Deposition of anthropogenic sulfate and Pb-210 in the western North Pacific area

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(Received April 16, 1984: Accepted November 19, 1984)

The monthly deposition rates of sodium, calcium, chloride, sulfate and Pb-210 from the atmosphere were measured at 12 stations in various parts of the Japanese Islands for two years. The deposition rates of sea salt particles were higher in the coastal region near the Sea of Japan in winter, demonstrating the fact that the strong winter monsoon produces many sea salt particles. Amounts of chloride, sulfate and calcium in excess of the sea salt component were always observed. The rather uniform annual deposition rates of excess sulfate ($3\text{--}10\text{g/m}^2/\text{y}$) suggest that a large part of this excess sulfate originates in global air pollution. Pb-210, much of which is of upper atmospheric origin, is also deposited in significant amounts in winter. This seasonal change may be due to the replacement of lower air masses over the continental margin area, which yields a two-layer model for the atmospheric transport of chemical constituents. The geographical variation of Pb-210 deposition can be explained using the two-layer model and by assuming a 12 day residence time for the tropospheric aerosols. The deposition rates for sulfate over the ocean area decrease more rapidly with distance from the continental coast than those for Pb-210. This result may show that the atmospheric residence time of sulfate is shorter than that of Pb-210.

INTRODUCTION

In recent years much attention has been paid to the behavior of atmospheric sulfur compounds in order to find a solution to problems induced by the anthropogenic sulfur emitted to the atmosphere (e.g., Rodhe, 1981). The behavior of a chemical constituent in the atmosphere depends upon its reactivity which in turn determines its atmospheric residence time. The geographical distribution of the deposition rates of sulfur compounds is also strongly related to their atmospheric residence times (Turekian *et al.*, 1977). Therefore we can predict the behavior of sulfur compounds in the atmosphere from the observed geographical variation of the anthropogenic sulfate deposited.

A coupling of the sulfur dioxide and sulfate system with the Rn-222 and Pb-210 system seems to be quite useful in elucidating this problem. Both sulfur dioxide and Rn-222 are unstable gases having similar life times in the atmosphere (Tsunogai, 1971). Both sulfate and Pb-210 are produced from their gaseous

precursors and soon become attached to aerosol particles (Junge, 1963). A difference between the geographical pattern of the sulfate deposition rates and that of the Pb-210 deposition rates can be mathematically analyzed to yield the atmospheric residence times of sulfate using the half life of Rn-222 (3.8d) and their source functions as presented by Tsunogai (1971).

Wet removal processes are most important in the removal of aerosol components such as sulfate, chloride and Pb-210, especially in the oceanic region (Tsunogai, 1975; Prospero, 1978). A quantitative estimate of the average wet deposition rate at any one place is not easy because the concentration of chemical constituents in rain or snow varies widely with time. This suggests that long term observation is necessary for the determination of the average wet deposition rate of any atmospheric constituent. Therefore, we established an observation network in the North Pacific region and for two years observed the monthly deposition rates of sulfate, chloride, sodium, calcium and Pb-210.

METHODS OF OBSERVATION AND DETERMINATION

Wet precipitation including dry sedimentation was collected with a cylinder and funnel type sampler of 302cm² or 165cm² mouth area. This sampler was placed on the roof of a building or in a plain grass field. To minimize the evaporation of the sample water and the exchange of water vapor of the sample water with the outside air, the bottom of the funnel was connected to the top of a polyethylene tubing 1m long and 1.0cm in diameter. The bottom of the tubing was then placed at the bottom of a 10l polyethylene bottle, which was replaced once a month to obtain water samples.

The sampling locations are listed along with their altitudes in Table 1. These 12 observation stations are distributed widely in the western North Pacific area.

Sample water was filtered through a Toyo No.5B (equivalent to Whatman No.40) filter. The solid material on the filter paper was ignited at 400 to 450°C and weighed. The Pb-210 content was radiochemically determined for both the solid and dissolved fractions principally by the method of Fukuda and Tsunogai (1975). The filtered sample water was analyzed for chloride and sulfate by the colorimetric methods of, respectively, Iwasaki *et al.* (1956) and Iwasaki *et al.* (1957), and for sodium and calcium by an atomic absorption method.

RESULTS AND DISCUSSION

Deposition rate of sea salt particles

Table 2 shows the average concentrations of the chemical constituents observed at the 12 stations in the western North Pacific area. These concentrations are calculated from the data given in the Appendix. Chloride and sodium are the most abundant, demonstrating the fact that the major component of aerosols in the coastal or maritime air masses is sea salt from the ocean surface. Ratios of Cl/Na found in the precipitation of this area, however, were always greater than that of seawater. This indicates that there are one or more extra sources of chloride in addition to sea salt in this atmospheric precipitation. Therefore, sodium was chosen as a representative sea salt component and we defined an excess amount of any chemical constituent derived from sources other than sea salt particles as follows:

$$M_{\text{excess}} = M_{\text{obs}} - (M/\text{Na})_{\text{sea}} \text{Na}_{\text{obs}} \quad (1)$$

where M is the concentration of the constituent in question and Na is that for sodium. The subscripts, *obs* and *sea*, refer to the observed value and the average concentration in seawater, respectively.

The deposition rates of sodium vary widely with place and season (Fig. 1). The variation

Table 1. Sampling stations*

Station**	Location	Height above sea level (m)	Height above ground level (m)	Surface area of the sampler (cm ²)
Kitami (Kt)	43°49'N 143°55'E	84	12	302
Hakodate (Hk)	41°49'N 140°45'E	3	1.2	1,452
Akita (Ak)	39°43'N 140°08'E	18	15	302
Sendai (Sn)	38°10'N 140°52'E	45	29	302
Hachijojima (Hc)	33°06'N 139°47'E	79	1.2	165
Chichijima (Cc)	27°05'N 142°11'E	20	1.2	165
Tokyo (Tk)	35°41'N 139°29'E	58	15	302
Kanazawa (Kn)	36°33'N 136°39'E	48	12	302
Misasa (Ms)	35°23'N 133°56'E	160	6	254
Tanabe (Tn)	33°43'N 135°23'E	17	1.2	302
Nagasaki (Ng)	32°44'N 129°52'E	19	9	165
Naha (Nh)	26°12'N 127°43'E	110	12	165

* The locations are plotted in Fig. 5a.

** Abbreviations are given in parentheses.

Table 2. Deposition rates and concentrations* of chemical constituents** over Japan and the western North Pacific

	Rainfall mm	Na	Cl	Δ Cl	SO ₄ g/m ² /y (mg/l)	Δ SO ₄	Ca	Δ Ca	Pb-210 kdpm/m ² /y (dpm/l)	Δ Cl Pb-210 10 ⁻⁴ g/dpm	Δ SO ₄ Pb-210 10 ⁻⁴ g/dpm	Δ Ca Pb-210 10 ⁻⁴ g/dpm
Kitami (Kt)	817	1.54 (1.88)	4.05 (4.96)	1.28 (1.57)	6.51 (7.97)	6.12 (7.49)	1.40 (1.71)	1.34 (1.64)	13.1 (16.0)	0.98	4.67	1.02
Hakodate (Hk)	966	3.40 (3.52)	7.45 (7.71)	1.33 (1.38)	5.89 (6.10)	5.03 (5.21)	1.83 (1.89)	1.70 (1.76)	15.5 (16.0)	0.86	3.25	1.10
Akita (Ak)	1512	10.93 (7.23)	22.60 (14.95)	2.98 (1.97)	7.39 (4.89)	4.64 (3.07)	2.76 (1.83)	2.34 (1.55)	21.8 (14.4)	1.37	2.13	1.07
Sendai (Sn)	988	1.01 (1.02)	2.23 (2.26)	0.41 (0.41)	4.28 (4.33)	4.03 (4.08)	3.54 (3.58)	3.50 (3.54)	11.8 (11.9)	0.35	3.42	2.97
Tokyo (Tk)	1604	0.81 (0.50)	2.86 (1.78)	1.40 (0.87)	4.77 (2.97)	4.57 (2.85)	1.26 (0.79)	1.23 (0.77)	13.4 (8.4)	1.04	3.41	0.92
Kanazawa (Kn)	2318	10.76 (4.64)	20.43 (8.81)	1.06 (0.46)	12.69 (5.47)	9.98 (4.31)	2.87 (1.24)	2.48 (1.07)	22.8 (9.8)	0.46	4.38	1.09
Hachijojima (Hc)	2792	10.66 (3.82)	20.56 (7.36)	1.37 (0.49)	6.08 (2.18)	3.40 (1.22)	1.73 (0.62)	1.32 (0.47)	19.7 (7.1)	0.70	1.73	0.67
Chichijima (Cc)	1330	5.54 (4.17)	11.85 (8.91)	1.88 (1.41)	4.43 (3.33)	3.04 (2.29)	1.68 (1.26)	1.47 (1.11)	10.0 (7.5)	1.88	3.04	1.47
Misasa (Ms)	1728	4.12 (2.38)	10.73 (6.21)	3.31 (1.92)	6.98 (4.04)	5.94 (3.44)	3.55 (2.05)	3.39 (1.96)	15.9 (9.2)	2.08	3.74	2.13
Tanabe (Tn)	1443	3.66 (2.54)	7.72 (5.35)	1.13 (0.78)	4.01 (2.78)	3.09 (2.14)	1.64 (1.14)	1.50 (1.04)	12.2 (8.5)	0.93	2.53	1.23
Nagasaki (Ng)	1742	3.63 (2.08)	6.88 (3.95)	0.34 (0.20)	6.80 (3.90)	5.89 (3.38)	1.43 (0.82)	1.29 (0.74)	21.6 (12.4)	0.16	2.73	0.60
Naha (Nh)	1743	13.95 (8.00)	27.00 (15.49)	1.89 (1.08)	7.83 (4.49)	4.32 (2.48)	4.38 (2.51)	3.84 (2.20)	15.8 (9.1)	1.20	2.73	2.43
Total mean	1582	5.83 (3.69)	12.07 (7.63)	1.57 (0.99)	6.58 (4.16)	5.11 (3.23)	2.34 (1.48)	2.12 (1.34)	16.1 (10.2)	0.98	3.17	1.32

* The concentrations are shown in parentheses.

** The symbol, Δ , denotes the excess amount subtracting the sea salt component.

appears to be a function of sea surface roughness where sea salt particles are produced. The roughness is a function of wind velocity integrated with time (Toba and Chaen, 1973). The largest deposition rates have been observed in the coastal region facing the Sea of Japan in winter. A strong north or west winter monsoon produces many sea salt particles at the sea surface and carries these particles to the coastal region near the Sea of Japan, where they are removed from the atmosphere by snowfall (Akita and Kanazawa in Fig. 1). On the other hand in the region near the Pacific Ocean (e.g., Tokyo and Sendai in Fig. 1) sea salt particles are transported largely by typhoons in summer or autumn (Tsunogai and Shinagawa, 1977), although there were no strong typhoons in this region during this observation period. On

isolated small islands (e.g., Okinawa), a large deposition rate of sea salt particles is always observed. The rather small deposition rate of sodium at Chichijima may be due to the geographical configuration of the sampling station which is surrounded by mountains 50 to 300m high.

Deposition rate of anthropogenic sulfate

The deposition rates of sulfate were comparable to those of sodium in the coastal area, but in the inland area or in the Pacific side area, they exceeded those of sodium (Table 2). This difference appears to be caused by the addition of a large amount of sea salt particles to precipitation over the coastal area.

The measured deposition rates of excess sulfate (3–10g/m²/y) show a rather small

Fig. 1. Monthly averaged deposition rates of sodium in $\text{mg/m}^2/\text{day}$ at Kanazawa, Akita, Tokyo and Sendai.

Fig. 2. Monthly averaged deposition rates of excess sulfate in $\text{mg/m}^2/\text{day}$ at Kanazawa, Akita, Tokyo and Sendai.

geographical variation in the western North Pacific area as compared to those of the above mentioned sea salt components (Table 2). Among these, larger deposition rates were found at the stations in northern Japan especially in winter (Fig. 2). We observed no marked seasonal variation in the deposition rates of excess sulfate at stations located on the Pacific side.

These results suggest that a part of the excess sulfate may come from local air pollution, chiefly from house heating in winter, but the major part may come from global air pollution, namely from anthropogenic sulfur compounds transported for a long distance through the atmosphere. The global transport of sulfate will be discussed later.

Deposition rate of Pb-210

The geographical variation of yearly deposition rates for Pb-210 (1.00 - 2.28 dpm/cm²/y) is the smallest among those of the chemical

constituents studied here. The monthly deposition rates were high in winter at stations along the coast of the Sea of Japan, whereas they were rather high in summer at stations located on the Pacific side (Fig. 3). This tendency is qualitatively similar to that for monthly rainfall amounts, but the concentration of Pb-210 (the ratio of deposition rate of Pb-210 to the amount of rainfall) is considerably lower in summer. The higher concentration of Pb-210 in winter precipitation may be largely due to the seasonal change in its concentration in air masses, because winter westerlies from the Asian continent usually contain more Pb-210. The seasonal change is more clearly seen in ratios of the deposition rate of Pb-210 in winter rather than in summer. Table 3 shows a marked contrast in the Pb-210 ratios. These ratios are much larger for stations facing the Sea of Japan.

The Rn-222 flux from the continent to the atmosphere has been estimated to be 0.7 atoms/

Table 3. Ratios of the deposition rates or concentrations* of various components in precipitation in winter (December to March) to those in summer (June to September)**

	Rainfall	Na	Cl	Δ Cl	SO ₄	Δ SO ₄ winter/summer	Ca	Δ Ca	Pb-210
Kanazawa (Kn)	1.46	28 (19)	26 (18)	15 (10)	4.3 (2.9)	3.4 (2.3)	14 (9.6)	13 (9.0)	2.6 (1.77)
Nagasaki (Ng)	0.57	2.1 (3.7)	2.0 (3.6)	1.00 (1.75)	1.20 (2.1)	1.09 (1.91)	2.2 (3.9)	2.2 (3.9)	1.92 (3.4)
Hakodate (Hk)	1.06	1.20 (1.13)	1.30 (1.23)	1.85 (1.75)	2.0 (1.89)	2.2 (2.1)	2.7 (2.6)	3.0 (2.8)	1.68 (1.59)
Akita (Ak)	0.50	5.0 (10)	4.9 (9.8)	4.1 (8.2)	6.0 (12)	6.6 (13)	4.1 (8.2)	4.0 (8.0)	1.41 (2.8)
Naha (Nh)	0.74	1.26 (1.70)	1.26 (1.69)	1.15 (1.55)	1.06 (1.43)	0.87 (1.17)	0.91 (1.23)	0.86 (1.16)	1.00 (1.35)
Hachijojima (Hc)	0.65	1.82 (2.8)	1.82 (2.8)	1.82 (2.8)	1.91 (2.9)	1.97 (3.0)	1.62 (2.5)	1.54 (2.4)	1.00 (1.54)
Misasa (Ms)	0.68	7.6 (11)	9.6 (14)	17 (25)	1.95 (2.9)	1.65 (2.4)	2.1 (3.1)	2.0 (3.0)	0.95 (1.40)
Chichijima (Cc)	0.65	1.30 (1.99)	1.13 (1.73)	0.43 (0.66)	0.67 (1.03)	0.45 (0.69)	1.04 (1.59)	1.00 (1.54)	0.91 (1.39)
Tanabe (Tn)	0.48	1.51 (3.2)	1.93 (4.0)	3.6 (7.6)	0.68 (1.41)	0.51 (1.07)	1.44 (3.0)	1.42 (3.0)	0.85 (1.77)
Kitami (Kt)	0.47	0.98 (2.1)	0.81 (1.71)	0.55 (1.16)	3.0 (6.4)	3.3 (6.9)	1.28 (2.7)	1.30 (2.8)	0.72 (1.52)
Sendai (Sn)	0.40	0.94 (2.4)	0.84 (2.1)	0.50 (1.25)	0.76 (1.90)	0.75 (1.87)	1.36 (3.4)	1.37 (3.4)	0.64 (1.60)
Tokyo (Tk)	0.32	0.60 (1.86)	0.60 (1.86)	0.60 (1.85)	0.97 (3.0)	0.99 (3.1)	1.64 (5.1)	1.66 (5.2)	0.62 (1.94)

* Those for concentrations are shown in parentheses.

** The stations are arranged in order of the ratios for the deposition rates of Pb-210.

Fig. 3. Monthly averaged deposition rates of Pb-210 in $\text{dpm/m}^2/\text{day}$ at Kanazawa, Nagasaki, Tokyo and Sendai.

Fig. 4. Monthly averaged deposition rates of excess calcium at Kanazawa, Akita, Tokyo and Hachiojima.

Fig. 5a

Fig. 5. Annual deposition rates of Pb-210 normalized to 1,000mm of rainfall. The geographical distribution is shown in Fig. 5a in the unit of $\text{dpm}/\text{cm}^2/\text{y}$. Figure 5b shows the relation between the deposition rates and the distance from the coastal line of the Asian Continent, where the solid curve is the calculated one in the text.

Fig. 5b

above, the deposition rates of Pb-210 depend to some extent on the rainfall amounts. We therefore have normalized the deposition rates to the annual rainfall amounts of 1,000mm, which is approximately equal to the average annual rainfall in the oceanic area (Sverdrup *et al.*, 1942). The normalization is carried out as follows.

If we can assume a simple first order removal of an atmospheric constituent with respect to the amount of rainfall, we get

$$dC/dp = -\beta C \quad (10)$$

where C is the amount of an atmospheric constituent in the air column, p is the rainfall amount and β is a constant. By integrating the equation (10), we obtain

$$C = C_0 \exp(-\beta p) \quad (11)$$

The amount removed from the air column by the rainfall (R) is given by

$$\begin{aligned} R &= \int_0^p C dp = \int_0^p C_0 \exp(-\beta p) dp \\ &= \alpha [1 - \exp(-\beta p)] \end{aligned} \quad (12)$$

where α is a constant and R is equal to the deposition rate. Although this equation is for a single instance of precipitation, we assume that this general form is also applicable to the annual average rainfall which is an assemblage of this precipitation.

To determine α and β in equation (12), we further assume that the normalized deposition rate in Kanazawa, where precipitation is higher, is equal to the average of the normalized rates at Kitami and Sendai, where the precipitation is less. This assumption is based on the fact that the distance from the coast line of the Asian Continent to Kanazawa (750 - 800km) lies between those of Kitami (550 - 600km) and Sendai (850 - 900km). Hence, we get

$$\alpha = 3.2 \quad \text{in } \text{dpm}/\text{cm}^2/\text{y}$$

$$\beta = 0.55 \quad \text{in } \text{m}^{-1}$$

The normalization equation is then given by

$$R_{lm} = 0.43 R_{obs} / [1 - \exp(-0.55p)] \quad (13)$$

where R_{lm} and R_{obs} are the deposition rate of Pb-210 at a rainfall amount of 1m (= 1,000mm) and the observed rate at the rainfall of p (m),

respectively.

In Fig. 5, we also plot the deposition rate of Pb-210 at Hawaii, which is a modified rate of Turekian *et al.* (1977) with a residence time for aerosols of 12 days. The flux observed at Assabu by Fukuda and Tsunogai (1974) is also shown. These observed values seem to be well fitted with the calculated curve.

Although the above result is not a direct demonstration of the longer residence time (12 days) for aerosols bearing Pb-210, the longer residence time is also possible when the two-layer model is used. In other words, calculated results suggest that the decrease in the deposition rate of Pb-210 with the distance from the coast line of the Continent is not only due to residence time (removal rate) but also due to the replacement of land air masses with masses of maritime origin in the lower atmosphere. Turekian *et al.* (1977) have ignored this latter effect.

In Fig. 6 ratios of excess sulfate/Pb-210 are plotted. If the behavior of excess sulfate in the atmosphere is similar to that of Pb-210, the ratio will be nearly constant. The geographical or temporal variation in the excess sulfate/Pb-210 ratios is smaller than those for the ratios of other chemical constituents to Pb-210 such as excess calcium/Pb-210, sodium/Pb-210 and excess chloride/Pb-210 (Table 2). The excess

sulfate/Pb-210 ratios (170 - 470 $\mu\text{g/dpm}$), however, are too scattered to deduce the relation between excess SO_4 and Pb-210 from our data.

It is interesting to compare our results with those observed by the SEAREX program (Turekian and Cochran, 1981; Prospero *et al.*, 1982) where the excess sulfate/Pb-210 ratio is around 50 $\mu\text{g/dpm}$ for aerosols over the Pacific. It therefore can be said that the excess sulfate/Pb-210 decreases with distance from the coast line and with time. This means that the residence time of excess sulfate is less than that of Pb-210. This is in agreement with the conclusion of Tsunogai (1971), where the residence time of sulfate is about half that of Pb-210.

Fig. 6. The relation between the ratio of excess sulfate to Pb-210 in 10^{-4}g/dpm and the distance from the coastal line of the Asian Continent.

Appendix. Monthly deposition rates of precipitation and chemical constituents

	H ₂ O (mm)	Na (g/m ²)	Cl (g/m ²)	SO ₄ (g/m ²)	Ca (g/m ²)	Pb-210 (10 ³ dpm/m ²)
Kitami						
Jan.	31	0.05	0.10	0.41	0.16	0.66
Feb.	39	0.10	0.19	0.76	0.08	1.02
Mar.	46	0.05	0.11	0.79	0.10	1.61
Apr.	38	0.17	0.36	0.52	0.15	0.65
May	92	0.11	0.34	0.25	0.19	1.14
June	113	0.28	0.81	0.41	0.10	1.45
July	83	0.06	0.22	0.23	0.13	2.34
Aug.	75	0.07	0.26	0.22	0.08	1.08
Sept.	91	0.07	0.17	0.30	0.08	0.88
Oct.	84	0.16	0.31	0.47	0.09	0.62
Nov.	70	0.15	0.40	0.60	0.08	0.81
Dec.	55	0.27	0.78	1.55	0.16	0.84
Total	817	1.54	4.05	6.51	1.40	13.1

To be cont'd.

cm²/s (Israel, 1951) or 1.2 atoms/cm²/s, excluding Europe where the emanation rate is assumed to be 70% of the continental rate (Turekian *et al.*, 1977). The latter Rn-222 emanation rate results in a deposition rate for Pb-210 of 0.85 dpm/cm²/y on an average for the whole northern hemisphere or 1.1 dpm/cm²/y for the latitudinal belt between 30°N and 60°N. Therefore, yearly deposition rates observed in the western North Pacific area are 1.0–2.0 times larger than the average emanation rate of Rn-222 from land to the atmosphere. This difference may be attributed to the following two causes. One is the amount of rainfall in this region where the average annual rainfall is about 1,600 mm. The other is the geographical location of the sampling stations for the global scale. According to Turekian *et al.* (1977) the atmospheric concentration of Rn-222 or Pb-210 is the highest at the east end of the Asian continent.

Deposition rate of calcium

Excess calcium is probably a component of soil dust (Tsunogai *et al.*, 1972). Therefore, local contamination is apparently unavoidable at sampling stations on land although care was taken to avoid contamination as much as possible.

Higher deposition rates of excess calcium were observed in winter or early spring at stations along the coast of the Sea of Japan where the surface was mostly covered with snow (Kanazawa and Akita in Fig. 4) and at the station on a small island, Hachijojima (Fig. 4). A considerable part of this excess calcium may come from the Asian continent as discussed by Duce *et al.* (1980).

On the other hand the larger values observed at Sendai on the Pacific coast and at Okinawa on a small coral island may be due to local contamination with soil dust, although there is no evidence demonstrating the origin.

Global transport of chemical constituents

Turekian *et al.* (1977) have proposed a global one-dimensional one layer model for the

transport of Rn-222 and its long-lived daughters. In this model, westerlies and removal of aerosols are considered along with the radioactive decay of Rn-222 and its daughters in the atmosphere as follows.

$$\frac{\partial N}{\partial t} = -U \frac{\partial N}{\partial X} + \lambda_P N_P - (\lambda + k)N \quad (2)$$

where N is the amount of a radon daughter nuclide in the air column, t is time, X is distance to the east, U is the average wind velocity, λ is the decay constant and k is the removal rate constant of aerosols equivalent to the reciprocal of the residence time. The suffix, p , refers to its parent nuclide. For Rn-222, the second term on the right is equal to the emanation rate and k is zero.

Turekian *et al.* (1977) have found that the calculated deposition rates (kN) of Pb-210 show a good agreement with the observed rates they compiled when there is a transit time across the North Pacific (9,000 km) of 12 days and the average aerosol residence time is 5 days. This shorter residence time is strong support for a residence time obtained from the Bi-210/Pb-210 ratio in Colorado precipitation, the inland area, by Poet *et al.* (1972), Gavini *et al.* (1974), however, have obtained a different result.

On the other hand Tsunogai and Fukuda (1974) have found that the average residence time obtained from the same Bi-210/Pb-210 ratios is 10–14 days in Hakodate where the climate is rather oceanic. We shall see that the observed deposition rates of Pb-210 can be explained by the longer aerosol residence time if we use a one dimensional two-layer model.

As discussed above, the deposition rates of Pb-210 largely depend on the concentration of Pb-210 in the lower air masses which seasonally or even daily alternate in the monsoon area. When the westerlies blow from the Asian continent, the Pb-210 content of the air is high. Whereas, east or south winds bring air masses containing less Pb-210 from the ocean. When we consider an average value obtained over a long period of observation, the alternation of air

masses is included in the above equation by adding a term for eddy diffusion as follows:

$$\frac{\partial N}{\partial t} = D \left(\frac{\partial^2 N}{\partial^2 X} \right) - U \left(\frac{\partial N}{\partial X} \right) + \lambda_p N_p - (\lambda + k) N \quad (3)$$

where D is the horizontal eddy diffusivity. However, these constants vary widely with altitude, because westerlies are prevailing in the upper layer. We have, therefore, divided the atmosphere into two layers to express this effect simply. For the lower layer:

$$\frac{\partial N_l}{\partial t} = D \left(\frac{\partial^2 N_l}{\partial^2 X} \right) + \lambda_p N_{pl} - (\lambda + k_l) N_l \quad (4)$$

For the upper layer:

$$\frac{\partial N_u}{\partial t} = -U \left(\frac{\partial N_u}{\partial X} \right) + \lambda_p N_{pu} - (\lambda + k_u) N_u \quad (5)$$

where the subscripts l and u refer to, respectively, the lower and upper layers. We regard the 500mb surface as the boundary. In steady state we obtain the following solutions;

$$A_l = A_{ol} \exp \left\{ -[(\lambda + k_l)/D]^{1/2} X \right\} - [\lambda P_{ol}/(\lambda + k_l - \lambda_p)] \exp \left\{ -[(\lambda + k_l)/D]^{1/2} X \right\} + [\lambda P_{ol}/(\lambda + k_l - \lambda_p)] \exp[-(\lambda_p/D)^{1/2} X] \quad (6)$$

and

$$A_u = A_{ou} \exp[-(\lambda + k_u)X/U] - [\lambda P_{ou}/(\lambda + k_u - \lambda_p)] \exp[-(\lambda + k_u)X/U] + [\lambda P_{ou}/(\lambda + k_u - \lambda_p)] \exp(-\lambda_p X/U) \quad (7)$$

where A and P are the radioactivities of Pb-210 and Rn-222, respectively, the subscript, o , refers to the value at the coast.

We assume the following values for the constants in the above equations:

$$D = 5 \times 10^9 \text{ cm}^2/\text{s}$$

$$T_l = 1/k_l = 12 \text{ d}$$

$$U = 9,000 \text{ km}/12 \text{ d} = 9 \text{ m/s}$$

$$T_u = 1/k_u = 50 \text{ d}$$

These assumptions, as well as those of Turekian *et al.* (1977), are not well founded. The horizontal eddy diffusivity has been deduced from the vertical diffusivity estimated by Jacobi and André (1963) and the ratio of the horizontal diffusivity to the vertical diffusivity in the free atmosphere, and by considering the concentration ratio of Rn-222 in the maritime air mass to that in the continental air mass (Junge, 1963). The speed of the westerlies, U , is the same as that of Turekian *et al.* (1977). The residence time of aerosol in the upper atmosphere (T_u) is deduced from those obtained by the cosmic ray produced nuclides and fission products (Katsuragi, 1976) and that of the upper atmospheric component obtained by Gavini *et al.* (1974).

At the eastern end of the Asian Continent we have assumed that the total amount of Rn-222 in the air column is 70 dpm/cm² which is in equilibrium with the exhalation rate of Rn-222 of 1.2 atoms/cm²/s, and that the partial amounts of Rn-222 are 55 dpm/cm² and 15 dpm/cm² for those in the lower and upper atmosphere, respectively. This is based on results obtained by Jacobi and André (1963). The following equations are obtained by introducing these constants into equations (6) and (7) above.

$$R_l = k_l N_l = 3.28 \exp(-1.4 \times 10^{-8} X) - 1.50 \exp(-2.1 \times 10^{-8} X) \quad (8)$$

$$R_u = k_u N_u = 0.54 \exp(-2.7 \times 10^{-10} X) - 0.06 \exp(-2.4 \times 10^{-9} X) \quad (9)$$

where the units of the deposition rate, R , and the distance from the Asian coast, X , are dpm/cm²/y and cm, respectively.

The calculated deposition rates ($R_{\text{calc}} = R_l + R_u$) are plotted in Fig. 5. In the figure we have plotted the observed deposition rates which are corrected for rainfall amounts. As shown

	H ₂ O (mm)	Na (g/m ²)	Cl (g/m ²)	SO ₄ (g/m ²)	Ca (g/m ²)	Pb-210 (10 ³ dpm/m ²)
Hakodate						
Jan.	94	0.23	0.59	0.56	0.18	2.17
Feb.	54	0.29	0.59	0.56	0.20	1.57
Mar.	61	0.27	0.50	0.51	0.21	1.52
Apr.	85	0.27	0.63	0.49	0.17	0.93
May	52	0.23	0.50	0.30	0.11	0.90
June	75	0.25	0.59	0.43	0.10	0.99
July	81	0.36	0.75	0.32	0.07	1.13
Aug.	69	0.28	0.56	0.24	0.07	1.02
Sept.	75	0.16	0.33	0.25	0.07	1.02
Oct.	135	0.25	0.48	0.47	0.12	1.40
Nov.	76	0.34	0.71	0.91	0.27	1.14
Dec.	109	0.47	1.22	0.85	0.26	1.74
Total	966	3.40	7.45	5.89	1.83	15.5
Akita						
Jan.	93	1.94	4.18	0.94	0.99	2.05
Feb.	59	1.29	2.69	1.69	0.30	1.32
Mar.	82	0.74	1.55	0.87	0.21	2.70
Apr.	101	0.41	0.89	0.69	0.20	2.97
May	143	0.37	0.84	0.53	0.25	1.83
June	192	0.40	0.83	0.14	0.08	2.10
July	131	0.28	0.60	0.12	0.10	1.18
Aug.	160	0.33	0.74	0.22	0.11	1.33
Sept.	156	0.20	0.43	0.23	0.13	1.23
Oct.	80	1.97	3.78	0.74	0.09	1.40
Nov.	232	0.89	1.84	0.48	0.10	1.56
Dec.	83	2.11	4.24	0.74	0.20	2.14
Total	1512	10.93	22.60	7.39	2.76	21.8
Sendai						
Jan.	26	0.07	0.16	0.19	0.24	0.62
Feb.	22	0.10	0.19	0.36	0.37	0.81
Mar.	83	0.10	0.20	0.49	0.58	1.02
Apr.	101	0.06	0.12	0.39	0.52	1.14
May	117	0.05	0.13	0.28	0.33	1.67
June	142	0.07	0.20	0.34	0.30	1.68
July	72	0.08	0.19	0.53	0.30	1.43
Aug.	99	0.10	0.21	0.47	0.25	0.99
Sept.	112	0.11	0.23	0.33	0.17	0.60
Oct.	104	0.12	0.26	0.42	0.14	0.65
Nov.	71	0.08	0.19	0.25	0.14	0.63
Dec.	39	0.07	0.15	0.23	0.20	0.56
Total	988	1.01	2.23	4.28	3.54	11.8
Tokyo						
Jan.	55	0.05	0.18	0.47	0.19	0.68
Feb.	33	0.05	0.13	0.27	0.12	0.76
Mar.	123	0.07	0.18	0.46	0.14	1.02
Apr.	126	0.08	0.25	0.35	0.13	1.26
May	125	0.07	0.27	0.35	0.12	1.43
June	205	0.05	0.15	0.31	0.09	2.19
July	241	0.03	0.10	0.45	0.08	1.61
Aug.	171	0.11	0.37	0.43	0.07	0.84
Sept.	253	0.16	0.53	0.54	0.09	0.99
Oct.	133	0.06	0.27	0.36	0.07	0.90
Nov.	70	0.04	0.23	0.31	0.07	0.63
Dec.	69	0.04	0.20	0.47	0.09	1.05
Total	1604	0.81	2.86	4.77	1.26	13.4

To be cont'd.

	H ₂ O (mm)	Na (g/m ²)	Cl (g/m ²)	SO ₄ (g/m ²)	Ca (g/m ²)	Pb-210 (10 ³ dpm/m ²)
Kanazawa						
Jan.	276	2.44	4.53	2.28	0.76	1.67
Feb.	189	1.86	3.60	1.56	0.38	1.79
Mar.	156	0.94	1.90	1.66	0.75	2.08
Apr.	121	0.68	1.42	0.91	0.29	2.01
May	124	0.19	0.37	0.53	0.10	1.09
June	155	0.05	0.09	0.53	0.05	1.32
July	92	0.02	0.04	0.24	0.02	0.93
Aug.	214	0.10	0.21	0.50	0.04	0.99
Sept.	192	0.09	0.18	0.53	0.04	0.69
Oct.	159	0.82	1.48	0.62	0.09	1.33
Nov.	307	1.57	2.88	1.13	0.13	4.26
Dec.	333	2.00	3.73	2.20	0.22	4.62
Total	2318	10.76	20.43	12.69	2.87	22.8
Hachijojima						
Jan.	204	1.31	2.51	0.72	0.14	2.05
Feb.	170	0.95	1.84	0.61	0.12	1.88
Mar.	186	0.95	1.91	0.66	0.20	1.49
Apr.	236	0.93	1.99	0.53	0.32	1.53
May	269	0.87	1.74	0.66	0.16	1.21
June	284	0.65	1.29	0.31	0.06	2.19
July	268	0.79	1.55	0.23	0.07	1.92
Aug.	237	0.54	1.01	0.29	0.10	1.27
Sept.	285	0.46	0.87	0.50	0.14	1.65
Oct.	326	0.91	1.63	0.53	0.15	1.61
Nov.	188	1.07	1.89	0.49	0.13	1.32
Dec.	139	1.23	2.33	0.55	0.14	1.61
Total	2792	10.66	20.56	6.08	1.73	19.7
Chichijima						
Jan.	67	0.64	1.23	0.27	0.17	0.60
Feb.	71	0.58	1.09	0.24	0.07	0.71
Mar.	54	0.60	1.24	0.24	0.18	0.99
Apr.	107	0.38	0.74	0.30	0.17	1.03
May	169	0.43	0.91	0.30	0.15	1.22
June	158	0.43	1.10	0.52	0.15	0.83
July	80	0.70	1.64	0.49	0.11	1.12
Aug.	138	0.37	0.72	0.38	0.15	0.85
Sept.	82	0.26	0.50	0.34	0.13	0.58
Oct.	148	0.23	0.54	0.35	0.12	0.64
Nov.	149	0.45	0.24	0.59	0.14	0.63
Dec.	107	0.47	0.90	0.41	0.14	0.77
Total	1330	5.54	11.85	4.43	1.68	10.0
Misasa						
Jan.	153	0.73	2.27	0.80	0.37	1.70
Feb.	128	0.58	1.75	0.75	0.38	1.56
Mar.	125	0.34	0.83	0.73	0.44	0.81
Apr.	110	0.16	0.31	0.67	0.51	0.85
May	61	0.07	0.17	0.45	0.38	0.72
June	93	0.05	0.15	0.29	0.17	1.53
July	165	0.05	0.14	0.29	0.13	2.04
Aug.	231	0.10	0.21	0.45	0.16	1.63
Sept.	245	0.11	0.22	0.50	0.21	0.98
Oct.	170	0.40	0.78	0.57	0.31	0.90
Nov.	156	0.82	1.83	0.58	0.26	1.39
Dec.	91	0.71	2.07	0.70	0.23	1.79
Total	1728	4.12	10.73	6.98	3.55	15.9

To be cont'd.

	H ₂ O (mm)	Na (g/m ²)	Cl (g/m ²)	SO ₄ (g/m ²)	Ca (g/m ²)	Pb-210 (10 ³ dpm/m ²)
Tanabe						
Jan.	60	0.44	0.88	0.23	0.20	0.92
Feb.	57	0.16	0.32	0.24	0.12	1.12
Mar.	91	0.42	1.07	0.21	0.22	1.17
Apr.	140	0.49	1.08	0.37	0.26	0.68
May	225	0.58	1.07	0.28	0.09	1.10
June	258	0.36	0.65	0.51	0.19	1.24
July	148	0.23	0.45	0.34	0.17	1.37
Aug.	77	0.20	0.43	0.23	0.07	1.09
Sept.	113	0.11	0.22	0.28	0.03	0.98
Oct.	70	0.18	0.52	0.57	0.08	0.66
Nov.	126	0.15	0.34	0.51	0.08	1.07
Dec.	78	0.34	0.69	0.24	0.15	0.76
Total	1443	3.66	7.72	4.01	1.64	12.2
Nagasaki						
Jan.	95	0.58	1.09	0.89	0.13	2.17
Feb.	96	0.55	1.02	0.53	0.26	2.69
Mar.	144	0.29	0.53	0.54	0.19	3.07
Apr.	198	0.27	0.54	0.58	0.12	2.22
May	209	0.14	0.26	0.72	0.06	2.05
June	242	0.11	0.21	0.53	0.07	1.29
July	246	0.14	0.28	0.41	0.08	0.96
Aug.	143	0.13	0.26	0.42	0.08	1.18
Sept.	101	0.46	0.87	0.61	0.09	1.47
Oct.	110	0.27	0.52	0.67	0.09	1.43
Nov.	75	0.34	0.64	0.49	0.12	1.62
Dec.	83	0.35	0.66	0.41	0.14	1.46
Total	1742	3.63	6.88	6.80	1.43	21.6
Naha						
Jan.	131	2.05	3.94	0.77	0.30	0.93
Feb.	104	1.98	3.77	0.61	0.20	1.18
Mar.	169	0.96	1.88	0.67	0.38	2.20
Apr.	166	0.28	0.59	0.52	0.45	1.92
May	109	0.82	1.53	0.59	0.42	2.26
June	138	1.02	2.00	0.52	0.28	1.89
July	135	1.42	2.72	0.61	0.34	1.49
Aug.	255	1.77	3.40	0.80	0.40	0.84
Sept.	145	0.95	1.83	0.74	0.39	0.78
Oct.	173	0.52	1.16	0.65	0.40	0.87
Nov.	125	0.60	1.19	0.58	0.42	0.75
Dec.	95	1.53	2.91	0.78	0.41	0.71
Total	1743	13.95	27.00	7.83	4.38	15.8

Acknowledgements—We are extremely grateful to the following persons for collecting the samples: Prof. M. Sasaki at Kitami; Prof. M. Shiikawa at Akita; Prof. S. Nishizawa, Drs. A. Taniguchi and K. Iseki at Sendai; Dr. N. Ogura at Tokyo; Mr. K. Ishida at Hachijojima; Messrs. T. Komatsu, T. Mori and N. Savory at Chichijima; Prof. K. Terada at Kanazawa; Prof. O. Matsubaya, Drs. Y. Tsutaki and M. Tsutsumi at Misasa; Dr. M. Suzuki at Tanabe; Mr. H. Hamada at Nagasaki; Prof. K. Kaneshima and Dr. T. Ohmori at Naha. We also wish to thank Prof. emeritus M. Nishimura and the colleagues in our laboratory for their valuable suggestions and encouragement throughout this work.

REFERENCES

- Duce, R. A., Unni, C. K., Ray, B. J., Prospero, J. M. and Merrill, J. T. (1980) Long-range atmospheric transport of soil dust from Asia to the tropical North Pacific: Temporal variability. *Science* **209**, 1522–1524.
- Fukuda, K. and Tsunogai, S. (1975) Pb-210 in precipitation in Japan and its implication for the transport of continental aerosols across the ocean. *Tellus* **27**, 514–521.
- Gavini, M. B., Beck, J. N. and Kuroda, P. K. (1974) Mean residence times of the long-lived radon daughters in the atmosphere. *J. Geophys. Res.* **79**, 4447–4452.

- Israel, H. (1951) Radioactivity of the atmosphere. *Compendium of Meteorology* 155–161. Edited by Malone, T. F. Am. Meteorol. Soc.: Boston.
- Iwasaki, I., Utsumi, S., Hagino, K. and Ozawa, T. (1956) A new spectrophotometric method for the determination of small amounts of chloride using the mercuric thiocyanate method. *Bull. Chem. Soc. Jpn.* **29**, 860–864.
- Iwasaki, I., Utsumi, S., Hagino, K., Tarutani, T. and Ozawa, T. (1957) Spectrophotometric method for the determination of small amounts of sulfate ions. *Bull. Chem. Soc. Jpn.* **30**, 847–851.
- Jacobi, W. and André, K. (1963) The vertical distribution of radon 222, radon 220 and their decay products in the atmosphere. *J. Geophys. Res.* **68**, 3799–3814.
- Junge, C. E. (1963) *Air chemistry and radioactivity*. Academic Press: New York. 382p.
- Katsuragi, Y. (1976) Radioactive fallout in Japan. *Tenki* **23**, 333–345.
- Poet, S. E., Moore, H. E. and Martell, E. A. (1972) Lead 210, bismuth 210 and polonium 210 in the atmosphere: accurate ratio measurement and application to aerosol residence time determination. *J. Geophys. Res.* **77**, 6515–6527.
- Prospero, J. M. (ed.) (1978) *The tropospheric transport of pollutants and other substances to the ocean*. National Academy of Sciences: Washington D.C. 243p.
- Prospero, J. M., Savoie, D. L., Nees, R. T., Duce, R. A., Uematsu, M. and Merrill, J. L. (1982) Sulfate and nitrate concentration in aerosol samples collected in the SEAREX Asian Dust Network. *SEAREX Newsletter* **5**, No. 2, 19–21.
- Rodhe, H. (1981) Current problems related to the atmospheric part of the sulphur cycle. *Some perspectives of the major biogeochemical cycles*. 51–60. Edited by Likens, G. E. SCOPE.
- Sverdrup, H. U., Johnson, M. W. and Fleming, R. H. (1942) *The oceans, their physics, chemistry and general biology*. Prentice-Hall: Englewood Cliffs, N. J. 1087p.
- Toba, Y. and Chaen, M. (1973) Quantitative expression of the breaking of wind waves on the sea surface. *Rec. Oceanogr. Works Japan* **12**, 1–11.
- Tsunogai, S. (1971) Oxidation rate of sulfite in water and its bearing on the origin of sulfate in meteoric precipitation. *Geochem. J.* **5**, 57–67.
- Tsunogai, S. (1975) Sea salt particles transported to the land. *Tellus* **27**, 51–58.
- Tsunogai, S. and Fukuda, K. (1974) Pb-210, Bi-210 and Po-210 in meteoric precipitation and the residence time of tropospheric aerosol. *Geochem. J.* **8**, 141–152.
- Tsunogai, S. and Shinagawa, T. (1977) Chemical components transported by the winter-monsoon. *Chikyu Kagaku* **11**, 1–8.
- Tsunogai, S., Saito, O., Yamada, K. and Nakaya, S. (1972) Chemical composition of oceanic aerosol. *J. Geophys. Res.* **77**, 5283–5292.
- Turekian, K. K. and Cochran, J. K. (1981) ^{210}Pb in surface air at Enewetak and the Asian dust flux to the Pacific: Corrigendum. *Nature* (London) **294**, 670.
- Turekian, K. K., Nozaki, Y. and Benninger, L. K. (1977) Geochemistry of atmospheric radon and radon products. *Ann. Rev. Earth Planet. Sci.* **5**, 227–255.