ABSTRACT

Cloud water and rainwater were examined at remote sites in southeastern Alaska and coastal Oregon using standardized collection and analytical techniques. Cloud water and rainwater were characterized by extremely low concentrations of most ions except SO$_4^-$, Na$^+$, and Cl$^-$. Acidity was greater than expected because of organic acids from unknown sources. Concentrations of NO$_3^-$ and NH$_4^+$ were extremely low, especially compared to samples collected similarly in the eastern USA. Rainwater did not differ between Alaska and Oregon except in concentrations of Ca$^2+$, Mg$^2+$, K, Na$^+$, and Cl$^-$. Cloud water generally had higher concentrations of ions than rainwater, especially in NO$_3^-$, NH$_4^+$, and SO$_4^2-$. Ion concentrations were highly variable and non-normally distributed. Sample sizes in future studies should be large (> 40). Cloud water deposition may be very important in terms of potential pollution effects and nutrient cycling in ecosystems with frequent cloud cover.

Cloud or fog water is an important hydrologic input to many forest ecosystems, but little is known about the chemistry of this form of precipitation. Chemicals carried in such finely dispersed water are deposited directly onto leaves and could be a significant factor in vegetative growth, especially at high elevations where forests are often bathed in clouds and fog for long periods.

In 1984, the Institute of Ecosystems Studies (IES) of the New York Botanical Garden began a cooperative research project. At each of 10 sites in North America, cloud water and rainwater were systematically collected from June to September 1984-1986.

The objective of this study was to develop a first approximation of the chemical input to ecosystems from cloud water and rainwater, in contrast to the more usual collection and analysis only of bulk precipitation. The study was designed to supply information only on chemical inputs to artificial collection devices; results are not directly comparable to natural water interception by plants.

Few studies of precipitation chemistry have been made in the Pacific Northwest (Junge, 1958; Moodie, 1964; Tarrant et al., 1968; Fredriksen, 1972; Roth et al., 1985), and most have been directed mainly at determining the nitrogenous content of rainfall. To help remedy this lack of information for the Pacific Northwest, we established and operated two cloud-water sampling sites, one at Marys Peak, OR, and one near Juneau, AK, as part of the IES project.

Results of the national IES study have been published (Weathers et al., 1988), and additionally, we highlight herein the relatively pristine condition of cloud water and rainwater in the Pacific Northwest compared with conditions along the east coast. We display concentrations of plant nutrients and of pollutant precursors.

METHODS

Collection sites in Oregon and Alaska were established where we expected frequent ground-level clouds, freedom from local sources of air pollution, case of access, and available operators for the collectors. Once the sites were selected, cloud-water and rainwater collectors were placed so that no large obstructions existed to the windward.

Our initial site in southeast Alaska was in a clearcut near Freshwater Bay on Chichagof Island (57°33'N, 135°10'W, 25 m elev.), about 65 km west of Juneau, AK. The local vegetation included coastal forest of Sitka spruce [Picea sitchensis (Bong.) Carr.], western hemlock [Tsuga heterophylla (Raf.) Sarg.], and scattered muskegs. Both collectors from 5 June to 30 July 1984 at this site, we collected 11 rain samples but only three cloud samples, because clouds rarely descended to the ground. We found in both Oregon and Alaska that cloud behavior was unpredictable at low elevations. As a result, this site was abandoned and a new collection site was established near the top of a ski lift on Douglas Island (58°16'N, 134°30'W, 800 m elev.), 7 km southwest of Juneau.

At the new site, the vegetation was alpine, mostly mountain hemlock [Tsuga mertensiana (Bong.) Carr.] scattered among sedge meadows [Carex spp.] and low shrubs. Eight cloud and nine rain samples were taken at this site from 30 July to 4 Sept. 1984. Collections continued from 12 July to 1 Sept. 1985 (12 samples each of rain and cloud water).

Marine air masses en route to this collection site pass over the islands and inland saltwater straits of the Alexander Archipelago. The islands are densely forested, very sparsely inhabited, and without industrial air pollution sources.

In 1984, we also established a collection site at Cascade Head, a coastal headland 16 km north of Lincoln City, OR (45°3'N, 124°W, 100 m elev.). The collector was placed in a grass-forb meadow within 200 m of the coast. We collected 16 rain samples from 8 August through 29 November, but were unable to collect any cloud samples because the collection site was below cloud level. In 1985, the Oregon collector was placed on Marys Peak, a mountain in the Coast Range of west-central Oregon (44°30'N, 123°34'W, 1245 m elev.), about 25 km WSW of Corvallis. Local vegetation included grass-forb meadows surrounded by noble fir (Abies procera Rehd.) forest. Samples from this site were collected from 29 June to 1 Nov. 1985. Most of the clouds sampled originated over the Pacific Ocean and subsequently passed over scattered small coastal communities and at least 40 km of forests. Timber harvesting and slash burning are common activities in the surrounding forests, and a paper mill 35 km west emits sulfur oxides.

We sampled clouds with an active collector described by Daube et al. (1987). A battery-powered fan draws air and water droplets through an intake on the lower side of the collector; the position of the intake excludes rain-sized water droplets. Cloud water droplets strike a vertical array of Teflon threads and accumulate, flowing into a polyethylene bottle. The fan allows sampling of clouds in the absence of wind. Rainwater was sampled with a standard polyethylene funnel rain collector (Likens et al., 1967). Both collectors remained sealed in plastic bags when not in use to eliminate dry deposition.

Sampling of a cloud event began after visibility had been reduced to < 1 km for > 15 min and continued for 5 h, unless...
visibility exceeded the 1-km maximum. Rain samples were collected concurrently with cloud samples except during rainless cloud events or when rain clouds remained above the elevation of our collection sites.

Cloud and rain sample pH was measured within 3 h of collection. The samples were refrigerated until shipped unrefigerated to the IES in Millbrook, NY, for further chemical analyses. At IES, the sample pH was remeasured and ion concentrations were determined by the following methods: Ca$^2+$ and Mg$^{2+}$ by inductively coupled plasma-emission spectroscopy, K$^+$ and Na$^+$ by flame-atomization absorption spectroscopy, NH$_3$, and Cl by automated colorimetry, SO$_4^{2-}$ and NO$_3^-$ by ion-exchange chromatography (Dionex 21 F AS4A & AG4A columns), and organic acids by the method of Keene et al. (1983). Further details on methods and quality control are available in Weathers et al. (1988).

Ion-concentration data were tested to determine if they were normally distributed (Shapiro and Wilk, 1965). Non-normal populations were log-transformed and retested for normalcy. Comparisons of sites and cloud vs. rain were made with t-tests ($P < 0.05$) on the transformed normal populations. Projected sample sizes were determined by setting various levels of the standard error as a percentage of the mean, and then solving for sample size.

### RESULTS

Sulfate, chloride, and sodium ions dominated rainwater and cloud water at both sites in Alaska and Oregon (Table 1). Other ions measured were mostly present in very low concentrations. Hydrogen ion concentrations (activities) were higher than expected, with some pH values falling as low as 3.80 in cloud water and 4.05 in rainwater. Seven of the 20 Alaska cloud-water samples were analyzed for carboxylic acid concentration. These samples, organic acids accounted for 13% of the total acidity on average.

Concentrations of all ions varied greatly. The coefficient of variation ranged from 98 to 216% for cloud water and 106 to 197% for rainwater (Fig. 1). Generally, concentrations of ions thought to come from oceanic sources—Mg$^{2+}$, Na$^+$, and Cl—varied the most, suggesting that clouds were formed separately over ocean and land. The higher variability of Mg$^{2+}$, Na$^+$, and Cl in cloud water samples relative to rainwater may have resulted from collection of cloud water but not rain from some clouds that originated as ocean fog.

Infrequent deposition events with relatively high ion concentrations were responsible for the large variablity and for the non-normal, skewed distributions of all ion concentrations ($P < 0.05$). The frequency distributions of H$^+$ concentration and log-transformed H$^+$ ion concentration (pH) of rainwater from both sites are shown as an example (Fig. 2). Logarithmic transformations normalized nearly all distributions, allowing statistical comparisons of sites and type of deposition. A few populations of transformed concentrations did not quite meet the test criteria for normalcy but were included in tests because they were more normal than untransformed data.

Average concentrations of all ions in our Alaska cloud water were not significantly different from our Oregon cloud water ($t$-test; $P > 0.05$). Alaska rainwater was not significantly different ($P > 0.05$) than Oregon rainwater in terms of pH, NO$_3^-$, NH$_4^+$, and SO$_4^{2-}$. Rainwater differed ($P < 0.05$) in the ions K$^+$, Ca$^{2+}$, Mg$^{2+}$,
Rainwater and cloud-water samples collected at sites in Alaska and Oregon have very dilute concentrations in our Alaska and Oregon samples. On average, cloud-water concentrations were three times greater than rainwater (Fig. 4). Ammonium, $\text{SO}_4^{2-}$, and $\text{NO}_3^-$ were 4.3 to 4.8 times more concentrated in cloud water, but $\text{Cl}^-$, $\text{Na}^+$, and $\text{Mg}^{2+}$ were only 1.1 to 1.9 times more concentrated. Higher concentrations of nutrient ions suggest that impaction of cloud water on vegetation may be an important mechanism for nutrient input, at least in areas with frequent cloud cover. These inputs have been ignored when most nutrient budgets reported in the literature were constructed.

Average concentrations of $\text{NO}_3^-$ and $\text{NH}_4^+$ can be converted to inorganic N weight per unit volume and multiplied by annual rainfall and cloud deposition to estimate annual inorganic N input. This analysis does not consider possible input of free amino acids, which have been found in some marine rains (Mopper and Zika, 1987). Although annual rainfall is measured in many areas, the magnitude of cloud-water deposition is unknown. Cloud-water deposition is thought to occur when cloud-water droplets impact fine vegetative surfaces. Thus, the amount of water deposited probably depends on cloud frequency, windspeed, and the exposed area of small-diameter vegetative surfaces. For the purpose of this analysis, we used a range of possible cloud-water deposition rates, expressed as the percentage of hydrological input of rainfall (Table 2).

The highest cloud-water deposition rate as a percentage of rain (50%) was chosen based on an estimate for montane coniferous forests of the northeastern USA (Lovett et al., 1982). Nitrogen input may range from $< 1 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in areas with low rainfall and infrequent clouds to $> 4 \text{ kg ha}^{-1} \text{ yr}^{-1}$ in areas with high rainfall, frequent cloud presence, and vegetation capable of capturing cloud moisture. Cloud water could account for a three- to fourfold increase in N deposition when cloud water contributes one-half of the hydrological input of rainfall.

High variability in ion concentrations points out the need for large sample sizes. To estimate average hydrogen ion concentration in cloud-water samples with a standard error that is 10, 15, or 20% of the mean, 192, 85, or 48 events must be sampled. About the same number of samples must be collected to achieve this precision for hydrogen ions in rainwater. Sample sizes for other ions varied from 24 to 116 to achieve a standard error that is 20% of the mean; 43 to 206 to achieve a standard error that is 15% of the mean; and 97 to 465 to achieve a standard error that is 10% of the mean. Clearly, large sample sizes are needed to estimate average concentrations of ions in cloud water and rainwater with reasonable precision.

**CONCLUSIONS**

Rainwater and cloud-water samples collected at sites in Alaska and Oregon have very dilute concentrations...
of most ions. Cloud water from Alaska and Oregon sites appear to be chemically similar. With small sample sizes (14–32 events), rainwater statistically differs only in the ions Ca$^{2+}$, Mg$^{2+}$, K$^+$, Na$^+$, and Cl$^-$. Both cloud water and rainwater from Alaska and Oregon are much more dilute than in the eastern USA. Differences of more than an order of magnitude in concentrations of important nutrient and pollutant-related ions point out the strikingly different precipitation regime on the east and west coasts of North America. Because of the potential for saltwater influence at our two sites, the validity of using our data as a control for many eastern U.S. sites is questionable.

Cloud-water deposition may be an important source of nutrients because it is more concentrated in some important nutrient ions. Cloud water could account for a three- to fourfold increase in annual N deposition if cloud water contributed one-half of the hydrological input as annual rainfall. Input of nutrients and pollutants into forest ecosystems via cloud water deposition needs to be more fully evaluated in areas with frequent clouds.

Cloud-water and rainwater concentration data are highly variable and must be transformed to be statistically analyzed by parametric statistics. Very large sample sizes are required to achieve minimal precision. Based on sample variances from this study, we recommend sampling a minimum of 40 rain or cloud events.

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REFERENCES


