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1. INTRODUCTION

We are now becoming more aware of the importance of atmospheric aerosols in the chemistry and physics of the atmosphere and as a means of transporting materials over long distances. In the stratosphere, atmospheric aerosols provide important surfaces for heterogeneous chemical processes leading to enhancement of the catalytic destruction of stratospheric ozone by chlorine. Aerosols are important as cloud condensation nuclei and play key roles in the hydrological cycle through their influence on the types and formation rates of clouds. Aerosols can also scatter or absorb incoming radiation from the sun or outgoing radiation from Earth, with important consequences for climate and weather. Indeed, their effects on clouds enable aerosols to alter the planet's thermal balance both indirectly and directly.

Aerosols at high concentrations have health impacts, particularly when they are associated with other air pollutant exposures. The killer smogs in London during the 1940s and 1950s were due to high levels of soots and sulfur dioxide trapped in a shallow boundary layer. In the United States, similar events in Donora, Pennsylvania, caused a number of deaths and led thousands of residents to be hospitalized. The result was the passage of legislation aimed at reduction of the levels of these primary pollutants.

We now recognize that the secondary formation of aerosols is also important. The oxidation of sulfur dioxide and nitrogen oxides to form submicron sulfate and nitrate aerosols is well documented. Large organic hydrocarbons, such as the natural monoterpenes and anthropogenically released hydrocarbons, can also react with ozone and hydroxyl radical to form secondary organic aerosols. Critical to our understanding of the roles that aerosols play in the atmosphere is the determination of their size, chemical composition, and physical properties. It is especially important to determine the ability of aerosols to take up water and grow to a size that can be removed by gravitational settling or washout processes.

In many cases, submicron secondary aerosols formed in the boundary layer can be transported for some distance, as they are removed slowly by gravity.

We define fine aerosols for this discussion as being 0.1-1 μm in aerodynamic diameter. Larger aerosols are considered coarse, and smaller aerosols are considered ultrafine. In past papers we have revisited the use of natural radioactivity on fine aerosols as a tool for determining transport and residence times of aerosols. This paper outlines the use of naturally occurring ^7Be for tracing and assessing effects of upper air parcels, along with the use of ^{210}Pb and its daughters, ^{210}Bi and ^{210}Po , to estimate submicron aerosol residence times.

We also discuss how ^7Be data can be used to address sampling problems on the network scale for PM-2.5 measurements. The reliability of high-volume measurements is often an issue in determining mass loadings of aerosols. Errors can be large if sampling volumes are not determined accurately. Power loss, filter loading leading to reduction in air flow, and a variety of other problems in city aerosol networks can result in inaccurate assessment of aerosol distributions. Beryllium-7 values, which should be reasonably consistent on network scales, can help both to identify problems and as a basis for correction of data.

Our past measurements of ^{210}Pb and its daughters were made with slower-flow cascade impaction systems. We present data taken with higher-volume, slotted cascade impactors that allow one-day measurements of apparent ages. The use of ^{210}Po to identify soil aerosol sources is presented and discussed in light of data from recent studies.

2. NATURAL RADIOACTIVITY ON AEROSOLS

The dominant radioactive isotopes in fine aerosols are ^7Be and ^{210}Pb and its daughters, ^{210}Bi and ^{210}Po (Gaffney et al. 1994). Cosmogenic particles hitting the atmosphere lead to the production of ^7Be in the lower stratosphere and upper troposphere. Radon gas emitted into the troposphere from continental crustal materials decays to form ^{210}Pb and its daughters. The sources, radioactive lifetimes, and decay schemes are shown in Figure 1.

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Radioactive Decay of Natural Atmospheric Tracers

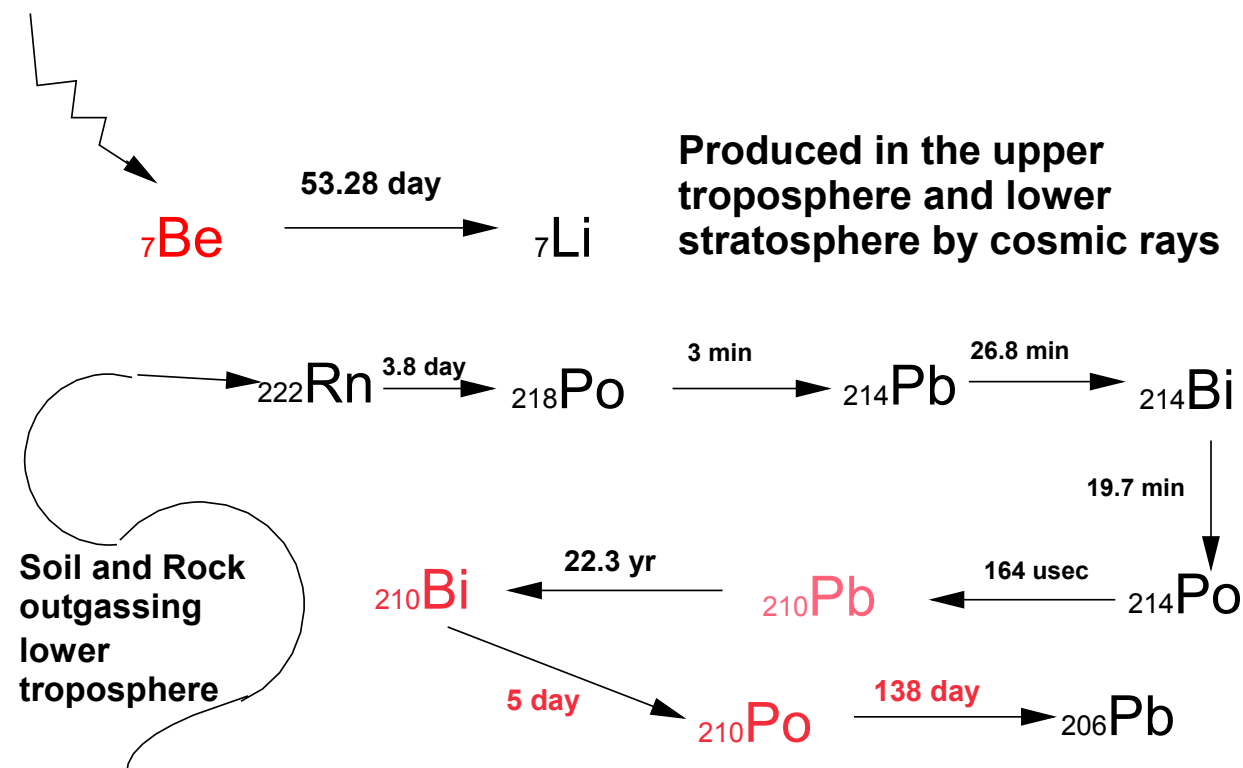


Figure 1. Sources of natural radioactivity in the atmosphere for ${}^7\text{Be}$ and ${}^{210}\text{Pb}$ and its daughters, ${}^{210}\text{Bi}$ and ${}^{210}\text{Po}$ (shown in red). Very short lived or stable isotopic species are shown in black.

Once ${}^7\text{Be}$ is produced in the upper troposphere and lower stratosphere, it attaches itself to available aerosol surfaces. This leads to a mean diameter of 0.3 μm for the size distribution of ${}^7\text{Be}$ -containing aerosol particles. Thus, measurement of the ${}^7\text{Be}$ content of fine aerosols can give a measure of the transport of this material from the upper troposphere/lower stratosphere to the surface where it is sampled. Past work suggested that this might be a useful way to determine stratospheric intrusions and also estimate whether stratospheric ozone is affecting tropospheric sites during these events.

The ${}^{222}\text{Rn}$ cycle leads to the formation of ${}^{218}\text{Po}$, that becomes attached to fine aerosols and decays to form the long-lived ${}^{210}\text{Pb}$ (see Figure 1). This species is deposited by wet and dry deposition, with precipitation being the dominant path (Gaffney et al. 1994). The size distribution for attached particles released in the boundary layer is somewhat larger than that for ${}^7\text{Be}$, with a median diameter upon initial attachment of 0.4 μm . In contrast with ${}^7\text{Be}$, which has a 53-day half-life, ${}^{210}\text{Pb}$ is present long enough in the soils where it is deposited to be measurable in wind-blown dusts.

In the absence of wind-blown dust contamination or other sources of ${}^{210}\text{Bi}$ and/or ${}^{210}\text{Po}$, the disequilibria in ${}^{210}\text{Bi}/{}^{210}\text{Pb}$ and ${}^{210}\text{Po}/{}^{210}\text{Pb}$ ratios are known to be useful estimates of atmospheric residence times (Marley et al. 2000). Key to the measurement is the ability to readily separate and determine the ${}^{210}\text{Pb}$ and its daughters. We have established a methodology for easily determining these species' activities in air samples size-fractionated by using cascade impactors (Marley et al. 1999).

3. EXPERIMENTAL METHODS

Impactors can be used to separate aerosols by size fraction for analysis. We have used two types of impactors in our work to date. Initial studies made use of an eight-stage Lundgren-type impactor with a flow rate of 1 L min^{-1} . Samples were collected on Teflon, with the final stage being quartz. Because of the low volume sampled, sufficient sample was collected in three to seven days.

By using this impactor, we have examined the fine and coarse fractions of aerosols from a number of cities and rural areas for ${}^7\text{Be}$ and for ${}^{210}\text{Pb}$ and its daughters.

The results are consistent with the findings of others in that we cannot detect ^7Be on aerosols above $1\ \mu\text{m}$ in diameter. We have used this fact to advantage in taking higher-volume samples for ^7Be species by collecting all of the aerosol below a $2.5\text{-}\mu\text{m}$ cutoff for gamma counting of the ^7Be . This approach allowed us to examine the concentrations of ^7Be in the Deer Park, Texas, area as part of the recent TexAQS 2000 field study (Gaffney and Marley 2002).

For ^{210}Pb and progeny determinations based on measurements at a number of sites, we have found that a system that allows us to look at the fine fraction

(diameters of $0.1\text{-}1.0\ \mu\text{m}$) and the coarse fraction ($>1.0\ \mu\text{m}$) enables separation of combustion-related and secondary aerosols from wind-blown soil. By using a slotted-plate cascade impaction system (Anderson-Sierra design), we have been able to collect samples of fine and coarse fractions at the no. 4 separation stage.

Reported here are those results, along with results of recent ^7Be data taken at Phoenix, Arizona, during the Department of Energy's Atmospheric Chemistry Program field study (Phoenix 2001; results are in Figure 2).

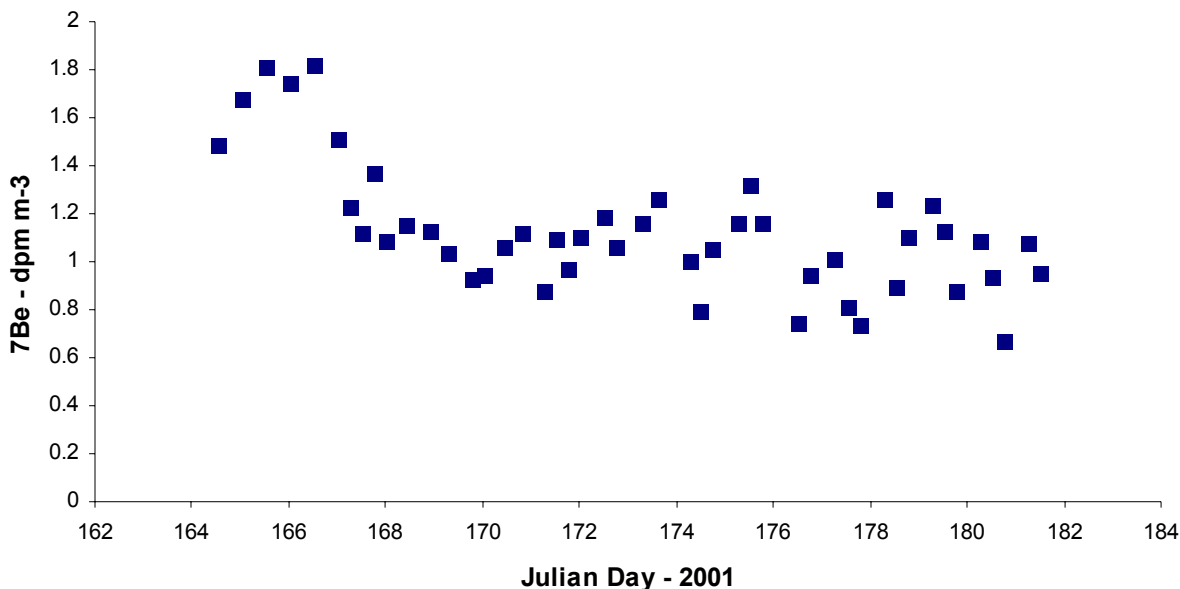


Figure 2. Beryllium-7 data taken at the western edge of Phoenix, Arizona, during the Phoenix 2001 field study.

4. RESULTS AND DISCUSSION

Data obtained from 6 hr of sampling at the University of Arizona Agricultural Experimental Station in Waddell, Arizona, are shown in Figure 2. These samples were taken with a high-volume sampling pump that collected $720\ \text{m}^3$ per day.

During the early part of this collection period, ^7Be was slightly elevated relative to the rest of the period. Note also that the ^7Be concentrations were fairly constant throughout the period. Modeling results from Lawrence Livermore National Laboratory showed that some stratospheric mixing might have occurred over the Phoenix area during the early part of the study, consistent with these observations (Atherton 2002).

Examination of the data and comparison with maximum ozone values for this period did not reveal significant correlation with ^7Be activity, consistent with results seen in the Houston, Texas, area for 12-hr filter samples. From these data, we derived an upper limit of 20-30 ppb for background from stratospheric input (Gaffney and Marley 2002).

Samples were also collected in the Pittsburgh, Pennsylvania, area during July 2001 and analyzed for ^7Be and ^{210}Pb and its daughters. For this study, the measurement method was modified to quantify ^{210}Pb , ^{210}Bi , and ^{210}Po in a shorter time frame. Samples were collected by using a slotted impactor that allowed a higher volume of air to be sampled in fine and coarse sample collection modes. Previously, we had used a lower-volume cascade impactor that yielded nine size

ranges for evaluation of size distributions (Marley et al. 2000).

The lower-flow system took 3-7 days for sample collection and thus limited the method in determinations of aerosol residence times. We found that ages for size fractions $<1 \mu\text{m}$ were very consistent from site to site, indicating that the aerosols had apparent atmospheric residence times of 10-40 days. This was consistent with typical values of 10 days that we found for precipitation (Gaffney et al. 1994). Our concept was that the washout of soluble aerosols such as sulfate and nitrate would be consistent with these observations for precipitation and that the longer lifetimes observed for the air samples were due to carbonaceous aerosols or other fine particulate matter that was not water soluble.

Note that the observed ages reported are not absolute but are representative of the compositions of the aerosols. For example, a mixture of 90% of a 5-day-old aerosol and 10% of a 100-day-old aerosol would have an apparent age of 14.5 days. Similarly, a 50:50 mixture of a 5-day-old aerosol and a 100-day-old aerosol would have a 52.5-day apparent residence time.

Samples collected in areas where wind-blown dust is significant, such as Phoenix and Mexico City, have exhibited high ages in the coarse fractions. Other sites where wind-blown dust is not significant, such as Argonne National Laboratory near Chicago and Centerton, New Jersey, have shown similar ages for some coarse fractions, probably because of aerosol coagulation processes. These results do indicate that the ^{210}Po content in the coarse fraction is an excellent indicator of wind-blown dust or soil contamination, because it is not dependent on soil type.

Results for the shorter-time sampling (24 hr) in the Pittsburgh area were consistent with our past measurements at many sites. Apparent residence times for the samples were 10-46 days, with an average of 23 days. At Centerton, New Jersey, with the lower-volume samples, we had obtained an average of 33 days.

The somewhat shorter lifetimes for the Pittsburgh samples could be due to local sources of aerosols. The coarse fraction in Pittsburgh had similar residence times, indicating that little ^{210}Po could have come from soils or from coal-fired power plants, which previously had been suggested as a source of excess ^{210}Po (Marley et al. 2000).

Recent studies on arctic haze have found similar lifetimes of 0-39 days for aerosol samples that were not size fractionated (Baskaran and Shaw 2001). These data indicate that a significant fraction of fine aerosols can be transported long distances.

The consistency of the data at many sites also indicates that the background concentration of fine aerosols is fairly constant over wide areas. Transport of fine aerosols will lead to difficulties in determining local source contributions to the fine particulate mass.

Over a short time period (12 hr) in a city-wide area, ^7Be levels are also usually quite constant. This observation could help to address errors in the volume of air sampled by high-volume filters and could be a means for correcting problems due to power failures during air sampling.

5. CONCLUSIONS

Natural radioactivity can be a very useful tool in understanding the physical processes affecting aerosols during their evolution in the atmosphere. These studies have shown that useful information can be obtained about the washout and transport of aerosols in the troposphere. We anticipate that significant information could be obtained about other radioactive elements in primary aerosols from coal-fired power plants to aid in assessment of their impacts.

Clearly, a significant fraction of fine aerosols is transported for more than 20 days. This means that regional if not global control strategies are needed to maintain adequate air quality and reduce the impacts of elevated levels of fine aerosols on our weather and climate.

6. ACKNOWLEDGEMENT

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