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Daphne McNeary

Wayne State University, ab7174@wayne.edu

Mark Baskaran

Wayne State University, baskaran@wayne.edu

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## Residence times and temporal variations of $^{210}\text{Po}$ in aerosols and precipitation from southeastern Michigan, United States

Daphne McNeary<sup>1</sup> and Mark Baskaran<sup>1</sup>

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[1] Daughter products of  $^{222}\text{Rn}$  (such as  $^{210}\text{Pb}$ , half-life = 22.1 years, and  $^{210}\text{Po}$ , half-life = 138 days) have been widely used as tracers to determine the removal rates of aerosols as well as to obtain analog information on the behavior of other chemical species in the lower atmosphere. To establish the first data set on the depositional fluxes of  $^{210}\text{Po}$  in bulk precipitation and concentrations in air samples from the midwestern United States, we measured the depositional fluxes of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  in the bulk (wet plus dry) and dry fallout by deploying a rain collector (dry and bulk) for a period of 17 months. We also collected 30 aerosol samples during this period to assess the temporal variations of these nuclides in the surface air in Detroit, Michigan. The activity of  $^{210}\text{Po}$  in the surface air ranged from below detection limit to  $0.118 \text{ mBq m}^{-3}$  (mean of  $0.072 \text{ mBq m}^{-3}$ ). The specific activities of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  in aerosols ranged between 0.28 and  $4.48 \text{ Bq g}^{-1}$  (mean of  $0.87 \text{ Bq g}^{-1}$ ) and 2.7 and  $30 \text{ Bq g}^{-1}$  (mean of  $13.6 \text{ Bq g}^{-1}$ ), respectively; these values are about 1–2 orders of magnitude higher than the surface soil. The mean activity ratios of  $^{210}\text{Po}/^{210}\text{Pb}$  in the bulk precipitation and dry fallout were found to be 0.049 ( $n = 27$ ) and 0.25 ( $n = 8$ ), corresponding to residence times of 15 and 75 days, respectively. Higher values in the dry fallout are attributed to resuspension of very fine older material from the ground. The  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratios in the aerosols varied between 0 and 0.210 (mean of 0.075), with corresponding residence times of 0–61 days (mean of 22 days). The mean deposition velocity and bulk washout ratio obtained using  $^{210}\text{Po}$  is compared with those obtained for  $^{210}\text{Pb}$ . From the measured aerosol mass concentrations and calculated values of the depositional velocity, the calculated depositional fluxes of aerosols are reported.

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### 1. Introduction

[2] Toxic substances are released daily into the atmosphere from anthropogenic sources that could potentially cause damage to the environment and human health. Once these pollutants enter the atmosphere, it is important to know how long they will remain in the atmosphere, what impact they will have on the environment, and what pathways will they take and where they will end up in the environment. Particle-reactive radionuclides that are present in the atmosphere provide analog information on the behavior of many of these pollutants.

[3] Radon-222 is a noble gas that emanates predominantly from the Earth's continental crust. The global  $^{222}\text{Rn}$  flux from continents ranges from  $1300$  to  $1800 \text{ Bq m}^{-2} \text{ d}^{-1}$ , but  $\sim 17 \text{ Bq m}^{-2} \text{ yr}^{-1}$  from oceanic areas [Samuelsson *et al.*, 1986; Nazaroff, 1992]. Thus the variations in the atmo-

spheric activities or fluxes of  $^{222}\text{Rn}$  and its daughter products in the atmosphere are primarily controlled by land-sea distribution. Lead-210 ( $T_{1/2} = 22.1$  years) is produced from the decay of  $^{222}\text{Rn}$  ( $T_{1/2} = 3.8$  days) and  $^{210}\text{Po}$  ( $T_{1/2} = 138$  days) is directly produced from  $^{210}\text{Bi}$ , after  $^{210}\text{Pb}$  decays to  $^{210}\text{Bi}$  ( $T_{1/2} = 5.01$  days). Since  $^{222}\text{Rn}$  is a noble gas that emanates predominantly from the Earth's continental crust, the activity of  $^{210}\text{Pb}$  in the air is longitudinal dependant, whether it is above the ocean or a continent, and its activity will decrease with elevation from the Earth's surface due to a decrease in the activity of  $^{222}\text{Rn}$  [Moore *et al.*, 1973].

[4] Naturally occurring particle-reactive radionuclides, have been utilized as effective tracers for the study of atmospheric transport processes [Lal, 1968; Wogman *et al.*, 1968; Bhandari *et al.*, 1970; Martell, 1970; Perkins *et al.*, 1970; Poet *et al.*, 1972; Martell and Moore, 1974; Kuroda *et al.*, 1978; Robbins, 1978; Moore *et al.*, 1980; Gaggeler, 1995; Suzuki and Shiono, 1995; Marley *et al.*, 2000; Baskaran and Shaw, 2001; Hirose *et al.*, 2004; Gaffney *et al.*, 2004; Duenas *et al.*, 2004, 2005; Papastefanou, 2006]. These radionuclide source terms are relatively well

<sup>1</sup>Department of Geology, Wayne State University, Detroit, Michigan, USA.

known, and are removed from the atmosphere by bulk precipitation, dry fallout, and radioactive decay, as well as removal by coagulation of smaller radionuclide-laden particles followed by gravitation settling. In particular, the activities of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  and their activity ratios in aerosols are useful to understand several atmospheric processes, including (1) residence times and removal rates of aerosols (the determination of the residence time using  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratios in aerosols can potentially provide information on the sources of aerosols, either of local or remote origin; rainout events will reduce these residence times considerably), (2) washout ratios (= specific activity in precipitation (mBq/kg)/specific activity in the air (mBq m $^{-3}$ )), (3) the depositional velocities ( $v$  = total flux (Bq m $^{-2}$  yr $^{-1}$ ) to the Earth's surface/activity in air (Bq m $^{-3}$ ) at some reference level) of these nuclides, (4) information on the sources and pathways of radionuclides, and (5) removal fluxes of aerosols using  $^{210}\text{Po}$ . In addition, the data on the activities in aerosols and bulk depositional fluxes of  $^{210}\text{Po}$  in the midwestern region of the United States is very limited. Information on the variations of the depositional fluxes of these nuclides is needed for utilizing these nuclides as tracers in the lacustrine system, as they provide insight on the long-range transport of radionuclides as well as to understand the differences in the behavior of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ .

[5] In our earlier study, we have reported the bulk and dry depositional fluxes of  $^7\text{Be}$  and  $^{210}\text{Pb}$  as well as the variations of their activities in aerosol samples [McNeary and Baskaran, 2003]. However, the activity ratios  $^{210}\text{Po}/^{210}\text{Pb}$  in aerosols enables us to estimate the residence time of aerosols and compare to the values obtained from bulk fallout. In addition, for the first time, we estimate the removal fluxes of aerosols using deposition velocities of aerosols and aerosol mass concentration. Since Po is highly volatile, this information could be quite useful for other species that behave geochemically similar to  $^{210}\text{Po}$  (such as Hg). The results and discussion presented in this paper do not overlap with what was presented by McNeary and Baskaran [2003].

## 2. Material and Methods

### 2.1. Collection of Bulk and Dry Fallout and Aerosol Samples

[6] The city of Detroit (42°25'N; 83°1'W; 175–205 m above msl; land area ~362 km $^2$ , and Metro Detroit area ~10,145 km $^2$ ) is located in Southeastern Michigan along the banks of the Detroit River and is the largest city in Michigan. A bulk rain collector (polyethylene drum of 200 L capacity, 2800 cm $^2$  surface area) was deployed in September 1999 at a site in the southwest area of Detroit, Michigan at ~1 m above the ground to avoid the resuspension of local dust particles getting into the collector, and a dry collector (lid of the drum) was deployed on the roof of a building at the same site at ~4 m above ground. The sampling site has been used as an air monitoring network station by the Michigan Department of Environmental Quality (MDEQ), Wayne County and U. S. Environmental Protection Agency (EPA) for a number of years. Prior to the collection of each sample, 100 mL of concentrated HCl with a 1 mL spike of  $^{209}\text{Po}$  (0.1768 ± 0.0018 Bq) and 1 mL of stable

Pb ( $\equiv$  1 mL of 1010  $\mu\text{g}/\text{mL}$ , Aldrich #05618DR) were added to the dry and bulk collectors. The  $^{209}\text{Po}$  obtained from NIST was used as a yield tracer. Details on the dry and wet collector are given by McNeary and Baskaran [2003]. The bulk rain samples were collected after each significant rainfall and after ~10 days of dry weather for the dry collector. Immediately after collection, the drum and/or the lid was cleaned with repeated rinsing of 6M HCl to remove adsorbed Pb and Po isotopes from the walls of the collector. The rinsings were combined with the rain sample and subsequently the solutions were further processed.

[7] A high-volume sampler equipped with a high purity glass microfiber filter was used to collect total suspended particulate matter (TSP) at the ground level. Details on the aerosol collection methodology are given by McNeary [2002]. The mass activity (mg m $^{-3}$ ) of aerosols in ambient air was determined gravimetrically.

### 2.2. Radiochemical Processing and Assay of Bulk and Dry Fallout and Aerosol Samples

[8] The bulk or dry deposition sample from the collector was transferred to a precleaned 3 L Pyrex glass beaker in the laboratory and evaporated to ~100 mL. Details on subsequent chemical processing for  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  are given by McNeary [2002]. The used glass fiber filter paper was weighed and cut into two halves. One half of the filter paper was stored in an envelope for future analysis while the other half was weighed and digested by adding 20 mL of hydrofluoric acid to bring the filter into solution. One milliliter of  $^{209}\text{Po}$  spike (0.1768 ± 0.0018 Bq mL $^{-1}$ ) was added. After evaporating the solution, the residue was treated with conc. HNO $_3$ , HCl and finally taken in 10 mL HCl. Details on the gamma counting are given by McNeary and Baskaran [2003]. After gamma counting, the solution was transferred from the counting vial quantitatively into a Teflon beaker and dried in a hot plate. The medium was converted into dilute HCl medium and the pH of the solution was adjusted ~2 after adding 8 mL of 20% hydroxylamine hydrochloride and 2 mL of 20% sodium citrate. The polonium was electroplated onto silver planchets and were assayed in a 8-input Octete-PC (ORTEC Company) alpha spectrometer with surface barrier detectors coupled to an integrated preamplifier, amplifier and multichannel analyzer in the Octete-PC system [McNeary, 2002].

[9] The decay correction for  $^{210}\text{Po}$  and an ingrowth correction for  $^{210}\text{Po}$  when determining the in situ  $^{210}\text{Po}$  activity ( $A_{\text{Po}-210}$ ) were applied as follows:

$$A_{\text{Po}-210} = \left\{ \left[ \frac{^{210}\text{N}}{^{209}\text{N}} \right] * A_{\text{Po}-209} * e^{\lambda_{\text{Po}t1}} \right\} - A_{\text{Pb}-210} * \left[ \frac{\lambda_{\text{Po}}}{(\lambda_{\text{Po}} - \lambda_{\text{Pb}})} \right] * e^{\lambda_{\text{Po}t1}} * \left[ e^{-\lambda_{\text{Po}t2}} - e^{-\lambda_{\text{Pb}t2}} \right] \quad (1)$$

where  $^{210}\text{N}$  and  $^{209}\text{N}$  are the background subtracted  $^{210}\text{Po}$  and  $^{209}\text{Po}$  counts, respectively,  $A_{\text{Po}-209}$  and  $A_{\text{Pb}-210}$  are the activities (mBq) of  $^{209}\text{Po}$  and  $^{210}\text{Pb}$ , respectively, and  $\lambda_{\text{Po}}$  and  $\lambda_{\text{Pb}}$  are the decay constants of  $^{210}\text{Po}$  (0.00502 d $^{-1}$ ) and  $^{210}\text{Pb}$  (0.0311 yr $^{-1}$ ) respectively;  $t1$  and  $t2$  are the time between rain collector removal and midcounting (days) and midcollection to polonium plating (days), respectively.

**Table 1.** Sampling Time Intervals, Annual Depositional Fluxes, and Activities of  $^{7}\text{Po}$  and  $^{210}\text{Pb}$  Measured in Detroit, Michigan From September 1999 Through February 2001<sup>a</sup>

Collection Interval	Days in Collection	Rainfall, cm	$^{210}\text{Po}$ , mBq L <sup>-1</sup>	$^{210}\text{Pb}$ , mBq L <sup>-1</sup>	$^{210}\text{Po}$ Flux, Bq m <sup>-2</sup> yr <sup>-1</sup>	$^{210}\text{Pb}$ Flux, Bq m <sup>-2</sup> yr <sup>-1</sup>	$^{210}\text{Po}/^{210}\text{Pb}$ , Activity Ratio	Residence Time, days
24 Sep to 1 Oct 1999	7 (3)	4.4	7.0	105	15.8 ± 1.3	240 ± 10	0.066 ± 0.005	20 ± 1
1–5 Oct 1999	4 (2)	1.2	2.2	402	2.4 ± 0.9	455 ± 15	0.005 ± 0.002	3.3 ± 0.7
5–14 Oct 1999	9 (3)	2.3	BD	500	BD	445 ± 10	-	-
14 Oct to 4 Nov 1999	21 (2)	1.8	36	195	14.5 ± 0.9	58.3 ± 3.3	0.194 ± 0.012	43 ± 3
4 Nov to 9 Dec 1999	35 (10)	3.6	13	462	4.8 ± 3.2	172 ± 3	0.028 ± 0.019	10.1 ± 4.8
9 Dec 1999 to 7 Jan 2000	29 (7)	4.4	4.9	375	2.7 ± 0.7	208 ± 4	0.013 ± 0.003	6.0 ± 0.8
7–27 Jan 2000	20 (7)	1.6	BD	685	BD	193 ± 6	-	-
27 Jan to 25 Feb 2000	29 (6)	1.9	32	685	7.7 ± 0.4	147 ± 4	0.059 ± 0.003	18 ± 1
25 Feb to 27 Mar 2000	31 (10)	3.3	BD	418	BD	162 ± 4	-	-
27 Mar to 22 Apr 2000	26 (11)	7.5	8.3	198	9.4 ± 2.2	183 ± 4	0.051 ± 0.012	16 ± 3
22 Apr to 12 May 2000	20 (5)	5.4	22	213	22.2 ± 1.3	212 ± 5	0.105 ± 0.006	30 ± 1
12–22 May 2000	10 (6)	4.6	21	288	35.4 ± 1.8	417 ± 10	0.085 ± 0.004	25 ± 1
22–29 May 2000	7 (2)	1.4	126	573	93.2 ± 5.1	328 ± 10	0.283 ± 0.016	88 ± 7
29 May to Jun 1 2000	3 (1)	0.56	47	1145	32.2 ± 1.4	382 ± 11	0.084 ± 0.004	24 ± 2
1–22 Jun 2000	21 (8)	2.7	21	343	10.0 ± 1.5	120 ± 4	0.084 ± 0.012	24 ± 4
22–30 Jun 2000	8 (5)	5.1	7.0	247	16.2 ± 1.0	365 ± 9	0.044 ± 0.003	14 ± 1
30 Jun to 29 Jul 2000	29 (9)	3.8	BD	768	BD	335 ± 5	-	-
29 July to 5 Aug 2000	7 (5)	4.8	BD	570	BD	1007 ± 18	-	-
5–21 Aug 2000	16 (5)	1.6	4.0	492	3.8 ± 0.5	175 ± 3	0.022 ± 0.003	8.5 ± 0.8
21–23 Aug 2000	2 (1)	2.6	9.0	540	42.4 ± 2.6	1718 ± 40	0.025 ± 0.002	9.3 ± 0.5
23 Aug to 17 Sep 2000	25 (8)	9.5	BD	208	BD	288 ± 9	-	-
17 Sep to 9 Oct 2000	22 (10)	5.6	10.5	290	9.8 ± 2.4	270 ± 9	0.036 ± 0.009	12 ± 2
9–26 Oct 2000	17 (7)	2.6	5.0	733	2.8 ± 1.5	250 ± 11	0.011 ± 0.006	5.3 ± 1.4
26 Oct to 26 Nov 2000	31 (11)	3.5	BD	410	BD	167 ± 6	-	-
26 Nov to 1 Jan 2001	36 (14)	5.1	BD	352	BD	180 ± 6	-	-
1 Jan to 1 Feb 2001	31 (8)	1.2	BD	1233	BD	155 ± 7	-	-
1 Feb to 1 Mar 2001	29 (3)	3.4	38	312	16.3 ± 1.4	133 ± 8	0.122 ± 0.011	35 ± 3

<sup>a</sup>BD is below detection. Numbers in parentheses denote number of rainy days. Reported propagated errors arise from the counting statistics, errors associated with calibration of the counting instruments, and error associated with the spike used.

As can be seen from equation (1), the final  $^{210}\text{Po}$  activities and deposition fluxes were corrected for radioactive decay from the end of sample collection to midcounting time as well as the for the ingrowth and decay during the deployment period and the details are given by *McNeary* [2002].

### 3. Results

#### 3.1. Precipitation

[10] The amount of precipitation, collection interval, specific activities, and depositional fluxes of  $^{210}\text{Po}$  for the 27 bulk samples and 12 dry deposition samples are given in Tables 1 and 2. We have published the data on the depositional fluxes of  $^7\text{Be}$  and  $^{210}\text{Pb}$  in an earlier article and hence we will limit our discussion on  $^{210}\text{Pb}$  to only those aspects that were not discussed in the earlier article [*McNeary and Baskaran, 2003*] and pertaining to the combined utility of  $^{210}\text{Po}/^{210}\text{Pb}$  ratio as a tracer. Of the 17 months for which the monthly precipitation was measured, the highest monthly precipitation accumulation occurred in the month of August 2000 and low precipitation occurred during winter months in 2000 (Figure 1).

#### 3.2. Activities and Depositional Fluxes of $^{210}\text{Po}$ and Activity Ratios of $^{210}\text{Po}/^{210}\text{Pb}$ in the Bulk Deposition Samples

[11] The specific activity (mBq L<sup>-1</sup>), depositional fluxes (Bq m<sup>-2</sup> yr<sup>-1</sup>) of  $^{210}\text{Po}$  and the activity ratios of  $^{210}\text{Po}/^{210}\text{Pb}$  in bulk deposition are given in Table 1. In nine samples, the time elapsed between the collection and plating of  $^{210}\text{Po}$  was too long, and as a result, the in growth correction

(in growth of  $^{210}\text{Po}$  from  $^{210}\text{Pb}$ ) was large. In those samples, the decay and in growth corrected  $^{210}\text{Po}$  values were either zero or negative. Those values are omitted from further discussion. In the remaining eighteen samples, the specific activity of  $^{210}\text{Po}$  in bulk precipitation samples varied between 2.4 and 126 mBq L<sup>-1</sup>, with a mean value of 23.0 mBq L<sup>-1</sup>. The corresponding depositional fluxes ranged from 2.4 to 93 Bq m<sup>-2</sup> yr<sup>-1</sup>, with a mean value of 18.1 Bq m<sup>-2</sup> yr<sup>-1</sup>. The monthly depositional  $^{210}\text{Po}$  flux (Figure 1) was calculated as follows:

[12] Calculated monthly flux = [total activity (mBq) during the deployment period + activity collected in the previous collection period that overlaps with the month of interest (days included in the previous sample) – activity collected after the retrieval that overlaps with the next month (days included in the next month sample)]/rain collector area (0.2800 m<sup>2</sup>). The activity was prorated based on the amount of rainfall during these periods under the assumption that the activity during a particular collection period is proportional to the amount of rainfall. Although there could be considerable variations in the activities of rainwater samples within a month, the errors introduced by this assumption are estimated to be small (less than 5%), since the fractional correction is rather small in most of the samples. The  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratios in those 18 samples varied between 0.005 and 0.283, with a mean value of 0.072, while in all the 28 samples, this mean ratio was found to be 0.029 (assuming  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratio to be zero in those nine samples). The frequency distributions of the specific activity of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  in aerosols as well as

**Table 2.** Dry Depositional Fluxes of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  Measured in Detroit, Michigan<sup>a</sup>

Sample Code	Collection Interval	Deployment Time, days	$^{210}\text{Pb}$ Flux, $\text{Bq m}^{-2} \text{yr}^{-1}$	$^{210}\text{Po}$ Flux, $\text{Bq m}^{-2} \text{yr}^{-1}$	$^{210}\text{Po}/^{210}\text{Pb}$ Activity Ratio
RW-D1	14–21 Oct 1999	4	$65 \pm 6$	$22.2 \pm 0.8$	$0.34 \pm 0.03$
RW-D2	24–31 Oct 1999	7	$28 \pm 4$	$15.9 \pm 2.3$	$0.57 \pm 0.12$
RW-D3 <sup>b</sup>	31 Oct to 13 Nov 1999	13	$255 \pm 8$	$12.5 \pm 0.9$	$0.049 \pm 0.004$
RW-D4 <sup>b</sup>	13–28 Nov 1999	15	$78 \pm 4$	$2.8 \pm 0.3$	$0.036 \pm 0.005$
RW-D6	26 Jan to 25 Feb 2000	6	$67 \pm 8$	0	0
RW-D7 <sup>b</sup>	25 Feb to 22 Apr 2000	6	$187 \pm 8$	$56 \pm 11$	$0.30 \pm 0.06$
RW-D10	8–30 Jun 2000	5	$53 \pm 11$	$33.9 \pm 2.5$	$0.64 \pm 0.14$
RW-D11	30 Jun to 19 Jul 2000	4	$47 \pm 10$	$12.4 \pm 0.8$	$0.27 \pm 0.06$
RW-D12	19 Jul to 23 Aug 2000	10	$37 \pm 5$	$1.0 \pm 0.6$	$0.028 \pm 0.017$
RW-D13	23 Aug to 22 Sep 2000	6	$55 \pm 15$	0	0
RW-D16	3–26 Nov 2000	4	$65 \pm 16$	$7.6 \pm 1.6$	$0.12 \pm 0.04$
RW-D17 <sup>b</sup>	26 Nov 2000 to 13 Jan 2001	7	$288 \pm 23$	0	0

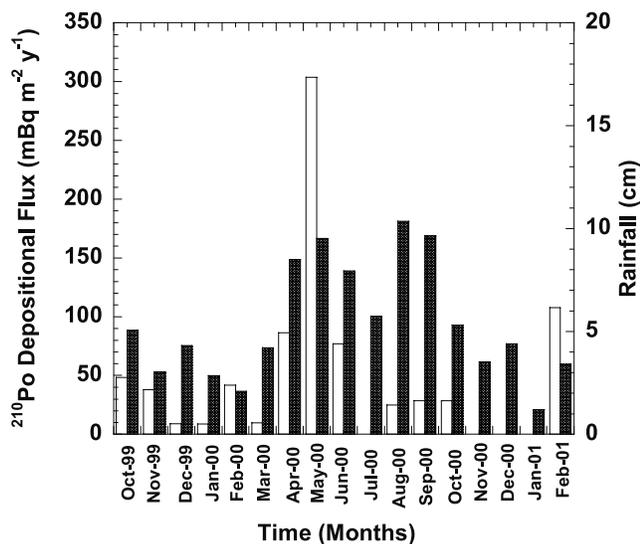
<sup>a</sup>Reported propagated errors arise from the counting statistics, errors associated with calibration of the counting instruments and error associated with the spike used.

<sup>b</sup>Likely exposure to precipitation.

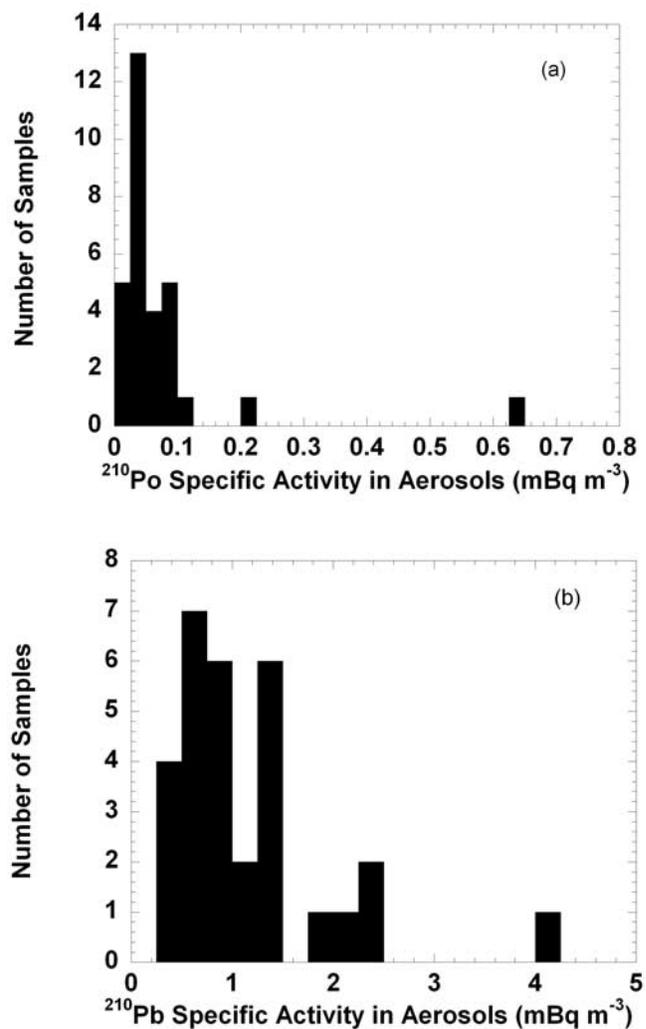
$^{210}\text{Po}/^{210}\text{Pb}$  activity ratios in aerosols and bulk precipitation are given in Figures 2 and 3, respectively.

### 3.3. Dry Depositional Flux of $^{210}\text{Po}$ and Activity Ratios of $^{210}\text{Po}/^{210}\text{Pb}$

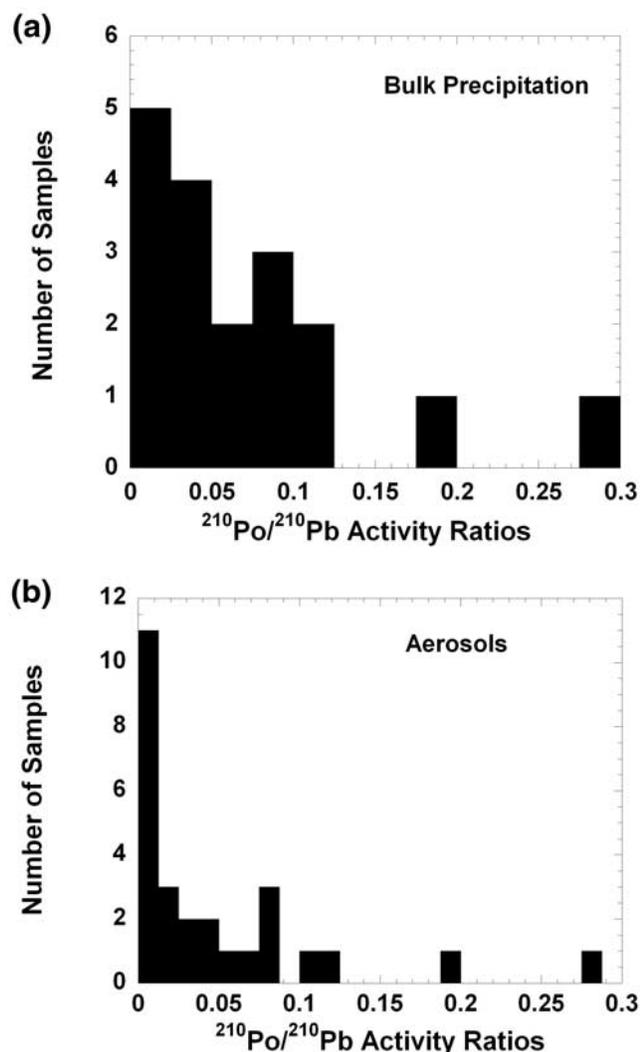
[13] The collection interval, depositional fluxes of  $^{210}\text{Po}$  and activity ratios of  $^{210}\text{Po}/^{210}\text{Pb}$  in the dry fallout for 12 samples are given in Table 2. In four samples (RW-D3, RW-D4, RW-D7 and RW-D17), very light showers contributed some amount of wet fallout into the dry collector and thus the data from these four samples will not be used for any further discussion. The dry depositional flux of  $^{210}\text{Po}$  was negligible in two of the eight samples measured. In the remaining six samples, the dry depositional flux varied between 1.0 and  $34 \text{ Bq m}^{-2} \text{yr}^{-1}$ , with a mean value of  $15.5 \text{ Bq m}^{-2} \text{yr}^{-1}$  (Table 2). The  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratios in those six samples varied between 0.05 and 0.63,



**Figure 1.** Monthly depositional fluxes of  $^{210}\text{Po}$  (shaded bar) and amount of precipitation in Detroit, Michigan.



**Figure 2.** (a) Frequency distribution of the activities of  $^{210}\text{Po}$  in aerosols collected in Detroit, Michigan. (b) Frequency distribution of the activities of  $^{210}\text{Pb}$  in aerosols collected in Detroit, Michigan.



**Figure 3.** (a) Frequency distribution of the activity ratios of  $^{210}\text{Po}/^{210}\text{Pb}$  in bulk precipitation collected in Detroit, Michigan. (b) Frequency distribution of the activity ratios of  $^{210}\text{Po}/^{210}\text{Pb}$  in aerosols collected in Detroit, Michigan.

with a mean value of 0.33 (Table 2). We realize that six samples are not sufficient to obtain any major conclusions.

### 3.4. Activities of $^{210}\text{Po}$ and Activity Ratios of $^{210}\text{Po}/^{210}\text{Pb}$ in Surface Air Samples

[14] The volume of air passed through the glass fiber filter varied between 1525 and 6636  $\text{m}^3$ , with a mean of 3975  $\text{m}^3$  (Table 3). The mass activities of the aerosol retained on the filter paper varied between 45 and 183  $\mu\text{g m}^{-3}$ , with a mean value of 91  $\mu\text{g m}^{-3}$  (Table 3). In cases when more than one air sample in a month was collected, the average value for that month is used for further discussion.

[15] Of the total 30 aerosol samples, in three samples the time elapsed between the collection and polonium plating was sufficiently long that the ingrowth correction (growth of  $^{210}\text{Po}$  from the decay of  $^{210}\text{Pb}$ ) was large and the corrected  $^{210}\text{Po}$  activity values were close to either zero or negative and thus no further discussion will be made on those

samples. In the remaining 27 samples, the  $^{210}\text{Po}$  activity varied between 0.018 and 0.65  $\text{mBq m}^{-3}$ , with a mean value of 0.075  $\text{mBq m}^{-3}$ . The  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratio in aerosols varied between 0 and 0.210, with a mean value of 0.070 (Table 3). The specific activity of  $^{210}\text{Po}$  in the aerosols (per gram of aerosol) varied between 0.28 and 4.48  $\text{Bq g}^{-1}$ , with a mean value of 0.87  $\text{Bq g}^{-1}$ . The corresponding values in  $^{210}\text{Pb}$  varied between 2.7 and 30  $\text{Bq g}^{-1}$ , with a mean value of 13.6  $\text{Bq g}^{-1}$ .

## 4. Discussion

### 4.1. Relationship Between Specific Activities of $^{210}\text{Po}$ and Amount of Precipitation

[16] The specific activities of  $^{210}\text{Po}$  in bulk precipitation samples varied between below detection limit and 126  $\text{mBq L}^{-1}$ , with a geometric mean of 15.2  $\text{mBq L}^{-1}$ . (Table 1). This range is comparable to the values reported in other places [Hussain *et al.*, 1998; Kim and Church, 2002]. The sample that had the second highest activity (1.1  $\text{Bq L}^{-1}$ ) had the least amount of precipitation (0.56 cm in one rainy day). Generally, samples with high amounts of precipitation had lower specific activities of  $^{210}\text{Po}$ , whereas samples with low amounts of precipitation had higher specific activity (Table 1). The relationship between low precipitation and high activities of  $^{210}\text{Po}$  can be attributed to the small raindrops that occur during drizzles having a much larger surface area and can scavenge more  $^{210}\text{Po}$  from the point of droplet condensation to the Earth's surface and/or quantitative washout of existing inventories of  $^{210}\text{Po}$ -laden aerosols followed by low activities in subsequent rains.

[17] The specific activity of  $^{210}\text{Po}$  (as well as  $^{210}\text{Pb}$ ) is plotted against the amount of rainfall in Figure 4. Although there is a considerable scatter in the data, there is a significant correlation ( $r = 0.45$ ,  $P < 0.01$ ) between the specific activity of  $^{210}\text{Po}$  and amount of rainfall. The weaker correlation for  $^{210}\text{Po}$  compared to  $^{210}\text{Pb}$  and  $^7\text{Be}$ , as shown by McNeary and Baskaran [2003], could be attributed to a fraction of the total Po to remain as volatile species that could escape from the scavenging by the water droplets. Of the three nuclides ( $^7\text{Be}$ ,  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ ) measured, we observe that the removal of  $^{210}\text{Po}$  by precipitation is the least efficient compared to  $^7\text{Be}$  and  $^{210}\text{Pb}$  [McNeary and Baskaran, 2003].

### 4.2. Volume-Weighted Activity of $^{210}\text{Po}$

[18] The volume-weighted activity of  $^{210}\text{Po}$  (= total annual  $^{210}\text{Po}$  deposited/annual precipitation,  $\text{Bq/L}$ ) during the 17 month study period was found to be 0.35  $\text{Bq L}^{-1}$  and is the highest value reported so far. Earlier, we reported the highest value for  $^{210}\text{Pb}$  from this site [McNeary and Baskaran, 2003]. This high value could be attributed to a number of factors including higher proportion of the air masses derived from continents, distance from the coastline, amount and frequency of rainfall, and altitude of the clouds. For example, the percentage of rainy days in Detroit (32%) is higher than those for Galveston, Texas (27%), although the total annual rainfall is significantly lower than Galveston, Texas [Baskaran *et al.*, 1993; McNeary and Baskaran, 2003]. The coastal site (Galveston) is likely to have a lower  $^{210}\text{Pb}$  value (and hence lower  $^{210}\text{Po}$ ), due to significant input of oceanic air mass (expected to be depleted in  $^{210}\text{Pb}$

**Table 3.** Sampling Time Intervals and Specific Activities in Aerosols of  $^7\text{Be}$ ,  $^{210}\text{Pb}$ , and  $^{210}\text{Po}$  Measured in Detroit, Michigan<sup>a</sup>

Collection Interval	Deployment Time, days	Volume of Air Filtered, $\text{m}^3$	Particulate Concentration, $\mu\text{g m}^{-3}$	$^{210}\text{Pb}$ , $\text{mBq m}^{-3}$	$^{210}\text{Po}$ , $\text{mBq m}^{-3}$	$^{210}\text{Po}/^{210}\text{Pb}$ Activity Ratio	Residence Time, days
28–29 Oct 1999	1	1873	183	$4.22 \pm 0.08$	$0.65 \pm 0.04$	$0.153 \pm 0.009$	$43 \pm 3$
31 Oct to 1 Nov 1999	1	2236	92	$2.45 \pm 0.06$	$0.093 \pm 0.020$	$0.038 \pm 0.008$	$13 \pm 2$
10–11 Jan 2000	1	2377	45	$1.28 \pm 0.04$	$0.20 \pm 0.01$	$0.156 \pm 0.009$	$45 \pm 3$
22–24 Jan 2000	2	3932	56	$2.11 \pm 0.03$	0	0	-
26–27 Jan 2000	1	2987	129	$1.05 \pm 0.03$	$0.037 \pm 0.004$	$0.036 \pm 0.004$	$12 \pm 1$
3–6 Feb 2000	3	6601	61	$1.34 \pm 0.02$	0	0	-
7–9 Feb 2000	2	4941	94	$1.34 \pm 0.03$	$0.018 \pm 0.003$	$0.014 \pm 0.002$	$6.3 \pm 0.3$
8–11 Mar 2000	2	5004	123	$0.44 \pm 0.03$	$0.093 \pm 0.001$	$0.210 \pm 0.013$	$61 \pm 5$
21–23 Mar 2000	2	3326	147	$0.58 \pm 0.03$	$0.042 \pm 0.002$	$0.073 \pm 0.005$	$22 \pm 1$
14–16 Apr 2000	2	4899	94	$0.72 \pm 0.02$	$0.055 \pm 0.006$	$0.075 \pm 0.010$	$22 \pm 3$
30 Apr to 2 May 2000	2	4279	73	$0.58 \pm 0.02$	$0.057 \pm 0.002$	$0.097 \pm 0.004$	$28 \pm 2$
2–4 May 2000	2	3615	57	$0.49 \pm 0.02$	$0.0400.001 \pm$	$0.082 \pm 0.005$	$24 \pm 1$
12–14 May 2000	2	3472	77	$0.51 \pm 0.02$	$0.040 \pm 0.003$	$0.078 \pm 0.006$	$23 \pm 1$
14–16 May 2000	2	4506	102	$0.55 \pm 0.02$	$0.042 \pm 0.002$	$0.077 \pm 0.005$	$23 \pm 1$
22–24 May 2000	2	3703	96	$0.92 \pm 0.02$	$0.033 \pm 0.002$	$0.037 \pm 0.002$	$12 \pm 1$
24–26 May 2000	2	3387	111	$0.30 \pm 0.03$	$0.033 \pm 0.001$	$0.111 \pm 0.008$	$32 \pm 2$
30 Jun to 2 Jul 2000	2	4239	97	$0.81 \pm 0.02$	$0.078 \pm 0.002$	$0.097 \pm 0.004$	$28 \pm 2$
8–9 Jul 2000	1	2086	84	$0.38 \pm 0.02$	$0.058 \pm 0.001$	$0.153 \pm 0.010$	$43 \pm 3$
13–14 Jul 2000	1	1525	127	$0.87 \pm 0.04$	$0.090 \pm 0.004$	$0.103 \pm 0.006$	$29 \pm 2$
24–26 Jul 2000	2	3387	80	$0.72 \pm 0.03$	0	NM	-
12–14 Aug 2000	2	4459	77	$0.75 \pm 0.02$	$0.035 \pm 0.002$	$0.045 \pm 0.002$	$14 \pm 1$
24–26 Aug 2000	2	4426	106	$0.94 \pm 0.03$	$0.038 \pm 0.001$	$0.041 \pm 0.002$	$13 \pm 1$
29 Aug to 1 Sep 2000	2	5548	75	$0.91 \pm 0.03$	$0.022 \pm 0.001$	$0.024 \pm 0.002$	$9.0 \pm 0.5$
20–22 Sep 2000	2	4382	68	$0.64 \pm 0.04$	$0.037 \pm 0.001$	$0.059 \pm 0.004$	$18 \pm 1$
29 Sep to 1 Oct 2000	2	3670	82	$1.40 \pm 0.06$	$0.077 \pm 0.002$	$0.055 \pm 0.002$	$17 \pm 1$
11–13 Oct 2000	2	4253	118	$2.00 \pm 0.06$	$0.067 \pm 0.002$	$0.034 \pm 0.001$	$12 \pm 1$
26–29 Oct 2000	3	6636	74	$1.19 \pm 0.04$	$0.035 \pm 0.002$	$0.029 \pm 0.002$	$10.4 \pm 0.5$
29 Nov to 1 Dec 2000	2	4331	54	$1.29 \pm 0.06$	$0.118 \pm 0.007$	$0.091 \pm 0.007$	$26 \pm 2$
21–23 Jan 2001	2	4155	81	$2.43 \pm 0.10$	$0.042 \pm 0.003$	$0.017 \pm 0.001$	$7.1 \pm 0.3$
2–4 Feb 2001	2	5055	67	$1.36 \pm 0.07$	$0.047 \pm 0.002$	$0.035 \pm 0.002$	$12 \pm 1$

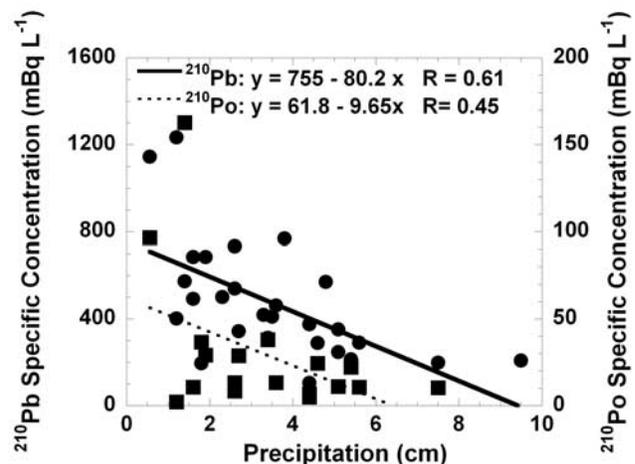
<sup>a</sup>NM is not measured. Reported propagated errors arise from the counting statistics, errors associated with calibration of the counting instruments and error associated with the spike used.

and  $^{210}\text{Po}$  due to low exhalation of  $^{222}\text{Rn}$  from the water). Detroit is farther away from the nearest coastal site and hence the relative proportion of the marine air is likely to be small. However, even a small portion of the marine air could pick up significant amounts of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  en route and hence the activity of  $^{210}\text{Po}$  (and  $^{210}\text{Pb}$ ) in air is expected to be higher.

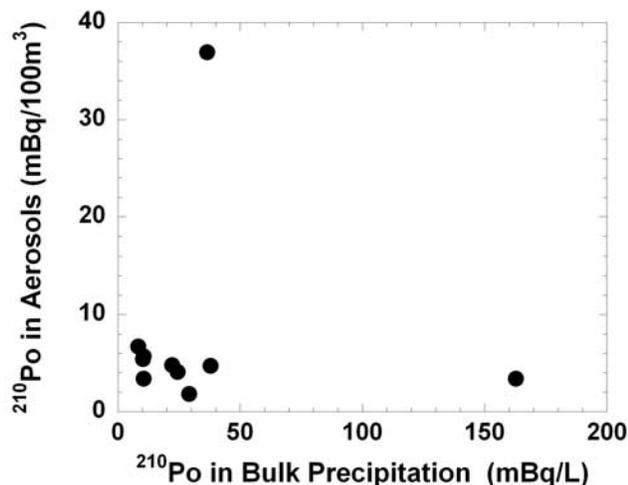
#### 4.3. Activities of $^{210}\text{Po}$ and Activity Ratios of $^{210}\text{Po}/^{210}\text{Pb}$ in the Precipitation Samples

[19] The specific activities of  $^{210}\text{Po}$  and the activity ratio of  $^{210}\text{Po}/^{210}\text{Pb}$  in air samples at any season depend upon three factors [Baskaran, 1995]: (1) The first factor is changes in the rate of transport of stratospheric air containing low activities of  $^{210}\text{Po}$  (with a relatively high  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratios, as residence time of these nuclides in stratosphere is  $\sim 1$  year), into the troposphere during the late winter and early spring seasons. (2) The second factor is decreased stability of the troposphere during the warmer months, resulting in movement of  $^{210}\text{Po}$ - and  $^{210}\text{Pb}$ -depleted aerosols from the upper troposphere to the middle and lower troposphere; this could result in lower  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratios (although the  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratios in stratospheric air mass is likely higher), as dynamic mixing of air masses could lead to active scavenging of aerosols during times of higher amounts of precipitation in late spring and summer months. (3) The third factor is variations of the rate of washout of the atmospheric aerosols that carry the  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  as seasonal changes in precipitation occur in the air masses reaching the sampling site. In addition to

these,  $^{210}\text{Po}$  could increase with longer residence time of aerosols. There is no relationship between the activities of  $^{210}\text{Po}$  in the aerosols to that in the bulk precipitation (Figure 5) while there is significant relationship between activities of  $^{210}\text{Pb}$  in aerosols to that in bulk precipitation (Figure 6). A lack of correlation again could be attributed to the volatile nature of  $^{210}\text{Po}$  some of which may not be present as adsorbed species onto aerosols, unlike  $^{210}\text{Pb}$ . As presented in section 3.3, the  $^{210}\text{Po}/^{210}\text{Pb}$  activity



**Figure 4.** Specific activities of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  ( $\text{mBq L}^{-1}$ ) versus amount of precipitation.



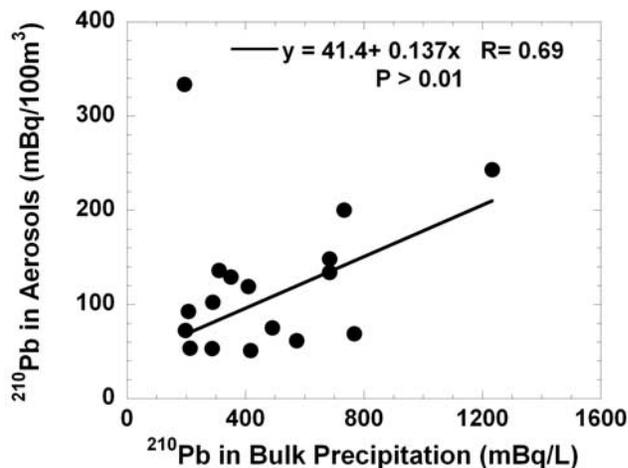
**Figure 5.** Specific activities of  $^{210}\text{Po}$  in aerosols versus in bulk precipitation.

ratios in dry precipitation are distinctly higher than those in the bulk precipitation, possibly indicating significant contribution from superfine resuspended soil particulate matter with  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratios  $\sim 1$  to the dry deposition.

#### 4.4. Activities of $^{210}\text{Po}$ , Activity Ratios of $^{210}\text{Po}/^{210}\text{Pb}$ , and Residence Time of Aerosols

[20] The temporal variation of the mass of the total suspended particulate matter retained on the filter indicates that the aerosol mass to be the highest during the month of June and generally higher during the summer months and lower during the winter months. The specific activities of  $^{210}\text{Po}$  (activity per gram of aerosols) and  $^{210}\text{Pb}$  varied between 0.28 and 4.48  $\text{Bq g}^{-1}$  (mean of 0.87  $\text{Bq g}^{-1}$ ) and 2.7 and 30  $\text{Bq g}^{-1}$  (mean of 13.6  $\text{Bq g}^{-1}$ ), respectively. There is a weak correlation ( $r = 0.38$ ,  $n = 27$ ,  $P < 0.1$ ) between the specific activities of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  (Figure 7). There is considerable scatter in the plot and this possibly could be attributed to varying amounts of volatile  $^{210}\text{Po}$  in the aerosols. The specific activity values of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  are about one to two orders of magnitude higher than those found in surface soils. The mean particle size in surface soil is about one to two orders of magnitude higher than those in the aerosols, and hence only extremely fine size (less than 10 micron) particles can undergo resuspension with high activities of  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ . If such resuspended soil particles were the source for the aerosols, then, the  $^{210}\text{Po}/^{210}\text{Pb}$  activity should be closer to 1 (any freshly deposited particulate matter that only contains  $^{210}\text{Pb}$  and no  $^{210}\text{Po}$  will attain a  $^{210}\text{Po}/^{210}\text{Pb}$  ratio of  $\sim 1$  in  $\sim 2$  years and most soil particles are expected to have a ratio of  $\sim 1$ ). In our data, this ratio is  $< 0.1$ , and hence resuspension of soil is not the major source of aerosols to the atmosphere.

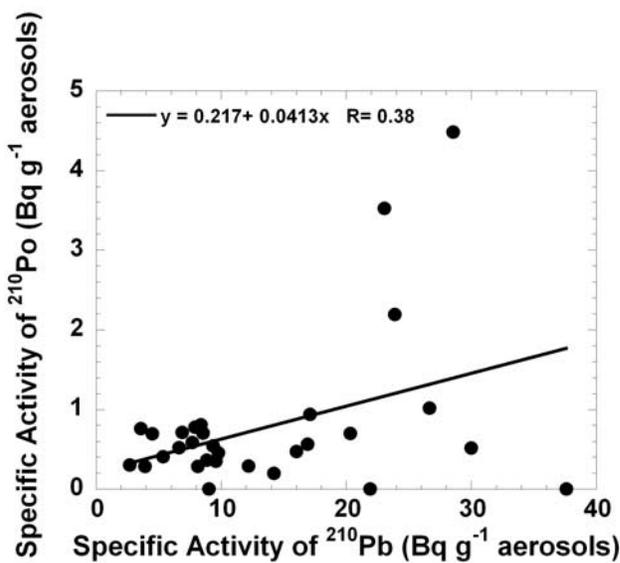
[21] If all the  $^{210}\text{Po}$  in our sampling site is derived from the atmospheric  $^{210}\text{Pb}$  via  $^{210}\text{Bi}$ , then, the  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratio in air can provide information on the sources of aerosols, of either local or remote origin as well as the 'age' of the aerosols. If Po and Pb are removed uniformly from the atmosphere, then, the  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratios in the bulk deposition samples should be the same as those in



**Figure 6.** Specific activities of  $^{210}\text{Pb}$  in aerosols versus in bulk precipitation.

the aerosol samples. The  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratios varied between 0.005 and 0.284, with a mean value of 0.072. This value is comparable to the range of 0 and 0.15 (mean of 0.05) in the precipitation samples collected from the San Francisco Bay area [Fuller and Hammond, 1983], and lower than the values reported in the north mid-Atlantic (0.11 to 0.42, mean = 0.24) on seven precipitation samples collected in 1989 [Hussain et al., 1998].

[22] Earlier studies have reported higher estimates of residence time based on  $^{210}\text{Po}-^{210}\text{Pb}$  disequilibrium than the estimates based on  $^{210}\text{Bi}-^{210}\text{Pb}$  and this difference was attributed to the extraneous sources of  $^{210}\text{Po}$  that must have been injected to the atmosphere from sources independent of the atmospheric radon. The extraneous sources of  $^{210}\text{Po}$  in the atmosphere include coal-burning power plants, forest fires, volcanoes and plant exudates [Moore et al., 1976;



**Figure 7.** Specific activities of  $^{210}\text{Pb}$  ( $\text{Bq g}^{-1}$  aerosols) versus specific activities of  $^{210}\text{Po}$  ( $\text{Bq g}^{-1}$  aerosols) in aerosols.

**Table 4.** Comparison of the Activity Ratios of  $^{210}\text{Po}/^{210}\text{Pb}$  and Residence Time of Aerosols With Those in the Aerosols<sup>a</sup>

Precipitation Sample	Deployment Time	$^{210}\text{Po}/^{210}\text{Pb}$		Sample Code	$^{210}\text{Po}/^{210}\text{Pb}$ , (Aerosols)	Residence Time, (Aerosols)
		Activity Ratio (Precipitation)	Residence Time (Precipitation)			
RWB-4 (1,2)	14 Oct to 4 Nov 1999	0.194 ± 0.012	56 ± 4	AF-1	0.153 ± 0.009	43 ± 3
RWB-4 (1,2)	14 Oct to 4 Nov 1999			AF-2	0.038 ± 0.008	13 ± 2
RWB-7 (3,4,5)	7–27 Jan 2000	-	-	AF-3	0.156 ± 0.009	45 ± 3
RWB-7 (3,4,5)	7–27 Jan 2000			AF-4	BD	-
RWB-7 (3,4,5)	7–27 Jan 2000			AF-5	0.036 ± 0.004	12 ± 1
RWB-8 (6,7)	27 Jan to 25 Feb 2000	0.059 ± 0.003	18 ± 1	AF-6	BD	-
RWB-8 (6,7)	27 Jan to 25 Feb 2000			AF-7	0.014 ± 0.002	6.3 ± 0.3
RWB-9 (8,9)	25 Feb to 27 Mar 2000	-	-	AF-8	0.210 ± 0.013	61 ± 5
RWB-9 (8,9)	25 Feb to 27 Mar 2000			AF-9	0.073 ± 0.005	22 ± 1
RWB-10 (10)	27 Mar to 22 Apr 2000	0.051 ± 0.012	16 ± 3	AF-10	0.075 ± 0.010	22 ± 3
RWB-11 (11, 12)	22 Apr to 12 May 2000	0.105 ± 0.006	30 ± 1	AF-11	0.097 ± 0.004	28 ± 2
RWB-11 (11, 12)	22 Apr to 12 May 2000			AF-12	0.082 ± 0.005	24 ± 1
RWB-12 (13, 14)	12–22 May 2000	0.085 ± 0.004	25 ± 1	AF-13	0.078 ± 0.006	23 ± 1
RWB-12 (13, 14)	12–22 May 2000			AF-14	0.077 ± 0.005	23 ± 1
RWB-13 (15, 16)	22–29 May 2000	0.283 ± 0.016	88 ± 7	AF-15	0.037 ± 0.002	12 ± 1
RWB-13 (15, 16)	22–29 May 2000			AF-16	0.111 ± 0.008	32 ± 2
RWB-17& 18 (17, 18, 19, 20)	30 Jun to 5 Aug 2000	-	-	AF-17	0.097 ± 0.004	28 ± 2
RWB-17& 18 (17, 18, 19, 20)	30 Jun to 5 Aug 2000			AF-18	0.153 ± 0.010	43 ± 3
RWB-17& 18 (17, 18, 19, 20)	30 Jun to 5 Aug 2000			AF-19	0.103 ± 0.006	29 ± 2
RWB-17& 18 (17, 18, 19, 20)	30 Jun to 5 Aug 2000			AF-20	NM	-
RWB-19 (21)	5–21 Aug 2000	0.022 ± 0.003	8.5 ± 0.8	AF-21	0.045 ± 0.002	14 ± 1
RWB-21 (22,23)	23 Aug to 17 Sep 2000	-	-	AF-22	0.041 ± 0.002	13 ± 1
RWB-21 (22,23)	23 Aug to 17 Sep 2000			AF-23	0.024 ± 0.002	9.0 ± 0.5
RWB-22 (24, 25)	17 Sep to 9 Oct 2000	0.036 ± 0.009	12±2	AF-24	0.059 ± 0.004	18 ± 1
RWB-22 (24, 25)	17 Sep to 9 Oct 2000			AF-25	0.055 ± 0.002	17 ± 1
RWB-23 (26)	9–26 Oct 2000	0.011 ± 0.006	5.3 ± 1.4	AF-26	0.034 ± 0.001	12 ± 1
RWB-24 (27)	26 Oct to 26 Nov 2000	-	-	AF-27	0.029 ± 0.002	10.4 ± 0.5
RWB-25 (28)	26 Nov 2000 to 1 Jan 2001	-	-	AF-28	0.091 ± 0.007	26 ± 2
RWB-26 (29)	1 Jan to 1 Feb 2001	-	-	AF-29	0.017 ± 0.001	7.1 ± 0.3
RWB-27 (30)	1 Feb to 1 Mar 2001	0.122 ± 0.011	35 ± 3	AF-30	0.035 ± 0.002	12 ± 1

<sup>a</sup>Numbers in parentheses denote corresponding air filter sample numbers. NM is not measured. BD is below detection limit. Errors reported with the activity ratios are the propagated errors on the activities of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ .

*Su and Huh, 2002; Le Cloarec et al., 1995; Nho et al., 1997*). Other probable sources include resuspension of topsoils [*Turekian et al., 1977; Turekian and Cochran, 1981; Nho et al., 1997*], stratospheric aerosols [*Tokieda et al., 1996*], sea spray of the surface microlayer [e.g., *Hussain et al., 1998; Kim et al., 2000*] and biovolatile  $^{210}\text{Po}$  species from the productive ocean [*Hussain et al., 1998*]. Under the assumption that all  $^{210}\text{Po}$  in the aerosol samples are derived from the decay of aerosol-laden  $^{210}\text{Pb}$  in the study site (i.e., no extraneous Po source) and there is no preferential removal of Po over Pb by aerosols, then, the residence time ( $T_R$ ) can be calculated using the equation:

$$A^{210}\text{Po}/A^{210}\text{Pb} = T_R^2 / (T_R + 1/\lambda_{\text{Bi}})(T_R + 1/\lambda_{\text{Po}}) \quad (2)$$

where  $\lambda_{\text{Bi}}$  and  $\lambda_{\text{Po}}$  are the decay constants of  $^{210}\text{Bi}$  ( $0.138 \text{ d}^{-1}$ ) and  $^{210}\text{Po}$  ( $0.00502 \text{ d}^{-1}$ ), respectively;  $A^{210}\text{Po}$  and  $A^{210}\text{Pb}$  are the activities of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$ , respectively.

[23] The calculated residence time varied between 6.3 and 61 days, with a mean value of 22 days (Table 3). The mean value is comparable to the mean residence time of 31 days obtained at Malaga, Spain [*Duenas et al., 2004*]. In three of the samples, the  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratios are not statistically indistinguishable from zero. The activity ratios of  $^{210}\text{Po}/^{210}\text{Pb}$  and residence time derived from this ratio in aerosols is compared to the corresponding values in the bulk precipitation in Table 4. As discussed earlier, the residence time of aerosol will be a realistic value, only if all atmospheric Po is derived from atmospheric  $^{210}\text{Pb}$ , and there is

no preferential removal of either Po or Pb by the atmospheric aerosols. There has been a considerable amount of controversy on the validity of using  $^{210}\text{Po}$ – $^{210}\text{Pb}$  disequilibrium to obtain the residence time of aerosols (summarized by *Robbins [1978]*). Recently, *Marley et al. [2000]* have shown that the residence times for smaller size aerosols ( $< 0.62 \mu\text{m}$ ) obtained using  $^{210}\text{Po}$ – $^{210}\text{Pb}$  activity ratios (47–57 days) are quite comparable to the residence times obtained using  $^{210}\text{Bi}$ – $^{210}\text{Pb}$  activity ratios (42–56 days). The differences in the residence times obtained using these two pairs of activity ratios become larger with the increase in the aerosol size. *Hussain et al. [1998]* reported a mean residence time of 5.4 days in April 1989 and 19.7 days in October 1989 for the marine aerosol from the North Atlantic. Our value of the residence time (mean value of 22.4 days) is quite comparable to these values. It should be pointed out that the residence time of aerosols in the lower atmosphere is about 4 days or less and increases with altitude within the troposphere by a factor of three or less [*Moore et al., 1973*]. *Kim et al. [2000]* compared the residence time obtained from  $^{210}\text{Po}/^{222}\text{Rn}$  and  $^{210}\text{Po}/^{210}\text{Pb}$  and attributed the longer residence time obtained from  $^{210}\text{Po}/^{210}\text{Pb}$  ratios to the excess  $^{210}\text{Po}$  derived from surface waters either by sea spray of the microlayer or by gas exchange.

#### 4.5. Monthly and Seasonal Variations in the Activities of $^{210}\text{Po}$ in the Aerosols

[24] The deployment periods were not strictly from the beginning to the end of a month. The monthly and seasonal

**Table 5.** Deposition Velocity of Aerosols Using  $^{210}\text{Pb}$  and  $^{210}\text{Po}$ <sup>a</sup>

Midcollection Time	$^{210}\text{Pb}$ Flux, $\text{Bq m}^{-2} \text{d}^{-1}$	$^{210}\text{Pb}$ Concentration, $\text{mBq m}^{-3}$	$^{210}\text{Po}$ Flux, $\text{Bq m}^{-2} \text{d}^{-1}$	$^{210}\text{Po}$ Concentration, $\text{mBq m}^{-3}$	$^{210}\text{Po}$ Deposition Velocity, $\text{cm s}^{-1}$	$^{210}\text{Pb}$ Deposition Velocity, $\text{cm s}^{-1}$
29 Oct 1999	240	4.22	15.8	0.650	0.07	0.04
1 Nov 1999	58.3	2.45	14.5	0.093	0.49	0.08
8 Feb 2000	147	1.34	7.7	0.018	1.33	0.35
15 Apr 2000	183	0.72	9.3	0.055	0.54	0.86
1 May 2000	212	0.58	22.2	0.057	1.24	1.16
3 May 2000	212	0.49	22.2	0.040	1.75	1.37
13 May 2000	417	0.51	35.3	0.040	2.80	2.78
15 May 2000	417	0.55	35.3	0.042	2.69	2.59
23 May 2000	328	0.92	93.2	0.033	8.86	1.29
25 May 2000	328	0.30	93.2	0.033	8.86	3.94
13 Aug 2000	175	0.75	3.8	0.035	0.34	0.75
20 Sep 2000	270	0.64	9.8	0.037	0.85	1.35
30 Sep 2000	270	1.40	9.8	0.077	0.41	0.61
12 Oct 2000	250	2.00	2.8	0.067	0.13	0.51
27 Oct 2000	167	1.19	0	0.035	34	0.45
Range					0.07–8.9	0.04–3.6
Mean					2.2	1.1

<sup>a</sup>The errors associated with the deposition velocities are estimated to be < 10% (based on the propagated errors arising from counting statistics, calibration of counting instruments, and the error associated with the spike).

variations of monthly and seasonal fluxes were calculated as described by *McNeary and Baskaran* [2003]. The monthly deposition varied between 2.3 and 93.2  $\text{Bq m}^{-2} \text{yr}^{-1}$ , with the highest values during the spring season (Figure 1). The increased deposition during spring could be attributed to exchange of air masses between stratosphere and troposphere, with larger inputs of stratospheric aerosols containing higher amounts of  $^{210}\text{Po}$  (due to longer residence times of aerosols in the stratosphere as there are no rainout or washout events).

#### 4.6. Deposition Velocity and Removal Fluxes of Aerosols Using $^{210}\text{Po}$

[25] The deposition velocity ( $V_d$ ) for any nuclide is determined by the following equation:

$$V_d = F/C_s \quad (3)$$

where  $F$  is the total flux of any species to the Earth's surface and  $C_s$  is the concentration of that species in air at the Earth's surface. The advantages of using  $^{210}\text{Po}$  to determine the deposition velocities are the following: (1)  $^{210}\text{Po}$  is mainly derived from Earth's surface and thus can be utilized for other species derived from Earth's surface (such as Hg). (2) The size distributions of  $^{210}\text{Po}$  in aerosols are likely similar to other particulate contaminants of interest, and therefore can be used to determine the fluxes of these contaminants to the Earth's surface. (3) The activities of  $^{210}\text{Po}$  in the aerosols and precipitation samples can be easily measured. In equation (3) the total flux includes dry and wet fallout.

[26] During periods when there is heavy precipitation, the deposition velocity of aerosols is expected to be significantly higher than those during drier periods. The deposition velocity for  $^{210}\text{Po}$  varied between 0.07 and 8.9  $\text{cm s}^{-1}$  (excluding one data point that has 34  $\text{cm s}^{-1}$ ) with a mean value of 2.2  $\text{cm s}^{-1}$  (Table 5). The corresponding value for  $^{210}\text{Pb}$  varied between 0.04 to 3.6  $\text{cm s}^{-1}$ , with a mean value of 1.1  $\text{cm s}^{-1}$  [*McNeary and Baskaran*, 2003]. This is the first data set reporting deposition velocities based on  $^{210}\text{Po}$  and hence there is no data to compare with. However, the

range of values is comparable to the values calculated using  $^7\text{Be}$  and  $^{137}\text{Cs}$  [*Papastefanou*, 2006].

[27] It has been reported that deposition velocity obtained from nuclides that have origin in the upper atmosphere (such as  $^7\text{Be}$ ) have generally yielded higher deposition velocities than  $^{210}\text{Pb}$  [*Turekian et al.*, 1983; *Todd et al.*, 1989; *McNeary and Baskaran*, 2003] and such differences were attributed to the differences in the source function of these two nuclides. Both  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  are derived from Earth's surface and thus the depositional velocities obtained are expected to be similar. *Duenas et al.* [2005] found correlation between the amount, frequency and duration of rainfall, and deposition velocities of  $^7\text{Be}$  and  $^{210}\text{Pb}$ , but did not observe between SPM and deposition velocities. The depositional velocities of aerosols containing  $^{210}\text{Po}$  plotted against those obtained using  $^{210}\text{Pb}$  (figure not shown) indicate significant correlation ( $R = 0.68$ ,  $P > 0.01$ ) between the two. However, the  $^{210}\text{Po}$ -based deposition velocities are generally higher than  $^{210}\text{Pb}$ -based deposition velocities, and this is likely due to preferential recycling of ultrafine dust particles containing lower  $^{210}\text{Po}$  in the soil dust. However there is no significant correlation between the depositional velocity of  $^{210}\text{Pb}$ -laden aerosols and total suspended particulate matter indicating the amount of aerosols does not control the rate at which aerosols are removed from the atmosphere. It is likely that only a small portion of the aerosol size spectrum scavenges effectively  $^{210}\text{Po}$  from the atmosphere and a major portion of the aerosols do not participate in the removal of particle-reactive nuclides, similar to the observation reported for  $^{210}\text{Pb}$  and  $^7\text{Be}$  [*McNeary and Baskaran*, 2003].

[28] The removal fluxes of aerosols,  $J_i^r$  ( $\text{mg m}^{-2} \text{d}^{-1}$ ), for nuclide 'i' can be calculated as:

$$J_i^r = V_d * \text{SPM} \quad (4)$$

where  $V_d$  is the deposition velocity ( $\text{m/d}$ ), and SPM is the suspended aerosol concentration ( $\text{mg/m}^3$ ). The removal fluxes of aerosols using  $^{210}\text{Pb}$  varied between 6 and 379  $\text{mg m}^{-2} \text{d}^{-1}$  (mean of 84  $\text{mg m}^{-2} \text{d}^{-1}$ ,  $n = 30$ ). The corresponding removal fluxes calculated using  $^{210}\text{Po}$  varied

between 11 and  $850 \text{ mg m}^{-2} \text{ d}^{-1}$  (mean of  $178 \text{ mg m}^{-2} \text{ d}^{-1}$ ,  $n = 14$ ). The distinctly higher removal fluxes based on  $^{210}\text{Po}$  is likely due to differences in the extent of recycling of aerosol-laden  $^{210}\text{Po}$ .

#### 4.7. Washout Ratio Using $^{210}\text{Po}$

[29] The washout ratio,  $W$ , is calculated for  $^{210}\text{Po}$  from the following relationship:

$$W = \rho C_{\text{rain}}/C_{\text{air}} \quad (5)$$

where  $\rho$  is the density of air at standard conditions ( $1.2 \text{ kg m}^{-3}$  at  $20^\circ\text{C}$  and  $0.76 \text{ m Hg}$ ) and  $C_{\text{rain}}$  and  $C_{\text{air}}$  are the radionuclide activities in bulk deposition (in  $\text{kg}^{-1}$ ) and a unit surface air (in  $\text{Bq m}^{-3}$ ), respectively. The washout ratio,  $W$ , relates the average activity of unit  $^{210}\text{Po}$  surface level precipitation to its average activity in unwashed surface level air. The washout ratio calculation is based on the assumption that the specific  $^{210}\text{Po}$  content of the air in the precipitating cloud is the same as that measured at the surface level in aerosol. However, if there is new air intruding into the area and the precipitation is from another air mass, considerable error will result.

[30] The washout ratio for  $^{210}\text{Po}$  varied between 68 and 4522 with a mean value of 762 (one value is omitted). This can be compared to  $^{210}\text{Pb}$  values that ranged between 55 and 2244 (mean of 637 [McNeary and Baskaran, 2003]). Because of the volatile nature of  $^{210}\text{Po}$  it is likely that  $^{210}\text{Po}$  can stay in the air as the gaseous phase for a longer time compared to  $^{210}\text{Pb}$  and hence could lead to lower washout ratios. The range of values of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  are close enough that we are unable to see any significant difference between the two. The possibility of differential washout of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  always exist which cannot be ruled out from our data. Duenas *et al.* [2005] observed significant correlation between SPM and washout ratios for  $^7\text{Be}$  ( $r = 0.42$ ,  $P < 0.05$ ) and  $^{210}\text{Pb}$  ( $r = 0.28$ ,  $P > 0.1$ ). There is no significant correlation between the washout ratios calculated for  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  (figure not shown). There is no washout ratio values published in literature using  $^{210}\text{Po}$  in aerosol and precipitation that can be compared with.

## 5. Conclusion

[31] Measurements of  $^{210}\text{Po}$  in bulk and dry precipitation as well as in aerosol samples were conducted at Detroit, Michigan, during a 17 month period in order to understand the depositional characteristics of  $^{210}\text{Po}$ . From this investigation, we draw the following conclusions.

[32] 1. The measured mean dry depositional flux ( $11.6 \text{ Bq m}^{-2} \text{ yr}^{-1}$ ) constitutes 64% of the bulk depositional flux ( $18.1 \text{ Bq m}^{-2} \text{ yr}^{-1}$ ) and is significantly higher than reported for other nuclides, such as  $^7\text{Be}$  and  $^{210}\text{Pb}$ . Such a high dry depositional flux is attributed to resuspended fine particulate material contributing to the dry fallout.

[33] 2. The specific activities of  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  in aerosols are about 1–2 orders of magnitude higher than those found in surface soil.

[34] 3. The mean activity ratios of  $^{210}\text{Po}/^{210}\text{Pb}$  in the bulk precipitation are significantly lower than those found in dry deposition samples. The mean residence time of aerosols,

calculated based on  $^{210}\text{Po}/^{210}\text{Pb}$  activity ratios, was found to be 22 days.

[35] 4. The activity ratios of  $^{210}\text{Po}/^{210}\text{Pb}$  in the bulk precipitation are slightly lower than the aerosols, indicating possible presence of volatile  $^{210}\text{Po}$  that are not completely scavenged by precipitation condensation; and

[36] 5. The mean deposition velocity of aerosols using  $^{210}\text{Po}$  was found to be  $2.2 \text{ cm s}^{-1}$ , a value higher than that reported for  $^{210}\text{Pb}$  in the same site. The differences in the velocities obtained using  $^{210}\text{Po}$  and  $^{210}\text{Pb}$  is likely due to the differences in the scavenging behavior of these nuclides. The removal fluxes of aerosols calculated using  $^{210}\text{Pb}$  and  $^{210}\text{Po}$  varied between 6 and  $178 \text{ mg m}^{-2} \text{ d}^{-1}$ . The mean washout ratio using  $^{210}\text{Po}$  activity was calculated to be 762.

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M. Baskaran, and D. McNeary, Department of Geology, Wayne State University, 0224 Old Main Building, Detroit, MI 48202, USA. (baskaran@wayne.edu)