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Comment on “How accurate are 234Th measurements in seawater based on the MnO2-impregnated cartridge technique?” by Pinghe Cai et al.

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Components: 2936 words, 2 figures, 1 table.

Keywords: 234Th; MnO2 cartridge method; small volume method; 234Th/238U equilibrium.

Index Terms: 4860 Oceanography: Biological and Chemical: Radioactivity and radioisotopes; 4866 Oceanography: Biological and Chemical: Sorptive scavenging; 1194 Geochronology: Instruments and techniques.

Received 27 July 2007; Accepted 5 November 2007; Published 13 February 2008.


1. Introduction

[1] The paper by Cai et al. [2006] poses the question whether the use of MnO2-impregnated cartridges can provide accurate measurements of dissolved 234Th concentrations in seawater. Cai et al. [2006] compared the MnO2-impregnated cartridge technique with the small-volume MnO2 coprecipitation technique in eight samples taken in the South China Sea. On average, ~30% of the dissolved 234Th appeared to be missing from their MnO2 cartridges, and this apparent loss they attributed to organic complexation of dissolved 234Th in seawater. If true, this calls into question previous measurements of 234Th made using MnO2-cartridges [e.g., Livingston and Cochran, 1987; Buesseler et al., 1992; Cochran et al., 1995; Moran et al., 1997; Baskaran et al., 1993, 1996; Santschi et al., 1999;]
Table 1. Results of Extraction Efficiency Determinations for Dissolved $^{234}$Th Using MnO$_2$ Impregnated Filters in Seawater From Various Investigators$^a$

<table>
<thead>
<tr>
<th>Reference</th>
<th>$^{234}$Th in Deep Water, dpm/L</th>
<th>Location</th>
<th>Flow Rate, L/min</th>
<th>Cartridge Type</th>
<th>Number (n) of Samples</th>
<th>Mean Extraction Efficiency (equation (1)), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bacon et al. [1996]</td>
<td>2.4</td>
<td>equatorial Pacific</td>
<td>1–8.5</td>
<td>0.5 $\mu$m$^b$</td>
<td>120</td>
<td>90.5 ± 12.7</td>
</tr>
<tr>
<td>Baskaran et al. [1993]</td>
<td>2.4</td>
<td>Gulf of Mexico</td>
<td>25–35</td>
<td>0.5 $\mu$m$^c$</td>
<td>20</td>
<td>93 ± 5</td>
</tr>
<tr>
<td>Baskaran et al. [1996]</td>
<td>2.4–2.5</td>
<td>Gulf of Mexico</td>
<td>20–30</td>
<td>0.5 $\mu$m$^c$</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>Buesseler et al. [1992]</td>
<td>2.4–2.5</td>
<td>JGOFS NABE</td>
<td>4–8</td>
<td>1 $\mu$m$^b$</td>
<td>40</td>
<td>87 ± 8</td>
</tr>
<tr>
<td>Cai et al. [2006]</td>
<td>2.5</td>
<td>South China Sea</td>
<td>4–7</td>
<td>5 $\mu$m$^d$</td>
<td>9</td>
<td>61 ± 53$^e$</td>
</tr>
<tr>
<td>Cochran et al. [1995]</td>
<td>-</td>
<td>Arctic</td>
<td>5–16</td>
<td>0.5 $\mu$m$^b$</td>
<td>83</td>
<td>50–95</td>
</tr>
<tr>
<td>Hartman and Buesseler [1994]</td>
<td>-</td>
<td>equatorial Pacific</td>
<td>4</td>
<td>5 $\mu$m$^d$</td>
<td>104</td>
<td>79 ± 8</td>
</tr>
<tr>
<td>Hung et al. [2004]</td>
<td>2.4</td>
<td>Gulf of Mexico</td>
<td>10–20</td>
<td>0.5 $\mu$m$^f$</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>Guo et al. [2002]</td>
<td>2.4</td>
<td>Gulf of Mexico</td>
<td>10–20</td>
<td>0.5 $\mu$m$^f$</td>
<td>NR</td>
<td>NR</td>
</tr>
<tr>
<td>Livingston and Cochran [1987]</td>
<td>2.4</td>
<td>North Atlantic</td>
<td>2–7</td>
<td>1 $\mu$m$^b$</td>
<td>12</td>
<td>83 ± 8</td>
</tr>
<tr>
<td>Moran et al. [1997]</td>
<td>2.4</td>
<td>Arctic Ocean</td>
<td>2–3</td>
<td>5 $\mu$m$^d$</td>
<td>30</td>
<td>90 ± 7</td>
</tr>
<tr>
<td>Santschi et al. [1999]</td>
<td>2.5–2.9</td>
<td>North Atlantic; Lab</td>
<td>10–35; 35</td>
<td>0.5 $\mu$m$^f$</td>
<td>18; 2</td>
<td>86 ± 95; 99 ± 1</td>
</tr>
<tr>
<td>L. Guo et al., unpublished data, 2007</td>
<td>1.9–2.0</td>
<td>northern Gulf of Mexico</td>
<td>10</td>
<td>0.5 $\mu$m$^f$</td>
<td>6</td>
<td>96.5 ± 1.5</td>
</tr>
</tbody>
</table>

$^a$NR, not reported.

$^b$CUNO Micro-WyndII Polypropylene, 25 cm.

$^c$Perforated Polypropylene (United Filters, Inc., Uoo.5R10P), 25 cm.

$^d$Hytrex II, 25 cm.

$^e$Recalculated from Cai et al. [2006], including the reported negative value.

$^f$Sparkling Clear Polypropylene, 25 cm.

$^g$Unpublished notebook data.

Guo et al., 2002; Hung et al., 2004]. However, previous applications of the MnO$_2$-cartridge method have found it to give good agreement with $^{238}$U in deep water and to agree with $^{234}$Th measured on small volume samples. Moreover, the analytical procedures applied by Cai et al. [2006] are not typical of other workers. Here we show that the two methods yield comparable results, within errors, when properly applied.

2. Methodology

[2] The MnO$_2$-cartridge method was developed initially for extraction of anthropogenic radionuclides (Pu isotopes and $^{241}$Am) from large volumes of seawater by in situ pumping [Winget et al., 1982; Mann et al., 1984] and adapted by Livingston and Cochran [1987] and Cochran et al. [1987] to also extract Th isotopes (Th-232, Th-230, Th-228). This sampling technique had the advantage of collecting both particulate and dissolved radionuclides. The method was subsequently used for measurement of dissolved and particulate $^{234}$Th and has been applied by many groups. Several different types, lengths and pore sizes of cartridges have been used (Table 1). Cartridges are generally wound fiber polypropylene with pore sizes of 0.5 $\mu$m [e.g., Buesseler et al., 1992; Cochran et al., 1993, 1995; Bacon et al., 1996; Baskaran et al., 1993, 1996; Santschi et al., 1999; Guo et al., 2002; Hung et al., 2004], 1 $\mu$m [Livingston and Cochran, 1987; Cochran et al., 1987; Colley and Thomson, 1994] or 5 $\mu$m [Hartman and Buesseler, 1994; Moran et al., 1997]. The cartridges are usually preceded by prefilters that are either untreated cartridges or a series of filters of different pore sizes (e.g., Nitex or Teflon, Whatman GF/F or QM-A) that separate particulate Th. Thorium retained on the MnO$_2$ cartridges is assumed to be “dissolved.” The extraction efficiency of dissolved Th is calculated from the activities on two cartridges in series (A and B [Livingston and Cochran, 1987]):

\[
\text{Efficiency(\%)} = 100(1 - \frac{B}{A}).
\] (1)

Dissolved Th is calculated from the activity on the A and B cartridges, decay-corrected to collection. Different flow rates and pumping systems have been used, but efficiencies are generally greater than 70%. Cai et al. [2006] used cartridges of 5 $\mu$m pore size and 5-inch (12.7 cm) length, while the pore size and cartridge length used by other groups are often very different (e.g., 0.5 $\mu$m, lengths from 8.3 to 25 cm; Table 1). Because adsorption of dissolved $^{234}$Th is related to the contact area of MnO$_2$, one could assume that larger pore sizes and
shorter cartridges would yield lower efficiencies at equal flow rates, a trend that is certainly evident from Table 1. As well, dependence of extraction efficiency on flow rate through the cartridge series has been observed [Cochran et al., 1995; Charette and Moran, 1999]. Cai et al. [2006] reported “theoretical collection efficiencies” (equation (1)) of −70 to 95% (mean 61 ± 53%). When used to calculate dissolved $^{234}$Th from the MnO$_2$ cartridges, Cai et al. [2006] noted an offset relative to dissolved values derived from small volume samples (total Th minus particulate Th) and concluded that Mn cartridges were undercollecting dissolved Th.

[1] Any method that involves determination of radioactivity requires rigorous calibration and evaluation of standards and any analytical artifacts that might occur. The method used by most investigators for analysis of $^{234}$Th on MnO$_2$ cartridges is nondestructive gamma spectrometry, applied to the ash remaining after igniting the cartridge in a furnace or to “pucks” produced by melting or compressing the cartridge. The method is standardized by adding a known amount of $^{234}$Th in equilibrium with $^{238}$U to a cartridge and counting it in the same geometry as the samples. This procedure works best with ashed samples because ashing more reliably produces a standard in which the $^{234}$Th is homogeneously distributed. Contrary to the assertion of Cai et al. [2006], “many researchers” (Buesseler et al. [1992] and Moran et al. [1997] are cited) do not “use deep water to calibrate their gamma detectors.” Instead, a $^{238}$U standard (or other U-containing standard such as pitchblende) is used and deep water analyses are used as an independent check on the standardization (see example below).

[2] In contrast to the gamma spectrometric analysis of ashed MnO$_2$ cartridges, Cai et al. [2006] used a leaching procedure (2M HNO$_3$, 30% H$_2$O$_2$) to remove the Th from the intact cartridge. The leachate was subsequently neutralized and Th was precipitated with Fe(OH)$_3$. Yield tracers were added and yields were determined via alpha spectrometry. This procedure entails considerably more manipulation of the sample than does gamma spectrometry of cartridge ash. The few other cases in which a wet chemical procedure has been applied used mixtures of HCl/HNO$_3$/H$_2$O$_2$ [Colley and Thomson, 1994], HNO$_3$/HF/NH$_2$OH HCl [Rutgers van der Loeff and Berger, 1993] and concentrated HCl/NH$_2$OH HCl [Shimmield et al., 1995]. Rutgers van der Loeff et al. [2006] cite a Soxhlet-type leaching technique using 6N HCl, requiring several days to produce a Th recovery of ~95% from the cartridge. Wet chemical methods require equilibration of the tracer with the $^{234}$Th on the cartridge, accurate calibration of all tracers and standardization of both alpha and beta counting systems.

[3] Cai et al. [2006] used the “dissolved” activity determined from small volume samples (total − particulate Th) to independently determine “derived collection efficiencies” for the A and B cartridges separately and found lower values than obtained from equation (1). However, such a discrepancy was not observed by others who used the same approach [e.g., Baskaran et al., 1993, 1996; Santschi et al., 1999]. For example, Santschi et al. [1999] found that field cartridge efficiencies were compatible with separate laboratory tests of MnO$_2$ cartridges using $^{234}$Th added to 200 L that gave 99% cartridge extraction efficiency (Table 1).

[4] In our experience, MnO$_2$-impregnated cartridges made by different individuals can vary in quality. As a consequence, QA/QC procedures when preparing MnO$_2$ cartridges for field sampling are essential, requiring laboratory calibration data to test that the MnO$_2$-impregnated cartridges quantitatively extract $^{234}$Th from seawater. However, Cai et al. [2006] did not provide such data.

3. Field Data: Method Verification and Intercomparison

[5] Our laboratories have applied the MnO$_2$-cartridge method for over 20 years. Initial efforts to verify the accuracy of the technique involved comparison of the values obtained in deep water with $^{238}$U activities. Because the cartridge method was independently calibrated in the laboratory, this comparison is a robust means of verifying the accuracy of the method. One such verification was undertaken in 1992–1993 as part of the JGOPS EqPac study (cartridge efficiency of 91 ± 13% [Bacon et al., 1996]). Figure 1 shows 42 analyses of total $^{234}$Th in deep water (depths >500 m; all MnO$_2$ cartridges ashed) of the equatorial Pacific. This location, although subject to upwelling, is far from the influences of ocean margins that might affect $^{234}$Th/$^{238}$U equilibrium. The results show that $^{234}$Th is in equilibrium with $^{238}$U (Figure 1). The standard deviation of the mean $^{234}$Th activity is ~8%, comparable to the 1σ error on an individual measurement.

[6] More recently, laboratories measuring $^{234}$Th have begun using a small volume method that offers...
increased sampling resolution but provides only total $^{234}$Th. Comparison of total $^{234}$Th derived from in situ pumping (gamma spectrometry; MnO$_2$ cartridges ashed) with total $^{234}$Th (beta counting) in small volume samples from diverse locations shows no clear bias toward lower activities on MnO$_2$ cartridge-derived $^{234}$Th (Figure 2a). A histogram treatment of the data shows that the mean ratio of small volume $^{234}$Th to MnO$_2$-derived $^{234}$Th is $1.11 \pm 0.23$ (Figure 2b). Figure 2b includes many samples from the upper water column, where $^{234}$Th/$^{238}$U disequilibrium is most pronounced. For these samples, some of the differences between the methods may be real, caused by short-term temporal variations of $^{234}$Th in the upper water column [Charette et al., 1999]. The data of Cai et al. [2006] stand out in Figure 2a as among the most discrepant of the data and are clearly distinct from large numbers of other data (Figure 2b versus Figure 2c).

Cai et al. [2006] implied that the $^{234}$Th deficit in nepheloid layers from continental slope areas as documented, for example, by Santschi et al. [1999] and Baskaran et al. [1996], was an artifact of the MnO$_2$-impregnated cartridge method. However, Santschi et al. [1999] documented high cartridge extraction efficiencies from both laboratory (99%, Table 1) and field (86 \(\pm\) 9%, Table 1) data, and equilibrium values of $^{234}$Th/$^{238}$U ratios were noted at depths where aggregate concentrations were lowest. Indeed the observed deficits coincid-
ed with increased abundances of aggregate numbers in nepheloid layers. Furthermore, deficits in $^{234}$Th/$^{238}$U disequilibria in deep waters have also been reported for other oceanic environments such as bottom nepheloid layers and ocean margins (e.g., Bacon and Rutgers van der Loeff [1989] for the Pacific, and Moran and Smith [2000] for the Arctic), and these documented deficits cannot be taken as a “proof” that the MnO$_2$-cartridge method is invalid. Finally, Hung and Gong [2007], using large-volume 0.5 cm$^3$ MnO$_2$ cartridge extraction methods (D of Table 1), found $^{234}$Th to be in equilibrium with $^{238}$U at 140 m in a nutrient-depleted region close to where Cai et al. [2006] reported their profile.

4. Summary

Our collective experience is that the preferred method for treating MnO$_2$ cartridges is ashing followed by nondestructive gamma spectrometry of the ash. This approach facilitates the independent preparation of standards and allows deep water to be used as a check on accuracy of the method (e.g., Figure 1). Such an approach provides a clear answer to the question “How accurate are $^{234}$Th measurements in seawater based on the MnO$_2$-impregnated cartridge technique?” In contrast to the assertions of Cai et al. [2006] based on eight samples, the large number of MnO$_2$ cartridge samples analyzed over the past 20 years shows that
the method provides acceptable accuracy, with precision on the order of 10%, and is in good agreement with total $^{234}$Th determined on small volume samples. However, there is clearly a need for future research on the speciation of Th in seawater. Organic complexation may well be important in coastal or freshwater settings and may affect the geochemical behavior of Th. In open

**Figure 2.** (a) Plot of $^{234}$Th activity determined by small volume (SV $^{234}$Th) versus in situ pump with MnO$_2$ cartridges (Pump $^{234}$Th) based on published or submitted data from: south Aegean Sea (FACTS [Speicher et al., 2006]); Chukchi Sea, western Arctic Ocean (HLY 04-02, HLY 04-03 [Lepore et al., 2007]); western Mediterranean Sea (EN 405 [Lepore et al., 2007]); northwest Atlantic, between RI and Bermuda (EN 400, 409; K. Lepore et al., Testing the $p$-ratio in the Mediterranean Sea and NW Atlantic Ocean: Implications for the accuracy of $^{234}$Th-derived POC export flux, unpublished manuscript, 2007); Mediterranean Sea, off Monaco (DYFAMED (K. Cochran et al., Time-series measurements of $^{234}$Th in water column and sediment trap samples from the northwestern Mediterranean Sea, submitted to Deep Sea Research, Part II, 2007)); South China Sea [Cai et al., 2006]. (b) Histogram of SV/Pump $^{234}$Th ratios indicating 11 ± 22% higher SV $^{234}$Th activities for field studies listed ($N$ = 76). (c) Histogram of SV/Pump $^{234}$Th ratios indicating 40 ± 22% higher SV $^{234}$Th activities based on a total eight samples reported in the South China Sea by Cai et al. [2006].
ocean settings, our results show that the extent of complexation, at least as reflected in MnO$_2$ cartridge measurements of $^{234}$Th, cannot be as great as Cai et al. [2006] suggest.

Acknowledgments

This work was supported, in part, by the National Science Foundation grants OCE0351559 to P.H.S. and C.C.H., OCE-0327721 to S.B.M., OCE0627820 to L.D.G., and OCE-0424845 and OCE-0622754 to J.K.C.

References


