The SO_4:Cl Ratio in Oceanic Rainwater[1]

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ABSTRACT: Rainwater samples collected on 20 islands in the Pacific and Atlantic oceans since 1961 have been analyzed for dissolved sulfate and chloride ion concentrations. Samples from sparsely populated islands have SO_4:Cl ratios approximately equal to that observed in seawater. Notable exceptions are samples from Midway and Christmas islands, which are enriched in sulfate, and those from the ocean stations Echo, Papa, and Victor, which are depleted in sulfate. The $\delta^{18}O$ of the oxygen in the SO_4 ion ranges from 9.5‰ in seawater and unpolluted rain to 11.2‰ in rain derived from a continental air mass. Aerosols and snow samples have higher $\delta^{18}O$ values of 11.2 to 14.8‰ due to their greater efficiency in trapping locally produced sulfate pollutants.

SULFUR AND CHLORINE are the major constituents of rainwater. The principal source of these components of airborne particles is thought to be sea salt, although continental and anthropogenic sources also must be considered (Lodge 1960, Kapoor and Ramana Murty 1966, Kellogg et al. 1972). However, the ratios of some chemical constituents in aerosols and rainwater over the ocean differ significantly from the analogous ratios in seawater (Koyama and Sugawara 1953, Komabayasi 1962). Numerous theories have been proposed to account for this discrepancy in terms of the chemical fractionation of sea salt, either as it leaves the sea surface or while it is being borne aloft. At present these theories are largely unsatisfactory and no mechanism that adequately explains the chemical fractionation of sea salt has been proposed (Lazrus, Baynton, and Lodge 1970, Tsunogai et al. 1972, Junge 1972). Enrichments of magnesium (Köhler and Bäth 1952), of calcium (Sugiura 1965), and of phosphate (MacIntyre 1970) have been observed during sea salt aerosol production in the laboratory. Chemical and isotopic fractionation due to the effects of surface tension have also been discussed recently by Bloch and Luecke (1972).

One of the problems involved in clarifying the mechanism of sea salt fractionation is that of inadequate data on the excess of constituents found in the air over the open ocean. This excess represents the increase in the concentration of a chemical above the concentration expected from the amount of sea salt in a sample:

$$[SO_4^=]_{xs.} = [SO_4^=]_{obs.} - \{[SO_4^=]/[Cl^-]\}_{sw} \times Cl^-_{obs.,}$$

where the seawater (sw) sulfate-to-chloride ratio is taken as 0.14. Chemical fractionation is only one of the several possible origins for the excess. Other sources include volcanic emanations, biological transport, eroded continental material, and man-made pollutants.

In an effort to clarify the cause of the excess sulfate frequently observed in rainwater (Junge 1963, 1972), I am presenting data here on the sulfate and chloride ion concentrations in rainfall collected from oceanic islands, ocean-going vessels, and coastal cities. Lazrus, Baynton, and Lodge (1970) collected the cloud water that impinged on an aluminum screen located at an altitude of 1020 m in eastern Puerto Rico. However, their experiment was designed specifically to exclude rainwater from the samples.

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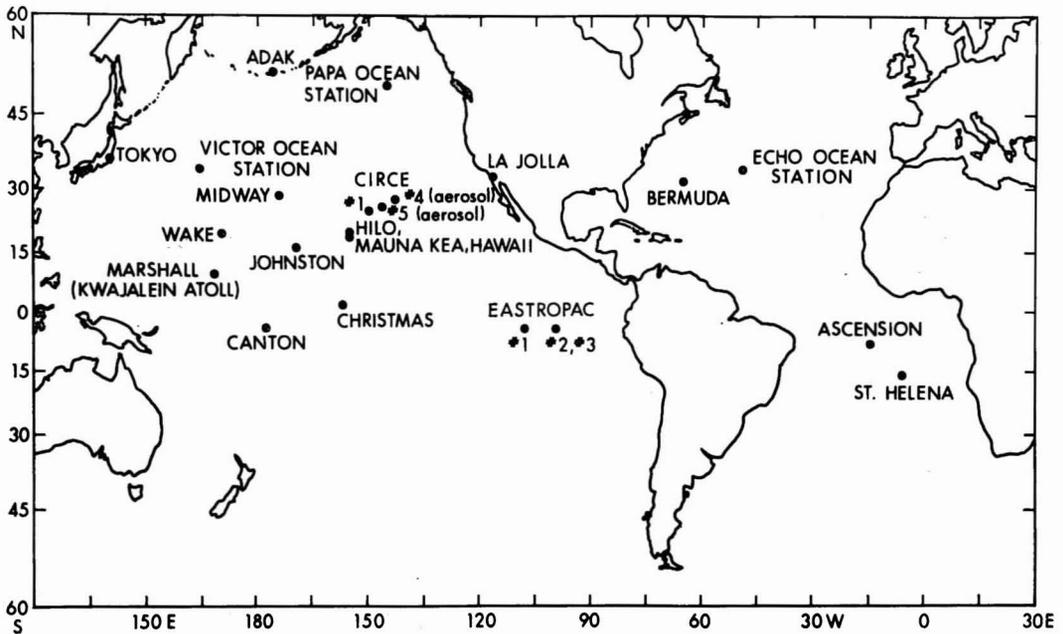
FIGURE 1. Map of the world showing the location of all sampling stations.

MATERIALS AND METHODS

The island and coastal city rainwater samples were collected by United States Weather Bureau personnel as part of the International Atomic Energy Agency/World Meteorological Organization Isotopes-in-Precipitation Network that monitors the concentrations of tritium and other stable and radionuclides in the atmosphere (IAEA 1969, WMO 1968). The samples used in this work were obtained from Dr. Hans Suess of the La Jolla Natural Tritium Laboratory where they were stored in flint glass bottles. The locations sampled are shown in Figure 1.

The Circe and Eastropac samples were obtained aboard the R.V. *Argo* of the Scripps Institution of Oceanography. The rain was collected in a 1.2 m × 2.4 m fiberglass tray with a drain in the bottom. The tray was covered with a weathertight seal around the edge when it was not in use, and this greatly reduced contamination. When the cover was opened the surface area of the collector doubled to 5.75 m², with the water running off the cover and tray into polyethylene bottles.

The La Jolla rain samples used for isotopic analyses were obtained from a 9 m² stainless steel collector located on the roof of Ritter Hall of the Scripps Institution of Oceanography (S.I.O.). The water flowed directly into my laboratory through Tygon tubing and was stored in polyethylene bottles. The aerosol samples were collected at the end of the S.I.O. pier (100 m offshore) at an elevation of 7 m above mean sea level or aboard the R.V. *Argo*, where a glycerol-wetted nylon screen with a mesh size of 1 mm was used.

I determined the concentration of sulfate ion on a Technicon AutoAnalyzer using an adaptation of the colormetric methyl thymol blue method (Lazrus, Lorange, and Lodge 1968, Kroopnick 1975). Most samples were run in duplicate and compared with seven standards containing between 0.96 and 24 ppm $SO_4^=$. One standard was run after every four samples. The average deviation between relicates of each standard was about 10 percent. The method for chloride is an adaptation of the procedures of Zall, Fisher, and Garner (1956), Skeggs (1965), Seto (1967), and Kroopnick (1975). Eleven Cl^- standards from 2 to 10 ppm were used. These were checked against six standards obtained from the United States Geological Survey in Menlo Park, California (Craig, personal com-
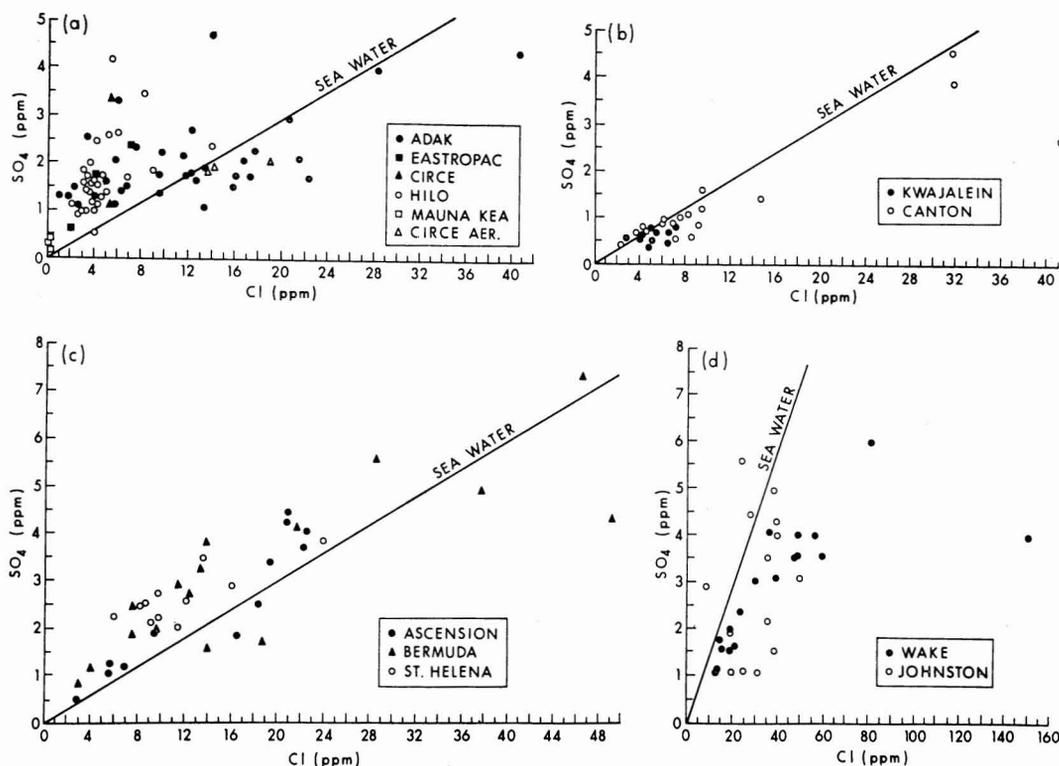
FIGURE 2. The concentrations of dissolved sulfate versus dissolved chloride in mg/liter. The solid line represents the average SO$_4$:Cl ratio in seawater of 0.14.

munication). A chloride standard was run after every four samples. The average deviation between replicates of each standard was about 5 percent.

The procedures used for extracting and measuring the $\delta^{18}O$ of the oxygen atoms in the sulfate molecules are too lengthy to be discussed here and have been described adequately elsewhere (Longinelli and Craig 1967, Longinelli 1968, Rafter and Mizutani 1967). Oxygen isotope data are expressed as the per mil enrichment of a sample in ^{18}O relative to the Standard Mean Ocean Water isotopic standard (Craig 1961): $\delta = [(R:R_{std}) - 1] \times 1000$ where R is the $^{18}O:^{16}O$ ratio.

RESULTS AND DISCUSSION

The final data tabulation includes the sample number, the concentrations of sulfate and chloride, the sulfate to chloride ratio, the date of collection, and the rainfall where appropriate (see appendix). Graphs of sulfate versus chloride are presented in Figures 2 and 3. The results from several locations have been combined on the same graph when they exhibit a similar pattern. The solid line on the graphs represents the SO$_4$:Cl ratio of average seawater, 0.14 (Morris and Riley 1966). The results from each location are summarized in Table 1, which also gives the standard deviation from the mean, the correlation coefficient between the SO$_4$:Cl ratio, and the order in which the samples were collected. A positive correlation coefficient of greater than 0.6 indicates that this ratio may have increased over time. In several cases large standard deviations from the mean of ± 100 percent occur. This may be due to natural variations, sample contamination during collection and processing, or analytical error. Sulfate and chloride standards run between every fourth sample had variations of only 10 and 5 percent, respectively (1 σ), which eliminates analytical error as a source of the large variations found in the natural samples.
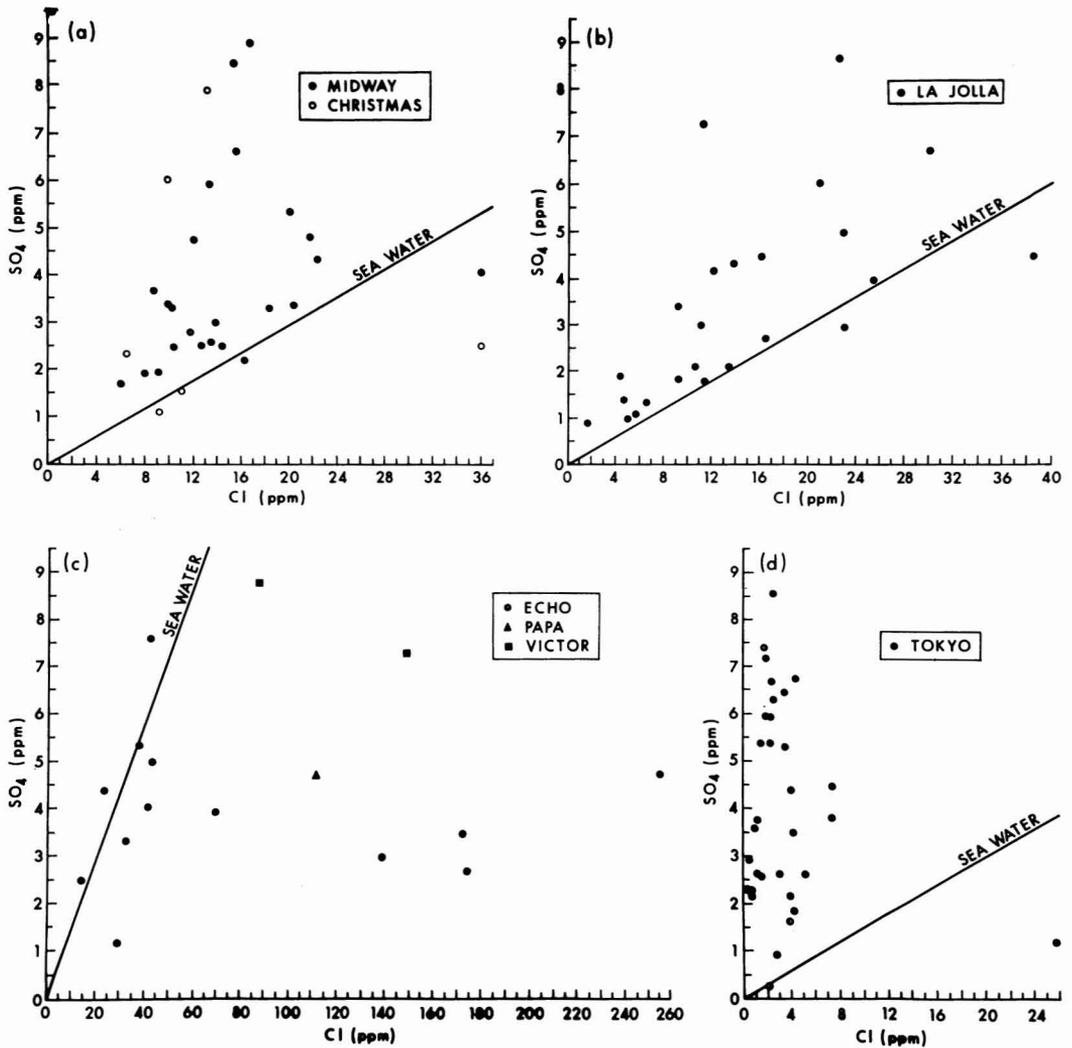
FIGURE 3. The concentrations of dissolved sulfate versus dissolved chloride in mg/liter. The solid line represents the average SO_4:Cl ratio in seawater of 0.14.

Some of the samples were stored as long as 7 years. Possible detrimental effects due to this prolonged storage include loss of water due to evaporation and microbial reduction of sulfate. The first process would increase the absolute sulfate and chloride values but should not change their ratios unless sufficient water had evaporated to cause precipitation. The extreme chloride enrichments observed in several samples from Canton, Wake, Bermuda, and the ocean stations Echo, Papa, and Victor may have been caused by sulfate reduction. However, in

all these cases the absolute chloride values also are very high. In addition, the presence of H_2S should have been noticeable when the glass bottles were opened, but none was ever detected. Therefore, SO_4 reduction probably can be ignored. Excess chloride has been observed previously in oceanic rains and aerosols and appears to be related to the wind speed (Handa 1969, Tsunogai et al. 1972). By dealing with the average value for a large number of samples we can ignore random natural variations. Systematic errors caused by

TABLE 1

SUMMARY OF SO$_4$ AND Cl DATA

AREA	NUMBER OF OBSERVATIONS	AVERAGE SO$_4$:Cl (wt.)	S.D.	CORRELATION COEFFICIENT	SAMPLING INTERVAL
Adak, Alaska	35	0.27	0.27	0.15	1962–1968
Ascension Island	12	0.18	0.03	0.06	1963–1966
Bermuda Island	16	0.20	0.08	0.11	1962–1967
Canton Island	19	0.13	0.04	0.66	1963–1966
Christmas Island	8	0.26	0.24	−0.75	1962–1964
Circe Expedition, Rains	3	0.31	0.27	–	1968
Circe Expedition, Aerosols	2	0.13	0.01	–	1968
Eastropac Expedition	3	0.37	0.05	–	1968
Echo, Ocean Station	13	0.09	0.07	0.59	1962–1966
Hilo, Hawaii	30	0.38	0.14	0.30	1964–1968
Johnston Island	14	0.12	0.10	−0.63	1964–1966
La Jolla, California	24	0.26	0.13	0.20	1958–1969
Marshall Islands	11	0.11	0.04	−0.17	1967
Mauna Kea, Hawaii	3	2.12	1.76	–	1968
Midway Island	24	0.28	0.13	−0.21	1964–1967
Papa, Ocean Station	2	0.04	–	–	1967–1968
St. Helena Island	12	0.28	0.12	−0.04	1965–1966
Tokyo, Japan	32	2.04	1.48	−0.09	1961–1962
Victor, Ocean Station	2	0.08	0.04	–	1962–1967
Wake Island	18	0.08	0.02	0.61	1964–1967
Average (Tokyo and Mauna Kea Excluded)		0.20	0.11	–	–
Seawater		0.14	–	–	–

sample contamination or sulfate reduction cannot be ignored but are probably negligible since chloride "enrichments" are rare, and the final conclusion is that no net enrichment of sulfate with respect to seawater was observed.

Samples from Midway, Christmas, La Jolla, Hilo, and Tokyo frequently are highly enriched in sulfate. For Tokyo this enrichment is certainly due to the burning of fossil fuels. The enrichments for Midway and Christmas islands may also be due to local pollution sources or, in the case of Christmas, to the oxidation of H$_2$S formed in several stagnant ponds located upwind of the rain gauge. The volcanic activity that is frequently observed in Hawaii does not appear to correlate directly with the high sulfate enrichments that are occasionally observed at the Hilo airport. Samples collected at three Atlantic islands (Ascension, Bermuda, St. Helena) show only slight sulfate enrichment, while at two Pacific islands (Wake, Johnston) a slight sulfate depletion is evident despite the presence of sulfur-emitting vehicles. The bulk of the data from Kwajalein, Canton, and Adak appears to scatter randomly about the seawater SO$_4$:Cl ratio of 0.14. Thus, uncontaminated rainwater collected on oceanic islands far from continental influences does not appear to differ significantly from the SO$_4$:Cl ratio of average seawater. This result is in contrast to the sulfate enrichment in cloud water observed by Lazrus, Baynton, and Lodge (1970). Their data give an average SO$_4$:Cl ratio of 0.40 ($\pm$ .23) due to higher sulfate but similar chloride values. Further evidence for a lack of ionic fractionation comes from two samples of marine aerosols collected on a nylon screen 50 feet above calm seas on a moving oceanographic research ship. The SO$_4$:Cl ratios of these samples (0.13, 0.12) were, within analytical error, the same as those of seawater.

Since samples were collected regularly for several years at most of the locations, the data were analyzed for possible increases or decreases in the SO$_4$:Cl ratio with time. The correlation coefficients in Table 1 indicate the probability of the SO$_4$:Cl ratio being related to the sampling date. Marginally significant, positive correla-

TABLE 2

$\delta^{18}O$ OF THE SO_4 RECOVERED FROM VARIOUS SAMPLES

SAMPLE DESCRIPTION	$\delta^{18}O\%_0$ SO_4	ORIGIN OF STORM (WIND DIRECTION)
La Jolla Rain		
31 Mar to 1 Apr 1967	9.4	NNW
1 Apr 1967	9.9	NNW
1 Apr to 4 Apr 1967	8.6±.1 (2)*	local
26 July 1967	11.2	NE
19 Nov 1967	10.0	SW
21 Nov 1967	9.0	local
Mont Laguna Snow		
1 Apr 1967	14.8	NNW
La Jolla Aerosols		
28 June 1967	13.5	NNW
7 Jul to 10 Jul 1967	13.2	W
30 Aug to 1 Sep 1967	11.2	Santa Ana
1 Sep to 5 Sep 1967	11.4	Santa Ana
Artificially Produced Spray		
Stock Solution	14.2±.1 (7)*	
Collected Spray	14.1±.2 (2)*	
Other Data		
Gracefield, New Zealand Rain†	10.7	
McQuaire Island Rain†	11.8	
Average Seawater‡	9.5	

NOTE:
* Number of analyses.
† Rafter and Mizutani 1967.
‡ Longinelli and Craig 1967.

tions are found for Canton and Wake Islands and Ocean Station Echo. The negative correlation shown for Johnston Island may also be significant. The strong negative correlation implied for Christmas Island is an artifact caused by a single, exceptionally high value.

Isotopic Results

The $^{18}O:^{16}O$ ratio of atmospheric sulfate sometimes differs from that measured for seawater sulfate and, thus, may be useful as a tracer that will allow us to distinguish other possible sources of atmospheric sulfate. Possible chemical reactions which modify the $\delta^{18}O$ of atmospheric sulfate particles also must be considered. The average $\delta_{SO_4}^{18}O$ value for seawater is 9.5‰ (Longinelli and Craig 1967). Sulfur dioxide produced by the combustion of fossil fuel at high temperatures is expected to have a $\delta_{SO_4}^{18}O$ that resembles atmospheric oxygen, 23.5‰ (Kroopnick and Craig 1972). Several mechanisms

have been proposed for the subsequent oxidation of this SO_2 to $SO_4^=$ (Gerhard and Johnstone 1955, Scott and Hobbs 1967). These mechanisms involve reaction with atmospheric oxygen to form SO_3 via an activated complex, SO_4^0. Thus, the resultant SO_3 should be more enriched in the heavier oxygen isotope than is seawater sulfate. Unfortunately, atmospheric water is highly depleted in $^{18}O(\delta_{H_2O}^{18}O$ $-14\%_0$ and $-5\%_0$, respectively, for southern California vapor and rains), making the exact isotopic composition of the final product difficult to predict. However, the resultant $SO_4^=$ should have a $\delta_{SO_4}^{18}O$ of $\sim 16\%_0$ following complete equilibration of the SO_2 with liquid water. The direct reaction of SO_2 with oxygen atoms (ozone) in industrially polluted environments or in the stratosphere should result in ^{18}O depleted sulfates, since these oxygen sources and reaction kinetics favor the lighter isotope. The mechanism for the low temperature oxidation of naturally produced H_2S to SO_2 is not

known and, therefore, it is premature to predict the isotope effects. Thus, a systematic survey of the $\delta_{SO_4}{}^{18}O$ in the various sulfate reservoirs is required before oxygen isotopes can be used to evaluate the relative importance of the several processes that contribute sulfate to the atmosphere. Unfortunately, the island rainwater samples discussed here were too small to permit isotopic analyses.

Preliminary measurements of rainwater collected in La Jolla, California, show that measureable differences can be detected in the oxygen isotope ratios of the sulfate (Table 2). High values of up to 11.2‰ occurred during a storm from the northeast. The lowest value of 8.6‰ occurred during a northwest wind and a prolonged, localized, low pressure cell. High values thus appear to be related to storms with a continental history, while the sea spray component has a lower $\delta_{SO_4}{}^{18}O$. A sample of snow that fell 40 miles inland (Mount Laguna) during the same storm that produced rain in La Jolla contained sulfate whose oxygen was several per mil higher ($\delta_{SO_4}{}^{18} = 14.8‰$, compared to 9.9‰). This increase may have been caused by the addition of continental sulfate.

Aerosols collected at the end of the S.I.O. pier on a glycerol-wetted nylon screen during westerly winds had an average $\delta_{SO_4}{}^{18}O = \sim 13.4‰$, while during a "Santa Ana" caused by a high altitude polar air mass a lower value of $\sim 11.3‰$ was obtained (Table 2). Thus, tropospheric aerosol samples appear to have a higher $\delta_{SO_4}{}^{18}O$ than do rainwater samples. This difference may be due to a dry oxidation mechanism for the conversion of SO_2 to SO_4 or perhaps to more efficient scavenging of locally produced anthropogenic SO_2 by aerosols.

Luecke and Nielson (1972) found that sulfur isotope fractionation occurred during experiments in which sea spray was artificially produced in the laboratory by bursting bubbles. However, I was unable to detect any oxygen isotope fractionation under similar experimental conditions (Table 2). Additional experiments are necessary to reconcile this difference.

CONCLUSIONS

Sulfate and chloride measurements of over 300 rainwater samples collected in the oceanic environment do not show any consistent evidence for ion fractionation during aerosol production and wet rainout. Preliminary measurements of the ^{18}O:^{16}O ratio of the oxygen in atmospheric and rainwater sulfates indicate that man-made and naturally produced continental sulfate can be distinguished from the sulfate in marine aerosols. Further measurements are needed before the relative contributions of industrial and naturally produced sulfates to the atmosphere can be evaluated.

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APPENDIX

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
		ADAK, ALASKA, 52° N, 177° W			
3	1.29	1.77	0.72	Jul 1962	6.05
5	1.76	17.23	0.10	5–7 Oct 1962	17.96
8	2.11	16.70	0.12	1 Dec 1962	–
9	1.14	5.78	0.19	1 Feb 1963	–
13	–	5.89	–	28 May 1963	1.57
23	1.08	13.30	0.08	10 Jun 1965	–

APPENDIX (*cont.*)

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
24	1.50	2.26	0.66	3 Aug 1965	0.71
25	1.65	12.60	0.13	Mar 1965	–
26	–	18.56	–	Apr 1965	24.31
32	1.42	6.25	0.22	Sep 1965	13.64
33	2.16	21.46	0.10	Oct 1965	16.92
35	4.67	95.97	0.04	Nov 1965	20.78
36	–	12.58	–	Dec 1965	14.05
37	1.52	15.76	0.09	31 Jan 1966	–
38	1.77	9.44	0.18	Jan 1966	–
39	3.00	20.57	0.14	Feb 1966	13.92
41	2.31	17.65	0.13	Mar 1966	3.18
42	2.24	9.64	0.23	Apr 1966	10.24
43	1.62	4.95	0.32	May 1966	–
44	4.74	13.96	0.33	Jun 1966	3.45
45	3.34	5.93	0.56	Jul 1966	–
46	1.77	11.71	0.15	Aug 1966	17.07
47	1.31	4.02	0.32	Sep 1966	9.55
48	2.19	11.48	0.19	Oct 1966	7.26
49	1.38	9.52	0.14	Nov 1966	29.57
50	4.06	28.29	0.14	Dec 1966	17.04
51	1.77	16.00	0.11	Jan 1967	11.33
52	4.45	40.62	0.10	Feb 1967	4.01
53	2.73	12.23	0.22	Mar 1967	11.30
54	2.34	7.47	0.31	Apr 1967	12.57
56	2.55	3.33	0.76	Jun 1967	4.14
57	1.31	0.98	1.34	Jul 1967	15.49
58	1.12	2.61	0.42	Aug 1967	11.99
59	1.95	13.30	0.14	Sep 1967	15.42
61	1.73	22.26	0.07	Nov 1967	24.79
62	1.51	6.70	0.22	Dec 1967	24.87
63	1.81	11.79	0.15	Jan 1968	22.40
65	2.79	--	–	Mar 1968	9.14
66	2.06	5.71	0.36	Apr 1968	12.70
65	–	13.67	–		
			ASCENSION ISLAND, 10° S, 15° W		
8	0.47	2.61	0.18	Mar 1963	116.50
9	1.89	9.28	0.20	Apr 1963	20.96
13	4.04	22.24	0.18	Aug 1963	16.12
15	3.38	19.12	0.17	Oct 1963	9.19
18	1.80	16.32	0.11	Jan 1964	11.44
20	1.18	6.70	0.17	Mar 1964	22.72
21	1.03	5.40	0.19	Apr 1964	55.20
22	4.45	20.59	0.21	Jun 1964	17.07
24	3.70	22.00	0.16	Aug 1964	17.91
30	1.23	5.50	0.22	Feb 1965	23.60
34	2.49	18.07	0.13	Jul 1965	14.94
43	4.23	20.59	0.20	Apr 1966	13.09

APPENDIX (*cont.*)

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
BERMUDA ISLAND (KINDLEY), 33° N, 65° W					
2	0.82	2.81	0.29	Aug 1962	–
3	1.16	3.89	0.29	Sep 1962	–
5	4.88	37.66	0.12	Nov 1962	–
7	5.52	28.33	0.19	Jan 1963	–
8	2.69	12.36	0.21	Feb 1963	–
9	7.25	46.35	0.15	Mar 1963	–
24	1.95	9.23	0.21	Jun 1964	10.95
26	1.54	13.80	0.11	Aug 1964	20.45
27	4.25	49.19	0.08	Sep 1964	27.48
28	1.69	18.55	0.09	Oct 1964	13.16
49	2.88	11.40	0.25	Jul 1966	15.27
50	1.84	7.43	0.24	Aug 1966	8.48
51	3.78	13.81	0.27	Sep 1966	12.73
52	2.45	7.52	0.32	Oct 1966	28.07
55	4.10	21.50	0.19	Jan 1967	9.73
60	3.23	13.30	0.24	Jun 1967	10.74
CANTON ISLAND, 3° S, 177° W					
16	0.59	8.55	0.06	Oct 1963	4.90
18	0.54	7.14	0.07	Dec 1963	24.38
20	3.90	31.67	0.12	Feb 1964	2.64
30	2.69	41.17	0.06	Jan 1965	–
31	4.56	31.48	0.14	Feb 1965	–
33	1.42	14.64	0.09	Apr 1965	–
35	1.01	7.52	0.13	Jun 1965	–
36	0.84	9.15	0.09	Jul 1965	5.36
37	0.78	4.94	0.15	Aug 1965	13.79
38	0.81	4.25	0.19	Sep 1965	9.02
39	0.43	2.34	0.18	Oct 1965	22.63
40	0.89	6.90	0.12	Nov 1965	42.80
41	0.97	6.10	0.15	Dec 1965	19.56
42	0.72	4.52	0.16	Jan 1966	52.04
43	1.07	8.25	0.12	Feb 1966	13.31
44	1.20	9.44	0.12	Mar 1966	6.60
45	1.60	9.40	0.17	Apr 1966	10.64
47	0.69	3.63	0.19	Jun 1966	10.31
48	0.88	6.00	0.14	Jul 1966	13.16
CHRISTMAS ISLAND, 2° N, 158° W					
1	7.94	12.97	0.61	May 1962	13.54
2	2.32	6.36	0.36	Jun 1962	4.98
3	6.04	9.59	0.62	Jul 1962	10.87
4	7.10	93.00	0.07	Aug 1962	0.53
5	2.52	35.92	0.07	Sep 1962	1.14
6	4.36	81.32	0.05	Oct 1962	0.58
7	–	13.55	–	Dec 1963	–
8	1.55	10.90	0.14	Jan 1964	–
9	1.10	9.08	0.12	Feb 1964	–

APPENDIX (*cont.*)

SAMPLE NUMBER	SO_4 (ppm)	Cl (ppm)	SO_4:Cl	DATE COLLECTED	RAINFALL (cm)
			CIRCE EXPEDITION, RAINS		
1*	3.39	5.40	0.62	16 Mar 1968	0.11 cm
3†	1.12	5.30	0.21	27 Apr 1968	0.3 cm
4	2.07	18.98	0.10	5 May 1968	–
			CIRCE EXPEDITION, AEROSOLS (NYLON SCREEN EXTRACTS)		
4‡	1.84§	13.93§	0.13	14 Mar 1968	$8 \times 10^4 \text{ m}^3$ (air)
5‡	1.90§	14.67§	0.12	15 Mar 1968	$7 \times 10^4 \text{ m}^3$ (air)
			EASTROPAC EXPEDITION		
1‖	2.38	7.00	0.34	14 Mar 1968	–
2‖	0.65	1.81	0.34	23 Mar 1968	–
3‖	1.75	4.10	0.42	23 Mar 1968	–
			ECHO, OCEAN STATION, 35° N, 48° W		
2	2.97	137.53	0.02	Aug 1962	–
3	–	273.91	–	Sep 1962	–
5	3.53	171.33	0.02	Nov 1962	–
6	–	166.41	–	Dec 1962	–
7	4.88	252.78	0.01	Jan 1963	–
8	–	74.64	–	Feb 1963	–
9	–	282.97	–	Mar 1963	–
10	2.71	173.44	0.01	Apr 1963	–
11	5.28	35.64	0.14	May 1963	–
14	3.93	68.36	0.05	Aug 1963	–
15	–	54.43	–	Sep 1963	–
16	5.04	40.57	0.12	Oct 1963	–
17	–	170.54	–	Nov 1963	–
18	–	220.85	–	Dec 1963	–
22	–	212.99	–	Apr 1964	–
24	4.11	38.45	0.10	Jun 1964	7.82
25	4.35	20.48	0.21	Jul 1964	8.26
26	7.58	40.04	0.18	Aug 1964	–
27	2.50	13.13	0.19	Sep 1964	12.12
30	–	274.72	–	Dec 1964	6.10
31	–	265.91	–	Jan 1965	–
34	–	169.76	–	Apr 1965	13.00
38	1.18	28.50	0.04	Aug 1965	4.57
40	3.30	31.00	0.10	Oct 1965	12.70
44	–	278.00	–	Feb 1966	4.78
45	–	243.15	–	Mar 1966	3.43
46	–	293.16	–	Apr 1966	–
			HILO, HAWAII, 20° N, 165° W		
17	0.55	4.12	0.13	May 1964	63.53
18	0.95	2.82	0.33	Jun 1964	17.81
19	1.56	4.38	0.35	Jul 1964	16.23
20	0.98	2.97	0.33	Aug 1964	18.69
21	1.61	3.90	0.41	Sep 1964	32.05

APPENDIX (*cont.*)

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
22	1.68	4.00	0.42	Oct 1964	29.36
23	1.40	5.10	0.27	Nov 1964	59.41
24	1.43	3.43	0.41	Dec 1964	24.51
25	1.14	4.32	0.26	Jan 1965	23.57
26	2.66	6.02	0.44	Feb 1965	9.42
27	1.78	3.84	0.46	Mar 1965	21.16
28	1.00	4.13	0.24	Apr 1965	46.96
29	–	2.68	–	May 1965	53.47
30	1.41	3.63	0.38	Jun 1965	22.48
31	2.03	3.74	0.54	Jul & Aug 1965	30.33
32	1.14	2.19	0.52	Sep 1965	14.53
33	1.30	4.70	0.27	Oct 1965	14.73
34	1.18	3.88	0.30	Nov 1965	48.72
35	1.87	8.95	0.20	Dec 1965	37.95
36	1.63	5.26	0.30	Jan 1966	31.90
37	1.73	3.49	0.49	Mar 1966	14.20
38	4.22	5.47	0.77	Apr 1966	13.31
39	3.49	8.12	0.43	May 1966	12.88
40	2.40	14.00	0.17	Jun 1966	19.02
41	1.76	4.76	0.36	Jul 1966	33.68
42	2.61	5.16	0.50	Aug 1966	18.34
43	2.49	4.27	0.58	Sep 1966	21.34
44	1.87	3.12	0.59	Oct 1966	39.60
45	1.61	3.22	0.50	Nov 1966	52.91
48	1.73	6.80	0.25	Feb 1967	26.29
63	–	2.68	–	23 Mar 1968	–
64	0.93	2.70	0.34	15 Apr 1968	–

JOHNSTON ISLAND, 16° N, 170° W

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
19	4.24	35.69	0.11	Feb 1964	–
20	5.61	22.96	0.24	Mar 1964	–
21	4.85	30.61	0.15	Apr 1964	–
22	2.81	6.85	0.41	May 1964	–
23	4.35	25.55	0.17	Jun 1964	–
25	1.04	24.36	0.04	Aug 1964	–
26	–	132.34	–	Sep 1964	–
27	3.94	39.36	0.10	Oct 1964	–
28	1.82	19.15	0.09	Nov 1964	–
40	3.49	34.28	0.10	Apr 1965	1.45
41	–	55.00	–	Jun 1965	2.74
42	1.06	19.44	0.05	Aug 1965	3.71
43	–	6.53	–	Oct 1965	8.28
44	2.18	35.00	0.06	Dec 1965	5.69
45	3.12	48.91	0.06	Apr 1966	0.79
46	1.48	38.70	0.03	Jun 1966	1.07
47	1.11	30.91	0.03	Jul 1966	3.18
48	–	73.00	–	Aug 1966	5.41

LA JOLLA, CALIFORNIA, 33° N, 117° W

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
32	4.45	16.20	0.27	25 Jan 1958	–
33	2.10	10.70	0.19	25 Jan 1958	–
34	6.70	30.10	0.22	26 Jan 1958	–
35	3.95	25.50	0.15	26 Jan 1958	–
36	8.65	22.50	0.38	3 Feb 1958	–

APPENDIX (*cont.*)

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
37	4.30	13.90	0.30	3 Feb 1958	–
38	1.80	11.50	0.15	4 Feb 1958	–
39	6.00	21.00	0.28	4 Feb 1958	–
43	–	48.00	–	6 Mar 1958	–
45	–	54.00	–	6 Mar 1958	–
55	2.95	23.00	0.12	1 Apr 1958	–
60	4.15	12.20	0.34	1 Apr 1958	–
61	3.40	9.30	0.36	1 Apr 1958	–
62	2.70	16.50	0.16	1 Apr 1958	–
29	–	6.90	–	19 Jan 1967	–
24	1.35	6.70	0.20	19 Nov 1967	–
25	1.40	4.75	0.29	19 Nov 1967	–
26	–	4.80	–	20 Nov 1967	–
27	0.90	1.75	0.51	21 Nov 1967	–
28	1.00	5.10	0.19	21 Nov 1967	–
30	2.10	13.50	0.15	15 Dec 1967	–
31	–	2.40	–	15 Dec 1967	–
65	1.83	9.31	0.19	26 Dec 1968	–
66	1.11	5.78	0.19	26 Dec 1968	–
67	4.44	38.65	p.11	30 Dec 1968	–
63	1.89	4.46	0.42	24 Jan 1969	–
64	2.98	11.16	0.26	24 Jan 1969	–
68	–	3.65	–	–	–
69	–	81.19	··	–	–
70	–	1.30	–	–	–
71	–	4.60	–	–	–
72	–	20.22	–	–	–
90	7.27	11.26	0.64	13 Dec 1967 (snow)	–
91	4.95	23.00	0.21	21 Jan 1962 (hail)	–

MARSHALL ISLANDS (KWAJALEIN ATOLL), 9° N, 168° E

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
21	0.79	7.14	0.11	Jan 1967	–
22	0.68	5.41	0.12	Feb 1967	24.69
23	0.76	4.85	0.15	Mar 1967	31.65
24	0.68	6.49	0.10	Apr 1967	19.41
25	0.45	6.40	0.07	May 1967	12.57
26	0.55	4.01	0.13	Jun 1967	27.91
27	0.56	2.76	0.20	Jul 1967	35.31
29	0.50	5.00	0.10	Sep 1967	34.80
30	0.35	4.72	0.07	Oct 1967	38.71
31	0.63	4.22	0.14	Nov 1967	28.35
32	0.45	6.40	0.07	Dec 1967	16.48

MAUNA KEA, HAWAII, 20° N, 165° W

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
1	0.39	0.23	1.65	21 Mar 1968	snow
2	0.32	0.08	4.06	21 Mar 1968	snow
3	0.18	0.28	0.64	21 Mar 1968	snow

MIDWAY ISLAND, 28° N, 175° W

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
18	2.63	13.45	0.19	Jan 1964	–
19	2.55	14.36	0.17	Feb 1964	6.99
20	2.85	11.71	0.24	Mar 1964	23.42
21	8.56	15.29	0.56	Apr 1964	5.21
22	5.99	13.21	0.45	May 1964	7.80

APPENDIX (*cont.*)

SAMPLE NUMBER	SO₄ (ppm)	Cl (ppm)	SO₄:Cl	DATE COLLECTED	RAINFALL (cm)
23	4.80	12.00	0.40	Jun 1964	5.64
24	8.98	16.66	0.53	Jul 1964	6.68
27	3.05	13.78	0.22	Oct 1964	15.57
28	2.24	16.19	0.13	Nov 1964	–
40	4.89	21.68	0.22	Feb 1965	–
41	4.11	36.05	0.11	Mar 1965	–
42	4.40	22.21	0.19	Apr 1965	–
43	3.38	10.20	0.33	Jun 1965	–
45	5.41	19.99	0.27	Nov 1965	–
46	–	28.29	–	Dec 1965	–
47	3.72	8.71	0.42	Jul 1966	–
48	6.70	15.50	0.43	Aug 1966	–
49	2.52	10.41	0.24	Sep 1966	–
50	1.99	9.17	0.21	Oct 1966	–
53	1.95	8.10	0.24	Jan 1967	–
54	1.74	6.10	0.28	Feb 1967	–
55	3.36	18.31	0.18	Mar 1967	–
56	3.41	20.34	0.16	Apr 1967	–
57	3.43	10.00	0.34	May 1967	–
58	2.55	12.68	0.20	Jun 1967	–

PAPA, OCEAN STATION, 50° N, 145° W

SAMPLE NUMBER	SO₄ (ppm)	Cl (ppm)	SO₄:Cl	DATE COLLECTED	RAINFALL (cm)
26	7.80	–	–	10 Apr–17 May 1967	–
27	–	252.03	–	1 May–22 May 1967	–
28	–	247.92	-	22 May–6 Jun 1967	–
29	–	182.13	–	6 Jun–7 Jul 1967	–
31	4.70	110.00	0.04	25 Aug–18 Sep 1967	–
32	–	235.61	–	19 Sep–6 Oct 1967	--
33	–	265.12	–	6 Oct–23 Oct 1967	–
34	1.70	–	–	11 Dec–24 Dec 1967	–
35	–	71.90	–	25 Dec 1967 20 Jan 1968	–
36	–	278.41	–	20 Jan–7 Feb 1968	1.68

ST. HELENA ISLAND, 15° S, 5° W

SAMPLE NUMBER	SO₄ (ppm)	Cl (ppm)	SO₄:Cl	DATE COLLECTED	RAINFALL (cm)
28	2.57	11.71	0.21	Apr 1965	7.14
30	2.51	8.32	0.30	Jun 1965	10.67
31	2.12	8.83	0.24	Jul 1965	10.19
32	7.75	12.60	0.61	Aug 1965	5.36
33	2.89	15.60	0.18	Sep 1965	7.39
34	3.86	23.48	0.16	Oct 1965	4.32
35	3.47	13.12	0.26	Nov 1965	2.31
37	2.20	9.40	0.23	Jan 1966	8.15
38	2.73	9.37	0.29	Feb 1966	11.46
39	2.47	7.89	0.31	Mar 1966	10.36
41	2.23	5.70	0.39	May 1966	13.72
42	2.00	11.05	0.18	Jun 1966	–

TOKYO, JAPAN, 36° N, 140° E

SAMPLE NUMBER	SO₄ (ppm)	Cl (ppm)	SO₄:Cl	DATE COLLECTED	RAINFALL (cm)
3	1.93	–	–	17–18 Nov 1961	0.55
27	5.32	3.54	1.50	9 May 1962	1.36
28	6.32	2.60	2.43	12 May 1962	1.41
29	2.64	1.23	2.14	17–21 May 1962	1.90
30	–	0.92	–	15–17 May 1962	1.70

APPENDIX (*cont.*)

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
31	0.93	2.72	0.34	23 May 1962	4.11
32	3.60	1.00	3.58	27–28 May 1962	2.81
33	6.70	2.45	2.73	29 May 1962	0.75
34	2.63	3.07	0.85	3–4 Jun 1962	1.81
35	3.50	4.22	0.82	4–8 June 1962	1.45
36	2.29	0.80	2.86	9–11 Jun 1962	5.42
37	2.93	0.61	4.80	11–12 Jun 1962	3.09
38	6.76	4.46	1.51	22 Jun 1962	0.81
39	7.19	1.91	3.76	24 Jun 1962	1.84
40	2.16	0.80	2.70	25–26 Jun 1962	3.55
41	7.43	1.83	4.06	26–29 Jun 1962	0.71
42	0.28	2.15	0.13	2 Jul 1962	2.29
43	2.60	1.60	1.62	2–3 Jul 1962	1.50
44	5.39	1.55	3.47	8–9 Jul 1962	2.12
45	5.97	1.97	3.03	9–10 Jul 1962	2.06
46	3.77	1.23	3.06	13 Jul 1962	3.28
47	1.20	25.76	0.04	28 Jul 1962	1.39
48	1.86	4.28	0.43	18–20 Aug 1962	3.60
49	2.63	5.30	0.49	25–27 Aug 1962	6.35
50	8.56	2.52	3.39	4–5 Oct 1962	0.66
51	6.47	3.50	1.84	11–12 Oct 1962	1.20
52	4.48	7.44	0.60	14–15 Oct 1962	1.34
53	3.83	7.43	0.51	15 Oct 1962	0.54
55	2.17	3.98	0.54	16–17 Nov 1962	1.27
56	1.63	3.87	0.42	16–17 Nov 1962	1.77
57	5.40	2.32	2.32	22 Nov 1962	1.23
58	2.31	0.40	5.77	26–27 Nov 1962	2.34
59	4.41	4.03	1.09	28 Nov 1962	0.56
60	5.95	2.33	2.55	5 Dec 1962	0.93

VICTOR, OCEAN STATION, 34° N, 164° E

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
1	–	222.86	–	Nov 1962	17.88
2	–	282.55	–	Dec 1962	22.43
28	–	275.54	–	Mar 1965	17.04
39	–	127.14	–	Feb 1966	12.62
40	–	281.30	–	Mar 1966	15.34
45	8.80	83.94	0.10	Aug 1966	–
56	–	156.99	–	Aug 1967	9.93
59	–	255.05	–	Nov 1967	8.79
60	7.40	144.92	0.05	Dec 1967	8.99

WAKE ISLAND, 20° N, 170° E

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
19	3.54	58.30	0.06	Feb 1964	1.55
20	3.95	148.08	0.02	Mar 1964	2.74
21	3.51	46.29	0.07	Apr 1964	9.35
25	1.45	18.94	0.07	Aug 1964	14.86
26	1.17	13.32	0.08	Sep 1964	17.22
27	1.57	21.00	0.07	Oct 1964	–
49	1.69	14.25	0.11	Aug 1966	12.32
50	1.54	15.58	0.09	Sep 1966	13.08
51	3.53	46.80	0.07	Oct 1966	6.43
55	5.90	79.00	0.07	Feb 1967	4.83

APPENDIX (*cont.*)

SAMPLE NUMBER	SO$_4$ (ppm)	Cl (ppm)	SO$_4$:Cl	DATE COLLECTED	RAINFALL (cm)
56	3.99	47.32	0.08	Mar 1967	15.60
57	3.01	29.60	0.10	Apr 1967	9.65
58	3.95	55.00	0.07	May 1967	2.54
59	2.32	22.51	0.10	Jun 1967	10.62
60	1.11	13.50	0.08	Jul 1967	26.82
61	1.94	18.80	0.10	Aug 1967	22.12
62	4.06	30.50	0.13	Sep 1967	10.11
63	3.07	37.42	0.08	Oct 1967	7.92

* Circe sample no. 1 was taken at 24° N, 150° W.

† Circe sample no. 3 was collected while the ship was approaching Singapore.

‡ Circe sample no. 4 was collected at 27° N, 141° W; sample no. 5 was collected at 25.5° N, 146° W.

§ SO$_4$ and Cl are given in mg/liter of wash water (112 ml).

‖ Eastropac sampling positions were: no. 1—4° S, 107° W; no. 2—5° S, 98° W; no. 3—5° S, 98° W.