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# Analysis of <sup>210</sup>Po, <sup>210</sup>Bi, and <sup>210</sup>Pb in atmospheric and oceanic samples by simultaneously auto-plating <sup>210</sup>Po and <sup>210</sup>Bi onto a nickel disc



Qiangqiang Zhong<sup>a</sup>, Viena Puigcorbé<sup>b</sup>, Christian Sanders<sup>c</sup>, Jinzhou Du<sup>a,\*</sup>

<sup>a</sup> State Key Laboratory of Estuarine and Coastal Research, East China Normal University, Shanghai, 200241, China

<sup>b</sup> School of Science, Centre for Marine Ecosystems Research, Edith Cowan University, Joondalup, WA, 6027, Australia

<sup>c</sup> National Marine Science Centre, Southern Cross University, Coffs Harbour, New South Wales, Australia

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#### ABSTRACT

<sup>210</sup>Po and <sup>210</sup>Pb are commonly measured to study particle cycling and particulate organic carbon export (POC) flux from the upper ocean. <sup>210</sup>Bi is a potential oceanographic tracer. However, no convenient and rapid analytical method for <sup>210</sup>Bi has been developed in the marine environment due to its short half-life (5 days). The aims are to study factors influencing the simultaneous auto-plating of <sup>210</sup>Po and <sup>210</sup>Bi onto nickel disc and to develop an effective ship-board procedure for the rapid measurement of <sup>210</sup>Po, <sup>210</sup>Bi, and <sup>210</sup> Pb at sea. The results suggest that the optimal conditions for auto-deposition of <sup>210</sup>Po and <sup>210</sup>Bi were achieved by using a 25 mm diameter nickel disc in 60 mL acidic solution (pH = 0.5) for 16 h at  $25 \pm 1$  °C. By adding <sup>209</sup>Po and <sup>210</sup>Bi as yield tracers to the sediments, recoveries of Po and Bi were >90%. If <sup>210</sup>Po or <sup>210</sup>Bi were in equilibrium with <sup>210</sup>Pb, <sup>210</sup>Po and <sup>210</sup>Bi ord for cainwaters and >60% for seawater samples, respectively, which indicates this analytical procedure is also applicable to marine and atmospheric environments. This method allows the rapid measurement of <sup>210</sup>Bi on a ship and help to obtain its vertical profile or spatial distribution in the marine environment within 1–2 days.

#### 1. Introduction

Products of the naturally occurring <sup>238</sup>U decay series include <sup>210</sup>Bi and <sup>210</sup>Po which are produced by the decay of <sup>210</sup>Pb. These three radionuclides are useful tracers to determine the mean residence times of atmospheric aerosols and to trace the particle dynamics and removal processes of heavy metals and particulate organic carbon (POC) from sea waters (Chen et al., 2016; Roca-Martí et al., 2016; Su et al., 2017). For instance, Fry and Menon (1962), Poet et al. (1972), Tsunogai and Fukuda (1974) and Moore et al. (1976), had found a large difference between the atmospheric residence times of aerosols estimated from <sup>210</sup>Bi/<sup>210</sup>Pb and <sup>210</sup>Po/<sup>210</sup>Pb activity ratios. However, simultaneous determination of these three nuclides in seawater or marine particle samples has not yet been widely reported because of the short half-life of <sup>210</sup>Bi (~5 days), which makes it difficult to separate <sup>210</sup>Bi from <sup>210</sup>Pb within that short period of time.

The classical method to determine <sup>210</sup>Po in environmental samples is based on its spontaneous deposition on a silver or nickel disk and the later measurement by alpha spectrometry (Blanchard, 1966; Fleer and Bacon, 1984; Lee et al., 2014; Murray et al., 2005; Su et al., 2017; Wei et al., 2011). <sup>210</sup>Pb concentrations are typically obtained by measuring either the ingrowth of <sup>210</sup>Po in a sample stored for six to twelve months after all Po in the plating solution had been cleared (Bacon et al., 1988; Baskaran et al., 2013), or by measuring the <sup>210</sup>Bi ingrowth after removing the Pb by electro-deposition (Narita et al., 1989), ion-exchange (Peck and Smith, 2000), or solvent extractions (Jia et al., 2000, 2001).

For land-based laboratories, <sup>210</sup>Bi is usually separated from <sup>210</sup>Pb by co-precipitation (Fry and Menon, 1962; Poet et al., 1972; Tsunogai and Fukuda, 1974; Nevissi, 1991), solvent extraction (Blais and Marshall, 1988), ion-exchange (Harada et al., 1989; Vreček et al., 2004), electro-deposition (Narita et al., 1989; Tokieda et al., 1994), or auto-deposition onto noble metals and subsequently measured using beta counter (Blanchard, 1966; Ehinger et al., 1986). These methods, however, present a series of limitations: Separation of <sup>210</sup>Bi from <sup>210</sup>Pb by co-precipitation using BiOCl may contain contamination of small amounts of <sup>210</sup>Pb (Narita et al., 1989); Using solvent extraction techniques to extract <sup>210</sup>Pb and/or <sup>210</sup>Bi in the presence of various amounts

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<sup>\*</sup> Corresponding author. *E-mail address:* jzdu@sklec.ecnu.edu.cn (J. Du).

of <sup>210</sup>Bi and/or <sup>210</sup>Po and to measure <sup>210</sup>Pb and <sup>210</sup>Bi by a liquid scintillation counter (LSC) is effective and time-saving (Blais and Marshall, 1988; Długosz-Lisiecka, 2019), but LSC requires high concentration (~100 Bq) and is expensive and not available in many marine laboratories (Lee et al., 2014); Ion-exchange is useful for quantitative separation of <sup>210</sup>Bi and <sup>210</sup>Pb, but the procedure is long and tedious, requiring up to 2 days (Narita et al., 1989; Tokieda et al., 1994), and may not be suitable to be used on boats or ships especially when sea conditions are very bad. The separation of <sup>210</sup>Bi by applying a controlled potential electrolysis requires to add nitric and perchloric acids and evaporate it to nearly dryness to decompose the reducing agent and to change the medium to a fluoroborate solution for electrodepositing Pb onto an anode as PbO<sub>2</sub> (Tokieda et al., 1994). In addition, many electrodeposition apparatuses are needed in order to increase the sample preparation and output in the ocean.

Therefore, a rapid sensitive spontaneous deposition method is usually chosen because of its relative simplicity and quickness, in addition, both <sup>210</sup>Bi and/or <sup>210</sup>Po can be spontaneously deposited onto a nickel disc and/or Ag disc quantitatively at temperatures above 80 °C with negligible interfering deposition of <sup>210</sup>Pb (Blanchard, 1966; Helmkamp et al., 1979; Church et al., 1994; Vesterbacka and Ikäheimonen, 2005; Lee et al., 2014). However, under most modestly equipped marine laboratories, especially on waterborne vessels, maintaining a near-constant temperature in an aqueous solution for hours or in a heated water bath (80-90 °C) may potentially be a safety hazard and limit the number of samples that could be processed without temperature-controlled devices. Another concern is the volatility of <sup>210</sup>Po at high plating temperatures (Lee et al., 2014; Matthews et al., 2007). Therefore, the objective of this study is to determine the optimum conditions for the deposition of both  $^{210}$ Po and  $^{210}$ Bi at room temperature (~25 °C) and to apply this technique to environmental samples. The outcome of this research will make possible onboard, rapid and simultaneous plating of <sup>210</sup>Po-<sup>210</sup>Bi by providing the most appropriate and reliable plating conditions when working with high temperatures may not be available.

#### 2. Methods and batch experiments

#### 2.1. Reagents and standards

 $A^{210}Pb^{-210}Bi^{-210}Po$  standard in radioactive equilibrium was obtained from the Beijing Geological Research Institute of Nuclear Industry (GBW04127). <sup>209</sup>Po and <sup>207</sup>Bi tracer were purchased from Eckert & Ziegler Isotopes Products (refs. 1526-81-1 and 1835-28-1, respectively). All chemicals/reagents used in this study were of analytical grade (purchased from Sinopharm Chemical Reagent Co., Ltd). Silver sheet (99.9% pure), nickel sheet (99.9%), copper sheet (99.5%) and stainless-steel discs, were bought from Tianjin Kemiou Chemical Reagent Co., Ltd. Seawater samples were collected from the East China Sea (ECS) (123.99 °E, 29.83 °N) in Jul. 2016. A marine sediment core for <sup>210</sup>Pb dating was collected from the ECS (Station DH3-6, 124.99 °E, 30.99 °N), in 2010, which had been frozen-dried and sealed and stored in plastic box at room temperature, and <sup>210</sup>Po, <sup>210</sup>Bi, and <sup>210</sup>Pb should be in radioactive equilibrium.

#### 2.2. Detectors

Measurement of <sup>210</sup>Bi activity was carried out using a gas-flow proportional low-level beta GM multicounter (Model RISØ GM-25-5A, DTU Nutech, Denmark). This unit runs through a PC and incorporates a discriminator/anticoincidence module for the five, 25-mm-diameter sample counters. The average counting efficiency for a<sup>210</sup>Bi source is calibrated as 37.39%. The background counting rates ranged from 0.14 to 0.19 cpm among the five detectors. The  $\alpha$  spectra of <sup>210</sup>Po (5.3 MeV) and <sup>209</sup>Po (4.8 MeV) were measured using an alpha spectrometer (Canberra series 7200–08, equipped with an A450-18AM PIPS detector with an active surface area of 450 mm<sup>2</sup>). The Canberra surface barrier

detector has a depletion depth of 60 µm thick, assembling with preamplifier, amplifier and biased amplifier units. The small depletion depth of the detector makes this system insensitive to  $\beta$  radiation so that counting signals are not recorded as a result of <sup>210</sup>Bi decay. A high purity germanium detector from ORTEC GMX70P4 was used for <sup>207</sup>Bi measurements. The overall detection efficiency at 569.60 keV for a thin layer of <sup>207</sup>Bi nickel source was 5.39%. The determination of stable lead (Pb<sup>2+</sup>) was carried out using an ICP-OES (Thermo Scientific iCAP 7400).

#### 2.3. Detector calibration

The detection efficiency for <sup>210</sup>Po was obtained by a standard mixture of <sup>241</sup>Am, <sup>239</sup>Pu, <sup>234</sup>U, and <sup>238</sup>U source (purchased from Seaboard Industrial Blvd. USA, ref. 67973–121) because <sup>241</sup>Am (5.6 MeV) has alpha particle energy similar to <sup>210</sup>Po. The detection efficiency for <sup>210</sup>Po ( $\eta_{det}$ (<sup>210</sup>Po)) was calculated based on the following equation:

$$\eta_{\rm det}(^{210}Po) = \frac{N(^{241}Am)}{t \times A^{241}Am} \tag{1}$$

where *t* is the counting time (s), *A* is the activity of the standard source  $(^{241}Am)$  (Bq) and *N* is the counts of the  $^{241}Am$  standard source in alpha spectrometry.

To obtain the counting efficiency of the beta counters, an aliquot of the stock standard solution was dried on all the types of the metallic discs, with care being taken to give the same source geometry as those deposition samples in the experiments. An aluminum absorber (6 mg cm<sup>-2</sup>) was placed over this disc to prevent the very low energy  $\beta$  ( $E_{\beta max}$  = 63.5 keV, from  $^{210}\text{Pb}$ ) and  $\alpha$  radiation ( $E_{\alpha}$  = 5.3 MeV, from  $^{210}\text{Po}$ ;  $E_{\alpha}$  = 4.8 MeV from  $^{209}\text{Po}$ ) from reaching the detector and to protect the beta counters from contamination.

The detection efficiency for  $^{210}$ Bi ( $\eta_{det}(^{210}$ Bi)) was calculated as follows:

$$\eta_{\rm det}(^{210}Bi) = \frac{N(^{210}Bi)}{t \times A_{\rm std}}$$
(2)

where *t* is the counting time (s), *A* represents the activity of the standard  $^{210}$ Bi dried on the disc (Bq) at the time of counting and *N* is the counts of the standard source.

## 2.4. Experimental set up to optimize the simultaneous plating of $^{210}\mathrm{Po}$ and $^{210}\mathrm{Bi}$

In order to determine the optimal conditions for the simultaneous auto-deposition of  $^{210}$ Po and  $^{210}$ Bi we tested the following factors: i) temperature and duration of the plating ii) surface area of the disc iii) volume of the plating solution iv) pH of the plating solution and v) type of metal discs used for the plating. The experiments were analyzed by considering the effect of each of these variables individually, while the remaining factors were kept constant to the previously established optimum conditions.

The solutions used for the batch experiments were prepared by adding 1-mL aliquots of the  $^{210}$ Po- $^{210}$ Bi- $^{210}$ Pb standard solution (9.36  $\pm$  0.12 dpm/mL) into filtrated seawater (40–100 mL; note that *in-situ*  $^{210}$ Po and  $^{210}$ Bi are negligible in these tens of milliliters of seawater compared to the added standard radionuclides). The solutions were acidified with HCl acid to reach the required pH for the plating (pH 0.5–1 for all the experiments except those where pH was the factor being examined).

Prior to use, circle metallic discs were cut from 0.1 mm thick sheets and washed with Milli-Q water and ethanol, and air dried. A thin adhesive Mylar backing was stuck on the unpolished side of the disc to prevent depositing. Later, the disc was tied using a thin nylon thread. The plating was carried out by suspending the prepared disc in the upper part of the solution contained in a Teflon beaker. Care was taken to prevent the clean surface of the disc from touching the side of the beaker. The plating solution was agitated gently via magnetic stirring.

After the completion of each experiment, the disc was removed from the solution, rinsed gently with Milli-Q water and ethanol and then air dried for half an hour. To prepare the samples for beta counting, the discs were fixed to a nylon disc and covered with a Mylar foil (<1 mg  $cm^{-2}$ ) and two layers of aluminum foil (<6 mg cm<sup>-2</sup>) to prevent  $\alpha$ particles from <sup>210</sup>Po decay registering counts. The prepared samples were stored for at least 10 h to allow for the decay of  $^{212}$ Bi (Energy = 2.25 MeV,  $T_{1/2} = 60$  min) and <sup>214</sup>Bi (Energy = 3.27 MeV,  $T_{1/2} = 20$  min) (this step is especially important for the natural environmental samples). When conducting the <sup>210</sup>Bi analyses, samples were counted at least 10 times over a period of more than 25 days (>5 half-life) to ensure that more than 95% of the <sup>210</sup>Bi had decayed away from the source (see supplementary material). Although  $^{228}$ Ac (half-life = 6.15 h) has similar  $E_{\beta max}$  (5.34 MeV) to that of <sup>210</sup>Bi (1.16 MeV), no signal of <sup>228</sup>Ac was observed for all the environmental sample, implying that there is no need to worry about the interference of  $^{228}$ Ac when Bi isotopes deposited onto Ni discs. After disassembling the sample, <sup>210</sup>Po activity was measured in the alpha spectrometer (Canberra series 7200-08). By checking all the alpha spectra of all the environmental sample discs deposited with <sup>210</sup>Po and <sup>209</sup>Po, no <sup>228</sup>Th (5.34 MeV) peak was observed although <sup>228</sup>Th has similar alpha energy to that of <sup>210</sup>Po (5.3 MeV). The background counting rate for each detector installed in this alpha spectrometer was carefully monitored and subtracted from the total counts for each peak region of interest.

#### 2.5. Environmental samples

Three different types of samples were used to test the effectiveness of this technique: i) an old sediment core collected from the ECS, ii) rainwater samples collected in Shanghai and iii) seawater samples from the ECS. Detailed treatments are presented in sections 3.2.1 and 3.2.2, but briefly, environmental samples were processed as follows:

-Sediment samples (0.5 g per sample) were spiked with suitable aliquots of <sup>209</sup>Po and <sup>207</sup>Bi and then completely digested using a mixture of mineral acids (HF: HClO<sub>4</sub>:HNO<sub>3</sub> = 1:1:1) at temperature <200 °C.

-Seawater (50–60 L) and rainwater (10–20 L) samples were also spiked with yield tracers of  $^{209}$ Po and  $^{207}$ Bi and had to be preconcentrated prior to their analyses. Based on the experiments, the pre-concentration method used was Fe(OH)<sub>3</sub> precipitates. The Fe(OH)<sub>3</sub> slurry was dissolved using a diluted HCl solution before plating.

The plating conditions used for all the environmental samples were those described as optimal during the experiments.

#### 3. Results and discussion

The specific activities of <sup>210</sup>Pb, <sup>210</sup>Pb and <sup>210</sup>Po in natural environment samples are typically low, 20–240 mBq/g (Persson and Holm, 2011), and even less than 20 mBq/g (Gao et al., 2017; Qiao et al., 2017). Due to those low specific activities, the volumes required to measure those radionuclides in marine samples (i.e. seawater and suspended materials in deep ocean) tend to be large, which can be a limiting factor. Therefore, improvements in recoveries of <sup>210</sup>Po and <sup>210</sup>Bi from limited sample sizes, can help us to process more samples, or allow greater precision for the same counting time.

#### 3.1. Optimization of the plating

In order to optimize the plating, we tested different factors that could have an influence: i) temperature and length of the plating time, ii) effect of surface area of the discs, iii) volume of the plating solution, iv) pH value of the solution, v) use of different metallic discs. The evaluation processes were iterated based on the previously established optimum conditions for each variable (Fig. 1). The results were reported as average  $\pm$  standard deviation based on three replicates.

#### 3.1.1. The effect of plating temperature and duration: auto-plating kinetics

In order to define the optimal plating time, we compared the autoplating kinetics of Po and Bi at room temperature (25  $^{\circ}$ C) and high temperature (80  $^{\circ}$ C). The recoveries of Po and Bi at different times are shown in Fig. 2. Plating of Po and Bi from solution onto the nickel discs were initially rapid, subsequently, the deposition rate decreased with time.

Hot plating at elevated temperature (e.g. 80 °C) can yield consistently higher recoveries of Po and Bi on to Ni disc than cold plating at room temperature (25 °C) before 8 h from our results (Fig. 2). Polonium begins to evaporate at high temperature (>150 °C), and organic complexes and halides of polonium are particularly volatile above 200 °C (Matthews et al., 2007). <sup>210</sup>Po losses due to evaporation are known to remain well below 1% in the temperature range of 150–250 °C, and increase to 14–90% at 300 °C–600 °C (Jia and Torri, 2007). In addition, maintaining a near-constant temperature in an aqueous solution on a hot plate for hours or in a heated water bath (higher than 80 °C) in shipborne laboratory could create safety concerns (e.g., possible empyrosis accident) and probable spills of solutions caused by unstable sea conditions. Considering these circumstances, cold plating at room temperature is recommended, although high temperature can induce a rapid deposition equilibrium.

At room temperature, the Po plating efficiency was found to increase



Fig. 2. Po and Bi recoveries as a function of plating time onto nickel discs at room temperature (25  $^\circ C$ ) and 80  $^\circ C.$ 



Fig. 1. Schematic of the work flow of the experiments. The titles of the different boxes indicate the factors being examined: Temperature and time, diameter of the metallic discs, volume of the plating solution, pH of the plating solution, different types of metallic discs. In italic blue font are the factors already tested and considered to be optimal. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

for the first stage (0–16 h) reaching a maximum value of ~80% at 16 h (Fig. 2). In addition, the lower yield of Po (~65%) is presumably due to the fact that the surface of nickel disc was seriously dissolved as a result of the oxidation of nickel metal to Ni<sup>2+</sup> (Porntepkasemsan et al., 2011) and we did observe that the solution became green. Hence, after a long plating time, the plated Po and Bi may have been removed from the disc surface as the nickel disc was badly corroded by H<sup>+</sup>, which caused the decrease of the recovery. Interestingly, the curve of Bi deposition efficiency for cold plating increased from 2 h (about 30%) to 36 h with a maximum value close to 88%. This suggests that the plating time should be more than 16 h, but no more than 24 h to obtain good recoveries for both radionuclides under cold plating conditions. Reducing the plating time at room temperature could be an option to improve the sample analysis throughput, but it will lower the recovery and increase the counting time.

The kinetic mechanism controlling and determining the efficiency of the auto-deposition process for <sup>210</sup>Po and <sup>210</sup>Bi was simulated using a pseudo-second order equation (Liu et al., 2016; Sun and Wang, 2006) to validate the experimental data. The pseudo-second-order kinetic model is based on the assumption that adsorption rates are controlled by chemical adsorption mechanisms that involve electron sharing or electron transfer between adsorbents and adsorbates. The pseudo-second order kinetic equation is given as follows:

$$\frac{t}{q_t} = \frac{1}{k \cdot q_e^t} + \frac{t}{q_e} \tag{3}$$

$$q_{i} = \frac{A_{disc}}{S_{disc}}$$
(4)

where  $q_t$  and  $q_e$  (dpm/490 mm<sup>2</sup>) are the amounts of deposited <sup>210</sup>Po or <sup>210</sup>Bi on the disc at time *t* and at equilibrium, respectively;  $A_{disc}$  is the activity of <sup>210</sup>Po or <sup>210</sup>Bi deposited on nickel (dpm);  $S_{disc}$  is the area of the disc (490 mm<sup>2</sup>); *k* is the rate constant of pseudo-second-order kinetic model (490 mm<sup>2</sup>/(h·dpm)). The pseudo-second order kinetics models of <sup>210</sup>Po and <sup>210</sup>Bi at room temperature were linear with a positive correlation with plating time (R<sup>2</sup> = 0.9688 and 0.9926 for <sup>210</sup>Po and <sup>210</sup>Bi, respectively) (Fig. 3). From these two parameters R<sup>2</sup> value and  $q_{e,cal}$  and  $q_{e,exp}$  for <sup>210</sup>Po and <sup>210</sup>Bi auto-deposition process noted in Table 1, from the agreement of  $q_{e,cal}$  and  $q_{e,exp}$  can be deduced that the pseudo-second order kinetic model fits the auto-plating process well, and that the plating process is chemically controlled (Liu et al., 2016; Sun and Wang, 2006) and related to electron transfer.

#### 3.1.2. The effect of the active surface area of the disc

The surface areas of the discs used in prior studies ranged from 100  $\text{mm}^2$  (Murray et al., 2005) to 1963  $\text{mm}^2$  (Sanchez-Cabeza et al., 1998). To estimate the effect of disc size on the recoveries of <sup>210</sup>Po and <sup>210</sup>Bi from the sample solution, six nickel discs with different diameter sizes, ranging from 17 mm (surface area: 227 mm<sup>2</sup>) to 30 mm (surface area: 707 mm<sup>2</sup>), were investigated for both radionuclides.

#### Table 1

Kinetic parameters derived from the pseudo-second order models for  $^{210}$ Po and  $^{210}$ Bi auto-deposition onto nickel discs at room temperature (25 °C).

Kinetic parameter	Value of <sup>210</sup> Po	Value of <sup>210</sup> Bi
k (490mm²/(h·dpm))	$9.40 imes10^{-2}$	$2.10 imes10^{-2}$
q <sub>e,cal</sub> (dpm/490 mm <sup>2</sup> )	6.67	9.09
R <sup>2</sup>	0.9688	0.9926
$q_{e,exp}$ (dpm/490 mm <sup>2</sup> )	6.79	8.22

The results indicated that the overall yield percentage of <sup>210</sup>Po and <sup>210</sup>Bi was highest for the 490 mm<sup>2</sup> (diameter = 25 mm) disc (Fig. 4). The maximum theoretical geometric counting efficiency for alpha and beta detectors would be achieved with a sample disc area equal to that of the detector (Fig. 4), and with the sample in proximity to the detector surface within a constant distance (0.6 cm for both alpha spectrometry and beta detector). Lee et al. (2014) pointed that due to differences in the solid angle subtended by the discs, the alpha detector efficiency was lower for areas that were smaller or larger than the size of the active area of the detector. Therefore, it is recommended to use nickel discs sized identically to the detector to obtain the best efficiencies.

#### 3.1.3. The effect of the volume of solution on auto-plating recoveries

Spontaneous deposition can be carried out either in a small volume of acid media or by simple immersion of a disc with one side covered in a larger volume of acid solution. Therefore, we tested the auto-plating efficiencies of <sup>210</sup>Po and <sup>210</sup>Bi from a series of solutions with different



Fig. 4. Effect of disc size on auto-deposition counting efficiency (%) of  $^{210}$ Po and  $^{210}$ Bi. The active area of the PIPS detector and the beta counter was 490 mm<sup>2</sup> (diameter = 25 mm).



Fig. 3. Pseudo-second-order kinetics plot for <sup>210</sup>Po and <sup>210</sup>Bi deposited on 25 mm discs at room temperature (25 °C).

volumes (40, 50, 60, 70, 80, 90, and 100 mL). The results of the experiments on plating solution volume are shown in Fig. 5. The yield of  $^{210}$ Po and  $^{210}$ Bi auto-plating onto nickel disc in seven different volumes ranged from 65% to 95% (Fig. 5). Recoveries of  $^{210}$ Po and  $^{210}$ Bi decreased with increasing volume, the ideal volume to plate both radionuclides would be 50 mL but 60 mL of solution was required to completely immerse the suspended disc and to thoroughly dissolve more inorganic salts residue after sediments or suspended matter were digested.

#### 3.1.4. The influence of the pH of solution on auto-plating recoveries

We assessed six solutions with H<sup>+</sup> concentration varying from 0.001 M (pH = 3) to 1 M (pH = 0) for three common acids (nitric, hydrochloric and sulfuric acid) and obtained the maximum recovery value at pH 0.5 (~0.3M) for both <sup>210</sup>Po and <sup>210</sup>Bi and for the three acids (Fig. 6). Deposition of <sup>210</sup>Po is slightly affected by variations of acidity within the studied range. In contrast, <sup>210</sup>Bi recoveries decreased substantially with increasing pH values > 0.5.

Previous reports indicate that most of the platings had been done with hydrochloric acid solution (Kim et al., 2009; Casacuberta et al., 2009; Desideri et al., 2009; Bonotto et al., 2009; Sadi et al., 2016), based on the possibility that silver discs were dissolved by nitric acid. However, our results suggest that no matter what kind of acid was chosen, the excessive corrosion of nickel discs at lower pH (<3) was prevalent. Therefore, the recommended acidity of the plating solution is a pH from 0.5 to 1 under nitric acid or hydrochloric media. The use of sulfuric acid is not recommended, due to the production of insoluble sulfate during plating especially for the soil/sediment's digestion solution.

#### 3.1.5. The effect of the type of metallic discs

Throughout the literature the application of all types of metals are mentioned for <sup>210</sup>Po analyses, including copper (Mackenzie and Scott, 1979; Vreček et al., 2004), nickel (Blanchard, 1966), stainless steel (Guérin and Dai, 2015), silver (Lee et al., 2014; Murray et al., 2005; Sanchez-Cabeza et al., 1998), bismuth (Figgins, 1961), and other noble metals such as platinum, palladium and gold. However, there are few reports about plating of <sup>210</sup>Bi onto metallic discs. Blanchard (1966) measured <sup>210</sup>Pb in environmental samples by depositing <sup>210</sup>Bi onto nickel disc. Church et al. (1994) developed an efficient quantitative technique for simultaneous analyses of <sup>210</sup>Pb, <sup>210</sup>Bi, and <sup>210</sup>Po in atmospheric and oceanic samples, in which purification and analysis of <sup>210</sup>Bi was achieved by auto-plating onto Ni. In this study, four common metallic materials, silver (Ag), nickel (Ni), copper (Cu) and stainless steel (SS) were used to investigate the deposition yield of both <sup>210</sup>Po and <sup>210</sup>Bi at room temperature (see Fig. 7A.)



Fig. 5. Effect of the solution volume (mL) on recoveries of  $^{210}\mathrm{Po}$  and  $^{210}\mathrm{Bi}$  plating.



Fig. 6. Effect of acidity of the plating solution on <sup>210</sup>Po and <sup>210</sup>Bi recoveries.

The results obtained showed similar Po recoveries for Ag and Ni discs (>80%) and lower values for Cu (68%) and SS (stainless steel) discs. Furthermore, good energy resolution for <sup>210</sup>Po alpha-spectrometry measurements were observed in all cases with relatively low FWHM values (Ni < Ag < Cu < SS) less than 30 keV (Fig. 7B). However, for Bi, spontaneous deposition does not occur on silver and copper discs at cold plating conditions (Fig. 7A) but recoveries >80% were found for nickel and stainless-steel discs. Mackenzie and Scott (1979) observed that <sup>210</sup>Bi and <sup>210</sup>Po are rapidly and efficiently removed from aqueous solution by spontaneous deposition of copper foils at high temperature (>90 °C), and then rapid desorption of <sup>210</sup>Bi occurs at room temperature, leaving a pure source of <sup>210</sup>Po on the copper disc.

On the basis of these observations and in regard to the resolution and recovery, subsequent experiments were carried out by plating both radionuclides onto nickel disc.

#### 3.1.6. Pre-concentration of <sup>210</sup>Bi from seawater samples

Due to the low specific activities of <sup>210</sup>Pb, <sup>210</sup>Bi and <sup>210</sup>Po in natural environment samples such as seawater, the volumes required to measure those radionuclides are large (tens of liters) and the sample processing, hence, require a pre-concentration step prior to the radiochemical analysis.

Previous research has reported many co-precipitation methods to pre-concentrate Po via ammonium pyrrolidinedithiocarbamate (APDC) co-precipitation with cobalt (APDC-Co, Fleer and Bacon, 1984), or with lead (APDC-Pb, Kadko, 1993), iron hydroxides (Fe(OH)<sub>3</sub>) and manganese dioxide (MnO<sub>2</sub>) precipitation (Lee et al., 2014). However, com-parison of co-precipitators to pre-concentrate <sup>210</sup>Bi from seawater has not been reported vet. Due to the short half-life of  $^{210}$ Bi (T<sub>1/2</sub> = 5.01 d), a fast and effective concentration method is needed. Here we compared five frequently-used co-precipitators (Fe(OH)<sub>3</sub>, Al(OH)<sub>3</sub>, MnO<sub>2</sub>, Cu<sub>2</sub>Fe (CN)6 and BaSO4) in order to find the most suitable method to co-precipitate <sup>210</sup>Bi from seawater. Seawater samples (50-60 L) were collected from the ECS. After acidification with HCl acid, a known quantity of <sup>207</sup>Bi (tracer for <sup>210</sup>Bi) was added and allowed to equilibrate for several hours to reach isotopic equilibrium. After adding FeCl<sub>3</sub> or AlCl<sub>3</sub> to the acidified solution, Fe(OH)<sub>3</sub> or Al(OH)<sub>3</sub> was generated by adjusting pH > 7 with NH<sub>4</sub>(OH). MnO<sub>2</sub> precipitate was produced by adding KMnO<sub>4</sub>, MnCl<sub>2</sub> and NH<sub>4</sub>(OH) to the acidified seawater sample. Cu<sub>2</sub>Fe(CN)<sub>6</sub> co-precipitator was generated by mixing a Cu(NO<sub>3</sub>)<sub>2</sub> and K<sub>4</sub>Fe(CN)<sub>6</sub> solutions. BaSO<sub>4</sub> was generated by adding BaCl<sub>2</sub> and Na<sub>2</sub>SO<sub>4</sub> solution to the acidified seawater. Precipitates were isolated by centrifugation at 5000 rpm for 30 min. The <sup>207</sup>Bi activities were then measured through  $\gamma$  spectrometry.



Fig. 7. Comparison of Po and Bi recovery on four different metallic discs (A). Energy resolution for <sup>210</sup>Po in all four cases was observed with relatively low full weight half maximum (FWHM) for Ag and Ni discs (B).

The <sup>210</sup>Bi recoveries for these five co-precipitators (two replicates for each precipitation method) are shown in Fig. 8. Cu<sub>2</sub>Fe(CN)<sub>6</sub> and BaSO<sub>4</sub> are not recommended due to their low recoveries (<60%). MnO<sub>2</sub> and Al (OH)<sub>3</sub> show high recoveries (>80%) for <sup>207</sup>Bi, however, these two precipitation methods take a relatively long time when filtering or centrifuging the precipitates. Interestingly, from this figure, it may be noted that Fe(OH)<sub>3</sub> can pre-concentrate almost 100% of <sup>207</sup>Bi from seawater.

Iron is widely present in most environmental samples such as sediments, soils, aerosols, biological tissues and water and Fe<sup>3+</sup> is frequently used to pre-concentrate Po and other radionuclides from seawater as a convenient method to reduce the sample volume (Huang et al., 2013; Su et al., 2017). Hence, Fe(OH)<sub>3</sub> co-precipitation is strongly recommended to simultaneously pre-concentrate <sup>210</sup>Po and <sup>210</sup>Bi from saewater samples.

However, iron interferes with the auto-plating of <sup>210</sup>Po onto metallic discs (Figgins, 1961; Benoit and Hemond, 1988; Lee et al., 2014), hence various reducing or complexing agents, containing ascorbic acid, hydrazine hydrochloride, hydroxylamine hydrochloride and citrate, have been used to avoid this interference. Lee et al. (2014) evaluated these reagents and concluded that ascorbic acid was more effective than hydroxylamine hydrochloride. Based on that study, we decided to use ascorbic acid as the reducing agent to eliminate the Fe<sup>3+</sup> present in the samples.

The amount of  $Fe^{3+}$  added to co-precipitate Po from seawater samples generally requires about 100 mg of  $Fe^{3+}$  per sample (10–20 L



Fig. 8. <sup>207</sup>Bi (<sup>210</sup>Bi) recovery (%) versus co-precipitation method.



Fig. 9. Effect of ascorbic acid amount (mg) on <sup>210</sup>Po and <sup>210</sup>Bi recoveries.

seawater) (Lee et al., 2014; Su et al., 2017). In order to assess the effects of the reducing agent on the Po and Bi recoveries, different amounts (from tens of mg to 500 mg) of ascorbic acid were added to each sample solution containing 100 mg of Fe<sup>3+</sup> (Fig. 9). The maximum recovery of <sup>210</sup>Po, i.e. 95%, was achieved by adding 300 mg of ascorbic acid. The highest deposition yield of <sup>210</sup>Bi was found to be 92.5 ± 2.7%, with 150 mg ascorbic acid. To obtain good recoveries for both <sup>210</sup>Po and <sup>210</sup>Bi, it is suggested that at least 200 mg ascorbic acid is suitable to eliminate the interference of 100 mg of Fe<sup>3+</sup> for auto-plating.

# 3.2. Application of the method for determination of $^{210}$ Po and $^{210}$ Bi in environmental samples

In the previous sections we have tested a number of factors that have an effect on the recoveries of Po and Bi to elucidate what are the optimal conditions to conduct a room temperature plating for both elements. The results are summarized in Table 2.

The optimized plating conditions where then applied to environmental samples. Three different types of samples were used to test the effectiveness of this technique: i) an old sediment core collected from the ECS, ii) rainwater samples collected in Shanghai and iii) seawater samples from the ECS. The analytical scheme for the determination of  $^{210}$ Po,  $^{210}$ Pi, and  $^{210}$ Pb in these environmental samples is outlined in Fig. 10.

The <sup>210</sup>Pb concentration in sediments were directly measured by gamma spectrometry as described in Huang et al. (2013) due to its high activity. But the <sup>210</sup>Pb in seawater and rainwater could be very low,

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#### Table 2

Recommended conditions for the plating of  $^{210}\mathrm{Po}$  and  $^{210}\mathrm{Bi}$  at room temperature.

Factor	Recommended condition
Plating time	16 h
Acid	HCl or HNO <sub>3</sub>
Disc diameter	25 mm
Volume of plating solution	60 mL
pH of plating solution	0.5
Disc metal type	Nickel
Pre-concentration method	Fe(OH) <sub>3</sub>
Ascorbic acid content	150–300 mg/100 mg ${\rm Fe}^{3+}$

hence, the determination of  $^{210}$ Pb in water samples was done following the procedure described in Bacon et al. (1988), where removing nearly all the residual  $^{209}$ Po and  $^{210}$ Po was done by auto-plating with another clean Ag disc. After 6 months storage,  $^{210}$ Pb was obtained by a second Ag auto-plating with the addition of new  $^{209}$ Po.

### 3.2.1. <sup>210</sup>Po and <sup>210</sup>Bi determination in sediments

The specific procedures for total dissolution of sediment samples are briefly described as follows: 0.5 g of sediment sample together with 20 mg Pb<sup>2+</sup> carrier, 2 dpm of <sup>209</sup>Po tracer, 30 dpm of <sup>207</sup>Bi tracer, and 10 mL of mixed acid (HF: HClO<sub>4</sub>: HNO<sub>3</sub> = 1:1:1) were added to a 100 mL Teflon beaker. The beaker was heated at <200 °C. The solution was evaporated to near dryness and 5 mL of HClO<sub>4</sub> were added. The solution was repeated until a colorless residue was obtained. The residue was finally dissolved with 60 mL of 0.3 M (pH ~ 0.5) HCl acid. Then, auto-plating of <sup>210</sup>Po and <sup>210</sup>Bi onto nickel discs was done at the recommended optimum conditions mentioned in section 3.2.

As mentioned in section 2.1, a sediment core from the ECS, station DH3-6, was collected in 2010. The sedimentary material was stored for long time (>2 years), thus <sup>210</sup>Po and <sup>210</sup>Bi are expected to be in secular equilibrium with <sup>210</sup>Pb, and the <sup>210</sup>Po and <sup>210</sup>Bi activities can be used as a proxy to determine the <sup>210</sup>Pb concentration in the sediment core.

The mean recovery was 91.1  $\pm$  4.2% for <sup>209</sup>Po and 92.7  $\pm$  12.9% for <sup>207</sup>Bi (Table 3). The vertical distributions of <sup>210</sup>Po, <sup>210</sup>Bi and <sup>210</sup>Pb along the core from the surface down to 21 cm depth, are illustrated in Fig. 11 and shown in Table 3. Except for some sediment layers (e.g., ~3 cm, ~15 cm, ~21 cm layers), the downcore variation of each profile and the specific activities of three radionuclides are in good agreement with

each other and within uncertainties ( $\pm 10\%$ ) (Table 3). These results suggest that <sup>210</sup>Po and <sup>210</sup>Bi can substitute the typical <sup>210</sup>Pb-dating method in some situations, for example, if one gets many fresh cores, and there is only one gamma spectrometer, then it will take many days to measure them all, but if we store the cores only for 25–30 days, then <sup>210</sup>Bi and <sup>210</sup>Pb will be in secular equilibrium and we could measure <sup>210</sup>Bi instead of <sup>210</sup>Pb to save time.

#### 3.2.2. <sup>210</sup>Po and <sup>210</sup>Bi determination in sea and rain waters

Seawater samples (50–60 L per sample) were collected at two stations and two depths (0 and 60 m) in the ECS. Samples were filtered through a 0.45  $\mu$ m pore membrane filter to separate it into the dissolved

#### Table 3

Recoveries of  $^{209}\text{Po}$  and  $^{207}\text{Bi}$  and the specific activities of  $^{210}\text{Po},$   $^{210}\text{Bi}$  and  $^{210}\text{Pb}$  found in sediment core DH3-6 samples. Uncertainties are  $1\sigma$  values of counting statistics.

Sample	Recovery <sup>209</sup> Po	<sup>210</sup> Po	Recovery <sup>207</sup> Bi	<sup>210</sup> Bi	<sup>210</sup> Pb
-	(%)	(Bq/	(%)	(Bq/	(Bq/
		kg)		kg)	kg) <sup>a</sup>
DH3-6	85.3	55.8 $\pm$	110.7	56.9 $\pm$	$43.9~\pm$
0–1 cm		3.5		5.5	7.8
DH3-6	89.4	$60.7~\pm$	91.3	59.4 $\pm$	59.1 $\pm$
1–2 cm		3.9		5.4	9.6
DH3-6	94.9	$65.3~\pm$	102.1	66.7 $\pm$	$68.2~\pm$
2–3 cm		4.2		6.2	6.0
DH3-6	95.6	51.1 $\pm$	78.1	$65.0~\pm$	46.2 $\pm$
3–4 cm		3.3		8.2	7.7
DH3-6	93.7	64.7 $\pm$	92.7	65.0 $\pm$	62.9 $\pm$
4–5 cm		4.0		5.0	8.7
DH3-6	86.6	44.5 $\pm$	97.5	46.7 $\pm$	$34.8~\pm$
9–10		2.9		4.4	10.2
cm					
DH3-6	91.4	33.1 $\pm$	85.9	40.5 $\pm$	30.1 $\pm$
14-15		2.2		4.2	9.8
cm					
DH3-6	95.9	$\textbf{28.4} \pm$	104.5	$29.0~\pm$	$18.9~\pm$
17–18		2.0		2.9	8.2
cm					
DH3-6	86.6	$21.1~\pm$	70.6	17.7 $\pm$	11.0 $\pm$
20-21		1.4		1.9	6.3
cm					
Average	$91.1 \pm 4.2$		$\textbf{92.7} \pm \textbf{12.9}$		

<sup>a</sup> Data obtained directly from γ spectrometry.



**Fig. 10.** Analytical scheme for the determination of  $^{210}$ Po,  $^{210}$ Bi, and  $^{210}$ Pb in sediment (line 1), seawater (line 2), and rainwater (line 3) samples. Procedures in red dashed boxes were accomplished on the scientific research ship (*Runjiang II*). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)



Fig. 11. Vertical distributions of  $^{210}\mathrm{Po},~^{210}\mathrm{Bi}$  and  $^{210}\mathrm{Pb}$  along the ECS sediment core.

(<0.45 µm) and particulate (>0.45 µm) phases (Fig. 10). The seawater sample preparation was completed on a small scientific research ship due to half-life of <sup>210</sup>Bi (Fig. 10). The particulate phases were digested by mixing with acid (HF: HClO<sub>4</sub>: HNO<sub>3</sub> = 1:1:1) until the filter was dissolved and there was a colorless residue, similar to the procedure applied to the sediment samples on the ship within 6–8 h.

A total of 10 rainwater samples (10–20 L per sample) were collected in Shanghai between September 2016 and April 2018. Rainwater and the dissolved fraction of seawater samples were treated by coprecipitation with Fe(OH)<sub>3</sub>. Samples were acidified by adding concentrated HCl acid until a pH of 1 was reached. For the large volume seawater sample (50–60 L), 500 mg Fe<sup>3+</sup> were added. For the rainwater sample (10–20 L), 100–200 mg Fe<sup>3+</sup> were added. Then, 20 mg of Pb<sup>2+</sup> carriers, 2 dpm of <sup>209</sup>Po tracer and 30 dpm <sup>207</sup>Bi were added to the acidified rainwater and seawater samples. After allowing for isotope equilibrium (1–2 h stirring), the solution was adjusted to a pH of 9 by adding a concentrated ammonia solution and mixing well to create the hydroxides precipitates. After 6–8 h, the precipitate had sunk, and the supernatant was carefully siphoned off. The hydroxide slurry was centrifuged at 5000 rpm and the remaining supernatant was discarded. The precipitate was dissolved within 60 mL of 0.3 M HCl solution. The subsequent analyses are the same as those described above for the sediment samples. All the experimental procedure was conducted within the following day of sample collection to minimize the decay and ingrowth of  $^{210}$ Bi.

In seawater samples, overall recoveries of  $^{209}$ Po,  $^{207}$ Bi and Pb $^{2+}$  were >60% (62-89% for <sup>209</sup>Po, 66-92% for <sup>207</sup>Bi, 65-80% for Pb<sup>2+</sup>) (Table 4). Concentrations ranged from 4.31 to 7.59 dpm/100L for  $^{210}$ Po, from 3.74 to 18.37 dpm/100L for <sup>210</sup>Bi and from 3.36 to 18.83 dpm/ 100L for <sup>210</sup>Pb. Biggin et al. (2002) reported the particulate and dissolved <sup>210</sup>Po, <sup>210</sup>Bi and <sup>210</sup>Pb activity concentrations in the Irish Sea by LSC method, which were much lower than those values reported in the ECS (Table 4). The results indicate that <sup>210</sup>Po and <sup>210</sup>Bi activity concentrations at station A8-4 at 60 m layer were higher than that of <sup>210</sup>Pb for the particulate phase, but at the surface of station A7-5, <sup>210</sup>Po and <sup>210</sup>Bi concentration were lower than <sup>210</sup>Pb for the dissolved and particulate phases, showing a deficiency of <sup>210</sup>Po and <sup>210</sup>Bi relative to <sup>210</sup>Pb. Besides, the percentages of particulate <sup>210</sup>Po, <sup>210</sup>Bi, and <sup>210</sup> Pb at 60 m layer of station A8-4 were 43.3% for <sup>210</sup>Po, 60.6% for <sup>210</sup>Bi, 31.3% for <sup>210</sup>Pb, respectively (Table 5). And the percentages in surface water of station A7-5 became 54.7%, 16.9%, and 44.2% for <sup>210</sup>Po, <sup>210</sup>Bi, and <sup>210</sup>Pb, respectively (Table 5). However, the percentages of particulate  $^{210}$ Po (83.4%) and  $^{210}$ Bi (90.6%) in the Irish Sea were much higher than those in the ECS (Table 5), indicating that marine particles in different sea areas have different accumulation ability for <sup>210</sup>Po, <sup>210</sup>Bi, and <sup>210</sup>Pb.

In rainwater samples, overall recoveries were >70% (75.0  $\pm$  9.4% for <sup>209</sup>Po, 73.5  $\pm$  11.2% for <sup>207</sup>Bi, and 76.9  $\pm$  6.7% for Pb<sup>2+</sup>), with <sup>210</sup>Po, <sup>210</sup>Bi, and <sup>210</sup>Pb activity concentrations ranging from 0.14 to 0.86 dpm/L , from 1.08 to 6.20 dpm/L and from 1.15 to 25.82 dpm/L, respectively (Table 6). In all the rainwater samples, the <sup>210</sup>Pb/<sup>210</sup>Po ratios were found to be in the range of 4–53, while the <sup>210</sup>Pb/<sup>210</sup>Bi ratios were 0.8–5.2. The <sup>210</sup>Pb which indicate that the equilibrium state between <sup>210</sup>Bi and <sup>210</sup>Pb may exist due to a longer residence time of aerosols in these three rainfall events. Although there are exceptions, disequilibrium between those two daughter radionuclides and <sup>210</sup>Pb did exist (Narita et al., 1989; Poet et al., 1972; Tokieda et al., 1994). The disequilibrium between <sup>210</sup>Po or <sup>210</sup>Bi and <sup>210</sup>Pb can be applied to estimate atmospheric residence times and atmospheric dynamics (Chen et al., 2016), because these three radionuclides are particle-reactive, and

Table 5

The calculated percentages of particulate <sup>210</sup>Po, <sup>210</sup>Bi, and <sup>210</sup>Pb.

Sample name	% Particul	ate	References		
	<sup>210</sup> Po	<sup>210</sup> Bi	<sup>210</sup> Pb		
A8-4-60m	43.3%	60.6%	31.3%	This study	
A7-5-0m	54.7%	16.9%	44.2%		
Irish Sea-SW	83.4%	90.6%	31.9%	Biggin et al. (2002)	

Table 4

Recoveries of <sup>209</sup>Po, <sup>207</sup>Bi and Pb<sup>2+</sup> and specific activity of <sup>210</sup>Po, <sup>210</sup>Bi and <sup>210</sup>Pb found in seawater samples.

Sample	Longitude	Latitude	Sampling date	Volume	Recovery (%)		Activity (dpm/100L)			References	
				(L)	<sup>209</sup> Po	<sup>207</sup> Bi	$Pb^{2+}$	<sup>210</sup> Po	<sup>210</sup> Bi	<sup>210</sup> Pb <sup>b</sup>	
A8-4-60m-D <sup>a</sup> A8-4-60m-P <sup>a</sup>	123.26°E	30.05°N	2017/5/8	55.3	89.1 83.3	66.0 91.6	72.9 80.3	$\begin{array}{c} 7.59\pm0.29\\ 5.79\pm0.34\end{array}$	$\begin{array}{c} 5.33\pm0.37\\ 8.19\pm0.57\end{array}$	$\begin{array}{c} 7.38\pm0.37\\ 3.36\pm0.17\end{array}$	This study
A7-5-0m-D <sup>a</sup> A7-5-0m-P <sup>a</sup>	123.49°E	30.26°N	2017/5/13	52.1	80.0 62.2	72.0 91.1	64.8 69.5	$\begin{array}{c} 4.31 \pm 0.30 \\ 5.21 \pm 0.33 \end{array}$	$\begin{array}{c} 18.37 \pm 1.29 \\ 3.74 \pm 0.26 \end{array}$	$\begin{array}{c} 18.83 \pm 0.94 \\ 14.89 \pm 0.74 \end{array}$	
Irish Sea-SW-D Irish Sea-SW-P	3.63°W	54.51°N	2000/9/11	20	NA NA	NA NA	NA NA	$\begin{array}{c} 0.61 \pm 0.09 \\ 3.06 \pm 0.23 \end{array}$	$\begin{array}{c} 0.54\pm0.12\\ 5.22\pm0.47\end{array}$	$\begin{array}{c} 3.84\pm0.40\\ 1.80\pm0.23\end{array}$	Biggin et al. (2002)

NA: not available.

<sup>a</sup> Note: D and P in sample code refer to dissolved (<0.45 μm) and particulate (>0.45 μm) fraction, respectively.

 $^{\rm b}~^{210}{\rm Pb}$  activity was derived from  $^{210}{\rm Po}$  ingrowth after storage for 1 year.

Table 6

RECOVERIES OF TO, DEALINED AND THE SDECTIL ACTIVITY OF TO, DEALINE TO INFAMILY ACTIVITY OF	Recoveries of <sup>209</sup> Pc	$^{207}$ Bi and Pb <sup>2+</sup> and the	specific activity of <sup>210</sup> Po.	<sup>210</sup> Bi and <sup>210</sup> Pb	in rainwater samp
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Sample	Sampling date	Volume	Recovery (%)	1		Activity (dpm/L)		<sup>210</sup> Pb/ <sup>210</sup> Po	<sup>210</sup> Pb/ <sup>210</sup> Bi	
		(L)	<sup>209</sup> Po	<sup>207</sup> Bi	Pb <sup>2+</sup>	<sup>210</sup> Po	<sup>210</sup> Bi	<sup>210</sup> Pb		
RW-1	2016/9/15	19.9	60.4	62.0	80.8	$0.14\pm0.01$	$1.36\pm0.11$	$1.15\pm0.13$	8.2	0.8
RW-2	2016/9/16	20.4	84.1	85.6	80.5	$0.19\pm0.01$	$1.08\pm0.08$	$1.49 \pm 0.15$	7.8	1.4
RW-3	2016/11/7	12.6	69.4	75.1	64.7	$\textbf{0.86} \pm \textbf{0.05}$	$6.20\pm0.50$	$18.71 \pm 1.71$	21.8	3.0
RW-4	2016/12/25	9.9	83.6	80.6	70.9	$0.53\pm0.06$	$3.86 \pm 0.27$	$3.15\pm0.30$	5.9	0.8
RW-5	2017/4/10	10.2	63.1	73.9	71.7	$0.83\pm0.04$	$6.19\pm0.46$	$25.82 \pm 1.55$	31.1	4.2
RW-6	2017/6/5	23.5	75.4	72.3	68.8	$0.22\pm0.01$	$\textbf{2.41} \pm \textbf{0.17}$	$11.73\pm1.06$	53.3	4.9
RW-7	2017/6/10	9.2	82.9	43.0	79.4	$0.47\pm0.03$	$2.33\pm0.18$	$12.11 \pm 1.33$	25.8	5.2
RW-8	2017/10/15	12.0	88.8	71.6	92.0	$0.50\pm0.03$	$2.29\pm0.17$	$1.79\pm0.16$	3.6	0.8
RW-9	2018/3/20	10.2	70.1	77.6	74.0	$0.65\pm0.09$	$3.69\pm0.26$	$18.30\pm1.35$	28.2	5.0
RW-10	2018/4/23	23.7	83.5	71.5	71.2	$0.35\pm0.03$	$\textbf{2.67} \pm \textbf{0.20}$	$3.57\pm0.30$	10.2	1.3
Mean $\pm \sigma$ :			$\textbf{76.1} \pm \textbf{9.4}$	$71.3 \pm 11.1$	$\textbf{75.4} \pm \textbf{7.5}$					
Range:						0.14-0.86	1.08-6.20	1.15 - 25.82	3.6–53.3	0.8–5.2

secular equilibrium between <sup>210</sup>Pb and its two daughters is generally not observed due to the limited existence of the aerosol particles in the air before their deposition (residence time).

#### 4. Conclusion

This study investigates the optimum conditions for the auto-plating of both <sup>210</sup>Po and <sup>210</sup>Bi at room temperature ( $25 \pm 1$  °C) to facilitate the sample processing for the determination of these radionuclides when high temperature plating is a limiting factor. The results indicate that the optimum conditions are achieved when the plating is conducted using 25 mm nickel disc, for 16 h with a 60 mL HNO<sub>3</sub> or HCl media solution with the presence of 150–300 mg ascorbic acid per 100 mg Fe added when Fe(OH)<sub>3</sub> co-precipitation is required.

The optimized method was then used on three types of environmental samples, sediments, seawater, and rainwater. Recoveries over 90% for <sup>209</sup>Po and <sup>207</sup>Bi were obtained in sediment samples and <sup>210</sup>Po, <sup>210</sup>Bi, and <sup>210</sup>Pb were found to be in secular equilibrium, as expected, confirming the applicability of this method in sediment samples and supporting the use of <sup>210</sup>Po and <sup>210</sup>Bi for sediment dating applications when those isotopes are expected to be in secular equilibrium with <sup>210</sup>Pb. Seawater and rainwater samples were also successfully analyzed, with recoveries >60%. This room temperature optimized plating method will facilitate the use of <sup>210</sup>Po, <sup>210</sup>Bi, and <sup>210</sup>Pb as tracers of particles in marine and atmospheric environment.

#### Declaration of competing interest

The authors declare no conflict of interest.

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#### Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jenvrad.2020.106301.

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