

**THE INFLUENCE OF THE MARINE ENVIRONMENT
IN THE PRECIPITATION CHEMISTRY OF A TROPICAL RAIN FOREST**

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INTRODUCTION

The ocean is a major contributor of aerosol and gases to the atmosphere. Seasalt aerosols are produced during the breaking of waves (e.g. Eriksson, 1959; Woodcock, 1980), and halogen and sulfur containing gases such as H_2S , $(CH_3)_2S$, SO_2 , COS , and SO_4^{-2} (e.g. Zafiriu, 1975) are formed by photochemical and/or marine biological processes. Since precipitation scavenges these components from the atmosphere, the chemistry of precipitation over the ocean and coastal areas will be dominated by the marine component.

METHODOLOGY

Weekly precipitation samples were collected from February 1985 to January 1986 in the El Verde area of the El Yunque rain forest as part of a nationwide monitoring being conducted by the National Atmospheric Deposition Program (NADP), and funded by National Oceanic and Atmospheric Administration (NOAA). Elevation at the site is 400 meters above sea level. The collector is placed on top of a 25 meter high tower.

An Aerochem Metric automatic collector which, minimizes the amount of dry deposition in the sample, was used. All plasticware used in the collector was scrupulously washed using a series of distilled-water rinses.

Immediately after a sample was collected, the pH and conductivity was measured at the field station laboratory using the procedures specified by NADP (NADP 1984). The samples were then shipped to the Central Analytical Laboratory (CAL), at the Illinois Water Survey, for analyses.

Once in CAL, conductivity and pH was measured again. The samples were analyzed for SO_4^{+2} , NO_3^- , Cl^- , NH_4^+ , Ca^{+2} , Mg^{+2} , Na^+ , PO_4^{-3} , and K^+ . The analytical techniques used included: ion chromatography for sulfate, atomic absorption spectrophotometry for calcium, magnesium, sodium and potassium, and Technicon AutoAnalyzer for nitrate, chloride, ammonia and phosphate.

The precision of the field pH and conductivity measurements was checked by using a dilute pH and conductivity standard solution provided periodically by CAL to the sites. In addition blind samples from the US Geological Survey were run on a quarterly basis. The agreement between the field and laboratory measurements was within ± 0.1 pH units. All other analytical techniques were evaluated using standard methods such as interlaboratory calibrations and standard additions.

During the sampling period 3 samples had very large seasalt components with $\text{Na}^-/\text{Mg}^{+2}$ ratios far from those of seawater. These poor ratios were probably the results of contamination, analytical error or dilution error. As these samples represent less than 5% of the total samples, their exclusion did not significantly affect the results of this study.

Three assumptions were made in calculating the contribution of seasalt to various components of rain.

- 1) all the reference species are contributed by seasalt.
- 2) no fractionation occurs during the formation of the aerosol.
- 3) no fractionation occurs during atmospheric transport and scavenging.

RESULTS AND DISCUSSION

The precipitation in El Yunque has two major components, seawater and acid. In order to determine the contribution of each component to precipitation composition, the ratios of $\text{Ca}^{+2}/\text{Na}^{+}$, $\text{Mg}^{+2}/\text{Na}^{+}$, $\text{K}^{+}/\text{Na}^{+}$, $\text{Cl}^{-}/\text{Na}^{+}$, and $\text{SO}_4^{-2}/\text{Na}^{+}$ were calculated from the average concentration of each element.

For the elements Mg^{+2} and Cl^{-} the mean ratios are 9% and 2% higher than those of the seawater ratio respectively. For SO_4^{-2} , Ca^{+2} , and K^{+} the ratios are significantly greater than the seawater value. This means that while seawater is the primary source of Mg^{+2} and Cl^{-} there are other sources of SO_4^{-2} , Ca^{+2} , and K^{+} .

Calcium

Seasalt contributed an average of 3.7 ueq/l, (SD= 2.4), or 34 % of the total Ca^{+2} . In almost 100% of our samples, the $\text{Ca}^{+2}/\text{Na}^{+}$ ratio were higher than the seawater ratio. Debris from the calcareous surface of the Island is probably responsible for this large excess of Ca^{+2} . Another source could be the presence of crustal dust transported from the Sahara region (Prospero, 1981) since maximum concentrations coincided with Sahara dust events. Similar results have been found in Bermuda sites (Galloway et al. 1983).

Potassium

There is an indication of potassium enrichment relatively to sodium since in 92% of the samples, the ratio compared to Na^{+} was higher than the mean seawater ratio. Sea salt contributed with 75% of the total potassium with a mean concentration of 1.8 ueq/l

(SD=1.19). Possible sources for this excess are crustal dust as well as local terrestrial sources.

Chloride

Seasalt accounted for 97% of the total chloride with an average concentration of 96.5 ueq/l (SD=63.3). There seems to be a small but significant excess of 3%. Only two of the samples (4%) were below the sea water ratio. Possible sources for this enrichment includes soil dust, degradation of organochloride compounds (Zafirliou, 1975; Cicerone, 1981, 1984), and desorption of inorganic gaseous chloride (Duce, 1969).

Magnesium

Apparently, there is a small (5%) enrichment of magnesium relative to sodium since 85% of the samples had a Mg^{+2}/Na^{+} ratio higher than the sea salt ratio. Seasalt magnesium accounted for 95% of the total. This raises the important question on whether this specie can be considered a strictly conservative tracer.

Sulfate

Seasalt was responsible for 48% of the total sulfate or 10.1 ueq/l (SD=6.6). All the ratios calculated were higher than the seawater ratio. Sources for these large excesses could be antropogenic transport of SO_4^{-2} or natural such as biogenic reduced sulfur gases from a marine source, or crustal dust.

IONIC RATIOS
ueq/l

	1 SEAWATER RATIO	EL VERDE P.R.	2 PICO ESTE P.R.	3 BERMUDA
Ca ⁺² /Na ⁺	0.0439	0.1701	0.2321	0.0652
Mg ⁺² /Na ⁺	0.227	0.247	0.243	0.223
K ⁺ /Na ⁺	0.022	0.033	0.063	0.029
Cl ⁻ /Na ⁺	1.16	1.19	0.98	1.19
SO ₄ ⁼ /Na ⁺	0.121	0.367	0.225	0.221

- 1 Wilson 1975
- 2 R. Trinidad (unpublished data)
- 3 Calculated from J.A. Galloway et al. 1982

AVERAGE CONCENTRATION
ueq/l

	SEASALT	NON SEASALT	TOTAL
SO ₄ ⁺²	10.1	10.9	21.0
Cl ⁻	96.5	2.8	99.3
Ca ⁺²	3.7	7.5	11.2
Mg ⁺²	18.9	1.0	19.9
K ⁺	1.8	0.6	2.4

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