1 **A methods assessment and recommendations for improving calculations and reducing uncertainties**

2 **in the determination of ^{210}Po and ^{210}Pb activities in seawater**

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14 **Running Head:** ^{210}Po and ^{210}Pb activity calculations in seawater

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Abstract

28

29   In marine systems, ^{210}Po and ^{210}Pb disequilibria are being increasingly used to examine oceanic

30   particle formation and export. Here, an updated assessment of current methods for determining ^{210}Po and

31   ^{210}Pb activity in marine samples is provided and includes a complete description of the vast number of

32   calculations and uncertainties associated with Po and Pb loss, decay, and ingrowth during sample

33   processing. First we summarize the current methods for the determination of ^{210}Po and ^{210}Pb activities in

34   dissolved and particulate seawater samples and recommend areas for improvement. Next, we detail the

35   calculations and associated uncertainties using principles of error propagation, while also accounting for

36   radionuclide ingrowth, decay and recovery. A spread-sheet reporting these calculations is included as a

37   downloadable Web Appendix. Our analysis provides insight into the contributions of the relative

38   uncertainty for each parameter considered in the calculation of final ^{210}Po and ^{210}Pb activities and gives

39   recommendations on how to obtain the most precise final values. For typical experimental conditions in

40   open seawater, we show that our method allows calculating ^{210}Pb activity with a relative uncertainty of

41   about 7%. However for ^{210}Po activities, the final relative uncertainty is more variable and depends on the

42   ^{210}Po/^{210}Pb activity ratio in the initial sample and the time elapsed between sampling and sample

43   processing. The lowest relative uncertainties on ^{210}Po that can be obtained by this method is 6% and can

44   only be obtained for samples with high ^{210}Po/^{210}Pb activity ratios (>1) that were rapidly processed.

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Introduction

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 eco-systems over the past several decades (Bacon *et al.* 1976; Nozaki *et al.* 1976; Thomson and Turekian 1976; Masqué et al 2002; Cochran and Masqué 2003; Rutgers van der Loeff and Geibert 2007). 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). While 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, while 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 regarding 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

72   and ^{210}Pb activities (>0.1 dpm), this agreement became rather poor (RSD up to 200%) for lower activity

73   samples. Although the authors were not able to precisely identify the sources of the disagreements, they

74   suggested that one possibility includes the manner in which the ^{210}Po and ^{210}Pb ingrowth, decay and

75   recovery calculations were conducted. Their study further revealed that there were various methodologies

76   in how uncertainties and error propagation were considered, which resulted in a large range in the specific

77   activity uncertainties reported. The inter-calibration effort by Church et al. (2012), therefore suggests that

78   there is a need for the scientific community to concur on "best practices" for ^{210}Po and ^{210}Pb measurement

79   as well as final data calculations.

80   In this context, the aims of this paper are: (1) to review the protocols used for ^{210}Po and ^{210}Pb

81   measurements in seawater and provide recommendations for improving the method's accuracy, (2) to

82   detail the calculations necessary for including isotopic recoveries and decay/ingrowth corrections during

83   sample processing, (3) to develop a protocol for error propagation and to identify the main sources of

84   uncertainty in the final data, and (4) to recommend methods for lowering the relative uncertainty. A

85   practical spread-sheet, which follows step wise the complex formulations reported in the paper, has been

86   made available as an downloadable Web Appendix.

87

88   **Materials and Procedures**

89   ***General procedure for sample collection and processing***

90   A typical protocol used for seawater sample processing of ^{210}Pb and ^{210}Po is presented in Figure 1

91   and assumes analysis of ^{210}Po and ^{210}Pb by alpha spectrometry as described by Fleer and Bacon (1984).

92   The seawater sample is collected as either total (unfiltered) or dissolved (filtered) with the particulate

93   fraction measured separately. After collection, the dissolved or total sample is acidified to pH 1-2 with

94   HCl, spiked with a well-calibrated ^{209}Po tracer solution (T$_{1/2}$=102 y) and a well-standardized stable lead

95   carrier added in order to monitor the losses of Po and Pb during sample processing. Some laboratories also

96   use ^{208}Po (T$_{1/2}$ = 2.9 y) in a double spike technique, the former added to monitor the initial yield and the

97   latter to act as a second yield tracer (Friedrich and Rutgers van der Loeff 2002). In the following, we limit

98   our discussions to the single-^{209}Po spike method, as tailing/peak overlap corrections for ^{208}Po (alpha

99   energy of 5.11 MeV) and ^{210}Po (5.31 MeV) add another level of complexity not necessary for this

100   discussion (Fleer and Bacon 1984).

101   For both total and dissolved samples, Po and Pb can be pre-concentrated from large volumes of

102   seawater via co-precipitation with $Fe(OH)_3$ (Thomson and Turekian 1976; Nozaki 1986), Co-APDC (Fleer

103   and Bacon 1984) or MnO_2 (Bojanowski et al. 1983). The precipitate is then dissolved in an acid solution

104   (generally HCl for $Fe(OH)_3$ and MnO_2, HNO_3 for Co-APDC) and, after evaporation to near-dryness,

105   recovered in a 0.5-2M HCl solution. For particulate samples, the solid phase is completely dissolved using

106   a mixture of strong acids (including HF) and, after evaporation to near-dryness, also recovered in 0.5-2 M

107   HCl solution. The Po nuclides are then plated by spontaneous deposition onto a silver disc (Flynn 1968).

108   Silver discs, typically 1-2 cm in diameter, can be obtained with greater than 99.99% purity. They are first

109   shined with a commercial silver polish and then washed using water and ethanol. One side of the disc is

110   covered by an inert substance, such as rubber cement, electronic spray (e.g glyptol) or plastic tape, so that

111   Po nuclides are plated on only one side. For samples processed using $Fe(OH)_3$ co-precipitation, ascorbic

112   acid should be added to the plating solution before plating in order to avoid $Fe(OH)_3$ formation on the

113   plate. The Po activities are measured after deposition by alpha spectrometry. Any remaining ^{210}Po and

114   ^{209}Po in solution is removed by either a second deposition onto another silver disc or scrap silver and/or

115   using anion exchange resin such as AG-1X8 (Sarin et al. 1992) or Sr Spec resin (Vajda, et al. 1994). Note

116   that the Po and Pb separation using Sr Spec resin can also be conducted prior to the first plating

117   (Bojanowski et al. 1983). After separation, the final eluate containing the ^{210}Pb is re-spiked with ^{209}Po and

118   stored for greater than 6 months to allow in-growth of ^{210}Po from ^{210}Pb. At that time, the ^{210}Pb activity of

119   the sample is determined by replating the eluate solution on a new silver disc and measuring the in-growth

120   of ^{210}Po (Figure 1). The determination of the initial activities of ^{210}Po and ^{210}Pb in the sample at the time of

121   collection requires several corrections that account for decay and ingrowth between the time of collection

122   and processing, together with corrections for Po and Pb chemical recoveries (detailed in Section 3).

123

124 ***Improved accuracy of the method***

125   *Use of ion exchange resin for Po and Pb separation*

126   Complete removal of Po isotopes after the initial plating procedure is a key component for

127 increasing the accuracy of the method. Indeed, incomplete removal of Po isotopes prior to storage will

128 affect the final calculated ^{210}Pb activity, and thus that of ^{210}Po. There are two methods to remove the

129 residual Po isotopes: replating the solution or separation onto ion exchange resin. Replating of samples

130 may not be sufficient to ensure complete removal of residual Po as a fraction of the Po nuclides may

131 remain in solution. Based on the Po recovery efficiency obtained on about 80 processed samples, we

132 found that 17±19% of the Po introduced into the plating solution can remain in solution after the first

133 plating. Note that such results are in agreement with previous findings (Flynn 1968). Assuming the same

134 efficiency for the cleaning plate, residual Po nuclides of 3±3% will remain in solution. In contrast, ion

135 exchange experiments with spiked solutions of known amounts of ^{209}Po and ^{210}Po showed a quantitative

136 removal of Po (98.9±1.4%, n=6, for AG-1X8 in HCl 9M; Rigaud unpublished results). Thus, although

137 both methods are valid, we recommend the use of ion exchange resin in order to obtain the most accurate

138 results.

139

140   *Precise determination of ^{210}Pb recovery efficiency during sample processing*

141   The Pb recovery is quantified by measuring stable lead concentrations in known aliquots of the

142 plating solution. Usually only one aliquot is collected after the second plating, providing information on

143 the total Pb loss that occurs during complete sample processing. This loss is generally assumed to occur

144 only during sample extraction (filtered or unfiltered) or dissolution (particulate). For example experiments

145 using the most common extraction protocols (Fe(OH)$_3$ and Co-APDC methods) on about 80 dissolved

146 seawater samples showed that the Pb extraction efficiency during initial seawater extraction were 70 ±

147 10% and 88 ± 18% for Fe(OH)$_3$ and Co-APDC respectively. However, Pb losses have also been shown to

148 occur during ion exchange resin procedure. For comparison, the Pb recovery during resin separation was

149 90 ± 17% and 96 ± 16% for the Fe(OH)$_3$ and Co-APDC method respectively. Thus, although the Pb

150   recovery during the separation onto resin is significantly higher than during the extraction procedure, it is

151   not always complete and can constitute a non-negligible loss of Pb during sample processing. In the case

152   of particulate samples, for which no extraction is required (Figure 1), ion exchange separation is the main

153   step for Pb loss during sample processing. Thus precise assessment of Pb isotope loss during both

154   extraction and ion exchange procedure needs to be considered to accurately correct for the actual ^{210}Pb

155   fraction that leads to ^{210}Po ingrowth between the extraction and the first plating dates as well as during the

156   storage period. Therefore we strongly recommend collecting another aliquot of plating solution between

157   the first plating and the resin procedure (Figure 1). Note also that the fraction of the solution removed with

158   the aliquot, although small, must also be accounted for during the activity correction process. Indeed, the

159   fraction of ^{210}Pb removed with the aliquot will not contribute to ^{210}Po ingrowth during the storage period,

160   resulting in an underestimation of ^{210}Pb and an overestimation of ^{210}Po (Cf. Section 3).

161

162   **Assessment**

163   ***Calculations and Associated Uncertainties***

164   In this section, calculations that correct for ^{210}Po and ^{210}Pb decay, ingrowth, and recovery are

165   presented along with their associated assumptions. The calculations are divided into several steps that

166   focus either on the activity of ^{210}Pb at the time of sample collection (Steps A) or ^{210}Po at the time of

167   sample collection (Steps B). The steps are presented in Figure 2 and consider three reservoirs: (1) the

168   sample (2) the plating solution in which Po and Pb are recovered after seawater extraction or particulate

169   dissolution, and (3) the two silver discs (the first one for the plating of *in situ* ^{210}Po and the second one for

170   the plating of ^{210}Po produced from the decay of ^{210}Pb during the storage period). A glossary of the terms

171   used is presented in Table 1. We also include equations that account for the combined uncertainty

172   calculated according to uncorrelated error propagation theory. The main sources of uncertainty we

173   consider here are those associated with (1) the counting of ^{210}Po and ^{209}Po by alpha spectrometry, (2) the

174   activity of the ^{209}Po spike, (3) the detector background, and (4) the Pb recovery. The uncertainties

175   associated with the radioactive decay constants of ^{210}Po, ^{210}Pb and ^{209}Po are ignored. The uncertainties

176   associated with the masses of sample, the spike and carrier amounts added into the sample, the mass of the

177   plating solution and the mass of aliquots taken for stable Pb analysis, are assumed to be of secondary

178   importance, and thus also ignored. However, if the additions of the ^{209}Po spike and Pb carrier are made

179   volumetrically, the volume used should be adapted to minimize uncertainties and the pipette should be

180   repeatedly calibrated for mass using the same solution and for each analyst. An analysis of the influence of

181   each of the uncertainties described above on the final ^{210}Po and ^{210}Pb calculated uncertainty, as well as

182   recommendations for minimizing some of these possible sources of error, are presented in Section 4.

183   An Excel spread-sheet including all calculations is available as a downloadable Web Appendix. In

184   these calculations the main assumptions are:

185   - (1) ^{210}Po and ^{209}Po are in chemical equilibrium at the time of co-precipitation and plating and are

186   scavenged and plated with the same efficiency. Such isotopic equilibrium is expected to be reached after

187   several hours of equilibration.

188   - (2) ^{210}Po activity on the silver discs decays only as a function of its own decay constant (i.e.,

189   ^{210}Pb is not plated onto the silver disc),

190   - (3) both ^{210}Po and ^{209}Po are completely removed from the plating solution after the first plating,

191   preferably using ion exchange resin or other quantitative procedure.

192   - (4) ^{210}Bi is at secular equilibrium with ^{210}Pb in the sample and plating solution, and thus, the in-

193   growth of ^{210}Po is only function of the ^{210}Pb decay.

194   - (5) ^{210}Pb activity in the sample and plating solutions decrease with time as a function of its own

195   decay constant (i.e. ^{210}Pb ingrowth from ^{226}Ra is assumed to be negligible during sample processing).

196

197   *Step A: Calculation of ^{210}Pb activity and associated uncertainty in the sample*

198   Step A-1: Calculation of ^{210}Po activity in the plating solution at the second plating date ((A_{210Po})$_{sol,tplat2}$),

199   dpm, Eq. 1a) and its associated uncertainty (σ((A_{210Po})$_{sol,tplat2}$), dpm, Eq. 1b) accounting for correction of

200 the detector background, Po recovery and ^{210}Po decay during counting and between the dates of second

201 plating and second counting:

202 $(A_{210Po})_{sol,t_{plat2}} = \left(\frac{C_{210Po,2}}{T_{c2}} - (A_{210Po})_{bg,2}\right)\frac{\lambda_{210Po}T_{c2}}{1-e^{-\lambda_{210Po}T_{c2}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}}{\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)\frac{\lambda_{209Po}T_{c2}}{1-e^{-\lambda_{209Po}T_{c2}}}}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}$

203 *Eq. 1a*

204 $$\sigma\left((A_{210Po})_{sol,t_{plat2}}\right) =$$

205 $$\sqrt{\begin{array}{l}\sigma(C_{210Po,2})^2\left(\frac{\lambda_{210Po}}{1-e^{-\lambda_{210Po}T_{c2}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}}{\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)\frac{\lambda_{209Po}T_{c2}}{1-e^{-\lambda_{209Po}T_{c2}}}}e^{\lambda_{210Po}(t_{c2,st}-t_{plat2})}\right)^2 \\ +\sigma((A_{210Po})_{bg,2})^2\left(\frac{\lambda_{210Po}T_{c2}}{1-e^{-\lambda_{210Po}T_{c2}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}}{\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)\frac{\lambda_{209Po}T_{c2}}{1-e^{-\lambda_{209Po}T_{c2}}}}e^{\lambda_{210Po}(t_{c2,st}-t_{plat2})}\right)^2 \\ +\sigma((A_{209Po})_{sp,t_{cal}})^2\left(\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)\frac{\lambda_{210Po}T_{c2}}{1-e^{-\lambda_{210Po}T_{c2}}}\frac{e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}}{\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)\frac{\lambda_{209Po}T_{c2}}{1-e^{-\lambda_{209Po}T_{c2}}}}e^{\lambda_{210Po}(t_{c2,st}-t_{plat2})}\right)^2 \\ +\sigma(C_{209Po,2})^2\left(\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)\frac{\lambda_{210Po}T_{c2}}{1-e^{-\lambda_{210Po}T_{c2}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}}{(C_{209Po,2}-T_{c2}(A_{209Po})_{bg,2})^2\frac{\lambda_{209Po}}{1-e^{-\lambda_{209Po}T_{c2}}}}e^{\lambda_{210Po}(t_{c2,st}-t_{plat2})}\right)^2 \\ +\sigma((A_{209Po})_{bg,2})^2\left(\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)\frac{\lambda_{210Po}T_{c2}}{1-e^{-\lambda_{210Po}T_{c2}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}T_{c2}}{(C_{209Po,2}-T_{c2}(A_{209Po})_{bg,2})^2\frac{\lambda_{209Po}}{1-e^{-\lambda_{209Po}T_{c2}}}}e^{\lambda_{210Po}(t_{c2,st}-t_{plat2})}\right)^2\end{array}}$$

206 *Eq. 1b*

207

208 Note that the recovery of ^{209}Po ($f_{Po,rec2}$) during the extraction and plating steps can be used as a quality

209 control check of sample processing. It is determined as:

210 $$f_{Po_{rec2}} = \frac{\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg}\right)\frac{\lambda_{209Po}T_{c2}}{1-e^{-\lambda_{209Po}T_{c2}}}}{\varepsilon(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}}$$ *Eq. 2a*

211

212 Step A-2: Calculation of ^{210}Pb activity in the plating solution at the ion exchange resin separation date

213 $((A_{210Pb})_{sol,tres}$, dpm, Eq. 3a) and its associated uncertainty $(\sigma((A_{210Pb})_{sol,tres})$, dpm, Eq. 3b) after correction

214 for ^{210}Po in-growth and decay between the dates of resin separation and second plating:

215 $$\left(A_{210Pb}\right)_{sol,t_{res}} = \frac{(A_{210Po})_{sol,t_{plat2}}(\lambda_{210Po}-\lambda_{210Pb})}{\lambda_{210Po}\left(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})}\right)}$$ *Eq. 3a*

216 $$\sigma\left(\left(A_{210Pb}\right)_{sol,t_{res}}\right) = \sqrt{\sigma\left(\left(A_{210Po}\right)_{sol,t_{plat2}}\right)^2\left(\frac{(\lambda_{210Po}-\lambda_{210Pb})}{\lambda_{210Po}\left(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})}\right)}\right)^2}$$ *Eq. 3b*

217

218 Step A-3: Calculation of ^{210}Pb activity in the sample at sampling date ($(A_{210Pb})_{spl,tspl}$, dpm, Eq. 4a) and its

219 associated uncertainty ($\sigma((A_{210Pb})_{spl,tspl})$, dpm, Eq. 4b) accounting for correction for ^{210}Pb decay between

220 the dates of resin separation and sampling, Pb recoveries and blank:

221 $$\left(A_{210Pb}\right)_{spl,t_{spl}} = \frac{(A_{210Pb})_{sol,t_{res}}e^{\lambda_{210Pb}(t_{res}-t_{spl})}}{f_{Pb_{rec,tot}}}\left(1+\frac{m_{al1}}{m_{sol1}}\right) - \left(A_{210Pb}\right)_B$$ *Eq. 4a*

222 $$\sigma\left(\left(A_{210Pb}\right)_{spl,t_{spl}}\right) = \sqrt{\begin{array}{l}\sigma\left(\left(A_{210Pb}\right)_{sol,t_{res}}\right)^2\left(\frac{e^{\lambda_{210Pb}\left(t_{res}-t_{spl}\right)}}{f_{Pb_{rec,tot}}}\left(1+\frac{m_{al1}}{m_{sol1}}\right)\right)^2 \\ +\sigma\left(f_{Pb_{rec,tot}}\right)^2\left(\frac{(A_{210Pb})_{sol,t_{res}}e^{\lambda_{210Pb}\left(t_{res}-t_{spl}\right)}}{\left(f_{Pb_{rec,tot}}\right)^2}\left(1+\frac{m_{al1}}{m_{sol1}}\right)\right)^2 \\ +\sigma\left(\left(A_{210Pb}\right)_B\right)^2\end{array}}$$ *Eq. 4b*

223

224 $f_{Pbrec,tot}$ and its associated uncertainty $\sigma(f_{Pbrectot})$ represents the total Pb recovery efficiency during the

225 sample processing, which includes Pb loss during the extraction from seawater samples or particulate

226 dissolution and during the ion exchange resin separation procedure. It is obtained by :

227 $$f_{Pb_{rec,tot}} = \frac{m_{sol2}[Pb]_{sol2}+m_{al1}[Pb]_{sol1}}{m_c[Pb]_c}$$ *Eq. 5a*

228 $$\sigma\left(f_{Pb_{rec,tot}}\right) = \sqrt{\begin{array}{l}\sigma([Pb]_{sol2})^2\left(\frac{m_{sol2}}{m_c[Pb]_c}\right)^2 \\ +\sigma([Pb]_{sol1})^2\left(\frac{m_{al1}}{m_c[Pb]_c}\right)^2 \\ +\sigma([Pb]_c)^2\left(\frac{m_{sol2}[Pb]_{sol2}+m_{al1}[Pb]_{sol1}}{m_c[Pb]_c^2}\right)^2\end{array}}$$ *Eq. 5b*

229

230   The parameters $(A_{210Pb})_B$ and $\sigma((A_{210Pb})_B)$ correspond to the activity (in dpm) and associated uncertainties,

231   respectively, of ^{210}Pb in the blank that may be due to contamination of reagents (e.g., lead carrier). The

232   blank is obtained by processing a volume of ultrapure water in the same manner as a sample, according to

233   the procedure outlined in Figure 1 and calculated following steps A1 and A2, and replacing the equations

234   of step A3 by:

235
$$(A_{210Pb})_B = \frac{(A_{210Pb})_{sol,t_{res}}e^{\lambda_{210Pb}(t_{res}-t_{car})}}{f_{Pb_{rec,tot}}}\left(1+\frac{m_{al1}}{m_{sol1}}\right) \qquad\qquad Eq.\ 6a$$

236
$$\sigma((A_{210Pb})_B) = \sqrt{\begin{array}{l}\sigma\left((A_{210Pb})_{sol,t_{res}}\right)^2\left(\frac{e^{\lambda_{210Pb}(t_{res}-t_{car})}}{f_{Pb_{rec,tot}}}\left(1+\frac{m_{al1}}{m_{sol1}}\right)\right)^2\\[2em] +\sigma\left(f_{Pb_{rec,tot}}\right)^2\left(\frac{(A_{210Pb})_{sol,t_{res}}e^{\lambda_{210Pb}(t_{res}-t_{car})}}{\left(f_{Pb_{rec,tot}}\right)^2}\left(1+\frac{m_{al1}}{m_{sol1}}\right)\right)^2\end{array}} \qquad Eq.\ 6b$$

237

238   Step A-4: Final calculation of ^{210}Pb activity in the sample at the sampling date $((A_{210Pb})_{spl,tspl}$ (dpm/100kg),

239   dpm/100kg, Eq. 7a) and its associated uncertainty $(\sigma((A_{210Pb})_{spl,tspl}$ (dpm/100kg)), dpm/100kg, Eq. 7b):

240
$$(A_{210Pb})_{spl,t_{spl}}\left(\frac{dpm}{100kg}\right) = \frac{(A_{210Pb})_{spl,t_{spl}}}{m_{spl}}100 \qquad\qquad Eq.\ 7a$$

241
$$\sigma\left((A_{210Pb})_{spl,t_{spl}}\left(\frac{dpm}{100kg}\right)\right) = \sqrt{\sigma\left((A_{210Pb})_{spl,t_{spl}}\right)^2\left(\frac{100}{m_{spl}}\right)^2} \qquad\qquad Eq.\ 7b$$

242

243   *Step B: Calculation of ^{210}Po activity and associated uncertainty in the sample*

244   Step B1: Calculation of ^{210}Po activity in the plating solution at the first plating date $((A_{210Po})_{sol,tplat1}$, dpm,

245   Eq. 8a) and its associated uncertainty $(\sigma((A_{210Po})_{sol,tplat1})$, dpm, Eq. 8b) after correction for detector

246   background, Po recovery and ^{210}Po decay during counting and between the dates of first plating and the

247   start of counting:

248    $(A_{210Po})_{sol,t_{plat1}} = \left(\frac{C_{210Po,1}}{T_{c1}} - (A_{210Po})_{bg,1}\right)\frac{\lambda_{210Po}T_{c1}}{1-e^{-\lambda_{210Po}T_{c1}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}}{\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)\frac{\lambda_{209Po}T_{c1}}{1-e^{-\lambda_{209Po}T_{c1}}}}e^{\lambda_{210Po}(t_{c1,st}-t_{plat1})}$

249   *Eq. 8a*

250                      $\sigma\left((A_{210Po})_{sol,t_{plat1}}\right) =$

251

$$\sqrt{\begin{aligned}
&\sigma(C_{210Po,1})^2\left(\frac{\lambda_{210Po}}{1-e^{-\lambda_{210Po}T_{c1}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}}{\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)\frac{\lambda_{209Po}T_{c1}}{1-e^{-\lambda_{209Po}T_{c1}}}}e^{\lambda_{210Po}(t_{c1,st}-t_{plat1})}\right)^2 \\
&+\sigma((A_{210Po})_{bg,1})^2\left(\frac{\lambda_{210Po}T_{c1}}{1-e^{-\lambda_{210Po}T_{c1}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}}{\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)\frac{\lambda_{209Po}T_{c1}}{1-e^{-\lambda_{209Po}T_{c1}}}}e^{\lambda_{210Po}(t_{c1,st}-t_{plat1})}\right)^2 \\
&+\sigma((A_{209Po})_{sp,t_{cal}})^2\left(\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)\frac{\lambda_{210Po}T_{c1}}{1-e^{-\lambda_{210Po}T_{c1}}}\frac{e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}}{\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)\frac{\lambda_{209Po}T_{c1}}{1-e^{-\lambda_{209Po}T_{c1}}}}e^{\lambda_{210Po}(t_{c1,st}-t_{plat1})}\right)^2 \\
&+\sigma(C_{209Po,1})^2\left(\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)\frac{\lambda_{210Po}T_{c1}}{1-e^{-\lambda_{210Po}T_{c1}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}}{(C_{209Po,1}-T_{c1}(A_{209Po})_{bg,1})^2\frac{\lambda_{209Po}}{1-e^{-\lambda_{209Po}T_{c1}}}}e^{\lambda_{210Po}(t_{c1,st}-t_{plat1})}\right)^2 \\
&+\sigma((A_{209Po})_{bg,1})^2\left(\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)\frac{\lambda_{210Po}T_{c1}}{1-e^{-\lambda_{210Po}T_{c1}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}T_{c1}}{(C_{209Po,1}-T_{c1}(A_{209Po})_{bg,1})^2\frac{\lambda_{209Po}}{1-e^{-\lambda_{209Po}T_{c1}}}}e^{\lambda_{210Po}(t_{c1,st}-t_{plat1})}\right)^2
\end{aligned}}$$

252   *Eq. 8b*

253

254   Step B2: Calculation of ^{210}Po activity in the plating solution at the date of extraction (dissolved or total

255   samples) or dissolution (particulate samples) ((A_{210Po})$_{sol,textr}$, dpm, Eq. 9a) and its associated uncertainty

256   (σ((A_{210Po})$_{sol,textr}$), dpm, Eq. 9b) after correction for ^{210}Po decay and in-growth between extraction and first

257   plating dates:

259   $(A_{210Po})_{sol,t_{extr}}$

260   $= \left((A_{210Po})_{sol,t_{plat1}} - \frac{\lambda_{210Po}\left((A_{210Pb})_{spl,t_{spl}}e^{-\lambda_{210Pb}(t_{extr}-t_{spl})} + (A_{210Pb})_B e^{-\lambda_{210Pb}(t_{extr}-t_{car})}\right)f_{Pb_{rec1}}}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}\right.\right.$

261   $\left.\left. - e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right)\right)e^{\lambda_{210Po}(t_{plat1}-t_{extr})}$

258   *Eq. 9a*

262

263
$$\sigma\big((A_{210Po})_{sol,t_{extr}}\big) =$$

264
$$\sqrt{\begin{array}{l} \sigma\left((A_{210Po})_{sol,t_{plat1}}\right)^2 \left(e^{\lambda_{210Po}(t_{plat1}-t_{extr})}\right)^2 \\[2mm] +\sigma\left((A_{210Pb})_{spl,t_{spl}}\right)^2 \left(\frac{\lambda_{210Po}e^{-\lambda_{210Pb}(t_{extr}-t_{spl})}f_{Pb_{rec1}}}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}-e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right)e^{\lambda_{210Po}(t_{plat1}-t_{extr})}\right)^2 \\[2mm] +\sigma((A_{210Pb})_B)^2 \left(\frac{\lambda_{210Po}e^{-\lambda_{210Pb}(t_{extr}-t_{car})}f_{Pb_{rec1}}}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}-e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right)e^{\lambda_{210Po}(t_{plat1}-t_{extr})}\right)^2 \\[2mm] +\sigma\big(f_{Pb_{rec1}}\big)^2 \left(\frac{\lambda_{210Po}\left((A_{210Pb})_{spl,t_{spl}}e^{-\lambda_{210Pb}(t_{extr}-t_{spl})}+(A_{210Pb})_Be^{-\lambda_{210Pb}(t_{extr}-t_{car})}\right)}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}-e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right)e^{\lambda_{210Po}(t_{plat1}-t_{extr})}\right)^2 \end{array}}$$

265
Eq. 9b

266

267 f_{Pbrec1} and its associated uncertainty $\sigma(f_{Pbrec1})$ represents the Pb recovery efficiency during sample extraction

268 (filtered or unfiltered samples). It is obtained by :

269
$$f_{Pb_{rec1}} = \frac{m_{sol1}[Pb]_{sol1}}{m_c[Pb]_c}$$
Eq. 10a

270
$$\sigma\left(f_{Pb_{rec1}}\right) = \sqrt{\sigma([Pb]_{sol1})^2\left(\frac{m_{sol1}}{m_c[Pb]_c}\right)^2 + \sigma([Pb]_c)^2\left(\frac{m_{sol1}[Pb]_{sol1}}{m_c[Pb]_c^2}\right)^2}$$
Eq. 10b

271

272 Note that for particulate samples, the date of extraction (t_{extr}) in Eq. 9a and Eq. 9b should be replaced by

273 the date of dissolution (t_{diss}), assuming that any loss of Pb that occurs during particulate sample processing

274 is during the dissolution procedure.

275

276 Step B3: Calculation of ^{210}Po activity in the sample at sampling date (($A_{210Po})_{sol,tspl}$, dpm, Eq. 11a) and its

277 associated uncertainty ($\sigma((A_{210Po})_{sol,tspl})$, dpm, Eq. 11b) after correction for the blank and for ^{210}Po decay

278 and in-growth between sampling date and extraction (dissolved or total) or dissolution (particulate) dates:

280      $(A_{210Po})_{spl,t_{spl}} = (A_{210Po})_{sol,t_{extr}} e^{\lambda_{210Po}(t_{extr}-t_{spl})}$

281      $- \dfrac{\lambda_{210Po}(A_{210Pb})_{spl,t_{spl}}}{\lambda_{210Po} - \lambda_{210Pb}} \left(e^{-\lambda_{210Pb}(t_{extr}-t_{spl})} - e^{-\lambda_{210Po}(t_{extr}-t_{spl})}\right) e^{\lambda_{210Po}(t_{extr}-t_{spl})}$

282      $- \dfrac{\lambda_{210Po}(A_{210Pb})_{B}}{\lambda_{210Po} - \lambda_{210Pb}} \left(e^{-\lambda_{210Pb}(t_{extr}-t_{car})} - e^{-\lambda_{210Po}(t_{extr}-t_{car})}\right) e^{\lambda_{210Po}(t_{extr}-t_{car})} - (A_{210Po})_{B}$

279   *Eq. 11a*

284      $\sigma\left((A_{210Po})_{spl,t_{spl}}\right)$

285      $= \sqrt{\begin{array}{c} \sigma\left((A_{210Po})_{sol,t_{extr}}\right)^2 \left(e^{\lambda_{210Po}(t_{extr}-t_{spl})}\right)^2 \\ + \sigma\left((A_{210Pb})_{spl,t_{spl}}\right)^2 \left(\dfrac{\lambda_{210Po}}{\lambda_{210Po} - \lambda_{210Pb}} \left(e^{-\lambda_{210Pb}(t_{extr}-t_{spl})} - e^{-\lambda_{210Po}(t_{extr}-t_{spl})}\right) e^{\lambda_{210Po}(t_{extr}-t_{spl})}\right)^2 \\ + \sigma((A_{210Pb})_{B})^2 \left(\dfrac{\lambda_{210Po}}{\lambda_{210Po} - \lambda_{210Pb}} \left(e^{-\lambda_{210Pb}(t_{extr}-t_{car})} - e^{-\lambda_{210Po}(t_{extr}-t_{car})}\right) e^{\lambda_{210Po}(t_{extr}-t_{car})}\right)^2 \\ + \sigma((A_{210Po})_{B})^2 \end{array}}$

283   *Eq. 11b*

286

287 In the case of particulate samples, t_{extr} should be replaced by t_{diss} in Eq. 11a and Eq. 11b.

288

289 The parameters $(A_{210Po})_B$ and $\sigma((A_{210Po})_B)$ correspond to the activity and its associated uncertainty,

290 respectively, of ^{210}Po in the blank, which should be obtained by processing a volume of ultrapure water

291 using the same reagents as would a sample, according to the procedure outlined in Figure 1. They are

292 calculated following step B1 and by replacing the equations of step B2 by:

293      $(A_{210Po})_B = (A_{210Po})_{sol,t_{plat1}} e^{\lambda_{210Po}(t_{plat1}-t_{car})}$

294      $- \dfrac{\lambda_{210Po}(A_{210Pb})_{B} e^{-\lambda_{210Pb}(t_{extr}-t_{car})} f_{Pbrec1}}{\lambda_{210Po} - \lambda_{210Pb}} \left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}\right.$

295      $\left. - e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right) e^{\lambda_{210Po}(t_{plat1}-t_{extr})}$

296      $- \dfrac{\lambda_{210Po}(A_{210Pb})_{B}}{\lambda_{210Po} - \lambda_{210Pb}} \left(e^{-\lambda_{210Pb}(t_{extr}-t_{car})} - e^{-\lambda_{210Po}(t_{extr}-t_{car})}\right) e^{\lambda_{210Po}(t_{extr}-t_{car})}$

297   *Eq. 12a*

298
$$\sigma\left((A_{210Po})_B\right) =$$

299
$$\sqrt{\begin{array}{l} \sigma\left((A_{210Po})_{sol,t_{plat1}}\right)^2\left(e^{\lambda_{210Po}(t_{plat1}-t_{car})}\right)^2 \\ +\sigma((A_{210Pb})_B)^2\left(\frac{\lambda_{210Po}e^{-\lambda_{210Pb}(t_{extr}-t_{car})}f_{Pb_{rec1}}}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}-e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right)e^{\lambda_{210Po}(t_{plat1}-t_{extr})}\right)^2 \\ +\sigma((A_{210Pb})_B)^2\left(\frac{\lambda_{210Po}}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{extr}-t_{car})}-e^{-\lambda_{210Po}(t_{extr}-t_{car})}\right)e^{\lambda_{210Po}(t_{extr}-t_{car})}\right)^2 \\ +\sigma\left(f_{Pb_{rec1}}\right)^2\left(\frac{\lambda_{210Po}(A_{210Pb})_Be^{-\lambda_{210Pb}(t_{extr}-t_{car})}}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}-e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right)e^{\lambda_{210Po}(t_{plat1}-t_{extr})}\right)^2 \end{array}}$$

300
Eq. 12b

301

302 Step B4: Final calculation of ^{210}Po activity in the sample at the sampling date ($(A_{210Po})_{spl,tspl}$ (dpm/100kg)),

303 dpm/100kg, Eq. 13a) and its associated uncertainty ($\sigma((A_{210Po})_{spl,tspl}$ (dpm/100kg)), dpm/100kg, Eq. 13b):

304
$$(A_{210Po})_{spl,t_{spl}}\left(\frac{dpm}{100kg}\right) = \frac{(A_{210Po})_{spl,t_{spl}}}{m_{spl}}100 \qquad\qquad Eq.\ 13a$$

305
$$\sigma\left((A_{210Po})_{spl,t_{spl}}\left(\frac{dpm}{100kg}\right)\right) = \sqrt{\sigma\left((A_{210Po})_{spl,t_{spl}}\right)^2\left(\frac{100}{m_{spl}}\right)^2} \qquad\qquad Eq.\ 13b$$

306

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

308 The final ^{210}Po/^{210}Pb activity ratio in the sample at the sampling date ($\frac{(A_{210Po})_{spl,t_{spl}}}{(A_{210Pb})_{spl,t_{spl}}}$) is simply obtained by

309 dividing $(A_{210Po})_{spl,t_{spl}}$(Eq. 11a) by $(A_{210Pb})_{spl,t_{spl}}$ (Eq. 4a). Its associated uncertainty ($\sigma\left(\frac{(A_{210Po})_{spl,t_{spl}}}{(A_{210Pb})_{spl,t_{spl}}}\right)$) can be

310 obtained using Eq. 14b. Note that Eq. 14b is only valid if the same ^{209}Po spike is used in steps A and B and

311 should be adapted if otherwise. Note also that for simplicity, influence of the blank in Eq. 14b was neglected.

312

313

314

315

$$\left(\frac{(A_{210Po})_{spl,t_{spl}}}{(A_{210Pb})_{spl,t_{spl}}}\right)$$

316

$$= \left(\sigma(C_{210Po,1})^2 \left(\frac{\left(\frac{1}{T_{c1}}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)} \right)^2 \right.$$

$$\sigma((A_{210Po})_{bg,1})^2 \left(\frac{(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)} \right)^2$$

$$\sigma(C_{209Po,1})^2 \left(\frac{T_{c1}\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})(C_{209Po,1}-T_{c1}(A_{209Po})_{bg,1})^2(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)} \right)^2$$

$$\sigma((A_{209Po})_{bg,1})^2 \left(\frac{\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)^2(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)} \right)^2$$

$$\sigma(C_{210Po,2})^2 \left(\frac{T_{c2}\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{(C_{210Po,2}-T_{c2}(A_{210Po})_{bg,2})^2(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)} \right)^2$$

$$\sigma((A_{210Po})_{bg,2})^2 \left(\frac{\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)^2(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)} \right)^2$$

$$\sigma(C_{209Po,2})^2 \left(\frac{\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{1}{T_{c2}}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)} \right)^2$$

$$\sigma((A_{209Po})_{bg,2})^2 \left(\frac{\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)} \right)^2$$

$$\sigma(f_{Pb_{rec,tot}})^2 \left(\frac{\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)} \right)^2$$

$$\left. \sigma(f_{Pb_{rec1}})^2 \left(\frac{\lambda_{210Po}e^{-\lambda_{210Pb}(t_{extr}-t_{spl})}}{\lambda_{210Po}-\lambda_{210Pb}}(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}-e^{-\lambda_{210Po}(t_{plat1}-t_{extr})})e^{\lambda_{210Po}(t_{plat1}-t_{spl})} \right)^2 \right)^{1/2}$$

317
Eq. 14b

318

17

319

Discussion

Influence of the relative uncertainty of individual parameters on the final ^{210}Po, ^{210}Pb and ^{210}Po/^{210}Pb

uncertainties

The main sources of uncertainty detailed in the previous calculations are: (1) the number of counts

for ^{210}Po ($C_{210Po,1}$ *and* $C_{210Po,2}$) and ^{209}Po ($C_{209Po,1}$ *and* $C_{209Po,2}$) detected by alpha spectrometry, (2) the

activity of ^{209}Po in the spike ($(A_{209Po})_{sp,tcal}$), (3) the detector background for each isotope ($(A_{210Po})_{bg}$ and

$(A_{209Po})_{bg}$) and (4) the estimated Pb recovery from sample processing ($f_{Pb,rec1}$ *and* $f_{Pb,rec,tot}$). For ^{210}Po, a fifth

source of uncertainty needs to be considered that includes the error associated with ^{210}Pb, since it is used in

the calculation to correct for ^{210}Po 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 ^{210}Po

and ^{210}Pb activities and the ^{210}Po/^{210}Pb activity ratio for typical experimental and environmental

conditions.

The influence of a specific parameter's uncertainty on the overall uncertainty of ^{210}Po and ^{210}Pb

activity, as well as the ^{210}Po/^{210}Pb 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 ^{209}Po and ^{210}Po 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 in order 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 ~ 200 dissolved

345   (<0.2 µm), particulate (>1 µm) and total (unfiltered) seawater samples collected from the North Atlantic

346   and Pacific Oceans during GEOTRACES transects (GA-02 and GA-03) and inter-calibration cruises

347   (Church et al. 2012). The range of values for the parameters considered within this large database (Table

348   2) is expected to reflect the typical range of experimental and environmental conditions that are

349   encountered during most ^{210}Po and ^{210}Pb determinations. The influence of each parameter was tested

350   separately (i.e.; one at a time), by using the equations presented previously and forcing the relative

351   uncertainty of the parameter of interest to vary from 0 to 15% (range of possible values) while fixing the

352   relative uncertainty of the other parameters at 0%. Please note that the relative uncertainty of each

353   parameter is defined to be similar between the two steps of sample processing (Steps A: ^{210}Pb

354   determination; Steps B: ^{210}Po determination).

355   Results are reported in Figure 3. Among the tested parameters, those that have the most important

356   influence on the final uncertainty of both *in situ* ^{210}Po and ^{210}Pb activities are: (1) the calibrated ^{209}Po

357   activity in the spike, (2) the number of counts of ^{210}Po and ^{209}Po detected by alpha spectrometry, and (3)

358   the Pb recovery efficiency (Figure 3). The uncertainty on the number of counts of ^{210}Po and ^{209}Po and the

359   Pb recovery efficiency has also an important influence on the final uncertainty of ^{210}Po/^{210}Pb activity ratio.

360   However, it is worth noting that the uncertainty on the spike activity does not impact the final uncertainty

361   of ^{210}Po/^{210}Pb activity ratio as such parameter cancel out in the ^{210}Po/^{210}Pb uncertainty calculation (Eq.

362   14b). Note that such observation is only valid if the same ^{209}Po spike is used between both steps A and B.

363   In the case of ^{210}Po, the ^{210}Pb uncertainty also has an important influence on the final relative uncertainty

364   (Figure 4). In contrast, the uncertainties associated with the detector backgrounds have a significantly

365   lower influence on the final calculated ^{210}Po and ^{210}Pb activities and the ^{210}Po/^{210}Pb activity ratio (Figure

366   3). It is worth noting that, for the dataset considered, the detector backgrounds were always <5% of the

367   ^{210}Po and ^{209}Po activities detected by individual alpha detectors.

368

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

370   ***uncertainties***

19

371   Reagents used during sample processing may be contaminated with ^{210}Po and ^{210}Pb and impact the

372   final ^{210}Po and ^{210}Pb activities and ^{210}Po/^{210}Pb activity ratios as well as their respective uncertainties. One of

373   the most important sources of contamination is the Pb carrier solution, which can contain significant

374   amounts of ^{210}Po and ^{210}Pb (e.g., Baskaran et al., 2013). Based on the dataset from the typical experimental

375   and environmental conditions stated above, we evaluate the influence of blank contamination by varying

376   the ^{210}Po and ^{210}Pb activities in blanks between 0.00 and 0.10 dpm and assuming radioactive equilibrium

377   between the two nuclides in blanks (Figure 5). The increase of ^{210}Po and ^{210}Pb activities in the blank results

378   in, as expected, a decrease in the final activity on ^{210}Po and ^{210}Pb, with ^{210}Pb slightly higher than ^{210}Po. As

379   such, it also induces a slight increase, on average, of the ^{210}Po/^{210}Pb activity ratio that can however induce

380   up to 20% variation for the highest blank activity tested (Figure 5). This clearly highlights the importance

381   of evaluating the blank contamination and to include it in the calculations.

382

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

384   In order to use ^{210}Po and ^{210}Pb as quantitative tracers for particles dynamic modeling in the ocean,

385   the determination in seawater samples should be as precise as possible (i.e., their relative uncertainty

386   should be as low as possible). In practice, the lowest relative uncertainties are assumed to be 3% for the

387   ^{209}Po spike calibration, 3.5% for counting statistics and 3% for the Pb recovery and ^{210}Po and ^{210}Pb

388   activities in the blank can be considered negligible (see next section). By applying these relative

389   uncertainties to the typical experimental and environmental conditions stated above, the mean relative

390   uncertainties on ^{210}Po and ^{210}Pb activities and the ^{210}Po/^{210}Pb activity ratio that can be obtained are 11 ±

391   6%, 7.4 ± 0.4% and 14 ± 7%, respectively. Such relative uncertainties may be considered acceptable for

392   oceanic process modeling for ^{210}Pb. However, the higher and more variable relative uncertainties on the

393   final calculated ^{210}Po and the ^{210}Po/^{210}Pb activity ratios is due to the fact that they incorporate the

394   uncertainty of the final calculated ^{210}Pb from the ingrowth correction (cf., Eq. 9b and Eq. 11b). The extent

395   of such a correction depends on two factors: (1) the ^{210}Po/^{210}Pb activity ratio in the sample (the lower the

396   ratio, the higher the correction) and (2) the time elapsed between the sampling and the first Po plating (the

397 longer the time elapsed, the higher the correction). The lowest ^{210}Po relative uncertainty obtainable for the

398 experimental conditions described is 6%, and then only obtained for those samples with a high ^{210}Po/^{210}Pb

399 ratio ($\geq$1) and the shortest delay between sampling and sample processing (<80 days) (Figure 6).

400 Variations in sample characteristics (e.g., ^{210}Po/^{210}Pb activity ratio) and experimental conditions (e.g., time

401 elapsed between sampling and first plating) can thus explain the high variability in the relative uncertainty

402 obtained for ^{210}Po.

403

404 **Comments and Recommendations**

405 ***Limitation of uncertainties on in situ ^{210}Po, ^{210}Pb and ^{210}Po/^{210}Pb determinations***

406 We previously identified the main sources of uncertainty in the ^{210}Po and ^{210}Pb determination. If

407 there is no way to modify the ^{210}Po/^{210}Pb activity ratio in the sample, there are however several other ways

408 to reduce the extent of the uncertainty for both ^{210}Po and ^{210}Pb and therefore ^{210}Po/^{210}Pb activity ratios.

409

410 *Time between sampling and first plating*

411 As the delay between the sampling and the first plating increases, the uncertainty on the ^{210}Po also

412 increases. Therefore, it is imperative to process samples as soon as possible after collection. However, it is

413 not always possible to practically limit this delay. This is particularly the case when considering long

414 sampling cruises. For typical seawater samples and the experimental conditions presented previously, a

415 delay of 3 months from time of collection at sea to first plating ashore will induce a relative uncertainty on

416 ^{210}Po of about 7% (^{210}Po/^{210}Pb activity ratio >2), 9% (^{210}Po/^{210}Pb activity ratio $\sim$ 1) and 13% (^{210}Po/^{210}Pb

417 activity ratio $\sim$ 0.5) (Figure 6b). In comparison, those uncertainties would be reduced to about 6% for

418 sample processed onboard and plated within a few days after collection. Onboard processing of samples,

419 including precipitation, filtration, dissolution/digestion and plating requires the use of specific equipment

420 (e.g., chemical fume hoods). As research vessels continue to become more modernized, we recommend

421 that such processing to be done onboard in order to minimize the impact of the needed corrections.

422

423   *Counting statistics*

424   One of the largest sources of uncertainty is that associated with the number of ^{210}Po and ^{209}Po

425   counts by alpha spectrometry. The uncertainty on counting is calculated using the square root of the

426   number of counts (e.g., Ludwig 2003), thus, the relative uncertainty on counting results decrease with an

427   increase in the number of counts following a $y=x^{1/2}/x$ shaped-curve. Consequently, it is relatively easy to

428   decrease this uncertainty by increasing the counting time, assuming detector backgrounds are relatively

429   minor. For practical reasons, however, it is also necessary to balance counting periods with the number of

430   samples that needs to be measured and counter availability. For an acceptable relative uncertainty <3.5%,

431   a minimum of ~820 counts is needed. For ^{210}Po, this can be obtained for a 10L dissolved seawater sample

432   with a ^{210}Po activity of 15 dpm.100L^{-1}, assuming a Po recovery of 80% and a detector efficiency of 15%,

433   in about 3 days of counting.

434

435   *Spike calibration*

436   The reported ^{209}Po activity in commercial stock solutions, from which ^{209}Po spikes are generally

437   made, is typically certified with a relative uncertainty < 5% (e.g., a ^{209}Po solution from Eckert & Ziegler is

438   certified at 3.1%; www.ezag.com). For the typical experimental and environmental conditions stated

439   above, such an uncertainty can impart a 5% relative uncertainty for ^{210}Pb final activities and as much as

440   20% for ^{210}Po activities (Figure 3). Since the spike solution activity can vary with storage (e.g., due to

441   evaporation) and because of the relatively high uncertainty on the ^{209}Po decay constant (102 ± 5y), we

442   recommend a regular calibration of the spike over time. Such calibrations imply the use of ^{210}Po certified

443   standards. The use of IAEA standard RGU-1 (IAEA 1987) is recommended for such calibrations due to its

444   low relative uncertainty on the ^{210}Po activity (<1%). We also recommend the use of the same ^{209}Po spike

445   during sample processing as it allows to significantly decrease the uncertainty on ^{210}Po/^{210}Pb activity

446   ratios.

447

448   *Pb recovery efficiency*

449   The uncertainty associated with Pb recoveries is essentially dependent on that associated with the

450   determination of stable Pb concentrations in the aliquots and carrier solution (Eq. 6b and Eq. 7b) as

451   obtained by routine analytical techniques (e.g., atomic absorption spectrometry, Fleer and Bacon 1984;

452   Friedrich and Rutgers van der Loeff 2002). In order to reduce the uncertainty associated with this analysis,

453   we recommend adding an amount of stable Pb to samples in sufficient quantity to ensure accurate

454   standardization. For example, an addition of ~10 mg of Pb into the sample easily allows the Pb

455   concentration to be determined by flame atomic absorption spectrometry (or ICPMS) with a relative

456   uncertainty ≤3%, as this will result in Pb concentrations ranging from 5 to 15 $\mu g\ g^{-1}$ in a 20 times diluted

457   10 ml plating solution assuming a 70-95% total Pb extraction efficiency.

458

459   *Blank consideration*

460   We showed that the blank could strongly impact the ^{210}Po and ^{210}Pb activities and the ^{210}Po/^{210}Pb

461   activity ratios and thus could induce an increase of their associated uncertainties. However, this essentially

462   depends on the purity of the reagents used. One of the main sources of contamination for ^{210}Po and ^{210}Pb is

463   the Pb carrier, which can contain significant amount of both isotopes. In order to minimize the blank, it is

464   recommended that the carrier be made using lead obtained from ancient sources (i.e., >200y) or pure

465   galena mineral that was shown to present the lowest ^{210}Pb activity (Cochran et al., 1983).

466

467   **Summary**

468   This paper presents methodologies for improving accuracy and precision in the determination of

469   ^{210}Po and ^{210}Pb activities in seawater samples. This will allow one to compare data reported by different

470   labs, and to use this isotope pair as a quantitative tracer for particle dynamics in marine systems.

471   First, we recommend that the accuracy of the method can be significantly improved by: (1)

472   systematic use of ion exchange resin for Po removal after the first plating, (2) accounting for recovery of

473   ^{210}Pb during both extraction/dissolution and ion exchange resin separation steps, (3) use of Pb yield tracer

474   made from sufficiently old lead material (>hundred of years) or lead old mineral (e.g., galena) and (4) use

475   of appropriate calculations for decay/ingrowth, recovery and blank corrections, as detailed herein. We also

476   provide as downloadable Web Appendix a spread-sheet outlining these calculations.

477   Second, the overall precision of the methodology is discussed by evaluating the impact of the

478   relative uncertainty on each individual parameter included in the calculations. Parameters that have the

479   most important influence on the final uncertainty of both *in situ* ^{210}Po and ^{210}Pb activities and thus the

480   ^{210}Po/^{210}Pb activity ratio are: (1) the calibrated ^{209}Po activity in the spike, (2) the number of counts of ^{210}Po

481   and ^{209}Po detected by alpha spectrometry, and (3) the Pb recovery efficiency. Blank contamination was

482   also showed to increase the final relative uncertainty on ^{210}Po, ^{210}Pb and ^{210}Po/^{210}Pb. For typical

483   experimental and environmental conditions, such relative uncertainties are about 7% for ^{210}Pb. However,

484   uncertainties can be considerably larger (up to 35%) for ^{210}Po, particularly for samples with low (<1)

485   ^{210}Po/^{210}Pb activity ratios and when there is a long delay (>80 d) between sampling and the first Po plating.

486   In contrast, for higher ^{210}Po/^{210}Pb activity ratios and shorter delays between sample collection and

487   processing, the method described herein allows determination of the ^{210}Po activity within a 6% relative

488   uncertainty.

489

490

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Figures and Figure Legends
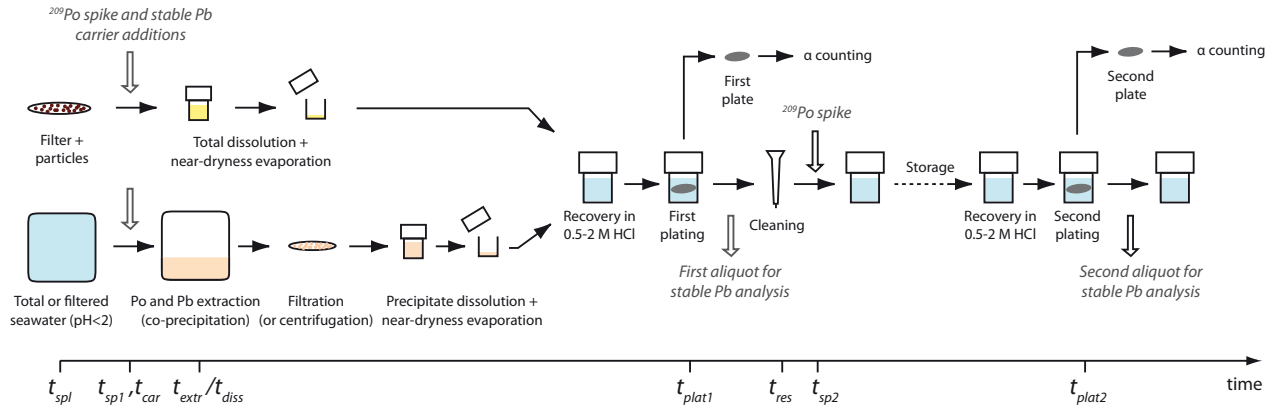
Figure 1: Sample processing scheme for the determination of total, dissolved and particulate ^{210}Po and ^{210}Pb activities. The times term (t) required for each step used in the calculation are provided.
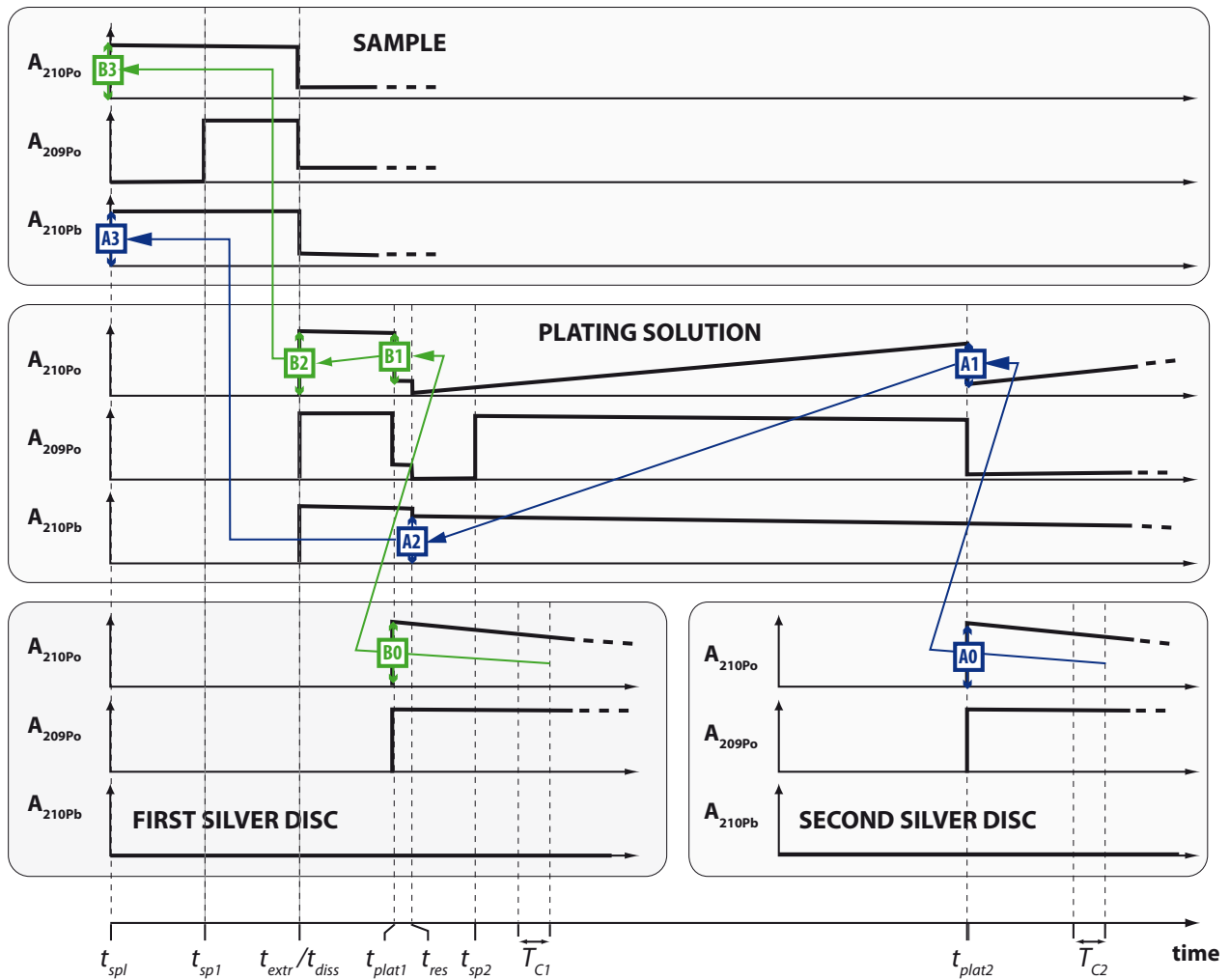
Figure 2: Schematic representation showing the temporal evolution of the activities of ^{210}Po, ^{209}Po and ^{210}Pb in the sample (total, dissolved or particulate), plating solution and silver discs during sample processing (from the left to the right). The steps followed to calculate the initial activity of ^{210}Pb (steps A) and ^{210}Po (steps B) in the sample are indicated.
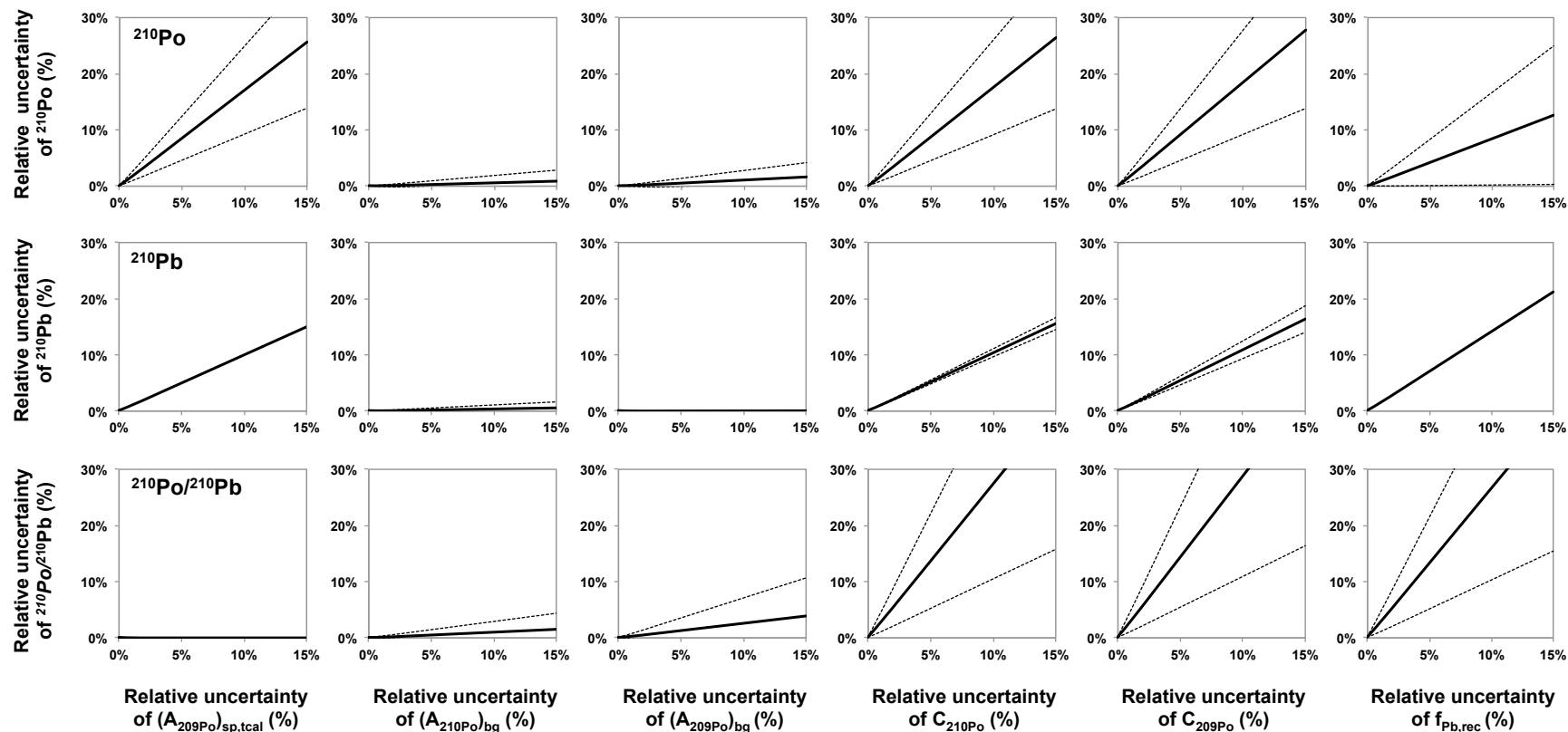
Figure 3: Evolution of the total relative uncertainty on the calculated ^{210}Po and ^{210}Pb activities and ^{210}Po/^{210}Pb activity ratios as a function of the relative uncertainty on parameters considered for the calculations of the activities of ^{210}Po and ^{210}Pb. The full line corresponds to the mean, and the dashed lines to the ±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 15%, while keeping the relative uncertainty on other parameters to 0%.

3
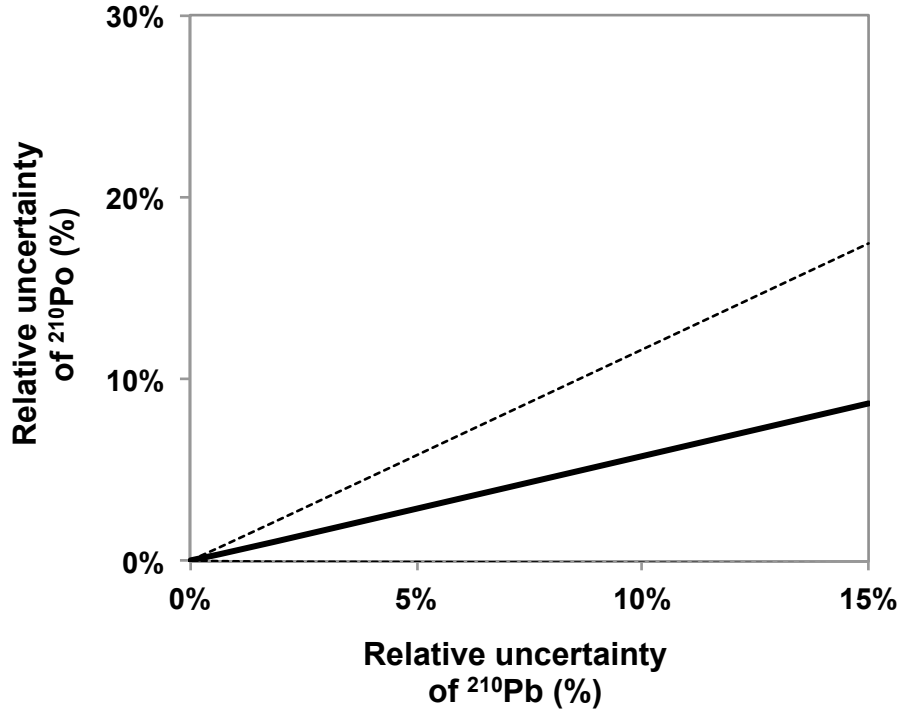
Figure 4: Evolution of the final relative uncertainty of [210]Po as a function of the final relative uncertainty of the ^{210}Pb activity. The full line corresponds to the mean, and the dashed lines to the ±1 standard deviation around the mean (note that the lower dashed line can not be distinguished 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%, while keeping the relative uncertainty of all other parameters at 0%.
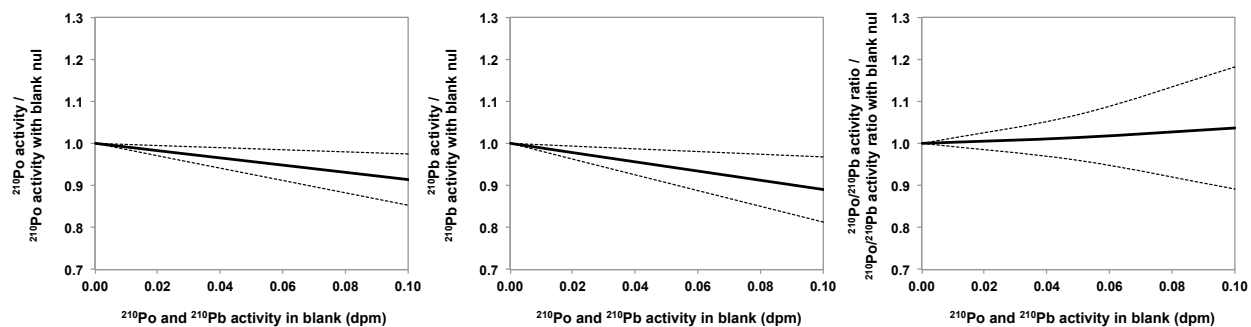
Figure 5: Influence of ^{210}Po and ^{210}Pb activities within blanks on ^{210}Po and ^{210}Pb activities and ^{210}Po/^{210}Pb activity ratios (expressed as the ratio between calculated values for the range of blank activity tested and the activity calculated with a null blank). The full line corresponds 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.
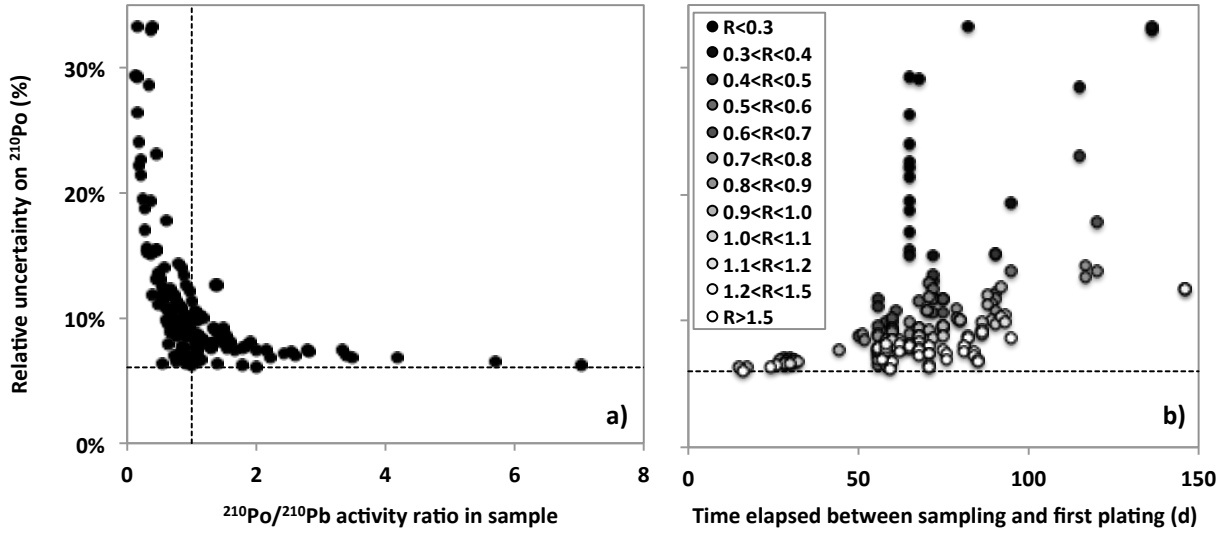
Figure 6: Relative uncertainty on the final calculated [210]**Po activity as a function of a)** [210]**Po/**[210]**Pb activity ratio in the sample at sampling time and b) time elapsed between sampling and first plating. These were estimated assuming relative uncertainties of 3% for the** [209]**Po spike 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** [210]**Po/**[210]**Pb activity ratio of 1. The horizontal dashed line represents the lowest** [210]**Po relative uncertainty obtained under these conditions, 6%. R corresponds to the** [210]**Po/**[210]**Pb activity ratio. In b), the data with high (>13%) relative uncertainty on** [210]**Po and plated 65-70 days after collection, correspond to samples with quite low** [210]**Po/**[210]**Pb activity ratios (<0.3) and were mostly dissolved surface samples from different stations, that were by chance processed with similar time delays.**

Tables

Table 1: List of parameters used in the calculations with their dimension and definition

Parameter	Dimension	Definition
CONSTANTS		
λ_{210Pb}	min^{-1}	^{210}Pb decay constant
λ_{209Po}	min^{-1}	^{209}Po decay constant
λ_{210Po}	min^{-1}	^{210}Po decay constant
SAMPLE INFORMATION		
t_{spl}		Sampling date
m_{spl}	kg	Mass of the sample.
DETECTOR INFORMATION		
ε		Detector efficiency
$(A_{210Po})_{bg,1}$ and $(A_{210Po})_{bg,2}$	cpm	First and second detector background for ^{210}Po
$(A_{209Po})_{bg,1}$ and $(A_{209Po})_{bg,2}$	cpm	First and second detector background for ^{209}Po
PROCESSING & ANALYSIS INFORMATION		
t_{sp1} and t_{sp2}		First and second spike addition dates
t_{extr} and t_{diss}		Extraction (filtered or unfiltered samples) or dissolution (particulate samples) dates
t_{plat1} and t_{plat2}		First and second plating dates
$t_{c1,st}$ and $t_{c2,st}$		Starting dates of the first and second counting
T_{C1} or T_{C2}	min	First and second counting times
t_{res}		Resin separation date
t_{car}		Carrier addition date
$t_{sp,cal}$		^{209}Po spike calibration date
m_{sp1} and m_{sp2}	g	First and second masses of the ^{209}Po spikes added
$C_{210Po,1}$ and $C_{210Po,2}$	cp	Total counts of ^{210}Po during the first and second counting
$C_{209Po,1}$ and $C_{209Po,2}$	cp	Total counts of ^{209}Po during the first and second counting
$(A_{209Po})_{sp,t_{cal}}$	dpm.g^{-1}	^{209}Po activity in the spike at the date of calibration
m_{al1}	g	Mass of the first aliquot of the plating solution collected after the first plating for stable Pb analysis.
m_c	g	Mass of Pb carrier solution added in the sample.
m_{sol1} and m_{sol2}	g	Mass of the plating solution when the first and second aliquots for stable Pb analysis were collected
$[Pb]_c$, $[Pb]_{sol1}$ and $[Pb]_{sol2}$	µg.g^{-1}	Pb concentration in the carrier solution and in the plating solution when the first and second aliquots for stable Pb analysis were collected
CALCULATED PARAMETERS		
$f_{Po,rec1}$ and $f_{Po,rec2}$		First and second Po recovery efficiencies
$f_{Pb,rec1}$ and $f_{Pb,rec_{tot}}$		Pb recovery efficiencies during extraction/dissolution only and during total sample processing (including also resin separation step) respectively
$(A_{210Po})_B$ and $(A_{210Pb})_B$	dpm	^{210}Po and ^{210}Pb activity in the blank, corresponding to their respective activity brought with carrier addition
$(A_{210Po})_{sol,t_{plat1}}$ and $(A_{210Po})_{sol,t_{plat2}}$	dpm	^{210}Po activity in the plating solution at the first and second plating dates respectively
$(A_{210Pb})_{sol,t_{res}}$	dpm	^{210}Pb activity in the plating solution at the resin separation date
$(A_{210Po})_{sol,t_{extr}}$ and $(A_{210Po})_{sol,t_{diss}}$	dpm	^{210}Po activity in the plating solution at the extraction (filtered or unfiltered samples) or dissolution (particulate samples) dates
$(A_{210Pb})_{spl,t_{spl}}$ and $(A_{210Po})_{spl,t_{spl}}$	dpm	^{210}Pb and ^{210}Po activity in the sample at the sampling date
$(A_{210Pb})_{spl,t_{spl}} (\frac{dpm}{100kg})$ and $(A_{210Po})_{spl,t_{spl}} (\frac{dpm}{100kg})$	dpm.100kg^{-1}	^{210}Pb and ^{210}Po activity in the sample at the sampling date

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.

Considered parameters in the uncertainty calculation[*]	Range of reported values (n=189)
$(A_{209Po})_{sp,tcal}$ (dpm/g)	1.3-53.4
$(A_{210Po})_{bg}$ (dpm)	<0.001-0.014
$(A_{209Po})_{bg}$ (dpm)	<0.001-0.047
C_{210Po} (counts)	100-2700
C_{209Po} (counts)	130-6700
$f_{Pb,rec}$ (%)	15-112

[*]parameters from the steps A and B of samples processing are here combined

A methods assessment and recommendations for improving calculations and reducing uncertainties in the determination of [210]Po and ^{210}Pb activities in seawater

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Equations Appendix A

Eq. 1a

$$(A_{210Po})_{sol,t_{plat2}} = \left(\frac{C_{210Po,2}}{T_{c2}} - (A_{210Po})_{bg,2}\right)\frac{\lambda_{210Po}T_{c2}}{1 - e^{-\lambda_{210Po}T_{c2}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}}{\left(\frac{C_{209Po,2}}{T_{c2}} - (A_{209Po})_{bg,2}\right)\frac{\lambda_{209Po}T_{c2}}{1-e^{-\lambda_{209Po}T_{c2}}}}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}$$

Eq. 1b

$$\sigma\left((A_{210Po})_{sol,t_{plat2}}\right) = \left[\begin{aligned} &\sigma(C_{210Po,2})^2 \left(\frac{\lambda_{210Po}}{1-e^{-\lambda_{210Po}T_{c2}}} \frac{(A_{209Po})_{sp,t_{cal}} e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})} m_{sp2}}{\left(\frac{C_{209Po,2}}{T_{c2}} - (A_{209Po})_{bg,2}\right) \frac{\lambda_{209Po}T_{c2}}{1-e^{-\lambda_{209Po}T_{c2}}}} e^{\lambda_{210Po}(t_{c2,st}-t_{plat2})} \right)^2 \\ &+\sigma\left((A_{210Po})_{bg,2}\right)^2 \left(\frac{\lambda_{210Po}T_{c2}}{1-e^{-\lambda_{210Po}T_{c2}}} \frac{(A_{209Po})_{sp,t_{cal}} e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})} m_{sp2}}{\left(\frac{C_{209Po,2}}{T_{c2}} - (A_{209Po})_{bg,2}\right) \frac{\lambda_{209Po}T_{c2}}{1-e^{-\lambda_{209Po}T_{c2}}}} e^{\lambda_{210Po}(t_{c2,st}-t_{plat2})} \right)^2 \\ &+\sigma\left((A_{209Po})_{sp,t_{cal}}\right)^2 \left(\left(\frac{C_{210Po,2}}{T_{c2}} - (A_{210Po})_{bg,2}\right) \frac{\lambda_{210Po}T_{c2}}{1-e^{-\lambda_{210Po}T_{c2}}} \frac{e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})} m_{sp2}}{\left(\frac{C_{209Po,2}}{T_{c2}} - (A_{209Po})_{bg,2}\right) \frac{\lambda_{209Po}T_{c2}}{1-e^{-\lambda_{209Po}T_{c2}}}} e^{\lambda_{210Po}(t_{c2,st}-t_{plat2})} \right)^2 \\ &+\sigma(C_{209Po,2})^2 \left(\left(\frac{C_{210Po,2}}{T_{c2}} - (A_{210Po})_{bg,2}\right) \frac{\lambda_{210Po}T_{c2}}{1-e^{-\lambda_{210Po}T_{c2}}} \frac{(A_{209Po})_{sp,t_{cal}} e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})} m_{sp2}}{\left(C_{209Po,2} - T_{c2}(A_{209Po})_{bg,2}\right)^2 \frac{\lambda_{209Po}}{1-e^{-\lambda_{209Po}T_{c2}}}} e^{\lambda_{210Po}(t_{c2,st}-t_{plat2})} \right)^2 \\ &+\sigma\left((A_{209Po})_{bg,2}\right)^2 \left(\left(\frac{C_{210Po,2}}{T_{c2}} - (A_{210Po})_{bg,2}\right) \frac{\lambda_{210Po}T_{c2}}{1-e^{-\lambda_{210Po}T_{c2}}} \frac{(A_{209Po})_{sp,t_{cal}} e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})} m_{sp2} T_{c2}}{\left(C_{209Po,2} - T_{c2}(A_{209Po})_{bg,2}\right)^2 \frac{\lambda_{209Po}}{1-e^{-\lambda_{209Po}T_{c2}}}} e^{\lambda_{210Po}(t_{c2,st}-t_{plat2})} \right)^2 \end{aligned} \right]^{1/2}$$

Eq. 2a

$$f_{Po_{rec2}} = \frac{\left(\frac{C_{209Po,2}}{T_{c2}} - (A_{209Po})_{bg}\right) \frac{\lambda_{209Po}T_{c2}}{1-e^{-\lambda_{209Po}T_{c2}}}}{\varepsilon (A_{209Po})_{sp,t_{cal}} e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})} m_{sp2}}$$

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Eq. 3a

$$(A_{210Pb})_{sol,t_{res}} = \frac{(A_{210Po})_{sol,t_{plat2}}(\lambda_{210Po} - \lambda_{210Pb})}{\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})} - e^{-\lambda_{210Po}(t_{plat2}-t_{res})})}$$

Eq. 3b

$$\sigma\big((A_{210Pb})_{sol,t_{res}}\big) = \sqrt{\sigma\big((A_{210Po})_{sol,t_{plat2}}\big)^2\left(\frac{(\lambda_{210Po} - \lambda_{210Pb})}{\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})} - e^{-\lambda_{210Po}(t_{plat2}-t_{res})})}\right)^2}$$

Eq. 4a

$$(A_{210Pb})_{spl,t_{spl}} = \frac{(A_{210Pb})_{sol,t_{res}}e^{\lambda_{210Pb}(t_{res}-t_{spl})}}{f_{Pb_{rec,tot}}}\left(1 + \frac{m_{al1}}{m_{sol1}}\right) - (A_{210Pb})_B$$

Eq. 4b

$$\sigma\left((A_{210Pb})_{spl,t_{spl}}\right) = \sqrt{\begin{array}{l} \sigma\big((A_{210Pb})_{sol,t_{res}}\big)^2\left(\dfrac{e^{\lambda_{210Pb}(t_{res}-t_{spl})}}{f_{Pb_{rec,tot}}}\left(1 + \dfrac{m_{al1}}{m_{sol1}}\right)\right)^2 \\[4mm] +\sigma\left(f_{Pb_{rec,tot}}\right)^2\left(\dfrac{(A_{210Pb})_{sol,t_{res}}e^{\lambda_{210Pb}(t_{res}-t_{spl})}}{\left(f_{Pb_{rec,tot}}\right)^2}\left(1 + \dfrac{m_{al1}}{m_{sol1}}\right)\right)^2 \\[4mm] +\sigma((A_{210Pb})_B)^2 \end{array}}$$

Eq. 5a

$$f_{Pb_{rec,tot}} = \frac{m_{sol2}[Pb]_{sol2} + m_{al1}[Pb]_{sol1}}{m_c[Pb]_c}$$

Eq. 5b

$$\sigma\left(f_{Pb_{rec,tot}}\right) = \sqrt{\begin{array}{l} \sigma([Pb]_{sol2})^2 \left(\dfrac{m_{sol2}}{m_c[Pb]_c}\right)^2 \\ +\sigma([Pb]_{sol1})^2 \left(\dfrac{m_{al1}}{m_c[Pb]_c}\right)^2 \\ +\sigma([Pb]_c)^2 \left(\dfrac{m_{sol2}[Pb]_{sol2} + m_{al1}[Pb]_{sol1}}{m_c[Pb]_c^2}\right)^2 \end{array}}$$

Eq. 6a

$$(A_{210Pb})_B = \frac{(A_{210Pb})_{sol,t_{res}} e^{\lambda_{210Pb}(t_{res}-t_{car})}}{f_{Pb_{rec,tot}}} \left(1 + \frac{m_{al1}}{m_{sol1}}\right)$$

Eq. 6b

$$\sigma((A_{210Pb})_B) = \sqrt{\begin{array}{l} \sigma\left((A_{210Pb})_{sol,t_{res}}\right)^2 \left(\dfrac{e^{\lambda_{210Pb}(t_{res}-t_{car})}}{f_{Pb_{rec,tot}}} \left(1 + \dfrac{m_{al1}}{m_{sol1}}\right)\right)^2 \\ +\sigma\left(f_{Pb_{rec,tot}}\right)^2 \left(\dfrac{(A_{210Pb})_{sol,t_{res}} e^{\lambda_{210Pb}(t_{res}-t_{car})}}{\left(f_{Pb_{rec,tot}}\right)^2} \left(1 + \dfrac{m_{al1}}{m_{sol1}}\right)\right)^2 \end{array}}$$

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Eq. 7a

$$(A_{210Pb})_{spl,t_{spl}}\left(\frac{dpm}{100kg}\right) = \frac{(A_{210Pb})_{spl,t_{spl}}}{m_{spl}}100$$

Eq. 7b

$$\sigma\left((A_{210Pb})_{spl,t_{spl}}\left(\frac{dpm}{100kg}\right)\right) = \sqrt{\sigma\left((A_{210Pb})_{spl,t_{spl}}\right)^2\left(\frac{100}{m_{spl}}\right)^2}$$

Eq. 8a

$$(A_{210Po})_{sol,t_{plat1}} = \left(\frac{C_{210Po,1}}{T_{c1}} - (A_{210Po})_{bg,1}\right)\frac{\lambda_{210Po}T_{c1}}{1-e^{-\lambda_{210Po}T_{c1}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}}{\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)\frac{\lambda_{209Po}T_{c1}}{1-e^{-\lambda_{209Po}T_{c1}}}}e^{\lambda_{210Po}(t_{c1,st}-t_{plat1})}$$

Eq. 8b

$$\sigma\left((A_{210Po})_{sol,t_{plat1}}\right) = \sqrt{\begin{aligned} &\sigma(C_{210Po,1})^2\left(\frac{\lambda_{210Po}}{1-e^{-\lambda_{210Po}T_{c1}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}}{\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)\frac{\lambda_{209Po}T_{c1}}{1-e^{-\lambda_{209Po}T_{c1}}}}e^{\lambda_{210Po}(t_{c1,st}-t_{plat1})}\right)^2 \\ &+\sigma((A_{210Po})_{bg,1})^2\left(\frac{\lambda_{210Po}T_{c1}}{1-e^{-\lambda_{210Po}T_{c1}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}}{\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)\frac{\lambda_{209Po}T_{c1}}{1-e^{-\lambda_{209Po}T_{c1}}}}e^{\lambda_{210Po}(t_{c1,st}-t_{plat1})}\right)^2 \\ &+\sigma((A_{209Po})_{sp,t_{cal}})^2\left(\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)\frac{\lambda_{210Po}T_{c1}}{1-e^{-\lambda_{210Po}T_{c1}}}\frac{e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}}{\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)\frac{\lambda_{209Po}T_{c1}}{1-e^{-\lambda_{209Po}T_{c1}}}}e^{\lambda_{210Po}(t_{c1,st}-t_{plat1})}\right)^2 \\ &+\sigma(C_{209Po,1})^2\left(\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)\frac{\lambda_{210Po}T_{c1}}{1-e^{-\lambda_{210Po}T_{c1}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}}{\left(C_{209Po,1}-T_{c1}(A_{209Po})_{bg,1}\right)^2\frac{\lambda_{209Po}}{1-e^{-\lambda_{209Po}T_{c1}}}}e^{\lambda_{210Po}(t_{c1,st}-t_{plat1})}\right)^2 \\ &+\sigma((A_{209Po})_{bg,1})^2\left(\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)\frac{\lambda_{210Po}T_{c1}}{1-e^{-\lambda_{210Po}T_{c1}}}\frac{(A_{209Po})_{sp,t_{cal}}e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}T_{c1}}{\left(C_{209Po,1}-T_{c1}(A_{209Po})_{bg,1}\right)^2\frac{\lambda_{209Po}}{1-e^{-\lambda_{209Po}T_{c1}}}}e^{\lambda_{210Po}(t_{c1,st}-t_{plat1})}\right)^2 \end{aligned}}$$

Eq. 9a

$$(A_{210Po})_{sol,t_{extr}} = \left((A_{210Po})_{sol,t_{plat1}} - \frac{\lambda_{210Po}\left((A_{210Pb})_{spl,t_{spl}}e^{-\lambda_{210Pb}(t_{extr}-t_{spl})}+(A_{210Pb})_B e^{-\lambda_{210Pb}(t_{extr}-t_{car})}\right)f_{Pb_{rec1}}}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}\right.\right.$$

$$\left.\left.- e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right)\right)e^{\lambda_{210Po}(t_{plat1}-t_{extr})}$$

Eq. 9b

$$\sigma\left((A_{210Po})_{sol,t_{extr}}\right) = \sqrt{\begin{array}{c} \sigma\left((A_{210Po})_{sol,t_{plat1}}\right)^2 \left(e^{\lambda_{210Po}(t_{plat1}-t_{extr})}\right)^2 \\ +\sigma\left((A_{210Pb})_{spl,t_{spl}}\right)^2 \left(\dfrac{\lambda_{210Po}e^{-\lambda_{210Pb}(t_{extr}-t_{spl})}f_{Pb_{rec1}}}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}-e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right)e^{\lambda_{210Po}(t_{plat1}-t_{extr})}\right)^2 \\ +\sigma((A_{210Pb})_B)^2 \left(\dfrac{\lambda_{210Po}e^{-\lambda_{210Pb}(t_{extr}-t_{car})}f_{Pb_{rec1}}}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}-e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right)e^{\lambda_{210Po}(t_{plat1}-t_{extr})}\right)^2 \\ +\sigma(f_{Pb_{rec1}})^2 \left(\begin{array}{c}\dfrac{\lambda_{210Po}\left((A_{210Pb})_{spl,t_{spl}}e^{-\lambda_{210Pb}(t_{extr}-t_{spl})}+(A_{210Pb})_B e^{-\lambda_{210Pb}(t_{extr}-t_{car})}\right)}{\lambda_{210Po}-\lambda_{210Pb}} \\ \left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}-e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right)e^{\lambda_{210Po}(t_{plat1}-t_{extr})}\end{array}\right)^2 \end{array}}$$

Eq. 10a

$$f_{Pb_{rec1}} = \frac{m_{sol1}[Pb]_{sol1}}{m_c[Pb]_c}$$

Eq. 10b

$$\sigma\left(f_{Pb_{rec1}}\right) = \sqrt{\sigma([Pb]_{sol1})^2 \left(\frac{m_{sol1}}{m_c[Pb]_c}\right)^2 + \sigma([Pb]_c)^2 \left(\frac{m_{sol1}[Pb]_{sol1}}{m_c[Pb]_c^2}\right)^2}$$

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Eq. 11a

$$(A_{210Po})_{spl,t_{spl}} = (A_{210Po})_{sol,t_{extr}} e^{\lambda_{210Po}(t_{extr}-t_{spl})} - \frac{\lambda_{210Po}(A_{210Pb})_{spl,t_{spl}}}{\lambda_{210Po} - \lambda_{210Pb}} \left(e^{-\lambda_{210Pb}(t_{extr}-t_{spl})} - e^{-\lambda_{210Po}(t_{extr}-t_{spl})} \right) e^{\lambda_{210Po}(t_{extr}-t_{spl})}$$

$$- \frac{\lambda_{210Po}(A_{210Pb})_B}{\lambda_{210Po} - \lambda_{210Pb}} \left(e^{-\lambda_{210Pb}(t_{extr}-t_{car})} - e^{-\lambda_{210Po}(t_{extr}-t_{car})} \right) e^{\lambda_{210Po}(t_{extr}-t_{car})} - (A_{210Po})_B$$

Eq. 11b

$$\sigma\left((A_{210Po})_{spl,t_{spl}} \right) = \sqrt{ \begin{array}{c} \sigma\left((A_{210Po})_{sol,t_{extr}} \right)^2 \left(e^{\lambda_{210Po}(t_{extr}-t_{spl})} \right)^2 \\ + \sigma\left((A_{210Pb})_{spl,t_{spl}} \right)^2 \left(\frac{\lambda_{210Po}}{\lambda_{210Po} - \lambda_{210Pb}} \left(e^{-\lambda_{210Pb}(t_{extr}-t_{spl})} - e^{-\lambda_{210Po}(t_{extr}-t_{spl})} \right) e^{\lambda_{210Po}(t_{extr}-t_{spl})} \right)^2 \\ + \sigma\left((A_{210Pb})_B \right)^2 \left(\frac{\lambda_{210Po}}{\lambda_{210Po} - \lambda_{210Pb}} \left(e^{-\lambda_{210Pb}(t_{extr}-t_{car})} - e^{-\lambda_{210Po}(t_{extr}-t_{car})} \right) e^{\lambda_{210Po}(t_{extr}-t_{car})} \right)^2 \\ + \sigma\left((A_{210Po})_B \right)^2 \end{array} }$$

Eq. 12a

$$(A_{210Po})_B = (A_{210Po})_{sol,t_{plat1}} e^{\lambda_{210Po}(t_{plat1}-t_{car})} - \frac{\lambda_{210Po}(A_{210Pb})_B e^{-\lambda_{210Pb}(t_{extr}-t_{car})} f_{Pb_{rec1}}}{\lambda_{210Po} - \lambda_{210Pb}} \left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})} - e^{-\lambda_{210Po}(t_{plat1}-t_{extr})} \right) e^{\lambda_{210Po}(t_{plat1}-t_{extr})}$$

$$- \frac{\lambda_{210Po}(A_{210Pb})_B}{\lambda_{210Po} - \lambda_{210Pb}} \left(e^{-\lambda_{210Pb}(t_{extr}-t_{car})} - e^{-\lambda_{210Po}(t_{extr}-t_{car})} \right) e^{\lambda_{210Po}(t_{extr}-t_{car})}$$

Eq. 12b

$$\sigma\left((A_{210Po})_B\right) = \sqrt{\begin{array}{l} \sigma\left((A_{210Po})_{sol,t_{plat1}}\right)^2 \left(e^{\lambda_{210Po}(t_{plat1}-t_{car})}\right)^2 \\[2mm] +\sigma((A_{210Pb})_B)^2 \left(\dfrac{\lambda_{210Po}e^{-\lambda_{210Pb}(t_{extr}-t_{car})}f_{Pb_{rec1}}}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}-e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right)e^{\lambda_{210Po}(t_{plat1}-t_{extr})}\right)^2 \\[2mm] +\sigma((A_{210Pb})_B)^2 \left(\dfrac{\lambda_{210Po}}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{extr}-t_{car})}-e^{-\lambda_{210Po}(t_{extr}-t_{car})}\right)e^{\lambda_{210Po}(t_{extr}-t_{car})}\right)^2 \\[2mm] +\sigma\left(f_{Pb_{rec1}}\right)^2 \left(\dfrac{\lambda_{210Po}(A_{210Pb})_B e^{-\lambda_{210Pb}(t_{extr}-t_{car})}}{\lambda_{210Po}-\lambda_{210Pb}}\left(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}-e^{-\lambda_{210Po}(t_{plat1}-t_{extr})}\right)e^{\lambda_{210Po}(t_{plat1}-t_{extr})}\right)^2 \end{array}}$$

Eq. 13a

$$(A_{210Po})_{spl,t_{spl}}\left(\frac{dpm}{100kg}\right) = \frac{(A_{210Po})_{spl,t_{spl}}}{m_{spl}}100$$

Eq. 13b

$$\sigma\left((A_{210Po})_{spl,t_{spl}}\left(\frac{dpm}{100kg}\right)\right) = \sqrt{\sigma\left((A_{210Po})_{spl,t_{spl}}\right)^2 \left(\frac{100}{m_{spl}}\right)^2}$$

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Eq. 14b

$$\left(\frac{(A_{210Po})_{spl,t_{spl}}}{(A_{210Pb})_{spl,t_{spl}}}\right) =$$

$$\sqrt{\begin{aligned}
&\sigma(C_{210Po,1})^2\left(\frac{\left(\frac{1}{T_{c1}}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)}\right)^2\\[6pt]
&\sigma((A_{210Po})_{bg,1})^2\left(\frac{(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)}\right)^2\\[6pt]
&\sigma(C_{209Po,1})^2\left(\frac{T_{c1}\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})(C_{209Po,1}-T_{c1}(A_{209Po})_{bg,1})^2(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)}\right)^2\\[6pt]
&\sigma((A_{209Po})_{bg,1})^2\left(\frac{\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)^2(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)}\right)^2\\[6pt]
&\sigma(C_{210Po,2})^2\left(\frac{T_{c2}\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{(C_{210Po,2}-T_{c2}(A_{210Po})_{bg,2})^2(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)}\right)^2\\[6pt]
&\sigma((A_{210Po})_{bg,2})^2\left(\frac{\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)^2(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)}\right)^2\\[6pt]
&\sigma(C_{209Po,2})^2\left(\frac{\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{1}{T_{c2}}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)}\right)^2\\[6pt]
&\sigma((A_{209Po})_{bg,2})^2\left(\frac{\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})f_{Pb_{rec,tot}}}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)}\right)^2\\[6pt]
&\sigma(f_{Pb_{rec,tot}})^2\left(\frac{\left(\frac{C_{210Po,1}}{T_{c1}}-(A_{210Po})_{bg,1}\right)(1-e^{-\lambda_{210Po}T_{c2}})\left(\frac{C_{209Po,2}}{T_{c2}}-(A_{209Po})_{bg,2}\right)(1-e^{-\lambda_{209Po}T_{c1}})e^{-\lambda_{209Po}(t_{c1,st}-t_{sp,cal})}m_{sp1}e^{\lambda_{210Po}(t_{c1,st}-t_{spl})}\lambda_{210Po}(e^{-\lambda_{210Pb}(t_{plat2}-t_{res})}-e^{-\lambda_{210Po}(t_{plat2}-t_{res})})}{\left(\frac{C_{210Po,2}}{T_{c2}}-(A_{210Po})_{bg,2}\right)(1-e^{-\lambda_{210Po}T_{c1}})\left(\frac{C_{209Po,1}}{T_{c1}}-(A_{209Po})_{bg,1}\right)(1-e^{-\lambda_{209Po}T_{c2}})e^{-\lambda_{209Po}(t_{c2,st}-t_{sp,cal})}m_{sp2}e^{\lambda_{210Po}(t_{c2st}-t_{plat2})}(\lambda_{210Po}-\lambda_{210Pb})e^{\lambda_{210Pb}(t_{res}-t_{spl})}\left(1+\frac{m_{al1}}{m_{sol1}}\right)}\right)^2\\[6pt]
&\sigma(f_{Pb_{rec1}})^2\left(\frac{\lambda_{210Po}e^{-\lambda_{210Pb}(t_{extr}-t_{spl})}}{\lambda_{210Po}-\lambda_{210Pb}}(e^{-\lambda_{210Pb}(t_{plat1}-t_{extr})}-e^{-\lambda_{210Po}(t_{plat1}-t_{extr})})e^{\lambda_{210Po}(t_{plat1}-t_{spl})}\right)^2
\end{aligned}}$$