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Inter-comparison of radium analysis in coastal sea water of the Asian region

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ABSTRACT

Laboratory inter-comparison is one of the methods used for regularly assessing the accuracy of the analytical data produced by laboratories for particular measurements. A working group at the 2010 GEOTRACES Asia Planning Workshop in Taipei recommended that a Ra inter-comparison experiment be conducted in the surface sea water of the Asian coastal region. In May 2011, we organized the Asian Ra Inter-comparison experiment. Analytes included ^{223}Ra, ^{224}Ra, ^{226}Ra, ^{228}Ra, and ^{228}Th. Nine laboratories joined this activity. One sample set was collected in the coastal region of the Yellow Sea, near Qingdao, China (YS1, YS2) and another in Tolo Harbor of Hong Kong (HK1, HK2). These waters are relatively high in Ra and low in suspended matter and can be considered representative of coastal waters in the region. The results show that most of the data reported by different labs is within two standard deviations of the mean. Radium extraction efficiencies based on two Mn-fiber columns attached in series averaged 95–99%. Results for ^{226}Ra, ^{223}Ra, and ^{228}Th in the Asia Inter-comparison are considerably less scattered than in the GEOTRACES Atlantic Inter-comparison. For ^{228}Ra the Asia and GEOTRACES results are similar; but for ^{224}Ra, the Asia results are considerably more scattered than the GEOTRACES results.

1. Background

There are four naturally occurring Ra isotopes, ^{223}Ra ($T_{1/2}$ = 11.4 days), ^{224}Ra ($T_{1/2}$ = 3.66 days), ^{226}Ra ($T_{1/2}$ = 1600 years), ^{228}Ra ($T_{1/2}$ = 5.7 years). As shown in Fig. 1, all the radium isotopes are produced from their parent nuclide thorium. The radium isotopes can be used to trace ocean processes such as mixing rates, water mass composition and age, and submarine groundwater discharge (SGD) (Burnett et al., 2006; Charette et al., 2003; Charette and Scholten, 2008; Moore, 2000a,b; Moore and Shaw, 1998). Moreover, because of the large variation in the rates of decay, these four Ra isotopes can be used to study the biogeochemical process with different time scales (Moore, 2000a). The half-life of ^{224}Ra is the shortest, so it is the best tracer for studying the mixing rate of estuarine and coastal sea water as well as the water exchange rate between the sediment interstitial water and the overlying seawater with the time scale of 1–10 days (Moore, 2000b; Moore and Krest, 2004). On a longer time scale, ^{228}Ra is used as a tracer for continental shelf influence in the sea with the time scale of 1–30 years (Kasemsupaya et al., 1993; Zhang, 2007; Moore et al., 2008).

To ensure that data reported by different laboratories are comparable, laboratory inter-comparison is required. Charette et al. (2012) reported the results of the 2008 GEOTRACES Atlantic Ra Inter-comparison study. They concluded that most laboratories could measure ^{228}Ra and ^{224}Ra very well; however, ^{226}Ra, ^{223}Ra and ^{228}Th were problematic. The most surprising of these was ^{226}Ra, as it is usually regarded as the easiest Ra isotope to measure accurately. Additionally, many laboratories reported radium extraction efficiencies from sea water on Mn-fibers well below the goal of 97 ± 3%.

In 2010 the GEOTRACES Asia Planning Workshop in Taipei recommended that another Ra inter-comparison study be conducted for laboratories in Asia. Several laboratories in the region only began measuring Ra isotopes recently and other labs that participated in the Atlantic inter-comparison received samples only after most of the ^{224}Ra had decayed.

Here, we report results of the 2011 Asian Laboratory Ra Inter-comparison. Nine laboratories joined this activity, including three from outside the region and two from the region that had participated

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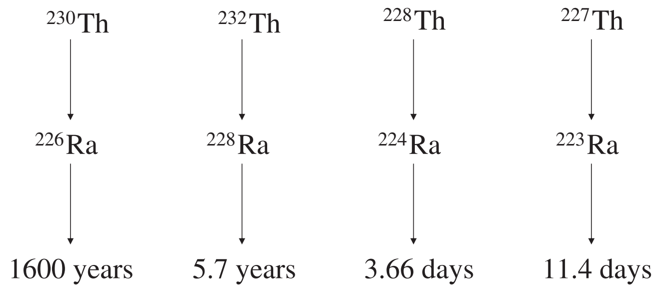

Fig. 1. Nuclear properties of Ra isotopes and their parent nuclide thorium isotopes.

in the GEOTRACES Atlantic Ra inter-comparison. Additional laboratories in Japan had to cancel because they were overwhelmed with samples from the Fukashima disaster.

The samples were collected in the Yellow Sea coast, near Qingdao, China, and in Tolo Harbor of Hong Kong in May–June 2011 (Fig. 2). The salinities of the water samples in Qingdao and Tolo Harbor were 31.3 and 34.0, respectively. The sampling location in Qingdao had a water depth of 10 m. Tolo Harbor is located in the northeastern part of Hong Kong's New Territories. In the inner harbor the water depth is less than 10 m, while along the channel the average depth is about 12 m. At each location, the water was relatively high in Ra isotopes and low in suspended matter. As such they are fairly representative of coastal waters in the region. Samples were sent by express mail to participating laboratories; most arrived within a few days, but some were delayed for up to 10 days.

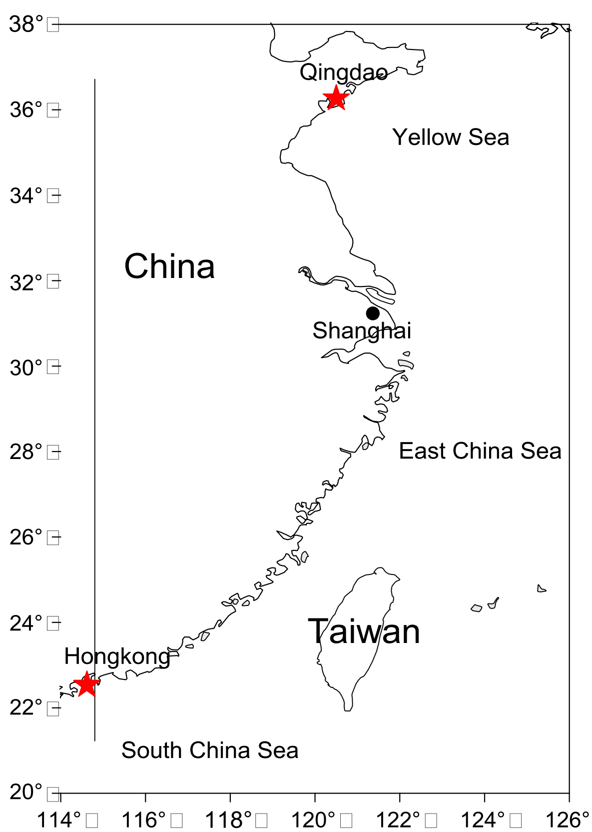

Fig. 2. Sampling locations (red star): one near Qingdao, China, and another in Tolo Harbor, Hong Kong, China.

2. Sampling and extraction procedure

The first sampling location is on the coast of the Yellow Sea, at a mariculcure laboratory around 30 km from Qingdao, China. We pumped the first sample (YS-1) from a recently-filled fish pond through a 1 μm filter column and then directly through Mn-fiber columns, which had been supplied by each participating laboratory. The second sample in Qingdao (YS-2) was directly pumped from coastal sea water through the filter into a holding tank and then through the Mn-fiber columns. The second sampling location was in Tolo Harbor, Hong Kong (HK-1 and HK-2). These samples were pumped through the 1 μm filter into a holding tank and then through the Mn-fiber columns.

The water distribution and extraction system is shown in Fig. 3. After filtration the water was passed through a pressure regulator and then to a hose containing emitters used in irrigation systems. Each emitter (RainBird #) was rated for a flow rate of 1 L/min at 40 psi pressure. This distribution system provided similar flow rates to each extraction column. Participating laboratories provided 2 columns (A and B) containing Mn-fiber (Moore, 1976), which were connected in series to extract radium. The water that passed through the columns was collected in plastic buckets and weighed to determine the weight processed. The time required to fill each bucket was recorded to estimate the flow rate. All the results from participating labs were reported by February 2012, 8 months after sampling.

3. Results

Most of the labs used RaDeCC systems (Moore and Arnold, 1996) to measure the short lived nuclides, ^{223}Ra and ^{224}Ra. The long-lived nuclides, ^{226}Ra and ^{228}Ra, were measured at a later date by gamma spectrometry, ingrowth of ^{228}Th using RaDeCC, or alpha spectrometry. One lab used a Dongtu system (FD-125 model, Beijing Nuclear Instrument Factory) to measure ^{224}Ra, ^{226}Ra and ^{228}Ra. The Dongtu system is a type of alpha counting system that includes a flow meter, scintillation cell, photomultiplier and preamplifier as well as a scaler. This instrument is used for determination of ^{224}Ra, ^{226}Ra and ^{228}Ra by $^{220,\ 222}$Rn emanation. In brief, a diffusion tube is filled with MnO_2-fiber and sealed to allow Rn ingrown. After 21 days the tube was connected to an evacuated ZnS scintillation counting cell and the Rn was transferred to the counting cell. The activities were subsequently measured by a Dongtu analyzer (Men et al., 2010; Chen et al., 2012).

The analytical methods used for the reported results are summarized in Table 1. Out of a possible 180 data points (5 isotopes, 4 stations, 9 laboratories), the reported data is 158, i.e. the percentage of the reported data is 88%. Missing data are due to the absence in some labs of RaDeCC system and some long delays between sampling and analysis date.

3.1. Extraction efficiency on Mn-fiber

The water was passed through two columns of Mn-fiber connected in series. Flow rates ranged from 0.19 to 0.64 kg min^{-1}. The extraction efficiency was determined from the relative amount of Ra recovered on columns A and B [Efficiency = 1 − (activity B/activity A)]. The summarized extraction efficiencies based on ^{228}Ra (or ^{224}Ra if ^{228}Ra was not reported) are showed in Table 2. If there was no reported value in column B, we could not assign a value to the recovery. The most common reason for not reporting a value for column B was that the value was listed as below detection by the analysis method, which would imply close to 100% extraction efficiency.

The individual recoveries ranged from 0.80 to 1.00 (n = 30); the average recoveries for each of the four samples ranged from 0.95 ± 0.07

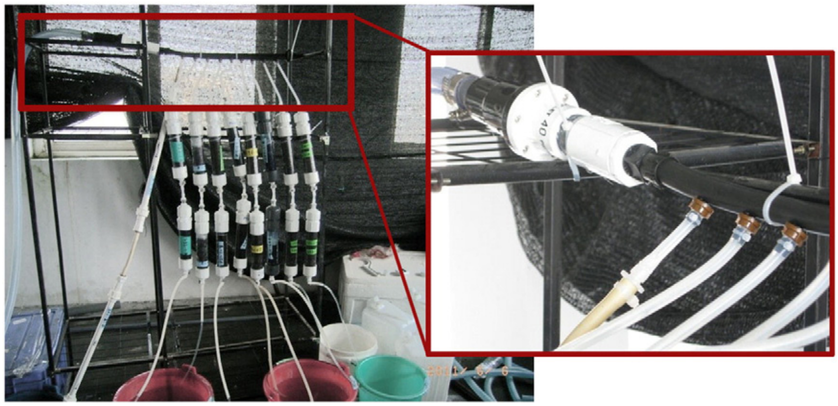

Fig. 3. Picture of pump water distribution for nine A and B manganese fiber columns (left). The lower insert shows the pressure regulator and emitter system.

Table 1
The analysis methods of the reported result by individual each laboratory.

Lab ID	Analysis methods and the number of reported data					
	^{226}Ra	^{228}Ra	^{224}Ra	^{223}Ra	^{228}Th	Total number
198	G, 4	G, 4	R, 4	R, 4	R, 4	20
287	G, 4	G, 4	R, 4	R, 4	R, 4	20
376	T, 4	T, 4	T, 2	0	0	10
465	G, 4	G, 4	R, 4	R, 4	R, 4	20
554	G, 4	R, 4	R, 4	R, 4	R, 4	20
643	A, 4	R, 4	R, 4	R, 4	R, 4	20
732	0	R, 4	R, 4	R, 4	R, 4	12
821	G, 4	G, 4	R, 4	R, 4	R, 4	20
910	G, 4	G,4	0	0	0	8
Total number	36	36	30	28	28	158

G, HPGe gamma spectrometry; A, alpha spectrometry; R, ReDeCC system; T, Dongtu system.

to 0.99 ± 0.02. We plotted extractions efficiency vs flow rate (Fig. 4) for all samples and found no correlation with flow rates in the range 0.19 to 0.64 kg min^{-1}.

3.2. Reported values for each isotope

Tables 3–7 give the reported values from each lab for the four samples. Because of the relatively low number of points, we have not applied any tests of outliers as such tests are not reliable for low sample size. However, we have excluded certain values from the summary statistics as noted on the tables.

For ^{226}Ra there are 36 reported results from participating labs (Table 1). The methods used for analysis include gamma spectrometry, alpha spectrometry, and Dongtu system. ^{226}Ra activities of YS-2 (0.38 ± 0.04 dpm/L), HK-1 (0.35 ± 0.04 dpm/L) and HK-2 (0.37 ± 0.03 dpm/L) are comparable, but that of YS-1 (0.71 ± 0.11 dpm/L) is significantly higher (Table 3, Fig. 5). This sample was pumped from a fish pond that may have been influenced by SGD.

For ^{228}Ra there are 36 reported results. The methods used for analysis include gamma spectrometry, alpha spectrometry, RaDeCC system and Dongtu system. From Table 1 and Fig. 6, it can be seen that there are 9/36 data considerably out of the range of average values even considering the errors. Similar to ^{226}Ra, the reported results

Table 2
Extraction efficiencies based on A and B columns. Efficiency = 1 − (activity B/activity A).

Lab ID	YS-1A	YS-1B	Eff.	YS-2A	YS-2B	Eff.	HK-1A	HK-1B	Eff.	HK-2A	HK-2B	Eff.
198	3.48	0.03	0.99	2.15	0.03	0.99	2.02	0.01	1.00	2.17	0.01	0.99
910	3.08	0.37	0.88	1.76	0.35	0.80	1.78	0.08	0.96	1.80	0.12	0.93
465	2.86	0.01	1.00	1.65	0.04	0.98	1.61	0.02	0.99	1.56	0.02	0.99
821	3.04	0.19	0.94	1.96	0.13	0.94	1.68	0.06	0.97	1.75	0.01	0.99
732*	1.61	0.00	1.00	1.82	bd		1.29	0.00	1.00	0.98	0.00	1.00
287	3.62	0.02	1.00	2.21	0.08	0.96	2.03	bd		2.05	0.03	0.99
554*	1.13	0.00	1.00	1.81	0.02	0.99	1.16	0.00	1.00	1.18	0.00	1.00
643*	1.04	0.00	1.00	2.08	0.03	0.99	1.17	0.00	1.00	1.12	0.00	1.00
376	1.35	bd		0.94	bd		1.22	bd		1.13	bd	
Average			0.98			0.95			0.99			0.99
Std. dev.			±0.04			±0.07			±0.02			±0.02
n			8			7			7			8

Based on ^{228}Ra except for *, which are based on ^{224}Ra.
bd is below detection.

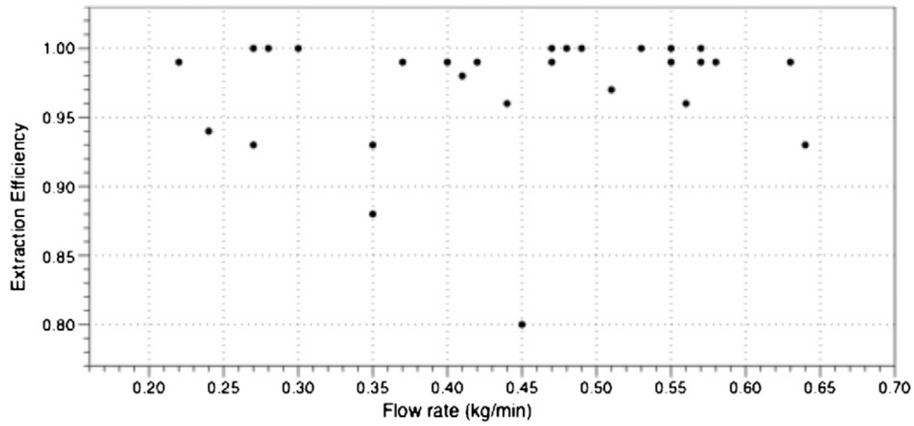

Fig. 4. Extraction efficiency vs flow rate for all samples.

Table 3
The reported of ^{226}Ra (dpm/kg) activities for each laboratory.

Laboratory code	YS-1		YS-2		HK-1		HK-2	
	Activity	Error	Activity	Error	Activity	Error	Activity	Error
198	0.95	0.002	0.46	0.002	0.32	0.005	0.37	0.005
287	0.70	0.000	0.39		0.40		0.39	
376	[0.23]	0.020	0.39	0.040	0.42	0.040	0.43	0.040
465	0.62	0.004	0.33	0.004	0.35	0.004	0.34	0.007
554	0.61	0.004	0.36	0.008	0.31	0.007	0.35	0.003
643	0.63	0.004	0.37	0.009	0.31	0.007	0.37	0.003
732	0.78	0.022	0.37	–	0.40	–	0.40	–
821	0.68	0.004	0.37	0.006	0.33	0.008	0.33	0.002
910	0.69	0.003	0.39	0.015	0.35	0.005	0.38	0.010
Average value	0.71		0.38		0.35		0.37	
Std. dev.	0.11		0.04		0.04		0.03	
Number of reported data	8		9		9		9	
CI (95%)	0.078		0.023		0.028		0.020	
CI as % value	11.0		6.0		7.8		5.5	

[] not used for calculation of average data.

of YS-2 (1.85 ± 0.45 dpm/L), HK-1 (1.77 ± 0.26 dpm/L) and HK-2 (1.80 ± 0.33 dpm/L) are comparable, with YS-1 being significantly higher (3.23 ± 0.40 dpm/L) (Table 4, Fig. 5).

For ^{224}Ra there are 28 reported results. One laboratory reported no data. The methods used for analysis are RaDeCC system, alpha and Dongtu system. Because of its short-half, some laboratory reported that at the time they made the first ^{224}Ra measurements of samples YS-1 and YS-2 only ~7% of the original signal remained. In this case all samples, including YS-1, were similar in activity (Table 5, Fig. 5).

For ^{223}Ra there are 28 reported results. One laboratory reported no data. Only the RaDeCC system was used. In this case samples from Tolo Harbor were almost twice the activity of the Yellow

Table 4
The reported of ^{228}Ra (dpm/kg) activities for each laboratory.

Laboratory code	YS-1		YS-2		HK-1		HK-2	
	Activity	Error	Activity	Error	Activity	Error	Activity	Error
198	3.50	0.001	2.18	0.001	2.03	0.001	2.19	0.001
287	3.64		2.29		2.03		2.08	
376	[1.35]	0.120	0.94	0.080	1.22	0.110	1.13	0.100
465	2.87	0.002	1.69	0.002	1.62	0.004	1.58	0.003
554	2.78	0.005	1.55	0.003	1.71	0.002	1.63	0.001
643	2.74	0.005	1.55	0.004	1.71	0.002	1.80	0.002
732	3.67	0.330	2.15	0.074	2.00	0.080	2.11	0.089
821	3.04	0.004	2.10	0.007	1.74	0.003	1.76	0.002
910	3.50	0.003	2.21	0.010	1.86	0.005	1.93	0.005
Average value	3.22		1.85		1.77		1.80	
Std. dev.	0.40		0.45		0.26		0.33	
Number of reported data	8		9		9		9	
CI (95%)	0.28		0.29		0.17		0.22	
CI as % value	8.6		15.9		9.6		12.0	

[] not used for calculation of average data.

Table 5
The reported of ^{224}Ra (dpm/kg) activities for each laboratory.

Laboratory code	YS-1		YS-2		HK-1		HK-2	
	Activity	Error	Activity	Error	Activity	Error	Activity	Error
198	0.66	0.035	1.53	0.307	1.24	0.045	1.27	0.032
287	1.88		2.03		1.85		1.60	
376	1.52	0.140	[3.12]	0.280				
465	[3.22]	0.037	[3.32]	0.005	[2.81]	0.016	[2.63]	0.017
554	1.13	0.002	1.83	0.005	1.16	0.003	1.17	0.002
643	1.04	0.002	2.11	0.002	1.17	0.005	1.11	0.005
732	1.61	0.090	1.82	0.025	1.29	0.002	0.98	0.001
821	1.05	0.019	2.20	0.017	1.34	0.005	1.42	0.004
910								
Average value	1.27		1.92		1.34		1.26	
Std. dev.	0.42		0.24		0.26		0.22	
Number of reported data	7		6		6		6	
CI (95%)	0.31		0.19		0.21		0.18	
CI as % value	24.3		10.2		15.4		14.2	

[] not used for calculation of average data.

Table 6
The reported of ^{223}Ra (dpm/kg) activities for each laboratory.

Laboratory code	YS-1		YS-2		HK-1		HK-2	
	Activity	Error	Activity	Error	Activity	Error	Activity	Error
198	0.061	0.004	0.049	0.003	0.112	0.006	0.110	0.006
287	0.069		0.052		0.077		0.110	
376								
465	0.059	0.001	0.042	0.001	0.081	0.001	0.092	0.001
554	0.071	0.002	0.086	0.007	0.117	0.005	0.121	0.005
643	0.060	0.010	0.074	0.014	0.124	0.016	0.152	0.026
732	0.085	0.000	0.042	0.003	0.114	0.005	0.074	0.010
821	0.058	0.039	0.051	0.043	0.113	0.024	0.113	0.009
910								
Average value	0.066		0.057		0.105		0.110	
Std. dev.	0.010		0.017		0.019		0.024	
Number of reported data	7		7		7		7	
CI (95%)	0.007		0.012		0.014		0.018	
CI as % value	10.9		22.1		13.0		16.3	

Sea samples. The reproducibility of the ^{223}Ra results was similar to that for ^{224}Ra (Table 6, Fig. 5).

For ^{228}Th there are 28 reported results. Two laboratories reported no data. The only method used for analysis was RaDeCC. Here the reproducibility is poor. The main problem for ^{228}Th analysis may be the low activity or variable extraction efficiency (Charette et al., 2012). The ^{228}Th measurements need further study in the future (Table 7, Fig. 5).

Table 7
The reported of ^{228} Th (dpm/kg) activities for each laboratory.

Laboratory code	YS-1		YS-2		HK-1		HK-2	
	Activity	Error	Activity	Error	Activity	Error	Activity	Error
198	0.149	0.005	0.110	0.005	0.078	0.003	0.083	0.004
287	0.104		0.081		0.037		0.061	
376								
465	0.075	0.001	0.053	0.005	0.035	0.003	0.033	0.002
554	0.128	0.005	0.071	0.014	0.061	0.005	0.072	0.007
643	0.122	0.009	0.086	0.007	0.068	0.016	0.067	0.020
732	0.048	0.001	0.037	0.002	0.073	0.004	0.054	0.019
821	0.106	0.018	0.071	0.049	0.044	0.024	0.048	0.002
910								
Average value	0.105		0.073		0.057		0.060	
Std. dev.	0.034		0.023		0.018		0.016	
Number of reported data	7		7		7		7	
CI (95%)	0.025		0.017		0.013		0.012	
CI as % value	24.0				23.2		20.5	

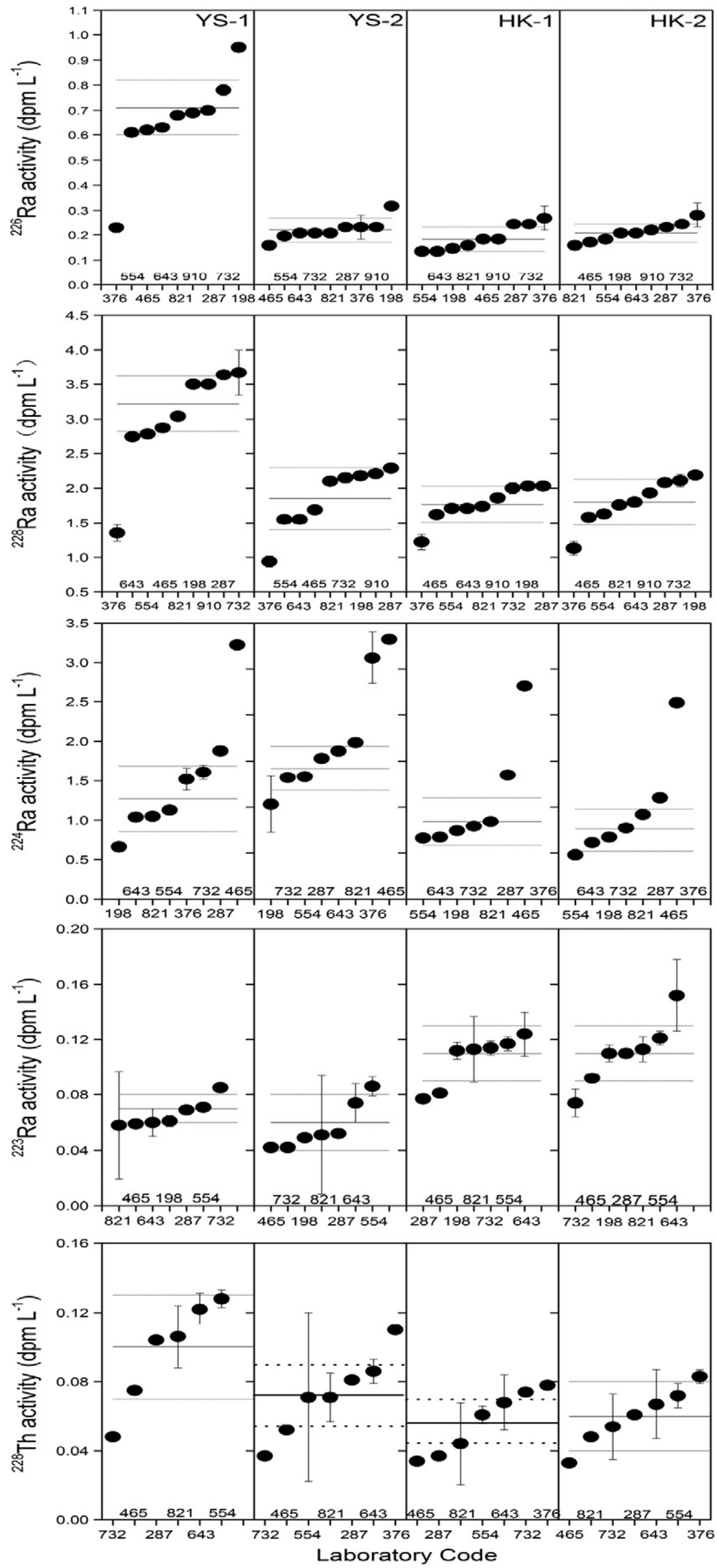

Fig. 5. The reported activities of ^{226}Ra, ^{228}Ra, ^{224}Ra, ^{223}Ra and ^{228}Th, the concerned average values and their errors.

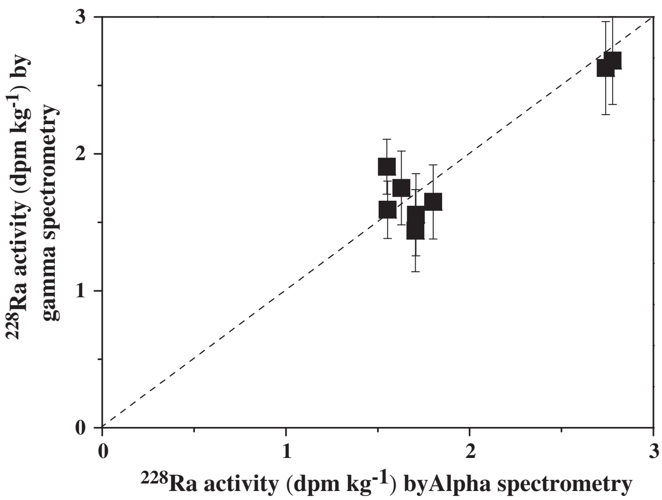

Fig. 6. Comparison of ^{228}Ra activities by HPGe-gamma spectrometry and alpha spectrometry.

4. Discussion

4.1. RaDeCC lower detection limits

Due to delays during shipping, some laboratories experienced long intervals (10 to 12 days) between the sampling date and the counting data. In such cases, the background and the limit of detection (LLD) may become important factors for controlling the uncertain of results. Moore (2008) has computed the LLD for ^{224}Ra to be about 0.5 dpm for a 400 minute counting period. Since all of our samples contained an initial ^{224}Ra activity of at least 50 dpm, even after 4 half lives (15 days) the sample will contain over 3 dpm, an easily measurable activity. However, after one or two half lives, the activity of ^{224}Ra is strongly influenced by the ^{228}Th activity on the Mn-fiber. Making ingrowth and decay corrections for aged samples is not straightforward, especially considering the problems in ^{228}Th analyses reported above. Without a good assessment of the ^{228}Th activity, the ^{224}Ra corrections cannot be made.

4.2. Comparison of Ra activities by different analysis techniques

There are several methods for analysis of ^{226}Ra and ^{228}Ra in seawater (Charette et al., 2012). If the activity is high enough and the equipment is available, gamma spectrometry is the easiest. After extraction of Ra from the Mn-fiber and precipitation with $BaSO_4$, the daughter nuclides, ^{214}Bi and ^{214}Pb, are used for ^{226}Ra and ^{228}Ac is used for ^{228}Ra after a 3-weeks equilibration (Elsinger et al., 1982). A more laborious technique, but one with considerably lower detection limits, is alpha spectrometry. This involves column separations of Ra from other elements and mounting of a thin source on a disk followed by sequential counting intervals (Hancock and Martin, 1991). A third method is based on a commercially-available system in China called a Dongtu system, which measures ^{224}Ra, ^{226}Ra and ^{228}Ra by $^{220,\,222}$Rn emanation (Men et al., 2010; Chen et al., 2012).

Fig. 6 compares results for ^{228}Ra analysis by HPGe-gamma spectrometry and alpha spectrometry. It is seen that there is no obvious difference between results obtained by the two methods. The results of ^{226}Ra and ^{228}Ra activity by the Dongtu system are lower in comparison with those by other methods. This could mean that the system used was not calibrated properly or that there is some problem in applying it to analyses of Ra isotopes in environment samples.

Table 8
The ±95% confidence interval expressed as % of average value.

Sample	^{226}Ra	^{228}Ra	^{224}Ra$_{ex}$	^{223}Ra	^{228}Th
YS-1	11	8.6	24.3	10.9	24
YS-2	6.0	15.9	10.2	22.1	23.9
HK-1	7.8	9.6	15.4	13.0	23.2
HK-2	5.5	12.0	14.2	16.3	20.5
Average	7.6	11.5	16.0	15.6	22.9
GEOTRACERS, stn 4[a]	19.7	9.3	8.9	42	74

[a] Charette et al. (2012).

4.3. Assessment

We can qualitatively compare the results of the Asian Ra Inter-comparison with the GEOTRACES Atlantic Ra Inter-comparison experiment. Table 8 shows the 95% confidence interval for each isotope and each sample expressed as % of the mean value. We also include results from Station 4 (the estuary sample) from the GEOTRACES inter-comparison reported by Charette et al. (2012). For ^{226}Ra, ^{223}Ra, and ^{228}Th the Asia results are considerably less scattered than the GEOTRACES results. For ^{228}Ra the Asia and GEOTRACES results are similar; but for ^{224}Ra, the Asia results are considerably more scattered than the GEOTRACES results. The ^{224}Ra analyses were compromised by excessive delays in some cases, but similar delays occurred in the Charette et al. (2012) study. Participating labs need to ensure that their RaDeCC systems are well calibrated and that they are making proper corrections for aged samples.

One significant difference between these experiments that does seem robust is the higher average Mn-fiber extraction efficiency for the Asian exercise. The average extraction efficiency for the Asia Inter-comparison was 98% compared to the GEOTRACES result of 87%. The GEOTRACES experiment utilized larger sample volumes and flow rates close to 1 L/min, while the Asia experiment samples averaged 45–75 L samples, which were processed at flow rates of 0.2 to 0.7 L/min. Whether the differences are due to the lower flow rates and volumes used in the Asian experiment or other factors is not known.

4.4. Comments and recommendations

We learned that most of the labs that participated in this inter-comparison could measure ^{226}Ra very well, better than the labs that participated in the GEOTRACES Atlantic inter-comparison. The ^{228}Ra results were a bit more scattered, but quite acceptable. The results for ^{224}Ra, ^{223}Ra, and ^{228}Th were not as good as expected.

The ^{224}Ra and ^{223}Ra results could probably be improved if the samples could reach the laboratory sooner. It may be worthwhile for each participant in a future inter-comparison to be present at the sampling site and return to the lab with the samples immediately. The IAEA reference fibers should be measured by each laboratory to improve their calibrations.

More attention is required regarding the uptake and measurement ^{228}Th on Mn-fibers. Without good ^{228}Th measurements corrections to the ^{224}Ra data for aged samples are problematic.

The lab that used Dongtu analysis system did not report very good results. We recommend they check the calibrations and perhaps partner with a nearby laboratory to improve their measurements.

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