

Phosphorus 32, phosphorus 33, beryllium 7, and lead 210: Atmospheric fluxes and utility in tracing stratosphere/troposphere exchange

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Abstract. The deposition of ³²P, ³³P, ⁷Be, and ²¹⁰Pb was measured in individual rain events at Woods Hole, Massachusetts, from March 1996 to February 1998 and in bimonthly integrated samples from Portsmouth, New Hampshire, from March to November 1997. Annual depositional fluxes of ³²P and ³³P were 0.178 and 0.165 disintegrations per minute (dpm) cm⁻² yr⁻¹, respectively, at Woods Hole and 0.212 and 0.175 dpm cm⁻² yr⁻¹ at Portsmouth. Beryllium 7 and ²¹⁰Pb fluxes averaged 12.8 and 1.43 dpm cm⁻² yr⁻¹, respectively, at Woods Hole and 16.6 and 0.95 dpm cm⁻² yr⁻¹ at Portsmouth. High ratios of ³³P/³²P were observed in rain during severe storm events, suggesting that these isotopes trace stratosphere/troposphere exchange processes. Similar occurrences, however, were not observed in ⁷Be/³²P, ⁷Be/³³P, and ⁷Be/²¹⁰Pb ratios. This indicates that there is substantial fractionation occurring among phosphorus, beryllium, and lead between time of production and atmospheric removal via precipitation.

1. Introduction

The processes that control stratosphere/troposphere exchange (STE) are of significant interest for elucidating the atmospheric cycling of many natural and anthropogenically produced trace elements. Many of these elements may play a role in controlling radiative forcing, a mechanism for inducing global change [Ramaswamy *et al.*, 1992; Toumi *et al.*, 1994]. Upward transport of anthropogenic trace chemical species, such as CFCs and other halocarbons, from the troposphere into the stratosphere, is one of the major causes of stratospheric ozone depletion. In contrast, downward transport from the stratosphere into the troposphere is a major removal pathway for many stratospheric components, including ozone and other reactive constituents.

Naturally produced radionuclides have proven to be useful tracers of a wide range of atmospheric processes [Bhandari *et al.*, 1966, 1970; Luyanous *et al.*, 1970; Viezee and Singh, 1980; Dibb *et al.*, 1992]. Beryllium 7 ($t_{1/2}$ = 53.3 days) and lead 210 ($t_{1/2}$ = 22.3 years), in particular, are two radionuclides which have been used to study aerosol residence times and air mass sources [Lal, 1959; Lal *et al.*, 1960; Bhandari *et al.*, 1966; 1970; Luyanous *et al.*, 1970; Dutkiewicz and Hussain, 1979, 1985; Dibb *et al.*, 1992; Baskaran *et al.*, 1993; Baskaran, 1995; Graustein and Turekian, 1996]. In this investigation we have included the additional measurement of phosphorus 32 ($t_{1/2}$ = 14.3 days), and phosphorus 33 ($t_{1/2}$ = 25.3 days). Our study encompasses, for the first time, the simultaneous

measurement of ³²P, ³³P, ⁷Be, and ²¹⁰Pb in individual rain events in order to determine day-to-day variability in radionuclide fluxes and the feasibility of using these isotopes to determine air mass mixing over short timescales.

The radioisotopes ³²P, ³³P, and ⁷Be are formed in the atmosphere by cosmic ray spallation of atmospheric argon (³²P and ³³P), oxygen, and nitrogen (⁷Be) [Lal and Peters, 1967]. Lead 210 is produced by the decay of radon 222, an inert gas which enters the troposphere predominantly from continental crust. All four radioisotopes are particle-reactive and are thought to become quickly associated with aerosols. These particles are then predominantly removed from the atmosphere via wet precipitation [Maenhaut *et al.*, 1979; Bondiotti *et al.*, 1988; Baskaran *et al.*, 1993; Waser and Bacon, 1995].

From March 1996 to February 1998 the radionuclides ³²P, ³³P, ⁷Be, and ²¹⁰Pb were measured in individual rain events at Woods Hole, Massachusetts. Additional samples, integrated over 1-2 week periods, were also measured from March to October 1997 at Portsmouth Harbor, New Hampshire. Our results indicate that ³²P and ³³P can be used in conjunction to trace STE events that occur during severe storms.

2. Materials and Methods

Bulk precipitation samples were collected from the roof of Clark Laboratory (height above sea level ~23 m) at the Woods Hole Oceanographic Institution (WHOI), Woods Hole, Massachusetts (41° 32'N, 70° 39'W) and at ground level at the U.S. Coast Guard Station at Portsmouth Harbor, New Hampshire (43° 04'N, 70° 42'W). No attempt was made to separate wet and dry deposition as both rain collectors were open to the atmosphere at all times. At Woods Hole the rain collector consisted of 2 x 5 m of plywood coated by thin polyethylene sheeting. At Portsmouth a circular, 1 m diameter stainless steel dish was used for collection. At

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Woods Hole, samples were immediately collected into acid-cleaned cubitainers, whereas at Portsmouth, rain samples were collected over 1-2 week intervals.

Rain samples were processed and measured for ^{32}P , ^{33}P , ^7Be , and ^{210}Pb according to the methods described by Benitez-Nelson and Buesseler [1998] and C.R. Benitez-Nelson et al. (Carbon export, eddy diffusivity, and horizontal transport in the Gulf of Maine, submitted to *Continental Shelf Research*, 1998). All activities were corrected to the midpoint of collection. Overall errors for ^{32}P and ^{33}P are 2σ and are derived from the propagation of uncertainties associated with multiple counting periods used in a nonlinear least squares curve fit, detector calibration, and chemical recoveries [Benitez-Nelson and Buesseler, 1998]. Uncertainties for ^{210}Pb and ^7Be are also 2σ , but were determined from a single counting period. Acid cleaning of the Woods Hole rain collector indicated that less than 3% of the annual bulk deposition of ^{210}Pb and ^7Be was lost by adsorption to the rain collector.

3. Results and Discussion

3.1. Radionuclide Activities and Flux Estimates

The activity of ^{32}P , ^{33}P , ^7Be , and ^{210}Pb in disintegrations per minute per liter (dpm L^{-1}) was measured in individual rain events at Clark Laboratory in Woods Hole, Massachusetts, beginning in March 1996 and in 1-2 week integrated samples at the U.S. Coast Guard Station in Portsmouth, New Hampshire, beginning in March 1997. It should be noted that each rain event collected at Woods Hole also includes the preceding days of dry fallout (0-17 days). The ^{32}P and ^{33}P activities were similar and ranged from 0.27 to 13.61 dpm L^{-1} (data available upon request). This activity range included

higher activities than the 0.06 to 3.78 dpm L^{-1} found previously [Goel et al., 1959; Lal et al., 1960; Walton and Fried, 1962; Waser and Bacon, 1995]. This is most likely due to the fact that prior sampling was often integrated over 1 to 3 week periods.

The average yearly flux of ^{32}P and ^{33}P at Woods Hole was 0.178 ± 0.004 and $0.165 \pm 0.004 \text{ dpm cm}^{-2} \text{ yr}^{-1}$, respectively, while the ^{32}P and ^{33}P flux at Portsmouth was 0.212 ± 0.004 and $0.175 \pm 0.003 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ (e.g., Figure 1). The ^{32}P and ^{33}P fluxes measured at Portsmouth were slightly higher than the ^{32}P and ^{33}P fluxes of 0.181 and $0.166 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ measured at Woods Hole during the time period when the Portsmouth samples were collected. The difference in flux between the two sites was probably due to differences in air mass source, since the rainfall amounts were indistinguishable over the period of comparison (64.7 versus 64.5 cm). The annual measured ^{32}P and ^{33}P fluxes at Woods Hole and Portsmouth were substantially higher than the annual ^{32}P flux of $0.086 \pm 0.015 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ and the ^{33}P flux of $0.082 \pm 0.021 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ measured previously at Bermuda [Waser and Bacon, 1995]. However, in this case, elevated fluxes were probably related to differences in both the source and precipitation rate (47 cm yr^{-1} at Bermuda versus 84.8 cm yr^{-1} at Woods Hole).

The ^7Be and ^{210}Pb activities also had a wide range in activity, 21 to 1442 dpm L^{-1} , and 2 to 160 dpm L^{-1} , respectively. These activities are similar to those found in other areas [Turekian et al., 1983; Olsen et al., 1985; Dibb, 1989; Todd et al., 1989; Baskaran et al., 1993]. The yearly flux of ^7Be and ^{210}Pb at Woods Hole was 12.8 ± 0.2 and $1.43 \pm 0.03 \text{ dpm cm}^{-2} \text{ yr}^{-1}$, respectively, while the flux of ^7Be and ^{210}Pb at Portsmouth was 16.6 ± 0.05 and $0.95 \pm 0.01 \text{ dpm cm}^{-2} \text{ yr}^{-1}$, respectively (e.g., Figure 2). The flux of ^7Be at

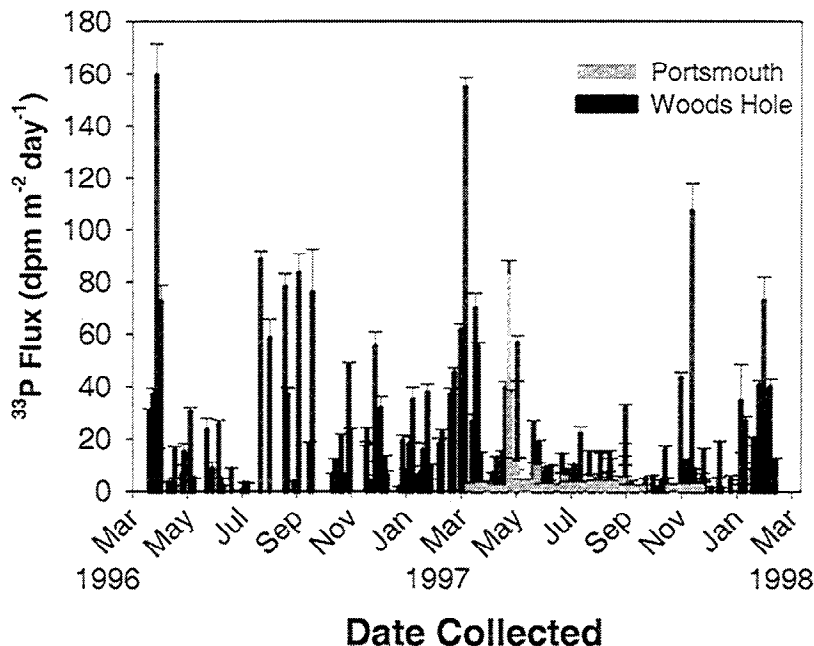


Figure 1. Daily ^{33}P flux measured at Woods Hole (heavily shaded bars) and Portsmouth (lightly shaded bars). Daily fluxes at Woods Hole are derived by multiplying the rainfall in the individual rain event by the specific activity of the sample. Fluxes at Portsmouth are derived by multiplying the cumulative rainfall by the specific activity found in the sample and dividing by the number of days in the collection period. Errors are 2σ (see text) and assume a 5% error in rainfall measurements. The magnitude of ^{33}P fluxes varies in the same manner.

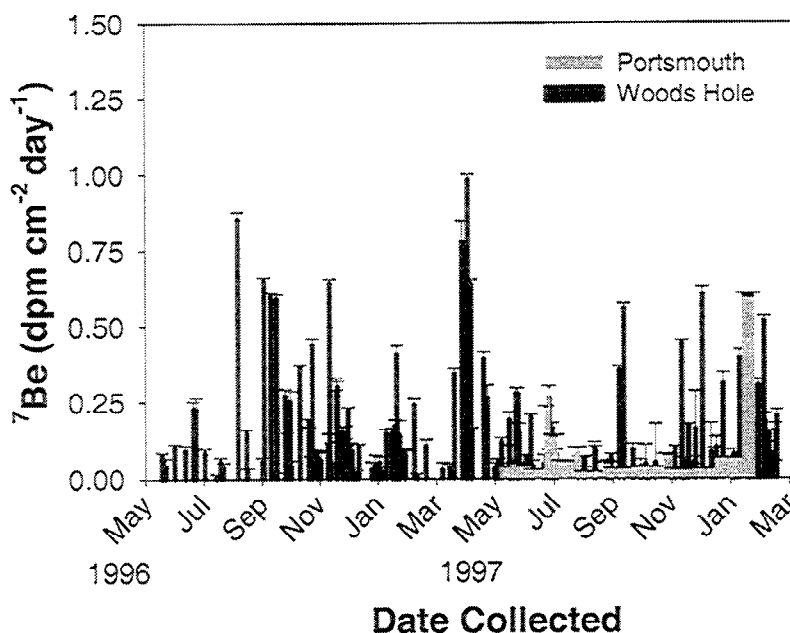


Figure 2. Daily ^7Be flux measured at Woods Hole (heavily shaded bars) and Portsmouth (lightly shaded bars). Daily fluxes at Woods Hole are derived by multiplying the rainfall in the individual rain event by the specific activity of the sample. Fluxes at Portsmouth are derived by multiplying the cumulative rainfall by the specific activity found in the sample and dividing by the number of days in the collection period. Errors are 2σ (see text) and assume a 5% error in rainfall measurements.

Portsmouth was again higher than that measured at Woods Hole, $12.07 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ over the same time period. In contrast, the ^{210}Pb flux at Woods Hole was substantially higher ($1.36 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ over the same time period). The dissimilarity in ^{210}Pb fluxes must be due to either differences in precipitation source (i.e., continental versus marine) and/or dry deposition rates.

It is unlikely that differences in dry deposition could account for the variation in total fluxes between Portsmouth and Woods Hole. Previous studies of dry deposition of ^{210}Pb and ^7Be have been found, in general, to be less than 15% of the total flux [Brown *et al.*, 1989; Todd *et al.*, 1989; Koch *et al.*, 1996]. However, the relative importance of dry versus wet deposition has been shown to increase during periods of low rainfall. Baskaran *et al.* [1993] found that dry deposition could account for as much as 41% of the total fallout measured at several stations in Texas.

A single dry deposition sample was taken during 7 days in July 1997 in order to evaluate the relative importance of dry deposition at our Woods Hole site. Our results, collected during a low-rainfall period, indicated that dry deposition accounts for less than 1% of the ^7Be flux, but accounts for 12% of the ^{210}Pb flux. The effect of dry deposition on the flux of ^{210}Pb and ^7Be can be further evaluated by examining the relationship between total deposition and the period between individual rain events, as the collector always remained open to the atmosphere. If dry deposition was a major contributor to the annual ^7Be and ^{210}Pb flux, then the time between rain events should be positively correlated with total deposition. However, no relationship was found.

Fluxes of ^7Be measured at Woods Hole are very similar to the ^7Be fluxes (4.3 to $22.7 \text{ dpm cm}^{-2} \text{ yr}^{-1}$) found previously on the northeastern coast. Our Woods Hole ^{210}Pb fluxes, on the

other hand, are 1.2 to 1.8 times higher than prior estimates of $1.20 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ at New Haven, Connecticut, and 0.79 and $0.85 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ at Norfolk, Virginia [Turekian *et al.*, 1983; Todd *et al.*, 1989]. Emission of ^{222}Rn from the continents has been found to range from 0.7 to $4.45 \text{ dpm cm}^{-2} \text{ yr}^{-1}$, with an average value of $0.9 \text{ dpm cm}^{-2} \text{ yr}^{-1}$ [Wilkening and Clements, 1975; Turekian *et al.*, 1977; Polian *et al.*, 1986]. Thus the wide range in continental sources can easily support our measured Woods Hole ^{210}Pb fluxes and may reflect precipitation from continental air masses at a higher relative rate than the other stations.

Given the relatively long half-life of ^{210}Pb , it is also possible that our precipitation samples reflect a recycled or soil component. Monaghan *et al.* [1986] estimated that between 8 and 35% of the ^{10}Be ($t_{1/2} = 1.5 \times 10^6$ years) flux at the Earth's surface was derived from soils. Although this fraction is most likely smaller for ^{210}Pb , a higher recycled component could also help to explain the differences between the Woods Hole ^{210}Pb flux and that measured in other areas.

3.2. Relationship Between Specific Activities and Fluxes With Rainfall

There was no significant correlation between the activity of ^{32}P , ^{33}P , ^7Be , or ^{210}Pb in individual rain events and rainfall at Woods Hole or at Portsmouth (e.g., Figure 3, $r^2 < 0.05$). A lack of correlation between the activity of ^{32}P and ^{33}P and rainfall was also found in measurements of ^{32}P and ^{33}P at Bermuda [Waser and Bacon, 1995]. In contrast, several investigations have found relationships between rainfall amount and the activity ^7Be and ^{210}Pb in rainfall samples integrated over longer timescales [Turekian *et al.*, 1983; Olsen *et al.*, 1985; Todd *et al.*, 1989; Baskaran *et al.*, 1993].

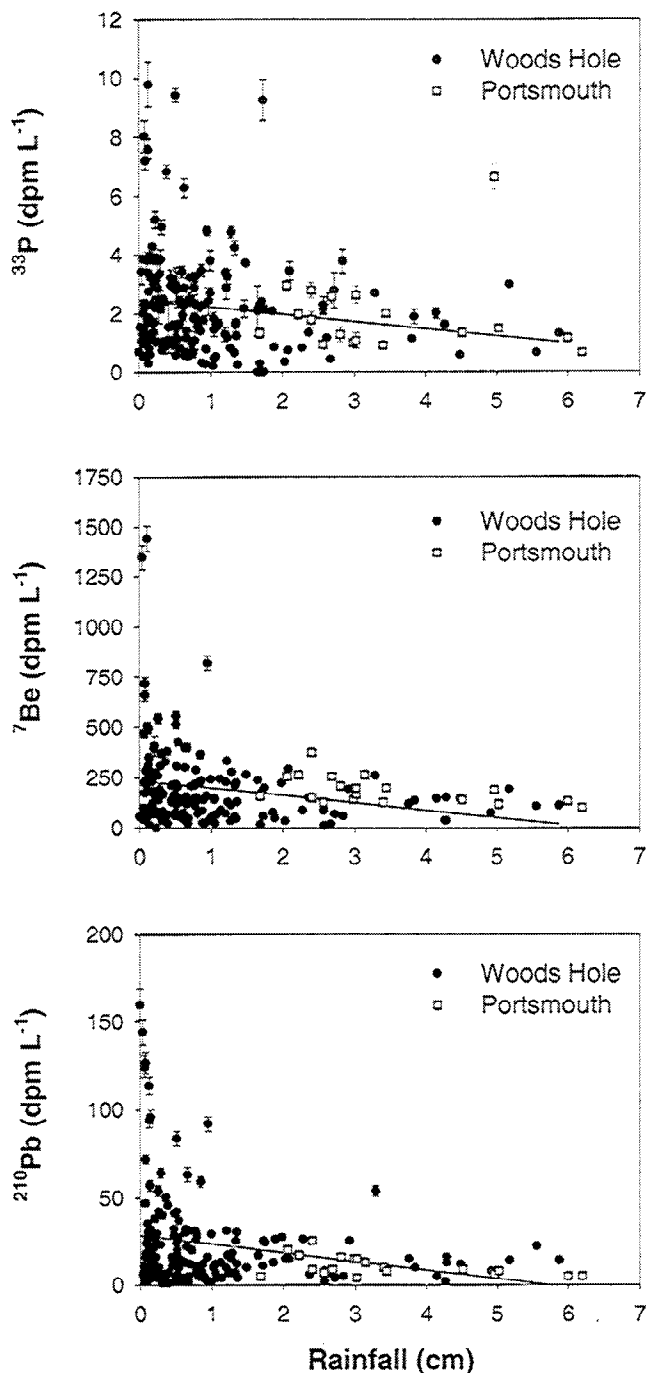


Figure 3. Specific activity of ^{33}P , ^7Be , and ^{210}Pb versus rainfall in samples measured at Woods Hole (solid circles) and at Portsmouth (open squares). The regression line is determined by a linear least squares fit through the data. The relationship between ^{33}P and rainfall is similar to that of ^{32}P .

The lack of a linear relationship found in this study suggests that radionuclide activities at our site were controlled by the interaction of complex processes, such as source and scavenging intensity.

Further insight into the processes that affect specific radionuclide activities can be conducted by measuring changes in the activity of ^{32}P , ^{33}P , ^7Be , and ^{210}Pb during a single rain event. Between four and six rain samples were

taken sequentially during individual rain events which occurred over a 12 hour period in December 1996, and in July, August, November, and December 1997. Our results showed no evidence of a decrease with time during single rain events (data available upon request, Figure 4). Again, these results differ from previous investigations which did find decreases in the activity of ^7Be during a single rain event [Olsen *et al.*, 1985; Dibb, 1989; Baskaran *et al.*, 1993]. However, it should be noted that these previous investigations characterized single rain events as spanning several days, whereas this study limited investigations to those rain events that occurred over less than a 12 hour period.

In contrast to activity, all four isotopes do show a correlation between flux and rainfall (e.g., Figure 5). This indicates that rain rate does play an important part in the removal of these isotopes from the troposphere. Similar relationships for ^7Be and ^{210}Pb have also been found in other studies [Turekian *et al.*, 1983; Dibb, 1989; Baskaran *et al.*, 1993]. Deviations in the relationships between flux and rainfall among the radionuclides can arise from differences in air mass sources, scavenging rates, and radioactive decay.

3.3. Radionuclide Ratios as an Indicator of Air Mass Source

3.3.1. Phosphorus 33/phosphorus 32. The average $^{33}\text{P}/^{32}\text{P}$ ratio measured in samples collected at Woods Hole and at Portsmouth was remarkably consistent, averaging 0.88 ± 0.14 . However, significantly elevated $^{33}\text{P}/^{32}\text{P}$ ratios of 1.1-1.5 were observed during specific rain events in September 1996 and in the winter (December-February) of 1997 and 1998. The elevated ratios in September 1996 all correspond to rain collected during hurricanes: Edouard, Fran, and Hortense (Figure 6). These hurricanes were all ranked as category 3 hurricanes on the Saffir-Simpson hurricane scale (winds 111-130 miles per hour (179-209 km h^{-1})) during their life history. The additional higher ratios measured in the winter of 1997 and 1998 also correspond to a series of events called nor'easters, intense storms from the northeast containing rain, sleet, snow, and hail. In contrast, lower ratios (<1.0) were almost always found between storm episodes.

The $^{33}\text{P}/^{32}\text{P}$ ratios observed during the storm events are much higher than expected. If it is assumed that the troposphere is relatively well mixed and that there is no fractionation of the radionuclides during condensation and precipitation, the following simple model can describe the change in radionuclide ratios with time:

$${}^a\text{A} / {}^b\text{A} = ({}^a\text{P} \lambda_b / {}^b\text{P} \lambda_a) (1 - \exp(-\lambda_a \tau_i)) / (1 - \exp(-\lambda_b \tau_i)) \quad (1)$$

where ${}^a\text{A}$ and ${}^b\text{A}$ are the activities of the longer-lived and shorter-lived radionuclide, respectively, ${}^a\text{P} / {}^b\text{P}$ refers to the production ratio of nuclide a to b, and λ_a and λ_b are the half-lives of the respective nuclides. Accordingly, the ratio of two radionuclides within an air mass can only vary between an initial production ratio R_0 and an equilibrium value, $R_e = {}^a\text{P} \lambda_b / {}^b\text{P} \lambda_a$ [Lal, 1959; Lal and Peters, 1967; Waser and Bacon, 1995].

The R_0 of $^{33}\text{P}/^{32}\text{P}$ has been estimated to range from 0.46 to 0.70 such that R_e has a maximum possible value of 1.2 [Lal and Peters, 1967; Waser and Bacon, 1995]. The activity ratio of $^{33}\text{P}/^{32}\text{P}$ measured in samples collected at Woods Hole and Portsmouth ranges from 0.55 ± 0.14 to 1.59 ± 0.26 (Figure 6), outside the predicted range. Thus our rain measurements

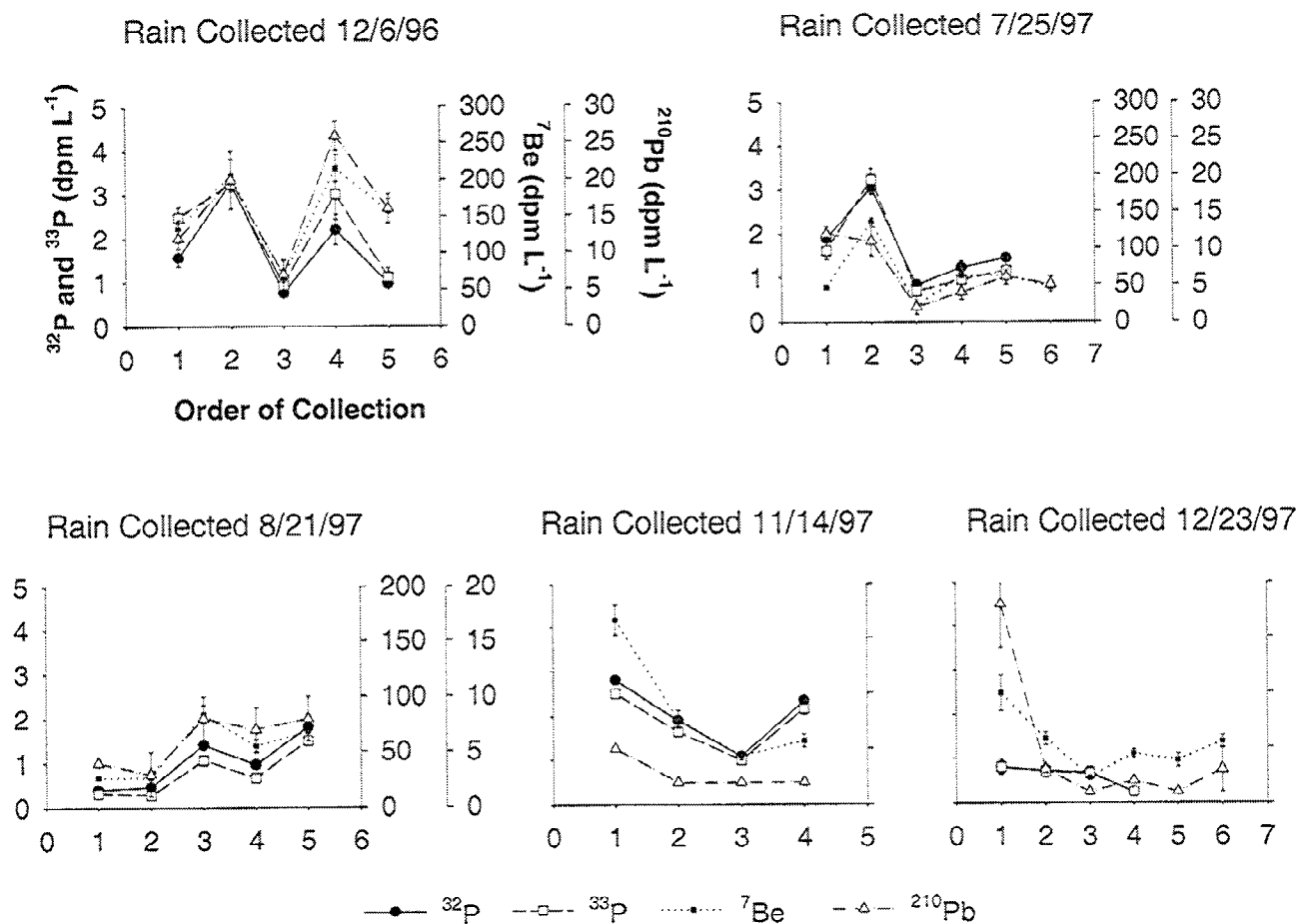


Figure 4. Specific activity of ^{32}P (solid circles), ^{33}P (open squares), ^7Be (solid squares), and ^{210}Pb (open triangles) in sequential samples taken during an 8-12 hour continuous rainfall period.

suggest that the severe storms encountered in this study were tapping higher $^{33}\text{P}/^{32}\text{P}$ ratio air. This source air appears to have a $^{33}\text{P}/^{32}\text{P}$ ratio of at least 1.5, the highest value measured in our rain samples.

Previous measurements of $^{33}\text{P}/^{32}\text{P}$ ratios suggested that the high ratio signal is predominantly of stratospheric origin. *Waser and Bacon* [1995] observed an increase in the ratio of $^{33}\text{P}/^{32}\text{P}$ in integrated rain samples at Bermuda to values as high as 1.20 during March, April, and July 1991, and January and February 1992. Increases in ^{90}Sr and ozone, two components predominantly derived from stratospheric air masses, were also noted to occur during the same months, although in previous years [*Waser and Bacon*, 1995].

Current evidence indicates that the production ratio of $^{33}\text{P}/^{32}\text{P}$ is similar throughout both the troposphere and stratosphere [*Lal and Peters*, 1967]. However, the absolute activity of ^{32}P and ^{33}P increases with increasing altitude and latitude, such that the highest activities are found in the upper stratosphere and at the poles [*Lal and Peters*, 1967]. One method of achieving an air mass with a high $^{33}\text{P}/^{32}\text{P}$ ratio is to invoke periodic mixing between higher-activity and lower-activity air (Figure 7). Simply put, once the higher-activity air mass is sequestered from its source and mixed with lower-activity air, it will decay with time, increasing the ratio of $^{33}\text{P}/^{32}\text{P}$. After some time period the activities of the mixed air

mass will have decayed to the point that the ratio will begin to decrease back to premixing levels.

Measurements of stratospheric air conducted in the early 1960s, while few in number, reported that the average $^{33}\text{P}/^{32}\text{P}$ activity ratio was 0.9 ± 0.2 [*Friend et al.*, 1961; *Rama and Honda*, 1961; *Drevinsky et al.*, 1964]. If it is assumed that the average $^{33}\text{P}/^{32}\text{P}$ stratospheric ratio is 0.9 and that the difference in activity of an air mass between specified regions is an order of magnitude [*Rama and Honda*, 1961; *Lal and Peters*, 1967], we are able to reproduce the highest ratios observed in our rain samples (Figure 7). If the ratio of $^{33}\text{P}/^{32}\text{P}$ in stratospheric air is higher, then even less decay and intermittent mixing between higher- and lower-activity air masses is required.

Numerous investigations have provided evidence for the intrusion of stratospheric air into the troposphere using both artificial and naturally occurring radionuclides [*Dutkiewicz and Hussain*, 1985; *Olsen et al.*, 1985; *Todd et al.*, 1989; *Viezee and Singh*, 1980; *Holton et al.*, 1995; *Appenzeller et al.*, 1996]. In general, STE appears to be maximized in the spring (February - April) and at midlatitudes in the Northern Hemisphere [*Dutkiewicz and Hussain*, 1979, 1985; *Todd et al.*, 1989]. If the ratio measured in our precipitation samples stems solely from this exchange, one would expect to observe a time lag of several weeks between STE and high $^{33}\text{P}/^{32}\text{P}$

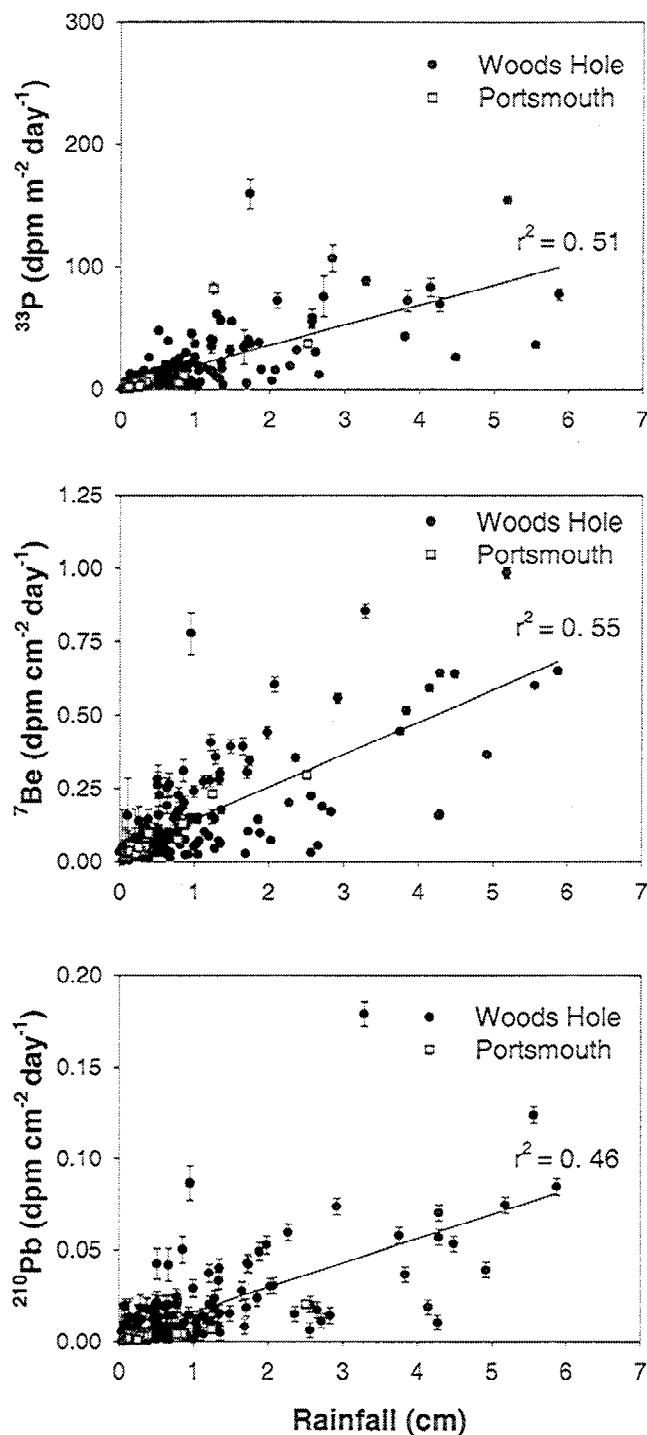


Figure 5. Daily flux of ^{33}P , ^7Be , and ^{210}Pb versus rainfall in samples measured at Woods Hole (solid circles) and at Portsmouth (open squares). The regression line is determined by a linear least squares fit through the data. The relationship between ^{33}P and rainfall is again similar to that of ^{32}P .

ratios. However, this time lag is not apparent in that high ratios are observed during severe storm events. In addition, high $^{33}\text{P}/^{32}\text{P}$ ratios tend to occur significantly earlier than expected, in December, January, and February.

Another process that can produce $^{33}\text{P}/^{32}\text{P}$ ratios that exceed equilibrium values invokes intermittent isentropic mixing

within the lower stratosphere between higher-activity polar regions and the lower-activity midlatitudes. Because the half-lives of ^{32}P and ^{33}P are short relative to the residence time of air in the lower stratosphere, localized differences in radionuclide concentrations can develop. These regional air masses may then be rapidly mixed between the polar and midlatitudes via breaking planetary waves, a process that appears to be maximized in winter. Furthermore, this isentropic mixing can occur on much more rapid timescales [McIntyre and Palmer, 1983]. Higher-ratio $^{33}\text{P}/^{32}\text{P}$ air could then be mixed into the troposphere during STE events caused by intense storms.

Unfortunately, the influence of stratospheric air in our precipitation samples does not allow for us to calculate tropospheric and stratospheric focusing factors [e.g., Monaghan *et al.*, 1986]. The half-lives of ^{32}P and ^{33}P are short, such that a significant amount of what is produced in both the troposphere and stratosphere decays there. As a result, it is not clear which fraction of the stratospheric production regularly enters the troposphere and what fraction of the tropospheric production reaches the Earth's surface. Small differences in either of these estimates can dramatically affect calculated stratosphere and troposphere focusing factors.

3.3.2. Beryllium 7/phosphorus 32 and beryllium 7/phosphorus 33. One would expect that the above STE processes would affect $^7\text{Be}/^{32}\text{P}$ and $^7\text{Be}/^{33}\text{P}$ ratios in the same manner as the ratio of $^{33}\text{P}/^{32}\text{P}$, given that aerosol scavenging of cosmogenic radionuclides is considered to be a rapid and indiscriminate process. The activity ratios of $^7\text{Be}/^{32}\text{P}$ and $^7\text{Be}/^{33}\text{P}$ varied dramatically between precipitation events, from 22 ± 2 to 423 ± 52 and 22 ± 2 to 501 ± 69 , respectively (e.g., Figure 8). This is over a factor of 10 higher than the model (equation (1)) estimated range of R_0 to $3.7R_0$ and $2.1R_0$, respectively. Similar large variations in $^7\text{Be}/^{32}\text{P}$ and $^7\text{Be}/^{33}\text{P}$ ratios have been previously reported [Lal *et al.*, 1960; Walton and Fried, 1962] and are probably more pronounced in this study due to the greater number of measurements and the sampling of individual rather than integrated rain events.

If higher $^7\text{Be}/^{32}\text{P}$ and $^7\text{Be}/^{33}\text{P}$ ratios are produced by the same mechanisms as for $^{33}\text{P}/^{32}\text{P}$, then one would expect to see a relationship. However, this is not found ($r^2 < 0.05$). Previous measurements of $^{33}\text{P}/^{32}\text{P}$ and $^7\text{Be}/^{32}\text{P}$ in precipitation [Goel *et al.*, 1959] and in ground air [Luyan *et al.*, 1970] also showed no correlation. In contrast, upper tropospheric (> 3 km) and stratospheric air measured by Rama and Honda [1961] showed a significant correlation for $^{33}\text{P}/^{32}\text{P}$ versus $^7\text{Be}/^{32}\text{P}$ ($r^2 = 0.61$).

Air mass mixing in the various atmospheric regions can occur on varying timescales. As a result, differences in decay may mask any ratio relationship. For this to be true, there should be little or no correlation between $^7\text{Be}/^{32}\text{P}$ and $^7\text{Be}/^{33}\text{P}$ ratios, given the differences in half-lives. Yet, the correlation between the ratios is substantial, having an $r^2 = 0.87$. This is not surprising, given that the difference between the half-life of ^{32}P and ^{33}P is small (10 days) relative to the difference in half-lives between ^7Be and ^{32}P and ^{33}P (39 and 28 days, respectively).

The addition of a variable amount of soil material in our measured precipitation samples may also play a role in the lack of correlation between $^{33}\text{P}/^{32}\text{P}$ and $^7\text{Be}/^{32}\text{P}$. One might expect that the importance of this recycled component in radioisotope fluxes would increase with decreasing chemical

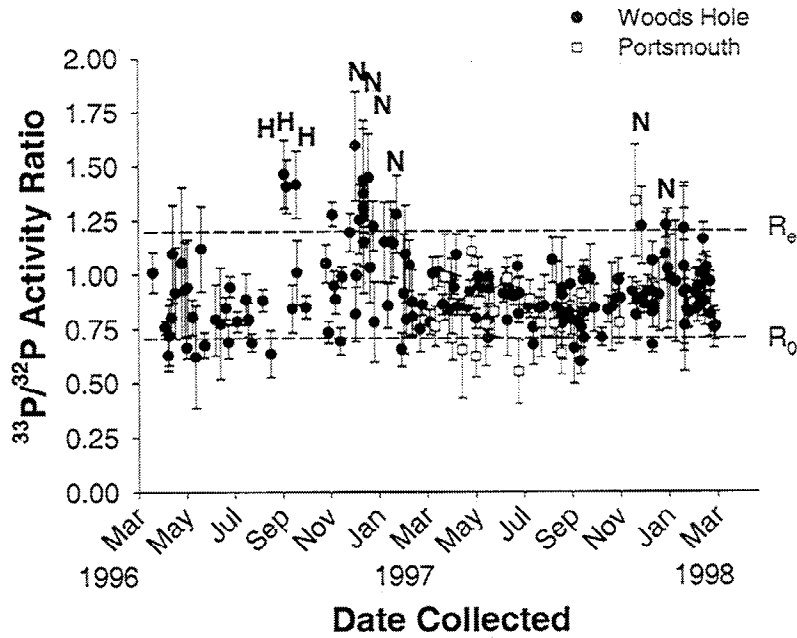


Figure 6. Activity ratio of $^{33}\text{P}/^{32}\text{P}$ in precipitation samples measured at Woods Hole (solid circles) and at Portsmouth (open squares). R_0 is the tropospheric production ratio of 0.7. R_e is the theoretical tropospheric steady state ratio of 1.2. H denotes a hurricane (Edouard, Fran, and Hortense), and N denotes a nor'easter.

reactivity and increasing half-life. Thus ^7Be would be more affected than ^{33}P , and any radionuclide ratio relationship would be obscured. However, this soil component is unlikely to be large as an average recycled fraction of only 24% was found for the much longer-lived radioisotope ^{10}Be [Monaghan *et al.*, 1986]. Furthermore, while the added flux to ^7Be might explain the presence of high ratios of $^7\text{Be}/^{32}\text{P}$ with low $^{33}\text{P}/^{32}\text{P}$ ratios, it does not explain why low $^7\text{Be}/^{32}\text{P}$ ratios are observed with high $^{33}\text{P}/^{32}\text{P}$.

Another more likely possibility for the lack of a relationship between the radioisotope ratios is fractionation. While fractionation is not expected between ^{32}P and ^{33}P , it is

entirely possible that it could be significant for the ratio of $^7\text{Be}/^{32}\text{P}$ and $^7\text{Be}/^{33}\text{P}$. Beryllium and phosphorus may be expected to behave differently under certain processes, that is, differences in scavenging may occur among various aerosol size classes and/or by precipitation. Evidence of fractionation is further demonstrated in that the correlation between $^7\text{Be}/^{32}\text{P}$ and $^{33}\text{P}/^{32}\text{P}$ in upper tropospheric and stratospheric air is significant, whereas in ground level air and in precipitation, it is not [Rama and Honda, 1961; Goel *et al.*, 1959; Luyanus *et al.*, 1970]. Fractionation processes would be expected to be minimized in upper atmospheric air samples, where filter samples efficiently collect aerosols of all types and sizes

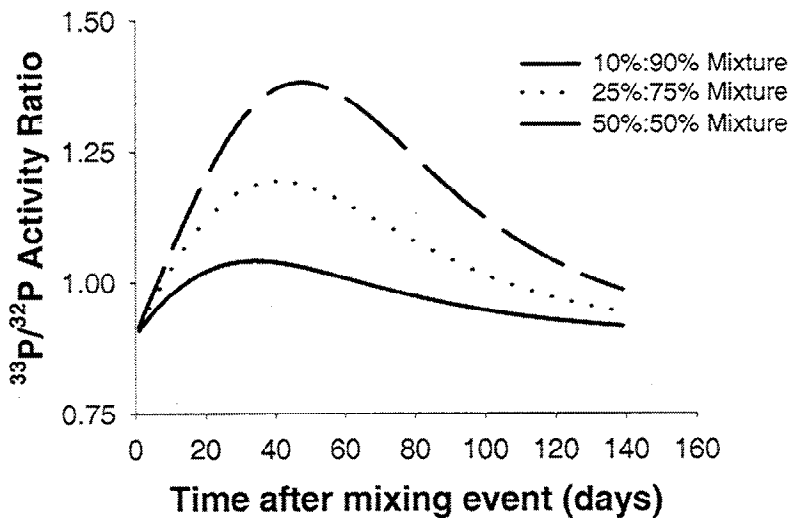


Figure 7. Model results of instantaneously mixing air masses with $^{33}\text{P}/^{32}\text{P}$ ratios of 0.9, but with an order of magnitude difference in absolute ^{32}P and ^{33}P activity: 10% higher activity air with 90% lower activity air, 25% with 75%, and 50% with 50%. Model assumed no further mixing after the initial event.

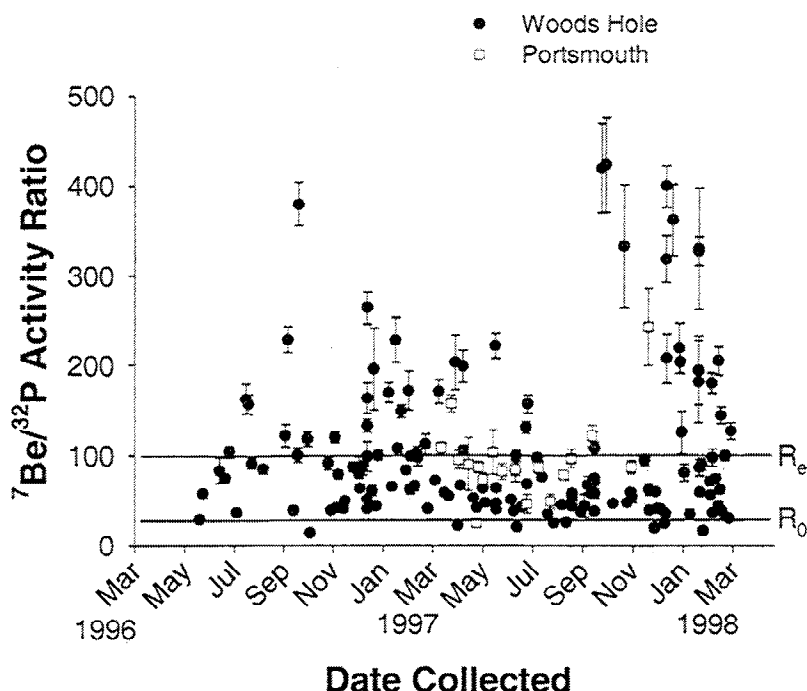


Figure 8. Activity ratio of ${}^7\text{Be}/{}^{32}\text{P}$ in precipitation samples measured at Woods Hole (solid circles) and at Portsmouth (open squares). R_0 is the tropospheric production ratio of 25. R_e is the theoretical tropospheric steady state ratio of 99. Ratios greater than 250 all occur during low-rainfall periods (<0.3 cm).

greater than the filter pore size ($\sim 0.7 \mu\text{m}$) [Rama and Honda, 1961; Gandrud *et al.*, 1989]. In the lower atmosphere and in rain, fractionation would be expected to be significantly greater, given differences in condensation and in the regional frequency of aerosol scavenging by precipitation. The lack of correlation found in our rain data suggests two possibilities. The first is that ${}^7\text{Be}$, ${}^{32}\text{P}$, and ${}^{33}\text{P}$ are scavenging differentially onto aerosol particle types and/or size classes that can have different origins, transport mechanisms, and/or residence times. The second is that precipitation may be scavenging aerosols at different efficiencies, a process that may be related to the altitude, magnitude, and duration of the precipitation event. It should also be noted that all of the high ${}^7\text{Be}/{}^{32}\text{P}$ and ${}^7\text{Be}/{}^{33}\text{P}$ ratios (> 250) occur during low-precipitation periods (<0.3 cm), which tend to scavenge aerosols from the lower troposphere.

It appears that the ratios of ${}^7\text{Be}/{}^{32}\text{P}$ and ${}^7\text{Be}/{}^{33}\text{P}$ cannot be used to trace STE. Only isotopes of the same element are appropriate, at least when used in conjunction with the simple model given in equation (1). However, further measurements of ${}^7\text{Be}/{}^{32}\text{P}$ and ${}^7\text{Be}/{}^{33}\text{P}$ in upper tropospheric and stratospheric air and in different aerosol particle sizes and types may provide information on the residence time and transport of various aerosol classes. For example, if the distribution of these radionuclides on various aerosol size classes and types is better constrained, then these isotopes could be used to describe atmospheric mixing processes over short timescales.

3.3.3. Beryllium 7/lead 210. If the ratio of ${}^7\text{Be}/{}^{32}\text{P}$ and ${}^7\text{Be}/{}^{33}\text{P}$ suffers from fractionation effects, so should the ratio of ${}^7\text{Be}/{}^{210}\text{Pb}$. Nonetheless, further evaluation of how the ratio of ${}^7\text{Be}/{}^{210}\text{Pb}$ varies in relationship to the other radionuclides may be useful. In previous studies the ratio of ${}^7\text{Be}/{}^{210}\text{Pb}$ has

been used to determine whether the source of a scavenged air mass is oceanic versus continental and/or upper versus lower tropospheric [Baskaran *et al.*, 1993; Graustein and Turekian, 1996; Koch *et al.*, 1996]. The major source of ${}^{210}\text{Pb}$ to the atmosphere is via decay of ${}^{222}\text{Rn}$, a gas predominantly emitted from continental material. Therefore the concentration of ${}^{210}\text{Pb}$ should decrease with increasing altitude and over the open ocean. Concentrations of ${}^7\text{Be}$ should increase with altitude and remain uniform at constant altitude over land versus sea. Thus an increase in the ${}^7\text{Be}/{}^{210}\text{Pb}$ ratio can indicate either STE events or changes in the extent of continental versus oceanic air masses.

The average activity ratio of ${}^7\text{Be}/{}^{210}\text{Pb}$ measured in rain collected at Woods Hole and at Portsmouth was 12.6 and 20.1, respectively. This is within the range of 11.3 to 25 observed by other investigators [Turekian *et al.*, 1983; Todd *et al.*, 1989; Baskaran *et al.*, 1993]. Lower ratios in previous studies tended to correspond to continental sites, whereas the highest ratio, 25, was measured at Bermuda. The difference in the ${}^7\text{Be}/{}^{210}\text{Pb}$ ratio between Woods Hole and Portsmouth suggests that the Woods Hole station measures precipitation derived from more continental air masses, whereas the Portsmouth station measures precipitation from more oceanic air. This is also evident in the higher ${}^{210}\text{Pb}$ fluxes measured at Woods Hole.

If high ${}^7\text{Be}/{}^{210}\text{Pb}$ ratios are also indicators of upper/lower tropospheric mixing, and increased ratios of ${}^{33}\text{P}/{}^{32}\text{P}$ are predominantly caused by STE, then one would expect to see a relationship. However, no such correlation is apparent in our data. Previous data, which include measurements of all four isotopes, are limited. Nonetheless, no correlations between ${}^7\text{Be}/{}^{32}\text{P}$ and ${}^7\text{Be}/{}^{210}\text{Pb}$ were found in precipitation or between

$^{33}\text{P}/^{32}\text{P}$ and $^7\text{Be}/^{210}\text{Pb}$ in stratospheric air samples [Rama and Honda, 1961; Bhandari et al., 1970], although a weak correlation ($r^2 = 0.49$, $n=12$) was found between $^7\text{Be}/^{32}\text{P}$ and $^7\text{Be}/^{210}\text{Pb}$ in stratospheric air samples.

There is the possibility that ^{210}Pb fluxes are more affected by a recycled component, which would serve to decrease the $^7\text{Be}/^{210}\text{Pb}$ ratio. However, the presence of high $^7\text{Be}/^{210}\text{Pb}$ ratios in the absence of high $^{33}\text{P}/^{32}\text{P}$ and $^7\text{Be}/^{32}\text{P}$ suggests that this process alone does not explain the lack of correlation between radionuclide ratios. Rather, these results again suggest a difference in either aerosol scavenging among beryllium, lead, and phosphorus and/or in scavenging of aerosols by precipitation. In addition, any relationship between upper and lower tropospheric mixing is probably diminished due to the additional dependence of ^7Be and ^{210}Pb on continental versus oceanic air mass sources. Thus the ratio of $^7\text{Be}/^{210}\text{Pb}$ may be a qualitative indicator of continental air masses, but it cannot be used to trace tropospheric mixing directly unless used in conjunction with regional atmospheric transport and mixing process models.

4. Conclusions

Elucidating stratosphere/troposphere exchange events and aerosol residence times is important for understanding the cycling of many natural and anthropogenically produced elements. Radioisotopes can be used to investigate these processes over a range of timescales. Our measurements of ^{32}P , ^{33}P , ^7Be , and ^{210}Pb are the first to be conducted in individual rain events over a seasonal cycle.

Annual depositional fluxes of ^{32}P , ^{33}P , and ^7Be measured at both Woods Hole and Portsmouth were similar in magnitude. Fluxes of ^{32}P and ^{33}P however, were significantly higher than those found previously, while ^7Be fluxes were similar to those found along the northeastern coast. Fluxes of ^{210}Pb measured at Woods Hole were 25% higher than those measured at Portsmouth, indicating that continental air masses were more prevalent at the Woods Hole site. No correlation was found between specific radionuclide activities and rainfall. Serial sampling during large rain events also showed no decrease in activity with time. In contrast, significant correlations were found between radionuclide fluxes and rainfall. This indicates that rainfall is an important removal pathway of these isotopes from the troposphere.

Our results suggest that elevated $^{33}\text{P}/^{32}\text{P}$ ratios are the result of lower stratospheric isentropic mixing followed by STE. Further elucidation of the atmospheric distribution of these isotopes may enable these isotopes to provide insight into the timing and spatial magnitude of STE. It appears that $^7\text{Be}/^{32}\text{P}$, $^7\text{Be}/^{33}\text{P}$, and $^7\text{Be}/^{210}\text{Pb}$ ratios, however, all suffer from fractionation effects associated with differences in either aerosol scavenging among beryllium, lead, and phosphorus and/or aerosol scavenging by precipitation. The $^7\text{Be}/^{210}\text{Pb}$ ratios are especially difficult to interpret given the differences in production between the two radionuclides. The ratio of $^7\text{Be}/^{32}\text{P}$ and $^7\text{Be}/^{33}\text{P}$ may prove useful in investigating differences in aerosol residence times within various particle size classes and types.

Acknowledgments. The authors wish to thank Carolyn Jordan at the University of New Hampshire for collecting and performing the initial processing of samples retrieved from Portsmouth, New Hampshire. We would also like to thank the U.S. Coast Guard

Station for allowing the collection of samples from their base of operations at Portsmouth Harbor, L. A. Ball for ICPES analyses, J. E. Andrews for rain collector construction, and J. MacFarlane for the map of the Gulf of Maine. The authors further wish to thank G. Crossin for help in collecting and processing samples retrieved from Woods Hole, Massachusetts, and D. Glover, W. Jenkins, M. Kurz, M. Follows, and B. Benitez-Nelson for insightful comments pertaining to the manuscript. The manuscript was further improved with the help of two anonymous reviewers. This work was funded in part by the Office of Naval Research Fellowship Program, STAR Environmental Protection Agency Fellowship Program, National Science Foundation (grant OCE-9633240), and the Woods Hole Oceanographic Institution (unrestricted funds). This is contribution 9705 from the Woods Hole Oceanographic Institution.

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(Received September 11, 1998; revised December 9, 1998; accepted December 14, 1998)