

THE EFFECT OF A MAJOR EMITTER ON THE RAIN CHEMISTRY OF SOUTHERN BRITISH COLUMBIA -A PRELIMINARY ANALYSIS

PART I

D. A. Faulkner Scientific Services Division Atmospheric Environment Service Pacific Region

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Scientific Services Division Atmospheric Environment Service, Pacific Region Environment Canada Vancouver, Canada

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Abstract

The ASARCO copper smelter in Tacoma, WA was a major emitter of sulphur dioxide and atmospheric arsenic prior to its closing in March 1985. Precipitation chemistry data collected from a network parallel to the US/Canada border in southwestern British Columbia were analyzed to determine changes in rain chemistry as a result of the closure. Significant decreases in arsenic concentrations were noted. Decreases in sulphate and nitrate concentrations were detected as well but it is not clear that these can be attributed to the smelter closure. Suggestions for future studies are offered.

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<u>The Effect of a Major Emitter on the Rain Chemistry of</u> <u>Southwestern British Columbia - A Preliminary Analysis</u>

D.A. Faulkner

1. Introduction

The opening or closing of a plant which emits large amounts of an air pollutant provides an opportunity to observe the effects of the emitter on the rain chemistry downwind of the source. Such an opportunity arose when the ASARCO copper smelter in Tacoma, Washington, (Figure 1a) ceased operation in March 1985. This smelter emitted, in 1983, an average of 199 t/d (75100 tons/year) of sulphur dioxide (SO_2) (Beck and Associates, 1985a). This amounted to about 29 and 87 percent, respectively, of the total SO_2 emissions of Washington State, and the Puget Sound Air Pollution Control Region (based on data from Beck and Associates, 1985a).

The ASARCO smelter, in addition to being a major source of SO_2 , was a major emitter of atmospheric arsenic (As). Crecelius <u>et al.</u> (1974) reported the smelter emitted approximately 300 t/yr of particulate material into the air. The stack dust was composed of approximately 30-40 percent As, 20-30 percent Pb, 2 percent Sb and smaller amounts of Zn, Cu, Hg and other metals.

The downwind effects of the smelter on the precipitation chemistry of the region have been indicated in several studies. In a study of a single storm, Larson <u>et al.</u> (1974) clearly showed depositions of sulphate and arsenic in precipitation out to about 60 km to the north-northeast of the plant. Maykut <u>et al.</u> (1985), in a modelling study - also reported in Beck and Associates (1985b) - indicated the downwind depositions from the Puget Sound area, in which the ASARCO smelter was the major SO₂ emitter, extended to the northeast and north of Puget Sound. The maps with this study suggest that pollutants from the Puget Sound region are advected into southwestern British Columbia.

The ASARCO smelter, before it closed, was the dominant source of SO2 in western Washington. However, several other sources in western Washington and southwestern B.C. remain and emit significant amounts of SO2. Chief among these is the electricity generating station in Centralia, Washington which emitted 96 t/d (38,720 ton/year, Duncan, 1985) in 1983. One natural source Mt. St. Helens, emitted 147 t/d (53,636 ton/year, Duncan, 1985). The emissions from that source have been decreasing and, as Pennel <u>et al.</u> (1985) point out, wind directions at the summit of Mt. St. Helens are generally such as to advect the emissions to the east or northeast. Other sources of note are the petroleum refineries and pulp mills in northern Washington near the Strait of Georgia. These sources, although relatively small, may have a greater effect than those in the southern part of the state on the precipitation chemistry of southern B.C. because of their proximity.

The major sources of SO2 in western Washington and southwestern B.C. are shown on Figure 1a. The emission rates depicted (t/d) are drawn from various sources and are estimates only. They are included here to indicate the relative magnitudes of the various sources.

Low and mid level air flows are favourable for the advection of pollutants northward to the region around the southern Strait of Georgia. The prevailing 850 mb wind at Quillayute, Washington (Tables 1 and 2) is southwesterly, particularly in winter. Faulkner (1984), in a study of synoptic scale trajectories for the year 1978, showed that, in precipitation cases, the mean trajectory of air parcels arriving at Vancouver, B.C., at the 850 mb level is southwesterly which implies that many parcels traverse the Puget Sound region before arriving in southwestern B.C. He also pointed out that the mean trajectory of lower level winds (925 mb) was directly over Puget Sound to Vancouver.

Schoenberg (1983) has shown that the low level air flow in the Puget Sound-Juan de Fuca Strait-Strait of Georgia complex is determined by synoptic scale pressure gradients but it is influenced strongly by the terrain (Figure 1b). She characterized the synoptic patterns by the 850 mb wind direction at Quillayute and observed that with a southerly 850 mb wind, the surface winds in Puget Sound were light southerly, in Juan de Fuca, light easterly. However, as 850 mb winds veered to south-southwest or southwest, the flow in Juan de Fuca reversed, and the southerly flows from Puget Sound extended northward into the southern Strait of Georgia where they turned northwestward following the channel

TABLE 1

	PERCENT	MEAN SPEED
DIRECTION	FREQUENCY	(m/s)
٦T	5.0	r 1
N	5.0	5.1
NNE	3.4	3.9
NE	2.9	5.6
ENE	2.1	4.0
E	1.7	3.1
ESE	1.9	2.5
SE	2.5	4.3
SSE	4.9	7.3
S	11.0	8.2
SSW	11.0	7.1
SW	9.7	9.7
WSW	8.0	5.4
W	11.2	5.5
WNW	9.0	5.7
NW	9.9	5.1
NNW	5.8	5.5
CALM	0.8	

Percent frequency of 850 mb wind direction and mean speed at Quillayute, Washington - June to August (1971-1977).

TABLE 2

DIRECTION	PERCENT FREQUENCY	MEAN SPEED (m/s)
N NNE NE ENE E SSE SSE SSW SW WSW WSW WSW WSW	3.4 1.8 2.4 2.1 1.0 1.3 3.0 4.3 13.6 12.0 16.3 10.2 12.3 6.7 5.9	6.1 6.2 8.8 10.7 7.2 6.3 9.5 11.8 14.3 14.9 13.7 11.8 11.8 11.8 10.3 9.8
CALM	0.0	0•2

Percent frequency of 850 mb wind direction and mean speed at Quillayute, Washington - December to February (1971-1977).

between Vancouver Island and the mainland. Thus, with 850 mb southwesterly flows, which tend to be rain-bearing flows (Faulkner, 1984), the situation is conducive to low-level advection of pollutants northward.

Pennell et al. (1985) proposed a conceptual model of wet deposition of pollutants from the Puget Sound area. They suggested a two-phase process: a Transient Purge phase and a Quasisteady Continuous phase. During the Transient Purge phase, reacted pollutants which have built up during a dry spell are wet-scavenged efficiently during the early stages of a period of precipitation. If precipitation continues for a sufficiently long period, all, or most of, these pollutants will be deposited within a short distance of the source. Then the Quasisteady Continuous phase may begin in which pollutants ingested into the cloud are scavenged much less efficiently and residence times increase. Pollutants may thus be transported a greater distance and, although deposition rates decrease, deposition may last over a longer period of time and total deposits may become significant. Pennell et al, could not estimate the relative importance of the two processes but suggested deposition from the Transient Purge would be confined to the Puget Sound lowlands and deposition at more distance receptors would be dominated by the Quasisteady process.

Some evidence exists to indicate that detectable amounts of pollutants from the Puget Sound region are advected northward to B.C.

Nikleva (1983) noted that measurements from the South Coast B.C. (SCBC) network extending from the west coast of Vancouver Island to the Fraser Valley showed that, in the mean, the most acidic precipitation falls on the southern Strait of Georgia area which lies in the path of low-level air flows from Puget Sound. However, in one instance of a <u>westerly</u> flow, he observed that the acidity in the Georgia Strait region was comparable to that of western Vancouver Island. Nikleva pointed out that the information was insufficient to determine the relative contributions from far and near sources.

The aim of this preliminary study is to analyze differences in precipitation chemistry in southwestern B.C. with the ASARCO smelter operating and not operating. Data from the SCBC network are available for the period January 1982 to April 1986, along a line extending from Bamfield on the west coast of Vancouver Island to Agassiz in the Fraser Valley (Figure 2). The approach taken will be to seek statistically significant changes and interpret them in the light of the known meteorology of the area. From that, recommendations on further study to more clearly determine the effect of the smelter will be made.

2. Data

Precipitation event sampling in the SCBC network began in December 1982. The original network consisted of 13 stations (Figure 2) but two stations, Jordan River and Chilliwack, closed well before March 1985 and

so were excluded from the analysis. Wilson Creek and Texada Island were added to the network in October, 1984. However, data from these two stations were not included in this analysis because of the shortness of the records. Table 3 depicts the periods of data collection at the sites used in this analysis. Volunteers along the network collected precipitation samples at the request of a co-ordinator in Vancouver. The coordinator attempted to obtain samples for events when widespread precipitation was expected. Events generally lasted 1-3 days. Details of the equipment used and handling procedures may be found in McLaren (1985).

Prior to December 1982 when sampling commenced along the SCBC network, the Atmospheric Environment Service (AES) operated a similar volunteer network on the B.C. lower mainland. Several stations of this network (Vancouver Airport, Ladner, Cloverdale, Abbotsford and Agassiz) became part of the SCBC network. Data from those stations dating back to January 1982 were included in the following analysis.

A different protocol was followed at the Vancouver International Airport (VAN) station. There, observers (employees of the AES) were instructed to collect samples whenever rain commenced. Also, beginning January 24, 1985, samples were collected at Vancouver Airport with a CAPMON (Canadian Air and Precipitation Monitoring Network) automatic sampler following the CAPMON protocol. (See AES, 1984 for details of the procedure.) Thus, many more samples, often of small precipitation amounts were collected at that station which may have implications for the analysis of the data as discussed below.

8.

Table 3

SOUTH COAST BRITISH COLUMBIA (SCBC) NETWORK DATA

	1982 JFMAMJJASDND	1983 JFMAMJJASOND	1984 JFMAMJJASOND	1985 JFMAMJJASOND	1986 JFMA
Bamfield (BAM)		X	X+		-+**
Port Renfrew (REN)		X	X+		-+**
Sooke (SOD)		X	X+		-+**
Saanichton (SAN)		X	X+		- ÷ **
Pender Island (PEN)	X		X+		-+ * *
Saltspring Island (SSI)	X		X+		-+**
Vancouver Airport (VAN)	X		X+		-+#*
Ladner (LAD)	X		X+		-+**
Cloverdale (CLO)	X		X+		+₹-¥
Abbotsford (ABB)	X		X+		+*-*
Agassiz (AGA)	X		X+		-+**

Legend:

- X--X Major ions only chemical analysis by North Vancouver IWD Laboratory
- +--+ Major ions and trace metals chemical analysis by Burlington CCIW Laboratory
- *--* Major ions only chemical analysis by Burlington CCIW Laboratory
- I Data not used for March 1985, the month of the ASARCO smelter closure.

Chemical analysis was carried out at two laboratories: at the Inland Waters Directorate, Environment Canada Laboratory in North Vancouver until September 1984, and at the Canada Centre for Inland Waters (CCIW), Environment Canada Laboratory in Burlington, Ontario, thereafter. Details of sampling and chemical analysis methods, together with data listings up to June 1984, may be found in McLaren (1985). A listing of chemical analysis methods employed at the CCIW Laboratory may be found in Appendix A.

It was necessary to meld the data from the two laboratories into one data set, a major problem since the two laboratories used different analysis techniques. It had been anticipated that differences attributable to laboratory techniques could arise and therefore duplicate samples were sent to both laboratories for comparison. Comparison results are presented in Appendix B for the 21 duplicate analyses available. As anticipated, the results differed. Correlations among the analyzed ion concentrations were calculated to determine if the differences were systematic. Among the major ions (sulphate, nitrate, ammonium, sodium, chloride and hydrogen), correlations were high (> 0.9), as shown in table 4 and Figure 3). Thus, it was decided to modify the results of one laboratory (North Vancouver Laboratory) using least squares regression analysis from the duplicate sample data. The results of these appear in Table 4. In general, linear regression proved adequate but in a few instances quadratic regression was required. It was discovered also that the regression equations were

inapplicable outside of the range of values measured in the duplicate samples. For these cases, as indicated in Table 4, simple linear relations were assumed and, in general, these took the form of equating one to the other. Table 4.

Comparison of Duplicate Sample Analyses at the North Vancouver (NVAN) and Burlington (CCIW) Laboratories.

(An	'N'	indicates	North	Vancouver,	а	'C'	indicates	'corrected')	1
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Ion	<u>Correlation</u>	Range (mg/L)	Regression Equation
Sulphate	0.96	S04N < = 1.75	S04NC =.326+1.317*S04N - 0.198*S04N *S04N
		SO4N > 1.75	SO4NC = SO4N
Nitrate	0.99	NO3N < .075 NO3N > =.075	N03NC = 0.157*N03N N03NC = .047+0.789*N03N 0.083*N03N*N03N
Calcium	0.87		CANC=0.32+0.896*CAN
Ammonium	0.92	NH4N < 0.25	NH4NC=0.005+0.118*NH4N+ 3.413*NH4N*NH 4N
		NH4N > ≈0.25	NH4NC=NH4N
Magnesium	0.80		MGNC=0.030+0.721*MGN
Sodium	0.89		NANC=0.033+0.969*NAN
Chlorine	0.93		CLNC=-0.119+0.996*CLN
Potassium	0.57		KNC=-0.010+0.741*KN
Hydrogen	0.96		HNC=1.3E-7+0.919*HN

The data collected prior to October 1984 (and analyzed at the North Vancouver Laboratory) were revised by application of the equations of Table 4. (Note that this is not meant to imply that the results from one laboratory were superior to the other; instead, the intent was to develop an internally consistent set of data to be used in a relative, rather than an absolute, sense). A Student's t-test of differences in mean concentrations (of revised data) before October 1984 and for the period October 1984 - February 1985 showed no significant differences in ionic concentrations of any of the elements. The applicability of the t-test to these data is discussed below.

The data were subjected to an ionic balance quality control check using the method described by Lau (1982). The ratio of cations to anions was calculated for each precipitation sample and, with the exception of the stations at Abbotsford and Cloverdale, were discarded if the ratio was outside the range 0.5-2.0. The two Fraser Valley stations are in a predominantly agricultural area and samples taken there frequently have high concentrations of ammonium. These cations are probably balanced by unknown anions (possibly phosphate) and hence the ionic balance cannot be determined accurately.

For any sample in which the concentration of an ion was below the minimum detectable limit (MDL) for that ion, rather than discard that measurement, a value equal to one-half of the MDL was assigned to it arbitrarily.

Listings of the data used in this report may be found in Appendices C and D which form Part II of this report.

3. Methods

Mean concentrations of the major ions and of some trace elements (such as arsenic) were compared using Student's t-test, a procedure of the SAS Institute Statistical Analysis System (SAS Institute, 1982a). Prior to using the t-test, the data were tested for normality by visually comparing a plot of the cumulative distribution function to a normal probability plot. Kolmogorov-Smirnoff normality tests (SAS Institute, 1982b) were also applied. Both tests indicated the data could be considered to have a normal distribution. (It should be pointed out that the plots of the data included 'outliers' on the high end of the plots. These cases of high concentrations of ions are probably very significant and should be examined in more detail.)

It is interesting to look first at the changes in concentrations of arsenic observed in the precipitation before and after March 1985. Larson <u>et al</u>. (1974) found in their study that the wet deposition of

arsenic followed the same pattern as sulphate deposition from the ASARCO smelter. Since no other significant sources of arsenic in the Puget Sound region or southwestern B.C. are known to exist, it is feasible to use arsenic as a tracer of opportunity.

Figure 4 is a plot of arsenic concentrations before and after March 1985 along the network as indicated. (For this figure and others depicting metals concentrations, only data analyzed at the CCIW Laboratory were employed.) Results of the t-test indicate that the differences at all sites east of Sooke (SOO) are significant at the 95% confidence level except for Vancouver (VAN) and Pender Island (PEN) where they are significant at better than the 90% confidence level.

This diagram, in conjunction with the known climatology of winds in the region, suggests strongly that prior to the closure of the ASARCO smelter, arsenic was being advected northward into the Strait of Georgia and the lower Fraser Valley region. Following the closure of the smelter, the arsenic levels dropped to the same as those on the southwest coast of Vancouver Island where southwesterly air flows predominate.

Since it is believed that arsenic may be used as a tracer of opportunity for emissions from the ASARCO smelter, it is interesting and instructive to examine correlations between concentrations of arsenic and other ions. Nikleva (1985) noted a correlation of 0.8 between <u>mean</u> arsenic and sulphate concentrations along the SCBC network from which he

suggested that a good part of the acidity in the southern Strait of Georgia region is associated with sources in the Puget Sound area.

Correlations between arsenic and other ion concentrations tend to be highest at the stations near the Strait of Georgia. The spatial variability of these correlations may be determined by examining the data on a station-by-station basis in which correlations are calculated from event data. Such correlation coefficients are listed in Table 4 for the major ions, sulphate and nitrate. Data in this table are based on event data before and after the smelter closure. From the table it is evident that the highest correlations are found at Pender Island, Vancouver, Ladner and Cloverdale. Correlations at Abbotsford are not as high as those at other mainland stations but this may be because of the relatively small number of samples at that station. The fairly good correlation between nitrate and arsenic at Bamfield may be misleading since the concentrations of both ions there were low and were often at or below the detection limit; the concentrations were consistent, but consistently low.

If only data <u>before</u> the smelter closure are used, a similar pattern emerges with significant correlations between sulphate and arsenic concentrations of .53 to .83 at Pender Island and east (Abbotsford excepted). After the smelter closure, only at one station, Vancouver Airport, is there a significant correlation (.69) and this again may be because arsenic levels decreased to near the detection level - (Figure 4).

Table 5

			Excess Sulphate*				Nitrate	
Station	Number of Samples	Mean As Conc. (ug/L)	Correlation	Significance Level**	Mean Conc. (mg/L)	Correlation	Significance Level	Mean Conc. (mg/L)
BAM	26	•11	•12	N/S	•42	•64	.99	•04
REW	29	•11	•30	N/S	•30	43	•95	•05
S00	28	•10	•00	N/S	•38	•00	N/S	•07
SAN	21	•24	•10	N/S	•71	02	n/s	•15
PEN	25	•21	•72	.99	•73	•85	.99	•15
SSI	25	•26	•51	.99	•67	•34	•90	•13
VAN	52	•22	•60	.99	1.22	•63	•99	•22
LAD	33	•44	•81	•99	•95	•86	•99	•21
CLO	23	•27	•63	.99	1.05	•72	•99	•22
ABB	18	•32	•38	•85	•72	•53	n/s	•16
AGA	26	•16	•53	.99	•44	•41	•95	•12

Correlations of Concentrations of Arsenic with Sulphate and Nitrate in Precipitation

* Excess sulphate is total sulphate less sulphate associated with sea salt.
** Only levels in excess of .85 are considered significant here.

The correlation between arsenic and sulphate concentrations would lead one to expect a decrease in sulphate concentrations corresponding to that of arsenic. Sulphate concentrations did decrease, at most stations, (Figures 5 and 6), but the decreases are less dramatic than those of arsenic. Nevertheless, a similar pattern emerges with stations near the Strait of Georgia indicating the most significant reductions. In general, changes are significant at the 95% confidence level except for the three western sites (for which changes are not significant), at Pender Island and Vancouver Airport where the concentration of sulphate increased slightly. (Note that Figure 6 depicts changes in excess sulphate defined as total sulphate less the sea salt contribution.)

The observed increase in sulphate concentration at Vancouver Airport is interesting and the reason for it is not apparent. One possibility is that because many of the Vancouver Airport data consist of daily samples, the equal weights given to events (days) of small precipitation amount bias the means in favour of larger concentrations which occur with small precipitation amounts. Calculated <u>weighted</u> means before and after the closure (Table 6) show a decrease in mean sulphate concentration at Vancouver Airport. However, this decrease was accompanied by corresponding decreases in nitrate and ammonium concentrations as well.

Table 6

Weighted Means of Ion Concentrations in Precipitation at Vancouver Airport Before and After Closure of the ASARCO Smelter (units = mg/L).

	Before	After
Number of samples	110	131
Sulphate	1.695	1.227
Nitrate	0.520	0.210
Ammonium	0.210	0.148
Sodium	0.681	0.385

(Because accurate measurements of precipitation were unavailable from the majority of stations, weighted means were not calculated for the comparisons at other sites. However, since the samples taken at all other sites were for cases of widespread precipitation, the variation in precipitation amounts from event to event at the other stations would be less than would occur with daily samples which are likely to include cases of barely greater than trace amounts.)

Figure 7 depicts mean nitrate concentrations prior to, and after the smelter closure. Again, the same pattern of significant decreases in nitrate in precipitation from the Saanich Peninsula eastward to the Fraser Valley with insignificant changes on southwestern Vancouver Island is evident. It is not known why the concentration of nitrate should decrease coincidentally with the decrease in sulphate.

An attempt was made to determine differences in concentrations of antimony before and after the smelter closure since Larson <u>et al</u>, (1974) suggested it might be used as a tracer of opportunity. However, the number of cases before the smelter closure was small (3-5) and many of the analyses indicated the concentrations were near, or below, the detection limit. No reliable differences could be detected. This may be due to the fact the emissions of antimony from the smelter were significantly lower than those of arsenic.

Changes in vanadium concentrations are shown in Figure 8 in which it is seen the concentration decreased at <u>every</u> site. All were highly significant changes with the exception of that at Port Renfrew (REN). No explanation of these changes is obvious but because vanadium is used in the refining of petroleum, and may therefore serve as a tracer of refinery pollutants, the changes are perhaps related to refinery operations at Cherry Point, just south of the U.S./Canada border. These refineries are much closer to the SCBC network and pollutants from them may be advected by the surface winds through the Strait of Juan de Fuca,

whereas pollutants from the southern Puget Sound are more likely to be advected by higher level winds which are less affected by the topography of southern Vancouver Island.

No significant changes in copper concentrations were observed which is consistent with the fact that copper emissions from the smelter were well below those of arsenic.

4. Conclusions and Recommendations for Further Study

Further evidence has been presented here to indicate that pollutant emissions from the Puget Sound area affect the precipitation chemistry of southwestern B.C. The significant decrease in concentration of arsenic in precipitation is the best evidence of this since the ASARCO smelter was, apparently, the major source of atmospheric arsenic in the region. Considering the meteorology of the Pacific Northwest and southwestern B.C., it is almost certain that the ASARCO smelter was the source of the arsenic monitored in precipitation in B.C.

A decline in concentration of sulphate near the southern Strait of Georgia was detected but it is less clear that this can be attributed to the closure of the ASARCO smelter. Previous precipitation monitoring (Nikleva, 1985) indicated that sulphur emissions in the Vancouver area undoubtedly contributed to the acidity of precipitation in the southern

Strait of Georgia. Changes in local emissions or variations in meteorology might have been the cause. Nevertheless, the fact that the sulphate and arsenic concentrations correlate well before the closure, but decrease after the closure suggest strongly a link to the ASARCO smelter.

An interpretation of the observations is consistent with the deposition model proposed by Pennell <u>et al.</u> (1985). Local (mainly Vancouver) emissions are scavenged by the Transient Purge process but longer duration depositions of transported sulphate occur during the Quasisteady Continuous phase. Furthermore, the analysis is consistent with the complex flow patterns of the region; that is, during periods of precipitation, surface and low level winds tend to be southerly in Puget Sound turning more southeasterly in the Strait of Georgia and undoubtedly do transport pollutants to southwestern B.C. but not necessarily in detectable quantities.

Further studies are required. It is recommended that these include:

- a) more powerful statistical analyses of the SCBC network data, such as factor and principal component analysis;
- b) case studies of particular events which examine the meteorological and chemical aspects of the problem;
- c) applications of models, both statistical and short-term types which include meteorological and chemical transformations.

These studies, it is hoped, would answer some of the questions which this analysis raises. Are the decreases in sulphate concentrations definitely related to the closure of the ASARCO smelter? If so, what are the magnitudes of these decreases? Why did the concentrations of vanadium and nitrate decrease coincidentally with the decrease of sulphate? The answers to these questions, and others, should be answered by a follow-up study. The results of such a study would have benefits in increasing our understanding of pollutant dispersion in southwestern B.C. and Puget Sound and would increase our knowledge of meso-scale transport processes which would have application elsewhere.

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List of Figures

- Figure la. Location chart. SO₂ point (P) and area (A) sources with <u>estimated</u> emissions are indicated in t/d. Example, P-96 indicates a point source of 96 t/d.
- Figure 1b. Topographic chart of Western Washington and southwestern B.C. (after Schoenberg, 1983).
- Figure 2. The South Coast British Columbia (SCBC) volunteer precipitation sampling network.
- Figure 3. Comparison of sulphate concentrations of duplicate samples analyzed by the Canada Centre for Inland Waters (CCIW) Laboratory and the Inland Waters Directorate North Vancouver (NVAN) Laboratory. The curve is a quadratic least squares regression line.
- Figure 4. Concentrations of arsenic (micrograms/L) along the SCBC network before and after the Tacoma ASARCO smelter closure.
- Figure 5. Same as Figure 4 but for total sulphate. Units mg/L.
- Figure 6. Same as figure 4 but for excess sulphate. Units mg/l. Excess sulphate = total sulphate less 0.245 x sodium concentration.

Figure 7. Same as Figure 4 but for nitrate. Units mg/L.

Figure 8. Same as Figure 4 but for vanadium. Units micrograms/L.



Figure 1(a)





- 1. Bamfield (BAM)
- 2. Port Renfrew (REN)
- 3. Jordan River (JOR)
- 4. Sooke (S00)
- 5. Saanichton (SAN)

- - 6. Saltspring Island (SSI)
 - 7. Pender Island (PEN)
 - 8. Ladner (LAD)
- 9. Vancouver (A) (VAN)
- 10. Cloverdale (CLO)

- 11. Abbotsford (A) (ABB)
- 12. Chilliwack (CHI)
- 13. Agassiz (AGA)
- 14. Wilson Creek (WIL)
- 15. Texada Island (TEX)















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Figure 7





APPENDIX A

Chemical Analysis Methods and Detection Limits For Samples Analyzed at the Canada Centre for Inland Waters, Burlington, Ontario Laboratory

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NAQUADAT (2) PARAMETER	IONS	ANALYSIS METHOD	DETECTION LIMIT
07315	Nitrogen Dissolved Nitrate	Ion Chromotography	0.01 mg/L
07505	Nitrogen, Total Ammonia	Colorimetric	0.001 mg/L
10301	рН	Electrometric	
11107	Sodium, Dissolved	Flame Photometry	0.1 mg/L
12106	Magnesium, Dissolved	Atomic Absorption	0.1 mg/L
16309	Sulphate, Dissolved	Ion Chromotography	0.01 mg/L
17209	Chloride, Dissolved	Ion Chromotography	
19107	Potassium, Dissolved	Flame Photometry	0.1 mg/L
20108	Calcium, Dissolved	Atomic Absorption	0.01 mg/L

TRACE METALS ANALYSIS (1)

NAQUADAT PARAMETER	IONS	ANALYSIS METHOD	DETECTION LIMIT
11311	Sodium, Extractable	ICAP (3)	1.0 mg/L
12005	Magnesium, Total	Plasma Emission Spectroscopy	0.05 mg/L
19005	Potassium, Total	11 11	0.2 mg/L
20005	Calcium, Total	11 11	0.05 mg/L
23311	Vanadium, Extractable	ICAP	0.001 mg/L
24311	Chromium, Extractable	ICAP	0.001 mg/L
25311	Manganese, Extractable	ICAP	0.001 mg/L
26311	Iron, Extractable	ICAP	0.001 mg/L
27311	Cobalt, Extractable	ICAP	0.001 mg/L
28311	Cobalt, Extractable	ICAP	0.001 mg/L
29311	Copper, Extractable	ICAP	0.001 mg/L
30311	Zinc, Extractable	ICAP	0.001 mg/L
33008	Arsenic, Total	ICAP	0.02 ug/L
34008	Seleniom, Total	ICAP	0.03 ug/L
38311	Strentium, Extractable	ICAP	0.001 mg/L
42311	Molybdenum, Extractable	ICAP	0.001 mg/L
48311	Calcium, Extractable	ICAP	0.001 mg/L
51008	Antimony, Total		0.1 ug/L
56311	Barium, Extractable	ICAP	0.001 mg/L
82311	Lead, Extractable	ICAP	0.001 mg/L

- From <u>NAQUADAT</u>, <u>Dictionary of Parameter Codes 1985</u> published by Data Systems Section, Water Quality Branch, Environment Canada, Ottawa KIA 0E7.
- (2) NAQUADAT = National Water Quality Data Bank
- (3) ICAP = Inductively Coupled Argon Plasma Spectroscopy

APPENDIX B

LABORATORY COMPARISON RESULTS

Duplicate samples from three CANSAP (Canadian Network for Sampling Precipitation) Stations, Vancouver Airport (YVR), Port Hardy (YZT) and Terrace (YXT) were analyzed at the Canada Centre for Inland Waters laboratory and the Inland Waters Directorate laboratory in North Vancouver. The following pages give comparison results. Units are mg/L except pH. A minus sign (-) indicates values below the detectable limit.

STN=YVR						
OBS	DATE	LAB	PH	S04	N03	CA
1	8310	NVAN	4.32000	2.30000	2.06000	0.330000
2	8310	CCIW	4.30000	2.29000	1.73000	0.330000
3	8311	NVAN	4.66000	0.60000	0.74000	0.120000
4	8311	CCIW	4.80000	0.79000	0.44000	0.100000
5	8402	NVAN	4.73000	0.90000	0.89000	0.170000
6	8402	CCIW	4.72000	1.26000	0.80000	0.190000
7	8404	NVAN	4,46000	2.60000	2.01600	0.510000
8	8404	CCIW	4,44000	2.31000	1.99000	0.500000
9	8406	NVAN	4.34000	2.40000	1.70600	0.550000
10	8406	CCIW	4.38000	2.51000	1.68000	0.560000
OBS		NH4	KG	NA	CL	K
1	0.	150000 -	0.040000	0.30000	0.80000	-0.20000
2	0.	070000	0.050000	0.31000	0.57000	0.07000
3	0.	060000	0.070000	0.80000	1.20000	-0.20000
4	0.	020000	0.050000	0.41000	0,89000	0.04000
5	0.	157000	0.075000	0.60000 -	1.70000	-0.20000
6	. 0,	131000	0.070000	0.59000	1.09000	0,11000
7	0.	237000	0.130000	1,10000	2.00000	0.20000
8	0.	215000	0.140000	1.08000	1,90000	0.26000
9	0.	164000	0.030000	0.40000	0,40000	-0.20000
10	0.	152000	0.040000	0.19000	0.54000	0.08000

 			CTN-	VVT			
				1.1			
OBS	DATE	LAB	PH	S04	N03	CA	
11	8310	NVAN	5.31000	-0.20000	0.030000	0.060000	
12	8310	CCIW	5.30000	0.46000	-0.010000	-0.050000	
13	8311	nvan	5.37000	-0.20000	-0.010000	0.100000	
14	8311	CCIW	5.30000	0.33000	-0.010000	0.130000	
15	8401	nvan	5.23000	-0.20000	0.022000	0.050000	
16	8401	CCIW	4.90000	0.27000		0.110000	
17	8402	NVAN	5.67000	0.20000	0.120000	0.080000	
18	8402	CCIW	5.20000	0.40000		0.130000	
19	8403	NVAN	5.10000	0.20000	0.146000	ı	
- 20	8403	CCIW	4.99000	0.48000	0.180000	0.06000	
21	8404	NVAN	5.09000	0.20000	0.244000	0.060000	
22	8404	CCIW	4.92000	0.59000	0.180000	0.050000	
23	8408	NVAN	4.70000	0.50000	0.315000	ı	
24	8408	CCIW	4.86000	0.81000	0.090000	0.040000	
OBS		NH4	NG	NA	CL	K	
11	-0.	010000	0.020000	-0.20000	0.30000	-0.20000	
12	0.	000000	0.020000	0.31000	0.32000	0.05000	
13	-0.	010000	0.020000	-0,20000	0.20000	-0.20000	
14	0.	010000	0.030000	0.15000	0.26000	0.05000	
15	-0.	003000	0.012000	0.20000	0.20000	-0.20000	
16	-0.	001000	0.200000	0,08000	0.21000	0.01000	
17	0.	027000	0.042000	0.20000	0.20000	-0.20000	
18			0.020000	0.15000	0.31000	0.02000	
19	0.	022000	1	-0.20000	-0.20000	-0.20000	
20	٥.	027000	0.010000	0.05000	0.14000	0.02000	
21	0.	031000	-0.010000	-0.20000	0.20000	-0.20000	
22	0.	026000	0.010000	0.12000	0.16000	0.04000	
23	0.	037000	•	-0,20000	2.20000	-0.20000	
24	0.	028000	0.020000	0.16000	0.26000	0.03000	

			STN=Y	ZT			
					•		
OBS	DATE	LAB	рн	· S04	ЮЗ	CA	
25	8311	NVAN	5.08000	0.60000	0.060000	0.130000	
26	8311	CCIW	5.10000	1.21000	-0.010000	0.160000	
27	8312	NVAN	4.93000	0.80000	0.240000	0.140000	
28	8312	CCIW	5.10000	1.42000	0.090000	0.380000	
29	8401	nvan	5.04000	-0.20000	0.151000	0.050000	
30	8401	CCIW	5,10000	0.79000	-0.040000	0.140000	
31	8402	NVAN	5.31000	0.30000	0.195000	0.120000	
32	8402	CCIW	5.40000	0.93000		0.160000	
33	8403	NVAN	5.10000	0.40000	0.301000	0.200000	
34	8403	CCIW	5.15000	0.91000	0.270000	0.160000	
35	8404	NVAN	4.89000	1.00000	0.195000	0.170000	
36	8404	CCIW	5.0000	1.46000	0.040000	0.180000	
37	8405	nvan	4.98000	0.40000	0.266000	0.240000	
38	8405	CCIW	4.82000	1.08000	0.180000	0.100000	
39	8407	NVAN	5.08000	0.30000	0.009000	0.070000	
40	8407	CCIW	4.92000	0.59000		0.050000	
41	8408	NVAN	4.66000	1.10000	0.089000	0.170000	
42	8408	CCIW	4.72000	1.41000		0.120000	
OBS		NH4	MG	NA	CL	K	
25	-0.0	10000	0.350000	3.20000	5.50000	0.20000	
26	0.0	00000	0.360000	3.17000	5.01000	0.12000	
27	0.0)90000	0.320000	2.70000	4.90000	-0.20000	
28	0.0	50000	0.340000	2.74000	6.17000	0.12000	
29	0.0	003000	0.130000	1.10000	2.10000	-0.20000	
30	-0.0	01000	0.130000	1.21000	2.23000	0.06000	
31	0.0	024000	0.180000	1.50000	2,80000	-0.20000	
32	0.0	03000	0.140000	1.17000	1.51000	0.03000	
33	0.0)13000	0.360000	1.10000	2.00000	-0.02000	
34	0.0	06000	0.140000	1.15000	2.10000	0.05000	
35	0.0	004000	0.200000	1.90000	3.40000	-0.20000	
36	0.0	00000	0.230000	2.02000	3.71000	0.09000	
37	0.0	197000	0.130000	0.80000	1.60000	-0.02000	
38	0.0)03000	0.110000	1.05000	1.65000	0.06000	
39	0.0	03000	0.040000	0.30000	0.50000	-0.20000	
40	0.0	06000	0.040000	0.32000	0.60000	0,03000	
41	0.0	003000	0.070000	0,60000	0.90000	-0.20000	
42	0.0	04000	0.060000	0,54000	0.94000	0.02000	

<u>The Effect of a Major Emitter on the Rain Chemistry of</u> <u>Southwestern British Columbia - A Preliminary Analysis</u>

D.A. Faulkner

Part I

Report No. PAES 87-1

Scientific Services Division Atmospheric Environment Service, Pacific Region Environment Canada Vancouver, Canada

April 1, 1987

		STN=Y	(UR		ويته فيله حمد ذكل بين عبد جمع جمع إيمار أيمو بلما جهد عالم المدر بمع رويد على وكار أيلم	الجمع بعدية بالجم مجمد محمة علمه الطلة اليوم مجمد معين محبود بالجم
		VIN	• • it			
DATE	LAB	РН	S04	NO3	CA	
8310	nvan	4.32000	2.30000	2.06000	0.330000	
8310	CCIW	4.30000	2.29000	1.73000	0.330000	
8311	nvan	4.66000	0.60000	0.74000	0.120000	
8311	CCIW	4.80000	0.79000	0.44000	0.100000	
8402	NVAN	4.73000	0.90000	0.87000	0.170000	
8402	CCIW	4.72000	1.26000	0.80000	0.190000	
8404	NVAN	4.46000	2.60000	2.01600	0.510000	
8404	CCIW	4.44000	2.31000	1,99000	0.500000	
8406	NVAN	4.34000	2.40000	1.70600	0.550000	
8406	CCIW	4.38000	2.51000	1.68000	0.560000	
	NH4	MG	NA	CL	К	
0.	150000	0.040000	0.30000	0.80000	-0.20000	
0.	070000	0.050000	0.31000	0.57000	0.07000	
0.	060000	0.070000	0.80000	1,20000	-0.20000	
0.	020000	0.050000	0.41000	0.89000	0.04000	
Ο.	157000	0.075000	0.60000 ¥	1.70000	-0.20000	
0.	131000	0.070000	0.59000	1.09000	0.11000	
0.	237000	0.130000	1,10000	2.00000	0.20000	
0.	215000	0.140000	1,08000	1.90000	0.26000	
0.	164000	0.030000	0.40000	0.40000	-0.20000	
0.	152000	0.040000	0.19000	0.54000	0.08000	
	DATE 8310 8310 8311 8402 8402 8404 8404 8404 8404 8406 8406 8406 8406	DATE LAB 8310 NVAN 8310 CCIW 8311 NVAN 8311 CCIW 8402 NVAN 8402 CCIW 8404 NVAN 8404 CCIW 8406 NVAN 8406 CCIW NH4 0.150000 0.070000 0.070000 0.060000 0.157000 0.131000 0.237000 0.215000 0.164000 0.152000	DATE LAB PH 8310 NVAN 4.32000 8310 CCIW 4.30000 8311 CCIW 4.30000 8311 NVAN 4.66000 8311 CCIW 4.80000 8402 NVAN 4.73000 8402 CCIW 4.72000 8402 CCIW 4.72000 8404 CCIW 4.44000 8404 CCIW 4.34000 8405 NVAN 4.34000 8406 CCIW 4.38000 NH4 MG 0.070000 0.150000 0.040000 0.070000 0.150000 0.050000 0.070000 0.020000 0.050000 0.070000 0.137000 0.070000 0.130000 0.131000 0.070000 0.130000 0.237000 0.130000 0.140000 0.164000 0.030000 0.152000	STN=YVR DATE LAB PH SO4 8310 NVAN 4.32000 2.30000 8310 CCIW 4.30000 2.29000 8311 CCIW 4.30000 2.29000 8311 NVAN 4.66000 0.60000 8402 NVAN 4.73000 0.90000 8402 CCIW 4.72000 1.26000 8402 CCIW 4.72000 1.26000 8404 NVAN 4.46000 2.31000 8404 CCIW 4.34000 2.31000 8406 NAN 4.34000 2.40000 8406 CCIW 4.38000 2.51000 NH4 MG NA 0.150000 0.070000 0.30000 0.020000 0.050000 0.41000 0.131000 0.075000 0.60000 0.131000 0.075000 0.59000 0.237000 0.130000 1.10000 0.152000 0.40000 0.40000	DATE LAB PH SO4 N03 8310 NVAN 4.32000 2.30000 2.06000 8310 CCIW 4.30000 2.29000 1.73000 8311 NVAN 4.66000 0.60000 0.74000 8311 CCIW 4.80000 0.79000 0.44000 8402 NVAN 4.73000 0.90000 0.89000 8402 NVAN 4.72000 1.26000 0.89000 8402 CCIW 4.72000 1.26000 2.01600 8402 CUWAN 4.4000 2.31000 1.99000 8404 NVAN 4.46000 2.40000 1.70600 8406 NVAN 4.34000 2.51000 1.68000 8406 CCIW 4.38000 2.51000 1.68000 0.150000 0.040000 0.30000 0.80000 1.2000 0.150000 0.050000 0.41000 0.89000 1.2000 0.150000 0.070000 0.59000 1.20000	DATE LAB PH S04 N03 CA 8310 NVAN 4.32000 2.30000 2.06000 0.330000 8310 CCIU 4.30000 2.27000 1.73000 0.330000 8311 NVAN 4.66000 0.60000 0.74000 0.120000 8311 NVAN 4.66000 0.79000 0.44000 0.100000 8402 NVAN 4.73000 0.90000 0.89000 0.170000 8402 CCIW 4.72000 1.26000 2.01600 0.510000 8404 CCIW 4.72000 1.26000 2.01600 0.50000 8404 CCIW 4.44000 2.31000 1.79900 0.50000 8405 NVAN 4.34000 2.51000 1.68000 0.550000 8405 CCIW 4.38000 2.51000 1.68000 -0.20000 8406 CCIW 4.38000 0.31000 0.57000 0.07000 0.150000 0.050000 0.30000 1

				C7N	VVT			
					1/1			
	OBS	DATE	LAB	РН	S04	N03	CA	
	11	8310	nvan	5.31000	-0.20000	0.030000	0.060000	
	12	8310	CCIW	5.30000	0.46000	-0.010000	-0.050000	
	13	8311	nvan	5.37000	-0,20000	-0.010000	0.100000	
	14	8311	CCIW	5.30000	0.33000	-0.010000	0.130000	
	15	8401	nvan	5.23000	-0.20000	0.022000	0.050000	
	16	8401	CCIW	4.90000	0.27000		0.110000	
	17	8402	nvan	5.67000	0.20000	0.120000	0.080000	
	18	8402	CCIW	5,20000	0.40000		0.130000	
	19	8403	NVAN	5.10000	0.20000	0.146000	4	
	20	8403	CCIW	4.99000	0,48000	0.180000	0.060000	
	21	8404	NVAN	5.09000	0.20000	0.244000	0.060000	
	22	8404	CCIW	4.92000	0,59000	0.180000	0.050000	
	23	8408	NVAN	4.70000	0.50000	0.315000	t	
	24	8408	CCIW	4.86000	0.81000	0.090000	0.040000	
	OBS		NH4	KG	NA	CL	K	
	11	_0 0	10000	0.00000	-0 20000	6 70000	0.0000	
	10	-0.0	10000	0.020000 0 020000	-0.20000	0,30000	-U.20000 A ASAAA	
/	12	0,0 	100000	0,020000 0 030000	-0 20000	0.32000	0,00000	
	10		10000	0.020000	-0.20000 A 150AA	0.20000	-0,20000 0 05000	
	17		07000	0,000000	0.13000	0,20000	0,0000	
	15	u.u _0 0	01000	0.012000	0.20000	0.20000	-U.20000 A A1AAA	
	10	0.0	01000	0,200000	0.00000	0.21000	0,01000	
	17	U , U	2/000	0,042000 A aganaa	0.20000 0 15000	0.20000	-U.20000 0 05000	
	10	, , ,	22000	0.020000	0.13000	0.01000	0.02000	
	20	0.0	27000	, a atagaa	0.20000	-0.20000 0 1A000	-0.20000	
	21	ט ט טיט	21000	-0.010000	0,0000 00000 0-	0,17000	U,UZUUU _0 20000	
	22	0.0 A A	26000	0.010000	0.20000	0.20000	0,20000 0 0A000	
	22	0 N	77000	0,010000	-0 20000	3 30000	-0.0000	
	23 24	υ.υ Λ Λ	28000	0,02000	-0,20000 0 12000	C.20000 A 32AAA	-0.20000 A A7AAA	
	£-7	0.0	20000	0,020000	h'TOAAA	0.20000	0,00000	

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COMPARISON OF LABORATORY ANALYSES NVAN = IWD LABORATORY, NORTH VANCOUVER CCIW = CCIW LABORATORY, BURLINGTON, ONTARIO

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			STN='	(ZT	ري وها بعد الله من هيد الله عنه الله عنه الله الله الله الله الله الله الله ال	ه مخلك فينت يكتر شاط مخل بخل يتنزه بتنت المد بابت سية يزما وكت أثن أنت أبتل الم ال	ه جون وزن وهم دون مرد مرد من وهم من وه من وهم من وهم مرد مرد مرد مرد مرد مرد مرد
OBS	DATE	LAB	PH	S04	NO3	CA	
25	8311	NVAN	5,08000	0.50000	0.060000	0.130000	
26	8311	CCIW	5.10000	1.21000	-0.010000	0.160000	
27	8312	NVAN	4.93000	0.80000	0.240000	0 140000	
28	8312	CCIW	5.10000	1.42000	0.090000	0.380000	
29	8401	NVAN	5.04000	-0.20000	0.151000	0.050000	
30	8401	CCIW	5.10000	0.79000	-0.040000	0.140000	
31	8402	NVAN	5.31000	0.30000	0.195000	0.120000	
32	8402	CCI₩	5.40000	0.93000		0.160000	
33	8403	NVAN	5.10000	0.40000	0.301000	0.200000	
34	8403	CCIW	5.15000	0.91000	0.270000	0.160000	
35	8404	nvan	4.89000	1.00000	0.195000	0.170000	
36	8404	CCIW	5.00000	1.46000	0.040000	0.180000	
37	8405	NVAN	4.98000	0.40000	0.266000	0.240000	
38	8405	CCIW	4.82000	1.08000	0.180000	0.100000	
39	8407	NVAN	5.08000	0.30000	0.009000	0.070000	
40	8407	CCIW	4.92000	0.59000		0.050000	
41	8408	NVAN	4.66000	1.10000	0.089000	0.170000	
42	8408	CCIW	4.72000	1.41000	,	0.120000	
OBS		NH4	MG	NA	CL	K	
25	-0.	010000	0.350000	3.20000	5.50000	0.20000	
26	0.	000000	0.360000	3.17000	5.01000	0.12000	
27	0.	090000	0.320000	2.70000	4.90000	-0.20000	
28	0.	050000	0.340000	2.74000	6.17000	0.12000	
29	0,	003000	0.130000	1,10000	2,10000	-0.20000	
30	-0.	001000	0.130000	1.21000	2.23000	0.06000	
31	υ.	024000	0.180000	1.50000	2.80000	-0.20000	
32	U.	003000	0.140000	1,17000	1.51000	0.03000	
33	V,	013000	0.360000	1.10000	2.00000	-0.02000	
54 75	υ.	006000	U.14UUUU	1.15000	2.10000	0.05000	
30	υ.	004000	0.200000	1.90000	3.40000	-0.20000	
35 70	U. 0	006000	0.230000	2.02000	3.71000	0.09000	
57	V.	07/000	0.130000	0.80000	1.60000	-0.02000	
<u>ა</u> ყ	υ.	003000	0.110000	1.03000	1.65000	U.U6UUU	
39	υ.	003000	U.U40000	U.30000	0.50000	-0.20000	
40	Ο.	005000	0.040000	9.32000	0.60000	0.03000	
41	υ.	000000	0.0/000	U.6UUUU	0.90000	-0.20000	
42	U,	004000	0,060000	0.54000	U.Y4000	V.V2000	