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M. Baskaran
Wayne State University, baskaran@wayne.edu

P. W. Swarzenski
U.S. Geological Survey, pswarzen@usgs.gov

B. A. Biddanda
Grand Valley State University, biddandb@gvsu.edu

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Constraints on the utility of MnO_2 cartridge method for the extraction of radionuclides: A case study using ^{234}Th

M. Baskaran
Department of Geology, Wayne State University, Detroit, Michigan 48202, USA (baskaran@wayne.edu)

P. W. Swarzenski
Pacific Science Center, U.S. Geological Survey, 400 Natural Bridges Drive, Santa Cruz, California 95060, USA

B. A. Biddanda
Annis Water Resources Institute, Lake Michigan Center, Grand Valley State University, Muskegon, Michigan 49441, USA

[1] Large volume (10^2–10^3 L) seawater samples are routinely processed to investigate the partitioning of particle reactive radionuclides and Ra between solution and size-fractionated suspended particulate matter. One of the most frequently used methods to preconcentrate these nuclides from such large volumes involves extraction onto three filter cartridges (a prefilter for particulate species and two MnO_2-coated filters for dissolved species) connected in series. This method assumes that the extraction efficiency is uniform for both MnO_2-coated cartridges, that no dissolved species are removed by the prefilter, and that any adsorbed radionuclides are not desorbed from the MnO_2-coated cartridges during filtration. In this study, we utilized ^{234}Th-spiked coastal seawater and deionized water to address the removal of dissolved Th onto prefilters and MnO_2-coated filter cartridges. Experimental results provide the first data that indicate (1) a small fraction of dissolved Th (<6%) can be removed by the prefilter cartridge; (2) a small fraction of dissolved Th (<5%) retained by the MnO_2 surface can also be desorbed, which undermines the assumption of uniform extraction efficiency for Th; and (3) the absolute and relative extraction efficiencies can vary widely. These experiments provide insight on the variability of the extraction efficiency of MnO_2-coated filter cartridges by comparing the relative and absolute efficiencies and recommend the use of a constant efficiency on the combined activity from two filter cartridges connected in series for future studies of dissolved ^{234}Th and other radionuclides in natural waters using sequential filtration/extraction methods.

1. Introduction

[2] The distribution of particle reactive radionuclides such as Th and ^{210}Pb in the U/Th series in seawater, have provided a wealth of information on marine particle dynamics. The activities of many of the short-lived U/Th series radionuclides in seawater are so dilute that most of these nuclides require considerable preconcentration prior to their radiochemical separation and analyses. Several methods have been developed to preconcentrate short-lived radionuclides from natural waters and include coprecipitation with Fe and Al hydroxides, and selective sorption on to Fe/MnO₂-coated surfaces. One of the widely used preconcentration methods for particulate and dissolved Th is to pass large volumes of seawater through a set of prefilters to retain particulate matter while the dissolved constituents are adsorbed onto two MnO₂-coated cartridges [e.g., *Buesseler et al.*, 1992; *Baskaran et al.*, 1993, 2003; *Colley and Thomson*, 1994; *Cochran et al.*, 1987, 1995; *Moran et al.*, 1997; *Charette and Moran*, 1999; *Rutgers van der Loeff and Moore*, 1999; *Benitez-Nelson et al.*, 2000; *Guo et al.*, 2002; *Rutgers van der Loeff et al.*, 2006]. Advantages of this method include the simultaneous measurement of a suite of gamma-emitting radionuclides, such as ^{234}Th, ^{210}Pb and Ra isotopes and selective removal of Th but not U which eliminates extensive chemical separation of U from Th isotopes in the field [e.g., *Baskaran et al.*, 1993; *Baskaran and Santschi*, 2002]. Furthermore, in studies that involve size-fractionated particulate Th determination, this method allows the filtration of large volumes of water (10^3–10^4 L) to assess the distribution of Th in various class-sized particles [e.g., *Guo et al.*, 2002]. Key assumptions in the filter cartridge method include (1) the prefilter does not sorb any dissolved Th and retains quantitatively particulate matter of sizes above the filter cutoff, (2) the two MnO₂ filters extract Th in a uniform manner (i.e., a constant percentage of the entering Th is removed by each MnO₂ fiber), and (3) any sorbed Th on the MnO₂-coated cartridge filters does not desorb during filtration. However, these assumptions have not been rigorously tested, although variations in reported extraction efficiencies have been summarized in detail [*Rutgers van der Loeff et al.*, 2006]. In this study, we present results from a series of experiments that specifically address the retention of dissolved Th onto prefilters and MnO₂-coated filter cartridges, release of sorbed Th from these MnO₂ filter cartridges and variations in the extraction efficiencies of the MnO₂-coated cartridge filters. This study is relevant to other nuclides that use three-cartridge method (one cartridge filter for particulate followed by two cartridge filters connected in series for radionuclides such as Ra, ^{210}Pb, ^{137}Cs, etc).

2. Materials and Methods

[3] Parameters that can cause variations in the extraction efficiency of MnO₂-coated cartridge filters include variations in: filtration volumes (sorption site density limiting the extraction efficiency), flow rates (changes in the contact time between seawater and MnO₂ surface), cartridge preparation techniques, loss of MnO₂ and Th from MnO₂ filter during filtration, retention of particulate Th in prefilter and electrostatic repulsion between the MnO₂ surface and colloid-bound Th [*Buesseler et al.*, 2001; *Rutgers van der Loeff et al.*, 2006]. For the following extraction efficiency experiments, we kept the volumes and flow rates constant. Thus the variations on the absolute extraction efficiencies in the MnO₂-coated cartridges due to changes in the preparation of MnO₂ cartridges, the amount of dissolved Th removed by the prefilter and loss of sorbed Th from MnO₂-coated filter cartridges could be quantified.

2.1. Preparation of Filter Cartridges

[4] The raw filters (25 × 7 cm; polypropylene fiber, Johnson Filtration, Amarillo, TX, Model: JP0.5R10P) were first cleaned by soaking a batch of 12 cartridges in 20-L plastic buckets at ~60°C for about 12 h sequentially in each of the following: (1) 2% Micro cleaning solution, (2) 2 M HCl, (3) 0.5 NaOH, and (4) 2 M HNO₃. The filters were rinsed in tap water before and after soaking them in cleaning solutions until the pH of the wash solution stabilized around ~7. The residual ash of a prefilter (at 500°C for 6 h) is <0.1% of its original weight (~150 g). Each precleaned filter was then soaked in a saturated KMnO₄ solution (250 g KMnO₄/L H₂O) in a plastic container at ~70°C. The soaking time in the KMnO₄ for the dark (D), normal (N) and light (L) cartridges were 24, 12 and 6 h, respectively. This counting procedure produced cartridges with MnO₂ weights ranging from 0.1 to 10% of the total weight of the prefilter cartridges. After the KMnO₄ bath, one batch of 6 cartridges was thoroughly washed with tap water. This water flow was connected directly to two Dark MnO₂-coated cartridges to remove any radionuclides and we periodically verified in blank cartridges that there was no blank ^{234}Th.

Table 1. Extraction Efficiency Experimental Conditions[a]

Experiment	F1: Type and Date Made	F2: Type and Date Made	F3: Type and Date Made	F4: Type and Date Made	F5: Type and Date Made
SET-1	D: 19 Jan 2005	D: 19 Jan 2005	D: 19 Jan 2005	none	none
SET-2	PF: Mar 2004	none	none	none	none
SET-3	N: 12 Aug 2003	N: 12 Aug 2003	N: 8 Aug 2003	none	none
SET-4	N: 12 Aug 2003	N: 12 Aug 2003	N: 12 Aug 2003	none	none
SET-5	D: 28 Aug 2003	PF: 11 Mar 2004	D: 28 Aug 2003	PF: 11 Mar 2004	none
SET-6	L: 19 Aug 2003	PF: 9 Mar 2004	L: 19 Aug 2003	PF: 9 Mar 2003	L: 18 Aug 2003
SET-7	N: 12 Mar 2003	PF: 6 Mar 2004	N: 12 Mar 2004	PF: 6 Mar 2004	N: 11 Mar 2004
SET-8	L: 18 Aug 2003	D: 19 Jan 2005	PF: 9 Mar 2004	none	none
SET-9	D: 19 Jan 2005	L: 19 Aug 2003	PF: 11 Mar 2004	none	none
SET-10	N: 11 Mar 2004	N: 11 Mar 2004	N: 18 Aug 2003	none	none
SET-11	D: 19 Jan 2005	D: 19 Jan 2005	D: 26 Jun 2005	none	none
SET-12	L: 12 Aug 2003	L: 12 Aug 2003	L: 11 Aug 2003	none	none

[a] D, dark (24 h coating); N, normal (12 h coating); L, light (6 h coating); PF, prefilter (dates when they were cleaned); $F_1, F_2, \ldots, F_5$ refer to the filter cartridges connected serially from inlet to outlet. Salinity of the water used: 23.89; flow rate: $4-5$ dpm L^{-1}; In all experiments except SET-4 (deionized water, 48 L), 100 L water was used.

2.2. Milking of ^{234}Th

[5] Thorium-234 spike was obtained by passing a uranyl nitrate solution through two large concentrated HCl-conditioned columns (Dowex-1 anion exchange column with 12 ml resin in each column; AG 1-X4, 100–200 mesh, chloride form) sequentially in order to quantitatively separate U from Th. The amount of U loaded onto the column and the saturation capacity of the anion exchange resin was taken into consideration in deciding the amount of resin needed to separate ^{238}U and ^{234}Th. This ^{234}Th fraction was subsequently isolated from impurities using an 8 M HNO$_3$ conditioned Dowex-1 anion exchange column. Thorium retained on the resin beads was eluted with MILLI-Q water. The purified ^{234}Th was evaporated to dryness and oxidized with concentrated HNO$_3$ twice, to destroy any organic matter that might have been introduced from the elution of the last resin column. One ml of the ^{234}Th spike was taken periodically over a period of one half-life of ^{234}Th and assayed by gamma counting [*Baskaran et al.*, 2003].

2.3. Extraction Efficiency Experiment

[6] For this experiment, 100L of seawater for each of the 11 experiments was collected from one site in Tampa Bay, Florida (salinity = 23.89) and initially prefiltered to remove the suspended particulate matter through a precleaned polypropylene filter cartridge (0.5 μm median pore size). In three sets of experiments, the prefiltered water samples were kept under UV light for 24 h to destroy a major portion of dissolved organic carbon (DOC). Changes in DOC concentrations were determined by high-temperature (680°C) oxidation with a Shimadzu TOC 5000 carbon analyzer [*Benner et al.*, 1997].

[7] One milliliter of pH-neutralized spike (29,048 dpm/ml ^{234}Th) was added to the sample, stirred vigorously for 30 min, and then allowed to equilibrate for 2 h. The dissolved ^{234}Th produced radiogenically from 100 L of seawater was calculated to be $\ll 1\%$ and thus ignored. One could argue whether equilibration was reached when the sample was allowed to equilibrate for 2 h, but it is of little relevance for this experiment studying whether retention and extraction equilibration with seawater is reached or not. After 2 h, the water sample was filtered through a manifold consisting of a set of preassigned cartridge filters (care was exercised in ensuring no bypass of water without identical contact with each of the filter). Details on what filters were used, their makeup and other details are given in Tables 1 and 2. None of the cartridges were rinsed with distilled water after filtration. The maximum saltwater retained in the prefilter could contribute up to $\sim 6-7$ g of salt (corresponding to about 250 ml of salt water), while the amount of salt retained on the MnO$_2$-coated filter cartridges were found to be negligible, implying that no salt water was retained in the pores and are completely closed with MnO$_2$. The fibers from extractor cartridges were cut away from the inert cartridge cores, packed into high-temperature-resistant crucibles, and ashed at 500°C for ~ 6 h. The homogenized ash was packed into a gamma vial and quantified using a NIST- and IAEA SRM-calibrated gamma ray spectrometer (U standard from NIST for ^{234}Th and RGU-1 from IAEA for ^{234}Th). Errors reported for ^{234}Th are the propagated errors arising from

Table 2. The ^{234}Th Activities and Absolute and Relative Efficiency for the Extraction Efficiency Experiment

Filter	Color of Filter[a]	DOC[b] (ppm)	Flow Rate (dpm L^{-1})	Total Ash Weight (g)	^{234}Th Total Activity (dpm)	Absolute Efficiency[c] (%)	Relative Efficiency[d] (%)
SET-I							
F1	**D**	4.74	4−5	24.993	28,336 ± 384	97.5	96.9
F2	D		4−5	39.170	883 ± 37	–	85.5
F3	D		4−5	36.722	128 ± 27	–	–
SET-II							
PF	PF	4.64	4−5	7.795	1104 ± 17	–	–
SET-III							
F1	N	4.64	4−5	8.270	25,882 ± 362	89.1	88.7
F2	N		4−5	3.250	2,912 ± 32	–	76.9
F3	N		4−5	2.218	673 ± 12	–	–
SET-IV							
F1	N	0.50	4−5	4.052	23,472 ± 279	80.8	88.7
F2	N		4−5	2.212	2655 ± 37		99.1
F3	N		4−5	8.746	237 ± 11		
SET-V							
F1	D	4.70	4−5	13.293	26,490 ± 354	91.2	87.5
PF1	PF		4−5	10.444	530 ± 13		
F2	D		4−5	9.274	3320 ± 67		
PF2	PF		4−5	7.741	277 ± 11		
SET-VI							
F1	L	4.13	4−5	2.279	21122 ± 140	72.7	77.5
PF1	PF		4−5	1.465	665 ± 23	–	71.4
F2	**L**		4−5	2.827	4747 ± 51		
PF2	PF		4−5	8.012	318 ± 18		
F3	L		4−5	7.847	1359 ± 21		
SET-VII							
F1	N	4.37	4−5	2.351	17,677 ± 146	60.9	73.6
PF1	PF		4−5	2.544	544 ± 19		
F2	N		4−5	2.535	4668 ± 44	–	65.2
PF2	PF		4−5	7.885	1192 ± 19		
F3	N		4−5	6.990	1626 ± 20		
SET-VIII							
F1	L	4.36	4−5	3.480	18,170 ± 147	62.6	76.7
F2	D		4−5	30.455	4240 ± 90		
PF	PF		4−5	7.963	238 ± 21		
SET-IX							
F1	D	3.95	4−5	21.58	24,361 ± 370	84.8	83.9
F2	L		4−5	2.692	3715 ± 37		
PF	PF		4−5	8.351	233 ± 11		
SET-X							
F1	N	2.19	4−5	2.161	30,068 ± 264	103.5	80.5
F2	N		4−5	3.617	5863 ± 61		49.2
F3	N		4−5	3.119	2979 ± 57		
SET-XI							
F1	D	2.12	4−5	14.483	23,360 ± 396	80.4	73.8
F2	D		4−5	38.136	6114 ± 145		76.6
F3	D		4−5	11.148	1433 ± 41		
SET-XII							
F1	L	2.59	4−5	2.317	14,711 ± 113	50.6	82.7
F2	L		4−5	1.804	2544 ± 25		36.1
F3	L		4−5	2.356	1626 ± 21		

[a] D, deep or dark as in Table 1 footnote (36 h); L, light (6 h); N, normal (12 h) soaking in hot KMnO₄ bath; PF, precleaned prefilter.
[b] Average of three samples, one collected before filtration started, one after 1/3 of filtration and the third after 2/3 filtration (1 ppm = 83.3 μM).
[c] The absolute extraction efficiency was calculated using equation (1).
[d] The relative extraction efficiency was calculated using equation (5).

Table 3. Activity of and Fraction of ^{234}Th Retained in the Prefilter Cartridges

Experiment	^{234}Th Activity (dpm)	% of Total[a]	$F_{PF/Mn}$[b] (%)
SET-II-PF	1104 ± 17	3.8	-
SET-V-PF1	530 ± 13	1.8	2.0
SET-V-PF2	277 ± 11	1.0	8.3
SET-VI-PF1	665 ± 23	2.3	3.1
SET-VI-PF2	318 ± 18	1.1	6.7
SET-VII-PF1	544 ± 19	1.9	3.1
SET-VII-PF2	1192 ± 19	4.1	25.3
SET-VIII-PF	238 ± 21	0.8	5.6
SET-IX-PF	233 ± 11	0.8	6.3

[a] Total ^{234}Th added in the experiment = 29048 dpm (details in section 2).
[b] $F_{PF/Mn}$ = activity in PF/Activity of ^{234}Th in the MnO₂-coated cartridge placed prior to the PF.

counting statistics and calibration of the detector and ^{234}Th spike.

3. Results and Discussion

3.1. DOC Concentrations

[8] The average concentration of dissolved organic carbon (DOC) in 7 samples was found to be 4.4 ± 0.3 ppm (range: 4.0–4.7 ppm; 1 ppm = 83.3 μM). The concentration of DOC after UV irradiation ranged from 2.12 to 2.59 ppm, with a mean value of 2.30 ppm, indicating about 54% of DOC is lost because of UV irradiation.

3.2. Variations in the Ash Weight

[9] We assumed that the cartridge ash weight is a reasonable proxy of the amount of MnO₂ coated on the fiber (Table 2). The ash weight varied considerably within one batch (e.g., in batch made on 19 January (dark coating): 14.48 to 39.17 g (mean = 29.36 g, n = 7); light coating (L): 1.80 to 7.85 g; mean = 3.20 g (n = 8); normal coating (N): 2.16 to 8.27 g, mean = 4.13 g, n = 12). Although all 12 cartridges in a batch were treated the same way and they were constantly moved around in the KMnO₄ bath, the possibility of nonuniform coating still exists and this can be due to factors such as location of a cartridge in the bath, contact with the precipitated KMnO₄ crystals, distance from the heating element(s), rate of mixing of the heated solution in the bath, etc., under which the cartridges were soaked in the KMnO₄ bath. *Mann et al.* [1984] also reported that the polypropylene filters do not impregnate uniformly with MnO₂. The question as to whether the ash content (mea-

sure of the amount of sorption sites) is related to the absolute or relative extraction efficiency of Th is discussed below.

3.3. Retention of Dissolved and Desorbed ^{234}Th Onto Prefilter Cartridges

[10] Although prefilter (PF) cartridges have been used extensively to retain particulate matter, no systematic studies have addressed if any dissolved ^{234}Th was retained by the prefilter. In SET-II, we passed ^{234}Th spiked seawater through a PF and found 3.8% of ^{234}Th was retained by the prefilter. While the nature and composition in the coastal water can be different than open ocean water, a Th colloid complex in the dissolved phase could play an important role in the removal of dissolved Th. In addition, when seawater is passed through MnO₂-coated cartridges, it is not known if any Th-laden MnO₂ particles can desorb and subsequently bleed through to the next cartridge. This could contribute to observed variable extraction efficiencies. To evaluate this, we placed prefilters in between MnO₂-coated cartridges (Tables 1–3) and our results indicate that 0.8 to 4.1% (mean: 1.7%, n = 8; Table 3) of the total ^{234}Th was sorbed onto these prefilters (Tables 1 and 2). Since the water was filtered through a 0.5 μm prefilter cartridge, we attribute this to the release of either Th-containing MnO₂ particles or fractional removal of dissolved Th. A comparison of the ratios of the activities in the prefilter to those in the previous MnO₂ filter ($F_{PF/Mn}$) suggests that the $F_{PF/Mn}$ varied from 2.0% to 8.3% (except one with a value of 25.3%). We are unable to unequivocally resolve whether the adsorbed Th on the prefilter is derived from MnO₂ fiber or dissolved Th passing through MnO₂ filter. Since dissolved Th goes through the first PF prior to entering a MnO₂ filter, it is presumed that "sorbable Th" is removed in the first PF and Th collected on the PF placed in between MnO₂-coated filter cartridges is likely derived from the desorption of Th from the MnO₂-coated filter. If Th is derived from the MnO₂ cartridge, then this could contribute to the variation in absolute efficiency (= activity retained in the filter/activity entering into the filter) between first and second MnO₂ filter cartridges.

[11] Recent controversy on the overestimation of extraction efficiencies (and hence underestimation of dissolved activities) led to the following observations [*Cai et al.*, 2006, 2008; *Hung et al.*, 2008]:

[12] 1. Larger pore sizes result in lower efficiencies for a given flow rates: while the raw filter will have
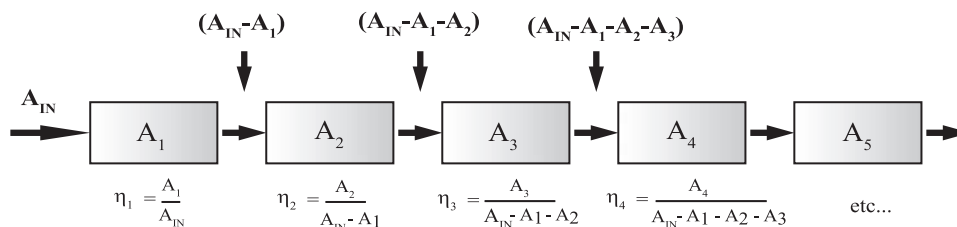
Figure 1.   Filtration assembly with absolute extraction efficiency equations.

distinct pore size, soaking in saturated KMnO₄ will result in filling of those pore spaces to a large extent and hence the pore sizes will be altered. Thus, relationship between pore sizes and extraction efficiency is not anticipated. The differences in the amount of residual salt found in the PF and MnO₂ filters support this (section 2.3). On the other hand, the flow rate is a measure of the contact time of dissolved ^{234}Th and MnO₂ surface and could affect the extraction efficiency.

[13]   2. ^{234}Th deficit observed at deeper depths (>500 m [*Cai et al.*, 2008, and references therein]) could be either due to sampling and analytical artifacts and/or real oceanographic phenomenon that remains undocumented. Even with the small-volume MnO₂ precipitation method, high ^{234}Th values have been reported (e.g., at 52 m: 2.45 ± 0.09 dpm L^{-1}, with ^{234}Th/^{238}U = 1.01 ± 0.04; at 110 m: 2.76 ± 0.10 dpm L^{-1}, with ^{234}Th/^{238}U = 1.13 ± 0.04; at 290 m: 3.52 ± 0.13 dpm L^{-1}, with ^{234}Th/^{238}U = 1.46 ± 0.05 [*Cai et al.*, 2008]). Extremely careful and rigorously tested sampling and analytical protocols will be needed to address this issue and resolve the new oceanographic phenomenon from analytical artifacts.

3.4. Derivation of the Relative Extraction Efficiency

[14]   A schematic of the five-cartridge filtration setup and the corresponding activity is shown in Figure 1. If we assume A_{IN} to be the initial activity of dissolved ^{234}Th entering the first MnO₂ filter cartridge, A_i and A_j are the activities in the ith and jth cartridges (i = 1–5 and j = i–1). The absolute extraction efficiency (η_i) in the ith cartridge can be derived as follows:

$$\eta_i = A_i{}^* 100 / \left(A_{IN} - \sum A_j \right) \qquad (1)$$

$$\eta_1 = A_1{}^* 100 / A_{IN} \qquad (2)$$

$$\eta_2 = A_2{}^* 100 / (A_{IN} - A_1) \qquad (3)$$

for uniform extraction efficiency in the first two cartridge filters ($\eta_1 = \eta_2$). Therefore,

$$A_1 / A_{IN} = A_2 / (A_{IN} - A_1)$$

$$\text{or } A_{IN} A_2 = A_{IN} A_1 - A_1^2 \qquad (4)$$

$$\text{or } A_{IN} = A_1^2 / (A_1 - A_2) = A_1 / (1 - A_2 / A_1) \qquad (5)$$

Equation (5) defines the relative extraction efficiency and is also the standard equation used to determine Th activity. The relative extraction efficiency given by the term $(1 - A_2/A_1)$ will yield a negative efficiency if $A_2 > A_1$.

3.5. Variations in Relative Extraction Efficiency

[15]   The relative extraction efficiency in percent (= $100*(1 - F_2/F_1)$) calculated using equation (5) for successive pairs of MnO₂-coated cartridges is presented in Table 2. The absolute efficiency was calculated only for the first MnO₂ filter while the relative efficiency was calculated for two sets of successive ones. The relative efficiency varied from 65.2 to 99.1% (excluding two values that are less than 50%, Table 2), similar to highly varying inter-sample extraction efficiencies reported in literature
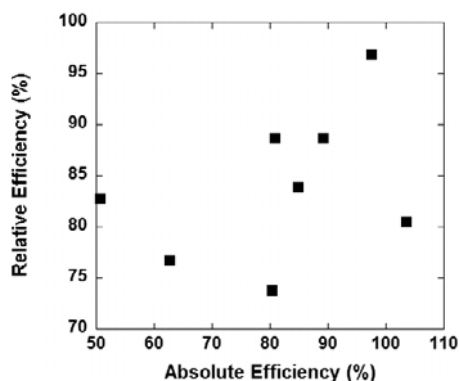

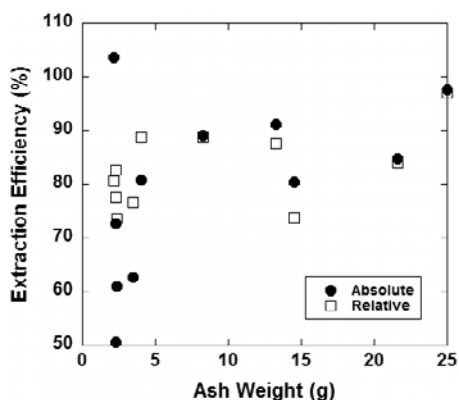**Figure 2.**   Relative efficiency versus absolute efficiency.

Figure 3. Extraction efficiency versus ash weight of the first cartridge (see comment in section 3.6).

(summarized by *Hung et al.* [2008]; in a small subset of samples, low efficiencies have also been reported; e.g., *Cochran et al.* [1995], less than 50%; *Baskaran et al.* [2003], less than 65%; and *Cai et al.* [2006], less than 60% and some negative values due to activity in $F_2 > F_1$). From such studies, it is evident that ~10% (±1 σ) variations in the reported efficiencies are common. In all MnO₂-coated cartridges connected in series, the relative efficiency is much more variable (36.1 to 99.1%) than the absolute efficiency (50.6 to 103.5%, Table 2). Thus, it is critical that we evaluate the variations on the individual absolute extraction efficiency of these cartridges.

3.6. Variations in the Absolute Extraction Efficiency and Comparison With Relative Efficiency

[16] An assumption that the absolute extraction efficiency (% = 100*(activity retained/activity going into the filter cartridge)) in the first and second MnO₂ extractor cartridges to be the same ($\eta_1 = \eta_2$) implies that the absolute and relative extraction efficiency should yield the same value. The relative extraction efficiency in the first two filter cartridges varied between 49.2 to 99.1% (excluding one light-coated cartridge, SET-XII-F2, Table 2). In 5 of the 7 experiments, the relative extraction efficiency in first-second MnO₂ pair was higher than that in second-third pair. A plot of the relative efficiency plotted against the absolute efficiency (Figure 2), suggests that there is no significant correlation between the relative and absolute efficiency. Coastal waters are generally enriched with organic colloidal material and it is likely that some of the spike added in the water readily forms a complex with the colloidal organic matter that is not retained

uniformly by the filter cartridges. If about 1–10% of the total ²³⁴Th added becomes colloid-bound ²³⁴Th and passes through the first cartridge, we can typically have absolute efficiencies similar to the values reported in this study. However, if varying amounts (>10%) of the colloidal ²³⁴Th are retained in subsequent cartridges, then the absolute and relative efficiencies will be highly variable. In SET-X through XII, we conducted a set of experiments with water exposed to UV rays where the DOC concentrations decreased by about 50% (Table 2). The relative efficiency in the Dark and Normal cartridges varied between 49 and 81% (excluding the Light cartridges in SET-XII). Thus, complexation of Th with UV degradable colloids does not appear to affect the variations in absolute and relative efficiencies. While previous studies have speculated that the organic complexation of Th could result in variations in extraction efficiency of Th, so far no experimental evidence has been published [*Cai et al.*, 2006; *Rutgers van der Loeff et al.*, 2006; *Santschi et al.*, 2006]. With our data, we are unable to exclude the possibility that only UV-resistant refractory DOM complexes with Th and is removed on to the filter cartridges. In the present case, the nature and composition of the colloidal material likely remained the same in all the water samples used in this study and hence the variations appears to suggest that complexation of Th with colloids is less likely to be the reason for the observed variations in the extraction efficiency (both absolute and relative). *Cai et al.* [2008] hypothesized that colloidal Th is not collected by MnO₂ cartridges, although colloidal Th in the size range of >1 kD could be as high as 64% (11 to 64%, mean = 20.0%, n = 16 [*Santschi et al.*, 1995]), most of colloidal Th ought to have been removed by MnO₂-coated cartridges, as mass balance was found in many of the samples. Other factors such as the amount of MnO₂ coated on the cartridges (i.e., the rate of reaction between the tracer and the extractor MnO₂), and temperature and duration of MnO₂ impregnation can also affect the extraction efficiency. However, there is no relationship between the absolute or relative extraction efficiency and the amount of ash weight of the first cartridge, although very low absolute efficiencies are found in low ash weight samples (Figure 3). A summary of earlier results on the relationship between extraction efficiency and flow rate through MnO₂ cartridges connected in series is given by *Rutgers van der Loeff et al.* [2006]. When the surface area of the fiber remains unsaturated with respect to any element of interest, we expect the volume of water filtration to be independent of the

extraction efficiency. It appears that contact time of the nuclide with MnO_2-coated surface in some cases plays a role while in other cases, the amount of contact time seems to be independent of the amount of nuclide extracted. Manganese oxide can exist in more than one form (α-MnO_2, β-MnO_2, γ-MnO_2, ε-MnO_2 and λ-MnO_2) on the surfaces of the polypropylene matrix and the variations in the form of MnO_2 could also affect the extraction efficiency, although pyrolusite (β-MnO_2) is expected to be the most common form [*Fong et al.*, 1994]. So far, the form of MnO_2 oxide coated on the filter has not been determined and/or reported and remains an unknown.

3.7. Use of Constant Extraction Efficiency in Calculating Dissolved [234]Th

[17] To address the potential error in dissolved [234]Th activities from the implied assumption of uniform extraction efficiency, we evaluated the possibility of combining the two filters and assuming constant extraction efficiency for the set of two cartridges. The constant extraction efficiency value used for a pair is taken to be the average value of all the relative extraction efficiencies in the two successive cartridge filters (in our case, calculated from the cartridges 1 and 2 and cartridges 2 and 3). The activity of [234]Th entering the first cartridge filter was then calculated as follows:

[18] Activity entering the first cartridge (which is the activity in the field sample)

$$= (A_1 + A_2)/[\eta + \eta(1.00 - \eta)] \qquad (6)$$

where η is the average of the relative extraction efficiency (0.842 in our study, average of 12 values; only those values when the MnO_2 filters are next to each other are used (PF next MnO_2 filters are not used; values below 50% are discarded as they are meaningless). The activity thus obtained is compared to the spike added to the experiment (i.e., activity entering the first filter cartridge) in Table 2. It was shown earlier [*Swarzenski and Baskaran*, 2004] that in ~30% of the samples (8 out of 25), the activity calculated using equation (5) assuming uniform extraction efficiency yielded meaningless values, either negative or with errors >80% while the activity calculated using constant extraction efficiency after combining the two successive cartridges yielded a much more realistic value. Thus, it appears that use of constant extraction efficiency on the combined activity in two filters provide a more meaningful measure of activity than the value obtained using the assumption of uniform extraction efficiency.

4. Conclusions

[19] The following results can be summarized from our extraction efficiency experiments:

[20] 1. Some amount of dissolved and/or desorbed [234]Th (although small, <6%) is removed by the prefilter cartridge. If this is a common occurrence, then the particulate activities reported in the literature may be overestimates.

[21] 2. There are indications that some amount of [234]Th is also desorbed from the MnO_2 cartridges, although the amount is relatively small (<5%).

[22] 3. There is a relatively large variation in the absolute efficiency of the first and second filter cartridges. Thus, the assumption of uniform extraction efficiency in two cartridges could introduce error on the value of dissolved [234]Th activity.

[23] 4. We suggest using constant extraction efficiency on the combined activity from two filter cartridges (activities in $F_1 + F_2$) connected in series to obtain a dissolved [234]Th activity. The average value of the relative efficiency from all the cartridges could be used as the constant efficiency value.

Acknowledgments

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