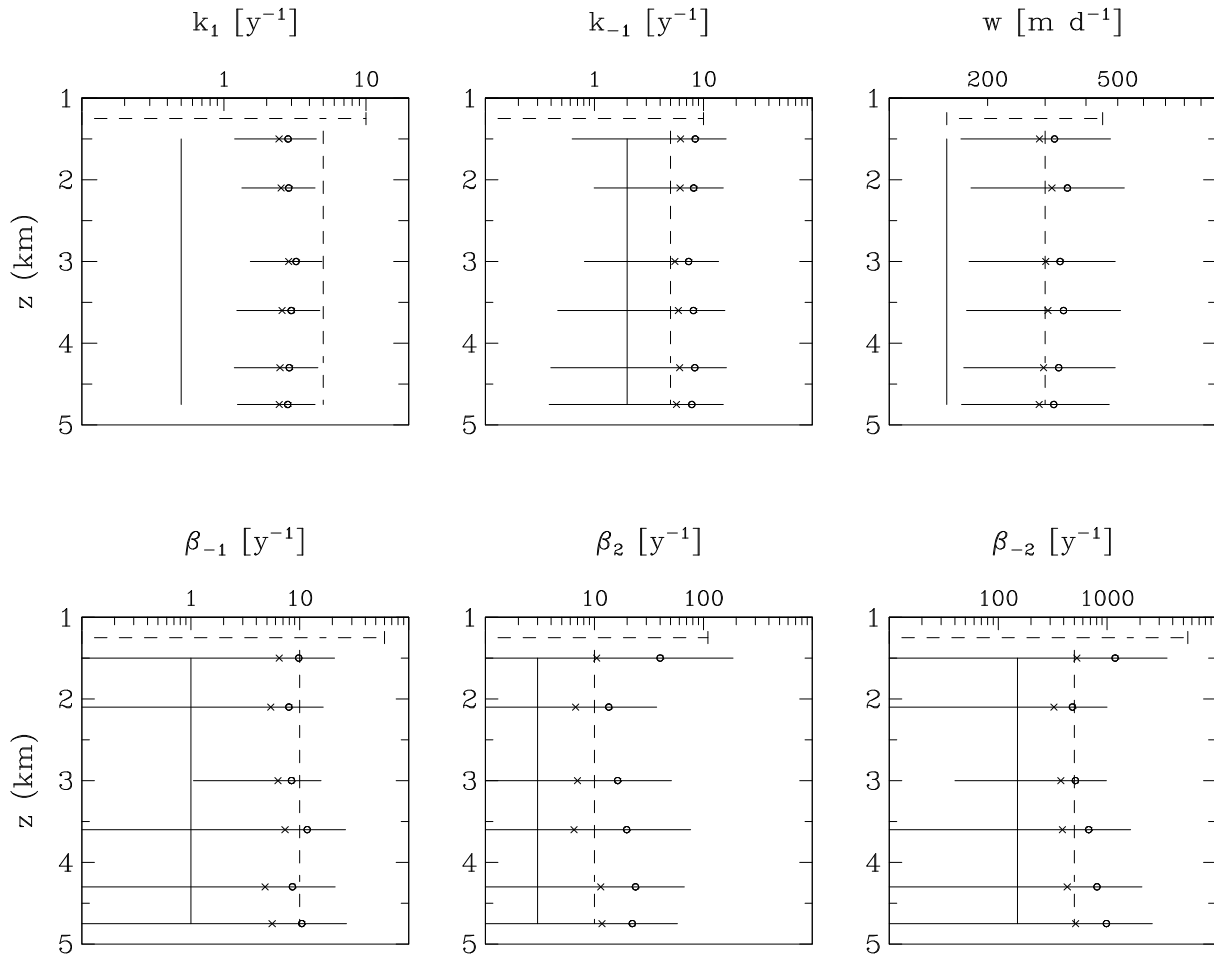


Figure 12: Rate constants of Th and particle cycling estimated in the presence of data errors, model errors, and limited sampling. The vertical solid lines indicate the values used to generate Th and particle data. The vertical (horizontal) dashed lines indicate the prior estimates (their errors) assumed in the inversions. The open circles (crosses) with horizontal bars show the means (medians) and their errors estimated in an inversion where (i) the errors and depths of the measurements would be those at GEOTRACES NA deep stations and (ii) the factor for model errors $p = 1$. The rate constants estimated by inversion are shown at six of the pumping depths at these stations.

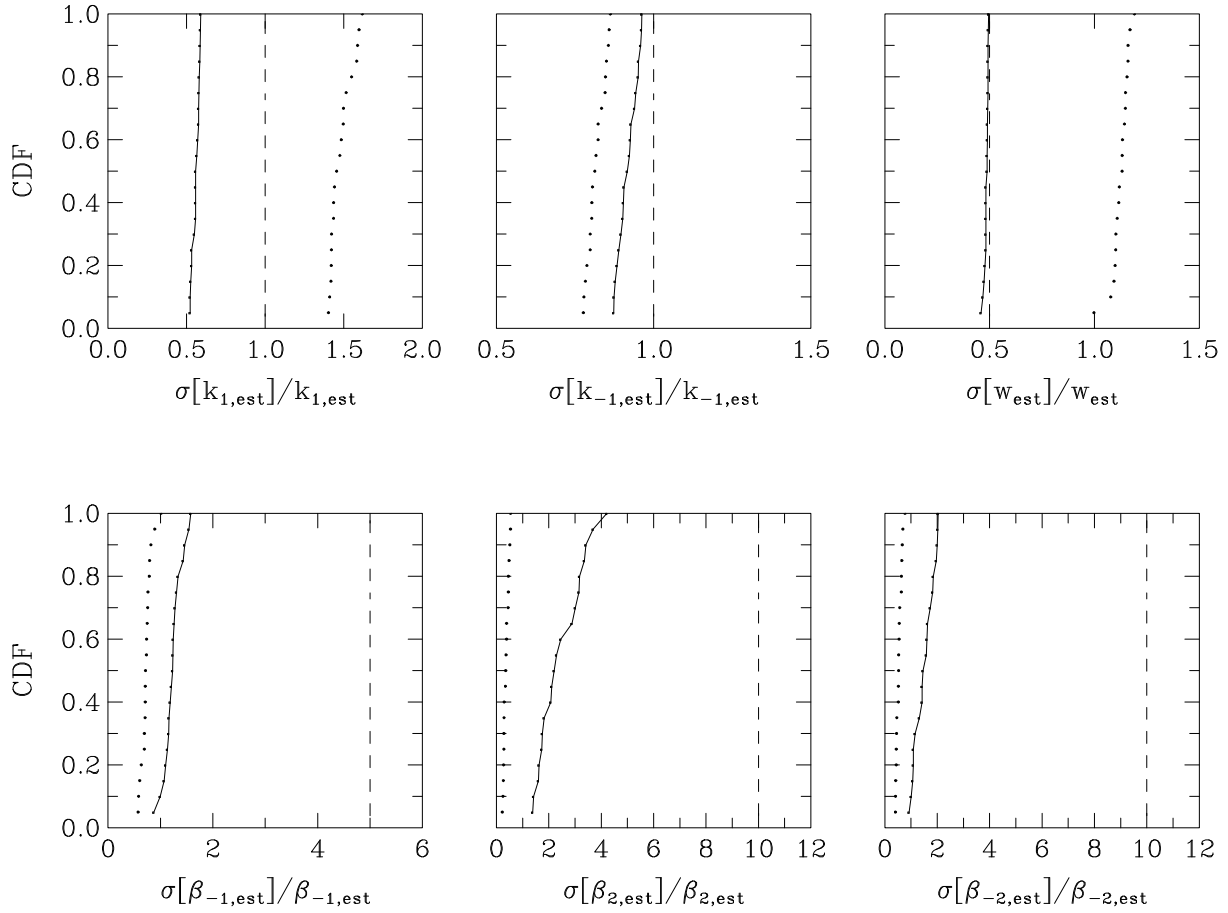


Figure 13: Cumulative distribution function (CDF) of the relative precision of the rate constants of Th and particle cycling, which are estimated in the presence of data errors, model errors, and limited sampling. The relative precision is the standard deviation of the rate constant divided by the value of the rate constant. The dashed (solid) line is the CDF for the prior (posterior) estimates. Also shown is the CDF of the difference between the estimated and actual value, divided by the standard deviation of the estimated value (dotted line). Note that the CDFs for the posterior estimates are based on values at all depths of the model grid.

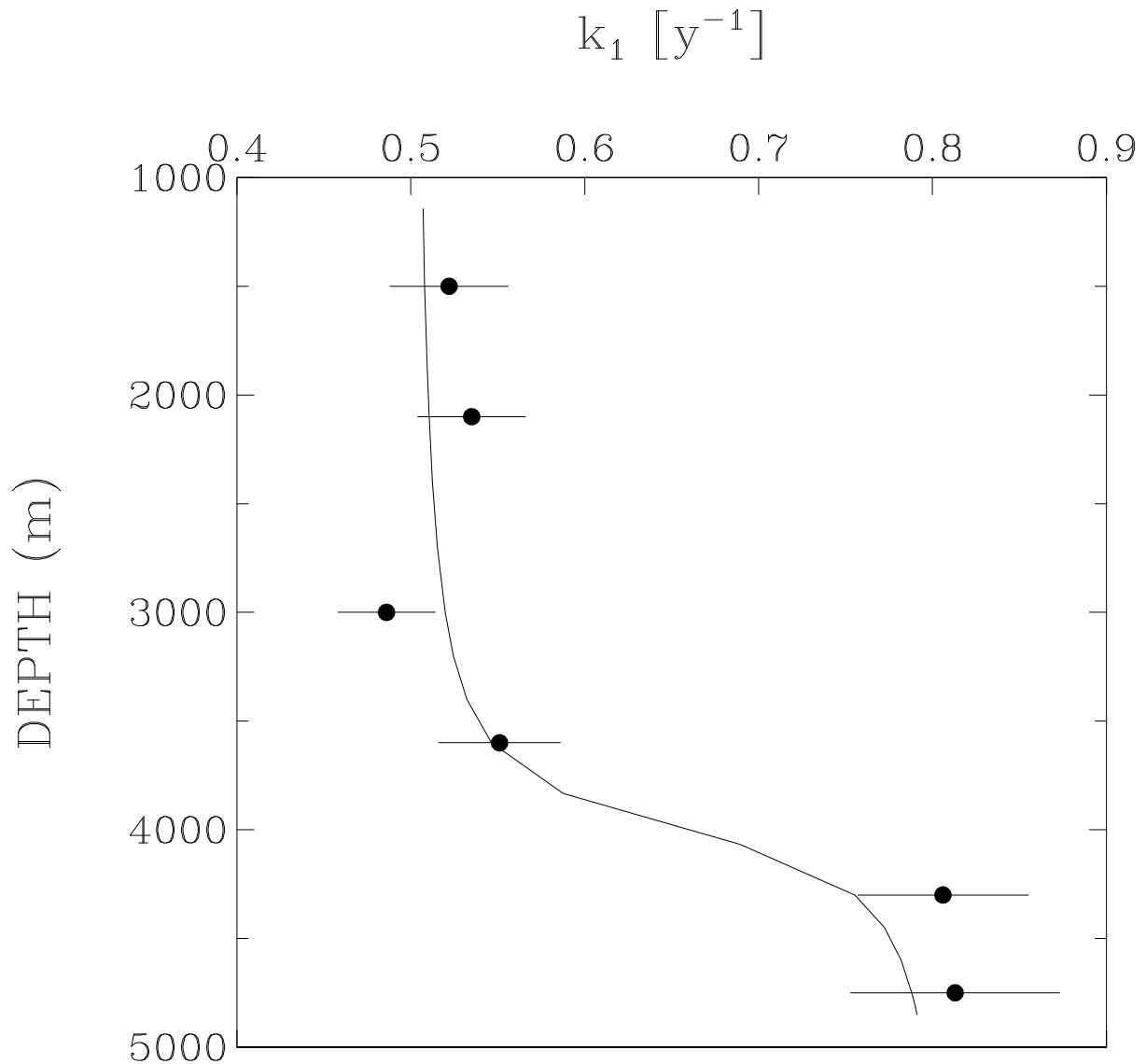


Figure 14: Recovery of vertical variations in the rate constant of Th adsorption. The solid line indicates values used to generate Th and particle data. The solid circles with horizontal bars show the means with their errors estimated in an inversion where the data have a relative error of 5%, they are available at all depths, and model errors are very small ($p = 10^{-5}$). Note that the values estimated by inversion are shown only at some of the pumping depths at GEOTRACES NA deep stations.

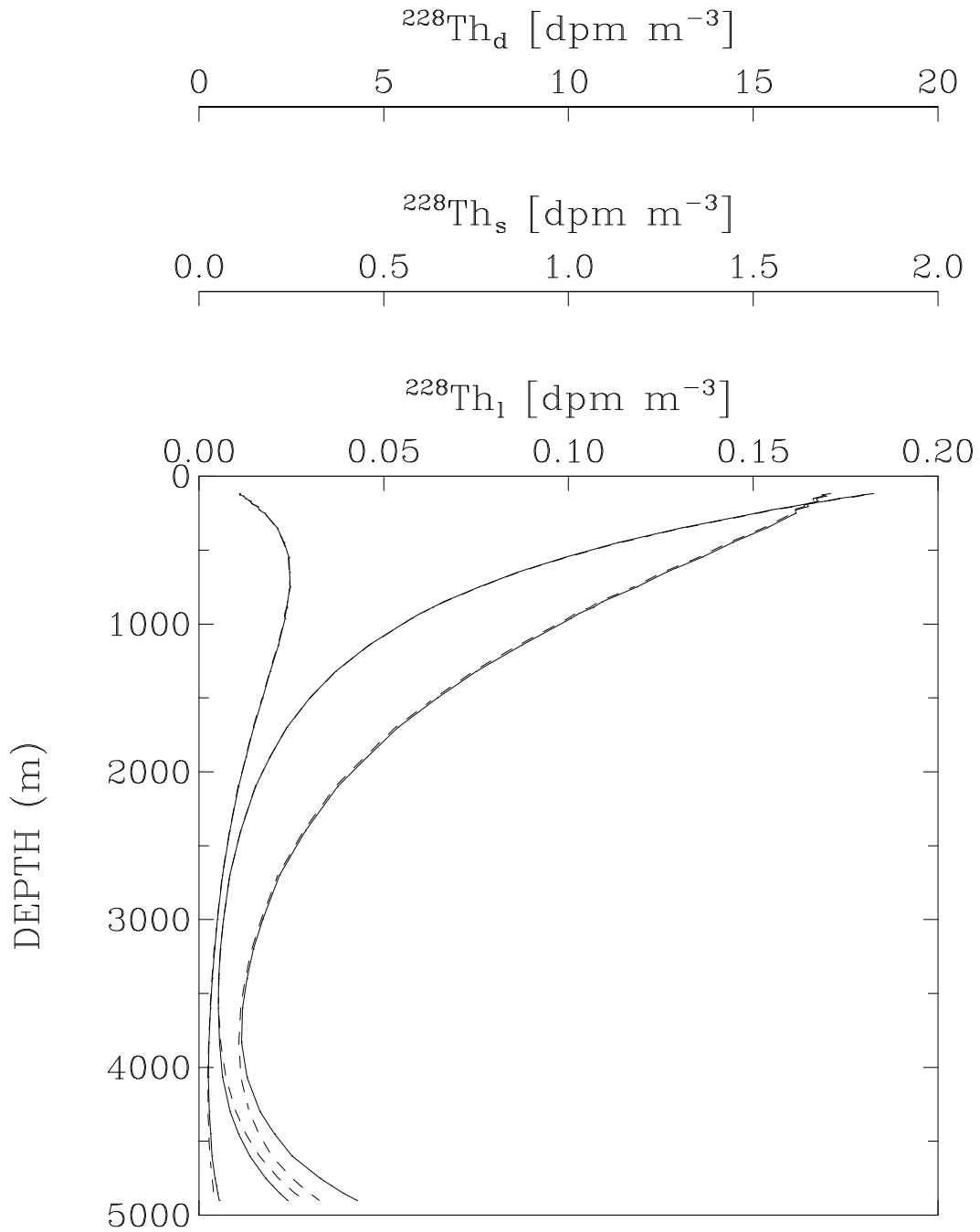


Figure 15: Vertical profiles of ^{228}Th activity in the dissolved phase (upper horizontal axis), the small particles (middle axis), and the large particles (lower axis). The ^{228}Th activities that are obtained by numerical solution with uniform (variable) rate of Th adsorption are shown by dashed (solid) lines (left most lines for large particles, middle lines for the dissolved phase, and right most lines for small particles).

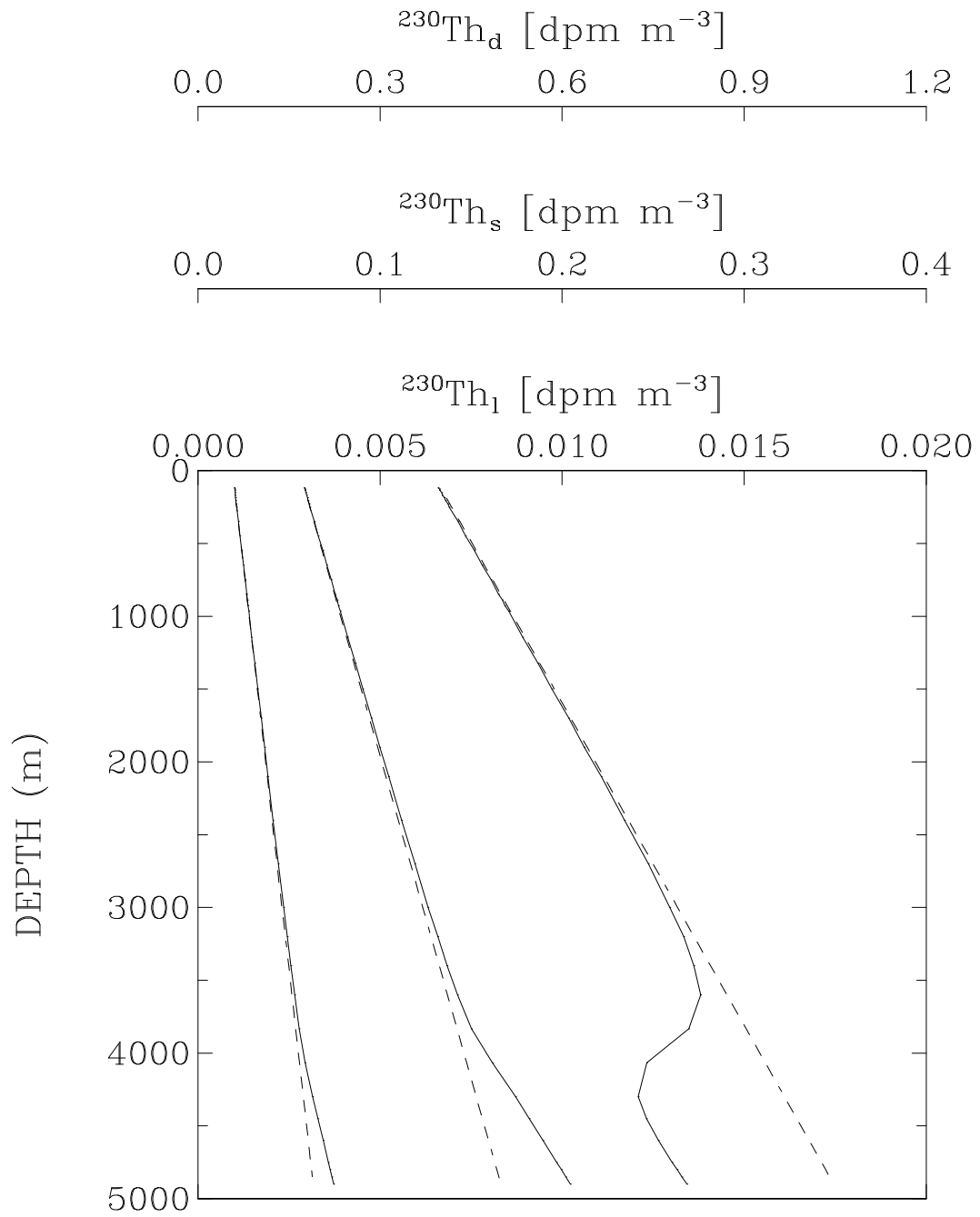


Figure 16: Same as Figure 15 but for ^{230}Th (left most lines for large particles, middle lines for small particles, and right most lines for the dissolved phase).

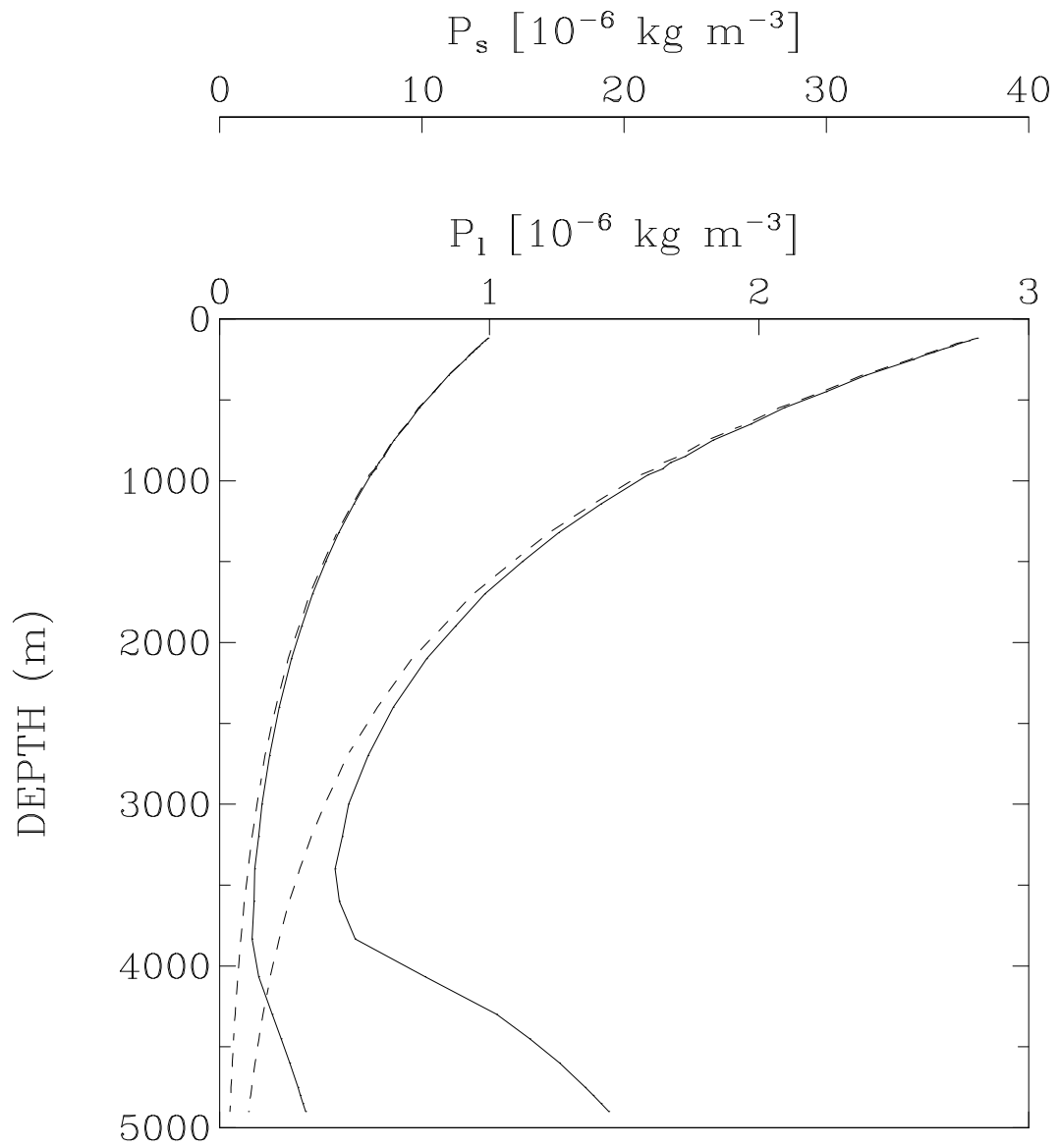


Figure 18: Same as Figure 15 but for the concentration of particles (left lines for large particles and right lines for small particles).

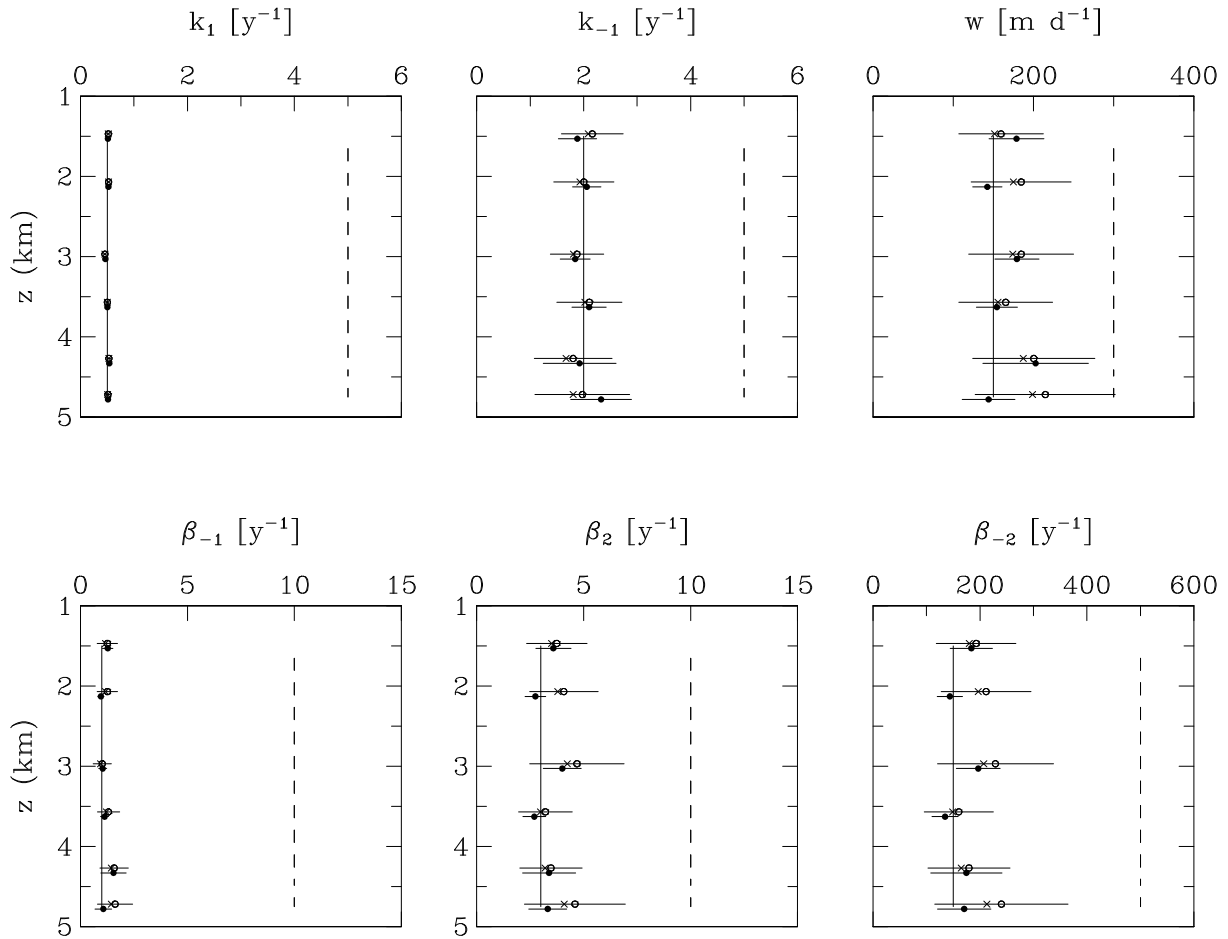


Figure 19: Rate constants of Th and particle cycling estimated with varying errors in the ^{228}Th equations. The vertical solid lines indicate the values used to generate Th and particle data. The vertical dashed lines indicate the prior estimates of the rate constants assumed in the inversions. The solid circles with horizontal bars show the means with their errors estimated in the reference inversion. The open circles (crosses) with horizontal bars show the means (medians) with their errors estimated in an inversion with a relatively large error for the ^{228}Th equations ($p = 1$). In both inversions, the data have a relative error of 5% and are available at all depths. The rate constants estimated by inversion are shown at six of the pumping depths at GEOTRACES NA deep stations.

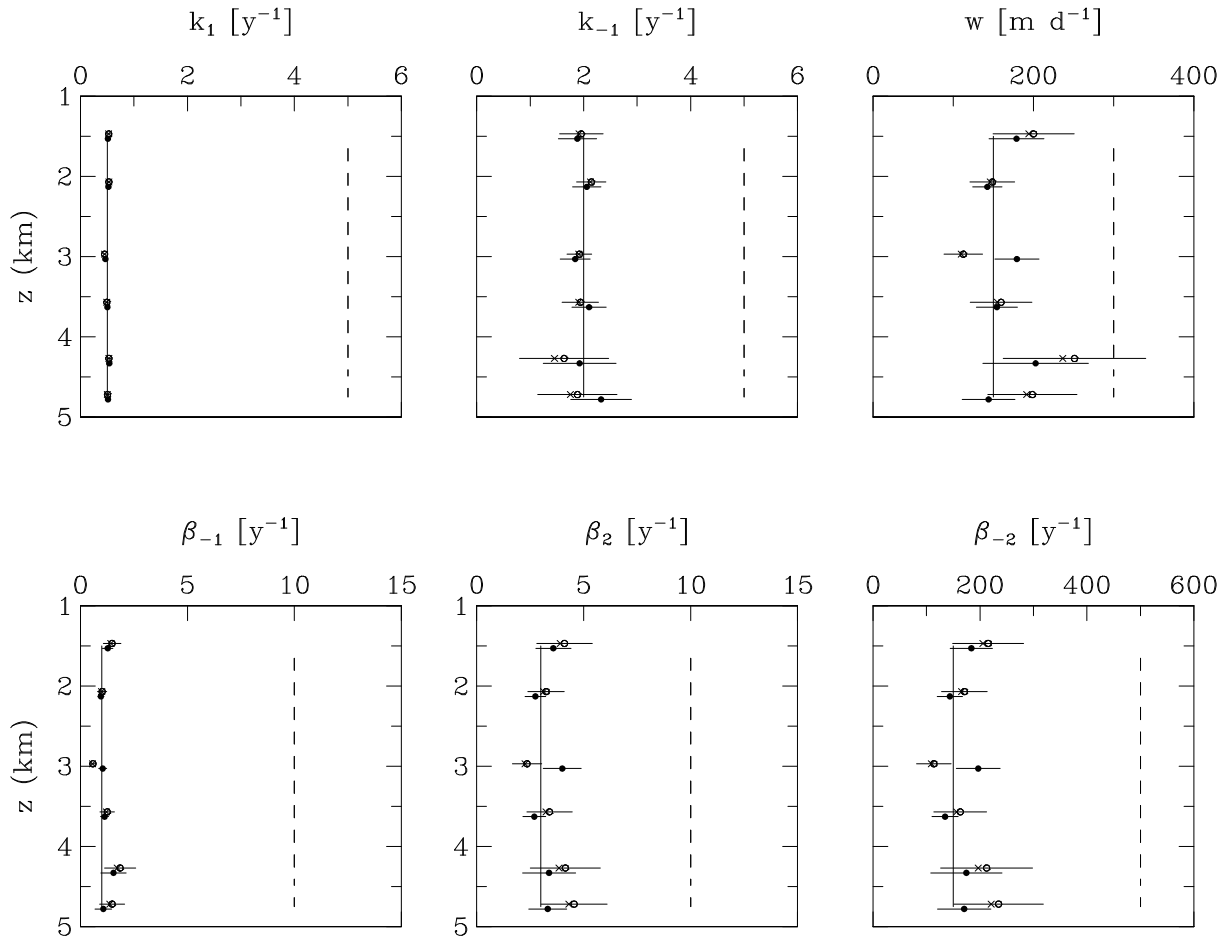


Figure 20: Rate constants of Th and particle cycling estimated with or without local ^{228}Ra data. The vertical solid lines indicate the values used to generate Th and particle data. The vertical dashed lines indicate the prior estimates assumed in the inversions. The solid circles with horizontal bars show the means with their errors estimated in the reference inversion. The open circles (crosses) with horizontal bars show the means (medians) with their errors estimated in an inversion where (i) ^{228}Ra activity is fixed to $2.4\ \text{dpm}\ m^{-3}$ at all depths and (ii) the error in the $^{228}\text{Th}_d$ equation is set equal to this value times the ^{228}Th radioactive decay constant. The rate constants estimated by inversion are shown at six of the pumping depths at GEOTRACES NA deep stations.