SENES CONSULTANTS LIMITED

Specialists in Energy, Nuclear and Environmental Sciences

ACIDIC DEPOSITION IN SOUTHWESTERN

BRITISH COLUMBIA

Prepared for: Wayne

Atmospheric Environment Service

Pacific Region

Environment Canada

Vancouver, B.C.

Prepared by:

SENES Consultants Limited

301 - 675 West Hastings Street

Vancouver, B.C.

V6B 1N2

May 1992

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1.0 INTRODUCTION

In 1991, the Atmospheric Environment Service (AES) of Environment Canada contracted with SENES Consultants Limited to undertake a study of acidic deposition in southwestern British Columbia and northwestern Washington. The overall objectives of the study were to:

- Incorporate field measurements from southern BC and Washington State into a quantitative assessment of acidic deposition;

- Determine any relationships between noted BC precipitation monitoring "episodes" and sources/events in Puget Sound (specifically any which relate to the ASARCO site in Tacoma, Washington); and

- Determine the relative importance of transboundary flow (and any seasonal variations) of pollutants to the Lower Mainland area.

The following report is not meant to provide a definitive assessment with respect to these objectives. Rather, the results presented represent a limited evaluation of the existing database within the budget constraints of the project.

Sources of the two main precursors of acid rain, sulphur dioxide (SO_2) and oxides of nitrogen (NO_x), in the region of interest are centred mainly in the Vancouver-Bellingham and the Seattle-Tacoma areas. These include petroleum refineries, pulp mills, automobiles and various industrial installations. Until its closure on March 24, 1985, the ASARCO copper smelter in Tacoma was one of the largest sources of SO_2 in the region with annual emissions ranging from 49611 to 81946 tonnes in the years 1979-1984, accounting for up to 45 percent of the SO_2 emissions of western Washington in 1984 (Duncan, 1985). The ASARCO smelter was also a significant source of arsenic (As). Crecelius *et al.*, (1974) reported that the smelter emitted approximately 300 t/y of particulate matter (TSP) of which 30-40 percent was As. Average annual total suspended particulate (TSP) emissions over the period 1979-84 were about 231 t/y. Other major constituents of the ASARCO particulate emissions included lead (Pb) at 20-30 percent, antimony

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(Sb) at 2 percent, and smaller amounts of zinc (Zn), mercury (Hg), copper (Cu) and other trace metals.

Since the smelter was the main source of As in the region, this element was a possible tracer of opportunity for evaluating the relative importance of transboundary transport of pollutant emissions. This report examines data collected by the AES over the period October 1984 to December 1986 by a network of volunteers from Bamfield on the west coast of Vancouver Island to Agassiz in the eastern Fraser Valley. In particular, the influence of the ASARCO smelter is examined.

As will be seen later, the Straits of Georgia and Juan de Fuca, and Puget Sound are an inter-connected system of valleys which determine, in large part, the meteorology of the region. Most particularly, the topographic orientation of Puget Sound-Strait of Georgia region has a profound influence on the low-level air flows with the result that these flows tend to have a southeast-northwest orientation.

Since the main pollutant sources are situated along the axis of Puget Sound-Strait of Georgia and given the local meteorology, it is likely that a reversing north to south flow of pollutants occurs in the region. However, the magnitudes of the cross-border fluxes are unknown and the determination of these quantities has been the object of several past and ongoing acid precipitation studies in B.C. and Washington State.

In this study, summary statistics are used to quantify rainwater chemistry as it relates to geographic location of sampling sites. The location of the sampling sites for this and previous studies are given in Figure D.1. This figure, located in Appendix D, is in foldout format so that it may be used throughout the report. For a limited high impact area (near the Strait of Georgia) mean concentrations of As in precipitation are calculated for a number of rainfall events. In addition, a few high As concentration events are described in terms of the synoptic meteorological situation. Assessment of transboundary contributions to SO_4 and NO_3 concentrations in rainwater were conducted for the Ladner sampling site.

2.0 PREVIOUS STUDIES

Nikleva (1985) reported on the first attempt to measure the concentration of pollutants in precipitation in southwestern BC. Using data from a monitoring network extending from Bamfield to Agassiz for the year 1983, he observed that excess sulphate[1] (XSO_4) concentrations ranged from about 0.2 mg/l at Bamfield (which he considered "background") to 0.9 mg/l in the Vancouver area. The XSO_4 concentration decreased eastward through the Fraser Valley and the influence of urban sources was clearly evident. However, Nikleva observed a similar pattern of As concentrations, and since the ASARCO smelter was the main source of As, it was suggested that the elevated levels of As and XSO_4 could be attributed, in part, to emissions from the smelter. Nikleva also observed a Seattle-Vancouver gradient of As and XSO_4 concentrations, consistent with the above conclusion. He was, however, unable to assess the relative importance of the local (BC) and Puget Sound emissions. The field observations continued during 1984-86 with an expanded and upgraded network.

In a study of data from the later network, Faulkner (1987), compared average concentrations of As and XSO_4 before and after the closure of the ASARCO smelter. He found a significant decrease in As concentrations after the closure at stations near the Strait of Georgia but no change at stations on the west coast of Vancouver Island. He observed a similar, although less significant, pattern of decreases in XSO_4. Although Faulkner attributed the decreases to the closure, he was unable to estimate the relative importance of the local and distant sources.

The effects of the ASARCO smelter on precipitation chemistry of the Seattle region were clearly shown in a study of a single storm event by Larson et al., (1975). High depositions of SO_4 and As to about 60 km downwind (north-northeast) of the plant were measured.

Vong et al. (1985) reported on one year of monitoring data collected at 4 monitoring sites in Washington State during the period February 1982 to February 1983. Multiple correlations

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[1] Excess sulphate is that portion of the sulphate ion concentration not of sea salt origin. In coastal regions, the sea salt influence is very marked and sulphate concentrations must be adjusted in order to observe the effects of anthropogenic and other natural (eg., volcanic) sources. For this study, the sulphate concentration is reduced by 0.253 of the sodium ion concentration to obtain the excess sulphate.

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among measured species were grouped into five categories which were interpreted to be indicative of the influence of sea salt, metals from the ASARCO smelter, an urban factor, soil, and acidic sulphate aerosol. Applying a simple washout model, Vong, et al. predicted that the copper smelter was the major contributor to the budget of rainwater sulphate in the Seattle region.

According to Vong et al. (1986a), the trace metal fingerprint for ASARCO smelter emissions consisted of As, Sb, Pb, Cu, and Fe. In his analysis of 14 storm events before and after closure of the smelter during the months of February-March 1985 and 1986, Vong et al. also listed Mn, Al, Ca, Ti, V and NO_3 concentrations as being indicative of a crustal component in rainwater samples, and the presence of Na, Cl and Mg as representative of saltwater contributions.

Maykut et al. (1985), developed a meso-scale, stochastic deposition prediction model which they applied to Washington State. (BC emissions were included in the study but predicted depositions ended at the Canada-USA border.) The effect of the ASARCO smelter was clearly evident in the modelled XSO_4 depositions for the year 1984. The model predicted a small area of deposition exceeding 20 kg/ha/y downwind (northeast) of the smelter. The predicted deposition for 1989, based on the elimination of the smelter and other minor reductions, showed a decrease of close to 70 percent. While the study also indicated a decrease in deposition near the Canada-USA border, these were indicated to be mainly in the eastern Fraser Valley with almost no change at Vancouver. (Wind directions in the study were based on pilot balloon measurements of winds at 500 m at the Seattle-Tacoma airport. Such measurements are likely to be biased toward southwesterly flows with the result that predicted depositions would be further east than anticipated.)

Pennell et al. (1985) proposed a conceptual model of wet deposition of pollutants for the Puget Sound region. They suggested a two-phase process - a Transient Purge stage and a Quasi-steady Continuous phase. They suggested that pollutants emitted during a dry spell react to form aerosols. The reactions are aided by oxidants which tend to form locally during the dry spells. These aerosols are wet-scavenged efficiently during the early stages of an ensuing period of rain, and if precipitation continued for a sufficiently long time, all or most of these pollutants could be deposited within a short distance of the source. After wet scavenging, further pollutant

emissions may be ingested into the cloud, then residence times increase and deposition will occur further downwind. Although the rate of deposition may be less in the latter phase, the deposition may continue for a longer period of time, and hence total deposition may become significant. Pennell et al. (1985) suggested that the transient stage would apply only in the Puget Sound region; deposition beyond that would be by the quasi-steady state process. It is not clear from the proposed model how far downwind the transient purge process might be effective. It is conceivable that aerosols produced in the Puget Sound region could be advected to the southern Strait of Georgia by strengthening southerly winds ahead of a Pacific low or trough and be scavenged in the Vancouver region.

Vong et al. (1985) also reported on precipitation quality monitoring conducted at Lake Ozette and Cheeka Peak on the Olympic Peninsula during short periods in the spring of 1984 and 1985. A primary purpose of the monitoring program was to assess the viability of using these remote sites to characterize "background" concentrations of SO_4, NO_3 and trace metals. Simultaneous measurements of sub-micron aerosols were collected with rainwater samples.

Table 2.1 lists the mean ion concentrations reported for the various monitoring programs conducted in these previous studies. As will be seen from the data, there was a clearly defined gradient in the As concentrations away from the smelter in the 1982-83 data reported by Vong, et al. (1985), with the highest average concentrations at 0.0032 mg/L in the West Seattle area, and decreasing concentrations northwards through Maple Leaf (0.0022 mg/L), Tolt River (0.0012 mg/L), and Bellingham (0.0006 mg/L). These results were in reasonably good agreement with the single event study reported by Larson et al. (1975) for one rainfall event in November 1973. The Carkeek Park concentration of 0.0044 mg/L is close to the 0.0032 mg/L average concentration observed ten years later in West Seattle.

The continuation of this gradient is confirmed by the average 1983 concentrations of As reported by MacLaren (1985) for the B.C. network which ranged from as low as 0.00008 mg/L at Bamfield to as high as 0.00043 mg/L at Saltspring Island. All of the sites in B.C. had As levels below the average 1982-83 level recorded at Bellingham of 0.0006 mg/L.

Table 2.1
MEAN ION CONCENTRATIONS FOR SELECTED SITES IN B.C. AND WASHINGTON FROM SELECTED STUDIES

	MEAN ION CONCENTRATION (mg/L)[1]								
	Na	SO_4	XSO_4	Cl	K	Ca	$N\text{-}NO_3$[2]	$N\text{-}NH_4$[2]	REFERENCES
Nov. '73 - Single Event									Larson, *et al.*, 1975
Neill Point, WA	0.250	1.300	NDR[3]	1.300	0.220	0.270	0.108	NDR	
Carkeek Park, WA	1.150	2.800	NDR	4.450	0.400	0.670	NDR	NDR	
Everett, WA	1.350	2.100	NDR	-	1.200	0.700	NDR	NDR	
Feb. '82 - Feb. '83									Vong, *et al.*, 1985
West Seattle, WA	0.026	0.142	0.133	0.059	0.003	0.013	0.010	0.006	
Maple Leaf, WA	0.022	0.134	0.127	0.044	0.003	0.010	0.012	0.009	
Tolt River, WA	0.022	0.082	0.076	0.041	0.003	0.005	0.010	0.005	
Bellingham, WA	0.023	0.089	0.082	0.041	0.003	0.005	0.011	0.008	
1983									McLaren, 1985
Bamfield, B.C.	1.780	0.420	0.153	3.310	0.100	0.090	0.030	0.012	
Ladner, B.C.	0.640	0.700	0.534	1.180	0.100	0.070	0.141	0.180	
Vancouver (A), B.C.	0.570	1.060	0.918	1.040	0.100	0.261	0.164	0.164	
Abbotsford, B.C.	0.190	0.340	0.295	0.350	0.100	0.040	0.086	0.681	
Agassiz, B.C.	0.190	0.280	0.229	0.360	0.100	0.030	0.083	0.314	
1984 - Apr./May Lake Ozette, WA	1.813	0.732	0.279	3.486	0.117	0.759	0.035		Vong, 1985
1985 - Apr.May									Vong, 1985
Lake Ozette, WA			0.307	3.870			0.037	0.037	
Cheeka Peak, WA			0.430	2.940			0.076	0.026	

Notes:
1. All data as reported in original reference except where converted to standard units.
2. Converted from NO_3 and NH_4 to $N\text{-}NO_3$ and $N\text{-}NH_4$.
3. NDR - no data reported.

Table 2.1 (continued)

HISTORICAL MEAN ION CONCENTRATIONS FOR SELECTED SITES IN B.C. AND WASHINGTON

	Pb	As	Cu	Zn	Cd	Fe	Mn	REFERENCES
MEAN ION CONCENTRATION (mg/L)								
Nov. '73 - Single Event								Larson, *et al.*, 1975
Neill Point, WA		0.0023	0.029	0.036	0.0015			
Carkeek Park, WA		0.0044	0.015	0.095	0.0010			
Everett, WA		0.0025	0.045	0.600	0.0060			
Feb. '82 - Feb. '83								Vong, *et al.*, 1985
West Seattle, WA	0.0035	0.0032	0.0045	0.0056	0.0003			
Maple Leaf, WA	0.0050	0.0022	0.0051	0.0046	0.0004			
Tolt River, WA	0.0018	0.0012	0.0019	0.0018	0.0009			
Bellingham, WA	0.0015	0.0006	0.0021	0.0051	0.0001			
1983								McLaren, 1985
Bamfield, B.C.	0.001	0.00008	0.002	0.001	0.0003	0.014	0.002	
Ladner, B.C.	0.003	0.00028	0.002	0.003	0.0002	0.014	0.001	
Vancouver (A), B.C.	0.009	0.00038	0.004	0.005	0.0003	0.023	0.002	
Abbotsford, B.C.	0.002	0.00021	0.002	0.003	0.0002	0.027	0.002	
Agassiz, B.C.	0.002	0.00010	0.001	0.001	0.0002	0.012	0.001	
1984 - Apr./May								Vong, 1985
Lake Ozette, WA	0.00015	NDR	0.00014	0.099	0.00012	0.0098	0.00049	
1985 - Apr.May								Vong, 1985
Lake Ozette, WA	0.00017	NDR	0.00011	0.075	0.000012	0.0094	0.00045	
Cheeka Peak, WA	0.00050	NDR	0.00012	0.057	0.000008	0.0479	0.00138	

It is worth noting that none of the other trace metal species showed similar gradients in concentration. For Washington State, the highest lead concentrations in 1982-83 were at the Maple Leaf site north of the Seattle city centre. Copper concentrations were also highest at this site, while zinc concentrations were highest in West Seattle. Cadmium concentrations were highest at the Tolt River site. All monitoring sites in the state had significantly elevated concentrations of trace metals over "background" levels recorded at Lake Ozette and Cheeka Peak. The oxide of arsenic is one of the few that is relatively soluble in water (clouds, precipitation, etc.). This means that it could be transported long distances while the other oxides, being relatively insoluble, would exist as particles and would deposit more quickly. Seinfeld (1986) suggests, however, that As is largely particulate so that some atmospheric oxidation mechanism would be needed. As_2O_3 is a 'soluble' particulate!   x

Comparisons for the other constituents measured in previous studies is somewhat more difficult. The average concentrations of sodium (Na), chloride (Cl), potassium (K), calcium (Ca) ammonium (NH_4) and nitrates (NO_3) recorded at Bamfield in 1983 were similar to concentrations reported for the "background" data at Lake Ozette in 1984. However, Bamfield reported significantly lower concentrations of total and excess SO_4 than those recorded at Lake Ozette. Both Abbotsford and Agassiz reported lower total SO_4 levels than Lake Ozette or Bamfield but higher excess SO_4 levels, indicating the declining influence of sea salt on sulphate concentrations with distance from the coast and the increasing influence of anthropogenic sources of sulphate. Nitrate concentrations were also higher at Abbotsford and Agassiz than at the "background" sites, but lower than at Ladner and Vancouver Airport. The Abbotsford and Agassiz sites had higher ammonium levels reflecting the influence of agricultural activities in these rural areas.

3.0 TOPOGRAPHY AND METEOROLOGY OF THE SOUTHWESTERN B.C. AND THE PUGET SOUND AREA

The local meteorology of northwestern Washington and southwestern BC is profoundly influenced by the topography of the region[1]. The Strait of Georgia, Puget Sound and the Chehalis gap form a semi-circular trough. The Strait of Juan de Fuca is a westward offshoot of this trough dividing the mountains of Vancouver Island and the Olympic Mountains. The relatively low land around Puget Sound forms a wide valley surrounded by peaks to over 2400 m in the Olympics and to over 3000 m in the Cascade Range east of the Sound. The Strait of Georgia, about 30 km wide, is narrower and is surrounded by relatively steep slopes and gradually narrows to its northern entrance. The terrain thus constricts flows from the southeast.

Most of the precipitation of the region is frontal in origin but is increased by upslope flow on the windward side of the mountains. Southwesterly upper flows that usually accompany precipitation events (see page 4-4) give rise to heavy precipitation on the west coast of Vancouver Island and on the western slopes of the Coast and Cascade ranges. A rain shadow in the Gulf Islands-San Juan Islands region lies downslope east of the Olympics.

Low-level flows are also strongly influenced by the terrain. In Georgia Strait, winds tend to blow either from the southeast or the northwest (Faulkner, 1982). In the Puget Sound area, winds tend to be southerly or northerly. In the Chehalis gap (southwest of Seattle), winds are generally southwest or northeast. In the Strait of Juan de Fuca, winds tend to be westerly with high pressure to the west, and easterly with high pressure to the east.

A synoptic-scale gradient with a strong southerly component tends to produce southwest winds through the Chehalis gap, southerly winds in Puget Sound and southeasterly winds in the Strait of Georgia, and easterly winds in Juan de Fuca Strait. As the gradient becomes more westerly or northwesterly, the low-level flow tends to reverse, although Schoenberg (1983) has indicated that southerly winds extend up to the southern part of the Strait of Georgia even with a westerly

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[1]   See map D.1 in Appendix D which can be folded out.

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gradient flow. As Danard (1973) has shown, the flow in Juan de Fuca reverses (i.e. becomes 'westerly') when the 850 mb wind direction veers from south to southwest.

In a study of surface winds from 6 February to 6 March, 1980, Schoenberg (1983) classified low-level flows of the Puget Sound-Georgia Basin based on the 850 mb wind direction at Quillayute, WA. She showed that with southwesterly winds at 850 mb, the low-level flow followed the valley northward in Puget Sound and then northwestward through the Strait of Georgia. Even with westerly winds at 850 mb, the low-level flow was southerly to near the Canada-USA border. Schoenberg developed 11 classifications that are functions of the 850 mb wind direction.

Faulkner (1984) analyzed 850 mb air parcel trajectories for four stations in BC. He found that the mean track of air parcels reaching Vancouver in precipitation cases was over the Olympic Peninsula from the Pacific. At other sites, it was almost directly from the west. This, together with Schoenberg's findings, strongly suggests that low-level flows in Puget Sound and the southern Strait of Georgia are southerly when precipitation falls at Vancouver. This contention is supported by the fact that PIBAL data at 460 metres above ground in the Seattle - Tacoma area have been shown to have a combined frequency of occurrence of over 70% for south, south-southwest and southwesterly wind directions on days with rain (Vong, 1982). This fact is significant in assessing the relative importance of emission sources in the Puget Sound and Strait of Georgia areas to acid rainfall in southern British Columbia.

4.0 EMISSIONS DATA AND RAIN WATER CHEMISTRY MONITORING PROGRAM

The data used in this study consist of observations of concentrations in rainwater of several ions and metals obtained for specific rainfall events at the various monitoring sites during the period 9 October 1984 through 6 February 1986. In addition, airflow back trajectories from Ladner and forward trajectories from the ASARCO smelter at 925 mb and 850 mb for 48 hours were obtained from the AES for some of the rainfall events with high As concentrations. Emissions data is limited and of variable quality. The quantity of information available far exceeded the limited budget available for the analysis. Both the quantity and quality of the available data had to be considered in deciding upon a suitable conceptual approach for the analysis and statistics to be generated.

4.1 PRECIPITATION COLLECTION AND CHEMICAL ANALYSIS

The AES conducted precipitation sampling with a volunteer network extending from Bamfield on the west coast of Vancouver Island to Agassiz in the Fraser Valley during 1982. Originally, the chemical analysis was performed at a local laboratory. Beginning in October 1984, the network was expanded and the chemical analysis was carried out by the Canada Centre for Inland Waters (CCIW), Environment Canada, Burlington, Ontario. When samples were sufficiently large, the CCIW laboratory divided the samples for two analyses; the main ions (pH, SO_4, NO_3, Cl, NH_4, Ca, Mg, Na, and K) and trace metals (Ca, Mg, Na, K, Ba, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, Sr, V, Zn, As, and Se). Where insufficient sample was available, only the main ions were analyzed.

4.1.1 Sampling Site Locations and Collection Procedure

The locations of the stations where samples were obtained are listed in Table 4.1 and are depicted in Figure D.1. Volunteers collected rain samples in clean, plastic bottles and funnels supplied by AES. When rain was forecast, the coordinator at AES Pacific Region Headquarters in Vancouver, contacted the volunteers to set out the collectors. At the conclusion of an "event",

Table 4.1

PRECIPITATION MONITORING SITES

STATION	IDENTIFIER	LATITUDE	LONGITUDE	ELEVATION (m)
Abbotsford	ABB	49 02	122 22	58
Agassiz	AGA	49 15	121 46	15
Bamfield	BAM	48 50	125 07	10
Cloverdale	CLO	49 07	122 45	20
Ladner	LAD	49 06	123 04	2
Pender Island	PEN	48 48	123 17	5
Port Renfrew	REN	48 33	124 24	10
Saanichton	SAN	48 37	123 25	61
Saltspring	SSI	48 50	123 29	120
Sooke	SOO	48 22	123 44	27
Texada Island	TEX	49 42	124 31	97
Vancouver (A)	VAN	49 11	123 10	3
Wilson Creek	WIL	49 26	123 41	30

usually 1-3 days in length, the coordinator again contacted the volunteers to close the collectors[1]. The bottles were mailed to Vancouver where they were kept in a refrigerator, then shipped to Burlington for analysis. Details of the equipment used and the handling methods are described in MacLaren (1985).

A different method of collection was employed at Vancouver Airport. There, AES meteorological technicians were instructed to collect samples whenever rain commenced. From January 25, 1985, samples were collected with a CAPMoN (Canadian Air and Precipitation Monitoring Network) sampler. *Daily samples over 24 hours* were collected using the CAPMoN protocol as described in the CAPMoN Technical Manual(AES, 1984). As a result, the data set for Vancouver (A) contains many more "events" than any of the other sites. The sample collection procedure for this program is arguably superior to the other sites which had volunteer collection. Since most of the Vancouver Airport samples were 24-hour samples, it was necessary to combine them for the period of the rain event. This was done by calculating a sample-amount weighted mean of the ion concentrations.

4.1.2   Collection and Laboratory Quality Control Procedures

The AES event coordinator checked each sample visually and noted those with obvious contamination (bugs, dust, etc.). For this study, all such sample data were rejected. As well, an ion check following the method described by Lau (1982) was applied to each sample analysis. If the ratio of positive to negative ions was outside of the range of 0.5 to 2.0, the observation was discarded. Exceptions to this were samples collected at Agassiz and Abbotsford Airport where the ratio was often outside of the range. At both of these stations, ammonium concentration was frequently high and it is believed that those cations were balanced by unknown anions of agricultural origin.

As a quality control procedure, the AES coordinator randomly forwarded two samples for the

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[1]   In this respect, precipitation values reported in the database represent total precipitation "catch" over periods of 1-3 days. In some cases, the collectors overflowed during the event and the total precipitation value reported in the database is therefore not an accurate estimate of precipitation amount and cannot be used to estimate deposition.

same event to the CCIW laboratory. If the ion check revealed both of the samples were acceptable, one was discarded. The decision of which are to discard was made by flipping a coin.

4.1.3   Quality Review of Database

Review of the extent and quality of the data base are described in Appendix A. There are contiguous time periods in the data set which show anomalous concentrations for several trace metals which are not readily explainable by physical processes. It is not clear whether these arise from changes in analytical procedure, database compilation or procedures for handling below minimum detectable limit (MDL) concentrations. Errors arising from reversing of concentrations of analytes are apparent from statistical analysis. In addition, some errors are evident when comparing major ion test concentrations to trace metal concentrations for a number of analytes measured in both tests. Overall the data appears to be of sufficient quality for the exploratory analyses of this study. The information presently available from this dataset has many intriguing aspects some of which are outlined in Chapters 6 and 7 of this report. However, the improvement in understanding of the emission and transport of pollutants in this region could be substantially improved with a thorough screening of the database.

4.2   EMISSIONS DATA

With respect to anthropogenic emissions, a complete inventory of emission sources was not available. However, several authors have estimated emissions in the area in previous studies. Development of an emissions database for the region would substantially enhance the understanding of atmospheric processes.

4.2.1   Sulphate Emissions

Vong *et al.* (1986b) reported that the two major sources of SO_2 emission in western Washington State were the ASARCO copper smelter (4 kg SO_2/sec) and a coal-fired power plant located near Centralia, WA (1.7 kg SO_2/sec). According to Duncan (1985), these two sources accounted for

about 45% of the SO$_2$ emitted in western Washington during 1983-84. The remaining 55% of the SO$_2$ emissions were due primarily to point sources such as pulp mills and industrial fuel combustion, as well as non-point sources. The Puget Sound Air Pollution Control Agency (PSAPCA) has reported SO$_2$ emissions from ASARCO at 70,295 tons (63,772 tonnes) in 1984, for an average of 2.0 kg SO$_2$/sec. The Centralia power plant was estimated to emit 59,000 tons SO$_2$ in 1981 (53,525 tonnes/year). The remaining 55% (160,557 tonnes/year) would be attributable to other sources in southwestern Washington and Puget Sound for a total emission rate of 262,954 tonnes per year in the region (excluding Mount St. Helens). By comparison, the estimated average annual SO$_2$ emission rate for the Greater Vancouver Regional District in 1985 was 12,252 tonnes (Levelton/Concord, 1989), less than 5% of the total emissions in western Washington. The bulk of GVRD emissions (i.e. 70%) were due to petroleum refineries and cement manufacturers located in Port Moody, Delta and Burnaby.

4.2.2 ASARCO Emissions Data

Stack monitoring data for arsenic concentrations in stack exhaust at ASARCO were obtained from PSAPCA. Most of the monitoring data seems to have been erased from the PSAPCA database files, and the remaining data records only cover the period from September 14, 1984 to February 21, 1985. The data do not include exhaust gas flow rates. Therefore, no estimate of total As emissions can be made although SO$_2$ daily emissions are reported. Table 4.2 lists the short period of overlapping As and SO$_2$ emission data in February, 1985. Taken as a whole, there is no correlation between As concentrations in stack emissions and total daily SO$_2$ emission rates. There are only 5 of 16 data points for which a reasonable linear correlation can be postulated (February 1, 2, 7, 12 and 13). This partially arises because the concentration need not necessarily be correlated with emissions. Additionally, the process stages at ASARCO may have been variable with respect to the emission of pollutants.

On an annual basis, the average ratio of particulate emissions to SO$_2$ emissions was 0.003 (i.e., 0.3% of SO$_2$ emissions). If, as reported by Crecelius (1974), arsenic was 30-40% of TSP emissions, a rough estimate of As emissions for the period of SO$_2$ emission data can be made. Though highly speculative, this would indicate a typical ratio of SO$_2$ to As in the order of about

Table 4.2

ASARCO STACK EMISSION MONITORING DATA
FEBRUARY, 1985

DATE (February)	AVERAGE As CONCENTRATION (ug/m^3)	TOTAL DAILY SO$_2$ (tons/day)
1	3.31	359.3
2	2.64	256.8
3	-	96.3
4	0.14	-
5	0.05	-
6	0.03	-
7	1.50	139.5
8	0.36	177.3
9	0.05	211.5
10	0.16	168.0
11	0.07	184.8
12	0.82	104.3
13	1.24	112.8
14	0.07	171.0
15	0.27	117.3
16	0.47	143.8
17	5.83	70.3
18	0.18	-
19	0.15	177.8
20	0.04	168.8
21	0.08	191.8

1000 to 1. Conversion from SO_2 to SO_4 gives an estimate of approximately 1500 to 1 for the ratio of SO_4 to As in ASARCO emissions. However the deposition process will be different for the two analytes. Arsenic, which is largely particulate (Seinfeld, 1986), would be expected to fall out sooner than SO_4.

According to Vong et al. (1986a), the trace metal fingerprint for ASARCO smelter emissions consisted of Sb, Pb, Cu and Fe, in addition to As. The largest of these, Pb, at 20 to 30% of particulate emissions has an emission rate slightly lower than As (Crecelius et al., 1974). However, other major sources of Pb are located in the region which would mask the emissions of ASARCO. The other elements are at much smaller emission rates and would be difficult to observe among the other sources in the area.

4.2.3 Other Emissions

As outlined in Figure 4.1, the Washington State Department of Ecology (1989) identifies the location of some major point sources of As in Cowlitz County in the extreme southwest portion of the state, but does not specifically identify the sources (Figure 4.1). Presumably, these sources are emissions from coal-fired utilities which make up the largest other source of As in the state. Other potential, more diffuse sources of As are in pesticides, herbicides, and fungicides, production of insecticides, herbicides and wood preservatives, sewage sludge incineration, forest and agricultural fires, as well as from industrial and residential wood combustion.

Other emission estimates for As and trace metals in Washington State are available from the WEDS data base compiled for the Washington State Department of Ecology (Radian, 1985). The emission estimates in WEDS are not measured emission rates. Rather, they are annual estimates based on published emission factors and production rates. In working with the database for the Washington State Department of Ecology, SENES has encountered discrepancies in the data which diminish its usefulness and raise doubts about its accuracy. The locations of major point sources for some trace metal species are identified in the Washington State Department of Ecology (1989) in an evaluation of public health risks. Those locations are depicted on Figure 4.1. The relative magnitudes of the emission sources could be obtained for future analyses.

FIGURE 4.1

Location of Emission Sources* of Some Trace Metals in Washington State
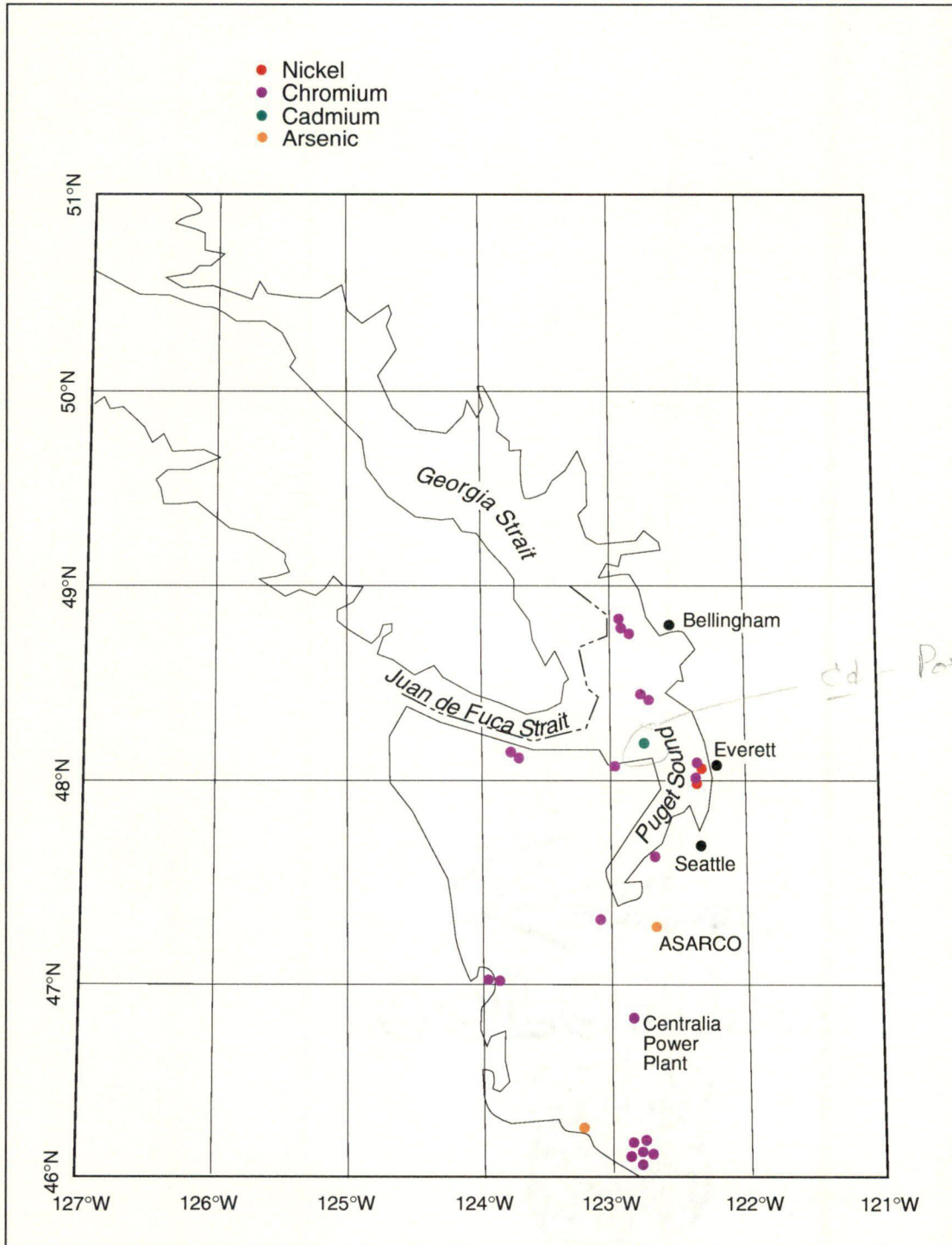
* Reference: Washington Environment 2010 (1989)
  (Sources not identified)

At present, there is no estimate of emission rates for trace metal species in British Columbia or the Greater Vancouver Regional District (GVRD). The 1985 GVRD emission inventory does not include trace metal species. An update to 1990 is in the process of being compiled for both the GVRD and the rest of B.C., and may contain trace metal data.

5.0   SUMMARY OF RAIN WATER CONCENTRATIONS

The concentration of a pollutant in rain water is affected by many factors. These can be classified into three major categories: variations in emission rates of the pollutant from multiple sources; dispersion and transformation of air pollutants; and, the scavenging of pollutants from the air mass during rainfall events.

In this particular study, only the concentrations in rain water samples are well known. The forward and back trajectory analyses calculated by the AES provide some information about variations in transport winds. There may also be some evidence of scavenging rates in the data for periods of consecutive day rainfall.

5.1   ASSOCIATIONS BETWEEN POLLUTANT CONCENTRATION AND SAMPLING SITES

Where a summarization of concentration that is indicative of the central tendency (i.e. a typical value) is required, the median has been calculated. The median is that value which has half the concentrations lower and half the concentrations higher. As such it is not influenced to as great an extent as the arithmetic mean when outliers or incorrect values are present in the dataset. A few very large or small data points dramatically influence the arithmetic mean but have little effect on the median.

The sites with the largest median concentration and largest maximum concentration during the period of the ASARCO operation are tabulated in Table 5.1. It must be recognized that the comparison among sites is influenced by the fact that data were not obtained from every site for identical events. For example, if on a day when the air concentrations were highest, and only one site had a measurement of rain water, that site would appear as the highest wet deposition on record. Another example is the impact of the amount of precipitation on the concentrations obtained at different sites. All else being equal (i.e. the concentration of analytes in the air mass above a site), differences in total precipitation catch between sites will influence the concentrations of analytes in the rain water. Those sites with higher precipitation will have lower concentrations. As such, the concentrations at sites with higher rainfall may be biased towards

Table 5.1

SITES WITH LARGEST MEDIAN AND MAXIMUM CONCENTRATIONS DURING THE PERIOD OF ASARCO SMELTER OPERATION

| Analyte | Site with Highest Median Concentration | | Site with Highest Maximum Concentration | | |
	Median Conc.	Site	Maximum Conc.	Site	Date of Maximum
Arsenic	0.0005	Ladner	0.0031	Ladner	04FEB85
Barium	0.0018	Cloverdale	0.0087	Cloverdale	21FEB85
Calcium	0.18	Vancouver	1.54	Ladner	19MAR85
Cadmium	0.0009	Saanich	0.0120	Saanich	17JAN85
Chloride	1.925	Ladner	12.85	Saanich	31OCT84
Cobalt	0.0004	Agassiz	0.0009	Texada Is.	31JAN85
Chromium	0.0007	Saanich	0.0024	Texada Is.	06DEC84
Copper	0.0087	Saanich	0.0530	Saanich	17JAN85
Iron	0.023	Vancouver	0.100	Cloverdale	19MAR85
Potassium	0.095	Saanich	1.230	Abbotsford	04FEB85
Magnesium	0.125	Ladner	1.15	Port Renfrew	10FEB85
Manganese	0.0022	Cloverdale	0.0210	Cloverdale	09OCT84
Molybdenum	0.0004	Agassiz	0.0011	Vancouver	31JAN85
Sodium	1.165	Ladner	9.62	Port Renfrew	10FEB85
Ammonium	0.428	Abbotsford	2.175	Abbotsford	04FEB85
Nickel	0.0011	Agassiz	0.0027	Texada Is.	31JAN85
Nitrate	0.220	Vancouver	1.22	Ladner	04FEB85
Lead	0.0098	Vancouver	0.0680	Vancouver	31JAN85
Selenium	0.0001	*	0.0005	Ladner	31JAN85
Sulphate	1.55	Vancouver	4.08	Ladner	04FEB85
Strontium	0.0011	Ladner	0.0062	Port Renfrew	10FEB85
Vanadium	0.0006	Ladner	0.0023	Abbotsford	24OCT84
Zinc	0.013	Saanich	0.098	Saanich	17JAN85

Note:

All concentrations in mg/L.

* Median concentration is below detection limit.

lower concentrations relative to the air concentration. In the following analyses, sites with low rainfall such as Saanichton will have generally higher concentrations than sites such as Bamfield which have substantially more precipitation. This must be kept in mind when using rain water concentrations to reflect air concentrations of pollutants.

5.1.1   Identification of Sites Associated with High Analyte Concentrations.

The median value of a set of concentrations indicates typical concentrations at a site. As such, a site with a higher median value usually has higher concentrations most of the time than a site with a lower median. Table 5.1 shows the largest median concentrations during the ASARCO operating period and the site at which the median was observed. It is interesting to note that there are groups of analytes at sites which can be explained by considering certain physical processes. For example, the high median concentration of As and V at Ladner could possibly be explained by the relative proximity of this site to petroleum refineries at Bellingham and to the ASARCO smelter. Abbotsford could be expected to have the highest NH_4 due to local agricultural activity. The reason for the highest median concentrations of Cd, Cr, Cu, Zn and K at Saanichton is not immediately apparent, but may be due to the low precipitation catch recorded at this site. Therefore, the higher concentrations reported for Saanichton may not be significant.

The maximum concentrations of pollutants not affected by transformation processes[1] will generally reflect days when a source is relatively close and the dilution is low. Thus, the site with the maximum concentration for a given analyte will usually reflect a site closer to a major source of the analyte. A review of the maximum concentrations shows Saanichton again with the highest Cd, Cu, and Zn; all on the same date, 17 January 1985. It is interesting to note that the maximum concentrations of both Co and Ni were recorded on the same date, 31 January 1985, at the extreme northerly site, Texada Island. The 4 February 1985, event produced the highest maximum As and NO_3 at Ladner, K and NH_4 at Abbotsford, and SO_4 at Vancouver. Concentrations of Mg, Na, Sr, and rainfall all have maximums at west Vancouver Island sites on the 10 February 1985, the date on which Bamfield reported the highest total precipitation.

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[1]   Secondary pollutants (e.g. SO_4) may have a long residence time in the atmosphere. This fact complicates the general type of analysis and suggests the use of an acid deposition model to screen the data.

SENES recommends a more detailed analysis of the meteorology associated with events on these dates.

5.1.2 Analyte Concentrations Related to Physical Location of Sites

Some examples of the relative median concentrations of Na, SO_4, NO_3, Pb, Cu, Zn and NH_4 during the period of the ASARCO operation are presented in Figure 5.1. The bars in the figure are scaled to the largest median concentration of the eight sites shown. This provides a relative assessment between the median concentration of the selected analytes. The most western site, Bamfield, has relatively low concentrations of NO_3, Pb, Cu, Zn and NH_4 while possessing relatively high concentration of Na and SO_4. The agricultural region around Abbotsford, to the east, has by far the highest median NH_4 concentration. The "highest concentrations" of Cu and Zn at Saanichton are also readily apparent. The Ladner site appears to have the "highest concentration" of Na, SO_4 and Pb.

The 90th percentile of the major ion and metals concentrations are shown in Figure 5.2. The events represented by the 90th percentile concentrations will indicate circumstances where the sites are close to a major source, the dilution is low, and the wind blows from the direction of the source. This plot reinforces the high NH_4 on Abbotsford, high Na for west Vancouver Island, high Cu and Zn at Saanichton, and high SO_4, NO_3 and Pb at Ladner seen in Figure 5.1.

As an overall assessment, the data suggest that a major source of NH_4 exists in Abbotsford area, a major source of Cu and Zn in the Saanichton area, and a major source of Pb in the Ladner area. Na concentrations are associated with proximity to sea water. NO_3 and SO_4 concentrations appear generally high in the Georgia Strait area with reduced concentrations to the east and minimal concentrations to the west.

The relative median concentrations of 7 trace metals are shown in Figure 5.3. It is apparent that Ni and V concentrations are relatively similar at the sites listed. Ladner had the highest median V, while Saanichton and Agassiz had the highest median Ni concentration. Vanadium is generally associated with petroleum refining and fuel oil combustion. Faulkner (1987) suggested

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FIGURE 5.1

MEDIAN CONCENTRATIONS OF MAJOR IONS AND METALS IN RAIN WATER DURING ASARCO SMELTER OPERATION

Analyte
- Sodium
- Nitrate
- Copper
- Ammonium
- Sulphate
- Lead
- Zinc

Concentrations of each analyte relative to highest site (i.e. relative scale)

Concentrations below detection limit shown as zero

FIGURE 5.2

90th PERCENTILE CONCENTRATIONS OF MAJOR IONS AND METALS IN RAIN WATER DURING ASARCO SMELTER OPERATION

Analyte		
Sodium		Sulphate
Nitrate		Lead
Copper		Zinc
Ammonium		

Concentrations of each analyte relative to highest site (i.e. relative scale)

Concentrations below detection limit shown as zero

FIGURE 5.3

MEDIAN CONCENTRATIONS OF TRACE METALS
IN RAIN WATER DURING ASARCO SMELTER OPERATION

Analyte

- Arsenic
- Cobalt
- Molybdenum
- Vanadium
- Cadmium
- Chromium
- Nickel

Concentrations of each analyte relative to highest site (i.e. relative scale)

Concentrations below detection limit shown as zero

the refinery operations at Cherry Point, just south of the US/Canada border, as a potentially large source of vanadium in southwestern B.C. rainwater. Cr is generally similar with the exception of Bamfield which had a median concentration below the detection limit. The median concentration of As is highest at Ladner with relatively high concentrations at Saanichton and Abbotsford, the three most southerly monitoring sites. A pronounced high median Cd level was apparent at Saanichton. Mo is highest at Wilson Creek and Agassiz while Co is high at those stations and Texada Island. The low median concentrations of Cd, Co, and Mo at the Ladner and Abbotsford sites is striking and suggests that sources of those contaminants are found outside the lower Fraser Valley.

A intercomparison with U.S. data shows that for Cu and Zn there are high values upwind of *?* Saanichton at Everett Washington (see Table 2.1).

Don't see data for Saanichton

The 90th percentiles of trace metal concentrations, shown in Figure 5.4, display less differentiation between sites than the median concentrations. This is possibly due to the low concentrations involved and a number of small sources scattered about the area. The As, Cd and V patterns seen in Figure 5.3 are repeated. The other analyte concentrations appear to be relatively similar throughout the geography with the exception of Texada Island. The largest 90th percentiles of Cr, Mo, and Ni are found at this site which may be a result of local mining activities or from the Canadian Force Air Base at Comox. *sic? ?*

Overall, a local source of Cd seems apparent near Saanichton. High As, though also apparent at Abbotsford and Saanichton, is associated with the Ladner site. Mo and Co appear associated with Agassiz and the north Georgia Strait sites. Cr seems dispersed about the area, as is Ni. V is dispersed but has the highest concentrations at Ladner. High Cd is consistent with the upwind Cd source identified in Puget Sound on Figure 4.1.

5.2   SUMMARY OF RAIN WATER CHEMISTRY BY ANALYTE AND SITE

The rainwater chemistry from the sampling program, from 1 October 1984 to 6 February 1986 inclusive, are presented in Appendix B. Note that due to the confounding of precipitation

suspected / not shown

Table 5.2

SUMMARY CONCENTRATIONS FOR SELECTED ANALYTES

	1983 Mean Concentration* (mg/L)	1 October 1984 to 6 February 1985 Median Concentration (mg/L)	1 October 1985 to 6 February 1986 Median Concentration (mg/L)
	Before	Before	After
Sulphate			
Bamfield	0.42	0.56	0.58
Ladner	0.70	1.37	0.75
Abbotsford	0.34	0.83	0.48
Agassiz	0.28	0.26	0.32
N-nitrate			
Bamfield	0.03	0.01	0.04
Ladner	0.14	0.18	0.17
Abbotsford	0.09	0.13	0.11
Agassiz	0.08	0.07	0.11
N-ammonia			
Bamfield	0.02	0.03	0.01
Ladner	0.19	0.14	0.16
Abbotsford	0.72	0.45	0.35
Agassiz	0.33	0.15	0.14
Sodium			
Bamfield	1.78	0.82	1.11
Ladner	0.64	0.65	0.45
Abbotsford	0.19	0.17	0.10
Agassiz	0.15	0.04	0.10

Note:

*   Reported by MacLaren (1985) and converted to $N\text{-}NO_3$ and $N\text{-}NH_4$.

FIGURE 5.4

90th PERCENTILE CONCENTRATIONS OF TRACE METALS IN RAIN WATER DURING ASARCO SMELTER OPERATION

Analyte

Arsenic
Cobalt
Molybdenum
Vanadium

Cadmium
Chromium
Nickel

Concentrations of each analyte relative to highest site (i.e. relative scale)

Concentrations below detection limit shown as zero

chemistry due to physical factors such as emission rate, wind speed, wind direction and precipitation quantity and possible errors in the database, median concentrations have been chosen to quantify precipitation. The median, the 50th percentile of a distribution, is influenced less by errors in the data or unusual events.

Reason for median values ?

did we check ?

Precipitation amounts are not available for the concentrations reported. This precludes the estimation of deposition rates. The original dataset has some indication of precipitation amounts but the measurements are right censored (i.e. some rainfall events overflowed the collection device resulting in measurements which are recorded as above the capacity of the collection device) and the units of precipitation catch are unclear.

No deposity

Median concentrations are reported for two periods. The first, during the ASARCO operation, covers the period from 1 October 1984 to 6 February 1985. The second, after the closing of ASARCO, covers the period from 1 October 1985 to 6 February 1986. The split based on the ASARCO operation is required since the smelter was an emission source of many pollutants. Since season of year could affect the concentrations in rain water, comparable time periods were chosen. Thus concentrations from 7 February 1985 to 30 September 1985 are not included in the tables. However, there were relatively few observations during this time period.

different

Vancouver (A) is an anomalous sampling site with respect to the other 12 sites. The first observation occurs on 25 January 1985. Only a few observations occur within the generally elevated concentration period of 31 January 1985 to ASARCO closure are available. This will bias Vancouver median values during the period high. As such, Vancouver will be the highest median site more often than it should be.

Also a median concentration over both time periods is calculated. It is not the average of the before and after ASARCO time period median concentrations but is the median over the grouped data. Overall there may be more observations in the post ASARCO period so that the median over both time periods will be slightly biased toward the post ASARCO period.

5.2.1 Major Ions

[handwritten: Sea water influenced]

Tabulated median concentrations are presented in Appendix B for the analytes measured in the major ions test. Median concentrations for XSO_4, calculated according to Appendix C, are also included. The overall quality of this data appears reasonable given the understanding of emissions and transport mechanisms in the region. There appear to be no systematic differences over the period of data collection.

Increases of pH post-ASARCO are apparent in the sites along typical trajectories from the smelter. This follows a decrease in XSO4 concentrations at those sites. NO_3 median concentrations do not appear to change substantially. However, NH_4 concentrations tend to increase in sites west of Abbotsford. This may be responsible for some of the increase in pH observed in the sites.

The analytes emitted primarily from sea water (Na and Cl), show increases at most stations between the two periods with the exception of the Ladner, Cloverdale and Vancouver (A) sites. The remaining analytes with substantial contributions from sea water (Ca, K, Mg and Sr) follow the pattern of Na and Cl.

5.2.2 Metals

The trace metals seem to fall into two major groups; 1) half fall from above MDL to below MDL concentration between the two periods, and 2) the remaining have varying patterns. There seems to be an overall trend to decreased concentrations between the two periods. The effect is more noticeable in the analytes with concentrations close to the MDL of the trace metals tests. This possibly reflects laboratory test procedure changes, change in procedure of handling below MDL levels, or systematic errors in data management or compilation.

[handwritten: more (road) activity lognie.]

There appears to be relatively no change in Fe concentrations but rather a possible slight overall increase between the periods. Pb and Zn show a general decrease at all sites with the exception of Vancouver Island sites. There is a possible decrease at the west Vancouver sites but no change

or possible increases in the Saanichton area. As discussed, Appendix B data has discrepancies in Cr, Ba and Mn concentrations which influence the median concentrations of these elements. Nickel is surprising in that the concentrations reported at all sites are extremely consistent both before and after closure of the ASARCO smelter. However the concentrations in the latter period are only about half the operating period levels.

A large group of elements have median concentrations at all sites below MDL for the post ASARCO period. This is quite surprising since most of the median concentrations for the ASARCO operating period are above the MDL. This situation occurs for As, Co, Cd, Mo, Se, and V.

This decrease is expected for As since the ASARCO smelter was generally agreed to be the major source of emissions in the region. The west Vancouver Island sites all have median concentrations below MDL during the ASARCO operation which supports the lack of transport to these areas. The interpretation of Cd concentrations is more difficult. Again all sites have median concentrations below MDL after the ASARCO closure (and at the west Vancouver Island sites before closure). The highest levels are extremely localized at Saanichton which does not correspond to the As (i.e. ASARCO) pattern. Statistically then, the decrease in Cd may be primarily a result of something other than the ASARCO operation.

The difference in Co, Mo, and V is disconcerting since median concentrations above the MDL across the whole monitoring network fall to below MDL after the ASARCO facility closes. It is unlikely that the ASARCO influence on the median concentrations would be seen at Bamfield and Port Renfrew. This suggests that a systematic change in concentration levels occurred which is unrelated to the ASARCO operation or a major problem with the data. Regardless of the reason for this change it effectively masks regional relationships for these analytes. Although the situation is apparent in V, the median at Cloverdale is above MDL after the ASARCO closure. This is possibly the effect of refineries at Cherry Point, WA; however, a decrease in the before and after period is apparent.

Selenium median concentrations are below MDL for all time periods and sites with the exception

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of Abbotsford which is reported at the MDL prior to closure. Selenium is a trace element in fertilizer and may be the source for Abbotsford.

5.3 COMPARISON TO PREVIOUSLY REPORTED CONCENTRATIONS

The concentrations of major ions and elements recorded in this study are similar to concentrations previously reported. Table 5.2 shows the median concentrations during the period from 1 October 1984 to 6 February 1985 compared to mean concentrations reported by MacLaren (1985) for the 1983 monitoring. It must be noted that median concentrations will generally be lower than mean concentrations. In general, there is good agreement in trends between sites with the earlier measured concentrations for most analytes. However, substantial differences are apparent in the comparison of 1983 monthly results with the 1 October 1984 to 6 February 1985 period. SO_4 in the 1983 period is generally lower than the later but NO_3 and NH_3 are substantially higher in the earlier period. Na appears similar in the two time periods.

When comparing the before and after ASARCO periods, it is evident that little change occurs for NO_3 and NH_3. However, large decreases in SO_4 and Na at Abbotsford and Ladner are observed between the two periods. This decrease was not observed at either Bamfield or Agassiz.

Although statistical significance could be calculated for these changes, observational studies, such as this one, do not allow cause and effect to be assigned. The data do, however, support the thesis that ASARCO was responsibile for these changes.

6.0   INFLUENCE OF ASARCO OPERATION ON B.C. RAIN WATER CHEMISTRY

The ASARCO facility has been assessed as a major emission source of several pollutants, primarily As and SO_2 in the Pacific Northwest prior to its closure in March, 1985. While other relatively large sources of most of the pollutants released by ASARCO exist, the smelter accounted for the largest percentage of As emissions in the study region. The following section attempts to establish an association between the operation of the smelter and the concentrations of pollutants in rain water samples collected in southern coastal British Columbia. Such a linkage could be enhanced by relating rain water concentrations to wind directions and speeds. However, the physical geography of the study area makes it difficult to establish precise wind directions and speeds for all the precipitation events and sites. Since the data record spans a long period both before and after the facility ceased operation, statisically, a precise knowledge of the wind directions is not necessarily required for the data to strongly suggest that ASARCO had an effect on the concentrations of As or SO_4 in southwestern B.C. if that effect was indeed significantly large.

6.1   GENERAL WIND TRAJECTORY ANALYSES

To facilitate airflow trajectory analysis, the concentration data were grouped into discrete events as listed in Table 6.1. This reduced data set, consisting of 20 events before, and 20 events after, the smelter closure was used for further analysis. Mean and maximum values of the eight monitoring sites in the Strait of Georgia were calculated for each event. (Event data after February 1986 were not considered since trace metal concentrations were unavailable.)

The AES provided 850 mb (about 1500 m above msl) and 925 mb (about 750 m above msl) trajectory data for each of the 40 events. These trajectories are based on the Canadian Meteorological Centre objective analyses of upper air data. They are thus based on synoptic scale analysis and do not totally reflect the regional or meso-scale flows which transport pollutants in the Puget Sound-Strait of Georgia Region. Nevertheless, they may be used as an indicator of the low-level flows during such events.

Table 6.1

LIST OF SOUTH COAST B.C. ACID RAIN EVENTS
(1984-86)

EVENT NO.	YEAR/MONTH	BEGINNING (day/hr)	END (day/hr)
1	84/10	05/14	08/05
2	84/10	09/18	11/00
3	84/10	24/15	25/15
4	84/11	01/01	02/15
5	84/11	05/15	07/15
6	84/11	22/15	24/01
7	84/12	7/01	08/17
8	84/12	13/15	15/00
9	85/01	17/15	19/03
10	85/02	01/03	02/01
11	85/02	04/15	06/01
12	85/02	06/01	07/15
13	85/02	11/02	12/03
14	85/02	14/01	15/15
15	85/02	19/01	20/15
16	85/02	21/00	22/17
17	85/02	23/00	25/18
18	85/03	19/18	22/02
19	85/03	22/02	23/01
20	85/01	23/01	25/04
21	85/04	26/01	27/02
22	85/04	27/02	29/15
23	85/06	07/01	08/04
24	85/10	09/23	11/15
25	85/10	16/00	16/14
26	85/10	17/00	19/07
27	85/10	19/05	21/15
28	85/10	29/01	30/15
29	85/10	31/02	01/15
30	85/11	02/02	04/15
31	85/11	04/02	06/03
32	85/12	04/02	06/03
33	85/01	02/15	03/15
34	86/01	07/01	09/02
35	86/01	09/15	13/01
36	86/01	13/01	16/15
37	86/01	16/16	18/00
38	86/01	17/15	18/23
39	86/01	21/15	23/15
40	86/01	29/03	31/04

Back trajectories for periods of greatest precipitation during each event were selected and classified by the direction of flow at each level. Table 6.2 shows the frequency of 925 mb trajectory direction versus event arsenic concentration (mean of 8 sites in the Strait of Georgia).

It is evident from Table 6.2 that trajectories with a southerly component predominated when As concentrations were high. A total of 19 out of 21 cases where the mean concentration over 8 sites was greater than 0.00014 mg/L were associated with directions from southwest to southsoutheast. It must be noted that this average, 0.00014 mg/L, is below the MDL of 0.0002 mg/L of As and will be strongly influenced by the substitution method[*]. (This also reflects the fact that, in general, precipitation tends to occur with southerly low-level flows.) However, two of the highest concentrations of As were associated with upper air *westerly* trajectories. Although the trajectories for these two cases (February 1-2 and 21-22, 1985) do not indicate a southerly flow, low-level southerly flow is evident from an examination of the synoptic situation and surface winds.

6.1.1 Wind Trajectories for High Arsenic Events

Investigation into forward airflow trajectories calculated for the high arsenic events suggests that the air masses passed over the ASARCO facility. Figure 6.1 depicts 3 forward airflow trajectories (and 6 back trajectories) at 925 mb for events that produced high As concentrations at the monitoring sites. While the highest As concentrations were observed to occur at the most southerly located stations (i.e., Saltspring Island and Saanichton on February 5, 1985; and, Vancouver, Ladner and Cloverdale on February 18, 1985), it is interesting to note that the two highest As concentrations recorded at Wilson Creek also occurred on February 5 and 18, 1985. The third forward trajectory analysis (December 12, 1984) had the most easterly trajectory, and the highest As concentrations for that event occurred at Abbotsford. Therefore, the forward trajectory analysis tends to corroborate the assessment that the smelter was responsible for elevated As concentrations.

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[*] Method used to quantify those observations which are below the detection limit (e.g. zero, MDL or ½ MDL).

Table 6.2

FREQUENCY OF 925 MB TRAJECTORY DIRECTIONS VERSUS EVENT MEAN As CONCENTRATIONS

EVENT MEAN (mg/L)	WIND DIRECTION					
	SSE	S	SSW	SW	WSW	W
<0.00015	7	5	0	5	0	0
0.00015-0.00019	1	3	1	0	0	0
0.00020-0.00024	2	5	3	4	0	2
TOTALS:	10	13	4	9	0	2

MDC = 0.00200

FIGURE 6.1

925 mb Airflow Trajectories

RAINFALL EVENT

841024 LAD — Year Month Day, Location of highest Arsenic concentration

AIR TRAJECTORY
- – – – Forward
- ——— Backward
- TIC = 6 hours
- 850219 O6Z — Year Month Day, Time
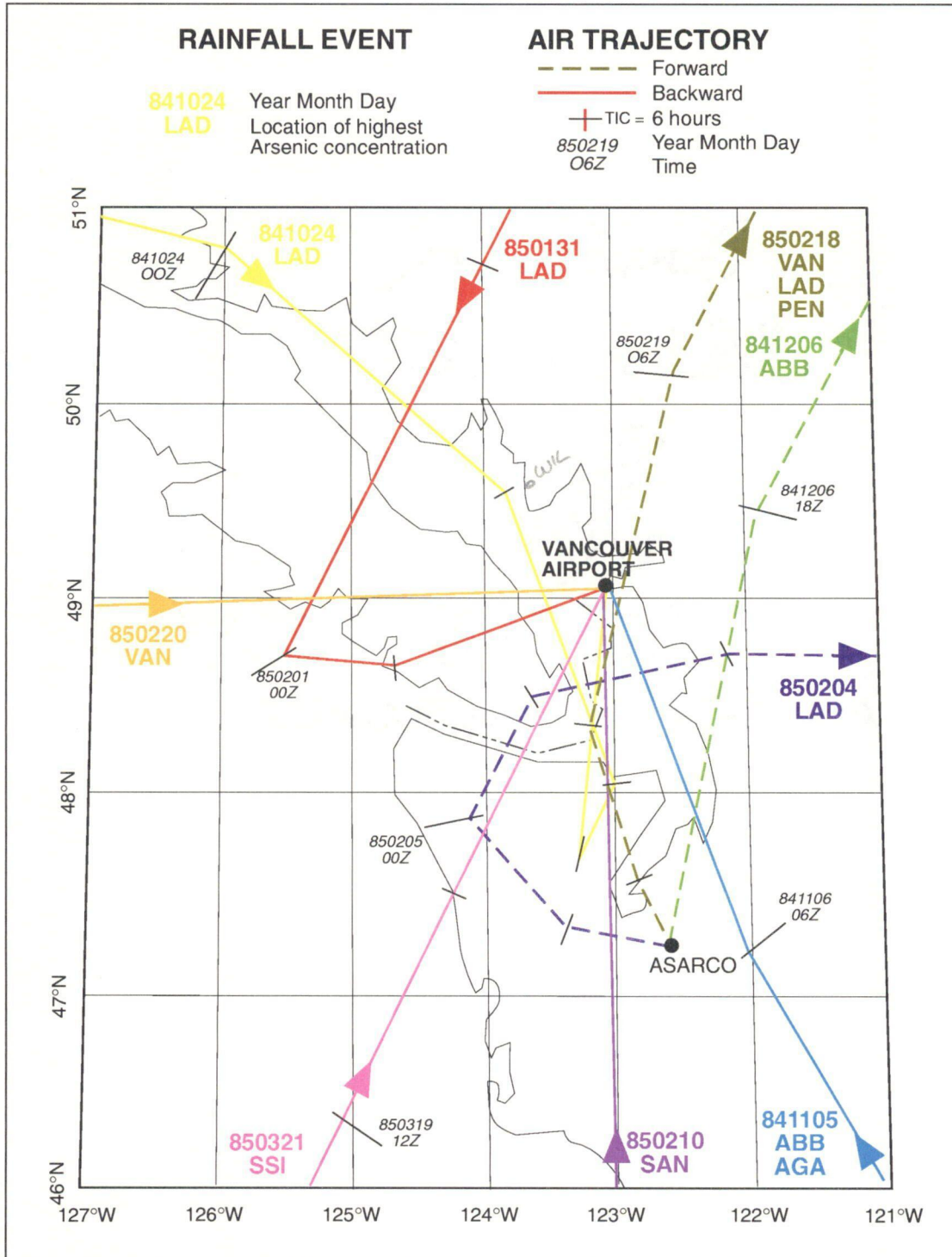
Unfortunately, the back trajectories from Ladner were less successful at identifying potential contributions from ASARCO emissions. Of 6 back trajectories depicted in Figure 6.1, only two (November 5, 1984 and February 10, 1985) passed close to the ASARCO facility. A third event (March 21, 1985) had a SW airflow trajectory which could be associated with northerly transport of pollutants through the Puget Sound-Georgia Strait region. A fourth event (October 24, 1984), had a flow from the north into the Olympic Peninsula region before returning towards the Lower Fraser Valley, and could have carried emissions from ASARCO to the Ladner monitoring site. However, the two remaining events (January 31 - February 1, 1985 and February 20, 1985) had westerly flows, and do not appear to correspond with emissions from ASARCO. However, as was noted previously, there was a generally low-level southerly airflow along the Puget Sound-Georgia Strait axis during these events which is not well represented by the calculated back trajectories at higher elevations. Therefore, the absence of a southerly flow in 925 mb back trajectory analysis does not automatically rule out the potential for transport of emissions from the Seattle-Tacoma area to southwestern B.C.

6.2 HIGH ARSENIC EVENTS

A strong indication that the ASARCO influence appeared in lower mainland B.C. can be established without the direct linkage of sample chemistry to wind direction and speed. For the purposes of statistical analysis, As concentrations can be subdivided for convenience into those reported at or below the method detection limit 0.0002 mg/L classified as low As concentration, and the remaining concentrations, those at 0.0003 mg/L or greater, classified as high As concentrations. Table 6.3 shows the number of high As concentrations at the sampling sites both prior to and following the smelter closure. It is immediately apparent that there were many high concentrations (56 of 191) before the closure and very few after (2 of 159). This is most apparent (about 80% of the events before closure and none after) at the sites of Cloverdale and Abbotsford which are located north of and closest to the ASARCO facility. Saanichton, Salt Spring Island, Pender Island, Ladner, Vancouver, and Agassiz all have about 50% high concentrations before the closure and a few after. (It is perhaps worth noting here again that, according to Vong (1982), approximately 70% of the rain events in the Seattle-Tacoma area are associated with S, SSW and SW winds. Therefore, an observed frequency of high As

Table 6.3

NUMBER OF RAINFALL EVENTS WHEN ARSENIC CONCENTRATION EXCEEDS THE MINIMUM DETECTABLE LIMIT

Site	Total Number of Rainfall Events	Rainfall Events While Smelter Operating	Rainfall Events After Smelter Closed
Abbotsford	9 (20)	9 (11) ~ 98%	0 (9)
Agassiz	6 (28)	6 (14)	0 (14)
Bamfield	0 (29)	0 (10)	0 (19)
Cloverdale	8 (25)	8 (11) ~ 78%	0 (14)
Ladner	9 (35)	9 (15) 60%	0 (20)
Pender Island	5 (26)	5 (13)	0 (13)
Port Renfrew	0 (33)	0 (17)	0 (16)
Saanich	6 (21)	5 (8)	1 (13)
Sooke	0 (29)	0 (15)	0 (14)
Salt Spring Island	8 (27)	7 (13)	1 (14)
Texada Island	1 (29)	1 (15)	0 (14)
Vancouver	4 (24)	4 (6)	0 (18)
Wilson Creek	2 (24)	2 (11)	0 (13)
Total Measurements	58 (350)	56 (191)	2 (159)

Note:

Number in brackets is total number of rainfall events during period.

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concentrations of 50% to 80% is entirely consistent with an observed frequency of airflows from the location of the smelter.)

The sites located at the north of the Georgia Strait, Texada Island and Wilson Creek, show a few high observations before closure. The west coast of Vancouver Island sites show no high As concentrations either before or after the ASARCO closure. One must recognize that there is some possibility of an arsenic source in the vicinity of Saanichton since 2 high observations occur after the smelter closure at Saanichton and Salt Spring Island sites.

Because of the large differences in concentration before and after closure, most of the sites, individually, would show a statistically significant difference between the As concentration before and after the smelter closure with a contingency table test. Since this is an observational study, this does not imply a causal relationship; however, it would be difficult to establish a physical explanation other than the ASARCO smelter being the cause of elevated As level. Such an explanation would require either the existence of an As source in the same general location as the ASARCO facility but much larger and at coincident times of closure, or the existence of an As source located in the lower mainland which also reduced its As output at the same time. There is no information to suggest that such an alternate source ever existed.

6.3   OTHER POLLUTANTS ASSOCIATED WITH ASARCO SMELTER OPERATION

In addition to As , other pollutants have been identified in emissions from the ASARCO facility. Aside from SO_2, these elements are trace metals (Pb, Cu and Zn) which have many other sources in the region. The interpretation of the trace metal changes affected by ASARCO operation are not pursued in this report. However, time plots of the concentrations of As, SO_4, NO_3, Na, and NH_4 at Ladner against date are presented in Figures 6.2 through 6.6. The huge reduction in As concentrations after the closure of the smelter is striking. All but the first measurement after closure of the smelter shows concentrations below detectable limits while only one of the events during the smelter's operation shows concentrations below the detection limit.

SO_4 also shows reductions in concentrations after closure of the smelter. The decrease in SO_4

6-4

FIGURE 6.2

ASSOCIATION BETWEEN ARSENIC CONCENTRATIONS (mg/L) AND DATE IN RAIN WATER COLLECTED AT LADNER
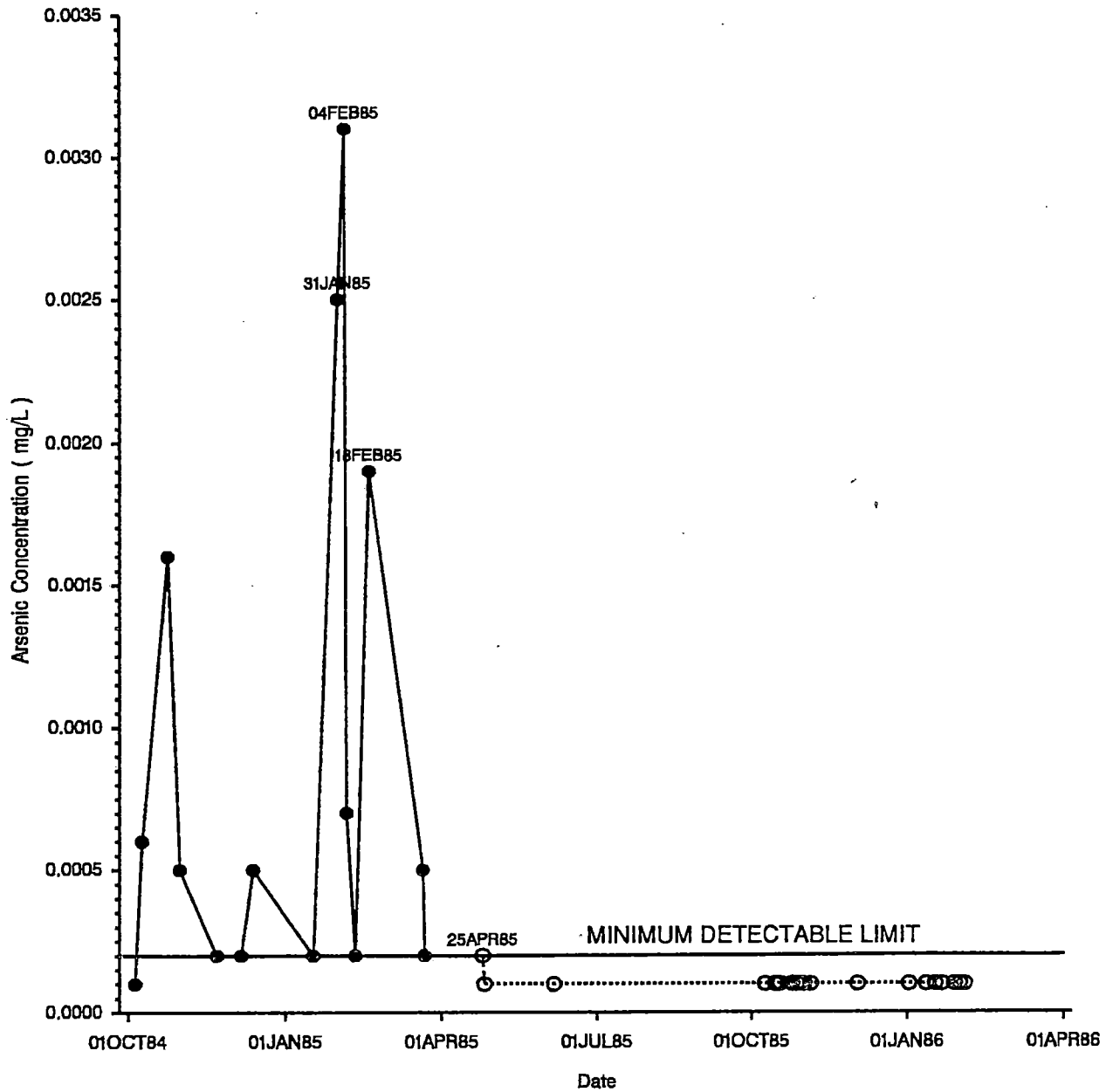
Time Plot of Analyte Concentration

FIGURE 6.3

ASSOCIATION BETWEEN SULPHATE CONCENTRATIONS (mg/L) AND DATE IN RAIN WATER COLLECTED AT LADNER

Time Plot of Analyte Concentration

FIGURE 6.4

ASSOCIATION BETWEEN NITRATE AS NITROGEN CONCENTRATIONS (mg/L) AND DATE IN RAIN WATER COLLECTED AT LADNER

Time Plot of Analyte Concentration
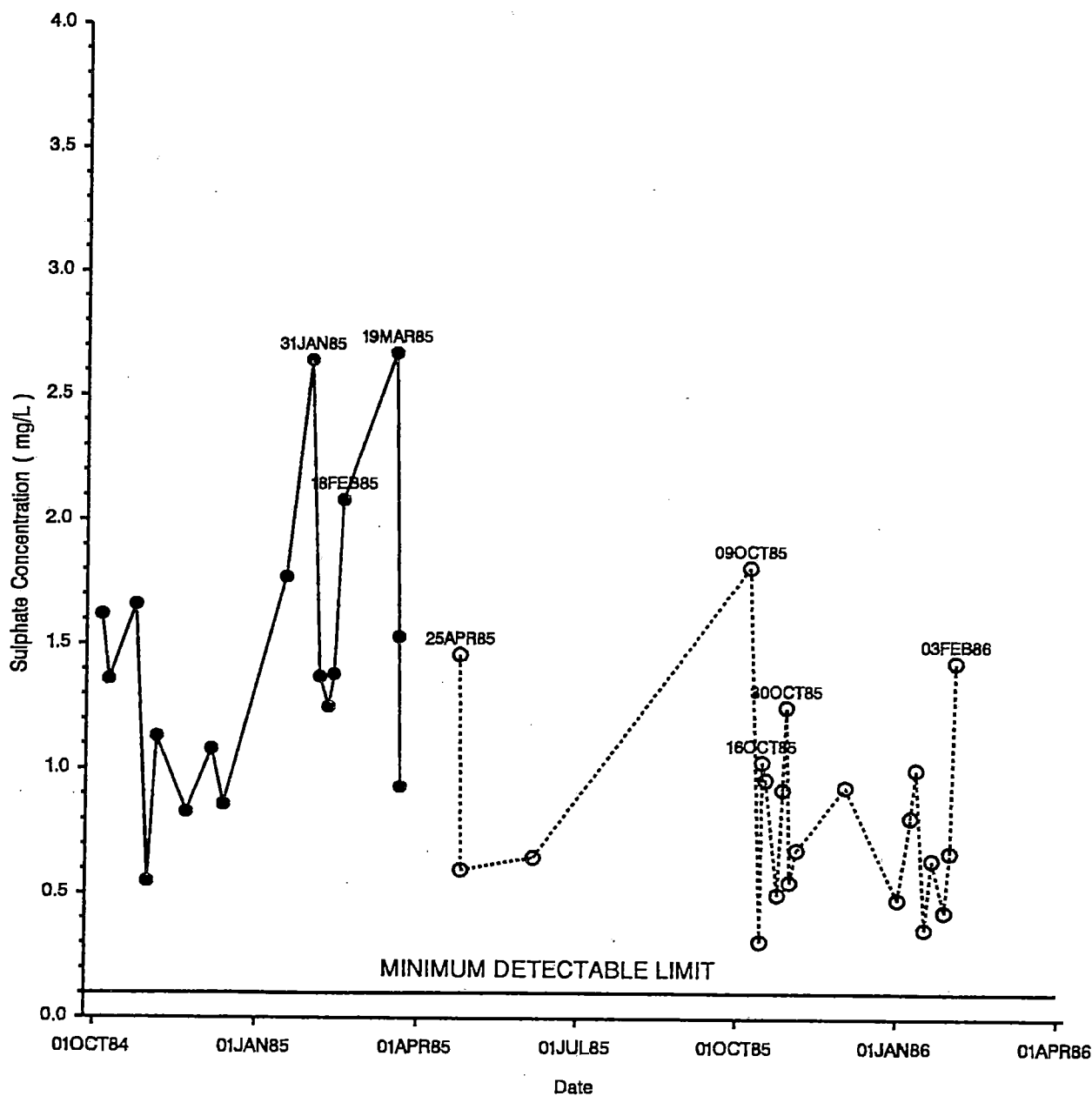
ASARCO Smelter ●—●—● Operating ⊙··⊙··⊙ Closed

FIGURE 6.5
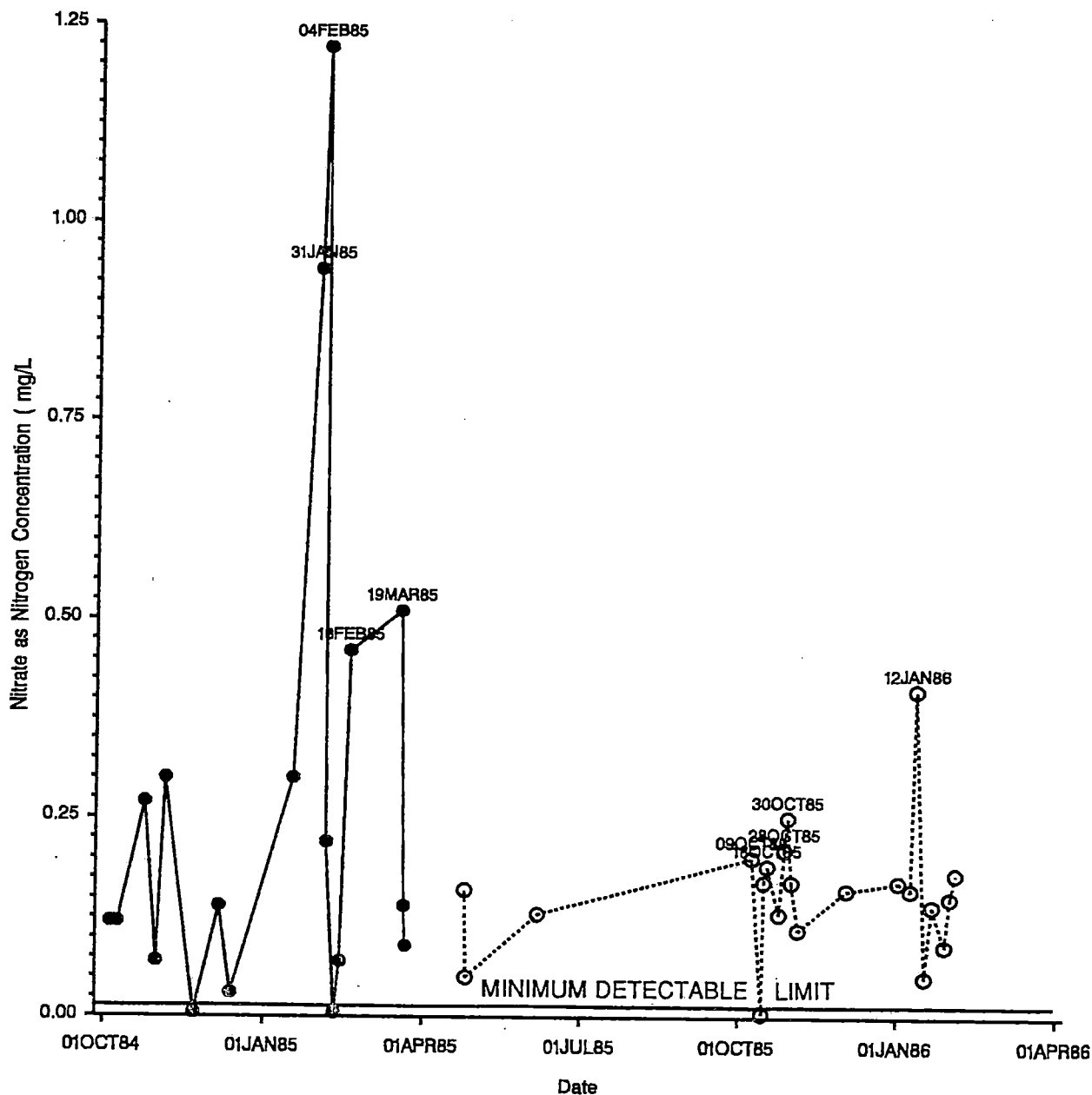
ASSOCIATION BETWEEN SODIUM CONCENTRATIONS (mg/L) AND DATE IN RAIN WATER COLLECTED AT LADNER

Time Plot of Analyte Concentration

FIGURE 6.6
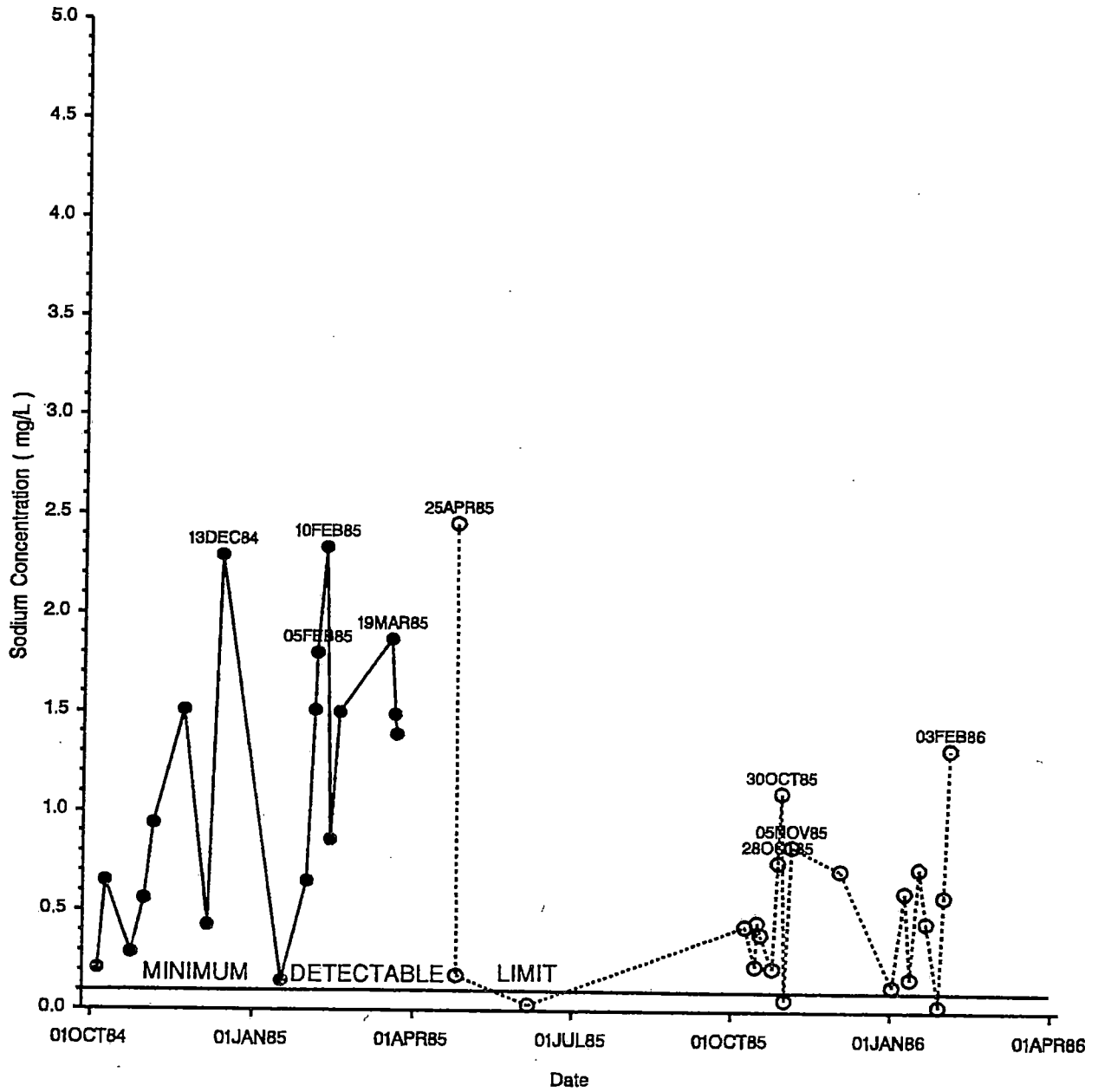
ASSOCIATION BETWEEN AMMONIUM AS NITROGEN (mg/L) AND DATE
IN RAIN WATER COLLECTED AT LADNER

Time Plot of Analyte Concentration

Date
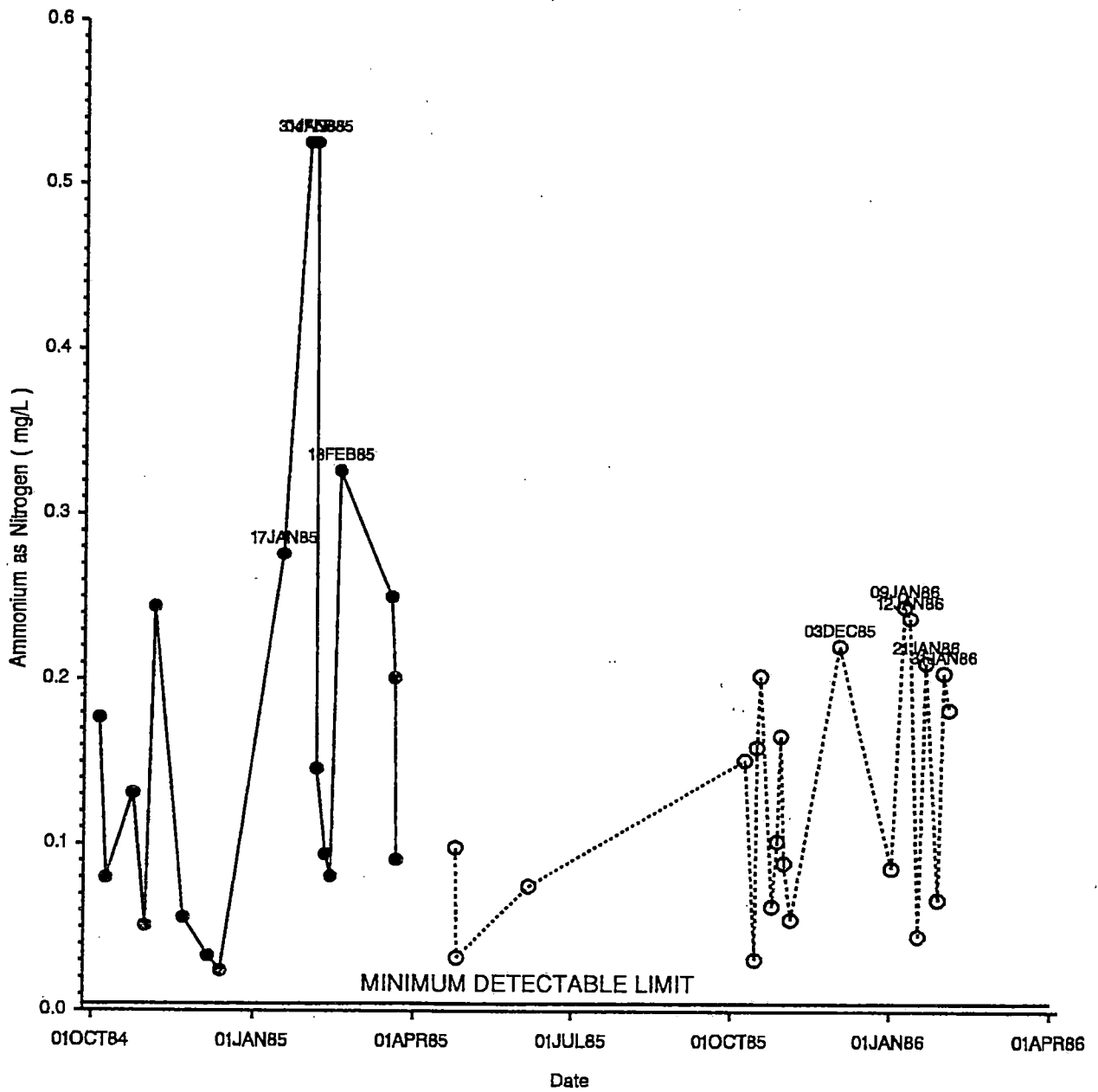
ASARCO Smelter ●—■—● Operating ⊙··⊙··⊙ Closed

after the closure of the facility could suggest that the ASARCO facility was also a source of this pollutant at this receptor location.

[handwritten marginal note: why even consider it as a smelter-related product?]

NO$_3$, however, shows roughly similar concentrations before and after the closure with the exception of a period of time from about the end of January to the end of March. If both the meteorological conditions and the emissions of NO$_3$ were similar before and after the closure, the similarity of NO$_3$ concentrations before and after the closure of the ASARCO would not be surprising. Within the GVRD, NO$_3$ emissions are mainly associated with mobile sources (i.e. 77% in 1985). A similarly large proportion of NO$_3$ emissions in the Puget Sound region (i.e. 88% in 1988) is also attributable to motor vehicles. Therefore, it is not all that surprising that the NO$_3$ concentrations remained relatively stable throughout the rain water sampling program.

The time plots for Na, largely indicative of sea water emissions, and NH$_4$, indicative of agricultural activities, show minimal change with respect to the ASARCO closure. *[handwritten: as expected.]*

7.0   MAGNITUDE OF TRANSBOUNDARY FLOW

It was impossible to infer the magnitude of the transboundary flux of pollutants within the limited scope of this project. It was possible, however, to use the analysis of precipitation chemistry data to estimate the contribution via rain from various sources. Since arsenic appeared in samples during times of generally southerly winds in rain events, some pollutants are transported to the lower mainland from U.S. sources. Without further modelling of the meteorology, it is difficult to precisely estimate the relative transboundary flux. Investigations into multivariate analysis were conducted to attempt to identify rainfall events by point of origin based on the relationships between analyte concentrations. Though promising, these analyses were plagued by confounding factors and the quality of the data set.

Concentrations are influenced by many factors which confound the association with emissions from a particular source. Information on emission rates, wind speed, atmospheric transformations, airflow trajectories and the scavenging rate would substantially improve the analyses by allowing for the removal of some of these confounding factors. Techniques for reducing the effect of these factors are available. One involves scaling the concentrations of pollutants to a single pollutant whose emission rate can be considered constant both temporally and spatially within the region. Limiting the analyses to common seasons may also reduce some of the confounding effects of meteorological variables. This is tested in a simple way in the next sections.

7.1   ASSESSMENT BASED ON ARSENIC AS A TRACER

A crude estimate of U.S. contribution of SO_4 and NO_3 can be established using the concentration of As to indicate rainfall events whose pollutants primarily arose from sources within the U.S. Background, sea salt contributions, and Canadian sources balance out the budget for these pollutants. Emissions data are used to estimate the ASARCO contribution for the pollutants. Unfortunately this can only be completed for the ASARCO operational phase. An analyte, other than As, which could act as an indicator for the post-closure period was not identified in this study.

7.1.1   Estimation of Sulphate Contribution

For each date during the ASARCO operation, contributions from the four sources (i.e. background sea water, Canadian and U.S.) were estimated. The contribution arising from seawater is calculated as 0.253 times the sodium concentration in mg/L for each date. A nominal background concentration, arising from non-regional influences, of 0.2 mg/L is assumed. Subtracting the nominal background and sea salt contribution from the SO_4 on each date gives the amount due to other sources. This is the SO_4, largely anthropogenic, which is to be apportioned between U.S. and Canadian sources. For simplicity, this anthropogenic SO_4 will be assigned completely to Canadian sources on dates with As concentration at or below the MDL of 0.0002 mg/L.   In a similar manner, anthropogenic SO_4 is assigned to U.S. sources on dates when the As concentrations are above the MDL. The mean for each of these contributions is presented in Table 7.1 .

The contribution of the U.S. anthropogenic SO_4 which can be assigned to ASARCO is not trivial. The method utilized in Appendix C for the removal of contributions from sea water could conceptually be utilized. This depends on the assumption that ASARCO was the only significant source of As emissions, the ratio in emissions for analytes from ASARCO is well known, and the deposition process is identical for all analytes.   While the first assumption is likely appropriate, the remaining are questionable. The ratio in emissions, possibly variable, is not well known. The deposition for As, associated with particulate matter, is different from the SO_4 process. Figure 7.1 shows a scatter plot of XSO_4 and As concentrations at Ladner with the ratio, 1500 to 1, of SO_4 to As emissions superimposed. This line should be the lower bound to the data. Obviously the ratio overpredicts the excess sulphate associated with As. This suggests that the emissions had a ratio much less than 1500 to 1. Therefore, this relationship cannot be used to estimate the ASARCO SO_4 contributions. However an estimate of 50% of SO_2 emissions in western Washington State as being from ASARCO is supported by the references. This suggests a mean ASARCO contribution of approixmately 0.4 mg/L which matches well the 0.5 mg/L decrease in median concentration of XSO_4 mean at Ladner.

7-2

SENES CONSULTANTS LIMITED

52 West Beaver Creek Road
Unit No. 4
Richmond Hill, Ontario
Canada L4B 1L9

Tel: (416) 764-9380
Fax: (416) 764-9386

38005

21 May 1992

Mr. Wayne Belzer
Atmospheric Chemist
Scientific Services Division
Pacific Region
Atmospheric Environment Service
Suite 700
1200 West 73rd Avenue
Vancouver, BC
V6P 6H9

Dear Wayne:

In response to the comments provided by AES on Project 1991-10-Acid Deposition in Southwestern British Columbia, I wish to document here SENES' response to the 47 items provided. In most cases, the item was accepted and corrected in text. The details are as follows:

1.   Table of Contents, Reference List and Annotated Bibliography added.

2.   U.S. data was requested but not received during the contract period. Whatever reference and use we could make of the published data we did.

3.   Explained.

4.   Corrected.

5.   Explained.

6.   Deleted.

7.   Corrected.

8.   There was not enough budget to go into any depth of analysis. Therefore, "dry spells" before "episodes" was not analyzed.

...*/2*

9. There are many examples of data problems. The order of magnitude differences were mentioned a couple of times in the text. The Seattle-Vancouver as one was not. (See also answer to items 44 and 45 below).

10. Deleted.

11. Table 2.1 remains the same since it is a direct copy from published data. SENES also has difficulty believing in three significant figures. A note was added to the table.

12. Explained.

13. Explained.

14. Corrected.

15. Expanded upon.

16. Changed.

17. Expanded upon. This statement is in conflict with Seinfeld - see new text.

18. Corrected.

19. Expanded.

20. Corrected.

21. Clarified.

22. No explanation can be given without an in-depth data quality check. It may be an error or it could be legitimate!

23. Removed.

24. Added.

25. Re-written.

26. Explained.

27. Added.

28. Corrected.

29. Two different types of analyses were done. One using meteorology and the other assuming that the data set stood alone (from which statistical conclusions were drawn). This comment was from the second type of analysis. Wind data were not ignored!

30. Explained.

31. Expanded.

32. The "high" and "low" were selected for convenience only in the analysis. This again points out a data problem.

33. Changed.

34. Expanded.

35. Added. You cannot ignore points below the MDL because they are a very real part of the data set. In fact how you deal with them can completely change your conclusions. *Right!*

36. Deleted.

37. Expanded.

38. "Means" used in Table 2.1 (a summary of historical reports) because most of the historical data used "means". The reason that SENES did not use "means" (but rather the "median") is explained in the report.

39. Changed.

40. This discussion focused on a couple of stations only for the sake of clarity on the figure. This is now explained in the text.

41. We are not lumping or comparing data here either. Rather some sites were not included so that the figure would be clear rather than crowded. *So what is the result of including them?*

42. Not used.

.../4
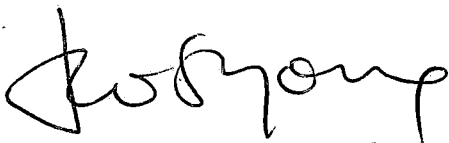
43.   Changed.

44.   You have picked out another potential error in the database. See Figure X.1 attached.

45.   This is another example of an order of magnitude error. See Figure X.2 attached.

46.   Corrected.

47.   Table corrected for sulphate. This error did not affect our analysis or conclusions. Note added to the table regarded Sr. It appears that all the references used the same original data and are in error. Sr should be 6.5 mg/L which corresponds to the B.C. data.

I must apologize for the delay in completing the report but I wanted to ensure that is was of the highest quality and to the extent possible met your needs. The fact that it was due at fiscal year end also always causes consultants a problem as may other clients need reports at that time.   Feb 15

I think that you will find the report delivers a substantial analysis for the size of the contract. We have enjoyed working with the data and look forward to proposing some follow-on analyses shortly.

Yours very truly,

SENES CONSULTANTS LIMITED

James W.S. Young, Ph.D., P.Eng.
General Manager Integrated
Environmental Studies

Bohdan (Dan) W. Hrebenyk, M.Sc.
Environmental Scientist
Manager, B.C. Office

Att.

:mf

FIGURE X.1

ASSOCIATION BETWEEN BARIUM CONCENTRATIONS (mg/L) AND DATE IN RAIN WATER COLLECTED AT PORT RENFREW

Time Plot of Analyte Concentration
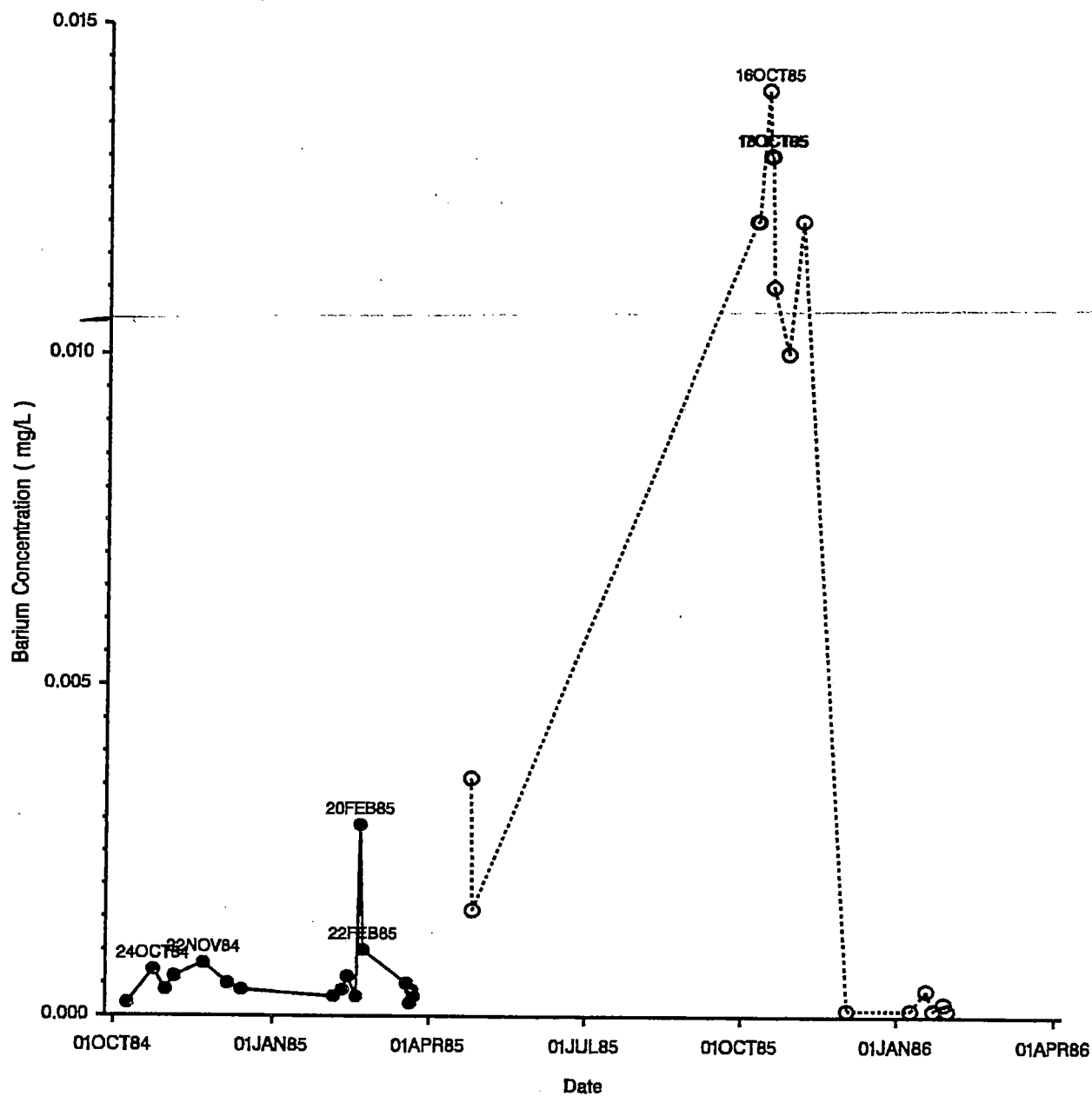
FIGURE X.2

ASSOCIATION BETWEEN COPPER CONCENTRATIONS (mg/L) AND DATE IN RAIN WATER COLLECTED AT PENDER ISLAND

Time Plot of Analyte Concentration
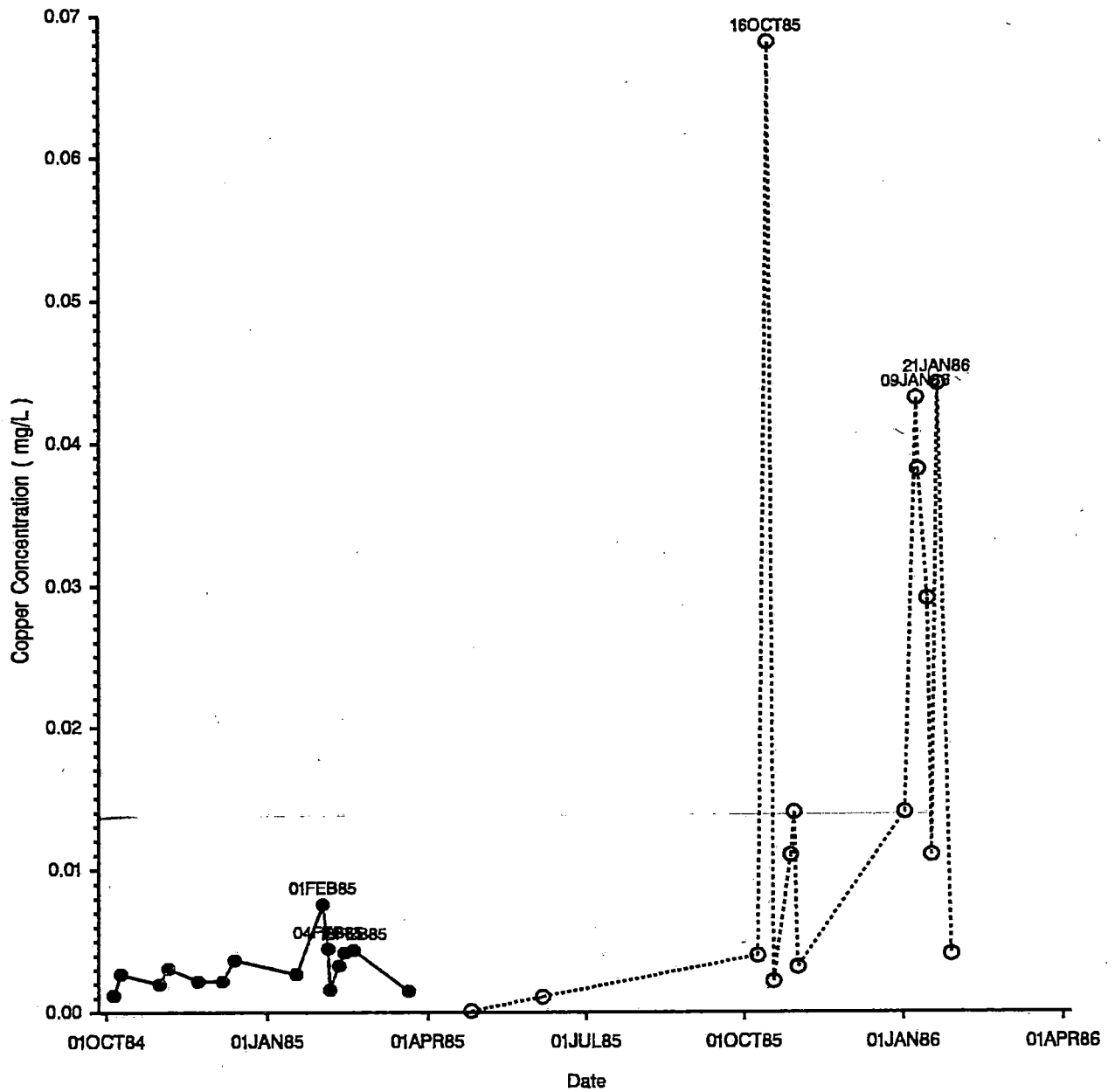
Questions:

1   Pg 5-4: I don't see the Saanichton/ Everett comparison in Table 2-1.

3   Pg 7-3: Multivariate analyses was discounted. Reason was "transformations of chemicals is highly variable". Is this correct? Isn't it the emissions that were highly variable?

MEMORANDUM
NOTE DE SERVICE

TO
À

Bruce Thomson   PAESS/BT

SECURITY - CLASSIFICATION - DE SÉCURITÉ
OUR FILE / NOTRE RÉFÉRENCE 8725-1(PAESS/WB)
YOUR FILE / VOTRE RÉFÉRENCE
DATE June 15, 1992

FROM
DE

Atmospheric Chemist   PAESS/WB
Scientific Services Division
AES, Pacific Region

SUBJECT
OBJET

Project 91-10: Acid Deposition in Southwestern British Columbia
- a report produced by Senes Consultants

This report had the objective of evaluating "Acid Deposition over the Pacific Northwest".
The project had several requirements that were to be met in the evaluation of this data.

Senes collected raw data from the SCBC studies and Trajectory plots from AES. This
covered the period 1982-1985. Senes also collected available data from Washington state's
PSAPC, for the ASARCO smelter shut-down period.

The trajectory plots produced were based on the presence of arsenic in the rainwater samples
collected during the SCBC study. The only known source of arsenic was the ASARCO
smelter near Tacoma. These trajectory plots generally show that air flows were from the
Tacoma/ASARCO smelter area when arsenic was found in the south coast stations. This
indicated that trans-boundary flow of pollutants occurred from Washington state to BC.

Sulfate contributions (from the ASARCO source) were calculated based on ASARCO's
emission ratios for sulfate and arsenic. These were found to be significant. "About 49% of
the sulfate and about 82% of the nitrate mean concentration can be attributed to U.S.
sources." Actual deposition rates however, were not calculated due to the poor quality of
rainfall data.

Wayne Belzer

cc: B. Thomson, PAES/AISB

(w6\p9119k.irk)

Comments on Project P91-10
Acid Deposition in Southwestern British Columbia

March 12, 1992

Comments to Senes:

Objective:

The report is large and appears to satisfy most of the contract requirements. The original objective were to:

A   Incorporate field measurements from Southern BC and Washington state into a quantitative assessment of acidic deposition;

B   Determine any relationships between noted BC precipitation monitoring 'episodes' and sources/ events in Puget Sound (specifically any which relate to the ASARCO site in Tacoma Washington);

C   Determine the relative importance of trans-boundary flow (and any seasonal variations) of pollutants to the Lower Mainland areas.

The funding for this project was limited to $10,000.00, and consequently resulted in some assistance from AES (trajectory work) and some limitation in the scope of the work.

Overview:

In general, the report meets almost all of the requirements of the contract. Ther are no problems with the report. A few areas need to be modified, deleted or added, but this is a minor problem. The following list indicates some of the areas that need addressing. Most of these are minor "housekeeping" items.

The report needs some work in the following areas:
1   There is no "Table of Contents", "Reference List" nor "Annotated Bibliography" in the report.
2   The data presented is sample-specific for the Canadian data, but only general reference is made to American data; I would like to see some American deposition/ concentration data in tables and referenced in the report.
3   Page 1-2, p 4, 1 2 "it is evident" -why is it evident?
4   Page 1-2, p 5, 1 3 "Figure 1.1" should be Figure D.1 or there is a figure missing.
5   Page 1-2, p 5, 1 6 "related to low-level airflows" - how are they related?
6   Page 2-1, p 2, 1 6 "also" - delete word
7   Page 2-1, p 2, footnote 1 "0.25" should be 0.256 (or 0.251 - see later discussion).
8   Page 2-2, p 4, 1 3 - mention is made of dry spells and the production of aerosols that could be scavenged during subsequent rainfalls. There is no follow up about the occurrence of 'dry spells' before the noted 'episodes' at Ladner. Maybe this

No budget

should be reviewed, and added.

Page 2-3, p 3,4 - There is an order of magnitude difference between the Seattle and Vancouver results for arsenic; is this true, and is it worth noting?

10 Table 2.1 has a title of "Historical ..", which implies to me that this has been the case for a long time; rather delete the word.

11 Table 2.1 shows data with three significant figures which I have some difficulty believing; suggest it be replaced with two significant figures.

12 Page 2-4, p 2 comments that the arsenic is the only metal to be tracked as far north as Vancouver. Possibly this is because the oxide of arsenic is one of the few that is relatively soluble in water (clouds, precipitation, etc..) and hence capable of being transported. The other oxides are relatively insoluble and would exist as particulates and hence be subject to particulate deposition.

13 Page 3-1, p 2, 1 2 - "Southwesterly upper flows that usually ..." probably needs to be justified via Don's work??

14 Page 4-3, p 2, 1 6 - "apparent" - from statistical evaluations?

15 "   , 1 9 "intriguing aspects" - what are they?

16 Page 4-4 - the data for emissions is difficult to read without commas (63772 tonnes -> 63,772 tonnes).

17 Page 4-5, p 1 1 2 "Arsenic, which is largely particulate,.." Is it?? I suspect that it is there as a readily soluble oxide.

18 Page 4-5, p 4, 1 8 "Figure D.1" should be "Figure 4.1".

19 Page 5-1, p 3, 1 1 - "median" is used here and later in the report (Page 5-4, 5-7) an explanation is given why means were not used; perhaps that could be done here?

20 Table 5.1 has a note that refers to "precipitation" which is not in the table. Should it be there??

21 Page 5-3, p 1 - data for other sites is not shown, but it does not state whether or not the data is similar for the excluded sites. Is it??

22 Page 5-3, p 3 1 2 - There is no major source of lead in the Ladner area; I live in the area and I know of no source there. This needs a better explanation - maybe from the nearby Vancouver area? or the ASARCO smelter??

23 Page 5-4, p 1, 1 3 "closely related in the data base" - What does this mean? If they are closely associated, why doesn't this show in Figure 5.3?

24 Page 5-4, p 2 -The higher incidence of Cr, Mo and Ni at Texada Island may have something to do with local mining activities, OR from the Canadian Forces air base across the channel at Comox.

25 Page 5-5, p 4, 1 4 "As previously discussed in Appendix B, ..." This is difficult to read and needs re-writing.

26 Page 5-7, p 1, 1 7 "The decrease in cadmium .." - I cannot see why this is not attributable to the ASARCO shutdown. ??

27 Page 5-7, p 3 - Selenium is a trace element in some fertilizers; is this a possible source here at Abbotsford?

28 Page 5-7, p 4, 1 4 - Again the concept of "median" results is used and should be referred to earlier.

29 Page 6-1, p 1, 1 9 "Since the data .." - This implies that the wind data doesn't support the conclusions, so it is being ignored; is this true?

✓ 30   Page 6-2, p 2, 1 5 "substitution method" - what is this?

31   Page 6-2, p 2, 1 7 "westerly" - Is this upper air direction? 850 mb?

cop-out ✓ 32   Page 6-3, p 2 - Arsenic has a detection limit (DL) of 0.0002 mg/l. How can we call anything less than this "low" and greater than it as "high"; it's either measurable or not measurable.

✓ 33   Table 6.3 - Is the "Limit of Quantification" another way of saying "Detection Limit"?

Expanded p-d ✓ 34   Page 7-1, p 2, 1 7 "Limiting the analyses .." - This infers that there should be seasonal analysis of the data, but then does nothing - no analysis and no reason why it wasn't done. This may require clarification.

✓ 35   Figure 7.1 (and others) - It would be useful to see a line denoting the MDC levels on the chart, so that the multitude of data points that are at or below this level can be ignored.

Deleted ✓ 36   Page 7-3, p 2, 1 7 "Relating ..." - What is this saying?

37   Page 7-4 - The Conclusions are rather limited. The reference to 25% of the SO_4 and 75% of the NO_3 are not well developed in the preceding discussion, although they can be inferred from Table 7.1.

38   Page 9-1, p 3 - Mean and median concentrations are again discussed, and I am drawn to ask the question why were mean values used in Table 2.1 if they are not desirable? Was it the only data available, and if so, why (if the other authors were using means) are means not useful here?

39   Page 9-1, p 5 and Page 9-2, p 1 - Better to replace "discrepancies" with "anomalies".

Expanded p-d ✓ 40   Page 9-2, p 2 - Were the Vancouver and Cloverdale data sets sufficiently similar to the Ladner data set to permit them to be ignored in this discussion??

41   Page 9-2, p 2 - The comparison of the Pender and Saltspring Islands may be okay, *only left out !* but we have some difficulty in including the Saanichton area with them; the *so what is result?* former are rural, but the latter is definitely an urban site.

✓ 42   Table A.4 - Missing and assumed to be detection limits.

✓ 43   Page A-3, p 3, 1 7 "analytical" may be confusing; suggest "statistical".

data pblm? → 44   Table B.3 for Barium - Port Renfrew is 0.0105 mg/l; is this correct as it is an order of magnitude different?

45   Table B.3 for Copper - Pender Island is 0.0140 mg/l; is this correct as it is an order of magnitude different?

✓ 46   Page C-2, p 2, 1 12 "C.2" - this should be "C.3".

47   Table C.1 - The data for sea salt concentrations is incorrect for Sulphate: 2,755 mg/L should be 2,652 mg/L. The reference for Sr concentrations also appears to be 13 mg/L; this raises some question as to the graph shown in Figure C.7. Maybe there is a problem with the chemical analysis?? My reference is the Handbook of Chemistry and Physics, 61st Edition, page F-206.

Table 7.1

**BALANCE SHEET FOR CONTRIBUTION TO OBSERVED
CONCENTRATIONS AT LADNER**

	SO_4 (mg/L)	NO_3 (mg/L)
Mean Concentration	1.57 (100%)	0.28 (100%)
Contribution from Sea Salt	0.29 (18%)	nil
Background	0.20 (13%)	0.01 (4%)
Canadian	0.32 (20%)	0.04 (14%)
U.S. (total)	0.77 (49%)	0.23 (82%)
	5̶3̶2̶	8̶6̶1̶

FIGURE 7.1

ASSOCIATION BETWEEN EXCESS SULPHATE AND ARSENIC CONCENTRATIONS (mg/L)
IN RAIN WATER COLLECTED AT LADNER

Association between Analytes
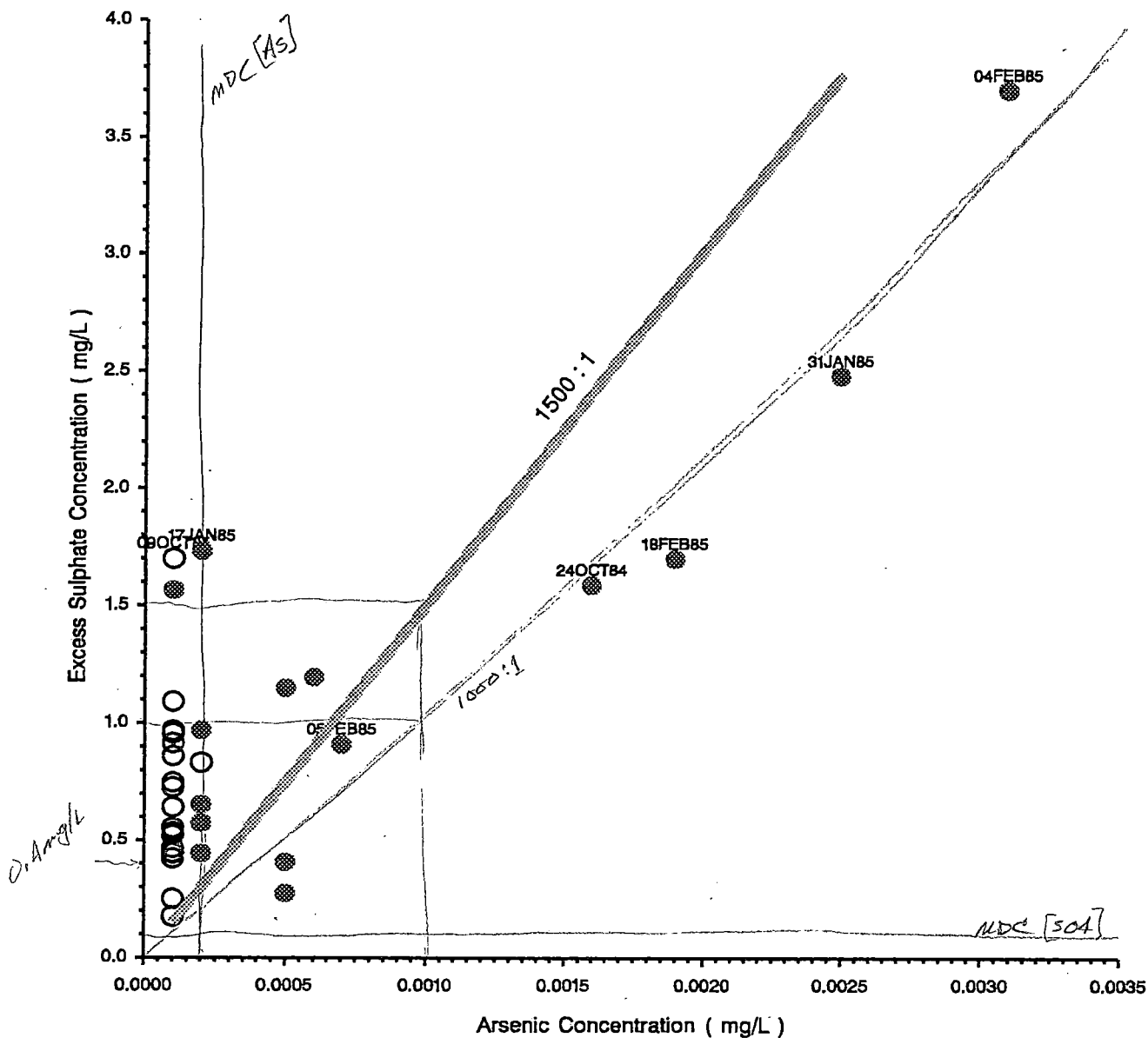
Legend   ● ● ● Before Shut–down   O O O   After Shut–down

ASARACO Emission

7.1.2 Estimates of Nitrate Contribution

The assigning of contribution of NO_3 is simpler than SO_4 since no appreciable contribution from either sea water or background exists. In a manner similar to SO_4, the contributions from U.S. and Canadian anthropogenic sources are calculated and presented in Table 7.1. The contribution from ASARCO can not be determined due to a lack of emissions data. However, it has not been indicated as a major source which is corroborated in no significant change in median concentration after ASARCO closure.

7.2   MULTIVARIATE ANALYSES

Multivariate analyses is useful in exploratory analysis to search for patterns in observations possessing many attributes. In the context of rainwater chemistry, groupings of observations (i.e. sites in combination with rainfall events) based on similarity in the relationships between analytes is plausible. This could lead to an empirical model which facilitates the identification of source types based on the correlations between the analytes. In theory, extending the technique would allow the proportioning of concentration arising from source types for each event and sampling site. Under conditions of constant emission rates (ratios between analytes maintained) for the sources and uniform transport other than wind direction, these techiques could generate empirical models relating rainwater chemistry to sources. Unfortunately one major confounding parameter is the atmopsheric transformation of chemicals whose rates are highly variable. This non-linear behaviour will limit the use of this type of analysis.

A number of multivariate analyses were explored in this study. On a coarse basis, logical groupings of analyte concentrations were identified. The sea water analytes of Na, Cl and Mg were grouped as associated elements. The influence of agricultural sources was identified by strong separation of NH_4 concentrations from the other analytes. The largely anthropogenic concentrations of SO_4, NO_3, Pb, and pH were also strongly associated.

The multivariate approach is promising with respect to identifying the relative contributions from multiple sources. Even within an individual rain event, the contributions from several defined

events could be assessed. However, the approach is limited in this study because of poor data quality and the required massaging of data prior to analysis. These techniques are extremely sensitive to systematic changes in laboratory procedure or errors of orders in magnitude in data compilation. With improvements in the data, substantial further understanding of the emission and deposition process would likely result.

7.3   SUMMARY

The attempt to determine the transboundary flow of pollutants, through the use of the database compiled around the closing of the ASARCO smelter, has been partially successful in that:

1) the appearance of elevated As in rainfall events indicates transboundary flow of pollutants from south of the border;

2) simple estimates using As as a tracer suggests that about 49% of the SO_4 and about 82% of the NO_3 mean concentration can be attributed to U.S. sources; and

3) estimates that ASARCO was the source of about 50% of the SO_2 emissions in western Washington are supported by the data from the AES rainwater sampling program.

8.0   AREAS FOR FURTHER STUDY

further study

The analyses carried out on the rainwater chemistry data support investigative analyses~~beyond this~~ ~~study.~~ In addition to multivariate analyses based on an improved data quality record, an analysis merging the limited U.S. and Canadian records and an investigation of scavenging effects would promote the understanding of atmospheric chemistry in the region.   *How?*

8.1   MERGING OF CANADIAN AND US DATA

Vong et al. (1986a, 1987) reported on 7 storm events during the two month period (February-March 1985) prior to closure of the ASARCO smelter. The study involved collection of rainwater samples at 38 sampling sites in the Seattle-Tacoma area. Subsequently, an additional 7 events were examined during the same two month period in 1986, one year after closure of the ASARCO facility, to determine what effect the closure had on precipitation quality in the region.

The analysis results for these two seasons showed that there is a statistically significant difference between upwind and downwind concentrations of pH and XSO_4 after closure of the facility, but no significant difference for nitrates. Principal component analysis of the trace metal species identified variations in As, Cu, Pb, and Sb concentrations as being indicative of smelter emissions, consistent with meteorology and the location of the copper smelter. It was concluded that the observed sulphate concentrations confirmed the hypothesis that only a relatively small fraction of the smelter's total SO_2 emissions were deposited within the U.S. sampling network, up to 60 km from the source. Within this distance, from 40 to 80 percent of the deposited excess sulphate was attributable to the smelter emissions. The remainder was assumed to be associated with low-level emissions from fuel oil burning in the local urban area.   *The next event month !*

The mean As concentration for grouped monitoring sites during two of the events sampled (February 14-15 and March 19-21, 1985) was reported as 0.00134 mg/L. This compares well with maximum As concentrations reported in the B.C. precipitation data for the February-March events of about 0.002 mg/L. Although it is tempting to try to compare As and other ion concentrations measured in B.C. with data from the Washington network for the same events,

8-1

But does the trajectory of air parcels give time-shifted co-incidence?

such an analysis is non-trivial because the reported event dates do not generally coincide for the two networks. The dates for rainfall events with measurable quantities of As in B.C. and the dates for the 7 events in Washington are as follows:

Washington, USA	British Columbia, Canada
	January 31 - February 1
	February 4-6
February 6-7	February 9-10
February 11-12	February 13-14
February 14-15	
February 19-20	February 18-23
	March 3-4
March 4-6	
March 19-20	March 19-23

+ Feb 6/7 ?

If one assumes that the periods of most interest would be those in which the rainfall event began in the Seattle-Tacoma region some time before the start of rainfall in BC, the selection of events for detailed analysis would be limited to the periods February 11-14, February 19-23, and March 19-23. In order to properly understand the observed concentrations, it would be necessary to disentangle the complex dynamics of the successive meteorological events accompanying each storm. The comparisons are complicated by the fact that the reported concentrations available in published reports for the Washington network are for station grouped and quality-screened data. Typically, there appear to be considerable gaps in the trace metal composition data in the

8-2

published tables. A copy of the original data was requested for use in future analyses, but such an analysis was considered to be beyond the scope of this study.

8.2 SCAVENGING EFFECTS

There appears to be evidence of changing scavenging rates in the As concentration data for periods of consecutive day rainfall. For example, a series of multiple-day events in February-March, 1985, appear to indicate that there was a decline in As concentrations as a function of the duration of precipitation events. During four such periods, the highest As concentrations, ranging from 0.0014 to 0.0031 mg/L, consistently occurred on the first day of the precipitation period. Concentrations on subsequent dates declined over a 2-3 day period to about 0.0004-0.0006 mg/L. The specific events and concentrations were as follows:

Event Date	Highest As Concen. (mg/L)	Location of Highest Concentration
January 31	0.0025	Ladner
February 1	0.0006	Pender Island
February 4	0.0031	Ladner
February 5	0.0013	Salt Spring Island
February 6	0.0004	Vancouver (A)
February 18	0.0022	Vancouver (A)
February 19	---	None
February 20	0.0017	Vancouver (A)
February 21	0.0009	Vancouver (A)
February 22	0.0004	Abbotsford
February 23	---	None
March 21	0.0014	Salt Spring Island
March 22	0.0004	Cloverdale
March 23	0.0004	Vancouver (A)

8-3

Total precipitation catch does not appear to have been a factor in determining concentrations, although this in itself may not be significant since there are doubts about the usefulness of the precipitation catch data in the database in general. The lower As concentrations appear to be consistent with a washout effect during periods of prolonged precipitation, and it may be worthwhile to examine these periods more closely in future. The effect may however arise from changes in wind speed or emission rates during the event.

Washout of several pollutants from the air mass was also observed for sites in close proximity but having different precipitation catches. In these cases, the site with the higher precipitation catch almost always had the lower concentration. If concentrations could be corrected for these effects, the identification of emission sources for various rain events would be enhanced .

9.0   SUMMARY AND RECOMMENDATIONS

The analysis of precipitation chemistry data for the period October 1984-February 1986 has identified a number of discrepancies and periods of anomalously high ion concentration levels in the data record which cannot be explained in terms of source emissions or physical atmospheric processes. Apart from occasional outliers, which are normal to any such data set, there are distinct time periods in the data record during which changes in concentration levels appear to have occurred at all or most of the monitoring sites at about the same time. Though not an exhaustive list, the following examples are representative:

- from October 1984 to December 13, 1984, the levels of Mo, Co, and Cr, as well as Cd, Ni and V at some sites, appear to be somewhat higher than after December 13. The reduction is sharply defined for Mo and Co from levels above the detection limit (i.e. 0.0002 mg/L) before December 13 to one-half the detection limit (i.e. non-detectable) after December 13.

- from the end of January to the end of March 1985, many of the analytes were reported at higher concentration levels during the two month period prior to closure of the ASARCO smelter. The higher concentrations during this period tend to elevate mean concentration levels when calculating mean concentrations before and after closure. Consequently, conclusions about potential effects of smelter operations which are based on mean concentrations are misleading. Concentrations based on median levels provide a better measure of concentration levels.

- from June to December, 1985, and again in February, 1986, the levels of Mn and Ba were one-to-two orders of magnitude higher than in the previous monitoring period, and levels of Cr increased to a lesser extent coincident with the rise in Mn and Ba levels.

Due to these anomolies, the analysis methodology chosen for this study has been restricted to

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[handwritten: → such as ? ---]

methods which would be relatively insensitive to database errors. However, the influence of these anomolies can not be eliminated entirely and the results of this analysis must be regarded as preliminary.

9.1   SUMMARY STATISTICS

Ion concentration levels were examined with respect to physical location of the monitoring sites in terms of the observed median and 90th percentile concentrations for specific analytes. Note that the Vancouver and Cloverdale sites were not included in the figures, due to their proximity to the Ladner station, for clarity in presentation. The relationships at these sites are expected to *[handwritten: No]* be similar to Ladner. The same applies to the figures including Pender and Salt Spring Island *[handwritten: No]* sites which are in close proximity to the Saanichton site. The results indicate the following *[handwritten: they ignored our comment]* geographical associations:

[handwritten: areas closest to the]

- NO$_3$ and SO$_4$ concentrations are highest in the Georgia Strait area with reduced concentrations both east and west of the strait

- Pb appears to be strongly associated with the Ladner site *[handwritten: !?]*

- Arsenic was primarily associated with Ladner, Saanichton and Abbotsford prior to ASARCO closure

- Cr, Ni and V appear to be widely dispersed throughout the region, but V is highest at Ladner

- NH$_4$ concentrations are highest at Abbotsford

- a possible source of Cu and Zn, as well as Cd, Cr, and As, may be associated with Saanichton

- Mo and Co are closely associated with Texada Island, Wilson Creek, and Agassiz

9-2

- relatively high concentrations of Na and SO_4 are associated with Bamfield and are most likely due to sea salt.

Local emission sources may be responsible for the higher NO_3 (mobile sources) and SO_4 (petroleum refineries and cement manufacturers) at Ladner and Vancouver. The As, and possibly the Pb, at Ladner could have been primarily associated with ASARCO prior to its closure, and the somewhat higher V concentrations at Ladner might be associated with this site's proximity to the petroleum refineries at Cherry Point, WA. The NH_4 concentrations at Abbotsford are almost certainly caused by agricultural sources. The potential sources of As, Cu and Zn (and possibly Cd and Cr) near Saanichton, as well as the potential sources of Mo and Co around Texada Island, Wilson Creek and Agassiz have not been identified. The evaluation of these trace metals would benefit from a review of the data quality and an emission inventory. Therefore, apart from the As, and possibly some of the Pb, V, NO_3 and SO_4, most of the variations in concentration levels observed in the data set are potentially attributable to local emission sources or natural background levels.

9.2   ASARCO CONTRIBUTIONS

Analysis of the average concentration levels of As and XSO_4 indicates that concentrations for these ions decreased substantially after closure of the ASARCO facility.

Using Ladner as a basis for comparison, the huge reduction in As concentrations following closure of the smelter is striking. All but the first measurement after closure were below detectable limits while only one of the events during the smelter's operations had concentrations below the detectable limit. For the monitoring sites as a whole, there were many elevated As concentrations (56 of 191) recorded before closure and very few (2 of 159) recorded after closure. This pattern was most apparent at the Cloverdale and Abbotsford sites with about 80% of the rainfall events having elevated concentrations before closure and none after closure. Other sites such as Saanichton, Salt Spring Island, Pender Island, Ladner, Vancouver and Agassiz all had elevated As concentrations in about 50% of the rainfall events before closure and few after closure. There is the possibility that another source of As exists or existed in the vicinity of

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Saanichton at the time of the observations since 2 of the elevated As observations were recorded at this site after the smelter shutdown (one immediately following and one about a year later).

Based on the 925 mb trajectory analysis, 19 of the 21 elevated As events were associated with SSE, S, SSW or SW airflows. The remaining 2 events were associated with W winds. Forward trajectory analysis for 3 of the events examined, and back trajectories for 3, and possibly a fourth event, tend to corroborate the assessment that the source region for the As concentrations was in the Puget Sound area near the ASARCO smelter. Back trajectories for 2 events were inconsistent with this interpretation, but examination of the synoptic conditions suggested a weak gradient flow up the Puget Sound - Georgia Strait axis, a condition which is not well represented by the 925 mb trajectory analysis.

It seems clear that most of the As in precipitation prior to closure of the smelter can be attributed to the smelter. The assessment of the magnitude of ASARCO's contribution of other pollutants to the precipitation quality in southwestern B.C. is complicated by the fact that the concentrations of most analytes increased in the two month period prior to closure of the facility. The NO_3 concentrations were an exception to this rule and remained relatively similar before and after closure, perhaps reflecting the fact that most of the NO_3 in the region as a whole results from automobile emissions.

9.3   ASSESSMENT OF CONTRIBUTION FROM DEFINED SOURCES

The data for Bamfield provide a suitable basis for evaluating the background contributions from sea salt and global sources. There is a strong linear relationship between Na and Cl, SO_4, Mg, Ca, K, and Sr. Using this relationship, the west-to-east sea water contribution to SO_4 concentrations ranges from about 50% at Bamfield to 10% at Abbotsford, with about 20%-30% at the sites around Georgia Strait. It appears that the source of Na and Cl is almost exclusively sea water. Substantial variations in the concentrations of Ca, Mg, K and Sr could be explained by the removal of the sea water contributions.

The concentration of As has been used as a tracer to indicate the physical location of the

9-4

emissions responsible for concentrations of NO_3 and SO_4 which are not explainable by sea water or background contributions. Based on this crude analysis, it appears that a level of approximately of 0.5 mg/L of the 1.6 mg/L average concentration of SO_4 at Ladner (~ 31%) is attributable to ASARCO emissions. Excluding ASARCO emissions, the contributions are about equally divided among background, sea water, Canadian sources, and U.S. sources. NO_3 appears to have little contribution from sea water, background, or ASARCO emissions. It appears that about 80% of the NO_3 arises from sources south of the border between the two countries.

9.4 RECOMMENDATIONS

There are several major sources of uncertainty which need to be addressed to answer the questions posed in this study, namely:

- data quality,
- location and magnitude of major emission sources or source regions,
- incomplete or inaccurate representation of the low-level dispersion and transformation processes, climatology for the region, and
- insufficient understanding of the scavenging rates for various pollutants in the air mass.

To address these uncertainties, the following measures are recommended:

Data Quality - conduct a review of the data quality, including possibly re-entry of the data using the original raw data and a strict QA/QC protocol for laboratory data. A review of chemical analysis methods also suggests that the minimum detectable limits are an order of magnitude too high suggesting a laboratory quality assurance problem.

Emissions - obtain a copy of the toxic emission inventory database (WEDS) from the Washington Department of Ecology (base year 1985), as well as a copy of the mobile source emission inventory (base year 1988) from the Puget

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Sound Council of Governments.

-   compile a trace metal emission inventory (base year 1985) for southwestern B.C. (An emission inventory is currently being compiled for base year 1990 which might be re-evaluated for 1984-85 production figures. A toxic emission inventory for B.C. is also being considered by Environment Canada.)

what is this? mentioned. First time mentioned

Meteorology -   consider using Schoenberg's (1983) synoptic classification scheme in conjunction with trajectory analysis to categorize dispersion conditions for comparison with rain water concentrations. Also extend the trajectory calculations from 2 days to 4-6 days to examine cyclical flows out over the ocean. ✓

Scavenging -   conduct a detailed evaluation of the four multiple-day rainfall events in the period January 31 - March 23, 1985, to determine whether the observed decreases in arsenic concentrations with duration of precipitation event were attributable to washout effects. An examination of transformation could also be undertaken at the same time. The entire period from January 31 to March 23, 1985, appears to be the most suitable for further analysis of the potential magnitudes of transboundary transport. It has not been possible to examine this period in detail for this study because the summary data for the monitoring studies conducted in the Seattle-Tacoma region just prior to the ASARCO shutdown were difficult to compare with the event data from B.C. However, a copy of the original data file for those events has just been obtained. Furthermore, this is the period for which there is still data on SO_2 emissions from the smelter, as well as some arsenic concentration stack monitoring data. Coupled with the trajectory analysis obtained for this study, this two month period has the most complete set of information available for evaluating potential smelter impacts. Therefore, it offers the most promising period for further

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evaluation. With a shorter period for analysis, it may be possible to concentrate efforts on improving the quality of the rainwater chemistry database in B.C. without a major effort.

The analysis in this study has demonstrated that it is possible to effectively differentiate between some local influences on precipitation quality and some effects of meso-scale transport. Although Dr. Jerry Gerlach of the USGS in Washington discounted the possibility, there remains the intriguing suggestion that long range transport of volcanic emissions from eruptions in Hawaii occurred. In a recently published paper, Whittlestone, et al. (1992) reported on the use of continuous radon monitoring at the Mauna Loa Observatory in Hawaii to evaluate long range transport from Asian sources. The Asian origin of elevated radon measurements was supported by wind trajectories. It would be useful to evaluate the potential for transport of particulate from volcanic eruptions in Hawaii as a source of trace metals in background concentrations in precipitation on the west coast of Vancouver Island.

With respect to quantifying the transboundary flows of pollutants, once emission inventories of sufficient quality exist, a model (such as the AES LRT model) could be used to estimate these flows and the ASARCO observational data used to validate the results.

REFERENCES

Crecelius, E.A., Johnson, C.J. and Hofer, G.C., 1974. *Contamination of Soils Near a Copper Smelter by Arsenic, Antimony and Lead.* Water, Air, and Soil Pollution, 3, 337-342.

Danard, M., 1973. *A Simple Model for Mesoscale Effects of Topoghraphy on Surface Winds.* Monthly Weather Review, Vol. 105, p. 572-581.

Duncan, C., 1985. *Precipitation Composition in Western Washington and the Washington Cascades.* Proceedings of the Acid Rain Symposium, Annual Conference of the Northwest Association for Environmental Studies, University of Victoria, Victoria, B.C.

Faulkner, D.A., 1987. *The Effect of a Major Emitter on the Rain Chemistry of Southwestern British Columbia - a Preliminary Analysis.* Report No. PAES 87-1, Scientific Services Division, Atmospheric Environment Service, Pacific Region, Environment Canada, Vancouver, Canada.

Faulkner, D.A., 1987. *The Effect of a Major Emitter on the Rain Chemistry of Southwestern British Columbia - A Preliminary Analysis (Part II - Data Listings).* Report No. PAE 87-2, Scientific Services Division, Atmospheric Environment Service, Pacific Region, Environment Canada, Vancouver, Canada.

Faulkner, D.A., 1984. *Trajectory Analysis for British Columbia.* Report No. PAES 84-1, Scientific Services Division, Atmospheric Environment Service, Pacific Region, Environment Canada, Vancouver, Canada.

Faulkner, D.A., 1982. *A Wind and Wave Climatology of the Strait of Georgia.* Report No. PAES 82-2, Scientific Services Division, AES Pacific Region, Environment Canada, Vancouver, B.C.

Larson, T.V., Charlson, R.J., Knudson, E.J., Christian, G.D. and Halstead, H., 1975. *The Influence of a Sulphur Dioxide Point Source on the Rain Chemistry of a Single Storm in the Puget Sound Region.* Water, Air and Soil Pollution, 4, 319-328.

Lau, Y.K., 1982. *Precipitation Chemistry.* Air Quality Control Branch, Pollution Control Division, Alberta Environment, Edmonton, AB, 75 pp.

Maykut, N., Beck, R.W., Harrison, H. and Ruby, M., 1985. *Stochastic Rain Model for Computing Dry and Wet Acid Deposition Patterns.* Proceedings of the 1985 APCA Joint Canadian Prairie and Northern Section/Pacific Northwest International Section Annual Meeting, 13-15 November 1985, Calgary, Alberta.

McLaren, R.R., 1985. *Lower Mainland and South Coast B.C. Precipitation Chemistry Data.* Report No. PAES 85-2, Scientific Services Division, Atmospheric Environment Service, Pacific Region, Environment Canada, Vancouver, Canada.

Nikleva, 1985. *Acid Rain Over Southwestern British Columbia.* Proceedings of the Acid Rain Symposium, Annual Conference of the Northwest Association for Environmental Sutdies, University of Victoria, Victoria, B.C.

Pennell, W.T., Hales, J.M. and Scott, B.C., 1985. *Wet Scavenging Processes in Puget Sound Storms.* Proceedings of the Acid Rain Symposium, Annual Conference of the Northwest Association for Environmental Studies, University of Victoria, Victoria, B.C.

Radian Corporation, 1985. *Washington Toxic Air Contaminants Study.* Prepared for Washington State Department of Ecology. Revised Final Report, 1 Feburary.

Schoenberg, S.A., 1983. *Regional Wind Patterns at the Inland Waters of Western Washington and Southwestern British Columbia.* Pacific River Environmental Laboratory, NOAA, Seattle, WA. Technical Memorandum ERL PMEL-43.

Seinfeld, J.H., 1986. *Atmospheric Chemistry and Physics of Air Pollution.* Wiley Interscience, John Wiley & Sons Ltd.

Vong, R.J., 1982. *Puget Sound Transport Winds - Application to Sulfate Wet Deposition.* Master of Science in Engineering Thesis, University of Washington, Seattle, WA.

Vong, R.J., Larson, T.V. and Zoller, W.H., 1986a. *A Multivariate Chemical Classification of Rainwater Samples.* Chemometrics and Intelligent Laboratory Systems.

Vong, R.J., T.V. Larson, W.H. Zoller, D.S. Covert, R.J. Charlson, I. Sweet, R. Peterson, T. Miller, J.F. O'Loughlin, and M.N. Stevenson, 1986b. *Rainwater Chemistry Near an Isolated SO_2 Emission Source.* Symposium on Acid Rain: I. Sources and Atmospheric Processes, R.W. Johnson, ed., Division of Petroleum Chemistry, American Chemical Society, Washington, D.C.

Vong, R.J., T.V. Larson, D.S. Covert, and A.P. Wagoner, 1985. "Measurement and Modelling of Western Washington Precipitation Chemistry", Water, Air, and Soil Pollution, 26, 71-84 (1985).

Vong, R.J., Moseholm, L., Covert, D.S., Sampson, P.D., O'Loughlin, J.F., Stevenson, M.N., Charlson, R.J., Zoller, W.H. and Larson, T.V., 1987. *Statistical Analysis of Spatial and Temporal Variations in Urban Rainwater Chemistry: Changes in pH and Sulphate Associated With the Closure of a Copper Smelter.* Paper Delivered at the International Acid Rain Conference, Lisbon, Portugal.

Washington State Department of Ecology, 1989. *Washington Environment 2010 Report: Human Health and Ecological Risks Associated with Ambient Air Pollution.* Draft Report, 15 June.

Whittlestone, S., Robinson, E and Ryan, S., 1992. *Radon at the Mauna Loa Observatory; Transport from Distant Continents.* Atmospheric Environment, Vol. 26A, No. 2, pp. 251-260.

ANNOTATED BIBLIOGRAPHY

ASARCO, 1985. "Resolutions SO1, SO2, and SO3, Quarterly Report, First Quarter 1985". Report submitted to the Puget Sound Air Pollution Control Agency, Seattle, WA.

> Details of results of the arsenic air monitoring program for the Dec. 14, 1984 to Mar. 7, 1985 period.

Atmospheric Environment Service, Pacific Region, Department of Environment, 1983. "Acid Rain on the West Coast of British Columbia", Presented to the Parliamentary Sub-Committee on Acid Rain, Vancouver, British Columbia.

> Preliminary results of a study to determine the precipitation chemistry of air masses approaching the coast from the Pacific Ocean and to determine the extent of change of these background values due to local emissions.

Brett, A.C., and S.E. Tuller, 1991. "The Autocorrelation of Hourly Wind Speed Observations", J. Appl. Meteor., June, 823-833.

> The autocorrelation of hourly wind speed observations is estimated for seven stations on the west coast of Canada at selected lags ranging from one hour to two months.

Canadian Forestry Services, 1985. "Acid Rain Research and Monitoring Studies in British Columbia, Yukon and the U.S. Pacific Northwest", Canadian Forestry Service, Victoria, B.C., Canada.

> A survey was conducted of research and monitoring studies relating to acid rain either being conducted or planned by agencies in British Columbia and the U.S. Pacific Northwest. Summaries of each program are presented. The survey is incomplete because not all agencies responded.

Core, J.E., N. Maykut, D. Weaver, J. Boylan, and M. Hooper, "PANORAMAS: Regional Haze in the Pacific Northwest States (A Summary of Major Findings From the Pacific Northwest Regional Aerosol Mass Apportionment Study)", 1986.

Presents an overview of the study's technical design and discusses each of the major elements of the Panoramas project. Discusses the extent and frequency of regional haze, regional haze; aerosol characterization; source attribution studies; and regional emission and air mass trajectory studies.

Duncan, L.C., 1988. "Assessment of the Composition of Winter Precipitation at Snoqualmie and Stevens Pass Sites: Winter 1896-1987". Final Report to the Washington State Department of Ecology (1988).

Precipitation samples were collected and analyzed for various quality parameters including SO_4, NO_3, and H concentrations. These data were combined with similar data collected in previous years. Analysis of the combined data set showed no significant change in mean concentrations coincident with the closure of the ASARCO smelter which was located upwind of the sampling sites.

Duncan, L.C., and K. Lillquist, 1986. "The Chemical and Physical Characteristics of Three Cascade Mountain Lakes", Final Report to Washington State Department of Ecology.

Water samples were obtained from three Cascade Mountain Lakes in the summer of 1985. The water chemistry of each sample was determined and compared with data obtained previously.

Faulkner, D.A., "The Effect of a Major Emitter on the Rain Chemistry of Southwestern British Columbia - A Second Look", Presented at the APCA Pacific Northwest International Section Meeting, 9-10 November 1987, Seattle, WA.

> A limited set of precipitation chemistry data collected in the Vancouver region during the 1984-1986 period (encompassing the closure of the ASARCO smelter), was analyzed statistically. The results indicate that significant reductions in arsenic concentrations occurred in certain regions after the closure of the smelter and that concentrations could likely be attributed to the closure.

Harrison, H., 1986. "A Source-Apportionment Study for Sulphate Aerosols and for Total- and Rainborne-Sulphur Flux to the Surface in Western Washington, Southern British Columbia, and Oregon During the Summer of 1984", A Report in Support of The Pacific Northwest Regional Aerosol Mass Apportionment Study (1986).

> A stochastic dispersion model is used to estimate the fractional contributions of six major sources of sulphur emissions in Western Washington, Southern British Columbia, and Northern Oregon including the ASARCO smelter.

Harrison, H., N. Maykut, and D. Weaver, 1986. "PANORAMAS: Quantification and Characterization of Regional Haze". Transactions of the APCA International Specialty Conference on Visibility Protection: Research and Policy Aspects, Grand Teton National Park, September 1986.

> Source-receptor relationships are quantified and the geographical extent and frequency of regional haze are assessed within the Pacific Northwest.

Hubbard, L.T., 1976. "Memo to File Re: ASARCO Smelter (Data Provided by the Puget Sound Air Pollution Control Authority)", (1976).

> Emission data on the ASARCO smelter including particulates. Also includes

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some physical characteristics of the stack and surrounding area.

Kotturi, M.S., B. Thomson, and S. Smythe, 1991. "High Elevation Fog Chemistry in Southwestern British Columbia", Presented at the 84th Annual Meeting and Exhibition of the Air and Waste Management Association, Vancouver, British Columbia.

A study of fog chemistry was conducted at Mt. Seymour, Vancouver to determine the concentration of various inorganic chemicals in fog at higher elevations. Source-receptor relationships were also investigated using local meteorological data. Generally, the concentration of $SO_4^=$ and NO_3 were found to be highest when the air mass trajectories were from the south, southwest and west passing over polluted point and urban sources.

Manna, B.B., and M.S. Kotturi, 1985. "Acid Precipitation: Presently Observed Situation in British Columbia", Presented to a Workshop on Mesoscale Monitoring and Modelling in Western Canada, Victoria, British Columbia (1985).

Major point sources of SO_2 within B.C. are identified as well as transboundary contributors. Results of monitoring programs are summarized and discussed.

McLaren, R.R., 1982. "Lower Mainland Precipitation Chemistry Data", Report No. PAES 82-4, Scientific Services Division, Atmospheric Environment Service, Pacific Region, Environment Canada, Vancouver Canada (1982).

Presents the precipitation chemistry data collected from January to April, 1982, by the Lower Mainland Sampling Program.

AB-4

Moseholm, L., 1986. "Analysis of Variance Components for pH, Excess Sulphate, and Nitrate in Western Washington Rainwater". A Master's thesis submitted to the University of Washington.

Rainwater samples were collected upwind and downwind of the ASARCO smelter before and after closure in 1985. An extensive data evaluation procedure and variance component analysis of measurements of pH, excess sulphate and nitrate showed that the smelter had a pronounced effect on the pH and excess sulphate in rainwater downwind.

Sirois, A., 1991. "The Relationship between Mean and Standard Deviation in Precipitation Chemistry Measurements across Eastern North America", Atmospheric Environment, Vol. 25A, No.2, 329-340.

A relationship between the mean and standard deviation of concentration and deposition of the major ions in precipitation is established for daily, weekly, and monthly sampled data. The same linear relationship is also shown to exist for seasonal precipitation-weighted-mean concentration and deposition of both sulphate and nitrate.

State of Oregon Department of Environmental Quality, 1986. "Pacific Northwest Regional Aerosol Mass Apportionment Study (PANORAMAS)", Vol. 5, Aerosol Chemistry (1986).

Discusses the aerosol chemistry aspects of the Panoramas regional haze study. Includes detailed data on aerosol chemistry for various locations within Oregon, Washington, and Idaho.

Vong, R.J. 1985. "Simultaneous Observations of Rainwater and Aerosol Chemistry at a Remote Mid-Latitude Site", Doctoral Dissertation Presented to the University of Washington (1985).

Vong, R.J., T.V. Larson, W.H. Zoller, D.S. Covert, R.J. Charlson, I.R. Sweet, R.E. Peterson, T.L. Miller, J.F. O'Loughlin, and M.N. Stevenson, 1986. "Rainwater Source - Receptor Relationships Near an Isolated SO_2 Emission Source", Presented at the Symposium on Acid Rain before the Division of Petroleum Chemistry of the American Chemical Society, New York, NY (1986).

Discusses regional rainwater chemistry and other measurements taken prior to the shutdown of the ASARCO smelter. Estimates of the impact of smelter emissions on mesoscale rainwater composition are also made.

APPENDIX A

REVIEW OF QUALITY AND EXTENT OF DATA USED

APPENDIX A: REVIEW OF QUALITY AND EXTENT OF DATA USED

The database supplied by the AES for this project consisted of event samples beginning in October 1984 and ending on 6 February 1986. Concentrations of 24 analytes are reported for 13 sites during this period. The data was reviewed to determine the extent of the data for each site, inconsistencies with respect to dates measured, and quality with respect to the concentrations reported. It appears that there are errors resulting from data management which could be removed by a thorough review of the data. SENES is confident that the quality of the data could be improved by this process (which is beyond the scope of this project).

A.1   Sites and Dates of Observations

Table A.1 summarizes the numbers of observations made at each site and whether the observation was made before or after the closure of the ASARCO smelter. In all, there are 13 sites with numbers of observations ranging from 24 to 39. There are 405 observations in total (combinations of sites and dates) in the data set. Since the ASARCO smelter was a source of many pollutants the number of observations before and after the closure on 24 March 1985 were determined. The observations are about equally divided between periods during the ASARCO operation and post the ASARCO operation (197 and 208 observations, respectively). Most sampling sites have about equal numbers of observations before and after the smelter closure. The exceptions are Vancouver (A) with more observations being made after closure, and Abbotsford with more being made before closure.

The number of sites with observations on the same day is presented in Table A.2. During the complete period of record, there was only one of the total of 73 days on which observations were made at all 13 sites. While more days of data (44) occurred after the smelter closed, many of these days have fewer sites reporting compared to the period prior to smelter closure.

A.2   Concentration Levels Observed

The individual observations consist of measurements of precipitation and pH as well as

Table A.1

NUMBER OF MEASUREMENTS BY SAMPLING SITE
AND PERIOD OF SMELTER OPERATION
FOR THE PERIOD OF RECORD

SITE	TOTAL NUMBER OF OBSERVATIONS	OBSERVATIONS WHILE SMELTER OPERATING*	OBSERVATIONS AFTER SMELTER CLOSED*
Abbotsford	24	15	9
Agassiz	31	16	15
Bamfield	36	15	21
Cloverdale	34	17	17
Ladner	39	18	21
Pender Island	30	15	15
Port Renfrew	33	17	16
Saanichton	27	12	15
Saltspring	34	19	15
Sooke	31	15	16
Texada Island	31	17	14
Vancouver (A)	27	9	18
Wilson Creek	28	12	16
Total Measurements	405	197	208

Note:

Measurements span period from 5 October 1984 - 3 February 1986.

* ASARCO smelter closed 24 March 1985.

Table A.2

NUMBER OF DAYS IN THE PRECIPITATION RECORD

Number of Sites Reporting on Same Date	Total Days in Period of Record	Number of Days While Asarco Operating	Number of Days After Asarco Closing
1	17	5	12
2	8	4	4
3	7	0	7
4	4	1	3
5	3	1	2
6	2	1	1
7	4	1	3
8	4	3	1
9	7	2	5
10	8	5	3
11	4	3	1
12	4	2	2
13	1	1	0
Total	73	29	44

concentrations of 23 ions and metals. Concentrations of Na, Mg, Ca, and K are reported twice in the data set since the laboratory measured these concentrations in both a major ion test and a trace metal test. For these four ions, the concentrations used in further statistical analysis are those obtained from the major ion test. Though not explored further, it was apparent that substantial variability exists in concentrations reported by the two tests for the common analytes. This variability should be studied before further analysis of the data is undertaken.

The concentrations of many of the analytes were frequently reported to be of the same low value. This is illustrated in Table A.3, where the three lowest reported concentrations for each analyte are listed along with the number of times each of those concentrations were reported. This serves to identify analytes with frequent concentrations below detection limits or which exhibit a discrete nature (many concentrations at the same value).

It is known that observations that were below the method detection limit (MDL) were assigned a numerical value of half the detection limit to facilitate analysis. This substantially increases the estimates of mean concentration for those analytes which have the majority of concentrations below the detection limit. This occurs because this substitution method generally overestimates the true concentration of the below detection limit observations. The median becomes affected by the substitution method when more than half of the observations are below the detection limit. If these statistics are of importance, methods of estimating the true concentration of the observations below the MDL should be implemented in future studies using a probaiblity distribution function fitted to the non-censored data.

From Table A.3, it is apparent that the detection limit for many of the analytes is 0.0002 mg/L. Trace metals such as Cd, Co, Cr, Mo, Se, and V all have substantial numbers of observations equal to 0.0001 and 0.0002 mg/L. Given the geographical separation of the sampling sites, it would not be surprising if all observations of some of these analytes were below the detection limit at some sites. For example, only 13 of 350 total observations of Se concentrations are at or above the detection limit of 0.0002 mg/L. Only Ladner, Cloverdale, and Pender Island sites report concentrations of Se above 0.0002 mg/L.

A-2

Table A.3

FREQUENCY OF LOWEST CONCENTRATIONS BY ANALYTE

Analyte	Total Number of Obs	Lowest Conc	Number of Times Lowest Reported	Second Lowest Conc	Number of Times 2nd Lowest Reported	Third Lowest Conc	Number of Times 3rd Lowest Reported	Comments on Data
Arsenic	350	0.0001	244	0.0002	48	0.0003	18	Detection Limits, Discrete Data
Barium	405	0.0001	29	0.0002	23	0.0003	31	Discrete Data
Calcium	405	0.010	9	0.020	30	0.022	2	
Cadmium	405	0.0001	305	0.0002	47	0.0003	25	Detection Limits, Discrete Data
Chloride	405	0.005	6	0.050	1	0.060	4	
Cobalt	405	0.0001	313	0.0002	6	0.0003	50	Detection Limits, Discrete Data
Chromium	405	0.0001	110	0.0002	55	0.0003	43	Detection Limits, Discrete Data
Copper	405	0.0001	13	0.0002	7	0.0003	3	
Iron	405	0.0007	1	0.0010	1	0.0011	5	
Potassium	405	0.0100	33	0.0200	61	0.0300	60	Discrete Data
Magnesium	405	0.0050	33	0.0100	43	0.0200	58	Discrete Data
Manganese	405	0.0001	1	0.0002	12	0.0003	18	
Molybdenum	405	0.0001	311	0.0002	22	0.0003	27	Detection Limits, Discrete Data
Sodium	405	0.0100	3	0.0200	3	0.0300	9	
Ammonium	405	0.0000	12	0.0005	22	0.0010	5	
Nickel	405	0.0001	53	0.0002	26	0.0003	49	Discrete Data
Nitrate	405	0.0050	44	0.0200	11	0.0300	19	Discrete Data
Lead	405	0.0001	3	0.0002	1	0.0003	4	
pH	404	3.8700	1	4.0400	2	4.0800	1	
Selenium	350	0.0001	337	0.0002	9	0.0004	1	Detection Limits, Discrete Data
Sulphate	405	0.0050	1	0.1000	1	0.1100	2	
Strontium	405	0.0001	33	0.0002	24	0.0003	47	Discrete Data
Vanadium	405	0.0001	172	0.0002	53	0.0003	41	Detection Limits, Discrete Data
Zinc	405	0.0001	6	0.0002	1	0.0003	1	

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Another artifact in the data, resulting from the precision of the laboratory measurement process, is a discrete nature at low concentrations. The discrete nature appears when many observations have the same concentration. This occurs when the concentrations approach the quantification limits of the laboratory test. Besides the analytes with high numbers of observations at or below detection limits, many observations for Ba, K, Mg, Ni, NO_3, and Sr were reported at these lower concentrations.

The discrete nature of much of the data limits the use of multivariate cluster analyses since cluster formation will tend to group together observations with discrete concentrations. In addition, Se and As concentrations are reported for only 350 of the 405 observations. The remainder of the observations are complete with the exception of pH which is missing one measurement in 405 observations.

A.3 DATA QUALITY

There are a large number of measurements within the data set. Not including the repeated measurements of Na, Mg, Ca, and K, there are a total of 10,014 measurements. With such a large data set, one should expect errors in the data. For a rigorous analysis of this data, a comprehensive review of the data quality is warranted. Several automatic outlier routines exist, but these should be used cautiously. Often, an apparent error will turn out to be a true value which provides a substantial amount of information. The data has not been checked with respect to quality because of budget constraints. However, for the most part, the statistical techniques employed in this study have been selected because they are insensitive to errors in data.

While it is difficult to determine the presence of contamination or incorrect recording of the site or date of the observation, some obvious errors were found during the analyses conducted for this study. Figure A.1 shows a time plot of manganese concentrations at Bamfield as a function of date. It is apparent that there are clumps in the concentration data for specific time periods. A similar sudden increase in Mn and Ba (and to a lesser extent Cr) was observed to occur at about the same time (June 1985 to December 1985) at all of the other monitoring sites. The primary known sources of manganese in the Puget Sound-Georgia Strait region are slash burning, wood,

ASSOCIATION BETWEEN MANGANESE CONCENTRATIONS (mg/L) AND DATE IN RAIN WATER COLLECTED AT BAMFIELD

Time Plot of Analyte Concentration
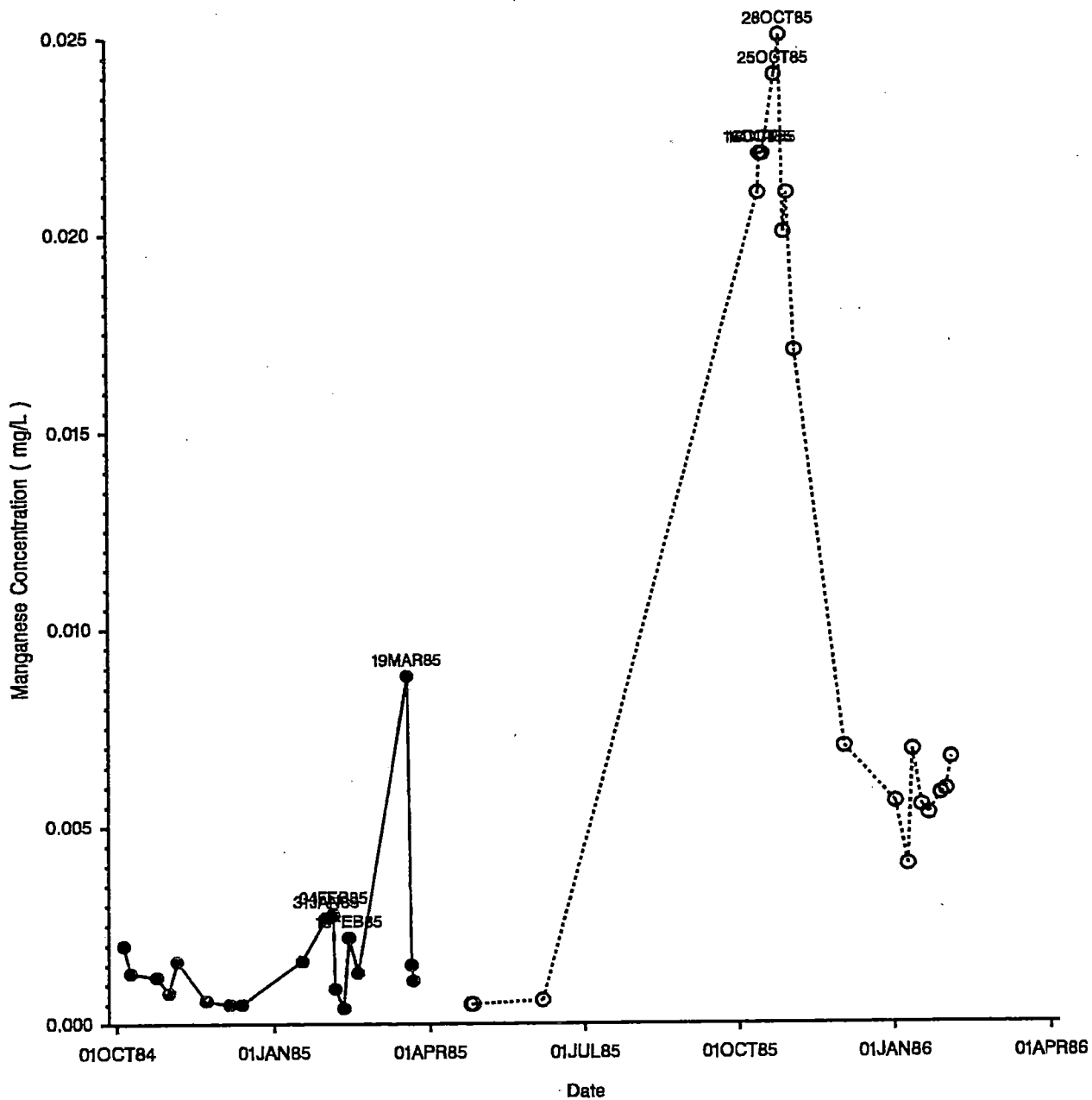
ASARCO Smelter ●─●─● Operating   ⊙··⊙··⊙ Closed

coal and oil fired industrial boilers, and residential woodstoves and fireplaces. Thus, the sources are widespread throughout the region, and it is difficult to imagine a physical process which would result in a sudden increase of one-to-two orders of magnitude spanning three seasons at all 13 monitoring sites. The possibility of long range transport from sources outside the region was at first considered as a potential explanation in view of the fact that the ratio of Mn to Ba in the precipitation data was similar to the ratio of these elements in volcanic dust from eruptions of El Chichon, Mexico (and possibly Pu'u O'O in Hawaii; Dr. K. Hickson, Pacific Geoscience Centre, Vancouver, B.C., personal communication). However, Dr. Jerry Gerlach, USGS in Washington State (personal communication) strongly discounted this possibility. Furthermore, it seems highly unlikely that such a sudden major increase in Mn and Ba would not be accompanied by similar increases in other trace elements.

Therefore, there remains a strong suspicion that these increases in concentrations may be due to analytical errors, changes in analytical techniques, or data entry errors in database compilations. There are, for instance, other curious patterns in the trace metal data. All of the monitoring sites reported lower concentrations of Co, Mo and Cr (and in some cases V, Cd and Ni) after December 13, 1984. In the case of Co and Mo, the levels went from slightly above detection limits (i.e. 0.0002 mg/L) to below detection limits (i.e. 0.0001 mg/L). There are no known major point sources of Co and Mo in the Puget Sound-Georgia Strait region, and the most likely sources are wood burning and crustal material. The higher values in the earlier part of the data record may be real, or they may be artifacts of the analytical procedures used at the laboratory. The method of reporting below MDL concentrations may also have changed at the laboratory or at the data base management stage.

A third period of anomalous concentrations in the database is the two month period of February-March, 1985, prior to closure of the ASARCO smelter. Concentration levels for most of the major ion and trace metal species are high across most monitoring sites. This suggests that atypical meterological conditions or increased production at ASARCO during this period may have contributed to the general increase in concentrations.

There may be other systematic anomalies in the data which are yet undiscovered. Non-systematic

errors such as sample contamination or incorrect recording of concentration are difficult to discover and interpret and require specific system knowledge to first identify and then resolve discrepancies. For example, if it is known that a high correlation with another analyte should exist, discrepancies from this relationship can be investigated.

Figure A.2 shows a scatter plot of magnesium concentration against sodium concentration which exhibits a strong linear relationship between the two ions. This would be expected from a coastal site such as Bamfield. Those data points far removed from the line are questionable and warrant further investigation as potentially erroneous results. One should not automatically consider these concentrations to be in error, since they may have a logical physical explanation which serves to illuminate the understanding of the process under investigation. However, on the basis of available information, there is a strong suspicion that these are errors in the database.

Additional data discrepancies are discussed in the individual analyses throughout the report. Possibly quality checked reentry of the original data would remove many of the discrepancies. This could dramatically reduce the effort required to address the remaining discrepancies of the data set and improve future analyses.

ASSOCIATION BETWEEN MAGNESIUM AND SODIUM CONCENTRATIONS (mg/L)
IN RAIN WATER COLLECTED AT BAMFIELD

Association between Analytes
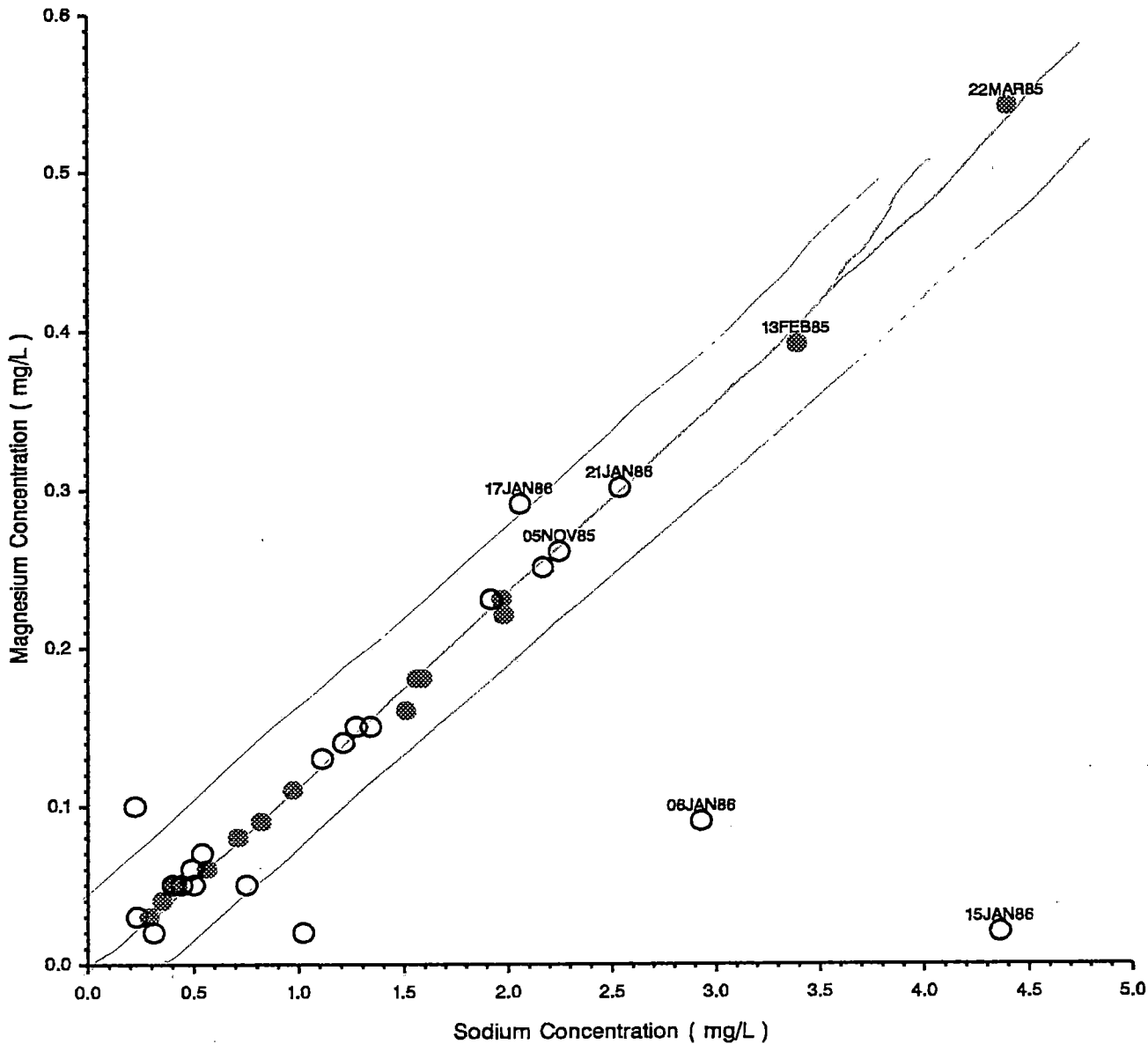
Legend   ● ● ●   Before Shut–down   O O O   After Shut–down

APPENDIX B

MEDIAN CONCENTRATION TABLES

CONCENTRATION OF MAJOR IONS

Median pH (pH units)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	5.41	5.58	5.56
Abbotsford	5.91	6.08	5.97 ***
Cloverdale	5.11	5.39	5.22
Ladner	4.56	5.04	4.82
Vancouver	4.27 *	4.76	4.74 **
Wilson Creek	4.66	4.88	4.82
Texada Island	4.82	5.08	5.06
Pender Island	4.80	4.80	4.80
Salt Spring Island	4.79	5.03	4.89
Saanichton	4.63	4.95	4.87
Sooke	5.07	5.16	5.12
Port Renfrew	5.12	5.05	5.05
Bamfield	5.11	5.20	5.17
Lowest Median (Site)	4.27 Vancouver *	4.76 Vancouver	4.74 Vancouver **
Highest Median (Site)	5.91 Abbotsford	6.08 Abbotsford	5.97 Abbotsford ***

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Sulphate Concentrations(mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.26	0.32	0.27
Abbotsford	0.83	0.48	0.61 ***
Cloverdale	1.09	0.88	0.95
Ladner	1.37	0.75	0.95
Vancouver	1.92 *	0.86	0.89 **
Wilson Creek	0.88	0.69	0.72
Texada Island	0.65	0.54	0.59
Pender Island	0.75	0.85	0.80
Salt Spring Island	0.97	0.72	0.73
Saanichton	1.05	0.74	0.81
Sooke	0.44	0.58	0.48
Port Renfrew	0.42	0.46	0.46
Bamfield	0.56	0.58	0.57
Lowest Median (Site)	0.26 Agassiz	0.32 Agassiz	0.27 Agassiz
Highest Median (Site)	1.92 Vancouver *	0.88 Cloverdale	0.95 Cloverdale

Notes:

Vancouver only has measurements beginning 25 January 1985.
*　　　Vancouver median before closure will be biased high.
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***　　Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Excess Sulphate Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.24	0.32	0.26
Abbotsford	0.65	0.41	0.60 ***
Cloverdale	1.01	0.68	0.90
Ladner	1.08	0.60	0.80
Vancouver	1.73 *	0.78	0.82 **
Wilson Creek	0.73	0.49	0.57
Texada Island	0.61	0.43	0.51
Pender Island	0.54	0.64	0.60
Salt Spring Island	0.66	0.62	0.62
Saanichton	0.67	0.50	0.60
Sooke	0.27	0.31	0.30
Port Renfrew	0.30	0.26	0.27
Bamfield	0.31	0.26	0.30
Lowest Median (Site)	0.24 Agassiz	0.26 Multiple Sites	0.26 Agassiz
Highest Median (Site)	1.73 Vancouver *	0.78 Vancouver	0.90 Cloverdale

Notes:

Vancouver only has measurements beginning 25 January 1985.
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**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Nitrate Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.07	0.11	0.08
Abbotsford	0.13	0.11	0.13 ***
Cloverdale	0.17	0.14	0.16
Ladner	0.18	0.17	0.17
Vancouver	0.61 *	0.13	0.14 **
Wilson Creek	0.14	0.12	0.13
Texada Island	0.14	0.09	0.12
Pender Island	0.10	0.14	0.13
Salt Spring Island	0.07	0.16	0.13
Saanichton	0.10	0.13	0.12
Sooke	0.06	0.04	0.05
Port Renfrew	0.02	0.06	0.05
Bamfield	0.01	0.04	0.04
Lowest Median (Site)	0.01 Bamfield	0.04 Bamfield	0.04 Bamfield
Highest Median (Site)	0.61 Vancouver *	0.17 Ladner	0.17 Ladner

Notes:

Vancouver only has measurements beginning 25 January 1985.
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**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Ammonium Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.186	0.143	0.145
Abbotsford	0.451	0.347	0.404 ***
Cloverdale	0.254	0.172	0.183
Ladner	0.139	0.155	0.148
Vancouver	0.283 *	0.069	0.070 **
Wilson Creek	0.023	0.043	0.030
Texada Island	0.008	0.016	0.012
Pender Island	0.031	0.059	0.055
Salt Spring Island	0.069	0.058	0.069
Saanichton	0.023	0.060	0.043
Sooke	0.001	0.013	0.010
Port Renfrew	0.001	0.012	0.006
Bamfield	0.030	0.010	0.011
Lowest Median (Site)	0.001 Multiple Sites	0.010 Bamfield	0.006 Port Renfrew
Highest Median (Site)	0.451 Abbotsford	0.347 Abbotsford	0.404 *** Abbotsford

Notes:

Vancouver only has measurements beginning 25 January 1985.
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**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Table B.2

CONCENTRATION OF IONS ASSOCIATED WITH SEA WATER

Median Calcium Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.03	0.03	0.03
Abbotsford	0.03	0.03	0.03 ***
Cloverdale	0.12	0.17	0.14
Ladner	0.12	0.09	0.10
Vancouver	0.19 *	0.10	0.10 **
Wilson Creek	0.05	0.07	0.06
Texada Island	0.06	0.23	0.08
Pender Island	0.04	0.05	0.04
Salt Spring Island	0.10	0.06	0.06
Saanichton	0.08	0.08	0.08
Sooke	0.04	0.06	0.05
Port Renfrew	0.04	0.06	0.05
Bamfield	0.06	0.06	0.06
Lowest Median (Site)	0.03 Multiple Sites	0.03 Multiple Sites	0.03 Multiple Sites
Highest Median (Site)	0.19 Vancouver *	0.23 Texada Island	0.14 Cloverdale

Notes:

Vancouver only has measurements beginning 25 January 1985.
* Vancouver median before closure will be biased high.
** Vancouver median overall will be biased towards later time period
*** Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Chloride Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.01	0.19	0.13
Abbotsford	0.24	0.24	0.24 ***
Cloverdale	0.58	0.45	0.51
Ladner	1.13	0.88	1.02
Vancouver	1.17 *	0.35	0.54 **
Wilson Creek	0.46	0.67	0.55
Texada Island	0.45	0.29	0.34
Pender Island	0.87	1.38	1.04
Salt Spring Island	0.52	0.59	0.59
Saanichton	1.45	1.27	1.43
Sooke	0.46	1.24	0.89
Port Renfrew	0.65	1.40	1.26
Bamfield	1.50	1.90	1.70
Lowest Median (Site)	0.01 Agassiz	0.19 Agassiz	0.13 Agassiz
Highest Median (Site)	1.50 Bamfield	1.90 Bamfield	1.70 Bamfield

Notes:

Vancouver only has measurements beginning 25 January 1985.
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**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Potassium Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.03	0.02	0.02
Abbotsford	0.06	0.05	0.05 ***
Cloverdale	0.05	0.08	0.07
Ladner	0.05	0.04	0.04
Vancouver	0.07 *	0.04	0.04 **
Wilson Creek	0.03	0.04	0.04
Texada Island	0.02	0.03	0.02
Pender Island	0.03	0.04	0.03
Salt Spring Island	0.04	0.05	0.05
Saanichton	0.06	0.05	0.06
Sooke	0.02	0.04	0.03
Port Renfrew	0.07	0.05	0.05
Bamfield	0.05	0.05	0.05
Lowest Median (Site)	0.02 Sooke	0.02 Agassiz	0.02 Multiple Sites
Highest Median (Site)	0.07 Vancouver *	0.08 Cloverdale	0.07 Cloverdale

Notes:

Vancouver only has measurements beginning 25 January 1985.
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**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Magnesium Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.01	0.01	0.01
Abbotsford	0.01	0.01	0.01 ***
Cloverdale	0.04	0.04	0.04
Ladner	0.07	0.06	0.06
Vancouver	0.06 *	0.03	0.03 **
Wilson Creek	0.02	0.07	0.04
Texada Island	0.02	0.03	0.02
Pender Island	0.07	0.09	0.08
Salt Spring Island	0.04	0.02	0.03
Saanichton	0.09	0.04	0.06
Sooke	0.04	0.05	0.04
Port Renfrew	0.04	0.10	0.08
Bamfield	0.09	0.09	0.09
Lowest Median (Site)	0.01 Multiple Sites	0.01 Multiple Sites	0.01 Mulitple Sites
Highest Media (Site)	0.09 Multiple Sites	0.10 Port Renfrew	0.09 Bamfield

Notes:

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***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Sodium Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.04	0.10	0.06
Abbotsford	0.17	0.10	0.11 ***
Cloverdale	0.36	0.24	0.27
Ladner	0.65	0.45	0.57
Vancouver	0.72 *	0.19	0.29 **
Wilson Creek	0.26	0.44	0.30
Texada Island	0.24	0.16	0.17
Pender Island	0.48	0.74	0.57
Salt Spring Island	0.29	0.36	0.32
Saanichton	0.78	0.68	0.78
Sooke	0.26	0.73	0.48
Port Renfrew	0.35	0.77	0.71
Bamfield	0.82	1.11	1.06
Lowest Median (Site)	0.04 Agassiz	0.10 Multiple Sites	0.06 Agassiz
Highest Median (Site)	0.82 Bamfield	1.11 Bamfield	1.06 Bamfield

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Strontium Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0001 <MDL	0.0003	0.0001 <MDL
Abbotsford	0.0004	0.0005	0.0005 ***
Cloverdale	0.0006	0.0009	0.0008
Ladner	0.0009	0.0006	0.0007
Vancouver	0.0010 *	0.0006	0.0007 **
Wilson Creek	0.0004	0.0006	0.0005
Texada Island	0.0003	0.0007	0.0004
Pender Island	0.0005	0.0006	0.0005
Salt Spring Island	0.0005	0.0007	0.0006
Saanichton	0.0008	0.0009	0.0009
Sooke	0.0004	0.0007	0.0005
Port Renfrew	0.0004	0.0008	0.0007
Bamfield	0.0006	0.0010	0.0010
Lowest Median (Site)	0.0001 <MDL Agassiz	0.0003 Agassiz	0.0001 <MDL Agassiz
Highest Median (Site)	0.0010 Vancouver *	0.0010 Bamfield	0.0010 Bamfield

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Table B.3

CONCENTRATION OF MAJOR METALS

Median Barium Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0005	0.0005	0.0005
Abbotsford	0.0007	0.0008	0.0008 ***
Cloverdale	0.0015	0.0016	0.0016
Ladner	0.0011	0.0006	0.0008
Vancouver	0.0034 *	0.0011	0.0012 **
Wilson Creek	0.0005	0.0007	0.0005
Texada Island	0.0005	0.0005	0.0005
Pender Island	0.0008	0.0007	0.0007
Salt Spring Island	0.0006	0.0014	0.0010
Saanichton	0.0007	0.0026	0.0012
Sooke	0.0010	0.0005	0.0009
Port Renfrew	0.0005	0.0105	0.0005
Bamfield	0.0003	0.0003	0.0003
Lowest Median (Site)	0.0003 Bamfield	0.0003 Bamfield	0.0003 Bamfield
Highest Median (Site)	0.0034 Vancouver *	0.0105 Port Renfrew	0.0016 Cloverdale

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Chromium Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0006	0.0004	0.0006
Abbotsford	0.0006	0.0006	0.0006 ***
Cloverdale	0.0005	0.0006	0.0005
Ladner	0.0006	0.0004	0.0006
Vancouver	0.0003 *	0.0003	0.0003 **
Wilson Creek	0.0006	0.0002	0.0005
Texada Island	0.0006	0.0003	0.0005
Pender Island	0.0005	0.0002	0.0005
Salt Spring Island	0.0005	0.0006	0.0006
Saanichton	0.0007	0.0003	0.0007
Sooke	0.0005	0.0003	0.0005
Port Renfrew	0.0006	0.0006	0.0006
Bamfield	0.0006	0.0003	0.0006
Lowest Median (Site)	0.0003 Vancouver *	0.0002 Multiple Sites	0.0003 Vancouver **
Highest Median (Site)	0.0007 Saanichton	0.0006 Multiple Sites	0.0007 Saanichton

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Copper Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0017	0.0012	0.0014
Abbotsford	0.0017	0.0012	0.0016 ***
Cloverdale	0.0016	0.0015	0.0016
Ladner	0.0017	0.0013	0.0016
Vancouver	0.0123 *	0.0016	0.0016 **
Wilson Creek	0.0032	0.0017	0.0027
Texada Island	0.0033	0.0015	0.0019
Pender Island	0.0027	0.0140	0.0040
Salt Spring Island	0.0029	0.0020	0.0023
Saanichton	0.0082	0.0040	0.0058
Sooke	0.0019	0.0021	0.0020
Port Renfrew	0.0016	0.0015	0.0015
Bamfield	0.0021	0.0013	0.0019
Lowest Median (Site)	0.0016 Multiple Sites	0.0012 Multiple Sites	0.0014 Agassiz
Highest Median (Site)	0.0123 Vancouver *	0.0140 Pender Island	0.0058 Saanichton

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Iron Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0054	0.0092	0.0080
Abbotsford	0.0074	0.0110	0.0078 ***
Cloverdale	0.0100	0.0190	0.0185
Ladner	0.0135	0.0110	0.0120
Vancouver	0.0475 *	0.0180	0.0180 **
Wilson Creek	0.0096	0.0105	0.0100
Texada Island	0.0043	0.0100	0.0065
Pender Island	0.0064	0.0110	0.0099
Salt Spring Island	0.0110	0.0120	0.0120
Saanichton	0.0160	0.0165	0.0160
Sooke	0.0092	0.0110	0.0093
Port Renfrew	0.0026	0.0073	0.0049
Bamfield	0.0037	0.0061	0.0060
Lowest Median (Site)	0.0026 Port Renfrew	0.0061 Bamfield	0.0049 Port Renfrew
Highest Median (Site)	0.0475 Vancouver *	0.0190 Cloverdale	0.0185 Cloverdale

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Lead Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0024	0.0012	0.0020
Abbotsford	0.0027	0.0013	0.0025 ***
Cloverdale	0.0044	0.0035	0.0037
Ladner	0.0067	0.0037	0.0046
Vancouver	0.0389 *	0.0070	0.0086 **
Wilson Creek	0.0033	0.0016	0.0027
Texada Island	0.0032	0.0020	0.0028
Pender Island	0.0023	0.0021	0.0023
Salt Spring Island	0.0030	0.0023	0.0026
Saanichton	0.0046	0.0044	0.0046
Sooke	0.0038	0.0021	0.0025
Port Renfrew	0.0020	0.0017	0.0018
Bamfield	0.0019	0.0011	0.0012
Lowest Median (Site)	0.0019 Bamfield	0.0011 Bamfield	0.0012 Bamfield
Highest Median (Site)	0.0389 Vancouver *	0.0070 Vancouver	0.0086 Vancouver **

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Manganese Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0004	0.0140	0.0046
Abbotsford	0.0009	0.0075	0.0027 ***
Cloverdale	0.0018	0.0155	0.0077
Ladner	0.0012	0.0120	0.0055
Vancouver	0.0043 *	0.0078	0.0078 **
Wilson Creek	0.0008	0.0065	0.0047
Texada Island	0.0006	0.0059	0.0054
Pender Island	0.0008	0.0078	0.0054
Salt Spring Island	0.0012	0.0210	0.0057
Saanichton	0.0009	0.0078	0.0054
Sooke	0.0004	0.0077	0.0049
Port Renfrew	0.0004	0.0180	0.0052
Bamfield	0.0004	0.0063	0.0051
Lowest Median (Site)	0.0004 Multiple Sites	0.0059 Texada Island	0.0027 *** Abbotsford
Highest Median (Site)	0.0043 Vancouver *	0.0210 Salt Spring Island	0.0078 Vancouver **

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Nickel Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0011	0.0003	0.0009
Abbotsford	0.0011	0.0004	0.0009 ***
Cloverdale	0.0010	0.0005	0.0007
Ladner	0.0010	0.0003	0.0005
Vancouver	0.0015 *	0.0004	0.0004 **
Wilson Creek	0.0010	0.0003	0.0006
Texada Island	0.0010	0.0004	0.0005
Pender Island	0.0010	0.0004	0.0005
Salt Spring Island	0.0009	0.0006	0.0006
Saanichton	0.0011	0.0005	0.0007
Sooke	0.0007	0.0003	0.0004
Port Renfrew	0.0009	0.0005	0.0006
Bamfield	0.0009	0.0003	0.0004
Lowest Median (Site)	0.0007 Sooke	0.0003 Multiple Sites	0.0004 Multiple Sites
Highest Median (Site)	0.0015 Vancouver *	0.0006 Salt Spring Island	0.0009 Multiple Sites

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Zinc Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0019	0.0017	0.0017
Abbotsford	0.0035	0.0019	0.0027 ***
Cloverdale	0.0034	0.0026	0.0029
Ladner	0.0037	0.0015	0.0017
Vancouver	0.0178 *	0.0051	0.0052 **
Wilson Creek	0.0052	0.0018	0.0025
Texada Island	0.0036	0.0020	0.0027
Pender Island	0.0032	0.0170	0.0066
Salt Spring Island	0.0049	0.0047	0.0049
Saanichton	0.0096	0.0135	0.0110
Sooke	0.0015	0.0017	0.0016
Port Renfrew	0.0021	0.0012	0.0013
Bamfield	0.0022	0.0009	0.0014
Lowest Median (Site)	0.0015 Sooke	0.0009 Bamfield	0.0013 Port Renfrew
Highest Median (Site)	0.0178 Vancouver *	0.0170 Pender Island	0.0110 Saanichton

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Table B.4

CONCENTRATION OF TRACE METALS

Median Arsenic Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0002	0.0001 <MDL	0.0001 <MDL
Abbotsford	0.0005	0.0001 <MDL	0.0002 ***
Cloverdale	0.0004	0.0001 <MDL	0.0002
Ladner	0.0005	0.0001 <MDL	0.0001 <MDL
Vancouver	0.0004 *	0.0001 <MDL	0.0001 <MDL
Wilson Creek	0.0002	0.0001 <MDL	0.0001 <MDL
Texada Island	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Pender Island	0.0002	0.0001 <MDL	0.0001 <MDL
Salt Spring Island	0.0002	0.0001 <MDL	0.0001 <MDL
Saanichton	0.0003	0.0001 <MDL	0.0001 <MDL
Sooke	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Port Renfrew	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Bamfield	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Lowest Median (Site)	0.0001 <MDL Multiple Sites	0.0001 <MDL All Sites	0.0001 <MDL Multiple Sites
Highest Median (Site)	0.0005 Multiple Sites	0.0001 <MDL All Sites	0.0002 Multiple Sites

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Cadmium Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0002	0.0001 <MDL	0.0001 <MDL
Abbotsford	0.0003	0.0001 <MDL	0.0001 <MDL
Cloverdale	0.0002	0.0001 <MDL	0.0001 <MDL
Ladner	0.0002	0.0001 <MDL	0.0001 <MDL
Vancouver	0.0005 *	0.0001 <MDL	0.0001 <MDL
Wilson Creek	0.0002	0.0001 <MDL	0.0001 <MDL
Texada Island	0.0003	0.0001 <MDL	0.0002
Pender Island	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Salt Spring Island	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Saanichton	0.0011	0.0001 <MDL	0.0001 <MDL
Sooke	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Port Renfrew	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Bamfield	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Lowest Median (Site)	0.0001 <MDL Multiple Sites	0.0001 <MDL All Sites	0.0001 <MDL Multiple Sites
Highest Median (Site)	0.0011 Saanichton	0.0001 <MDL All Sites	0.0002 Texada Island

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Cobalt Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0005	0.0001 <MDL	0.0001 <MDL
Abbotsford	0.0004	0.0001 <MDL	0.0001 <MDL
Cloverdale	0.0003	0.0001 <MDL	0.0001 <MDL
Ladner	0.0003	0.0001 <MDL	0.0001 <MDL
Vancouver	0.0002 *	0.0001 <MDL	0.0001 <MDL
Wilson Creek	0.0003	0.0001 <MDL	0.0001 <MDL
Texada Island	0.0003	0.0001 <MDL	0.0001 <MDL
Pender Island	0.0003	0.0001 <MDL	0.0001 <MDL
Salt Spring Island	0.0003	0.0001 <MDL	0.0001 <MDL
Saanichton	0.0003	0.0001 <MDL	0.0001 <MDL
Sooke	0.0003	0.0001 <MDL	0.0001 <MDL
Port Renfrew	0.0003	0.0001 <MDL	0.0001 <MDL
Bamfield	0.0003	0.0001 <MDL	0.0001 <MDL
Lowest Median (Site)	0.0002 Vancouver *	0.0001 <MDL All Sites	0.0001 <MDL All Sites
Highest Median (Site)	0.0005 Agassiz	0.0001 <MDL All Sites	0.0001 <MDL All Sites

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Molybdenum Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0005	0.0001 <MDL	0.0001 <MDL
Abbotsford	0.0004	0.0001 <MDL	0.0002 ***
Cloverdale	0.0003	0.0001 <MDL	0.0001 <MDL
Ladner	0.0003	0.0001 <MDL	0.0001 <MDL
Vancouver	0.0008 *	0.0001 <MDL	0.0001 <MDL
Wilson Creek	0.0003	0.0001 <MDL	0.0001 <MDL
Texada Island	0.0003	0.0001 <MDL	0.0001 <MDL
Pender Island	0.0003	0.0001 <MDL	0.0001 <MDL
Salt Spring Island	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Saanichton	0.0002	0.0001 <MDL	0.0001 <MDL
Sooke	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Port Renfrew	0.0002	0.0001 <MDL	0.0001 <MDL
Bamfield	0.0003	0.0001 <MDL	0.0001 <MDL
Lowest Median (Site)	0.0001 <MDL Mulitple Sites	0.0001 <MDL All Sites	0.0001 <MDL Multiple Sites
Highest Median (Site)	0.0008 Vancouver *	0.0001 <MDL All Sites	0.0002 Abbotsford ***

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Selenium Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Abbotsford	0.0002	0.0001 <MDL	0.0001 <MDL
Cloverdale	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Ladner	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Vancouver	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Wilson Creek	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Texada Island	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Pender Island	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Salt Spring Island	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Saanichton	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Sooke	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Port Renfrew	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Bamfield	0.0001 <MDL	0.0001 <MDL	0.0001 <MDL
Lowest Median (Site)	0.0001 <MDL Multiple Sites	0.0001 <MDL All Sites	0.0001 <MDL All Sites
Highest Median (Site)	0.0002 Abbotsford	0.0001 <MDL All Sites	0.0001 <MDL All Sites

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

Median Vanadium Concentrations (mg/L)			
Station	Smelter Operating	Smelter Closed	Both Periods
Agassiz	0.0006	0.0001 <MDL	0.0001 <MDL
Abbotsford	0.0006	0.0001 <MDL	0.0005 ***
Cloverdale	0.0006	0.0003	0.0004
Ladner	0.0007	0.0001 <MDL	0.0004
Vancouver	0.0009 *	0.0001 <MDL	0.0002 **
Wilson Creek	0.0006	0.0001 <MDL	0.0001 <MDL
Texada Island	0.0006	0.0001 <MDL	0.0002
Pender Island	0.0006	0.0001 <MDL	0.0004
Salt Spring Island	0.0005	0.0001 <MDL	0.0003
Saanichton	0.0006	0.0001 <MDL	0.0003
Sooke	0.0005	0.0001 <MDL	0.0002
Port Renfrew	0.0005	0.0001 <MDL	0.0002
Bamfield	0.0005	0.0001 <MDL	0.0001 <MDL
Lowest Median (Site)	0.0005 Multiple Sites	0.0001 <MDL Multiple Sites	0.0001 <MDL Multiple Sites
Highest Median (Site)	0.0009 Vancouver *	0.0003 Cloverdale	0.0005 *** Abbotsford

Notes:

Vancouver only has measurements beginning 25 January 1985.
*   Vancouver median before closure will be biased high.
**   Vancouver median overall will be biased towards later time period
***   Abbotsford both period median will be biased towards smelter operating period
Before closure is time period from 1 October 1984 to 6 February 1985.
Post closure is time period from 1 October 1985 to 6 February 1986.

APPENDIX C

SEA SALT INFLUENCE ON ION CONCENTRATIONS

APPENDIX C: SEA SALT INFLUENCE ON ION CONCENTRATIONS

The Bamfield site, located on the western shore of Vancouver Island, is expected to be least affected by anthropogenic sources with respect to rain water chemistry. This is due to its distance from large anthropogenic sources and the general lack of easterly winds which could transport pollutants to this site. Consequently, the data from this site can provide information on the analytes which arise from either the influence of sea water or from global background levels.

C.1   Association Between Analytes

A correlation analysis was conducted on the measured analyte concentrations at Bamfield. Spearman correlations, based on the ranks of concentrations, were determined in order to reduce the influence of questionable data on the correlations which could result if Pearson correlations were used. These correlations showed strong associations between Na, SO_4, Ca, K, Mg, and Sr, with Na associated with the highest correlations. This suggests that a common source contributes to the observed concentrations of these analytes. Furthermore, Na is possibly the best predictor of SO_4, Ca, K, Mg, and Sr contributions to rain water concentration arising from the common source.

Plots of concentrations were produced for the Bamfield data. Figures C.1 through C.3 show the association between Cl, NO_3 and SO_4 concentrations and Na concentration. Figure C.1 shows a very strong linear relationship between Cl and Na concentrations. However, there is one data point with a Na concentration of about 2.0 mg/L which falls substantially below the line. This indicates a high concentration of Na relative to Cl in this sample which, if real, suggests a large source of Na relative to Cl appearing on a single date or a condition in which the Cl has been removed from the atmosphere relative to the Na. Whether this is an error in the recording of the laboratory analysis, contamination of the sample, or a true representation of the rainfall, is unknown and further investigation of this data point is warranted. If this one data value is ignored, there exists a high correlation between the Cl and Na.

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FIGURE C.1

ASSOCIATION BETWEEN CHLORIDE AND SODIUM CONCENTRATIONS (mg/L)
IN RAIN WATER COLLECTED AT BAMFIELD

Association between Analytes

Legend   ⊛ ⊛ ⊛ Before Shut – down   O O O After Shut – down

FIGURE C.2
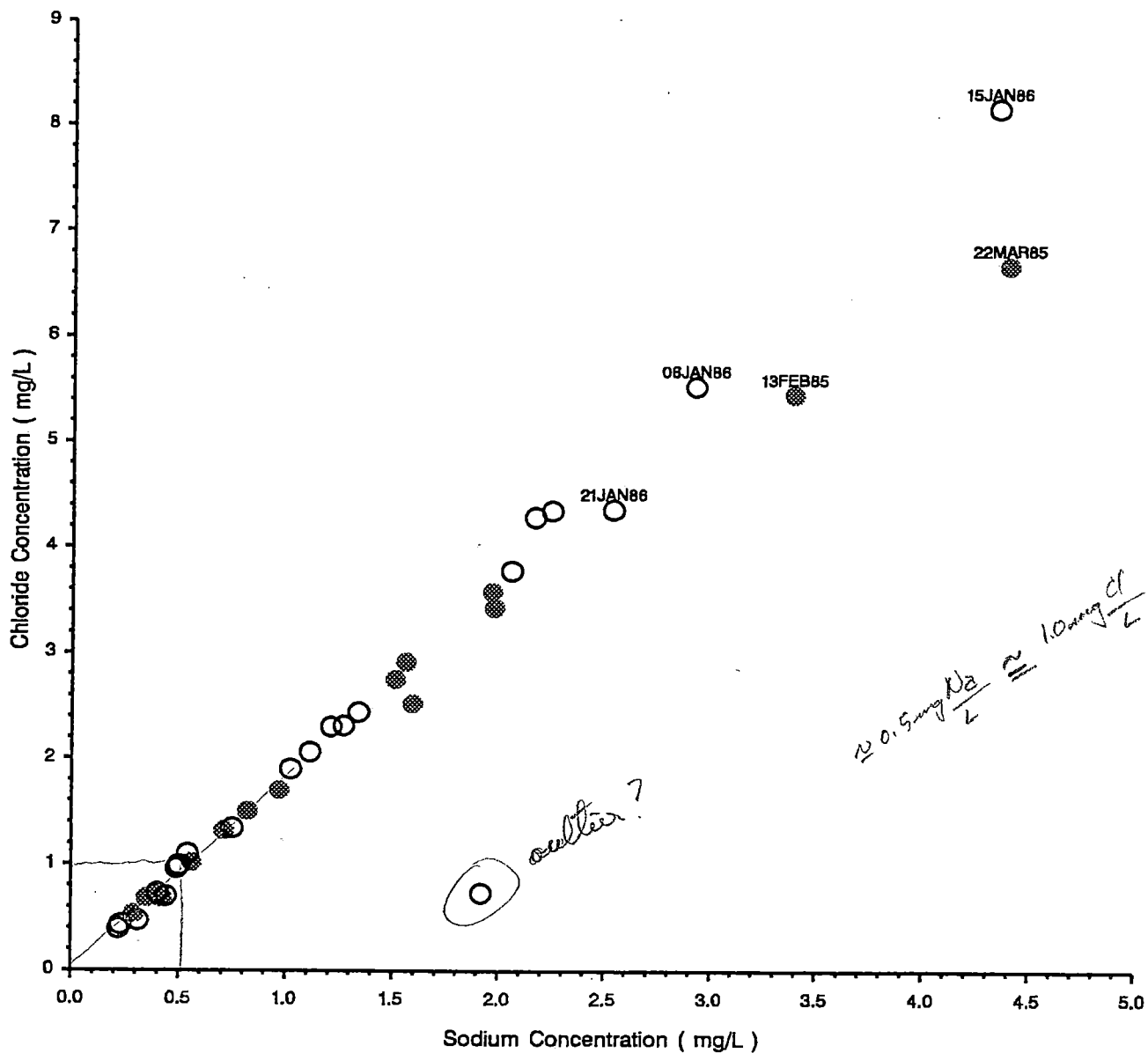
ASSOCIATION BETWEEN NITRATE AS NITROGEN AND SODIUM CONCENTRATIONS (mg/L) IN RAIN WATER COLLECTED AT BAMFIELD

FIGURE C.3

ASSOCIATION BETWEEN SULPHATE AND SODIUM CONCENTRATIONS (mg/L) IN RAIN WATER COLLECTED AT BAMFIELD
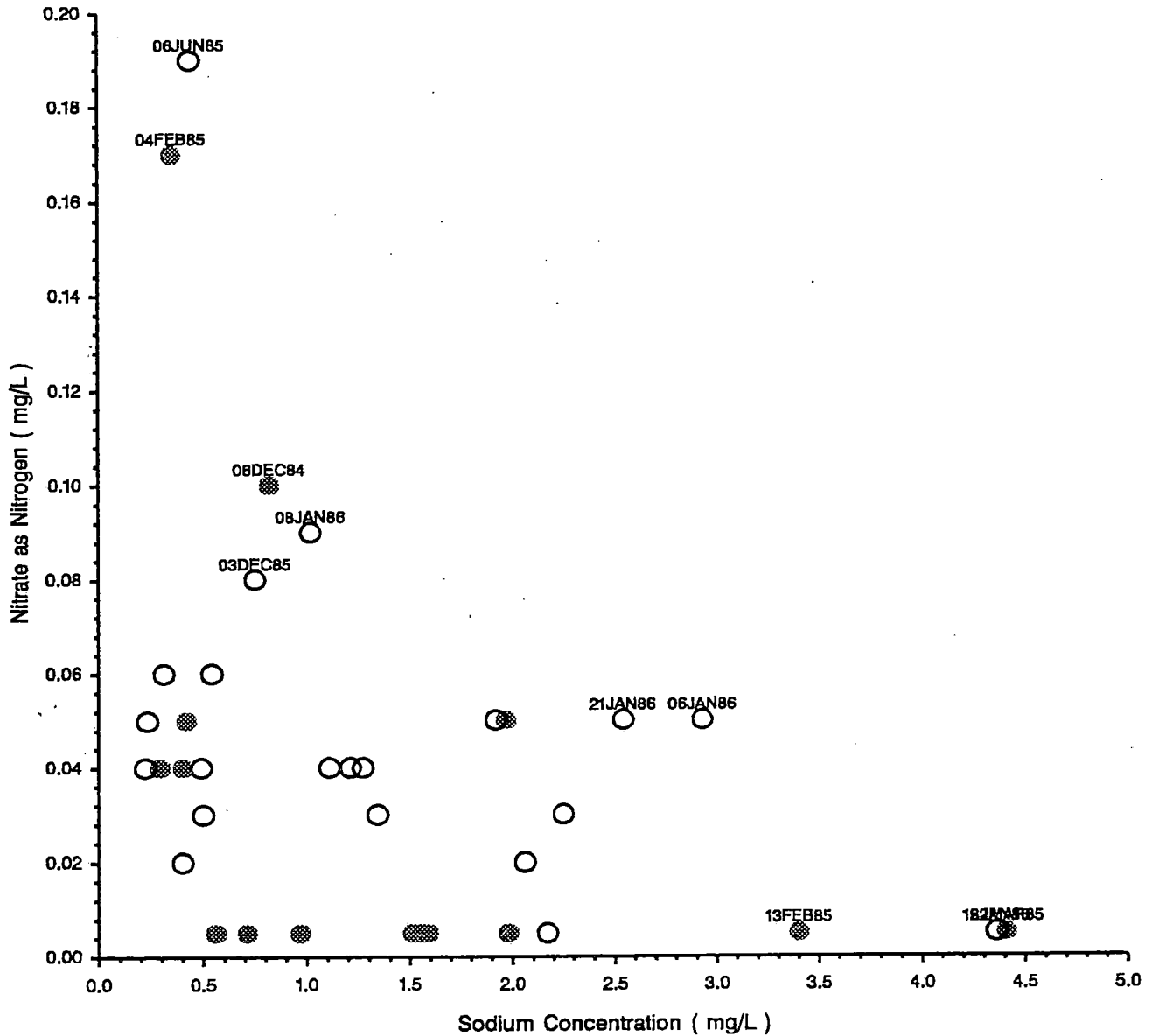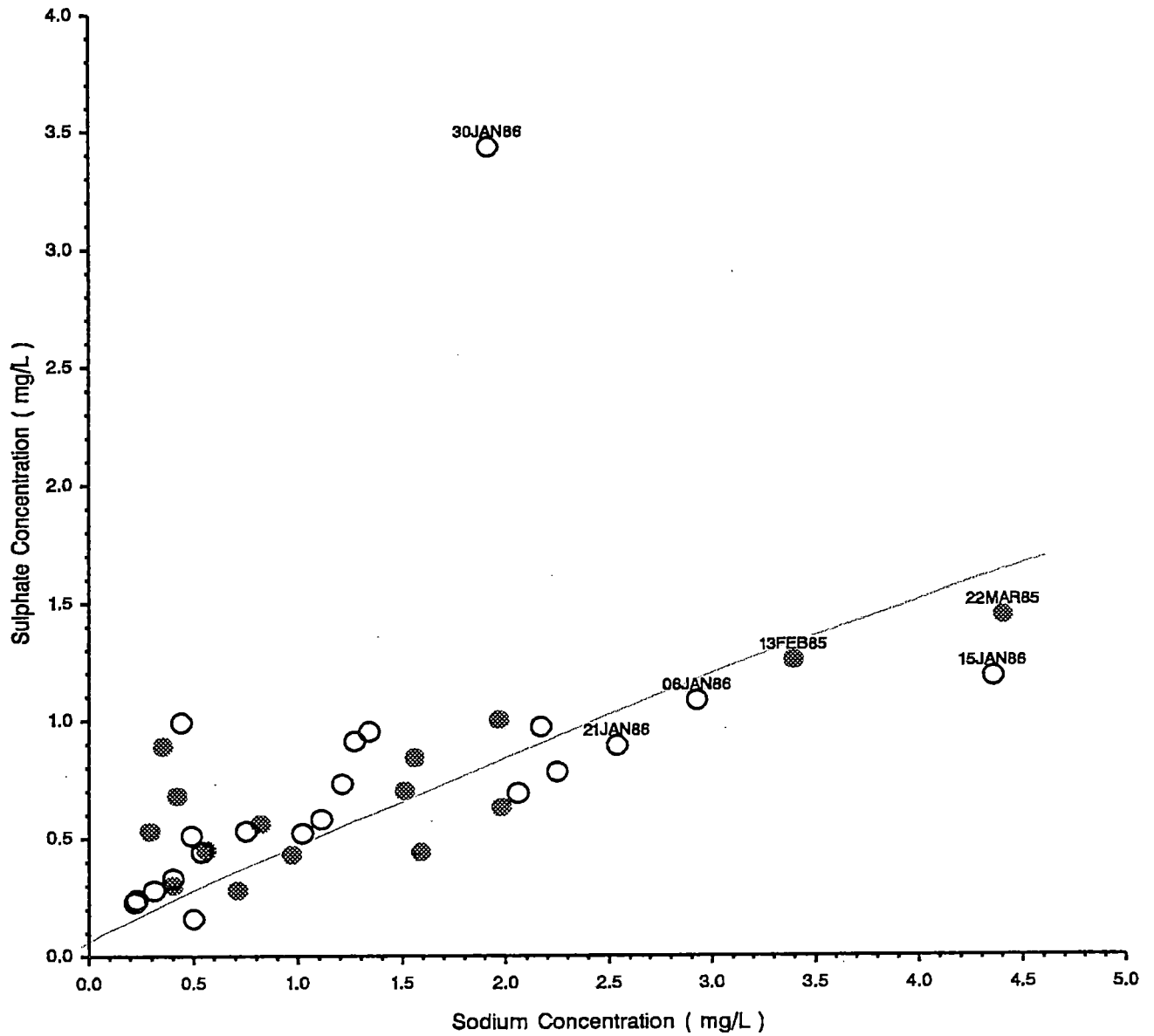
Association between Analytes

Legend   ⊛ ⊛ ⊛ Before Shut-down   O O O After Shut-down

Figure C.2 shows an association that is typical of most of the analytes plotted against sodium. The relationship between NO_3 and Na concentrations displays a pronounced hyperbolic shape, suggesting that the sources of these two analytes are located in different directions relative to the site. This is entirely reasonable since Na is most likely associated with sea salt from the Pacific and NO_3 is associated with mobile sources in the Lower mainland and eastern Vancouver Island. It is interesting to note that although many analyte concentration plots display this shape, plots of NO_3 and Na for other sites such as Ladner and Abbotsford do not display a hyperbolic relationship and the events with highest analyte concentrations relative to sodium are also different. However, there are groupings such as high Pb, NO_3 and NH_4 (i.e. automobile and agricultural sources) which occur for common events. Cr and Ni were high relative to Na on coincident dates although these dates do not coincide with the dates of high Pb, NO_3 and NH_4 concentrations. This suggests possibly different sources for these groups as well as different directions of wind prior to the rainfall events.

The relationship between SO_4 and Na is shown in Figure C.3. There is a definite linear association between these analytes, indicating that SO_4 concentration increases with Na. This suggests they share a common source. The relationship is less well defined than the association with Cl indicating the presence of other factors: additional sources of SO_4 other than the Na related source (i.e., sea salt), or varying scavenging rates from the atmosphere being two such factors. An outlying point, which occurred on 30 January 1986, lies substantially above the linear association, indicating that there was an unusually high ratio of sulphate to sodium on that date. This is the same date with the outlying point on the plot of Cl against Na in Figure C.1. This suggests a data management error in which the concentrations for Cl and SO_4 may have been reversed. Switching the database concentrations of about 0.7 mg/L about 3.4 mg/L respectively would result in the date, 30 January 1986, following the relationships evident in Figures C.1 and C.3.

C.2   SEA WATER AS A SOURCE OF ANALYTES IN RAIN WATER SAMPLES

Based on the strong correlations between some of the measured analytes, an hypothesis that sea water is a major source of Na, Cl, SO_4, Mg, Ca, K, and Sr seems likely. If this is true the

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relationship of Cl, SO_4, Mg, Ca, K and Sr to Na could be used to remove the effect of sea salt from rain water concentrations. This is similar to the estimation of XSO_4 in previous studies. A review of typical concentrations of various dissolved elements in sea water is presented in Table C.1. The concentrations of the ions in were used to determine ratios of Cl, SO_4, Mg, Ca, K and Sr to Na in sea water. These ratios should correspond to the relative concentrations observed in rain water chemistry on dates when the major source of the pollutants is sea water.

The ratios of the analyte concentrations in sea water were superimposed on the scatter plots of the rain water concentrations of Cl, SO_4, Mg, Ca, K and Sr against Na concentration. The association between Na and Cl, previously depicted in Figure C.1, is precisely superimposed by the sea water ratio of the two elements. This suggest Cl and Na share the only significant source, sea water emissions, at the Bamfield site. Figures C.4 through C.7 show the results for Mg, Ca, K, and Sr. In the cases of Cl and Mg, the sea water ratio again falls coincident with the linear association between the analytes. This suggests that the only significant source of Cl and Mg at Bamfield is sea water.

In the Mg plot of Figure C.4, there are apparent discrepancies in the data. The concentration reported on 15 January 1986 falls substantially below the linear relationship indicated in the figure. This would require a large source of Na on these dates which is not consistent with the concentration of other analytes relative to Na. This strongly indicates that the magnesium concentrations are incorrect for this date. This is substantiated by the value of 0.44 mg/L reported from the trace elements laboratory test for that date. The trace element reported concentration would agree well with the linear relationship.

Figures C.5 to C.8, for Ca, K, Sr and SO_4 respectively, all show the sea water ratio describing a lower bound for the concentration ratio of the analytes at Bamfield. Furthermore, the sea water ratio generally parallels the association between the specific analyte and the sodium concentration. Some dates show larger deviations from this association suggesting that sea water is a major source of the analytes in rain water, but that there also exist substantial amounts of analyte contribution from a global background for most events. In addition, there are events when a substantial fraction of the analyte concentration can be attributed to neither the global

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Table C.1

**RATIO OF CONCENTRATION OF SELECTED IONS
TO CONCENTRATION OF SODIUM IN SEA WATER**

Analyte	Sea Water Concentration (mg/L) ≡ ppm	Ratio of Analyte To Sodium *(in mg/L/mg/L)*
Chloride	19,000	1.810
Sodium	10,500	1.000
Sulphate *(5]885 mg/L)*	2,655**	0.253
Magnesium	1,275	0.119
Calcium	400	0.0381
Potassium	380	0.0362
Strontium	6.5*	0.0006

Notes:

Source of Concentrations - Table 7-8 Composition of Sea Water, Handbook of Tables for Applied Engineering Science, 2nd Edition CRC Press, 1976.

* Strontium reported in reference as 13 mg/L converted to 6.5 mg/L (appears to be miscalculated in original document). Further the 13 mg/L is not supported by the data. Using 13 mg/L on Figure C.7 would indicate another source of Na_o. We suspect that there is an error in most reference documents.

** Concentration of Sulphate Calculated by Conversion of Elemental Sulphur (885 mg/L) completely to Sulphate.

FIGURE C.4

ASSOCIATION BETWEEN MAGNESIUM AND SODIUM CONCENTRATIONS (mg/L) IN RAIN WATER COLLECTED AT BAMFIELD
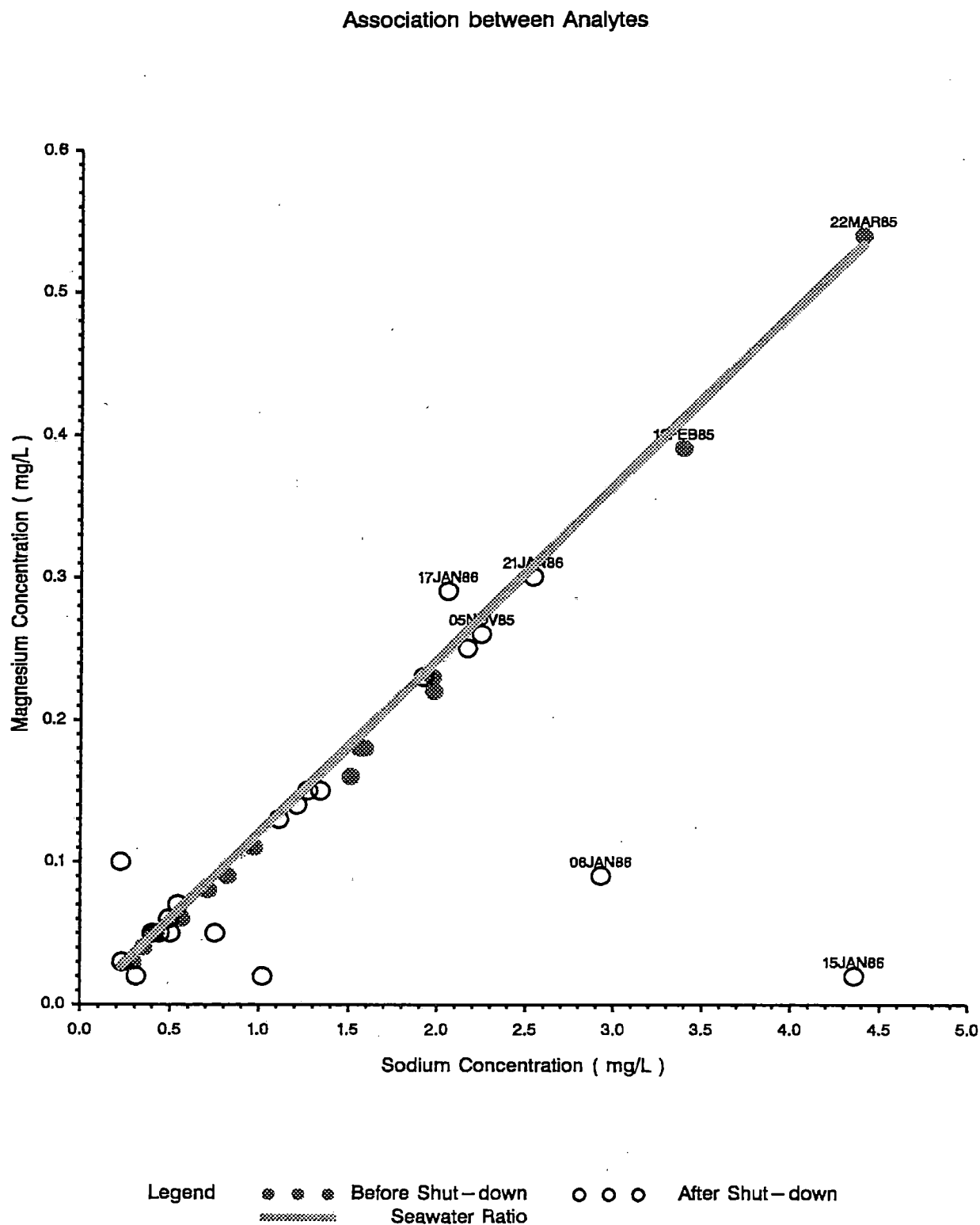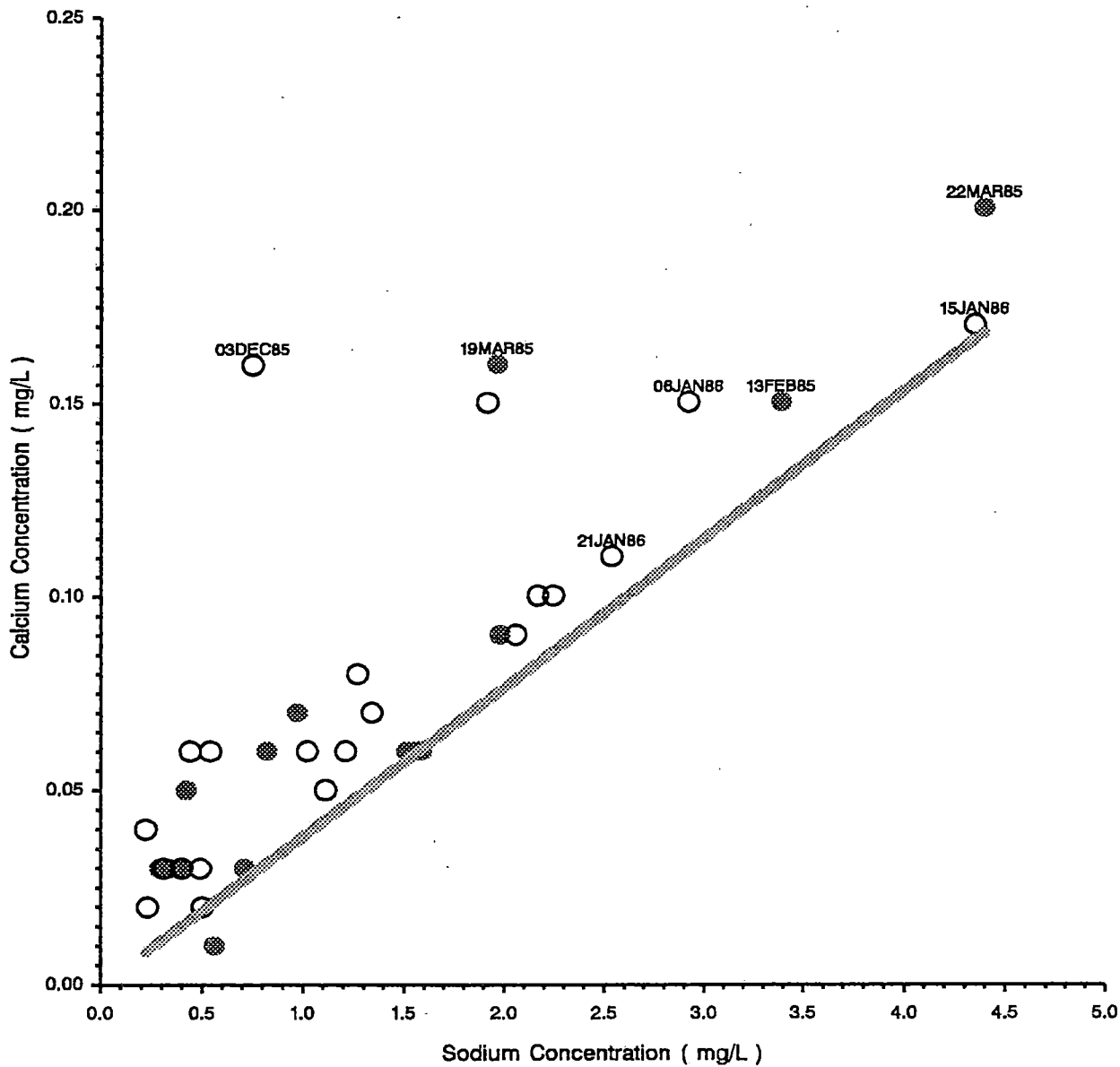
Association between Analytes

FIGURE C.5

ASSOCIATION BETWEEN CALCIUM AND SODIUM CONCENTRATIONS (mg/L) IN RAIN WATER COLLECTED AT BAMFIELD

Association between Analytes

Legend — Before Shut–down — After Shut–down — Seawater Ratio

FIGURE C.6

ASSOCIATION BETWEEN POTASSIUM AND SODIUM CONCENTRATIONS (mg/L)
IN RAIN WATER COLLECTED AT BAMFIELD

Association between Analytes

FIGURE C.7

ASSOCIATION BETWEEN STRONTIUM AND SODIUM CONCENTRATIONS (mg/L) IN RAIN WATER COLLECTED AT BAMFIELD

Association between Analytes

FIGURE C.8

ASSOCIATION BETWEEN SULPHATE AND SODIUM CONCENTRATIONS (mg/L) IN RAIN WATER COLLECTED AT BAMFIELD
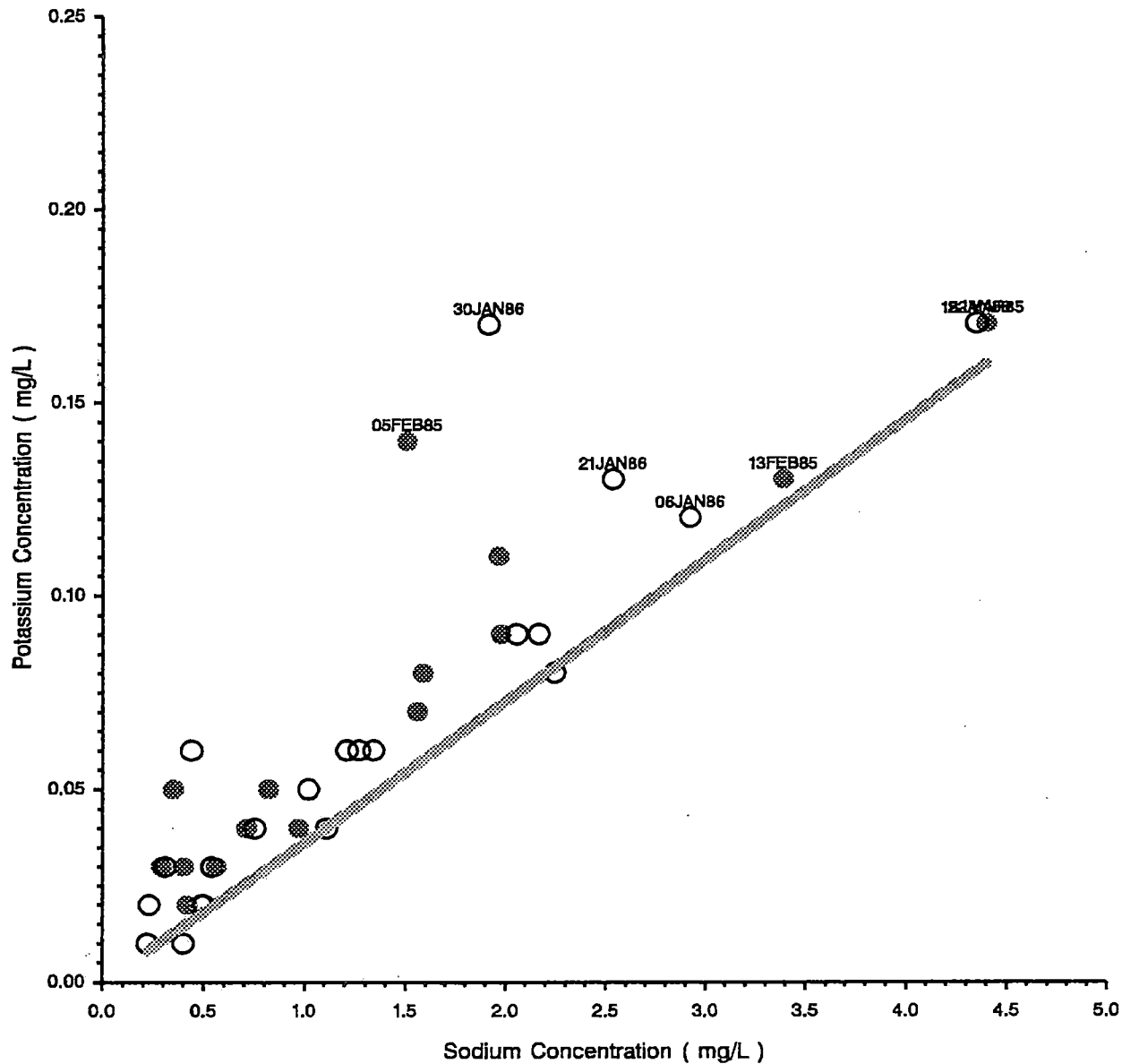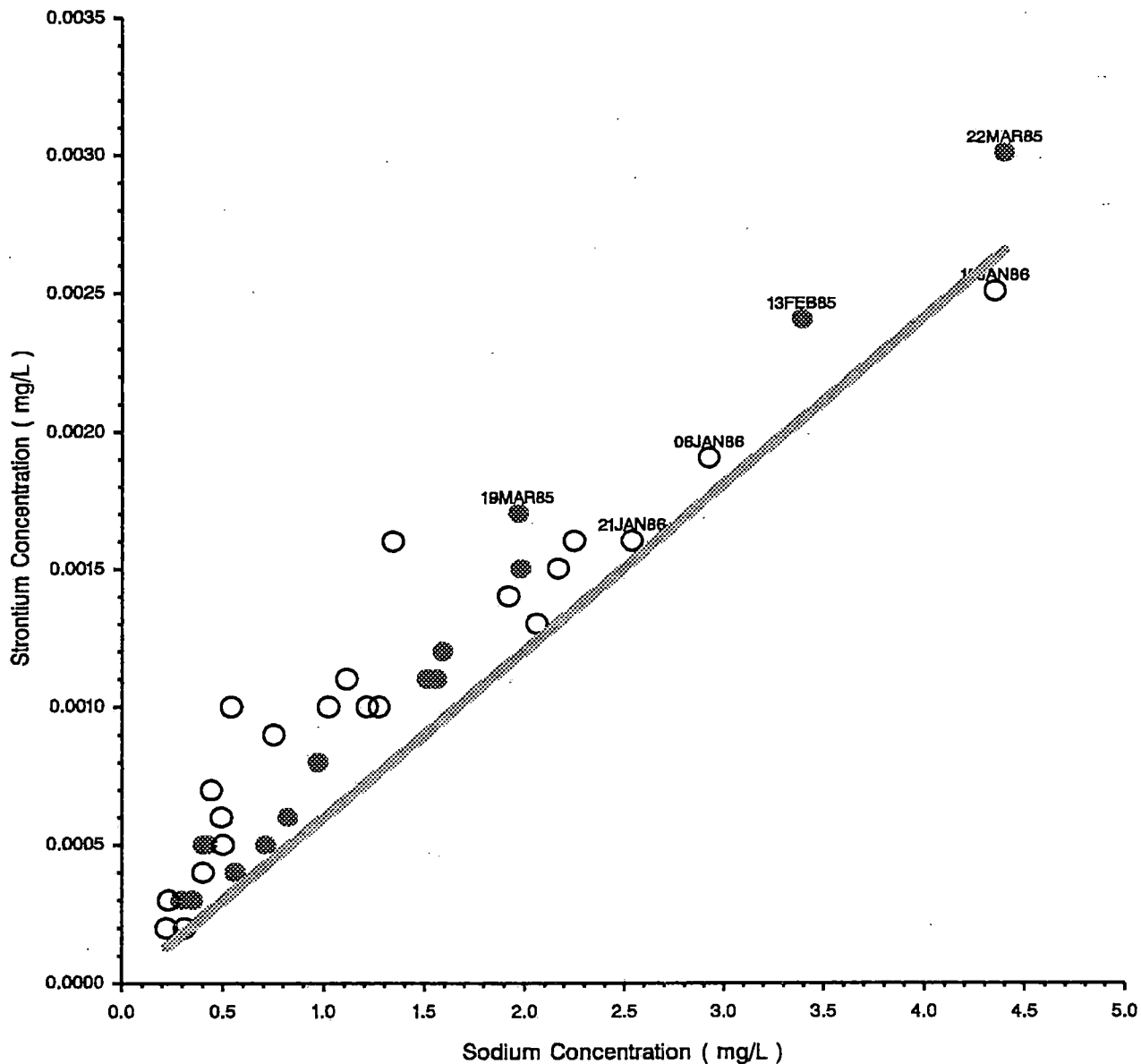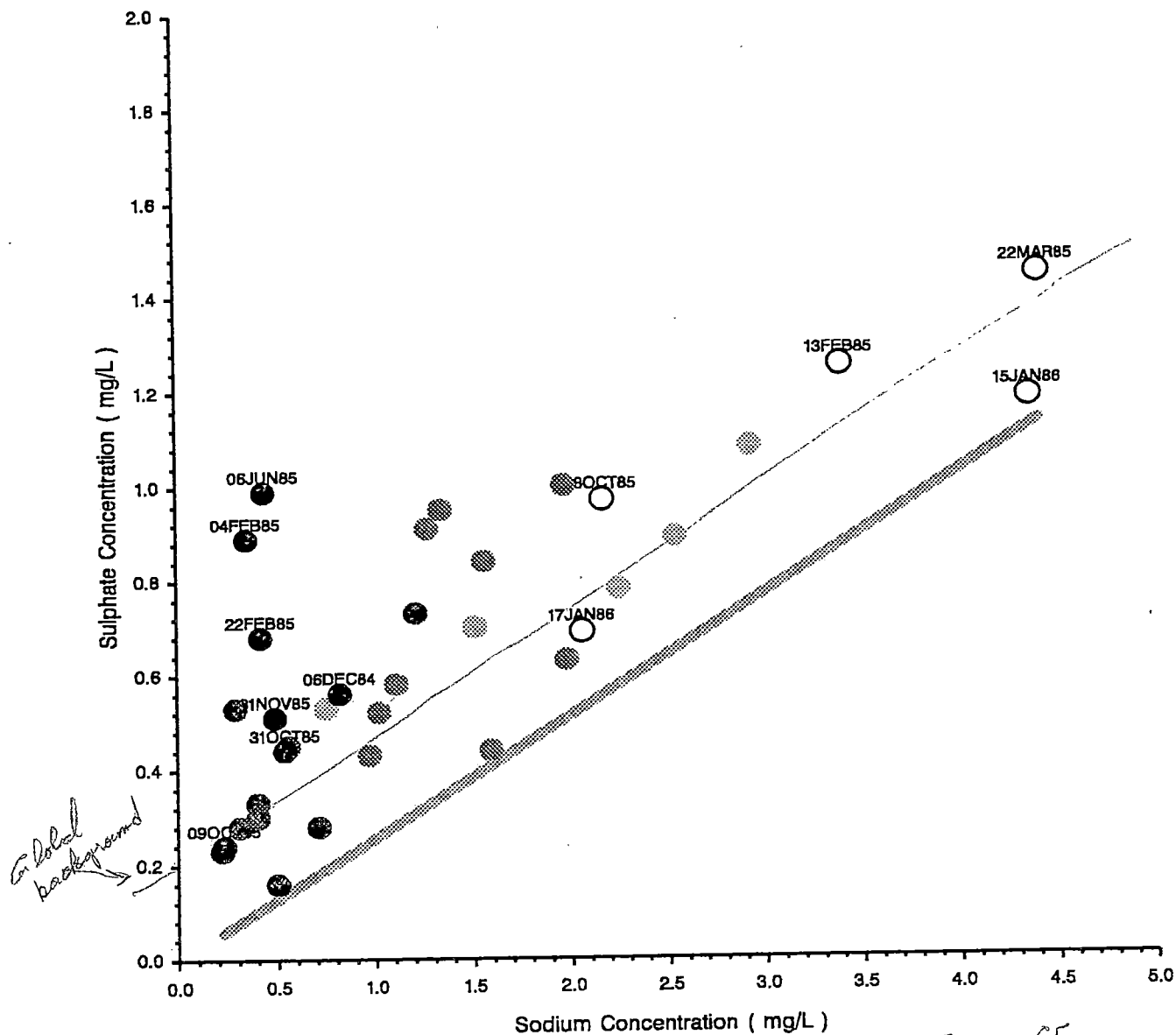
Association between Analytes

Comparison to Sodium

Seawater Ratio	0 Analytes High
1 – 2 High	3 – 4 High
5 – 7 High	>7 High

background nor the sea water. These occasions are plausibly related to anthropogenic sources delivered by easterly winds.

It must be noted that the relationship for Sr has been derived by adjusting the reported concentrations for sea water concentration. When the ratio based on report concentrations was plotted, the ratio had a slope of 2 times the relationship of the data. This was disconcerting, so based on some confusion regarding the conversion between uEq/L and ppm, the reported concentration of Sr was divided by 2 (the valence of Sr is +2). This resulted in the ratio, falling on the relationship, shown in Figure C.7. This is quite interesting and suggests the concentrations reported in the reference are incorrect. A confirmatory chemical analysis on sea water may be necessary.

These relationships apply in general to all sites. However at locations impacted by other emission sources of the analytes, the association between the analyte and sodium concentration will be less pronounced. It is worth noting that a strong linear relationship exists for Na and Cl at Ladner and Abbotsford which suggests that there are no significant sources of Na or Cl, other than sea water, in the region. The Na and Mg relationships follow well at Ladner, but not Abbotsford, which suggests a source of Mg other than sea water in the region, perhaps local soil.

The linear relationships between Na and Ca (or Sr) remain evident at Ladner, but appear to break down further inland around Abbotsford. This is similar to the previous elements and the interpretation is similar. The weak linear association between Na and SO_4 at Ladner, and a low association between these analytes at Abbotsford are not unexpected considering the large sources of SO_4 in those areas.

C.3   REMOVING THE EFFECT OF SEA WATER SOURCES FROM OBSERVATIONS

The strong relationship between the ratios of the analytes to Na in sea water and the observed concentrations in rainfall suggest that the effect of sea water could be removed from most observations. This would involve calculation of the sea water contribution by multiplying the ratio in sea water by the sodium concentration in the rain water. Subtracting this amount from

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the total concentration yields the amount of analyte arising from global background, anthropogenic and natural sources other than sea water. This could be completed for SO_4, Ca, K, Mg, and Sr to estimate excess concentrations for the listed analytes. Of course this requires that the only significant source of Na is sea water emissions.

The global background for these sea water analytes could be determined by regressing the concentrations of the analyte against Na for those dates on which there was no apparent contribution from anthropogenic sources. In this case, the intercept of a regression (with slope possibly constrained to the sea water ratio) would be indicative of background levels. These would be concentrations arising from transportation from areas far removed from the region.

Dates free from regional anthropogenic sources could be assessed either from indicated concentrations or the relationship between anthropogenic analytes and sodium. As noted previously, certain analytes display an hyperbolic association with sodium concentration. In the absence of information about wind back trajectories, concentration data relating to these analytes can indicate whether rainfall events were influenced by offshore winds or anthropogenic sources. For example, rainfall events where the concentrations of anthropogenic analytes are high relative to sodium concentration suggest the influence of an offshore wind. Repeating this process for several analytes, having hyperbolic relationships, will produce a list of dates on which some offshore contamination is indicated. A regression on sodium using a data set with those events having substantial anthropogenic contamination removal should quantify the global background level as the intercept term.

This process was initiated for SO_4 in Figure C.8. Here the events are coded by the number of anthropogenic analytes whose concentrations are relatively higher than the sodium concentration on that date. Setting the slope of the regression to be equal to the sea water ratio, a global background SO_4 concentration of about 0.2 mg/L seems quite plausible. This process could be repeated for Sr, Ca and K, all of which have substantial background and anthropogenic source contributions above the sea water component. In fact, this procedure could be extended to develop global backgrounds for anthropogenic pollutants such as Pb and Zn.

From this investigation, a estimate of excess SO_4 concentration calculated by subtracting the sea water ratio of SO_4 to Na times the Na concentration appears reasonable. The background level, although approximately 0.2 mg/L, appears quite variable and corrections for background contribution are not made. This is because this apparent background is a relatively major portion of the total sulphate concentration. In this report, SO_4 is calculated as follows:

$$SO_{4\ net} = SO_{4\ Total} - (0.253 \times Na_{Total}) \tag{1}$$

where

$SO_{4\ net}$	=	is the contribution (mg/L)from sources other than global background or sea water;
$SO_{4\ Total}$	=	is the concentration (mg/L) of SO_4 in the rain water sample;
Na_{Total}	=	is the concentration (mg/L) of sodium in the rain water. Note that the equation assumes minimal sources of Na from other than sea water;
0.253	=	is the ratio of concentration in mg/L of SO_4 to Na in sea water.

This process could be repeated for Cl, Mg, Ca, K, and Sr to derive excess concentrations for these analytes. Some of these pollutants have substantial contributions from sources other than sea water and the removal of the sea water effect would aid in the understanding of these anthropogenic or crustal sources.

The contributions from background and sea water emissions of SO_4 are presented in Table C.2 for several selected sites. By subtraction, the contribution from other sources is calculated and presented. A gradient from west to east in the contribution from sea water is readily apparent. Also the proportion arising from other sources was largest in the eastern sites indicating the influence of anthropogenic emissions in those areas.

Table C.2

RELATIVE CONTRIBUTIONS TO SULPHATE
CONCENTRATION IN RAIN WATER SAMPLES

	Mean Concentration (mg/L)	Percent from Global Background (%)	Percent from Sea Water (%)	Mean Concentration from Sea Water (mg/L)	Percent from Other Sources (by Subtraction) (%)	Mean Concentration from Other Sources (mg/L)
Bamfield						
ASARCO operating	0.68	29	59	0.40	12	0.08
ASARCO closed	0.80	25	46	0.37	29	0.23
Texada Island						
ASARCO operating	0.65	31	14	0.09	55	0.36
ASARCO closed	0.49	41	14	0.07	45	0.22
Ladner						
ASARCO operating	1.35	15	21	0.28	64	0.86
ASARCO closed	0.69	25	17	0.12	58	0.40
Abbotsford						
ASARCO operating	0.89	22	8	0.07	69	0.61
ASARCO closed	0.46	43	8	0.04	49	0.23

Note:

*   Concentrations weighted by precipitation catch.

APPENDIX D

MAP OF THE REGION

FIGURE D.1

Location of Precipitation Monitoring Sites

ABB	Abbotsford	MPL	Maple Leaf	SOO	Sooke
AGA	Agassiz	NPT	Neill Point	SSI	Saltspring Island
BAM	Bamfield	OZE	Lake Ozette	TAC	Tacoma
CHE	Cheeka Peak	PEN	Pender Island	TEX	Texada Island
CKK	Carkeek Park	QYT	Quillayute	TLT	Tolt River
CLO	Cloverdale	REN	Port Renfrew	VAN	Vancouver Airport
LAD	Ladner	SAN	Saanichton	WIL	Wilson Creek
				WST	West Seattle

TEX · WIL
Georgia Strait
VAN · ABB · AGA
BAM · SSI · LAD · CLO · BEL
REN · PEN
SCO · SAN
Juan de Fuca Strait
CHE
· OZE
· QYT
OLYMPIC PENINSULA
Puget Sound
EVE
MPL · TLT
· CKK
WST · SEA
NPT
· ASARCO
TAC
Chehalis Gap
· Centralia Power Plant

51°N 50°N 49°N 48°N 47°N 46°N

127°W 126°W 125°W 124°W 123°W 122°W 121°W