2.2 RAINWATER INTERACTIONS WITH NATURAL RADIONUCLIDES ON CARBONACEOUS SOOT

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1. INTRODUCTION

Natural radionuclides can be useful indicators of aerosol lifetimes and sources. We are becoming more aware of the importance of atmospheric aerosols in the chemistry and physics of the atmosphere and as agents for 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 they play key roles in the hydrologic 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.

Critical to our understanding of the roles that aerosols play in the atmosphere is determination of their size, chemical composition, and physical properties. Especially important is their ability to take up water and grow to a size that can be removed by gravitational settling or washout processes.

In past work we have discussed the use of naturally occurring ^{7}Be for tracing and assessing effects of upper air parcels, along with the use of ^{210}Pb and its daughters, ^{210}Bi and ^{210}Pb, to estimate residence times of submicron aerosols (*1*–*4*).

To evaluate how strongly several natural radionuclides are bound to carbonaceous soots, we have performed some preliminary laboratory and field studies on the interactions of ^{7}Be, ^{210}Pb, and ^{210}Pb daughters (^{210}Bi and ^{210}Po) with rainwater. Soot samples were exposed to radionuclides in filtered rainwater with added diesel soot (NIST standard) to evaluate the binding strengths of the radionuclides to soot surfaces as a function of pH. The behavior of the radionuclides with "aged" soot (soot exposed to ozone in the laboratory) was also studied.

We made field measurements of ^{7}Be in dry-air events versus precipitation events to evaluate washout of ^{7}Be attached to aerosol species. Rainfall was characterized simultaneously in the precipitation events. These preliminary studies are presented here and discussed in terms of the potential use of natural radionuclides to examine lifetimes of soots (i.e., black carbon).

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2. NATURAL RADIOACTIVITY ON AEROSOLS

The dominant radioactive isotopes in fine aerosols are ^{7}Be and ^{210}Pb and its daughters, ^{210}Bi and ^{210}Po (*1*–*4*). Cosmogenic particles hitting the atmosphere lead to the production of ^{7}Be 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. These natural radioactive tracers then attach themselves to the surfaces of pre-existing aerosols. Analysis of the size distributions of these natural radionuclides shows that most of their contributions from the air are in the submicron aerosol component. Since ^{210}Pb has a 22.3-yr half-life, it and its daughters can have significant concentrations in wind-blown dust and can act as indicators of that material when they occur in higher concentrations in the size range > 1 μm (*5*).

The major radionuclides in the aerosol size range 0.1–1.0 μm are ^{7}Be, ^{210}Pb and its daughters (^{210}Bi and ^{210}Po), and ^{40}K (*1*–*4*). Gamma counting can be used to measure ^{7}Be, ^{40}K, and ^{210}Pb. Alpha counting and beta counting are used for ^{210}Po and ^{210}Bi, respectively (*1*–*4*). If low-energy gamma counting is not available, ^{210}Pb can also be determined by stripping it from its daughters and allowing them to grow during a fixed measurement time, then back-calculating the ^{210}Pb activity (*2)*.

3. DISTRIBUTION COEFFICIENT DETERMINATIONS

Diesel soot samples (NIST standard diesel soot) were mixed into rainwater collected at Argonne National Laboratory (southwest suburban Chicago) for use in distribution coefficient determinations. The samples of rainwater were prefiltered with ultrafiltration methods to remove particulate matter.

A small amount of soot, typically 25 mg, was mixed into 300 mL of rainwater. The radionuclide of interest was added and mixed again, and the pH of the solution was adjusted. The distribution coefficient, K_d, was determined by separating the particulates from the water and then counting the two media. Here

K_d = activity on carbon soot/activity in water,

normalized to the mass of carbon and the water volume.

Low activity levels were used for all of these experiments. Low-level detection of the species was accomplished with the appropriate counting system. For ^{7}Be, gamma counting was done directly on filtered soot. For ^{210}Pb and daughters, we used analytical methods developed at Argonne (*2*).

The results for untreated diesel soot in rainwater are shown in Figure 1 for ^{7}Be and Figure 2 for ^{210}Pb and daughters, as a function of pH.

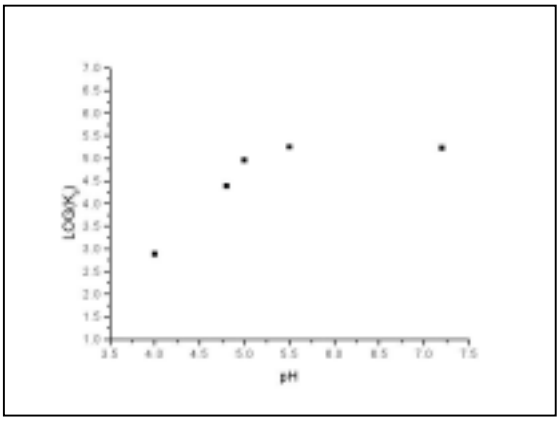

Figure 1. Log K_d for ^{7}Be attached to untreated soot in rainwater, as a function of pH.

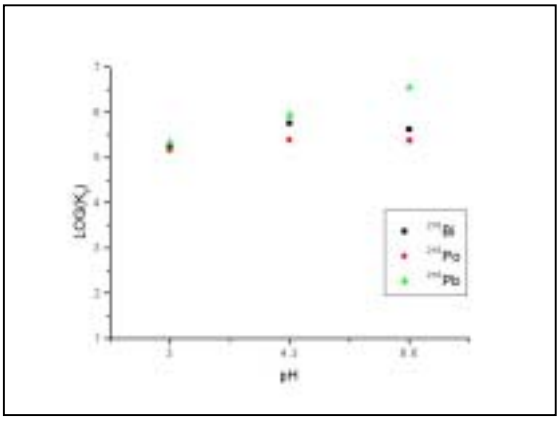

Figure 2. K_d for ^{210}Pb and its daughters on untreated soot in rainwater, as a function of pH.

The results indicate that ^{210}Pb and its daughters are strongly bound to soot particles. Beryllium-7 is also bound reasonably tightly at neutral pH levels with and becomes more soluble at lower pH. The normal pH of rainwater considered to be unaffected by acidic species is 5.6. Acid rain typically has pH = 4–4.5. Thus, these studies indicate that the natural radionuclides we have used as clocks (^{210}Pb and daughters) are unlikely to be significantly redistributed among particles in cloud droplets.

Soot samples were next exposed to ozone from a calibrated source for periods that would allow an integrated dose of up to two weeks at ozone levels of 60 ppb. These exposures were done for a few hours to a day at ppm levels. The results for ^{7}Be at pH = 5 are shown in Figure 3. Similar results were observed for ^{210}Pb, ^{210}Bi, and ^{210}Po, with stronger binding observed after longer ozone exposures.

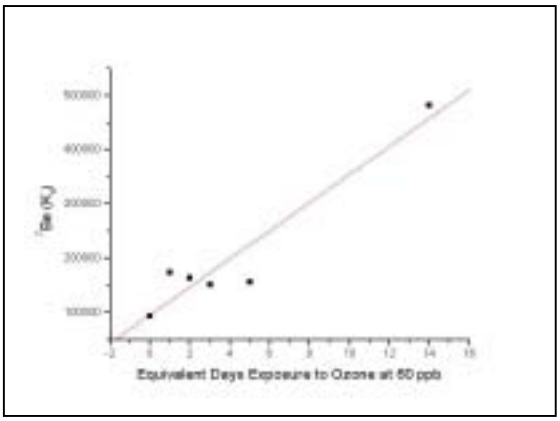

Figure 3. Log K_d as a function of exposure time for ^{7}Be attached to ozone-treated soot in rainwater at pH 5.

These results indicate that K_d for soot increased at longer exposure times. Thus, aged soots will be bound more strongly to the radionuclides, consistent with oxidation of soot surfaces to form carboxylate or hydroxycarboxylate structures that are known to be strong chemical chelating agents.

4. WET- AND DRY-AIR MEASUREMENTS OF ^{7}BE

A sampling system was set up during wet and dry periods for collection of submicron aerosols on quartz filters for gamma counting. The sampler uses a wetness detection switch that turns on the wet sampler during precipitation events and collects precipitation simultaneously. When the switch is off, the dry sampler is activated to collect comparison ^{7}Be values. High-volume samplers were used, and for some periods five-stage cascade impactors (Anderson-Sierra Instrument Design) collected samples in size ranges of 10, 4, 1, 0.5, and <0.5 μm (50% cutoff). As in past observations, the samples collected at Argonne had the most activity in the submicron aerosol fraction. Data for high-volume samplers in periods of wet and dry sampling are shown in Table 1. These data were taken on 8–15 June 2004 at the deposition site that Argonne has run

Table 1. Beryllium-7 activity in air and rainwater samples from the Argonne sampling site.

Julian Days	Dry/ Wet	Air		Rainwater	
		Volume (m^3)	^{7}Be (mBq m^{-3})	Volume (mL)	^{7}Be (Bq L^{-1})
160–163	Dry	1570	1.99	-	-
163–165	Dry	2738	1.57	-	-
163–165	Wet	1305	1.88	2200	0.18
165–167	Dry	2372	2.09	-	-
166–167	Dry	869	1.88	-	-
166–167	Wet	203	0.21	4600	0.32
167–173	Dry	5469	0.47	-	-

for years as part of the National Atmospheric Deposition Program (NADP), as well as for routine meteorological monitoring.

During the sampling period we attempted to examine both wet and dry air by coupling the systems to an automated rain sampler that collects rain in buckets for further analysis. The dry periods all had ^{7}Be levels of 1.57–2.09 mBq m^{-3}. During one rain event we were able to obtain samples of interstitial air for comparison. For the one-day sample on days 166–167, the error for ^{7}Be during the wet period could be large because of the small sample volume. However, for days 163–165, the ^{7}Be levels in wet and dry interstitial air were similar to the levels before and after the rain event. This observation indicates that an insignificant amount of the ^{7}Be was removed during this event. For the one-day event on days 166–167 the concentration dropped more significantly in the wet sampler, a finding consistent with the lower ^{7}Be levels during the subsequent dry period. We interpreted this result to indicate that the more productive storm system on days 166–167 was accompanied by arrival of an air mass with lower levels of ^{7}Be. The increased levels of ^{7}Be in the washout might also indicate that the aerosol was removed more efficiently, possibly because the aerosol was more "aged."

Building on these preliminary results, we plan to conduct more measurements and couple the ^{7}Be data with results for ^{210}Pb and daughters to examine the rainout of black carbon and determine its removal rates. This will be done in conjunction with measurements of ^{14}C (a good indicator of biogenic material) and ^{40}K (indicative of wood smoke sources).

5. CONCLUSIONS

Our laboratory experiments using filtered rainwater and standard diesel soots clearly indicate that natural radionuclides are strongly attached to soot surfaces at most pH levels anticipated in cloud droplets and in rainfall; thus, the radionuclides should be useful in evaluating the lifetimes of soots. Results of the preliminary field studies also indicate that the washout of fine aerosols containing ^{7}Be is not a very efficient process, contrary to results from current models. We are using these preliminary results to plan further experiments on aerosol removal and lifetimes as part of field efforts to determine the key properties of fine aerosols that are important in atmospheric radiative forcing.

5. ACKNOWLEDGEMENT

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