Lead Precipitation Fluxes at Tropical Oceanic Sites Determined From ^{210}Pb Measurements

D. M. Settle and C. C. Patterson

Division of Geological and Planetary Sciences, California Institute of Technology, Pasadena, California 91125

K. K. Turekian and J. K. Cochran

Department of Geology and Geophysics, Yale University, New Haven, Connecticut 06511

Concentrations of lead, ^{210}Pb, and ^{210}Po were measured in rain selected for least influence by local sources of contamination at several tropical and subtropical islands (Enewetak; Pigeon Key, Florida; and American Samoa) and shipboard stations (near Bermuda and Tahiti). Ratios expressed as ng Pb/dpm ^{210}Pb in rain were 250–900 for Pigeon Key (assuming 12% adsorption for ^{210}Pb and no adsorption for lead), depending on whether the air masses containing the analyzed rain came from the Caribbean or from the continent, respectively; about 390 for the northern Sargasso Sea downwind from emissions of industrial lead in North America; 65 for Enewetak, remote from continental emissions of industrial lead in the northern hemisphere; and 14 near Tahiti, a remote location in the southern hemisphere where industrial lead emissions to the atmosphere are much less than in the northern hemisphere. (The American Samoa sample yielded a higher ratio than Tahiti; the reason for this is not clear but may be due to local Pb sources.) The corresponding fluxes of lead to the oceans, based on measured or modeled ^{210}Pb precipitation fluxes, are about 4 ng Pb/cm^{2}y for Tahiti, 10 for Enewetak, and 270 for the Sargasso Sea site, and between 110 to 390 at Pigeon Key.

Introduction

The aim of this study, as part of the SEAREX Program sponsored by the National Science Foundation [*Duce*, 1981], is to determine atmospheric input fluxes of Pb from remote sources to the oceans by combining information concerning the natural input flux of ^{210}Pb to the oceans with measurements of lead and ^{210}Pb in rain. ^{210}Pb can be used as an analog of remote source lead at present because both are ultimately derived from gaseous sources on land. These nuclides differ in this respect from bomb-produced and cosmogenic nuclides precipitating to the earth's surface from the stratosphere and upper troposphere. ^{210}Pb (22 year half-life) is produced by the decay of ^{222}Rn (3.8 day half-life) emanating from the ground (see *Turekian et al.* [1977] for a summary), whereas lead is now derived principally from smelter fumes and leaded gasoline exhausts [*Settle and Patterson*, 1980], although soil dusts, volcano fumes, and sea spray also contribute relatively small natural amounts of lead to the atmosphere (see Ng and *Patterson* [1981] for a summary). In prehistoric times these latter natural sources were the only ones contributing lead to the atmosphere [*Schaule and Patterson*, 1981a, b] and deliverable to the oceans.

Our strategy is to measure lead and ^{210}Pb concentrations in rain and air samples collected at various tropical and subtropical oceanic sites. At some locations a number of rain samples were collected over a period of a few days and at other locations only one rain sample was collected and analyzed. Using the best estimate of the Pb/^{210}Pb ratio in precipitation at each site, we determine the precipitation flux of lead based on an independently determined ^{210}Pb flux at or near each site.

Methods and Results

The sites studied were Pigeon Key, Florida; Enewetak; American Samoa; a shipboard station near Tahiti; and a

shipboard station near Bermuda. Analytical methods for Pb and ^{210}Pb already have been described [*Patterson and Settle*, 1976; *Turekian et al.*, 1973]. In addition to rain samples analyzed and discussed in this paper, samples of air pumped through filters, dry deposition, and seawater were also collected at some of these locations. The results obtained on most of these samples will be presented and discussed elsewhere, although a few of the immediately relevant data will be used in this paper.

Pigeon Key, Florida. Sampling was done at the University of Miami Florida Keys Environmental Field Station at Pigeon Key (24°40'N, 81°9'W) in May 1978. The rain collector was placed on top of a 9-m tower located south of highway U.S. 1, which runs through the Florida Keys. An automatic system monitored meteorological parameters: wind direction and speed, condensation nuclei, and temperature. Rain uncontaminated by the highway or by mainland Florida could be collected when the winds were from the south or east. The rain collector was a shallow funnel custom-made of conventional polyethylene, with a cross-sectional area of 8000 cm^2. A 2-l polyethylene collection bottle was force fitted onto the tip of the funnel and was protected from rain running down the outside of the funnel and bottle by a skirt welded into the underside of the funnel. The collector was wrapped in acid-cleaned polyethylene to protect it from contamination between events and during a collecting event was handled only by persons wearing polyethylene gloves. The collecting funnel was washed with ultra-pure 0.1% HNO$_3$ (a better procedure, not used at Pigeon Key, is then to wash the acid off with ultra-pure water) immediately before a rain sample was collected. After each rain sample had been collected, the funnel was immediately rinsed with 1% HNO$_3$, followed by a rinse with ultra-pure water. Sampling was done in three modes: (1) for rain alone during a specific shower, (2) the funnel was deployed both during and between rains to collect a composite sample of both rain and some dry deposition that could be washed

TABLE 1.   Concentrations of Lead, ^{210}Pb, and ^{210}Po in Pigeon Key Precipitation and Dry Deposition, 1978

Sample Number	Date	Collection Times, EDT	Wind Direction	Collection	Volume Water Collected or Volume Acid Wash, l	ng Pb/kg Solution	dpm ^{210}Pb/kg Solution	dpm ^{210}Po/kg Solution
1	May 18	0845–0850	ESE	5 m rain	2	960	3.5 ± 0.17	0.06 ± 0.20
2	May 18	0850–0915	SSE	25 m rain	1	770	...	...
3	May 18	0915–1300	E	3.5 hour dry deposition followed by 15 m rain	0.5	2900	...	...
4	May 18	1300–1800	ENE	3.0 hour dry deposition, 30 m rain, 1.5 hour dry deposition	2	1100	3.45 ± 0.16	0.10 ± 0.15
5a	May 20–21	2240–0700	NE	8 hour dry deposition followed by 20 m rain	2	5440	4.41 ± 0.18	0.11 ± 0.19
5b	May 20–21	2240–0700	NE	acid wash of sample funnel after collection and transfer of 5a	1	2020	1.26 ± 0.08	0.13 ± 0.20
6	May 21	1140–1645; 1805–2210	NE	acid wash of funnel after 9.2 hour dry deposition only	1	4740	0.16 ± 0.02	0.10 ± 0.03

Concentrations of Pb corrected for dry deposition in samples 1, 4, and 5a were 960, 700, and 4400 ng Pb/kg, respectively. Concentrations of ^{210}Pb corrected for 12% adsorption in samples 1, 4, and 5a were 3.89, 3.83, and 4.90 ^{210}Pb dpm/kg, respectively. ng Pb/dpm ^{210}Pb in samples 1, 4, and 5a were 250, 180, and 900, respectively.

off by the rain, and (3) the funnel was exposed without rain to measure the total dry deposition flux. Five rain samples were collected and analyzed. An acid rinse of the funnel after 9.2 hours of exposure without rain was also analyzed. These data are listed in Table 1.

Oceanic station near Bermuda. A rain sample was collected aboard the R/V *Endeavor* 250 km northwest of Bermuda as part of a SEAREX expedition in July 1979. The same type of collector described above with an area of 2000 cm^2 was used. The funnel, although previously cleaned in a series of acid baths [*Patterson and Settle*, 1976], was rinsed with 0.1% HNO$_3$, followed by an ultra-pure distilled water rinse immediately before the rain was collected. This latter step was introduced because it greatly reduced the collector blank. In a separate experiment with ^{205}Pb tracer in simulated rain using this procedure it was found that a negligible (<5%) amount of lead was adsorbed by the collector.

The ship tracked a squall and then headed into it so that the rain was uncontaminated by ship exhaust while the

collector was hand held into the rain off the bow of the ship. The rain was acidified in the container in which it was collected and analyzed for Pb and ^{210}Pb. These results are shown in Table 2.

Enewetak. A series of rain samples was collected at Enewetak (11°20'N, 162°20'E) for Pb and ^{210}Pb assay during the dry and wet periods of 1979. The collector was located on top of an 18-m tower that had been constructed on a small uninhabited island just north of Enewetak, at the most easterly edge of the atoll. An automated system for monitoring meteorological conditions was available. The winds were from the east 90% of the time and samples were collected only when winds were in a sector which presumably excluded contamination from leaded gasoline exhausts emitted on Enewetak. The rain collector was the same one used at Pigeon Key (8000 cm^2), and the procedure followed was the same as that followed aboard the R/V *Endeavor* near Bermuda. At Enewetak the collector, previously cleaned in a series of acid baths at CIT, was not used for dry deposition so that

TABLE 2.   Lead and ^{210}Pb Concentrations in Rain From Enewetak and American Samoa and Shipboard Samples Taken Near Tahiti and Bermuda

	ng Pb/kg	dpm ^{210}Pb/kg	ng Pb/dpm ^{210}Pb
Near Bermuda (34°N 66°W)			
Shipboard (July 16, 1979)	520	1.34 ± 0.10	390
Enewetak (11°20'N 162°20'E)			
Dry season (May 16, 1979)	110	0.48 ± 0.04	230
Wet season (July 27, 1979)	15	0.18 ± 0.03	83
Wet season (Aug. 2, 1979)	63	0.98 ± 0.06	64
Wet season (Aug. 3, 1979)	6	0.097 ± 0.005	62
Near Tahiti (15°S 150°W)			
Shipboard (Jan. 2, 1980)			
Acidified in collection bottle	9	0.644 ± 0.079	14
Shipped to Yale unacidified; acidified in bottle at Yale	...	0.714 ± 0.029	...
Shipped to Yale unacidified; transferred to another bottle and acidified	...	0.567 ± 0.027	...
American Samoa (14°S 170°W)			
Wet season (Feb. 3, 1981)	7	0.053 ± 0.004	132

No corrections for adsorption have been made for either Pb or ^{210}Pb. The methods of sampling in these experiments differed from the Pigeon Key experiment; see text.

it was rinsed with 0.1% HNO₃, followed by ultra-pure distilled water immediately before taking each rain sample, and was not rinsed with 1% HNO₃ afterward. One sample was collected on May 16, 1979, during the dry season and three were collected in July and August of that year during the wet season. All samples were acidified in the collection bottle to a pH of 1-2. The analytical results for these rains are shown in Table 2.

Equatorial South Pacific. A sample from a tropical South Pacific site was taken aboard a ship north of Tahiti (15°S, 105°W) in January 1980 with the collector used aboard the R/V *Endeavor* (2000 cm²). The sample was acidified in the collection bottle to a pH of 1 at the time of collection. Part of this sample was analyzed for Pb and part for ²¹⁰Pb. Two additional samples from the same rain were collected in another container for ²¹⁰Pb assay. One of these was an unacidified sample returned to Yale and acidified there in the conventional polyethylene bottle in which it had been transported. Another sample of this unacidified rain shipped to Yale was transferred at Yale from its shipping bottle (conventional polyethylene) to another container where it was then acidified. The aim of these experiments was to establish the fractional loss of ²¹⁰Pb from solution by adsorption without prior acidification. The transfer from one bottle to another after sitting in the laboratory for a month without acidification resulted in about a 20% loss of ²¹⁰Pb due to adsorption. The sample acidified in the bottle at the time of collection was smaller than the other two samples and therefore had a large counting uncertainty for the same counting times. Thus while the value of 0.714 dpm/kg obtained on the larger volume sample has a smaller error, both lead and ²¹⁰Pb were measured in the smaller sample. Therefore this sample was used to calculate the ratio. Analytical data for these samples are listed in Table 2.

American Samoa. A rain sample was collected near the NOAA GMCC Station at Cape Matatula, an easternmost promontory on Tutuila Island (170°34'W, 14°16'S), for Pb and ²¹⁰Pb assay during the wet season in 1981. The collector was located on the top of a 14-m tower. The collection procedure was the same as that used at Enewetak. Attempts were made to collect rain from storms that approached the island within a sector ranging from the northeast to the southeast. Analytical results for this rain are given in Table 2.

DISCUSSION

Measurements of ²¹⁰Pb and Pb on the same samples of rain or other precipitation (including dry deposition) allow the determination of the manner in which ²¹⁰Pb and Pb concentrations are coupled in the aerosol. With this knowledge it may then be possible to determine the flux of Pb (or any other chemical species behaving in the same manner) by combining the Pb-²¹⁰Pb relationship with ²¹⁰Pb fluxes measured in a number of ways described by *Turekian et al.* [1977].

Pigeon Key. Dry deposition fluxes of ²¹⁰Pb, ²¹⁰Po, and lead onto the rain collector used in this experiment during May 21, 1978, at Pigeon Key can be calculated from the data for sample 6 in Table 1. These are 0.017 dpm ²¹⁰Pb/h, 0.011 dpm ²¹⁰Po/h, and 510 ng Pb/h onto the collector (area = 8000 cm²). The ²¹⁰Po/²¹⁰Pb activity ratio of 0.6 ± 0.2 is close to equilibrium, which indicates that most of the ²¹⁰Pb in dry

deposition at this location and under these conditions did not originate from the decay of radon in the atmosphere. The deposition flux of lead at Pigeon Key of 1.5 ng/cm² day is about one-fifteenth that observed in urban Los Angeles [*Huntzicker et al.*, 1975]. The Pigeon Key collection site was adjacent to a highway, and the wind was blowing from the highway toward the collector when the flux was measured. The ng Pb/dpm ²¹⁰Pb ratio of 30,000 in the dry deposition sample is a hundred times higher than the ratio measured in rain formed in air masses traveling toward the collection site from the sea (= 274, sample 1, Table 1). The high Pb/²¹⁰Pb ratio is characteristic of urban dusts contaminated with industrial lead, and it indicates that the source of lead is probably the adjacent highway.

The rain samples collected in the funnel are of two kinds (Table 1). Two samples were exposed only during the time when rain actually fell (only one of which was analyzed for both Pb and ²¹⁰Pb), and three samples (only two were analyzed for both Pb and ²¹⁰Pb) were exposed to dry deposition for varying lengths of time (hours) prior to and, in one sample after, the rain collection. We can attempt to correct for the dry deposition contribution to the mixed samples by subtracting out the dry flux estimates for Pb, ²¹⁰Pb, and ²¹⁰Po from Table 1, if indeed these fluxes were constant over time. The correction is trivial for ²¹⁰Pb and ²¹⁰Po but can be quite significant for Pb.

The problem of the role of adsorption of Pb, ²¹⁰Pb, and ²¹⁰Po by the funnel in affecting the concentrations of these nuclides in the collection bottle was addressed by using the collection made on May 20 (samples 5a and 5b) and information obtained on the May 21 dry deposition experiment (sample 6). The funnel had been exposed for 8 hours to dry deposition prior to a 20-min rain. The collected water (sample 5a) and an acid leach of the funnel (sample 5b) were both analyzed. The funnel leach showed significant amounts of Pb, ²¹⁰Pb, and ²¹⁰Po. This indicates incomplete transfer of these nuclides through the funnel.

As the ²¹⁰Pb and ²¹⁰Po dry deposition fluxes were shown to be extremely small, any retention of these two nuclides by the funnel must be ascribed primarily to adsorption from the rain. We can evaluate the adsorption correction for the Pigeon Key sample by using the information from the May 20 (samples 5a and 5b) experiment. Over the 8 h 20 min of exposure a dry total ²¹⁰Pb accumulation of 0.14 dpm was deposited in the collector for the 8 hours when no rain fell, if we use the dry flux from sample 6. The total accumulation over that time was 10.1 dpm so that the dry deposition ²¹⁰Pb is clearly a small fraction of the total ²¹⁰Pb, although much more significant for lead because of the strong local source from the highway. The acid wash indicated that 1.26 dpm ²¹⁰Pb was retained by the collector by adsorption during the transfer process. Therefore, ~12% of the ²¹⁰Pb collected was left behind during the transfer process. The acid-washed sample also shows a ²¹⁰Po/²¹⁰Pb ratio higher than the total sample. This cannot be assigned to the dry fall-out component because of its very small contribution but rather is because ²¹⁰Po is more easily adsorbed than ²¹⁰Pb on surfaces [*Turekian and Nozaki*, 1980].

The dry deposition and adsorption corrected concentrations for wet precipitation can be obtained by the experiments described above. Three rains with variable amounts of dry fallout so corrected (i.e., a dry deposition of 0.017 dpm ²¹⁰Pb/h and an adsorption loss of 12%) yield concentrations

of 3.98, 3.88, and 4.93 dpm ^{210}Pb/kg for the precipitation with an average concentration of 4.26 dpm ^{210}Pb/kg.

A dry deposition flux of 510 ng Pb/hr on the funnel was measured in sample 6 collected on May 21. This complicates the determination of lead concentrations in those rains collected after the funnel had been left uncovered for extended periods in regions such as Pigeon Key that are affected by automobile traffic. Part of such dry deposition lead deposits is washed into the collection bottle by rain. If no lead in rain is adsorbed on the funnel then the entire amount remaining on the funnel can be assigned to dry deposition not washed off by rain. Since about 12% of the ^{210}Pb in rain was observed to collect on the funnel, a similar fraction of lead in rain might also be expected to be adsorbed on the funnel if the chemical speciation of ^{210}Pb and Pb were the same in rain. On the other hand, it has been found that less than 5% of ^{205}Pb tracer in simulated rain was adsorbed by the collecting funnel. This suggests that the chemical speciation of Pb which originates mainly from leaded gasoline exhausts and ^{210}Pb are different in rain if the ^{205}Pb tracer properly represents lead in rain. If most of the Pb remaining on the funnel after being washed by rain is assigned to dry deposition (on the basis of the ^{205}Pb tracer experiment), the fraction of the total dry deposition deposit of lead washed off by rain can be estimated from the May 20 experiment (samples 5a and 5b). In this case the funnel probably collected about 4100 ng Pb by dry deposition during 8 hours of exposure. Two liters of rain were then collected by the funnel during the next 20 min. A separate acid rinse of the funnel (sample 5b) contained 2000 ng Pb, indicating that the rain had washed off about 50% of the dry deposition Pb. The concentration of Pb in the rain (4400 ng Pb/kg in sample 5a) was calculated after subtracting 2000 ng of dry deposition lead. A similar type of correction was made for dry deposition Pb in samples 3 and 4 where the collector was opened to air for about 3 hours in each case before collecting rain.

As the source of dry deposition aerosols is predominantly the local highway, it is not possible to correct unambiguously for the dry deposition flux of Pb during all the sampling periods at this station by using the measured flux over any one period, since wind direction strongly influences that flux. Without a sure value for the dry deposition flux, it is not possible to determine accurately the concentration of Pb in rain in regions impacted by automobile traffic such as this. This was possible, however, for the May 20 samples 5a and 5b because the dry deposition experiment (sample 6) followed soon after, when the wind direction remained the same.

Only the May 18 (sample 1) rain can be used to determine the Pb/^{210}Pb ratio in upper air coming from a seaward direction because it was collected when the wind came from the ESE and the collection interval was so brief the dry deposition collection was negligible. If we assume that no lead was adsorbed from the rain by the funnel and that 12% of the ^{210}Pb was adsorbed, the Pb/^{210}Pb ratio is 250. An estimate of the Pb/^{210}Pb ratio of the May 20 rain, which was from the NE direction, can be made on the basis of the calculations discussed above. The resultant value is 900 ng Pb/dpm ^{210}Pb. As this is air from a NE direction it is obviously from a more lead-rich continental region (probably the Miami area).

The mean annual rainfall at Key West is about 100 cm. If the ^{210}Pb concentration in this rain was the same as the average concentration for all rains in Table 1, the precipitation flux would be 0.41 dpm ^{210}Pb/cm^2 y. This value is uncertain because the ^{210}Pb concentration in rain can vary considerably over time [see Benninger, 1978; L. K. Benninger et al., manuscript in preparation, 1981]. Dry fallout provides an additional 0.02 dpm ^{210}Pb/cm^2 y.

The ratio of ng Pb/dpm ^{210}Pb is strongly dependent on whether the rain is marine or continental in origin, varying from 250 for a rain of marine origin to 900 for a rain of continental origin. Since our data do not characterize the ng Pb/dpm ^{210}Pb ratio in precipitation at Pigeon Key for the entire year, the annual precipitation flux of lead at Pigeon Key using a ^{210}Pb flux of 0.43 probably lies within the range of 110 to 390 ng Pb/cm^2 y, depending on the relative importance of rains originating from marine and continental regions. The measured dry deposition flux of lead at Pigeon Key in one experiment is equivalent to about 560 ng/cm^2 y, which is large, if maintained over a year, compared to the precipitation flux of lead. Onshore winds dominate the wind rose at this location so that the contribution of the dry deposition component to the total eolian input flux of lead to the ocean around Pigeon Key is less than 560 ng/cm^2 y. Experiments at Pigeon Key were not carried out under the presumption that it was a representative site for Atlantic air. Atmospheric lead concentrations and lead dry deposition fluxes at Pigeon Key were observed to be about one tenth of those typical in the urban Los Angeles basin [Huntzicker et al., 1975].

Northwest of Bermuda. The concentration of ^{210}Pb in the sample of rain analyzed in this study is near the lower limit of monthly average concentrations reported by L. K. Benninger et al. (manuscript in preparation, 1981) at the Bermuda Biological Station. The concentration of lead in this rain, as in the Pigeon Key rains, is high compared to that in Pacific rains, which probably reflects the input of industrial lead emissions to the atmosphere from the United States. The ng Pb/dpm ^{210}Pb ratio of 390 yields a precipitation flux of lead of 270 ng Pb/cm^2 y to the eastern North Atlantic, if the annual ^{210}Pb flux of 0.7 dpm/cm^2 y measured at Bermuda by L. K. Benninger et al. (manuscript in preparation, 1981) is used.

Although Pb and ^{210}Pb are both generated as submicron-sized aerosols over land, the proportions of these two lead species are different in air masses that have passed over different continental areas. Therefore, the Pb/^{210}Pb ratio at a given marine location may exhibit seasonal variations. As a consequence, the above value for the precipitation flux of lead to the eastern North Atlantic may be modified when studies are made of additional rains collected at different seasons.

Enewetak. Rains were collected at Enewetak from two climatic regimes, the dry season and the wet season. During the two seasons air masses tend to originate from separate regions having different continental and marine areas, which could alter the relative proportions of lead and ^{210}Pb in the air masses. In the North Pacific, westerlies from Asia contain relatively low concentrations of lead but high concentrations of ^{210}Pb compared to easterlies from North America which contain comparatively higher concentrations of lead and lower concentrations of ^{210}Pb. Dry season silicate dusts in air, which were about 40-fold higher than those in air during the wet season [Duce et al., 1980; Settle and Patterson, 1981], were found to originate from Asia
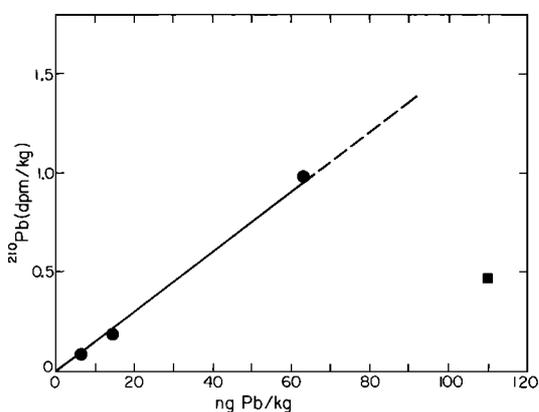
Fig. 1. Relationship between ^{210}Pb and Pb in rain collected at Enewetak. Circles represent samples collected during the wet season in July and August 1979, and they show a slope of 65 ng Pb/dpm ^{210}Pb (assuming no selective adsorption of ^{210}Pb relative to Pb by the funnel). The value of this ratio in air at the site during this period was 82. The square represents a rain sample collected during the dry season in May 1979. We believe that local exhaust emission contamination may be included in this rain, because the ratio in easterly trades air during the dry season in April and May 1979 was much lower, about 79.

[*Duce et al.*, 1980; *Patterson and Settle*, 1981]. It has been observed on the basis of Pb isotopic composition that lead aerosols in the wet season came predominantly from North America [*Patterson and Settle*, 1981]. Air at these two different seasons at Enewetak could contain different proportions of Pb to ^{210}Pb as they do for aluminum relative to ^{210}Pb [*Turekian and Cochran*, 1981].

The three rain samples collected during the wet season regime show a strong linear correlation between Pb and ^{210}Pb concentrations over a large concentration range. The regression line goes through the origin and has a slope of 65 ng Pb/dpm ^{210}Pb (Figure 1). Concentrations of ^{210}Pb in air collected on filters during the wet season averaged about 1.2 dpm/10^3 m^3 [*Turekian and Cochran*, 1981] while concentrations of common Pb in this same air during this period averaged about 100 ng Pb/10^3 m^3 [*Settle and Patterson*, 1981] yielding a ratio of about 82 ng Pb/dpm ^{210}Pb. This agrees well with the ratio of 65 observed in rain collected during this same period. This agreement indicates that precipitation mechanisms for both Pb and ^{210}Pb apparently must be operating in the same manner.

Rain from the dry season regime exhibits a higher Pb/^{210}Pb ratio than in the wet season. Since no other rain samples were collected for simultaneous Pb and ^{210}Pb assay during this season, it is not known whether this ratio is characteristic of that different season or is simply an artifact of local vehicular exhaust contamination. This latter possibility is raised since that particular rain came from air masses whose trajectories were questionable and could have passed over Enewetak before the rain fell. Lead associated with silicate dusts contained in the rain collected during the dry season contributes only 1% of the total lead in that rain, and cannot account for the extra lead in the rain. If anything, we would expect the Pb/^{210}Pb ratio from Asia to be lower than that from North America because of the relative source strengths for Pb and ^{210}Pb. Concentrations of ^{210}Pb in air collected on filters during the dry season averaged about 2.9 dpm ^{210}Pb/10^3 m^3 [*Turekian and Cochran*, 1981] while concentrations of common lead in air during this same period averaged

about 230 ng Pb/10^3 m^3 [*Settle and Patterson*, 1981] yielding a ratio of about 79 ng Pb/dpm ^{210}Pb, which is nearly identical with the ratio observed during the wet season despite a greater than two-fold change in concentrations. This consistency derived from measurements integrated over long periods strongly suggests that the single event rain sample collected during the dry season does not characterize the more general situation.

The annual precipitation flux of ^{210}Pb at Enewetak is 0.15 dpm/cm^2 y [*Turekian and Cochran*, 1981]. The Pb/^{210}Pb ratio in rain which fell during the wet season can be combined with this ^{210}Pb flux to compute a lead precipitation flux at Enewetak of 10 ng Pb/cm^2 y.

When the precipitation flux of lead is computed directly from measured concentrations of lead in three samples of rain collected duirng the wet season, the value for this flux is 3.5 ng Pb/cm^2 y. The three rain events used to obtain this average value showed lead concentrations that varied by an order of magnitude. The 10 ng Pb/cm^2 y value for the lead flux is more significant because it is computed from an observed integrated concentration of ^{210}Pb in rain applicable to an 8-month period and a ng Pb/dpm ^{210}Pb ratio in rain observed to be uniform during the wet season, and similar to air samples collected during both the dry and wet seasons.

It is difficult to measure the remotely derived lead precipitation flux directly. To avoid contamination effects from local lead emissions, the number of meteorologically permissive sampling events must be greatly restricted. Since these restrictions do not apply to ^{210}Pb, it is best to determine the ng Pb/dpm ^{210}Pb ratio in precipitation during meteorologically acceptable events and then apply this ratio to an integrated ^{210}Pb precipitation flux to obtain a net lead precipitation flux free of local contamination effects.

Southern hemisphere near Tahiti. It is of great interest to determine the eolian flux of lead to the oceans in the southern hemisphere because the input of lead to the oceans of the northern hemisphere originates mainly from industrial sources [*Schaule and Patterson*, 1981a, b; *Settle and Patterson*, 1981]. Of the total industrial lead emitted to the earth's atmosphere, about 90% is introduced to the northern hemisphere. Because of this, fluxes of lead to the oceans in the southern hemisphere should be considerably less than those in the northern hemisphere. Data from an oceanic site near Tahiti confirm this expectation.

Turekian et al. [1977] have modeled the ^{210}Pb precipitation flux for the South Pacific as a function of longitude. Two measured fluxes used in setting the parameters of the model were those reported for Fiji (0.48 dpm/cm^2 y) and Raratonga (0.31 dpm/cm^2 y). By coupling the ng Pb/dpm ^{210}Pb ratio of 14 measured in rain near Tahiti (Table 2) with the Raratonga value, we obtain a lead precipitation flux of 3.9 ng Pb/cm^2 y. This flux south of the equator in the Pacific easterlies is about 40% of the precipitation flux of lead north of the equator in the Pacific easterlies, which we determined at Enewetak, and less than 2% of the lead precipitation flux we measured in westerlies of the North Atlantic near Bermuda.

American Samoa. Rain collected on the island of Tutuila, American Samoa, illustrates the problem created by the possible inclusion of locally derived lead. Updrafts created by mountains can inject locally produced industrial lead aerosols into air masses being sampled for rain. The rain collected February 3, 1981, originated from a storm that approached the island from the north. But surface winds at

the collection site however, were from the northwest, characteristic of such a situation. We would expect the $Pb/^{210}Pb$ ratio in this rain to be similar to that found in the rain collected on shipboard near Tahiti. The much larger ratio observed in the Samoa rain may be due to the island contamination effect discussed above. We cannot exclude the possibility that the higher $Pb/^{210}Pb$ ratio observed in rain at Samoa could be a reflection of a remotely derived higher $Pb/^{210}Pb$ ratio in an air mass that had a different origin compared to that from which the Tahiti rain was collected. A number of additional samples of rain have been collected at different seasons at American Samoa, and we hope that data from these samples will help resolve this question.

CONCLUSIONS

The lead precipitation flux is found to be about 4 ng/cm² y in the South Pacific easterlies, 10 ng/cm² y in the North Pacific easterlies, and 270 ng/cm² y in the North American westerlies. This is in accord with effects expected from industrial lead emissions to the atmosphere [*Schaule and Patterson*, 1981a, b; *Settle and Patterson*, 1981]. The lead precipitation flux is best determined from measurements of ^{210}Pb concentrations in rain integrated over a long interval combined with a series of measurements of the $Pb/^{210}Pb$ ratio in rain (or possibly air) during selected meteorologically permissible events that would exclude contamination effects from local lead emissions to the atmosphere.

It should be recognized that in the northern hemisphere at least, dry deposition may be an important component of the total net atmospherically derived flux of lead to the oceans, after correction for recycled lead in sea spray. At Enewetak it has been found to amount to about one third of the total [*Settle and Patterson*, 1981; *Settle et al.*, 1981]. Since the ^{210}Pb flux determined by *Turekian and Cochran* [1981] included both wet and dry fluxes, the lead flux calculated for Enewetak from the $Pb/^{210}Pb$ ratio is larger than the lead precipitation flux alone. In sourthern California, near the coast, it amounts to about 10 times the precipitation flux [*Patterson and Settle*, 1974], while at Pigeon Key it may equal the precipitation flux.

Concentrations of silicate dusts and seasalts have been measured in the rain samples studied in this report [*Settle and Patterson*, 1981; *Unni*, 1978; *Ng et al.*, 1981]. These data indicate in every instance that these two substances cannot provide the major portion of the lead or the ^{210}Pb found in the rains. Additional studies have shown that most of the lead in marine air is associated with particles <0.2 μ diameter [*Duce et al.*, 1976]. These two facts show that both Pb and ^{210}Pb reside in aerodynamically similar types of particles so that it could be expected that they would be transported from land to marine locations and precipitated in similar ways. Since the proportion of Pb to ^{210}Pb can be expected to vary seasonally, the lead precipitation fluxes given in this report are tentative because rain samples collected at representative seasons at the different sites have not yet been studied. Such data are needed to provide more representative values for the precipitation fluxes.

REFERENCES

Benninger, L. K., ^{210}Pb balance in Long Island Sound, *Geochim. Cosmochim. Acta, 42,* 1165–1174, 1978.

Duce, R. A., SEAREX: A multi-institutional investigation of the sea/air exchange of pollutants and natural substances, in *Marine Pollutant Transfer Processes,* edited by M. Waldichuk, G. Kullenberg, and M. Orren, Elsevier, New York, in press, 1981.

Duce, R. A., G. L. Hoffman, B. J. Ray, I. S. Fletcher, G. T. Wallace, J. L. Fasching, S. R. Piotrowicz, P. R. Walsh, E. J. Hoffman, J. M. Miller, and J. L. Heffter, Trace metals in the marine atmosphere: sources and fluxes, in *Marine Pollutant Transfer,* edited by H. Windom and R. Duce, pp. 77–119, Lexington Books, Lexington, Mass., 1976.

Duce, R. A., C. K. Unni, B. J. Ray, J. M. Prospero, and J. T. Merrill, Long range atmospheric transport of soil dust from Asia to the tropical North Pacific: temporal variations, *Science, 209,* 1522–1524, 1980.

Huntzicker, J. J., S. K. Freidlander, and C. I. Davidson, Material balance for automobile-emitted lead in the Los Angeles basin, *Environ. Sci. Tech., 9,* 448–457, 1975.

Ng, A., and C. C. Patterson, Natural concentrations of lead in ancient Arctic and Antarctic ice, *Geochim. Cosmochim. Acta, 45,* 1981.

Ng, A., B. Schaule, K. Bruland, and C. C. Patterson, The relationship between Pb and ^{210}Pb in air, rain, and surface seawater, submitted to *Earth Planet. Sci. Lett.,* 1981.

Patterson, C. C., and D. M. Settle, Contribution of lead via aerosol deposition to the Southern California Bight, *J. Rech. Atmos., 8,* 957–960, 1974.

Patterson, C. C., and D. M. Settle, The reduction of order of magnitude errors in lead analyses of biological materials and natural waters by evaluating and controlling the extent and sources of industrial lead contamination introduced during sample collecting and analysis, in Accuracy in Trace Analysis, edited by P. La Fleur, *Spec. Publ. 422,* pp. 321–351, Nat. Bureau of Stand., 1976.

Patterson, C. C., and D. M. Settle, Enewetak: Lead isotope tracers identify Asian dusts, *SEAREX Newslett., 4,* 13, 1981.

Schaule, B. K., and C. C. Patterson, Lead concentrations in the Northeast Pacific: Evidence for global anthropogenic perturbations, *Earth Planet. Sci. Lett., 54,* 97–116, 1981a.

Schaule, B. K., and C. C. Patterson, Large historic increases of the eolian input of industrial lead to the North Atlantic have combined with short residence times of lead in the water column to greatly perturb the natural lead depth profile in the Sargasso Sea, in *Trace Metals in Sea Water,* in press, Plenum, New York, 1981b.

Settle, D. M., and C. C. Patterson, Lead in albacore: Guide to lead pollution in Americans, *Science, 207,* 1167–1176, 1980.

Settle, D. M., and C. C. Patterson, Magnitudes and sources of precipitation and dry deposition fluxes of industrial and natural leads to the North Pacific at Enewetak, submitted to *J. Geophys. Res.,* in press, 1982.

Settle, D. M., R. A. Duce, and C. C. Patterson, Importance of transfer in the atmosphere of metal-rich sub-micrometer particles to large particles in determining magnitudes of dry deposition fluxes of metals, paper presented at the IAMAP Third Scientific Assembly, Symposium on the role of oceans in atmospheric chemistry, Germany, 1981.

Turekian, K. K., and J. K. Cochran, ^{210}Pb in surface air at Enewetak and the Asian dust flux to the Pacific, *Nature, 292,* 522–524, 1981.

Turekian, K. K., and Y. Nozaki, ^{210}Po and ^{210}Pb in the eastern South Pacific: The role of upwelling on their distributions in the water column, in *Isotope Marine Chemistry,* edited by E. D. Goldberg, Y. Horibe, and K. Saruhashi, pp. 157–164, Uchida Rokakuho, Tokyo, 1980.

Turekian, K. K., D. P. Kharkar, and J. Thomson, Uranium and

thorium decay series nuclide abundances in marine plankton, Final Report, Adv. Res. Project Agency, Washington, D. C., 1973.

Turekian, K. K., Y. Nozaki, and L. K. Benninger, Geochemistry of atmospheric radon and radon products, *Ann. Rev. Earth Planet. Sci, 5,* 227–255, 1977.

Unni, C. K., Analyses of Pigeon Key rain and dry deposition samples, *SEAREX Newslett., 1,* 13, 1978.