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Is the Extraction of Thorium onto MnO$_2$-coated Filter Cartridges Uniform?

by

P. W. Swarzenski[1] and M. Baskaran[2]

1:    U.S. Geological Survey, Center for Coastal and Watershed Studies, St. Petersburg, FL 33701

2:    Department of Geology, Wayne State University, Detroit, MI 48202

Abstract:

Large-volume (i.e., $10^2 - 10^3$ L) seawater samples are traditionally required to study the partitioning of particle-reactive radionuclides between solution and size-fractionated particulate matter. One of the most frequently used methods to preconcentrate the short-lived isotopes of Th (^{234}Th and ^{228}Th) from such large volumes of water involves the effective extraction of Th onto two MnO_2-coated polypropylene cartridges. Determination of dissolved Th activities assumes that the two MnO_2-coated filter cartridges extract Th uniformly (same extraction efficiency), but this assumption has not been rigorously validated. Any variability in the extraction efficiency of the two cartridges connected in series will directly introduce an error in the determination of final dissolved Th activity. In this article, we evaluated the variability in the extraction efficiency of MnO_2-coated filter cartridges that were prepared under varying conditions.

Thorium-234-spiked seawater was filtered in series through a manifold consisting of six MnO_2-coated cartridges. From the activities of ^{234}Th retained in each cartridge, the relative (calculated from the activities in two successive cartridges) and absolute (ratio of ^{234}Th activity retained to the activity entered) extraction efficiency for each of the cartridges was calculated. At a constant flow rate and constant $KMnO_4$ saturation, the absolute extraction efficiency varied by ~40% (from 54.1 to 93.8%) within the first two filter cartridges, and over 50% (from 32.3 to 89.3%) on all six MnO_2 cartridges. Our results confirm that a uniform extraction efficiency using two filters connected in series is rarely achieved. Using the average extraction efficiency of all cartridges, we propose a new approach that assumes a constant extraction efficiency. This method will reduce the error introduced by the assumption of uniform extraction efficiency in the determination of dissolved Th activities.

1. Introduction:

In seawater, the distribution of particle-reactive radionuclides such as Th and ^{210}Pb in the U/Th-series has provided a wealth of information on marine particle dynamics, while the more soluble radioisotopes, such as radium, have been effectively utilized to trace water masses and to estimate horizontal and vertical mixing coefficients. The activities of many of the short-lived U/Th-series radionuclides in aqueous systems are so dilute that most of these nuclides require considerable preconcentration prior to their radiochemical separation and analyses. With the advent of new mass spectrometric methods (e.g., thermal ionization mass spectrometry and inductively coupled plasma mass spectrometry), many U/Th-series radionuclides that have higher atomic abundances (half-lives greater than ^{226}Ra, 1,620 yrs), such as ^{232}Th, ^{230}Th, ^{231}Pa, ^{234}U, ^{235}U and ^{238}U, have successfully been measured in small-volume samples (Chen et al., 1986; Toole et al., 1991; Cohen et al., 1992; Luo et al., 1997; Fietzke et al., 1999; Hinrichs and Schnetger, 1999; Stirling et al., 2000). However, radiometric counting methods are still the only way of measuring environmental levels of nuclides with half-lives less than 100 yrs, due to their low atomic abundances. For example, the longest-lived radionuclide in the U/Th decay series below ^{222}Rn is ^{210}Pb, with a half-life of 22.3 yrs. If ^{210}Pb were to remain in secular equilibrium with ^{238}U in ocean water, its atomic abundance would be ~ 4.1 x 10^{7} atoms L^{-1}, as opposed to 8.5 x 10^{15} atoms L^{-1} for ^{238}U (neglecting atmospheric input to the surface waters). With a relatively short residence time of ^{210}Pb in the water column, the concentration of ^{210}Pb is $\sim$ two orders of magnitude lower than this value, and hence the atomic abundance would be $\sim 10^{5}$ atoms L^{-1}. Similarly, the atomic abundance of ^{234}Th would be $\sim$ 1.2 x 10^{5} atom L^{-1}, if ^{234}Th and ^{238}U are assumed to be in secular equilibrium.

Therefore, several methods have been developed to preconcentrate radionuclides from natural waters. These include co-precipitation with Fe- and Al-hydroxides, and selective sorption onto Fe-and/or Mn-coated surfaces. The most widely used preconcentration method for

particulate and dissolved Th is to pass a large volume of water through a set of prefilters that ideally retain particulate Th, while dissolved Th will be adsorbed onto the two MnO_2-coated cartridges (e.g., Buesseler et al., 1992; Baskaran et al., 1993, 1996, 2003; Colley and Thomson, 1994; Cochran et al., 1987, 1996; Moran et al., 1997; Charette and Moran, 1999; Benitez-Nelson et al., 2000; Guo et al., 2002). The fundamental assumption inherent to this technique is that the two Mn filters connected in series extract Th in a uniform and consistent manner (i.e., exactly the same extraction efficiency). However, this assumption has not been rigorously tested, and any significant deviation from uniform extraction of Th will significantly affect the determination of Th activities. In this article, we present results from a series of experiments that address the variability of the extraction efficiency of traditional MnO_2 filters as a function of variable degree of $KMnO_4$ saturation and provide a new method to standardize the extraction efficiency calculations.

2. Review of Earlier Methods of Preconcentration For Radionuclides:

Many methods have been developed to preconcentrate radionuclides from large volumes of seawater. Merrill et al. (1960) were among the first to propose the use of dispersed insoluble hydroxides on cation-exchange columns to remove Be from large volumes of seawater. Lal et al. (1964) developed the first method to extract a subset of trace elements such as Si, Be, Al, and Ti from coastal seawater by filtering seawater through a low-resistance matrix of ferric hydroxide. Krishnaswami et al. (1972) used synthetic acrilon fiber coated with ferric hydroxide to extract Th, Pb, Si, and Ra from seawater. Moore (1976) used fluffy acrylic fiber coated with MnO_2 to extract [228]Ra from seawater quantitatively. Fluffy acrylic fiber was also shown to extract Ra, Th and Ac, isotopes quantitatively (Reid et al., 1979). A potential problem with the use of acrilon fiber is that the ash content is relatively high (10-15% of the raw fiber weight) and thus reduces the effective volume of water samples that will be counted in a Ge-well detector (for a typical 10-ml geometry). Furthermore, acrilon fiber has been shown to contain high blank levels of select

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radionuclides (^{226}Ra: 0.1-1.0 dpm/100 g of acrylic fiber, Moore and Reid, 1973; Reid et al., 1979; ^{228}Ra: 0.1 to 0.2 dpm/100 g of acrylic fiber, Knauss et al., 1978; Reid et al., 1979; ^{232}Th, ^{230}Th, ^{228}Th: 0.05 to 0.16 dpm/100 g of acrylic fiber, Moore, 1976; Knauss et al., 1978; Moore et al., 1985). Mann et al. (1984) observed higher blank levels for Pu in cotton fibers as compared to polypropylene fiber material. Moore and Reid (1973) used MnO_2-impregnated acrylic fiber cartridges to extract dissolved Ra from natural waters. Wong et al. (1979) was the first one to determine the concentration of Pu from seawater using two filter cartridges connected in series and assumed uniform extraction efficiency in the two filters. The distinct advantage of using fiber cartridges is that the filtration process can occur in the field (either *in situ* or in a field-based laboratory), instead of having to bring large volumes of seawater back to the lab for subsequent processing. Many researchers have started using *in-situ* filtration pumps to preconcentrate radionuclides at various depths in the deep ocean using such a cartridge methodology (e.g., Nozaki et al., 1981; Bacon and Anderson, 1982; Baskaran et al., 1993, 1996, 2003; Buesseler et al., 1995; Cochran et al. 1996; Guo et al., 1995; Moran et al., 1997). Mann and Casso (1984) extended the concept of Wong et al. (1979) to determine the concentrations of ^{137}Cs by passing water through a tandem cartridge consisting of twin beds of ion-exchange resin impregnated with cupric ferrocyanide. Mann et al. (1984) first used a three-cartridge series to extract transuranics from seawater, the first being employed to retain the particulate matter and the remaining two to extract dissolved radionuclides. Since then, many other researchers have utilized this method to obtain particulate and dissolved phases of Th and ^{210}Pb (e.g., Buesseler et al., 1992; Baskaran et al., 1993; Baskaran and Santschi, 2003). The advantages and disadvantages of this method include:

a) Simultaneous measurement of gamma-emitting radionuclides, such as ^{234}Th (although the most useful gamma line at 63 keV has a branching ratio of only 4%), ^{210}Pb and Ra isotopes, although relatively higher amounts of extraction of Th and Pb can be accomplished while Ra extraction is highly variable (e.g., Baskaran et al., 1993; Colley

and Thomson, 1994; Baskaran and Santschi, 2003). However, activity ratios of Ra (^{228}Ra/^{226}Ra, ^{223}Ra/^{226}Ra, and ^{224}Ra/^{228}Ra) can be readily obtained from large samples.

b) Large volume sampling is still required for ^{228}Th measurements, although atom abundances of ^{230}Th and ^{232}Th in seawater are sufficiently high for detection via modern mass spectrometric techniques.

c) Selective removal of Th but not U, which eliminates extensive chemical separation of U from Th isotopes in the field, as in the case of the $Fe(OH)_3$-precipitation method;

d) Simultaneous determination of both dissolved and particulate phases is possible; and

e) 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), which is not possible with other methods.

In addition, to estimate particulate organic carbon (POC) export from the euphotic zone using ^{234}Th as a tracer, POC/^{234}Th ratios on sinking particulate matter are needed and obtained by size-fractionated filtration of large seawater samples. The distinct disadvantage lies with the assumption that the first and second MnO_2-coated cartridges extract Th uniformly. In fact, some earlier studies have shown that this efficiency to be highly variable and can range from < 50% to 100% (e.g., Bacon et al., 1989; Cochran et al., 1996) for Th isotopes. This range reflects the variability in the extraction efficiency from sample to sample, under the assumption that both cartridges extract Th uniformly. However, it remains unknown whether these variabilities are due to differences in the cartridges or in the samples. The discrete variability in the extraction efficiency of the two cartridges has not been systematically determined and is the subject of this paper.

3. Materials and Methods:

The most commonly reported parameters that cause variations in the extraction efficiency of the MnO_2-coated cartridge filters include: variations in the volume of water filtered, fluctuations in the flow rates, and variations in the cartridge-preparation techniques, including the temperature during MnO_2-impregnation (e.g., Buesseler et al., 2001). For the following extraction efficiency experiments, we kept the volume of water filtered, and the cartridge preparation and temperature during MnO_2 impregnation constant. The flow rates varied between 2.8 and 7.5 L min^{-1}. We believed this variation in flow rates would not cause any major difference in the extraction efficiency, and thus, absolute variations in the extraction efficiencies of the MnO_2-coated cartridges due to changes in the preparation of MnO_2 cartridges can be quantitatively assessed.

3.1 Preparation of filter cartridges:

We used 7- x 25-cm filter cartridges, consisting of a spun, woven special polypropylene fiber wound over a cylindrical core of perforated polypropylene (Johnson Filtration, Amarillo, TX, Polypropylene Media Filter Cartridge, Model: JP0.5R10P). Because the manufacturing process of these commercially-available cartridges involves the addition of large amounts of anti-wetting surfactant that can interfere with the impregnation of MnO_2, a rigorous cleaning of this surfactant was required. The raw filters were first cleaned by soaking a batch of 12 cartridges in 20-L plastic buckets at ~60°C for ~ 12 hrs in a bath of: 1) 2% Micro cleaning solution; 2) 2 M HCl; 3) 0.5 NaOH; and 4) 2 M HNO_3. The filters were rinsed in tap water before and after soaking them in cleaning solutions until the pH of the wash solution stabilized at around ~7. An average weight of an uncleaned prefilter is ~150 g, and the ash weight of the cleaned prefilter is less than 0.1% of its original weight. Each precleaned filter was then soaked in a saturated $KMnO_4$ solution (250 g $KMnO_4$ per liter of water) in a plastic container for a specific period of time at ~70°C. The soaking time in the $KMnO_4$ bath varied from 36 hrs (DARK, D) to 6 hrs (LIGHT, L) with a normal soaking time of 12 hrs (NORMAL, N) for this set of experiments.

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This procedure for coating the precleaned polypropylene cartridges produced extraction cartridges with MnO_2 weights ranging from 0.1 to 10% of the total weight of the prefilter cartridges, depending on how long the filters were soaked in the $KMnO_4$ bath. After the $KMnO_4$ bath, one batch of six cartridges was thoroughly washed with tap water. This water flow was connected directly to two DARK MnO_2-coated cartridges to remove any radionuclides of interest that may be present. We periodically ashed the MnO_2-cartridges to determine potential blank Th activities, and we did not find any. The filter cartridges were bagged wet.

3.2 Milking of ^{234}Th:

Thorium-234 spike was obtained by passing a uranyl nitrate solution through two large concentrated HCl-conditioned columns (Dowex-1 anion-exchange column: AG 1-X4, 100-200 mesh, chloride form) successively in order to separate U from Th quantitatively. The amount of U loaded onto the column and the saturation capacity of the anion-exchange resin were 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 by passing the spike through 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 using the 63-keV photopeak.

3.3 Extraction efficiency experiment:

For this experiment, a large seawater sample (150 L) was collected from Tampa Bay, Florida, (salinity of 26) and initially prefiltered through a precleaned polypropylene filter cartridge (0.5-μm median pore size). A known amount of pH-neutralized spike (31074 dpm/ml ^{234}Th) was added to the sample, stirred vigorously for ~30 min, and then allowed to equilibrate

for ~2 hrs. After 2 hrs, the water sample was filtered through a manifold consisting of six pre-assigned cartridge filters. We ensured that the cartridge housings were operating correctly in that flow of water passed directly through the cartridge filters without any leaks or malfunctions. After filtration, the cartridges were rinsed with distilled water to remove any salts. From previous laboratory experiments, it has been demonstrated that the loss of ^{234}Th during rinsing process was negligible (Santschi et al., 1999). The fibers from the extractor cartridges were cut away from the inert cartridge cores, packed into crucibles, and ashed at 500°C for ~6 hrs. The ash was homogenized and a known weight of this ash was packed into a gamma-counting vial and gamma counted for ^{234}Th (63 keV peak) in a Ge-well detector coupled to InSpector (CANBERRA Inc.). The amount of ash utilized for gamma counting varied from 14.3% to 100% (53% of the samples) of the total ash weight. The gamma-counting system was calibrated with liquid and sediment standards obtained from NIST and IAEA (U-standard from NIST for ^{234}Th and RGU-1 from IAEA for ^{234}Th). The densities of the sample and standards were comparable; thus, no self-absorption correction was applied (Baskaran et al., 1993).

4. Results and Discussion:

4.1 Variations in the ash weight:

In these experiments, we assumed that a cartridge ash weight is a reasonable proxy for the amount of MnO_2 coated on the fiber (Table 1). Nonetheless, the ash weight varied considerably within one batch; for example, for the batch made on 27th June (all DARK cartridges – 36-hr soak in $KMnO_4$ bath), the ash content varied between 12.21 and 15.09 g, with a mean value of 13.99 g (n=7). In contrast, during the LIGHT coating (6-hr soak in $KMnO_4$ bath), the ash content varied between 1.73 and 10.76 g with a mean value of 3.72 g (n=12). However, there were two cartridges that had significantly higher ash content (10.53 and 10.76 g), which could be due to direct contact with the precipitated MnO_2 at the bottom of the $KMnO_4$ bath. Although all cartridges in a batch (twelve) were treated the same way and they were constantly moved around

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in the $KMnO_4$ bath, the possibility of non-uniform coating still exists. Excluding the outliers, the mean value of 2.34 g (range: 1.73 to 2.83 g) was considerably lower (with a higher percentage range) than those for the DARK-coated cartridges. In two other batches of DARK cartridges, the variations were fairly large. The range in ash content for a normal coating (12-hr soaking in $KMnO_4$ bath) was also wide (1.83 to 4.21 g). Thus, there are variations in the ash content that could be, at least in part, attributed to cartridge-preparation methods [such as location of a cartridge in a bath, contact with the precipitated $KMnO_4$ crystals, distance from the heating element(s), rate of mixing of the heated solution in the bath, etc.)]. For example, Mann et al. (1984) reported that polypropylene filters do not impregnate uniformly with MnO_2. It is possible that the surfactants utilized in making these cartridges were not cleaned properly prior to soaking in the $KMnO_4$ bath and caused poor impregnation. The question as to whether the ash content (measure of the amount of sorption sites) is related to the absolute or relative extraction efficiency of Th is discussed below.

4.2 Derivation of the absolute and relative extraction efficiency:

A schematic of the six-cartridge filtration setup and the corresponding activity in each cartridge is shown in Figure 1. If we assume A_I to be the initial activity of dissolved ^{234}Th entering the first MnO_2 filter cartridge, A_i and A_j are the activities in the 'i'th and 'j'th cartridges $(i = 1,2,3,4, \ldots..$ and $j = i-1)$. Thus, the absolute extraction efficiency (η_i) in the 'i'th cartridge can be derived as follows:

$$\eta_i = A_i *100 / (A_I - \Sigma A_j) \qquad (1)$$

$$\eta_1 = A_1 *100 / A_I \qquad (2)$$

$$\eta_2 = A_2 *100 / (A_I - A_1) \qquad (3)$$

For uniform extraction efficiency in the first two cartridge filters (i.e., $\eta_1 = \eta_2$)

Therefore, $\qquad\qquad\qquad A_1/A_I = A_2 / (A_I - A_1)$

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

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

Equation (5) is the standard equation used to determine the Th activity if one assumes that the two filter cartridges extract Th uniformly.

4.3 Variations in relative extraction efficiency:

The relative extraction efficiency is calculated using Eq. (5) for the first five cartridges and the results are presented in Table 1. The calculated relative efficiency, using [234]Th activities from the first three cartridges (two values for each set), in all five sets varied from 64.3 to 96.4% similar to highly varying extraction efficiencies reported from sample to sample in literature. For example, Mann et al. (1984) reported an extraction efficiency using MnO_2-coated cotton filter cartridges that varied between 16 and 100% for Pu and 76 to 100% for Am. Livingston and Cochran (1987) found that the extraction efficiency using MnO_2-polypropylnene filter cartridges varied between 69 to 93% (mean: 82.7%, n=12) and 71 to 94% (mean: 87.1%, n=12), for Th and Am, respectively. Bacon et al. (1989) reported extraction efficiencies of 97 to 100% for Th, and 55 to 80% for Pa using MnO_2-coated acrylic fiber cartridges. Using MnO_2-treated polypropylene cartridges, Cochran et al. (1987) observed very low extraction for Pu (~10%), and this was attributed to the lower scavenging of the oxidized Pu present in the water column. Those authors also observed that the extraction efficiency for [230]Th and [241]Am varied between 76.4 and 91.2% (83.8±7.4%, 1SD), and 71.2 and 96.0% (83.6±12.4%, 1SD), respectively. Buesseler et al. (1992) reported an extraction efficiency that ranged between 70 and 95% (87±8%, 1SD, Buesseler et al., 1992; 79±9%, 1 SD, Buesseler et al., 1995) for [234]Th. Cochran et al. (1996) observed a large range in the extraction efficiency, from 65 to 100% (74.0±17.0%, 1SD), with a few samples less than 50%, in the Arctic waters in the Nansen Basin. For the Amerasian Basin, Moran et al. (1997) reported an extraction efficiency that varied between 82.3 to 96.9% (89.6 ±7.3%, 1SD) for

^{234}Th, whereas Baskaran et al. (2003) reported the extraction efficiency to vary between 72 to 98% for ^{234}Th in the Canada Basin. Baskaran et al. (2003) also reported that a couple of samples had less than 65% efficiency, and discarded those samples from further interpretation. Guo et al. (2002) found the extraction efficiency to vary between 70 and 92%. From such studies, it is evident that ~20% (+/- 1SD) variations in the efficiency from sample to sample are quite common.

The relative efficiency in all filters varied from negative values (indicating that the second of two cartridges had a higher activity than the first one; such observations have been made with Ra isotopes; unpublished data) to values greater than 95% (Table 1). More discussion on observed low-extraction efficiencies in 3rd to 5th cartridges is given below. In all six cartridges connected in series, the relative efficiency is much more variable than the absolute efficiency. Thus, it is critical that we evaluate the variations on the individual extraction efficiency (absolute) of these cartridges.

4.4 Variations in the Absolute Extraction Efficiency:

In this experiment, we had six cartridges connected in series, and hence 'i' varied from 1 and 6 and 'j' from 2 to 6. Equation (1) does not assume uniform efficiency, and the ratio of the activity retained in the filter to that entering activity yields an absolute efficiency. The mass-balance of Th activity is shown in Table 1. In five of the six sets, the mass-balance was within 5%, while in one it was off by ~9%. The summation of the activities in all six cartridges is used as the total activity instead of the actual activity added to the experiment. The difference in absolute efficiency ([measured activity in F_1/amount of spike added] x 100 – [measured activity in F_1/summation of activity in all the filter cartridges in a set] x 100) for the first cartridge calculated using the amount of spike added and the summation of ^{234}Th in each cartridge is relatively small (less than 5%, except Set III, where it is ~10%, Table 1). The absolute efficiencies calculated from Equation (1) are shown in Table 1. Prior work assumed that the

extraction efficiency in the first and second MnO$_2$-extractor cartridges is identical ($\eta_1 = \eta_2$). Experimental results show that the absolute extraction efficiency in the first two filter cartridges varied between 54.1 to 93.8%, with a much large variation in the absolute extraction efficiency, as compared to the relative extraction efficiency (Table 1). The absolute extraction efficiency in a given set of six cartridges varied by almost over a factor of two, from 32.3 to 89.3% in the DARK cartridges, and 39.3 to 93.8% in the LIGHT cartridges. It is noteworthy that the first cartridge filter always had the highest absolute extraction efficiency (Table 1). In addition, the absolute and relative extraction efficiencies in the first cartridge (relative efficiency was calculated using the activity of ^{234}Th retained on the first two cartridges in each set) varied between 88.9 and 93.8%, and 89.4 and 94.2%, respectively. There is a general trend that the 3rd, 4th, and 5th filter cartridges have the lowest extraction efficiency (Table 1). The plot of the relative efficiency against the absolute efficiency (Figure 4) indicates scatter in the plot, suggesting that the relative efficiency and absolute efficiency vary, although the correlation is significant (P>0.001). Coastal water samples are often 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 and is not retained uniformly by the filter cartridges. If we assume ~ 1-10% of colloid-bound ^{234}Th passes through the first cartridge, we can expect absolute efficiencies as calculated in this study. However, if varying amounts of this colloidal ^{234}Th are retained in subsequent cartridges, then the absolute and relatively efficiencies will be highly variable. Our data appear to suggest this. The question then becomes, is this what is causing the variations in the extraction efficiency from region to region? It is likely that this is a major factor that causes variability in the relative extraction efficiency in seawater. An experiment similar to the one conducted in this study with ultrafiltered and UV-treated water could perhaps shed more light on this issue.

Using the relative efficiency of 'i'th filter cartridge calculated from the activity of ^{234}Th retained on 'i'th and 'i+1' cartridges, the activity of ^{234}Th entering the 'i'th cartridge was

calculated and compared to the actual value entering the 'i'th cartridge (Figure 5). The actual

activity going to the 'i+1'th cartridge was calculated by subtracting the value of ^{234}Th retained by

the 'i'th cartridge from the value that enters the 'i'th cartridge. The deviation from the calculated

activity to the actual activity for each of the cartridges (Table 2) indicated the following,

a) In the first two cartridges, the deviation between the actual activity and the activity

calculated under the assumption that the first three cartridges (to calculate the relative

extraction efficiency in the first two) extract Th uniformly, ranged between 0.6 - 18.8%.

Thus, there could be an error as high as 18.8% on the determination of ^{234}Th from the

assumption that the cartridges extract uniformly.

b) The uniform extraction efficiency varied between 32.3 and 89.3% (Set I) in the DARK

MnO_2-coated cartridge filters and was comparable to the range of the LIGHT-coated

filters (Set II). The lower efficiencies (less than 60% in 11 out of 15) are commonly

found in the 3rd to 5th filter cartridges, although values >60% (four out of 15) are also

observed. As discussed before, this could be due to a small fraction of total Th forming a

Th-ligand complexation that escapes MnO_2 surfaces without sorption.

c) The relative efficiency calculated using equation (5) becomes negative when ^{234}Th

activity in F_i is < F_{i+1}. In four of the 25 samples, the relative extraction efficiency was

negative (Table 1).

As discussed, factors that may affect the extraction efficiency are the flow rate (i.e., direct

measure of the contact time of the nuclide with the MnO_2), the amount of MnO_2 coated on the

cartridges (i.e., the rate of reaction between the tracer and the extractor MnO_2), and the

temperature and duration of MnO_2 impregnation. There is no relation between the absolute or

relative extraction efficiency and the amount of ash weight (Figure 2), suggesting that the amount

of MnO_2 coated on the filter cartridge does not control the amount of Th absorbed. This is

similar to the observation reported for the relative extraction efficiency for Th and the ash weight

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by Baskaran et al. (1993). The extraction (both absolute and relative) efficiency is found to be independent of the flow rate that ranged from 2.8 to 7.5 L min^{-1} (Figure 3). When the surface area of the fiber remains unsaturated with respect to any element of interest, we expect the volume of water filtered to be independent of the extraction efficiency. Mann et al. (1984) did not find any clear relation between flow rate and/or volume and extraction efficiency of Pu. Several researchers also did not find any correlation between the flow rates (up to 6 L/minute, Buesseler et al., 1992; up to 35 L/minute, Baskaran et al., 1993) and extraction efficiency for ^{234}Th in MnO_2-coated, polypropylene filter cartridges, while others have observed only a weak dependence of the extraction efficiency on flow rate (~5-16 L/minute, Cochran et al., 1995b; 4.8 to 13 L/minute, Charette and Moran, 1999; Guo et al., 2002). Charette and Moran (1999) also reported the extraction efficiency is independent of the amount of volume, up to 2,000 L on an 8.5-cm cartridge ($\equiv$ 6,000 L for the cartridge used for this experiment). Thus, it seems that contact time of the nuclide with a 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.

4.5 Use of constant extraction efficiency in calculating dissolved ^{234}Th:

As discussed earlier, both the absolute and relative extraction efficiency of the cartridge filters varied considerably from filter to filter, and this variation will introduce an error in the final dissolved ^{234}Th activities. In order to circumvent the error on dissolved ^{234}Th activity from the implied assumption of uniform extraction efficiency, we evaluated the possibility of combining the two filters and assumed 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 first two 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:

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

$$= (A_1 + A_2) / [\eta + \eta (1.00 - \eta)] \tag{6}$$

where η is the average of the relative extraction efficiency (0.852 in our study, average of 12

values) of all the pairs of filter cartridges (one for each sample). The activity thus obtained is

compared to the spike added to the experiment (i.e., activity entering the first filter cartridge) in

Table 2. In ~ 30% of the samples (eight out of 25), the activity calculated using equation (5) that

assumes uniform extraction efficiency yielded meaningless values, either negative or with errors

>80%, while the activity calculated using a 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 provides a more meaningful activity

than the value obtained using the assumption of uniform extraction efficiency.

4.7 How does the variation in extraction efficiency affect the rate of removal of dissolved

and particulate ^{234}Th as well as residence time of particulate and dissolved ^{234}Th in the

euphotic zone?

We have taken three data points for ^{238}U, and dissolved and particulate ^{234}Th activities

from the Canada Basin of the Arctic Ocean: case I (^{234}Th$_d$ = 1.97 dpm L^{-1}; ^{234}Th$_p$ = 0.20 dpm L^{-1};

^{238}U = 2.27 dpm L^{-1}); case II (^{234}Th$_d$ = 1.23 dpm L^{-1}; ^{234}Th$_p$ = 0.09 dpm L^{-1}; ^{238}U = 2.22 dpm L-

1L-1); and case III (^{234}Th$_d$ = 1.79 dpm L^{-1}; ^{234}Th$_p$ = 0.19 dpm L^{-1}; ^{238}U = 2.35 dpm L^{-1}). The

removal fluxes of dissolved and particulate ^{234}Th and the residence times were calculated using

±5, ±10, and ±15% errors on the dissolved ^{234}Th activities and the corresponding residence times

and rate constants and plotted in Figures 6a and 6b. Up to a ±15% variation on the ^{234}Th$_d$

activities could result in up to orders of magnitude higher or lower rate constants and residence

times, depending on how close ^{234}Th$_{total}$ is to the ^{238}U activity. When the ^{234}Th$_{total}$/^{238}U AR is close

to 1, the errors on the residence times and rate constants could become very high (Figures 6a, 6b).

For example, in case I, with ±15% error on the ^{234}Th$_d$ values, the removal fluxes of dissolved

^{234}Th (J_{Thd}) varied between 0.00013 to 0.0171 dpm L^{-1} d^{-1} (0.00863 dpm L^{-1} d^{-1} for 0% error) while the removal fluxes of particulate ^{234}Th (J_{Thp}) values varied between negative and 0.0114 dpm L^{-1} d^{-1} (0.00288 dpm L^{-1} d^{-1} for 0% error; Figure 6a). The residence times of dissolved ^{234}Th varied between 98 and 732 d (228 d for 0% error, neglecting one value in which ^{234}Th$_{total}$/^{238}U activity ratio is 1.0), while the corresponding values for the particulate ^{234}Th varied between negative values to 4636 d (70 d for 0% error, neglecting two negative values and 4,636 days in Figure 6b). Thus, the residence times and removal fluxes of particulate and dissolved ^{234}Th could vary over orders of magnitude due to non-uniform extraction efficiency of MnO$_2$ cartridge filters, especially in waters where ^{234}Th$_{total}$/^{238}U is close to equilibrium. In case II, the ^{234}Th$_{total}$/^{238}U ratio is 0.59. In this case, the residence times and removal rate constants varied within a factor of 2 (J_{Thd}: 0.023 to 0.034 dpm L^{-1} d^{-1}; J_{Thp}: 0.0205 to 0.0312 dpm L^{-1} d^{-1}; residence time of dissolved ^{234}Th: 31 and 61 days; residence time of particulate ^{234}Th: 2.9 and 4.4 days; Figure 6a). In case III, the ^{234}Th$_{total}$/^{238}U ratio is 0.84. In this case, the residence times and removal rate constants varied within a factor of ~6 (J_{Thd}: 0.00838 to 0.0238 dpm L^{-1} d^{-1}; J_{Thp}: 0.00292 to 0.01836 dpm L^{-1} d^{-1}; residence time of dissolved ^{234}Th: 64 and 246 days; residence time of particulate ^{234}Th: 10 and 465 days; Figure 6a).

5. Conclusions:

1) There is a relatively large variation in the absolute efficiency of the first and second filter cartridges, and thus, the assumption of uniform extraction efficiency could introduce a large error on the dissolved ^{234}Th activity when uniform extraction efficiency is assumed using the two Mn-cartridge system.

2) We suggest using constant extraction efficiency on the combined activity of two filter cartridges connected in series to obtain a dissolved ^{234}Th activity. The average value of the relative efficiency from all the cartridges appears to provide a reasonable value.

3) In cases where $^{234}Th_{total}/^{238}U$ activity ratios are close to 1 or >1.0, even a relatively small error in the extraction efficiency could introduce very high errors in the removal-rate constants and residence times of particulate and dissolved ^{234}Th.

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Table 1: ^{234}Th activities, absolute and relative efficiency for the extraction efficiency experiment[+].

Filter Number	Color of filter[++]	Flow Rate (L/min)	Date made	Total ash weight (g)	^{234}Th total activity (dpm)	[*]Absolute efficiency (%)	[**]Relative efficiency (%)
SET I:							
F1	D	2.8	6/27/2003	13.4647	217132±3946	89.3 (87.3)	92.4
F2	D	2.8	6/27/2003	13.6647	16578±622	63.9	64.3
F3	D	2.8	6/27/2003	15.747	5912±225	63.0	81.0
F4	D	2.8	6/26/2003	2.3155	1122±41	32.3	-60.7
F5	D	2.8	6/27/2003	13.8596	1803±131	76.8	69.8
F6	D	2.8	6/26/2003	2.3686	544±18	-	-
SET II							
F1	L	6.0	8/19/2003	2.3981	226605±2107	93.8 (91.2)	96.4
F2	L	6.0	8/19/2003	1.7252	8083±130	54.1	66.7
F3	L	6.0	8/19/2003	2.2773	2690±99	39.3	1.5
F4	L	6.0	8/19/2003	10.7581	2648±127	63.7	66.3
F5	L	6.0	8/19/2003	2.8317	892±42	59.2	31.1
F6	L	6.0	8/19/2003	2.2672	614±22	-	-
SET III							
F1	D	6.0	6/27/2003	15.0897	182317±3101	91.8 (83.8)	93.5
F2	L	6.0	8/19/2003	2.2985	11852±226	72.8	88.1
F3	D	6.0	6/27/2003	12.2105	1416±45	32.0	-0.3
F4	L	6.0	8/19/2003	2.5089	1420±58	47.2	53.2
F5	D	6.0	6/27/2003	13.9214	665±68	41.8	-39.4
F6	L	6.0	8/19/2003	10.5353	927±63	-	-
SET IV							
F1	D	7.5	2/5/2003	5.3276	227046±3346	88.9 (91.3)	89.4
F2	D	7.5	2/5/2003	2.7194	23971±363	84.9	93.0
F3	D	7.5	6/26/2003	10.7278	1681±94	39.4	20.8
F4	L	7.5	8/19/2003	2.2298	1332±53	51.5	50.7
F5	L	7.5	8/19/2003	2.4789	657±17	52.3	8.8
F6	L	7.5	8/19/2003	2.356	599±44	-	-
SET V							
F1	N	6.5 -- 7.0	8/8/2003	10.8926	219011±3377	92.3 (88.1)	94.2
F2	N	6.5 -- 7.0	8/8/2003	10.1489	12771±406	69.6	73.8
F3	N	6.5 -- 7.0	8/12/2003	2.1353	3351±36	60.0	70.4
F4	N	6.5 -- 7.0	8/12/2003	4.2065	993±47	44.4	40.0
F5	N	6.5 -- 7.0	8/12/2003	1.8255	595±14	47.9	-8.6
F6	N	6.5 -- 7.0	8/18/2003	3.223	646±57	-	7.9

+: Spike added: set I, II, IV and V: 2.49 x 10^5 dpm; set III: 2.18 x 10^5 dpm; Mass balances in five sets are: 97.8%, 97.2%, 91.3%, 102.7% and 95.6% in sets I through V, respectively.

++: D: Deep (36 hrs); L: Light (6 hrs) and N: Normal (12 hrs) soaking in $KMnO_4$ bath

*: The absolute extraction efficiency (= amount retained on the filter / summation of the activities in all the filters in a set) calculated using Equation (1); number in parenthesis denotes the value calculated based on the amount of spike added.

**: The relative extraction efficiency was calculated using Equation (5).

Table 2: Activities of measured ^{234}Th, and calculated ^{234}Th based on constant and relative extraction efficiency

Sample Code	Measured ^{234}Th (dpm)	^{234}Th entry (dpm)	^{234}Th dpm (constant effi.)[*]	^{234}Th dpm (relative effi.)[**]
SET I				
F1	217132±3946	243091	245941	235080
F2	16578±622	25959	23667	25768
F3	5912±225	9381	7402	7297
F4	1122±41	3469	3077	-1847
F5	1803±131	2347	2470	2582
F6	544±18	544		
SET II				
F1	226605±2107	241533	246970	234987
F2	8083±130	14928	11336	12114
F3	2690±99	6845	5618	174195
F4	2648±127	4155	3726	3994
F5	892±42	1507	1586	2865
F6	614±22	614		
SET III				
F1	182317±3101	198596	204330	194993
F2	11852±226	16279	13962	13460
F3	1416±45	4427	2985	-505715
F4	1420±58	3011	2194	2669
F5	665±68	1591	1674	-1686
F6	927±63	926		
SET IV				
F1	227046±3346	255286	264153	253847
F2	23971±363	28240	26994	25779
F3	1681±94	4269	3171	8100
F4	1332±53	2588	2093	2628
F5	657±17	1256	1322	7495
F6	599±44	599		
SET V				
F1	219011±3377	237367	243912	232573
F2	12771±406	18356	16965.67	17314
F3	3351±36	5585	4570.612	4761
F4	993±47	2234	1670.986	2479
F5	595±14	1241	1306.571	-6927
F6	646±57	646		

*: Assuming a constant efficiency of 85.2% (see text for details)
**: Assuming Equation (5) in the text
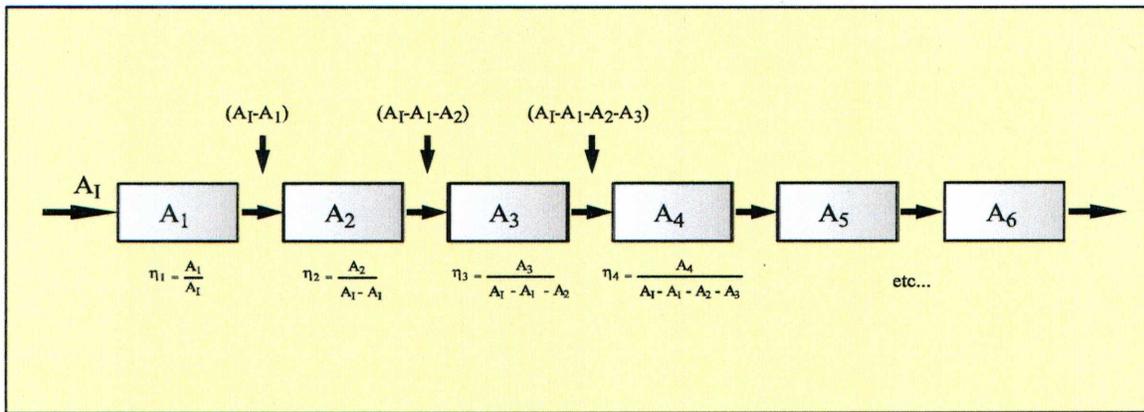
Figure Caption

Figure 1:   Filtration assembly with absolute extraction-efficiency equations.
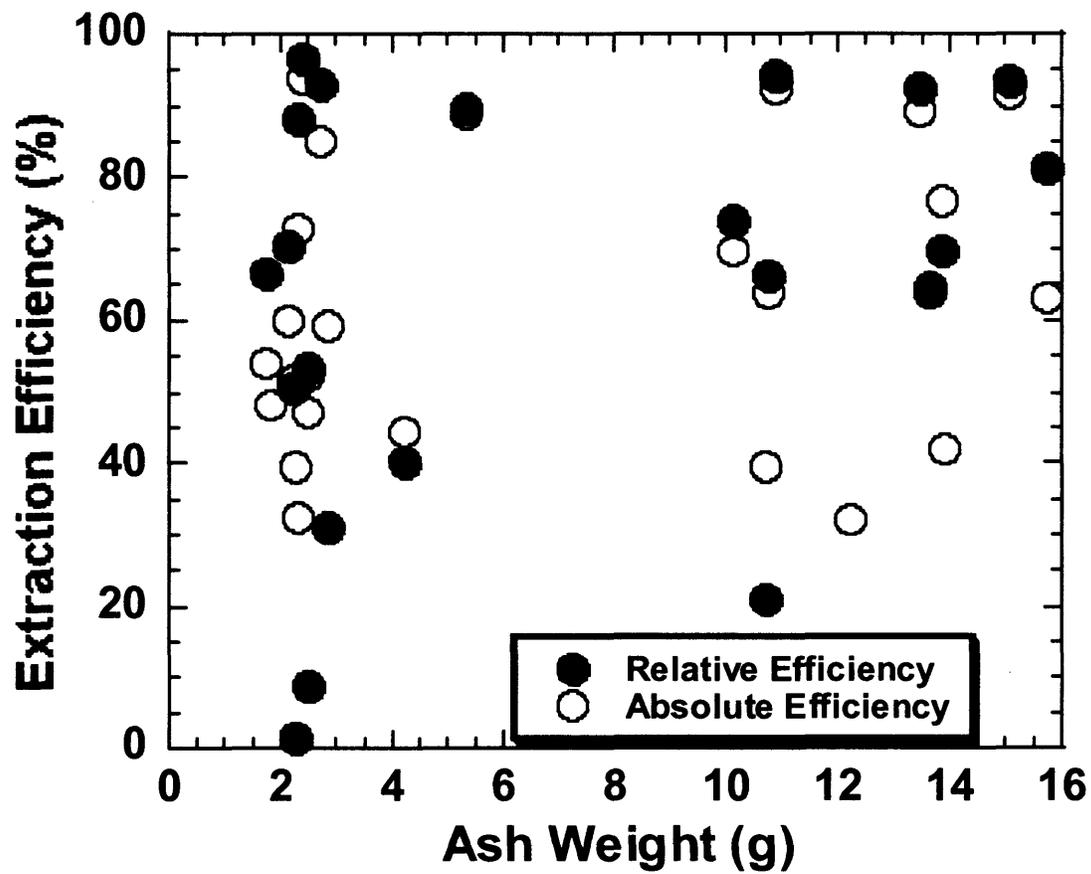
Figure 2:   Extraction efficiency versus ash weight.

Figure 3:   Extraction efficiency versus flow rate (L min^{-1}).

Figure 4:   Relative efficiency versus absolute efficiency.

Figure 5   The measured and relative efficiency-based calculated ^{234}Th were normalized by dividing the F_1 by 1000, F_2 by 100, F_3, F_4 and F_5 by 10.

Figure 6a: Removal flux of dissolved and particulate ^{234}Th versus percentage error introduced in the determination of dissolved of ^{234}Th due to variable extraction efficiency in filters 1 and 2.

Figure 6b: Residence times of dissolved and particulate ^{234}Th versus percentage error introduced in the determination of dissolved of ^{234}Th due to variable extraction efficiency in filters 1 and 2. The data used are: Case-I: ^{234}Th$_d$ = 1.97 dpm L^{-1}; ^{234}Th$_p$ = 0.20 dpm L^{-1}; ^{238}U = 2.27 dpm L^{-1}; Case II: ^{234}Th$_d$ = 1.23 dpm L^{-1}; ^{234}Th$_p$ = 0.09 dpm L^{-1}; ^{238}U = 2.22 dpm L^{-1}; and Case III: ^{234}Th$_d$ = 1.79 dpm L^{-1}; ^{234}Th$_p$ = 0.19 dpm L^{-1}; ^{238}U = 2.35 dpm L^{-1}; Data taken from Baskaran et al. (2003).

Figure 1:   Filtration assembly with absolute extraction efficiency equations.

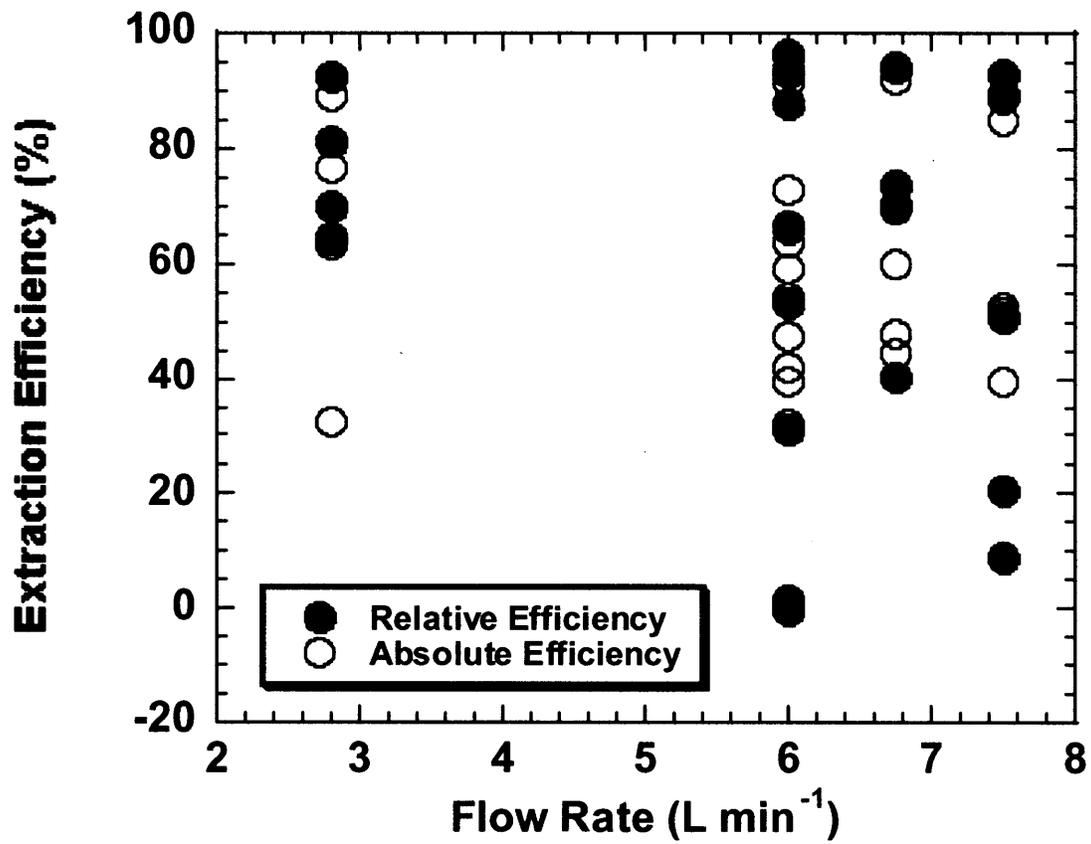Figure 2: Extraction efficiency versus ash weight.
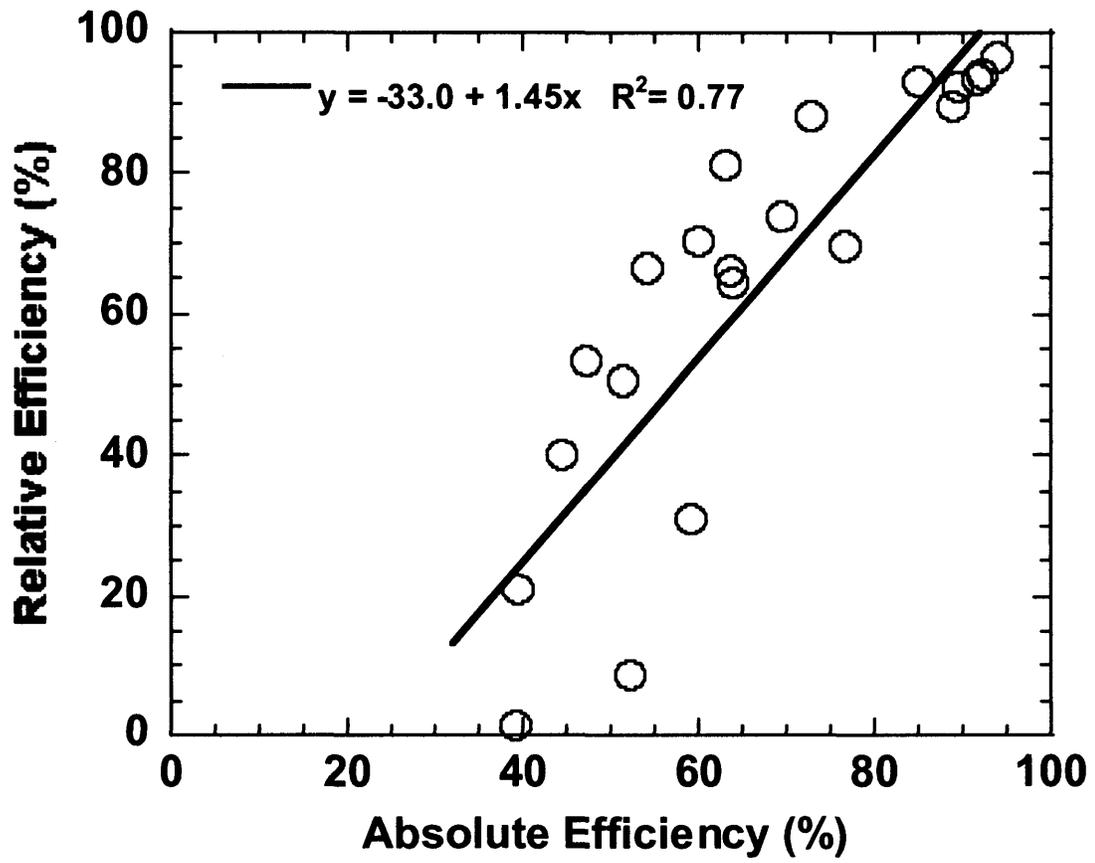
Figure 3: Extraction efficiency versus flow rate (L min^{-1}).
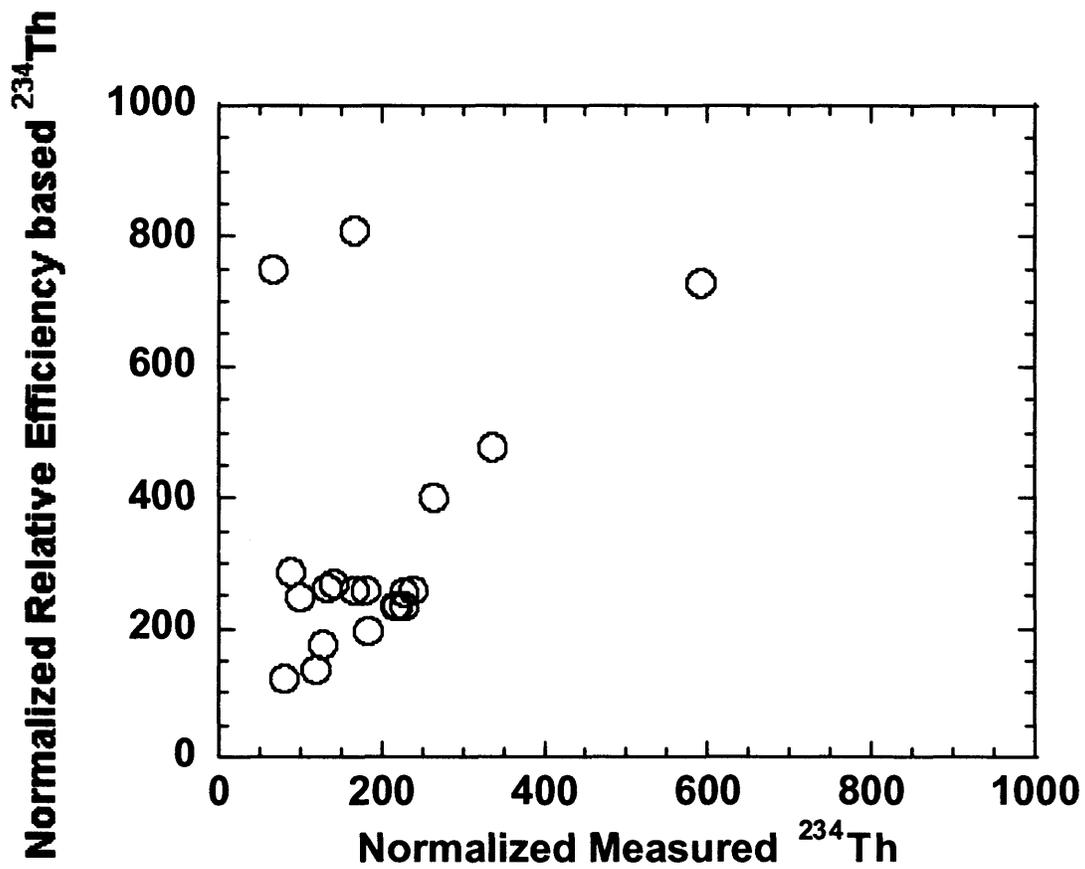
Figure 4: Relative efficiency versus absolute efficiency.

Figure 5 The measured and relative efficiency-based calculated ^{234}Th activities (dpm) were normalized by dividing the F_1 by 1000, F_2 by 100, F_3, F_4 and F_5 by 10.
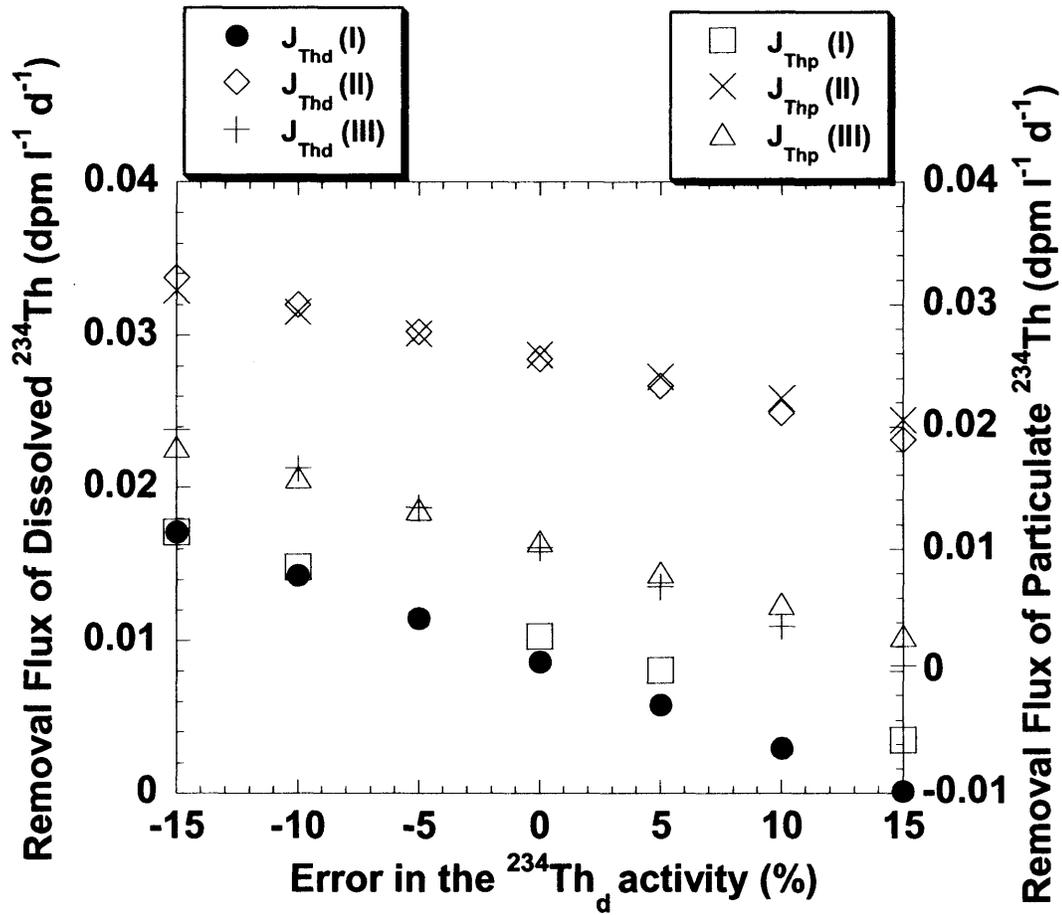
31

Figure 6a: Removal flux of dissolved and particulate ^{234}Th versus percentage error introduced in the determination of dissolved of ^{234}Th due to variable extraction efficiency in filters 1 and 2.
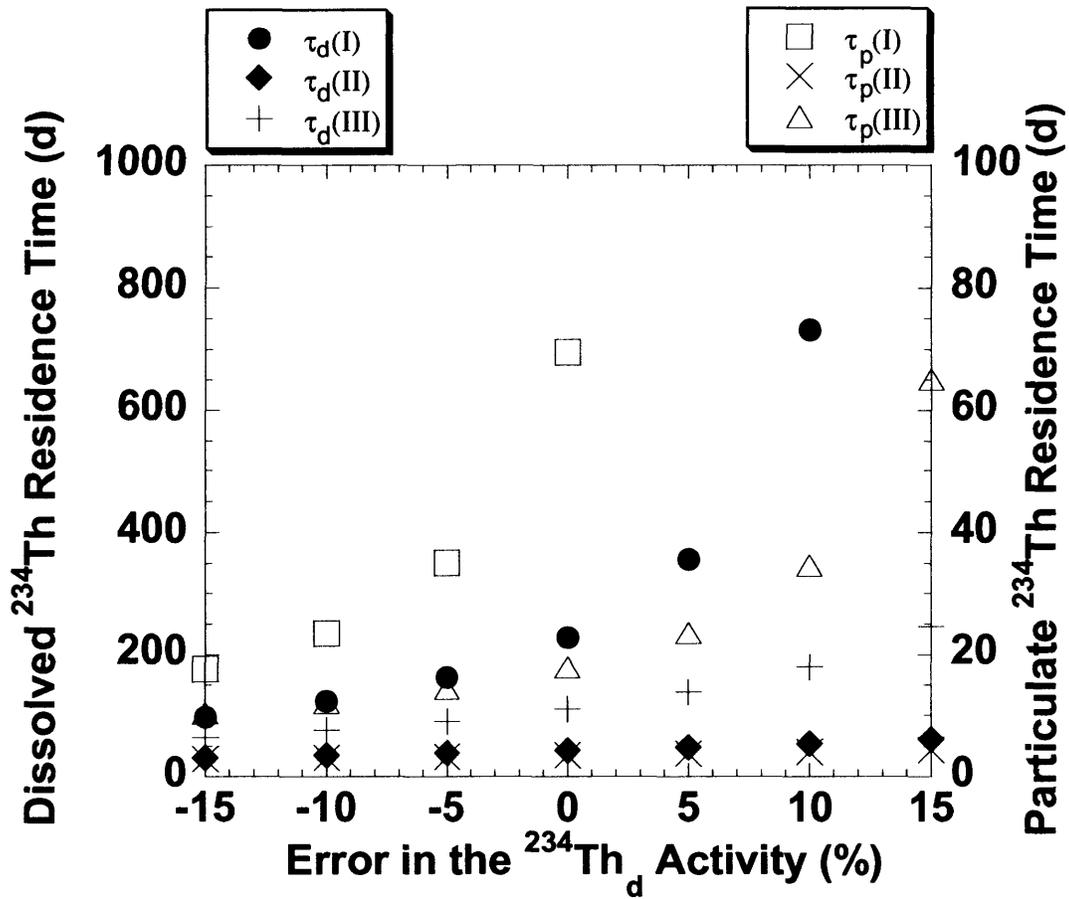
Figure 6b: Residence times of dissolved and particulate ^{234}Th versus percentage error introduced in the determination of dissolved of ^{234}Th due to variable extraction efficiency in filters 1 and 2. The data used are: Case I: ^{234}Th$_d$ = 1.97 dpm l^{L1}; ^{234}Th$_p$ = 0.20 dpm L^{-1}; ^{238}U = 2.27 dpm L^{-1}; Case II: ^{234}Th$_d$ = 1.23 dpm L^{-1}; ^{234}Th$_p$ = 0.09 dpm L^{-1}; ^{238}U = 2.22 dpm L^{-1}; and Case III: ^{234}Th$_d$ = 1.79 dpm L^{-1}; ^{234}Th$_p$ = 0.19 dpm L^{-1}; ^{238}U = 2.35 dpm L^{-1}; Data taken from Baskaran et al. (2003).