A methods assessment and recommendations for improving calculations and reducing uncertainties in the determination of 210Po and 210Pb activities in seawater

9 AUTHORS, INCLUDING:

Sylvain Rigaud
Université de Nîmes
47 PUBLICATIONS  84 CITATIONS

Claudia Benitez-Nelson
University of South Carolina
109 PUBLICATIONS  2,697 CITATIONS

Jordi Garcia-Orellana
Autonomous University of Barcelona
80 PUBLICATIONS  730 CITATIONS

Pere Masqué
Autonomous University of Barcelona
152 PUBLICATIONS  1,896 CITATIONS
A methods assessment and recommendations for improving calculations and reducing uncertainties in the determination of $^{210}$Po and $^{210}$Pb activities in seawater

S. Rigaud¹, V. Puigcorbé²,³, P. Cámara-Mor²,³, N. Casacuberta²,³, M. Roca-Martí²,³, J. García-Orellana²,³, C. R. Benítez-Nelson⁴, P. Masqué²,³, and T. Church¹*

¹School of Marine Science and Policy, University of Delaware, Newark, DE 19716 USA
²Departament de Física, Universitat Autònoma de Barcelona, Barcelona 08193, Spain
³Institut de Ciència i Tecnologia Ambientals, Universitat Autònoma de Barcelona, Barcelona 08193, Spain
⁴Marine Science Program and Department of Earth and Ocean Sciences, University of South Carolina, SC 29208, USA

Abstract

In marine systems, $^{210}$Po and $^{210}$Pb disequilibria are being increasingly used to examine oceanic particle formation and export. Here, an updated assessment of current methods for determining $^{210}$Po and $^{210}$Pb activity in marine samples is provided and includes a complete description of the vast number of calculations and uncertainties associated with Po and Pb loss, decay, and ingrowth during sample processing. First, we summarize the current methods for the determination of $^{210}$Po and $^{210}$Pb activities in dissolved and particulate seawater samples and recommend areas for improvement. Next, we detail the calculations and associated uncertainties using principles of error propagation, while also accounting for radionuclide ingrowth, decay, and recovery. A spreadsheet reporting these calculations is included as a downloadable Web Appendix. Our analysis provides insight into the contributions of the relative uncertainty for each parameter considered in the calculation of final $^{210}$Po and $^{210}$Pb activities and gives recommendations on how to obtain the most precise final values. For typical experimental conditions in open seawater, we show that our method allows calculating $^{210}$Pb activity with a relative uncertainty of about 7%. However, for $^{210}$Po activities, the final relative uncertainty is more variable and depends on the $^{210}$Po/$^{210}$Pb activity ratio in the initial sample and the time elapsed between sampling and sample processing. The lowest relative uncertainties on $^{210}$Po that can be obtained by this method is 6% and can only be obtained for samples with high $^{210}$Po/$^{210}$Pb activity ratios (>1) that were rapidly processed.

The naturally occurring $^{210}$Po ($T_{1/2} = 138.4$ d) and $^{210}$Pb ($T_{1/2} = 22.3$ y) radionuclide pair has been widely used to examine dissolved and particle dynamics in marine ecosystems over the past several decades (Bacon et al. 1976; Nozaki et al. 1976; Thomson and Turekian 1976; Masqué et al. 2002; Cochrane and Masqué 2003; Rutgers van der Loeff and Geibert 2008). Both nuclides are part of the $^{238}$U decay chain, with $^{210}$Po produced from the decay of $^{210}$Pb via $^{210}$Bi ($T_{1/2} = 5.0$ d). In seawater, both $^{210}$Pb and $^{210}$Po are particle reactive, but $^{210}$Po also bio-accumulates within organic tissues (Stewart and Fisher 2003a, 2003b; Stewart et al. 2005). As such, differences in the specific activity of these two radionuclides in the water column have been increasingly used to quantitatively assess export fluxes of sinking particulate material, such as organic carbon, from the surface ocean to depth (Moore and Dymond 1988; Sarin et al. 1999; Friedrich and Rutgers van der Loeff 2002; Stewart et al. 2007; Verdeny et al. 2009; Yang et al. 2011).

Since the fundamental measurement techniques described by Fleer and Bacon (1984), there have been significant improvements in sample processing that rely on the use of exchange resins (Sarin et al. 1992, Vajda et al., 1994). Whereas these methods have proven to be very successful in the separation of Po and Pb, losses of $^{210}$Pb can occur during processing. Unfortunately, there is no clear consensus as to how such losses should be assessed during subsequent calculations. Some laboratories consider the loss as minor and ignore it, whereas others include extensive correction procedures. In addition, each laboratory has their own approach for calculating radionuclide ingrowth, decay, and recovery during sample processing as well as error treatment, which relies on a range of assumptions. As a result, questions have been raised regard-

*Corresponding author: E-mail: tchurch@udel.edu
Phone: (302) 831-2558, Fax: (302) 831-4575

Acknowledgments

Full text appears at the end of the article.

DOI 10.4319/lom.2013.11.561
ing the accuracy and precision of $^{210}$Po and $^{210}$Pb measurements in seawater (Church et al. 2012).

An initial assessment of the precision and accuracy of current procedures for $^{210}$Po and $^{210}$Pb measurement was conducted as part of a recent intercalibration exercise using dissolved and particulate seawater samples (Church et al. 2012). One of the major conclusions was that while the results reported by laboratories agree relatively well (relative standard deviation, RSD < 50%) for samples with high $^{210}$Po and $^{210}$Pb activities (> 0.1 dpm), this agreement became rather poor (RSD up to 200%) for lower activity samples. Although the authors were not able to precisely identify the sources of the disagreements, they suggested that one possibility includes the manner in which the $^{210}$Po and $^{210}$Pb ingrowth, decay, and recovery calculations were conducted. Their study further revealed that there were various methodologies in how uncertainties and error propagation were considered, which resulted in a large range in the specific activity uncertainties reported. The intercalibration effort by Church et al. (2012), therefore, suggests that there is a need for the scientific community to concur on "best practices" for $^{210}$Po and $^{210}$Pb measurement as well as final data calculations.

In this context, the aims of this paper are (1) to review the protocols used for $^{210}$Po and $^{210}$Pb measurements in seawater and provide recommendations for improving the method's accuracy, (2) to detail the calculations necessary for including isotopic recoveries and decay/ingrowth corrections during sample processing, (3) to develop a protocol for error propagation and to identify the main sources of uncertainty in the final data, and (4) to recommend methods for lowering the relative uncertainty. A practical spreadsheet, which follows step-wise the complex formulations reported in the paper, has been made available as a downloadable Web Appendix.

**Materials and procedures**

**General procedure for sample collection and processing**

A typical protocol used for seawater sample processing of $^{210}$Pb and $^{210}$Po is presented in Fig. 1 and assumes analysis of $^{210}$Po and $^{210}$Pb by $\alpha$ spectrometry as described by Fleer and Bacon (1984). The seawater sample is collected as either total (unfiltered) or dissolved (filtered) and the particulate fraction measured separately. After collection, the dissolved or total sample is acidified to pH 1-2 with HCl, spiked with a well-calibrated $^{209}$Po tracer solution ($T_{1/2} = 102$ y) and a well-standardized stable lead carrier added to monitor the losses of Po and Pb during sample processing. Some laboratories also use $^{208}$Po ($T_{1/2} = 2.9$ y) in a double spike technique, the former added to monitor the initial yield and the latter to act as a second yield tracer (Friedrich and Rutgers van der Loeff 2002). In the following, we limit our discussions to the single-$^{209}$Po spike method, as tailing/peak overlap corrections for $^{208}$Po ($\alpha$ energy of 5.11 MeV) and $^{210}$Po (5.31 MeV) add another level of complexity not necessary for this discussion (Fleer and Bacon 1984).

For both total and dissolved samples, Po and Pb can be pre-concentrated from large volumes of seawater via co-precipitation with Fe(OH)$_3$ (Thomson and Turekian 1976; Nozaki 1986), Co-APDC (Fleer and Bacon 1984) or MnO$_2$ (Bojanowski et al. 1983). The precipitate is then dissolved in an acid solution (generally HCl for Fe(OH)$_3$ and MnO$_2$, HNO$_3$ for Co-APDC) and, after evaporation to near-dryness, recovered in a 0.5-2M HCl solution. For particulate samples, the solid phase is completely dissolved using a mixture of strong acids (including HF) and, after evaporation to near-dryness, also recovered in 0.5-2M HCl solution. The Po nuclides are then plated by spontaneous deposition onto a silver disc (Flynn 1968). Silver discs, typically 1-2 cm in diameter, can be obtained with greater than 99.99% purity. They are first shined with a commercial silver...
polish and then washed using water and ethanol. One side of the disc is covered by an inert substance, such as rubber cement, electronic spray (e.g. glyptol) or plastic tape, so that Po nuclides are plated on only one side. For samples processed using Fe(OH)_3 co-precipitation, ascorbic acid should be added to the plating solution before plating in order to avoid Fe(OH)_3 formation on the plate. The Po activities are measured after deposition by a spectrometry. Any remaining 210Po and 209Po in solution is removed by either a second deposition onto another silver disc or scrap silver and/or using anion exchange resin such as AG-1 × 8 (Sarin et al. 1992) or Sr Spec resin (Vajda et al. 1994). Note that the Po and Pb separation using Sr Spec resin can also be conducted prior to the first plating (Bojanowski et al. 1983). After separation, the final eluate containing the 210Pb is re-spiked with 209Pb and stored for greater than 6 months to allow in-growth of 210Pb from 210Po. At that time, the 210Pb activity of the sample is determined by re-plating the eluate solution on a new silver disc and measuring the in-growth of 210Po (Fig. 1). The determination of the initial activities of 210Po and 210Pb in the sample at the time of collection requires several corrections that account for decay and ingrowth between the time of collection and processing, together with corrections for Po and Pb chemical recoveries (detailed in Calculations and associated uncertainties section).

Improved accuracy of the method

Use of ion exchange resin for Po and Pb separation

Complete removal of Po isotopes after the initial plating procedure is a key component for increasing the accuracy of the method. Indeed, incomplete removal of Po isotopes prior to storage will affect the final calculated 210Pb activity, and thus that of 210Po. There are two methods to remove the residual Po isotopes: re-plating the solution or separation onto ion exchange resin. Re-plating of samples may not be sufficient to ensure complete removal of residual Po as a fraction of the Po nuclides may remain in solution. Based on the Po recovery efficiency obtained on about 80 processed samples, we found that 17 ± 19% of the Po introduced into the plating solution can remain in solution after the first plating. Note that such results are in agreement with previous findings (Flynn 1968). Assuming the same efficiency for the cleaning plate, residual Po nuclides of 3 ± 3% will remain in solution. In contrast, ion exchange experiments with spiked solutions of known amounts of 209Po and 210Po showed a quantitative removal of Po (98.9 ± 1.4%, n = 6, for AG-1 × 8 in HCl 9M; Rigaud unpubl. data). Thus, although both methods are valid, we recommend the use of ion exchange resin to obtain the most accurate results.

Precise determination of 210Pb recovery efficiency during sample processing

The Pb recovery is quantified by measuring stable lead concentrations in known aliquots of the plating solution. Usually only one aliquot is collected after the second plating, providing information on the total Pb loss that occurs during complete sample processing. This loss is generally assumed to occur only during sample extraction (filtered or unfiltered) or disso-
mass of aliquots taken for stable Pb analysis, are assumed to be of secondary importance, and thus ignored. However, if the additions of the 209 Po spike and Pb carrier are made volumetrically, the volume used should be adapted to minimize uncertainties and the pipette should be repeatedly calibrated for mass using the same solution and for each analyst. An analysis of the influence of each of the uncertainties described above on the final 210 Po and 210 Pb calculated uncertainty, as well as recommendations for minimizing some of these possible sources of error, are presented in Discussion section.

An Excel spreadsheet including all calculations is available as a downloadable Web Appendix. In these calculations the main assumptions are (1) 210 Po and 209 Po are in chemical equilibrium at the time of co-precipitation and plating and are scavenged and plated with the same efficiency. Such isotopic equilibrium is expected to be reached after several hours of equilibration. (2) 210 Po activity on the silver discs decays only as a function of its own decay constant (i.e., 210 Pb is not plated onto the silver disc); (3) both 210 Po and 209 Po are completely removed from the plating solution after the first plating, preferably using ion exchange resin or other quantitative procedure. (4) 210 Bi is at secular equilibrium with 210 Pb in the sample and plating solution, and thus, the in-growth of 210 Po is only function of the 210 Pb decay. (5) 210 Pb activity in the sample and plating solutions decrease with time as a function of its own decay constant (i.e., 210 Pb ingrowth from 226 Ra is assumed to be negligible during sample processing).

Step A: Calculation of 210 Pb activity and associated uncertainty in the sample

Please note: Equations 1a to 14b discussed this section can be found in Equations Appendix A.

Step A-1: Calculation of 210 Po activity in the plating solution at the second plating date \([A_{210Po}^{\text{sol,plat2}}] \text{ dpm, Eq. 1a}\) and its associated uncertainty \(σ[A_{210Po}^{\text{sol,plat2}}], \text{ dpm, Eq. 1b}\) accounting for correction of the detector background, Po recovery and 210 Po decay between the dates of second plating and second counting.

Note that the recovery of 209 Po \(f_{Po,rec2}\) during the extraction and plating steps can be used as a quality control check of sample processing. It is determined as Eq. 2a.

Step A-2: Calculation of 210 Pb activity in the plating solution at the ion exchange resin separation date \([A_{210Pb}^{\text{sol,tres}}] \text{ dpm, Eq. 3a}\) and its associated uncertainty \(σ[A_{210Pb}^{\text{sol,tres}}], \text{ dpm, Eq. 3b}\) after correction for 210 Po in-growth and decay between the dates of resin separation and second plating.

Step A-3: Calculation of 210 Pb activity in the sample at sampling date \([A_{210Pb}^{\text{spl,tspl}}] \text{ dpm, Eq. 4a}\) and its associated uncertainty \(σ[A_{210Pb}^{\text{spl,tspl}}], \text{ dpm, Eq. 4b}\) accounting for correction for 210 Pb decay between the dates of resin separation and sampling, Pb recoveries and blank.
Table 1. List of parameters used in the calculations with their dimension and definition

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Dimension</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \lambda_{210\text{Pb}} )</td>
<td>( \text{min}^{-1} )</td>
<td>( ^{210}\text{Pb} ) decay constant</td>
</tr>
<tr>
<td>( \lambda_{209\text{Po}} )</td>
<td>( \text{min}^{-1} )</td>
<td>( ^{209}\text{Po} ) decay constant</td>
</tr>
<tr>
<td>( \lambda_{210\text{Po}} )</td>
<td>( \text{min}^{-1} )</td>
<td>( ^{210}\text{Po} ) decay constant</td>
</tr>
<tr>
<td>( t_{\text{spl}} )</td>
<td>kg</td>
<td>Sampling date</td>
</tr>
<tr>
<td>( m_{\text{spl}} )</td>
<td></td>
<td>Mass of the sample</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td></td>
<td>Detector efficiency</td>
</tr>
<tr>
<td>( (A_{210\text{Po}})<em>{\text{bg,1}} ) and ( (A</em>{210\text{Po}})_{\text{bg,2}} )</td>
<td>cpm</td>
<td>First and second detector background for ( ^{210}\text{Po} )</td>
</tr>
<tr>
<td>( (A_{209\text{Po}})<em>{\text{bg,1}} ) and ( (A</em>{209\text{Po}})_{\text{bg,2}} )</td>
<td>cpm</td>
<td>First and second detector background for ( ^{209}\text{Po} )</td>
</tr>
<tr>
<td>( (A_{210\text{Po}})<em>{\text{B}} ) and ( (A</em>{210\text{Pb}})_{\text{B}} )</td>
<td>dpm</td>
<td>( ^{210}\text{Po} ) and ( ^{210}\text{Pb} ) activity in the blank, corresponding to their respective activity brought with carrier addition</td>
</tr>
<tr>
<td>( m_{\text{spl}} )</td>
<td>g</td>
<td>First and second masses of the ( ^{209}\text{Po} ) spikes added</td>
</tr>
<tr>
<td>( C_{210\text{Po}} ) and ( C_{210\text{Po,2}} )</td>
<td>cp</td>
<td>Total counts of ( ^{210}\text{Po} ) during the first and second counting</td>
</tr>
<tr>
<td>( C_{209\text{Po}} ) and ( C_{209\text{Po,2}} )</td>
<td>cp</td>
<td>Total counts of ( ^{209}\text{Po} ) during the first and second counting</td>
</tr>
<tr>
<td>( (A_{209\text{Po}})(A_{210\text{Pb}})_{\text{sp,1}} )</td>
<td>dpm.g(^{-1} )</td>
<td>( ^{209}\text{Po} ) activity in the spike at the date of calibration</td>
</tr>
<tr>
<td>( m_{\text{pl,1}} ) and ( m_{\text{pl,2}} )</td>
<td>g</td>
<td>Mass of the first aliquot of the plating solution collected after the first plating for stable Pb analysis</td>
</tr>
<tr>
<td>( m_{\text{pl,1}} ) and ( m_{\text{pl,2}} )</td>
<td>g</td>
<td>Mass of Pb carrier solution added in the sample</td>
</tr>
<tr>
<td>([\text{Pb}]<em>{\text{f,1}}) and ([\text{Pb}]</em>{\text{f,2}})</td>
<td>( \mu\text{g.g}^{-1} )</td>
<td>Pb concentration in the carrier solution and in the plating solution when the first and second aliquots for stable Pb analysis were collected</td>
</tr>
<tr>
<td>( f_{\text{PO},\text{rec},1} ) and ( f_{\text{PO},\text{rec},2} )</td>
<td></td>
<td>First and second Po recovery efficiencies</td>
</tr>
<tr>
<td>( f_{\text{Pb,rec},\text{tot}} )</td>
<td></td>
<td>Pb recovery efficiencies during extraction/dissolution only and during total sample processing (including also resin separation step), respectively</td>
</tr>
<tr>
<td>( (A_{210\text{Po}})<em>{\text{pl,1}} ) and ( (A</em>{210\text{Po}})_{\text{pl,2}} )</td>
<td>dpm</td>
<td>( ^{210}\text{Po} ) activity in the plating solution at the first and second plating dates, respectively</td>
</tr>
<tr>
<td>( (A_{210\text{Pb}})_{\text{pl,1}} )</td>
<td>dpm</td>
<td>( ^{210}\text{Pb} ) activity in the plating solution at the resin separation date</td>
</tr>
<tr>
<td>( (A_{210\text{Pb}})<em>{\text{pl,1}} ) and ( (A</em>{210\text{Pb}})_{\text{pl,2}} )</td>
<td>dpm</td>
<td>( ^{210}\text{Pb} ) activity in the plating solution at the extraction (filtered or unfiltered samples) or dissolution (particulate samples) dates</td>
</tr>
<tr>
<td>( (A_{210\text{Pb}})<em>{\text{pl,1}} ) and ( (A</em>{210\text{Po}})_{\text{pl,2}} )</td>
<td>dpm</td>
<td>( ^{210}\text{Pb} ) and ( ^{210}\text{Po} ) activity in the sample at the sampling date</td>
</tr>
<tr>
<td>( (A_{210\text{Pb}})<em>{\text{pl,1}} ) and ( (A</em>{210\text{Po}})_{\text{pl,2}} )</td>
<td>dpm.100 kg(^{-1} )</td>
<td>( ^{210}\text{Pb} ) and ( ^{210}\text{Po} ) activity in the sample at the sampling date</td>
</tr>
</tbody>
</table>
Step B4: Final calculation of 210Po activity in the sample at the sampling date \( (A_{210\text{Po}})_{\text{pl,tspl}} \) (dpm/100 kg), dpm/100 kg, Eq. 13a) and its associated uncertainty \( (\sigma (A_{210\text{Po}})_{\text{pl,tspl}}) \) (dpm/100 kg), dpm/100 kg, Eq. 13b).

**Step C: Calculation of the 210Po/210Pb activity ratio and associated uncertainty in the sample**

The final 210Po/210Pb activity ratio in the sample at the sampling date \( \left( \frac{A_{210\text{Po}}}{A_{210\text{Pb}}} \right)_{\text{pl,tspl}} \) is simply obtained by dividing \( \left( \frac{A_{210\text{Po}}}{A_{210\text{Pb}}} \right)_{\text{pl,tspl}} \) (Eq. 11a) by \( \frac{A_{209\text{Po}}}{A_{209\text{Pb}}} \) (Eq. 4a). Its associated uncertainty \( (\sigma \left( \frac{A_{210\text{Po}}}{A_{210\text{Pb}}} \right)_{\text{pl,tspl}}) \) can be obtained using Eq. 14b.

Note that Eq. 14b is only valid if the same 209Po spike is used in steps A and B and should be adapted if otherwise. Note also that for simplicity, influence of the blank in Eq. 14b was neglected.

**Discussion**

Influence of the relative uncertainty of individual parameters on the final 210Po, 210Pb, and 210Po/210Pb uncertainties

The main sources of uncertainty detailed in the previous calculations are (1) the number of counts for 210Po \((C_{210\text{Po,}\text{1}})\) and \((C_{210\text{Po,}\text{2}})\) and 209Po \((C_{209\text{Po,}\text{1}})\) and \((C_{209\text{Po,}\text{2}})\) detected by a spectrometer, (2) the activity of 209Po in the spike \((A_{209\text{Po}})_{\text{sp,1}-\text{cal}}\), (3) the detector background for each isotope \((A_{210\text{Po}})_{bg} \) and \((A_{209\text{Po}})_{bg}\) and (4) the estimated Pb recovery from sample processing \((f_{\text{rec,tot}})\) and \((f_{\text{rec,1}})\). For 210Po, a fifth source of uncertainty needs to be considered that includes the error associated with 210Pb, since it is used in the calculation to correct for 210Po ingrowth during sample processing (i.e., Eq. 9 and Eq. 11). In this section, we report the relative influence each source of error has on the cumulative uncertainty of 210Po and 210Pb activities and the 210Po/210Pb activity ratio for typical experimental and environmental conditions.

The influence of a specific parameter’s uncertainty on the overall uncertainty of 210Po and 210Pb activity, as well as the 210Po/210Pb activity ratio, is dependent on two factors: (1) the relative uncertainty of all parameters considered in the calculations, and (2) the relative weight that each parameter has in the final calculated activity. The relative uncertainty of each parameter (factor 1) is only dependent on individual experimental conditions. These include uncertainty of the spike calibration for spike activity, counting statistics for 209Po and 210Po in the sample and during background measurements, and on the analysis of stable Pb concentrations in the aliquots used for determining the recovery. In contrast, the relative weight of each parameter’s uncertainty on the final calculated activity (factor 2) is dependent on the uncertainty calculations.
obtained by error propagation. These need to be precisely estimated to identify which parameter listed above has the most influence on the uncertainty of the final results, and therefore, will provide information on areas where additional effort is needed.

We estimated the influence of the relative uncertainty of each parameter on the final calculated $^{210}$Po and $^{210}$Pb activities and $^{210}$Po/$^{210}$Pb activity ratio based on the data obtained from $\sim$ 200 dissolved ($< 0.2 \mu m$), particulate ($> 1 \mu m$), and total (unfiltered) seawater samples collected from the North Atlantic and Pacific Oceans during GEOTRACES transects (GA-02 and GA-03) and intercalibration cruises (Church et al. 2012). The range of values for the parameters considered within this large database (Table 2) is expected to reflect the typical range of experimental and environmental conditions that are encountered during most $^{210}$Po and $^{210}$Pb determinations. The influence of each parameter was tested separately (i.e., one at a time), by using the equations presented previously and forcing the relative uncertainty of the parameter of interest to vary from 0 to 15% (range of possible values) while fixing the relative uncertainty of the other parameters at 0%.

Please note that the relative uncertainty of each parameter is defined to be similar between the two steps of sample processing (Steps A: $^{210}$Pb determination; Steps B: $^{210}$Po determination).

Results are reported in Fig. 3. Among the tested parameters, those that have the most important influence on the final uncertainty of both in situ $^{210}$Po and $^{210}$Pb activities are (1) the calibrated $^{209}$Po activity in the spike, (2) the number of counts $^{210}$Po and $^{209}$Po detected by $\alpha$ spectrometry and (3) the Pb

**Table 2.** Range of values for the parameters considered for typical experimental and environmental conditions. These originate from about 200 data representing dissolved, particulate, or total seawater samples processed for $^{210}$Po and $^{210}$Pb determination.

<table>
<thead>
<tr>
<th>Considered parameters in the uncertainty calculation</th>
<th>Range of reported values ($n = 189$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$(A_{209Po})_{sp,tocal}$ (dpm.g$^{-1}$)</td>
<td>1.3–53.4</td>
</tr>
<tr>
<td>$(A_{210Po})_{bg}$ (dpm)</td>
<td>$&lt;0.001–0.014$</td>
</tr>
<tr>
<td>$(A_{209Po})_{bg}$ (dpm)</td>
<td>$&lt;0.001–0.047$</td>
</tr>
<tr>
<td>$C_{210Po}$ (counts)</td>
<td>100–2700</td>
</tr>
<tr>
<td>$C_{209Po}$ (counts)</td>
<td>130–6700</td>
</tr>
<tr>
<td>$f_{Pb,rec}$ (%)</td>
<td>15–112</td>
</tr>
</tbody>
</table>

*Parameters from the steps A and B of samples processing are here combined

**Fig. 3.** Evolution of the total relative uncertainty on the calculated $^{210}$Po and $^{210}$Pb activities and $^{210}$Po/$^{210}$Pb activity ratios as a function of the relative uncertainty on parameters considered for the calculations of the activities of $^{210}$Po and $^{210}$Pb. The full line corresponds to the mean, and the dashed lines to the $\pm 1$ standard deviation around the mean. They were calculated using the experimental data from the processing of 200 seawater samples by varying their individual relative uncertainty from 0 to 13%, whereas keeping the relative uncertainty on other parameters to 0%.
recovery efficiency (Fig. 3). The uncertainty on the number of counts of $^{210}$Po and $^{209}$Po and the Pb recovery efficiency has also an important influence on the final uncertainty of $^{210}$Po/$^{210}$Pb activity ratio. However, it is worth noting that the uncertainty on the spike activity does not impact the final uncertainty of $^{210}$Po/$^{210}$Pb activity ratio as such parameter cancel out in the $^{210}$Po/$^{210}$Pb uncertainty calculation (Eq. 14a). Note that such observation is only valid if the same $^{209}$Po spike is used between both steps A and B. In the case of $^{210}$Po, the $^{210}$Pb uncertainty also has an important influence on the final relative uncertainty (Fig. 4). In contrast, the uncertainties associated with the detector backgrounds have a significantly lower influence on the final calculated $^{210}$Po and $^{210}$Pb activities and the $^{210}$Po/$^{210}$Pb activity ratio (Fig. 3). It is worth noting that, for the dataset considered, the detector backgrounds were always < 5% of the $^{210}$Po and $^{209}$Po activities detected by individual α detectors.

**Influence of the $^{210}$Po and $^{210}$Pb activities in blanks on the final $^{210}$Po and $^{210}$Pb activities and associated uncertainties**

Reagents used during sample processing may be contaminated with $^{210}$Po and $^{210}$Pb and impact the final $^{210}$Po and $^{210}$Pb activities and $^{210}$Po/$^{210}$Pb activity ratios as well as their respective uncertainties. One of the most important sources of contamination is the Pb carrier solution, which can contain significant amounts of $^{210}$Po and $^{210}$Pb (e.g., Baskaran et al. 2013). Based on the dataset from the typical experimental and environmental conditions stated above, we evaluate the influence of blank contamination by varying the $^{210}$Po and $^{210}$Pb activities in blanks between 0.00 and 0.10 dpm and assuming radioactive equilibrium between the two nuclides in blanks (Fig. 5). The increase of $^{210}$Po and $^{210}$Pb activities in the blank results in, as expected, a decrease in the final activity on $^{210}$Po and $^{210}$Pb, with $^{210}$Pb slightly higher than $^{210}$Po. As such, it also induces a slight increase, on average, of the $^{210}$Po/$^{210}$Pb activity ratio that can however induce up to 20% variation for the highest blank activity tested (Fig. 5). This clearly highlights the importance of evaluating the blank contamination and to include it in the calculations.

**Implications for the final uncertainty on $^{210}$Po and $^{210}$Pb activities and $^{210}$Po/$^{210}$Pb activity ratios**

To use $^{210}$Po and $^{210}$Pb as quantitative tracers for particle dynamics in the ocean, the determination in seawater samples should be as precise as possible (i.e., their relative uncertainty should be as low as possible). In practice, the lowest relative uncertainties are assumed to be 3% for the $^{209}$Po spike calibration, 3.5% for counting statistics and 3% for lead recovery, and also $^{210}$Po and $^{209}$Pb activities in the blank are considered negligible (see *Comments and recommendation* section). By applying these relative uncertainties to the typical experimental and environmen-

---

**Fig. 4.** Evolution of the final relative uncertainty of $^{210}$Po as a function of the final relative uncertainty of the $^{210}$Pb activity. The full line corresponds to the mean, and the dashed lines to the ± 1 standard deviation around the mean (note that the lower dashed line cannot be distinguished from the X-axis). They were calculated using the experimental data from the processing of 200 seawater samples by varying the relative uncertainty of $^{210}$Pb from 0 to 15%, whereas keeping the relative uncertainty of all other parameters at 0%.

**Fig. 5.** Influence of $^{210}$Po and $^{210}$Pb activities within blanks on $^{210}$Po and $^{210}$Pb activities and $^{210}$Po/$^{210}$Pb activity ratios (expressed as the ratio between calculated values for the range of blank activity tested and the activity calculated with a null blank). The full line corresponds to the mean, and the dashed lines to the ± 1 standard deviation around the mean. They were calculated using the experimental data from the processing of 200 seawater samples.
tal conditions stated above, the mean relative uncertainties on $^{210}\text{Po}$ and $^{210}\text{Pb}$ activities and the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratio that can be obtained are $11 \pm 6\%$, $7.4 \pm 0.4\%$, and $14 \pm 7\%$, respectively. Such relative uncertainties may be considered acceptable for oceanic process modeling for $^{210}\text{Pb}$. However, the higher and more variable relative uncertainties on the final calculated $^{210}\text{Po}$ and the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratios is due to the fact that they incorporate the uncertainty of the final calculated $^{210}\text{Pb}$ from the ingrowth correction (cf., Eq. 9b and Eq. 11b). The extent of such a correction depends on two factors: (1) the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratio in the sample (the lower the ratio, the higher the correction) and (2) the time elapsed between the sampling and the first Po plating (the longer the time elapsed, the higher the correction). The lowest $^{210}\text{Po}$ relative uncertainty obtainable for the experimental conditions described is $6\%$, and then only obtained for those samples with a high $^{210}\text{Po}/^{210}\text{Pb}$ ratio ($\sim 1$) and the shortest delay between sampling and sample processing ($<80$ d) (Fig. 6). Variations in sample characteristics (e.g., $^{210}\text{Po}/^{210}\text{Pb}$ activity ratio) and experimental conditions (e.g., time elapsed between sampling and first plating) can thus explain the high variability in the relative uncertainty obtained for $^{210}\text{Po}$.

Comments and recommendations

Limitation of uncertainties on in situ $^{210}\text{Po}$, $^{210}\text{Pb}$, and $^{210}\text{Po}/^{210}\text{Pb}$ determinations

We previously identified the main sources of uncertainty in the $^{210}\text{Po}$ and $^{210}\text{Pb}$ determination. If there is no way to modify the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratio in the sample, there are however several other ways to reduce the extent of the uncertainty for both $^{210}\text{Po}$ and $^{210}\text{Pb}$ and therefore $^{210}\text{Po}/^{210}\text{Pb}$ activity ratios.

Time between sampling and first plating

As the delay between the sampling and the first plating increases, the uncertainty on the $^{210}\text{Po}$ also increases. Therefore, it is imperative to process samples as soon as possible after collection. However, it is not always possible to practically limit this delay. This is particularly the case when considering long sampling cruises. For typical seawater samples and the experimental conditions presented previously, a delay of 3 months from time of collection at sea to first plating ashore will induce a relative uncertainty on $^{210}\text{Po}$ of about $7\%$ ($^{210}\text{Po}/^{210}\text{Pb}$ activity ratio $> 2$), $9\%$ ($^{210}\text{Po}/^{210}\text{Pb}$ activity ratio $\sim 1$), and $13\%$ ($^{210}\text{Po}/^{210}\text{Pb}$ activity ratio $\sim 0.5$) (Fig. 6b). In comparison, those uncertainties would be reduced to about $6\%$ for sample processed onboard and plated within a few days after collection. Onboard processing of samples, including precipitation, filtration, dissolution/digestion, and plating requires the use of specific equipment (e.g., chemical fume hoods). As research vessels continue to become more modernized, we recommend that such processing to be done onboard to minimize the impact of the needed corrections.

Counting statistics

One of the largest sources of uncertainty is that associated with the number of $^{210}\text{Po}$ and $^{209}\text{Po}$ counts by $\alpha$ spectrometry. The uncertainty on counting is calculated using the square

---

**Fig. 6.** Relative uncertainty on the final calculated $^{210}\text{Po}$ activity as a function of a) $^{210}\text{Po}/^{210}\text{Pb}$ activity ratio in the sample at sampling time and b) time elapsed between sampling and first plating. These were estimated assuming relative uncertainties of 3% for the $^{209}\text{Po}$ spike calibration, 3.5% for the counting statistics, and 3% for the Pb recovery, for the 200 samples representing typical experimental and environmental conditions presented in the text. The Y-axis is the same for both panels. The vertical dashed line represents the lowest $^{210}\text{Po}$ relative uncertainty obtained under these conditions, 6%. R corresponds to the $^{210}\text{Po}/^{210}\text{Pb}$ activity ratio. In b), the data with high (>13%) relative uncertainty on $^{210}\text{Po}$ and plated 65-70 d after collection, correspond to samples with quite low $^{210}\text{Po}/^{210}\text{Pb}$ activity ratios (<0.3) and were mostly dissolved surface samples from different stations, that were by chance processed with similar time delays.
root of the number of counts (e.g., Ludwig 2003), thus, the relative uncertainty on counting results decrease with an increase in the number of counts following a $y = x^{1/2}/x$ shaped-curve. Consequently, it is relatively easy to decrease this uncertainty by increasing the counting time, assuming detector backgrounds are relatively minor. For practical reasons, however, it is also necessary to balance counting periods with the number of samples that needs to be measured and counter availability. For an acceptable relative uncertainty < 3.5%, a minimum of ~ 820 counts is needed. For $^{210}$Po, this can be obtained for a 10 L dissolved seawater sample with a $^{210}$Po activity of 15 dpm.100 L$^{-1}$, assuming a Po recovery of 80% and a detector efficiency of 15%, in about 3 days of counting.

**Spike calibration**

The reported $^{209}$Po activity in commercial stock solutions, from which $^{209}$Po spikes are generally made, is typically certified with a relative uncertainty < 5% (e.g., a $^{209}$Po solution from Eckert & Ziegler is certified at 3.1%; www.ezag.com). For the typical experimental and environmental conditions stated above, such an uncertainty can impart a 5% relative uncertainty for $^{210}$Pb final activities and as much as 20% for $^{210}$Po activities (Fig. 3). Since the spike solution activity can vary with storage (e.g., due to evaporation) and because of the relatively high uncertainty on the $^{209}$Po decay constant (102 ± 5 y), we recommend a regular calibration of the spike over time. Such calibrations imply the use of $^{210}$Po certified standards. The use of IAEA standard RGU-1 (IAEA 1987) is recommended for such calibrations due to its low relative uncertainty on the $^{210}$Po activity (<1%). We also recommend the use of the same $^{209}$Po spike during sample processing as it allows to significantly decrease the uncertainty on $^{210}$Po/$^{210}$Pb activity ratios.

**Pb recovery efficiency**

The uncertainty associated with Pb recoveries is essentially dependent on that associated with the determination of stable Pb concentrations in the aliquots and carrier solution (Eq. 6b and Eq. 7b) as obtained by routine analytical techniques (e.g., atomic absorption spectrometry, Fleer and Bacon 1984; Friedrich and Rutgers van der Loeff 2002). To reduce the uncertainty associated with this analysis, we recommend adding an amount of stable Pb to samples in sufficient quantity to ensure accurate standardization. For example, an addition of ~ 10 mg of Pb into the sample easily allows the Pb concentration to be determined by flame atomic absorption spectrometry (or ICPMS) with a relative uncertainty ± 3%, as this will result in Pb concentrations ranging from 5 to 15 μg g$^{-1}$ in a 20 times diluted 10 mL plating solution assuming a 70% to 95% total Pb extraction efficiency.

**Blank consideration**

We showed that the blank could strongly impact the $^{210}$Po and $^{210}$Pb activities and the $^{210}$Po/$^{210}$Pb activity ratios and thus could induce an increase of their associated uncertainties. However, this essentially depends on the purity of the reagents used. One of the main sources of contamination for $^{210}$Po and $^{210}$Pb is the Pb carrier, which can contain significant amount of both isotopes. To minimize the blank, it is recommended that the carrier be made using lead obtained from ancient sources (i.e., > 200 y) or pure galena mineral that was shown to present the lowest $^{210}$Pb activity (Cochran et al. 1983).

**Summary**

This article presents methodologies for improving accuracy and precision in the determination of $^{210}$Po and $^{210}$Pb activities in seawater samples. This will allow one to compare data reported by different labs, and to use this isotope pair as a quantitative tracer for particle dynamics in marine systems.

First, we recommend that the accuracy of the method can be significantly improved by (1) systematic use of ion exchange resin for Po removal after the first plating, (2) accounting for recovery of $^{210}$Pb during both extraction/dissolution and ion exchange resin separation steps, (3) use of Pb yield tracer made from sufficiently old lead material (>100 y) or lead old mineral (e.g., galena) and (4) use of appropriate calculations for decay/ingrowth, recovery and blank corrections, as detailed herein. We also provide as downloadable Web Appendix a spreadsheet outlining these calculations.

Second, the overall precision of the methodology is discussed by evaluating the impact of the relative uncertainty on each parameter included in the calculations. Parameters that have the most important influence on the final uncertainty of both in situ $^{210}$Po and $^{210}$Pb activities and thus the $^{210}$Po/$^{210}$Pb activity ratio are (1) the calibrated $^{209}$Po activity in the spike, (2) the number of counts of $^{210}$Po and $^{209}$Po detected by $\alpha$ spectrometry, and (3) the Pb recovery efficiency. Blank contamination was also showed to increase the final relative uncertainty on $^{210}$Po, $^{210}$Pb, and $^{210}$Po/$^{210}$Pb. For typical experimental and environmental conditions, such relative uncertainties are about 7% for $^{210}$Pb. However, uncertainties can be considerably larger (up to 35%) for $^{210}$Po, particularly for samples with low (<1) $^{210}$Po/$^{210}$Pb activity ratios and when there is a long delay (>80 d) between sampling and the first Po plating. In contrast, for higher $^{210}$Po/$^{210}$Pb activity ratios and shorter delays between sample collection and processing, the method described herein allows determination of the $^{210}$Po activity within a 6% relative uncertainty.

**Acknowledgments**

The National Science Foundation grants (OCE-0851462) contributed to the manuscript and (OCE-0961653) provided support for S. Rigaud. V. Puigcórbe, P. Cámara-Mor, and M. Roca-Martí acknowledge funding through PhD grants from the Ministerio de Educación y Ciencia (Spain). Funding was also obtained through the ICREA Academia prize of the Generalitat de Catalunya and MEC CTM2007-31241-E/ MAR (P. Masqué) and EU FP7-MC-IF-220485 (C.R. Benitez-Nelson and P. Masqué). S. Rigaud also wishes to thank Rachel Shelley for her initial assistance in writing the paper.
References


