An Evaluation of Precipitation Scavenging Rates of Background Aerosol[1]

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ABSTRACT

Concentrations of radon daughters in falling rain have been used to derive precipitation scavenging rates of those particles with which radon daughters are associated; presumably these are the particulate component of natural, background aerosol. Scavenging rates ranging from 10^{-4} to 10^{-3} s^{-1} are deduced from a comparison of the observations with the predictions of simple models of in-cloud scavenging processes.

1. Introduction

It seems clear that scavenging rates of particles by precipitation depend upon enough variables to make precise prediction exceedingly difficult, if not impossible. Among the controlling parameters, such factors as the chemical and physical form of the contaminant in question, the type and duration of prevailing precipitation, and the natural (background) aerosol characteristics are obvious influences. Even though accurate formulation of the precipitation scavenging process may not be possible in the immediate future, there is an obvious need for simple but improved methods of introducing wet removal into schemes for regional assessment of the environmental impact of industrial pollution.

The experiment described here was an attempt to obtain information on the rates at which raining clouds cleanse the atmosphere, utilizing natural radioactivity as a tracer of naturally occurring aerosols. The analysis presented here is a revised version of one performed earlier (Hicks, 1967), using results from a study of the most easily detectable gamma-emitting daughters of radon throughout several periods of rainfall at Argonne, Ill., during 1966. This reanalysis is stimulated by recent interest in regional-scale pollutant transport, such as is addressed in the MAP3S program of DOE and the MISTT program of the EPA[2].

Fluxes of radon into the atmosphere result in readily detectable concentrations of radon daughters in air. The gas and its daughters have been used in many experiments and their behavior in the lower atmosphere is now reasonably well understood. The effects of meteorological conditions on the distributions of radon and thoron, for example, were investigated by Moses *et al.* (1960), who found a daily radon concentration cycle resulting from variations in atmospheric mixing. In the atmosphere, the air concentrations of the radioactive daughters would be expected to approach equilibrium with increasing height. In a theoretical study, Jacobi *et al.* (1959) showed that the short-lived first daughter of radon (^{218}Po, 3 min half-life) is in equilibrium with radon above about 20 m for vertical diffusivities $\gtrsim 0.1$ m^2 s^{-1}. By extrapolation of their results, ^{214}Pb and ^{214}Bi approach equilibrium concentrations at about 100 m. Measurements made by Fontan *et al.* (1966) support this, but we might expect to find some degree of disequilibrium in the vicinity of clouds due to the presence of large convective updrafts and electric fields (Jonassen and Wilkening, 1970).

2. Radon-daughter concentrations in rain

Gamma-ray spectrometry was used to measure the isotopes of interest in successive samples of precipitation collected at ground level during nine rainfall occasions. Samples were collected using an acrylic-coated tray of ~ 4 m^2 area mounted on the roof of the analyzing laboratory. Water was channeled to the laboratory by plastic tubing.

Typically, about 3 ℓ of rainwater were analyzed. Lead and bismuth were removed from the rain chemically, after the addition of appropriate carriers. In this way, a sample was prepared for analysis in about 10 min. Most samples were counted for the first time within 30 min after collection, using a 5 inch$\times$4 inch NaI (Tl) crystal coupled to a 400-channel pulse analyzer. Efficiencies of the collection system and of the chemical scavenging procedure were checked using prepared standard solutions of radon daughters. No significant loss of radioactivity was detected.

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[2] The Midwest Interstate Sulfur Transformation and Transport experiment, directed by Dr. W. Wilson of the U. S. Environmental Protection Agency.

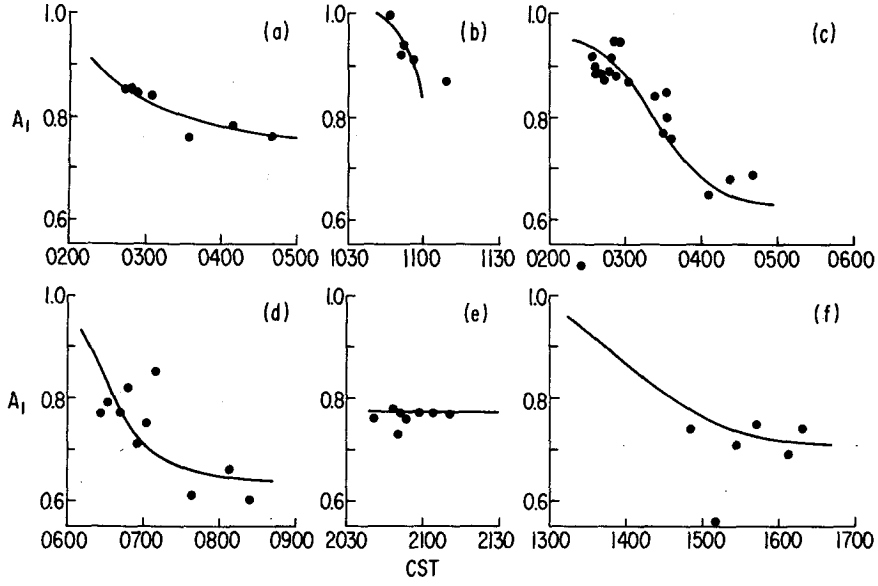

FIG. 1. Isotope activity ratios at the cloud base on 11 July (a), 13 July (b), 27 July (c, d), 1 August (e) and 10 August (f), 1966. Lines drawn by eye correspond to the scavenging rates and rainfall durations listed in Table 1.

Gamma-ray spectra of freshly collected rainfall are typically dominated by the photopeaks at 0.352 (^{214}Pb) and 0.609 MeV (^{214}Bi). After these isotopes have decayed, the ^{212}Pb photopeak at 0.323 MeV becomes apparent (^{212}Pb is a thoron daughter.) In the present work, an initial count was used to determine the radon daughters. A second spectrum was obtained about 4 h later in order to measure ^{212}Pb. Fission products in the rainwater were measured after a further time lapse of several days; these measurements were reported previously (Hicks *et al.*, 1966). The fission product spectra were used as backgrounds for the ^{212}Pb measurements, while the latter were used as the appropriate background levels in the ^{214}Pb and ^{214}Bi determinations.

Standard radon-daughter gamma-ray spectra were obtained from electrostatically collected samples of the emissions from solutions of radium in known concentration.

3. Results

Measured concentrations of ^{214}Pb ranged from 100 to 4000 pCi ℓ^{-1}, averaging about 1000 pCi ℓ^{-1}. The activity ratio of ^{214}Bi to ^{214}Pb was usually about 0.8, with an estimated error of about 5%.

Fig. 1 illustrates the results obtained during six periods of continuous rainfall. Data are corrected for decay, as explained later, to represent results applicable at cloud base. Isotope ratios are chosen for illustration here because these are far less scattered than the separate isotopic concentrations, from which some information could doubtlessly be obtained but with greatly diminished reliability. Details of the six occasions illustrated in Fig. 1 are given in Table 1, where it is seen that two situations of warm frontal rain are included. All other cases probably represent convective situations.

TABLE 1. Geometric means and specific details of the six occasions illustrated in Fig. 1.

Date	Cloud base (m)	Mean rainfall rate (mm h^{-1})	f_* (s^{-1})	f (s^{-1})	t_1 (min)	Comments
(a) 11 July	900	6.2	2×10^{-4}	2×10^{-4}	70	Moderate thunderstorm
(b) 13 July	800	21.6	1×10^{-4}	1×10^{-3}	5	Thunderstorm
(c) 27 July	250	13.2	2×10^{-4}	5×10^{-4}	10	Warm frontal rainfall
(d) 27 July	250	14.8	5×10^{-4}	5×10^{-4}	40	Warm frontal rainfall
(e) 1 August	1200(?)	22.3	2×10^{-4}	2×10^{-4}	60	Severe thunderstorm
(f) 10 August	370	1.3	5×10^{-4}	5×10^{-4}	10	Shower; no ^{212}Pb data
Geometric means	520	9.5	3×10^{-4}	5×10^{-4}	20 160	

4. Discussion

The lines drawn through the data points of Fig. 1 represent an interpretation of the results in terms of rainout rates and assumed secular equilibrium within the cloud air masses prior to the onset of rainfall. A similar assumption is made by Perkins *et al.*, (1970), who suppose that cosmogenic radionuclides are in equilibrium at the time of nucleation in a cloud. This type of assumption tends to be supported by the data of Fig. 1: the general monotonic decrease of the radon-daughter activity ratios has already been mentioned. It is conceded, though, that some other aspects of rainfall scavenging might be critical and must be considered.

For the moment, consider ^{218}Po, ^{214}Pb and ^{214}Bi to be in equilibrium with atmospheric radon in and near a cloud before rain starts to fall out. The generation of water droplets will not disturb this equilibrium, even though many of the radioactive particles change their physical and chemical form. Only after precipitation commences will the overall equilibrium be modified.

The original equilibrium in the air mass is described by

$$\lambda_0 N_0 = \lambda_i N_i = C, \qquad (1)$$

where C is the activity concentration of radon, N_i the atom concentration of the ith radon daughter and λ_i the corresponding decay constant.

Gat *et al.*, (1966) showed that little ^{218}Po is attached to particles, a result of its 3 min half-life. The longer-lived isotopes, ^{214}Pb (26.8 min) and ^{214}Bi (19.7 min), will be largely associated with particles. Thus, when considering the effect of rainfall scavenging, ^{218}Po is not necessarily scavenged in the same way as the other isotopes.

Consider first a simple cloud model in which precipitation, commencing at time $t=0$, removes a constant proportional fraction f (s^{-1}) of the aerosol available per unit time. The behavior of the radon-daughter system is described (in a similar manner to Gat *et al.*) by

$$(dn_i/dt) = \lambda_{i-1} n_{i-1} - \lambda_i n_i - f n_i - \nabla \cdot \mathbf{F}_i, \qquad (2)$$

where n_i is the atom concentration of the ith radon daughter at time t, and where $\mathbf{F}_i$ is the flux of n_i into the cloud air mass due to the circulation through the cloud and due to mixing. It is assumed in this discussion that ^{218}Po, ^{214}Pb and ^{214}Bi are each removed by rainfall at precisely the same rate. There is evidence that this last assumption may be incorrect in that ^{218}Po, in particular, might be subject to enhanced scavenging due to its electric charge in ionized form, but it is difficult to see how allowance for any such effect is possible in the present theoretical format. In fact, (2) is already a simplification, neglecting all effects of ion migration (Wilkening, 1970).

It is possible that the flux divergence term in (2) may be significant, particularly in the case of an extremely vigorous convective cell. However, it can be shown that in most situations the error involved in disregarding the divergence term will be less than 10%. If we assume that $\nabla \cdot \mathbf{F}_i$ is negligible, solutions are readily obtained for the set of equations (2), corresponding to the first three daughters of radon, subject to the boundary condition that equilibrium existed at time $t=0$. Such solutions are illustrated in Fig. 2, where A_1 (the activity ratio ^{214}Bi/^{214}Pb) is shown as a function of elapsed time for a range of rainout rates f. Scavenging causes gross distortions in the initial equilibrium between radon daughters. For each scavenging rate, a new steady state can be defined in which the isotope ratio remains constant with time so long as f remains constant. Thus, if the cloud has been raining for a sufficient time, measurements of this ratio in the cloud environment should permit an estimate of the mean rate of removal of aerosols during the cloud's life.

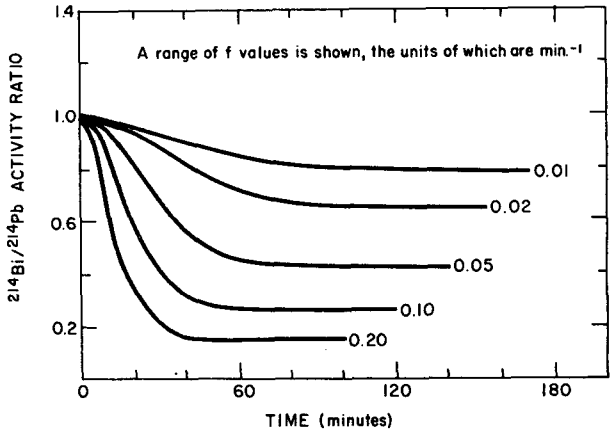

FIG. 2. The ^{214}Bi to ^{214}Pb activity ratio in a cloud as a function of time after the initiation of a scavenging function f.

Recalculation for the case in which no ^{218}Po is scavenged causes only minor changes in the form of the curves shown.

Thus it should be possible to estimate the value of f appropriate to each of the six experimental occasions shown in Fig. 1, provided sufficiently accurate correction can be made for radioactive decay during the time lapse between the rain leaving the cloud base and measurement at ground level (as has been done in Fig. 1). It should also be possible to locate the measured values on the time scale of Fig. 2 and so estimate the time at which rain first started falling from the cloud in question.

Generally, the time involved in preparation of the samples was much greater than the time needed for the rain to fall from the cloud base. The sample preparation time was directly measured. For the present study, the fall time was estimated from measurements of the cloud base altitude made at Midway Airport, near Argonne, and the terminal velocity associated with 2 mm drops. On the basis of raindrop size spectra (Mueller, 1966) the droplet sizes which contribute most

to the net transport of water fall into a narrow range, centered at about 2 mm diameter. This median diameter depends only slightly on rainfall rate, following approximately a quarter-power relationship. For the present, effects of evaporation, changes in rainfall rate and scavenging during descent of the rain have been neglected.

Some justification for the neglect of scavenging of the radon and thoron daughters by falling raindrops can be derived from the results of Greenfield (1957). Since the isotopes of interest here are largely associated with particles having diameters <1 μm (Jacobi *et al.*, 1959), the amount of radioactivity collected by impaction during the descent of the rain should be sufficiently small to be disregarded in the present analysis. Consequently, the data have been corrected for radioactive decay on the basis that ^{212}Pb and ^{214}Pb decay exponentially after rain falls from the cloud base and that ^{214}Bi concentrations change according to growth from its parent and radioactive decay. However, recent work by Graedel and Franey (1974) suggests that subcloud processes might be much more efficient than previously thought, in which case the present correction for the time of fall of the rain might be a considerable oversimplification.

The curves drawn through the radon-daughter activity ratio data of Fig. 1 are fitted by eye from the family of Fig. 2. In the curve-fitting procedure, two degrees of freedom are available: the scavenging rate f and the time t_1 since rain first started falling from the clouds. The values of f and t_1 (considered as the raining age of the storm at arrival) which give the most satisfactory agreement are listed in Table 1. For example, in Fig. 1a, A_1 appears to have reached its asymptotic value by about 0300 on 11 July. The best fit is obtained by using a scavenging rate of 2×10^{-4} s^{-1}. To obtain a satisfactory agreement with the earlier data, it is necessary to assume that the cloud commenced precipitating approximately 70 min before the first rain fell at Argonne.

A simpler interpretation neglects the time dependence and assumes that each measurement represents a final and static value of the isotope ratio resulting from a specific scavenging rate. Reference to Fig. 2 enables a range of scavenging rates to be determined for each occasion, the means of which are also listed in Table 1 as f_*. It should be noted that all the estimates of f and of f_* are confined to the semi-logarithmic series (1, 2, 5, 10, etc), since further resolution is not warranted.

Comparison of the values listed in the table shows that the two estimates of the scavenging rate agree closely except for the thunderstorm occasion of 13 July. In Fig. 1, it is seen that the measured isotope ratios dropped markedly through this particular rainfall, suggesting that neglect of the time-dependence implicit in the determination of f_* is, in fact, not valid in this case. The lack of scatter in the derived values of f and f_* is encouraging. Not surprisingly, it appears that the most efficient scavenging is associated with "young" storms.

The present results can be compared with a number of similar evaluations which have appeared in the literature in recent years. Some of these results have been conveniently tabulated by McMahon *et al.* (1976), who conclude (on apparently somewhat tenuous evidence) that a linear relationship exists between f and the rainfall rate J (mm h^{-1}). Their expression is based on eight evaluations of f, four of which are from field studies. The four experimental determinations are 2×10^{-4} $J^{0.8}$ (Engelmann, 1965), 8×10^{-5} (Makhon'ko, 1967), 4×10^{-6} (Esmen, 1972), and 7×10^{-6} (accredited to Acres Consulting Services, 1974), all in units of reciprocal seconds. To this list may be added 3×10^{-5} (Bakulin *et al.*, 1970) and about 3×10^{-3} (Perkins *et al.*, 1970). The scatter in these results must cause some concern, but clearly the present results of 10^{-4} to 10^{-3} s^{-1} are not out of line. However, they do not support the dependence between f and J reported by Engelmann and McMahon *et al.* A recent study by Graedel and Franey (1974) of washout (i.e., subcloud scavenging) rates gave results similar to those obtained here, with no discernible influence of the rainfall rate. Instead, they find a strong dependence on particle size. This matter cannot be addressed with the present data, nor is it clear how the strong variability seen in Table 1 of Graedel and Franey for subcloud processes will influence the total scavenging rates under consideration here.

5. Conclusions

A severe limitation of the present work is its reliance, almost entirely, upon self-consistency to confirm the results. The validity of one of the two alternative analysis schemes rests on the assumption that the flux of radioactivity into a raining cloud is small in comparison with the removal rate due to scavenging by the rainfall processes. The fact that the radon-daughter data closely follow curves of the predicted shape lends some support to the assumption. However, it seems quite likely that the results obtained here may represent the net effect of an input flux and simultaneous rainfall scavenging.

Nevertheless, the present simple mathematical model of rainfall scavenging of particulate natural radioactivity enables estimates to be made of the aerosol scavenging rates of raining clouds. These rates can be deduced from sequential rainfall samples collected at the ground surface. The values obtained ranged between 10^{-4} and 10^{-3} s^{-1}, and feature the overall characteristics that one would expect: in particular, younger rainfall systems are considerably more active as scavenging agents. It is also possible to deduce estimates of the time at which rain first started falling from the air mass under consideration. This feature might lend itself to verification using radar.

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