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The cycle of atmospheric cadmium over the North Pacific Ocean

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ABSTRACT

Bulk aerosol, cascade impactor, precipitation, and seawater samples were collected for a study of atmospheric cadmium at two sites in the Central North Pacific Ocean. The results of the analyses of these samples strongly suggest that the primary source of atmospheric Cd is the long-range transport of anthropogenic pollutant aerosol from Asia and Japan. The atmospheric concentration of Cd ranged from 1 to 60 pg m^{-3} and was strongly correlated with the atmospheric Pb concentration. The deposition rate of atmospheric Cd was estimated to be between 6 and 70 ng m^{-2} d^{-1} during the spring, and this flux is an insignificant source of Cd found in the surface waters of the Central North Pacific. The dissolubility of atmospheric Cd in seawater was determined. Virtually all of the Cd was released into an operationally defined dissolved state within 6 h.

1. Introduction

Little is known about the cycle of Cd in the remote marine atmosphere. The major reason for our lack of knowledge is the difficulty in properly measuring the concentration of this metal in aerosols and precipitation in remote regions. This is due to the extremely low concentration of Cd in the remote marine atmosphere and the ease with which samples can be contaminated.

However, the sources, concentrations and fates of this trace metal in the remote marine atmosphere are potentially important since it is well known that Cd is a toxic heavy metal, and it has been determined that the primary sources of Cd in the global atmosphere are anthropogenic (Nriagu and Pacyna, 1988; Nriagu, 1979; Nriagu, 1989). Furthermore, it has been conclusively demonstrated that Cd is substantially enriched in remote marine air with respect to crustal and oceanic source materials (Duce et al., 1983; Rahn, 1976). The primary candidates for sources of Cd which would cause such an enrichment are the preferential partitioning of Cd into sea-salt aerosols during sea-salt aerosol generation and the long range transport of anthropogenic or naturally enriched continental aerosols.

The deposition of continentally derived atmospheric Cd to the open ocean may have an effect on the oceanic cycle of Cd. Furthermore, if the primary source of atmospheric Cd is pollutant material, then atmospheric deposition may be perturbing this cycle. To gauge the extent of this possible perturbation, it is necessary to estimate the atmospheric deposition rate of Cd to the ocean surface and to determine the dissolubility of atmospheric Cd in seawater.

In this research, ultra-clean trace metal techniques were used to measure Cd in aerosols, rain and seawater from remote locations in the North Pacific. Relationships between Cd and three source indicator elements (Na, an indicator for marine aerosol, Al for mineral aerosol, and Pb for anthropogenic or pollutant aerosol) were examined to determine the primary sources of atmospheric Cd. The depositional flux of Cd to the North Pacific was estimated and laboratory experiments were undertaken to determine the dissolubility of atmospheric Cd in surface seawater.

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2. Experimental methods

2.1. Description of the sampling sites

Samples for this research were collected at sites in the central North Pacific (Fig. 1), including the two SEAREX (Sea-Air Exchange) Program's North Pacific Westerlies cruises aboard the R/V Moane Wave. The first cruise took place from 5 May to 3 June, 1986, and sampling was within the area bounded by 22°N to 57°N and 149°W to 170°W. The second cruise was from 10 June to 11 July 1986 and was within 22°N to 40°N and 155°W to 171°W. However, during much of the second cruise, the ship was positioned in a zone bounded by 35° to 40°N and 165° to 170°W.

Bulk aerosol, rain, and seawater samples were collected on these cruises. Aerosol samples were collected at the top of a tower on the bow of the ship, approximately 15 m above the sea surface. Rain samplers were mounted at the end of long anodized aluminum poles about 1.5 m forward of the bow of the ship and about 4 m above sea level. Surface seawater samples were collected from an inflatable launch following the procedure of Bruland (1980).

A second sampling site was located on the windward side of Oahu, Hawaii in the North Pacific trade wind regime. Bulk aerosol, cascade impactor and rain samples were collected at the top of a 20 m sampling tower from 19 March to 17 April 1987.

All sample processing was done in a portable class 100 clean room on the Moana Wave. At Oahu, sample processing was done in a laminar flow clean hood. All samples were stored frozen until analysis, and the rain and seawater samples were acidified to pH < 1 before freezing.

2.2. Sampling control

Precautions were taken so that the samples were not contaminated with material of local origin. Automatic sampling control systems were used to control the air sampling. On the Moane Wave, samples were collected when the relative wind direction was within ±110 degrees of the bow of the ship; the wind speed was $>2\ m\ s^{-1}$; the con-

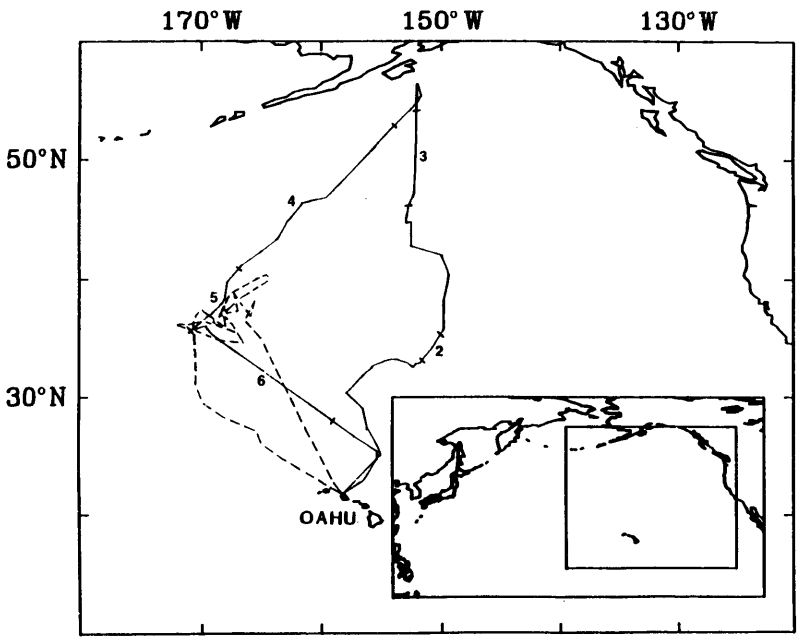

Fig. 1. SEAREX cruise tracks and Oahu sampling area. Solid line is the first SEAREX cruise, dashed line is the second. The areas where samples were collected during the first cruise are shown. All samples during the second cruise were collected between 30°N and 40°N and between 160°W and 170°W.

densation nuclei count was below 900 cm^{-3}; and there was no rain or fog. At Oahu, samples were collected when the wind was blowing from 020° to 140° and the wind speed was >2 m s^{-1}. The Oahu station sampling control system did not allow for control with respect to CN or precipitation.

Locally generated contamination was also a factor for the rain samples. Aboard the Moana Wave the ship maintained a heading that kept the rain samplers upwind of the ship while it was raining to decrease the possibility of contamination. At Oahu rain was sampled only when the aerosol sampling conditions had been in-sector before the precipitation began, stayed in-sector during the event, and remained in-sector after the rain ended.

2.3. Sampling systems and analytical methods

The sampling systems, sampler preparation and analytical methods used in this research are described in detail in Patterson (1988). Briefly, all aerosol samples were collected on acid-washed 90 mm Millipore HA filters at a flow rate of approximately 5.5 m^3 hr^{-1}. On the Moana Wave, replicate aerosol samples were collected for each sampling period. At Oahu, only one bulk aerosol sample was collected for each sampling period. Several of the replicate samples and aliquots of the Oahu samples were reserved for the aerosol dissolubility experiments.

Cascade impactor aerosol samples were collected using an Andersen Mark II low volume impactor (Andersen Samplers Inc., Atlanta, GA) mounted inside a polyethylene rain shelter. The impaction substrate was 80 mm acid-washed Millipore HA filters supported on acid-washed quartz collection plates.

The rain collection procedure is very complex and is described in detail by Arimoto et al. (1986). Briefly, the procedure involved carefully deploying an acid-washed polyethylene funnel of approximately 0.5 m surface diameter at the onset of a precipitation event. The rainwater was collected in acid-washed 2 L polyethylene bottles that were attached to the base of the funnel.

The bulk aerosol and cascade impactor samples were ashed for 16 hours in an LTA-505 low temperature asher (LFE Plasma Systems, Waltham, Mass.) at a power of 50 W and an O_2 flow rate of 1.5 l min^{-1}. These settings maintained the ashing temperature below 50° C and provide the shortest ashing time with greater than 99% recovery for volatile heavy metals such as Cd (Walsh et al., 1976; Mulford, 1966). After ashing, the residue was digested in 0.4 mL 1:1 DD-Q HNO_3: sub-boiling distilled hydroflouric acid for 24 h (DD-Q HNO_3 is concentrated nitric acid purified twice by distillation in quartz). The acid was then evaporated, and the residue was dissolved in 1.0 ml 0.1% DD-Q HNO_3.

The seawater samples were preconcentrated by a factor of up to 250 using a procedure similar to the APDC/DDDC liquid-liquid extraction technique of Bruland et al. (1979). The rain samples were preconcentrated using a sub-boiling evaporation procedure. For concentrated rain samples with unusually high salt concentrations (which interfered with the chemical analysis), another aliquot of the sample was concentrated by a factor of 10 using the same liquid-liquid extraction used for the seawater samples.

All samples were analyzed for Cd, Pb and Al by flameless atomic absorption spectrophotometry with Zeeman background correction using a Perkin-Elmer Model 5000 spectrophotometer with an HGA-500 graphite furnace. The samples were analyzed for Na by flame atomic absorption. The conditions for analysis of each metal are presented in Patterson (1988). The method of standard additions was used for all flameless AA.

2.4. Aerosol dissolubility experiments

The dissolubility of aerosol Cd was measured using a procedure adapted from that of Maring and Duce (1987). Each bulk aerosol sample was leached in 100 g of filtered seawater of known Cd concentration for 6 h. After exposure to the seawater, the leached sample filter and the leachate seawater were analyzed for Cd. The resultant mass of Cd was compared to the initial mass of Cd in each fraction to determine the dissolvable fraction of atmospheric Cd.

The cutoff between dissolved and particulate Cd was operationally defined as 0.2 μm. This is the 99% particle retention efficiency diameter for Millipore HA filters.

3. Results and discussion

3.1. Bulk aerosol data

3.1.1. Bulk aerosol samples. The atmospheric Cd, Pb, Al and Na concentrations for the bulk

aerosol filters samples are presented in Table 1. The atmospheric Cd concentrations in the region of the North Pacific covered by the Moana Wave are approximately a factor of two higher than previous measurements at Enewetak Atoll in the remote trade wind regime of the North Pacific (Duce et al., 1983), and much lower than measurements over the Atlantic Ocean (Duce et al., 1976b). At Oahu, the overall range of Cd concentrations is notably higher than the concentrations measured on the Moana Wave, but it is still lower than in the North Atlantic.

3.1.2. Relationships among cadmium, lead and aluminum concentrations. In Table 1, it is apparent that the peaks in the Pb and Al concentrations coincide with periods of high atmospheric Cd concentration at both sampling sites, and that there is no apparent relationship between the Cd and Na concentrations. The Cd concentrations of the bulk aerosol samples are plotted versus the Pb and Al concentrations in Figs. 2a and b, respectively. The relationship between Cd and Pb suggests that these two metals follow similar cycles. Pb in the North Pacific atmosphere is anthropogenically derived material from Asian and North American continental sources (Settle and Patterson, 1982; Duce et al., 1983; Schaule and Patterson, 1981). This relationship between atmospheric Cd and Pb suggests that the primary source of Cd in the remote North Pacific is also the long range transport of continental aerosol, probably of anthropogenic origin.

The relationship between Cd and Al concentrations (Fig. 2b) also suggests that atmospheric Cd has a continental source since atmospheric Al in this region is primarily from the long range transport of mineral aerosol from Asia (Uematsu et al., 1983; Parrington et al., 1983; Duce et al., 1980). There is more scatter among the points in the Cd-Al plot than in the Cd-Pb plot. This suggests

Table 1. *Trace metal concentration data for the bulk aerosol samples*

Sample ID	Volume (m^3)	Sampling period	Cd (pg SCM^{-1})	Pb (pg SCM^{-1})	Al (ng SCM^{-1})	Na (μg SCM^{-1})	Pb/Cd
MW2	496	4–8 May 1986	17 (3)*	580 (70)	114 (7)	3.0 (0.1)	34
MW3	340	13–16 May 1986	8 (4)	220 (30)	39 (3)	1.7 (0.1)	28
MW4a	397	19–24 May 1986	4.8 (1.6)	150 (40)	12 (1)	3.2 (0.1)	31
MW4b	411	19–24 May 1986	5.2 (1.5)	180 (50)	12 (1)	2.4 (0.1)	35
MW5	427	24–28 May 1986	29 (5)	1200 (100)	120 (10)	1.6 (0.1)	41
MW6	508	28 May–1 June 1986	15 (2)	460 (10)	70 (7)	1.4 (0.1)	31
MW7a	473	12–17 June 1986	1.5 (0.6)	74 (10)	14 (1)	0.85 (0.03)	49
MW7b	440	12–17 June 1986	1.5 (0.6)	60 (10)	14 (1)	0.90 (0.05)	40
MW8	478	17–24 June 1986	4.3 (0.6)	180 (5)	14 (1)	1.1 (0.1)	42
MW9a	520	24–30 June 1986	2.6 (0.5)	12 (1)	29 (2)	1.1 (0.1)	4.6
MW9b	496	24–30 June 1986	2.3 (0.5)	10 (1)	31 (3)	1.2 (0.1)	4.4
MW10	875	30 June–9 July 1986	1.7 (0.3)	7.2 (0.6)	14 (1)	1.7 (0.1)	4.2
OA1A	306	19–22 March 1987	6.1 (0.8)	120 (13)	21 (3)	4.3 (0.4)	20
OA2C	353	22–25 March 1987	8.6 (1.1)	210 (27)	24 (3)	3.4 (0.4)	24
OA3A	283	25 March–1 April 1987	43 (3)	1200 (170)	78 (13)	3.9 (0.4)	28
OA4C	121	1–2 April 1987	62 (3)	3800 (420)	530 (62)	6.3 (0.7)	61
OA5B	371	2–5 April 1987	58 (3)	4300 (960)	190 (10)	2.2 (0.1)	74
OA6D	361	5–8 April 1987	18 (4)	620 (57)	110 (19)	4.1 (0.4)	34
OA7B	349	8–11 April 1987	5.2 (0.9)	230 (21)	27 (2)	2.0 (0.1)	44
OA8C	264	11–14 April 1987	3.8 (0.9)	150 (14)	88 (12)	3.3 (0.3)	40
OA9A	369	14–17 April 1987	18 (4)	230 (31)	45 (8)	3.4 (0.3)	13
Avg. filter blank		——	0.36 (0.16)**	0.62 (0.27)	n.d.	n.d.	
Avg. sample blank		——	0.42 (0.14)	1.1 (0.83)	210 (70)	3.1 (1.4)	

* Values in parentheses are the propagated error from one standard deviation of the analytical error.

** Values for blanks given in ng $filter^{-1}$ for cadmium, lead and aluminum, and in μg $filter^{-1}$ for sodium. n.d. means below detection limit ($=0.01$ μg $filter^{-1}$ for Na, 1 ng $filter^{-1}$ for Al).

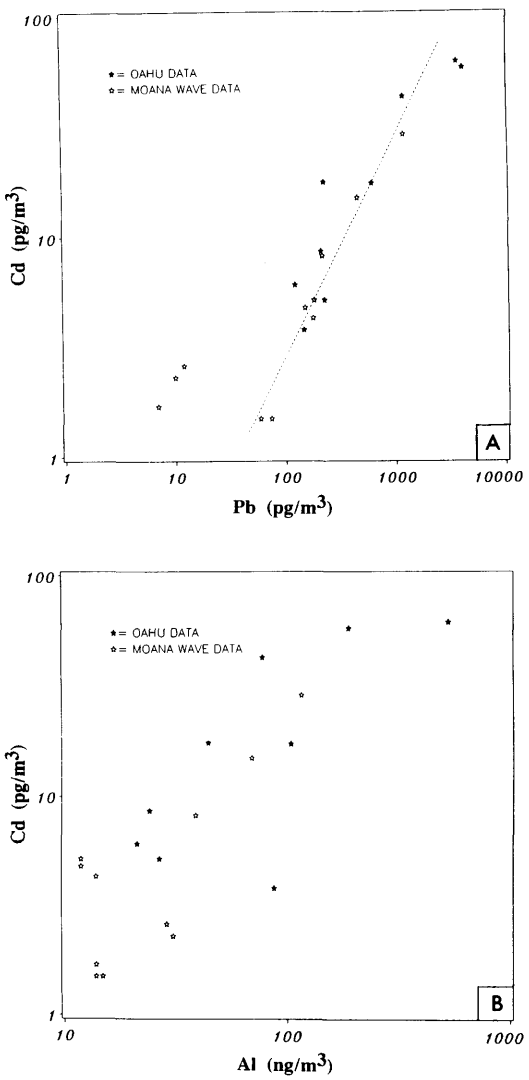

Fig. 2. Plots of the bulk aerosol cadmium concentration versus (a) the lead concentration and (b) the aluminum concentration. In (a), the dashed line represents a constant Pb/Cd ratio of 37.

separate sources for Al (mineral aerosol) and Cd and Pb (primarily pollutant aerosol). If all three metals have a continental source, then episodic transport of continental air to the remote North Pacific will result in coincident elevated concentrations for all three metals. However, differences between the physical characteristics, suspension mechanisms, and source regions of the two types of continental aerosols will result in a less coherent relationship between metals associated with different types of particles than between metals associated with the same type. Thus, the greater scatter in the Cd-Al plot is consistent with a continental pollutant source of Cd.

The mean Cd crustal enrichment factor (EF_{crust}) for the Moana Wave data is 170 ± 90, the mean for the Oahu data is 220 ± 130 and the overall mean is 200 ± 110. The Cd EF_{crust} is defined as:

$$EF_{crust} = ([Cd]/[Al])_{air}/([Cd]/[Al])_{avg.\ crust}.$$

In the present study, we used the globally averaged crustal abundances of Cd and Al reported by Taylor and McLennan (1985) in the denominator. While our enrichment factors are not extraordinarily high, they are substantially greater than one, supporting the hypothesis of a non-crustal source for Cd.

3.1.3. Lead to cadmium ratios. If Cd and Pb had precisely the same cycles in the remote marine atmosphere, one would expect a linear relationship between the logarithms of the Cd and Pb concentrations with a slope of about 1, indicating a constant Pb/Cd ratio. The dashed line in Fig. 2a represents such a relationship for a Pb/Cd ratio of 37. Many of the points in Fig. 2a approach such a linear relationship. Those that don't are generally those with the high and low extreme concentrations of Pb. These observations suggests either conservative mixing of air from two sources of Pb and Cd or varying source strengths for the two metals relative to each other within the source region. The latter explanation is likely because of the different primary sources for Pb (i.e., automobile exhaust) and Cd (non-ferrous ore smelting and fossil fuel combustion). However, our data set is too small to conclusively determine what controls of the Pb/Cd ratio.

Recent estimates of global anthropogenic emissions (Nriagu and Pacyna, 1988) and global natural emissions (Pacyna, 1986) of Cd and Pb can be used to estimate a global Pb/Cd emissions ratio. The global combined atmospheric emission rate is estimated to be 8.6 million kg $year^{-1}$ for Cd and 350 million kg $year^{-1}$ for Pb. The emission rates of both metals are vastly dominated by continental industrial and municipal emission processes. The mean Pb/Cd emissions ratio is about 40, roughly the same as the mean Pb/Cd

ratio measured during the present study (37, not including samples MW9 and MW10). Furthermore, Dulac et al. (1987) report that the Pb/Cd ratio in aerosols over the Mediterranean Sea ranges from 15 to 60 with a geometric mean of 46, again similar to the results of this study.

It is interesting that these three Pb/Cd ratios are so similar. Perhaps this is an indication of a global anthropogenic perturbation to the background aerosol. However, it may also be due to an internally mixed aerosol from a specific type of source or group of sources.

3.2. *Cascade impactor data*

Cd, Pb, and Al concentrations for a representative cascade impactor sample collected at Oahu are plotted against the fifty percent cutoff diameter for each stage in Fig. 3. It is clear that Cd is associated primarily with the submicrometer size particles. For this sample, there was a significant large particle Cd component, consistent with previous Cd mass-size distribution measurements made in Bermuda by Duce et al. (1976a). They attributed this large particle mode to an oceanic source via sea-salt aerosol production.

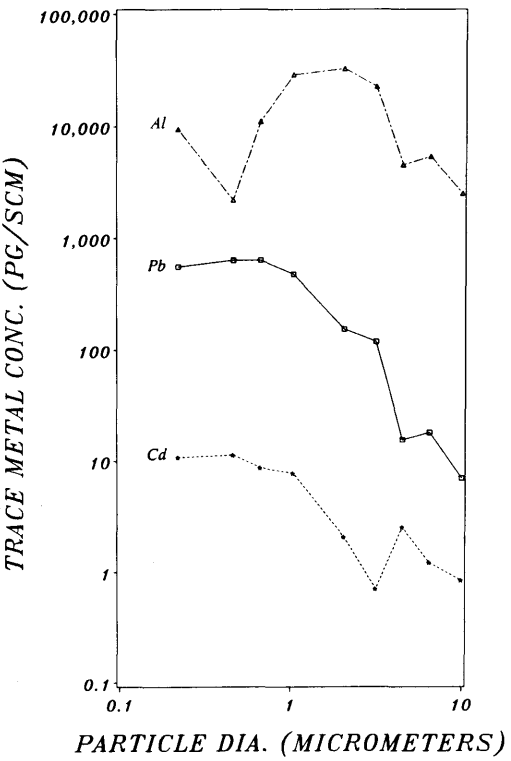

Fig. 3. Plot of the size distributions of cadmium, lead and aluminum determined from cascade impactor sample OACI2.

The aerodynamic mass-size distribution (AMSD) for Pb in Fig. 3 is remarkably similar to that of Cd. This was typical of all the cascade impactor samples. The abundance of Pb on the small particle fraction is consistent with the well documented high temperature continental source for Pb in the remote marine atmosphere (Settle and Patterson, 1982; Duce et al., 1983). Thus the similarity between the Cd and Pb AMSDs supports the suggestion that Cd over the remote North Pacific also has a high temperature anthropogenic source.

The Al AMSD in Fig. 3 and in all the other cascade impactor samples we collected has a substantially different shape from those of Cd. This is consistent with the hypothesis that Al and Cd may come from the same source region (i.e., the continents), resulting in similar total concentration trends, but that the specific sources of the two metals are very different in the source region.

3.2.1. Mass median diameters. The mass median diameters (mmd) for Cd, Pb, Al and Na measured in each of the four cascade impactor samples, and their 95% confidence limits, are presented in Table 2. Also included in Table 2 are the goodness-of-fit chi-square values for the log-normal mass-size distribution. The goodness-of-fit chi-square parameter is an indication of how well the cascade impactor data fit a log-normal mass-size distribution. In this study, the size distribution parameters for samples with chi-squared values higher than about 20 are questionable.

The Cd mmds in Table 2 are statistically the same as the Pb mmds and significantly different from the Al mmds for each sample at the 95% confidence level. This supports the hypothesis that Cd and Pb have a similar type of source. Furthermore, the great difference between the Cd and Al mmds emphasizes that the particles containing Cd are not the same as the particles containing Al, in support of the suggestion that Cd and Al may have a similar source region, but have different sources and behavior in the remote marine atmosphere.

3.3. *Air mass trajectory analyses*

Figs. 4 and 5 present selected backwards isentropic air mass trajectory analyses which roughly

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Table 2. *Mass median diameters from the cascade impactor data*

Metal	Sample ID	MMD (μm)	0.95 conf. limits lower	0.95 conf. limits upper	Goodness-of-Fit χ^2
cadmium	OACI1	0.46	0.24	0.66	17
	OACI2	0.76	0.64	0.89	10
	OACI3	0.61	0.55	0.68	1.3
	OACI4	0.21	<0.0	0.56	105
lead	OACI1	0.42	0.33	0.51	1.6
	OACI2	0.76	0.67	0.85	4.5
	OACI3	0.67	0.58	0.75	2.8
	OACI4	0.40	0.32	0.49	1.6
aluminum	OACI1	2.7	1.7	4.0	85
	OACI2	2.3	2.0	2.5	10
	OACI3	2.0	1.9	2.3	10
	OACI4	2.5	2.0	4.1	17
sodium	OACI1	1.8	1.1	2.7	50
	OACI2	4.4	4.0	4.9	4.3
	OACI3	4.1	3.7	4.5	3.9
	OACI4	1.8	1.6	2.0	7.4

show the transport path followed by air masses reaching the Moana Wave. These air mass trajectories were calculated according to the method of Merrill et al. (1986). These trajectory analyses were selected from a large set of trajectory analyses that were calculated at 12 hours intervals during both the Moana Wave cruises and the Oahu sampling period. They were selected on the basis of being the most representative trajectories for the discussion of trends in the Cd concentration at these sites.

The trajectory presented in Fig. 4 is representative of trajectories which occurred during periods of high Cd, Pb, and Al concentration. Notice that air which has been lifted into the upper troposphere over Asia is rapidly transported offshore to the Central North Pacific where it descends into the marine atmospheric boundary layer.

Fig. 5 presents a trajectory representative of those that occur during periods of low Cd, Pb and Al concentrations. This analysis shows that some of the air that was being sampled during the collection of Moana Wave sample 8 had been moving very slowly in the marine boundary layer during the previous 10 days.

The air mass trajectory analyses suggest that Cd follows the same atmospheric transport pathway as that followed by other continentally-derived atmospheric particulate material in the North Pacific, i.e., the uplifting of continental air in Asia, then rapid eastward transport in the upper troposphere, followed by subsidence down to the marine boundary layer (Duce et al., 1980; Avila, 1983; Merrill et al., 1985; Merrill et al., 1989). Therefore, the air mass trajectory analyses further support the suggestion that the primary source for atmospheric Cd in the remote North Pacific is the long-range transport of continental material.

3.4. *Relative importance of the various sources of atmospheric cadmium*

Our data strongly suggest that the long range transport of continentally derived pollutant material is the primary source of atmospheric Cd over the remote North Pacific. However, the importance of other sources still needs to be determined. To more quantitatively describe the importance of anthropogenic, crustal and sea-salt aerosol sources for atmospheric Cd, rough estimates of the crustal and oceanic components of the bulk aerosol have been calculated. The crustal component of atmospheric Cd was calculated using the Al concentration in each bulk aerosol sample and the Cd/Al ratio in average crustal

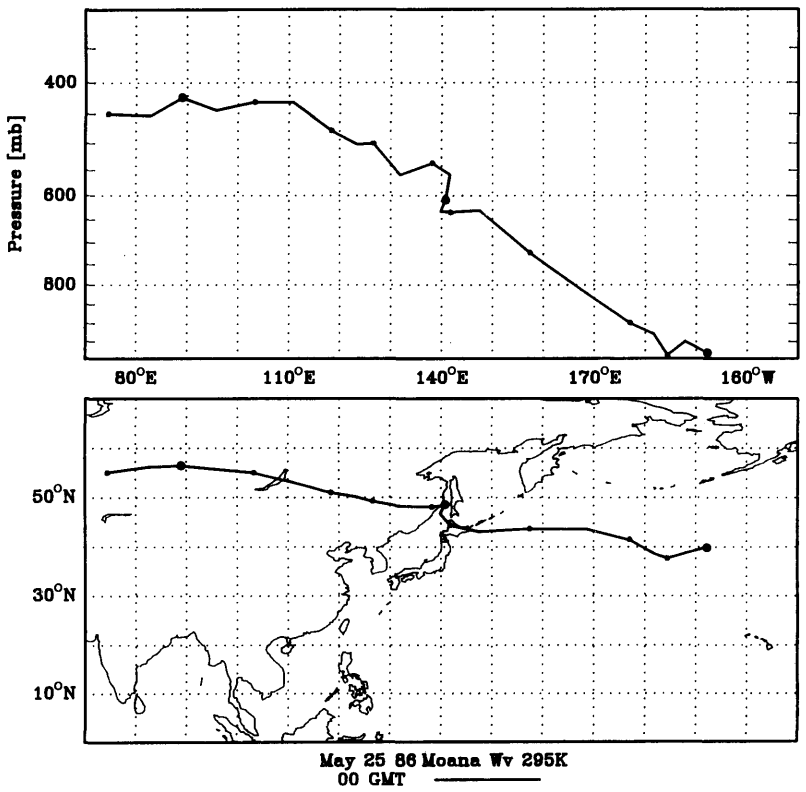

Fig. 4. Isentropic air mass trajectory calculated for the 295 K surface ending at the position of the Moana Wave at 00 GMT, 25 May, 1986. Each small dot along the trajectory represents one day of travel. Each large dot represents a five day period.

material (Taylor and McLennan, 1985). The sea-salt component of atmospheric Cd was calculated using the atmospheric Na concentration, the Cd/Na ratio in surface seawater, and by assuming that Cd is preferentially partitioned into sea-salt aerosols with respect to Na by a factor of 500. The surface seawater concentration of Cd that was used is the mean of the surface seawater Cd concentrations measured for this research (3.4 ng kg^{-1}, Table 5), and the enrichment factor of 500 is estimated from measured enrichments of other trace metals (Piotrowicz et al., 1979; Weisel, 1981; Weisel et al., 1984). An excess Cd component, which is expected to be primarily anthropogenic Cd, was determined by subtracting the crustal and oceanic components from the total Cd concentration in each bulk aerosol sample. The results of these calculations are presented in Table 3 as the mean percentage of each component. The excess (anthropogenic) component accounts for an average 93% of the total Cd in each bulk aerosol sample. The sea-salt component comprises about 6%, and the crustal component makes up less than one percent of the total Cd.

The results in Table 3 are supported by multiple linear regression analysis. If stepwise multivariate linear regression analysis is applied to the bulk aerosol trace metal concentration data, the Pb concentration is the variable that is the most significantly correlated with the Cd concentration ($r = 0.96$). The Na concentration is the only other variable that significantly contributes to the multivariate regression, and the correlation coefficient for the model after entering this variable is 0.98.

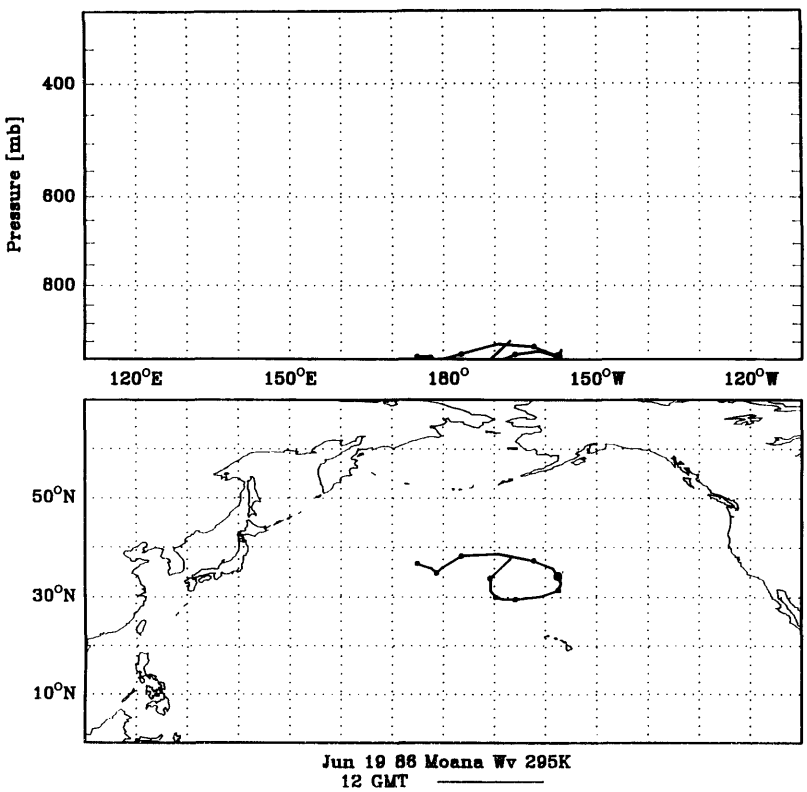

Fig. 5. Same as Fig. 4, except ending at the position of the Moana Wave at 12 GMT, 19 July, 1986.

Table 3. *Estimated fractions of marine, crustal and excess atmospheric cadmium in the remote North Pacific*

Source	Mean (%)	s.d. (absolute) (%)	Maximum (%)	Minimum (%)	Std. error (absolute) (%)
crustal	0.8	0.6	2.7	0.2	0.1
marine	6.1	4.3	18	0.6	1.0
excess	93	5	99	84	1.0

3.5. Trace metal concentrations in rain

The Cd and Pb concentrations in the rain samples are presented in Table 4. They were much higher at Oahu than on the Moana Wave. This can be attributed to the higher atmospheric concentrations of these metals at Oahu since the source of Cd and Pb in rain is the scavenging of aerosol particles by the raindrops. The concentrations of Cd and Pb in the rain vary together.

The Pb/Cd ratios of the main samples are very similar to the Pb/Cd ratios in the bulk aerosol (Table 1). This supports the suggestion that Cd and Pb behave similarly in the remote North Pacific atmosphere since it appears that Pb is scavenged by precipitation in roughly the same proportion as Cd.

3.6. Cadmium concentrations in seawater

The Cd concentrations measured in the surface seawater samples collected during the Moana

Table 4. *Cadmium and lead concentrations in rain*

Sample ID	Sampling period	Position	Volume (ml)	Cadmium (ng kg^{-1})	Lead (ng kg^{-1})	Pb/Cd
MWR1	12 May 1986: 1030–1500	44°N, 153°W	960	2.1 (0.2)	39 (9)	19
MWR2	14 May 1986: 1500–1730	46°N, 152°W	430	5.6 (1.2)	56 (10)	10
MWR3A	20 May 1986: 2330–0345	47°N, 158°W	1700	3.9 (0.2)	130 (4)	33
MWR3B	21 May 1986: 0420–0600	47°N, 158°W	1300	4.2 (0.4)	78 (3)	19
MWR4	19 June 1986: 1400–1800	37°N, 166°W	100	5.4 (0.6)	230 (20)	43
MWR5	21 June 1986: 0020–0230	38°N, 166°W	520	9.9 (0.7)	190 (30)	19
MWR6	22 June 1986: 0100–0500	40°N, 165°W	290	6.7 (0.5)	270 (20)	40
MWR7	23 June 1986: 1930–0930	40°N, 164°W	610	1.2 (0.2)	33 (5)	28
MWFW1	26 June 1986: 1700–0830	38°N, 168°W	320	3.8 (0.3)	26 (5)	7
Mean Moana Wave Sample Blank		———	2L	<0.08	<0.55	
OAR1	27 March 1987: 1330–1900	OAHU	560	62.0 (14.0)	1100 (100)	18
OAR2	31 March 1987: 1000–1115	OAHU	1300	12.0 (1.0)	85 (9)	7
OAR3	31 March 1987: 1130–1345	OAHU	770	13.0 (1.0)	230 (20)	18
OAR4	31 March 1987: 1400–1815	OAHU	30	120 (8)	3800 (400)	32
OAR5	15 April 1987: 0645–1130	OAHU	150	32.0 (3.0)	380 (40)	12
Mean Oahu Sample Blank		———	2L	<0.08	<0.055	

Error values are one standard deviation of the mean calculated from three separate analyses of each sample.

Table 5. *Surface seawater cadmium concentrations*

Sample ID	Collection date (1986)	Position	Cadmium (ng kg^{-1})	Cadmium (pmol kg^{-1})
MWSW1	5 May	33°08′N, 150°05′W	1.8 (0.3)	16 (3)
MWSW2	11 May	42°42′N, 151°01′W	5.0 (0.7)	44 (4)
MWSW3	26 May	35°34′N, 170°50′W	2.5 (0.3)	22 (3)
MWSW4	17 June	38°44′N, 167°14′W	4.8 (0.7)	43 (6)
MWSW5	26 June	36°19′N, 169°00′W	3.0 (0.3)	27 (3)

Error values are one standard deviation of the mean calculated from three separate analyses of each sample.

Wave cruises are presented in Table 5. The mean Cd concentration for the five samples is 30 ± 13 pmol kg^{-1}. These concentrations are similar to those measured previously in a nearby area by Boyle et al. (1981). Our data show a latitudinal dependence of the surface water Cd concentration, with the concentration decreasing with decreasing latitude. We believe that this latitudinal dependence may be due to water mass mixing across the Subarctic Convergence in the North Pacific. Unfortunately, no hydrographic data were collected during the Moana Wave cruises, so the position of this water mass boundary could not be determined. Further study is necessary to verify the existence and determine the cause of the observed gradient in the Cd concentration in North Pacific surface water.

3.7. Cadmium dissolution from bulk aerosols

Seven of the bulk aerosol samples were tested for Cd dissolubility. A summary of the results of the aerosol dissolubility experiments for these seven samples is presented in Table 6. Notice that the recoveries were good for all of the samples (i.e., mass balance was achieved to within the propagated analytical error) and that essentially all of the Cd in the bulk aerosol samples was released into the seawater fraction within the

Table 6. *Summary of the aerosol dissolubility experiments*

Sample ID	Initial mass of Cd in filter aliquot*	Mass of Cd released to seawater	Mass of Cd remaining in filter aliquot	Mass recovered
Oahu 5B	11 ± 1	10 ± 1 ($94\% \pm 13\%$)	<0.32 (0 to 3%)	75 to 103%
Oahu 7B	0.94 ± 0.15	1.1 ± 0.1 ($113\% \pm 20\%$)	<0.32 (0 to 34%)	92 to 192%
Moana Wave 2E	2.5 ± 0.3	2.4 ± 0.2 ($96\% \pm 13\%$)	<0.32 (0 to 13%)	79 to 133%
Moana Wave 3C	0.94 ± 0.16	1.2 ± 0.2 ($127\% \pm 33\%$)	<0.32 (0 to 34%)	100 to 218%
Moana Wave 5C	5.7 ± 0.5	3.7 ± 0.4 ($66\% \pm 9\%$)	2.0 ± 0.1 ($26\% \pm 4\%$)	$92\% \pm 10\%$
Moana Wave 6F	2.7 ± 0.3	2.4 ± 0.2 ($88\% \pm 12\%$)	<0.32 (0 to 12%)	73 to 122%
Moana Wave 8F	0.84 ± 0.14	0.82 ± 0.16 ($98\% \pm 25\%$)	<0.32 (0 to 38%)	67 to 186%
Moana Wave 10F	1.4 ± 0.2	1.2 ± 0.2 ($90\% \pm 18\%$)	<0.32 (0 to 23%)	63 to 143%

* All data are in ng Cd. The errors are one standard deviation of the propagated analytical errors.

exposure period (6 h). A much smaller fraction of the total Cd dissolved in Moana Wave sample 5C. It is unclear why.

The mean and standard deviation of the percentage of the Cd released to the seawater fraction from the bulk aerosol samples is $97\% \pm 18\%$. This result is consistent with the results of a study by Chester et al. (1986) in the remote North Atlantic who found that roughly 75% of the Cd in aerosol samples dominated by mineral aerosol from the Sahara Desert could be released into water buffered to a pH of 7. However, some caution should be used in comparing the result of the present work with that of Chester et al. (1986) because of differences between the methods used to determine aerosol dissolubility. The aerosol samples tested by Chester et al. (1986) were collected using a polyethylene mesh. Such aerosol collectors have a low efficiency for collecting the small particles on which most of the Cd is evidently present. Furthermore, the aerosol particles were removed from the mesh using a distilled water rinse before testing for Cd dissolubility. The distilled water rinse was meant to remove the sea-salt aerosol component, but considering the results of the present study, it probably also washed away much of the Cd.

3.8. Deposition of cadmium to the remote North Pacific surface waters

We believe that the Cd data collected for this research are representative of the spring and early summer only, when long range atmospheric transport from Asia is most active. This assertion is based on previous studies of long range atmospheric transport of mineral dust and anthropogenically derived trace metals to the North Pacific (Uematsu et al., 1983; Parrington et al., 1983; Duce et al., 1983; Merrill et al., 1989).

3.8.1. Wet deposition. Two different models were used to estimate the wet deposition rate of Cd. This was done because of the limitations and uncertainties intrinsic to both wet deposition models. The wet flux of Cd was first calculated by multiplying the volume weighted mean Cd concentration in rain by an estimate of the seasonal rainfall for the latitudinal band between 30°N and 45°N over the North Pacific. Maximum and minimum estimates were made using this model by varying the seasonal precipitation and the Cd concentration of the rain. For the minimum estimate, 2.0×10^{-3} m day^{-1} of rain (U.S. Navy, 1977) and the volume weighted mean Cd concentration of the rain collected on the Moana Wave in the

spring and early summer of 1986 (4.6 ng kg^{-1}) were used. For the maximum estimate, 2.7×10^{-3} m day^{-1} of rain and the volume weighted mean Cd concentration of the rain collected at Oahu in the spring of 1987 (25 ng kg^{-1}) were used. The resulting total wet deposition rates were multiplied by 0.93 (the magnitude of the excess component, Table 3) to obtain an estimate of the net wet Cd deposition. (Net deposition is the deposition of continentally derived atmospheric Cd.) The wet deposition rate of the recycled (i.e., oceanically derived) component was determined by subtracting the net from the total. The results are presented in Table 7 as Method 1.

The second wet deposition model that was used is based on the use of the scavenging ratio (S):

$$S = (C_{x,\text{rain}}/C_{x,\text{air}}) \cdot \rho,$$

where $C_{x,\text{rain}}$ is the concentration of the element of interest, x, in rain (in ng kg^{-1}); $C_{x,\text{air}}$ is the concentration of the element of interest in the air (in ng SCM^{-1}); ρ is the density of air at standard conditions (1.2 kg SCM^{-1}) to make S dimensionless.

The use of scavenging ratios to estimate wet deposition is described by Slinn (1983). For the present calculations, a value for S of 250 was used to obtain a minimum estimate of wet deposition and a value of 1000 was used for a maximum estimate. Both of these scavenging ratios are in the range of reliably measured values for either Cd or Pb in remote marine areas (Settle and Patterson, 1982; Arimoto et al., 1985; Davidson et al., 1985; Arimoto et al., 1987). The precipitation rate was also varied as in the previous model.

The total, net and recycled components of wet deposition were determined in the same manner as for Method 1. The results are presented in Table 7 as Method 2. Both methods result in similar estimates, although Method 2 produced somewhat lower estimates than Method 1. In both cases, net wet deposition is greater than recycled.

3.8.2. Dry deposition. Unlike wet deposition, total dry deposition cannot be directly estimated from the data collected for this research. The dry deposition rates for the net and recycled components were calculated separately and then added together to obtain the total dry deposition rate. The net deposition rate was calculated using three separate models. The recycled component of the dry depositional flux of Cd could be estimated using only one empirical method.

The first and simplest method was to use experimentally determined net dry deposition velocities and the geometric mean Cd concentrations adjusted by multiplication by 0.93 to account for the net-only component. Unfortunately, there are few data on dry deposition velocities for Cd. However, because Cd and Pb appear to have similar mass-size distributions, it will be assumed that they have similar dry deposition velocities. The net dry deposition velocity for Pb reported by Settle and Patterson (1982) (0.11 cm s^{-1}) will be used for a minimum estimate and the dry deposition velocity for ^{210}Pb of Turekian et al. (1977) (0.85 cm s^{-1}) will be used for a maximum estimate of the dry deposition rate for Cd(^{210}Pb can be used as an analog of non-marine Pb, Turekian et al. (1977)). The results of the calculation are presented in Table 8 as Method 1.

The other methods that were used to estimate the net dry deposition flux of Cd to the ocean are based on the similar models of Slinn and Slinn (1980) and Williams (1982). The major difference between these models is that the Williams (1982) model attempts to include the effect of white-caps

Table 7. *Wet deposition flux estimates*

Method	Flux			Description
	total	net	recycled	
1 (minimum)	9.8	9.4	0.4	Cr × P
(maximum)	63	60	3	Cr × P
2 (minimum)	4.5	4.3	0.2	scavenging ratio method
(maximum)	19	18	1	scavenging ratio method

Fluxes are given in ng Cd m^{-2} day^{-1}. For a full description of each method, see text.

Table 8. *Dry deposition flux estimates*

Method	Flux	Type	Description
1 (minimum)	0.8	net	$C_{air} \times V_{dd}$ $(Pb)_{exp}$.
(maximum)	6.2	net	$C_{air} \times V_{dd}$ $(Pb)_{exp}$.
2	1.1	net	using V_{dd} (diam.) from model of Slinn and Slinn (1980) with geometric mean atmospheric cadmium concentration.
3	1.7	net	using V_{dd} (diam.) from model of Williams (1982) with geometric mean atmospheric cadmium concentration.
4 (minimum)	0.3	recycled	using V_{dd} $(Pb)_{exp}$.
(maximum)	0.9	recycled	using V_{dd} $(Na)_{exp}$.
total dry deposition			
(minimum)	1.1		sum of the minimum estimates from methods 1 and 4.
(maximum)	7.1		sum of the maximum estimates from methods 1 and 4.

Fluxes are given in ng Cd m^{-2} day^{-1}. For a full description of each method, see text.

and breaking waves while the Slinn and Slinn (1980) model is for a smooth unbroken water surface. The two different models can give quite different results, particularly for elements present primarily on small particles (Arimoto and Duce, 1986).

For this study, the models have been generalized for hydrophilic aerosol particles. Particle growth in the deposition layer was calculated according to the model of Fitzgerald (1975), and the relative humidity was assumed to be 98 %. The wind speed was assumed to be 7 m s^{-1}, the climatological mean wind speed in the study area during the spring (US Navy, 1977). The broken surface transfer coefficient in the Williams (1982) model, K_{bs}, was set at a constant value of 7 cm s^{-1}. Williams (1982) recommends a value of 10 cm s^{-1} for K_{bs}, but Slinn (1983) has argued that while it is likely that K_{bs} is large, 10 cm s^{-1} is probably an overestimate.

Both models result in dry deposition velocities that are a function of particle size. To use these models properly, one must divide the atmospheric mass of Cd into fractional masses in a range of particle size intervals. Using the cascade impactor results, the Cd concentration was fit to a function of particle size using the procedure described in Patterson (1988). The results of the net dry deposition calculations are presented in Table 8 as Methods 2 and 3.

To calculate the dry deposition rate for the recycled component of atmospheric Cd, a model similar to dry deposition Method 1 was used. However, for the recycled component, the geometric mean Cd concentration was adjusted by multiplying it by 0.06 to obtain an estimate of the mean recycled Cd concentration. In addition, the net Pb dry deposition velocities were replaced by recycled Pb and sea-salt dry deposition velocities. The dry deposition rate of recycled Pb in remote regions has been estimated by Settle and Patterson (1982). From their data, a dry deposition velocity of 1.1 cm s^{-1} can be calculated. This value is used to obtain the minimum estimate of recylced Cd dry deposition. The maximum estimate for the dry deposition rate of recycled Cd was calculated using a sea-salt dry deposition velocity measured by McDonald et al. (1982) (3.4 cm s^{-1}). The resultant recycled Cd dry deposition rate estimates are presented in Table 8 as Method 4.

Methods 2 and 3 result in net dry fluxes that are encompassed by the maximum and minimum fluxes from Method 1, and are skewed toward the minimum estimate for Method 1. Contrary to the

case for wet deposition, recycled Cd can account for a considerable percentage of the total dry deposition. This is because the recycled Cd is on the large sea-salt aerosol particles which have a high dry deposition velocity.

3.8.3. Total (Wet + Dry) deposition. The wet and dry deposition estimates are summarized in Table 9. The dry depositional fluxes of Cd are substantially less than the wet fluxes for all models. This is the expected result for trace elements with submicrometer mmds and log-normal AMSDs (Arimoto and Duce, 1986).

We believe it would be unrealistic and an oversimplification of the system to present mean deposition estimates or try to constrain the estimates to produce a smaller range of depositional fluxes. The actual total depositional flux of Cd will vary from season to season and from year to year over a range perhaps similar to that reported in Table 9. This should be kept in mind when comparing these atmospheric deposition estimates to other sources of Cd in the surface waters of the North Pacific and to estimates of atmospheric deposition in other areas.

The data in Table 9 can be used to approximate the significance of the various components and processes to the overall total deposition. In general, the wet component probably accounts for about 80 to 90 percent of the overall total deposition of Cd to the remote North Pacific. Similarly, about 90 to 100 percent of the overall total deposition of Cd is net deposition.

3.9. Effect of atmospheric Cd deposition on the surface waters of the north Pacific Ocean

The primary sources of Cd in the surface waters of the central North Pacific are believed to be the horizontal mixing of nutrient and Cd-rich outcroppings of thermocline water with nutrient and Cd depleted central gyre surface water and the nutrient-like regeneration of Cd by upward vertical advection and diffusion of remineralized Cd in the thermoline (Boyle et al., 1981; Bruland, 1980). Very few estimates of the flux of Cd to the surface waters of the North Pacific have been made. However, rough estimates of these sources of Cd to the surface waters of the central North Pacific Ocean can be made using data from other studies, and these estimates can be used to obtain an estimate of the importance of the atmospheric deposition of Cd to these waters.

Table 9. *Summary of the estimates of the deposition of atmospheric cadmium to the remote North Pacific during the spring*

	Total (net + recycled)	Net	Recycled
wet	4.5 – 63	4.3 – 60	0.2 – 3
dry	1.1 – 7.1	0.8 – 6.2	0.3 – 0.9
total (wet + dry)	5.6 – 70	5.1 – 66	0.5 – 4

Fluxes are given in ng Cd m^{-2} day^{-1}.

Since the cycle of Cd in the open ocean appears to be closely linked to the phosphate cycle (Bruland, 1984), one method of estimating the vertical flux of Cd is to use the vertical phosphate flux together with a pseudo-stoichiometric relationship between Cd and phosphate (Bruland, 1980). For the present estimates, vertical phosphate fluxes of 120 nmol cm^{-2} yr^{-1} (Eppley and Peterson, 1979), 260 nmol cm^{-2} yr^{-1} (Duce, 1986), and 400 nmol cm^{-2} yr^{-1} (Bruland, 1980) were used. The Cd flux can be estimated from these data by using the linear relationship between the Cd and phosphate concentrations determined by Bruland (1980). The vertical Cd flux estimates calculated using this method are 130, 280 and 430 ng Cd m^{-2} d^{-1}, respectively.

Another method that can be used to estimate the vertical flux of Cd to the surface waters of the North Pacific is to use a very simple advection-diffusion model. The advection-diffusion equation is:

$$F = wR_t + K_z(dC/dz)$$

where F is the flux in ng m^{-2} d^{-1}, w is the vertical velocity in m day^{-1}, R_t is the concentration of Cd in the upper thermocline where the vertical concentration gradient of Cd is greatest, in ng m^{-3}, K_z is the vertical diffusion coefficient in m^2 day^{-1}, and dC/dz is the vertical concentration gradient of Cd at the top of the thermocline in ng m^{-4}.

To make the present estimate, w was assumed to be 0.01 m day^{-1} (Munk, 1966), R_t was assumed to be 2×10^4 ng m^{-3} (using the data of Bruland (1980)), K_z was assumed to be 10 m^2 s^{-1} (Gammon et al., 1982), and dC/dz was assumed to be 1.8×10^2 ng m^{-4} (from the vertical profile of Bruland (1980)). The resultant flux estimate is 3000 ng Cd m^2 d^{-1}. This estimate is approxi-

mately 10 times the estimates produced using the phosphate fluxes. The large difference between the two estimates is an indication of the uncertainty of the estimates.

The horizontal flux of Cd into the study region can also be estimated using the simple advection-diffusion model. Similar to the vertical advection-diffusion calculation, the equation used to estimate the horizontal flux of Cd to the central and eastern North Pacific is:

$$F = uR_h + K_h(dC/dx)$$

where F is the flux in ng m^{-2} d^{-1}, u is the horizontal velocity in m day^{-1}, u is the horizontal velocity in m day^{-1}, R_h is the Cd concentration where the horizontal concentration gradient is the greatest in ng m^{-3}, K_h is the horizontal diffusion coefficient in m^2 day^{-1}, and dC/dx is the horizontal concentration gradient of Cd in ng m^{-4}. In the estimates made for the present study, it was assumed that all horizontal transport of Cd is from the western North Pacific (Tchernia, 1980).

For the present estimates, R_h and dC/dx were determined from the data of Boyle et al. (1981) to be 1×10^4 ng m^{-3} and 7×10^{-3} ng m^{-4}, respectively. The values of K_h that were used are 10^2 m^2 day^{-1} for the low estimate and 10^3 m^2 day^{-1} for the high estimate (Kullenberg, 1982). The horizontal velocities used to make the minimum and maximum estimates are 0.05 m s^{-1} and 0.15 m s^{-1}, respectively. These horizontal velocities are in the range of the current velocities expected in this region (Tchernia, 1980). The minimum horizontal flux estimate is 0.6×10^8 ng m^{-2} d^{-1} and the maximum estimate is 2×10^8 ng m^{-2} d^{-1}.

To compare the atmospheric, vertical and horizontal fluxes of Cd to the study region, a simple box model can be constructed. The dimensions of the box will be defined as 35°N to 45°N and from 170°W to 150°W, roughly the area covered during the Moana Wave cruises, and down to a depth of 50m (the depth of the mixed layer in this area according to Bathen (1972) and Tabata and Giovando (1963)). The vertical and atmospheric fluxes of Cd into this box can be determined by multiplying the respective fluxes by the area of the lower and upper surfaces of the box, which are both 1.3×10^{12} m^2. The horizontal flux of Cd into the box can be determined by multiplying the horizontal flux by the area of the westward facing surface of the box, which is 5×10^7 m^2. The results of these calculations are presented together with an estimate of the total flux of Cd into the box in Table 10.

Table 10. *Summary of fluxes of cadmium to the surface waters of the study region (box model estimates)*

Source	Flux into box* (ng day^{-1})
horizontal advection-diffusion	$3 - 9 \times 10^{15}$
vertical advection-diffusion	$0.2 - 3 \times 10^{15}$
atmospheric deposition	$0.007 - 0.09 \times 10^{15}$
total flux into box	$3 - 12 \times 10^{15}$

* The box is defined as the volume enclosed by 35°N to 45°N by 170°W to 150°W, to a depth of 50 m (see text).

The results in Table 10 show that the horizontal flux of Cd into the mixed layer of the ocean in the study area can be equal to or up to 40 × more than the vertical flux. Furthermore, the atmospheric flux is negligible compared to either of the other two sources. This result is consistent with the cycle of Cd in the open ocean (Bruland, 1984). Cd has a "nutrient-type" vertical distribution in the open ocean, characterized by a minimum concentration in the surface mixed layer, a strong concentration gradient in the thermocline, and relatively high concentrations in the deep water. If the atmosphere were the primary source of Cd to the surface waters of the open ocean, then one would expect a concentration maximum in the surface mixed layer. If atmospheric deposition of Cd to the open ocean were a minor but significant source of Cd in the surface mixed layer, then one would not expect the very strong Cd concentration gradient in the thermocline, and periodic surface maxima may be observed. Since such phenomena have not been observed, it seems likely that results of our very crude box model calculation are correct.

4. Conclusions

The primary source of Cd (>90%) in the remote North Pacific atmosphere is the long-range transport of continental anthropogenic material.

However, there may be other sources which contribute to the excess component, and the importance of these other sources cannot be determined without further study.

Sea-salt aerosol generation is probably the second most important source of Cd to the remote North Pacific atmosphere, comprising $< 10\%$ of the total mass of atmospheric. Mineral aerosol transport from Asia is apparently a negligible source, comprising $< 1\%$ of the total atmospheric Cd.

The Pb/Cd ratios of the bulk aerosol samples were relatively constant and were similar to estimates of the Pb/Cd atmospheric emissions ratio and the Pb/Cd ratio in a very distant area (the Mediterranean Sea). Further study of the Pb/Cd ratio is warranted to determine what controls this ratio and its value as a tracer for modeling studies.

Atmospheric Cd is removed primarily by wet depositional processes, with dry deposition comprising only about ten to twenty percent of the total. Furthermore, the net deposition (i.e., the deposition of the excess, presumably anthropogenic, component) of Cd is much greater than the deposition of recycled (i.e., oceanically derived) Cd.

The atmospheric deposition of Cd is insignificant as a source of Cd found in the surface waters of the central North Pacific Ocean.

Virtually 100% of the Cd in the bulk particulate samples was soluble in seawater, dissolving within 6 h.

A latitudinal gradient of the surface seawater Cd concentration was observed. The Cd concentration decreased with decreasing latitude in our study area.

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