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Concentrations, Sources, and Fluxes of Trace Elements in the Remote Marine Atmosphere of New Zealand

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The concentrations of trace elements were determined for aerosol particle, dry deposition, and precipitation samples collected from Ninety Mile Beach on the North Island of New Zealand. Major objectives for the studies, which were conducted as part of the SEAREX (Sea/Air Exchange) Program, were to investigate the concentrations, sources and geochemical cycling of trace elements in the westerly wind field over the South Pacific Ocean. Many of the trace elements were associated with natural materials such as atmospheric sea salt or mineral aerosol. The mean concentration of atmospheric sea salt (~7.9 μg m^{-3}) was 5 to 30% higher than that predicted by models based on relationships between salt concentrations and wind speed. Mineral aerosol particles were transported through the atmosphere from Australia, and the concentration of atmospheric dust (~200 ng m^{-3}) was lower than the expected long-term average due to the fact that the sampling at Ninety Mile Beach was conducted during the climatological low-dust season. Estimates of the atmospheric deposition rates suggest that eolian material constitutes a significant fraction of the nonbiogenic deep-sea sediments of the region. Certain trace elements, including Ag, Cd, Cu, I, Mo, Pb, Sb, Se, Ni, and Zn, were enriched over the concentrations expected from natural sources. Anthropogenic emissions from Australia and New Zealand evidently affected the concentrations of several of these elements on local to regional scales.

INTRODUCTION

A major objective of the multi-institutional SEAREX (Sea/Air Exchange) Program was to investigate the concentrations, sources and geochemical cycling of a variety of trace substances in the atmosphere over the North and South Pacific Ocean. The first two SEAREX experiments were at Enewetak in 1979 (11°20'N, 162°20'E) and at American Samoa in 1981 (14°15'S, 170°34'W). Results of the earlier trace element studies conducted for SEAREX have been published by Duce et al. [1980, 1983], Arimoto and Duce [1987], and Arimoto et al. [1985, 1987, 1989].

We present here information on trace element concentrations and fluxes determined from atmospheric samples collected at the northern tip of the North Island of New Zealand (34°33'S, 172°45'E, see Figure 1). The principal objectives for these experiments, which took place from June to August 1983, were (1) to measure the concentrations of trace elements in the atmosphere, (2) to determine the sources for the trace elements, and (3) to estimate the rates of exchange across the air/sea interface. Studies on atmospheric phosphorus that were conducted during the SEAREX experiments at New Zealand have been previously published [*Chen et al.*, 1985] as have studies on organic compounds [*Gagosian*, 1986; *Gagosian et al.*, 1987; *Atlas and Giam*, 1986; *Sicre et al.*, 1990] and mercury [*Fitzgerald*, 1986].

Mass balance calculations have shown that atmospheric deposition supplies geochemically significant quantities of various trace elements, nitrogen compounds, and synthetic organic chemicals to the world's oceans [*Group of Experts on Scientific Aspects of Marine Pollution* (GESAMP), 1989]. The GESAMP assessment focussed on comparing the global atmospheric and riverine inputs of trace substances to the world's oceans. A major conclusion of that study was that overall rivers supply a greater quantity of particulate trace metals to the oceans than is delivered by atmospheric deposition, but much of the river-borne particulate material is deposited nearshore. As a result the atmospheric pathway was thought to be especially important for trace elements in the open ocean. Moreover, the GESAMP assessment indicated that atmospheric transport and deposition most strongly affect the soluble forms of trace elements: the riverine and atmospheric inputs of soluble Fe, P, Cu, Ni, and As were judged to be approximately equal while the atmospheric pathway was dominant for soluble Zn, Cd, and Pb.

The transport and deposition of mineral aerosol have been shown to be highly episodic, and the sporadic inputs of mineral dust and other types of aerosol particles to the oceans via atmospheric deposition are important as a source of (1) suspended particles [*Uematsu et al.*, 1983], (2) deep-sea sediments [*Blank et al.*, 1985; *Sirocko and Sarnthein*, 1989]; and (3) a variety of dissolved trace elements including Al [*Orians and Bruland*, 1985; *Prospero et al.*, 1987; *Maring and Duce*, 1987], micronutrients such as Fe [*Duce*, 1986; *Martin and Gordon*, 1988], and pollution-derived elements such as Pb [*Schaule and Patterson*, 1981]. Collectively, these studies have shown that the atmospheric transport and deposition of trace elements not only effects the chemistry but also the biology of the oceans.

Certain trace elements associated with mineral dust, especially Fe and Mn, are important for atmospheric chemistry because they catalyze the oxidation of sulfur from S(IV) to S(VI) and in so doing affect the *p*H of clouds and fogwater [*Jacob et al.*, 1989]. *Pandis and Seinfeld* [1989] modeled a fog event and suggested that the Fe^{3+} catalyzed pathway for S(IV) oxidation was nearly comparable in yield to that involving H_2O_2. Other studies have shown that various iron oxides are involved in photochemical reactions tied to the atmospheric S

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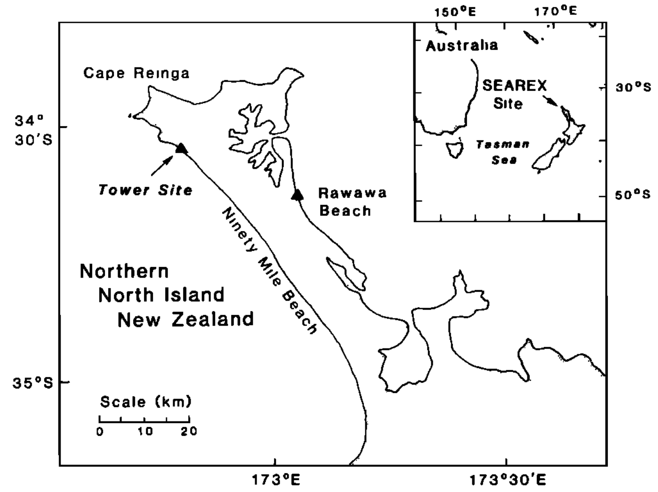

Fig. 1. Location of the Sea/Air Exchange sampling sites on the North Island of New Zealand. Precipitation samples also were collected from the Tasman Sea region.

cycle [*Faust et al.*, 1989]. Thus the chemistry of trace elements in the atmosphere is linked to dynamic cycles of broad significance.

METHODS

Field Operations

Samples of aerosol particles, dry deposition, and rain were collected from May to August 1983 from the tops of two aluminum, scaffold-type, walk-up towers erected on Ninety Mile Beach of the North Island of New Zealand (Figure 1). The sampling site was in the westerly wind regime, approximately 1500 km southeast of Australia. The towers were situated on a vast sandy beach with dunes 1 to 2 km inland, and the towers were approximately 15 km from the northernmost tip of the island. Our intention was to collect samples representative of the clean atmosphere of this remote region, and the towers were used to minimize the collection of locally generated sea-salt particles and other materials from nearby sources. One tower was 20 m tall, and it was used for the collection of aerosol samples. Wet and dry deposition samples were collected from the top of a second tower that was 15 m tall.

Power for the site was supplied by an 85 kW diesel generator. The exhaust from the generator was cleaned through the use of a custom-made system that included a catalytic converter (Engelhard PTX Diesel Purifier, model 623D, Exhaust Controls, Incorporated, Union, New Jersey), a baghouse (Torit TD-486-55, Donaldson Company, Minneapolis, Minnesota), and HEPA filters (Flanders Filters, Incorporated, Washington, North Carolina). To ensure that emissions from the generator did not contaminate the samples, the exhaust from the generator could be vented at either of two strategic locations depending upon wind conditions.

Sensors and equipment for monitoring wind speed and direction, condensation nuclei (CN), ozone, and rainfall, were installed on the towers. Information obtained with this equipment was used to automatically control the aerosol samplers [*Schwartze et al.*, 1988]. The sampling pumps automatically shut off whenever (1) the ambient wind speed fell below a threshold of 1.3 m s^{-1}, (2) the winds were not from the preselected oceanic sampling sector, which was from 200° to 290°, or (3) the CN concentration exceeded 750 CN cm^{-3}. A scientific watch was maintained continuously at the site, and when meteorological conditions were favorable, sampling was conducted 24 hours a day. A radar system was used for tracking precipitation and the position of ships upwind of the sampling site. All sampling was interrupted whenever emissions from ships or motor vehicles threatened to contaminate the samples. Aerosol sampling also was interrupted during precipitation.

A total of 11 bulk aerosol samples was collected with custom-made samplers constructed of polyethylene and polypropylene; as discussed below, the number of samples was limited, owing to conditions that were unfavorable for sampling. Each aerosol sampler was enclosed in a separate polypropylene rain shelter that was mounted on the top rail of the 20-m-tall tower. Each acid-washed sampler held two 24-cm-diameter acid-washed Whatman 41® filters (Whatman, Incorporated, Clifton, New Jersey). We summed the concentrations determined from double Whatman 41® filters for the aerosol sampling because of concerns over the collection efficiency of this filter medium for submicrometer particles [*Lodge*, 1986]. We note that concerns over the collection efficiency of these filters have been addressed by others [*Lowenthal and Rahn*, 1987; *Watts et al.*, 1987; *Prospero* 1989]. The two filters were separated by a polyethylene screen and a 12-mm-thick polypropylene support grid ("egg-crate"). In general, most of the mass (~95%) of the elements was concentrated on the first filter, but for lead and copper the collection efficiency of the first filter was lower, about 75% to 80% of the total mass collected.

Twelve size-separated aerosol particle samples were collected with modified Sierra model 235 cascade impactors (Andersen Samplers, Incorporated, Atlanta, Georgia). The standard units were modified to provide discrete samples of ultragiant (>10 μm diameter) particles. Modifications to the cascade impactor (CI) consisted of the addition of a stage (denoted stage 0) to the top of the impactor and the machining of an additional slot into stage 1. The calculated 50% cutoff characteristics, in micrometers aerodynamic equivalent diameter (μmAED), of the modified impactor are as follows (A. A. P. Pszenny, personal communication, 1983):

stage 0 = 16.8 μmAED
stage 1 = 9.3 μmAED
stage 2 = 3.6 μmAED
stage 3 = 2.1 μmAED
stage 4 = 1.0 μmAED
stage 5 = 0.52 μmAED
filter < 0.52 μmAED

The high-volume aerosol samplers (bulk samplers and cascade impactors) operated at ~68 m^3 h^{-1}. Initial plans were to sample until the volumes of the samples approached 10,000 m^3, but it became necessary to collect samples with smaller volumes (>3000 m^3) owing to unfavorable meteorology. Normal airflow patterns over the South Pacific were disrupted by the El Niño/Southern Oscillation (ENSO) in 1983 [e.g., *Rasmusson and Wallace*, 1983; *Harrison*, 1987], and this large-scale disturbance clearly affected the conditions at the sampling site during the SEAREX studies. Approximately 32% of the time, the winds and other meteorological conditions were suitable for aerosol particle sampling. Detailed information on meteorological conditions during sampling is available from the authors.

Paired blanks for the aerosol particle samples were obtained from filter assemblies that were not connected to pumps but were located in the same shelters as the samples. These blanks were used to assess the passive accumulation of materials on the filter during the time the aerosol samples were on the tower. A blank was collected for each high-volume bulk and size-separated aerosol particle sample. The concentrations of trace elements in the samples were corrected for the paired blanks.

Blank and sample aerosol filters were loaded and unloaded in a clean bench housed in a laboratory built especially for the trace element studies. During transport to and from the tower, the air sampling cassettes and deposition samplers were enclosed in acid-washed plastic bags. All sample handling on the ground and on the towers was done by persons wearing clean-room garb and clean plastic gloves. The exposed aerosol filters were hermetically sealed in acid-washed bags and stored frozen until aliquots were removed for analysis. The filter holders were washed between collections with dilute acid and water purified with the use of a Milli-Q® system (Millipore Corporation, Bedford, Massachusetts).

Low-volume samples (~1 m^3 h^{-1}) were collected using acid-washed 0.4-μm porosity, 47-mm diameter Nuclepore® filters (Nuclepore Corporation, Pleasanton, California). For these collections, single membrane filters were mounted in an acid-washed Nuclepore® polycarbonate filter holder. Each low-volume unit, along with a blank, was enclosed in an individual, custom-made, polypropylene precipitation shelter. The low-volume samples were collected without wind-sector controls over ~1-day intervals; a total of 37 daily low-volume samples were collected, but the use of these data was limited to studies of precipitation scavenging.

Dry deposition samples were collected with a custom-made, low-density polyethylene sampler designed and built at the California Institute of Technology by C. C. Patterson and D. M. Settle. This device had both upward facing and downward facing collection surfaces (both surfaces 57.5-cm diameter). The sampling unit we used was designed to provide some information on the relative importances of the various mechanisms involved in the dry deposition process, and it was deployed on the shorter (15 m tall) of the two sampling towers. It is worth noting that dry deposition sampling is especially difficult: a vigilant watch is required because the collector must be covered in event of rain or if other circumstances threaten to contaminate the sample. After the collection of each dry deposition sample, the plate was covered, enclosed in an acid-washed plastic bag, and transported to the trace-element laboratory. The deposits on the plate were removed by rinsing the plate with double-distilled 1.5 N HNO_3 while gently scraping the surface of the plate with a quartz rod. The dry deposition samples collected in this manner were stored frozen in acid-cleaned polyethylene bottles until aliquots were removed in a class 100 clean room for analysis. The plate was rigorously cleaned with ultra-pure acid between collections.

Rain samples were collected on an event basis, using a custom-made, low-density polyethylene funnel (77.5-cm diameter) and a polyethylene bottle. Samples were collected from three sites: (1) the top of the 15 m tower on Ninety Mile Beach, (2) Rawawa Beach on the eastern side of the North Island (see Figure 1), and (3) the Research Vessel (R/V) *Tangaroa* during a cruise in the Tasman Sea. Before each collection, the precipitation sampler was rinsed with 0.1% HNO_3 and Milli-Q® water. Shortly after collection, the samples were acidified to *p*H 1 to 2 with HNO_3 redistilled in quartz and then frozen until aliquots were removed for analysis.

Meteorological support was provided by the New Zealand Meteorological Service (NZMS) during the experiments at Ninety Mile Beach. Current and forecast surface and upper air maps were obtained several times each day through the use of a radiofacsimile receiver. Computer-generated, low-level trajectory analyses and forecasts covering a 72-hour back trajectory and a 24-hour prognostic trajectory also were received from the NZMS each day. In addition, special weather forecasts for SEAREX were prepared by the forecast center in Wellington. If meteorological forecasts indicated that unfavorable sampling conditions were likely to persist, the aerosol samplers were carefully covered with acid-cleaned, custom-made, tight-fitting polyethylene lids. The dry deposition and rain collectors were kept covered whenever they were not in use.

Chemical Analyses

Chemical analyses were performed using atomic absorption (AA) spectrophotometry and instrumental neutron activation (INAA). Details of the analytical procedures have been published by *Duce et al.* [1983] and *Arimoto et al.* [1985]. The elements analyzed by AA were Ag, Ca, Cd, Cu, Fe, K, Mg, Mn, Mo, Na, Pb, V, and Zn. The AA analyses were performed using flameless and flame techniques with a model 5000 atomic absorption spectrophotometer with Zeeman background correction (Perkin-Elmer Corporation, Norwalk, Connecticut). A short irradiation INAA procedure (~120 s irradiation, ~120 s decay period) using the 2 MW reactor (thermal neutron flux of 4×10^{12} n cm^{-2} s^{-1}) of the Rhode Island Nuclear Science Center was used to determine the concentrations of Al, Br, Ca, Cl, I, Mg, Mn, Na, and V. The concentrations of Ba, Ce, Co, Cs, Eu, Fe, Hf, Rb, Sb, Sc, Se, Ta, Tb, Th, and Zn were determined in different aliquots of the samples through a long irradiation INAA procedure, which included an irradiation time of 85,000-125,000 s, a decay period of 1,800,000-4,300,000 s, and counting for ~80,000 s. The detection limits for each element vary as a function of sampling time and blank concentrations, and this information is available from the authors upon request.

RESULTS AND DISCUSSION

Trace Element Concentrations Over Northern New Zealand

The weather in northern New Zealand (called Northland) typically is dominated by a progression of anticyclones and troughs of low-pressure. Climatologically, the winds over Northland are from the southwest [*de Lisle and Kerr,* 1964], and the frequency of winds from that direction is greatest in the austral winter and spring. During the experiments, the passage of the high- and low-pressure systems often brought air to Ninety Mile Beach that was uncontaminated based on the concentrations of condensation nuclei and ozone. Sampling conditions were the best during June and August, but during July there were several extended periods when the air mass trajectories reaching Northland had passed over more southern parts of New Zealand. As mentioned above, the strong ENSO in 1983 affected the conditions during the SEAREX experiments, and this phenomenon reduced the number of samples that could be collected.

The concentrations of radon in the atmosphere were measured during the SEAREX experiments, and the data for this trace constituent were used to assess the continental influences on the air sampled during the experiments. When the air mass trajectories indicated that air being sampled had come from the Southern Ocean south of Tasmania, the radon concentrations were low, of the order of a few tenths of 1 pCi $^{-3}$ (R. Arimoto et al., unpublished data, 1983). At other times similarly low Rn concentrations were obtained when the transport was directly from Australia, across the Tasman Sea. Samples influenced by local sources were not considered representative of the clean marine atmosphere of the South Pacific. Therefore, with the exception of data for some daily samples, which are specifically identified, the results presented below are only for the samples that were collected under clean marine conditions.

Atmospheric sea salt. The concentration of atmospheric sea salt at Ninety Mile Beach, as represented by Na, was typical of that expected in the westerly wind field of the South Pacific [e.g., *Erickson et al.*, 1986]. The geometric mean Na concentration at the top of the 20-m tower based on the AA and INAA analyses of eleven high-volume samples was 7.9 μg m^{-3} (Table 1), and thus the sea salt concentration was approximately 26 μg m^{-3}. Differences between the Na concentrations determined by AA and INAA were not significant as determined by a paired t-test (probability for chance occurrence, $p = 0.28$).

The mean wind speed at the site during the sector-controlled aerosol sampling was 9.1 m s^{-1}. Based on the numerical relationship between wind speed and atmospheric salt con-

TABLE 1. Concentrations of Trace Elements in Aerosol Particles from New Zealand

Element	Method*	Units**	*n*†	Arithmetic Mean	Standard Deviation	Geometric Mean
Br	INAA	ng	11	43	14	41
Ca	AA	ng	11	240	120	210
Ca	INAA	ng	11	230	79	220
Cl	INAA	µg	11	13.6	4.4	13
I	INAA	ng	11	1.1	0.52	0.95
K	AA	ng	11	360	160	330
Mg	AA	µg	9	0.84	0.33	0.80
Mg	INAA	µg	11	0.87	0.28	0.84
Na	AA	µg	11	8.4	2.1	8.1
Na	INAA	µg	11	7.9	2.5	7.6
Al	INAA	ng	11	18	8.1	16
Ba	INAA	pg	8	230	140	190
Ce	INAA	pg	10	13	3.7	12
Co	INAA	pg	11	3.4	1.6	3.0
Cs	INAA	pg	11	1.9	0.82	1.7
Eu	INAA	pg	11	0.28	0.12	0.25
Fe	AA	ng	11	10	5.4	8.4
Fe	INAA	ng	11	11	4.8	9.6
Hf	INAA	pg	9	0.77	0.38	0.68
Mn	AA	pg	11	150	86	130
Mn	INAA	pg	9	120	60	100
Rb	INAA	pg	11	49	40	37
Sc	INAA	pg	11	3.9	1.8	3.5
Tb	INAA	pg	3	0.21	0.086	0.20
Th	INAA	pg	11	2.4	1.0	2.2
V	AA	pg	10	39	14	35
V	INAA	pg	11	49	30	40
Ag	AA	pg	5	26	29	12
Cd	AA	pg	5	36	59	16
Cu	AA	pg	8	120	150	82
Mo	AA	pg	10	20	20	13
Pb	AA	pg	10	210	200	130
Sb	INAA	pg	11	4.4	3.1	3.7
Se	INAA	pg	11	97	30	93
Zn	INAA	pg	8	130	100	91

*AA stands for atomic absorption, INAA for instrumental neutron activation analysis.
**Units per cubic meter at standard temperature and pressure.
†*n* stands for number of samples.

centration published by *Lovett* [1978], one would predict a salt concentration of 18 µg m^{-3}, which is approximately 10 to 30% lower than that determined from the aerosol particle samples. If the standard deviation of the wind speed (1.8 m s^{-1}) is taken into account, as recommended by *Erickson et al.* [1986], the predicted salt concentration would be only ~5% to 15% lower than the measured value. Even though the difference in the observed and predicted salt concentrations is small, Ninety Mile Beach has an extensive surf zone, and it is possible that some locally generated sea-salt aerosol raised the concentrations slightly.

The elements exhibiting significant correlations with Na in bulk aerosols, i.e., a probability for chance occurrence of less than 1% ($p < 0.01$), include Br, Cl, K, and Mg (Table 2). In addition, Na was correlated with some elements, such as Sc, that are generally associated with mineral aerosol [*Rahn*, 1976; *Duce et al.*, 1976, 1983] and with several elements whose concentrations are enriched over those expected from sea water and mineral dust. These correlations suggest the possibility, discussed in further detail below, that some of the sea-salt and other types of aerosol particles existed as internal mixtures [e.g., *Andreae et al.*, 1986].

It is also possible that the correlations among certain elements were in part a consequence of the multicollinearity of variables caused by meteorology, i.e., the trace element concentrations covaried as a result of short-term trends in meteorological conditions [e.g., *Henry*, 1989]. For example, iodine was well correlated with sodium and the other sea-salt elements, but the I/Na ratio in the aerosol samples was enriched several hundred-fold over seawater levels (see "Enriched Elements" below). Some of the enrichment of I in aerosol particles results from the physical processes involved in the generation of the sea-salt aerosol [*Seto and Duce*, 1972], but the sorption of gas phase I-containing species also may contribute to the enrichment [*Cicerone*, 1981; *Duce et al.*, 1983].

Previous studies [e.g., *Duce et al.*, 1983] as well as data presented below have shown that sea salt and I are concentrated on aerosol particles of different sizes. Thus it is difficult to invoke a plausible physical model, other than a broad response to meteorological conditions, that explains the correlation between I and Na in the bulk aerosol particle samples. Other elements that were enriched over the levels expected from seawater, including Se, Sb, and Mo, also were correlated with Na; this is a further indication that meteorological factors, such as removal by wet deposition or the passage of frontal systems, may have caused the concentrations of the various particulate trace species to covary.

The cascade impactor data were used to evaluate the enrichments and depletions of several trace elements relative to

TABLE 2. High-Volume Samples: Correlations Among Trace Elements

	Ag	Al*	Ba*	Br*	Ca	Cd	Ce*	Cl*	Co*	Cs*	Cu	Eu*	Fe	Hf*	I*
Ag	1														
Al*		1													
Ba*			1												
Br*				1											
Ca					1										
Cd						1									
Ce*		0.64		*0.76*			1								
Cl*				*0.96*			*0.77*	1							
Co*		0.63		*0.78*			*0.91*	*0.82*	1						
Cs*		*0.73*					0.61		0.66	1					
Cu	0.92										1				
Eu*		0.63						*0.69*	0.61	0.66		1			
Fe		0.65							0.61	0.64			1		
Hf*		*0.73*		0.63			0.66	*0.75*	*0.73*	*0.76*		*0.70*		1	
I*		0.56		*0.86*			*0.75*	*0.82*	*0.73*			0.56		0.69	1
K				0.65			0.58	0.68	0.65				0.57	0.53	
Mg*				*0.98*			*0.73*	*0.99*	*0.76*			0.62		0.67	*0.80*
Mn*		0.57								0.61				0.62	
Mo				*0.82*	*0.78*		*0.74*	*0.74*	*0.77*						0.68
Na*				*0.95*			*0.76*	*0.99*	*0.80*			0.66		*0.74*	*0.80*
Pb					0.58										
Rb*				*0.79*	*0.73*		*0.86*	*0.87*	*0.87*	0.64		0.64		0.65	0.56
Sb*					*0.72*				0.63						
Sc*		*0.89*		*0.72*			*0.86*	*0.82*	*0.89*	*0.73*		*0.76*		*0.81*	*0.78*
Se*				*0.71*				*0.83*	0.61			*0.80*		0.64	0.56
Ta*															
Tb*								0.59							
Th*		*0.72*		*0.72*			*0.79*	*0.88*	*0.84*	*0.78*		*0.87*		*0.82*	0.66
V*		0.60								0.58				0.72	
Zn															

	K	Mg*	Mn*	Mo	Na*	Pb	Rb*	Sb*	Sc*	Se*	Ta	Tb*	Th*	V*	Zn
K	1														
Mg*	0.66	1													
Mn*			1												
Mo	0.65	*0.75*		1											
Na*	0.68	*0.98*		*0.74*	1										
Pb	0.63					1									
Rb*	*0.77*	*0.83*		*0.75*	*0.87*		1								
Sb*	*0.81*			0.69		*0.88*	*0.71*	1							
Sc*		*0.76*			*0.80*		*0.78*		1						
Se*	*0.70*	*0.82*			*0.80*		*0.73*		*0.72*	1					
Ta*											1				
Tb*												1			
Th*	0.66	*0.81*			*0.86*		*0.90*		*0.90*	*0.86*			1		
V*			*0.81*											1	
Zn															1

*Elements analyzed by instrumental neutron activation. All others analyzed by atomic absorption spectrometry.

Only correlations with a probability for chance occurrence of less than 5% ($p < 0.05$) are shown; correlations with $p < 0.01$ are italicized. Not all samples had data for all elements, and thus the critical values for the correlation coefficients varied among pairs of elements.

the composition of sea water (Table 3*a*). On the largest particles (CI stages 0 and 1) the Br/Na concentration ratio was essentially the same as that typical of bulk seawater, but Br was depleted by 15 to 30% relative to Na on CI stages 2 to 5. In contrast, Br was enriched by a factor of 2.5 on the backup filters of the CIs; similar enrichments of Br on final filters of CIs have been observed for aerosol particle samples from earlier SEAREX experiments [*Duce et al.*, 1983; *Arimoto et al.*, 1987] and over the North Pacific [*Zhou et al.*, 1990].

The Cl to Na concentration ratio for the aerosol particles collected on CI stages 0 to 3 was slightly depleted (~5%) relative to bulk seawater, and the Cl/Na ratio became increasingly depleted relative to seawater on CI stages 4 and 5 and on the backup filter (Table 3*a*). The depletion of Cl in submicrometer aerosol particles is well documented [e.g., *Robbins et al.*, 1959; *Moyers and Duce*, 1972; *Okada et al.*, 1978; *Maenhaut et al.*, 1983], and model calculations by *Brimblecombe and Clegg* [1988] indicate that methane sulfonic acid and nitric acid may expel HCl from the sea-salt aerosol particles. More recently, Keene et al. (1990) suggested that photochemical reactions involving some unidentified Cl-containing species could be responsible for the observed Cl deficits.

The alkali and alkaline earth elements generally were in seawater proportions, especially in the particles greater than 1 μm AED (Table 3*a*). The apparent enrichments of Ca, Mg, and K relative to Na in some of the smaller particle fractions probably were due to the higher relative proportions of mineral dust on the impactor stages that collect the smaller particles. As shown in Figure 2, the mass-particle size distribution (MSD) of Na was such that a significant fraction of the total mass of sea salt occurred on particles greater than 10 μm AED.

Mineral aerosol. Three potential sources for the Al in the aerosol particle samples will be discussed; these are (1) oceanic dissolved Al that became incorporated in the sea-salt aerosol, (2) mineral dust particles transported from Australia, and (3) particles generated in the surf zone. First, we show that the contribution of dissolved Al is most likely negligible. The concentration of Na in seawater collected near the SEAREX site was 0.38 mol L^{-1} [*Chen et al.*, 1985], the dissolved Al concentration for seawater from the Tasman Sea reported by *Maring and Duce* [1987] was 9 nmol L^{-1}, and a typical enrichment of Al in sea-salt aerosols is of the order of 5000 [*Weisel et al.*, 1984]. Thus one would predict an Al/Na mass ratio of $\sim 1.4 \times 10^{-4}$ in the sea-salt aerosols based on the seawater data. The arithmetic mean Al/Na ratios for the first three stages of the cascade impactor, where most of the mass of sea salt occurred, ranged from 4.2×10^{-3} to 6.7×10^{-3}. The difference between the observed and predicted Al/Na ratios indicates that only a few percent of the Al in the cascade impactor samples can be attributed to ocean-derived dissolved Al.

Air-mass trajectory analyses presented by *Merrill* [1989] demonstrate that Australia was a probable source of mineral aerosol particles and other continentally-derived materials during the SEAREX experiments in New Zealand. The atmospheric transport of dust from Australia to New Zealand was first reported in the scientific literature at the beginning of the twentieth century, and particularly strong events were noted in 1902 [*Dixon and Dove*, 1903; *Marshall*, 1903], in 1928 [*Marshall and Kidson*, 1929; *Healy*, 1970], and in 1929 [*Kidson*, 1930]. In more recent studies, Australia has been identified as the most likely source of the soil dust sampled at Hokitika on the South Island of New Zealand [*Collyer et al.*, 1984]. These authors used air-mass trajectory analyses, an assessment of antecedent weather in Australia, and mineralogical data to investigate the source regions for the dust and to study its transport through the atmosphere.

Mineral dust particles are produced via the weathering of crustal rock that typically contains approximately 8% Al by weight [*Taylor and McLennan*, 1985]. The geometric mean concentration of Al for the high-volume bulk aerosol samples collected using the automatic sampling control system was 16 ng m^{-3}. Based on these data, a representative atmospheric dust concentration for the two and one-half months of sampling at Ninety Mile Beach was of the order of 200 ng m^{-3}.

The mineral dust concentration we observed at New Zealand during the austral winter is comparable to a seasonally adjusted dust concentration for Norfolk Island, which is typically of the order of 100 ng m^{-3} but ranges from ~30 to 200 ng m^{-3} [*Prospero et al.*, 1989]. Based on the distances of these sites from the major dust source regions in Australia, one might expect the dust concentrations to be lower at New Zealand because it is farther from Australia than Norfolk Island. However, the relative efficiency of transport from Australia to Norfolk compared with New Zealand is likely to be much more complex than a simple linear function of the distances between the sites. Therefore it is probably too simplistic to expect that the concentrations of mineral aerosol at the two sites would be in direct proportion to their distances from the source region.

The SEAREX aerosol samples from Ninety Mile Beach were collected during the climatological low-dust season, and therefore the observed mineral aerosol concentrations were less than one would expect for a representative annual average. Dust storms in the arid and semi-arid source regions of Australia peak in the austral spring and summer, especially from October to January, and the climatology of the dust storms is reflected in the record of mineral dust concentrations over the South Pacific [*Prospero et al.*, 1989]. Moreover, their data show that at Norfolk Island the concentrations of atmospheric dust during June, July, and August (i.e., the austral winter) are approximately 6 times lower than those during the high-dust austral summer.

The mass-particle size distribution for Al (Figure 3), shows that the mineral aerosol concentrations on CI stages 4 and 5 and on the backup filter were variable, suggesting that the MSD

TABLE 3*a*. Elemental Ratios for Cascade Impactor Samples: Sea-Salt Elements

Ratio		Seawater*	Stage 0 16.8**	Stage 1 9.3	Stage 2 3.6	Stage 3 2.1	Stage 4 1.0	Stage 5 0.52	BUF <0.52
Br/Na	Mean	6.2×10^{-3}	6.4×10^{-3}	6.0×10^{-3}	5.1×10^{-3}	4.7×10^{-3}	4.2×10^{-3}	4.8×10^{-3}	15×10^{-3}
	Standard deviation		0.39×10^{-3}	0.51×10^{-3}	0.83×10^{-3}	0.50×10^{-3}	0.82×10^{-3}	1.4×10^{-3}	7.0×10^{-3}
	n†		9	12	12	12	12	12	12
Ca/Na	Mean	38×10^{-3}	34×10^{-3}	29×10^{-3}	24×10^{-3}	32×10^{-3}	30×10^{-3}	37×10^{-3}	43×10^{-3}
	Standard deviation		8.2×10^{-3}	5.3×10^{-3}	10×10^{-3}	7.9×10^{-3}	14×10^{-3}	29×10^{-3}	31×10^{-3}
	n		9	12	11	11	12	12	11
Cl/Na	Mean	1.8	1.7	1.7	1.7	1.7	1.6	1.4	1.2
	Standard deviation		0.052	0.19	0.14	0.096	0.13	0.27	0.59
	n		9	12	12	12	12	12	12
Mg/Na	Mean	120×10^{-3}	110×10^{-3}	110×10^{-3}	110×10^{-3}	110×10^{-3}	110×10^{-3}	170×10^{-3}	380×10^{-3}
	Standard deviation		5×10^{-3}	8×10^{-3}	15×10^{-3}	12×10^{-3}	10×10^{-3}	160×10^{-3}	880×10^{-3}
	n		9	12	12	12	12	12	12
K/Na	Mean	37×10^{-3}	32×10^{-3}	34×10^{-3}	31×10^{-3}	32×10^{-3}	35×10^{-3}	37×10^{-3}	65×10^{-3}
	Standard deviation		4.0×10^{-3}	4.0×10^{-3}	4.8×10^{-3}	9.6×10^{-3}	11×10^{-3}	18×10^{-3}	74×10^{-3}
	n		7	8	8	8	8	8	8

* Seawater data compiled by *Broecker and Peng*, [1982].

**Aerodynamic equivalent mass median diameter.

† *n* stands for number of samples.

TABLE 3*b*. Elemental Ratios for Cascade Impactor Samples: Crustal Elements

Ratio		Crustal* Rock	Stage 0 16.8**	Stage 1 9.3	Stage 2 3.6	Stage 3 2.1	Stage 4 1.0	Stage 5 0.52	BUF <0.52
Ce/Al	Mean	800 x 10^{-6}	680 x 10^{-6}	750 x 10^{-6}	710 x 10^{-6}	3800 x 10^{-6}	7100 x 10^{-6}	5500 x 10^{-6}	1400 x 10^{-6}
	Standard deviation		370 x 10^{-6}	440 x 10^{-6}	520 x 10^{-6}	3200 x 10^{-6}	9900 x 10^{-6}	4500 x 10^{-6}	930 x 10^{-6}
	n†		8	11	11	6	4	8	3
Co/Al	Mean	120 x 10^{-6}	150 x 10^{-6}	160 x 10^{-6}	140 x 10^{-6}	1100 x 10^{-6}	400 x 10^{-6}	740 x 10^{-6}	440 x 10^{-6}
	Standard deviation		51 x 10^{-6}	61 x 10^{-6}	53 x 10^{-6}	1800 x 10^{-6}	460 x 10^{-6}	610 x 10^{-6}	460 x 10^{-6}
	n		9	11	10	6	5	6	9
Cs/Al	Mean	46 x 10^{-6}	87 x 10^{-6}	250 x 10^{-6}	210 x 10^{-6}	1900 x 10^{-6}	640 x 10^{-6}	460 x 10^{-6}	280 x 10^{-6}
	Standard deviation		30 x 10^{-6}	550 x 10^{-6}	330 x 10^{-6}	2500 x 10^{-6}	520 x 10^{-6}	560 x 10^{-6}	150 x 10^{-6}
	n		7	12	11	9	7	7	7
Eu/Al	Mean	11 x 10^{-6}	14 x 10^{-6}	43 x 10^{-6}	45 x 10^{-6}	90 x 10^{-6}	140 x 10^{-6}	84 x 10^{-6}	66 x 10^{-6}
	Standard deviation		5 x 10^{-6}	94 x 10^{-6}	92 x 10^{-6}	95 x 10^{-6}	140 x 10^{-6}	81 x 10^{-6}	53 x 10^{-6}
	n		6	12	11	8	4	4	5
Fe/Al	Mean	440 x 10^{-3}	560 x 10^{-3}	800 x 10^{-3}	540 x 10^{-3}	760 x 10^{-3}	760 x 10^{-3}	950 x 10^{-3}	420 x 10^{-3}
	Standard deviation		70 x 10^{-3}	740 x 10^{-3}	250 x 10^{-3}	740 x 10^{-3}	1100 x 10^{-3}	910 x 10^{-3}	290 x 10^{-3}
	n		9	12	11	10	10	10	10
Hf/Al	Mean	72 x 10^{-6}	83 x 10^{-6}	44 x 10^{-6}	35 x 10^{-6}	82 x 10^{-6}	190 x 10^{-6}	69 x 10^{-6}	23 x 10^{-6}
	Standard deviation		130 x 10^{-6}	21 x 10^{-6}	14 x 10^{-6}	79 x 10^{-6}	160 x 10^{-6}	39 x 10^{-6}	
	n		9	12	10	5	5	3	1
Sc/Al	Mean	140 x 10^{-6}	205 x 10^{-6}	320 x 10^{-6}	200 x 10^{-6}	310 x 10^{-6}	270 x 10^{-6}	240 x 10^{-6}	130 x 10^{-6}
	Standard deviation		27 x 10^{-6}	390 x 10^{-6}	120 x 10^{-6}	340 x 10^{-6}	400 x 10^{-6}	210 x 10^{-6}	130 x 10^{-6}
	n		9	12	11	11	10	10	10
Th/Al	Mean	130 x 10^{-6}	130 x 10^{-6}	140 x 10^{-6}	130 x 10^{-6}	250 x 10^{-6}	350 x 10^{-6}	410 x 10^{-6}	130 x 10^{-6}
	Standard deviation		31 x 10^{-6}	99 x 10^{-6}	58 x 10^{-6}	201 x 10^{-6}	370 x 10^{-6}	270 x 10^{-6}	69 x 10^{-6}
	n		8	12	11	6	6	6	6
V/Al	Mean	750 x 10^{-6}	1500 x 10^{-6}	2300 x 10^{-6}	2400 x 10^{-6}	1800 x 10^{-6}	3200 x 10^{-6}	3000 x 10^{-6}	5900 x 10^{-6}
	Standard deviation		160 x 10^{-6}	1300 x 10^{-6}	3500 x 10^{-6}	1100 x 10^{-6}	2600 x 10^{-6}	2300 x 10^{-6}	5100 x 10^{-6}
	n		6	5	7	6	6	7	10

* Crustal rock data from *Taylor and McClennan*, [1985].

**Aerodynamic equivalent mass median diameter.

† *n* stands for number of samples.

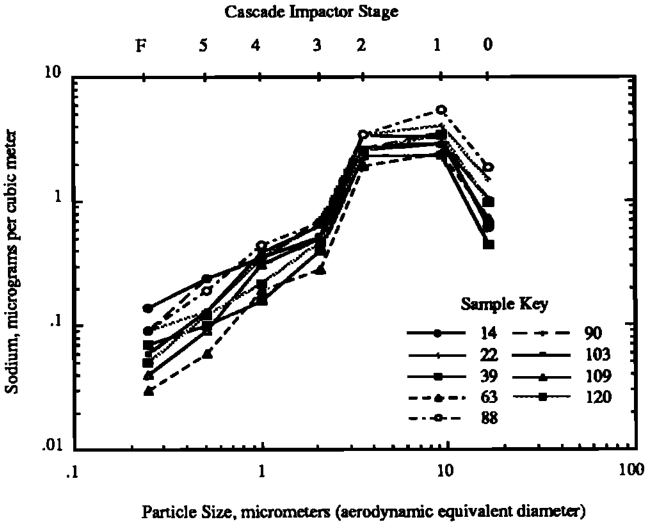

Fig. 2. Mass-particle size distribution of sodium determined from high-volume cascade impactor samples.

of mineral aerosol was bimodal or multimodal. In three of the cascade impactor samples, the concentration of Al for one or more of the CI stages was below detection limits, and thus the data for those samples are not plotted in Figure 3. Even though the Al concentrations in the finer particle-size fractions were more variable than those of Na, the mass median diameters of both elements occurred on particles between 9.3 and 16.8 µm AED (i.e., more than 50% of the total mass of both elements occurred on particles larger than 9.3 µm AED).

We recognize the possibility that some mineral particles from the surf zone of Ninety Mile Beach were injected into the atmosphere along with the sea salt. However, it is unlikely that any such particles originating from the local surf zone were a major component of the aerosol. As discussed above, neither the sea-salt concentrations nor the mineral aerosol concentrations were appreciably higher than those predicted by models or expected from complementary data, respectively. The neutron activation data could not be used to distinguish the precise origins of either sea salt or mineral particles based, but *Sicre et al.* [1990] have used data for long-chain alkenones to investigate the origins and atmospheric transport of marine-derived aerosol particles. Their results demonstrate the importance of local sources for marine particles at Ninety Mile Beach, but their methods cannot be used to evaluate the impact of the particles that are actually produced in the surf zone.

Several elements (i.e., Ce, Co, Cs, Eu, Fe, Hf, Sc, Th, and V) generally existed in proportions relative to Al which are similar to those in crustal rock, indicating that mineral aerosol dominated their concentrations at New Zealand (Table 3*b*). The greatest apparent departures from the crustal ratios occurred on the CI Stages that collected the fine particles. Much of this difference is most likely due to the low concentrations of the elements in the fine particles and hence analytical uncertainty.

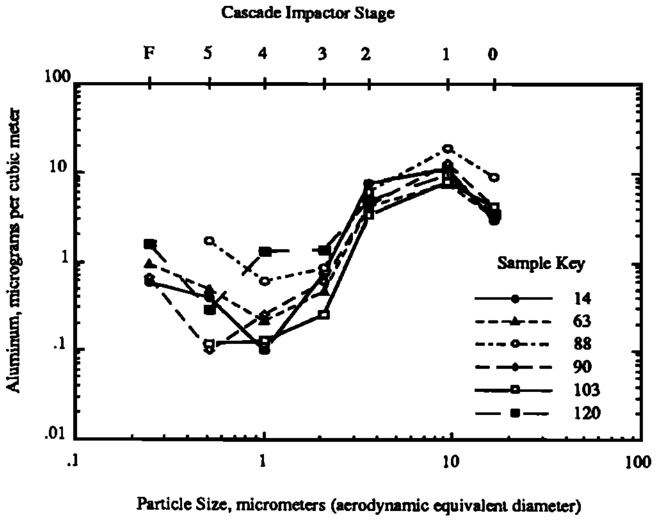

Fig. 3. Mass-particle size distribution of aluminum determined from high-volume cascade impactor samples.

We expect that these deviations from crustal ratios also may be a consequence of differences in the sources for the various mineral aerosol modes, but contributions from other sources not related to mineral aerosol also may have been responsible. This is known to be true for V, which is released into the atmosphere as a result of the burning of heavy fuel oil [*Zoller*, 1973; *Rahn*, 1981; *Duce et al.*, 1983].

Internal mixtures of sea salt and mineral aerosol particles. Previous SEAREX studies at Enewetak [*Duce et al.*, 1983; *Arimoto et al.*, 1985] showed that the mass median diameter for sea-salt particles was of the order of 10 μm AED, while that for mineral aerosol particles was much smaller, ~2 μm AED. The present results indicate the mass median diameters for Al and Na at Ninety Mile Beach were similar, and while it is not possible to provide a definitive explanation for the difference in MSDs for mineral aerosol, the possibility that the salt and mineral aerosol existed as internal mixtures is briefly discussed below.

Maenhaut et al. [1983] previously observed that the size distributions for sea salt and mineral aerosol were similar over the eastern equatorial Pacific, and these authors recognized that coagulation processes in the atmosphere may have been the cause. The occurrence of internally mixed aerosol particles was documented through single-particle analyses by *Andreae et al.* [1986], and they hypothesized that the mixtures resulted from a series of processes involving the activation of cloud condensation nuclei (CCN), the scavenging of mineral particles by cloud droplets, and the coalescence of cloud droplets containing mineral particles with droplets containing salt. These authors emphasized that the internal mixing process would effectively bring together various types of chemical reactants, including atmospheric sea salt, mineral aerosol, sulfate-rich particles, and anthropogenic aerosol particles. We observed that the concentrations of Al in the finer particle fractions of the New Zealand samples were more variable than those of Na, and therefore a subpopulation of the dust particles evidently was not mixed with sea salt. Furthermore, if mixing did occur, it clearly was of lesser importance for the enriched elements discussed below.

Anomalously enriched elements. Several trace elements (Ag, Cd, Cu, I, Mo, Pb, Sb, Se, Ni, and Zn) were substantially enriched over the levels expected from sea salt or mineral aerosol. In general, these anomalously enriched elements (AEEs) were poorly correlated with one another, but some significant correlations did exist (Table 2). Often multivariate statistics are used to unravel the relationships in data sets containing concentrations for a suite of trace elements [e.g., *Henry et al.*, 1984; *Gordon*, 1988]. However, a constraint on the minimum number of samples needed for a robust interpretation makes this type of analysis unwarranted for the Ninety Mile Beach data set. Despite these data limitations, some general observations about the relationships among the enriched elements can be made. The discussion begins with Se and I, whose concentrations are thought to be affected by gas-phase species and then continues with Pb, Sb, Mo, Cd, Ag, and Zn, which are are thought to be more strongly influenced by anthropogenic emissions.

Selenium was correlated with iodine in the bulk aerosol samples with a probability of chance occurrence of less than five percent ($p < 0.05$). Both of these elements are thought to enriched in the marine aerosol as a result of the evasion of gas-phase species from the oceans (e.g., *Mosher and Duce* [1983, 1987], *Zafiriou* [1974], *Rasmussen et al.* [1982], respectively). Emissions of biogenic substances have been implicated in the enrichment process, but the issue is not fully resolved because volatile anthropogenic substances also may be involved.

The MSD for Se was such that the highest concentrations of this element occurred on particles ≤ 3.6 μm AED (Figure 4). The MSD of selenium is presumably controlled by steady state processes that depend upon (1) the evasion of gas-phase Se from the oceans due to biological activities in surface waters, (2) the emission of Se-containing compounds from anthropogenic sources, (3) the sorption of the Se-containing compounds by the aerosol particles, (4) the evolution of the aerosol particle-size spectrum as a function of production, transport, and deposition, and (5) the scavenging and removal of gases and particles by wet deposition. There were insufficient data to reliably determine the MSD of iodine, but the existing data suggested that this element also tended to be most highly concentrated in the smaller particle-size fractions. In addition, the cascade impactor data show that the MSDs of I and Se were clearly different from the MSDs of atmospheric sea salt or mineral aerosol.

The geochemical cycling of Pb presents one of the clearest cases for a global-scale perturbation of trace metal chemistry caused by human activities. Before anthropogenic emissions became the dominant source for Pb, the Pb in the atmosphere was divided more-or-less equally between soil dusts and volcanic emissions (see review by *Patterson and Settle* [1987]). At present most of the atmospheric Pb originates from motor vehicles and from metal smelters [*Patterson and Settle*, 1987; *Nriagu*, 1989]. Our data indicate that at Ninety Mile Beach, Pb was enriched about 30- to 50-fold over crustal abundances; these estimates are based on the Pb/Al ratios of *Mason* [1966] and *Taylor and McLennan* [1985]. The geometric mean atmospheric Pb concentration we determined (130 pg m^{-3}) was comparable to that determined by *Patterson and Settle* [1987]. Unlike Se or I, the MSD of Pb in remote ocean regions (Figure 4) is most strongly influenced by two factors: (1) the evolution of the particle-size spectrum as the pollution aerosol is transported from the continents to the open ocean, and (2) the incorporation of Pb into sea-salt particles. The sorting of the aerosol particles by size is affected by coagulation, dry deposition, and wet deposition. Some Pb is recycled from the oceans along with atmospheric sea-salt particles, but this amounts to only 1 to 15% of the Pb in the remote marine atmosphere [*Settle and Patterson*, 1982].

A highly significant correlation between Sb and Pb was evident in the New Zealand data for the bulk high-volume aerosol particles, suggesting that Sb, too, was derived from pollution sources. *Rahn* [1976] observed that atmospheric Sb exhibited an enormous range of enrichments relative to crustal rock (<5 to 24,000), and *Rahn and Lowenthal* [1984] have used this element in their scheme for identifying regional sources

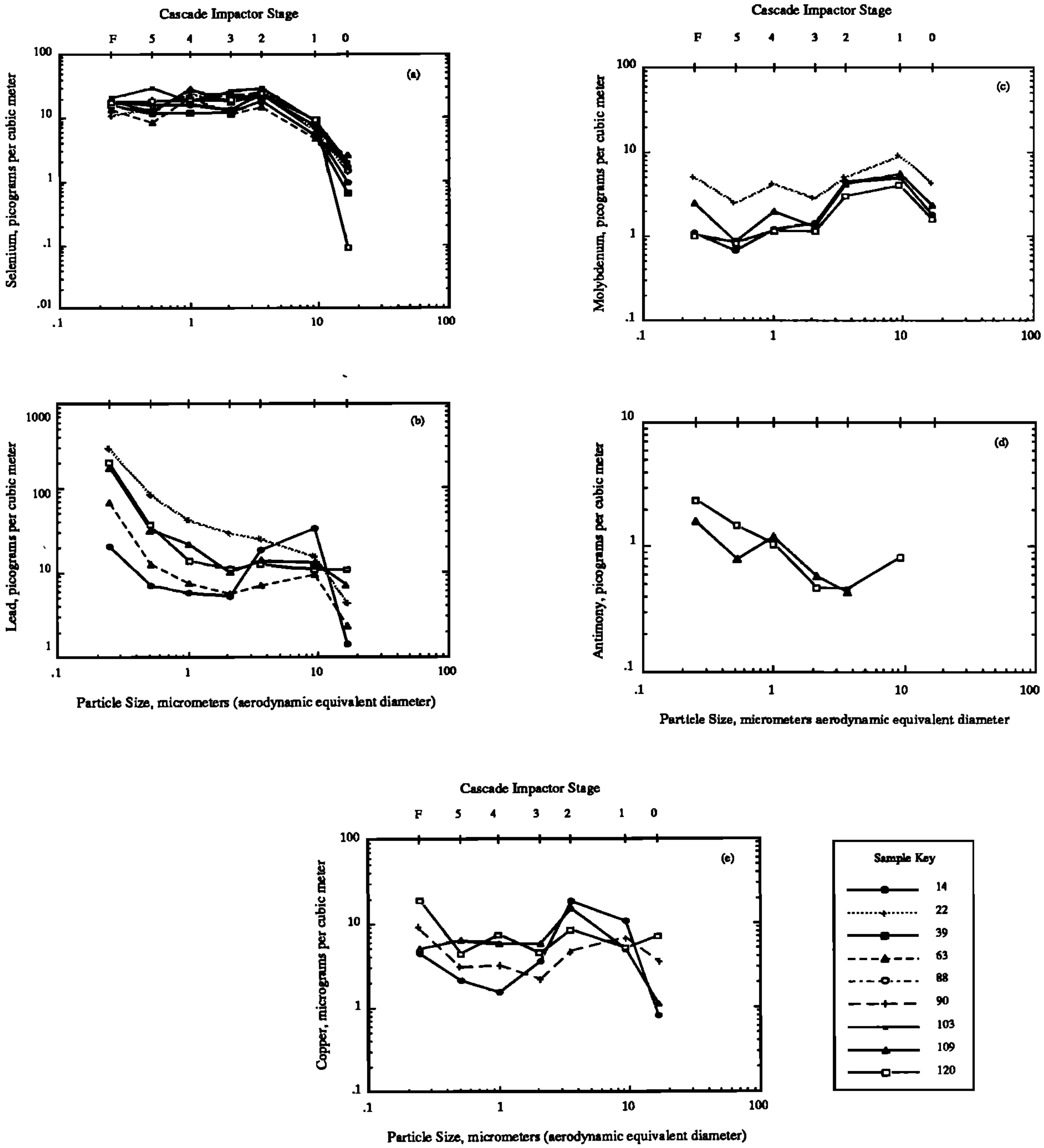

Fig. 4. Mass-particle size distribution of enriched trace elements determined from high-volume cascade impactor samples: (*a*) selenium, (*b*) lead, (*c*) molybdenum, (*d*) antimony, (*e*) copper.

for atmospheric pollutants. The enrichments of Sb in aerosol particles are thought to be due to emissions from coal combustion and from municipal waste incinerators [e.g., *Nriagu*, 1989], but details of the biogeochemical cycling of Sb in the marine atmosphere are limited.

The Ninety Mile Beach cascade impactor samples showed that high concentrations of Pb and Sb occurred on the backup filters, i.e., particles ≤ 0.52 μm AED. The cascade impactor data for Sb are not plotted owing to the fact that Sb was below detection limits for all CI stage 0 samples and because only three of the samples had a complete set of data for the remaining stages. In general, a pattern of high trace element concentration in submicrometer particles is consistent with materials derived from that high-temperature sources that often are associated with air pollution [e.g., *Church et al.*, 1989]. As discussed above, trace elements that are enriched in aerosol particles as a result of gas-to-particle conversion also tend to be concentrated on small particles, but at present there is no evidence for volatile antimony-containing compounds.

Relatively little is known about the atmospheric chemistry of Mo, but the concentration of Mo in the bulk aerosol particle samples from Ninety Mile Beach was correlated with Sb (Table 2), suggesting that some of the Mo originated from pollution sources. *Rahn* [1976] observed that Mo was enriched relative to crustal rock in some atmospheric samples, but he concluded that the data were too limited for a detailed discussion of this element. In our samples, the highest concentration of Mo occurred on CI stage 1, but Mo also exhibited high concentrations on the backup filters of the impactors, which is another indication that a pollution source was important. The Mo/Al ratio for the large particles captured by first two stages of the cascade impactor ranged from 0.88 x 10^{-3} to 3.5 x 10^{-3}; this is approximately 50 to 200 times higher than the ratio in crustal rock. On the other hand, the Mo/Na ratio for CI stages 0 and 1 were 13 x 10^{-6} and 2.1 x 10^{-6}, respectively, which compares reasonably well with the Mo/Na ratio in seawater [3.1 x 10^{-6}, Collier, 1985], suggesting that the large-particle Mo is associated with sea salt.

The concentrations of three other enriched elements, Cd, Ag, and Zn, were too low to reliably determine their MSDs. Cadmium and zinc are generally thought to be influenced by a mixture of natural and anthropogenic sources [*Church et al.*, 1989; *Nriagu*, 1989], but information relative to the sources for Ag is severely limited. The limited aerosol data from New Zealand do not permit us to characterize the sources for these elements in detail. This is particularly unfortunate because Cd and Zn are biogeochemically important in the ocean, and their distributions in the ocean are tied to the chemistry of certain nutrients [*Bruland*, 1983]. However, the geochemistry of Cd recently has been investigated [*Patterson and Duce*, 1990]. These authors concluded that most of the Cd in the marine atmosphere was transported from the continents and that pollution sources were important.

Details concerning the fluxes of Zn in the atmosphere are generally lacking, but some data exist for the concentrations of Zn in atmospheric samples from the Pacific [*Duce et al.*, 1983; *Arimoto et al.*, 1985, 1987]. More provocative than the data for Zn concentrations are results suggesting that the cycling of Zn in the atmosphere is affected by chemical reactions involving mineral aerosol and anthropogenic acids. In rain water from the western Mediterranean region, the solubility of Zn varies with pH, and the partitioning of Zn is thought to be controlled by adsorption-desorption equilibria [*Losno et al.*, 1988]. These authors also proposed that calcium carbonate associated with desert dusts at least partially neutralizes the various acids in rain, and therefore the mineral particles not only affect the *p*H of the rain but also indirectly influence the Zn partitioning in rainwater.

Dry Deposition of Particulate Trace Elements

The dry deposition velocities of aerosol particles are affected by an aerodynamic resistance in the atmospheric boundary layer and by a surface resistance in the laminar sublayer adjacent to the receptor surface [e.g., *Slinn and Slinn*, 1981]. Aerodynamically large particles (> ~1 μm diameter) are mainly removed from the atmosphere by gravitational settling, and these particles may skid across streamlines and impact on receptor surfaces. The movements of small particles (≤ ~0.01 μm diameter) are dominated by Brownian motion, and diffusion generally is most important for their fluxes. Particles of intermediate size (~ 0.1 μm diameter) are not effectively removed by dry deposition, and consequently in the absence of precipitation, the aerosol particles of this approximate size tend to have relatively long residence times in the atmosphere. *Giorgi* [1988] suggested that when averaged over long-term simulations, the dry deposition velocities of nucleation mode particles (<0.1 μm diameter) are 0.015 to 0.15 cm s^{-1}; accumulation mode particles (0.1 to 2 μm diameter) are 0.002 to 0.03 cm s^{-1}; and coarse particles (>2 μm diameter) are 1.25 to 3.5 cm s^{-1}. For comparison, the parameterizations for dry deposition velocities recommended by *GESAMP* [1989] are as follows:

1. Submicrometer aerosol particles = 0.1 cm s^{-1}.
2. Supermicrometer crustal particles, not associated with sea salt = 1.0 cm s^{-1}.
3. Large sea-salt particles and associated materials = 3.0 cm s^{-1}.

The uncertainties associated with the GESAMP parameterizations for the submicrometer aerosol particles and supermicrometer crustal particles were estimated to be plus or minus a factor of 3; for the large sea-salt particles the uncertainty was concluded to be a factor of 2.

The fine particle fraction (<2 μm diameter) is particularly important for pollutant transport studies because it contains much of the air-borne particulate load of trace-metal contaminants [*Rahn*, 1976; *Church et al.*, 1989]. Unfortunately, the uncertainties in the dry deposition velocities of submicrometer particles are especially large; for example, *Sievering* [1984] concluded that the dry deposition velocities of submicrometer aerosols were uncertain by an order of magnitude or more.

A passive artificial collector with both upward and downward facing collection surfaces was used to sample dry deposition at New Zealand. We are aware that the results obtained with this collector may be considered limited in interpretive value because one cannot relate the results obtained for this surrogate surface to a natural receptor, such as the surface of the ocean. Such criticisms have been summarized by *Hicks et al.* [1980]. In a reassessment of the techniques used for measuring dry deposition, *Hicks* [1986] suggested that results obtained with artificial collectors are most credible for rapidly falling (i.e., generally large) particles. He also indicated that for particles small enough to be influenced by turbulence, the significance of results obtained with artificial collectors diminishes rapidly.

The importance of large particles in the dry deposition to marine regions has been inferred from measurements using surrogate surfaces by *Arimoto et al.* [1985, 1987], *Dulac et al.* [1989], and *Schneider et al.* [1990] Sensitivity analyses by *Dulac et al.* [1989] have shown that the modelled dry deposition rates of trace elements are strongly affected by assumptions made about the mass-particle size distributions of the elements. More specifically their analyses demonstrated that assumptions about the right tail of the distribution (i.e., the giant particles) significantly affected the modelled dry deposition rate.

Following the experiments of *Davidson* [1977] and *Muhlbaier-Dasch* [1983], we used a dry deposition sampler with an upward- and a downward-facing collection surface to determine the relative importance of gravitational settling in the dry deposition process. In almost all of the cases, the upward facing surface collected more material than the downward facing surface (Table 4). More important the deposition rates were consistent between the two samples, demonstrating that the measured dry deposition rates are reproducible and thus can be compared with those from other studies using similar collection devices. The percentage of the dry deposition due to sedimentation was calculated as follows:

$$\%\ \text{Sedimentation} = 100 \times \frac{\text{Collection}_{Up} - \text{Collection}_{Down}}{\text{Collection}_{Up}}$$

where Collection_{Up} is the dry deposition flux to the upward facing surface and Collection_{Down} is the dry deposition flux to the downward facing surface.

For all of the elements analyzed, with the exception of Zn in the first sample (which probably was contaminated with this element), the percentage of the dry deposition attributable to gravitational settling was fifty percent or greater. Thus as suggested by *Hicks* [1986], sedimentation was the mechanism responsible for most of the dry deposition of aerosol particles to the artificial collector. Further, there was no clear difference

TABLE 4. Dry Deposition of Trace Elements

Sample	Hours Exposed	Dry Deposition Rate, ng cm^{-2} d^{-1} Na	Mg	K	Zn
1 Down	46.45	1300	110	039	0.056
1 Up		530	660	230	0.035
% Sedimentation		76	83	83	-60
V_d, cm s^{-2}		7.4	8.8	8.6	5.8
2 Down	59.48	1500	0180	66	0.018
2 Up		580	690	230	0.10
% Sedimentation		74	74	72	83
V_d, cm s^{-2}		7.2	7.3	7.9	5.8

Sample	Dry Deposition Rate, ng cm^{-2} d^{-1} Fe	Pb	Cd	Cu	Mn
1 Down	1.0	0.0027	≤0.0010	0.0062	0.018
1 Up	2.5	0.016	≤0.0010	0.013	0.080
%Sedimentation	59	83		50	77
V_d, cm s^{-2}	2.0	2.1		1.5	4.8
2 Down	1.3	0.0049	≤0.00035	0.0029	0.020
2 Up	3.5	0.012	≤0.00083	0.023	0.091
%Sedimentation	62	59		87	78
V_d, cm s^{-2}	3.5	2.2		3.9	6.5

in the relative importance of sedimentation for the dry deposition rates of the elements derived from different sources.

The dry deposition sampler we used was subject to two possible problems: first, some material deposited on the collection surfaces may not have adhered, and second, phoretic effects may have introduced artifacts. The problem of particle loss clearly was more serious for the downward-facing surface, and any such sampling artifacts would of course invalidate the simple interpretation of the data presented above. On the other hand, observations of the deposition plate during sampling showed that soon after deployment it became coated with a moist layer of sea salt. Even though it is not possible to evaluate quantitatively the collection and retention efficiency of the sampler, this circumstantial evidence suggests that the loss of particles from the collection surfaces was not a serious problem. Neither are there data that can be used to evaluate any artifacts that result from thermophoresis, electrical forces, or other phoretic processes.

Dry deposition velocities (V_d) for several of the trace elements were calculated by dividing the dry deposition rates (Collection_{Up}) determined from the deposition plate by the atmospheric concentrations (C_{Air}):

$$V_d = \frac{\text{Collection}_{Up}}{C_{Air}}$$

The dry deposition velocities for the sea-salt elements (Na, Mg, and K) ranged from 7.2 to 8.8 cm s^{-1} (Table 4); these are comparable to the dry deposition velocities for sea salt determined with a similar deposition plate deployed during the previous SEAREX experiments at Enewetak and American Samoa [*Arimoto et al.*, 1985, 1987]. The dry deposition velocity for sea salt was less than a factor of 3 higher than the GESAMP value.

The dry deposition velocity for Na was 2 to 4 times higher than that for Fe, and this result appears paradoxical because the evidence presented above indicates that at least some of the sea-salt and mineral dust particles evidently were internally mixed. However, the difference in deposition velocities may yet be explained by differences in the MSDs of sea salt and mineral aerosol. This is because the aerosol sampling apparatus we used does not effectively collect or separate particles >10 μm, and these giant particles are important for dry deposition. We note that the difficulty in collecting giant particles is not unique to our studies: for example, *Dulac et al.* [1989] have stressed the need for developing samplers capable of collecting and separating giant particles.

More compelling is the fact that the deposition velocities observed for mineral aerosol at New Zealand were higher than at other sites where a similar deposition collector was deployed. For Fe, which was considered representative of mineral dust, V_d was of the order of 2.8 cm s^{-1}; this is higher than the V_d determined from the previous SEAREX studies at Enewetak (0.41 cm s^{-1} [*Arimoto et al.*, 1985]) or American Samoa (1.8 cm s^{-1} [*Arimoto et al.*, 1987]) and also higher than that measured at Oahu (0.36 to 0.98 cm s^{-1} [*Schneider et al.*, 1990]), where the same deposition plate was deployed. The fact that relatively high deposition velocities were observed at New Zealand may be another indication that the internal mixing occurred and that the particle aggregates increased the deposition velocity for mineral aerosol.

The dominant role of giant particles in the dry deposition of mineral aerosol has been recognized by *Betzer et al.* [1988]. More recently, *Schneider et al.* [1990] presented evidence that the particle-size spectra for mineral particles in the air and in dry deposition samples differ significantly. In particular these authors observed that the mass median diameter for particles collected by a dry deposition sampler was 8.6 μm while that for the aerosol particles in the air was much smaller, 2.6 μm. Furthermore, they found that the particle-size distribution for the material collected by the dry deposition sampler was narrower, i.e., the standard deviation was smaller, than that for the particles in air. These observations are further evidence that giant particles are important for dry deposition, and they are directly relevant to our results from New Zealand.

Wet Deposition of Trace Elements

Precipitation samples were collected from three sites: at the main SEAREX sampling facility at Ninety Mile Beach, at Rawawa Beach on the eastern side of the North Island, and during a cruise aboard the R/V *Tangaroa* in the Tasman Sea. The small number of precipitation samples collected does not permit a detailed site-by-site comparison of the data, but in general the concentrations of trace elements in precipitation from Ninety Mile Beach were comparable to if not lower than those from the other sites. All of the precipitation data are combined in Table 5, and volume-weighted means and standard deviations are calculated for the ensemble of all samples.

The relationship between the concentration of a trace substance in air and in precipitation is often evaluated by calculating a scavenging ratio (SR), i.e., the concentration of the substance of interest in rain (C_{Rain}, ng kg^{-1}) divided by the corresponding concentration in aerosol particles (C_{Air}, ng m^{-3}). Scavenging ratios commonly are adjusted for the density of air (ρ, ~1.2 kg m^{-3}) so that the units are dimensionless but calculated on a per unit mass basis:

$$\text{SR} = \frac{\rho C_{Rain}}{C_{Air}}$$

While the calculation of a scavenging ratio is straightforward, the meaningfulness of SRs is often debated. First, the concentration of the substance in the air most frequently is determined for samples collected at or near ground level, but the concentration of the substance aloft probably is a

TABLE 5. Concentrations of Trace Elements in Precipitation Samples From New Zealand

Date in 1983	Local Time	Volume mL	[Na] $\mathrm{mg\ kg^{-1}}$	[Mg] $\mathrm{mg\ kg^{-1}}$	[K] $\mathrm{mg\ kg^{-1}}$	[Zn] $\mathrm{\mu g\ kg^{-1}}$	[Fe] $\mathrm{\mu g\ kg^{-1}}$	[Pb] $\mathrm{ng\ kg^{-1}}$	[Cd] $\mathrm{ng\ kg^{-1}}$	[Cu] $\mathrm{ng\ kg^{-1}}$	[Mn] $\mathrm{ng\ g^{-1}}$
June 24	1115	900	0.23	0.03	≤0.010	0.04	0.2	15	≤2.9	5	12
June 30	0726	900	2.66	0.33	≤0.113	0.08	0.5	90	≤0.6	5	11
June 30	0811	300	4.03	0.49	≤0.157	0.24	0.3	62	≤0.5	8	20
June 30	1020	200	3.44	0.42	≤0.135	0.54	0.3	85	≤0.8	7	17
June 30	1544	1200	4.23	0.52	≤0.168	0.05	0.6	59	≤3.8	12	21
July 19	0829	500	5.88	0.71	0.24	0.15	1.6	21	≤0.4	12	38
July 24*	1520	1500	2.13	~0.24	≤0.08	0.01	1.4	530	4.9	18	52
July 24*	1543	700	3.02	~0.37	≤0.113	0.01	0.7	180	≤2.3	16	30
Aug. 10	1203	1000	0.70	0.09	≤0.45	nd	0.8	nd	nd	nd	nd
Aug. 10	1223	700	0.17	0.02	≤0.010	nd	0.7	nd	nd	5	6
Aug. 20	0913	1900	1.11	0.14	≤0.56	0.41	2.2	nd	nd	7	50
Aug. 20	1049	1900	0.17	0.02	≤0.01	0.1	0.5	nd	nd	nd	10
Aug. 20	1144	700	0.42	0.05	≤0.02	nd	nd	nd	nd	nd	nd
Sept. 12†	0700	650	5.78	0.71	0.25	0.06	0.4	118	≤2.9	23	37
Sept. 14†	1650	2000	2.13	0.26	≤0.09	nd	3.3	186	≤4.6	39	218
Volume weighted mean			1.95	0.24	<0.25	<0.14	<1.3	<180	<4.9	<16	<56
Volume weighted standard deviation			0.43	0.05		<0.05	<0.3	<54		<3.4	<19

nd not detected.

*Samples collected from Rawawa Beach.

†Samples collected from the Tasman Sea.

more important influence on its concentration in precipitation. Thus if the concentration of a substance changes with height, the meaningfulness of SRs is diminished. Second, meteorological conditions, especially relative humidity [*Engleman*, 1988], exert a major influence on the concentrations of trace substances in rain, and these effects are transferred directly into the empirical scavenging ratios.

The calculation of meaningful SRs requires that the aerosol particle and precipitation samples are collected over representative time scales, and SRs may be calculated in two different ways depending upon their intended application. Often SRs are calculated on an event basis (SR_{event}) and these are useful for studying the processes actually responsible for the wet deposition of gases and particles. In practice aerosol particle sampling often is interrupted by precipitation, and therefore the air and rain samples are not collected simultaneously. Another complicating factor relative to time scales is that precipitation samples often are collected over periods of minutes while it may take hours or days to collect a sufficient amount of material to determine the concentrations of trace elements in the aerosol particle samples.

Scavenging ratios also can be calculated from long-term averages of the concentrations ($\mathrm{SR}_{average}$). In general, the most reliable $\mathrm{SR}_{average}$ for trace elements are thought to range from 200 to 2000 [*GESAMP*, 1989]. It is the $\mathrm{SR}_{average}$ that are useful for estimating wet deposition rates from representative atmospheric concentrations.

The daily aerosol particle samples from Ninety Mile Beach were analyzed by neutron activation analysis only, and thus the only data sets for aerosol particles and rain matched by day of collection are for sea salt (Na, Mg, and K), mineral aerosol (Fe), and for one enriched element (Zn). The SR_{event} for Na, which is considered representative of sea salt, ranged from 27 to 1300; those for mineral aerosol (Fe) ranged from 13 to 1800, and those for zinc ranged from 88 to 4300 (Table 6). The wide range in the SR_{event} presumably is a measure of the variability in the wet removal of particles caused by meteorology.

The SR_{event} for Na at Ninety Mile Beach (arithmetic mean 330) was almost identical to that determined during the SEAREX experiments at Enewetak (mean 360), but these two values are somewhat lower than that at American Samoa (mean 900). At Ninety Mile Beach, the SR_{event} for Fe (mean 220) also was relatively similar to that at Enewetak (mean 390) but lower than at Samoa (mean 1900). This was also true for Zn: the mean SR_{event} for Zn at Ninety Mile Beach (mean 1300) was similar to that at Enewetak (mean 790) but lower than at Samoa (mean 4900). The reasons for the differences in the values of the SRs calculated from the three SEAREX experiments are not entirely clear, but this observation is sufficiently interesting to warrant a brief discussion.

One of the main differences between the sites is that the sampling towers at Enewetak and New Zealand were close to sea level while at Samoa the tower was situated on a sheer 30-m cliff; thus there is a possibility that the topography affected the vertical distributions of the trace elements and hence their SR_{event}. Another fact to consider is that the concentrations of trace elements in air and rain at Samoa are among the lowest ever reported for the near-surface troposphere anywhere on the Earth. The precipitation scavenging of particles is a function of nucleation, scavenging during the growth of the cloud droplets or ice crystals, and below-cloud scavenging

TABLE 6. Scavenging Ratios for Trace Elements

Sample	Iron	Sodium	Zinc
June 24 (I)	13	91	720
June 30 (I)	110	340	500
June 30 (II)	63	520	1500
June 30 (III)	63	440	3400
June 30 (IV)	130	540	310
July 17	24	1300	1400
July 24 (I)	34	260	4300
July 24 (II)	19	360	140
Aug. 10 (I)	28	110	
Aug. 10 (II)	19	27	
Aug. 20 (I)	1800	170	360
Aug. 20 (II)	410	26	88
Aug. 20 (III)		63	
Mean	220	330	1300
Standard deviation	500	340	1500

[*Engleman*, 1988]. Cloud condensation nuclei must be activated before cloud droplets form, and as a result there may be a practical lower limit for the number of aerosol particles scavenged by a unit volume of rain. In this context, *Buat-Ménard and Duce* [1986] have proposed that in remote marine regions the in-cloud scavenging of aerosol particles by hydrometeors is independent of particle size and that virtually all particles are activated. Further studies of the scavenging of aerosol particles, involving both field and modeling efforts, would appear desirable.

The SR_{event} for each element were highly variable, but the data from New Zealand suggest that the SR_{event} for Fe were the lowest, while those for Na were intermediate, and those for Zn were the highest. The low SR_{event} for Fe may be an artifact due to the difficulty in dissolving all of the particulate Fe. In addition, the SR_{event} for Zn varied markedly among samples, and given the large relative standard deviation in the Zn, we do not consider the scavenging ratio for the AEEs to be well constrained. Much of the variability in the SR_{event} undoubtedly is due to the difficulties in collecting matched aerosol particle and precipitation samples. As previously discussed, the observed SR_{event} also may be affected by the vertical distributions of the elements, i.e., those elements exhibiting relatively low scavenging ratios may be relatively enriched near the surface and depleted aloft. There is no information available on the vertical distributions of any of the trace elements analyzed during the SEAREX experiments, but such studies are becoming technically feasible. For future studies of wet deposition it will be important to investigate the relationships between the vertical distributions of trace elements in the atmosphere and their scavenging by precipitation.

Long-Range Transport and the Air/Sea Exchange of Trace Elements

One major objective for our studies was to estimate of the inputs of trace elements to the waters bordering New Zealand, and we used our data for the concentrations of trace elements in the atmosphere for this purpose. *Smith* [1985] reviewed the existing data relative to the heavy metal inputs to the region, and from that review it is clear that the SEAREX experiments were the first systematic attempt to quantify the transfer of trace elements from the atmosphere to the waters of the New Zealand region.

Calculation of Trace Element Fluxes. Our approach for estimating trace element fluxes was to use our experimental results together with the parameterizations for wet and dry deposition developed by GESAMP Working Group 14 [*GESAMP*, 1989] to estimate the fluxes. We opted for this strategy so that the results from the two studies would be more-or-less comparable and because the differences between the direct measurements and parameterizations were small, given the uncertainties attached to the calculations. An important limitation of our deposition estimates is that the concentrations we used in the calculations were extrapolated from a limited number of samples collected during only 3 months. This limitation in data obviously introduces a potential bias in our results, especially for mineral aerosol whose concentration is known to vary strongly with season.

The dry deposition of the trace elements was calculated as the product of their geometric mean concentrations in the atmosphere and estimated dry deposition velocities. For mineral particles we used a dry deposition velocity of 1 cm s^{-1}. This is the value recommended by GESAMP, and given the fact that the uncertainty associated with this parameterization is a factor of 3, it is consistent with the dry deposition velocity determined from our studies. For sea salt, the dry deposition value we used, 5 cm s^{-1}, is a compromise between the observed deposition velocities (7.2 to 8.8 cm s^{-1}) and the GESAMP value (3 cm s^{-1}). The dry deposition velocity for the AEEs used for the calculations, 0.1 cm s^{-1}, is 10 to 20 times lower than those determined at New Zealand using the plastic plate. This lower velocity was used because of evidence that only about 10 percent of the total dry deposition of Pb (which is taken as a representative AEE) constitutes a true flux, i.e., a net transfer of material from the atmosphere to the ocean [*Settle and Patterson*, 1982; *Arimoto et al.*, 1985]. The remaining 90% of the dry deposition of the AEEs is attributed to material recycled with sea spray. This is likely to be an oversimplification because the recycled fraction probably varies among elements.

The wet deposition of the trace elements was calculated from the concentration of the element of interest in the air, the density of air, a scavenging ratio ($SR_{average}$), and the annual precipitation amount. The scavenging ratios recommended by *GESAMP* [1989] were used in the calculations; these are sea salt 300, mineral dust particles 300, and the AEEs 200. For sea salt and mineral aerosol the $SR_{average}$ used in the calculations were similar to the SR_{event} observed at New Zealand (Table 6). For the AEEs, the $SR_{average}$ used to estimate the flux was lower than the SR_{event}. This decision was made because there is no theoretical basis indicating that precipitation should scavenge the AEEs more effectively than sea salt or mineral aerosol and because the SR for Zn was not well constrained (Table 6). The mean annual precipitation at the northern tip of New Zealand for 1941 to 1970 was 145 cm [*Chen et al.*, 1985], and this value was used in the flux calculations, which are summarized in Table 7.

Transport and deposition of mineral aerosol. Mineral particles that originate in the deserts of central and western Australia are transported through the atmosphere over distances of thousands of kilometers, and the air-to-sea transfer of this material is an important source for ocean sediments of the region. For example, *Glasby* [1971] observed that the atmospheric input of mineral aerosol was comparable to the nonbiogenic sedimentation rate on Lord Howe Rise and on an adjacent area of the Tasman Sea. Thus he concluded that the atmospheric deposition of mineral particles supplies a major component of the nonbiogenic sediments of the Tasman Sea.

The concentrations of mineral aerosol observed during the SEAREX experiments at Ninety Mile Beach cannot be considered representative of long-term average owing to the limited sampling campaign and to the climatology of dust storms in Australia. The total flux of mineral dust calculated from the SEAREX samples was of the order of 0.1 g m^{-2} yr^{-1}, but the annual average flux of mineral aerosol is most likely several times higher than this because of the seasonality of dust storm activity. Nevertheless, as discussed below the atmospheric deposition of mineral dust determined from the SEAREX experiments is generally consistent with the rate at which nonbiogenic sediments accumulate in the South Pacific.

Windom [1970] compared the accumulation of trace metals in sediments from the Central Pacific with the flux of dust to the Franz Josef and the Tasman snowfields on the South Island of New Zealand. This comparison showed that the atmospheric deposition of Fe, Cu, Ni, Co, Cr, and Sr to the snowfields was within a factor of 3 of their accumulation in sediments, suggesting that atmospheric transport and deposition supplies geochemically significant quantities of these trace metals to the South Pacific Ocean. Our results (Table 7) provide further support for this hypothesis because the air/sea exchange rate we calculated for mineral aerosol was equivalent to one-sixth of the sediment accumulation rate used by *Windom* [1970]. Given the fact that the present data, which are limited to one season of the year, underestimate the eolian fluxes to the region, it is clear that the results of the SEAREX studies in the New Zealand

TABLE 7. Atmospheric Deposition of Trace Elements

Element	Dry Deposition Rate	Wet Deposition Rate
Br	65,000	15,000
Ca	360,000	84,000
Cl	20,000,000	4,700,000
I	1,500	340
K	520,000	120,000
Mg	1,300,000	300,000
Na	12,000,000	2,900,000
Al	5,000	5,800
Ba	60	69
Ce	3.8	4.4
Co	0.95	1.1
Cs	0.54	0.62
Eu	0.079	0.091
Fe	2,800	3,300
Hf	0.21	0.25
Mn	38	44
Rb	12	13
Sc	1.1	1.3
Tb	0.063	0.073
Th	0.70	0.80
V	12	14
Ag	0.38	2.9
Cd	0.51	3.9
Cu	2.6	20
Mo	0.41	3.1
Pb	4.1	31
Sb	0.12	0.89
Se	2.9	23
Zn	2.9	22

All fluxes in $\mu g\ m^{-2}\ yr^{-1}$.

area support the hypothesis that eolian material becomes an important component of deep-sea sediments.

Despite the geochemical significance of the air/sea exchange of mineral aerosol, the atmospheric loadings of dust in the New Zealand region are not so strong as in areas affected by the deserts in northwestern China or the Sahara Desert. Our data indicate that the annual atmospheric deposition of mineral aerosol to the waters in the vicinity of the North Island of New Zealand is greater than 0.1 $g\ m^{-2}\ yr^{-1}$ but less than 1 $g\ m^{-2}\ yr^{-1}$, and this is in agreement with the calculations done by *GESAMP* [1989]. For comparison, the GESAMP calculations show that the flux of mineral aerosol to the western Pacific bordering Asia and to the eastern Atlantic bordering Africa exceeds 10 $g\ m^{-2}\ yr^{-1}$. Thus the atmospheric deposition of mineral aerosol to the New Zealand region is less than 10% of the flux to more heavily impacted areas.

The estimated air-to-sea transfer of mineral aerosol to the New Zealand area is similar to the dust flux to the other areas of the open Pacific investigated for SEAREX. For example, at Enewetak, the mineral aerosol flux was estimated to be ~0.15 $g\ m^{-2}\ yr^{-1}$ [*Arimoto et al.*, 1985] and at American Samoa the flux was not well constrained but estimated to be between 0.02 and 0.2 $g\ m^{-2}\ yr^{-1}$. Interestingly, the *GESAMP* [1989] analysis indicates that only a few oceanic areas have dust fluxes significantly lower than those in New Zealand. The areas of very low dust flux include: (1) the central South Pacific, between approximately 170°W and 80°W and 0° to 50°S, (2) the southern oceans, south of ~50°S, and (3) a small area southeast of Greenland in the North Atlantic.

Transport and atmospheric deposition of the enriched trace elements. There are few atmospheric trace element data from the New Zealand region with which we can compare our results. The volume-weighted mean concentration of lead in the precipitation samples we analyzed from northern New Zealand and from the Tasman Sea was ≤ 180 ng kg^{-1}(Table 5). This value is comparable to the Pb concentration in precipitation samples from the SEAREX experiments (three samples ranging from 17 to 490 ng kg^{-1}) analyzed by C. C. Patterson and D. M. Settle and reported by *Steiner and Clarkson* [1985]. Based on the Pb data of Patterson and Settle and a consideration of air-mass trajectories, Steiner and Clarkson concluded that the long-range transport of pollution aerosol from Australia influenced the concentration of Pb in the New Zealand area. These authors found that the highest levels of Pb occurred in the sample whose air-mass back trajectory was directly from Australia.

Further consideration of the data shows that the concentration of Pb in precipitation from the remote SEAREX site on Ninety Mile Beach (≤ 180 ng kg^{-1}) was much lower than in rain from more heavily populated regions of New Zealand. For example, the mean concentration of Pb in precipitation from Christchurch, which is on the South Island of New Zealand, was reported to be 16,800 ng kg^{-1} [*Stevenson*, 1980]. The concentration of Pb in rain from Hamilton on the North Island of New Zealand was 5600 ng kg^{-1}, and this is also much higher than that observed during the SEAREX studies.

The SEAREX precipitation data indicate that emissions of air pollutants from New Zealand affect the concentration of atmospheric lead on local and perhaps regional scales. Automobiles in New Zealand continue to use leaded gasoline, and this is likely to be the source for much of the lead in the atmosphere. According to *Hughes* [1985], the New Zealand government has planned to phase-out leaded additives from gasoline in 1990, but even after that, some high-octane fuels will continue to contain lead at concentrations of 0.15 g L^{-1}. Thus it is likely that the anthropogenic perturbation of atmospheric lead in the New Zealand region will persist, at least for the near future.

In a broader context, the atmospheric lead flux to the New Zealand region was calculated to be 35 $\mu g\ m^{-2}\ yr^{-1}$; this is consistent with the estimates made by *GESAMP* [1989] (between 10 and 100 $\mu g\ m^{-2}\ yr^{-1}$) and similar to an estimate by *Patterson and Settle* [1987] (100 $\mu g\ m^{-2}\ yr^{-1}$). The atmospheric deposition of Pb to New Zealand evidently is of the same order as the eolian Pb fluxes at American Samoa, in the tropical South Pacific (20 to 30 $\mu g\ m^{-2}\ yr^{-1}$, [*Patterson and Settle*, 1987; *Arimoto et al.*, 1987], respectively; see Table 8) and those at Enewetak, in the tropical North Pacific, (70 $\mu g\ m^{-2}\ yr^{-1}$, [*Settle and Patterson*, 1982; *Arimoto et al.*, 1985]).

On the other hand, the atmospheric Pb flux at New Zealand was lower than the deposition rate characteristic of the westerly wind regime of the North Pacific (150 $\mu g\ m^{-2}\ yr^{-1}$; *Maring et al.*, 1989). This difference in fluxes undoubtedly reflects the fact that ~90% of the industrial lead emissions to the atmosphere occur in the westerly wind field of the northern hemisphere [*Patterson and Settle*, 1987]. Atmospheric inputs to the westerlies of the southern hemisphere account for most of the remaining ~10% of the anthropogenic Pb emissions. The fact that the difference between the eolian Pb flux to New Zealand and the North Pacific is not greater is most likely a result of the geographical distribution of sources for Pb in the Australia/New Zealand region.

Uncertainties in the air-to-sea transfer rates of the other elements are considerable, and this is a result of the few data available as well as limitations in our understanding of the critical parameters for calculating deposition. For example, *Patterson and Duce* [1990] concluded that the net air/sea rate for Cd to the open North Pacific (~45°N) during the spring was between 6 and 70 ng $m^{-2}d^{-1}$ (which, if extrapolated to an annual value would be between 2 and 26 $\mu g\ m^{-2}yr^{-1}$). For reference, estimates of the Cd fluxes at New Zealand and Enewetak are 4.4 and 3.5 $\mu g\ m^{-2}yr^{-1}$, respectively (see

Table 8). Given the substantial uncertainties, the atmospheric fluxes of Cd show a zonal pattern somewhat similar to Pb, suggesting that atmospheric Cd, too, is affected by pollution sources.

The atmospheric deposition rates for Zn in the major wind regimes over the Pacific Ocean appear qualitatively different from those of the enriched elements discussed above (Table 8). This is in part a reflection of geographical differences in atmospheric concentrations of the enriched elements, which can be demonstrated by a consideration of elemental ratios. The compilation by *GESAMP* [1989] indicates that the mean Zn/Pb ratio at twelve remote sites, including Enewetak and Samoa, ranged from 0.85 to 5.4. In contrast, the Zn/Pb ratio for the samples from Ninety Mile Beach study was lower (~0.7), and this is noteworthy because the Zn/Pb ratio in anthropogenic emissions evidently is lower than that resulting from natural sources. The Zn/Pb ratio in global anthropogenic emissions ranges from 0.19 to 0.67 (ratio of representative values = 0.40 [*Nriagu and Pacyna*, 1988]) while a ratio typical of natural sources is 3.8 [*Nriagu*, 1989]. Thus the relatively low Zn/Pb ratio observed at Ninety Mile Beach may be indicative of local or regional-scale anthropogenic perturbations of the concentrations of trace elements in the atmosphere of New Zealand.

Zonal differences in the estimated atmospheric deposition rates for Zn (Table 8) appear greater than those of the other enriched trace elements. However, this is largely an artifact resulting from difficulties in selecting the appropriate parameters for the flux calculations. In fact, the Zn/Pb concentration ratios for aerosol particles from Samoa and Enewetak were 4 and 1.4, respectively [*Arimoto et al.*, 1987; *Duce et al.*, 1983]; and if both of these two elements were in the fine particle mode, it would be reasonable to assume that the ratios of Zn/Pb fluxes would be proportional to their concentration ratios. Differences in the Zn/Pb flux ratios relative to atmospheric concentrations could occur if the deposition of the two elements were controlled by different processes, but we consider this improbable. It is more likely that the previous estimates of fluxes [*Arimoto et al.*, 1985, 1987]) were biased by several samples contaminated with Zn and the concomitant overestimates of dry and wet deposition.

In summary, the deposition estimates indicate that air-to-sea transfer of trace elements in the New Zealand regions is important as a source for abiogenic deep-sea sediments. It is likely that the atmospheric deposition of the enriched trace elements is geochemically important, but there are few supporting data for trace element concentrations in the water column of the region that can be used for comparisons. For example, the atmospheric deposition of copper to New Zealand appears comparable to that at Enewetak and Samoa (Table 8), but there are few if any data that can be used for evaluating the significance of the fluxes. *Smith* [1985] reviewed the natural and anthropogenic sources for heavy metals in the New Zealand aquatic environment, and this author concluded that the data for heavy metal inputs to New Zealand waters were not sufficiently comprehensive for a thorough assessment. Further, Smith noted that trace metal pollution of the water was not likely to be a major problem, but he also recommended that the contribution of trace metals from the atmosphere should be assessed to complete mass balances and to evaluate environmental impacts. The data obtained during SEAREX are a major achievement in this regard.

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TABLE 8. Atmospheric Deposition of Trace Elements to the Pacific Ocean

	Lead		Cadmium		Copper		Zinc	
South Pacific westerlies	35 to 100	(1, 2)	4.4	(1)	23	(1)	25	(1)
South Pacific easterlies	20 to 30	(2, 3)			55 to 105	(3)	140 to 580	(2)
North Pacific easterlies	70	(2, 4)	3.5	(4)	44	(4)	670	(4)
North Pacific westerlies	150	(5)	5.1 to 66	(6)				

All deposition rates in $\mu g\ m^{-2}\ yr^{-1}$; References in parentheses: (1) this paper, (2) *Patterson and Settle* [1987], (3) *Arimoto et al.* [1987], (4) *Arimoto et al.* [1985], (5) *Maring et al.* [1989], and (6) *Patterson* [1988].

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