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► **To cite this version:**

Thomas Church, Sylvain Rigaud, Mark Baskaran, Anupam Kumar, Jana Friedrich, et al.. Intercalibration studies of Po-210 and Pb-210 in dissolved and particulate seawater samples. *Limnology and Oceanography: Methods*, 2012, 10, pp.776-789. 10.4319/lom.2012.10.776 . hal-01061553

HAL Id: hal-01061553

<https://hal.science/hal-01061553v1>

Submitted on 19 Sep 2024

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Intercalibration studies of ^{210}Po and ^{210}Pb in dissolved and particulate seawater samples

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Abstract

Documented is an intercalibration (IC) exercise for both ^{210}Po and ^{210}Pb in seawater aliquots distributed between up to eight international laboratories that followed individual protocols. Dissolved and particulate samples were provided by GEOTRACES during two IC cruises at baseline stations in the North Atlantic and North Pacific oceans. Included were surface and/or deep dissolved and particulate samples at each site, plus complete profiles analyzed by the laboratory of the lead author. An unspecified solid phase standard was also distributed with ^{210}Po and ^{210}Pb in secular equilibrium to confirm spike calibrations. The ^{210}Po activities reported ($n = 8$) for the standard were very similar with a relative standard deviation (RSD) of 3.6% and mean value indistinguishable from the certified value, confirming accurate calibration of Po spikes. For seawater samples, the agreement was strongly dependent for both nuclides on the activity of the samples. The agreement was relatively good for dissolved seawater samples (RSD = 9% to 29%, $n = 4$), moderate for the particulate samples (RSD = 12% to 80%, $n = 8$), and poor for particulate dip blanks (RSD = 50% to 200%, $n = 8$). Noted is the higher apparent affinity of ^{210}Po versus ^{210}Pb for polysulphone filter material. Some lack of reproducibility between labs may have been caused by unspecified differences in individual lab protocols and calculations. A minimum sample activity of 0.1 dpm for both nuclides is recommended for an adequate reproducible sample activity. It is suggested that a consistent set of procedures and calculations be used to optimize future ^{210}Po and ^{210}Pb analyses in seawater samples.

Rationale for precise and accurate ^{210}Po and ^{210}Pb assay in the ocean

The ^{210}Pb ($t_{1/2} = 22.3$ y) and ^{210}Po ($t_{1/2} = 138$ d) parent and granddaughter radionuclide pair has proven to be effective tracers of oceanographic processes. Studies of particulate and dissolved ^{210}Po and ^{210}Pb in the marine environment have been used for quantifying the scavenging and removal of par-

ticle-reactive species including organic carbon integrated over sub-annual time scales not attainable by direct measurement synthesized in Verdeny et al. (2009).

The GEOTRACES (Geochemical Trace Element/Isotope Studies) program has been initiated to study trace elements and isotopes (TEIs) and to quantify processes across major ocean boundaries. The ^{210}Po and ^{210}Pb radionuclide pair is a useful suite of radiometric TEIs that are both geochemically (e.g., Pb) and biochemically (e.g., Po) active. Thus these isotopes complement the other particle reactive nuclides operating on comparable time scales (e.g., ^{234}Th , ^{228}Th) included in GEOTRACES. As such, ^{210}Po and ^{210}Pb were identified as priority tracers by the U.S. GEOTRACES Scientific Steering Committee in their "Principles and Pri-

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Acknowledgments

Full text appears at the end of the article.

DOI 10.4319/lom.2012.10.776

orities of the U.S. GEOTRACES Intercalibration Initiative" (www.geotraces.org).

To use the $^{210}\text{Po}/^{210}\text{Pb}$ radionuclide pair under the international auspices of the GEOTRACES program, a thorough intercomparison was deemed necessary leading to intercalibration across participant laboratories. This work is also intended to assess the protocols suggested in the methods manual prepared for the program. This process will allow adjusting the methods so that reliable and consistent data can be generated along multiple transects sponsored by the international community and across the variety of interfaces being targeted.

Why intercalibration is necessary: In general and for GEOTRACES

The $^{210}\text{Po}/^{210}\text{Pb}$ disequilibrium in the surface ocean is evidenced as a deficiency of ^{210}Po in the dissolved phase relative to ^{210}Pb ($^{210}\text{Po}/^{210}\text{Pb} < 1.0$) and corresponding excess in particulates ($^{210}\text{Po}/^{210}\text{Pb} > 1.0$). This is largely recognized as due to preferential extraction of Po by phytoplankton and regeneration in the subsurface reviewed in Stewart et al. (2008). This disequilibrium is one means for modeling organic carbon export e.g., Stewart et al. (2007) and to derive vertical eddy diffusion coefficients to model the transport of new nitrogen production in Sarin et al. (1994). Such modeling demands relatively high precision for analyzing this granddaughter/parent pair by any given laboratory, and accuracy between laboratories conducting contiguous sampling across oceanic regimes.

Previously, the global distribution of the ^{210}Po and ^{210}Pb pair was studied during the GEOSECS (Geochemical Ocean Section Study) program by 3 groups that identified sampling and analytical problems with the $^{210}\text{Po}/^{210}\text{Pb}$ measurements (Scripps, Yale and Woods Hole; Cochran et al. 1983; Chung and Craig 1983). The causes of differences between results included problems with water sampling materials (e.g., preferential loss of ^{210}Pb on stainless steel or PVC) and filtration apparatus to accurately differentiate the dissolved fractions. These discrepancies were largely reconciled during a final intercomparison representing the only prior attempt for a thorough intercomparison for dissolved ^{210}Pb . This was made toward the end of GEOSECS at Station 500 (28°27'N and 122°11'W) to help resolve the differences outlined above Chung et al. (1983). At that time there was good agreement between the two extraction methods being used by the Yale-WHOI groups (Co-APDC) and Scripps (Fe-OOH) for ^{210}Pb (5% to 10% at all depths). Other artifacts including different methods of filtration had been resolved, and residual ^{210}Pb carry over between sampling bottles minimized to a few percent (Chung and Craig, 1983). The particulate burden was so minor as to not be resolved unless large volume samples of 6-20 L are obtained (Bacon et al. 1976). However the corresponding ^{210}Po data were either not completed or not reported. This supports the rationale for an intercalibration of ^{210}Po and ^{210}Pb in future studies as well as for the employment of submersible pumps to collect particulate nuclides of sufficient activities.

Oceanographic perspective for the intercalibration

Observations and discussions continue on the exact nature of the ^{210}Po and ^{210}Pb granddaughter/parent distribution, including the cause of reported large scale deficiency of ^{210}Po ($^{210}\text{Po}/^{210}\text{Pb}$ activity ratios < 1) in both pelagic and meso-pelagic waters of some oceanic regimes (e.g., western and eastern Indian Ocean: Chung and Finkel 1988 and Cochran et al. 1983, respectively; East China and Philippine Seas: Nozaki et al. 1990; Equatorial Pacific and Bering Sea: Nozaki et al. 1997; Sargasso Sea: Kim and Church 2001; South China Sea: Chung and Wu 2005; Antarctic Circumpolar Current: Friedrich and Rutgers van der Loeff 2002). Proposed processes in benthic waters include preferential extraction of ^{210}Po onto the suspended particulate phase versus adsorption of ^{226}Ra supported ^{210}Pb at the sediment water interface (Bacon et al. 1976; Cochran et al. 1983). However to reach such conclusions, an ideal analytical uncertainty of less than 10% needs to be obtained.

Thus, a thorough intercalibration for both ^{210}Po and ^{210}Pb is timely to ascertain whether mid-waters and deeper ^{210}Po deficiencies are accurate and not due to inadequacy in the analytical techniques. Furthermore, if such deficiencies are shown to exist, they could reveal those meso-pelagic processes that might be operational and modeled on the sub-annual time scales commensurate to that of the ^{210}Po half-life (Turekian and Nozaki 1980; reviewed in Rutgers van der Loeff and Geibert 2008).

Approach to intercalibration and participation

The present article reports an inter-laboratory comparison for the assay of ^{210}Po and ^{210}Pb conducted on identical dissolved and particulate aliquots using lab specific protocols and calculations. The international laboratories with published peer-reviewed articles on the ^{210}Po and ^{210}Pb nuclide pair were invited to participate and those responded received samples. Not all laboratories elected to participate and those reporting partial data (i.e., only ^{210}Po without a subsequent ^{210}Pb ingrowth measurement) were excluded from this manuscript. The approach to the intercalibration exercise was to first distribute a solid standard of higher activity (IAEA-RGU-1), and also to collect and distribute common aliquots of dissolved and particulate marine samples at lower natural activity. The natural intercalibration samples were taken at the GEOTRACES baseline station (BATS) in the North Atlantic at (31°40'N; 64°10'W) as well as a coastal (SHELF) site on the slope off Chesapeake Bay (37.0°N, 74.4°W, depth 1655 m), and at the baseline station (SAFE) in the North Pacific at (30°00'N; 140°00'W). The present article basically reports the inter laboratory comparison of the same dissolved and particulate aliquots using their own protocols and calculations.

Materials and procedures

Intercalibration solid standard

The certified reference material (IAEA-RGU-1) was distributed to the participating groups as an unidentified solid. The participating laboratories were not informed of the activity in the certified material, thus we do not anticipate the labs read-

justed their data as a result. The RGU-1 was prepared at the IAEA by dilution of a uranium ore (BL-5 7.09% U) with floated silica powder of uniform grain size distribution. This material is certified at 400 ± 2 ppm of ^{238}U , corresponding to 0.298 ± 0.001 dpm.mg $^{-1}$, in equilibrium with all the members of the ^{238}U -series, and reported as such for the ^{210}Po nuclide at time of plating (IAEA, 1987). About 100 mg of this standard were distributed to the laboratories with a general range of activity for proper spiking, and a guide for dissolving the silica matrix.

Intercalibration of dissolved seawater

The seawater was collected using Niskin bottles deployed at the designated depths of the two GEOTRACES baseline stations and used to fill a common well-mixed tank for dispensing. This was accomplished at one depth (2000 m) in the North Atlantic (BATS) during the July 2008 IC-I Intercalibration cruise, and at two depths (6 and 3000 m) in the North Pacific (SAFe) during the May 2009 IC-II Intercalibration

cruise. The 20 L Cubitainers® were filled with filtered (<0.2 μm) seawater using AcroPak® capsules with Supor® membranes, and acidified to pH 2 using Optima grade HCl. The cubitainers were then sealed in dark bags at sea and transferred to cold storage before distribution and analysis ashore. The filtered and acidified seawater samples on board were assumed to be isolated from further storage artifacts, including biological activity based on earlier findings (e.g., Chung et al.1983).

The dissolved seawater samples were distributed promptly with information on the date of sampling to the participating international laboratories. The samples were then processed by all laboratories using their own protocols. The generic steps for sample processing are outlined in Fig. 1. The dissolved samples were all processed by application of the Fe coprecipitation method (Nozaki 1986; Sarin et al. 1992) followed by α spectrometry as described in detail (pp. 27-35) of the GEOTRACES procedures manual found at: <http://www.geotraces.org/science/>

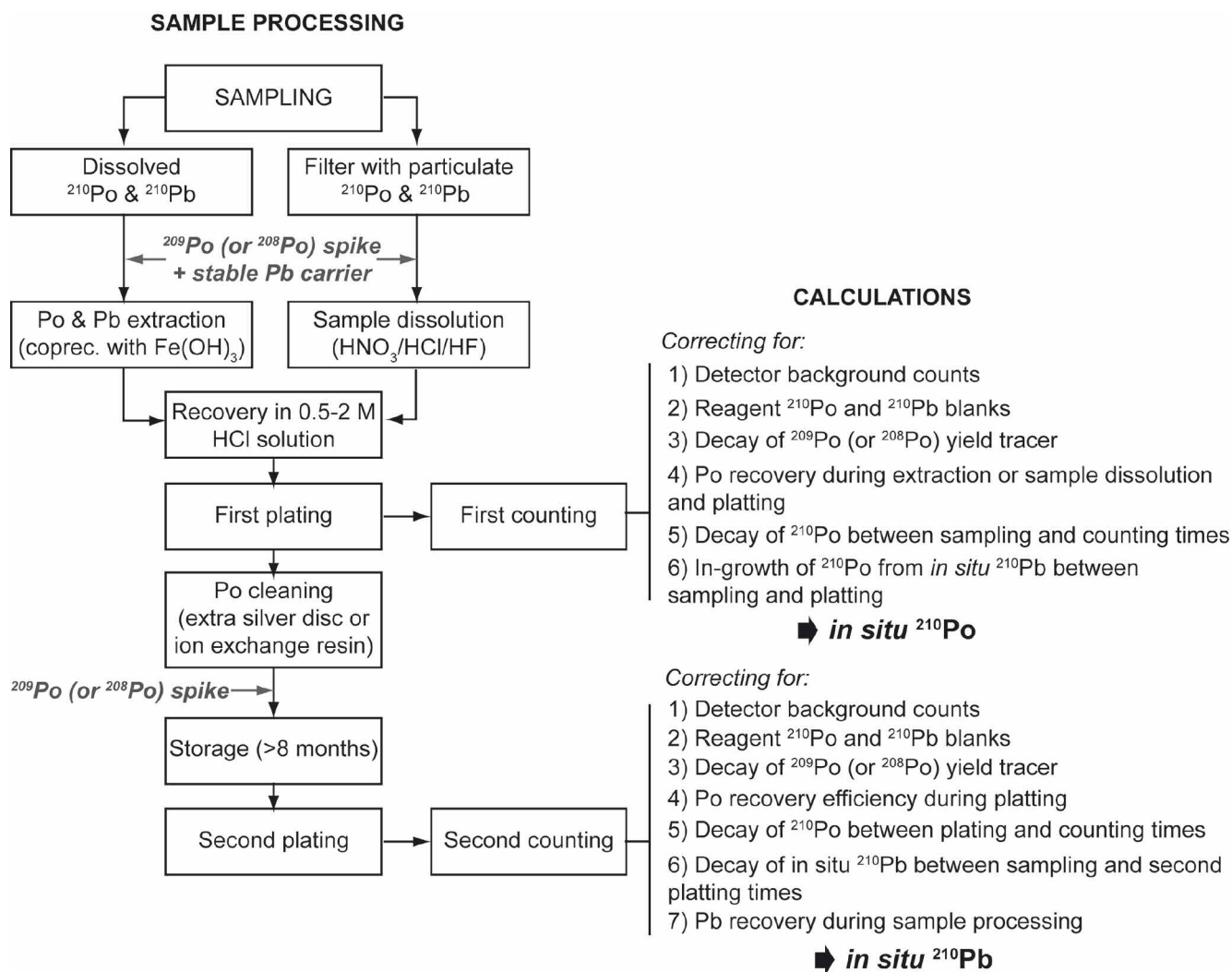


Fig. 1. General protocol for ^{210}Po and ^{210}Pb activity measurement in dissolved or particulate seawater samples with correction accounted for in the calculation.

intercalibration/222-sampling-and-sample-handling-protocols-for-geotraces-cruises and reviewed elsewhere (Mathews et al. 2007; Baskaran et al. 2009). Most laboratories followed these suggested protocols with minor variation. Only one laboratory used a double spike technique with both ^{208}Po used to trace the initial ^{210}Po and ^{209}Po after separation of the ^{210}Pb . Other variants include removing the residual Po from the plated solution before ^{210}Pb in-growth either by using a second Ag plate or passing the initial plating solution through anion exchange resin. In both later cases, the goal is to separate the ^{210}Pb from any residual ^{209}Po spike or under plated ^{210}Po , before subsequent ingrowth of ^{210}Po traced by an additional ^{209}Po spike before the following months of ingrowth. An analysis of the effect of residual polonium in the solution after the first plate on the in-situ determination of ^{210}Po is discussed in a related paper Baskaran et al. (in prep.).

The in situ ^{210}Po and ^{210}Pb activities need to be calculated by applying several corrections, such as blanks of either nuclide arising from reagents contamination, ingrowth/decay of the parent/granddaughter pair, with monitors of Po efficiencies and Pb recovery during processing (Fig. 1). We confirmed that most labs applied such corrections using the appropriate equations as outlined in the GEOTRACES methods manual. These calculations are also expected to include accurately compounded errors using appropriate error propagation equations. Most laboratories appear to have performed these corrections and used spread sheets that appropriately integrate these important parameters. This was confirmed in some cases when labs provided raw data to capture errors in data entry to check for the above corrections, and confirm the reported results.

Intercalibration of seawater particulates

Particulate samples were collected using in situ pumps, and the methods of collecting the particulates are described in another companion article (Maiti et al. 2012). Two types of filters were chosen by GEOTRACES for the comparison; quartz microfiber [QMA and polysulphone membrane (Supor) of nominal 1 μm pore size with 147 mm diameter]. Seawater samples (volumes between 201 to 718 L) were pumped through these filters at about 5 L/min at two depths (100 and 2000 m) in the North Atlantic at BATS and one depth (80 m) at the slope site off Chesapeake Bay. Blank filters (so-called dip blanks) were placed inside a 53 μm Nitex® screen bag and deployed on the side of the pump allowing the filter to be in complete contact with the water being filtered and were treated similarly as samples. These dip blanks are meant to simulate the passive sorption of ^{210}Po and ^{210}Pb from the water onto the filter.

A total of 13 (22 mm diameter) punches were cut-out from each filter representing an active filtration diameter of 130 mm. Thus each punch corresponded to 2.86% of the total volume of water filtered (equivalent to 5.8 to 20.5 L per filter aliquot). Punches of samples and dip blank filters were distributed promptly for analysis to about a dozen international labs within months after collection, of which 8 responded

with complete results for both nuclides. The laboratories were informed of the dates of collection and volume filtered through the filter. Each of the participating group used their own dissolution protocols for particles as well as their own correction calculation (Fig. 1). All of the groups used combinations of concentrated strong acids ($\text{HNO}_3\text{-HCl-HF}$) to digest the filters as suggested in the GEOTRACES protocol noted above and reviewed elsewhere (Mathews et al. 2007; Baskaran et al. 2009). The QMA filters dissolved completely, but residue was left behind from the Supor filters. Note here that the dip blank values were not subtracted from the sample value but considered separately as samples.

Complete seawater depth profiles

During the IC cruises, samples were also collected over a complete depth profile at SAFe (dissolved and particulate QMA) and BATS (particulate QMA) stations using the same sampling protocol as reported for IC samples. The ^{210}Po and ^{210}Pb activities were analyzed by the laboratory of the lead author (University of Delaware) and used in order to interpret the results obtained for the IC intercalibration at the same corresponding depths both for confirmation and discussion in the context of oceanographic processes.

Assessment

Intercalibration standard

The ^{210}Po activity reported by participating labs ($n = 8$) for the RGU-1 certified standard was 0.295 ± 0.011 dpm mg^{-1} (Table 1). The associated RSD is very low (3.6%) indicating a very good agreement for ^{210}Po activity reported by the different labs. Moreover, this value is comparable with those certified for this referenced material (0.298 ± 0.001 dpm mg^{-1}) indicating accurate ^{210}Po determination. The assessment is that all labs have achieved an adequate dissolution of the standard with an accuracy that also verifies reliability their ^{209}Po spikes.

Intercalibration of dissolved seawater

The intercomparison results were satisfactory for ^{210}Po and ^{210}Pb in dissolved fractions from the participant labs ($n = 4$) as

Table 1. Intercalibration data for the IAEA Standard Reference Material RGU-1. The material is certified by the IAEA (1987) at 400 ± 2 ppm of ^{238}U to be in equilibrium with all daughters, including ^{210}Pb and ^{210}Po , at 0.298 ± 0.001 dpm mg^{-1} .

Participating groups	^{210}Po (dpm. mg^{-1})	\pm	RSD
A	0.273	0.005	
B	0.300	0.010	
C	0.299	0.012	
D	0.297	0.010	
E	0.299	0.025	
F	0.290	0.007	
G	0.294	0.004	
H	0.310	0.003	
MEAN	0.295	0.011	3.6%

presented in Table 2 and plotted in Fig. 2. All mean activities reported ranged from 7.9 ± 0.8 dpm/100 L to 21.8 ± 1.9 dpm/100 L for ^{210}Po and from 10.4 ± 1.5 dpm/100 L to 28.5 ± 6.3 dpm/100 L for ^{210}Pb . The individual reported data agrees well between themselves ($\text{RSD} \leq 14\%$) for both isotopes in the 2000m BATS sample, for ^{210}Pb in surface SAFe sample and for ^{210}Po in 3000m SAFe sample. However, the results agree less well for ^{210}Pb in 3000m SAFe sample (22% RSD) and for ^{210}Po in surface SAFe sample (29% RSD).

However, it is worth noting that for most of the samples, the difference between values reported by each laboratory reported value is significantly higher than the uncertainties reported for each measurement. Such uncertainties correspond to those reported by labs B, C, and D for a single individual analysis ($n = 1$), but to standard deviation on replicates ($2 < n < 4$) for labs A and E (Table 2). The source of the large deviation between duplicates such as Lab E is unknown, but suggests potentially significant differences among individual laboratory procedures.

When considering the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratios, all measurements agree well with each other and indicate a significant ^{210}Po deficiency throughout the water columns. This deficiency is most significant in the SAFe surface sample (0.41 ± 0.17) and lower but still significant in deep samples from BATS and SAFe (0.74 ± 0.06 and 0.80 ± 0.11 , respectively).

Intercalibration of particulate samples

The ^{210}Po and ^{210}Pb activities in filter aliquots for both QMA and Supor filters at each of the three depths (Shallow, Deep,

and Shelf; 6, 2000-3000, and 80 m, respectively) reported by the participating laboratories ($n = 8$) are shown in Fig. 3, whereas the range (minimum and maximum values) and the mean with the standard deviation for both samples and dip blank filters summarized in Table 3. For the 6 filter samples (three sites and two filter types), the values reported for both isotopes by different labs range from 0.00 ± 0.03 dpm to 0.34 ± 0.03 dpm for ^{210}Po and from 0.050 ± 0.002 dpm and 0.22 ± 0.02 dpm for ^{210}Pb . Comparison between labs showed that results generally agree, with better for ^{210}Pb than ^{210}Po . The RSD ranged for ^{210}Pb from 12% to 47% and for ^{210}Po from 29% to 80%.

For dip blanks, the values reported in each filter aliquot ranged from -0.03 ± 0.02 dpm to 0.24 ± 0.02 dpm for ^{210}Po and from -0.01 ± 0.02 dpm and 0.14 ± 0.01 dpm for ^{210}Pb (Table 3). The negative values were not significantly different than zero. The dip blank comparison between labs is poorer than for particulate samples, but still remains better for ^{210}Pb than for ^{210}Po . Relatively the individual RSD ranged from 50% to 80% for ^{210}Pb and from 80% to 210% for ^{210}Po . Here the fraction of samples represented by these blanks corresponds to a significant proportion of ^{210}Po ($22 \pm 30\%$) and ^{210}Pb ($30 \pm 27\%$) activities found in sample filters (Table 4). Here again, the differences between each reported value are generally higher than the associated uncertainties for each measurement and correspond only to calculated uncertainties from error propagation for the single reported value as limited by sample size.

Table 2. ^{210}Po and ^{210}Pb activities and $^{210}\text{Po}/^{210}\text{Pb}$ activity ratios reported by participating laboratories, with the corresponding mean, one standard deviation and relative standard deviation, in dissolved seawater during IC-I and II in the North Atlantic (BATS) and North Pacific (SAFe). The number of replicates obtained by each laboratory is also reported.

Participating groups	^{210}Po				^{210}Pb				$^{210}\text{Po}/^{210}\text{Pb}$		
	(dpm 100 L ⁻¹)	±	RSD	n	(dpm 100 L ⁻¹)	±	RSD	n		±	RSD
Atlantic IC-I, BATS 2000m											
A	8.2	1.1		2	12.1	1.1		2	0.68	0.11	
C	n.d.				9.3	0.5		1	n.d.		
D	8.5	0.4		1	11.1	1.1		1	0.77	0.08	
E	7.0	5.4		2	9.0	2.1		3	0.78	0.63	
MEAN	7.9	0.8	10%		10.4	1.5	14%		0.74	0.06	8%
Pacific IC-II, SAFe 6m											
B	7.8	0.7		1	28.3	1.2		1	0.28	0.03	
C	7.4	1.7		1	26.9	1.6		1	0.27	0.07	
D	13.5	0.5		1	21.2	1.0		1	0.64	0.04	
E	10.8	4.7		3	24	13		3	0.5	0.3	
MEAN	9.9	2.9	29%		25.1	3.2	13%		0.39	0.21	53%
Pacific IC-II, SAFe 3000m											
B	23.2	1.2		1	34.5	1.2		1	0.67	0.04	
C	22.4	2.0		1	25.2	1.0		1	0.89	0.09	
D	19.0	0.7		1	21.3	1.3		1	0.89	0.06	
E	22.5	2.6		4	33.0	3.3		4	0.73	0.11	
MEAN	21.8	1.9	9%		28.5	6.3	22%		0.82	0.13	15%

n.d.: not determined

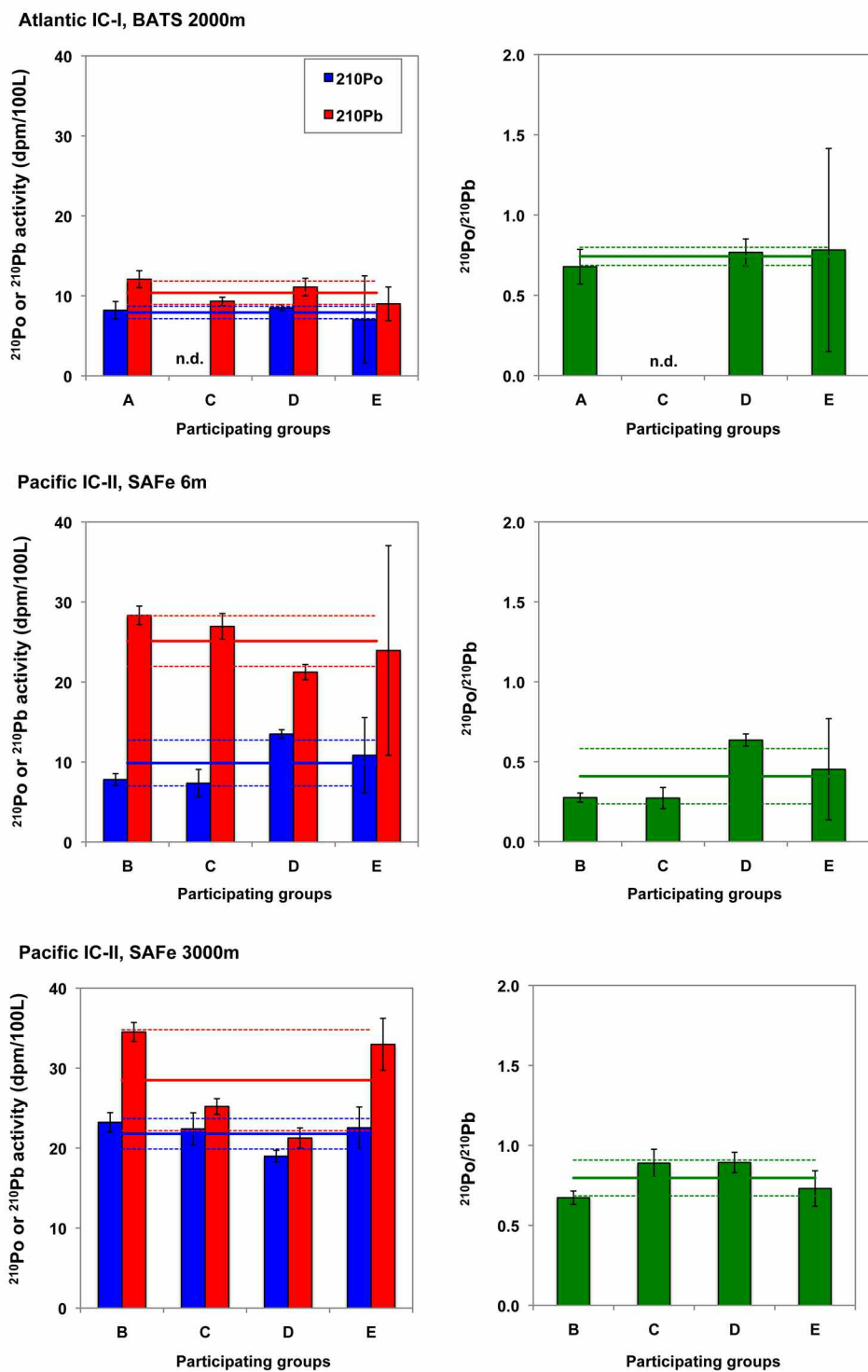


Fig. 2. ^{210}Po and ^{210}Pb activities and $^{210}\text{Po}/^{210}\text{Pb}$ activity ratios in dissolved seawater intercalibration during IC-I and II in the North Atlantic and Pacific Ocean. The straight and dashed horizontal lines represent the mean \pm one standard deviation, respectively.

Because of the relatively high uncertainty of the final activity of both isotopes, the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratios in particulates can only be poorly defined. They seem to indicate ^{210}Po deficiency at the Shelf station at 80 m (0.46 ± 0.33 with QMA

and 0.70 ± 0.58 with Supor) as equilibrium or slight excess at the BATS station (1.00 ± 0.37 for QMA and 1.17 ± 0.55 for Supor at shallow depth and 1.53 ± 0.61 with QMA and 1.73 ± 1.07 with Supor at depth [3000 m]). However, the large asso-

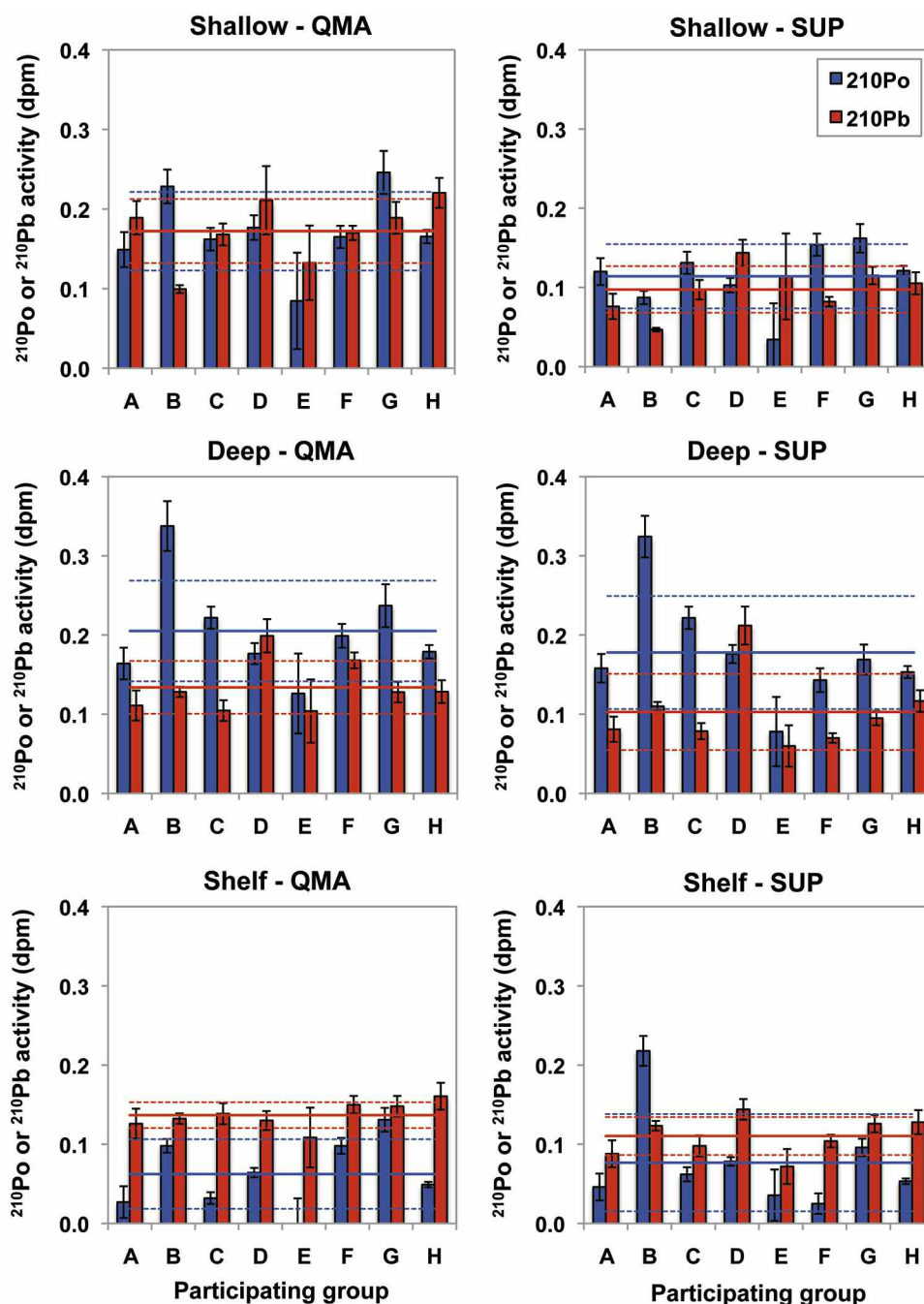


Fig. 3. ^{210}Po and ^{210}Pb activities in particulate intercalibration samples taken on IC-1 (North Atlantic), BATS and Shelf stations. The straight and dashed horizontal lines represent the mean \pm one standard deviation, respectively.

ciated uncertainties do not allow a precise conclusion.

The comparison between particulate filter type, based on volume normalized activity, show that the ^{210}Po activity is higher in the Supor filters in comparison to the QMA filters Supor/QMA activity (ratio = 1.7 ± 0.8) an effect that could be attributed to the stronger affinity of Po to polysulphone material. There is no such significant difference in the volume normalized activity for ^{210}Pb (Supor/QMA = 1.3 ± 0.5). The range

of ^{210}Po values reported for the dip blank filter is large, and thus, we are unable to see statistically significant differences in the Supor/QMA ratios.

Discussion

The intercalibration exercise

The overall purpose of this intercalibration exercise for ^{210}Po and ^{210}Pb in marine samples is to compare the results

Table 3. Activities* of ^{210}Po and ^{210}Pb in QMA/Supor IC-1 Intercalibration filters in the North Atlantic (BATS) taken at shallow (100 m), deep (2000 m), and shelf (80 m) depth.

Depth, Filter, Volume	Sample ^{210}Po dpm	Dip BLK ^{210}Po dpm	Sample ^{210}Pb dpm	Dip BLK ^{210}Pb dpm
BATS Shallow-QMA (19.9 L)	0.08-0.25 (0.17 ± 0.05; 29%)	-0.01-0.08 (0.02 ± 0.03; 121%)	0.10-0.22 (0.17 ± 0.04; 23%)	0.02-0.14 (0.06 ± 0.04; 60%)
BATS Shallow-Supor (5.8 L)	0.03-0.16 -0.03-0.06 (0.11 ± 0.03; 36%)	0.05-0.14 (0.01 ± 0.03; 209%)	0.03-0.09 (0.10 ± 0.03; 30%)	(0.05 ± 0.03; 53%)
BATS Deep-QMA (20.5 L)	0.13-0.34 (0.20 ± 0.06; 31%)	0.00-0.09 (0.03 ± 0.03; 111%)	0.10-0.20 (0.13 ± 0.03; 25%)	-0.01-0.08 (0.04 ± 0.03; 86%)
BATS Deep-Supor (15.8 L)	0.08-0.32 (0.18 ± 0.07; 40%)	-0.01-0.11 (0.02 ± 0.04; 181%)	0.06-0.21 (0.10 ± 0.05; 47%)	0.03-0.13 (0.05 ± 0.04; 73%)
SHELF-QMA (13.4 L)	0.00-0.13 (0.06 ± 0.04; 70%)	0.00-0.08 (0.03 ± 0.03; 84%)	0.11-0.16 (0.14 ± 0.02; 12%)	-0.01-0.11 (0.05 ± 0.04; 83%)
SHELF- Supor (10.0 L)	0.03-0.22 (0.08 ± 0.06; 80%)	-0.01-0.24 (0.05 ± 0.08; 184%)	0.07-0.14 (0.11 ± 0.02; 22%)	0.02-0.11 (0.05 ± 0.03; 60%)

*The range of activities reported by the 8 participating groups is given; numbers in parenthesis denote the mean along with the standard deviation and the corresponding relative standard deviation, on the 8 data points. The negative values reported are due to very low activities in the dip blank and a larger reagent blank was subtracted from the dip blanks.

Table 4. Activities of ^{210}Po and ^{210}Pb in dip blank as % of sample activity and $^{210}\text{Po}/^{210}\text{Pb}$ ratios in dip blank for IC-1 Intercalibration filters

Depth and Filter	^{210}Po in dip blank (%)	^{210}Pb in dip blank (%)	$(^{210}\text{Po}/^{210}\text{Pb})_{\text{mean}}$ in dip blank
Shallow-QMA	-7-33 (12 ± 14)	8-70 (39 ± 22)	-0.1-0.9 (0.4 ± 0.4)
Shallow-Supor	-22-62 (12 ± 27)	24-141 (57 ± 40)	-0.5-0.8 (0.3 ± 0.5)
Deep-QMA	-1-37 (13 ± 14)	-13-63 (28 ± 24)	-3.9-1.1 (-0.4 ± 1.8)
Deep-Supor	-3-41 (10 ± 17)	38-98 (49 ± 22)	-0.1-2.6 (0.5 ± 0.9)
Shelf-QMA	2-87 (50 ± 30)	-8-74 (32 ± 26)	-3.2-2.0 (0.16 ± 1.44)
Shelf-Supor	15-110 (38 ± 48)	22-64 (48 ± 24)	-0.2-2.2 (0.56 ± 0.76)

The range of fractional activities reported by the 8 participating groups is given; numbers in parenthesis denote the mean along with the standard deviation on the 8 data points. The negative values reported are due to very low activities in the dip blank and a larger reagent blank was subtracted from the dip blanks.

reported by participant laboratories using their own sample processing protocol and calculations. This blind intercomparison was conducted on identical aliquots from the same samples collected during dedicated cruises in two different major ocean basins. Comparison between labs showed that agreement was very good for the RGU-1 standard, relatively good for the dissolved samples, relatively low for particulate samples and poor for the dip blank. As such, the following questions are addressed.

Why does the reproducibility between labs depend on sample type?

The first task is to understand why the comparison between laboratories was so variable depending the sample used. For this purpose, a plot is provided reporting the RSD of the mean obtained for the values reported by participating labs for the 17 samples (1 standard, $n = 8$; 3 dissolved samples, $n = 4$; 6 particulates samples and 6 dip blank filters, $n = 8$) as a function of the mean total ^{210}Po and ^{210}Pb activity in the samples (Fig. 4). Note that here the RSD value of the

blanks are treated as operational in the form of dip blanks, thus plotted the same way as would low activity samples. It shows that the higher the total ^{210}Po and ^{210}Pb activity in the sample, the higher the reproducibility between labs. This clearly suggests that the agreement between labs is fundamentally influenced by the activity in the sample analysis. Also from Fig. 4, a threshold value of 0.1 dpm can be proposed as a minimum activity in a given marine sample to obtain an meaningful comparison of ^{210}Po and ^{210}Pb between individual labs and achieve a RSD < 40%. For samples representing activities < 0.1 dpm (e.g., the dip blank and most particulate samples in this study), it appears that the differences between individual protocols are the main source of the poor agreement between labs. Indeed, for these samples, the absolute standard deviation does not increase proportional to the sample activity, and thus corresponds to a systematic error associated with the individual methods used by the participating labs. For samples presenting activity > 0.1 dpm, the differences originating from individual lab proce-

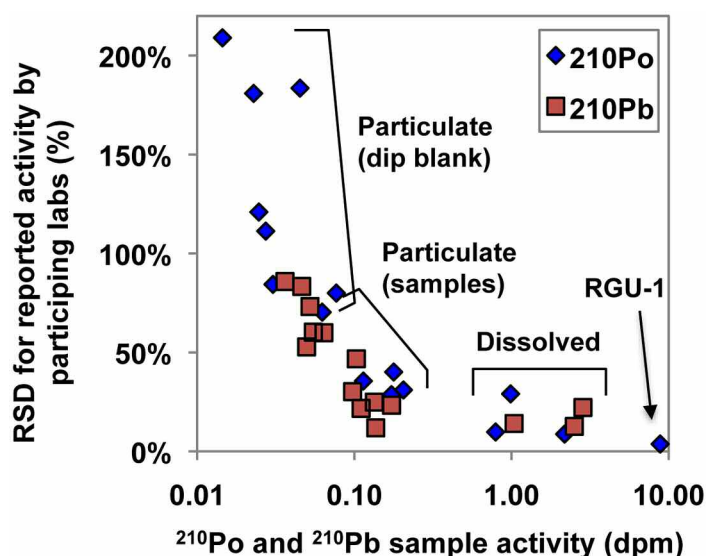


Fig. 4. One relative standard deviation (RSD) in the reported ^{210}Po and ^{210}Pb activity by the participant labs for all samples considered in this study as a function of ^{210}Po and ^{210}Pb absolute activity in the sample. Included are the reference solid standards of RGU-1, dissolved seawater and particulates samples, and dip blank. Note the logarithmic scale for ^{210}Po and ^{210}Pb activity.

dures are secondary, whereby the absolute standard deviation increases proportional to activity in the samples.

Thus in practice, the 0.1 dpm threshold constitutes a limit for the current method of ^{210}Po and ^{210}Pb measurement. Such an activity was achieved for the solid material standard RGU-1 (≥ 30 mg of solid) and for the dissolved water (> 10 L samples) as well, but not for most of the particulate samples (limited to between 5.8 and 20.5 L filtered seawater) or for the dip blank. For adequate measurement of ^{210}Po and ^{210}Pb particulate activity, it implies that the amount of filtered seawater should represent an optimal volume of at least 30 L for similar oceanographic sites.

Why is the intra-lab uncertainty lower than inter-lab variability?

It was observed that for most dissolved and particulate marine samples or dip blanks, the differences in the values reported between the different labs are larger than the uncertainties associated within each lab measurement. Three hypotheses can be drawn to explain this observation: 1. there is a significant difference in the ^{210}Po and ^{210}Pb activity between the sample aliquots, 2. some uncertainties are not taken into account, or error propagation calculations are not uniformly or properly applied, and 3. there exists some differences in protocols or calculations applied by the different labs that lead to significantly different final results.

The first hypothesis can be practically ruled out, as there should not be much variability between aliquots to explain the differences observed. Indeed, for particulate samples it was shown that the inter-variability for another isotope ^{234}Th

between pump or between punches of filter was not more than 18% (Maïti et al. 2012), and we can expect similar variability for ^{210}Po and ^{210}Pb . For dissolved samples, the variability between aliquot are also expected to be low since aliquots were withdrawn from well-homogenized tanks.

Concerning the second hypothesis, it is possible that the uncertainty in calculations or error propagation differed among the participating labs. Indeed the results of a questionnaire sent to all participating labs indicated that the extent of analytical errors varied widely; from only counting statistics, and for many others. These errors include pipetting/weighting (spike, carrier, and sample), spike calibration, reagent blank and detector background. In addition, there are those uncertainties compounded with error propagation arising during the ^{210}Pb ingrowth corrected ^{210}Po . Thus, in the future special attention should ensure sharing appropriate and commonly agreed calculations leading to the final assay of activities. This is the specific objective of another related paper Rigaud et al. (in prep.).

Finally, the third hypothesis considers some methodological differences between labs that may contribute to significant differences between individually reported values. Such differences may be associated with small but significant differences between commonly reported procedures for sample processing, including differences in the calculation used for correcting in-growth/decay or isotope recoveries. The labs reported generally following the same procedure as described in the previously referenced GEOTRACES cookbook, although some specific differences are reported. These include differences in the amount of spike, Pb and Fe carrier added, a double spike technique using both ^{208}Po and ^{209}Po , absence or variable procedures for residual Po removal, blank/background corrections, different assumptions on decay/ingrowth calculation or corrections. Until resolved, such differences are expected to be significant sources of the inter-lab variability, and to constitute potential limits for the accurate determination of ^{210}Po and ^{210}Pb in natural marine samples. Note that such limits are particularly evident for samples with low activity as demonstrated by this study (Fig. 4).

Implication for oceanographic processes

The ^{210}Po and ^{210}Pb activity profiles as well as the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratio is often used as a tracer for processes involving particulate scavenging in the oceans (e.g., Stewart et al. 2008). Specifically the aim is to compare the IC data with complete ^{210}Po , ^{210}Pb and $^{210}\text{Po}/^{210}\text{Pb}$ activity profiles obtained by the lab of the lead author (UDE) at the SAFE station (dissolved and particulate) and BATS station (particulate) during the same cruises (Fig. 5, Table 5).

The results from both this intercalibration exercise and synchronous profiles are in good agreement with those previously reported for dissolved profiles near SAFE, and less for the particulate profile at BATS (Fig. 6). As mentioned previously, the lower agreement for particulate samples seems principally due to the low activity in those samples. For the dissolved samples from

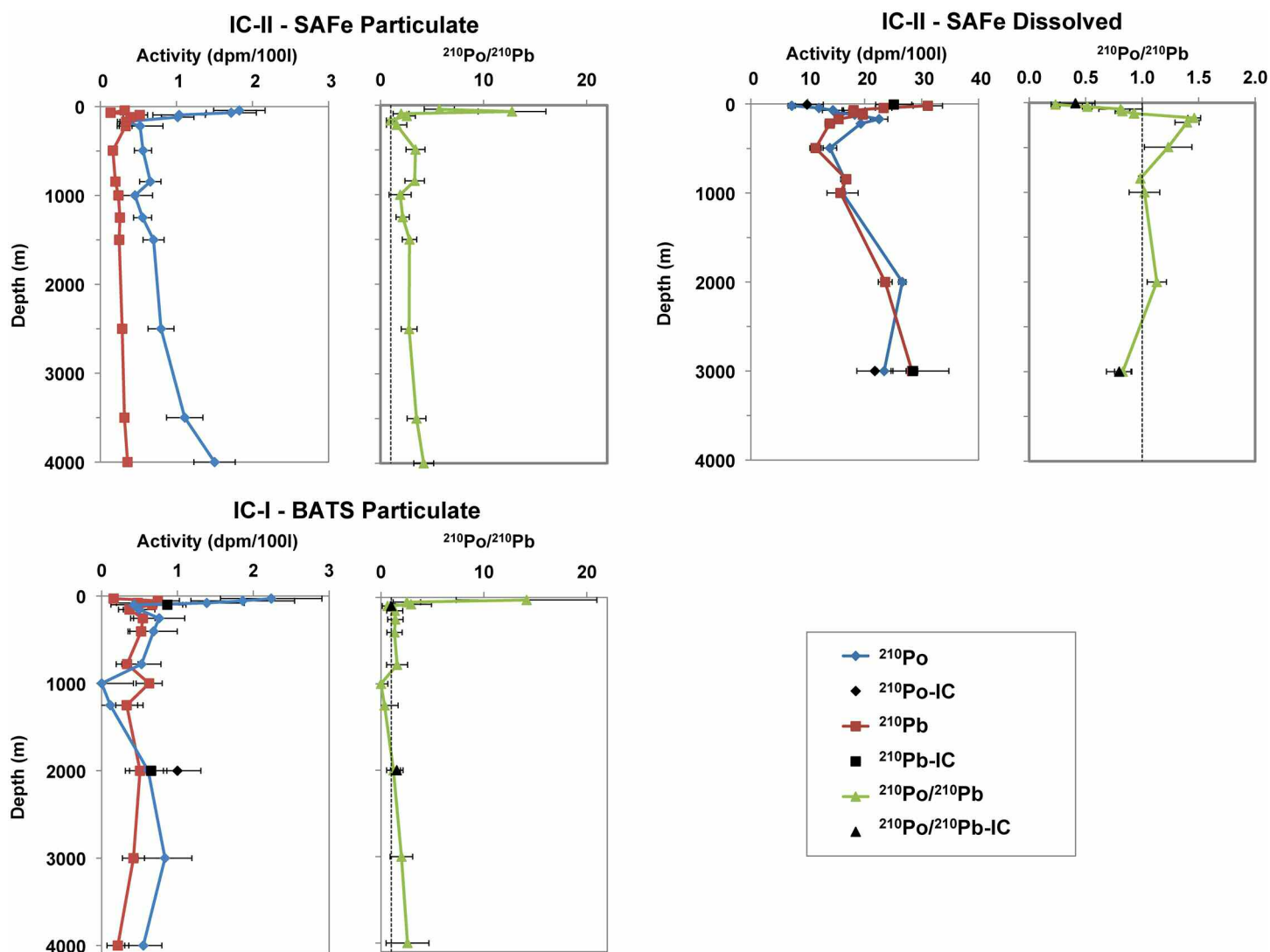


Fig. 5. Profiles of ^{210}Po and ^{210}Pb activities and $^{210}\text{Po}/^{210}\text{Pb}$ activity ratios obtained in seawater samples at the GEOTRACES IC-II SAFe (dissolved and particulate) and IC-I BATS (particulate) stations as reported by the lab of the lead author. Results obtained in dissolved samples for the intercalibration exercise for surface (IC-6m) and deep (IC-3000m) at the SAFe station, and in particulate samples (QMA filters) for surface (100m) and deep (2000m) at the BATS station are also plotted for comparison.

SAFe, it is apparent that the large and significant ^{210}Po deficiency at 6 m depth obtained for IC samples (0.39 ± 0.21 , Table 2) corresponds to a more general deficiency occurring over the upper 100 m of the water column (Fig. 5). This ^{210}Po deficiency is due to the selective uptake of ^{210}Po by biological activity relative to ^{210}Pb (reviewed in Stewart, et al. 2008). Evidenced also here is both the ^{210}Po excess observed between 200 and 800 m attributed to ^{210}Po regeneration from mineralization of settling organic material, and the significant enrichment of ^{210}Po relatively to ^{210}Pb in the particulate phase (Fig. 5). Deeper, the $^{210}\text{Po}/^{210}\text{Pb}$ ratio approaches equilibrium but still seems to reach a significant (0.80 ± 0.11) deficiency at 3000 m depth. Similar ^{210}Po deficiencies at depth were also observed at BATS (activity

ratio 0.74 ± 0.06 , Table 2) and was also reported elsewhere (Bacon et al. 1976; Cochran et al. 1983; Kim et al 1999; Kim 2001). The causes for this deficiency have been debated as due to preferential scavenging of Po during C cycling in deep waters, or differential ^{210}Po and ^{210}Pb uptake by benthic nepheloid particles and adsorption at the sediment water interface. However, any of these options would have to be operating on the sub-annual scale of the ^{210}Po half-life (138 days). Analytically, there is also the potential for differential extraction of spike ^{209}Po versus in situ ^{210}Po isotopes during phases of seawater extraction. Such potential methodological bias is being tested by comparing different extraction methods, which should confirm the observed disequilibria in deep waters Casacuberta et al. (in prep.).

Table 5. ^{210}Po and ^{210}Pb activities and $^{210}\text{Po}/^{210}\text{Pb}$ activity ratios mean \pm 1 standard deviation, ($n = 2$) along depth profiles of dissolved and particulate samples in IC-II North Pacific (SAFe) and in particulates samples IC-I in North Atlantic (BATS). Results (mean \pm 1 standard deviation) obtained for the intercalibration (IC) exercise are also reported.

Depth (m)	^{210}Po (dpm/100 L)	\pm	^{210}Pb (dpm/100 L)	\pm	$^{210}\text{Po}/^{210}\text{Pb}$	\pm
DISSOLVED - SAFe Station						
6 (IC)	9.9	2.9	25.1	3.2	0.39	0.21
20	7.2	0.6	31.1	2.6	0.23	0.03
45	12.0	0.3	23.3	1.4	0.51	0.03
70	14.4	1.9	18.1	2.0	0.80	0.14
95	14.8	0.2	18.0	1.6	0.82	0.07
120	18.2	0.5	19.7	0.8	0.93	0.05
170	22.5	1.5	15.4	0.5	1.46	0.11
220	19.3	0.3	13.9	0.8	1.39	0.09
495	13.9	1.2	11.4	1.0	1.22	0.15
845	16.5	0.7	16.8	0.5	0.98	0.05
1000	16.1	2.7	15.8	0.6	1.02	0.18
2000	26.6	0.6	23.6	1.2	1.13	0.06
3000	23.4	1.2	28.3	1.0	0.83	0.05
3000 (IC)	21.8	1.9	28.5	6.3	0.82	0.13
PARTICULATE - SAFe Station						
45	1.8	0.3	0.32	0.06	5.7	1.5
70	1.7	0.3	0.13	0.02	12.8	3.3
95	1.0	0.3	0.52	0.10	2.0	0.8
120	1.0	0.2	0.40	0.10	2.6	0.8
170	0.33	0.11	0.34	0.08	1.0	0.4
220	0.5	0.3	0.33	0.08	1.6	1.0
495	0.6	0.1	0.16	0.03	3.4	0.9
845	0.7	0.1	0.20	0.04	3.3	0.9
1000	0.5	0.2	0.24	0.06	1.9	1.1
1250	0.6	0.1	0.26	0.05	2.2	0.6
1500	0.7	0.1	0.25	0.04	2.8	0.7
2500	0.8	0.2	0.29	0.05	2.8	0.8
3500	1.1	0.2	0.32	0.05	3.5	0.9
4000	1.5	0.3	0.36	0.05	4.2	1.0
PARTICULATE - BATS Station						
30	2.2	0.7	0.16	0.06	14.2	6.8
55	1.9	0.7	0.74	0.29	2.5	1.3
80	1.4	0.49	0.48	0.28	2.9	2.0
100	0.43	0.30	0.67	0.24	0.64	0.51
100 (IC)	0.87	0.25	0.87	0.20	1.0	0.4
155	0.49	0.21	0.37	0.14	1.3	0.8
255	0.76	0.34	0.54	0.16	1.4	0.7
405	0.69	0.31	0.52	0.17	1.3	0.7
780	0.53	0.26	0.34	0.14	1.6	1.0
1000	0.00	0.42	0.63	0.17	0.0	0.7
1250	0.11	0.43	0.33	0.14	0.35	1.3
2000	0.61	0.25	0.51	0.19	1.2	0.7
2000 (IC)	1.00	0.31	0.65	0.16	1.5	0.6
3000	0.84	0.35	0.42	0.15	2.0	1.1
4000	0.55	0.25	0.21	0.14	2.6	2.1

Literature comparison

As shown in Fig. 6, the profile for dissolved ^{210}Pb obtained during GEOTRACES at SAFe (30°00'N; 140°00'W) agrees with that reported earlier at GEOSECS station 202 (33°9.5'N, 139°36.3'W) nearby (Nozaki et al. 1980). Also both the surface ^{210}Po and ^{210}Pb activities at SAFe agree within the uncertainties to those reported previously at station 202 (Nozaki et al. 1976). Specifically here, the surface ^{210}Po and ^{210}Pb activities are 11.8 ± 0.5 and 23.7 ± 1.2 dpm/100 L respectively, while for SAFe at 6 m they are 11.4 ± 4.5 and 23.5 ± 5.0 (dpm/100L), statistically identical.

There is relatively good agreement also for particulate ^{210}Pb activities at BATS, noting the relatively few and low particulate activities reported by this study and that reported in Kim and Church (2001), where the particulate ^{210}Pb is calculated by the difference between total and dissolved assays. The limited agreement for particulate ^{210}Po in surface waters at BATS may be related to its high seasonality in association with the spring bloom.

Comments and recommendations

Spike calibration

Calibration of the yield tracer spikes using the IAEA RGU-1 solid standard, though successful, used a silica solid material that must first be digested. While this may be a good matrix for replicating silicon containing marine particulate samples (litho- or bio-genic), its complete digestion requires the use of hydrofluoric acid, which needs special hazard training not common in all labs. In the future, other additional standards material might be used, such as the ^{210}Pb calibrated lead wire (NIST SRM 983; certified at 433 ± 43 dpm/g) that is more readily soluble in nitric and hydrochloric acids.

Dissolved seawater procedures

Based on the Atlantic intercomparison, it appears possible to obtain satisfactory agreement for ^{210}Po and ^{210}Pb in the dissolved phase. The cause of lower agreement in the Pacific water samples may reflect small, yet random differences between ocean basins of unidentified origin specific to individual laboratory procedures, in either extraction technique or dissolved spike equilibration during the assay of both nuclides. However, both ^{210}Po and ^{210}Pb activities values reported in surface and deep water samples at SAFe during this intercalibration exercise agree with the profile at surface (6 versus 20 m depth) and deep (both at 3000 m depth) obtained during the same cruise (Fig. 5). Comparing the ^{210}Pb activities reported during the GEOSECS intercalibration exercise in the NE Pacific, this agreement is also the case at both depths (Chung, et al., 1983).

Experiments are continuing to compare alternative preconcentration techniques both for efficiency and precision of radionuclide analyses as required by future GEOTRACES expeditions. One recommendation is to consider processing of dissolved samples as soon as possible after collection. If not, this can induce a larger uncertainty on the final calculation of ^{210}Po activity, especially for samples with a low initial $^{210}\text{Po}/^{210}\text{Pb}$ ratio (Rigaud et al. in review). Under GEOTRACES, this could be accomplished by allowing for processing the shorter-lived radionuclides onboard or at intermediate laboratories during transit. Also within the prolonged time interval between sampling and final data calculation, it is necessary for labs to carefully record the dates and times of all steps between sampling and final data calculations.

Particulate procedures

Due to the low volume of water samples filtered (5.8 to 20.5 L) during this intercalibration, the errors associated with the

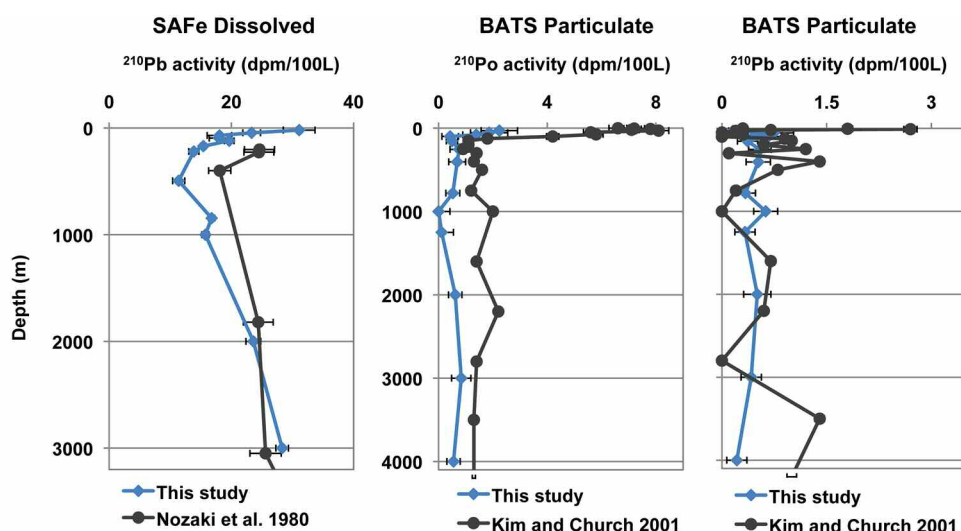


Fig. 6. Comparison between dissolved and particulate profiles obtained during this study with data published at or near the same location.

particulate ^{210}Po and ^{210}Pb were relatively high. In principle, based on a 30 L sample (typical large sampling bottle), it is possible to obtain accurate particulate activity concentrations for both ^{210}Pb and ^{210}Po to several percent precision with good chemical recovery. Once sources of blanks and other systematic errors have been distinguished, even smaller volumes could be used. However to ensure consistency of analysis or separate size fractions, it is recommended that minimum volumes for particulate assay should be at least fifty to hundreds of liters using submersible pumps, as recommended in the GEOTRACES Intercalibration manual. The particulate activities submitted here in do not reveal any consistent trend, so significant deviations from the average value may be due to relatively high background or blanks in some instruments or labs, respectively. Thus, it is recommended that labs routinely monitor blank levels very closely, particularly when dealing with low activities, as was the case in this study. In fact, it is possible to achieve essentially zero ^{210}Pb blanks in the stable Pb carrier by using lead refined centuries ago, or pure crystals of galena mineral. In any case, an overall procedural blank should still be conducted for both ^{210}Pb and ^{210}Po using all reagents, including an ancient stable Pb carrier.

Acknowledgments

We thank the scientists and crew of the R.V. *Knorr* for their assistance in obtaining our samples on both the North Atlantic and North Pacific US GEOTRACES cruises. We particularly acknowledge Dr. Greg Cutter (Old Dominion University) and the LDEO radionuclide sampling team in providing the seawater samples from the Atlantic and the Pacific, respectively. The WHOI pumping team provided particulate filters in both the Atlantic and Pacific for intercalibration exercises. The National Science Foundation provided support for both TC (OCE-0851462) and MB (OCE-0851032). PM was supported by the Generalitat de Catalunya through the prize ICREA. The authors also acknowledge the following for their laboratory assistance: Maria W. Ruocco, Ma Qiang, Ingrid Stimac, Lily Leon, and both Ms. H.M. Lee and Dr. S.H. Kim (funded by KORDI E98564). The thorough and insightful review of Michiel Rutgers van der Loeff, and one other anonymous reviewer are gratefully acknowledged.

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Submitted 14 November 2011

Revised 22 June 2012

Accepted 3 July 2012