Atmospheric Bismuth-212: Measurement and Some Geophysical Applications

Abstract. *The concentrations of lead-212 and its short-lived daughter bismuth-212 in air near the ground were determined simultaneously by adaptation of the immersed-filter, delayed-coincidence technique of Assaf and Gat to measurement of the* 3×10^{-7}*-second bismuth-212 and polonium-212 pair. The radioactive disequilibrium between lead-212 and bismuth-212 depends strongly on the efficiency of the ground in acting as a sink for these nuclides. This efficiency is low under dry conditions.*

Natural radioactivity in air in the troposphere results predominantly from radon-222 and its short-lived decay products (*1*); their distribution and the extent of radioactive disequilibrium between parent and daughter products has provided information on transport rates and on scavenging processes (*2*) in the atmosphere. Complementary information can be obtained from the airborne decay products of thorium-232 (*3*). However, measurement of the Bi^{212} decay product from this series has not been possible by conventional counting methods (*4*) in which the radioactivity of the thoron daughter on air filters is determined only after the decay of radioactivity of daughter products of Rn^{222}, when a transient equilibrium is attained between Bi^{212} and its parent Pb^{212} regardless of their relative concentrations in the air.

We have adapted the delayed-autocoincidence method (*5*) to detection of the 3×10^{-7}-second Bi^{212}-Po^{212} pair for measurement of the concentrations of Bi^{212} and Pb^{212} and for determination of the extent of disequilibrium between them (*6*). The airborne particulates were collected on filters (*7*) that were immersed in a liquid-scintillation solution (*8*); the scintillation pulses were counted with a photomultiplier tube and two delayed-coincidence circuits. This system differs from an earlier one (*5*) by the addition of a fast delayed-coincidence gate (delay time τ_d, 0.1 μsec; gate-open time τ_g, 1.5 μsec) which detects the double scintillations, due to β and α disintegrations of the Bi^{212}-Po^{212} pair, with an efficiency of about 76 percent (*9*). The short open-time of the fast-coincidence gate ensures a small background counting rate from random pulses in that channel. Of the disintegrations of the Bi^{214}-Po^{214} pairs, 0.75 percent are also counted in the fast-coincidence channel. One must correct for this background (*10*); the correction can be made quite accurately, for the disintegrations of the Bi^{214}-Po^{214} pairs are simultaneously measured in the slow-coincidence channel.

The relative amounts of Bi^{212} and Pb^{212} can be computed by analysis of the decay of the Bi^{212}-Po^{212} activity on the filters (*5, 11*). The optimum sampling time for obtaining maximum sensitivity in measurement of the Pb^{212}:Bi^{212} activity ratio was 2 hours. In order to measure the airborne Pb^{212}:Bi^{212} activity ratio with a 10-percent standard error, 16 count/min of thoron-daughter activity must be intercepted per minute on the filters; thus one must take 1- to 10-m^3 samples of air each minute.

The results of our first attempts to measure the Pb^{212} : Bi^{212} radioactivity within 1 meter of the ground and on top of an 8-m-high building (Table 1) show that measurement of short-lived radioactive decay products, such as Bi^{212}, contributes information relative to the problem of transport conditions at the interface (*12*).

The source of the thorium-series activity in the atmosphere is the exhalation of Rn^{220} in gaseous form from Earth's surface (*13*); because of its short life, Rn^{220} is transformed into the 10.6-hour Pb^{212} close to the ground. This isotope is responsible for dispersion of the thorium-series activity throughout the atmosphere. In an undisturbed system the rate of attainment of a transient equilibrium between Bi^{212} and its parent Pb^{212} resembles the buildup of Bi^{214} activity from radon gas (Rn^{222}), because of the similarity of the radioactivity-decay rates of daughter products. However, distribution of the products in the atmosphere may vary considerably even under ideal steady-state conditions, since the daughter products do not possess noble-gas characteristics and are rapidly attached to the natural

Table 1. Concentrations of airborne natural radioactivity at Rehovoth, Israel; *sharav*, hot and dry weather caused by subsidence.

Sampling							
Day (1967), hour	Duration (hr)	Height above ground (m)	Pb^{212} : Bi^{212}	Pb^{214} : Bi^{214}	$\Sigma(Bi\text{-}Po)^{212}$* ($\times$ 100)	Σ Radon: Σ thoron†	Conditions during preceding 2 hours‡
23 Jan, 0915	1	0.60	0.9 ± 0.2	1.1 ± 0.05	115	2.8	Ground frozen
25 Jan, 0815	1	.15	1.1 ± .2	0.9 ± .1	122	1.3	
26 Jan, 1400	1	.15	1.45 ± .3	1.25 ± .05	50	4.8	SW winds
9 Apr, 1440	1	.60	1.3 ± .2	1.1 ± .1	60	2.1	Wind 320°, 5 k
11 Apr, 0840	2	8	0.85 ± .1	1.15 ± .05	450	1.35	Still air, *sharav*
12 Apr, 1350	2	8	1.25 ± .15	1.25 ± .05	150	3.2	Wind 160°, 4 k
14 Apr, 0612	1	8	1.2 ± .1	1.25 ± .05	250	1.8	Wind 250°, 8 k
16 Apr, 0720	2	8	1.8 ± .4	0.8 ± .1	14	4.8	W wind, cloudy, rain nearing
17 Apr, 1430	2	8	1.6 ± .3	1.2 ± .1	32	3.5	Wind 270°, 3 k
19 Apr, 1730	2	8	1.45 ± .15	1.2 ± .1	125	1.2	Still air
20 Apr, 1030	2	8	1.45 ± .2	1.1 ± .1	100	0.95	Wind 250°, 16 k
27 Apr, 0915	1.5	8	1.4 ± .3	1.0 ± .1	29	1.4	Still air
29 Apr, 0830	2	8	1.4 ± .2	1.25 ± .1	200	1.7	Wind 250°, 9 k
2 May, 1230	2	8	2.4 ± .25	1.1 ± .1	85	1.2	Rain, wind 230°, 8 k

* Sum of $(Bi\text{-}Po)^{212}$ pairs counted on fast-coincidence channel. † Ratio of sums of $(Bi\text{-}Po)^{214}/(Bi\text{-}Po)^{212}$ pairs. ‡ Wind at Beth Dagan Meteorological Station; k, knots.

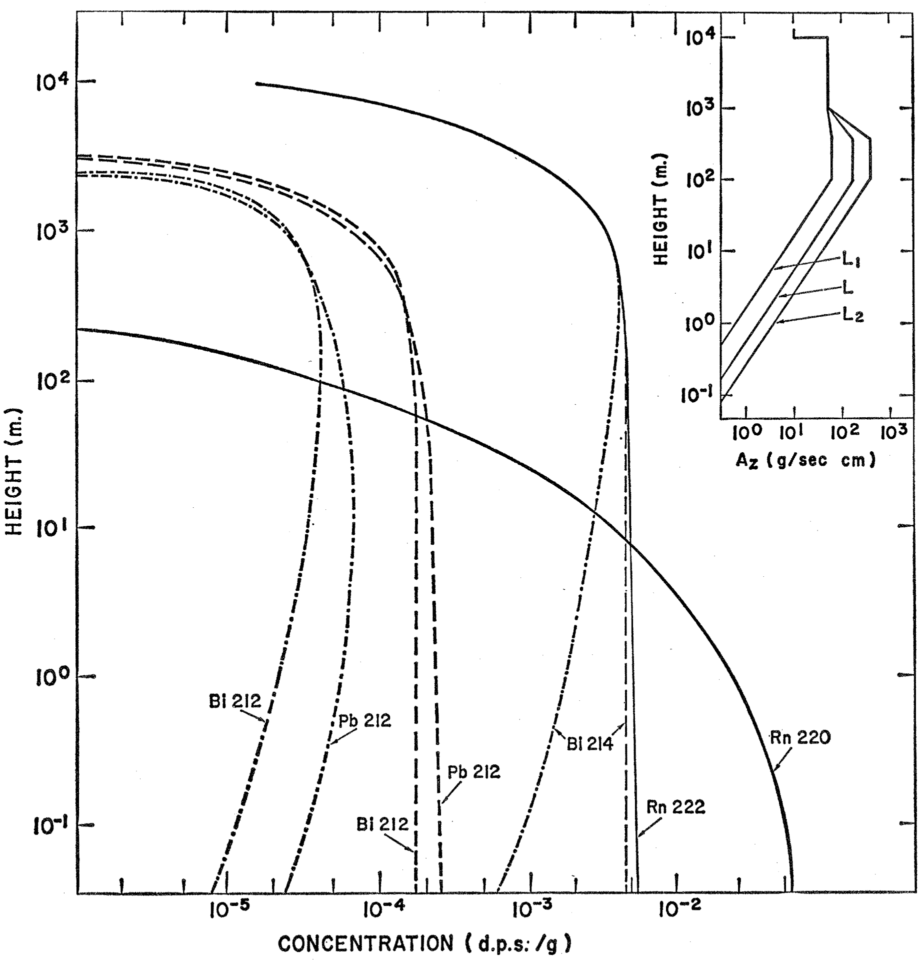

Fig. 1. Vertical distribution of Rn^{220}, Rn^{222}, and their short-lived decay products in the atmosphere. Calculated distribution based on the Austausch-coefficient profile L (inset) for Rn^{222} exhalation rates of 1 atom/sec·cm² and Rn^{220} exhalation rates of 0.02 atom/sec·cm². Solid lines, radon isotopes; broken line, daughter products, with total reflection at the surface; dotted lines, daughter products, with vanishing concentrations at the surface. Inset: Profiles of the vertical-exchange coefficients (Austausch) used in the calculations.

aerosol particles in the air (*14*); thus they are subject to gravitational settling, scavenging, and interception at the phase boundaries. If one assumes uniformity and steady-state conditions, the vertical distribution of the nuclides may be described by a diffusion equation (*15*) such as

$$\frac{\delta}{\rho \delta z}\left(A_z \frac{\delta c_i}{\delta z}\right) - \lambda_i c_i = P_i$$

where c_i is the concentration of nuclide per gram of air, where i is 0, 1, 2, 3 . . ., depending on the position in the decay chain; z is height above ground; A_z is the vertical turbulent-exchange coefficient (Austausch); λ_i is the radioactivity-decay constant; ρ is the air density; P is production, being 0 for radon, and P_i being $-\lambda_{i-1}c_{i-1}$ for daughter products. For radon the boundary condition requires the vertical flux to equal the exhalation rate at Earth's surface. For the daughter products a removal term must be added at the boundary (*12*), whose magnitude depicts the detailed happenings at the interface.

We have calculated the vertical profiles of the nuclides concerned for three idealized, representative, turbulent-diffusion profiles (Fig. 1, inset). Profile L is a simplified version of the eddy-diffusion profile that has been measured by Mildner under stable atmospheric conditions and reanalyzed by Lettau (the Leipzig profile) (*16*); it consists of a linear profile up to 100 m, followed by a flat maximum from 100 to 350 m; A_z then decreases upward to 50 g/cm·sec at a height of 1 km. As Lindner did not measure higher than 1 km, we assumed a constant A_z from that height upward. Profiles L_1 and L_2 are two extreme variants of this basic profile that include the range of conditions under stable atmospheric conditions. A roughness

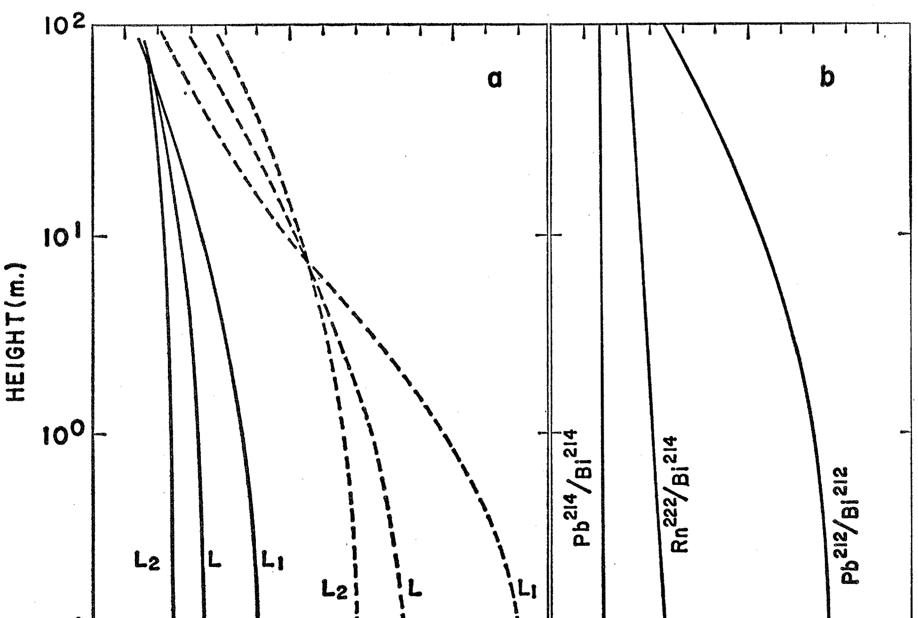

Fig. 2 (left). (a) Activity ratio Pb^{212}:Bi^{212} (airborne), as a function of height, calculated for Austausch-coefficient profiles L, L_1, and L_2 (Fig. 1, inset). Solid lines, for boundary condition of total reflection of radon daughter products at the surface ($E_i = 0)_{z=0}$; broken lines, for boundary condition $(c_i = 0)_{z=0}$. (b) Activity ratios in air of different nuclides after prolonged scavenging by rain; the L Austausch-coefficient profile, boundary condition of $(E_i = 0)_{z=0}$, and a rain-scavenging rate constant of $\lambda_r = 5 \times 10^{-5}$ second throughout the air column up to a height of 5 km are assumed.

parameter (z_0) of 1 cm was assumed in all calculations.

The diffusion equations were solved for two extreme boundary conditions: (i) vanishing daughter concentrations near the ground (*17*); and (ii) a vanishing concentration gradient near the ground, corresponding to a complete reflection of the aerosol-bound daughter products at the surface.

The vertical distribution of the radon isotopes and of their decay products, as calculated numerically for the *L* profile, is shown in Fig. 1. The boundary conditions have a spectacular effect on the near-surface concentration of the short-lived nuclides in the thoron series. Measurement of the disequilibrium between these daughter products seems to be an excellent tool for probing conditions at the interface. The calculated values of the $Pb^{212}:Bi^{212}$ ratios for the different conditions described above appear in Fig. 2a. For the first boundary condition [that is, $(c_i)_{z=0}=0$], this calculated ratio is greater than 2 up to a height of about 10 m. At our sampling height of 8 m, this ratio is 2.1 for all three vertical-diffusion conditions L, L_1, and L_2. However, the measured activity ratios never approached such a high value (except during rain), averaging 1.38; this value is very close to that predicted for the height of 8 m by the model for the *L* profile with complete reflection at the boundary.

Although the true wind-speed profiles were not determined during these preliminary experiments, the measured activity ratios of the daughter products of Rn^{222} gave values consistent with the assumed diffusion conditions. The experimental results thus seem to indicate that during fair weather the transport of the natural aerosol to the surface is considerably hindered. Probably there is a "Brownian barrier" through which molecular diffusion is the dominant mode of transport; such a barrier then effectively limits the removal of aerosol particles whose rate of diffusion is very low. These findings agree with recent results (*18*) on the rate of deposition of Aitken nuclei on rough surfaces. This technique could be used to measure the particle flux into the sea; the very low radioactivities encountered in marine atmosphere may, however, limit its usefulness to areas near the coast.

Figure 2b shows an example of the great disequilibrium between the thoron daughter products that results from continuous scavenging by rain throughout the air column; during rainy periods, however, assumption of a steady-state exhalation of Rn^{220} becomes extremely doubtful and must be verified in every instance.

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References and Notes

1. C. E. Junge, in *Air Chemistry and Radioactivity* (Academic Press, New York, 1963).
2. J. R. Gat, G. Assaf, A. Miko, *J. Geophys. Res.* **71**, 1525 (1966).
3. Radon-220, 54 seconds; Pb^{212}, 10.6 hours; Bi^{212}, 1 hour; Po^{212}, 3×10^{-7} second.
4. L. R. Lockhart and R. L. Patterson, *The Natural Radiation Environment* (Rice Univ. Centennial Series, Univ. of Chicago Press, Chicago, 1964), pp. 279–90.
5. G. Assaf and J. R. Gat, *Nuclear Inst. Methods* **49**, 29 (1967).
6. In principle the β-α coincidence technique of Fontan *et al.* [*Tellus* **18**, 623 (1966)] also could be used for such measurements, but with less sensitivity.
7. Type GM-4; Gelman Manufacturing Co.
8. Of 5 g of terphenyl and 0.38 g of *p*-bis-[2-(5-phenyloxazole)]-benzene in 1 liter of toluene.
9. The counting efficiency of the α and β disintegrations is 98 percent. However, only 76 percent of the disintegrations of all $(Bi\text{-}Po)^{212}$ pairs are expected to occur during the time interval between 0.1 and 1.5 μsec. The overall counting efficiency of Bi^{212} by our method is 49.3 percent because of the branching in the Bi^{212} decay scheme.
10. The particular gate-open time of the fast-coincidence channel was chosen so as to minimize the standard counting error of Po^{212} in the presence of such a background. Specifically the value of τ_g' that minimizes the expression,
$$\frac{\sigma(c')}{c'} = \{c_4'[1\text{-exp}\,(\lambda_4'\tau_g')] + c_4[1\text{-exp}\,(-\lambda_4\tau_g')]\}^{1/2}/c_4'[1\text{-exp}\,(-\lambda_4\tau_g')]$$
was computed for a typical case of $c_4' = c_4/30$, c_4 and c_4' being the mean count rates of Po^{214} and Po^{212} , respectively, and λ_4 and λ_4' being their radioactivity-decay constants.
11. M. Kawano and S. Nakatani, in *The Natural Radiation Environment* (Rice Univ. Centennial Series, Univ. of Chicago Press, Chicago, 1964), pp. 291–312.
12. B. Bolin, in *Nuclear Radiation in Geophysics* (Academic Press, New York, 1962), pp. 136–68.
13. H. Israel, in *Nuclear Radiation in Geophysics* (Academic Press, New York, 1962), pp. 76–96.
14. L. Lassen, *Geofis. Pura Appl.* **50**, 281 (1961); ——— and G. Rau, *Z. Phys.* **160**, 504 (1960); W. Jacobi, *Geofis. Pura Appl.* **50**, 260 (1961).
15. The "diffusion equation" approached is valid for a long averaged concentration profile under steady-state conditions; its validity becomes questionable for short-lived isotopes or for conditions in which the atmospheric-residence times are short relative to the scale of turbulence, which is responsible for the transport. Such effects have been discussed by G. Assaf (thesis, in preparation) and by D. O. Staley, *J. Geophys. Res.* **71**, 3357 (1966).
16. H. Lettau, *Tellus* **2**, 125 (1950).
17. These are the conditions assumed by Jacobi and André [*J. Geophys. Res.* **68**, 3799 (1963)] in their extensive calculations of the radioactive profiles in the atmosphere; they imply that Earth's surface acts as an efficient sink for particulate matter in the atmosphere.
18. A. C. Chamberlain, *Proc. Roy. Soc. London* **A296**, 45 (1967).

3 January 1968

DDT Residues and Declining Reproduction in the Bermuda Petrel

Abstract. *Residues of DDT [1,1,1-trichloro-2,2-bis(*p*-chlorophenyl)ethane] averaging 6.44 parts per million in eggs and chicks of the carnivorous Bermuda petrel indicate widespread contamination of an oceanic food chain that is remote from applications of DDT. Reproduction by the petrel has declined during the last 10 years at the annual rate of 3.25 percent; if the decline continues, reproduction will fail completely by 1978. Concentrations of residues are similar to those in certain terrestrial carnivorous birds whose productivity is also declining. Various considerations implicate contamination by insecticides as a probable major cause of the decline.*

Many oceanic birds nested on Bermuda in 1609 when the first settlers arrived, the most abundant apparently being the Bermuda petrel, *Pterodroma cahow*. Within 20 years man and his imported mammals virtually exterminated this species; for nearly 300 years it was considered extinct. Several records of specimens since 1900 were followed in 1951 by discovery of a small breeding colony (*1*), and in 1967 22 pairs nested on a few rocky islets off Bermuda. With a total population of about 100 the petrel is among the world's rarest birds.

A wholly pelagic species, *P. cahow* visits land only to breed, breeds only on Bermuda, and arrives and departs only at night. The single egg is laid underground at the end of a long burrow. When not in the burrow the bird feeds far at sea, mainly on cephalopods; when not breeding it probably ranges over much of the North Atlantic (*1*).

Reproduction by *P. cahow* has declined recently. The data since 1958 (Table 1) show an annual rate of decline of 3.25 ± 1.05 percent; the negative slope of a weighted regression is significant (P, .015; F test). If this linear decline continues, reproduction will fail completely by 1978, with extinction of