MEASUREMENT AND MODELING OF WESTERN WASHINGTON PRECIPITATION CHEMISTRY

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Abstract. Precipitation was collected and chemically analyzed for a 1 yr period at four sites in Western Washington. Spatial and seasonal variabilities in concentrations were identified with the highest concentrations nearest emission sources and in the summer. Multiple correlations among measured species revealed five groupings which were interpreted as the influences of seasalt, metals from a Cu smelter, an urban factor, soil, and acidic sulfate aerosol. A simple washout model predicted that the Cu smelter was the major contributor to a budget for rainwater sulfate. Measurement uncertainties were estimated for each analyte.

1. Introduction

We are reporting the results of a 1 yr study involving the collection and chemical characterization of precipitation in Western Washington. Previous measurements of precipitation chemistry in Western Washington include two single event studies at multiple sites near a SO_2 emission source (Larson *et al.*, 1975; Knudson *et al.*, 1977), monthly sampling at a single site in Seattle (Feeley and Larsen, 1981) and a 6 mo study at five locations traversing Snoqualmie Pass in the Cascade Mountains (Logan *et al.* 1982). Our work extends the sampling period to 1 yr at four sites.

The study location provided a relatively simple system for data analysis. Clean air masses move inland from the Pacific Ocean past a small number of air pollution emission sources in the Puget Sound area. Figure 1 shows the location of the sampling sites and the relevant pollutant sources. Location in a mid-latitude marine climate results in frequent west-east passages of precipitating cyclonic synoptic systems which in our study region experience additional lifting due to the presence of the north-south oriented Cascade and Olympic Mountain ranges. Cyclonic southwest flow aloft frequently accompanies precipitation while low level wind flow patterns include the effect of orographic north-south channeling by mountain ranges bordering the Puget Sound lowland basin (Overland and Walter, 1983). In the Seattle area, 850 mb winds during rain are predominately from the SSW and corresponding surface winds are more variable but generally from the SW during rain (Vong, 1982).

In addition to the four sites we operated in the Puget Sound area, data were obtained from the National Atmospheric Deposition Program (NADP) for a 5th site that is operated by the National Park Service near the coast of Washington in the Hoh River valley (Yanish, 1983). This site was chosen because it is generally upwind of our other monitoring sites during rain events and usually not influenced by anthropogenic

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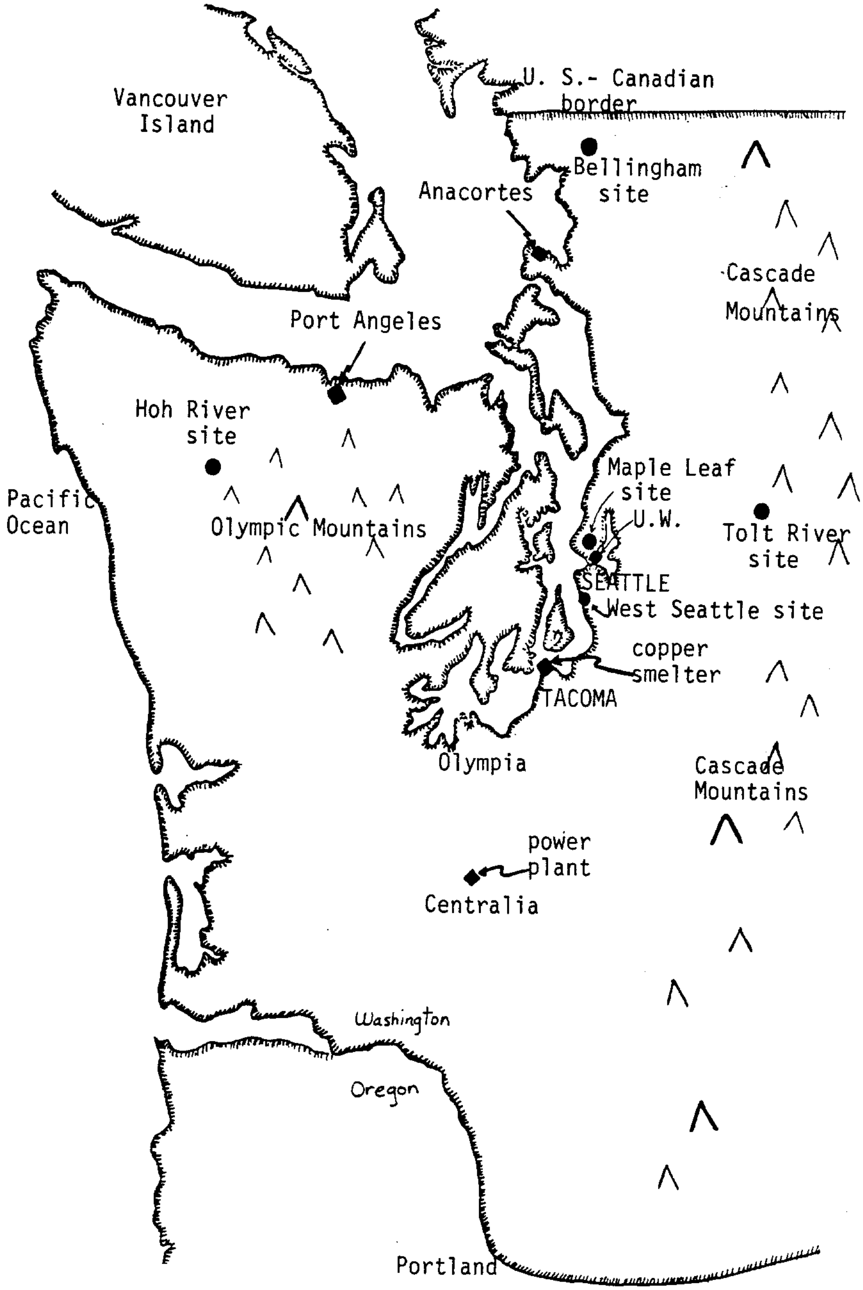

Fig. 1. Map of Western Washington precipitation monitoring sites, major industrial and urban air pollution emission locations, and topographical features.

emissions (Tanner *et al.*, 1972; Fox and Ludwick, 1976; Rancitelli and Perkins, 1970; Charlson *et al.*, 1984).

2. Experimental

Our precipitation samples were collected weekly in automated rain sensing collectors in a manner similar to the NADP sampling protocol. Samplers were located in grassy areas (minimum 0.8 ha) as far away from roadways and local emission sources as possible. Collection buckets were rinsed with 0.5 HCl followed by repeated rinses in deionized, distilled water until the conductivity of the final rinse fell below 1.5 μS cm^{-1}. This rinse was subsequently sent to the USEPA laboratory for chemical analysis. Samples were analyzed in the field for pH, conductivity, temperature, and volume. All samples were transported and stored in new (rinsed) Nalgene bottles. Samples were stored at 4 °C prior to analysis.

After transport to the USEPA water quality laboratory in Manchester, WA. the samples were analyzed for 15 chemical species and solution conductivity. SO_4^{2-}, NO_3^-, Cl^-, PO_4^{3-} and NH_4^+ were determined by colorimetric auto-analyzer techniques while Na^+, Mg^{2+}, K^+, and Ca^{2+} were determined by flame atomic absorption spectroscopy (AAS). Five trace metals (As, Pb, Cu, Cd, and Zn) were analyzed on graphite furnace AAS. Solution pH was measured by glass electrode in the University of Washington and the USEPA laboratories.

Sampling and analysis errors were quantified by duplicate analyses of split samples and from analysis of samples collected in co-located samplers. Selected samples were also analyzed for SO_4^{2-} and NO_3^- by ion chromatography (Dionex, model 10). All samples were analyzed for Ca^{2+}, Na^+, Mg^{2+}, and K^+ without prior filtration and for SO_4^{2-}, NO_3^-, NH_4^+, and Cl^- with prior filtration. A subset of 27 samples was reanalyzed for Na^+, K^+, Ca^{2+}, and Mg^{2+} after filtration through 0.45 μm pore size Millipore filters. Sampler collection efficiency was determined by the operation of a weighing rain gauge at each monitoring site.

3. Results

Table I presents the volume-weighted mean ion concentrations, pH, conductivity, and rainfall amount for samples collected from February 14, 1982 until February 15, 1983. The annual volume-weighted mean pH of precipitation in the Puget Sound area was between 4.4 and 4.6, compared to a rainwater pH value of 5.4 for a site 35 km from the coast. The cation concentrations represent unfiltered samples. We have reported the excess sulfate and Ca concentrations by correcting for seasalt contributions as calculated from rainwater Cl and the bulk chlorinity ratio in seawater (Junge, 1963). PO_4^{3-} was not detected in any samples (detection limit = 2μg L^{-1}).

We have attempted to evaluate the effect of two factors that could alter the observed ion concentrations: sample handling and collection and laboratory analytical imprecision. Handling and collection influences were evaluated by operation of two samplers

TABLE I

Summary of rainwater chemistry measurements: volume weighted mean (std. dev.)

	Hoh River[a]	West Seattle	Maple Leaf	Tolt River	Bellingham
H^+	4.1 [1.6]	36.4 [23.4]	38.8 [24.2]	25.5 [24.0]	26.9 [22.3]
SO_4	8.2 [5.6]	29.6 [17.8]	27.8 [16.9]	17.1 [12.4]	18.5 [11.8]
SO_4[b]	4.6 [3.5]	27.9 [17.3]	26.5 [16.3]	15.8 [12.4]	17.1 [11.7]
NO_3	1.3 [1.2]	7.2 [5.2]	8.7 [7.3]	7.1 [7.4]	8.1 [6.9]
NH_4	0.7 [1.4]	4.5 [3.6]	5.8 [6.1]	3.7 [4.3]	5.3 [4.8]
Cl^-	33.6 [36.1]	16.5 [17.7]	12.4 [12.2]	11.6 [9.1]	11.6 [11.8]
Na	28.8 [29.7]	11.5 [13.7]	9.5 [9.5]	9.6 [8.0]	10.0 [8.8]
Mg	7.0 [7.1]	3.4 [3.7]	2.7 [3.3]	2.8 [2.1]	2.6 [2.3]
K	1.0 [0.9]	0.7 [0.8]	0.7 [0.9]	0.7 [0.8]	0.9 [1.1]
Ca	2.7 [4.1]	6.4 [8.6]	4.9 [5.2]	2.3 [1.1]	2.5 [1.9]
Ca[b]	1.4 [1.5]	5.8 [7.7]	4.4 [5.0]	1.9 [1.7]	2.1 [2.1]
Pb (ppb)	–	3.5 [4.1]	5.0 [6.6]	1.8 [2.6]	1.5 [2.1]
As (ppb)	–	3.2 [4.6]	2.2 [2.8]	1.2 [2.3]	0.6 [1.4]
Cu (ppb)	–	4.5 [4.7]	5.1 [4.5]	1.9 [3.7]	2.1 [4.7]
Zn (ppb)	–	5.6 [5.7]	4.6 [6.3]	1.8 [3.0]	5.1 [22.7]
Cd (ppb)	–	0.3 [0.7]	0.4 [2.5]	0.9 [2.9]	0.1 [0.3]
Conductivity (uS cm^{-1})	7.6 [6.0]	15.6 [6.6]	15.3 [6.5]	9.9 [7.0]	10.3 [5.9]
Rainfall (cm yr^{-1})	306.8	99.6	100.9	218.4	87.4
Volume-weighted pH	5.39	4.44	4.41	4.59	4.57
$\Sigma(+)/\Sigma(-)$	1.03(0.30)	1.17(0.29)	1.15(0.22)	1.21(0.40)	1.19(0.29)

[a] Hoh river data from NADP (Yanish, 1983).

[b] Corrected for seasalt based on chlorinity ratio (see text).

located 5 m apart at the Maple Leaf monitoring site during the summer. We collected 16 pairs of samples and compared the concentrations of each chemical species in both buckets. We have calculated the relative mean deviation for each species as follows: first absolute value of the difference between each measurement and its sample pair mean was determined and then that value was divided by the pair mean value with the quotient averaged over the data set. This is similiar to rainwater sampling error calculations performed by Topol *et al.* (1982).

Laboratory analytical precision was evaluated by duplicate analysis of 19 split rainwater samples collected in the winter. The calculation procedure for these duplicate samples was identical to the evaluation of relative mean deviation for co-located samplers which was described above. Table II presents these estimates of our measurement uncertainties.

Results for these two subsets of our rainwater samples suggest that the measurement uncertainties were less than 30% of the reported concentrations for all measurements except Cu, Cd, Zn, and K. These four species were not utilized beyond reporting annual volume weighted concentrations and their associated uncertainties. The subset of rainwater samples which were used for the split sample analysis had concentrations near the detection limits for all trace metal species resulting in high relative uncertainties.

The effect of filtration on the reported concentrations for Ca, Na, Mg, and K was investigated by comparison of AAS measurements on filtered and unfiltered aliquots.

TABLE II

Estimate of experimental uncertainty[a] (%)

Analyte	Subset I ($N = 38$) duplicate analysis[a]	Subset II ($N = 32$) co-located samplers[a]	Subset III ($N = 54$) removed by filtration[b]
SO_4	1.8	9.1	
NO_3	0.5	5.7	
NH_4	6.0	13.3	
Cl	6.4	6.5	
Na	5.2	10.8	2.9
Mg	9.2	14.5	5.0
K	43.6	33.5	6.7
Ca	18.8	11.5	21.5
Pb	23.6	13.3	
As	29.8	17.8	
Cu	57.8	20.5	
Zn	56.6	33.4	
Cd	62.4	38.5	
H	9.2	13.8	
Conductivity	0.6	4.0	
Rainfall		6.5	

[a] Uncertainty $\cong$ relative mean deviation = $1/N\Sigma(|x_i\text{-pair mean}|/\text{pair mean})$.

[b] Removed by filtration for a given specie = $1/N\Sigma(x_1 - x_2)/x_2$

where: x_1 is the concentration for an unfiltered aliquot

x_2 is the concentration for a filtered aliquot.

Detection limits ($\mu g\ L^{-1}$): SO_4 = 500; $NO_3 - N$, $NH_4 - N$, Cl = 2; Na, Mg, K = 10; Ca = 20; As, Pb, Cu = 1; Cd = 0.1; Zn = 5.

Filtration was performed approximately one week after sample collection. The mean concentrations of all four species were higher in the unfiltered samples compared to the filtered samples although only the Ca concentrations were significantly ($p \leq 0.01$) decreased due to filtration.

To further evaluate the quality of our precipitation data we reanalyzed 29 samples for sulfate and nitrate on an ion chromatograph. These results agreed ($r = 0.99$, $p \leq 0.01$) with the colorimetric autoanalyzer data.

Unmeasured species of potential interest include HSO_3^- and HCO_3^-. For ambient CO_2 of 340 ppm, temperature of 20 °C. and pH = 4.5, equilibrium calculations were used to show that the HCO_3^- is less than 0.5 $\mu eq\ L^{-1}$. At pH = 5.0 HCO_3^- is less than 1.0 $\mu eq\ L^{-1}$ (Vong and Charlson, 1985). Similar calculations for ambient SO_2 of 10 ppb indicate that at equilibrium HSO_3^- could reach 20 $\mu eq\ L^{-1}$ and affect the sample charge balance but this occurs infrequently in our monitoring area and would not be important due to its oxidation to $SO_4^=$ in the sample during collection and storage. Both forms of S are detected as $SO_4^=$ by the colorimetric autoanalyzer technique.

The collection efficiency of the rainwater samplers was evaluated by the operation of a rain gauge at each site. Results indicated that each of our four samplers collected at least 96% of total rainfall with good correlation ($r = 0.99$, $p \leq 0.01$) between the gauge and sampler except for summer periods of low rainfall when evaporation in the gauge occurred.

Finally, analytical accuracy and completeness were verified by calculation of the charge balance as the ratio of cations to anions. Results of these calculations are presented in Table I for each of our sampling sites. These data show a 15% excess of cations over anions for the unfiltered samples, but only a 2% excess for the filtered

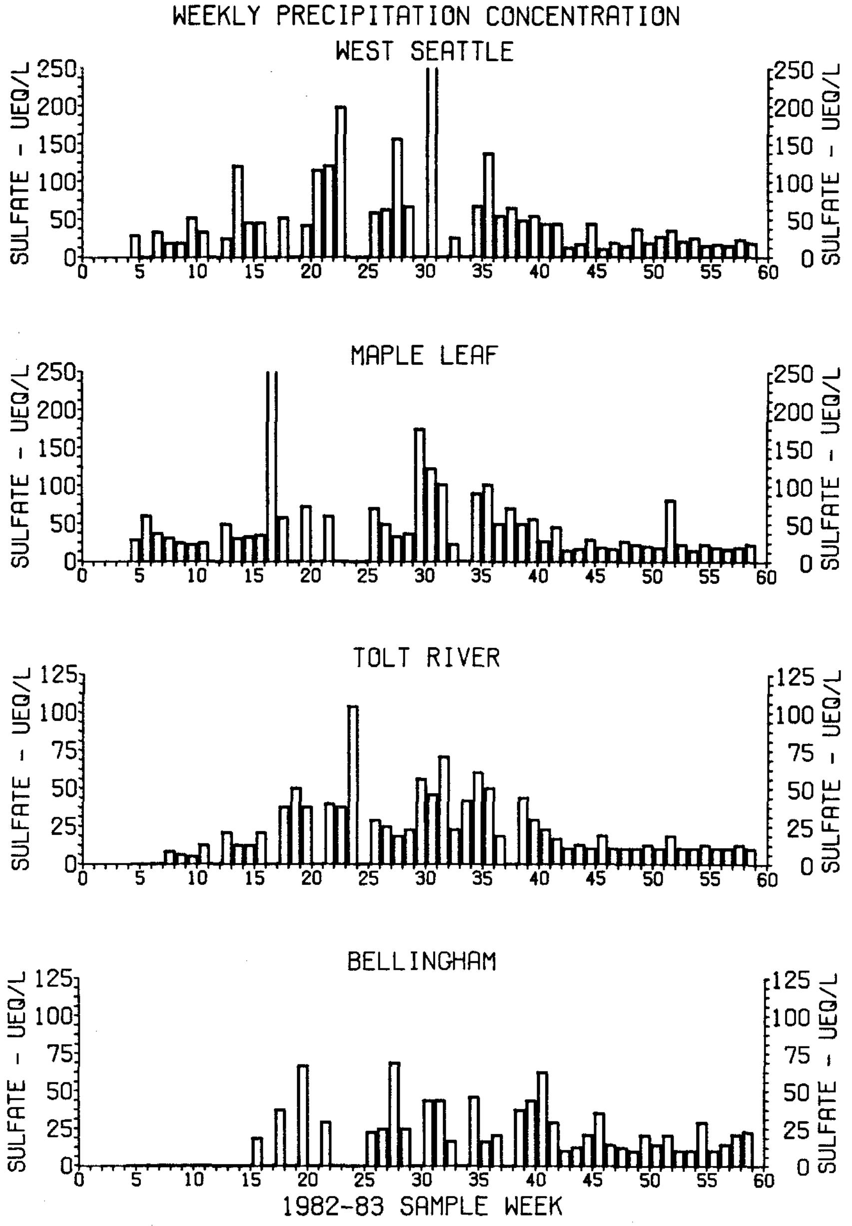

Fig. 2. Weekly precipitation sulfate concentration at four sites in Western Washington for 1982–83.

samples. This is consistent with the work of Peden and Skowron (1978). This charge imbalance may have been due to un-ionized Ca, Mg and K present in the unfiltered samples.

Seasonal variability was observed in the concentration of all species, with 200 to 400% higher concentrations in summer compared to winter (Vong and Waggoner, 1983). Figures 2 and 3 present time series for sulfate and nitrate ion concentrations at

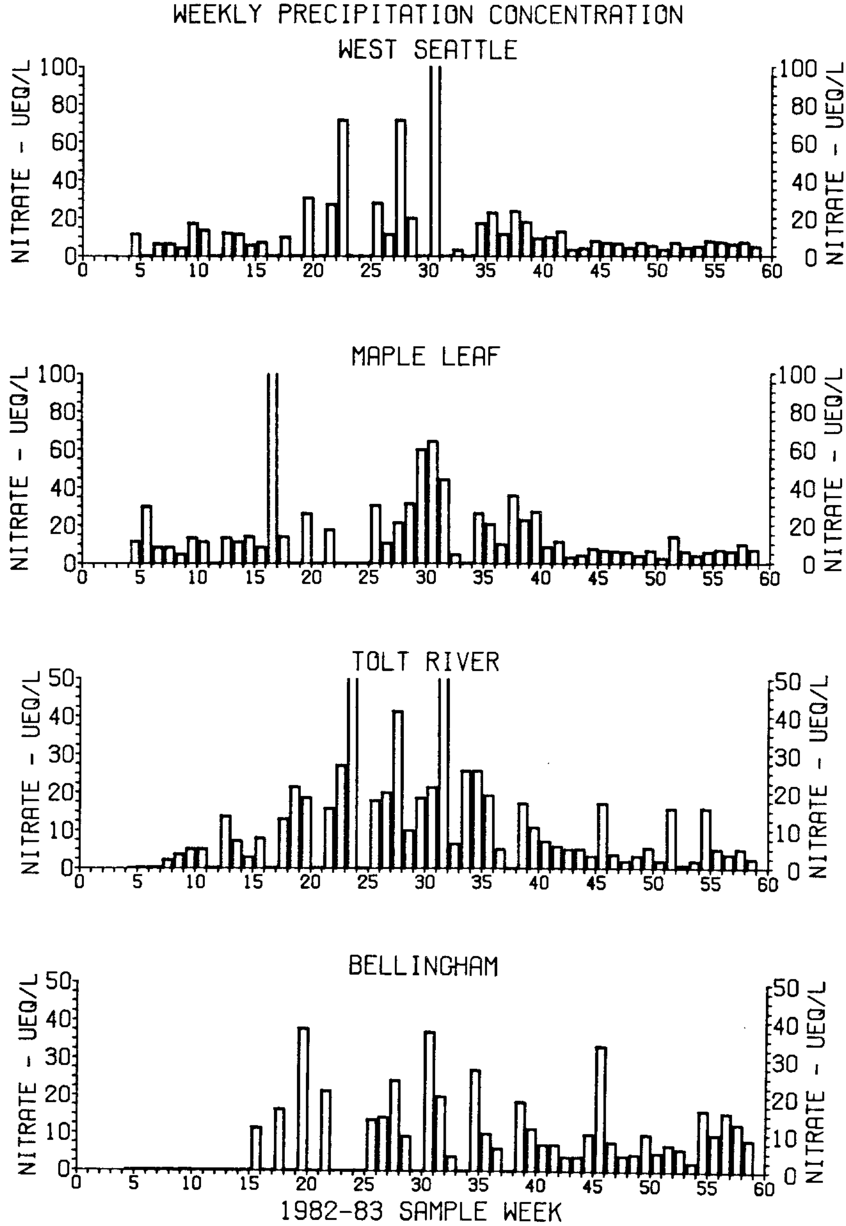

Fig. 3. Weekly precipitation nitrate concentration at four sites in Wetern Washington for 1982–83.

our 4 sampling sites. Analysis of rainfall data for Seattle indicated generally higher rainfall rates in winter than summer (1.15 mm h^{-1} compared to 0.71 mm h^{-1}) and longer duration of rainfall in winter than summer (29.8 hr $week^{-1}$ compared to 8.1 hr $week^{-1}$). This is different from most Eastern U.S. sites at which rainfall rates are generally higher in summer. Figure 4 presents time series for sample volume at the rainwater collection sites.

Rainfall quantity displayed a negative correlation ($0.1 \leq r \leq 0.5$) with the concentration of all species. To account for the potential effect of rainfall amount on our observed rainwater concentrations, we normalized the mass concentrations of any one species to the total mass concentration of all measured species in that sample. This procedure was previously applied to aerosol (Hansson *et al.*, 1984) and precipitation data (Gatz, 1983). Table III presents the normalized mass concentrations of four species for summer and winter samples. Summer has been defined as the period April 25 to September 4 with the remainder of the sampling period defined as winter. Seasonal

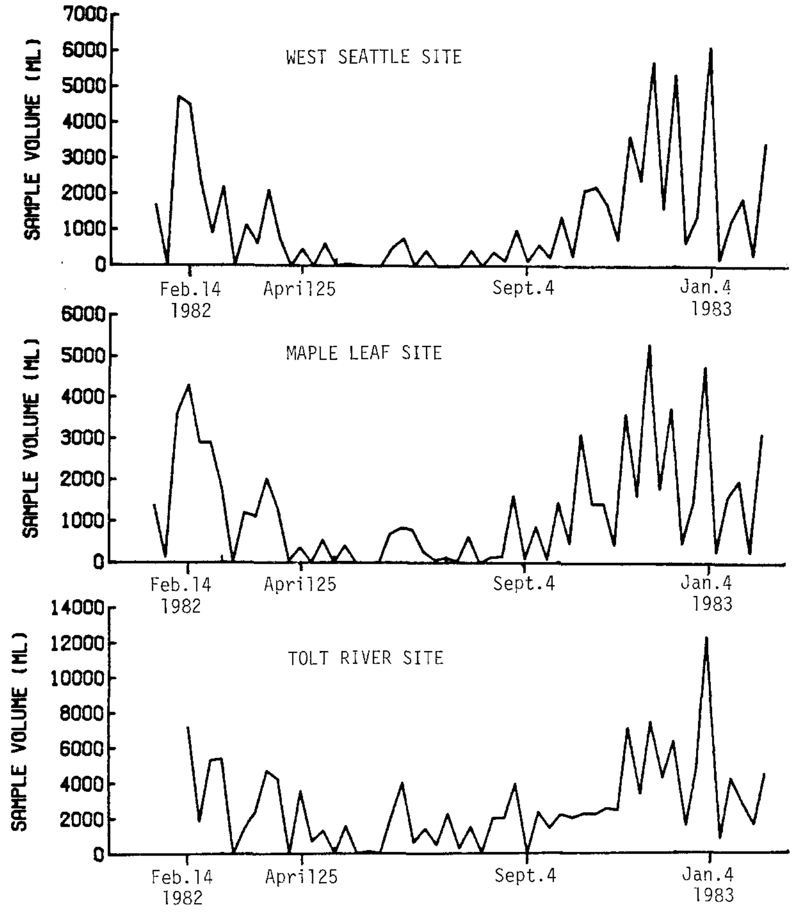

Fig. 4. Precipitaion volume for three Seattle area sites. Samples were collected at weekly intervals.

TABLE III

Fractional composition by season[b]

Site	West Seattle		Maple Leaf		Tolt River	
Specie	Winter[d]	Summer[c]	Winter[d]	Summer[c]	Winter[d]	Summer[c]
SO_4[a]	0.443	0.492	0.454	0.463	0.332	0.427
NO_3	0.167	0.171	0.180	0.212	0.191	0.271
Cl	0.176	0.118	0.159	0.118	0.230	0.102
Ca[a]	0.028	0.042	0.028	0.029	0.019	0.016

[a] Excess sulfate and calcium calculated from chlorinity ratio in seawater (Junge, 1963).

[b] Fraction = mass of specie/total ionic mass.

[c] Summer season = April 25 to September 4, 1982.

[d] Winter season = February 14 to April 25, 1982 and September 4, 1982 to February 15, 1983.

variation in the fractional composition was less pronounced than for the absolute concentration suggesting that the effect of rainfall volume was an important influence on rainwater concentrations.

Not all of the observed seasonal variability could be accounted for by the rainfall volume. Chloride was a larger fraction of the ions in winter than in summer in agreement with an expected source of seasalt associated with high wind speed in the winter. Excess sulfate and nitrate represented a larger fraction of the ions in the summer. Closure problems are possible for this type of normalization procedure and caution must be used in its application (Johansson *et al.*, 1984).

Table IV presents pair-wise correlation matrices for 11 chemical species at each site. Only those correlation coefficients greater than 0.5 are reported (significant at $p \leq 0.01$). Principal component factor analysis (Nie *et al.*, 1975) of rainwater concentrations at our four sites revealed the following groupings of species with similar factor loadings: (1) Cl, Na, Mg; (2) NH_4 and NO_3; (3) SO_4 and H ; (4) Ca and Pb; (5) As and Pb (at West Seattle only). A detailed discussion of the methodology and results of principal component factor analysis of these data are presented by Vong *et al.*, 1984. Knudson *et al.* (1977) observed similiar groupings in data for a single storm in the Puget Sound area.

Finally, we examined the relationship between surface wind direction (PSAPCA, 1983) and species concentration at the West Seattle site. This analysis has the following limitations: no single wind direction fully characterizes a weekly sample; surface wind direction is not exactly the same as the higher elevation transport wind direction. Sulfate, As, and Pb were 60, 300, and 110% higher, respectively, at this site for 26 weeks with predominantly southerly surface winds compared to 26 weeks with variable surface winds.

4. Discussion

Our measurements show relatively high values of excess sulfate at all four inland sites. The sulfate concentration is also highly correlated with H^+, with both concentrations

TABLE IV

Correlation matrix for rainwater concentrations (all values of $r \geq 0.5$ reported; $p \leq 0.01$)

	NH_4	NO_3	Cl	SO_4[a]	As	Pb	Na	Mg	Ca[a]	H
A: West Seattle monitoring site										
NH_4	1									
NO_3	0.850	1								
Cl			1							
SO_4[a]		0.587		1						
As					1					
Pb		0.501		0.550	0.573	1				
Na			0.714				1			
Mg			0.710	0.528			0.702	1		
Ca[a]		0.547		0.501		0.772			1	
H		0.500		0.784						1
B: Maple Leaf monitoring site										
NH_4	1									
NO_3	0.835	1								
Cl			1							
SO_4	0.803	0.805		1						
As					1					
Pb	0.674	0.556		0.673	0.548	1				
Na			0.876				1			
Mg			0.832				0.753	1		
Ca[a]	0.640	0.567		0.842		0.649			1	
H	0.662	0.814		0.861		0.577			0.587	1
C: Tolt River monitoring site										
NH_4	1									
NO_3	0.942	1								
Cl			1							
SO_4[a]	0.632	0.657		1						
As					1					
Pb	0.569	0.621		0.537		1				
Na			0.791				1			
Mg[a]			0.914				0.735	1		
Ca[a]	0.651	0.659		0.605		0.591			1	
H	0.696	0.769		0.867		0.710			0.622	1
D: Bellingham monitoring site										
NH_4	1									
NO_3	0.617	1								
Cl			1							
SO_4[a]		0.691	1							
As					1					
Pb		0.548				1				
Na			0.770				1			
Mg			0.572				0.832	1		
Ca[a]		0.524		0.515					1	
H		0.783		0.558		0.503			0.527	1

[a] Ca and SO_4 were corrected for seasalt (see text).

2 to 4 times higher in summer than in winter. In an attempt to account for the sources of the sulfate ion in our samples, we have constructed a simple empirical model that describes the concentration of sulfate in rainwater due to large SO_2 point sources and to the marine background. This model predicts the annual average sulfate concentration in rainwater as a function of location within the Puget Sound region.

The point source washout model assumes that the downwind concentration of sulfate in the rainwater that is due to the source is independent of rainfall rate and linearly proportional to the SO_2 emission rate (Hutcheson and Hall, 1974). A washout coefficient which represents the combined effects of oxidation of SO_2 to sulfate and of removal of S by precipitation has been determined from the results of a single storm study in the Puget Sound area (Larson *et al.*, 1975). Atmospheric dispersion is treated by a modified box model which uses climatological values for aloft wind speed and direction during rain to disperse emissions into a 16 sector wind rose (Vong, 1982). Sulfate deposition: $D_s(x)$, ($\mathrm{g\,m^{-2}\,yr^{-1}}$) is given by:

$$D_s(x) = \left[\frac{96}{64}\right][J_s\{x\} f_s Q W\{x\}] \div [(\pi/8)\, u_s x]$$

where the washout coefficient, $W\{x\}$, in fraction per millimeter of rain is given by:

$$W\{x\} = 0.012 + (0.047)(x - 1)/24, \text{ for } x \leq 25\,.$$

$$W\{x\} = 0.06 \text{ for } x \geq 25$$

and where:

x is the downwind distance (km)

f_s and u_s are the wind direction frequency (dimensionless) and speed ($\mathrm{m\,s^{-1}}$) from sector s

$J_s\{x\}$ is the rainfall rate in sector s at x ($\mathrm{mm\,yr^{-1}}$)

Q is the SO_2 emission rate ($\mathrm{g\,s^{-1}}$).

The annual volume-weighted sulfate ion concentration ($\mathrm{mg\,L^{-1}}$) is given by:

$$C_s\{x\} = D_s\{x\}/J\,.$$

About 75% of the SO_2 emitted in Western Washington during 1982 comes from two point sources shown in Figure 1 (PSAPCA, 1982). Transport wind direction frequency during rain was constucted from 6 yr of rawindsonde data available at sites near these two sources (Vong, 1982). The remaining 25% of the SO_2 emissions were due primarily to pulp mills and industrial fuel burning. These sources were approximated by two composite point sources centrally located in the cities of Seattle (King County) and Tacoma (Pierce County).

Marine background sulfate consists of two distinct parts: the SO_4 in seawater and the excess SO_4 associated with acidic compounds (Charlson and Rodhe, 1982; Galloway *et al.*, 1982). The seasalt SO_4, was computed from the observed Cl concentration measured at each monitoring site using a SO_4^{2-} : Cl^- mass ratio of 0.14. The marine excess SO_4 concentration at our sites in the Puget Sound region was computed using the values for the Hoh River NADP site. Galloway *et al.* (1982) present data for the background excess SO_4 concentration in areas with either low or high rainfall rates which are consistent with the Hoh River NADP annual volume- weighted mean value of about 5 μeq L^{-1} excess SO_4. Therefore, we have added background concentration to the model calculations to complete our S budget for rain in the Puget Sound area.

The results of the SO_4 washout model are presented in Table V. The model underpredicts the 1982–83 annual average SO_4^{2-} concentration from 5 to 19% depending on the site. The model indicates that the Tacoma Cu smelter contributed from 34 to 62% of measured total precipitation SO_4 for 1982–83 and that all anthropogenic sources accounted for from 60 to 78%. The assumption of linearity between SO_2 emissions and sulfate deposition and the determination of the washout coefficient from a single storm imply that the results of this simple model should be considered as an approximation. This result is qualitatively consistent with our analysis of concentration versus ground level wind direction presented earlier and also with the principal component analysis which identified an independent source of As and Pb, two elements emitted by the Cu smelter.

TABLE V

Results of model calculations for sulfate concentration (contribution to rainwater annual average SO_4 in μeq L^{-1})

Location	West Seattle	Maple Leaf	Tolt River
Predicted sulfate:			
Seasalt[a]	1.7	1.3	1.3
Background[b]	4.6	4.6	4.6
Cu smelter	18.3	12.5	5.8
Power plant	1.9	1.7	1.5
Pierce county[c]	1.9	1.3	0.6
King county[d]	Neglible	4.8	0.6
Sum of predicted	28.4	26.2	14.4
Measured sulfate	29.6	27.8	17.1

[a] Seasalt sulfate calculated from chlorinity ratio in sea water and measured chloride in rainwater at the site (Junge, 1963).

[b] Background excess sulfate concentration calculated from Hoh River NADP data (Yanish, 1983).

[c] Pierce county includes Tacoma.

[d] King county includes Seattle.

Our prediction of the contribution of sulfate ion from the Cu smelter was further tested by using As as a conservative tracer of the smelter plume. We compared the measured As concentration to the measured rainwater SO_4 at each site. This approach assumes that background As in the Puget Sound region is nearly zero (Rancitelli and Perkins, 1970; Tanner *et al.*, 1972) and that the smelter is the only significant source of As in the region (Carpenter *et al.*, 1978; Crecelius, 1974; Larson *et al.*, 1975; Knudson *et al.*, 1977).

Using this measured As to SO_4 ratio we calculated the percentage contribution of the smelter to total sulfate at each site. If the washout model prediction for smelter sulfate (62% of measured) for the West Seattle site is assumed correct, the As to SO_4^{2-} ratios indicate that the washout model predictions of 45% and 34% smelter contribution to measured sulfate at the Maple Leaf and Tolt River sites, respectively, are reasonable. As to SO_4^{2-} ratios predict smelter contributions at the Maple Leaf and Tolt River sites of 46% and 40%, respectively. In other words, the decline in measured rainwater As with downwind distance from the smelter is consistent with the decline in smelter sulfate as predicted by the washout model.

5. Conclusions

The annual volume-weighted mean pH of precipitation in the Puget Sound area in 1982–83 ranged from 4.4 to 4.6 compared to coastal rainwater with a value of 5.4. After subtracting out the contribution of sea-salt from 65 to 80% of the total remaining anion equivalents were sulfate ions and the remainder were nitrate ions. Seasonal variability was observed and can be explained in part by the reduced volume of rainfall in the summer compared to winter.

The following groupings of species varied independently of one another at all four sites: (1) Cl^-, Na^+, Mg^{2+}; (2) NH_4^+ and NO_3^-; (3) H^+ and SO_4^{2-}; (4) Ca^{2+} and Pb. The first grouping can reasonably be ascribed to incorporation of sea-spray into the rain. The second grouping appears to be an urban factor, possibly from automobiles, buses and trucks. The third grouping is either due to incorporation of acidic sulfate aerosol into the rainwater or to absorption and subsequent oxidation of SO_2 to H_2SO_4 in clouds or in the rain collection buckets. The last grouping may represent the presence of soil or road dust.

A simple budget of sulfate ion can account for from 81 to 95% of the observed sulfate ions in these rainwater samples. The budget indicates that a local Cu smelter accounted for 34 to 62% of the sulfate ions depending on site location, with the largest contributions occuring near the source. This same budget indicates that all anthropogenic sources accounted for 60 to 78% of the sulfate ions in the rainwater depending on site location.

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