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Eolian inputs of lead to the South Pacific via rain and dry deposition from industrial and natural sources

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Abstract—Virtually all lead in air at American Samoa is industrial. About 63% of total lead in the air originated from industrially produced, lead-rich, carbonaceous-oxide aerosols. Another 30% of total lead in air originated from industrial lead recycled in sea spray salt, while about 6% originated from industrial lead-rich aerosols which had been deposited on plant leaf surfaces and reintroduced to the atmosphere as plant aerosols. Natural volcanic and soil dust lead in air each amounts to about 1% of the total. The net eolian input flux of lead to the ocean at Samoa was 1.61 ng Pb/cm^{2}yr from rain after a 15% correction (0.28 ng/cm^2 yr) had been applied to the above flux for lead recycled in sea salt contained in rain. 73% of the net input of lead originated from industrially produced carbonaceous-oxide aerosols, while 25% originated from natural lead and 2% from industrial lead in soil dust. Natural lead in volcanic SO_4 amounts to about 1% of the net input. The bulk of the mass of dry deposition to the ocean consists of recycled sea salt. This recycled sea salt returns an amount of lead to the ocean by dry deposition that is equivalent to the net amount added by rain. This recycled lead in sea spray salt (1.6 ng/cm^2 yr) originated from lead contained in industrially produced aerosols that had been previously added to the ocean surface microlayer by rain. The maximum contribution of natural soil dust lead to the dry deposition flux is less than 1% of the total (<0.02 g/cm^2 yr). At this location four times as much sea salt is returned to the ocean by dry deposition (1900 μg/cm^2 yr) compared to that returned by rain (490 μg/cm^2 yr). Thirty times more dust is added to the ocean at this location by rain (60 μg/cm^2 yr) than is added by dry deposition (2 μg/cm^2 yr). ^{206}Pb/^{207}Pb ratios of atmospheric lead, when correlated with isotopic compositions of industrial lead emissions from various regional sources, suggest that lead in air collected during the summer came from industrial sources in New Zealand and Australia, and that lead in air collected during the winter was either from industrial sources in northern South America or was lead from North American sources that had been exported to the Southern Hemisphere and used there. These assignments are validated because they correlate well with isentropic air mass trajectories assigned to periods when the air was sampled.

INTRODUCTION

IT HAS BEEN SHOWN (PATTERSON and SETTLE, 1987a) that during preindustrial times about half the lead in the troposphere came from soil dusts, while the remainder came from volcanic gases. Today the proportion of this natural lead in the atmosphere is overwhelmed by industrial lead emitted from smelters, automobile exhausts, and power plants. About 85% of industrial lead emissions to the global atmosphere are introduced into the Northern Hemisphere Westerlies from North America, Europe, and Japan, with most of the remainder being introduced into the Southern Hemisphere Westerlies from Brazil, South Africa, Australia, and New Zealand. This creates a negative north-south gradient in global atmospheric lead concentrations across boundaries between the northern hemisphere Westerlies and Easterlies meridional tropospheric circulation cells, as well as across the equatorial boundary between the northern and southern Easterlies cells, because their convergence barriers restrict latitudinal mixing and the residence time of lead-rich aerosols is about ten days. Atmospheric lead concentrations in a pole to pole strip across the central Pacific show declines within meridional cells on either side of the Westerlies, with the northern hemispheric set containing higher lead concentrations than the corresponding southern hemispheric set, and with the Antarctic polar cap being the least lead polluted tropospheric cell within the Earth's atmosphere.

Eolian anthropogenic lead inputs added to the oceans during the past century were discovered to far outweigh ancient natural riverine inputs (CHOW and PATTERSON, 1962). Later work showed that these industrial inputs now account for about 90% of the total marine lead reservoir (SCHAULE and PATTERSON, 1981, 1983; SHEN and BOYLE, 1987). Present-day riverine anthropogenic lead inputs are sequestered on shelf deposits before that lead enters the open oceans (SCHAULE and PATTERSON, 1981; NG and PATTERSON, 1982; FLEGAL *et al.*, 1986; TREFREY and PRESLEY, 1976). Most of this lead is stored in the thermocline above 1000 m, creating steep negative concentration gradients with depth down to the base of the thermocline where magnitudes of concentration changes with depth are highest in the North Atlantic region, intermediate

in the North Pacific region, and lowest in the South Pacific (CHOW and PATTERSON, 1962; FLEGAL and PATTERSON, 1983; FLEGAL *et al.*, 1986; SCHAULE and PATTERSON, 1981, 1983). Such regional differences exist because of the slowness of horizontal mixing at depth on a time scale of centuries. Lead isotopic compositions of marine leads can be used for identification of regional origins of industrial lead to oceanic lead reservoirs at various locations (FLEGAL and PATTERSON, 1983; FLEGAL *et al.*, 1984, 1986; MARING *et al.*, 1987, 1990).

The aims of this investigation were (1) to establish separate *net* eolian input fluxes of natural soil dust lead, volcanic lead, and industrial lead to the oceans; and (2) to quantitatively evaluate fluxes via rain and dry deposition, together with the separate eolian input fluxes of lead, salt, and dust recycled in sea spray aerosols through rain and dry deposition. It was also our purpose to identify regional sources of inputs of industrial lead by use of isotope tracers.

SAMPLE COLLECTION

The sample collection site was located in the South Pacific Easterlies on the eastern end of Tutuila Island (American Samoa 14°S, 170°W). Sampling devices were mounted on the top of an 18 m tower located at the edge of a 30 m cliff on the coast. Air was monitored continuously by meteorological recording devices, and decisions to collect samples were made manually on the basis of both local and antecedent wind trajectory characteristics, selecting only parcels of air believed to represent large regional character not contaminated by local emissions of anthropogenic lead. This experiment was part of the NSF SEAREX Program operation carried out at American Samoa in 1981. Descriptions of the program, site, and relation to other major wind systems are given in DUCE (1981) and ARIMOTO *et al.* (1987).

Samples of sea salts, soil dusts, volcanic and industrial fume aerosols in South Pacific Easterlies boundary layer air were collected on total air filters, cascade air impactors, and dry deposition plates at various times during winter and summer seasons. Seawater was collected by dipping bottles attached to long poles from the bow of a small U.S. Coast Guard boat as the boat moved slowly forward. Samples of rain formed at high altitudes were collected in the boundary layer near the ocean surface during these periods, together with surface seawater samples that were collected at distances of 20 to 30 miles from the shore site of rain collection. Ultra-clean *manual* collection procedures together with ultra-clean sampling equipment and analytical techniques were used for all samples. Actual sampling times for air, rain, and dry deposition were severely restricted to small windows within the total site occupation time because of interference from local atmospheric emissions. Pathway sources of sampled air were continuously monitored by meteorological recording devices and meteorological network information input. These data were continuously evaluated and used to make decisions over short time intervals whether to collect or not collect air, impactor, dry deposition, and rain samples. Only those air parcels believed not to be contaminated by local emissions of anthropogenic lead were accepted. Some of these constraint evaluation techniques have been described in ARIMOTO *et al.* (1987).

Descriptions of the rain and air collection apparatus are given in MARING *et al.* (1989). The dry deposition collector was a 40-cm diameter rimless 1-cm thick polyethylene disk supported from the bottom center. Deposits were removed by sweeping (by means of an ultra-pure quartz rod) a 1 cm^3 drop of dilute HCl over the entire surface, twice. Crucial aspects of control of contamination in cleaning apparatus and containers and in handling, transport and storage of samples are outlined in MARING *et al.* (1989).

ANALYTICAL METHODS

Sizes of samples were: air ~250 m^3; rain 0.2 to 2 liters; dry deposition 30 to 140 hrs; and seawater ~2 liters. Concentrations of Pb, Ca, Sr, Ba, K, and Rb, together with isotopic compositions of lead, were determined in the samples by thermal ionization high-resolution magnetic scanning isotope dilution mass spectrometry under ultra-low level lead contamination control in the ultra-clean biogeochemical laboratory of the Geology Division at the California Institute of Technology. Descriptions of the methods have been given elsewhere (PATTERSON and SETTLE, 1976, 1977; PATTERSON *et al.*, 1976; EVERSON and PATTERSON, 1980; SETTLE and PATTERSON, 1980; BOUTRON and PATTERSON, 1983). A known amount of stable ^{208}Pb isotope spike was added to all samples being analyzed for lead. This mixture of spike and sample was dissolved in $HNO_3/HClO_4$ in an ultra-pure quartz dish and taken to dryness. The redissolved residue was complexed with citrate and cyanide and extracted with dithizone in $CHCl_3$ to isolate mixtures of intrinsic ^{207}Pb and spike ^{208}Pb isotopes free from other metals. Isolated lead samples were evaporated on rhenium filaments and the $^{208}Pb/^{207}Pb$ ratios in them were measured in the mass spectrometer.

Contamination introduced from each container and reagent was determined separately and then summed as 11 separate additions which varied slightly for each analysis, yielding a total of about 340 pg with an uncertainty of about 20 pg. Amounts of sample lead ranged from 1 to 10 ng, with an uncertainty of ±0.5% in reported concentrations. Calcium and barium were determined by IDMS by adding stable ^{42}Ca and ^{136}Ba isotope tracers to aliquots of acid solutions of some of the dissolved samples being analyzed for lead. These mixtures of sample and tracer isotopes of calcium and barium were evaporated on oxidized tantalum filaments and inserted into the source of the mass spectrometer for isotopic analysis. Leads were separately isolated from unspiked samples to measure $^{206}Pb/^{207}Pb$ ratios of lead intrinsic within the samples. Representative contamination values from various sources introduced during collection and analyses are reported in MARING *et al.* (1989).

RESULTS

Eolian input fluxes from rain and dry deposition of lead, salt, and dust to the ocean determined from these concentrations are listed in Table 2. Characteristic isotopic compositions of lead measured in the fluxes are also listed.

Table 1. Summary of observed concentrations of lead, salt, and dust, distributions of industrial and natural lead among different types of aerosols, and isotopic compositions of lead in air and rain collected at American Samoa during 1981. Concentrations and isotopic concentrations of lead in seawater collected at the time and place are also listed

Type of sample	Date (1981)	Sea salt	Soil dust	Total lead	Distribution of total lead: Soil dust Nat.	Soil dust Ind.	Sea salt Nat.	Sea salt Ind.	Indust. from plant leaves	Indust. aerosols	Volcanic aerosols	Pb isotopic composition 6/7	6/8	6/4
Air		$\mu g/m^3$	ng/m^3	pg/m^3	pg/m^3									
Summer	1/14–2/27	5.5	12	40	0.08	0	—	14	2.1	24	0.3	1.1948	0.4911	18.31
Winter	7/04–7/21	13	48	22	0.32	0	—	4.0	1.4	16	0.3	1.1766	0.4872	18.31
Mean air		9	30	31	0.2	0		9	1.8	20	0.3			
Rain		$\mu g/m^3$	ng/m^3	pg/m^3	ng/kg									
Summer	1/19	0.6	0.3	12.6	2.1	0.15	—	1.5	—	8.8	0.1	—	—	—
Summer	2/3	2.7	1.0	9.0	7.0	.5	—	4.3	—	0	.06	1.2240	0.4998	19.12
Winter	7/25	2.1	0.05	24.8	0.35	0.02	—	0.6	—	23.9	0.1	—	—	—
Winter	7/26	6.9	0.13	0.9	0.9	0.06	—	0.6	—	0	.03	—	—	—
Mean rain		3.1	0.6	12	2.6	0.18		1.7		7.5	0.07			
Sea Water			ng/kg											
Summer	1/27		3.5									1.1820	0.4830	18.36
Winter	7/28		4.3									1.1799	0.4833	18.26

Table 2. Summary of eolian inputs and dry deposition fluxes of lead, salt, and dust to the ocean, together with the isotopic compositions of the flux leads at American Samoa during 1981

Type of flux	Date (1981)	Sea salt	Soil dust	Total lead	Recycled Pb in sea salt	Net input Pb flux	Pb isotopic composition 6/7	6/8	6/4
Via Rain*		$\mu g/cm^2\ yr$	$\mu g/cm^2\ yr$	$ng/cm^2\ yr$	$ng/cm^2\ yr$	$ng/cm^2\ yr$			
Summer	1/19	96	48	2.01	0.25	1.76	—	—	—
Summer	2/3	440	160	1.44	0.69	0.75	1.2240	0.4998	19.12
Winter	7/25	340	8	3.96	0.10	3.86			
Winter	7/26	1100	21	0.14	0.10	0.05			
Mean Rain		490	60	1.89	0.28	1.61			
Via Dry Dep.*									
Summer	1/19–2/6	950	2.3	2.43	2.4	0	1.2291	0.4994	19.21
Winter	7/3–7/18	2800	2.7	0.83	0.83	0	1.2223	0.4992	19.07
Mean Dry Dep.		1900	2.5	1.6	1.6	0			

* Seasonal fluxes converted to annual fluxes.

Observed concentrations of lead, salt, and dust and distributions of industrial and natural lead among different types of aerosols in air and rain and lead concentrations in seawater are summarized in Table 1. Soil dust concentrations in air and rain were determined from measured barium concentrations × 2500 (wt. ratio in silicate source rock) × 1.33 (correction applied for humus component, PATTERSON and SETTLE, 1987a). Sea salt concentrations in air and rain were determined from measured total calcium minus calcium contributed by dust × 86 (wt. ratio in sea salt) and/or from total measured potassium minus potassium contributed by dust × 91. Volcanic lead concentrations in rain were determined from measured average non-sea salt SO_4 concentrations in rain (reported by PSZENNY *et al.*, 1982) × 0.1 (fraction that is volcanic, ZEHNDER and ZINDER, 1980) × S/SO_4 wt. ratio × Pb/S volcanic wt. ratio (PATTERSON and SETTLE, 1987a, 1988), yielding a mean for both season and year of 0.1 ng volcanic lead per 3 mg sea salt per kg rain. A mean concentration of volcanic lead in air was obtained from this value for volcanic lead in rain by multiplying it by three to yield a mean of 0.3 pg volcanic lead per 9 μg sea salt per m^3 air, for season and year. Concentrations of natural lead in soil dust contained in both air and rain were determined from measured dust concentrations × 7 ppm (concentration in total silicate fraction, PATTERSON and SETTLE, 1987a). Concentrations of industrial lead in contaminated humus of soil dust (in the Southern Hemisphere) were determined from measured dust concentrations × 0.5 ppm (PATTERSON and SETTLE, 1987a). Concentrations of lead contained in sea salt contained in both rain and air (all of the lead was industrial—see below) were obtained from measured concentrations of sea salt in air and rain × Pb/salt in sea water × enrichment factors that were 2500 in winter and 25,000 in summer (see below). Concentrations of industrial lead in plant leaf aerosols contained in air were set equal to 8% of total industrial lead in <1.5 μm aerosols (see below). Such lead was set equal to 0% in rain. The sum of leads in soil dust, sea salt, volcanic aerosols, and in plant leaf aerosols was subtracted from total lead in air to yield concentrations of lead in industrially produced lead-rich aerosols. Concentrations of net industrial lead in industrially produced lead-rich aerosols contained in rain were assigned to the net remaining after total lead was corrected for lead in sea salt, dust, and volcanic aerosols.

Uncertainties in measurements of metal concentrations in air are about 10%, determined mainly by an uncertainty of this magnitude in air volumes. Error in measurement of air volumes was reduced to about 10% through use of three calibration methods in the field at the time of collection: integrated rotameter flow, hot wire conductivity flow meter, and integrated bellows gas meter. Uncertainties of metal concentrations (except Ba) in rain ranged from <1% to 10% with smaller concentrations being less certain. Uncertainties for Ba concentrations ranged from 3 to 30%. Uncertainties for Pb concentrations in seawater were about 1%. These values were not determined from statistical considerations but were derived essentially from human interpretative knowledge, gained through measurement, of influences by errors in contamination control, which greatly exceeded instrumental

errors and varied with sample type and element being studied. Measurement errors were about ±0.1% of the $^{206}Pb/^{207}Pb$ ratio, about ±0.2% of the $^{206}Pb/^{208}Pb$ ratio, and about ±0.5% of the $^{206}Pb/^{204}Pb$ ratio.

Other investigators determined the following constituents in samples related to those we studied: Cl, Br, I, Na, Mg, K, Ca, Al, Fe, Mn, V, Pb, Ag, Cd, Cu, Zn, Sc, Co, Hf, Rb, and Se by ARIMOTO *et al.*, (1987); sea salts, NO_3, SO_4, pH by PSZENNY *et al.* (1982); Hg by FITZGERALD (1989); organic compounds by ATLAS and GIAM (1989) and by PELTZER and GAGOSIAN (1989); and ^{210}Pb by TUREKIAN *et al.* (1989).

Our salt and dust data were compatible with that determined by our colleagues R. Arimoto, R. Duce, P. Harder, B. Ray, and C. Unni at the University of Rhode Island. Investigators in the SEAREX group used our expertise and guidance in development of ultra-clean collection and analytical methods for their studies of trace metals by means of sharing of samples and collection apparatus.

DISCUSSION

Lead in rain and dry deposition impacting the ocean's surface originates from four major types of lead-containing aerosols in marine air: soil dust, industrial smokes, volcanic sulfate, and sea salt. Net oceanic inputs of lead at various locations and times are determined by magnitudes of scavenging of the first three types of aerosols from air into rain. However, lead-rich industrial aerosols originating from the ocean surface microlayer (originating there, in turn, from such aerosols contained in rain impacting the surface) introduced into sea spray salt and scavenged by rain constitutes a major component of the gross flux which must be corrected out of the measured total in rain to obtain the true input. Net lead introduced to the oceans originates from two kinds of continental and island sources: natural and industrial. Natural lead is contained in soil dust silicates and volcanic sulfate aerosols, while industrial lead is contained in industrially contaminated soil dust humus, industrially contaminated plant leaf debris, and industrially produced lead-rich carbonaceous and oxide aerosols. Although the magnitude of dry deposition input of lead to the ocean's surface at Samoa is quite significant and equal to the net input via rain, the former consists virtually entirely of recycled industrially produced lead-rich aerosols contained in sea spray salt that had originated from the ocean surface microlayer. These data indicate that dry deposition of soil dust is not a significant pathway by which lead enters the oceans.

Atmospheric occurrences

As shown in Table 1, concentrations of salts and dusts were three to four times higher in winter air compared to summer air at Samoa, while concentrations of lead were twice as high in the summer. The mass of sea salt aerosols in air was about a thousand-fold greater than the mass of dust particles, which in turn exceeded by a thousand-fold the mass of aerosol lead. About 99% of the lead in Samoan air originated from industrial sources, with about two-thirds being net input occurring in industrially produced carbonaceous-oxide aerosols, about one-third being recycled industrial lead occurring in sea salt aerosols, and about one-fifteenth occurring in industrial lead-rich aerosols attached to larger plant-leaf aerosols. The remaining one percent of atmospheric lead originated from natural clay lead in soil dusts and from natural volcanic fume lead trapped in oxidized and hydrolyzed volcanic sulfur.

Soil dusts. Soil dust in air at Samoa was a net introduction and was not present as a recycled constituent of sea spray. Concentrations of natural clay lead in these dusts are about 7 ppm, showing that the average 30 ng dust/m^3 air contributes about 1% of total lead in air. This amount compares favorably with the estimated amount of volcanic lead in the air (see below). On the basis of relative global inputs to the atmosphere, dust and volcanic eolian deposition flues should be approximately the same.

Indications have been found suggesting that about one-third of the average total 11 ppm lead in the upper 3 cm of soil in non-urban, non-agricultural regions of the northern hemisphere (about 3.7 ppm) is industrial lead, contained in the humus fraction (from unpubl. data by G. KOLBASUK, R. ELIAS, Y. HIRAO, and C. PATTERSON; summary reported in PATTERSON and SETTLE, 1987a). Differences in tropospheric lead concentrations between the Northern and Southern Hemispheres suggest that soil humus in the Southern Hemisphere is contaminated about one-seventh of that in the Northern Hemisphere, so that it can be assumed that the concentration of industrial lead in soil dusts in the Southern Hemispheric troposphere is about 0.5 ppm. This indicates that industrial lead in soil dust is less than 0.1% of the total lead in air.

Leaf particles. Cascade impactor aerosol size studies also disclosed that a significant fraction of industrial atmospheric lead was contained in a new category of intermediate-sized (1 ↔ 1.5 μm) leaf wax particles. It is known that about two-thirds of the eolian input flux of industrial Pb to vegetated regions is introduced via momentum and diffusion

impact collection of fine Pb-rich aerosols onto leaf surfaces (ELIAS *et al.*, 1982). It had also been found that 1 ↔ 1.5 μm sized leaf wax particles are transported large distances over the oceans (PELTZER and GAGOSIAN, 1989). The cascade impactor findings (ROSMAN *et al.*, 1990) showed that these leaf wax particles contain industrial lead deposits which amounted to about 8% of total lead contained in <1.5 μm particles in air and about 6% of total lead in air.

Volcanic sulfate aerosols. In preindustrial times the emission flux of volcanic lead to the troposphere was about the same as the emission flux of soil dust (PATTERSON and SETTLE, 1987b, 1988). Most volcanic lead is probably emitted in the form of molecular halides which become attached to sulfur aerosols within a few seconds after emission. This sulfur becomes oxidized, and then hydrolyzed, where it accounts today for about 10% of global non-sea salt sulfate in the atmosphere (PATTERSON and SETTLE, 1987b, 1988; ZEHNDER and ZINDER, 1980). It was assumed that the ratio of total non-sea salt SO_4 aerosols to sea salt in rain formed at high altitudes was similar to that in boundary layer air. This is an overestimate because the ratio is probably smaller in boundary layer air. If this ratio is assigned to the yearly mean of 9 μg sea salt/m^3 air, and volcanic lead is computed from it and the measured global mean volcanic Pb/S ratio (PATTERSON and SETTLE, 1987b, 1988), an average concentration of 0.3 pg volcanic lead/m^3 air is estimated, which amounts to about 1% of the total lead in air and at the same time compares favorably with the equal amount of natural dust lead measured in marine boundary layer air.

Sea salt aerosols. It is proved from lead isotopic tracers that lead in sea spray salt originates virtually entirely from industrial lead in the sea surface microlayer, and at concentrations in the salt aerosol that are greatly enriched over seawater concentrations (see *Dry Deposition* section below). The amount of recycled (non-net input) industrial lead (9 pg/m^3) in average 9 ug sea salt/m^3 air comprises 30% of total average lead in air.

Industrially produced lead-rich aerosols. Impactor aerosol size studies (ROSMAN *et al.*, 1989) showed that lead in air not contained in sea salt or dust was divided: 8% on 1 ↔ 1.5 um plant leaf particles and 92% on <0.5 μm industrially produced carbonaceous-oxide aerosols. The proportions of air lead measured in salt and dust on the impactor were not reliable because of loss of the latter on entry surfaces before the air entered the impactor. Bulk air filter data obtained in this study show, reliably, that the net amount of industrial lead in <0.5 μm aerosols, obtained by subtracting lead in soil dust, volcanic SO_4, sea salt, and plant leaf particles amounts to an average 20 pg/m^3 air, or 63% of total lead in air.

Regional origins. $^{206}Pb/^{207}Pb$ ratios of atmospheric lead in boundary-layer air below 1000 m, when correlated with isotopic compositions of industrial lead emissions from various regional sources, show that: (1) lead in such air collected at American Samoa within the Easterlies meridional cell in the Southern Hemisphere during a specific meteorological regime in the winter (ratio = 1.1766) came from industrial sources in New Zealand and Australia, because the values of the ratio of leads emitted from those regions were low; and (2) lead in air collected during a specific meteorological regime in the summer (ratio = 1.1948) came from industrial sources in northern South America, because the values of the ratio of leads emitted from that region were high (PATTERSON and SETTLE, 1987a). These assignments derived from isotopic tracers correlate well with specific isentropic air mass trajectories assigned to air (MERRILL, 1989) that was sampled at various periods. Such isotopic assignments serve, in this manner, to validate those isentropic trajectories.

Air masses, identified as originating from specific regions in the Southern Hemisphere by means of both isentropic trajectories and lead isotopic tracers, appear to contain lead with somewhat higher values of $^{206}Pb/^{207}Pb$ ratios than would be expected. An estimate of the mean value for this ratio in Australian lead alkyls would be about 1.135 for early 1980s (see *Global Context* section below), while alkyls made of Chilean lead should have had values for the ratio equal to about 1.18 for that time. The average value of $^{206}Pb/^{207}Pb$ in U.S. lead alkyls for 1980 was about 1.225 (MANEA-KRICHTEN *et al.*, 1991). This suggests that lead alkyls containing leads from the U.S.A. were being exported to and used within the Southern Hemisphere, so that emissions of this lead within the Southern Hemisphere mixed with emissions of Australian and Chilean lead to elevate $^{206}Pb/^{207}Pb$ ratios of the latter.

Occurrences in rain

The isotopic composition of lead in rain is quite unlike that in boundary-layer air, indicating that the collected rain had formed in high altitude air masses originating from a different meteorological regime than that responsible for the lower altitude air mass sampled close to the time the rain was collected. Isotopic tracers indicate that the high altitude lead in rain originated from industrial aero-

sols emitted from restricted regions of southern United States and northern Mexico, while the low altitude lead in air originated from mixtures of the above type of air mass with air that originated from northern swirls of Westerlies from Australia and New Zealand.

Proportions of dust relative to salt and industrially produced lead-rich aerosols scavenged from air by rain at high altitudes differ from those measured in air at lower boundary layer altitudes because (1) concentrations of salt decrease while concentrations of dust and lead-rich industrial aerosols increase with altitude, and (2) scavenging ratios (conc. in rain/conc. in air) for salt are greater than for dust while those for dust are greater than for lead-rich aerosols (MARING *et al.*, 1989; CHURCH *et al.*, 1991a,b). These factors account (aside from meteorological regime differences) for the greater proportion of dust lead in total lead in rain compared to its proportion of total lead in boundary-layer air (23% vs. 1%), the smaller proportion of sea salt lead in rain lead compared to air lead (15% vs. 30%), and the unchanged proportion of industrial lead-rich aerosols in both rain lead and air lead (64%). The average concentration of volcanic lead in rain was computed from the observed average non-sea salt concentration.

Sea salt is the only effective source of recycled lead in rain, amounting to 15% of the total, leaving a net input of 1.6 ng pb/cm^2 yr to the oceans from the Easterlies at Samoa (computed from an annual rainfall of 160 cm/cm^2, DORMAN and BOURKE, 1979). 73% of this net input lead originated from industrially produced carbonaceous-oxide aerosols, while 25% originated from natural lead and 2% from industrial lead in soil dust. Natural lead in volcanic SO_4 aerosols amounts to about 1% of the net input. The eolian input of sea spray salt returned to the oceans in rain is 490 μg/cm^2 yr. The eolian input of dust in rain is 60 μg/cm^2 yr.

Occurrences in dry deposition

The bulk of the mass of dry deposition to the ocean consists of recycled sea salt. This recycled sea salt returns an amount of lead to the ocean by dry deposition (1.6 ng/cm^2 yr) that is equivalent to the net amount added by rain. This recycled lead originated from lead contained in industrially produced aerosols that had been previously added to the ocean surface microlayer by rain. The maximum contribution of natural soil dust lead to the dry deposition flux is less than 1% of the total (<0.02 ng/cm^2 yr). The amount of sea spray salt returned to the ocean by dry deposition is 1900 μg/cm^2 yr, which is four times that returned in rain. The sum of dust added by dry deposition of both pure dust aerosols and dust contained in recycled sea salt (1.7 μg/cm^2 yr) is only one-thirtieth of dust in such forms added to the oceans in rain (60 μg/cm^2 yr). The small amount of dust added to the ocean surface by dry deposition indicates that not much dust is sequestered in the sea surface microlayer, and dust is therefore probably not greatly enriched in sea spray. This means that lead/dust ratios are probably greatly increased in sea spray when lead-rich industrial aerosols are enriched in sea spray. It follows that most of the dust observed in dry deposition and in rain probably originates from pure dust aerosols.

There is no discernible amount of lead-rich industrial aerosols added in pure form by dry deposition to the ocean surface. $^{206}Pb/^{207}Pb$ ratios in rain and in large particles on the dry deposition plate were nearly identical, 1.2240 vs. 1.2223, but quite different from those ratios in bulk air filters (1.1766), and surface seawater (1.1799), all collected within the same brief time period. This proves that lead in sea spray originates from undissolved particles in rain which are sequestered in the sea surface microlayer and then incorporated in sea spray particles. Lead isotopic tracers force us to assign all of the dry-deposition lead to recycled sea salt, and the ratio of lead to salt in dry deposition compared to the ratio of lead to salt in nearby seawater gives a measurement of the enrichment factor for lead in sea spray salt. Such measured enrichment factors were 26,000 for summer sea spray and 2400 for winter sea spray. Our impactor studies indicated an enrichment factor of 1200 for winter sea spray salt deposited on the coarse particle sized stages. This measurement of the ratio in size separated particles (even though some of the salt and dust in air had been lost) concurred with and verified the measurement of the ratio in dry-deposition deposit mixtures of all-sized particles. This conclusion is based on the indication by isotopic tracers that contributions of lead from small-sized particles was insignificant.

It is not known now why the enrichment factor changes with season, but it is known from isotopic tracers that the enriched lead in sea spray salt aerosols originates from lead-rich industrial aerosols that are first scavenged from air by rain and collected by the oily ocean microlayer after the rain impacts on the ocean surface. The lead dissolves from the collected particles into seawater at a slow rate of about 50% per day (MARING, 1986) to provide added lead to seawater. It is during this short period before dissolution that the lead is added to sea spray, where its quantities greatly outweigh dissolved sea-

water lead in the spray. The isotopic compositions of lead in rain fluctuate with time at any given location, but the isotopic composition of lead in seawater is an average of both added and advected lead and changes only slowly with time. The global average value of the enrichment factor has been put at 5000, based on a number of similar type of measurements carried out at various locations (PATTERSON and SETTLE, 1987a).

Global context

There is a clear demarkation between air concentrations and eolian input fluxes of lead to the mid-Pacific on either side of the equatorial boundary separating the Northern and Southern Easterlies. Concentrations in boundary layer air are 160 pg Pb/m^3 north of the Equator, and 31 ng Pb/m^3 south of the Equator, while net eolian input fluxes (corrected for recycled lead in sea salt) from these meridional cells are 6 and 1.6 ng Pb/cm^2 yr, respectively (northern Easterlies data from SETTLE and PATTERSON, 1982). About 7% of the larger amount of lead in rain north of the Equator originates from natural sources, compared to about 30% of the smaller amount of lead in rain south of the Equator. There is also a demarkation between air concentrations and eolian input fluxes of lead to the mid-Pacific on either side of the boundary separating the southern Easterlies and Westerlies. Lead concentrations in boundary layer air are 30 and 150 pg/m^3 and net lead fluxes are 1.6 and 10 ng/cm^2 yr in Easterlies and Westerlies, respectively (southern Westerlies data from SETTLE and PATTERSON, 1985).

Industrial lead enters the atmosphere of the Southern Hemisphere mostly by injection into the Westerlies meridional cell, so that eolian inputs to the Earth's surface from tropospheric meridional cells on either side of the southern Westerlies cell can be reliably expected to be smaller. However, eolian input fluxes from the Easterlies cell to the oceans should greatly exceed those from the Antarctic polar cap cell to the snow pack because lead concentrations in the latter atmosphere should be much smaller. The rationale for this is that the Antarctic circumpolar convergence provides a much stronger barrier to mixing from the Westerlies on its southern edge compared to effectiveness against mixing by the intertropical convergence on its northern edge. Furthermore, some industrial lead is injected directly into the Easterlies cell. Therefore, eolian input fluxes of lead to the snow surface of the Antarctic, being driven by much smaller atmospheric lead concentrations, must be considerably smaller than those from the Easterlies, so values of eolian inputs to the oceans measured in this study have served as valuable restrictive guides to studies and measurements of eolian lead inputs to snow in the Antarctic (BOUTRON and PATTERSON, 1987).

The $^{206}Pb/^{207}Pb$ ratios of lead in surface seawater underlying the Antarctic meridional cell (avg. ~1.160) reported by (FLEGAL *et al.*, 1991) are considerably higher than that observed underlying the Westerlies meridional cell by us in 1983 (1.1347, SETTLE and PATTERSON, 1985). These values for lead in water reflect sums of eolian contributions over a period of several years earlier than the dates of collection of the waters. The elevated values in the Antarctic cell may reflect the greater use of lead alkyls of U.S. origin within the Southern Hemisphere since 1980 (FLEGAL *et al.*, 1991), because U.S. lead has possessed values for this ratio of about 1.225 since 1980 and about 1.230 since 1985 (MANEA-KRICHTEN *et al.*, 1991), and much greater amounts of U.S. lead alkyls have been exported to the Southern Hemisphere during the last decade than was the case previously.

Future work

Scavenging ratios of salts, dusts, and metals determined in this work are not true values because atmospheric concentrations were measured in boundary layer air and concentrations were measured in rain that had formed in high altitude air. There is a need to determine true values, and this can be done by collecting samples of both air and fog-water formed in that air at elevated altitudes and collected from an airplane or blimp before and after the fog formed. At the same time there is need for reliable enrichment factors for metals in sea salt spray determined directly from cascade impactor aerosol size-sorted samples. These data are required for reliable measurement of eolian input fluxes of metals corrected for recycled metals in sea salt spray.

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