PRECIPITATION AND STREAMWATER CHEMISTRY FROM UNDISTURBED WATERSHEDS IN THE CASCADE MOUNTAINS OF OREGON

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(Received May 14, 1988; revised September 6, 1988)

Abstract. Long-term records of precipitation and streamwater chemistry are rare; such records from forested watersheds relatively free of acidic deposition are even rarer. Precipitation and streamwater chemistry have been measured on two undisturbed forested watersheds at the H. J. Andrews Experimental Forest located on the western slopes of the Cascade Mountains of Oregon. Data from one watershed spans the period 1973–1985, the other 1969–1985. The mean annual pH of precipitation was 5.5 with a range of 4.7 to 6.0. HCO_3^- was the dominant anion; Ca^{2+} and Na^+ were the dominant cations. The mean annual pH of streamwater was 7.3, and was dominated by HCO_3^- and Ca^{2+}. These data contrast sharply with data from other calibrated watersheds in the north Cascade Mountains of Washington and British Columbia, and with data from New Hampshire and North Carolina where pH of precipitation averages 4.14 and 4.43, respectively, with SO_4^{2-} the dominant anion.

1. Introduction

The effects of acidic precipitation on forests and forested watersheds has been of concern in the United States for nearly two decades (Likens *et al.*, 1972). Research indicates that acidic precipitation poses a threat to aquatic systems (Schindler, 1974; Schofield, 1977), and to terrestrial systems (Johnson, 1979) including threats to trees (Siccama *et al.*, 1982), forest nutrition (Johnson *et al.*, 1982), soils (Reuss and Johnson, 1986), and streams (Hall *et al.*, 1980).

For many years, acidic precipitation in North America was perceived to be an eastern problem (Cogbill and Likens, 1974). Recent research has suggested that acidic precipitation may be a problem throughout the United States and Canada (Wisniewski and Keitz, 1983; Harte *et al.*, 1985; Powers and Rambo, 1981). Volume weighted average pH of precipitation from the western slopes of the Rocky Mountains of Colorado averaged 4.9 from 1981 to 1984, with seasonal values as low as 4.3 (Harte *et al.*, 1985). Leonard *et al.* (1981) reported that the volume-weighted pH of precipitation at Lake Tahoe, California, had dropped from 5.10 to 4.67 between 1972–1973 and 1977–1978. Acidic precipitation has been reported from the San Francisco Bay area (McColl and Bush, 1978) to the Puget Sound area of western Washington (Vong *et al.*, 1985), and

Water, Air, and Soil Pollution **42** (1988) 203–219.

in the North Cascade Mountain Range of Washington (Cole and Johnson, 1977; Dethier, 1979).

Two limitations to the study of the effects of acidic precipitation on forests are a lack of long-term continuous precipitation records and a lack of reference areas that receive unpolluted precipitation. In this paper we present precipitation and streamwater chemistry data from sites at two elevations at the H. J. Andrews Experimental Forest in the Cascade Mountains of Oregon. Data from the lower elevation site have been collected continuously since 1969, and from the higher elevation site since 1973.

2. Site Description

The study areas are located at the H. J. Andrews Experimental Forest 72 km east of Eugene, Oregon, and consist of two small watersheds designated WS 8 (high elevation) and WS 9 (low elevation). WS 8 is 21.4 ha located between 955 and 1190 m in elevation with a southerly aspect and slopes from 20 to 40%. The watershed is underlain with two units of the Sardine Formation; one contains welded and nonwelded ash flows, the other, basalt and andesite lava flows (Swanson and James, 1975). The soils are an association of an Andic Cryumbrept and typic Haplorthods. The surface soils are sandy or silty loams while the subsoils are loams or clay loams. As a result of fire, the watershed is forested primarily by 130-yr-old Douglas-fir (*Pseudotsuga mensiezii* (Mirb.) Franco) with scattered 450-yr-old stands (Harr *et al.*, 1982).

The maritime climate of the study area is influenced greatly by the Pacific Ocean 160 km to the west. Daily mean January and July temperatures averaged 2 °C and 11 °C, respectively. Annual precipitation, measured at the weather station approximately 0.5 km west of the watershed at about 925 m elevation, averaged 219 cm during the 1964–1979 water years, ranging from 125 cm in 1977 to 290 cm in 1972. About 80% of the annual precipitation occurs from October to March. Most precipitation is rain, but snow is common. The snowpack generally begins to develop in early December. Pack depth may reach more than 225 cm and contain more than 85 cm of water equivalent. Streamflow has been measured continuously with an H-flume since October 1963 (Harr *et al.*, 1982).

WS 9 is 8.5 ha located between 425 and 700 m in elevation with a southeasterly aspect, and with steep slopes between 60 and 100%. The watershed is underlain by the Little Butte Formation consisting of blocky breccias derived from mudflows and pumice-deficient pyroclastic flows (Swanson and James, 1975). The soils are deep loamy-skeletal, mixed, mesic Lithic Dystrochrepts and Lithic Haplumbrepts (Brown and Parsons, 1973). The forest of WS 9 is predominantly 450-yr-old Douglas-fir with an understory of western hemlock (*Tsuga heterophylla* (Raf.) Sarg.). Precipitation is measured at the primary meteorological station at the administration site of the H. J. Andrews Experimental Forest at 426 m elevation about 1.3 km northwest of WS 9. Average annual precipitation from 1972 through 1984 was 230 cm. At this elevation nearly all of the precipitation occurs as rain. For the same period of record, daily mean

January and July temperatures averaged 1 °C and 18 °C, respectively. Streamflow has been measured continuously with a trapezoidal flume since 1969.

3. Methods

Samples of precipitation for chemical analyses were collected in large openings in the forest. Stainless steel funnels caught the precipitation, which passed through plastic tubing to an acid-washed polyethylene carboy in an underground chamber to keep the sample cool. The carboys were collected after a 3-week interval. Precipitation samples were 3-week composite samples of bulk precipitation for each watershed. References to 'individual samples' refer to these 3-weeks composites. Methods of sample handling and chemical analyses were the same as for streamwater samples. Composite samples collected over a 3-week period, even when stored in a cool dark environment, are subject to change. Comparisons were made between the 3-week composite bulk samples from the low-elevation collector, and the weekly wet-only precipitation samples collected for the National Atmospheric Deposition Program at the same site for 1985. The differences were minor.

Streamwater samples were collected in acid-washed polyethylene carboys by a proportional water sampler at the stream gage (Fredriksen, 1969). The discrete samples were composited into one sample for each watershed, which was collected every 3 weeks and transported to the laboratory. Once the samples reached the laboratory they were warmed to room temperature and divided into two aliquots. One of the aliquots was immediately filtered through a glass-fiber filter. A Whatman GF/C* filter was used prior to 1983, and a GF/F since. Specific conductance, pH, and HCO_3^- were measured on the unfiltered sample within 24 hr. PO_4–P was analyzed within 48 hr. Aliquots for the measurement of particulate and dissolved organic P were fixed and stabilized with 6N H_2SO_4 and potassium persulfate within 48 hr. The other analyses were performed as soon as possible on samples stored at 4 °C and warmed to room temperature. To test whether or not the composite streamwater samples had changed over the 3-week period, two grab samples were collected at each sampling interval during 1981–1982. One was analyzed immediately; the other was stored with the carboy at the stream gage for the 3 weeks. Comparisons of the data indicated that none of the constituents changed because of the 3-week storage. There were no consistent differences in concentrations between samples during the test period of 1 yr.

The pH of filtered samples was measured potentiometrically at room temperature; pH was converted to H^+ for all data analyses and subsequently reconverted to pH. HCO_3^- was determined from filtered samples, at room temperature, by potentiometric titration to pH 4.5 with 0.02 N H_2SO_4 and reported as HCO_3^- or as HCO_3–C. Specific conductance of filtered samples was measured on a Wheatstone Bridge at room tem-

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perature, corrected to 25 °C, and reported in μS. NO_3–N has been measured continuously by the Cd reduction method, manually from the inception of the study until 1978 with color measured by spectrophotometer, and automatically since 1978 on a Technicon Autoanalyzer (Armstrong *et al.*, 1967; Franson, 1980). Total N is defined as particulate N plus dissolved organic N plus NH_4–N and was determined by Nesslerization following macro-Kjeldahl digestion (Franson, 1980). PO_4–P was determined by the ascorbic acid method. Particulate and dissolved organic P were determined by the ascorbic acid method following persulfate digestion of unfiltered samples (Franson, 1980). Ca^{2+}, Mg^{2+}, Na^+, and K^+ were determined by atomic absorption spectroscopy.

Dissolved silica was measured by the molybdosilicate or molybdate yellow method manually until 1978; since 1978 the automated molybdate blue method has been used (Franson, 1980). Suspended sediment was measured by filtration through washed and weighed GF/C filter papers prior to 1983 and through GF/F filters since. Filter papers were then dried at 70 °C for not less than 48 hr, cooled in a desiccator, and weighed.

All concentration data are volume weighted by multiplying the concentrations of individual samples by the volume of the sample and dividing by the sum of the volume for the water year. Input-output budget data were calculated by multiplying the mean annual concentrations times the volume of precipitation or streamwater for the water year. A water year is from October 1 to September 30.

4. Results

4.1. SPECIFIC CONDUCTANCE

Precipitation falling on the watersheds of the H. J. Andrews Experimental Forest can be characterized as a dilute solution of low ionic strength (Table I). Specific conductance averaged only 5 μS (Table II) and ranged from 2 to 3 μS during the winter rainy season to about 14 μS during the late summer and autumn; occasional values were as high as 50 μS.

The specific conductance of the high elevation stream in WS 8 averaged 33 μS over the 8 yr of record (Table III). There was a strong seasonal periodicity, with summer low flows averaging 54 ± 1.3 μS and winter high flows averaging only 28 ± 1.0 μS. The specific conductance of the low-elevation stream at WS 9 averaged 41 μS, with summer highs of 75 ± 2 μS and winter lows of 32 ± 2 μS.

4.2. PH

From 1973 through 1985, the volume weighted pH of precipitation at the Andrews watersheds averaged 5.5 ± 0.1 (Table II) with a range of annual means of 4.7 to 6.0. These values are characteristic of unpolluted precipitation coming off the Pacific Ocean without passing over major sources of pollution, since unpolluted precipitation in equilibrium with CO_2 should have a pH of 5.6 (Barrett and Brodin, 1955; Likens *et al.*, 1976).

TABLE I

Cation-anion balance for the volume-weighted mean precipitation and streamwater chemistry data from two reference watersheds at the H. J. Andrews Experimental Forest in the Cascade Mountains of Oregon

Ion	Years	Precipitation		Streamwater	
		WS 8	WS 9	WS 8	WS 9
	n	μeq L^{-1}			
H$^+$	11	4	2	0	0
Ca^{2+}	10	9	8	145	186
Mg^{2+}	13	3	4	48	86
Na$^+$	13	11	11	108	97
K$^+$	13	2	3	11	5
HCO_3^-	13	33	36	326	380
NO_3^-	12	2	1	0	0
PO_4^{3-}	9	0	0	2	2
Cation sum	–	29	28	312	374
Anion sum	–	35	37	328	382
Error %	–	9	14	3	1

Streamwater pH at both watersheds averaged 7.3 ± 0.1 throughout the study. This neutralization was due to cation exchange as precipitation passed through the forest canopy and the soil on its way to becoming streamflow.

TABLE II

Comparison of precipitation chemistry at two reference watersheds at the H. J. Andrews Experimental Forest, Oregon, 1973–1985

Constituent	Yr	Watershed 8		Watershed 9	
		Mean	SE	Mean	SE
Conductance, (μS)	8	5	0.3	5	0.6
pH	11	5.4	0.1	5.6	0.1
HCO_3^-, mg L^{-1}	13	2.0	0.1	2.2	0.2
NO_3–N, mg L^{-1}	12	0.031	0.002	0.017	0.002
Total N, mg L^{-1}	7	0.069	0.005	0.082	0.010
PO_4–P, mg L^{-1}	9	0.004	0.001	0.004	0.001
Particulate P, mg L^{-1}	10	0.005	0.001	0.007	0.001
Diss. organic P, mg L^{-1}	13	0.002	0.001	0.004	0.001
Ca^{2+}, mg L^{-1}	10	0.18	0.03	0.17	0.10
Mg^{2+}, mg L^{-1}	13	0.04	0.01	0.05	0.01
Na$^+$, mg L^{-1}	13	0.25	0.03	0.26	0.03
K$^+$, mg L^{-1}	13	0.09	0.02	0.10	0.02
SiO_2, mg L^{-1}	13	0.26	0.07	0.21	0.05
Sediment, mg L^{-1}	13	1.62	0.19	2.19	0.32

TABLE III

Comparison of streamwater chemistry from two reference watersheds at the H. J. Andrews Experimental Forest, Oregon, 1973–1985

Constituent	Yr	Watershed 8		Watershed 9	
		Mean	SE	Mean	SE
Conductance, μS	8	33	0.8	41.	1.1
pH	11	7.3	0.04	7.3	0.04
HCO_3^-, mg L^{-1}	13	19.9	0.60	23.2	0.67
NO_3–N, mg L^{-1}	12	0.003	0.001	0.003	0.001
Total N, mg L^{-1}	7	0.042	0.003	0.066	0.003
PO_4–P, mg L^{-1}	9	0.022	0.001	0.022	0.001
Particulate P, mg L^{-1}	10	0.008	0.001	0.009	0.001
Diss. organic P, mg L^{-1}	13	0.018	0.001	0.019	0.001
Ca^{2+}, mg L^{-1}	10	2.91	0.02	3.73	0.19
Mg^{2+}, mg L^{-1}	13	0.58	0.02	1.05	0.03
Na^+, mg L^{-1}	13	2.49	0.06	2.22	0.06
K^+, mg L^{-1}	13	0.43	0.03	0.19	0.02
SiO_2, mg L^{-1}	13	12.35	1.01	14.57	0.99
Sediment, mg L^{-1}	13	7.05	1.41	2.90	0.71

4.3. ALKALINITY (HCO_3^-)

Bicarbonate (HCO_3^-) was by far the predominant anion in both precipitation and streamwater at the Andrews watersheds (Table I). The mean annual alkalinity of precipitation averaged 2.1 ± 0.1 mg L^{-1} over the period with little variation from year to year (Table II). These concentrations resulted in average annual additions of 8.5 ± 0.7 kg ha^{-1} of HCO_3–C to the watersheds (Table IV).

Stream HCO_3^- averaged 20 mg L^{-1} in the stream from WS 8, and 23 mg L^{-1} in the stream from WS 9 over the period 1973–1985. There was little year-to-year variability (Table III). There were, however, seasonal variations with lower concentrations occurring during winter high-flow periods and higher concentrations during the summer low-flow periods. These concentrations resulted in average annual losses of 48 and 58 kg ha^{-1} from WS 8 and WS 9, respectively.

4.4. NITROGEN

Mean annual NO_3–N concentrations in precipitation averaged 0.031 mg L^{-1} and 0.017 mg L^{-1} at WS 8 and WS 9, respectively, over the period of record (Table II). These concentrations resulted in deposition rates of less than 1.0 kg ha^{-1} at both sites (Table IV). NO_3^- concentrations in streamwater were so low that they were not a factor in the cation-anion balance (Table I). Annual losses of NO_3–N averaged only 0.1 kg ha^{-1} from both watersheds.

Total N, which includes particulate, dissolved organic, and NH_4–N, averaged 0.07 ± 0.01 mg L^{-1} in precipitation (Table II). The highest concentrations occurred during late summer and early autumn, the period of least precipitation. Total N in

TABLE IV

Comparison of deposition of nutrients dissolved in precipitation at two watersheds at the H. J. Andrews Experimental Forest, kg ha^{-1} yr^{-1}

Constituent	Yr	Watershed 8		Watershed 9	
		Mean	SE	Mean	SE
HCO_3–C	13	8.6	0.65	8.4	0.66
NO_3–N	12	0.7	0.06	0.3	0.06
Particulate–N	7	0.4	0.03	0.7	0.09
Diss. Org. N plus NH_4–N	13	1.0	0.05	1.0	0.10
PO_4–P	9	0.1	0.01	0.1	0.01
Particulate P	10	0.1	0.01	0.1	0.02
Dissolved organic P	13	0.1	0.01	0.1	0.01
Ca^{2+}	10	3.7	0.68	3.4	0.58
Mg^{2+}	13	0.9	0.09	0.9	0.10
Na^+	13	5.4	0.58	5.0	0.55
K^+	13	2.0	0.29	1.8	0.27
SiO_2–Si	13	2.4	0.63	1.9	0.43
Suspended sediment	13	32.8	3.13	41.2	5.66

streamwater from WS 8 averaged 0.04 mg L^{-1} while WS 9 averaged 0.07 mg L^{-1} (Table III). The highest values occurred during the periods of lowest flow in late summer and early autumn.

Nitrogen additions to these watersheds, in precipitation, as particulate nitrogen, dissolved organic N, NH_4–N, and NO_3–N averaged 2.0 ± 0.1 kg ha^{-1} yr^{-1} (Table IV). Nitrogen losses from the watershed averaged 0.8 ± 0.1 kg ha^{-1} yr^{-1} (Table V).

4.5. PHOSPHORUS

PO_4–P in precipitation averaged 0.004 mg L^{-1} with a range from near zero to 0.013 mg L^{-1} (Table II). No annual cycles were discernible. PO_4–P in streamwater from both watersheds averaged 0.022 mg L^{-1} over the period of the study with no seasonal cycles.

Particulate P concentrations in precipitation averaged 0.006 ± 0.001 mg L^{-1}, and dissolved organic P concentrations averaged 0.003 ± 0.001 mg L^{-1} (Table II). Streamwater concentrations of particulate P averaged 0.008 ± 0.001 mg L^{-1}, and dissolved organic P averaged 0.018 ± 0.001 mg L^{-1} (Table III). The highest concentrations occurred in the dry summer months in both precipitation and streamwater.

The average annual deposition of P as the sum of particulate, dissolved organic, and PO_4–P was 0.3 kg ha^{-1} (Table IV) for both watersheds. The average annual loss from the watersheds was 0.6 kg ha^{-1} for a net loss of 0.3 kg ha^{-1} (Table V).

4.6. CATIONS

Ca^{2+} concentrations in precipitation averaged 0.2 ± 0.1 mg L^{-1} during the period of record with little year-to-year variation (Table II). There was a strong seasonal cycle

TABLE V

Comparison of losses via streamwater from two reference watersheds at the H. J. Andrews Experimental Forest, kg ha^{-1} yr^{-1}

Constituent	Yr	Watershed 8		Watershed 9	
		Mean	SE	Mean	SE
HCO_3–C	13	47.9	4.29	57.7	5.63
NO_3–N	12	0.1	0.01	0.1	0.01
Particulate N	7	0.2	0.03	0.2	0.04
Diss. Org. N plus NH_4–N	13	0.5	0.07	0.6	0.07
PO_4–P	9	0.3	0.04	0.3	0.05
Particulate P	10	0.1	0.01	0.1	0.02
Dissolved organic P	13	0.2	0.04	0.2	0.03
Ca^{2+}	10	35.0	4.46	44.6	6.00
Mg^{2+}	13	7.1	0.63	13.4	1.45
Na^+	13	30.7	2.83	28.9	3.36
K^+	13	5.6	0.85	2.5	0.36
SiO_2–Si	13	72.0	8.23	88.7	10.95
Suspended sediment	13	95.1	21.2	44.4	14.52

with low values often near zero during the wet winters and occasional values as high as 1.4 mg L^{-1} during the dry summer months. Ca^{2+} deposition averaged 3.6 ± 0.6 kg ha^{-1} yr^{-1} over the 10 yr of record. Ca^{2+} concentrations in streamwater from WS 8 averaged 2.9 mg L^{-1} for the 10 yr of record (Table III). Concentrations averaged 2.4 ± 0.2 mg L^{-1} during the winter high-flow period, and averaged 4.8 ± 0.2 mg L^{-1} during the dry summer periods. Ca^{2+} concentrations in the stream at WS 9 averaged 3.7 mg L^{-1} with winter low flows averaging 3.1 ± 0.3 mg L^{-1}, and summer highs averaging 7.4 ± 0.3 mg L^{-1}. Ca^{2+} outflow from WS 8 averaged 35 ± 4 kg ha^{-1} yr^{-1} (Table V). This represents a net loss of 31 kg ha^{-1} yr^{-1} of Ca^{2+} from the ecosystem. WS 9 averaged a loss of 45 ± 6 kg ha^{-1} yr^{-1} for a net loss averaging 41 kg ha^{-1} yr^{-1}. Ca^{2+} outflow in streamflow is 10 times the input in precipitation.

Mg^{2+} concentrations in precipitation averaged 0.04 ± 0.01 mg L^{-1} over the course of the study with no apparent seasonal cycles (Table II). Concentrations of individual samples ranged from near zero to 0.28 mg L^{-1}. As a result, Mg^{2+} deposition averaged 0.9 kg ha^{-1} yr^{-1} with a range of 0.5 to 2.0 kg ha^{-1} yr^{-1}. Mean annual concentrations of Mg^{2+} in streamwater from WS 8 averaged 0.6 mg L^{-1} while WS 9 averaged 1.1 mg L^{-1} (Table III). The lowest concentrations occurred during the wet winter months. The highest concentrations occurred during the dry summer months. The mean volume-weighted output from WS 8 averaged 7.1 ± 0.6 kg ha^{-1} for an average net loss of 6.2 kg ha^{-1} yr^{-1}. WS 9 lost an average of 13.4 ± 1.5 kg ha^{-1} yr^{-1} for a net loss of 12.5 kg ha^{-1} yr^{-1}.

Na^+ concentrations in precipitation averaged 0.25 ± 0.03 mg L^{-1} with year-to-year variation of 0.11 to 0.43 mg L^{-1} (Table II). Na^+ deposition averaged

5.2 ± 0.6 kg ha^{-1} yr^{-1} (Table IV). Average concentrations of Na$^+$ in streamwater were 2.5 mg L^{-1} and 2.2 mg L^{-1} for WS 8 and WS 9, respectively, for the 13 yr of record (Table III). Na$^+$ was lost from WS 8 at the annual rate of 30.7 ± 2.8 kg ha^{-1} and at the rate of 28.9 kg ha^{-1} from WS 9.

K$^+$ concentrations in precipitation averaged 0.09 ± 0.02 mg L^{-1} (Table II) with a range from 0.03 mg L^{-1} to 0.24 mg L^{-1}. Deposition of K$^+$ averaged 1.9 ± 0.3 kg ha^{-1} yr^{-1}. Concentrations of K$^+$ in streamwater averaged 0.4 mg L^{-1} and 0.2 mg L^{-1} at the two watersheds with little seasonal variation. K$^+$ output in the stream from WS 8 averaged 5.6 kg ha^{-1} yr^{-1} with a range of 1.7 to 14.4 kg ha^{-1} yr^{-1} for an average net loss of 1.6 kg ha^{-1} yr^{-1}. Net loss from WS 9 averaged less than 1.0 kg ha^{-1} yr^{-1} (Table V).

4.7. Dissolved Silica (SiO_2)

Concentrations of SiO_2 in precipitation averaged 0.26 ± 0.07 and 0.21 ± 0.05 mg L^{-1} (Table II) for WS 8 and WS 9, respectively. Seasonal cycles were apparent with wet-season lows near zero and peak values each year at about 1.0 mg L^{-1} for a single sample. The maximum value measured, 2.8 mg L^{-1} in 1980, probably was associated with an eruption of Mount St. Helens. Deposition of SiO_2–Si to WS 8 averaged 2.4 kg ha^{-1} yr^{-1} (Table IV) with a maximum of 8.0 kg ha^{-1} yr^{-1} in 1980 and a minimum of 0.6 kg ha^{-1} yr^{-1} in 1975. WS 9 averaged 1.9 ± 0.4 kg ha^{-1} yr^{-1}.

Concentrations of SiO_2 in the stream of WS 8 averaged 12.4 mg L^{-1} over the period of record (Table III). WS 9 averaged 14.6 ± 1.0 mg L^{-1}. SiO_2–Si losses from WS 8 averaged 72.0 kg ha^{-1} yr^{-1} (Table V) with a range of 19.8 to 123.2 kg ha^{-1} yr^{-1}. Losses from WS 9 averaged 88.7 kg ha^{-1} yr^{-1} with a range from 26 to 158 kg ha^{-1} yr^{-1}.

4.8. Particulate Matter

Concentrations of particulate matter in precipitation at WS 8 averaged 1.6 mg L^{-1} (Table II). Concentrations during the winter season when most precipitation occurred averaged 0.4 ± 0.05 mg L^{-1}. Concentrations in the dry summer months averaged 9.7 ± 2.5 mg L^{-1}. The maximum value of 35.8 mg L^{-1} occurred during the yarding and trucking of logs from an adjacent harvested watershed. These figures translate to an annual deposition of 32.8 ± 3.1 kg ha^{-1} yr^{-1} (Table IV). Dust in the collector near WS 9 averaged 2.2 ± 0.3 mg L^{-1} for an average annual deposition rate of 41.2 ± 5.7 kg ha^{-1} yr^{-1}. Wet-season minimums were near zero while midsummer maximums averaged 15.8 ± 5.4 kg ha^{-1} with an absolute maximum value of 77 mg L^{-1}.

Concentrations of suspended sediment in the stream from WS 8 averaged 7.1 mg L^{-1} (Table III) with a range of annual means from 0.9 to 16.9 mg L^{-1} and individual values as high as 164.5 mg L^{-1}. WS 9 averaged 2.9 mg L^{-1} with annual means from 0.9 to 9.6 mg L^{-1} and a maximum value of 59 mg L^{-1}, about 3 times as much suspended sediment left WS 8 in streamflow as was deposited by precipitation. But at WS 9, deposition and loss were nearly equal.

5. Discussion

5.1. Precipitation

The chemistry of precipitation falling on the watersheds at the H. J. Andrews Experimental Forest was dominated by the anion HCO_3^- (Table I). NO_3^- was a minor contributor to the ion balance and PO_4^{3-} was not a factor. All of the measured cations were required to balance HCO_3^- in the following order of importance: $Na^+ > Ca^{2+} > H^+ > Mg^{2+} > K^+$.

In terms of deposition, the major element added to the watershed from precipitation was HCO_3–C (Table IV). In all likelihood, the source of this C was the dissociation of carbonic acid (H_2CO_3) formed in the atmosphere by the dissolution of CO_2 in water vapor. Na^+ was the next major element in terms of deposition, presumably derived from salt from the Pacific Ocean. Ca^{2+} was the third most important element, and may have been derived locally from dust from agricultural activities in the Willamette Valley and from unpaved truck roads in and near the Andrews Forest. Nitrogen was next in importance followed by K^+, Mg^{2+}, and P.

Unfortunately, SO_4^{2-} and Cl^- were not measured in our study. Comparative data from our 3-week composite bulk samples and the weekly wet-only samples are presented for 1985 (Table VI). Mean annual conductance and mean annual concentrations of NO_3^-, NH_4^+, and Mg^{2+} of the two data sets were within the standard errors. The weekly wet-only collections were more acidic and contained lower concentrations of Ca^{2+}, Na^+, and K^+ than the 3-week bulk collections. Unfortunately, HCO_3^- was not

TABLE VI

Precipitation chemistry data from the main meteorological station at the H. J. Andrews Experimental Forest comparing data from the bulk collector with wet-only data collected for the National Atmospheric Deposition Program during water year 1985

Constituent	Bulk		Wet only	
	Mean	SE	Mean	SE
	mg L^-		mg L^-	
Conductance	5.5	0.5	5.8	0.6
pH	5.7	–	5.3	–
HCO_3^-	2.29	0.22	–	–
NO_3^-	0.10	0.03	0.12	0.06
SO_4^{2-}	–	–	0.27	0.06
Cl^-	–	–	0.42	0.06
NH_4^+	0.02	0.01	0.03	0.01
Ca^{2+}	0.13	0.02	0.03	0.03
Mg^{2+}	0.05	0.01	0.03	0.02
Na^+	0.39	0.05	0.24	0.04
K^+	0.07	0.02	0.02	0.01

measured in the wet-only collection. But these comparative data seem to indicate that precipitation at the Andrews Forest is dominated by HCO_3^-, with Cl^- and SO_4^{2-} as important anions. The cations are dominated by Na^+ followed by H^+, Mg^{2+}, and Ca^{2+}. These seem to be minor differences that do not seem to jeopardize the value of the long-term data at the Andrews Forest. Nor do they compromise the conclusions of this paper: that precipitation at the Andrews Forest is dominated by the influence of the Pacific marine environment and is relatively free from local or long-range air pollution with the exception of local road and agricultural dust and seasonal ash falls from slash burning.

Our precipitation chemistry data agreed well with values reported by Sollins *et al.* (1980) for the same lower elevation site at the Andrews Forest for the period 1972–1975. They reported a pH of 5.2, 33 $\mu eq\ L^{-1}$ of HCO_3^-, with Na^+ the dominant cation. Deposition rates reported by Sollins *et al.* (1980) were nearly identical to ours. Fredriksen (1972) reported only 3 to 5 $kg\ ha^{-1}\ yr^{-1}$ of particulate matter in precipitation at the lower elevation collector. Our values were an order of magnitude higher, which may reflect greater use of the roads in the 1970's than in the 1960's.

Stednick (1981) reported nutrient deposition onto calibrated watersheds in southeast Alaska also from unpolluted air masses. At that site, pH averaged 6.5 from 1977 to 1980. He reported that in terms of deposition, Na was dominant followed by Cl followed by $Ca > Mg > S > N > HCO_3\text{–}C > K > P$ (Table VIII).

However, data published by Feller (1977) and Feller and Kimmins (1979) for gaged watersheds in southwestern British Columbia just east of Vancouver, B.C., Canada, indicated that air pollution can be a factor in western North America. They reported precipitation from 1971 to 1975 with an average pH of 4.5 with H^+ and SO_4^{2-} the dominant ions. Dethier (1979) also reported acid deposition in the North Cascades of Washington with high SO_4^{2-} deposition (Table VII).

Chemistry of precipitation at the Andrews Forest was in marked contrast with the chemistry of precipitation on forest lands in the Eastern United States, including the Hubbard Brook Experimental Forest (HBEF) in New Hampshire. HBEF is downwind of major industrial centers of the Northeastern United States and receives the results of anthropogenic emissions as acidic deposition (Munn *et al.*, 1984). At HBEF from 1963 through 1974 (Likens *et al.*, 1977), SO_4^{2-} was the predominant anion rather than HCO_3^- as at the Andrews (Table VII). NO_3^- was next and CL^- third. H^+ was the major cation in precipitation at HBEF with a pH of 4.14 compared with a pH of 5.6 at the Andrews. At HBEF, NH_4^+ was the second major cation with 12.2 $\mu eq\ L^{-1}$. The 6 yr of NH_4^+ data at the Andrews averaged only 2.1 $\mu eq\ L^{-1}\ yr^{-1}$. Ca^{2+}, Na^+, Mg^{2+}, and K^+ occurred at HBEF at concentrations similar to those at the Andrews.

In terms of deposition, C input as HCO_3–C to HBEF was negligible (Table VIII). SO_4–S was added to the ecosystem at the rate of 12.7 $kg\ ha^{-1}\ yr^{-1}$. In the only year SO_4–S was measured at the Andrews, 2.6 $kg\ ha^{-1}$ was added to the watershed. NO_3–N inputs to HBEF are sixfold higher than at the Andrews. While PO_4–P at 0.04 $kg\ ha^{-1}\ yr^{-1}$ is 2.5-fold less than at the Andrews.

The Fernow Experimental Forest in West Virginia (Helvey and Kunkle, 1986) and

TABLE VII

Concentrations of nutrients dissolved in precipitation for several sites in the Western and Eastern United States, μeq L^{-1}

Location	pH	H^+	HCO_3^-	NO_3^-	PO_4^{3-}	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Na^+	K^+	NH_4^+
Alaska[a]	5.65	2	80	–	–	10	60	30	40	4	–
British Columbia[b]	4.5	32	5	11	–	27	10	8	13	3	–
Washington[c]	5.4	4	–	1	–	8	3	7	29	1	–
Washington[d]	4.6	26	–	7	–	17	2	3	10	1	–
Washington[e]	4.85	14	–	–	–	22	4	2	10	2	–
California[f]	5.0	10	21	4	2	60	26	6	53	9	–
New Hampshire[g]	4.14	72	0	24	0	60	8	3	5	2	12
North Carolina[h]	4.43	37	–	10	1	33	10	4	9	2	7
H. J. Andrews WS 9	5.6	2	36	1	0	6	8	4	11	3	1

[a] Johnson, 1981, Wadleigh, Alaska, August–September 1974.
[b] Feller and Kimmins, 1979, 1972–1973.
[c] Vong *et al.*, 1985, Hoh River, February 1982–February 1983.
[d] Vong *et al.*, 1985, Tolt River, Cascade Mountains east of Seattle, 1982–1983.
[e] Dethier, 1979, North Cascade Range, 1974–1975.
[f] McColl and Bush, 1978, San Francisco Bay area, 1974–1975.
[g] Likens *et al.*, 1977, Hubbard Brook, 1963–1974.
[h] Swank and Douglass, 1977, Coweeta Hydrologic Lab, 1972–1976.

TABLE VIII

Deposition of nutrients dissolved in precipitation for several sites in the Western and Eastern United States, kg ha^{-1} yr^{-1}

Location	pH	HCO_3–C	NO_3–N	PO_4–P	SO_4–S	Ca	Mg	Na	K
Alaska[a]	6.5	4.6	0.5	0.5	9.6	18.8	12.3	38.4	4.0
British Columbia[b]	4.5	–	3.7	0.0	6.5	3.7	0.9	4.4	0.9
British Columbia[c]	–	1.5	0.3	0.1	2.2	7.3	2.2	13.2	0.9
Washington[d]	4.9	–	–	–	15.7	3.5	1.3	10.3	3.4
California[e]	5.0	1.7	0.2	0.3	4.8	2.2	0.3	6.6	1.7
California[f]	5.1	–	0.8	0.0	2.8	3.0	0.6	4.5	2.6
New Hampshire[g]	4.1	0.0	4.3	0.0	12.7	2.2	0.6	1.6	0.9
North Carolina[h]	4.4	–	2.9	0.1	10.7	4.8	1.0	4.3	2.1
H. J. Andrews WS 9	5.6	8.4	0.3	0.1	2.6	3.4	0.9	5.0	1.8

[a] Stednick, 1981, Indian River, 1979–1980.

[b] Feller and Kimmins, 1979, Haney, B.C., average of three watersheds – one year 1972–1973.

[c] Zeman, 1975, Jameson Creek – one year 1970–1971.

[d] Dethier, 1979, Copper Lake, Washington – one year 1974–1975.

[e] McColl and Bush, 1978, San Francisco Bay area, December 1974–April 1975.

[f] Leonard *et al.*, 1981, Lake Tahoe, October–April 1972–1973.

[g] Likens *et al.*, 1977, Hubbard Brook, 1963–1974.

[h] Swank and Douglass, 1977, Coweeta Hydrologic Lab, 1972–1976.

the Coweeta Hydrologic Laboratory in North Carolina (Swank and Douglass, 1977) are also downwind of sources of air pollution. As at HBEF, H^+ is the dominant cation and SO_4^{2-} is the dominant anion in precipitation (Table VII). At Coweeta, S > Cl > inorganic N > Ca > Na. At the Fernow Forest, however, inorganic N and S are deposited equally at the rate of about 13 kg ha^{-1} yr^{-1}, followed by Ca.

5.2. Streamwater Chemistry

The chemistry of the streamwater draining from the reference watersheds at the Andrews Forest was dominated by the anion HCO_3^-. Concentrations of other anions were negligible in the cation-anion balance (Table I). Ca^{2+} was the predominant cation and the concentrations were nearly twice those of Mg^{2+} and Na^+. The other cations, K^+ and H^+, were inconsequential to the ion balance. These high HCO_3^- concentrations represented an average net loss of 48 to 58 kg ha^{-1} yr^{-1} of C as HCO_3–C from these watersheds. This increase in HCO_3–C as precipitation passed through the plant-soil continuum to become streamflow seemed to be the result of the dissociation of H_2CO_3 produced by the production of CO_2 and organic acids during respiration of tree roots and soil microorganisms (Sollins *et al.*, 1980).

These results agreed well with streamwater concentrations previously reported for a nearby watershed covered by an old-growth Douglas-fir forest at the Andrews (Sollins *et al.*, 1980). They reported that HCO_3^- was the dominant anion at about 350 μeq L^{-1} essentially balanced by Ca^{2+} at 160 μeq L^{-1}, Mg^{2+} at 85 μeq L^{-1}, and Na^+ at 69 μeq L^{-1}.

While the data from the watershed covered with mature 130-yr-old Douglas-fir agreed well with data reported from a 450-yr-old, old-growth Douglas-fir forest, they differ widely from data reported for a 60-yr-old, second-growth northern hardwood forest at HBEF in New Hampshire (Likens *et al.*, 1977). Some of these differences may be attributed to differences in soils, geology, forest type and land-use history, but many of the differences may be attributed to the fact that forests of the Northeast are subject to acidic deposition. At HBEF, the average stream pH is 4.9 vs pH 7.3 at the Andrews Forest. As a result, HCO_3^- averages only 15 μeq L^{-1}, while SO_4^{2-} is the dominant anion at 131 μeq L^{-1}.

Nitrogen output from the Andrews watersheds was remarkably low. This output level represents an average accumulation of about 1.0 kg ha^{-1} yr^{-1}. At the HBEF, there was a net gain of about 2.5 kg ha^{-1} yr^{-1} (Table IX). Streams from reference watersheds at Coweeta and the Fernow Forest also gained about 5 kg ha^{-1} yr^{-1} of inorganic N.

Particulate, dissolved organic, and PO_4–P in streamwater at the Andrews averaged 0.6 kg ha^{-1} yr^{-1} over 10 yr, 1972 through 1981, for a net loss of 0.3 kg ha^{-1} yr^{-1}, also nearly a balanced budget. These P losses are an order of magnitude greater than those reported for Hubbard Brook. Coweeta reported a small net gain of PO_4–P.

Ca^{2+} averaged a net loss of 31 to 41 kg ha^{-1} yr^{-1} at the Andrews. Ca^{2+} outflow in streamwater was 10 times the input in precipitation. Net losses at the HBEF averaged 11.5 kg ha^{-1} yr^{-1} and 3 to 4 kg ha^{-1} yr^{-1} at the Coweeta and the Fernow forests. Net loss of Mg^{2+} at the Andrews averaged 6 to 13 kg ha^{-1} yr^{-1}. At HBEF there was an

TABLE IX

Loss of nutrients dissolved in streamwater for several sites in the Western and Eastern United States, kg ha^{-1} ha^{-1}

Location	pH	HCO_3–C	NO_3–N	PO_4–P	SO_4–S	Ca	Mg	Na	K	NH_4–N
Alaska[a]	7.2	36.1	2.2	0.4	22.8	275.0	24.0	39.6	10.3	1.4
British Columbia[b]	6.8	–	1.0	0.0	7.3	16.9	3.4	10.8	1.6	–
British Columbia[c]	–	7.3	0.2	0.2	3.0	41.7	8.8	25.6	2.6	0.4
New Hampshire[d]	4.9	1.5	3.6	0.0	17.6	13.7	3.1	7.2	1.9	0.3
North Carolina[e]	6.7	–	0.1	0.0	1.4	7.7	3.7	11.0	5.6	0.1
H. J. Andrews WS 9	7.3	57.7	0.1	0.3	–	44.6	13.4	28.9	2.5	–

[a] Stednick, 1981, Indian River, 1979–1980.

[b] Feller and Kimmins, 1979, Haney, B.C., average of three watersheds 1972–1973.

[c] Zeman, 1975, Jameson Creek – 1970–1971.

[d] Likens *et al.*, 1977, Hubbard Brook, 1963–1974.

[e] Swank and Douglass, 1977, Coweeta Hydrologic Lab, 1972–1976.

average net loss of 2.5 kg ha^{-1} yr^{-1}, with net losses of 2.7 kg ha^{-1} yr^{-1} at Coweeta. The average net loss of Na^+ from the reference watersheds at the Andrews was 25 kg ha^{-1} yr^{-1}. The net loss at HBEF was 5.6 kg ha^{-1} yr^{-1}, and 6.8 at Coweeta. K^+ loss from the reference watersheds averaged 1 to 4 kg ha^{-1} yr^{-1}. The net loss at HBEF was 1.0 kg ha^{-1} yr^{-1}, and 3.5 kg ha^{-1} yr^{-1} at Coweeta. SiO_2 losses from the reference watersheds at the Andrews averaged 167 kg ha^{-1} yr^{-1}. Net losses at HBEF averaged 38 kg ha^{-1} yr^{-1}, and 99 kg ha^{-1} yr^{-1} at Coweeta. Suspended sediment in streamwater at the Andrews Forest averaged 44 to 95 kg ha^{-1} yr^{-1}. Eight years of data at HBEF (1965–1973) averaged only 7 kg ha^{-1} yr^{-1}.

The watersheds at the Andrews Forest currently are relatively free of anthropogenic deposition. As such, they may be useful as reference forests as research progresses on the effects of acid deposition on the forest environment throughout North America. Precipitation chemistry should continue to be monitored at the Andrews Forest in the event that global changes in atmospheric chemistry begin to affect the forests of western Oregon.

Acknowledgments

This study was initiated by R. L. Fredriksen. We gratefully acknowledge field work by A. Levno, R. Mersereau. G. Lienkaemper, and C. Creel, and data management by D. Henshaw and T. Larrabee. Water chemistry analyses were performed by E. Holcombe and C. Jones under Supplement Nos. PNW-82-321 and PNW-83-341 to the Master Memorandum of Understanding between USDA Forest Service and Oregon State University. Financial support for field facilities and data collection, management, and analysis was also provided through grants from the National Science Foundation (DEB 7611978, DEB 7925939, DEB 8012162, and BSR 8300370, and Oregon State University.

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