Progress Report to Western LRTAP Committee on AES Pacific Region Program

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Introduction

The main objective of the AES Pacific Region LRTAP studies ~~is~~ ~~to obtain a better understanding of the background precipitation chemistry along the B.C. coast. This requires a knowledge of~~ the precipitation chemistry of ~~the~~ air masses approaching the coast from the Pacific Ocean and ~~an understanding of~~ the extent and degree of change to these background values due to ~~widespread~~ emissions from the Vancouver urban and industrial area ~~as well as from other large individual point sources~~.

In support of the study objective two monitoring programs were established in January 1982. The data obtained during the three month period January to March 1982 are available in two Scientific Services Internal Reports. This report discusses some preliminary results of the data analysis.

CANSAP Coastal Stations - Event Sampling

Data from the CANSAP network have been used to portray precipitation chemistry on a regional level. However the three CANSAP stations located along the B.C. coast are all near potential sources of local pollution. The Vancouver station is situated at a major airport within a large urban/industrial area and the data cannot be considered representative of the background values. The stations at Port Hardy and Terrace are located at regional airports near fairly small communities. Although the effect of immediate local sources are not known, it is thought they should not greatly affect the precipitation chemistry. Of more concern at Port Hardy and Terrace is the potential effect from large emission sources some distance from the samplers. A large aluminum smelter and a pulp mill are located 60 km from the Terrace monitoring site at Kitimat. A similar situation exists at Port Hardy where a pulp mill is located at Port Alice 35 km south of the monitoring site. Although the data from these stations are used to portray regional differences in pH, it is not at all certain that the data are representative of regional conditions.

The CANSAP data themselves provide only limited opportunity to investigate the factors contributing to the precipitation chemistry since the monthly averages are a composite of individual events with quite different air trajectories and air mass histories. The continual event sampling program was therefore initiated to provide data that would indicate the contribution of individual storms. A classification of specific precipitation events with regard to air mass trajectories should provide an indication of the effects of local and regional emission sources.

Although three months of data are insufficient for classification purposes, some interesting results are available from the Port Hardy data. During the three month sampling period the mill at Port Alice was closed from January 27 to March 4, 1982. Out of a total of 33 samples collected 16 samples were obtained when the mill was closed and 17 when the mill was in operation. This provided an excellent opportunity for a comparison study.

PORT HARDY EVENT SAMPLING - JANUARY TO MARCH 1982

	H+	pH	Cond	Ca++	Mg++	NH_4+	Fe++	Na+	Cl-	SO_4--	NO_3-	EXCESS SO_4
Mill Operating	7.49	5.13	16.8	.111	.177	.038	.014	1.72	3.13	1.00	.221	.58
Mill Closed	5.30	5.28	10.3	.054	.164	.038	.002	1.03	1.9	0.43	.115	.17
Student t	0.91	0.74	0.97	.99	.17	.10	.99	0.91	0.90	0.995	.96	

Table 1. Ion concentrations are in mg/l.
Sulphate values less than detectable level (.2 mg/l) are taken as .1 mg/l in calculating averages.

The average concentrations of the various ions for the mill closed and mill operating data sets are shown in Table 1. It is evident that the concentrations of most of the ions increased significantly when the mill was in operation. The conductance, measuring total ion activity, increased from 10.3 to 16.8 under mill operating conditions. The cation/anion fraction was 1.2 for mill closed and 1.0 for mill operating conditions suggesting that most of the important ions were identified.

PORT HARDY EVENT SAMPLING - JANUARY TO MARCH 1982

	H+	pH	Cond	Ca++	Mg++	NH_4+	Fe++	Na+	Cl-	SO_4--	NO_3-	EXCESS SO_4
Mill Operating	7.49	5.13	16.8	5.52	14.53	2.106	.734	74.7	88.3	20.82	3.560	12.076
Mill Closed	5.30	5.28	10.3	2.71	13.47	2.086	.118	44.9	53.2	8.95	1.849	3.539

Table 2. Ion concentrations are in micro equivalents.

Table 2 lists the ion concentrations in micro equivalents. It can be seen that sea salt is the main ionic component during both mill operating and non-operating periods. Since Port Hardy is a coastal community, sea salt originating directly from ocean spray can be expected to be present in the atmosphere and in precipitation. This was the main source of sodium and chloride ions when the mill was closed and during this period an average of 1 mg/l of sodium and 1.9 mg/l of chloride was measured in precipitation. When the mill was in operation additional sodium and chloride ions would be expected since the wood waste power boiler burns bark obtained from logs which have been transported and stored in booms in ocean water. The addition of sea salt from this source increased the sodium ion concentration to 1.7 mg/l and the chloride ion concentration to 3.1 mg/l. If, as assumed, the additional sodium and chloride ions from the mill originated from sea salt, the proportion of chloride to sodium should be near 1.8, the value found in sea water. This is indeed the case since Cl/Na (no mill) = 1.9 and Cl/Na (mill operating) = 1.8. From Table 1 it appears, therefore, that at Port Hardy the amount of sea salt in precipitation was increased by approximately 70% over the natural coastal levels due to the additional salt emitted from operating the waste wood power boiler.

From Table 1 we also see that the total amount of sulphate ion more than doubled during mill operating conditions. Of more importance, however, is the excess sulphate, that is the non sea salt associated sulphate, since this is the component contributing to the acidity. It is noted that the concentration of excess sulphate ions was more than three times as great during mill operations as compared with mill closed conditions. However, this increase in sulphate ion resulted in only a slight lowering of the pH from 5.28 (mill closed) to 5.13 (mill operating), indicating that other neutralizing and buffering substances were also present.

Since there were no obvious local emissions during the mill closed period, the concentrations observed at that time should be a first approximation to background levels. If we examine the 16 mill closed events, Table 3, it is evident that three of the samples (No.'s, 5, 6 and 8) form a group with characteristics quite different from the remainder of the set. The three samples noted recorded the highest excess sulphate values and the highest values for nitrate. Furthermore they are the only samples with values for iron above the detectable level of .001. A similar situation exists for lead where the same three events were included in the four samples reporting values above detectable level. The association of the above ions strongly suggests an urban/industrial source. As could be expected the three events identified reported the lowest pH values (5.09, 4.87 and 5.12).

The meteorology of the low pH events was examined and although not conclusive, there was some evidence to suggest the low pH precipitation was associated with a low level southeasterly flow pattern. Advection of polluted air from local sources or from the Georgia Strait area is therefore a possibility. This will be investigated further. If we delete the three occurrences noted above from the mill closed data, the remainder of the data may be more representative of air masses reaching the coast from the Pacific. The average values for these data are given in Table 4. The value of 5.37 for pH compares favourable with the pH values obtained from the other samples taken at sites away from local sources.

PORT HARDY EVENT SAMPLING - JANUARY TO MARCH 1982

Event	H+	pH	Cond	Cu++	Ca++	Mg++	NH_4+	Fe++	Pb++	Mn++	K+	Na++	Zn++	Cl-	SO_4--	NO_3-	EXCESS SO_4
1.	5.25	5.28	7.4	.001	.05	.075	.021	.001	-.001	-.001	-.2	.7	-.001	1.2	.3	.120	.1
2.	3.39	5.47	4.7	.003	.06	.045	.027	-.001	-.001	-.001	-.2	.4	-.001	.6	.2	.084	.1
3.	2.75	5.56	7.1	.002	.07	.082	.015	.001	-.001	.002	-.2	.7	-.001	1.2	.2	.062	.0
4.	3.98	5.40	4.6	.001	.02	.042	.006	.001	-.001	-.001	-.2	.3	-.001	.6	-.2	.049	.1
5.	8.13	5.09	7.6	.003	.05	.032	.075	.007	.003	.001	-.2	.3	-.001	.7	.7	.248	.6
6.	13.49	4.87	13.3	.002	.07	.130	.037	.005	.003	-.001	-.2	.9	.001	1.8	.8	.279	.6
7.	5.01	5.30	5.9	.001	.01	.050	.009	.001	-.001	-.001	-.2	.4	-.001	.8	.2	.044	[illegible]
8.	7.59	5.12	11.4	.002	.04	.110	.062	.010	.002	-.001	-.2	.9	-.001	2.0	.6	.217	.4
9.	4.47	5.35	3.2	.002	.03	.010	.015	.001	-.001	-.001	-.2	-.2	-.001	.2	-.2	.058	.2
10.	5.50	5.26	5.6	.002	.01	.040	.013	-.001	.003	-.001	-.2	.4	-.001	.7	-.2	.071	.1
11.	3.72	5.43	25.6	.001	.13	-.900	.010	.001	-.001	-.001	.2	3.4	-.001	6.1	.9	.035	.1
12.	4.07	5.39	4.5	.003	-.01	.032	.019	.001	-.001	-.001	-.2	.4	-.001	.6	-.2	.044	.1
13.	3.55	5.45	12.1	.003	.07	.300	.180	-.001	.001	-.001	-.2	1.3	.004	2.2	.6	.106	.3
14.	4.27	5.37	20.4	.003	.10	.590	.050	-.001	.001	.002	-.2	2.5	-.001	4.6	.8	.115	.2
15.	5.01	5.30	14.1	.001	.06	.400	.021	-.001	-.001	.007	-.2	1.6	-.001	3.0	.5	.151	.1
16.	4.68	5.33	17.9	.003	.09	.520	.042	.001	-.001	-.001	-.2	2.1	-.001	3.9	.7	.151	.2

Table 3. Port Hardy event sampling during mill closed period. Conductance is expressed in US/CN. Missing data are designated as -.9. Minus signs indicate that values are below detectable limits. Ion concentrations are in mg/l.

AVERAGE VALUES FOR 13 MILL CLOSED EVENTS

H+	pH	Cond	Cu++	Ca++	Mg++	NH_4+	Fe++	Pb++	Mn++	K+	Na++	Zn++	Cl-	SO_4--	NO_3-	EXCESS SO_4
4.28	5.37	10.24	.002	.055	.237	.033	.001	.001	.002	.200	1.108	.001	1.98	.400	.084	.131

Table 4. Port Hardy event sampling during mill closed event with three samples deleted. Ion concentrations are in mg/l.

Lower Mainland Study

The Lower Mainland area is the economic centre of the province. Over one-half of the population of B.C. reside in its boundaries. However it is also a sensitive ecological area of great interest. It encompasses the Fraser River estuary with its important salmon fisheries and wildfowl reserves. The area contains some of the best agricultural land in the world. The mountain slopes have valuable forests. The chemistry of the precipitation is therefore of concern to a number of interests.

Although CANSAP data are available from Vancouver Airport, there are indications these data may not be representative of the entire area. The Lower Mainland monitoring network was therefore established to better define the spatial and temporal variability of the precipitation chemistry.

The network consists of 14 stations (Fig. 1). For the study, precipitation samples were obtained during individual storm events employing a manually operated collector. A description of the collector, sampling methods and the data analysis for the January-March period have been published in Scientific Services Report No.4.

The average conductivity for the 12 events sampled are plotted in Fig. 2. It can be seen that the largest values are associated with the city centre and the industrial area along Burrard Inlet (T-6, T-7). Values are lower at the high elevation stations (Grouse Mtn. and Mt. Seymour Park) and Seymour Falls, T-40, located in a narrow valley between the mountain slopes. Lower values are also found at the four Fraser Valley stations.

The average pH values for each station is plotted in Fig. 1. The lowest pH values are found in the city centre and Burrard Inlet industrial area. To provide a better overview with the limited data available the stations have been combined into three groups - city, valley and mountains. The average values are summarized in Table 5. Slightly higher pH readings were observed at the mountain stations with substantially higher readings from the valley stations. The group averages of 4.77, 4.91 and 5.40 bring this out quite clearly.

LOWER MAINLAND EVENT SAMPLING - JANUARY TO MARCH 1982

	H+	pH	Cond	Ca++	Mg++	NH_4+	Fe++	Pb++	Mn++	K+	Na+	Zn++	Cl-	SO_4--	NO_3-
Fraser Valley	4.00	5.40	7.2	.10	.039	.704	.004	.003	.002	.2	.32	.002	.45	.65	.737
Vancouver City	17.0	4.77	14.9	.28	.091	.382	.015	.008	.002	.2	.68	.002	1.16	1.32	1.356
Mountain Area	12.33	4.91	8.6	.06	.026	.073	.003	.005	.002	.2	.3	.003	.4	.5	.475

Table 5. Ion concentrations in mg/l.

Fraser Valley group includes Agassiz, Chilliwack, Abbotsford and Cloverdale.
Vancouver City includes T2, T6, T7 and Ladner.
Mountain area includes Grouse Mtn., Mt. Seymour and T40.
Twelve events were sampled. Not all stations reported for each event.

The city group shows the highest values in iron, lead, sulphates and nitrates reflecting the effect of anthropogenic sources.

Nitrate concentrations seemed to be particularly sensitive to transportation corridors. For example at the Alta Lake station (Fig.1 insert) located adjacent to the highway the concentrations were ten times as great as those observed at the nearby station on top of Whistler Mountain. This was the main factor causing the large difference in pH at the two stations.

Sulphate levels were highest in the city. At the mountain and the valley stations there was little difference in the sulphate values obtained, notwithstanding the large difference in pH values. The reason for this may be found in the ammonium concentrations. The Fraser Valley is primarily a farming and agricultural area and may be an important source of ammonia. This would explain the large concentrations of ammonium measured and may explain the corresponding smaller values in the hydrogen ion concentration.

Although the Ladner station was included in the city group, it is located south of the city in a residential/rural area with conditions similar to the valley sites. During rain periods the air trajectories are primarily from the southeast. Since there are a number of emission sources in the Puget Sound area, there is a possibility that the lower values reported at Ladner result from sources in the state of Washington.

Snowpack Samples

In addition to the two programs outlined, snow samples were taken at a number of sites over the mountain areas north of Vancouver. The snow sampling locations are indicated in Fig. 3. Snow profile samples were obtained from 9 pit locations. Surface grab samples were taken at the same sites plus an additional 3 sites. A complete description of the sites, sample collection techniques and processed data is available in SSD Internal Report Number 3. An analysis of the data is proceeding.

Conclusions

Since this preliminary analysis was based on limited data, the conclusions must be considered tentative. Additional data will provide a better insight into the factors contributing to acidic precipitation along the coast. Nevertheless some interesting results are indicated.

There is strong evidence that the Port Alice pulp mill has an effect on the precipitation chemistry at the Port Hardy CANSAP station. A substantial increase in sea salt ions was observed at Port Hardy due to the burning of hog fuel in the mill's waste wood boiler. During the mill closed period the average excess sulphate ion concentration was .17 mg/l. This increased to .58 mg/l when the mill was in operation.

The average pH of precipitation from air masses that did not appear to be affected by coastal urban/industrial pollution was estimated at 5.36.

A strong gradient in the pH of precipitation was observed in the lower mainland area where the pH in the Fraser Valley was much higher than in the city (5.40 against 4.77).

Both the Port Hardy and Vancouver Airport sites are influenced by local emission sources. The data obtained therefore casts considerable doubt on the accuracy of current maps depicting precipitation pH less than 5 along the southern B.C. coast. The data obtained suggest that the pH in areas not affected by local pollution may in general be nearer 5.4.

Recommendations

The data available to date have yielded some valuable information and the monitoring should be continued to provide an adequate data base for further analysis.

There is some evidence that pollution from Washington may be affecting the Georgia Strait area. It is proposed that the Lower Mainland monitoring network be expanded to investigate transboundary effects.

Acknowledgements

Mr. Ron McLaren was responsible for sample collection and data management. Chemical analysis was carried out by IWD Water Quality Laboratory, North Vancouver, B.C.

AVERAGE pH

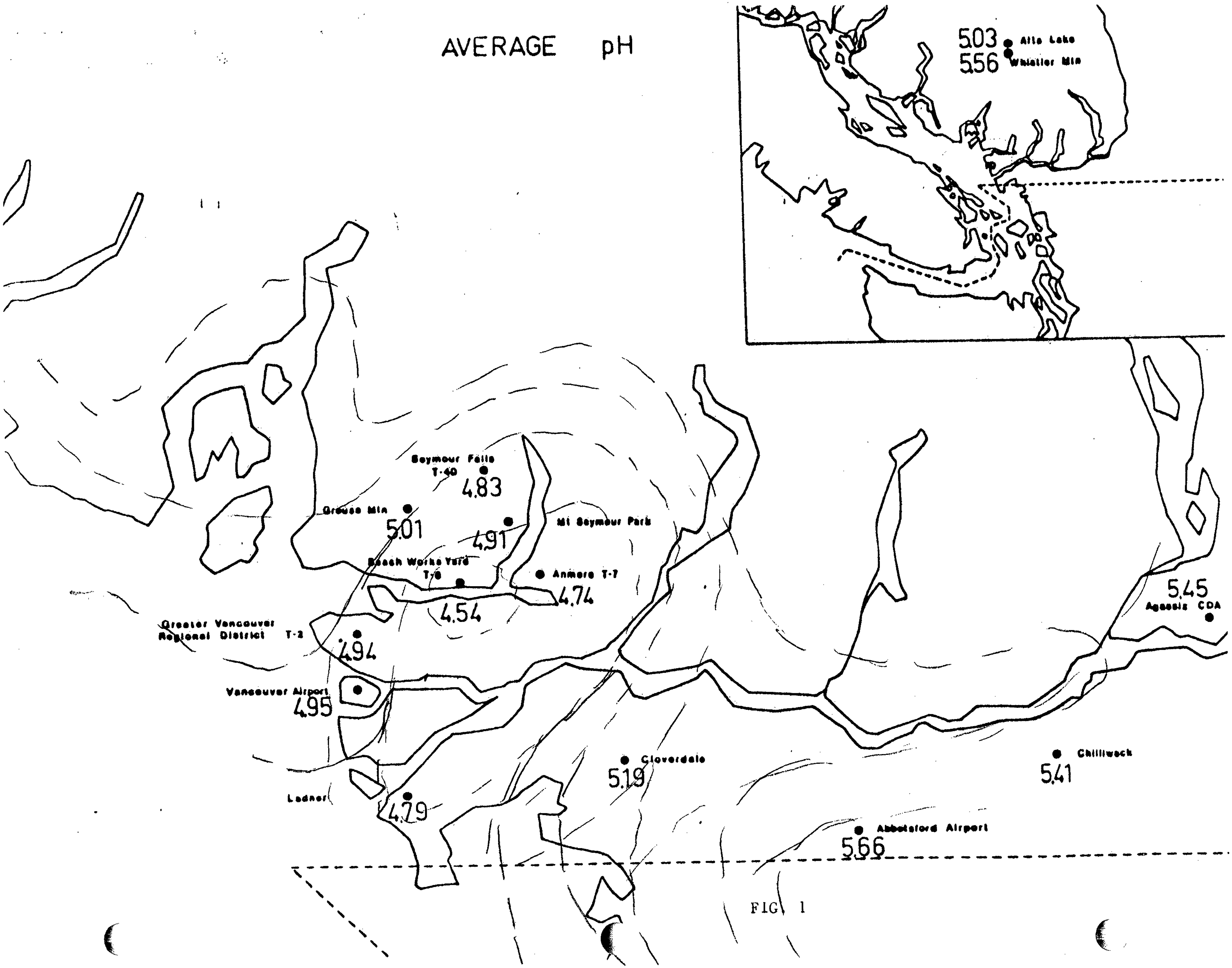
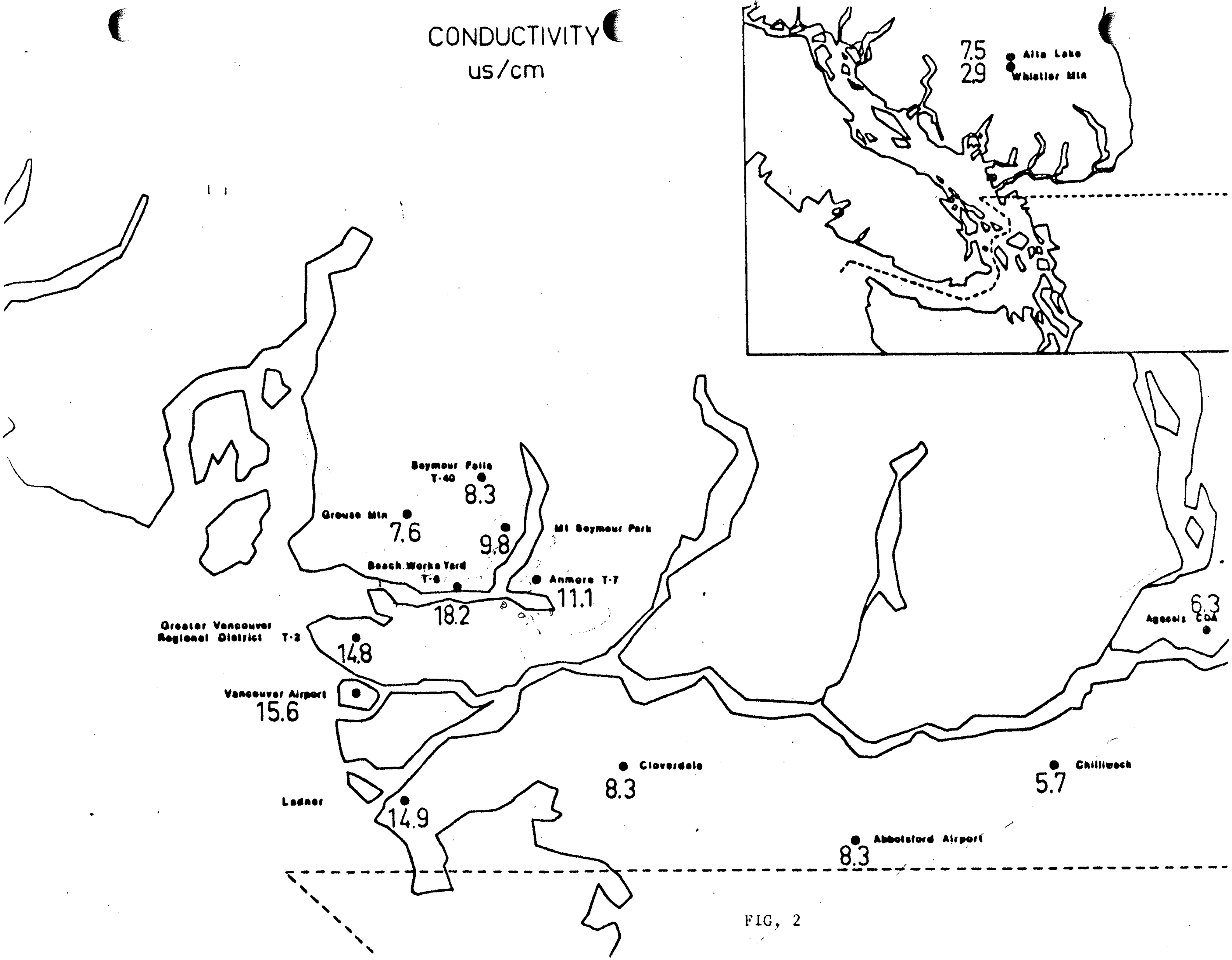
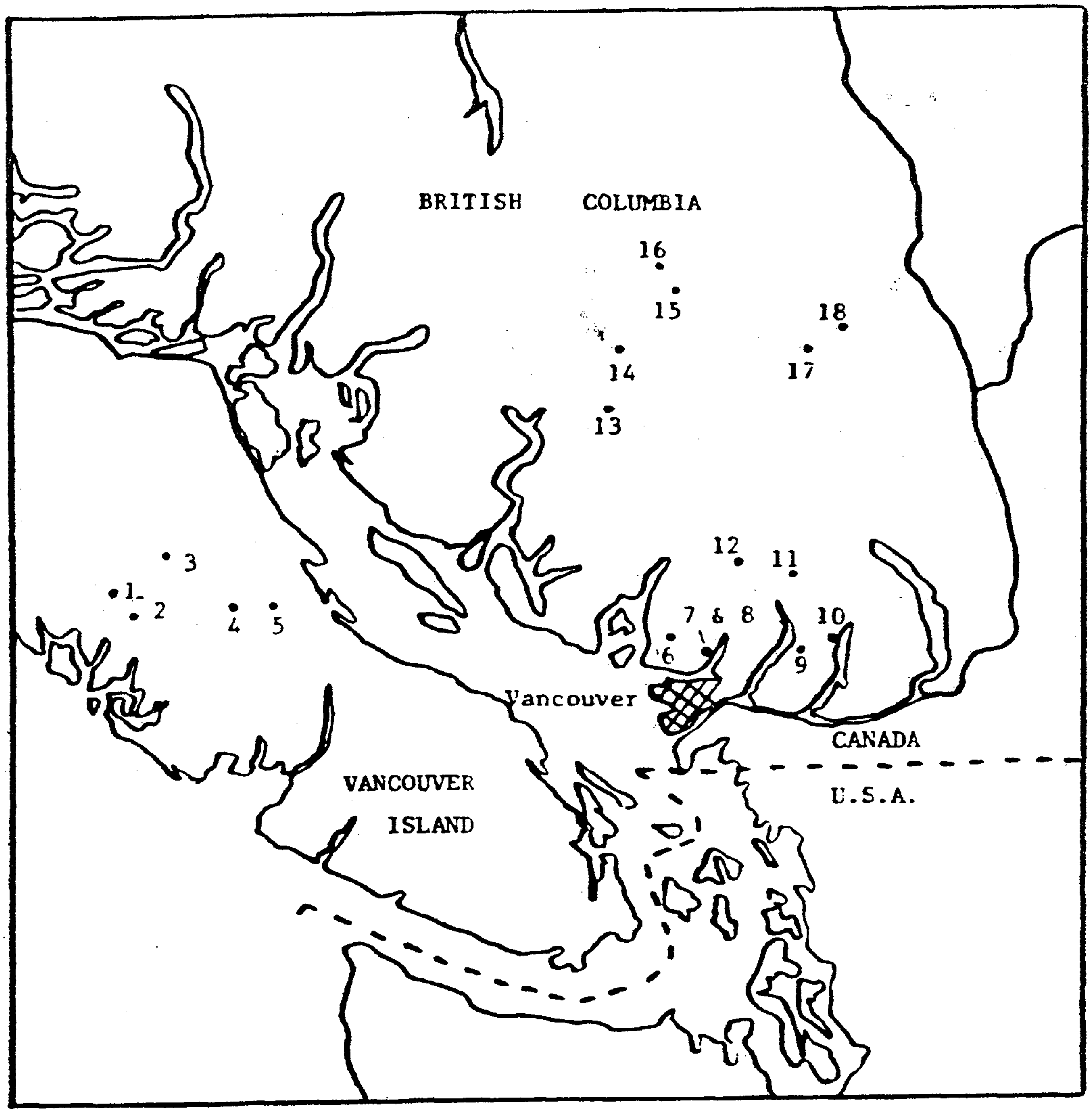


FIG 1


CONDUCTIVITY
us/cm
7.5 Alta Lake
2.9 Whistler Mtn
Seymour Falls
T-40
8.3
Grouse Mtn
7.6
9.8
Mt Seymour Park
Beach Works Yard
T-8
18.2
Anmore T-7
11.1
Greater Vancouver
Regional District T-2
14.8
Vancouver Airport
15.6
Ladner
14.9
Cloverdale
8.3
6.3
Agassiz CDA
Chilliwack
5.7
Abbotsford Airport
8.3

FIG, 2



SNOW SAMPLING LOCATIONS

*01. SPLENDOR MTN LAKE
*02. KOWUS CREEK VALLEY
*03. MT MCBRIDE
*04. COMOX GLACIER
*05. W. OF HAMILTON LAKE
06. THE LIONS
07. MT SEYMOUR (PEAK)
08. MT SEYMOUR (LOGGED AREA)
09. MT BLANSHARD
10. MT ROBIE REID
11. REMOTE PEAK
12. PINECONE LAKE
13. S.W. OF MT CALLAGHAN
14. N.W. OF MT CALLAGHAN
15. NORTH CREEK (1)
16. NORTH CREEK (2)
17. W. OF DUFFEY LAKE
18. CAYOOSH RANGE

*NOTE: Data for Vancouver Island locations are available in a separate report by S & B Research Etc., 6-70 Dallas Rd. Victoria, B.C. V8V 1A2

FIG. 3