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GEOTRACES radium isotopes interlaboratory comparison experiment

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Abstract

In anticipation of the international GEOTRACES program, which will study the global marine biogeochemistry of trace elements and isotopes, we conducted a multi-lab intercomparison for radium isotopes. The intercomparison was in two parts involving the distribution of: (1) samples collected from four marine environments (open ocean, continental slope, shelf, and estuary) and (2) a suite of four reference materials prepared with isotopic standards (circulated to participants as 'unknowns'). Most labs performed well with ^{228}Ra and ^{224}Ra determination, however, there were a number of participants that reported ^{226}Ra, ^{223}Ra, and ^{228}Th (supported ^{224}Ra) well outside the 95% confidence interval. Many outliers were suspected to be a result of poorly calibrated detectors, though other method specific factors likely played a role (e.g., detector leakage, insufficient equilibration). Most methods for radium analysis in seawater involve a MnO_2 fiber column preconcentration step; as such, we evaluated the extraction efficiency of this procedure and found that it ranged from an average of 87% to 94% for the four stations. Hence, nonquantitative radium recovery from seawater samples may also have played a role in lab-to-lab variability.

GEOTRACES is an international study of the global marine biogeochemical cycles of trace elements and their isotopes. "GEOTRACES seeks to identify processes and quantify fluxes that control the distributions of key trace elements and isotopes (TEIs) in the ocean, and to establish the sensitivity of these distributions to changing environmental conditions" (GEOTRACES Science Plan 2006).

Within the GEOTRACES program, radium isotopes (^{223}Ra, ^{224}Ra, ^{226}Ra, and ^{228}Ra) will be applied as tracers and proxies in coastal environments and also in the open ocean. Some of the primary applications will be to determine land-ocean sources of TEIs such as submarine groundwater discharge (SGD) (e.g., Moore 1996; Burnett et al. 2006) and to quantify exchange rates between the coastal and open ocean (e.g., Moore 2000). In the open ocean, radium isotopes will be used to investigate vertical and horizontal transport of TEIs at the surface, midwater column, and bottom boundary layer (e.g., Trier et al. 1972; Kaufman et al. 1973; Ku and Luo 2008). In concert with its thorium daughter (^{228}Th), ^{228}Ra can be used to trace particle transport processes and source/sink pathways for biolimiting elements such as iron (e.g., Li et al 1980). Inventories of ^{228}Ra in the upper water column can be used to determine the total input of SGD to the ocean (Moore et al 2008).

A major component of the GEOTRACES objectives will be met by sampling along ocean basin sections, and as an international program, many countries have conducted or are planning GEOTRACES cruises focusing on specific regions. It was determined by the GEOTRACES community that prior to the commencement of the sampling program, intercomparison activities were necessary to assure the accuracy of all the collected data. To this end, the goal for the intercomparison phase of GEOTRACES was to achieve the best precision and accuracy possible (lowest random and systematic errors) for

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the suite of GEOTRACES' TEIs as a prelude to the sampling program, with continuing effort throughout the sampling and analysis process. For the radium isotopes, we included all four naturally occurring isotopes of radium (^{224}Ra, ^{223}Ra, ^{226}Ra, ^{228}Ra) as well as thorium-228, a biogeochemically useful particle reactive decay product of ^{228}Ra (see Fig. 1, decay series, for half lives and sources). Although ^{228}Th was not a target isotope in this investigation, measurements of ^{228}Th are required to correct for supported ^{224}Ra. In estuarine and nearshore waters, this correction is usually minor; but for samples containing low activities of ^{224}Ra, the correction is important. Additionally, the large number of cruises and associated samples necessitated a reevaluation of techniques for preconcentration and analysis of radium isotopes in seawater.

Materials and procedures

In 2008 the U.S. GEOTRACES program organized a two-leg intercomparison cruise between Norfolk and Bermuda. The radium intercomparison sampling was assigned to the second leg of the cruise aboard the R/V *Knorr* in June 2008. Three stations were sampled during the cruise: open ocean, continental slope, and inner continental shelf (Fig. 2). These locations were selected to represent a range of globally expected radium activities. In addition to the cruise, the radium intercomparison also included a coastal estuarine sample with high-end radium activities that was collected in Waquoit Bay, MA, during October 2008.

A list of the participating laboratories is shown in Table 1 and the methods they employed are summarized in Table 2. Each lab was randomly assigned a laboratory identification number before the start of the experiment. The laboratories supplied their own Ra sorption media or requested that unprocessed acidified (to pH 2 with HCl) water subsamples to be shipped to them. The most common method of Ra sample processing was concentrating Ra on MnO_2-coated filtration media: acrylic fiber, acrylic wound cartridges, cellulose Hytrex cartridges, and acrylic Hytrex cartridges.

For regular sample processing, the flow rate for each sample was carefully restricted to 1 L/min or slower as in the case of MnO_2 filters that were very tightly packed. Those providing MnO_2-coated media were required to provide two filters per sample, which allowed us to process water samples through filters placed in series. This provided quantitative information on the radium extraction efficiency (A/B cartridge method by Livingston and Cochran 1987) of the MnO_2-coated filters provided by each laboratory. Results from each lab were reported as the sum of the primary and secondary Mn fiber column.

At each station a 1250 L polypropylene tank was filled 1-3 times (depending on per sample volume requirement) from the ship's seawater intake and each fill was well mixed prior to sub-sampling (Fig. 3). Upon filling, the water was filtered using a 1-µm polypropylene cartridge filtration system. All tanks had one sub-sample processed and counted immediately on a delayed coincidence counter (RaDeCC, Moore and Arnold 1996) on the ship for reference, and again in regular time intervals, to follow the decay/ingrowth of the short-lived radium and thorium isotopes. The RaDeCC instrument is an α scintillation counter with an electronic pulse gating system

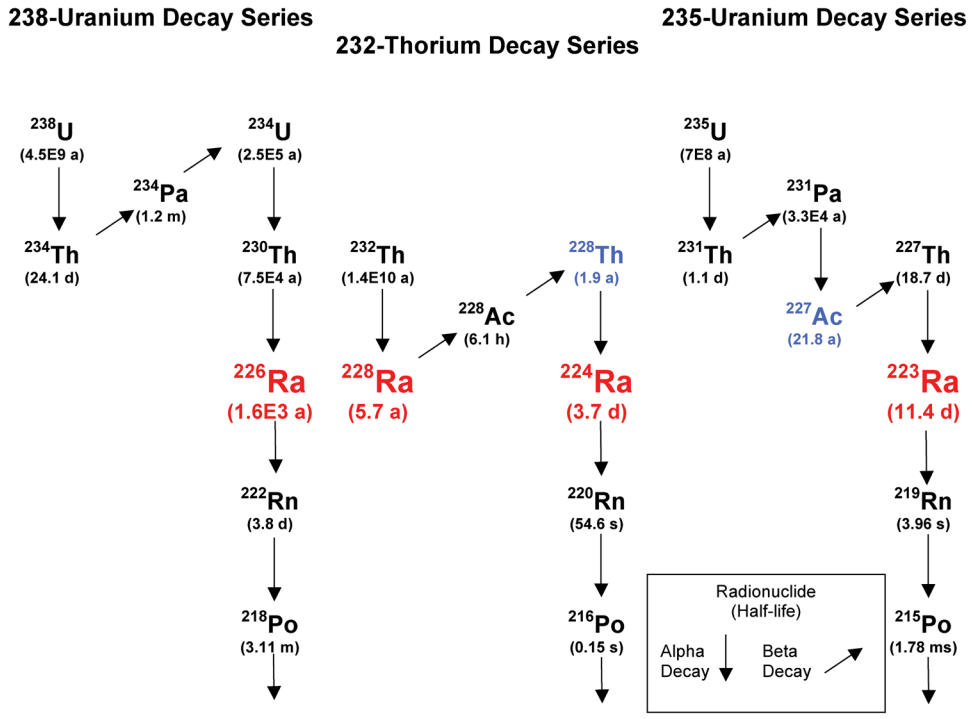

Fig. 1. Radionuclides of the uranium and thorium decay series.

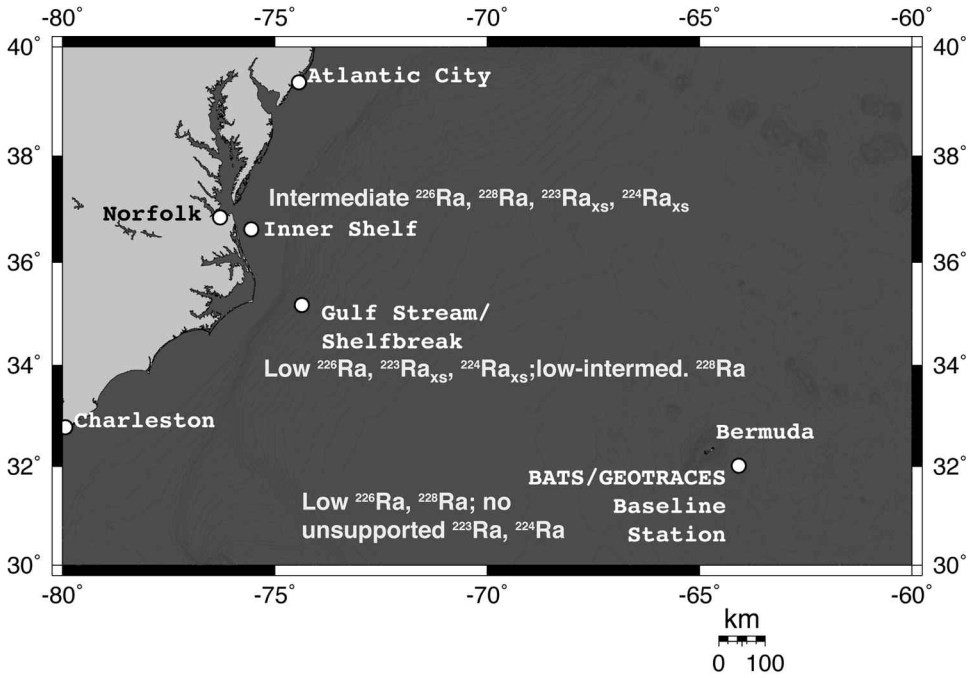

Fig. 2. Location of the Atlantic GEOTRACES Intercalibration Cruise stations for radium isotopes and expected Ra isotope activities.

Table 1. List of laboratories that participated and reported results in the GEOTRACES radium laboratory intercomparison exercise (23 laboratories from 11 countries). Each laboratory was randomly assigned a number in no particular order under which the results were reported and announced to the community.

Last name	First name	Institution	Country
Burnett	William	Florida State U.	USA
Charette	Matt	WHOI	USA
Cochran	Kirk	State University of New York (SUNY)-Stony Brook	USA
Crusius	John	United States Geological Survey (USGS)	USA
Dai	Minhan	Xiamen U.	China
de Oliveira	Joselene	U. Sao Paulo	Brazil
Du	Jinzhou	East China N. U.	China
Godoy	José Marcus	Instituto de Radioprotecao e Dosimetria (IRD)	Brazil
Hammond	Doug	U. Southern Calif.	USA
Hancock	Gary	CSIRO	Australia
Henderson	Gideon	Oxford U.	England
Kadko	David	U. Miami	USA
Kim	Guebuem	Seoul National Univ.	S. Korea
Masque	Pere	U.A. Barcelona	Spain
Moore	Willard	Univ. SC	USA
Moran	Brad	U. Rhode Island	USA
Orellana	Jordi Garcia	U.A. Barcelona	Spain
Paytan	Adina	Stanford U.	USA
Rutgers van der Loeff	Michiel	AWI	Germany
Scholten	Jan C.	International Atomic Energy Agency (IAEA)	Monaco
van Beek	Pieter	Laboratoire d'Etudes en Géophysique et Océanographie Spatiales (LEGOS)	France
Vengosh	Avner	Duke	USA
Zaggia	Luca	Consiglio Nazionale delle Ricerche-Istituto di Scienze Marine (CNR-ISMAR)	Italy

Table 2. Methods used for each radium isotope and ^{228}Th by the participating laboratories.

Method	^{226}Ra	^{228}Ra	^{224}Ra	^{223}Ra	^{228}Th
γ spectrometry	4, 7, 8, 11, 12, 13, 15, 16, 18, 23	7, 8, 12, 13, 15, 16, 18, 23			
^{222}Rn emanation-α scintillation counting	5				
Delayed coincidence counting (RaDeCC)		5, 26	4, 5, 6, 7, 10, 11, 12, 13, 15, 16, 18, 21, 23, 26, 28	4, 5, 6, 7, 10, 11, 12, 13, 15, 16, 18, 21, 26, 28	4, 5, 6, 7, 10, 12, 13, 15, 16, 18, 21, 23, 26, 28
Mean of γ and α spectrometry		11			11
Inductively coupled plasma mass spectrometry (ICP-MS)	15				

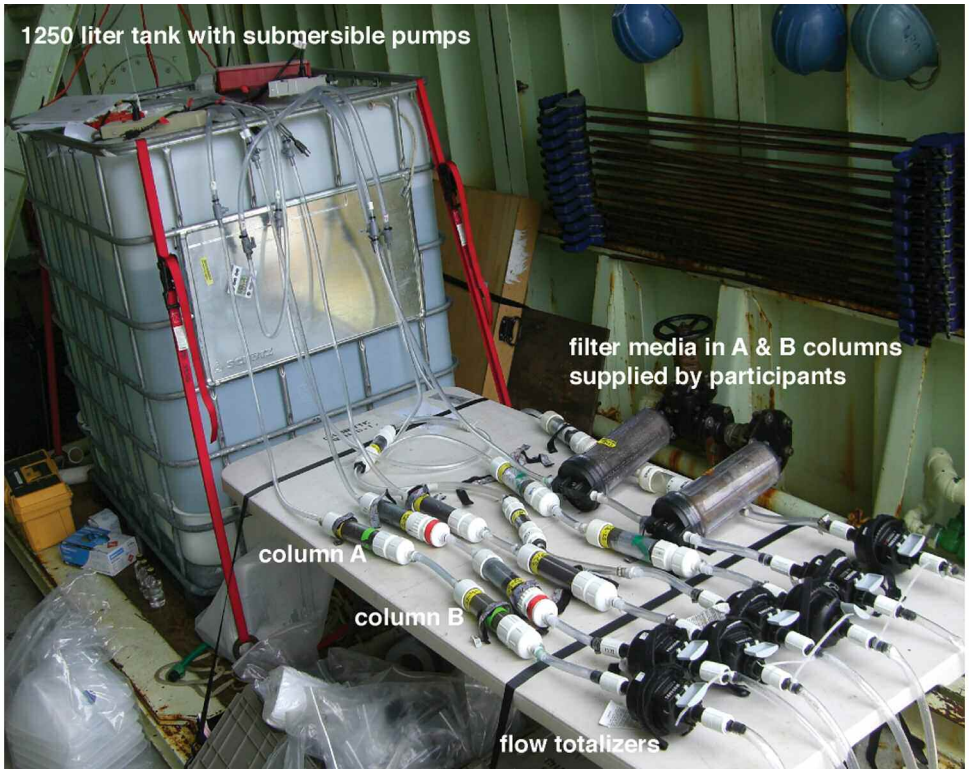

Fig. 3. Intercomparison samples were distributed from this system, which allowed up to 8 replicate samples to be processed simultaneously through A and B columns of MnO_2-fiber. The flow rates were controlled by inline valves and monitored by flow meters. Each outlet was capable of recording the volume processed.

that distinguishes decay events of short-lived radium daughter products based on their contrasting half-lives. Upon arrival to the port the samples sorbed to MnO_2 media or acidified water subsamples were express shipped to the participating laboratories.

All measurement results were reported to us along with metadata and information about sample handling. A deadline of approximately 9 months after the cruise was set for participating laboratories to report their results, which was met by sixteen laboratories. Station 1 was occupied early in the cruise such that 90% of the original activity of excess ^{224}Ra had decayed from the samples upon our arrival at the dock. Further decay during transit meant that most laboratories were not able to properly assess this sample for short-lived radium activity. Not all laboratories analyzed all four isotopes or ^{228}Th. Tables 3-6 show the reported values for each isotope at the

Table 3. Radium isotopes and ^{228}Th (dpm/100 L) from station 1 (open ocean) as measured by the participating laboratories. $^{224}Ra_{xs}$ and $^{223}Ra_{xs}$ are excess values after correction of total radium for supported radium from ^{228}Th and ^{227}Ac. Lab 15 reported ^{226}Ra values analyzed by two different methods (γ-spectrometry and ICP-MS). Statistical outliers (*) were not used to calculate the median, mean, or standard deviation.

Lab ID	^{226}Ra	Error	^{228}Ra	Error	$^{224}Ra_{xs}$	Error	$^{223}Ra_{xs}$	Error	^{228}Th	Error
4	8.52	6.22			0.16		0.05			
5	7.19	0.52	3.00	0.44	3.36	1.54	0.03	0.02	0.80	0.06
6							0.07	0.06	0.76	0.04
7	12.0*	0.32	4.70*	0.45					1.28*	0.10
8	7.10	0.22	2.41	0.25						
10							0.04	0.03	0.44	0.09
11	8.08	0.18	2.98	0.07			0.13*	0.09	0.68	0.09
12	7.28	0.16	2.94	0.28	3.83	1.03	0.04	0.05	0.70	0.18
13	7.28	0.22	3.03	0.41	2.44	0.10	0.05	0.02	0.65	0.04
15	6.88	0.24	3.00	0.34						
15 ICP-MS	8.23	0.21								
16	12.6*		2.03						0.91	
18	8.27	0.49	3.24	0.25			0.08	0.03	0.74	0.04
23	5.43*	0.34	1.90	0.19	8.61	0.74			0.33*	0.03
26			3.40	0.22						
N	12		11		5		8		10	
Mean	7.65		2.79		3.7		0.05		0.71	
Median	7.28		2.99		3.4		0.05		0.72	
Std. Dev.	0.62		0.5		3.1		0.02		0.14	
95% Conf. Int.	7.1-8.27		2.03-3.24		0.16-8.61		0.03-0.08		0.65-0.80	
Outliers (%)	25		9		0		13		20	
Shipboard mean (n = 8)	7.25		3.14		2.36		0.01		0.70	
Std. Dev.	0.34		0.61		0.30		0.02		0.08	

Table 4. Radium isotopes and ^{228}Th (dpm/100 L) from station 2 (slope) as measured by the participating laboratories. $^{224}Ra_{xs}$ and $^{223}Ra_{xs}$ are excess values after correction of total radium for supported radium from ^{228}Th and ^{227}Ac. Lab 15 reported ^{226}Ra values analyzed by two different methods (γ-spectrometry and ICP-MS).

Lab ID	^{226}Ra	Error	^{228}Ra	Error	$^{224}Ra_{xs}$	Error	$^{223}Ra_{xs}$	Error	^{228}Th	Error
4	10.3	5.2					0.06			
5	7.2	0.4	16.3	0.4	1.4	0.2	0.07	0.02	0.29	0.05
6					3.6	1.0	0.03	0.03	0.47	0.07
7	11.7	0.3	14.1	0.7					0.91	0.04
8	13.4	0.3	16.7	0.8						
10							0.02	0.01	0.57	0.08
11	9.7	0.1	15.2	0.1			0.07	0.02	0.87	0.12
12	9.1	0.6	16.1	1.1	1.3	0.3	0.05	0.01	0.72	0.06
13	8.4	0.3	13.1	0.7	1.0	0.0	0.03	0.01	0.76	0.04
15	8.2	0.3	13.4	0.5						
15 ICP-MS	9.5	0.2								
16	12.3		14.9		0.7				0.40	
18	11.4	0.7	16.4	1.1			0.06	0.02	0.66	0.04
21	12.7	0.3			1.4	0.6	0.10	0.04	1.29	0.54
22										
23	5.5	0.1	11.3	0.5	3.3	0.5			0.04	0.00
26			13.2	0.6						
N	13		11		7		9		11	
Mean	10.0		14.6		1.8		0.05		0.63	
Median	9.7		14.9		1.4		0.05		0.66	
Std. Dev.	2.3		1.74		1.1		0.02		0.34	
95% Conf. Int.	8.2-12.3		13.2-16.3		0.7-3.3		0.03-0.07		0.40-0.87	
Outliers (%)	0		0		0		0		0	
Shipboard mean (n = 4)	9.8		15.6		1.3		0.05		0.64	
Std. Dev.	1.1		0.9		0.3		0.03		0.10	

Table 5. Radium isotopes and ^{228}Th (dpm/100 L) from station 3 (shelf) as measured by the participating laboratories. $^{224}Ra_{xs}$ and $^{223}Ra_{xs}$ are excess values after correction of total radium for supported radium from ^{228}Th and ^{227}Ac. Lab 15 reported ^{226}Ra values analyzed by two different methods (γ-spectrometry and ICP-MS). Statistical outliers (*) were not used to calculate the median, mean, or standard deviation.

Lab ID	^{226}Ra	Error	^{228}Ra	Error	$^{224}Ra_{xs}$	Error	$^{223}Ra_{xs}$	Error	^{228}Th	Error
4	20.4	6.2			8.4*		0.69			
5	10.8	0.5	40.1	1.2	18.7	0.3	1.59	0.08	0.02	0.14
6					16.8	0.6	1.77	0.12	1.51	0.10
7	24.3	0.9	39.6	1.9	15.2	1.2	1.60	0.14	2.52	0.12
8	24.5	0.8	41.5	2.3						
10					8.3*	0.2	0.93	0.20	1.06	0.36
11	14.9		37.9				2.37		1.81	
12#	10.4	0.6	30.4	1.8	13.0	1.2	0.87	0.09	0.98	0.08
13	15.1	0.4	32.9	1.0	15.6	0.4	1.12	0.09	1.49	0.13
15	13.2	0.6	36.2	1.5						
15 ICP-MS	14.6	0.3								
16	24.8		36.3		14.1		1.00		1.88	
18	16.2	1.0	35.9	2.7	13.4	0.7	1.77	0.19	1.19	0.09
21	17.1	0.6			14.8	1.5	1.56	0.35	1.99	1.33
23	11.5	1.2	37.7	1.6	13.1	0.4				
26			34.2	1.1	10.4	0.0	0.78	0.27	0.78	0.10
N	13		11		12		12		11	
Mean	16.5		36.6		14.5		1.34		1.38	
Median	15.1		36.4		14.5		1.34		1.49	
Std. Dev.	5.30		3.3		2.29		0.51		0.68	
95% Conf. Int.	11.6-24.3		34.2-39.6		13.0-16.8		0.87-1.77		0.98-1.86	
Outliers (%)	0		0		17		0		0	

*Statistical outlier.
#Problem with flow meter.

Table 6. Radium isotopes and ^{228}Th (dpm/100 L) from station 4 (estuary) as measured by the participating laboratories. $^{224}Ra_{xs}$ and $^{223}Ra_{xs}$ are excess values after correction of total radium for supported radium from ^{228}Th and ^{227}Ac. Statistical outliers (*) were not used to calculate the median, mean, or standard deviation.

Lab ID	^{226}Ra	Error	^{228}Ra	Error	$^{224}Ra_{xs}$	Error	$^{223}Ra_{xs}$	Error	^{228}Th	Error
4	21.5	7.1			64.8		6.1			
5	12.2	0.4	64.6	7.27	81.5	0.9	11.7	0.2	0.16	0.44
6										
7	19.5	0.9	60.5	2.53	74.0	4.8	10.7	0.9	2.50	0.31
8	17.6	0.5	63.2	2.10						
11	19.1	0.6	55.2	3.00	67.6	1.5	2.4	0.3		
12	14.6	0.6	59.9	3.13	64.5	3.4	6.3	1.0	1.66	0.12
13	14.5	0.4	55.2	1.40	68.2	3.1	6.2	0.1	1.58	0.24
15					42.5*	4.3	3.6	0.4	1.28	0.13
16	14.6		52.4		59.2		4.5		0.43	
17										
18	23.7	2.2	62.4	9.91	67.1	2.1	10.3	0.9	1.91	0.11
21	24.3	0.8			74.8	2.4	8.5	1.6	3.27	1.90
23	14.4	0.9	49.1	2.04	46.3*	1.1			0.33	0.02
26			56.9	5.74	62.6	1.7	4.6	0.7	1.50	0.10
N	11		10		10		11		10	
Mean	17.8		57.9		68.4		6.8		1.46	
Median	17.6		58.4		67.3		6.2		1.54	
Std. Dev.	4.13		5.0		6.61		3.1		0.98	
95% Conf. Int.	14.5-21.5		52.4-63.2		62.6-74.8		4.5-10.3		0.33-2.5	
Outliers (%)	0		0		17		0		0	

*Statistical outlier.

individual stations. The tables also include shipboard measurements of the reference tank sub-samples, which were subsequently remeasured for ^{228}Th on the RaDeCC and long-lived radium isotopes by γ spectrometry at Woods Hole Oceanographic Institution (WHOI). Note that the WHOI reference value ('Shipboard Mean' in Tables 3 and 4) is not to be considered the "accepted" value, rather it was meant to quantify potential tank-to-tank variability for stations where more than one tank filling (sometimes separated by multiple days) was required to process samples for all participants. For all stations and isotopes, this variability was minor compared with the analytical uncertainties reported by the participating labs.

This exercise was also coordinated with the RaDeCC system laboratory performance test via reference materials prepared by the IAEA-Environment Laboratories, Monaco, which were distributed as unknowns to participating laboratories. Because of their short half-lives, reference materials for ^{224}Ra and ^{223}Ra must include activities of their long lived parents. Hence, the reference materials included ^{227}Ac, ^{232}Th, and mixed ^{227}Ac + ^{232}Th standards loaded on Mn-fibers, where activities and the radium isotope ratios were close to those expected in natural samples. The procedure used to prepare the reference fibers for ^{224}Ra and ^{223}Ra used in this laboratory performance test are described elsewhere (Scholten et al. 2010). After the fibers were prepared, they were measured repeatedly at the IAEA lab. The ^{224}Ra bearing fibers (with ^{232}Th as the parent) were shown to be stable; however, the ^{223}Ra fibers (with ^{227}Ac as the parent) showed decreasing activity in the ~ 6 months after their preparation and then the activity remained relatively stable (Scholten et al. 2010). The reason for this decrease is uncertain at present. The fibers were distributed to labs in Europe, Asia, Australia, and South America from Monaco and to labs in North America from the University of South Carolina (SC). The samples were rigorously controlled between runs by the laboratories to ensure that proper humidity and activity levels were preserved on the fibers. After each lab completed the measurements, the fibers were returned to the original lab, where measurements were repeated. In this way, we were able to determine that no significant change in the reference materials occurred during the period of distribution. These results are shown as lab code 'SC' in Tables 7 and 8. The first row gives the initial results measured at the University of South Carolina; the second row gives the mean value of all of the repeated measurements at SC as fibers were returned from each lab.

Detailed statistical treatment of all 4 stations' intercomparison data were performed with methods used by the IAEA for their interlaboratory comparisons and/or proficiency tests (e.g., Pham et al. 2011). Calculations were based on the assumption of nonparametric distribution of data to which distribution-free statistics were applicable. The results were checked for the presence of outliers using a box and whisker plot test (STATGRAPHICS PLUS 4.0). Mean values were calculated from all results passing the test ('N [cal]' in Tables 3-6). These values are considered to be the most reliable estimates of the true values. Confidence intervals were taken from a nonparametric sample population. They represent a two-sided interval for the 95% confidence limits.

As recommended by the International Union of Pure and Applied Chemistry (IUPAC) (Thompson et al. 2006) and the International Organization for Standardization (ISO 1997), we also use a Z-score evaluation to assign participating laboratories a normalized performance score for bias. The performance of a laboratory was considered to be acceptable if the difference between the robust mean of the laboratory and the assigned value is less than or equal to two. A laboratory analysis is regarded as being an outlier when Z > 3. The Z-score is calculated according to the formula:

$$Z = (X_i - X_a) / S_b,$$

where X_i is the robust mean of the reported values of volumetric activity in the sample, X_a is the assigned value (a mean value of accepted results), and S_b is the target standard deviation, i.e., the standard deviation of accepted values.

Assessment and discussion

Intercomparison of samples

The main goal of the Intercomparison Exercise and the Proficiency Test was to determine how proficient the participants were in quantifying radium isotopes. At station 1 (Bermuda Atlantic Time Series station, BATS), we counted 8 shipboard samples immediately after collection. Because surface waters at this station have not been in contact with coastal waters within the lifetime of ^{224}Ra there should be no excess ^{224}Ra. As discussed in more detail later, contamination from the ship's seawater intake resulted in some excess ^{224}Ra in the distributed samples (Table 3). However, by the time the participants received them, at most 10% of the excess remained in the sample. Station 2 (Table 4) was on the continental slope and station 3 (Table 5) was on the shelf. Both of these had measureable excess ^{224}Ra and ^{223}Ra above the shipboard blank derived from the seawater intake system. Station 4 in Waquoit Bay, MA, had high activities of all four radium isotopes (Table 6).

The counting methods used by the laboratories included RaDeCC for ^{223}Ra, ^{224}Ra, and ^{228}Th, γ-spectrometry for ^{226}Ra and ^{228}Ra (e.g., Moore 1976; Charette et al. 2001; Dulaiova and Burnett 2004, van Beek et al. 2010), radon emanation followed by cryogenic extraction for ^{226}Ra (e.g., Mathieu et al. 1988), α spectrometry for ^{228}Ra and ^{228}Th (e.g., Hancock and Martin 1991) and ICP-MS for ^{226}Ra (e.g., Foster et al. 2004; Hsieh and Henderson 2011) (Table 2). The RaDeCC system consists of a scintillation cell attached to a photomultiplier tube that records α particles during the decay of Rn daughter products of the short-lived Ra isotopes (Moore and Arnold 1996; Moore 2008). The photomultiplier tube is connected to a delayed coincidence system that utilizes the differences in the decay constants of the short-lived Po-daughters of ^{219}Rn and ^{220}Rn to

Table 7. Radium-224 (dpm) in the IAEA reference fiber as measured by the participating laboratories. Laboratories indicated by * were not a part of the original GEOTRACES intercomparison exercise. 'SC' is the University of South Carolina, which served as a reference laboratory for the distribution of these IAEA fibers. The amount of tracer retained by each fiber is reported as the IAEA mean. Results marked with # were excluded from the mean. For further information on the preparation of these reference materials, please see Scholten et al. (2010).

Lab ID	Std C	Std G	Std I	Lab ID	Std H	Std U	Std J
SC T1	15.11	10.94	9.90	6	13.73	10.87	10.02
SC Mean	14.55	10.80	9.17	15	15.42	12.64	10.58
21	14.10	9.99	9.62	8	13.1	11.97	9.55
28	12.51	9.52	8.92	*	22.11	18.75	14.17
5	13.3	9.9	8.6	13	15.8	13.8	11.3
10	12.00	8.64	8.67	21	14.1	11	9.01
13	14.87	10.43	10.3	*	12.52	10.57	8.35
4	12.90	11.10	10.10	*	22.25	17.6	14.17
23	20.04	9.71	10.02	20	2078#	1114#	1829#
*	16.85	12.57	11.35	26	16.37	12.46	8.66
16	16.41	11.78	10.79	*	20.94	18.77	15.35
7	13.64	10.01	9.13	*	17.16	11.71	12.26
			*	14.7	11.3	8	
Mean	14.69	10.45	9.71	Mean	16.52	13.45	10.95
Std. Dev.	2.24	1.06	0.86	Std. Dev.	3.44	3.11	2.51
IAEA	14.64	11.1	9.64	IAEA	14.5	12.09	9.59
Mean/IAEA	1.00	0.94	1.01	Mean/IAEA	1.14	1.11	1.14

#Statistical outlier.

Table 8. Radium-223 (dpm) in the IAEA reference fiber as measured by the participating laboratories. Laboratories indicated by * were not a part of the original GEOTRACES intercomparison exercise. 'SC' is the University of South Carolina, which served as a reference laboratory for the distribution of these IAEA fibers. The amount of tracer activity retained by each fiber is reported as the IAEA mean, however, these activities were shown by Scholten et al. (2010) to have decreased by up to 30% before their distribution to participants, but were stable during the course of the intercomparison. It is, therefore, recommended that the IAEA values not be used for RaDeCC system calibration. Results marked with # were excluded from the mean. For further information on the preparation of these reference materials, please see Scholten et al. (2010).

Lab ID	Std C	Std E	Std I	Lab ID	Std H	Std F	Std J
SC T1	1.74	6.88	0.81	6	1.81	7.50	0.89
SC Mean	1.67	6.37	0.69	15	2.19	10.60	1.2
21	1.44	6.17	0.72	8	2.24	10.91	1.21
28	2.01	6.53	0.82	*	1.76	9.06	1.13
5	1.66	6.00	0.77	13	1.52	6.79	0.7
10	2.20	7.45	1.07	21	1.24	5.57	0.66
13	2.33	10.05	1.24	*	1.73	9.14	0.83
4	2.30	8.70	0.83	*	2.27	8.31	1.13
23	1.75	7.67	1.09	20	6.24#	0.61#	3.7#
*	1.99	6.58	0.75	26	2.27	10.03	1.06
16	3.00	10.16	1.07	*	3.46	9.73	1.77
7	1.61	5.35	0.73	*	1.93	8.68	0.8
Mean	1.98	7.33	0.88	Mean	2.04	8.76	1.03
Std. Dev.	0.43	1.56	0.18	Std. Dev.	0.58	1.63	0.31
IAEA	2.31	10.18	1.05	IAEA	2.11	10.10	1.05
Mean/IAEA	0.86	0.72	0.84	Mean/IAEA	0.97	0.87	0.98

#Statistical outlier.

determine the activity of ^{223}Ra and ^{224}Ra. To analyze ^{226}Ra and ^{228}Ra via γ spectrometry, the fibers can be either ashed (e.g., Charette et al. 2001) or have the radium removed from the fiber via chemical leaching followed by barite precipitation (e.g., Moore 1976). The sample is then placed within a γ-spectrometer and ^{226}Ra can be measured via the daughter ^{214}Pb peak at 352 keV, whereas ^{228}Ra can be measured via daughter ^{228}Ac peaks at 338 and 911 keV. Further details on these and other methods for determining Ra isotopes in natural waters can be found in Rutgers van der Loeff and Moore (1999).

The participating laboratories generally performed well with ^{224}Ra and ^{228}Ra, especially for samples that had high activities. Measurements of ^{226}Ra via ICP-MS by lab 15 agreed well with traditional counting methods. There was no systematic bias in the reported results for any one of the methods described above suggesting that calibration and preconcentration methods were the main cause of the variability.

Because station 4 had high activities of all 4 Ra isotopes and the samples could be dispatched quickly to participants, we discuss these results in detail. Results from the other stations generally echo the results from Station 4. Excluding statistical outliers, the relative confidence interval for ^{224}Ra (9%) at station 4 was similar to the expected analytical error for RaDeCC ^{224}Ra measurements of samples with relatively high activities (Garcia-Solsona et al. 2008). The relative confidence interval for ^{223}Ra at station 4 (43%) was considerably greater than the uncertainty normally associated with RaDeCC ^{223}Ra measurements (Garcia-Solsona et al. 2008). For ^{228}Ra, the relative confidence interval was 9%, which is excellent; in fact nine of ten labs reported a value with error that was within the confidence interval of the mean. But for ^{226}Ra, the relative confidence interval was 20%, considerably greater than for ^{228}Ra. One difference is that ^{226}Ra is counted via its granddaughters, ^{214}Bi and ^{214}Pb, which may be lost from the sample by radon gas diffusion and emanation; this applies to all methods of ^{226}Ra determination used by participants (γ, α scintillation, RAD7) except ICP-MS. However, this is not a problem if $BaSO_4$ is used to scavenge Ra as this matrix does not leak Rn (Moore 1984). A more likely explanation for the discrepancy among γ measurements is coincidence summing, which occurs at certain energies if the source is close to the detector. If the efficiency of the detector is determined by the typical mixture of standards, the apparent efficiencies of sum-coincidence peaks will not match the efficiency curve (Moore 1984). In summary, these results imply that the labs are well calibrated for ^{224}Ra and ^{228}Ra, but their calibrations for ^{223}Ra and ^{226}Ra need to be improved. Calibration issues pertaining to ^{223}Ra are discussed in the ensuing section.

At station 4 the relative confidence interval for ^{228}Th (74%) was higher than the theoretical minimum error of 10%, though this should not be entirely unexpected for such low activity samples. Regardless, similar levels of disagreement among labs were obtained from the other stations. Measurements of ^{228}Th by Mn-fiber counting on the RaDeCC system clearly require a re-evaluation of the method, with better controls on recovery and counting protocols. Because sample counts for ^{228}Th are usually low, the problem may be that some ^{228}Th ingrowth occurred before the samples were measured for supported ^{228}Th.

Figure 4 gives a more detailed statistical treatment of the data from station 4, employing methods used by the IAEA for their interlaboratory comparisons (e.g., Pham et al. 2011). In Fig. 4a-e, we present the radium isotopes and ^{228}Th data for station 4 with the corresponding standard deviation in order of ascending volumetric activity (dpm/100 L). In addition, we calculated the Z-score for all data received for station 4 (Fig. 4f-j). For the vast majority of the isotopes and labs the distributions of Z-scores were < 2 and symmetric, which indicates that the overall performance of the laboratories was satisfactory. The only exception was ^{224}Ra for labs 15 (Z = 3.9) and 23 (Z = 3.4), which were considered to be statistical outliers both based on their deviation from the 95% confidence interval and their high Z-score.

Proficiency test of reference materials

For the IAEA prepared radium reference materials, most laboratories were well calibrated for ^{224}Ra but 3 labs were 40% to 50% high and lab 20 had reported values ~100 times greater than the mean (Tables 7-8). If these labs are excluded, the remaining labs are all within 10% of the IAEA assigned value. Figure 5 shows the peaked histogram of the ^{224}Ra values adjusted to the activity of the "U" fiber.

Conversely, there is disagreement on the calibration of ^{223}Ra: about half of the labs agree well with the IAEA assigned activity, while the other half were 30% to 40% low. Fig. 5 shows the broad histogram of these results. This cannot be explained by the apparent decrease in activity of the ^{227}Ac fibers, as they proved to be stable during the course of the performance exercise. Since most labs use the same type pumps and the same volume detectors and the standards were measured in the same columns, it is unlikely that the large differences can be explained by differences in gas flow or system volume. Instead, we must conclude that there is a fundamental difference in calibration, with some labs calibrated to a different reference value. To raise the low values to the assigned value, the efficiencies of the ^{223}Ra channel on RaDeCC for these labs would have to be reduced from ~45% to ~30%. There is no inherent reason why the ^{223}Ra channel should have an efficiency ~30% while the ^{224}Ra channel has an efficiency ~50% (Moore and Arnold 1996). There is a clear need for a well-calibrated, stable ^{227}Ac reference fiber and a better understanding of factors that control the efficiency of the ^{223}Ra channel of the RaDeCC system.

Shipboard contamination

Research vessel seawater intake systems are commonly used to collect surface ocean water for radium analysis. However, Charette et al. (2007) reported the potential for these systems to contaminate for short-lived Ra isotopes. The source of this contamination is believed to be from thorium isotopes, which

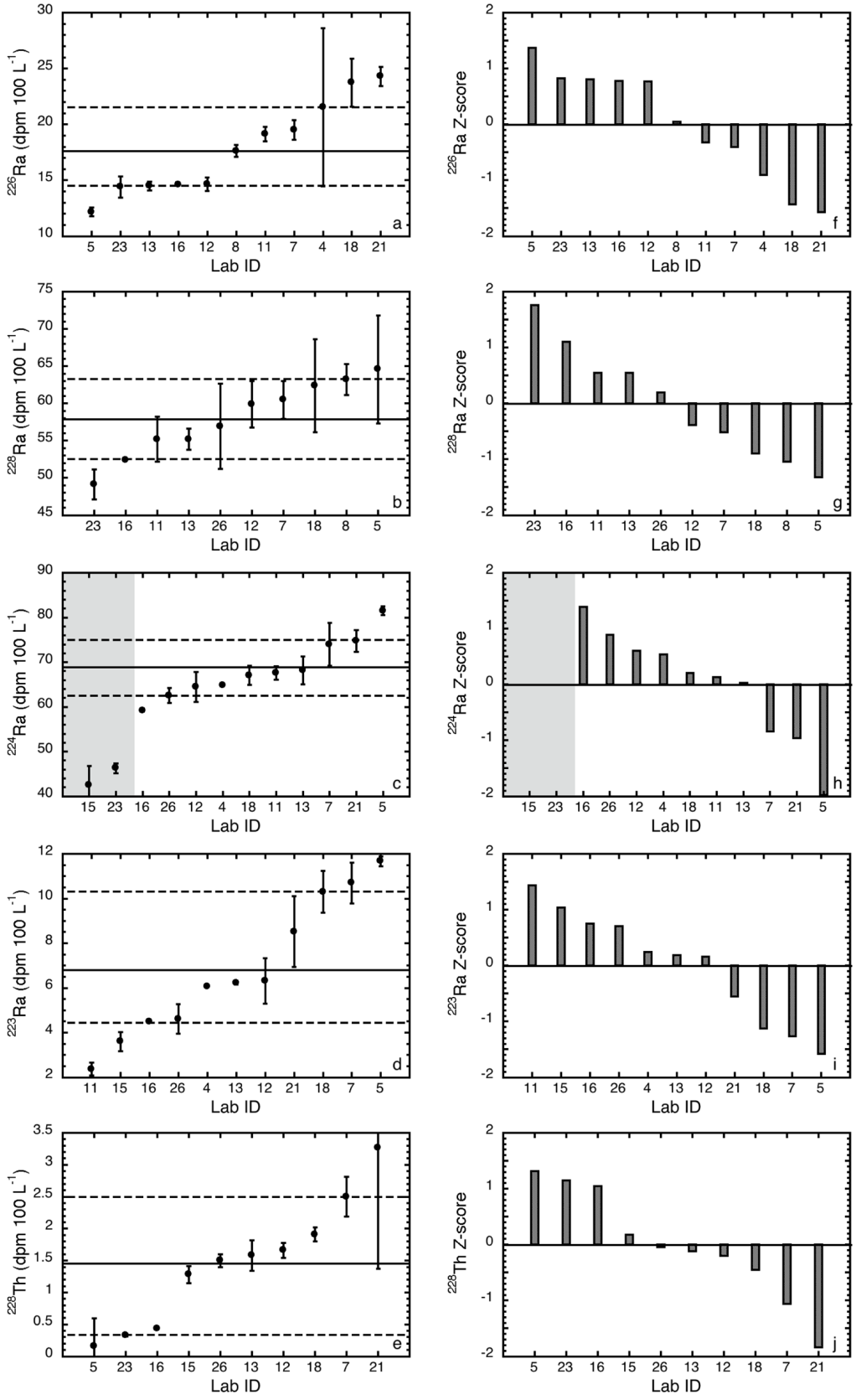

Fig. 4. Station 4 intercalibration results with 95% confidence interval (dashed lines), mean (solid line), and statistical outliers (shaded areas).

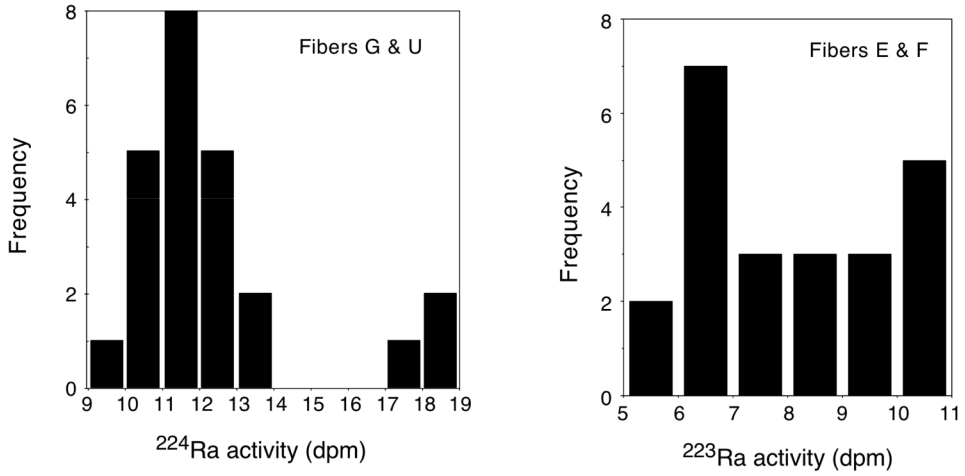

Fig. 5. Histograms of ^{224}Ra and ^{223}Ra measurements of IAEA performance standards. The results from labs that measured fiber G (11.1 dpm) have been increased by 1 dpm to bring them into line with the activity of standard U (12.1 dpm). The activities of fibers E and F were almost the same, 10.1 dpm.

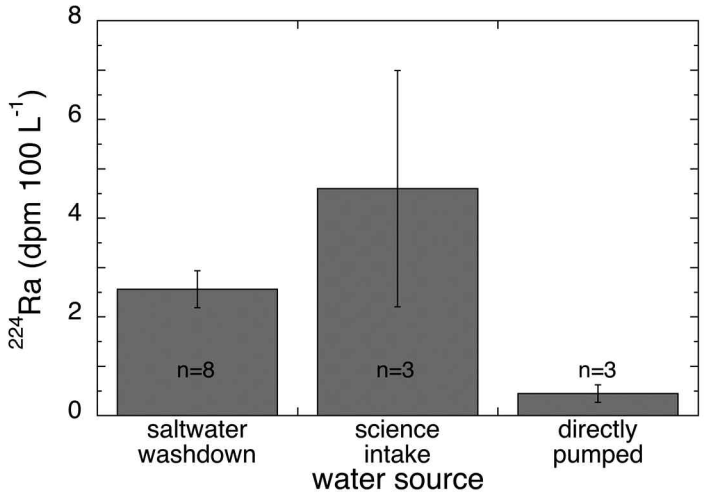

Fig. 6. Testing for ^{224}Ra contamination from the R/V *Knorr* intake systems.

can irreversibly sorb onto the walls of pipes in the plumbing system, and by radioactive decay, provide a continuous supply of their daughter products, mainly ^{224}Ra, which has a short half-life (and therefore a high production rate). Moore et al. (2008) reported similar problems for samples stored overnight in Niskin bottles.

During the GEOTRACES Intercomparison cruise (Station 1), we tested three methods for collecting surface seawater: (1) the ship's science supply, (2) the ship's saltwater wash-down supply, and (3) an over-the-side trace metal clean pump with Teflon plumbing (Fig. 6). The ship's science supply had the highest ^{224}Ra contamination, with values ranging from 3-7 dpm/100 L. The ship's regular seawater intake had lower ^{224}Ra (2-3 dpm/100L), but was still elevated in comparison to water sampled directly via a trace-metal clean pump (0.2-0.5 dpm/100 L, an activity supported by the dissolved ^{228}Th). There are two primary differences between the science supply and the saltwater wash-down intake. First, the science supply is constructed mostly of nonmetallic parts. Second, the pumping rate of the science supply is slower than that of the wash-down system. Since we would not expect *more or less* thorium sorption to the walls of the all-plastic intake system, we are left with the pumping rate as a likely cause of the varying degree of ^{224}Ra contamination. Assuming similar thorium sorption between the two systems (and therefore equal ^{224}Ra production rates), a water sample from the fast flow rate system would accumulate less ^{224}Ra during transit through the plumbing. In future radium studies, we recommend all ship's intake systems be checked for contamination by comparing to a CTD or directly collected sample. If contamination is found to be present, we would recommend against using the ship-based seawater supply for that cruise.

Extraction efficiency of Ra using Mn-coated filter media

On the cruise, we determined the radium sorption efficiency of each medium supplied by the participants by pairing two columns from each laboratory, with the first-in-line column defined as column "A" and the second as column "B." In this configuration, the B column should sorb any radium that passes column A. Both columns were analyzed for radium by the laboratories. Table 9 lists the individual results for the laboratories at the 4 stations. As the laboratories generally performed the best with ^{228}Ra determination, we used this isotope to calculate extraction efficiency. The average reported extraction efficiency was only 87-94%, which is below the > 97% assumed for flow rates of under 1 L/min (Moore 1976, 2008; Reid et al. 1979). Some labs reported a range of extraction efficiencies at the 4 stations (75% to 95%) that was similar to the reported range for all labs at all stations. Other labs had a narrow range of extraction efficiencies (90% to 100%). One laboratory had extraction efficiencies between 33% and 57%. Whereas this lab used a similar amount of fiber per column as

Table 9. Radium extraction efficiencies based on ^{228}Ra in paired A and B columns using Mn coated acrylic fiber and a flow rate of < 1 L/min. If ^{228}Ra data were not provided, the next most abundant Ra isotope was used to derive the extraction efficiency. Stations 1-3 are from the cruise and station 4 is from Waquoit Bay, MA. Samples indicated by an * were considered outliers, and therefore, were not used to compute the overall average.

Lab ID	^{226}Ra	error	^{228}Ra	error
4			0.84	0.87
5	0.76	0.95	0.71	0.80
6	0.95	1.00	1.00	
7	0.76	0.91	0.82	0.89
8	0.77	0.84	0.91	0.95
11	0.90	0.99	0.99	
12	1.00	1.00	0.97	0.99
13	0.89	0.96	0.96	0.98
15	0.78	0.88	0.80	
16			0.92	0.99
18	0.91	0.97	0.96	0.99
21		0.33*	0.57*	0.55*
23	0.96		0.80	0.85
Average	0.87	0.94	0.89	0.92
Std. Dev.	0.09	0.06	0.09	0.07
N	10	9	12	9
95% Conf. Int.	0.05	0.03	0.05	0.05

the other groups, the diameter of their column holders was significantly larger. This resulted in a fiber path length that was half or less of the other groups, resulting in a shorter contact time between the water and the fiber. Labs with better, yet still low, extraction efficiencies used the same column diameter and amount of fiber per column; shortcomings in the fiber preparation method (amount of MnO_2 sorbed per unit of filter media) may be one area where labs could make improvements. Additionally, we have found that fiber "fluffing" is an important step toward achieving quantitative radium recovery as poorly fluffed fibers will have a greatly reduced active MnO_2 surface area. Reduced surface area is also a concern for overcooked MnO_2 fiber, which tends to form large clumps too dense and fragile to fluff. Another possible explanation for the apparent low recoveries could be an undetected blank, which could cause the activity on the B column to be too high.

Comments and recommendations

The Ra intercomparison exercise has been very constructive. We learned that most labs could measure ^{228}Ra and ^{224}Ra very well; however, ^{226}Ra, ^{223}Ra, and ^{228}Th were problematic. The most surprising was ^{226}Ra as it is usually regarded as the easiest Ra isotope to measure accurately. We recommend that labs experiencing difficulty here purchase a well-calibrated standard (e.g., NIST 4696) and refine their measurement protocol accordingly to eliminate problems with sum-coincidence peaks. Also, since the γ-spectrometric measurement of ^{226}Ra is made indirectly via ^{214}Bi and ^{214}Pb, which are the decay products of radon, special care has to be made so that no radon can escape the sample via diffusion or emanation (co-precipitation with $BaSO_4$ or a well-sealed high density container) and that adequate time is allowed for the establishment of the equilibrium.

Disagreement among GEOTRACES ^{223}Ra results acquired via RaDeCC may be related to aging of the ^{227}Ac-based Mn-fiber standard as reported in Scholten et al. (2010). However, similar levels of disagreement between laboratories were observed with IAEA reference material, which was known to be stable at the time of distribution. This leads us to the conclusion that there is a fundamental difference in calibration, with some labs calibrated to a different reference value. These findings highlight the community need for a widely available ^{227}Ac standard reference solution.

Many labs reported extraction efficiencies well below the goal of 97 ± 3%. These labs should further test and refine their procedures using A and B columns and multiple replicate samples. It is not clear what causes some labs to report consistent near 100% recovery, while other labs have a wide range of recoveries. Potential problems that were observed during the intercomparison exercise were large diameter sample columns resulting in short Ra to fiber contact time and improperly rinsed fibers that leaked MnO_2, even $KMnO_4$ when passing water. For Mn-fiber columns, we recommend a maximum of 1 1/4 inches (as schedule 40 PVC) for the diameter and a length of 25 cm. Based on our experience, the amount of fiber in the column should be no less than half of the column length when observed under filtration. Leaky fibers and filter materials also have the potential to contaminate other TEI samples especially if deployed on high-volume pumps. Finally, there could also be a small blank, which would cause the B column to have too high an activity. This highlights the importance of determining Ra blanks on filtration media.

Measurements of ^{226}Ra via ICP-MS (one lab) agreed well with counting methods. We encourage other labs to further develop and streamline this technique as it requires smaller sample volumes. It is recommended that the ship's seawater intake systems be tested for short-lived radium isotope contamination and that the system is well flushed before sample collection.

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