Measuring bismuth-210, its parent, and daughter in aquatic systems

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Abstract

$^{210}$Bi ($t_{1/2}: 5.01$ d)—the daughter of $^{210}$Pb and parent of $^{210}$Po—has rarely been measured in aquatic systems, and its behavior in the water column is poorly understood. In this article, I present a method for quickly measuring $^{210}$Pb, $^{210}$Bi, and $^{210}$Po in aquatic samples, where (1) $^{210}$Bi and $^{210}$Po are scavenged onto an anion solid-phase extraction disk within 15 min of pretreating the sample; (2) beta decay of $^{210}$Bi is counted on the disk immediately thereafter; (3) $^{210}$Po is subsequently removed from the disk and redeposited on a copper plate for alpha-spectroscopy; and (4) $^{210}$Pb is determined via the ingrowth of $^{210}$Bi. I present decay-corrected calculations for total, dissolved, and particle-bound fractions of each nuclide and conclude with an analysis of $^{210}$Pb, $^{210}$Bi, and $^{210}$Po activities in rain, dreissenid (quagga) mussels, and water samples from the Milwaukee Inner Harbor in Lake Michigan. Results show that the loss of lead on the anion solid-phase extraction disks was negligible ($0.2\% \pm 2.1\% \pm 1$ SD, $n = 4$), and the sorption of bismuth was complete ($99\% \pm 2\% \pm 1$ SD, $n = 16$). Relative mean absolute deviations of duplicate sample analyses of lake water were $2.4\% \pm 1.9\%$ for $^{210}$Pb (geometric mean of total sample activity: 3.0 disintegrations per minute [dpm], $n = 6$), $7.7\% \pm 5.8\%$ for $^{210}$Bi (geometric mean of total sample activity: 2.6 dpm, $n = 8$), and $2.7\% \pm 1.7\%$ for $^{210}$Po (geometric mean of total sample activity: 1.4 dpm, $n = 8$).

Over the past 50 years, the naturally occurring radionuclide of lead-210 ($^{210}$Pb $t_{1/2}: 22.3$ years) and its granddaughter polonium-210 ($^{210}$Po $t_{1/2}: 138.4$ d) have been measured and used as a tracer of particle flux in the water column (e.g., Shannon et al. 1970; Bacon et al. 1976; Rutgers van der Loeff and Geibert 2008; Verdeny et al. 2009). Over that same timeframe, the daughter of $^{210}$Pb, bismuth-210 ($^{210}$Bi $t_{1/2}: 5.01$ d), has rarely been measured and its behavior in the water column is poorly understood.

Fowler et al. (2010) encouraged the radiotracer community to measure $^{210}$Bi in aquatic systems based on bismuth’s apparent affinity for biogenic particles and suggested that the $^{210}$Bi/$^{210}$Pb nuclide pair could serve as a useful tracer for short-term scavenging processes in the upper water column. Wang et al. (2019) and Kim and Hong (2019) have recently repeated this call. The primary advantage of a short-lived radionuclide tracer is its ability to rapidly respond to any change in scavenging flux, with the $^{210}$Bi/$^{210}$Pb tracer capable of reaching a new steady-state disequilibrium as much as $\sim 30$ times faster than the $^{210}$Po/$^{210}$Pb pair. If radionuclide profiles are mistakenly assumed to be at steady-state, tracer-derived particle fluxes can greatly underestimate or exceed true flux conditions.

Interest in measuring $^{210}$Bi waxed and waned from the early-1990s to the early-2000s (e.g., Church et al. 1994; Tokieda et al. 1994; Marley et al. 1999; Katzberger et al. 2001; Biggin et al. 2002). Unfortunately, none of these techniques have been exploited, and the application of $^{210}$Bi as a tracer of aquatic scavenging processes has still not been explored. To date, only a few estimates of in situ $^{210}$Bi activity exist, from the thermal springs in Bad Gastein (Austria) (Katzberger et al. 2001), and the waters of Funka Bay (Tokieda et al. 1994) and the Irish Sea (Biggin et al. 2002).

The methods referenced above all have their strengths. Procedures for separating $^{210}$Bi make use of precipitation, solvent extraction, ion exchange chromatography, and electrochemical techniques (Marley et al. 1999, and references therein). However, we have found—from our work with the short-lived nuclide yttrium-90 ($^{90}$Y $t_{1/2}: 2.67$ d; Waples and Orlandini 2010)—that time is of essence due to the rapid decay of the analyte. With respect to $^{210}$Pb, $^{210}$Bi, and $^{210}$Po, the analyses of $^{210}$Pb and $^{210}$Po activity are secondary to the speed and ease with which $^{210}$Bi can be isolated and counted. Given this criterion, the method of Marley et al. (1999) stands out.

Marley et al. (1999) used an anion solid-phase extraction (SPE) disk to separate the $^{210}$Bi and $^{210}$Po progeny from their $^{210}$Pb parent with less than 1% interference, where the anionic chloride complexes of bismuth and polonium have affinities...
(K_d > 10^4) for the disk’s anionic chelating particles that greatly exceed those of lead (K_d ~10). Because the disk itself was then counted directly on an alpha/beta gas-flow proportional counter, both the separation and initial measurement of 210Bi were quickly achieved. However, Marley et al. (1999) also counted 210Po on the SPE disk with the proportional counter, and here the method is problematic. While Marley et al. (1999) advocated their method for measuring 210Pb, 210Bi, and 210Po in aquatic samples, they only applied their technique to rain and snow, where natural activities were high and the whole sample could be eluted through the disk. In large samples with low natural activities, the total or dissolved fraction activities of 210Pb, 210Bi, and 210Po must be concentrated by scavenging. Unknown and variable scavenging efficiencies require that an isotope of the target nuclide must also be added as a yield monitor. Because both 210Po and its yield monitor 209Po decay by alpha particle emission, α-spectroscopy is required to resolve and quantify the activity of each isotope, and this cannot be done while polonium is still strongly sorbed to the SPE disk.

In this study, I modify the method of Marley et al. (1999) slightly, so that polonium is removed from the SPE disk and redeposited on a copper plate for α-spectroscopy. I also expand on procedural topics that were either not discussed or only briefly developed, including sample pretreatment, anion SPE disk sorption efficiencies, detector efficiencies and backgrounds, and decay-corrected calculations for total, dissolved, and particle-bound fractions of 210Pb, 210Bi, and 210Po. I conclude with an analysis of 210Pb, 210Bi, and 210Po activities in rain, dreissenid (quagga) mussels, and water samples from the Milwaukee Inner Harbor in Lake Michigan, where the emphasis here is placed on method assessment and precision, and comparison with reported activities in the literature. An additional manuscript describing a larger environmental data set of 210Pb, 210Bi, and 210Po activities—including the values presented here—and an analysis of their scavenging in the water column is in preparation (J. T. Waples unpubl.).

**Materials and procedures**

**Measuring 210Pb, 210Bi, and 210Po in a water sample**

My approach to measuring both dissolved and particle-bound fractions of 210Pb, 210Bi, and 210Po in a water sample is shown in a schematic in Fig. 1 and a more detailed timeline in Fig. 2. The description of this method is organized with the timeline. After sample pretreatment (where both particle-bound and dissolved nuclide fractions that have been scavenged on a ferric hydroxide precipitate are filtered and digested in nitric acid), the approach, in brief, calls for the immediate and complete separation of bismuth and polonium from lead on an anion SPE disk and counting the disk—first for 210Bi via β-decay, then for 207Bi via γ-emission to determine yield. Polonium is then removed from the SPE disk, plated to copper, and α-counted for 210Po and the yield monitor 209Po. Total and particle-bound 210Pb fractions are held for approximately 1 month and finally measured via 210Bi that has grown into secular equilibrium with its parent.

**Sample collection (t_0)**

The volume of water required to measure the activity of any radionuclide in both dissolved and particle-bound fractions will depend on many factors. These include the activity of the nuclide, the nuclide’s affinity for particle sorption, the

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**Fig. 1.** A schematic of separation procedures for the determination of 210Pb, 210Bi, and 210Po.
half-life of the nuclide and the speed at which the sample can be processed, and the degree of accuracy required by any specific application of the nuclide as a tracer (Waples and Orlandini 2010). Based on previous measurements of $^{210}$Pb in Lake Superior (Chai and Urban 2004) and the Clinton River in southeastern Michigan (Mudbidre et al. 2014), an initial estimate of ~ 50 L of water was considered adequate for the analysis of both dissolved and particle-bound fractions of $^{210}$Pb, $^{210}$Bi, and $^{210}$Po in Lake Michigan.

Water samples were collected with a submersible pump and stored in large plastic barrels. At least one ~ 50 L water sample (S1) was collected for the immediate analysis of dissolved and particle-bound fractions of $^{210}$Bi and $^{210}$Po and the subsequent analysis of particle-bound $^{210}$Pb. At least one additional ~ 50 L water sample (S2) was collected for the eventual analysis of total (dissolved + particle-bound) $^{210}$Pb. Time of sample collection was noted as $t_0$.

The S2 sample was immediately weighed, acidified with 500 mL of concentrated HCl (12 M), spiked with a calibrated yield monitor of $^{207}$Bi (e.g., 0.6 Bq), and stored for later analysis.

**$^{210}$Bi analysis timeline**

- $t_0$: collect samples (S1 and S2)
- $t_{1a}$: collect and process S1 particulate fraction
- $t_{1b}$: collect and process S1 dissolved fraction
- $t_{2a}$: run S1 particle fraction through SPE disk 1
- $t_{2b}$: run S1 dissolved fraction through SPE disk 2
- $t_3$: γ-count SPE disks 1 and 2
- $t_4$: γ-count SPE disks 1 and 2

proceed to $^{210}$Po analysis

**$^{210}$Po analysis timeline**

- $t_5$: separate S1 Po from SPE disks 1 and 2
- $t_6$: plate Po
- $t_7$: α-count Po plates

proceed to $^{210}$Pb analysis

**$^{210}$Pb analysis timeline**

- $t_8$: collect and process S2 total fraction
- $t_{9a}$: run S2 total fraction through SPE disk 3
- $t_{9b}$: run S1 particle fraction effluent through SPE disk 4
- $t_{10}$: β-count SPE disks 3 and 4
- $t_{11}$: γ-count SPE disks 3 and 4

**calculate radionuclide activity**

Fig. 2. A timeline of separation procedures for the determination of total, particle-bound, and dissolved fractions of $^{210}$Pb, $^{210}$Bi, and $^{210}$Po.
**Nuclide separation on anion SPE membrane disks (t3)**

Empore™ anion SPE membrane disks (3 M, 47 mm, product number 2252, now manufactured by CDS Analytical) were placed in a Nalgene filter apparatus with a 250-mL receiver. Vacuum (~ 400 mbar) was applied using a water aspirator. The filters were wetted with ~ 10 mL of ethanol and then rinsed three times with ~ 10 mL of 0.5 M HCl. The filter apparatus receiver was emptied and cleaned with distilled water before loading the S1 sample fractions onto the anion SPE disks. Sample elution times were generally less than 5 min. The time of elution was noted as t3a for the S1 particle-bound fraction and t3b for the S1 dissolved fraction.

Each anion SPE disk was again rinsed three times with ~ 10 mL of 0.5 M HCl. Bismuth and polonium isotopes from both sample fractions were now sorbed to the disks. The eluate from the S1 particle-bound fraction was carefully transferred to a clean beaker, spiked with 207Bi (e.g., 0.6 Bq), and covered for later analysis of particle-bound 210Pb (via the ingrowth of 210Bi). The eluate from the S1 dissolved fraction was generally discarded. However, this eluate can be used to determine the dissolved 210Pb fraction if a lead yield monitor is added to the original sample (see “Comments and recommendations” section).

To prepare the anion SPE disks for β-counting, the filters were again placed under vacuum and rinsed three times with ~ 10 mL of distilled water. The disks were then transferred to covered beakers and exposed to vapors of 50% NH4OH for 5 min, which effectively neutralized any residual acid (Marley et al. 1999). Finally, the disks were placed onto cupped stainless steel planchets (2-in. diameter, available from A. F. Murphy Die & Machine) and allowed to air-dry for ~ 30 min.

**β-Counting 210Bi decay on the anion SPE membrane disk (t4)**

The dried anion SPE disks in cupped stainless steel planchets were placed in a low background gas-flow proportional counter with eight 2,25-in.-diameter detectors and anti-coincidence circuitry (G542 System, Gamma Products) and counted over a series of four sessions spanning a ~ 30-d period (e.g., at 0, 5, 10, and 25 d after sample preparation). Each counting session consisted of a series of 10, 150-min counting intervals. The time of each counting interval (t4) was recorded.

**γ-Counting 207Bi recovery on the anion SPE membrane disk (t5)**

The anion SPE disks in planchets were then put in plastic Petri dishes and placed (face down) in an HPGe planar detector (models GMX-23210-P and LO-AX-70450/30-S, Ortec). Gamma counts were measured over an average period of ~ 2 x 10^5 s. 207Bi recovery was determined by peak analysis in the 570 keV region. Gamma spectrum analysis was performed using Maestro software (v. 6.04, Advanced Measurement Technology). Peak analyses reported net peak areas and net area uncertainty (± 1 SD). The time of the count (t5) was noted.

**Removal of Po isotopes from the anion SPE membrane disk (t6)**

After β- and γ-counting, the anion SPE disks were again mounted in a 47-mm filtration apparatus (Nalgene), placed under vacuum, and rewetted with ~ 10 mL of ethanol. The disks were then carefully rinsed four times with a total of ~ 40 mL of distilled water and the filter apparatus receiver was emptied and cleaned with distilled water.

After the anion SPE disks had been wetted and rinsed—and “the ethanol in the filter apparatus receiver removed”—the disks were placed under vacuum and rinsed with 80 mL of 8 M HNO3 to elute the polonium isotopes of 210Po and 209Po. I emphasize the importance of removing all ethanol from the eluate sample because “ethanol and nitric acid will react violently when heated.”

The eluate of nitric acid and polonium isotopes was then transferred from the filter apparatus receiver to a 500-mL beaker and evaporated to near dryness on a hotplate, with the sample temperature not exceeding ~ 100°C.

**Plating Po isotopes on a copper disk (t7)**

The polonium isotopes of 210Po and 209Po were spontaneously deposited on a copper disk using a modified methodology of Robbins and Edgington (1975), MacKenzie and Scott (1979), and Kostenko (1982). Briefly, the dried polonium sample was first reconstituted with 50 mL of 0.1 M HCl. Next, 0.1 g of L-ascorbic acid (Sigma Aldrich) was added to the beaker to prevent any iron in the sample from interfering with the plating of polonium. The pH of the solution was adjusted to ~ 1 with 6 M HCl and the entire contents of the beaker was transferred to a 125-mL Nalgene wide-mouth plastic bottle. A flat copper disk (7/8-in. diameter, available from A. F. Murphy Die & Machine), which was polished on one side and sealed with a thin layer of polyurethane on the other, was added to each sample bottle (polished side up) and the bottles were capped tight, put in an oven, and heated to 95°C for ~ 12 h (i.e., overnight). After heating, the copper disks were retrieved, rinsed with distilled water and ethanol, and allowed to dry.

**α-Counting 210Po and 209Po on a copper disk (t8)**

The dried copper disks were then placed in an alpha counter (Octete Plus alpha spectrometry workstation with Ultra-AS detectors, Ortec). Alpha counts were measured over a period of 1.8 x 10^5 s. 210Po and 209Po activities were determined by peak analyses of the 5.31 and 4.88 MeV regions, respectively. Alpha spectrum analysis was performed using Maestro software (v. 6.06, Advanced Measurement Technology). The time of the count was noted as t8.

**210Pb analysis (t8-t14)**

After approximately 1 month, the second water sample S2 and the saved eluate from the S1 particle-bound fraction (see t2) were processed to measure total and particle-bound 210Pb—via 210Bi—using the same procedures outlined in time steps t1 through t4 above.

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Specifically, the S2 water sample was processed using the same procedure described in the t1 "S1 sample processing (t1)" section above, except that both dissolved and particle-bound fractions of $^{210}\text{Bi}$ were collected onto one nitrocellulose filter to determine total $^{210}\text{Pb}$. Because the sample was already acidified and spiked with $^{209}\text{Bi}$, the procedure started with the addition of ferrous iron. The time of filtration was noted as t8.

The separation of bismuth isotopes from the total and particle-bound $^{210}\text{Pb}$ sample fractions on anion SPE disks proceeded as described in time step t2, except that eluates from both sample fractions were discarded. The time of elution was noted as t9a for the S2 total $^{210}\text{Pb}$ sample and t9b for the S1 particle-bound $^{210}\text{Pb}$ fraction.

Beta ($t_{10}$) and gamma ($t_{11}$) counting of the activities of $^{210}\text{Bi}$ and $^{207}\text{Bi}$ proceeded as described in time steps t3 and t4.

**Yield monitors and standards**

Standards of $^{207}\text{Bi}$ (half-life: 32 years; cat. no. 7207; reference date: 01 August 2017; National Institute of Standards and Technology (NIST) traceable; total uncertainty ± 3.1% at 99% confidence interval) and $^{209}\text{Po}$ (half-life: 125.3 years; cat. no. 7209; reference date: 01 August 2017; NIST traceable; total uncertainty ± 3.0% at 99% confidence interval) and $^{210}\text{Pb}$ (half-life: 22.3 years; cat. no. 7210; reference date: 01 June 2018; NIST traceable; total uncertainty ± 4.1% at 99% confidence interval) were purchased from Eckert & Ziegler Isotope Products. Progeny nuclides of $^{210}\text{Bi}$ and $^{210}\text{Po}$ were in secular equilibrium with the $^{210}\text{Pb}$ standard (Eckert & Ziegler Isotope Products).

A secondary standard of $^{210}\text{Pb}$, $^{210}\text{Bi}$, and $^{210}\text{Po}$ (in secular equilibrium) was made by digesting ~ 10 g of Lake Michigan sediment (collected in 1994) in 50 mL of concentrated HNO3. The mixture was covered and heated gently overnight and allowed to dry the following morning. The dried sediment was then reconstituted with 50 mL of 0.5 M HCl and allowed to sit for an additional day before removing the sediment by filtration through a nitrocellulose filter (0.45 μm, 47 mm, Whatman). Calibration of the sediment standard eluate was eventually achieved via $^{210}\text{Po}$, using weighed aliquots of the NIST-calibrated $^{209}\text{Po}$ standard.

**Anion SPE disk sorption efficiencies**

**Bismuth**

The sorption efficiency of bismuth on the anion SPE disks was determined by the recovery of $^{207}\text{Bi}$ on rain, mussel tissue, and particle-bound water fraction samples, where the transfer of $^{207}\text{Bi}$ to the SPE disks was complete (i.e., lossless). Procedural details are described in the “Assessment: Materials and procedures” section below.

**Lead**

The sorption efficiency of lead on the anion SPE disks was determined by digesting four samples of ~ 0.5 g of Lake Michigan sediment (collected in 1994) in 20 mL of concentrated (16 M) HNO3. Each sample was spiked with measured volumes of the NIST-calibrated $^{207}\text{Bi}$ and $^{209}\text{Po}$ standards. The samples were heated until dry, reconstituted in 20 mL 0.5 M HCl, and stirred before removing the sediment by filtration through a nitrocellulose filter. The four samples were then run through four separate anion SPE disks and the disks were beta counted repeatedly to determine the initial $^{210}\text{Bi}$ activity in counts per minute (cpm) in the extracted sediment digestion.

The eluate from the four samples (containing any $^{210}\text{Pb}$ that passed through the SPE disks) was spiked again with the same volumes of $^{207}\text{Bi}$ and $^{209}\text{Po}$ standards and covered. After 57 d—and the complete ingrowth of $^{210}\text{Bi}$ to secular equilibrium with its parent—the four samples were again run through separate SPE disks and beta counted to determine the $^{210}\text{Bi}$ activity (cpm) in the eluate.

Because the SPE disks for each sample were beta counted on the same detector, and the transfer of lead from the eluant of the first SPE disk to the second SPE disk was complete, any decrease in $^{210}\text{Bi}$ activity on the second SPE disk could be attributed to the sorption of $^{210}\text{Pb}$ on the first SPE disk.

**Detector efficiencies and backgrounds**

**$^{210}\text{Bi}$ beta efficiency**

A two-standard, eight-point calibration curve was used to determine the $^{210}\text{Bi}$ beta counting efficiency of the low background gas-flow proportional counter.

Four samples containing measured masses of the sediment-derived standard, $^{207}\text{Bi}$, and $^{209}\text{Po}$ were run through four anion SPE disks. The four disks were repeatedly counted in all eight beta detectors over a period of several weeks to determine initial ($t_2$) $^{210}\text{Bi}$ activities in cpm. The four disks were then placed in gamma counters to determine activities of the added $^{207}\text{Bi}$ and the filter extraction efficiency of bismuth. Next, the polonium isotopes were carefully extracted from each disk using 8 M nitric acid. $^{210}\text{Po}$ and $^{209}\text{Po}$ were spontaneously plated on copper disks and alpha counted to determine $^{210}\text{Po}$ activity in disintegrations per minute (dpm; where 60 dpm = 1 Bq) per gram of sediment-derived standard.

To check the calibration of the sediment-derived “house standard,” and the validity of my alpha counting procedure, another calibration curve was measured using the NIST-calibrated $^{210}\text{Pb}$ standard from Eckert & Ziegler Isotope Products. Four samples containing measured masses of the calibrated $^{210}\text{Pb}$ standard and $^{207}\text{Bi}$ were run through four anion SPE disks and the four disks were then repeatedly counted in four of the eight detectors over a period of several weeks. Again, the decay of beta activity over time was used to calculate the initial ($t_2$) $^{210}\text{Bi}$ activity on the disks (cpm). The four disks were then placed in gamma counters to determine activities of the added $^{207}\text{Bi}$.

**$^{207}\text{Bi}$ gamma efficiency**

To determine the efficiency of our gamma detectors at measuring $^{207}\text{Bi}$, two samples were prepared using the NIST-
calibrated $^{207}$Bi standard. The anion SPE disks were first placed in cupped stainless steel planchets and wetted with ethanol. Weighed aliquots of $^{207}$Bi standard were then spread evenly across the disks. The disks were dried on low heat, placed in plastic petri dishes, and counted face down using the same geometry employed for other standard or environmental samples.

Counts in the region of 569.7 keV were measured over an average interval of 16 d to determine the detector response to $^{207}$Bi, where the efficiency of the response is expressed in units of cpm dpm$^{-1}$. Gamma spectrum analysis was performed using Maestro software (v. 6.04, Advanced Measurement Technology). Peak analyses reported net peak areas and net area uncertainty (± 1 SD).

**Alpha-detector background**

Alpha-detector backgrounds for $^{210}$Po and $^{209}$Po activities in the regions of 5.31 MeV (for $^{210}$Po) and 4.88 MeV (for $^{209}$Po) were determined by counting blank polished copper disks for $5 \times 10^5$ s.

**Radionuclide activity calculations**

Radionuclide activities at the time of sample collection ($t_0$) were first calculated for $^{210}$Pb, followed by $^{210}$Bi, and finally $^{210}$Po because activities of $^{210}$Pb and $^{210}$Bi were needed to make small corrections in the $t_0$ activities of $^{210}$Bi and $^{210}$Po, respectively.

**$^{210}$Pb total activity**

Because $^{210}$Pb activities were calculated via the ingrowth of $^{210}$Bi, the first step to determining the total $^{210}$Pb activity involved calculating the $^{210}$Bi activity on the anion SPE disk 3 at time $t_9$. This was done by repeatedly beta counting the SPE disk over a significant fraction of the sample’s $^{210}$Bi lifetime. The time series of 150-min measurements of gross beta activity (cpm) were then plotted as a function of $e^{-\lambda t}$, where $\lambda$ is the decay constant for $^{210}$Bi (0.13835 d$^{-1}$) and $t$ is the time elapsed between the start of each beta count and the separation of $^{210}$Bi on the anion SPE disk at time $t_9$. For a linear regression of the data:

$$A_{\text{gpm}}^\text{cpm} = A_{\text{gpm}}^\text{cpm} + A_{\text{bi}}^\text{cpm} e^{-\lambda t},$$  

where $A_{\text{gpm}}^\text{cpm}$ is the gross beta count and $A_{\text{gpm}}^\text{cpm}$ is the initial activity of $^{210}$Bi at time $t_0$ or $t_9$. For a linear regression of the data:

$$A_{\text{gpm}}^\text{cpm} = A_{\text{gpm}}^\text{cpm} + A_{\text{bi}}^\text{cpm} e^{-\lambda t},$$  

where $A_{\text{gpm}}^\text{cpm}$ is the gross beta count and $A_{\text{bi}}^\text{cpm}$ is the initial activity of $^{210}$Bi at time $t_0$ or $t_9$. For a linear regression of the data:

$$A_{\text{gpm}}^\text{cpm} = A_{\text{gpm}}^\text{cpm} + A_{\text{bi}}^\text{cpm} e^{-\lambda t}. $$  

The $^{210}$Bi activity (in dpm) per unit sample volume at time $t_9$ ($A_{\text{Bi}}(t_9)$) was calculated as

$$A_{\text{Bi}}(t_9) = \frac{A_{\text{bi}}^\text{cpm}}{\text{eff} \times \text{yield} \times \text{vol}}.$$

where eff is the beta detector efficiency for $^{210}$Bi expressed in units of cpm/dpm, yield is the fraction of bismuth recovered from the sample (as determined by the $^{207}$Bi yield monitor), and vol is the initial sample volume.

Between the time steps of collecting the $^{210}$Pb, $^{210}$Bi, and $^{210}$Po nuclides on the ferric hydroxide precipitate ($t_8$) and the separation of $^{210}$Bi and $^{210}$Po from $^{210}$Pb on the anion SPE disk ($t_9$), an additional small correction can be applied for the decay of $^{210}$Bi caused by any preferential scavenging of $^{210}$Bi over $^{210}$Pb by ferric hydroxide (where $S_{\text{Pb/Bi}}$ is the ratio of lead to bismuth scavenged). The corrected activity of $^{210}$Bi at $t_8$ was calculated as

$$A_{\text{Bi}}(t_8) = \frac{A_{\text{gpm}}^\text{cpm} \times (S_{\text{Pb/Bi}} \times A_{\text{Bi}}(t_9)) \times (e^{-\lambda t} - e^{-\lambda t_9})}{e^{-\lambda t_9}}.$$

where $\lambda$ is the decay constant for $^{210}$Pb (8.51 $\times 10^{-5}$ d$^{-1}$), $S_{\text{Pb/Bi}}$ was taken as 1, and $t$ is the time elapsed between time steps $t_8$ and $t_9$. The $S_{\text{Pb/Bi}}$ value of 1 was based on analyses of duplicate lake water samples, where the ratio between the $^{210}$Bi activity in secular equilibrium with $^{210}$Pb in the water sample and the $^{210}$Bi activity in secular equilibrium with $^{210}$Pb in the saved eluate from SPE disk 3 was 95% ± 5% ($n = 2$).

$A_{\text{Bi}}(t_9)$ represents the activity of $^{210}$Bi in the S2 sample at the time of nuclide scavenging with ferric hydroxide. If the S2 sample was held for at least 30 d before processing, $^{210}$Bi activities are assured to be at least 98.5% in equilibrium with their parent $^{210}$Pb, assuming initial $^{210}$Bi activities were zero. If initial $^{210}$Bi activities in field samples were within 80% of secular equilibrium with $^{210}$Pb at the time of sample collection (a likely scenario), then holding the S2 sample for 30 d results in final $^{210}$Bi activities that are at least 99.7% in equilibrium with $^{210}$Pb. This increases to 100.0% after 40 d.

A final small correction for the decay of total $^{210}$Pb ($A_{\text{Pb}}^{\text{total}}$) between time steps $t_8$ and sample collection at $t_9$ was calculated as

$$A_{\text{Pb}}^{\text{total}} = \frac{A_{\text{gpm}}^\text{cpm}}{e^{-\lambda t}},$$

where $t$ is the time elapsed between time steps $t_8$ and $t_9$.

The propagated uncertainty of the estimate ($\sigma_{A_{\text{Pb}}^{\text{total}}}$) was calculated as

$$\sigma_{A_{\text{Pb}}^{\text{total}}} = A_{\text{Pb}}^{\text{total}} \sqrt{\left(\frac{\sigma_{A_{\text{Pb}}^{\text{total}}}}{A_{\text{Pb}}^{\text{total}}}\right)^2 + \left(\frac{\sigma_{\text{eff}}}{\text{eff}}\right)^2 + \left(\frac{\sigma_{\text{yield}}}{\text{yield}}\right)^2}.$$

Uncertainties in the activity of total $^{210}$Pb associated with the ratio of lead to bismuth scavenged by ferric hydroxide were negligible.

**$^{210}$Pb particle-bound activity**

The activity of $^{210}$Pb on particulate matter was calculated in a manner similar to the method described above for total
$^{210}$Pb. After the anion SPE disk 4 was beta counted repeatedly over a significant fraction of the sample’s $^{210}$Bi lifetime, the 150-min measurements of gross beta activity (cpm) were plotted as a function of $e^{-\lambda t}$, where $t$ is the time elapsed between the start of each beta count and the separation of $^{210}$Bi on the anion SPE disk at time $t_0$. A linear regression of the data gave the initial activity of $^{210}$Bi ($A_{Bi}^{pm}$) at time $t_0$ (Eq. 1). The $^{210}$Bi activity (dpm) per unit sample volume at time $t_{9b}$ ($A_{Bi(t_{9b})}$) was calculated using Eq. 2.

Because the loss of lead on the anion SPE disks was negligible (0.2% ± 2.1%; ± 1 SD, $n = 4$), and the sorption of bismuth on the disks was complete (99% ± 2%; ± 1 SD, $n = 16$) (as shown in the “Assessments: Materials and procedures” section below), the activity of particle-bound $^{210}$Pb ($A_{Pb}^{part}$) at the time of initial separation ($t_{2a}$) on SPE disk 1 was calculated as

$$A_{Pb(t_{2a})} = \frac{A_{Bi(t_{2a})}}{\lambda_{Bi} \times (e^{-\lambda_{Bi} t} - e^{-\lambda_{Bi} t_{2a}})}$$  \hspace{1cm} (6)

where $t$ is the time elapsed between the elution of $^{210}$Pb on SPE disk 1 at $t_{2a}$ and the separation of $^{210}$Bi on SPE disk 4 at $t_{9b}$. Because the time between $t_{2a}$ and sample collection at $t_0$ was less than 1 d, $A_{Pb}^{part}$ at $t_{2a}$ was taken as $A_{Pb}^{part}$ at $t_0$. The propagated uncertainty of the estimate ($\sigma_{A_{Pb}^{part}}$) was calculated using Eq. 5.

$^{210}$Bi particle-bound fraction activity

As with the lead fractions described above, repeated beta counts of the anion SPE disk 1 were plotted as a function of $e^{-\lambda_{Bi} t}$, and the slope of the linear regression of the data gave the initial activity of $^{210}$Bi ($A_{Bi}^{pm}$) at time $t_{2a}$ (Eq. 1). The $^{210}$Bi activity in dpm per unit sample volume at time $t_{2a}$ ($A_{Bi(t_{2a})}$) was calculated using Eq. 2.

A small correction was applied for the decay of $^{210}$Pb during the time elapsed between the separation of particles from the original sample matrix at time $t_{1a}$ and the removal of $^{210}$Pb at $t_{2a}$. The activity of $^{210}$Bi in the particle-bound fraction ($A_{Bi}^{part}$) of sample S1 at time $t_{1a}$ was calculated as

$$A_{Bi(t_{1a})} = \frac{A_{Bi(t_{2a})} \times (\lambda_{Bi} t_{2a} - \lambda_{Bi} t_{1a}) \times (e^{-\lambda_{Bi} t_{2a}} - e^{-\lambda_{Bi} t_{1a}})}{\lambda_{Bi} t_{2a} - \lambda_{Bi} t_{1a}}$$  \hspace{1cm} (7)

where $t$ is the time elapsed between time steps $t_{1a}$ and $t_{2a}$. Because the time between $t_{1a}$ and sample collection at $t_0$ was on the order of 1 h, $A_{Bi}^{part}$ at $t_{1a}$ was taken as $A_{Bi}^{part}$ at $t_0$. The propagated uncertainty of the estimate ($\sigma_{A_{Bi}^{part}}$) was calculated using Eq. 5.

$^{210}$Bi dissolved fraction activity

Repeated beta counts of the anion SPE disk 2 were plotted as a function of $e^{-\lambda_{Bi} t}$ in the same manner as described above, and the slope of the linear regression of the data gave the initial activity of $^{210}$Bi ($A_{Bi}^{pm}$) at time $t_{2b}$ (Eq. 1). The $^{210}$Bi activity (in dpm) per unit sample volume at time $t_{2b}$ ($A_{Bi(t_{2b})}$) was calculated using Eq. 2.

Two small corrections (< 1%) were applied for the decay of $^{210}$Pb. Between the scavenging of the dissolved fractions of $^{210}$Pb, $^{210}$Bi, and $^{210}$Po on ferric hydroxide precipitate at $t_{1b}$ and the removal of $^{210}$Pb at $t_{2b}$, ~ 70% of the dissolved $^{210}$Pb fraction that was scavenged by the precipitate was decaying to $^{210}$Bi. The use of a 70% recovery value is based on three findings: (1) Rigaud et al. (2013) reported that scavenging of the dissolved lead fraction with Fe(OH)$_3$ in 80 seawater samples was consistently efficient at 70% ± 10%; (2) scavenging of $^{207}$Bi with Fe(OH)$_3$ in this study averaged 60% ± 9% ($n = 9$), but included samples that were partially discarded after filtration; and (3) the Pb/Bi scavenging ratio in this study was ~ 1 (see $^{201}$Pb total activity” section above). The corrected $^{210}$Bi activity in the dissolved fraction ($A_{Bi}^{diss}$) at $t_{1b}$ was calculated as

$$A_{Bi}^{diss(t_{1b})} = \frac{A_{Bi(t_{2b})} \times (0.7 \times A_{Pb}^{diss(t_{1b})}) \times (e^{-\lambda_{Bi} t_{2b}} - e^{-\lambda_{Bi} t_{1b}})}{e^{-\lambda_{Bi} t_{2b}} - e^{-\lambda_{Bi} t_{1b}}},$$  \hspace{1cm} (8)

where the activity of $^{210}$Pb in the dissolved fraction ($A_{Pb}^{diss}$) was taken as $A_{Pb}^{total} - A_{Pb}^{part}$ and $t$ is the time elapsed between time steps $t_{1b}$ and $t_{2b}$. The second correction for $^{210}$Bi decay between the removal of particles at $t_{1b}$ and $t_{2b}$ accounted for the whole of the dissolved $^{210}$Pb fraction contributing to $^{210}$Bi activity. The corrected $^{210}$Bi activity in the dissolved fraction ($A_{Bi}^{diss}$) at $t_{1b}$ was calculated using Eq. 8 and an $A_{Bi}^{diss}$ multiplier of 1.0; $t$ was the time elapsed between time steps $t_{1a}$ and $t_{1b}$. Because the time between $t_{1a}$ and sample collection at $t_0$ was on the order of 1 h, $A_{Bi}^{diss}$ at $t_{1a}$ was taken as $A_{Bi}^{diss}$ at $t_0$.

The propagated uncertainty of the estimate ($\sigma_{A_{Bi}^{diss}}$) was calculated using Eq. 5. Uncertainties in the activity of dissolved $^{210}$Bi associated with the ratio of lead to bismuth scavenged by ferric hydroxide were negligible.

$^{210}$Po activity

The $^{210}$Po activities of both particle-bound and dissolved fractions of sample S1 were determined by alpha counting the isotopes of $^{210}$Po and the added yield monitor $^{209}$Po. Both the yield of polonium recovered from the original sample and the alpha detector efficiency for $^{210}$Po and $^{209}$Po were calculated together as

$$\text{eff}_{Po} = \frac{A_{Po}^{pm(t_{7})}}{A_{Po}^{pm(t_{7})}},$$  \hspace{1cm} (9)

where $A_{Po}^{pm(t_{7})}$ was the measured background-corrected activity of $^{209}$Po (in cpm) at the start of the alpha count at time $t_7$, and $A_{Po}^{pm(t_{7})}$ was the activity of the added $^{209}$Po standard (in dpm) at the start of the alpha count ($t_7$).
The activity of $^{210}$Po (in cpm) at $t_f$ was corrected for background and decay during the count as

$$A_{^{210}Po(t_f)} = \frac{\text{count}_{^{210}Po} - \text{bg}_{^{210}Po}}{t} e^{-\lambda_{^{210}Po} t_f},$$

(10)

where count$_{^{210}Po}$ was the gross alpha count, bg$_{^{210}Po}$ was the measured background in the 5.31 MeV region, $\lambda_{^{210}Po}$ is the decay constant for $^{210}$Po ($5.7975 \times 10^{-8}$ s$^{-1}$), and $t$ was the length of the alpha count ($s$). The $^{210}$Po activity (in dpm) per unit sample volume at time $t_f$ was calculated as

$$A_{^{210}Po(t_f)} = \frac{A_{^{210}Po(t_f)}}{\text{eff}_{^{210}Po} \times \text{vol}},$$

(11)

where vol is the initial sample volume.

Because bismuth was scavenged along with polonium on the anion SPE disks, and $^{210}$Bi decayed to $^{210}$Po before polonium separation, a final correction for both $^{210}$Bi and $^{210}$Po decay to the time of the initial separation on the SPE disks was calculated as

$$A_{^{210}Po(t_0)} = \frac{A_{^{210}Po(t_f)} - \frac{\lambda_{^{210}Po}}{t_2 a_{^{210}Po(t_2)}} - \frac{\lambda_{^{210}Bi}}{t_2 a_{^{210}Bi(t_2)}}}{e^{-\lambda_{^{210}Bi} t_2}} e^{-\lambda_{^{210}Po} t_2},$$

(12)

where $^{210}$Po particle-bound fraction activities at $t_2$ ($A_{_{^{210}Po(t_2)}}$) and dissolved fraction activities at $t_2$ ($A_{_{^{210}Bi(t_2)}}$) used corresponding particle-bound and dissolved $^{210}$Bi activities, and $t$ was the time elapsed between time steps $t_f$ and $t_0$. Because the time between $t_2$, and sample collection at $t_0$ was less than 1 d, $A_{^{210}Po}$ at $t_2$, was taken as $A_{^{210}Po}$ at $t_0$.

The propagated uncertainty of the estimate ($\sigma_{A_{^{210}Po}}$) was calculated as

$$\sigma_{A_{^{210}Po}} = A_{^{210}Po} \sqrt{\left(\frac{\sigma_{A_{^{209}Po(t_0)}}}{A_{^{209}Po(t_0)}}\right)^2 + \left(\frac{\sigma_{A_{^{210}Bi(t_2)}}}{A_{^{210}Bi(t_2)}}\right)^2},$$

(13)

where $\sigma_{A_{^{209}Po(t_0)}}$ and $\sigma_{A_{^{210}Bi(t_2)}}$ were simply calculated as the square root of the background and decay corrected gross alpha counts divided by the alpha count time. Uncertainties associated with the decay of $^{210}$Bi on the anion SPE disk were negligible.

**Assessment: Materials and procedures**

**Anion SPE disk sorption efficiencies**

**Bismuth**

The efficiency of bismuth retention on the anion SPE disks was determined using $^{207}$Bi (Fig. 3). In rain, mussel tissue, and particle-bound water fraction samples, where the transfer of the $^{207}$Bi spike to the SPE disk was complete, the first elution for the measurement of $^{210}$Bi (Fig. 3, filled circles) showed $^{207}$Bi recoveries of $100\% \pm 2\%$ (± 1 SD, n = 9). The eluate of these samples was saved for $^{210}$Pb analysis (via the ingrowth of $^{210}$Bi) and spiked once more with $^{207}$Bi. The second elution (Fig. 3, open circles) again showed $^{207}$Bi recoveries of $99\% \pm 2\%$ (± 1 SD, n = 7). From these results, I conclude that the anion SPE disks are essentially $100\%$ efficient at scavenging bismuth.

**Lead**

Four digested sediment samples (with $^{210}$Bi in equilibrium with $^{210}$Pb) were run through SPE disks and repeatedly beta counted. The beta counts were plotted against the decay time ($e^{-\lambda_{^{210}Bi} t}$) so that the slope of the linear regression gave the $^{210}$Bi activity (cpm) at the time of elution (Fig. 4, nablas). After 57 d (i.e., ~11 half-lives of $^{210}$Bi), the sample eluates (containing any $^{210}$Pb that passed through the first set of SPE disks) were run through a second set of SPE disks and the disks were repeatedly beta counted to determine the $^{210}$Bi activity in secular equilibrium with $^{210}$Pb (Fig. 4, circles). Differences in the activities (slopes) of $^{210}$Bi in the original samples and the $^{210}$Bi in (equilibrium with $^{210}$Pb) in the sample eluates averaged $-0.01 \pm 0.07$ cpm (± 1 SD, n = 4). If I also consider the decay of $^{210}$Pb over the 57-d ingrowth period, relative differences between the original and eluate activities shrank to $0.2\% \pm 2.1\%$ (± 1 SD, n = 4). Had any significant amount of $^{210}$Pb
sorbed to the SPE disks during the first elution, the activities of $^{210}$Bi in the second elution disks should have been lower than the first. From these results, I conclude that the sorption of lead to the anion SPE disks is negligible.

Detector efficiencies

$^{207}$Bi gamma efficiency

Plates with the NIST-calibrated $^{207}$Bi standard were prepared according to the method described in “Materials and procedures” section. The two detector efficiencies for the 569 keV peak were $0.0272 \pm 0.0010$ and $0.0346 \pm 0.0012$ cpm dpm$^{-1}$, respectively. The relative uncertainty in efficiency for both detectors averaged $\pm 3.5\%$.

$^{207}$Bi beta efficiency

Because gamma counting efficiencies are, in general, low, it is tempting to speed up bismuth yield analysis and sample throughput by increasing the $^{207}$Bi activity of the yield monitor. However, internal conversion processes associated with $^{207}$Bi decay release high-energy electrons that register as beta counts in the proportional counter.

To examine the effect of $^{207}$Bi activity on gross beta activity, four samples containing $4.79 \pm 0.02$ dpm of $^{210}$Bi were spiked with $0$, $17.6$, $35.5$, and $71.0$ dpm of $^{207}$Bi. The samples were run through anion SPE disks and the disks were repeatedly beta counted over a period of several weeks (Fig. 5). The mean slope of all four counts (indicating initial $^{210}$Bi activities at time of separation on the SPE disks) was $2.195 \pm 0.026$ cpm ($\pm 1$ SD, $n = 4$), with a standard deviation of the mean ($\pm 0.026$ cpm) smaller than the individual standard errors of each slope (Fig. 5A). This demonstrated that the activity of the $^{207}$Bi yield monitor does not interfere with the calculated activity of $^{210}$Bi. However, the uncertainty of each $^{210}$Bi estimate ($\pm 1$ SD) is taken as the standard error of the slope, and this did increase with increasing $^{207}$Bi activity (Fig. 5B). The increase in the standard error of the slope amounted to $0.0004 \pm 0.00004$ cpm per dpm of $^{207}$Bi. In practical terms, for a sample with a total $^{210}$Bi activity of $\sim 5$ dpm, a $^{207}$Bi spike of $\sim 35.5$ dpm (0.6 Bq) added approximately $\sim 1\%$ to the total relative error of the sample activity estimate when compared to a sample with no $^{207}$Bi spike.
Calibration curves for \(^{210}\text{Bi}\) beta efficiencies in three of the four detectors used to measure \(^{210}\text{Pb}\) and \(^{210}\text{Bi}\) activities in environmental samples are shown in Fig. 6. Each curve was composed of eight calibrated samples, and the same eight samples were counted in each detector. Four of the eight standard samples were derived from a solution of digested lake sediment that was calibrated using the NIST-calibrated \(^{210}\text{Po}\) standard (Fig. 6, filled circles). The other four standard samples were made using the NIST-calibrated \(^{210}\text{Pb}\) standard (Fig. 6, open circles). \(^{210}\text{Pb}\) and \(^{210}\text{Bi}\) were in secular equilibrium with \(^{210}\text{Po}\) in both the sediment-derived and \(^{210}\text{Pb}\) standards.

\(^{210}\text{Bi}\) recovery in the sediment-derived standard samples averaged 99.5% ± 1.7% (± 1 SD, \(n = 4\)). A uniform recovery of bismuth was also indicated by the low standard error of each slope estimate in Fig. 6 (< 3% relative error).

\(^{210}\text{Bi}\) beta efficiencies (eff) were taken as the slope of each calibration curve and averaged 0.504 ± 0.004 cpm dpm\(^{-1}\) (± 1SD, \(n = 3\)) for Detectors 1b, 1c, and 1d. The fourth detector used for environmental sample analysis (i.e., Detector 2a, not shown) had a \(^{210}\text{Bi}\) beta efficiency of 0.506 ± 0.017 cpm dpm\(^{-1}\).

The \(y\)-intercept of each calibration curve for all four detectors used for environmental sample analysis (i.e., those shown in Fig. 6 and Detector 2a) averaged 0.019 ± 0.108 cpm and did not differ significantly from zero. This indicated that blank background activities of \(^{210}\text{Pb}\), \(^{210}\text{Bi}\), and \(^{210}\text{Po}\) in, for example, anion SPE disks, nitrocellulose filters, and reagents were negligible at least as far back as procedural time step \(t_{1b}\).

The concordance between slopes of both sediment-derived and \(^{210}\text{Pb}\) standards gave credence to both the accuracy of the NIST-calibrated standards and that my \(\alpha\), \(\beta\), and \(\gamma\)-counting procedures were synchronized (in the sense that the activity of \(^{210}\text{Bi}\) as determined by \(\alpha\)-counting \(^{210}\text{Po}\) in equilibrium with \(^{210}\text{Bi}\) was equal to the activity of \(^{210}\text{Bi}\) as determined by \(\beta\)- and \(\gamma\)-counting).
Table 1. Activities of $^{210}$Pb, $^{210}$Bi, and $^{210}$Po in rain and lake water.

| Sample       | Typea | Collected date (2018) | $^{210}$Pb b dpm m$^{-3}$ | $^{210}$Bi dpm m$^{-3}$ | $^{210}$Po dpm m$^{-3}$ |
|--------------|-------|-----------------------|---------------------------|--------------------------|--------------------------|
| Rain A       | T     | 11/4                  | 16627 ± 588               | 10040 ± 383              | 853 ± 44                 |
| Rain B       | T     | 11/4                  | 17342 ± 336               | 9961 ± 614               | 893 ± 87                 |
| Water (LS10P) | P     | 11/15                 | 39 ± 1                    | 48 ± 1                   | 21 ± 0                   |
| Water (LS11P) | P     | 11/15                 | 41 ± 4                    | 47 ± 4                   | 21 ± 1                   |
| Water (LS12P) | P     | 11/20                 | 51 ± 3                    | 51 ± 4                   | 34 ± 1                   |
| Water (LS13P) | P     | 11/20                 | 47 ± 3                    | 45 ± 4                   | 32 ± 1                   |
| Water (LS9D)  | D     | 11/15                 | 49 ± 2                    | 48 ± 3                   | 33 ± 1                   |
| Water (LS10D) | D     | 11/15                 | 79 ± 7                    | 36 ± 2                   |                           |
| Water (LS11D) | D     | 11/20                 | 90 ± 8                    | 33 ± 1                   |                           |
| Water (LS12D) | D     | 11/20                 | 33 ± 5                    | 25 ± 1                   |                           |
| Water (LS13D) | D     | 11/20                 | 46 ± 4                    | 25 ± 1                   |                           |
| Water (LS14T) | T     | 11/20                 | 106 ± 7                   |                           |                           |
| Water (LS15T) | T     | 11/20                 | 105 ± 7                   |                           |                           |

aT = total; P = particulate fraction; D = dissolved fraction (< 0.45 μm).
bActivities reported with ± 1 SD propagated counting errors.
cMean (± MAD) activities of replicate (rain) and duplicate (water) sample analyses.

Assessment: Field application

Field sample collection

Environmental samples of rain, lake water, and dreissenid (quagga) mussels were collected from the University of Wisconsin-Milwaukee School of Freshwater Sciences campus and its adjacent slip in the Milwaukee Inner Harbor (Fig. 7). The slip measures 365 m long and 29 m wide, with an average water column depth of 4 m.

Rainwater was collected at ground level (43.017719° N, 87.903000° W) in a large plastic barrel fitted with a funnel and its adjacent slip in the Milwaukee Inner Harbor (Fig. 7). The slip measures 365 m long and 29 m wide, with an average water column depth of 4 m.

Lake water

Particle-bound, dissolved (< 0.45 μm), and total activities of $^{210}$Pb, $^{210}$Bi, and $^{210}$Po in lake water on 15 November and 20 November are shown in Table 1. Relative MADs of duplicate sample analyses of lake water were 2.4% ± 1.9% for $^{210}$Pb (geometric mean of total sample activity: 3.0 dpm, n = 6), 7.7% ± 5.8% for $^{210}$Bi (geometric mean of total sample activity: 2.6 dpm, n = 8), and 2.7% ± 1.7% for $^{210}$Po (geometric mean of total sample activity: 1.4 dpm, n = 8), and compared favorably to the precision of other methods employing α-spectroscopy for the analysis of $^{210}$Po and the determination of its mussel shell length in mm (Waples et al. 2017).
of $^{210}$Pb via the ingrowth of $^{210}$Po (e.g., Church et al. 2012; Baskaran et al. 2013; Rigaud et al. 2013).

The relative propagated counting errors for all three nuclides averaged 7% ± 3% ($n = 22$). Importantly, the relative MADs for all 11 pairs of duplicate samples averaged 4% ± 4% ($n = 11$), which gave some indication that all significant counting errors were being considered.

The total $^{210}$Pb activity of 105 dpm m$^{-3}$ on 20 November and the range of total (dissolved + particle-bound) $^{210}$Po activities from 56 to 58 dpm m$^{-3}$ on 15 November and 20 November were in general agreement with other reported activities of total $^{210}$Pb and $^{210}$Po in Lake Superior (48–131 and 16–54 dpm m$^{-3}$, respectively; Chai and Urban 2004), the Clinton River in Michigan (90–684 and 78–438 dpm m$^{-3}$, respectively; Mudbidre et al. 2014), and Crystal Lake in Wisconsin (113 ± 40 and 95 ± 47 dpm m$^{-3}$, respectively; Talbot and Andren 1984).

The total (dissolved + particle-bound) $^{210}$Bi activity of 88 dpm m$^{-3}$ and total $^{210}$Bi/$^{210}$Pb activity ratio of 0.84 on 20 November is significant because it shows, for the first time, a substantial disequilibrium between the daughter and parent in the water column (see Tokieda et al. 1994; Biggin et al. 2002).

**Mussel tissue**

Activities of $^{210}$Pb, $^{210}$Bi, and $^{210}$Po in quagga mussel tissue are shown in Table 2. Mean activities (± MAD) of $^{210}$Pb, $^{210}$Bi, and $^{210}$Po in both small and large mussel samples were 2.8 ± 0.4, 0.7 ± 0.3, and 43 ± 3 dpm DW g$^{-1}$, respectively, with nuclide activity ratios of 1 : 0.3 : 15.4. The $^{210}$Po activity in mussel tissue was roughly 1.7 times higher than what was found on suspended particulate material on 20 November (i.e., 26 ± 1 dpm g$^{-1}$; J. T. Waples unpubl.). The enhanced bioconcentration of $^{210}$Po is commonly observed in marine organisms (e.g., Stewart and Fisher 2003).

By comparison, mean $^{210}$Pb and $^{210}$Po activities in (Mytilus) mussels from the Atlantic coast of Portugal were remarkably similar at 3 ± 1 and 46 ± 17 dpm g$^{-1}$, respectively, with a $^{210}$Po/$^{210}$Pb activity ratio of 16.9 (Carvalho et al. 2011). Similar $^{210}$Po/$^{210}$Pb activity ratios have been found in bivalves from, for example, the Aegean coast of Turkey (Uğur et al. 2002) to the western English Channel (Connan et al. 2007).

The low activities of $^{210}$Bi in quagga mussel tissue ($^{210}$Bi/$^{210}$Pb: ~ 0.3) are consistent with the study by Fowler et al. (2010), which found a bismuth assimilation efficiency of only ~ 4% in copepods fed with $^{207}$Bi-labeled phytoplankton, and another study by Noshkin et al. (1984), which found whole fish $^{210}$Bi/$^{210}$Pb activity ratios of ~ 0.4 in composite samples made up of bone, mussel, and liver tissue from the Bikini and Rongelap Atolls.

**Table 2. Activities (± 1 SD) of $^{210}$Pb, $^{210}$Bi, and $^{210}$Po in dreissenid (quagga) mussels.**

| Sample               | Collected date (2018) | $^{210}$Pb dpm g$^{-1}$ | $^{210}$Bi dpm g$^{-1}$ | $^{210}$Po dpm g$^{-1}$ |
|----------------------|-----------------------|-------------------------|-------------------------|-------------------------|
| Small mussel tissue  | 11/29                 | 3 ± 2                   | 0 ± 1                   | 46 ± 1                  |
| Large mussel tissue  | 11/29                 | 2 ± 1                   | 1 ± 1                   | 39 ± 1                  |

**Discussion**

The method described here (as modified from Marley et al. 1999) allows for quick measurement of $^{210}$Pb, $^{210}$Bi, and $^{210}$Po in aquatic samples and should enable the radiotracer community to determine: (1) if the $^{210}$Bi/$^{210}$Po nuclide pair can serve as a useful tracer for short-term scavenging processes in the upper water column (Fowler et al. 2010) and (2) whether or not the scavenging of $^{210}$Bi can significantly alter particle flux estimates derived from $^{210}$Po/$^{210}$Pb disequilibrium (Kim and Hong 2019).

This method fundamentally differs from current methods to measure $^{210}$Po and $^{210}$Pb in that instead of measuring $^{210}$Pb via the ingrowth of $^{210}$Po (e.g., Church et al. 2012, references therein), $^{210}$Pb is measured via the decay of isolated $^{210}$Bi that was in secular equilibrium with $^{210}$Pb. An immediate benefit of this approach is that $^{210}$Pb can be determined after ~ 1 month instead of > 6 months. The method described here also eliminates the need for a lead yield monitor, which can be a significant source of background $^{210}$Po and $^{210}$Pb (Rigaud et al. 2013).

Early studies of $^{210}$Pb in the environment included methodologies where $^{210}$Pb was determined by the ingrowth of $^{210}$Po (e.g., Burton and Stewart 1960; Hill 1960; Holtzman 1966; Shannon et al. 1970) as well as $^{210}$Bi (e.g., Blifford et al. 1952; Burton and Stewart 1960; Rama and Goldberg 1961; Fry and Menon 1962; Craig et al. 1973). Comparisons of the two approaches showed similar levels of precision. Burton and Stewart (1960) estimated the precision of their $^{210}$Bi technique at approximately ± 10% and their $^{210}$Po technique at ± 15%, although it is not immediately clear if total sample activities in both sample sets were similar. An intercomparison of $^{210}$Pb measurements at GEOSECS station 500 showed that the $^{210}$Bi technique for measuring $^{210}$Pb had a precision of ~ 5% for total sample activities of ~ 4 dpm $^{210}$Pb (Chung et al. 1983). A follow-up study showed the precision of the $^{210}$Po technique for measuring $^{210}$Pb ranged from ~ 2% to 15% for total sample activities of ~ 1–3 dpm $^{210}$Pb, (Fler and Bacon 1984).

A significant constraint of this method (and the measurement of all short-lived nuclides, including $^{210}$Po) is the necessity to rapidly separate and count the nuclides. In this study, the shore-based processing of a ~ 50 L water sample took an
average of 8 h—from sample collection to starting the $^{210}\text{Bi}$ β-count. This included filtration of both particulate and dissolved sample fractions, acid digestion of both fractions, and nuclide separations on an anion SPE disk, with acid digestion taking the longest amount of time. Offshore applications of this method will require shipboard processing of samples; and the use of strong acids for sample digestion will necessitate the availability of a chemical fume hood (Rigaud et al. 2013). Microwave digestion of samples could reduce both the volume of acid used and time of digestion considerably (e.g., Michel et al. 2008; Szarłowiecz 2019) and should be considered in our evolving approach to measuring $^{210}\text{Pb}$, $^{210}\text{Bi}$, and $^{210}\text{Po}$ in aquatic systems.

**Comments and recommendations**

This method is amenable to any modification in sample pre-treatment or polonium analysis (see http://www.geotraces.org/sic/intercalibrate-data/cookbook; last accessed on 23 August 2019). It may be preferable, for instance, to use ferric chloride instead of ferrous sulfate to create a ferric hydroxide precipitate so as to prevent the precipitation of calcium sulfate in a seawater sample.

If sample volume or storage space is limited, and the collection of a separate (S2) sample for total $^{210}\text{Pb}$ is impractical, then a stable Pb yield monitor (Rigaud et al. 2013) should be added to the S1 sample so that the in situ dissolved $^{210}\text{Pb}$ fraction can be quantified using the eluate from SPE disk 2 (time step $t_{2b}$).

Because anion exchange is selective (e.g., Saito 1984), other beta emitting radionuclides that might also sorb to the anion SPE disk and interfere with the determination of $^{210}\text{Bi}$ activity are not likely to be encountered in offshore waters. When sampling in coastal waters near large urban centers, however, several short-lived radiopharmaceuticals in treated sewage effluent could sorb to the SPE disk and spuriousy increase beta counts attributable to $^{210}\text{Bi}$ activity. Of special concern is the beta emitter, iodine-131 ($^{131}\text{I}$; $t_{1/2}$: 8.01 d) (e.g., Montenero et al. 2017). For this reason, it is good practice to confirm that beta activity is decaying at a rate that is consistent with $^{210}\text{Bi}$ by fitting beta decay as a function of time with a three-parameter exponential decay curve, where the fitted decay constant ($\lambda$) should equal the expected $^{210}\text{Bi}$ decay constant of 0.13835 d$^{-1}$.

**References**

Bacon, M. P., D. W. Spencer, and P. G. Brewer. 1976. Pb-210/Ra-226 and Po-210/Pb-210 disequilibria in seawater and suspended particulate matter. Earth Planet. Sci. Lett. 32: 277–296. doi:10.1016/0012-821X(76)90068-6

Baskaran, M., and others. 2013. Effects of flow rates and composition of the filter, and decay/ingrowth correction factors involved with the determination of in situ particulate $^{210}\text{Po}$ and $^{210}\text{Pb}$ in seawater. Limnol. Oceanogr. Methods 11: 126–138. doi:10.4319/lom.2013.11.126

Biggin, C. D., G. T. Cook, A. B. MacKenzie, and J. M. Pates. 2002. Time-efficient method for the determination of $^{210}\text{Pb}$, $^{210}\text{Bi}$, and $^{210}\text{Po}$ activities in seawater using liquid scintillation spectrometry. Anal. Chem. 74: 671–677. doi:10.1021/ac0107599

Bliford, I. H., L. B. Lockhart Jr., and H. B. Rosenstock. 1952. On the natural radioactivity in the air. J. Geophys. Res. 57: 499–509. doi:10.1029/JZ057i004p00499

Burton, W. M., and N. G. Stewart. 1960. Use of long-lived radioactivity as an atmospheric tracer. Nature 186: 584–589. doi:10.1038/186584a0

Carvalho, F. P., J. M. Oliveira, and G. Alberto. 2011. Factors affecting $^{210}\text{Po}$ and $^{210}\text{Pb}$ activity concentrations in mussels and implications for environmental bio-monitoring programmes. J. Environ. Radioact. 102: 128–137. doi:10.1016/j.jenvrad.2010.11.003

Chai, Y., and N. R. Urban. 2004. $^{210}\text{Po}$ and $^{210}\text{Pb}$ distributions and residence times in the nearshore region of Lake Superior. J. Geophys. Res. 109: C10S07. doi:10.1029/2003JC002081

Chung, Y., R. Finkel, M. P. Bacon, J. K. Cochran, and S. Krishnaswami. 1983. Intercomparison of $^{210}\text{Pb}$ measurements at GEOSECS station 500 in the Northeast Pacific. Earth Planet. Sci. Lett. 65: 393–405. doi:10.1016/0012-821X(83)90178-4

Church, T. M., H. Hussain, T. G. Ferdelman, and S. W. Fowler. 1994. An efficient quantitative technique for the simultaneous analyses of radon daughters $^{210}\text{Pb}$, $^{210}\text{Bi}$, and $^{210}\text{Po}$. Talanta 41: 243–249. doi:10.1016/0039-9140(94)80115-0

Church, T. M., and others. 2012. Inter-calibration studies of $^{210}\text{Po}$ and $^{210}\text{Pb}$ in dissolved and particulate sea water samples. Limnol. Oceanogr. Methods 10: 776–789. doi:10.4319/lom.2012.10.776

Connan, O., P. Germain, L. Solier, and G. Gouret. 2007. Variations of $^{210}\text{Po}$ and $^{210}\text{Pb}$ in various marine organisms from Western English Channel: Contribution of $^{210}\text{Pb}$ to the radiation dose. J. Environ. Radioact. 97: 168–188. doi:10.1016/j.jenvrad.2007.04.004

Craig, H., S. Krishnaswami, and B. L. K. Somayajulu. 1973. $^{210}\text{Pb}$,$^{226}\text{Ra}$: Radioactive disequilibrium in the deep sea. Earth Planet. Sci. Lett. 17: 295–305. doi:10.1016/0012-821X(73)90194-5

Flear, A. F., and M. P. Bacon. 1984. Determination of $^{210}\text{Pb}$ and $^{210}\text{Po}$ in seawater and marine particulate matter. Nucl. Instrum. Methods Phys. Res. 223: 243–249. doi:10.1016/0167-5087(84)90655-0

Fowler, S. W., J.-L. Teyssie, and T. M. Church. 2010. Scavenging and retention of bismuth by marine plankton and biogenic particles. Limnol. Oceanogr. 55: 1093–1104. doi:10.4319/lo.2010.55.3.1093

Fry, L. M., and K. K. Menon. 1962. Determination of the tropospheric residence time of lead-210. Science 137: 994–995. doi:10.1126/science.137.3534.994
Hill, C. R. 1960. Lead-210 and polonium-210 in grass. Nature 187: 211–212. doi:10.1038/187211a0

Holtzman, R. B. 1966. Concentrations of the naturally-occurring radionuclides Pb-210, Po-210 and Ra-226 in aquatic fauna, p. 82–89. In Argonne National Laboratory, Radiological Physics Division Annual Report, July 1966 through June 1967. ANL-7360. Argonne National Laboratory

Katzberger, C., G. Wallner, and K. Irlweck. 2001. Determination of 210Pb, 210Bi and 210Po in natural drinking water. J. Radioanal. Nucl. Chem. 249: 191–196. doi:10.1023/A:1013230124145

Kim, S. H., and G.-H. Hong. 2019. On the role of 210Bi in the apparent disequilibrium of 210Pb–210Po at sea. J. Environ. Radioact. 208-209: 106024. doi:10.1016/j.jenrrad.2019.106024

Kostenko, J. J. 1982. Fractionation of lead-210 in Lake Michigan sediments. M.S. thesis. Univ. of Wisconsin-Milwaukee.

MacKenzie, A. B., and R. D. Scott. 1975. Determination of bismuth-210 and polonium-210 from aqueous solutions by spontaneous adsorption on copper foils. Analyst 104: 1151–1158. doi:10.1039/AN9790401151

Marley, N. A., J. S. Gaffney, K. A. Orlandini, P. J. Drayton, and M. M. Cunningham. 1999. An improved method for the separation of 210Bi and 210Po from 210Pb by using solid-phase extraction disk membranes: Environmental applications. Radiochim. Acta 85: 71–78. doi:10.1524/ract.1999.85.12.71

Michel, H., D. Levent, V. Barci, G. Barci-Funel, and C. Hurel. 2008. Soil and sediment sample analysis for the sequential determination of natural and anthropogenic radionuclides. Talanta 74: 1527–1533. doi:10.1016/j.talanta.2007.09.030

Montenero, M. P., E. K. Dilbone, and J. T. Waples. 2017. Using medically-derived iodine-131 to track sewage effluent in the Laurentian Great Lakes. Water Res. 123: 773–782. doi:10.1016/j.watres.2017.07.022

Mudbidre, R., M. Baskaran, and L. Schweitzer. 2014. Investigations of the partitioning and residence times of Po-210 and Pb-210 in a riverine system in Southeast Michigan, USA. J. Environ. Radioact. 138: 375–383. doi:10.1016/j.jenvrad.2014.01.007

Noshkin, V. E., K. M. Wong, R. J. Eagle, and T. A. Jokela. 1984. Concentrations of 208Bi and 210Pb, 210Bi-210Po disequilibrium in fish. Pacific Science 38: 350–355.

Rama, M. K., and E. D. Goldberg. 1961. Lead-210 in natural waters. Science 134: 98–99. doi:10.1126/science.134.3472.98

Rigaud, S., and others. 2013. A methods assessment and recommendations for improving calculations and results in the marine environment. Limnol. Oceanogr. Methods 11: 561–571. doi:10.4319/lom.2013.11.561

Robbins, J. A., and D. N. Edgington. 1975. Determination of recent sedimentation rates in Lake Michigan using Pb-210 and Cs-137. Geochim. Cosmochim. Acta 39: 288–304. doi:10.1016/0016-7037(75)90198-2

Rutgers van der Loeff, M. M., and W. Geibert. 2008. U/Th series nuclides as tracers of particle dynamics, scavenging and biogeochemical cycles in the oceans, p. 227–268. In S. Krishanswami and J. K. Cochran [eds.], U/Th-series radionuclides in aquatic systems, v. 13, chap. 7. Elsevier. doi:10.1016/S1569-4860(07)00007-1

Saito, N. 1984. Selected data on ion exchange separations in radioanalytical chemistry. Pure Appl. Chem. 56: 523–539. doi:10.1351/pac198456040523

Shannon, L. V., R. D. Cherry, and M. J. Orren. 1970. Polonium-210 and lead-210 in the marine environment. Geochim. Cosmochim. Acta 34: 701–711. doi:10.1016/0016-7037(70)90072-4

Stewart, M. S., and N. S. Fisher. 2003. Bioaccumulation of 210Po in marine copepods. Limnol. Oceanogr. 48: 2011–2019. doi:10.4319/lo.2003.48.5.2011

Szarlowicz, K. 2019. Optimization of the radiochemical procedure of 210Po determination in small amounts of sediment samples. Int. J. Environ. Sci. Tech. 16: 5735–5740. doi:10.1007/s13762-018-2156-2

Talbot, R. W., and A. W. Andren. 1984. Seasonal variations of 210Pb and 210Po concentrations in an oligotrophic lake. Geochim. Cosmochim. Acta 48: 2053–2063. doi:10.1016/0016-7037(84)90386-7

Tokieda, T., H. Narita, K. Harada, and S. Tsunogai. 1994. Sequential and rapid determination of Po-210, Bi-210, and Pb-210 in natural waters. Talanta 41: 2079–2085. doi:10.1016/0039-9140(94)00182-0

Tokieda, T., K. Yamanaka, K. Harada, and S. Tsunogai. 1996. Seasonal variations of residence time and upper atmospheric contribution of aerosols studied with Pb-210, Bi-210, Po-210 and Be-7. Tellus B Chem. Phys. Meteorol. 48: 690–702. doi:10.3402/tellusb.v48i5.15940

Uğur, A., G. Yener, and A. Bassari. 2002. Trace metals and 210Po (210Pb) concentrations in mussels (Mytilus galloprovincialis) consumed at Western Anatolia. Appl. Radiat. Isot. 57: 565–571. doi:10.1016/S0969-8043(02)00141-0

Verdeny, E., P. Masque, J. Garcia-Orellana, C. Hanfland, J. K. Cochran, and G. Stewart. 2009. POC export from ocean surface waters by means of 234Th/238U and 210Po/210Pb disequilibrium: A review of the use of two radiotracer pairs. Deep-Sea Res. II 56: 1502–1518. doi:10.1016/j.dsr2.2008.12.018

Wang, J., Q. Zhong, M. Baskaran, and J. Du. 2019. Investigations on the time-series partitioning of 210Pb, 207Bi and 210Po between marine particles and solution under different salinity and pH conditions. Chem. Geol. 528: 119275. doi:10.1016/j.chemgeo.2019.119275

Waples, J. T., H. A. Bootema, and J. V. Klump. 2017. How are coastal benthos fed? Limnol. Oceanogr. Lett. 2: 18–28. doi:10.1002/lol2.10033

Waples, J. T., and K. A. Orlandini. 2010. A method for the sequential measurement of yttrium-90 and thorium-234 and their application to the study of rapid particle dynamics in aquatic systems. Limnol. Oceanogr. Methods 8: 661–677. doi:10.4319/lom.2010.8.0661

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