



Environment Environnement Canada Canada

Atmospheric Environment Service Service de l'environnement atmosphérique

BACKGROUND CONCENTRATIONS OF

SULPHATE IN PRECIPITATION

ALONG THE B.C. COAST

Report PAES-86-1

Scientific Services Division Pacific Region Atmospheric Environment Service Vancouver, Canada

March 31, 1986

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PAES 86-1

EXECUTIVE SUMMARY

The acidity of coastal precipitation will not be determined solely by its sulphur content, but instead by all the ions that contribute to its acidbase chemistry. The pH of precipitation is not, by itself, sufficient to characterize the acid-base components of the precipitation as discussed in this report.

The mechanisms of precipitation formation and its transformation during its descent to the ground (i.e. rain, snow, melting) are key factors in the determination of chemical constituents of precipitation in West Coast environments. With the oceanic biota as a source of atmospheric aerosol sulphate, the chemistry of rainfall in remote locations along the coast will be dominated by "background" sulphate. At this time, it is not possible to say how far inland the sulphate aerosol remains the dominant influence. It is probable that, within the Coast Range, it is important, and that more than one to two days downwind, its importance will depend strongly on local natural and anthropogenic factors. Nitrate and formate from oceanic sources are of secondary importance in determining the chemistry.

For the purposes of this report, "background" was defined as a nearby remote site, upwind of urban areas, with the further requirement that data with evidence of possible anthropogenic source contamination be excluded. Data from long-term precipitation measurement sites along the coasts of British Columbia, Washington, and Oregon were evaluated in order to estimate a "background" sulphate concentration in rainfall. The data were screened for precipitation collection efficiency and precipitation type, charge balance, sea-salt ratios and the possible contamination of the air mass by continental and/or anthropogenic materials (ie., nitrate, ammonia and calcium). The remaining data were corrected for sulphate associated with sea-salt. The data were compared both as averages at each of the five sites and as a grand average across all the data. The consistency of the frequency histograms in these two averages gives confidence in the screening technique.

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The results of this analysis suggest a background excess sulphate concentration in rainfall along the B.C. coast that occurs most frequently in the range of 6 to 10 microequivalents per litre. The distribution has a mode at approximately 8 microequivalents per litre. Other studies suggest background nitrate is approximately 1 to 3 microequivalents per litre, formate about 1 microequivalent per litre, and ammonium about 1 to 2 microequivalents per litre, leading to a pH close to 5.0.

Further studies that would provide better definition of this result and would potentially broaden its application are suggested.

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ACKNOWLEDGEMENTS

The report was prepared by the following study team:

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The study was authorized and funded by the Atmospheric Environment Service of Environment Canada under Contract Number 06SB.KM759-5-0517. The cooperation of Don Faulkner, AES Project Manager, Peter Summers, Ron MacLaren, the computer services staff and the Canada Centre for Inland Waters facilitated the preparation of the report.

In addition the B.C. Ministry of Environment, Waste Management Branch and their Environmental Laboratory provided information which assisted in the preparation of the report. The assistance of Dr. R.G. Wilson, Dr. Murthi Kotturi, Dr. Neil McQuaker and Doug Sandberg facilitated the evaluation of the B.C. Ministry of Environment data.

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Along the B.C. Coast, pH values are near 5.0 These are the most acidic values reported outside of Eastern Canada. Since rain with a pH of less than 5 has the potential to cause environmental damage, the Department of the Environment initiated a research study in 1982, under the Western Long Range Transport of Atmospheric Pollutants (Western LRTAP) program, to determine the precipitation chemistry of air masses approaching the Coast from the Pacific Ocean, and the extent and degree of change to these background values due to local emissions. The 1985 Western LRTAP objectives (Western LRTAP, 1985) and three year program recommended a series of research thrusts. One Western LRTAP objective recognized that "precipitation chemistry over Western Canada is different than over Eastern Canada. The difference in climate is a factor and the role played by dust may be important in characterizing the precipitation chemistry. It is expected that these studies would assist in evaluating the respective contributions to acid depositions from anthropogenic, local and background sources". This study focuses on the background sulphate component of the overall research program.

A careful review of the data led to the suggestion that the higher pH values recorded at the remote prairie sites were associated with natural alkaline soil aerosols and the lower pH values on the B.C. Coast were associated with natural sulphate aerosols originating over the Pacific Ocean. It is the purpose of this study to explore that hypothesis further and to estimate the concentration of sulphate and other acid ions in the precipitation as it arrives from the Pacific Ocean.

The acidity of precipitation is determined by both the mechanism of precipitation formation (i.e., rain, snow, hail, etc.) and the acid-base character of the solute precursors present (e.g., the alkaline prairie aerosols, mentioned above). Nucleation scavenging tends to produce the highest concentrations when the nucleation scavenging effects are high. Vapour deposition with no riming produces much lower concentrations. This study will concentrate on low-elevation marine rain and ignore snow and other

forms of precipitation. Further, this study looks beyond sulphate and considers other ions that determine the "background" in the study area. These include reduced sulphur compounds from oceanic biological activity, as well as ammonia from continental biological activity.

The potential effectiveness of industrial control programs to reduce the acidity of precipitation will depend, in part, on the nature, amounts, and relative proportions of acid-base species present in the "background". Background concentrations are most commonly measured at sites remote from anthropogenic sources, although sites at great distances may not be representative of the background for the study regions. Thus it is necessary to carefully define the meaning of background relative to the use of the data. A purely theoretical definition might require an estimate of the ionic composition of rainfall in the hypothetical world-wide absence of all anthropogenic sources while a purely environmental policy analysis definition might be the fraction of ions that are not from local anthropogenic sources subject to the control of regional pollution control officials.

Recognizing that "acid rain" is potentially a different phenomenon on the West Coast of British Columbia compared to eastern North America and that an understanding of background concentrations is important to the development of any acid rain control policies, the Atmospheric Environment Service of Environment Canada authorized a study of background sulphate concentrations in precipitation along the B.C. and Northwestern U.S. coastlines. In December of 1985, CIRRUS Consultants was selected to conduct this study in association with experts at the University of Washington and Central Washington University, who had been conducting similar studies in the United States. This report describes the activities and conclusions of this study.

2.0 STUDY OBJECTIVES

The objectives for this study may be inferred from the Environment Canada and Department of Supply and Services Terms of Reference as follows:

- to evaluate the relevant literature with respect to probable sources of sulphur and other acid-base species in remote atmospheres;
- to collect all available background precipitation measurements from the Northwest Coast of North America;
- to evaluate the measurement techniques used in order to determine the validity and comparability of the data. This evaluation would include site selection and collection methods as well as chemical analysis techniques;
- to develop and implement data analysis techniques to screen the data for relevant measurements and eliminate clearly invalid data;
- to provide a rationale for the removal of any measurements from the data base;
- to discuss the appropriate definition of "background" concentrations of acid-base species in precipitation;
- to provide an estimate of the background concentration of sulphate and to describe the uncertainty in these estimates;
- to develop conclusions and recommendations for future data collection and analysis.

These objectives are addressed in the subsequent sections of this report.

3.0 SUMMARY OF RELEVANT LITERATURE

In recent years there has been a significant increase in research on atmospheric chemistry in remote areas. Many of the chemical measurements made at remote sites have included an analysis of rainwater. From these results a better understanding of the acid-base chemistry of precipitation in remote locations has developed and is summarized in this report. This work has also led to the identification of important natural sources of acidic and basic materials and a better understanding of the transformation, transport, and deposition of the emissions in the remote atmosphere. This section will briefly review the scientific literature on these topics as it has emerged in the past few years. It will conclude with a summary of some of the data from these measurement programs.

3.1 The Acid-Base Chemistry of Precipitation

The acidity of precipitation is determined dynamically by an on-going titration of the acidic (e.g., CO₂, SO₂, H₂SO₄, HNO₃, HCOOH) by basic (e.g., NH₃ and CaCO₃) materials in air and in atmospheric liquid water. Thus "background" cannot be described only by the pH in the absence of local or anthropogenic sulphate, but must also include ammonia and other important acid-base species (Morgan, 1982).

Sulphate in the cloud-water solution, for example, will increase in proportion to the sulphuric acid (H₂SO₄) added to the system, but the presence of basic materials, such as ammonia, means that the H⁺ does not increase in proportion to the amount of H₂SO₄ added. This inherent non-linearity in weakly buffered rainwater means that pH is not, by itself, sufficient to characterize the acid-base chemistry of precipitation. The non-linear change in pH as acids are added to a system is illustrated in Figure 3-1. The expected pH of cloud-water is shown for five different initial concentrations of a total ammonia (NH₃ and NH₄⁺) and varying concentrations of aerosol sulphate input to the cloud-water. For an unrealistically and initially high concentration of base, the change in pH is almost linear with increasing sulphate loads, but for all the other cases shown, the change in equilibrium pH is distinctly non-linear. This fundamental concept of atmospheric chemistry should be incorporated into any analysis of precipitation chemistry data.



Figure 3.1. pH sensitivity to $SO_4^{=}$ and NH_4^+ . Expected pH of cloud water for atmospheric water content of 0.5 g/m³, .10 ppb of SO₂, 330 ppm of CO₂, and no NO₃⁻. The initial concentration of total ammonia (NH₃⁺ NH₄⁺) is given in ug/m³ of cloudy air on each parametric line (Vong and Charlson, 1985)

In order to fully describe the acid-base character of rainwater, it is necessary to understand the total acid or base neutralizing capacity and the equilibrium properties of the acids and bases present, as well as the H^+ concentration. Strong acids (e.g., H₂SO₄) will almost entirely dissociate and all the H^+ will be available. Weak acids (e.g., CH₃COOH) will also be strongly dissociated in dilute solutions, but at higher concentrations, a



smaller proportion of the H^+ will be released. However as bases are added to the weak acid solution, additional H^+ will become available as neutralization proceeds. Thus the base neutralizing capacity can be the same even though the pH of the strong acid solution is significantly lower. For a mixture of strong and weak acids, which is typical of most precipitation, the strong acid will repress the dissociation of the weak acid at high pH. The total neutralizing capacity will then depend on the amount of strong acid, the amount of weak acid and the pH corresponding to neutralization.

Ultimately, the H⁺ availability and the base neutralizing capacity of precipitation are determined by:

- the emissions of acids and bases into the air mass
- the production of acids in the air or clouds.
- the pre-existing acidic and basic aerosol and gaseous species that are transferred or scavenged into the cloud-water
- the oxidation of organic acids to CO₂.

While measurements of non-cloud aerosol and gases will sufficiently describe the prior conditions in those phases, estimates of ongoing emission and current chemical balances require knowledge of both the gas phase precursor concentrations and the rates of conversion. At present the appropriate rates for many of the important production reactions are unknown. Although gas-phase emission and conversion (e.g., from NO) may be an important consideration in agricultural or industrialized areas, it is expected that in remote locations along the northwest coast the concentrations of background gases will be small. Consequently, an understanding of the pre-existing aerosol and soluble gases and information on the atmospheric water content should be enough to initially approximate the acid-base character of the cloud-water and rainwater (Charlson and Rodhe, 1982).

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3.2 Probable Sources of Acid-Base Species in Remote Marine Atmospheres

3.2.1 Natural Mechanisms

The primary acid-base components influencing precipitation chemistry in air masses moving onshore along the northwest coast are sulphuric acid, nitric acid, formic acid, methane-sulphonic acid, ammonia, and with a small effect, sea-salt.

One of the more important sources of rainwater solute in marine air is seawater droplets (Pszenny et al., 1982). These droplets are produced when air bubbles burst at the sea surface or seawater is separated by high The ions in the droplets will be similar to that of bulk seawater winds. (which is slightly basic) but may be enriched in some species (Junge, 1963; Duce et al., 1976). While most of the sea-salt that enters the atmosphere is quickly redeposited in the ocean, some of it will remain airborne and eventually deposit on land. The sea salt contains many species besides sodium and chloride, in a sufficiently constant composition that the fraction of those species attributable to sea-salt usually can be subtracted from the measured values. Thus sulphate (almost always) and calcium (sometimes) will be expressed as "excess", that is, the amount not associated with sea-salt. Sodium concentrations are almost always used as the tracer of sea-salt associated components as chloride can be lost to the atmosphere as HCl, from reaction with H₂SO₄.

Emissions from the oceanic biosphere are the principal source of solutes in marine air rainwater. The primary source of sulphuric acid (H₂SO₄), is expected to be the oxidation of dimethyl-sulphide, {(CH₃)₂S, or DMS}, with sulphur dioxide (SO₂) as an intermediate compound. The measured concentrations of DMS in surface sea water leads to a calculated flux to the atmosphere of about 2 to 6 mmol/m²/yr. The lower values appear to be characteristic of open ocean and the higher ones of coastal and upwelling regions (i.e., along the edge of the continental shelf). The close match between the estimated flux to the atmosphere of DMS and the measured deposition of sulphur (in excess of that associated with sea-salt) to ocean surfaces in



remote locations, about 3 mmol/m²/yr, suggests that DMS is the source of most of the excess sulphate in these regions (Prospero et al., 1985)

The oxidation of DMS takes apparently on the order of about one day, as does the oxidation of SO_2 , such that the bulk of sulphur of importance to acid-base chemistry in the marine atmosphere tends to be in the form of sulphate particles. Measured levels of DMS and SO_2 in air, along with calculated oxidation rates result in a flux that is close to the calculated source strength. These calculated conversion rates and fluxes agree with the observed flux of $SO_4^=$ out of the marine atmosphere in rain, which is approximately 3 mmol/m²/yr. This suggests that dry removal of DMS, SO_2 and sulphate aerosol are minor removal pathways for sulphur, which should be the case if lifetimes of DMS and SO_2 are short and are determined mainly by reactions in the atmosphere. Figure 3-2 illustrates this marine sulphur cycle, with a check on the internal consistency of the fluxes shown by comparing data from different researchers.

Some of the H₂SO₄ observed along the northwest coast of North America might be derived from long-distance transport from Asia or from an elevated northern hemispheric background. The amount of this possible anthropogenic contribution cannot be estimated accurately at this time and is a matter for further research. As described in the next section, this level is expected to be a small portion of the sulphate arriving at the northwest coast of North America in marine air masses.

Nitric acid, HNO₃, is created from the oxidation of various nitrogen compounds, including N₂ in air, N₂O and NO. The chief pathways for its production in marine air are thought to be the oxidation of N₂O in the stratosphere (making NO) and the production of NO by high-altitude lightning in the Inter-Tropical Convergence Zone (N₂ + O₂ --> 2NO). Both of these sources result in HNO₃ formation via oxidation of NO to NO₂ with subsequent oxidation by OH to HNO₃. Gaseous HNO₃ can react with the surface of basic



Figure 3.2. The Sulphur Cycle in the Remote Marine Troposphere. (Crutzen et al., 1985)

sea-salt, be dissolved in cloud water or captured by falling raindrops, all of which result in a flux of about 1 mmol/m²/yr. There is a rough balance in the estimates of sources and removal (Galloway et al., 1985).

Formic acid, HCOOH, most likely derives from the oxidation of methane, CH4, and/or formaldehyde HCHO. Its amount is surprisingly large in comparison to H₂SO₄ and HNO₃ and it measurably contributes to the anion concentration of marine rainwater. It is usually classified as a weak acid; however, in the context of rainwater chemistry, with pH > pK, the formic acid is fully dissociated and is therefore just as effective a proton donor as the strong acids.

Methane-sulphonic acid, CH₃SO₃H, is probably produced by the oxidation of DMS. The amount of it is almost insignificant in an acid-base sense; however, its presence may serve as a useful tracer for marine excess sulphur.

Ammonia, NH₃, appears to be the only important base in the marine atmosphere. Its source over the oceans is not well known, although it is likely that the atmospheric species derive from a Henry's law equilibrium with the sea-surface. The flux of $\rm NH_4^+$ out of the atmosphere is largely in rainwater and is approximately equimolar with excess sulphate.

3.2.2 Anthropogenic Long Range Transport

Immediately to the west of the northwest coast of North America is the relatively unpopulated Kamchatka Peninsula and western Siberia. To the west southwest, some 6900 km away, is Japan. Korea and China are about 2400 km farther. With an average horizontal velocity of 5 to 10 m/sec, an air mass would take from 8 to 16 days to cross the Pacific if it moved constantly along a straight line. This contrasts to a travel time of about 1.5 to 3 days between the Ohio River valley and New England or Eastern Canada.

It is reasonable to expect that air masses will often follow a circuitous route across the Pacific and the total travel time will be much longer than 8 days. However, even in only 8 days, the SO₂ emitted into the air from industrial centers in Asia can be reasonably expected to be almost entirely converted to sulphate aerosol (or removed to the ocean surface) before the air mass arrives at the northwest coast.

If we assume, solely for the purposes of illustration and establishing an approximate upper bound, a 1/e decay lifetime of about 2 days for total sulphur species in marine air (as suggested by the data in Figure 3-2), less than 2% of the initial sulphur burden will remain in the air mass after 8 days and less than 0.04% after 16 days. If the lifetime is as long as 4 days the remaining sulphur burden would be 13% after 8 days and 2% after 16

days. If an initial average value (averaged throughout the entire 2500 m mixing layer) of 2.5 ug/m³ of sulphur dioxide (expressed as sulphur) in a polluted air mass leaving the Asian Coast is assumed, a 2% residual implies a final concentration of 50 ng S/m^3 , which is one-third of the estimated concentration of excess sulphate in marine air shown in Figure 3-2. At a 0.04% residual the concentration would be 1 ng S/m^3 , or less than 1% of the excess sulphate. In either case, current precipitation chemistry analysis techniques probably would not be able to resolve those cases where anthropogenic sulphur accounted for a measurable portion of the excess sulphate. However, the use of methane-sulphonic acid as a tracer of natural excess sulphate may provide a way to estimate the anthropogenic fraction after a long over-sea transit.

3.3 Mechanisms for Transformation and Removal of Acid-Base Species

Sea-salt aerosols are injected into the atmosphere as a droplet which may dry through evaporation into a particle. These particles are relatively large, mostly greater than 2 micrometers. Because of their size they are removed from the atmosphere by sedimentation and washout with lifetimes of several hours or less. The rapid falloff in the sea-salt content of precipitation as an air mass moves inland is easily detected (Granat and Soderlund, 1975). The relatively few smaller sea-salt aerosols (diameter less than 1 micrometer) will remain in the air mass for much longer.

The precursors of most other acid-base species of interest to precipitation chemistry are introduced into the atmosphere as gases. They will be removed from the atmosphere by dissolution in atmospheric water (cloud-water or rain), absorption directly at the earth's (or ocean) surface, or by oxidation and physical transformation to aerosol or cloud particles. Particles created by gas-to-particle conversion generally will be less than 0.5 micrometer in diameter and will remain airborne with a potential lifetime on order of a few days.

Sulphur dioxide absorbed into cloud water may also be oxidized and when the cloud mass evaporates, the oxidized species may be left behind as an aerosol

if the product is non-volatile (e.g., sulphate). The rates of the oxidation reactions that produce these particles are poorly understood and for many species it is not possible even to identify the dominant reaction. However measurements do suggest that lifetimes for the oxidation of DMS and SO₂ are in the order of less than a few hours to 1-2 days. Thus the gas content of remote atmospheres will be of immediate practical interest only if the concentrations are significantly higher at the coastal margins, which is still a matter of research.

The primary removal mechanism for remote atmospheric sub-micrometer aerosols appears to be nucleation scavenging and transport to the surface with precipitation (Sievering et al., 1984). Cloud droplets tend to grow by the diffusion of water vapour onto the cloud condensation nuclei (CCN). Because the CCN tend to be soluble this produces solute in the droplet. When cloud droplets form on the aerosols as nucleation centers the concentration of acid-base species will initially be high but will be diluted by many orders of magnitude as additional vapour condenses on the new droplet. The scavenging of particles below clouds by falling rain is slow. The equilibrium concentration of rain can be estimated from the simple Junge (1963) equation

$$C_{rain} = C_{aerosol} e(ED)/L$$

where e is the scavenging efficiency, E is the below cloud evaporation of droplets (which will increase the concentration), D is an index of the in-cloud dilution of droplets (which will decrease the concentration), and L is the liquid water content of the cloud air. Nucleation scavenging efficiencies have been reported for rain in the range of 0.5 to 1.0 (Hegg et al., 1984) and an estimate of nearly 1.0 is reasonable for rain in remote locations (Jensen and Charlson, 1984). The (ED) term may be assumed to be near 1.0 for rain (Charlson and Rodhe, 1982).

Snowflakes may grow almost entirely by vapor condensation on the ice nuclei, which are not the same type of particles as the cloud condensation nuclei and generally are not soluble. The snow crystal thus may contain very little solute. In contrast, hail (or graupel) grows by the collection of

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super-cooled cloud droplets onto an ice core by collision. Similarly snow may become rimed by the collection of super cooled droplets. Thus the solid-phase precipitation potentially is both chemically different and more dilute than rain or very similar to rain. Conversely, rain which is melted snow will reflect the character of snow. Thus it is extremely important to know the immediate past history of precipitation when background chemistry measurements are taken (Scott, 1981). It is also important to separate snow core and glacier meltwater measurements when making comparisons of precipitation chemistry data.

3.4 Measurements of Acid-Base Species at Remote Sites

At remote marine sites the dominant anion in precipitation will usually be excess sulphate (Charlson and Rodhe, 1982). MSA has been detected in marine precipitation and may be an indicator of the marine origin of the sulphate species (Saltzman et al., 1983; Vong, 1985). At remote continental sites organic acids can be important to the total anion concentrations (Galloway et al., 1984). Formate and acetate were detected in Katherine, Australia rainwater by Keene et al. (1983a,b). At the South Pole three strong mineral acids, HCl, HNO₃, and H₂SO₄, were present in snow representing a continuous 10 year period (Legrand and Delmas, 1984).

If low trace metal concentrations are used as the criteria, the cleanest (measured) precipitation on the earth falls in Antarctica and Greenland (Galloway <u>et al.</u>, 1982b). Precipitation studies along the northwest coast of North America have also found low concentrations of trace metals. Rancitelli and Perkins (1970) and Tanner et al. (1971) collected three 5 minute samples of rainwater near Quillayute, Washington and reported trace metal concentrations for Sb, Mn, and Hg which approach the values recorded in Antarctica and Greenland. Their Cu, Ag, and Zn concentrations were an order of magnitude higher than the lowest values (Pb, Cd, and V were not determined). Sampling during April and May, 1984 by Vong (1985) confirmed these low levels of trace metals, and found low values for excess $S04^=$, $N03^-$ and $NH4^+$ with on-shore synoptic wind flow patterns.

Table 3.1 summarizes the lowest concentrations of several trace metals found in remote area precipitation. Most of these concentrations are below the detection limits of all but the most sensitive analytical techniques and were obtained utilizing extremely careful sampling and analysis techniques.

Analyte	(ug/L)	Site Location
Sb	0.03	Greenland
Cd	0.02	Greenland
Cu	0.04 0.06	Antarctica Greenland
Рb	0.1-0.4 0.02-0.04	Greenland Antarctica
Mn	0.1-0.3 0.02	Greenland Antarctica
Hg	0.01-0.05	Greenland
Ag	0.007	Antarctica/Greenland
v	0.02	Greenland
Zn	0.01-0.03	Antarctica Greenland

TABLE :	3.1.	Trace	Metals	in	Remote	Precipitation	(Galloway	et	al.,	1982))
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A summary of the chemical composition of rainwater measured at other remote sites is given in Table 3.2. After sea-salt, the dominant anion species influencing the acid-base chemistry are SO4, NO3 and RCOOH (mainly formate). The important cations are H^+ and NH_4^+ . If these data are representative, they suggest a preliminary estimate of SO4⁼ concentration between 4 and 10 microequivalents per litre (ue/1), NO3 around 1 to 3, formate about 1, and ammonium around 1 to 2 ue/1, leading to a pH close to 5.

Site	Lake (zette	Amsterdam Is.	Poker Flat	Katherine	Eniwetok	B. C.	Bermuda
	Washi	ngton	Indian Ocean	Alaska	Australia	South Pacific	Coast	S. Atlantic
Reference	Vc	ong	Galloway and	Galloway	et al.(1982)	Arimoto	Nikleva	Jickels
	(19	85)	Gaudry (1984)	-		(1985)	(1984)	(1984)
Units	ueq/L	ug/L	ueq/L	ueg/L	ueq/L	ug/L	ug/L	ug/L
	F 0	F 0		11 0	10.0			
H+	5.2	5.2	8.8	11.0	16.6			
SO4	15.2	730.	29.2	7.2	6.3		_	
S04(xs)	5.8	280.	4.9	7.1	5.5	280.	280.	
Na	78.8	1800.	206.5	1.0	7.0	1100.	100140.	3400.
C1	98.2	3500.	237.7	2.6	11.8	2000.		6800.
Br						7.1		
Mg	18.3	220.	45.9	0.2	2.0	170.	1030.	490.
NO3	2.5	160.	1.3	1.9	4.3			
NHA	2.3	41.	1.8	1.1	2.0			
ĸ	3.0	120.	4.4	0.6	0.9	39.	3050.	160.
Ca	3.8	76.	8.6	0.1	2.5	50.	2090.	310.
Mn		0.49				0.012	0.5-1.4	0.27
Fe		9.8				1.0	1.1-9.8	4.8
Cu		0.14				0.013	0.9-1.7	0.66
7n		0.99				0.052	0 9-2 2	1 15
Ph		0.15				0.035	1 3-2 0	0 77
C d		0.012				0.002	2.0.2.0	0.06
τu τ		0.012				0.002		0.00
v C -						0.021	0.2 - 0.3	
50						0.021	(0.1-0.2	
AL						2.1	~ ~ ~ ~	
Cr						×	0.3-0.5	
NI							0.7-1.3	
As							0.1	
RCOOH	0.97	43.4	2.2		0.6-53.0a			
MSA	0.07	6.6						
$NH_4/SO_4(xs)$) 0.39	5.2	0.36Ъ	0.15b	0.37Ъ			
Notes:							н. Н	
a: Keene et	t al. (]	.983)						
b: Galloway	y (1985))						

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TABLE 3-2. Chemical Composition of Rainwater Samples Collected at Remote Sites

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4.0 DATA ANALYSIS

4.1 Inventory and Evaluation of Data from Remote Sites on the Northwestern Coast of North America

Data from precipitation chemistry measurement sites in the Canadian Network for Sampling Precipitation (CANSAP), the U.S. National Acid Deposition Program (NADP), the South Coastal Event Sampling Network in British Columbia, B.C. Ministry of Environment (Sandberg, 1984) and several individual sites operated by other agencies, researchers, and private organizations were obtained and examined for their usefulness in this analysis. After a preliminary review of all the data only long-term data from five sites, three in the U.S. and two in Canada, were used in developing the results presented in this report.

4.1.1 Primary (Long Record Length) Sites

The CANSAP and NADP networks have been operating precipitation chemistry sites in British Columbia, Washington, Alaska, and Oregon for a number of years. Only the results for the coastal sites located at Port Hardy and Terrace, British Columbia (for 1980-83), Alsea Guard Station (1980-85) and Schmidt Farm (1980-83), Oregon, and Hoh River, Washington (1980-85) were utilized in the data analysis. Other stations were eliminated because the site locations were judged less likely to produce results which could be described as background. For example, the site in Denali National Park, Alaska was not included because of possible influences from Anchorage area emissions and its inland, higher elevation location.

Data from a long-term site operated by the Washington State Department of Ecology (WDOE) near Copalis Crossing on the Washington coast were obtained, but only a 14 week record during 1985 was available. Data for several sites operated by the B.C. Ministry of the Environment were provided by the Ministry but rain volumes were not consistently reported and volume-weighted averages could not be calculated except by manual extraction of data from the laboratory files. A one-year data set from a site operated by U.S.

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Borax at Quartz Hill, Alaska was obtained but the sampling periods were irregular and many of the samples were contaminated with insects and other debris. None of these data were used in the analyses reported here.

4.1.2 Secondary (Event and Shorter Record Length) Sites

A number of investigators have collected and analyzed marine precipitation in the Pacific Northwest over periods of hours to days. Event samples are potentially valuable in developing a definition of background concentrations. Unlike long-term sampling programs, with an event sampling program it is possible to distinguish among several meteorological flow regimes and avoid those that may include offshore flow from populated areas or onshore flow with historic trajectories that indicate a residence period over land. In short term sampling it is not necessary to use automated samplers and it is thus possible to avoid long exposures of the sample or the sample container to the environment (and possible chemical changes or contamination) during dry weather periods. Logan et al, (1982) and Vong et al. (1985b) observed seasonal trends in precipitation composition due to sulphate changes.

Event sample data was obtained from the South Coastal Event Sampling Network in British Columbia. These data include sites at (in order of decreasing number of samples) Port Hardy, Terrace, Bamfield, Pt. Renfrew, Jordan River, and Cape St. James. Data were available from the event sampling conducted by Galloway et al. (1982) and Dayan et al. (1985) at Poker Flat, Alaska as a part of the World Meteorological Organization background precipitation sampling network.

Data were also available from the event sampling conducted by Vong (1985) during the spring of 1984 at Lake Ozette and Cheeka Peak on the northern Washington coast and by Vong et al. (1986) during the spring of 1985 at Cheeka Peak. These data have been previously analyzed in detail and can be used as a standard for comparison for the other data presented in this report.

Data from snow samples taken on Vancouver Island during 1982 at Splendor Mountain and Mt. McBride were obtained. Data were provided by the U.S. Geological Survey for a sequence of snow cores taken along the crest of the Cascade Mountains from the U.S. border to California. The Vancouver Island samples may represent background conditions. These samples may be of interest for a preliminary examination of differences between background rainwater and snow composition. No analysis of these data is provided in this report.

4.2 Evaluation of Measurement Techniques

4.2.1 Site Selection and Collection Methods

Precipitation chemistry sampling sites must be free from local or regional anthropogenic influences, local soil or vegetation contamination, or rain shadow influences from near-by mountains or other large, physical features. The site selection criteria for federal and provincial research and monitoring in British Columbia are presented by McQuaker et al. (1983) in <u>Precipitation and Surface Waters: Recommended Methods for Sampling and Site</u> Selection.

Local influences can be an important source of error. Vong and Waggoner (1983) present data to suggest that a collector located on a rooftop receives significantly different levels of contaminants than those instruments located on grassy areas as required by the NADP criteria. The importance of local industrial sources is illustrated by the comments of Nikleva (1983,1985) regarding an aluminum smelter that may affect the Terrace site, a pulp mill that may influence the Port Hardy site, and the possible influence of Puget Sound area emissions on the South Coast sampling network sites located east of Jordan River. Although the source is not identified, Barrie and Sirois (1982) suggest that some CANSAP samples before 1980 may be high in excess calcium. An inspection of data from the Port Hardy site (Vong and Larson, 1983) indicates it is high in excess calcium, making pH higher than would be obtained from a more representative site. Nikleva

(personal communication, 1985) has suggested that early event sampling at Bamfield may also suffer from high excess calcium.

The containers used for collecting precipitation for later chemical analysis may be either constantly open to the atmosphere, which is referred to as a bulk sampler, or mechanically opened when a sensor detects rain. The collectors utilized by the NADP use a heated plate to detect wet conditions and activate the lid-lifting mechanism. The container is closed at the end of the rainfall when the sensor dries. Some collectors in use in Scandinavia use a spinning disk with a small electrical gap. The latter have the advantage of reacting more quickly to the end of the rainfall period. Chan et al. (1984) and Dasch (1985) suggest that the differences between bulk samples and wet-only samples are significant. They report higher concentrations for the ions of calcium, magnesium, sodium, potassium, as well as ammonium, sulphate, chloride and nitrate in the bulk collection samples. Dasch (1985) reported the pH of the wet samples to be lower than that measured in the bulk samples.

Conversely, the automated collectors appear to miss about 7% of the precipitation because of sensor-mechanical lag. Sisterson et al. (1985) present evidence for changes in ion concentration in rainfall during the precipitation period. Because the change may be in either direction, i.e., toward more or less acidity as the rainfall progresses, the mechanical lag would produce indeterminate errors in the ion concentration measurements as well as a negative bias in the volume measurements.

Manually operated wet-only collectors can be expected to display a similar bias. If the container is opened prior to the forecasted event, dry deposition will be collected. On the other hand, if the collector is to be opened at the onset of the event, a decision is required as to when the event has started. The action would, more often than not, be late. Consequently, there will be an indeterminate error associated with the opening and closing of the collector. This would also produce a negative volume bias.

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The choice of sampling periods or event only sampling may give rise to differences in the reported concentrations of the acid-base species. Sisterson et al. (1985) examined the chemical differences between event samples and accumulated weekly samples that were collected in northeastern Illinois over a two-year period. They calculated an equivalent weekly composite sample by summing the event measurements over the appropriate time periods. The weekly samples had less ammonium and higher pH than the equivalent composite event samples in all seasons and more sulphate in every season except summer. Weekly samples had significantly more calcium and magnesium during the seasons with low precipitation. However, event and weekly nitrate values were not significantly different.

4.2.2 Chemical Analysis

Analytical errors may be classified as determinate or indeterminate. Determinate errors are errors of instrument, method, or operator. They can be identified by spiking, inter-laboratory exchange, or by examining certified samples. Indeterminate errors arise from propagation of the random measurement errors associated with each operation of the analysis.

The magnitude of determinate and indeterminate errors must be considered and stated when a series of analytical measurements are used to define a property of a set (i.e., "background sulphate" concentrations). These errors are also considered when members of the set are rejected as "outliers". Table 4.1 illustrates the error magnitudes observed in two U.S analytical laboratories.

Sisterson et al. (1985) examined the determinate and indeterminate errors associated with the analysis of precipitation components at the Argonne Analytical Chemistry Laboratory (ACL) and the Central Analytical Laboratory (CAL). Both of these laboratories should be considered "state-of-the-art." Table 4-1 reports measures of both bias (percent difference between mean value and certified value) and precision (plus or minus two times the standard deviation divided by the mean) for the precipitation chemistry

measurements. At low concentrations, the percentage error can be substantial as this value is near the analytical detection level.

An additional consideration in the evaluation of analytical data is the ability of a measurement to detect a small concentration. This is particularly critical for measurements at remote sites. The minimum detection limit (MDL) of an instrument or technique corresponds to the minimum signal magnitude that can be ascribed to the presence of analyte in a sample. The actual MDL of a measurement is a function of the number of bland samples. Long and Winefordner (1983) suggest using an MDL of 3 times the standard deviation of the blank signal. Table 4.2 gives the estimated MDL from several reports, expressed in micro-normal (uN) concentrations.



		ACL	<u>.</u>		CAL	
Analyte	Conc.	Bias	Precision	Conc.	<u>Bias</u>	Precision
Volume	2g		+/-100.0%	2g		+/-100.0%
	300ັ	0.0	1.9	300ັ	+2.0%	1.9
	1300	0.0	0.5	1300	1.5	0.5
H+	83.2ueq/1	+4.5	10.1	83.2ueq/1	+4.5	10.1
	871.0	+3.4	3.0	871.0	+3.4	30
Ca ⁺⁺	0.50		100.0	1.0		100.0
	6.84	+9.6	17.4	3.34	-10.4	6.7
	15.97	-15.8	1.6	17.47	+4.4	4.0
	68.86	-12.7	6.8	72.36	+3.1	2.6
Mg++	0.25		100.0	0.17		100.0
	4.69	+14.0	4.5	1.97	-14.3	3.0
	13.98	+13.3	0.0	9.38	+2.0	3.1
	32.90	0.0	0.0	24.68	-0.2	2.0
к+	1.28		100.0	0.10		100.0
	3.35	+15.1	38.6	0.84	-7.4	10.7
	9.97	+4.3	5.3	6.90	+0.5	3.1
Na ⁺	0.87		100.0	0.17		100.0
	2.74	+41.9	16.3	3.05	-14.3	6.7
	3.78		4.2			
	5.66	+3.0		6.83	+0.4	1.4
	19.58		8.0	21.75	+0.1	1.5
	34.45	-12.2				
NH4+	0.55	-5.3		0.55	+8.0	
	1.11		100.0	1.11	+1.1	100.0
	5.54		2.1	5.54		37.0
	51.00	-3.2		16.63		10.1
	7872		3.5	113.65	+0.1	3.3
NO3-	0.16		100.0	0.32		100.0
-	7.42	-4.2	12.3	7.90	+1.6	13.5
	19.36	-2.4				
	23.71		7.6	27.10	-0.5	3.6
	61.29	-3.5				
	63.39		5.0			

TABLE 4.1 Bias and Precision for Individual Components in Sample Inter-comparison at Two Laboratories (Sisterson et al., 1985)

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TABLE 4.1 Bias and Precision for Individual Components in Sample Inter-comparison at Two Laboratories (Sisterson et al., 1985)- Continued

		ACL			CAL	
Analyte	Conc.	Bias	Precision	Conc.	Bias	Precision
504 ⁼	1.04		100.0	0.29		100.0
•	13.21	+6.6	12.3	15.00	-2.2	13.5
	20.41	-0.2				
	73.82		4.6			
	126.35		4.1	106.65	+0.3	1.7
	163.93	-0.2	-	213.30	-0.2	1.2
C1-	1.13		100.0	0.56		100.0
	2.99		17.0			
	4.80	-5.6				
	6.86		8.7	9.87	+10.4	11.6
	28.21	+0.3		39.78	+4.6	1.4
				79.27	+4.4	2.1

Notes:

- 1. Replicate analyses and stating the result in terms of the standard deviation of the set.
- 2. Bias is the percentage difference between mean value and certified value.
- 3. Precision is plus or minus two times the standard deviation divided by the mean.

4. ACL = Analytical Chemistry Laboratory (Argonne)

5. CAL = Central Analytical Laboratory (EPA)

Analyte:	<u>S04</u>	NO3	<u>C1</u>	Na	<u>Ca</u>	Mg	<u>K</u>	<u>NH4</u>
Argonne ACL	70	TO	TO	TO			TO	тс
Method: MDL:	1.6	•24	1.7	1.3	.75	•38	1.9	1.6
NADP CAL								
Method: MDL:	C •84	C •48	C •43	AA •26	AA 1.5	AA •25	AA .15	C 1.7
MAP3S/RAINE								
Method: MDL:	AWC •4	AWC •4	IC •2	IC .4	AA •5	AA .•8	IC .25	IC .6
IWD(original)								
Method: MDL:	С 4.2	с 0.3	С 5.7	FE 8.7	AA • 5	AA .42	FP 5.1	C 0.17
IWD(current)					,			
Method: MDL:	IC .31	IC •24	1C .42	FP 1.3	AA 3.7	AA 1.2	FP .76	с •08
BC MOE								
Method: MDL:	IC .20	IC .16	IC .3	IC .4	ICP 1.0	ICP •8	IC .26	IC .6
Notes: C= Colo IC= Ion AA= Ato FP= Flav	urimetric Chromatograp mic Absorptio me Photometri	ACL= CAL= IWD= BC N	Analyti Central Inland 10E=B.C.	.cal Chem Analyti Waters D Ministr	nistry L Lcal Lab Director	aborator orator ate	ory y ent	

TABLE 4.2Minimum Detection Limits for Precipitation ChemistryMeasurements (expressed as micro-normal or uN)

Sources: NAQUADAT (1984), MAP3S/RAINE (1982), McQuaker (1983), Sisterson

ICP= Inductively Coupled Plasma. AWC= Automated Wet Chemistry

(1985),

Estimates of MDL, defined as 2 times the standard deviation, have been recalculated for the U.S. laboratories and included in Table 4-2. The Canadian laboratory MDL's were based on their published material and are based on either a testing procedure or the stated detection limits of the instrumentation.

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4.3 Data Analysis Techniques for Validity Screening

4.3.1 Techniques Used

Analysis of precipitation chemistry data from the northwest coast of North America was initially focused on five coastal sites, Hoh River, Alsea Guard Station, Schmidt Farm, Port Hardy, and Terrace. The location of the sites are:

- Hoh River, also called Olympic National Park, in Northwestern Washington State, latitude, 47° 52'N, longitude 123° 55'W
- Alsea, in Suislaw National Forest, NW of Eugene Oregon, latitude 44° 23'N, longitude 123° 37'W
- Schmidt Farm, also called Hyslop, near Alsea, Oregon, latitude 44° 38'N, longitude 123° 11'W
- Port Hardy, on Vancouver Island, latitude 50°, 41'N, longitude 127°, 22' W
- Terrace, in Northwestern B.C., latitude 54°, 28' N, longitude 128°, 35' W.

The sampling records were examined and found to be without serious gaps and the analytical procedures were determined to be constant throughout the record period. Three screening tests were applied to the data to eliminate samples which might not be valid or representative of background conditions. The screening was designed to be conservative in the sense that a sample would be rejected only if it was clearly unsuitable.

First, all samples were examined for sample integrity. This is defined in terms of the internal consistency of the chemical and volume measurements. As a preliminary step, samples were eliminated when precipitation did not fall during a sampling period, the field-site operator reported obvious

problems with the sample's quality, or the sample was not recorded as rain (as opposed to snow). Next, a charge balance was calculated as the absolute value of the difference between anions (C1, NO₃, SO₄) and cations (Na, Mg, K,Ca, NH₄, H⁺) divided by the sum of anions and cations. This is slightly less stringent that an alternate form of charge balance which calculates the ratio of cations divided by anions. The approach chosen is preferred because it is less sensitive to small errors (e.g., ions near their detection limit) in concentration for samples with very low overall ionic strength (as is possible in background locations when sea salt concentrations are low). To pass this screening step, a sample was required to have less than a 40% charge balance error. Samples surviving the entire four step screening procedure had a mean charge balance error of 7%.

Thus, the 40% charge balance screen, in combination with the efficiency and chloride/sodium ratio screens, produces a final data set for the sites where the typical uncertainty in charge balance (+/-7%) is equal to the estimated excess sulphate value of 5.5 microequivalents/litre. Therefore, if all the charge balance error was in the excess sulphate, it would still be significantly greater than zero. This is the least restrictive screen that guarantees the excess sulphate is significantly greater than zero.

Second, sampling efficiency (comparison of rain gauge depth with sample volume) and sea salt (Cl/Na) ratios were utilized to further identify samples of questionable integrity. Poor sampling efficiency could indicate problems with the sampler or possibly a spilled sample, either of which would reflect on the integrity. A factor of two deviation from the expected 100% efficiency was chosen as a limit. Samples retained for further data analysis had an efficiency greater than 50% or less than 200%.

Rainwater collected within several hundred kilometers of the ocean generally has the same Cl/Na ratio as bulk seawater (1.8 by mass) unless local sources of Na (e.g., pulp mills) or Cl (e.g., coal combustion) are present or sample contamination (e.g., human hands) has occurred (Holland, 1978). In remote marine sites it is especially important to correctly evaluate Na concentration if the sulphate correction for sea salt is applied to determine excess

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SO4. This is less important when sea salt concentrations are small since the actual magnitude of the SO4 attributed to sea salt would be small. Therefore, in this analysis samples were eliminated if the sea salt ratio varied from the expected value by a factor of two, unless sodium was less than 1 mg/L. When sodium is equal to 1.0 mg/L, the sea salt sulphate will be equal to 0.25 mg/L, which is the global average of excess SO4 at remote sites. This implies the Cl/Na criteria would eliminate samples which could <u>potentially</u> have an error in the SO4 sea salt correction as large as the expected value of excess SO4. To survive the second step of the data screening a sample was required to be within a factor of two of the expected Cl/Na mass ratio, i.e., 0.9 < Cl/Na > 3.6 (in additional to passing the efficiency test described above).

Third, samples were examined to determine if they reveal evidence of a period of overland residence for the air mass. If we want to estimate the background concentrations from precipitation measurements, it is important to know if the weekly or monthly average samples include rainfall with significant anthropogenic contributions. Few sampling sites in mid-latitude locations in North America are <u>always</u> isolated from anthropogenic emissions sources. Fox and Ludwick (1976) demonstrated that aerosol Pb concentrations were much lower along the coast of Washington during on-shore flow that when air trajectories had passed over continental areas. Although rain along the northwest coast generally occurs under southwest flow from the Pacific (Overland and Walter, 1983) it is possible to collect rain from weather systems having continental back-trajectories, as demonstrated for the Washington Coast by Vong (1985).

It would be desirable to screen rain samples to eliminate any rain collected during off-shore flow or during on-shore flow with a past overland trajectory. Even with a thorough meteorological analysis there would remain an uncertainty in the weekly or monthly data since no one trajectory can describe most weekly or monthly precipitation sampling periods. As an alternative, samples were screened for ions that would suggest anthropogenic or terrestrial contamination of the air mass.

Studies of remote precipitation in very isolated locations (Galloway <u>et al.</u>, 1982; Galloway and Gaudry, 1984) or which utilized meteorological analysis (Vong, 1985) were utilized to suggest upper limits for three components of background precipitation. Nitrate, ammonia, and calcium are all indicative of terrestrial emission sources. Vong, for example, reported that 30 of 31 rain samples collected during on-shore flow contained less than 5 ueq/L of nitrate and only 3 of 31 samples had ammonium ion greater than 5 ueq/L. Calcium, especially as calcium carbonate, is a major earth mineral and may be evidence of contamination by wind-blown dust, but it is also a significant component of seawater. A loose screen for dust contamination was defined by first calculating the excess calcium as (Ca - 0.0378 Na) and then requiring this value to be less than 10 ueq/L.

To survive the third screening step the sample had to have nitrate less than 5 ueq/L, ammonia less than 5 ueq/L, and excess calcium less than 10 ueq/L.

4.3.2 Effects on Data Set

A total of 385 rainwater samples survived the four step screening procedure, 62% of the 617 samples of rain fully analyzed by the NADP and CANSAP laboratories for these five sites (Alsea Guard Station and Schmidt Farm, Oregon, Hoh River, Washington, Port Hardy and Terrace, British Columbia). Table 4.3 details the samples eliminated by site and procedure.

Site	Alsea	Schmidt	Hoh	Pt. Hardy	Terrace
Dates Type Network	1/80-1/85 Weekly NADP	1/80-1/83 Weekly NADP	1/80-1/85 Weekly NADP	1/80-12/83 Monthly CANSAP	1/80-12/83 Monthly CANSAP
Number Possible Number Analyzed	180	125	219	47	46
Number with 40% Charge Balance	177	122	212	46	45
Number with sea	salt				
within 50-200%	164	83	182	42	30
Number with NO3 <5 ueq/L	133	46	167	38	30
Number with both excess Ca <10ueq	/L 128	35	162	31	29

TABLE	4.3	Number	of	Samples	Remaining	After	Each	Step	of	the	Screening
		Proced	lure	e							

4.4 Limitations on the Use of Other Data Sets

The non-sea salt sulphate concentrations reported at the Bamfield, Port Renfrew, and Jordan River sites in the report "Lower Mainland and South Coast B.C. Precipitation Chemistry Data" requires further examination. Examination of that data set indicates that the minimum detectable level (MDL) sulphate concentration is 4.16 uN while the MDL Na concentration reported is 8.7 uN. It is assumed that the standard deviation here can be taken as .5 of the reported MDL yielding values of 2.1 uN and 4.4 uN


respectively for the standard deviations associated with the sulphate and sodium determinations.

Excess or no sea-salt SO4 concentrations are estimated by subtracting from the analytical sulphate concentration the concentration of sulphate which would have occurred if all of the sodium in the sample were sea-salt derived. That correction is applied by subtraction of .117 uN SO4 for every uN Na in the sample.

TABLE 4.4 Precipitation Data From 'Lower Mainland Study'

NUMBER OF EVENTS

Site	Total	Where SO4 (MDL(SO4)	Where $Na(.12)>SO_4$
Bamfield	. 37	17	19
Port Renfrew	29	18	13
Jordan River	29	23	12

As illustrated in Table 4.2, the average Na concentrations at the three sites yield sea-salt concentrations in excess of the total sulphate concentrations for almost half of the events studied. The reported sulphate concentrations were also less than the minimum detection limit for sulphate in almost half of the events studies.

There is considerable uncertainty in analytically derived values even if they slightly exceed the detection limit. Quantitative measurements were rarely made at the limit of detection since the relative standard deviation at that concentration is typically 25-100%.

5.0 DEFINITION OF "BACKGROUND" CONCENTRATION OF ACID-BASE SPECIES IN PRECIPITATION

In casual speech, environmental policy analysts use "background" to describe a variety of concepts, from the amount of atmospheric pollutants that are derived from natural sources to the pollutants that are imported into a region and are beyond the control of local officials. The correct definition of the term will depend on the use to which it is being put. Summers, (1985) developed definitions which form the basis for Sections 5.1 and 5.2.

5.1 Definition for Separation of Natural vs Anthropogenic Sources

If it is desired to scientifically define the relative importance of natural and anthropogenic sources then one of the following definitions might be appropriate:

- 1. The lowest concentrations of pollutants observed anywhere on the globe over some appropriate averaging period.
- 2. The fraction of pollutants at remote sites that cannot be attributed to any anthropogenic source.
- 3. The average concentrations that would occur if all the natural emissions were distributed uniformly over the globe.
- 4. The average concentrations that could be expected if all anthropogenic sources had never existed.

Using the first definition, it may be possible to establish a background value for an extremely isolated site, such as the Antarctic continent, but there would be no reason to believe that it would be an appropriate value in another location with a different climate and different naturally occurring local sources. The second would solve that problem, if a remote site could be found within a local climate regime, but raises the additional problem of

how to differentiate between the possible sources of pollutants. The third addresses the question of local variability by averaging over the entire globe but it does not add any understanding to the processes of generation and removal of pollutants from the atmosphere. The fourth definition offered is most precise in addressing the question, but it would require much research over a very long period to develop the information necessary to confidently calculate even a local result.

Any definition of background must always be qualified not only to location but also to meteorology. For example, at Mauna Loa observatory, the air is clean virtually all the time (as long as cane is not being burned and the volcano is not erupting). Still, the study of data for carbon dioxide and aerosols at that site (at 3400 m elevation) indicates three different background regimes, one observable during upslope winds and the other two observed with downslope winds. The first appears to represent the marine boundary layer and the latter two the upper troposphere. One upper tropospheric condition is relatively clean and the other includes dust identifiable as being transported from Asia (Shaw, 1980). At low elevation sites along the west coast of B.C. a similar difference should be observed in on-shore marine air masses and off-shore moving continental air masses.

The elevation of the Mauna Loa site points up another important aspect of defining background from remote site measurements. Several factors, which are not yet fully understood, must be considered when rain samples are acquired from higher altitudes. First, liquid water content decreases and the washout ratio¹ increases, resulting in an <u>increased</u> aqueous phase concentration of the substances removed by nucleation scavenging. Second, temperature decreases and precipitation formation increasingly involves snow-flake growth by vapor deposition, which results in a <u>decrease</u> in the concentration of the solutes in the water. Third, precipitation amount varies with altitude with increased amounts of rain at lower altitudes due

¹. Washout ratio is the ratio of the concentration in the rain divided by the concentration in the air. The units of this ratio vary according to local practice.

to the lifting of the cloud masses and decreased amounts at greater altitudes due to decreased liquid water content of the clouds (Millar and Yoshinaga, 1981). Fourth, the acid-base species available in pre-cloud air in the boundary layer are likely to be different from those in the upper troposphere.

Thus measurements made at a nearby remote site which is at a much higher elevation or where the precipitation is dominated by snowfall would not be appropriate for estimation of background in lower elevation coastal regions. Nor would snow collected in areas such as Antarctica provide useful comparisons. However, evidence from recent research by Vong (1985) suggests that rain falling at low altitude from on-shore air masses along the northwest coast of North America is not measurably different from rain falling at low altitudes in other remote, mid-latitude marine settings. Thus, data collected at remote coastal sites in B.C., Washington, and Oregon should be useful in defining a background value for non-anthropogenic sources along the entire North Pacific Coast.

5.2 Definitions for Environmental Planning

If the purpose is to understand the atmospheric transport into and generation of pollutants in an area in order to understand the limits of effectiveness of control programs, then other definitions may be offered:

- 5. Average values observed at sites on the upwind edges of the control region.
- 6. Typical values observed at remote sites upwind and near the control region.
- 7. The concentration of pollutants in the control region atmosphere that cannot be accounted for by anthropogenic sources in the control region.

These definitions are more oriented to the functional reality of environmental policy decisions but each still presents some difficult issues.

Number 5 has been widely used in the development of air quality control plans for many years. It assumes and accepts whatever is coming into a region as a given. However, it may not fall cleanly under the concept of "background" because a significant fraction of the imported pollution may be of obvious anthropogenic origin on the immediate other side of the chosen boundary line for the control area. Definition 6 avoids this difficulty by asking for values from sites that are clearly not under such local influence. However such a site may be less relevant because pollutants from local natural sources may be removed from the atmosphere (and not replaced from other natural sources) between the remote site and the control region. Finally, the last definition speaks most directly to the needs of the policy analyst but again may be very difficult to confidently calculate. Definition 7 has many of the same faults as Definition 5 and, in addition, would rely on highly unreliable modelling techniques to determine the expected concentrations in the control region from local sources.

The most appropriate choice of a background value to be used in local air quality management planning must consider each of these possible definitions. In developing such a value it is important to have available data from nearby remote sites at similar elevations. However only along the Pacific coast and in some areas of Western Canada can these values be expected to reflect primarily natural sources and to be devoid of anthropogenic influences. In Central and Eastern Canada and in urbanized areas along the Pacific Coast (e.g., Victoria and the Lower Mainland), the contribution of acidic and basic materials from other political jurisdictions should be significant and may equal or exceed the natural contribution.

This suggests that a definition of background should consider data from remote sites screened to remove potentially anthropogenically-influenced air masses (Definition 2), from nearby, remote sites (Definition 6), and an evaluation of anthropogenic sources in neighboring jurisdictions (Definitions 5 and 7). By considering and carefully evaluating each of these elements a graded series of background definitions can be provided to the environmental policy officials which will serve the needs of control program development.

6.0 ESTIMATES OF BACKGROUND IN ACCORD WITH DEFINITION

6.1 Mean Values and Variability in the Estimates

For purposes of this report, a combination of Definition 2 and 5, described in Section 5.0, was selected as the definition of background sulphate in rainwater. The measurement sites selected for analysis were relatively remote and upwind of the mainland control area and, in addition, it was possible to identify, and exclude, individual measurements that appeared to be influenced by anthropogenic sources. For reasons stated earlier, this definition also excludes measurements taken during precipitation in the form of snow. As described in detail in Section 4, five sites that meet the above criteria, two in B.C., one in Washington, and two in Oregon were selected for analysis. There is no "<u>a priori</u>" reason to believe that these sites are different with respect to observed background sulphate values.

Following selection of these sites, the aqueous concentrations of sulphate in rainwater, rather than the deposition rate of sulphate via rain, was selected as the appropriate variable. This decision was based on the fact that the total amount of rain in a year varies considerably between the west coast and the inland regions of interest. The removal of sulphur species from the air via rain is a relatively inefficient mechanism with a corresponding large atmospheric residual amount of sulphur that is not significantly removed in a given rain event. Therefore, if deposition is chosen, the geographic variability in the amount of rain between the coast and the inland regions becomes the single most important determinant of sulphate deposition rate on an annual basis. The choice of sulphate concentration in rainwater, rather than deposition rate, eliminates this potential rainfall bias.

Based on the above approach, the sulphate concentration measurements at these five sites were screened according to the criteria described in Section 4. These criteria require internal consistencies of sample volume to rain gauge measurement, of ionic charge balance, and of sodium to chloride in ratio relative to seawater. Histograms of the total and

minimally screened sulphate concentration data for each site are shown in Figure 6.1 (a to e) for the following sites:

- Port Hardy, Figure 6.1 (a)

- Terrace, Figure 6.1 (b)

- Schmidt, Figure 6.1 (c)

- Alsea, Figure 6.1 (d)

- Hoh River, Figure 6.1 (e)

A principal component analysis of the entire chemical data set for these minimally screened cases consistently showed that sea-salt was the predominant source of chemical variability of the major ionic species. Therefore, the sulphate measurements were adjusted to remove sea-salt sulphate using sodium ion concentration as an index of sea-salt. Additional sources were weakly indicated, with the suggestion of a soil derived factor as well as a combustion (or fertilizer) factor. Figure 6.1 (a to e) therefore shows the original total sulphate histogram and the adjusted "excess sulphate" histograms resulting from this correction. The "excess" sulphate values are always less than the measured sulphate values. Also, a significant portion of the high sulphate observations (greater than or equal to 20 ueq/L) were associated with high sea-salt levels as illustrated in Figure 6.1 (a to e).

The sea-salt correction alone is not adequate for this analysis. It is required that no known anthropogenic or local sources should influence the measurements. To this end, an additional set of screening criteria was established based on source information gained from principal component analysis. The nitrate and ammonium ion restriction is based on the ocean not being a significant source of these ions, whereas local anthropogenic sources may be (e.g., combustion or fertilizer). The calcium restriction eliminates the possibility of soil derived sulphate ion. Figure 6.1 (a to e) shows the resulting shift in the excess sulphate frequency distribution

due to this final screening procedure as the "fully screened" value. The occurrence of high values (greater than or equal to 20 ueq/L) is virtually eliminated. The remaining number of samples at each site were reduced during screening and the base for the percentage calculations is the number of total samples after screening.

These distributions provide a working definition of "background" sulphate. It is not expected that the local sources of sulphate at these sites (including sea spray) will be significant at the downwind regions of interest. However, it is expected that these "excess" sulphate distributions will persist for several hours to a day or more downwind, as described in Section 3. Essentially, these sulphate distributions reflect the influence of a widely distributed fine particle sulphate aerosol of marine origin. This aerosol is expected to influence lowland rainwater chemistry in a similar way at these sites as it does at the downwind region of interest.

Support for this notion of a widely distributed source is found when comparing the average excess sulphate distributions computed from the data given here by two different techniques, giving equal weight to the distributions at each site and giving equal weight to each measurement independent of site. The latter procedure weighs two sites more heavily (Hoh and Alsea Guard Station) because their record length is longer and thus emphasizes data over a long time period rather than over a wide geographical area. Both average distributions are approximately the same, suggesting a general widespread background source relatively invariant over time and space, as illustrated in Figure 6.2. Figure 6.2 was prepared based on the number of screened excess sulphate samples in contrast to the number of total sulphate samples for Figure 6.1 (a to e). This approach is also supported by the similarity among the distributions at each of the sites and the overall distribution.

Thus, the sulphate ion concentration distribution shown in Figure 6.2 is our best estimate of the background sulphate in rainwater. A distribution is more appropriate than a single average value, as the background and/or

natural source is expected to vary. It should be emphasized that this distribution is applicable over an annual sampling period with a one-week averaging time. The relatively frequent occurrence of very low levels (0-2 ueq/L) may be, in part, an artifact of the sea-salt correction procedure, related to the analytical accuracy of the sodium and sulphate measurements at these low levels (see Section 4.2). However, these very low sulphate levels cannot be completely attributed to analytical errors in the sea-salt correction, as data from at least one site (Hoh River) show the same phenomena in the total sulphate measurement {refer to Figure 6.1 (a to e)}.

TABLE 6.1 Precipitation Comparison for Various Sites

(Concentrations reported as micro-equivalents per litre or ue/1)

<u>Site</u>	<u>Alsea</u>	Schmidt	Hoh	Pt.Hardy	Terrace	<u>5 sites</u>
Rain mm/wk	48.3	44.1	73.2	46.7	28.5	
Baland	ce .05	•08	.07	.07	.19	.07
C1/Na	1.8	2.2	2.5	1.7	2.1	2.1
# SO4 < L.D.	. 5	5	33	1	3	47
N	128	35	162	31	29	385
Na SO4xs NO3 H ⁺ NH4 Caxs	45. 5.5 1.7 3.6 1.4 3.8	13. 5.0 2.5 3.2 2.0 2.0	24. 4.4 1.4 3.7 1.4 1.3	66. 6.4 1.4 8.3 0.7 3.4	5.4 7.8 0.6 7.5 0.4 4.1	34. 5.5 1.4 5.1 1.2 2.2
Princi	ipal Compo	onents:				
1 1	Na,Cl,Mg	Na,Cl,Mg	Na,Cl,Mg	g Na,Cl,Mg	Na,Cl	Na,Cl,Mg
2	Caxs S04xs	Caxs H ⁺	H ⁺ SO4xs NO3	nh4 NO3	Caxs Mg	H ⁺ SO4xs CAxs
3	-		(Caxs)			(NO3,NH4)

Note: components in () are not necessarily statistically valid.



6.2 Limitations in Projections of Background Estimates

The results reported here are expected to be useful as an estimate of background concentration only along the northwest coast of North America. It is not known at this time how far inland the air masses will be dominated by the marine sulphate aerosol. Naturally occurring terrestrial emissions and wind-blown dust could change the acid-base chemistry significantly.



SULPHATE TOTAL FIGURE Qo CONCENTRATION EXCESS **6**. 1 **(a)** SULPHATE PORT HARDY EVALUATION ATE LEVELS



TOTAL

EXCESS

FULLY SCREENED



FIGURE 6.1 (c) SCHMIDT SULPHATE CONCENTRATION EVALUATION TOTAL & EXCESS SULPHATE



FIGURE 6.1 (d) ALSEA SULPHATE CONCENTRATION EVALUATION TOTAL & EXCESS SULPHATE LEVELS



FIGURE 6.1 (e) HOH RIVER SULPHATE CONCENTRATION EVALUATION TOTAL & EXCESS SULPHATE LEVELS



FIGURE 6.2 EXCESS SULPHATE CONCENTRATION FOR ALL STATIONS SITE AND NUMBER WEIGHTED AVERAGES



7.0 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

The description in Section 3.0 of this report of the acid-base chemistry of precipitation and mechanisms of precipitation formation imply that any useful interpretation of precipitation measurements must reflect this broader perspective. In particular, data derived from rain must be separated from data derived from snow measurements. Presentation of pH measurements alone and interpretations of such results as delineating regions of concern for "acid rain" can be potentially misleading unless a supporting analysis of other important acid-base species has been made.

For the purposes of this report, "background" sulphate was defined as the concentration in rainfall obtained at nearby remote sites, upwind of urbanized areas, with the further requirement that data with evidence of possible anthropogenic source contamination be excluded. This had the effect of reducing the anthropogenic contribution to this background estimate of possible local and regional anthropogenic sulphur sources. The screening techniques used appear to have been successful in eliminating the spurious data without increasing the data noise to an unacceptable level.

As shown in Section 6.0, values obtained from several long-time record sites along the northwest coast of North America were mutually consistent and suggest a background excess sulphate concentration in the range of 6 to 10 microequivalents per litre. The distribution has a mode at approximately 8 microequivalents per litre. There is a secondary mode of very clean rain, with an excess sulphate concentration near or below the minimum detection limit of the instrumentation being used. The implications of this bi-modal distribution are not understood at this time.

In the marine air masses studied in this report, sulphate was the dominant ion in the acid-base balance, although other ions were present and potentially important. In other areas of Canada there may not be a single dominant ion and the interpretation of the data may be much more difficult.

The importance of sulphate in coastal areas appears to derive from a substantial atmospheric burden of sulphate aerosol which is only slowly removed by rainfall. This suggests that the region of marine sulphate dominance may extend from a few hours to possibly several days downwind from the coast.

7.2 Recommendations

British Columbia has two coastlines, the outer and inner (i.e., Pacific Ocean and Strait of Georgia). Sites for future collection of background precipitation data, for the outer coast, should be located:

- at low elevations

- such that no land areas lie upwind

- with immediate exposure to on-shore flows from the north Pacific
- away from geographic features that would create a "rain shadow"
- with reasonable access but without opportunity for public interference

Sampling should be conducted so as to avoid significant impact from the outflow of pre-frontal easterlies from the Straits of Juan de Fuca and the anthropogenic sources of Puget Sound and the Strait of Georgia. Any proposed sampling strategy should be tested, eg. with measurements of trace metals in rain (Vong, 1985).

For the "inner" coast, background levels of sulphate are expected to be about the same level as the outer coast while nitrate and ammonia levels may increase due to natural terrestrial sources. Based on this study, two recommendations can be made:

- meteorological monitoring should be employed at any inner coastal



site so trajectory analysis could be used to eliminate data with potential anthropogenic contamination;

- studies should be attempted to ascertain whether the local natural background can be objectively quantified, or whether it will be necessary to extrapolate from the outer coast.

In the course of conducting this study, several avenues for progress in measurements of the acid-base chemistry of precipitation along the B.C. Coast were suggested by the study team.

First, the chemical criteria screening techniques used in this study for controlling the contamination of the data by air masses with a trajectory over terrestrial areas remain unproven even though the results presented here suggest strongly that they are valid. Stronger evidence for the conclusions of this report and support for the screening techniques (which could be used elsewhere if confirmed) could be obtained by analysis of the event data sets described in Section 4.1.2, and in particular, the South Coastal Event Sampling Network. This would not have to be a substantial effort, but its results could provide important support to these estimates of background sulphate and significant additional data. Besides excess sulphate, a full ion balance is needed to complete the acid-base picture.

Second, there should be a careful review of the data collection and analysis procedures of all the stations along the B.C. Coast that might be used for future studies of the acid-base chemistry of precipitation. This review would be oriented to ensuring that all the necessary ions are being measured and recorded and that other data are being recorded in such a manner as to be useful for acid-base chemistry studies. Integration of data being collected in Washington into a B.C. data base should be investigated.

Third, the supposition and apparent result of this study that marine sulphate aerosol along the coast is carried inland and has an effect there should be further studied. The results of such a study would support or contradict the choice of concentration rather than deposition as the more

important variable. At this time it is not possible to say that the results presented here are not highly influenced by the amount of rainfall at the sites. It is suggested that the west coast of Vancouver Island may present an opportunity unique in the world for such a study. If a string of temporary rain collection sites were established along the road from Ucluelet to Port Alberni it would be possible to collect from a selected single storms' rain with widely varying deposition rates. The results from this experiment would make a major contribution to resolving this issue.

Fourth, measurement programs should be repeated for precipitation monitoring sites inland of the Coast Range to define the background acid-base chemistry there, where it is not expected to be dominated by marine sulphate aerosol.

This study, emission inventories and modelling are being conducted as part of the Environment Canada/B.C. Ministry of Environment/Greater Vancouver Regional District planning to protect the atmospheric environment. A more detailed evaluation of anthropogenic and natural sources would assist in determining the relative importance of these various sources and their effect on precipitation on the Coastal Range mountains. Data of this sort, as well as a more complete and fundamental understanding of the natural background are absolutely necessary for any attempt to predict (e.g. with region-specific models) the potential impact of new sources or control programs.

8.0 REFERENCES

8.1 Annotated Bibliography

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Rainwater and dry deposition chemical composition and scavenging ratios for samples collected at Eniwetok Atoll in the Marshall Islands are reported. Rainwater concentrations of trace metals are 3 to 10 times lower than average Northwest Coast values.

Barrie,L.A., Fisher,D., and Koerner,R.M. (1985), <u>Atmospheric Environment</u>, 19: 2055-63.

Arctic snow cores from Agassiz in the Northwest Territories of Canada were analyzed for pH and conductivity. Summer background H⁺ averaged 6 ueq/L while winter H⁺ was about 8 ueq/L from 1912 until 1956 and increased to a mean of about 14 ueq/L by 1977.

Barrie,L.A. and Hoff,R.M. (1984), <u>Atmospheric Environment, 18</u>: 2711-2722. SO4 aerosol and SO2 gas measurements were performed at several Arctic sites including Barrow,AK, and Igloolik and Mould Bay, Canada. Concentrations were well above remote values. Mean SO2 residence times were estimated to be between 10-32 days, depending on season,with the highest residence times in winter.

Barrie,L.A. and Neustadter,J. (1983), <u>The Dependence of Sulphate Scavenging</u> <u>Ratios on Meteorological Variables</u>, in Precipitation Scavenging, Dry <u>Deposition, and Re-suspension</u>, ed. H.Pruppacher, (The Hauge: Elsevier Science), pp. 203-211.

Scavenging ratio depends upon precipitation amount and type for samples collected in eastern Canada. Sulphate scavenging ratio (precipitation SO₄) was corrected for the calculated value of dissolved (equilibrium) SO₂.

50

Barrie,L.A. and Sirois,A. (1982), <u>An Analysis and Assessment of Precipi-</u> <u>tation Chemistry Measurements Made by CANSAP: 1977-80</u>, (Downsview, Ont.: Atmospheric Environment Service), Report AQRB-82-003-T This review of CANSAP data includes 5 B.C. sites, including the Vancouver airport and Port Hardy. Port Hardy data are described as excessively influenced by high Ca concentrations (possibly increasing pH) while Vancouver site is criticized for locating near a major airport.

Barrie,L.A., Wiebe,H.A., Fellin,P., and Anlauf,K. (1981), <u>Results of the</u> <u>Canadian Air and Precipitation Monitoring Network: July 1979 to June 1980</u> (Downsview, Ont.:Atmospheric Environment Service), Report AQRB-81-026-T Aerosol and precipitation chemical composition data are presented for 6 sites in Eastern Canada.

Bates,T.S. and Cline,J.D. (1985), <u>J.Geophys.Res.</u>, 90:9168-72. DMS concentrations were measured in ocean water near the northwest coast of the U.S. during 1983-84. The flux of sulphur estimates from their DMS measurements represents 4-13% of total anthropogenic sulphur emissions from the Western U.S.

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South Pole prehistoric snow (trace element) chemical composition is presented. SO4 was present at 0.07 mg/L with the sea-salt correction being negligeable based on Na. Cd (3 pptm), Zn (60 pptm), Cu (18 pptm), Mn (85-134pptm), Al (3-4 pptm), and Fe (3-4 ppb) are among the elements reported for prehistoric ice samples. Present day surface snow concentrations in Antarctica (from the literature) are presented for these same species as follows: SO4 (0.02-0.10 mg/L), Cd(1-10 pptm), Zn (15-80 pptm), Cu (10-70 pptm), Mn (10-30 pptm), Al (0.5-1.5 ppbm), and Fe (0.5-1.5 ppbm).

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Calculations indicate that pre-existing sulphate aerosol can explain the SO4 content of remote precipitation and, therefore, equilibrium pH. Remote rain



is predicted to have a pH of 4.5 to 5.6 based on liquid H₂O content and variability in the sulphur cycle.

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Total aerosol samples collected near Quillayute were analyzed for a number of trace metals with Pb $(19ng/m^3)$, Mn $(6 ng/m^3)$, V $(1.7 ng/m^3)$, Zn $(31 ng/m^3)$, Cu $(2.2 ng/m^3)$, Fe $(230 ng/m^3)$, and Ti $(21 ng/m^3)$ data higher than concentrations reported for sub-micron aerosol by Vong (1985) or total aerosol by Fox and Ludwick (1976) or Ludwick <u>et al.</u> (1977). This may be caused by a lack of data stratification according to meteorological conditions.

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The composition of precipitation at Point Barrow and Poker Flat, AK are reported for the period 1979 until 1982. Trajectory analysis was used to stratify the data according to synoptic air flow pattern. Under westerly air flow, excess sulphate dominated the anion content with a volume weighted mean concentration of 7.1 ueq/L at Poker Flat.

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Size segregated aerosol samples were collected at Eniwetok Atoll in the Marshall Islands. Enrichments were similar to average values along the Northwest Pacific coast. Periodic transport of dust from Asia is described as a possible source of V, Cr, Ni, and Cu. Geometric mean concentrations for the total aerosol were as follows (in ng/m3): Na (4000), A1 (21), V (0.08), Cr (0.09), Mn (0.3), Fe (17), Cu (0.04), Zn(0.17), Cd (0.004), and Pb (0.12). Pb and Zn were primarily in the sub-micron size range.

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The sulphur cycle of the globe is discussed. The anthropogenic and natural contributions are of the same order of magnitude although the anthropogenic portion is very patchy and corresponds to the continental portions of the northern Hemisphere.

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Cl, Na, K, Ca, and SO4 were measured for rainwater collected by a network covering much of the United States. This represents the first high quality study of the chemical composition of precipitation in the U.S. A site on Tatoosh Island, WA was used for their background site. Reported excess sulphate levels are very similar to average Northwest Pacific coast values reported here.

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Data are reported for a U.S. network that included a site at Neah Bay,WA. One of the authors (Lazrus) has reported (personal communication) that the Neah Bay station was never visited and may suffer from bad data.

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McLaren, R.R. (1985), Lower Mainland and South Coast B.C. Precipitation Chemistry Data (Vancouver, B.C.: Atmospheric Environment Service Pacific Region), Report PAES 85-2

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Raw data for precipitation collected in B.C. (trace metals and major anions and cations) are reported.

McLaren,R.R. (1982), <u>Sampling of Snowpacks for Chemical Analysis in South-</u> western British Columbia, (Vancouver, B.C.: Atmospheric Environment Service Pacific Region), Report PAES82-3 Raw data for snow cores collected in B.C. are reported with trace metals, anions, and cations included.

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Detailed description of procedures for B.C. Ministry of Environment pH and acidity procedures are outlined.

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The ICP/Aes method for trace element analysis are described and discussed.

Miller, J.M. and Yoshinaga, A.M., (1981), <u>Geophysical Research Letters</u>, 8: 779-82.

Preliminary data on Hawaiian rain indicate a mean pH of about 5 but a range of values from 4 to 5.6 are reported.

Moodie,C.D. (1964), <u>Nutrient Inputs in Rainfall at Nine Selected Sites in</u> <u>Washington</u>, Washington Agricultural Experimental Station, Bulletin (Pullman, WA; Washington State University).

Rain composition for several sites are reported but these data are of uncertain quality. A site near the coast at Long Beach is included.

Nikleva, S. (1984), <u>Acid Rain Over Southwestern British Columbia</u> (Vancouver, B.C.: Atmospheric Environment Service)

This report is similar to Nikleva (1983) except that some comparisons to Washington data have been included along with results of pH from the trans-boundary network. He concludes that background pH is 5.3 to 5.4 with

excess sulphate near 0.2 mg/L, similar to the average values reported in this study.

Nikleva,S. (1983), <u>Acid Rain on the West Coast of British Columbia</u> (Vancouver, B.C.: Atmospheric Environment Service), Report 8305-4 PAES pH values near the coast of B.C. averaged about 5, prompting further study of rain chemistry in that area. Sites at Port Hardy, Terrace, in the Lower Mainland, and along the southern coast indicate a depression of pH near Vancouver.

Nikleva,S. (1982), <u>Progress Report to Western LRTAP Committee on AES Pacific</u> <u>Region Program</u> (Vancouver, B.C.: Atmospheric Environment Service), Report PAES82-6

The information in this report is covered in Nikleva (1983). Raw data for Port Hardy event sampling are included here.

Overland, J.E. and Walter, B.A. (1983), <u>Marine Weather of the Inland Waters of</u> <u>Western Washington</u>, (Seattle, WA: National Oceanic and Atmospheric Admin.), NOAAERL-PEML-44

A useful discussion of the meteorology of Western Washington is included. This document would be useful to anyone planning to sample air or rain under selected wind flow regimes.

Powers, C.F. and Rambo, D.L. (1981), <u>Environmental Monitoring and Assessment</u>, 1: 93-105.

The only review of Western U.S. rain chemistry studies prior to Vong and Larson (1983). Included are a state by state breakdown of existing data. A number of the studies referenced contain data of uncertain quality and are not so identified in this review.

Pszenny, A.A.P., MacIntyre, F. and Duce, R.A. (1982), <u>Geophysical Research</u> Letters, 9: 751-4.

A very useful article on the influence (very small) of sea-salt on the pH of marine rain. Data for the composition of marine rains on the windward side of Samoa indicate pH values of 5.4 to 5.9.

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Rancitelli,L.A. and Perkins,R.W. (1970), <u>J.Geophysical Research</u>, 75: 3055-64.

This article and Tanner <u>et al.</u> (1972) report a large number of trace metals in precipitation collected over a five minute period near Quillayute,WA. These metals are very low in these samples. Note that the sampling period is so short as to make interpretation of the data difficult.

Sandhu,H.S., Mann,A.S., Wilson,R.G., Lechner,L.J., and Morelli,M., (1981) Western Canada LRTAP Activities.

This report provides a progress report on the acid rain activities of the 4 Western Provinces and Environment Canada. The activities are summarized with contact points for further information.

Summers, P.W., (1985), <u>Regional Background Atmospheric Sulphate Levels in</u> <u>Canada: Preliminary Estimates and Implications for Control Strategies</u>, prepared for Federal Provincial Advisory Committee on Air Quality. This report contains definitions of "background" that are addressed in detail in Section 5 of this report.

Summers, P.W., (1980), <u>Note on the Potential for Acid Rain in Western</u> <u>Canada</u>, prepared at the request of the Joint Consultation Meeting on Regional Scale Transport of Pollutants in Western Canada, September, 4, 1980.

This report concludes that potential for acid rain is more of a local than regional problem in Western Canada in contrast to Eastern Canada.

Tanner, T.M., Rancitelli, L.A. and Haller, W.A. (1972), <u>Water, Air, and Soil</u> <u>Pollution, 1</u>: 132-43.

Trace metals in rain near Quillayute, WA. See Rancitelli and Perkins (1970).

Vong,R.J. (1985), Simultaneous Observations of Rainwater and Aerosol Chemistry at a Remote Mid-latitude Site, PhD dissertation, University of Washington, Seattle,WA.

Measurements of rainwater and sub-micron aerosol chemical composition are reported. This study was specifically designed to investigate the northern Pacific Ocean background. Considerable analysis of meteorology, experimental errors, and possible sources of rain water solute are included.

Vong,R.J. and Charlson,R.J. (1985), <u>Chemical Education, 62</u>: 141-3. An equilibrium model for the pH of rainwater is described. Included is a Sillen diagram for rainwater composition at the Hoh River, WA, indicating that sulphate controls the pH.

Vong,R.J., Frank,I.E., Charlson,R.J., and Kowalski,B.R. (1985a), Exploratory Data Analysis of Rainwater Composition, in <u>Environ. Applications of</u> <u>Chemometrics</u>, Breen,J.J. and Robinson,P.E., eds., ACS Symposium Series <u>292</u>, 34-52

This paper is a discussion of the multivariate statistical analysis techniques applied to rainwater data and their application to the data set reported by Vong et al. (1986).

Vong,R.J., Larson,T.V., Covert,D.S. and Waggoner,A.P.,(1985b), <u>Water, Air,</u> and Soil Pollution, 26: 71-84.

Data are presented for the composition of rain in the Seattle and Bellingham areas of Washington State. Twelve months of NADP data from the Hoh River are summarized for comparison to urban data. Results indicate that background contributes about 16% of Seattle sulphate in rain.

Vong,R.J., Larson,T.V., and Charlson,R.J. (1984), <u>Precipitation Chemistry in</u> <u>the Pacific Northwest</u>, presented to the Annual Meeting of the Pacific Northwest International Section-Air Pollution Control Assoc., Portland,OR. This is an updated version of Vong and Larson (1983). Tables provide considerable data on precipitation chemical composition in Washington State with data for comparable sites in B.C. and Oregon included.

Vong,R.J. and Larson,T.V. (1983), <u>A Critical Review of Acid Deposition</u> <u>Research in the Pacific Northwest</u>, (Seattle,WA: Puget Power and Light Co.), Research Project 1983-1, Final Report

An annotated bibliography of mainly Washington State rainwater chemistry studies, which includes a discussion of the conclusions reached, typical values (summarized for coastal, urban, and mountainous sites), and numerous data from other sources.

Vong,R.J., Noone,K.J., Covert,D.S., and Charlson,R.J. (1986), The Chemical Composition of Marine Rain Collected at Cheeka Peak, Makah Indian Reservation, Washington, unpublished data, University of Washington, Seattle,WA. Newly available data for major anions and cations in rain collected during May 1985 near the Washington coast (unpublished) are similar to Lake Ozette and Cheeka Peak data published by Vong (1985).

Vong,R.J. and Waggoner,A.P. (1983), <u>Measurements of the Chemical Composition</u> of Western Washington Rainwater, 1982-83, (Seattle, WA: US EPA Region X), EPA-910/9-83-105

This technical report summarizes the same data as Vong <u>et al.</u> (1985), except that the Hoh River data reported here covers a longer time period (2 1/2 years).

Wang, P.Y. and Hobbs, P.V. (1983), <u>J. Atmospheric Sciences</u>, <u>40</u>: 1959. This paper includes measurements of the liquid water content of Pacific frontal clouds.

Welch,E.B., Chamberlain,W.H., and Spyridakis,D.E. (1984), Chemical Content of Snow and Effect of Melting on Cascade Mountain Lakes, <u>Northwest Science</u>, 58:885.

Data are provided for the chemical content of snow cores collected at sites in the Olympic and Cascade Mountains of Washington State. Excess sulphate in the Olympic snow cores was similar to average northwest coastal data for rainwater (3.3 ueq/L). Cations were higher than for rain, possibly due to incorporation of dust into the snow pack.

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Wooldridge, D.D. and Larson, A.G. (1980), <u>Non-point Source Pollution in Forest</u> <u>Streams of the Western Olympic Mountains (Washington, DC: Office of Water</u> Research & Technology), Project report B-076-WASH

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