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Effects of flow rates and composition of the filter, and decay/ingrowth correction factors involved with the determination of in situ particulate ^{210}Po and ^{210}Pb in seawater

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Abstract

Accurate measurements of particulate ^{210}Po (^{210}Po$_p$) and ^{210}Pb (^{210}Pb$_p$) are required in the investigation of (i) partitioning of Po and Pb between particulate and dissolved phases and (ii) export estimates of carbon and other key trace metals from the euphotic zone via sinking particulate matter. Based on the intercomparison of different composition of the filter material (QMA, Supor, Millipore, and Pall GN6) and flow rates (2 to 8 L min), we show how these factors affect the measured concentrations of ^{210}Po$_p$ and ^{210}Pb$_p$ and their activity ratios (AR). As such, we recommend using Supor 0.4 μm filter and a flow rate of up to 8 L/min for the measurements of ^{210}Po$_p$ and ^{210}Pb$_p$. Furthermore, we inter-compared ^{210}Po$_p$ and ^{210}Pb$_p$ obtained by small-volume McLane and large-volume MULVFS pumps. The activities of ^{210}Po$_p$ in MULVFS filter samples are somewhat higher than that of McLane filter samples, whereas the ^{210}Po/^{210}Pb AR collected by McLane pump is distinctly lower, suggesting some fractionation in the collection process by the pumping systems. Likewise comparison of vertical profiles of ^{210}Po$_p$ and ^{210}Pb$_p$ obtained using McLane pumps by two independent research groups at the two intercalibration stations in the Pacific Ocean show quite similar values except in the mesopelagic waters, suggesting possible uneven loading and presence of larger gelatinous plankton in the filter. Finally, we append a detailed analysis of various correction factors for the accurate calculation of in situ ^{210}Po and ^{210}Pb. Presented results are relevant to the worldwide community that uses ^{210}Po-^{210}Pb as tracers in aquatic systems.

Suspended particulate matter in the sea is composed of terrestrial material, derived from the upper continental crust, primarily delivered from discharges of rivers and streams and atmospheric deposition, biogenic material (e.g., opal, calcium carbonate, and organics) formed both in the marine and terrestrial environments, and authigenic minerals formed within the sea. The formation, transport, decomposition, dissolution, burial, and ultimate fate of the biogenic particulate matter is primarily controlled by physico-chemical and ecological parameters such as nutrients, light, temperature, upwelling, food chain dynamics, which in turn could be affected by the changing global climate. The biogeochemical dynamics of particulate matter controls scavenging, cycling, and transport of the so-called GEOTRACES particle-reactive Trace Elements and Isotopes (TEIs) in the marine environment. Understanding the behavior of particle-reactive TEIs in the sea requires accurate determination of their dissolved and particulate concentrations.

Separation of the particulate matter for the determination of radionuclides concentration (activity) from the seawater involves seawater sampling and filtration through a finite

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pore-size filter. The dissolved and particulate phases are defined operationally by the pore size of the filter used. The most widely used pore sizes range from 0.2 to 1.0 µm. A majority of the filters also have only nominal pore sizes rather than absolute cut-off. The pore size, filtration rate (which is a measure of the contact time of the water containing dissolved species with the filter and also a measure of the pressure exerted onto particles during filtration) and the chemical composition of the filter (due to possible sorption of radionuclide onto filter matrix) could affect the measured concentrations of particulate radionuclides and may differ from the in situ concentration. To assess the effects of pore size, flow-rates, and the composition of the filter material on the measured concentrations of particulate ^{210}Po (^{210}Po$_p$) and ^{210}Pb (^{210}Pb$_p$), we conducted a series of experiments with different pore sizes, flow rates, and filter composition to answer the following questions: (1) How do the concentrations of ^{210}Po$_p$ and ^{210}Pb$_p$ vary with different pore sizes (0.2, 0.4 and 0.8 µm Supor), flow rates (2.25 to 8.25 L/min through 1 µm QMA) and composition of the filter (QMA, Supor, Millipore HA, and Pall GN6)? (2) How do the ^{210}Po$_p$ and ^{210}Pb$_p$ concentrations compare in samples collected using small-volume pumps (4-8 L/min) with that in the large-volume pumps (MULVFS, 59 L/min)? (3) What is the distribution between the concentrations of ^{210}Po$_p$ and ^{210}Pb$_p$ measured in the top filter (F_1) to that in the back-up filter (F_2) and what are the possible sources of these artifacts; and (4) How do the concentrations of ^{210}Po$_p$ and ^{210}Pb$_p$ in vertical profiles from the Pacific inter-calibrated between two laboratories compare?

In a related paper (Church et al. 2012), we presented analytical results from the intercalibration of dissolved and particulate samples at several GEOTRACES intercalibration sites in the North Atlantic and Pacific. In this article, we append for general use the various factors and assumptions in calculating final ^{210}Po and ^{210}Pb data, such as correction factors due to in situ decay and growth of final ^{210}Po from the presence of ^{210}Pb before and between times of separation.

Materials and procedures

General considerations

The chemical procedure and radiochemical assay followed by most of the research groups for the measurement of ^{210}Po and ^{210}Pb in seawater (either particulate and/or dissolved) are mostly similar (Fleer and Bacon 1984; Friedrich and Rutgers van der Loeff 2002; Hong et al. 1999; IAEA 2009; Kim et al. 1999; Masque et al. 2002; Mathews et al. 2007; Radakovitch et al. 1998; Rutgers van der Loeff and Moore 1999; Sarin et al. 1992; Stewart et al. 2007). The determination of ^{210}Po and ^{210}Pb in seawater (either particulate or dissolved phase) is routinely conducted in the same sample, first by measuring ^{210}Po (called 'in situ' ^{210}Po) and then keeping the same sample for a period of about 6 months to 2 years for the ingrowth of ^{210}Po from the decay of in situ ^{210}Pb. The second ^{210}Po (called 'parent-supported') measurement provides the data on ^{210}Pb. The most widely used instrument for seawater (both dissolved and particulate) ^{210}Po and ^{210}Pb analysis is an α spectrometer with surface barrier detectors (see reviews in Mathews et al. 2007 and Baskaran et al. 2009a). Currently, the recommended assay of both dissolved and particulate sea water samples are outlined in the GEOTRACES procedures manual (GEOTRACES 2010)

Sampling of particulate matter

Details on the collection of small-volume (McLane) and large-volume (MULVFS) particulate matter as well as sub-sampling of the filters are given in Maiti et al. (2012) and Bishop et al. (2012). Water samples were filtered through McLane in situ pumps from two stations during IC-2 cruise: North Pacific at SAFe (Sampling and Analysis of Iron) (30°00′N; 140°00′W, 4000 m depth) and Santa Barbara Basin (SBB; 34°17′N; 120°03′W, 850 m depth) stations. All the filters (QMA-Quartz microfiber membrane, Supor-polyethersulfone membrane, Millipore HA-mixed cellulose ester membrane and Pall GN6-mixed nitrocellulose membrane) used in the present study are nominal pore sizes and were acid leached with 10% HCl, to remove any metals present in the filter, in a shore-based laboratory before use in the field. The McLane pumps were programmed to operate within a range of 4-8 L/min. The QMA filters used in MULVFS were also acid-leached prior to use in the field (Bishop et al. 2012).

For ^{210}Po$_p$ and ^{210}Pb$_p$, filtering through a conventional filtration set-up, such as passing the requisite volume (10s L) through 0.45 µm Supor membrane filters, is time consuming. Also longer contact time of the seawater with the filter material due to filter loading or clogging could result in the sorption of dissolved and colloidal ^{210}Po and/or ^{210}Pb onto the filter. Although capsule filters are more efficient with respect to filtration, quantitative retrieval of particulate matter from such filter cartridges is quite difficult. Results from the IC-1 cruise for ^{210}Po$_p$ and ^{210}Pb$_p$ indicate that 10-20 L water samples from open ocean filtered through 380 mm^2 area of the filter paper (22-mm diameter circular punch from a 142-mm diameter filter) have a relatively high error on the activities of ^{210}Po and ^{210}Pb (>20%; Church et al. 2012).

Digestion of the filter sample

In the open ocean, the suspended particulate matter is usually comprised of < 5% lithogenic material (Chester 1990) and hence most of the Pb and Po are present in association with biogenic particulate matter. In the case of ^{210}Po, there could be some possible transport within the cell material in the biota (Stewart and Fisher 2003a, 2003b). A number of procedures have been followed in the digestion of the filter material. Since the ^{210}Po- and ^{210}Pb-laden particulate matter is retained on the filter material, digestion with a combination of HF (to break the Si matrix), HNO_3 (to break the organic matrix), and HCl (to convert to chloride medium) should be sufficient. It is likely that almost all of the biogenic matter is decomposed by concentrated nitric acid digestion method. The Quartz Microfiber (QMAs, with a nominal pore size) as well as glass

fiber filter (GFFs, with a typical nominal pore size) were found to be totally dissolved with HF-HNO_3-HCl acid digestion while Supor filters resulted in some amount of residual material. Because most of the particulate matter is biogenic, we do not recommend use of dissolution with $HClO_4$, which requires a special fume-hood that may not be readily available with many research groups.

A flow chart showing the analysis of filters for $^{210}Po_p$ and $^{210}Pb_p$ is given in Fig. 1. The filter containing the particulate matter was transferred to a 100 mL Teflon beaker, and then a known amount of ^{209}Po (~1 dpm) SRM Standard (NIST-SRM-4326) and 1 mg stable Pb (AAS Standard) were added as yield monitor (Pb yield monitor for the entire chemical processing steps including ion-exchange separation of Pb and Po). One of the 8 intercalibration groups used ^{208}Po spike, although the α energy difference between ^{209}Po and ^{210}Po is higher (423.5 keV) than that of ^{208}Po and ^{210}Po (189.4 keV) allowing better resolution with ^{209}Po spike. Furthermore, it is widely recognized that ^{208}Po spike contains some amount of ^{209}Po impurity, and hence those groups that use double spike method (^{209}Po for in situ ^{210}Po and ^{208}Po for in situ ^{210}Pb via ^{210}Po determination) will have to take the presence of ^{209}Po in the ^{208}Po spike in to consideration, because the correction for ^{209}Po present in ^{208}Po spike becomes more serious with time as the decay rate of ^{208}Po [$t_{1/2}$ = 2.898 years] is more than 35 times faster than that of ^{209}Po [$t_{1/2}$ = 102.5 years]).

Two digestion methods were employed: (i) In the open digestion method, 5 mL each of trace-metal grade HF, conc. HNO_3 and conc. HCl was added to the Teflon beaker after adding a known amount of ^{209}Po (~1 dpm) and stable Pb (1 mg) and the solution was digested at ~90°C on a hot plate. After the solution completely dried, 5 mL each of HF-HNO_3-

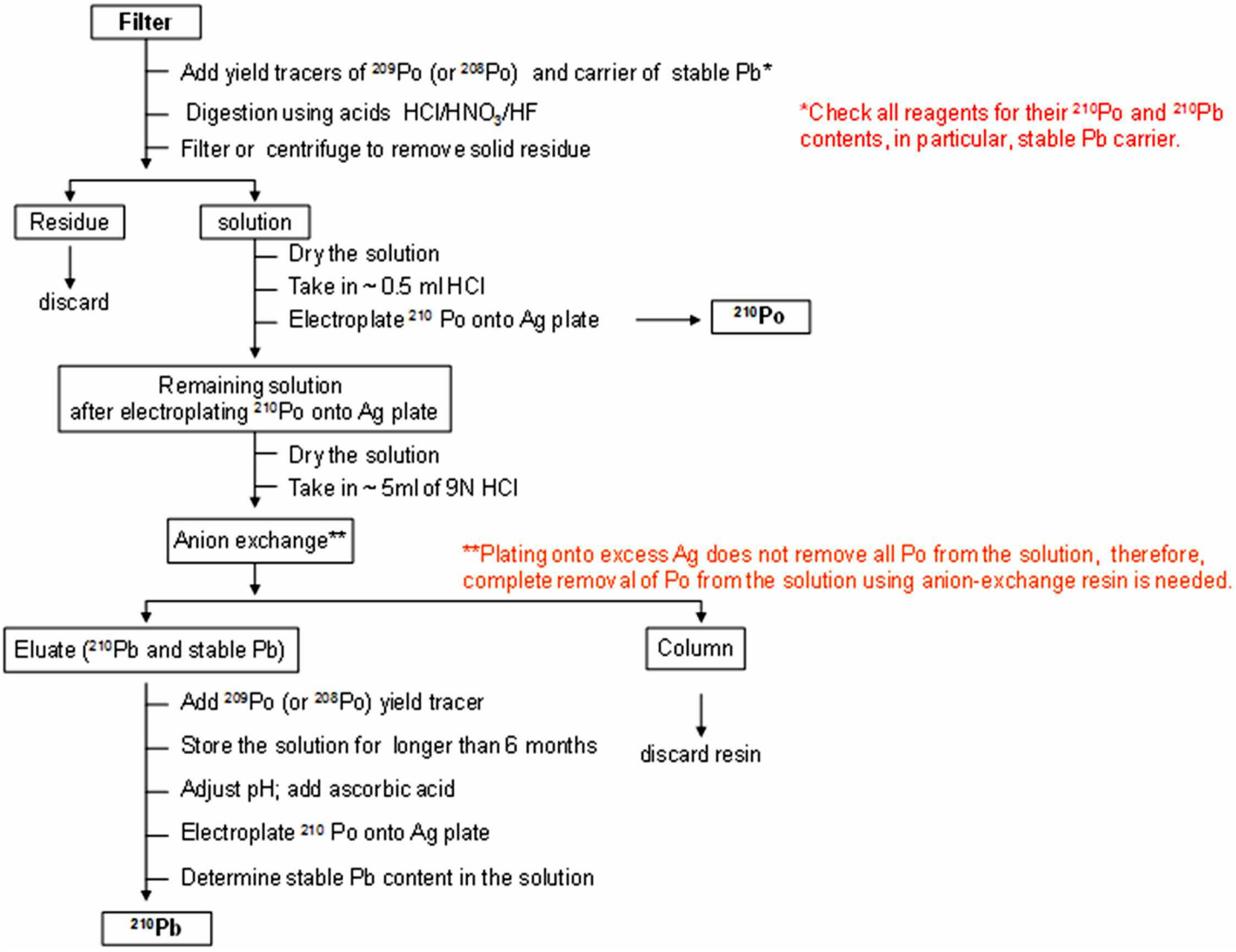


Fig. 1. Flow chart for the analysis of particulate ^{210}Po and ^{210}Pb.

HCl digestion was repeated twice and to the final residue, another 5 mL of conc. HCl was added and dried; the residue was finally taken in 5 mL 6M HCl; and (ii) in the closed digestion method, 10 mL each of conc. HF-HNO_3- HCl were added to the Teflon digestion vessel after adding a known amount of ^{209}Po (~1 dpm) and 1 mL of stable Pb (= 1 mg Pb). The solution was digested at 100°C for 6 h; the digested solution was dried followed by another drying with 5 mL conc. HCl. The final residue obtained from both open and closed digestion methods was taken in 5 mL 6M HCl. To this solution, 20 mL of distilled water was added and the solution was centrifuged to remove solid residue, if needed. This 25 mL of 1.2 M HCl solution was used for electroplating on to a Ag planchet for 4 h at 90°C. A detailed discussion on optimizing various factors to obtain maximum plating efficiency is given in Lee et al. (in press). The GEOTRACES procedures manual (GEOTRACES 2010) recommends plating each sample for at least 4-6 h at 80-90°C, although a wide range of temperatures (80°C-90°C) and time (1.5-24 h) have been reported (summarized in Mathews et al. 2007; Lee et al. in press).

Quantitative separation of ^{210}Po and ^{210}Pb after plating for the assay of in situ ^{210}Pb

To determine the in situ ^{210}Pb, the plated solution used for in situ ^{210}Po is stored for 6 to 24 months for the ingrowth of ^{210}Po and the ingrown ^{210}Po is again assayed by most laboratories. After the plating of in situ ^{210}Po, often some amount of Po (^{210}Po and the spike, ^{209}Po) is left behind in the solution. Many research groups use additional Ag plates to remove the residual Po, but this is reported to remove only a portion of the residual ^{210}Po (Cochran et al. 1983). Anion exchange resin column separation will only ensure complete separation of Po from Pb (Chung et al. 1983; GEOTRACES procedure manual [GEOTRACES 2010]). Some research groups assume that allowing the plated solution to sit for 1-2 y will result in the decay of ^{210}Po to negligible amounts (in 1-2 y, 84% to 94% of the residual ^{210}Po would have decayed), but there is very little decay of ^{209}Po (0.7% to 1.3%) that takes place during this period. Therefore, when ^{209}Po spike is also used for the determination of in situ ^{210}Pb via ^{210}Po, the presence of residual ^{209}Po will underestimate the results. The effect of residual Po on the determination of activity of in situ ^{210}Pb is graphically shown in Fig. 2 under different scenarios based on varying amounts of residual Po and time for the ingrowth of ^{210}Po from in situ ^{210}Pb, assuming that the activity ratio ^{210}Po/^{210}Pb = 1 in the sample; spike ^{209}Po activity = in situ ^{210}Po activity (Fig. 2). The percentage difference in the ^{210}Po/^{209}Po ratios with and without residual Po is plotted as a function of time (Fig. 2). It is evident that quantitative removal of Po from the plated solution, which is used for in situ ^{210}Pb determination, is required. The chemical procedure (Fig. 1) that we have adopted (recommended in the GEOTRACES procedure manual [GEOTRACES 2010]) involves ion-exchange column separation (DOWEX-1, anion exchange AG-1-X8 [100-200 mesh], 9M HCl column, e.g., Baskaran et al. 2009a) of Po and Pb in the presence of HCl to effect passage of the ^{210}Pb as the chlorocomplex and the quantitative retention of ^{210}Po and ^{209}Po on to resin beads.

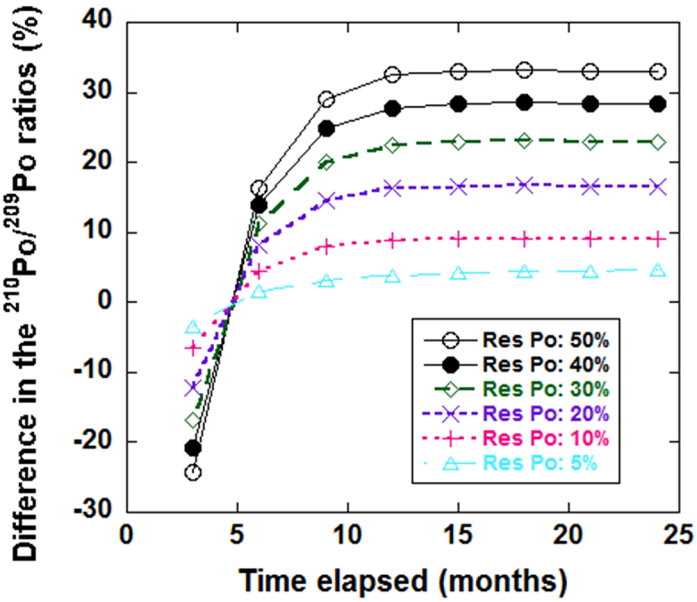


Fig. 2. The model curve showing the percent error introduced on the ^{210}Po/^{209}Po ratio in the second plating if 5 to 50% of the Po remains in the solution after the first plating. The error introduced depends on the ^{210}Po/^{210}Pb ratio and the amount of ^{209}Po added. The assumptions made here are: activities of $^{210}Po_{in\ situ}$ = $^{210}Pb_{in\ situ}$ = ^{209}Po added for first plating as well as second plating. The error was calculated as follows: Error (%) = 100 × [(^{210}Po/^{209}Po)$_{when\ no\ residual\ Po\ present}$ − (^{210}Po/^{209}Po)$_{residual\ Po\ present}$]/(^{210}Po/^{209}Po)$_{when\ no\ residual\ Po\ present}$].

Assessment

Blanks

The possible sources of blanks to the activities of ^{210}Po and ^{210}Pb in the samples include the chemical reagents, filter, the silver planchet used for the plating of ^{210}Po, and the stable Pb carrier used to monitor the chemical yield of ^{210}Pb. The dip blank QMA filters were kept in a 51 µm Nitex screen and placed alongside the McLane pumps while the filtration was going on, exposing the QMA filter to the seawater. The ^{210}Po and ^{210}Pb activities on three dip blank 1 µm QMA filters varied between 0.028 and 0.102 dpm for ^{210}Po and 0.105 and 0.155 dpm for ^{210}Pb (Table 1; the dip blank = sorbed radionuclide from the water + reagent blank). The mean dip blank activities of ^{210}Po and ^{210}Pb were subtracted from all the particulate activities of the corresponding samples from both McLane and MULVFS filer samples.

The stable Pb is another potential source of blank ^{210}Po and ^{210}Pb. It was demonstrated during GEOSECS inter-comparison study that the best Pb carrier was obtained from galena (PbS) which was reported to have essentially zero ^{210}Pb (Cochran et al. 1983). We further evaluated the ^{210}Pb levels in two Pb standards from two laboratories: Fisher AAS Standard and Baker

Table 1. Concentrations of ^{210}Po and ^{210}Pb in QMA (1 µm) dip blanks.

Depth (m)	^{210}Po activity* (dpm)	^{210}Pb activity* (dpm)
70	0.077 ± 0.007	0.148 ± 0.017
160	0.055 ± 0.004	0.105 ± 0.012
845	0.028 ± 0.003	0.155 ± 0.016
3000	0.102 ± 0.009	0.146 ± 0.015
Mean	0.066 ± 0.003	0.139 ± 0.008

The dip blank filters represent the dip blanks + reagent blanks.
*The average dip blank for the Supor filter (data from 2009 Atlantic intercalibration cruise) for ^{210}Po and ^{210}Pb was found to be 0.007 dpm and 0.088 dpm, respectively, and is considered to be upper limit for the blank filter.

AAS Standard in lab-I and one $Pb(NO_3)_2$ salt standard in lab-II. The Fisher Co. AAS-standard was found to contain 13.7 dpm ^{210}Pb per gram of Pb (or 0.0137 dpm in 1 mg stable Pb carrier) whereas in the Baker AAS-standard it was much lower, 0.62 dpm ^{210}Pb per gram of Pb (or 0.00062 dpm in 1 mg stable Pb carrier, Table 2). In lab-II, the standard had 54 dpm per gram of Pb carrier (or 0.054 dpm per mg stable Pb carrier; Table 2). Although the amount of ^{210}Po and ^{210}Pb in the Pb carrier is not a very serious issue (1 mg Pb addition will add 0.0137 dpm of ^{210}Po and ^{210}Pb to the blank level), addition of 10 mg of Pb with 54 dpm/g Pb will contribute substantial blank of ^{210}Po and ^{210}Pb in small-volume samples, and thus, it is important to evaluate the amount of ^{210}Pb present in the stable Pb carrier before the carrier is used, even if old Pb is used for this purpose. Details on the chemical yield calculation and its use in the determination of in situ ^{210}Pb concentrations are given in Appendix A.

Intra-filter inhomogeneity of the retained particulate matter

There are inhomogeneities in the distribution of particulate matter retained on the whole surface of the filter, if a whole filter is not used for analysis. A quadrant of 142-mm diameter QMA or Supor filter was found to have inter-filter variability (due to uneven particle loading resulting from particle nature, filter type, pumping system, etc.) of 2.0-2.5%, as opposed to 22 mm-diameter punches that have ~18% inter-punch variability for ^{234}Th (Maiti et al. 2012). The inter-pump variability for 22 mm Supor punches (one from each pump) was also found to be ~16% to 18% for ^{234}Th, ~12% for biogenic silica and 11% for particulate inorganic carbon (Maiti et al. 2012). Although we do not have inter-filter and inter-pump variability data for ^{210}Po and ^{210}Pb, it is likely such differences as with ^{234}Th do exist.

Comparison of the activities of ^{210}Po and ^{210}Pb in the first and second filters

Although a filter is used for the separation of particulate phase of a chemical species from the dissolved phase in seawater, the distinction between particulate and dissolved phases are operationally defined, with the nominal pore-size (usually 0.2-0.8 µm) as the cut-off for the separation of the phases. However, sorption of the dissolved constituents of seawater on to the filter as well as the accuracy of the nominal size with respect to the particle size has remained an area of concern in selecting appropriate filters for various chemical analyses.

Table 2. ^{210}Pb blank in stable Pb carrier.

Sample code	Number of samples	^{210}Pb activity (dpm/g Pb)
Lab-I-Fisher-AAS Std.	2	13.7
Lab-I-Baker-AAS Std.	2	0.62
Lab-II- $Pb(NO_3)_2$ salt	2	54

In filters stacked in sets of two, it is traditionally assumed that the top filter quantitatively collected 'particles' above the nominal cut-off of the filter while the bottom filter placed directly underneath was only exposed to the particles smaller than the pore-sized particles and dissolved and colloidal phases (< cut-off of the pore size of the filter). In the present study, the percentage of the $^{210}Po_p$ and $^{210}Pb_p$ in the second filter (F_2) over the total combined activities of the first and second filter (F_1 + F_2) varied between 3.1 and 32.2% (mean: 10.2%, n = 15) and 0 and 46.0% (mean: 11.8%, n = 15), respectively (Table 3, Fig. 3). The dip-blank subtracted particulate ^{210}Po and ^{210}Pb activities in the second filter with positive values was observed in 11 (out of 15) for ^{210}Po and 7 (out of 15) for ^{210}Pb. Similar results are reported for ^{234}Th also (Maiti et al. 2012).

Effects of filter chemical composition on the measured particulate ^{210}Po and ^{210}Pb activities

To evaluate how the chemical composition of the filter material affect the activities of $^{210}Po_p$ and $^{210}Pb_p$, we filtered seawater collected at 100 m depth at the SAFe station on 15 May 2009 (IC-2 cruise) through 4 different filter types (Supor, Millipore HA, Supor 0.4 µm, Pall GN6 and QMA) with different nominal pore sizes (0.2 to 1.0 µm). The Supor filters are made up of polyethersulfone (PES) membrane, whereas Millipore-HA consists of mixed cellulose esters, and the Pall GN6 is made up of nitrocellulose. Water volumes between 286 and 679 L were filtered through for a period of 205 min (Table 4). The highest concentrations of ^{210}Po and ^{210}Pb were found in Supor 0.2 µm and 0.45 µm Pall GN6, respectively. We do not have ^{210}Po and ^{210}Pb blank activity levels for 0.45 µm Millipore HA and Pall GN6 filters, but it is very unlikely that the blank levels for ^{210}Po and ^{210}Pb are very different for Pall GN6. Filters are at least 6 months old from the time of acquisition and were cleaned with 10% HCl before use in the field.

For $^{210}Po_p$, the activity decreases in the order: Supor 0.2 µm > Millipore HA 0.45 µm > Supor 0.4 µm > Pall GN6 0.45 µm > Supor 0.8 µm > QMA 1 µm (Table 4, Fig. 4A). The $^{210}Pb_p$ activity decreases in the order: Pall GN6 0.45 µm > Supor 0.8 µm > Millipore HA 0.45 µm > Supor 0.4 µm > Supor 0.2 µm (Table 4, Fig. 4A). It appears that the ^{210}Pb-laden (largely lithogenic) particles are more efficiently retained by larger pore size Supor

Table 3. Activities of particulate ^{210}Po and ^{210}Pb and their ^{210}Po/^{210}Pb activity ratios in F_1 and F_2 in 1 µm QMA filters (except at 100 m) from the SAFe and SBB Stations in the Pacific Ocean (IC-2).

Depth (m)	^{210}Po-F_1 dpm/100 L	^{210}Po-F_2 dpm/100 L	^{210}Pb-F_1 dpm/100 L	^{210}Pb-F_2 dpm/100 L	^{210}Po/^{210}Pb Ratio in F_1	^{210}Po/^{210}Pb Ratio in F_2
30 (SBB)	0.68 ± 0.02	0.025 ± 0.005	0.42 ± 0.06	0.13 ± 0.03	1.59 ± 0.23	0.18 ± 0.05
45 (SAFe)	3.77 ± 0.19	1.79 ± 0.15	0.54 ± 0.18	BD	6.97 ± 2.37	—
60 (SBB)	0.73 ± 0.03	0.089 ± 0.014	0.34 ± 0.05	0 ± 0.015	2.17 ± 0.33	—
70 (SAFe)	LCY	0.48 ± 0.04	LCY	0.54 ± 0.18	—	0.89 ± 0.31
95 (SAFe)	1.60 ± 0.10	0.26 ± 0.02	1.28 ± 0.39	0.43 ± 0.14	1.24 ± 0.38	0.59 ± 0.20
100 (Supor)	0.77 ± 0.03	0.18 ± 0.01	1.71 ± 0.25	0.38 ± 0.05	0.45 ± 0.07	0.47 ± 0.10
120 (SAFe)	0.72 ± 0.05	0 ± 0.004	1.56 ± 0.47	0.82 ± 0.38	0.46 ± 0.14	—
130 (SABa)	0.46 ± 0.03	0.077 ± 0.023	0.56 ± 0.10	0 ± 0.015	0.82 ± 0.16	—
160 (SABa)	0.93 ± 0.05	0.11 ± 0.02	0.84 ± 0.0.10	0 ± 0.014	1.12 ± 0.15	—
170 (SAFe)	0.32 ± 0.02	0 ± 0.003	0.54 ± 0.14	0.46 ± 0.17	0.59 ± 0.16	—
220 (SAFe)	0.30 ± 0.02	0.091 ± 0.017	0.95 ± 0.28	0.22 ± 0.09	0.31 ± 0.09	0.41 ± 0.18
230 (SABa)	1.02 ± 0.06	0.091 ± 0.014	0.79 ± 0.08	0 ± 0.011	1.28 ± 0.14	—
480 (SABa)	1.08 ± 0.06	0.20 ± 0.03	1.49 ± 0.16	0 ± 0.012	0.73 ± 0.09	—
495 (SAFe)	0.098 ± 0.010	0 ± 0.003	1.78 ± 0.56	0.28 ± 0.11	<0.1	—
530 (SABa)	0.079 ± 0.007	0.012 ± 0.008	2.25 ± 0.22	0 ± 0.014	<0.1	—
845 (SaFe)	0.17 ± 0.02	0 ± 0.003	1.30 ± 0.41	0.24 ± 0.11	0.13 ± 0.04	—

BD, below detection limit; LCY, low chemical yield.

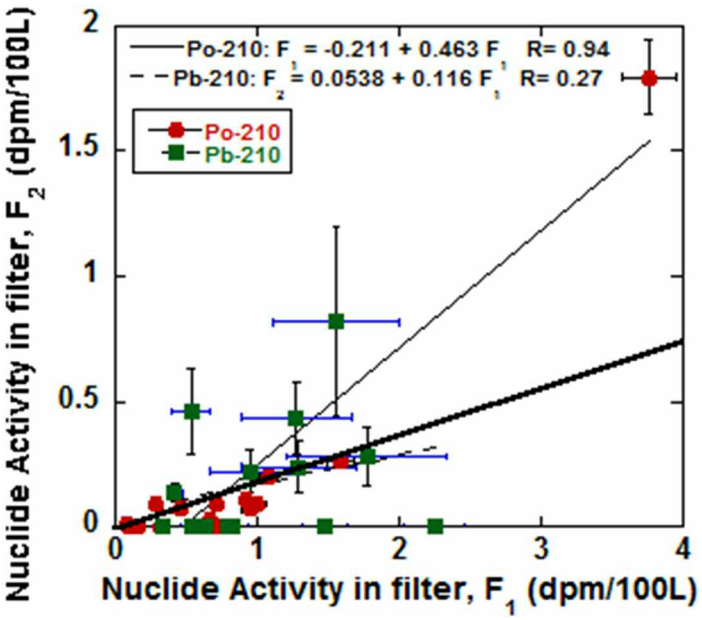


Fig. 3. Activities of ^{210}Po and ^{210}Pb in the back-up filter (QMA, 1 µm) versus activity in the top filter (samples for IC-2 cruise, data given in Table 3).

filters while ^{210}Po-laden (largely biogenic) are retained by smaller pore size filters. Higher activities of ^{210}Po in Supor could also be due to the nature of the matrix, with polyethersulfone membrane having stronger affinity for Po-containing biogenic material.

The blank levels for ^{210}Po and ^{210}Pb in QMA filters were found to be negligible, although the blank level for ^{210}Pb was slightly higher than that for ^{210}Po (Church et al. 2012). This can be compared with blank levels for ^{234}Th, which was reported to be generally higher in 1 µm QMA compared to 0.7 µm GFF (e.g., Rutgers van der Loeff et al. 2006), although recent study found negligible ^{234}Th blank in QMA filters (Maiti et al. 2012). Thus it appears that there are inhomogeneities in the nature of QMA blank levels depending on the batch and place where they are manufactured and the rigor of acid cleaning before their use in the field.

The ^{210}Po/^{210}Pb activity ratios in different filter material show a wide range, between 0.4 and 3.9, indicating the filter material affects the concentrations of $^{210}Po_p$ and $^{210}Pb_p$ differently (Table 4, Fig. 4B). Pall GN6 has the lowest value due to significantly higher $^{210}Pb_p$ activities.

Effects of different flow rates on the measured particulate ^{210}Po and ^{210}Pb activities

At 100 m at the SAFe station, 452 to 519 L water samples were filtered through QMA filters at flow rates between 2.25 L/min to 8.25 L/min, with an increment of 1 L/min on 12 May 2009 (Table 5). Highest concentrations of $^{210}Po_p$ were found at 3.25 and 4.25 L/min, with the lowest value found at 2.25 L/min. Between 5.25 and 8.25 L/min, the $^{210}Po_p$ activity remains relatively constant, 1.16 ± 0.08 dpm/100 L (Table 5, Fig. 5A). The variation in the $^{210}Pb_p$ activity with the flow rates is given in Fig. 5A. The ^{210}Po/^{210}Pb activity ratio (AR) varied between 0.85 and 1.46, again without any variance with the flow rates (Table 5, Fig. 5B) and is indistinguishable from each other within ± 2σ. In summary, one can pump at least up to 8.25 L/min without creating any artifacts on the $^{210}Po_p$ and $^{210}Pb_p$ activities, if large volume water samples are needed.

Table 4. Effects of particulate ^{210}Po and ^{210}Pb concentrations* in different filter matrices in SAFe Station at 100 m on 15 May 2009 (205 min filtration) in the North Pacific (IC-2).

Filter material	Total volume (L)	^{210}Po (dpm/100 L)	^{210}Pb (dpm/100 L)	^{210}Po/^{210}Pb AR
QMA^2 1.0 μm	678.6	0.80 ± 0.04	LCY	—
SUPOR 0.2 μm	285.6	2.66 ± 0.11	0.68 ± 0.09	3.91 ± 0.56
SUPOR 0.4 μm	245.7	2.23 ± 0.05	0.70 ± 0.09	3.18 ± 0.43
SUPOR 0.8 μm	555.2	1.10 ± 0.04	1.73 ± 0.14	0.64 ± 0.06
Millipore HA 0.45 μm	608.0	2.35 ± 0.08	1.62 ± 0.17	1.45 ± 0.16
Pall GN6 0.45 μm	316.2	1.94 ± 0.08	4.58 ± 0.35	0.42 ± 0.04
SUPOR 0.8 μm -F_1	494.4	0.77 ± 0.03	1.71 ± 0.25	0.45 ± 0.07
SUPOR 0.8 μm -F_2		0.18 ± 0.01	0.38 ± 0.05	0.47 ± 0.07

LCY, Low chemical yield and data are not reliable.
*Only for QMA the dip blank (dip blank + reagent blank) was subtracted, and no dip blanks were subtracted for other filters, as dip blanks were not collected. The reagent blanks were found to be negligible in most of the IC-1 filters analyzed.

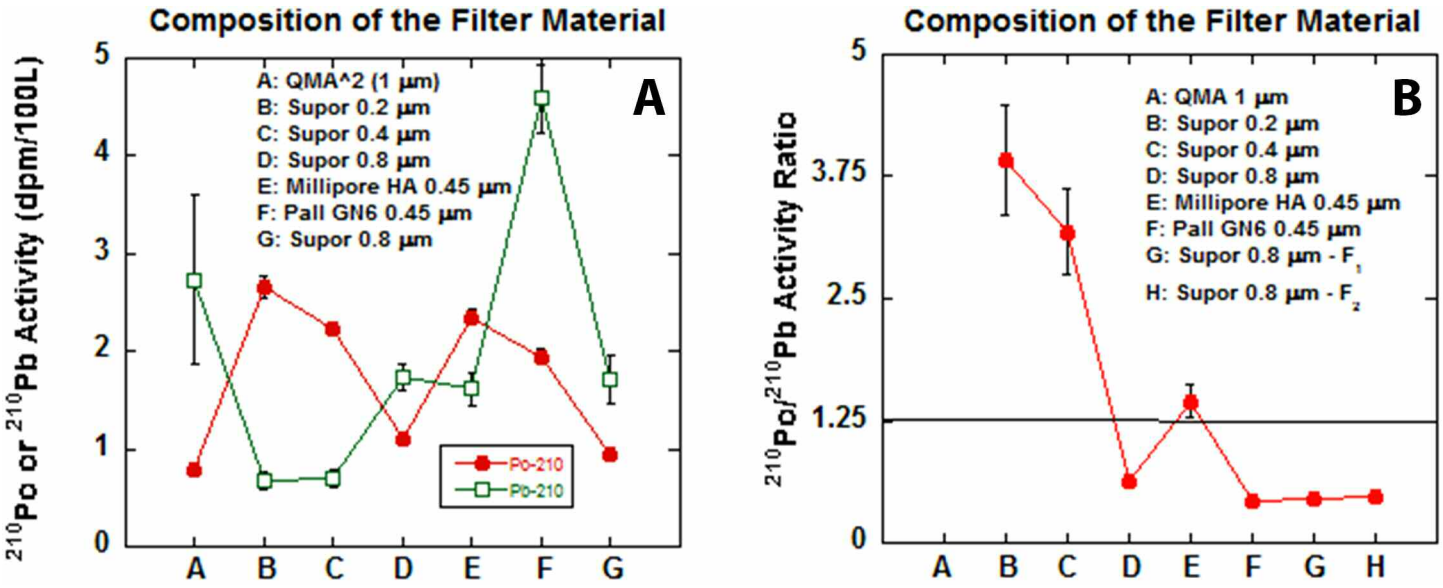


Fig. 4. Variations in: A) the activities of ^{210}Po and ^{210}Pb as a function of the composition of the filter material (samples from IC-2 cruise); and B) the activity ratios; Note that D (single filter) and G (with a back-up filter) are Supor 0.8 μm filters.

Intercomparison of particulate ^{210}Po and ^{210}Pb activity between small-volume (McLane) and large-volume (MULVFS) filtration

The filtration rate of the McLane pump varied between 6 and 8 L/min while the filtration rate with the MULVFS pump was 59 L/min at SAFe sampling station in the North Pacific during IC-2 cruise. The concentrations of $^{210}Po_p$ and $^{210}Pb_p$ and $^{210}Po_p/^{210}Pb_p$ AR obtained by both pumps (1.0 μm nominal pore-size QMA in both cases; prefilter: 51 μm) are given in Table 6 and Fig. 6A,B. The concentrations of $^{210}Po_p$ in the prefilter (> 51 μm) indicates a steep gradient below 120 m, from 0.11 to 0.15 dpm/100 L in the upper 120 m and below 0.05 dpm/100 L below 120 m. The $^{210}Po_p$ activities appear to be strongly coupled to the biological activity and are attributed to enrichment by the active biological community in the euphotic zone. The corresponding values for ^{210}Pb did not vary significantly, and the dip blank-subtracted values below 120 m are less than 0.02 dpm/100 L.

An inter-comparison of $^{210}Po_p$ in small-volume with large-volume pumps indicates that the activities in MULVFS filter samples are higher by a factor of 1.1 to 2.1 than that of McLane filter samples (Table 6). In the case of $^{210}Pb_p$, the McLane pump filter values are somewhat higher by a factor of 1.6 to 4.5 in 5 out of 7 samples. The range of ^{210}Po/^{210}Pb ratios are somewhat larger in MULVFS-QMA filter (3.4 to 13.0, mean = 7.0, n = 10) compared with the prefilter (4.5 to 8.9, mean = 6.5, n = 6), and this is attributed to higher concentrations of ^{210}Po in 1-51 μm range compared with > 51 μm. The ^{210}Po/^{210}Pb AR in particulate matter collected by McLane pump is distinctly lower (0.6 to 6.3 except one sample, Table 6, mean = 3.8, n = 7) than that of MULVFS (4.1-13.0, Table 6), possibly suggesting some fractionation of $^{210}Po_p$ and $^{210}Pb_p$ in the col-

Table 5. Concentrations* of particulate ^{210}Po and ^{210}Pb at different flow rates filtered through 1-μm QMA filter at 100 m in SAFe Station in the North Pacific (IC-2) on 12 May 2009.

Flow Rate (L/min.)	Total volume (L)	^{210}Po (dpm/100 L)	^{210}Pb (dpm/100 L)	^{210}Po/^{210}Pb AR
2.25	470.4	0.81 ± 0.04	LCY	—
3.25	487.6	1.39 ± 0.06	1.21 ± 0.26	1.14 ± 0.25
4.25	470.5	1.38 ± 0.06	1.02 ± 0.16	1.35 ± 0.21
5.25	456.8	1.16 ± 0.05	1.15 ± 0.22	1.00 ± 0.19
6.25	456.5	1.16 ± 0.05	0.80 ± 0.22	1.46 ± 0.41
7.25	472.0	1.08 ± 0.05	1.28 ± 0.32	0.85 ± 0.21
8.25	452.7	1.21 ± 0.05	0.97 ± 0.16	1.24 ± 0.21

LCY, Low chemical yield and data are not reliable.
*The dip blank (dip blank + reagent blank) subtracted values are reported.

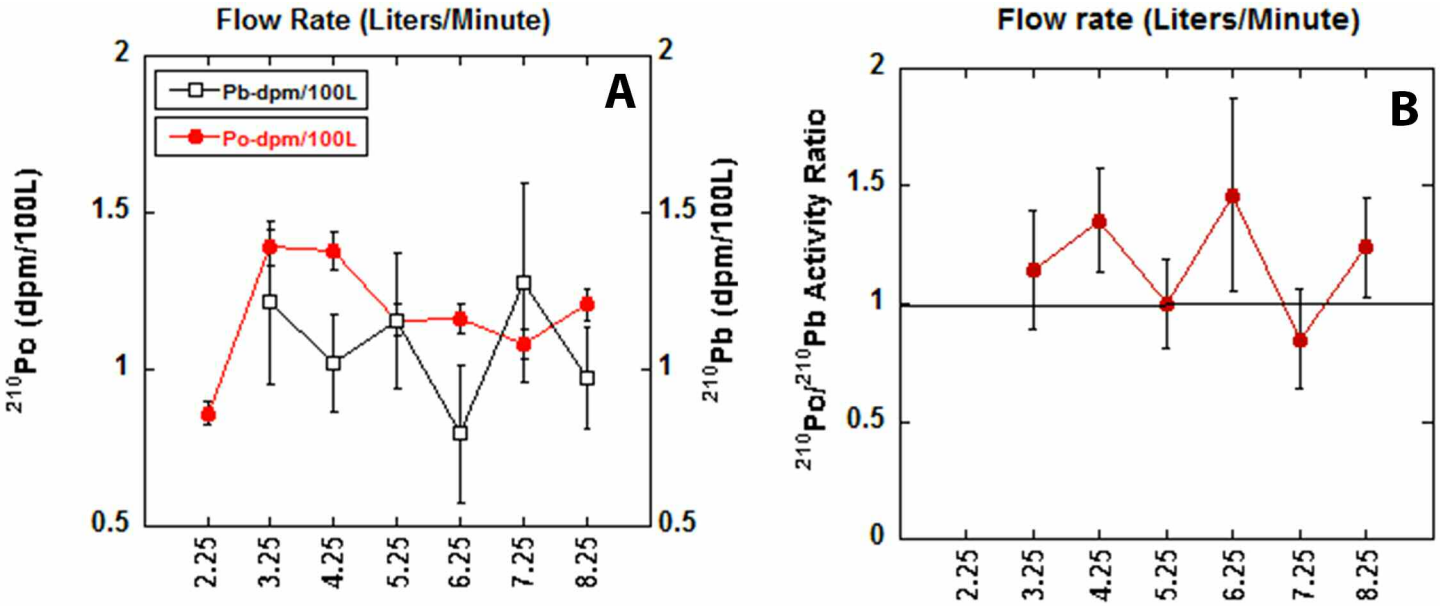


Fig. 5. A) Activities of particulate ^{210}Po and ^{210}Pb and B) ^{210}Po/^{210}Pb activity ratios as a function of flow rates in 1 μm QMA filter from IC-2 Cruise.

lection process by the pumping systems. The concentrations of ^{210}Po and ^{210}Pb and their activity ratios in particulate matter collected by both McLane and MULVFS appear to be oceanographically consistent.

Intercomparison of vertical profiles of particulate ^{210}Po and ^{210}Pb between two laboratories

We have intercompared the $^{210}Po_p$ and $^{210}Pb_p$ activities in two vertical profiles: SAFe deep water station and Santa Barbara Basin (SBB) station. One quarter of the filters was sent to each of two labs (A and B), and the filters were completely digested and analyzed for $^{210}Po_p$ and $^{210}Pb_p$. The vertical profiles obtained by these two labs are shown in for ^{210}Po, ^{210}Pb, and ^{210}Po/^{210}Pb AR in Figs. 7, 8, and 9A,B, respectively. The vertical profiles of in situ ^{210}Pb in SAFe station show quite similar values (within the propagated errors), except in the mesopelagic waters (Fig. 8). However, there appears to be a consistent difference between the two labs for ^{210}Po. This suggests possible calibration issues in one of the ^{209}Po spikes. The ratio of the ^{210}Po-A/^{210}Po-B appears likewise to be quite consistent in both the profiles, with the largest deviation at some mid-depths, primarily due to differences in the activities and associated errors of ^{210}Po. Both labs have used RGU-1 primary standard to consistently validate the ^{209}Po spikes as intercalibrated in the SRM exercise (Church et al. 2012). Thus, we strongly recommend that collaborative labs periodically intercalibrate their primary spikes and aliquots gravimetrically. The intercomparison of the ^{210}Po/^{210}Pb activity ratios for both SAFe and SBB station are generally good, except in the meso-pelagic depth at SAFe and surface water of SBB station, and it could be due to uneven loading of particulate matter (such as presence of larger gelatinous plankton) in the filter.

Discussion

Volume of water samples:

In the measurements of particulate and dissolved ^{210}Po and ^{210}Pb, large volume samples are needed and in situ pumps with

Table 6. Intercomparison of particulate ^{210}Po and ^{210}Pb between large-volume MULVFS* (>51 μm (PF) and 1 μm QMA) and small-volume McLane† in situ pumps (1 μm QMA) at SAFe Station in the North Pacific (IC-2).

Depth (m)	^{210}Po-PF-MULVFS dpm/100 L	^{210}Po-QMA-MULVFS dpm/100 L	^{210}Po- QMA-McLane dpm/100 L	^{210}Pb-PF-MULVFS dpm/100 L	^{210}Pb-QMA-MULVFS dpm/100 L	^{210}Pb-QMA McLane dpm/100 L	^{210}Po/^{210}Pb AR – PF in MULVFS	^{210}Po/^{210}Pb AR – QMA in MULVFS	^{210}Po/^{210}Pb AR – QMA in McLane
20	0.152 ± 0.012	3.98 ± 0.10	ND	0.0 ± 0.005	0.306 ± 0.036	ND	—	13.0 ± 1.6	—
45	0.129 ± 0.014	3.54 ± 0.14	2.77 ± 0.12	0.0 ± 0.006	0.280 ± 0.028	0.44 ± 0.03	—	12.6 ± 1.4	6.3 ± 0.5
70	0.106 ± 0.008	2.28 ± 0.11	1.62 ± 0.19	0.0 ± 0.005	0.293 ± 0.024	0.11 ± 0.01	—	7.8 ± 0.7	14.7 ± 2.2
95	0.119 ± 0.010	1.44 ± 0.07	1.29 ± 0.07	0.017 ± 0.006	0.242 ± 0.015	0.93 ± 0.10	7.0 ± 2.5	6.0 ± 0.5	1.4 ± 0.2
120	0.136 ± 0.009	1.24 ± 0.07	0.84 ± 0.06	0.020 ± 0.004	0.249 ± 0.011	1.01 ± 0.12	6.8 ± 1.4	5.0 ± 0.4	0.83 ± 0.12
170	0.048 ± 0.005	0.50 ± 0.03	0.29 ± 0.02	0.010 ± 0.003	0.149 ± 0.006	0.46 ± 0.04	4.8 ± 1.5	3.4 ± 0.2	0.63 ± 0.07
220	0.031 ± 0.004	0.81 ± 0.04	0.38 ± 0.04	0.007 ± 0.002	0.148 ± 0.003	0.67 ± 0.07	4.5 ± 1.4	5.5 ± 0.3	0.56 ± 0.08
345	0.043 ± 0.003	0.84 ± 0.04	ND	0.006 ± 0.002	0.125 ± 0.002	ND	7.2 ± 2.4	6.7 ± 0.3	—
495	0.028 ± 0.003	0.64 ± 0.03	0.30 ± 0.03	0.0 ± 0.002	0.156 ± 0.002	0.14 ± 0.01	—	4.1 ± 0.2	2.1 ± 0.3
695	0.027 ± 0.003	0.73 ± 0.04	ND	0.003 ± 0.002	0.119 ± 0.002	ND	8.9 ± 6.0	6.1 ± 0.4	—

ND, No data.
*MULVFS cast M8, Event 2041 (details given in Bishop et al. 2012)
†The average values of ^{210}Po and ^{210}Pb data obtained by Lab-A and Lab-B are given.

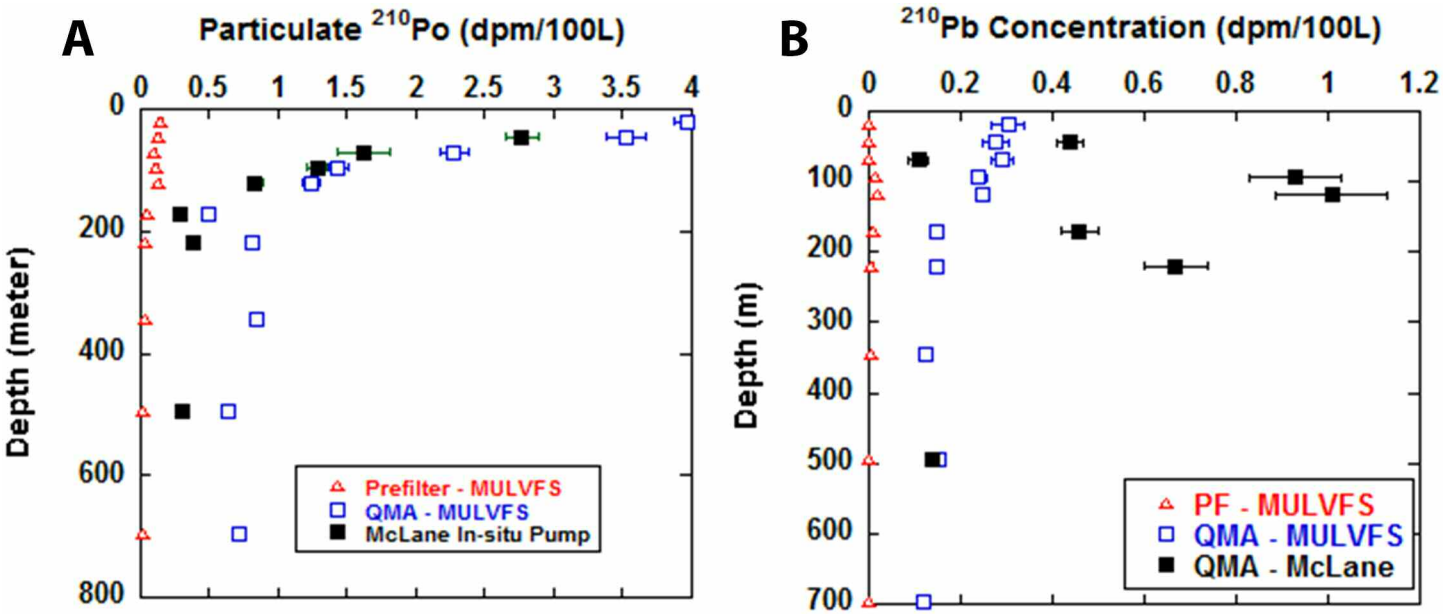


Fig. 6. Inter-comparison of: A) particulate ^{210}Po and B) particulate ^{210}Pb between large-volume MULVFS and McLane in situ pumps (both pumps used: 1 μm QMA filter); PF: pre-filter >51 μm at SAFe site.

Supor filters appear to be superior for collecting particulate matter from larger volumes of water. If in situ pumps are not readily available, it is recommended to use 50 L volume composited from multiple Niskin bottles and filtration to be done through 0.4 μm, 142 mm diameter Supor filters. As a general rule, the required volume for particulate ^{210}Po and ^{210}Pb measurements should be at least 5 times the volume used for dissolved ^{210}Po and ^{210}Pb and due to finite blank corrections (reagents and spikes), we recommend water volume of at least 10 L for the dissolved ^{210}Po and ^{210}Pb measurements (Church et al. 2012).

Why high activities of ^{210}Pb and ^{210}Po in the second filter

The activities in the second filter (back-up filter) are quite significant and could be from any or a combination of the following sources: (i) fine particulate matter including colloidal material containing these nuclides sorbed on to the second filter; (ii) break-through of the filter material from the first filter; and (iii) particulate matter passing through the filter paper as the cut-off is only nominal, not absolute, and a certain fraction of the particulate matter above the pore size of the filter is expected to pass through the pores of the filter. If the second filter retains some of the dissolved Pb and Po, then we

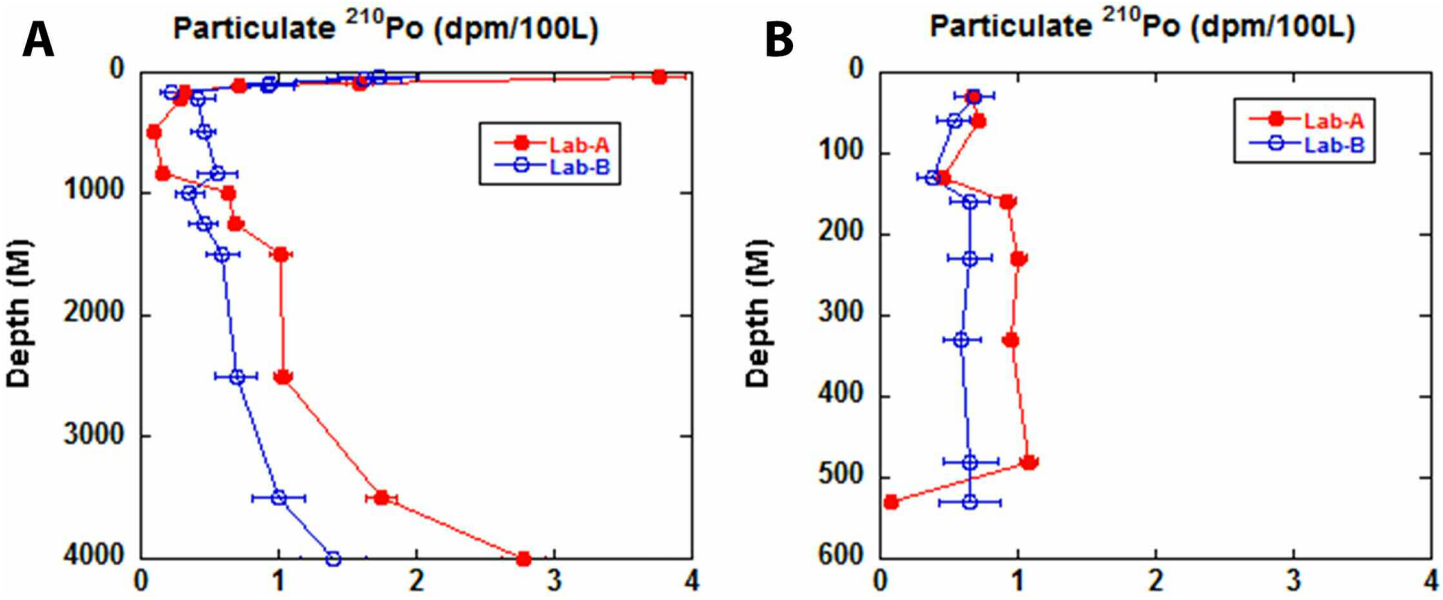


Fig. 7. Inter-comparison of particulate ^{210}Po (QMA filter, 1 μm) between Lab-A and Lab-B in two vertical profiles at the IC-2 North Pacific A) SAFe site and B) the SBB site.

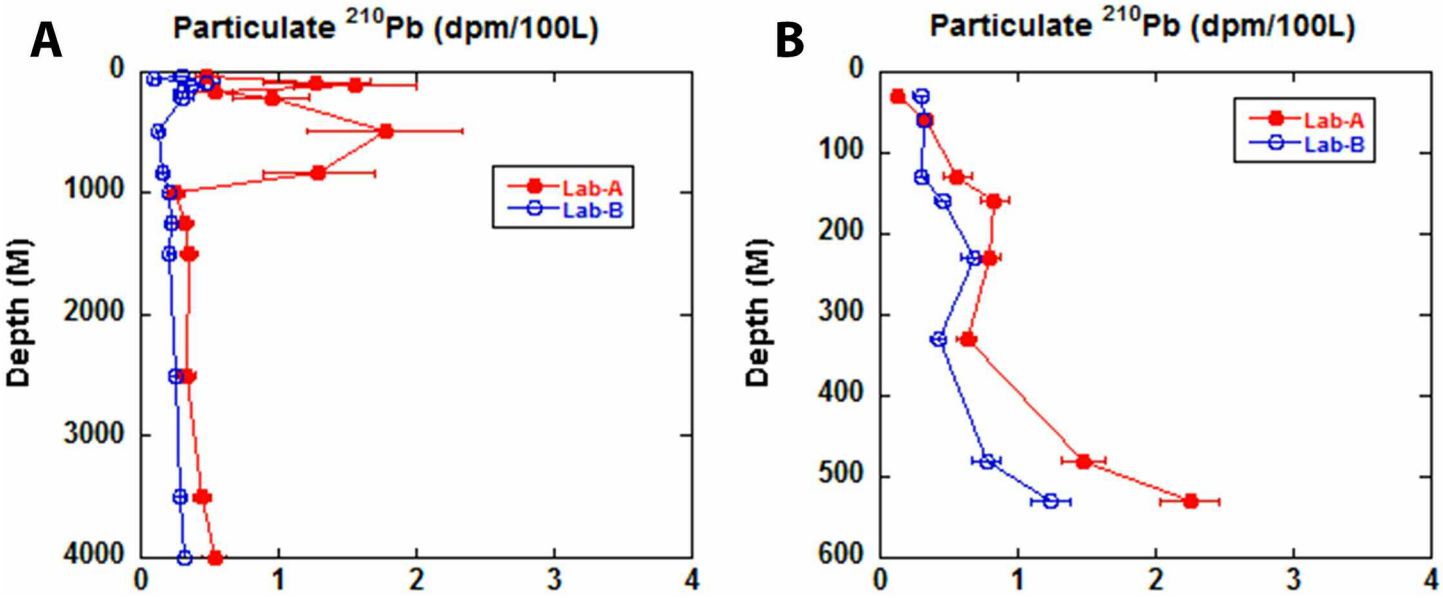


Fig. 8. Inter-comparison of particulate ^{210}Pb (QMA filter, 1 μm) between Lab-A and Lab-B in two vertical profiles at the IC-2 North Pacific A) SAFe site and B) the SBB site.

expect the removal of some of the dissolved Po and Pb on to the first filter also. It has been shown that colloidal C and ^{234}Th in 0.45 μm-10-kD accounts for ~10% of the dissolved (< 0.45 μm) fraction whereas 0.45 μm-1-kD accounts for about 20% to 60% (e.g., Santschi et al. 1995). Some of the colloidal material that passes through the first filter could also be retained in the second filter. The blank filters did not have significant amount of dissolved ^{210}Po or ^{210}Pb (Table 1 and Table 4 in Church et al. 2012) suggesting that the passive sorption of ^{210}Po and ^{210}Pb are likely negligible, as evidenced by the activities in the dip blanks (Table 1). Therefore, the bottom filter appeared to collect particulate ^{210}Po and ^{210}Pb that passed through the first filter. When water samples were pumped through a filter, the amount of dissolved and colloidal ^{210}Po and ^{210}Pb retained on the filter could be different than those retained from the passive sorption. Similar observation that GFFs and QMAs also retain dissolved Th and DOC (but not Ag or Nuclepore filters that have absolute cut-off pore-sizes) have been reported earlier and this was attributed to the filter composition, matrix and the volume of water filtered through

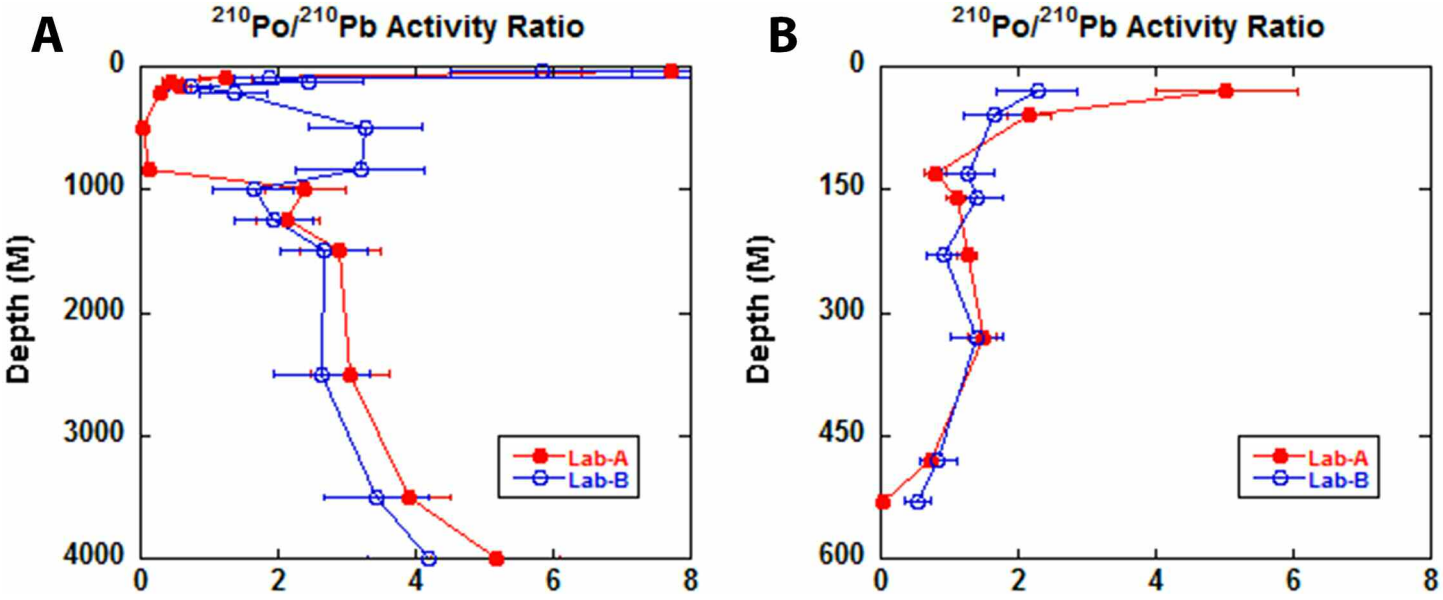


Fig. 9. Inter-comparison of particulate ^{210}Po/^{210}Pb activity ratios between Lab-A and Lab-B in two vertical profiles: A) at the IC-2 North Pacific SAFe site and B) the SBB site (QMA filter, 1 μm).

(Buesseler et al. 1998; Moran et al. 1999; Benitez-Nelson et al. 2001; Rutgers van der Loeff et al. 2006). Because the pore sizes of all the filters used in this study are nominal, it is very likely that a fraction of the particulate matter could also be caught in the second filter. Note that the activities in the back-up filter of the GFF filter in aerosol studies are comparable (~25% of the ^{210}Pb in the first filter was found in the back-up filter, summarized in Baskaran 2011; Turekian and Cochran 1981; Turekian et al. 1989) to the present study, and thus, it appears that the nature of the pore size (nominal versus absolute cut-off) could be the major reason for finding relatively significant activity in the back-up filter. Other possibilities include retention of colloidal fraction on the bottom filter, particles smaller than the nominal pore size of the filter passing through the top filter, and breakdown of the particulate matter from the first filter going to the second filter. There is a strong correlation between the activities retained on the filters F_1 and F_2 for ^{210}Po (r = 0.94, n = 15, Fig. 3), but poor correlation (r = 0.27) for ^{210}Pb. This can be due to constant fractional amount of removal in F_1 and F_2 of ^{210}Po-laden biogenic particulate matter. In this case, the total ^{210}Po activity can be calculated using the following equation (Eq. 1):

$$\text{Total activity} = \text{Activity in Filter} - 1\ /(1 - F_2/F_1) \qquad (1)$$

where F_1 and F_2 are the ^{210}Po activity in the first filter (top) and second filter (bottom), respectively (Baskaran et al. 2009b).

It appears that the extent of retention of ^{210}Po-laden biogenic and ^{210}Pb-laden lithogenic matter on to F_1 and F_2 filters appears to be different. The ^{210}Po/^{210}Pb activity ratios (AR) in the upper 120 m depth are higher in the top filter (F_1) whereas it is generally lower in waters > 120 m depth, and this is likely due to retention of higher amounts fine-sized biogenic particulate matter. The concentrations of biogenic particulate matter generally decrease below euphotic zone, and this may reflect in the ^{210}Po/^{210}Pb AR in waters > 120 m depth (Table 3).

Comments and recommendations:

The TEI community in GEOTRACES has recommended the use of polysulfone Supor filter based on factors such as low blanks, faster filtration rate, ease of handling, and high level of recovery (e.g., Cullen and Sherrell 1999). However, groups that investigate POC export flux studies using a small-volume ^{234}Th β counting method, have recommended QMA filters due to lower β blank and measurements of C, N on the same filter (Rutgers van der Loeff et al. 2006). As a compromise on the flow rate and low blanks and faster filtration rates, we recommend that future inter-comparison of particulate (and dissolved) samples between laboratories should always be on the same type of filter. We recommend using Supor 0.4 μm filter for the measurements of particulate ^{210}Po and ^{210}Pb.

There are differences in the concentrations of ^{210}Po$_p$ and ^{210}Pb$_p$ obtained by the small-volume McLane and large-volume MULVFS pumps. More work needs to be conducted in characterizing the particulate matter (Al, organic C, biogenic Si, etc.) collected by these pumps and assessing which is the most suitable pump for the collection of particulate matter for ^{210}Po, ^{210}Pb, and other radionuclides.

Based on the analysis of a suite of particulate filter samples collected during May 2009 in the Intercalibration-2 cruise in the Pacific Ocean to evaluate how factors such as the composition, pore size, flow rates affect the measured particulate ^{210}Po and ^{210}Pb, we draw the following conclusions: (i) The chemical composition of the filter material plays a major role

on the measured concentrations of particulate ^{210}Po and ^{210}Pb activities. Pall GN6 filter (0.45 µm) has the highest ^{210}Pb activity, about 2.6 times higher than that of the Supor 0.8 µm filter, and this is likely due to preferential retention of ^{210}Pb-laden particulate matter. Smaller pore-size Supor filters generally have higher ^{210}Po activities, and it is likely due to preferential retention of biogenic material on the Supor filter. To have an optimum filtration rate, lower blank levels for ^{210}Po and ^{210}Pb and higher particulate ^{210}Po and ^{210}Pb, we recommend Supor 0.4 µm filter for the measurements of particulate ^{210}Po and ^{210}Pb measurements; (ii) There is no measurable difference in the activities of ^{210}Po and ^{210}Pb between different flow rates, from 3.25 L/min to 8.25 L/min, and thus we recommend using higher flow rates (8.25 L/min) for the collection of particulate matter; (iii) The intercomparison of particulate ^{210}Po obtained from small-volume McLane pumps and large-volume MULVFS appears reasonably good; however, for ^{210}Pb, the activities obtained by MULVFS filter is higher by a factor 1.6 to 4.5 in 5 of the 7 samples than that of the McLane filter samples. There appears to be some fractionation of particulate matter based on ^{210}Po/^{210}Pb activity ratios; (iv) In many back-up QMA filters, we found an average value of 10% to 12% of the total (top + bottom filter) ^{210}Po and ^{210}Pb in the bottom filter, and this is attributed to the 'nominal' pore-size of the filter; in those filters that have absolute cut-off (such as Nuclepore), the activities are expected to be negligible, as was reported for ^{234}Th (Rutgers van der Loeff et al. 2006); and (v) A detailed analysis of the ingrowth/decay corrections for determining the concentrations of in situ ^{210}Po and ^{210}Pb is appended. Here the application of a growth and decay correction for determining the in situ activity of ^{210}Po is included. The importance of a quantitative separation of ^{210}Po and ^{210}Pb after the first plating is emphasized. The correction for the contribution from the decay of in situ ^{210}Bi intermediate to in situ ^{210}Po is not included, but an estimate based on dedicated analyses of this nuclide should be included in future research work. This is especially important for any excess amounts of ^{210}Bi (^{210}Bi/^{210}Pb > 1), such as particles that could contribute significantly to preformed amount of ^{210}Po.

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Effects of flow rates and composition of the filter, and decay/ingrowth correction factors involved with the determination of in situ particulate ^{210}Po and ^{210}Pb in seawater

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Appendix A

Correction factors in the calculations of the final activities of ^{210}Po and ^{210}Pb

Because the production of ^{210}Po from ^{210}Pb involves an intermediate daughter, ^{210}Bi, the correction factors (decay and ingrowth) are more complicated than other parent-daughter pair radionuclide (e.g., ^{234}Th-^{238}U pair). In this section, we outline the correction factors that need to be applied for obtaining correct in situ ^{210}Po and ^{210}Pb values.

In situ ^{210}Po

In low-level counting of ^{210}Po measurements with α spectrometry, the backgrounds of each detector need to be monitored and included explicitly in the calculation. Ideally, the count rate of the samples should be at least 5 times higher than that of the background of the detectors. The background is obtained by counting an unused cleaned Ag planchet, and subtracting the counting rate from the Po isotope regions of interest. It is also recommended checking the detector chamber backgrounds without the Ag planchet to inspect for any spurious Po contamination, to ensure that two backgrounds are the same within the counting uncertainty. The following corrections need to be applied in the determination of in situ ^{210}Po:

A) Background subtraction of the α spectrum for each detector and chamber geometry for each ^{208}Po, ^{209}Po ($^{209}N_n$), and ^{210}Po ($^{210}N_n$) regions being used;

B) Decay of ^{210}Po from the time of plating to mid-counting time (t_1) of the sample;

C) Decay of ^{209}Po (or ^{208}Po) spike from the time of last calibration (or from the time of certification for SRMs) to first plating (t_2);

D) Ingrowth correction from the decay of assayed *in situ* ^{210}Pb to ^{210}Po via ^{210}Bi;

E) Subtraction from the measured ^{210}Po activity for the decay of *in situ* ^{210}Bi to ^{210}Po; and

F) Decay of ^{210}Po from the time of collection to first plating (T) on Ag planchets.

If $^{210}N_n$ and $^{209}N_n$ are the background-subtracted net counts of ^{210}Po and ^{209}Po, respectively, t_1 and t_2 are the time elapsed between the first plating and mid-counting and time elapsed between spike polonium (either ^{209}Po or ^{208}Po) assayed and mid-counting, respectively; A_{spike} is the amount of Po spike added (dpm); λ_{Po210} and λ_{Pos} are decay constants of ^{210}Po and the spike (either ^{209}Po or ^{208}Po), respectively.

The ^{210}Po activity at the time of plating ($^{210}A'_{Po\text{-}210}$) is given by (correction factors for terms B and C above):

$$^{210}A'_{Po\text{-}210}\ (\text{dpm}) = (^{210}N_n/^{209}N_n)\ exp(\lambda_{Po210}t_1)\ exp(-\lambda_{Pos}t_2)\ A_{spike} \qquad (1)$$

Two sources of ^{210}Po contribute to the $^{210}A'_{Po\text{-}210}$ activity: (i) in situ ^{210}Po present in the sample that had decayed from sample collection till plating; and (ii) ingrowth from ^{210}Pb, from the time of sampling to the time of first plating. Whereas in situ ^{210}Po activity decreases with time from the time of collection, the amount of ^{210}Po derived from the ingrowth of ^{210}Po via ^{210}Bi from the decay of in situ ^{210}Pb increases with time. The ingrowth of ^{210}Po (correction term D above) from the in situ ^{210}Pb activity ($^{210}A_{ingrowth}$) can be calculated using the Bateman's equation as

$$^{210}A_{ingrowth} = {}^{210}A_{Pb\text{-}in\text{-}situ}\ [\lambda_{Bi}\lambda_{Po}\,e^{-\lambda PbT}/(\lambda_{Bi}-\lambda_{Pb})(\lambda_{Po}-\lambda_{Pb}) + \lambda_{Bi}\lambda_{Po}\,e^{-\lambda BiT}/(\lambda_{Pb}-\lambda_{Bi})(\lambda_{Po}-\lambda_{Bi}) + \lambda_{Bi}\lambda_{Po}\,e^{-\lambda PoT}/(\lambda_{Pb}-\lambda_{Po})(\lambda_{Bi}-\lambda_{Po})] \qquad (2)$$

where λ_{Pb}, λ_{Bi}, and λ_{Po} are decay constants of ^{210}Pb, ^{210}Bi, and ^{210}Po, respectively; T is the time elapsed between collection and first plating; the term $^{210}A_{Pb\text{-}in\text{-}situ}$ (= $N_1^\circ\,\lambda_{Pb}$) denote in situ ^{210}Pb activity.

The amount of ingrowth correction for ^{210}Po depends on the concentration of in situ ^{210}Pb and the time elapsed between collection and in situ ^{210}Po plating. For the data given in this article (Tables 3-6), the amount of ^{210}Po without correction for in situ ^{210}Pb is found to be 7 to > 100% more than the activity with the correction. Thus, it is not possible to obtain reliable in situ ^{210}Po activity in marine samples without measuring in situ ^{210}Pb, unless the complete ^{210}Po analysis is done optimally within 1-2 weeks. Even in 4 days, 2% of ^{210}Po activity would have grown (= 4 days/mean-life of ^{210}Po, 199.7

days; 7% in 2 weeks), if all three ^{210}Pb, ^{210}Bi, and ^{210}Po nuclides were in secular equilibrium in the sample. Thus, this correction must be applied in all studies.

Most of the researchers do not apply the correction (step-E above) for the contribution from the decay of in situ ^{210}Bi to ^{210}Po, as this requires independent and precise determination of ^{210}Bi. However, one can evaluate this contribution to the measured in situ ^{210}Po activity as follows: If A_{Bi} is the in situ ^{210}Bi activity (dpm/100 L), then, the maximum contribution from this activity is given by: $A_{Bi} * \lambda_{Po}/\lambda_{Bi} = 0.036\ A_{Bi}$ (or 3.6% of the in situ ^{210}Bi activity). If ^{210}Po and ^{210}Bi were in equilibrium in seawater (particulate and dissolved), then the error in the ^{210}Po activity introduced by not making this correction is ≤ 3.6%. However, if the in situ ^{210}Bi activity is in excess (in situ ^{210}Bi/^{210}Pb AR > 1.0), as suggested from a recent study of its particle reactivity in the marine biota (Fowler et al. 2010), then the contribution to measured in situ ^{210}Po could be much greater than this estimate. It is important to note that the biological uptake and physical adsorption characteristics among ^{210}Pb, ^{210}Bi, and ^{210}Po in seawater are not the same. Thus equilibrium between these pairs is not expected to exist in the sea (Tokieda et al. 1994; Biggin et al. 2002). Further work is required to resolve the overestimation associated with the contribution from in situ ^{210}Bi to the measured in situ ^{210}Po.

The final correction (term F above) is for the decay of in situ ^{210}Po from the time of collection to first plating.

Thus the equation to calculate the in situ ^{210}Po activity is given by:

$$A^{Po\text{-}210}{}_{in\ situ}\ (dpm) = [{}^{210}A'_{Po\text{-}210}\ (dpm) - {}^{210}A_{ingrowth}]\ e^{-\lambda PoT} \qquad (3)$$

Calculation of in situ ^{210}Pb activity

The in situ ^{210}Pb activity calculation involves the following corrections

G) Background subtraction of the α spectrum for each detector and chamber geometry for each ^{209}Po ($^{209}N_{n2}$) (or ^{208}Po) and ^{210}Po ($^{210}N_{n2}$) regions being used;

H) Decay of ^{210}Po from the time of second plating to mid-counting (t_3);

I) Decay of ^{209}Po (or ^{208}Po) spike from the time of last calibration (or from the time of certification for SRM) to second plating (t_4);

J) Ingrowth factor for ^{210}Po from the decay of ^{210}Pb for the time elapsed between Po-Pb separation (after first plating) and second Po plating (t_5);

K) Chemical yield for ^{210}Pb; and

L) Correction factor for the decay of ^{210}Pb from the time of collection to the second plating (t_6)

The activity of ^{210}Po (ingrown, from the decay of ^{210}Pb) at the time of second plating corrected for the decay of ^{210}Po from plating to mid-counting (term H above) and for the decay of spike due to time elapsed between the last assay of spike Po (^{209}Po or ^{208}Po) and the time of second plating (term I above) is given by:

$${}^{210}A^{m}{}_{Po\text{-}210}\ (dpm) = ({}^{210}N_n/{}^{209}N_n)\ exp(\lambda_{Po210}t_3)\ exp(-\lambda_{Pos}t_4)\ A_{spike} \qquad (4)$$

The ingrowth of ^{210}Po from the decay of ^{210}Pb from the time elapsed between Po and Pb separation after the first plating to second plating (term J) is given by:

$${}^{210}A_{Pb\text{-}210} = {}^{210}A^{m}{}_{Po\text{-}210}\ /[1- exp(\lambda_{Po210}t_5)] \qquad (5)$$

The chemical yield of $^{210}A_{Pb\text{-}210}$ is corrected by (term K above):

$${}^{210}A_{Pb}{}' = {}^{210}A_{Pb\text{-}210}\ /\ \text{chemical yield} \qquad (6)$$

where the chemical yield (η_c) = amount of stable Pb carrier assayed/amount of stable Pb carrier added. An aliquot of the sample (about 5%) taken after the ion-exchange column (after Po and Pb separation, Fig. 1), was used to determine the stable Pb concentration using an Atomic Absorption Spectrometer or other appropriate instruments.

The in situ ^{210}Pb activity is corrected for the decay of ^{210}Pb from collection to plating is given by

$${}^{210}A_{Pb\text{-}in\text{-}situ} = {}^{210}A_{Pb\text{-}210}{}'\ exp(\lambda_{Pb}t_6) \qquad (7)$$

where t_6 is the time elapsed between collection and second plating and λ_{Pb} is the decay constant of ^{210}Pb.

Thus the equation to calculate the in situ ^{210}Pb activity is given by:

$${}^{210}A_{Pb}\ in\ situ = ({}^{210}A^{m}{}_{Po\text{-}210})\ exp(\lambda_{Pb}t_6)/\eta_c\ [1- exp(-\lambda_{Po210}t_5)] \qquad (8)$$

where $^{210}A^{m}{}_{Po\text{-}210}$ is calculated using Eq. 4.

Finally a spreadsheet will be posted that link these equations to explicit decay/ingrowth corrections, blank/background subtractions and error propagation on pp. 27-35 of the GEOTRACES procedures manual found at http://www.obs-vlfr.fr/GEOTRACES/science/intercalibration/222-sampling-and-sample-handling-protocols-for-geotraces-cruises