

Atmospheric Input of Phosphorus to Remote Tropical Islands¹

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ABSTRACT: Atmospheric particulate phosphorus has been measured in the tradewinds of the Hawaiian and Samoan islands. The concentration of phosphorus ranges from 300 to 800 $\mu\text{g m}^{-3}$ and averages about 500 $\mu\text{g m}^{-3}$. Reactive phosphorus comprises 20–35 percent of the total phosphorus, persulfate releasable phosphorus 20–35 percent, and acid-soluble phosphorus 40–60 percent. The reactive phosphorus appears to be of crustal origin, while the acid-soluble fraction is of marine origin. The origin of the persulfate releasable phosphorus is not readily apparent. The acid-soluble fraction may be either organic or inorganic in nature. The persulfate releasable fraction appears to be comprised of organic material. The net phosphorus input to the vegetation on the windward sides of these islands is estimated to be 0.025–0.030 $\text{kg ha}^{-1} \text{yr}^{-1}$. The value amounts to 15–20 percent of the phosphorus deposition measured at an island site. It appears that bulk precipitation samples are easily contaminated in regions of intense biological activity.

THE INPUT OF PHOSPHORUS COMPOUNDS from the atmosphere to forests, croplands, and inland water bodies has been widely measured in temperate zones as part of ecological and water quality studies. However, very few data are available from tropical regions. The most comprehensive study appears to be that of Ungemach (1972) at Manaus, Brazil, in the Amazon Basin. Other measurements of phosphorus input from the atmosphere in tropical regions have been made in Ghana (Nye 1961), Nigeria (Jones 1960), The Gambia (Thorton 1965), and the Kerala coast of India (Vijayalakshmi and Pandalai 1963). Phosphorus inputs reported by these investigations range from 0.14 to 4.3 $\text{kg ha}^{-1} \text{yr}^{-1}$.

Almost no data are available on the flux and sources of atmospheric phosphorus to the vegetation of islands. An Antarctic island has been studied by Allen, Grimshaw,

and Holdgate (1967). Based on their analysis of rain water, calculations show that precipitation on this island, located in the midst of phosphate-rich Antarctic waters, contributed about 0.15 $\text{kg ha}^{-1} \text{yr}^{-1}$ of phosphorus to the vegetation of the island. In a study of mineral cycles in the El Verde Forest of Puerto Rico, Jordan and Drewry (1969) report an input of phosphorus in rain of 1.81 $\text{kg ha}^{-1} \text{wk}^{-1}$. This is the equivalent of 94 $\text{kg ha}^{-1} \text{yr}^{-1}$ and seems to be high compared to the other available data.

Many major Pacific tropical islands are of volcanic origin. Soils of these islands are often acid, have relatively high contents of amorphous ferric and aluminum oxides, and consequently have a very high fixation capacity for phosphorus (Fox, Plucknett, and Whitney 1968; Younge and Plucknett 1966). Because of the strong fixation capacity of these soils, losses of available phosphorus in leaching and runoff should be very low. However, some loss most assuredly does occur. Natural sources of phosphorus that replace this loss appear to be weathering and input from the atmosphere. Estimating the magnitude of the atmospheric input is the concern of this paper.

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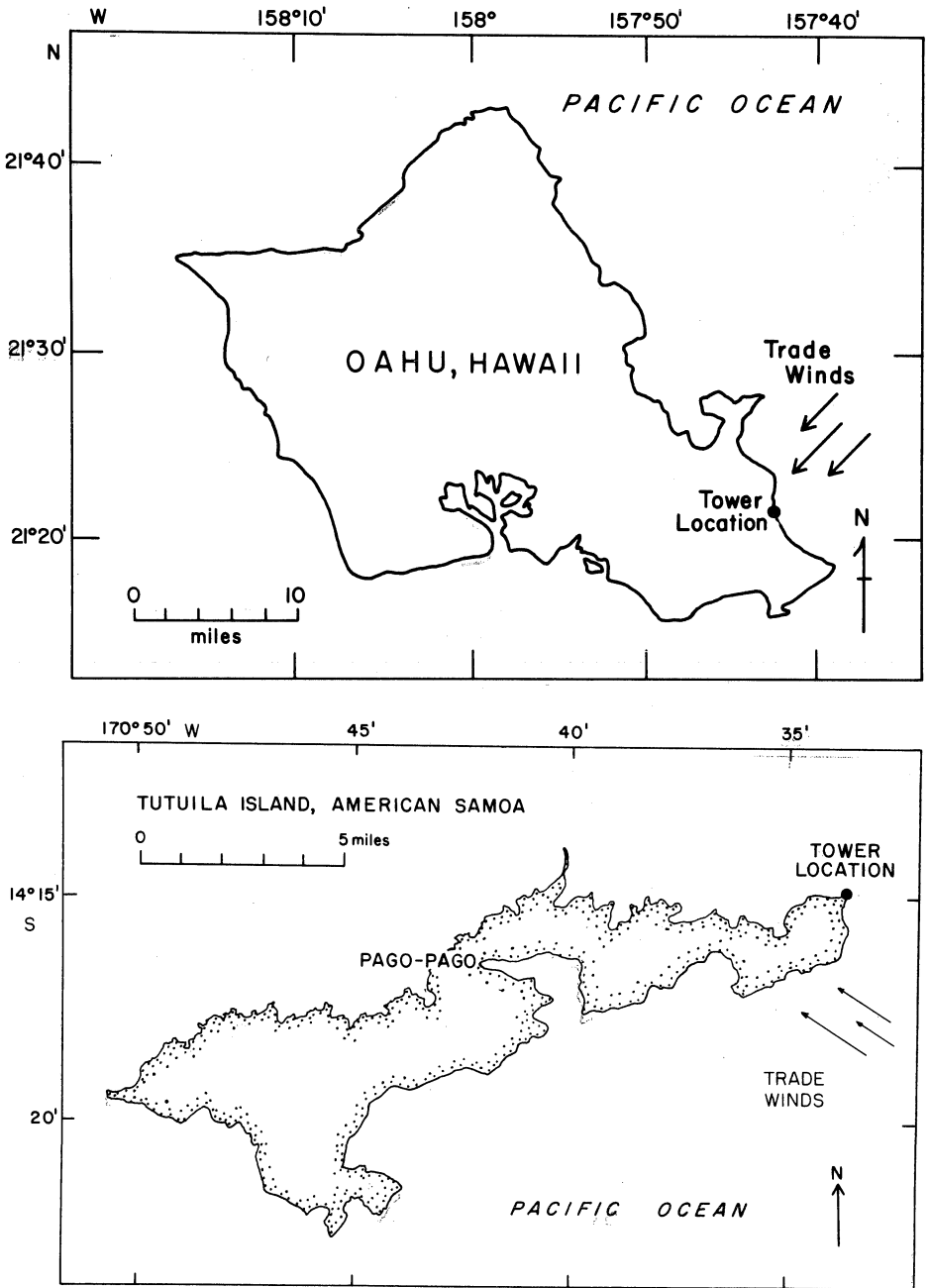


FIGURE 1. Sampling sites on the islands of Oahu, Hawaii, and Tutuila, American Samoa.

SITES AND METHODS

Our study of atmospheric input of phosphorus was carried out at sampling stations at Bellows Air Force Station on the island of Oahu, Hawaii, and at the National Oceanic and Atmospheric Administration (NOAA) GMCC station at Cape Matatula, Tutuila Island, American Samoa. Both locations are on the windward sides of the respective island in locations that provide maximum exposure to the onshore winds from the prevailing tradewinds (Figure 1).

Sampling Methods

Samples of atmospheric particulate matter were collected from the top of 20-m towers situated at each site. The samples were collected with Cadillac sampling pumps connected to 20 × 25 cm polystyrene filters (Delbag Microsorban 97/99). The time of sampling ranged from 3 to 7 days, during which 5000–14,000 m³ of air passed through the filters. Due to the persistence of the northeast tradewinds at Hawaii during the sampling period (August–October 1975), samples were collected continuously. At American Samoa, where the winds were more variable over a longer sampling period, the sampling pumps were connected to an automatic control system that shut down sampling during periods of nonmarine winds, calm, rain, or high counts of Aitken nuclei. The sampling system has been described in detail by Duce et al. (1976a). A size-separated aerosol sample for phosphorus analysis was collected at the Hawaii site with a Sierra Model 235 high-volume cascade impactor. Delbag collection strips and backup filters were used. According to the manufacturer, the equivalent aerodynamic radius cutoffs at 50 percent collection efficiency for particles with a density of 1 g cm⁻³ are as follows: stage 1 = 3.6 μm; stage 2 = 1.5 μm; stage 3 = 0.75 μm; stage 4 = 0.48 μm; stage 5 = 0.25 μm; final filter ≤ 0.25 μm. The impactor sample was collected over a 7-day period.

In addition to samples of atmospheric particulates, bulk precipitation samples were

collected at Samoa on the roof of the National Oceanic and Atmospheric Administration (NOAA) laboratory. A 0.36-m² rain sampling funnel was connected to a 20-liter polyethylene jerrycan. The funnel was covered with polyethylene screening to exclude insects and large particles. The jerrycan was emptied into 1-liter glass bottles after each rain. We added 40 mg of Hg₂Cl₂ to each 1-liter precipitation sample as a preservative. All filter and precipitation samples were shipped to the University of Rhode Island for analysis.

Chemical Analysis

Each filter sample was divided into four quarters for analysis. Two quarters were pelletized and then analyzed for sodium and aluminum by neutron activation analysis. The pellets were irradiated for 30 s in the Rhode Island Nuclear Science Center swimming pool reactor at a flux of 4×10^{12} n cm⁻²s⁻¹. Within 2 min, the samples were counted for 400s on a Ge(Li) detector (resolution of 2.3 keV for the 1332-keV gamma ray of ⁶⁰Co) coupled to a Nuclear Data 2200 4096 channel analyzer with a computer-compatible magnetic tape output (Ampex TM-7) for spectrum analysis. A computer program (J. L. Fasching, personal communication) was used to process the Ge(Li) spectra acquired. Absolute standards for sodium and aluminum were prepared on blank filters, pelletized, irradiated, and counted in the same manner as the unknowns. Constant geometry was maintained during the counting of all standards and unknowns. Corrections were made for dead time and half-life discrimination.

After decay of any residual radioactivity, these quarters were ashed at 500°C in the presence of excess magnesium. The residue was dissolved in 1 ml of 1 N HCl, diluted to 40 ml, and filtered. Any arsenate present was reduced to arsenite by the method of Johnson and Pilson (1972). Phosphorus was determined using the ascorbic acid method of Murphy and Riley (1962). Phosphorus determined in this manner is called "total phosphorus."

Commercially available aluminum, iron, and calcium phosphates are detected by this method, along with low-molecular-weight polyphosphates. The degree of recovery of more complex phosphorus minerals or of phosphorus occluded or substituted in silicate minerals is unknown.

One quarter of the filter sample was extracted with agitation for 30 min using doubly distilled water. After filtration and arsenate reduction, the phosphorus present was determined colorimetrically, as above. Phosphorus determined on this portion of the filter is called "reactive."

The last quarter was treated with 5 ml of 6.4 percent potassium persulfate solution in 40 ml of doubly distilled water, and autoclaved for 25 min at 125°C (Menzel and Corwin 1965). After filtration, the solution was analyzed for phosphorus, as above. Due to interference by the oxidizing agent, arsenate was not reduced in this analysis. However, much of the arsenate is probably lost in the autoclaving step. In any case, the error introduced is small, as total atmospheric arsenic compounds found at these sites is only about 4 percent of the phosphorus (P. R. Walsh, personal communication). Phosphorus determined by persulfate oxidation includes reactive phosphorus, phosphorus that is liberated during the oxidation of organic material, and inorganic phosphorus that is soluble at the final pH of the oxidation reaction ($\text{pH} \approx 2$). Studies with a variety of organophosphorus compounds showed that the efficiency of oxidation ranged between 80 and 90 percent, averaging 85 percent. The phosphorus determined in this analytical step is called "total available phosphorus."

The "persulfate releasable" phosphorus fraction is the difference between the total available phosphorus and the reactive phosphorus. A fraction called "acid-soluble" is defined as the difference between the total phosphorus value and the total available phosphorus value.

Analytical precision in the atmospheric samples has been calculated as follows: total P, ± 10 percent; total available P, ± 15 percent; reactive P, ± 20 percent; sodium, ± 9 percent; aluminum, ± 16 percent.

Only total persulfate phosphorus was determined on the precipitation samples using the persulfate oxidation technique after filtration in the laboratory. Because the samples could not be analyzed immediately after collection, meaningful values for reactive phosphorus could not be obtained. The analytical precision in the measurement of phosphorus in precipitation was about ± 4 percent.

RESULTS AND DISCUSSION

The analytical results on the filter samples, along with the pertinent meteorological data, are shown in Tables 1 and 2. Table 3 summarizes these concentrations and gives the distribution of the different phosphorus fractions. In the dry season, about the same amount of phosphorus is found in the marine air of Hawaii and Samoa; the major difference is that the reactive phosphorus level in Samoan air is about one-half that of Hawaiian air. Soluble and organic phosphorus levels are similar at the two sites. The major difference between wet and dry season samples in Samoa is the lower level of organic phosphorus during the wet season. Acid-soluble and reactive phosphorus do not appear to be greatly affected by the change in seasons.

Figure 4 illustrates the distribution of phosphorus, sodium, and aluminum on a cascade impactor sample taken in Hawaii. Due to the low levels of phosphorus on each stage, only total phosphorus could be determined. For comparison, the figure also shows the size distribution of total organic carbon in Hawaiian air as determined by Hoffman and Duce (1977). For the larger size particles, the phosphorus distribution matches that of sodium fairly well. In the finer fractions, the behavior is more complex and subject to some uncertainty in interpretation.

The analyses of the bulk precipitation samples are shown in Table 4. The total available phosphorus content in the precipitation samples ranged from 2 to 145 $\mu\text{g liter}^{-1}$. However, input rates on a unit time basis proved to be more constant, ranging from

TABLE 1

METEOROLOGICAL CONDITIONS AND CONCENTRATIONS OF PHOSPHORUS IN SAMPLES OF ATMOSPHERIC PARTICULATE MATTER FROM THE MARINE AIR OF HAWAII, 1975

SAMPLE	DATE	AVG WIND VELOCITY (m s ⁻¹)	PERCENT "GOOD" WINDS	PPTN (cm)	PHOSPHORUS (pg m ⁻³)						
					TOTAL	TOTAL AVAIL.	REACTIVE	PERSULFATE RELEASABLE	ACID- SOLUBLE	SODIUM (μg m ⁻³)	ALUMINUM (ng m ⁻³)
1	11 August	7.1	100	0.03	500	460	90	370	40	2.5	11
2	14 August	10.0	100	0.13	860	370	300	70	490	4.3	22
3	18 August	8.1	100	0.03	480	380	160	220	100	3.2	8
4	22 August	8.4	100	0.20	470	250	60	190	220	3.8	20
5	28 August	6.6	95	0.46	420	220	150	70	200	2.2	18
6	3 September	8.0	99	0.03	500	220	110	110	280	3.6	11
7	8 September	8.1	100	0.28	390	170	110	60	220	2.9	7
8	12 September	5.4	76	0.10	430	320	190	130	110	1.6	11
9	18 September	8.4	100	0.03	770	550	450	100	220	2.9	21
10	24 September	7.6	100	0.03	530	350	140	210	180	3.0	13
11	30 September	7.2	98	0.20	440	270	220	50	170	2.6	14
12	6 October	9.1	100	0.71	380	170	70	100	210	3.5	4
13	12 October	7.9	98	0.03	260	130	70	60	130	2.5	5
Mean		7.8	97	0.17	490	300	170	130	200	3.0	13
Standard deviation		±1.1		±0.21	±160	±120	±110	±90	±110	±0.7	±6

TABLE 2

METEOROLOGICAL CONDITIONS AND CONCENTRATIONS OF PHOSPHORUS IN SAMPLES OF ATMOSPHERIC PARTICULATE MATTER FROM THE MARINE AIR OF AMERICAN SAMOA, 1976

SAMPLE	DATE	AVG WIND VELOCITY (m s ⁻¹)	PERCENT "GOOD" WINDS	PPTN (cm)	PHOSPHORUS (pg m ⁻³)						
					TOTAL	TOTAL AVAIL.	REACTIVE	PERSULFATE RELEASABLE	ACID- SOLUBLE	SODIUM (μg m ⁻³)	ALUMINUM (ng m ⁻³)
1	11 January*	5.8	80	11.53	400	190	60	130	220	2.7	3
2	18 January	6.8	85	13.38	425	180	130	50	240	3.2	8
3	25 January	4.2	96	1.37	330	180	100	80	150	2.3	17
4	1 February	3.9	86	1.42	320	100	70	30	220	1.8	3
5	5 February	4.1	73	3.84	560	140	80	60	430	2.5	1
Mean		5.0	84	6.34	410	160	90	70	250	2.5	6
Standard deviation		±1.3		±5.77	±100	±40	±30	±40	±100	±0.5	±6
1	16 June [†]	5.9	94	2.80	510	380	40	340	140	3.4	5
2	25 June	5.0	86	2.84	590	520	160	360	60	2.9	2
3	2 July	10.4	87	1.57	510	170	60	110	360	3.7	5
4	9 July	5.9	95	5.03	400	130	20	110	270	3.9	2
5	16 July	6.9	48	3.96	800	200	N.D.	200	600	2.4	13
6	23 July	8.6	80	2.82	340	100	50	50	230	2.7	8
7	1 August	7.0	80		440	150	120	30	290	3.1	7
8	8 August	7.1	56	2.64	650	160	N.D.	160	490	2.6	4
9	15 August	12.7	73	0.38	500	140	N.D.	140	400	3.9	14
10	22 August	5.3	92	0.28	620	220	120	100	390	6.2	8
11	28 August	8.9	100	0.25	450	170	20	150	280	3.5	8
12	4 September	4.5	100	0.01	320	140	40	100	190	4.8	6
13	11 September	5.6	86	0.07	410	270	200	70	130	2.3	7
14	18 September	4.9	58	3.10	430	180	170	10	240	1.6	7
Mean		7.0			500	210	70	140	290	3.4	6
Standard deviation		±5.5			±130	±110	±70	±100	±150	±1.1	±±4

N.D. = not detected above blank.

*Wet season.

[†]Dry season.

TABLE 3

THE CONCENTRATION AND DISTRIBUTION OF
ATMOSPHERIC PARTICULATE PHOSPHORUS
COMPOUNDS IN THE MARINE AIR OF HAWAII
AND SAMOA

FRACTION	HAWAII		SAMOA*			
	DRY SEASON [†]		RAINY SEASON		DRY SEASON	
	pg m ⁻³	%	pg m ⁻³	%	pg m ⁻³	%
Total P	500	100	370 [‡]	100	470	100
Total avail. P	290	58	160 [§]	43	240	51
Reactive P	160	34	90	24	90	19
Persulfate rel. P	130	26	70 [#]	19	150	32
Acid-soluble P	210	42	210	57	230	49

* Excludes all samples with less than 80% "good" winds.

[†] Hawaii: dry season, July–October 1976. Samoa: rainy season, December–February 1976; dry season, June–September 1976.

[‡] Significantly less than other values at 92% confidence level (c.l.).

[§] Significantly less than other values at 93% c.l.

^{||} Significantly higher than other values at 98% c.l.

[#] Significantly less than other values at 90% c.l.

0.09 to 0.90 mg ha⁻¹ day⁻¹. The annual input of total available phosphorus is estimated to be 0.14 kg ha⁻¹ yr⁻¹.

Sources of Phosphorus in the Atmosphere

Data matrices consisting of the various phosphorus fraction concentrations along with the concentrations of aluminum and sodium were analyzed by factor analysis and by multivariate linear regression. Factor analysis is a statistical technique for the grouping of linear combinations of similar variances from variables that are highly correlated. The theory of factor analysis has been presented in detail by Harman (1967). The application of factor analysis to the measurement of trace elements in the atmosphere has been described by Hopke et al. (1976) and Duce et al. (1976b). The results of the factor analysis of the experimental data are presented in Table 5. Using an eigenvalue cutoff of 1, three factors are found to account for 87 percent of the variation of the Hawaiian data, 86 percent of the Samoan data, and 89 percent of the pooled data.

The first factor contains most of the sodium variation and certainly must represent sea

salt particles ejected from the ocean by bubble action. Sodium concentration correlates with the square of the wind velocity ($r = 0.35$, sig. = 0.95), as would be expected from the work of Woodcock (1953) and Blanchard (1963).

Most of the acid-soluble phosphorus variation also appears in factor 1, indicating that the ocean is the most likely source for this phosphorus fraction. Figure 2 shows that the concentration of acid-soluble phosphorus in marine air at these sites increases as the sodium concentration increases. The type of phosphate that comprises this fraction is not obvious. One possibility is the presence of organic phosphates that are resistant to persulfate oxidation. This would imply that only 30–50 percent of the organic matter present on the filters was oxidized by the persulfate method. While the composition of organic phosphorus compounds in seawater is still poorly known, laboratory studies suggest that recoveries are more typically in the 80–90 percent range. In addition, relatively large amounts of acid-soluble phosphorus are not found on filters collected over waters with known high organic phosphorus content (Graham, Piotrowicz, and Duce 1979). It seems unlikely, then, that this fraction is unoxidized organic material.

A possible source of acid-soluble phosphorus might be the polyphosphates known to be present in bacteria. Polyphosphate chains of up to 300–500 units in length are found in bacteria and algae (Zajic 1969). Bacteria are known to be highly concentrated in the surface microlayer of the ocean (Sieburth 1963; Sieburth et al. 1976), and the ability of bursting bubbles to inject water droplets containing bacteria into the atmosphere has been well documented (Bezdek and Carlucci 1972, Blanchard and Syzdek 1970).

Factor 2 associates the aluminum and reactive phosphorus variations, which indicates a crustal source for this factor. Reactive phosphorus concentration generally increases with increasing aluminum concentration, but there is a large amount of scatter in the data. Multivariate linear regression of the pooled data gives a significant (99.7 percent) regression of reactive phosphorus on aluminum.

TABLE 4
THE INPUT OF PHOSPHORUS IN BULK PRECIPITATION AT SAMOA, 1975-1976

SAMPLE	DATE	DAYS EXPOSED	PPTN (cm)	TOTAL AVAILABLE P	
				IN PPTN ($\mu\text{g liter}^{-1}$)	AS BULK DEPOSITION ($\text{mg ha}^{-1}\text{day}^{-1}$)
1	10 December	6	10.64	3.1	0.55
2	16 December	17	8.33	10.4	0.51
3	2 January	6	10.62	3.2	0.55
4	8 January	5	2.87	4.0	0.22
5	13 January	4	6.93	1.9	0.33
6	17 January	3	6.48	2.7	0.57
7	20 January	17	4.37	11.9	0.30
8	6 February	8	8.81	3.5	0.39
9	14 February	5	2.82	3.7	0.21
10	25 June	1	0.78	4.6	0.36
11	26 June	2	0.83	5.5	0.23
12	28 June	1	1.19	4.8	0.56
13	29 June	3	0.03	145	0.12
14	2 July	1	0.20	52	0.95
15	3 July	1	0.03	99	0.25
16	4 July	2	0.13	58	0.38
17	6 July	1	0.25	31	0.74
18	9 July	3	0.18	38	0.23
19	12 July	1	1.47	6.2	0.97
20	13 July	1	1.21	3.7	0.39
21	14 July	4	2.03	5.2	0.24
22	18 July	1	0.84	3.7	0.32
23	19 July	1	0.71	5.6	0.40
24	20 July	2	0.28	6.5	0.09
25	22 July	1	0.30	9.9	0.31
26	23 July	2	0.36	12	0.21
27	25 July	2	1.14	3.0	0.17
28	27 July	1	0.70	13	0.95
29	28 July	1	1.52	4.0	0.61

NOTE: Total days = 103; total input of available phosphorus = 40.1 g ha^{-1} ; estimated annual input = $0.14 \text{ kg ha}^{-1}\text{yr}^{-1}$.

The regression coefficient for aluminum is 0.0082 ± 0.0025 . This value is reasonably close to the values of 0.009-0.015 found for the ratio of phosphorus to aluminum in soils and crustal material (Rahn 1976).

Further evidence that crustal material is the main source of reactive phosphorus results from a comparison of the ratios of reactive phosphorus and aluminum in Hawaii to the same quantities in Samoa. These ratios are 1.9 and 2.2, respectively. The trajectories of the air masses that were sampled at the Hawaiian site have been obtained from the NOAA. These trajectories indicate that the most likely source of crustal material is the North American continent between Canada and Mexico. Some of the acid-soluble phos-

phorus variation also appears to be associated with factor 2 and may represent phosphate minerals in the crustal material.

Air mass trajectory data are not available for the Samoa site. However, inspection of surface wind and pressure charts suggests that the desert areas of Chile and Peru are possible sources of the crustal material in the Samoa samples.

The persulfate releasable phosphorus stands alone as the third factor. Overall, this phosphorus fraction appears to have little association with either sea salt or crustal material, although there is some aluminum variation associated with the persulfate fraction of the Samoa samples.

The persulfate releasable fraction could

TABLE 5

RESULTS FROM FACTOR ANALYSIS PERFORMED ON THE DATA MATRIX FROM THE HAWAIIAN AND SAMOAN SAMPLE SETS

	HAWAII			SAMOA			COMBINED DATA		
	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 1	FACTOR 2	FACTOR 3	FACTOR 1	FACTOR 2	FACTOR 3
Eigenvalues	2.84	1.37	0.99	1.91	1.30	0.91	1.95	1.48	1.02
Portion	0.47	0.23	0.17	0.38	0.30	0.18	0.39	0.30	0.20
Cumulative portion	0.47	0.70	0.87	0.38	0.68	0.86	0.39	0.69	0.89
Variance									
Reactive P	-0.097	0.891	-0.216	-0.125	-0.905	-0.027	-0.066	-0.898	-0.041
Persulfate releasable P	-0.149	-0.074	0.969	0.002	0.116	0.934	0.023	0.069	0.979
Acid-soluble P	0.714	0.440	-0.393	0.769	-0.391	-0.453	0.761	-0.137	-0.566
Sodium	0.926	0.054	0.083	0.982	0.126	0.141	0.963	0.037	0.110
Aluminum	0.309	0.874	0.117	0.044	0.454	0.675	0.108	-0.891	-0.086

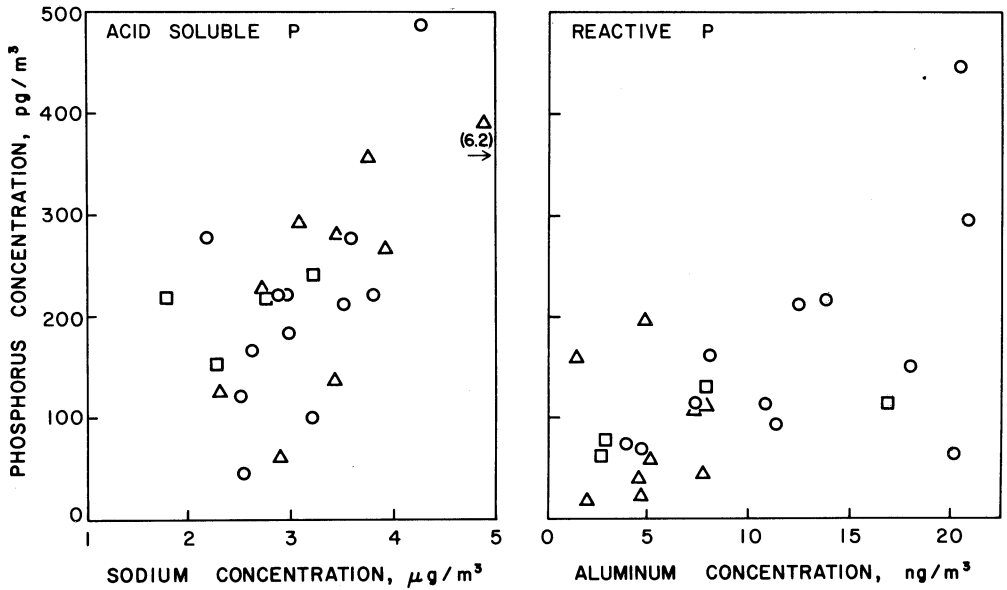


FIGURE 2. *Left*: The concentration of acid-soluble phosphorus versus the concentration of sodium in marine air at Hawaii and Samoa. *Right*: The concentration of reactive phosphorus versus aluminum at the same sites. ○, Hawaii; △, Samoa, rainy season; □, Samoa, dry season.

include both organic and dilute acid-soluble inorganic phosphates. To determine whether a significant amount of dilute acid-soluble phosphate was present in this fraction, nine Samoa filters were extracted with 0.025 *N* HCl (pH \approx 1.6) and the extracts analyzed for phosphorus. The amount of phosphorus recovered was somewhat less than that found by the deionized water extractions and much less than the recoveries from the persulfate analysis (Table 6). Thus, it appears that the phosphorus recovered in the persulfate fraction is entirely organic in nature.

Large-particle biological material, which would be expected to contain organic phos-

phorus, has been reported over both the Atlantic and Pacific oceans (Delany et al. 1967, Folger 1970, Prospero and Bonatti 1968). These particles have been identified as marine and freshwater diatoms, fungal spores, phytoliths, and pollen grains. Because of their low densities and irregular shapes, large organic particles are likely to be transported much further than mineral grains or salt particles of equivalent size.

It appears, however, that approximately 80 percent of the total organic carbon (TOC) in the marine atmosphere at both Hawaii and Samoa is found on particles of less than 0.5 μm diameter (Hoffman and Duce 1977). This size fraction, then, is also a possible source of organic phosphorus. Due to the very low levels of total phosphorus on the impactor samples, it was not possible to determine organic phosphorus as a function of particle size directly. However, from the data presented in Table 3 and in Figures 2 and 3, some inferences can be made. The concentration of organic phosphorus in the marine air of Samoa in the rainy season is about one-half the concentration in the dry

TABLE 6

EXTRACTION STUDIES OF SAMOA FILTER SAMPLES

EXTRACTION METHOD	PHOSPHORUS FOUND ($\mu\text{g m}^{-3}$)
0.025 <i>N</i> HCl	40 \pm 20
Deionized water	70 \pm 50
Persulfate oxidation	220 \pm 140

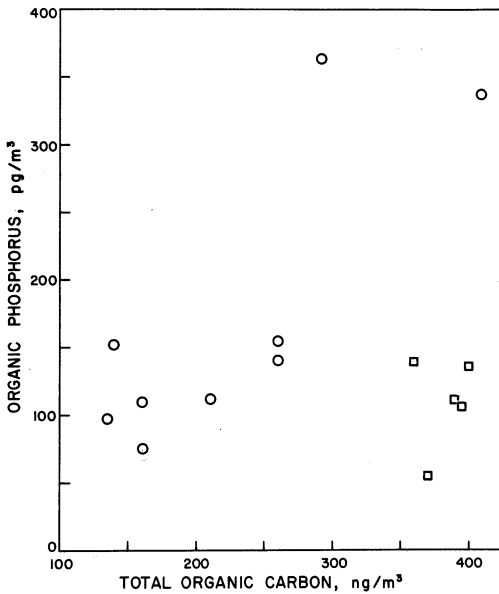


FIGURE 3. The concentration of organic phosphorus versus total organic carbon in the marine air of Hawaii and Samoa. □, Hawaii; ○, Samoa.

season. This would suggest that these particles are being effectively removed by rainout in the wet season, and so are relatively large since removal by rain is most efficient for large particles (Gatz 1975).

Figure 4 shows that if two anomalous Samoa points are excluded, there is little correlation between the organic phosphorus and the organic carbon concentrations of Hoffman and Duce (1977) measured on simultaneous samples. The TOC in the marine air at Samoa is about one-half the concentration found in Hawaii. On the other hand, organic phosphorus levels are very similar. The two samples at Samoa with high organic phosphorus and TOC values were the first two samples taken at the start of the dry season sampling period, and it is possible that these samples are contaminated with construction debris. The impactor data, however, indicate that some fraction of the organic phosphorus may be associated with the fine fraction of organic carbon. The increase in total phosphorus on the impactor backup filter may be related to the large mass

of fine-particle organic carbon also found on the impactor filters.

In summary, the data suggest that the organic phosphorus input to these islands is mostly biologically derived particles of greater than $0.5 \mu\text{m}$ diameter, but that some small fraction may be associated with the 80 percent of organic carbon found to be less than $0.5 \mu\text{m}$ in diameter.

INPUT OF PHOSPHORUS TO THE WINDWARD VEGETATION

The measured input of total available phosphorus is estimated to be $0.14 \text{ kg ha}^{-1}\text{yr}^{-1}$, based on the precipitation samples taken at Samoa. However, Ungemach (1972) points out that it is not easy to distinguish true input from simple recycling of locally derived material, especially in the tropics where biological activity is intense. A calculation of input based on atmospheric concentrations, deposition velocities, and rainout factors should permit us to estimate the amount of recycled material present in the precipitation samples.

The particle size distribution used in our calculation is that obtained for total phosphorus on the Hawaiian impactor sample. Using this distribution, the average wind velocity at the time of sampling, and the data on the deposition velocity as a function of particle size and wind velocity of Sehmel and Sutter (1974), we obtain a weighted average deposition velocity of approximately 3 cm s^{-1} . This is in reasonable agreement with the average deposition velocity of 2.4 cm s^{-1} for phosphorus compounds measured in an English woodland by White and Turner (1970). It is significantly higher than the value of 0.6 cm s^{-1} by Delumyea and Petel (1978) for deposition of phosphorus compounds over Lake Huron. However, the mass median diameter of particles sampled by Delumyea and Petel was less than $1 \mu\text{m}$ as compared to approximately $3 \mu\text{m}$ for our Hawaiian sample. The differences in deposition velocity are consistent with this difference in diameter.

Based on a deposition velocity of 3 cm s^{-1}

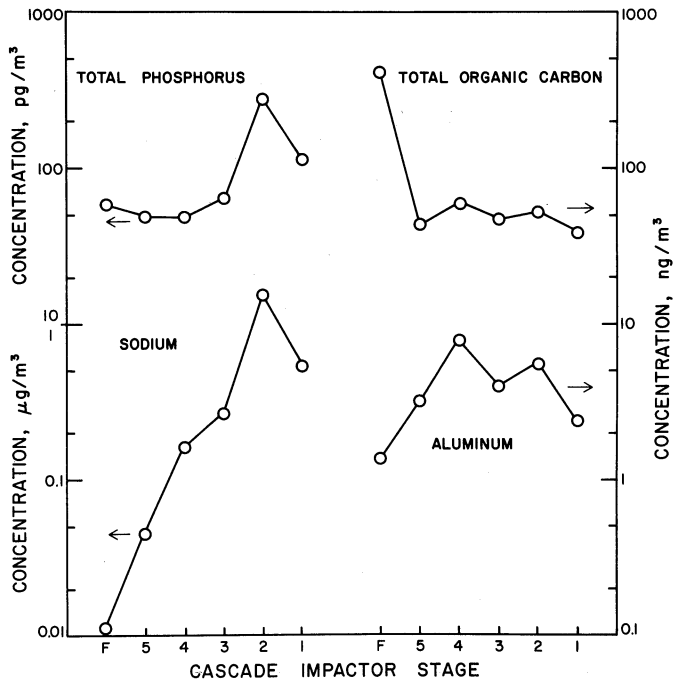


FIGURE 4. The concentration of total phosphorus, sodium, aluminum, and total organic carbon as a function of cascade impactor stage. Largest particles on stage 1, smallest on stage 5; F = backup filter.

and an atmospheric concentration of 500 pg m^{-3} , a dry deposition flux of approximately $5 \text{ g ha}^{-1}\text{yr}^{-1}$ is obtained. Additional input will occur in rainout and washout. We can estimate the wet input using the data of other investigators on the wet/dry input ratio of phosphorus at other locations. Nihlgard (1970) and Kluesener (1972) have measured precipitation and dry fallout inputs in Sweden and Wisconsin, areas that have rainfalls of approximately 80 cm yr^{-1} . Ratios of phosphorus input in precipitation to that of dry fallout are 0.33 and 0.65, respectively. White and Turner (1970) find a ratio of 2.85 for an English woodland with a rainfall of 155 cm. Cape Matatula, Samoa, where both the filter and bulk precipitation samples were taken, has an estimated rainfall of 250 cm yr^{-1} . Based on this rainfall, we estimate the ratio of phosphorus input by precipitation to that of dry fallout to be between 4 and 5. This gives a total phosphorus input of 0.025 to $0.030 \text{ kg ha}^{-1}\text{yr}^{-1}$. This amount is approximately 20–25 percent of the $0.14 \text{ kg ha}^{-1}\text{yr}^{-1}$

phosphorus input estimated from the bulk precipitation analysis and suggests that perhaps 75–80 percent of that phosphorus content was from recycling of locally derived material.

Williams (1967) has reported the results of a phosphorus analysis on one rain sample taken on shipboard 30 mi north of Samoa. The phosphorus concentration was found to be $0.08 \text{ } \mu\text{m liter}^{-1}$. The composition of the phosphorus was 50 percent reactive and 50 percent organic. Based on rainfall of 133 cm yr^{-1} over the oceans at this latitude (Baumgartner and Reichel 1975) and an estimated rainout to dry deposition ratio of 3:1, we obtain a phosphorus input of $0.045 \text{ kg ha}^{-1}\text{yr}^{-1}$. Since this estimate is based on only one sample, it is a tenuous number. However, it appears that a true phosphorus input rate for these islands is certainly less than $0.1 \text{ kg ha}^{-1}\text{yr}^{-1}$ and is most likely less than $0.05 \text{ kg ha}^{-1}\text{yr}^{-1}$. While this input of phosphorus is small compared to the amounts reported in continental areas, it

may be important to the nutrient balance of the island vegetation. The intense rainfall (up to 500 cm yr⁻¹) on the windward side of these islands results in strongly leached acid soils. Under these conditions, the soil phosphorus below the humus layer is tightly fixed and unavailable. Atmospheric input may be significant in balancing the nutrient losses that occur from runoff or fixation.

SUMMARY

The concentration of phosphorus in the prevailing tradewinds of the Hawaiian and Samoan islands ranges from 300 to 800 pg m⁻³, averaging about 500 pg m⁻³. Of the total phosphorus, reactive phosphorus comprised 20–35 percent, organic phosphorus 20–35 percent, and acid-soluble phosphorus 40–60 percent. Factor analysis suggests that the source of the reactive phosphorus is crustal material, and the acid-soluble phosphorus fraction may be derived from the surrounding oceans. The source of organic phosphorus is more complex. This fraction is most likely biological particles from either continental or oceanic sources. It appears to have a fairly large particle size and is not a major portion of the total organic carbon content of the marine air at these sites.

The phosphorus input to the vegetation on the windward sides of these island chains is estimated to be 0.025–0.030 kg ha⁻¹yr⁻¹, based on the atmospheric concentration, a calculated deposition velocity, and an assumed ratio of input in precipitation to that in dry fallout. This value amounts to 15–20 percent of the phosphorus deposition measured in a bulk precipitation collected at a nearby site. We conclude that bulk precipitation samples are easily contaminated in tropical regions where biological activity is intense.

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