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Pacific and Yukon Region Workshop on Acidic Depositions January 20, 1983

Edited by

D. A. Faulkner

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Summary of Proceedings

Pacific and Yukon Region Workshop on Acidic Depositions

at

B.C. Research Auditorium Vancouver, Canada January 20, 1983

Co-sponsored by: Environment Canada British Columbia Ministry of Environment

Editor: D.A. Faulkner

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#### Foreword

The Pacific and Yukon Region DOE (Department of the Environment) Acid Rain Committee, soon after its formation in 1982, recognized that considerable acid rain-related research and monitoring were on-going on Canada's West Coast. At the same time the Committee recognized a need to co-ordinate the efforts of the many agencies doing the work. A workshop of scientists from the Federal and Provincial Governments was recommended as one means to improve co-ordination.

Accordingly, Environment Canada and the British Columbia Ministry of Environment sponsored and arranged a joint workshop in Vancouver on January 20, 1983. The objectives of the workshop were to:

- (i) assist in co-ordinating agency activities and plans,
- (ii) identify acid rain-related concerns,
- (iii) identify information gaps, and
- (iv) provide a means to establish contacts among participants.

This report contains summaries (mine) or author's abstracts of the presentations made at the workshop. Also included is a summary of the statements made at the end of the workshop by the members of a panel, who were given the difficult task of assessing the magnitude and nature of acid rain problems in B.C. and the Yukon.

The organizing committee for the workshop comprised Les Swain, Dr. Neil McQuaker, Steve Nikleva and myself. On behalf of the committee, I wish to thank; B.C. Research for making their facilities available to us; the chairman, speakers and panel members for their efforts in making the workshop worthwhile; Ron McLaren, Doug Sandberg and Lorne McGregor who assisted with the program arrangements. As a member of the organizing committee my thanks go to the other members. As editor, I offer my thanks to Lori Nicholson who somehow always manages with my infamous scribbling.

D.A. Faulkner

#### Abbreviations Used in this Report

- AES Atmospheric Environment Service
- APN Air and Precipitation Monitoring Network

ASB - Air Studies Branch

BAPMON - Background Air Pollution Monitoring Network

CANSAP - Canadian Network for Sampling Precipitation

- CANSOC Canadian Network for Sampling Organic Compounds
  - DOE Department of the Environment (=Environment Canada)
  - EC Environment Canada (= Department of the Environment)
  - EPS Environmental Protection Service

DFO - Department of Fisheries and Oceans

IPSFC - International Pacific Salmon Fisheries Commission

IWD - Inland Waters Directorate

LRTAP - Long Range Transport of Atmospheric Pollution

MOE - Ministry of Environment

NH&W - National Health and Welfare

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# Emissions of Sulphur Dioxide and Oxides of Nitrogen in B.C. and Yukon

## E. Wituschek Environmental Protection Service, DOE, West Vancouver (Editor's Summary)

An inventory of emissions of the primary pre-cursors of acid rain began in North America in 1972 based on a Source Industrial Classification Index. Data for Canada and the U.S.A are published in the June 1982 report of the Canada/U.S. Working Group.

Current and projected North America emissions of  ${\rm SO}_2$  and  ${\rm NO}_{\mathbf{x}}$  are given in Table I.

{	SO <sub>2</sub> (10	<sup>6</sup> t/yr)	NO $_{\rm x}$ (10	<sup>6</sup> t/yr)	Primary SO4	(kilotonne/yr)
Year	Canada	U.S.A.	Canada	U.S.A.	Canada	U.S.A.
1980	4.8	24.1	1.8	19.3	192	480
2000	4.5	26.6	2.4	24.1	ł	1
	1				1	

Table I Emissions of primary pre-cursors

(Source: Canada/U.S. Working Group Report, June 1982)

l	SO <sub>2</sub> (1	0 <sup>6</sup> t/yr)	NO $_{\rm x}$ (10	<sup>6</sup> t/yr)
Source	Canada	U.S.A.	Canada	U.S.A.
Electric Utilities	.75	15.8	.25	5.6
Industrial Boilers	.62	2.4	.30	3.5
Non-ferrous Smelters	2.13	1.4	.01	0.0
Residential/Commercial	.21	.8	.09	0.7
Other Industrial	.92	2.9	.07	0.7
Transportation	•16	0.8	1.11	8.5
Total	4.8	24.1	1.8	19.3

The emissions by source (1980) are listed in Table II.

Table II Emissions of primary pre-cursors by source classification (Source: Canada/U.S. Working Group Report, June 1982)

Emissions in B.C. (1978) by source are given in Table III.

Source	Emissions	(10 <sup>3</sup> t/yr)
ł	so <sub>2</sub>	NOx
Industrial Process	164	11
Fuel Combustion	56	29
Transportation	10	123
Incineration	0.3	1.9
Miscellaneous	<u> </u>	7
Total	231	173

Table III Emissions of acid rain precursors in B.C. (1978). Note units are kilo-tonnes/year vs. mega-tonnes/year in the previous tables.

The major sources of  $SO_2$  are industrial processes and fuel combustion; of  $NO_x$  are transportation and fuel combustion. The B.C. emissions of  $SO_2$  are about 1/5 of the total Canadian Emissions; B.C. emissions of  $NO_x$  are 1/10 of the Canadian total.

Major B.C. sources (1978) are:

	$SO_2$ (t/day)	NO <sub>X</sub> (t/day)
Kitimat	4	
Alcan smelter	17	6
Eurocan pulp & paper	2	1.4
Trail		
Cominco smelter	62	2.4
Fort Nelson		
Westcoast Transmission		
natural gas plant	240*	4
Vancouver		
Chevron refinery	1.5	1.4

(The proposed Hat Creek thermal generating plant emissions were expected to be 150 t/day  $SO_2$  and 17 t/day  $NO_x$ ).

In the lower mainland of B.C. the total emissions of  $SO_2$  are 47,000 t/yr; of  $NO_x$  86,000 t/yr. The  $NO_x$  emissions include 33,000 and 28,000 t/yr from gasoline and diesel powered vehicles respectively.

\* This figure has been reduced substantially by about 90% in 1982.

## Precipitation Monitoring

# M. Kotturi Air Studies Branch, Victoria (Editor's Summary)

The Air Studies Branch (ASB), MOE, initiated a pilot study in September 1980 of the impact of local sources on precipitation acidity. Impetus for this came from noting the low pH of precipitation at the Terrace CANSAP station. A network of 5 sampling stations in the Skeena and Kitimat valleys was set up to take precipitation event samples. The stations were located at Prince Rupert, Terrace, Kitimat, Onion Lake and Salvus Camp. The latter was intended to serve as a background site since it is some distance from industries located at Kitimat, Terrace and Prince Rupert.

The daily emissions from the Alcan smelter were (in 1981) about 1.47 t/day of fluoride and 13 t/day of sulfate. These emissions are low-level and are almost constant. The sulfation rates as a result of these emissions in 1979 were about .27 mg  $SO_3/(100 \text{ cm}^2.\text{day})$ ; this may be low compared to the Province of Ontario standard of .7 mg  $SO_3/(100 \text{ cm}^2.\text{day})$ .

Ambient fluoride can only be detected to a distance of about 3 km downwind from the smelter. It is believed this is because of the combined effect of high solubility of HF in rain water and the high annual precipitation in the area (Prince Rupert, 2414 mm, Kitimat, 2826 mm and Terrace 1301 mm) washes out the fluoride.

Rain samples were collected in a collector made from a 20 cm diameter funnel and a polyethylene bottle.

An examination of the Terrace CANSAP data shows that when precipitation amounts are high, the pH is high. Usually, when precipitation amounts are low, sulfate concentrations are high. Similarly it is noted the fluoride concentrations in precipitation at Terrace (70 km downwind from Kitimat) vary inversely with precipitation amount.

It is found the concentration of strong acid in the ASB Terrace samples is almost constant. One reason for this is that the method of detection is not sufficiently sensitive.

The study has found that fluoride concentrations in precipitation at the Kitimat sampling site are dependent on wind direction. With northerly winds, concentrations at the site (about 1.2 km north of the smelter) are low; with southerly or southwesterly winds they are relatively high. Also, the concentration of fluoride at the site is inversely proportional to precipitation amount, as was the case with sulfate at Terrace. The Atmospheric Environment Service provided back trajectories of air parcels for each of the events. A few interesting features have been noted from these:

- (i) A comparison of two trajectories, one with a slowly moving parcel, the other with a rapidly moving parcel, showed that the parcel moving more slowly picked up more fluoride than did the rapidly moving parcel;
- (ii) In one case of high pH (low acidity) it was found the trajectory was from the southeast, and it is suggested the high pH was a result of the parcel picking up calcareous soil particles from the B.C. Interior.

In summary, the study has found the lowest pH values at the pollution control site in Kitimat (4 km north-northeast of the smelter). There, the median pH based on data for the period August 1980 - June 1981 is 4.52. The median pH at the background station (Salvus Camp) was 5.2.

In another ASB project, snow core samples are taken at high altitude stations in south central B.C. The pH of these samples (winter 81-82) ranged from 4.97 to 6.51. This project is to be continued in spring 1983.

For the future, it is planned to install six automatic (Sangamo) collectors at sites chosen to complement the CANSAP network.

- Q. Do you have a feeling of the percentage of contribution of sea salts to the ion deposition?
- A. Yes we did conventional calculations. The data are available.
- Q. Did you consider dry deposition on the Kitimat study?
- A. Yes. Both ambient gaseous and particulate fluoride concentrations decrease with distance from the smelter.
- Q. What about sulfates?
- A. No. We didn't monitor sulfate dry depositions.

#### AES Pacific Region Acid Rain Monitoring and Studies

S. Nikleva Atmospheric Environment Service, DOE, Vancouver (Editor's Summary)

The Atmospheric Environment Service (AES) operates, or participates in the operation of several precipitation chemistry networks. These are:

(i) BAPMON (Background Pollution Monitoring Network)

This is a World Meteorological Organization (WMO) sponsored network and includes nine sites in Canada, one of which is in B.C. Originally, the site was at Puntzi Mountain, opened ca. 1974 but was closed two years later and moved to Kelowna.

(ii) CANSAP (Canadian Network for Sampling Precipitation)

This network, the major one in Canada, consists of 54 stations, 8 of them in B.C. Monthly samples are shipped to the Canada Centre for Inland Waters, Burlington, Ont. for analysis.

(iii) APN (Air and Precipitation Monitoring Network)

APN comprises eight stations in eastern Canada - the farthest west station is Cree Lake, Sask. Daily samples of air and precipitation are collected. All stations are in rural areas and are intended to determine background concentrations and depositions.

(iv) CANSOC (Canadian Network for Sampling Organic Compounds).

This Inland Waters Directorate (IWD) network has 12 stations with one at Vancouver International Airport. Monthly samples are analyzed for organic compounds.

(v) Canadian Arctic Aerosol Network

This network includes three Arctic stations.

CANSAP data are published every three months but are not up-to-date; the latest currently available are for December 1980. B.C. data are available on computer at AES Regional Office in Vancouver and some data later than 1980 are available.

It was recognized that CANSAP had several deficiencies and a review of the network was undertaken. As a result, the network, beginning in April 82 in the east and fall 1983 in the west is being changed. The revised network will be named CAPMON, Canadian Air and Precipitation Monitoring Network. The objectives of the new program are to (i) measure temporal variations and long-term trends of chemical composition of precipitation and wet and dry deposition, (ii) to provide a data-base for LRTAP models, and (iii) to provide a standard set of monitors for all regions of Canada. Dry depositions will be estimated from ambient concentrations.

With the new networks, several changes will be implemented. Stations may be closed or re-located (in B.C. and other western provinces); improvements will be made to the sampler; daily rather than monthly samples will be taken; improved quality control procedures will be implemented; and new management procedures will be initiated.

For the 1977-79 CANSAP data, it appears that an area of mean pH less than 5 exists along the B.C. coast. This compares to the large area with mean pH less than 5 in eastern Canada, the main area of concern about acid rain. However, this analysis is based on the assumption that data are representative and gradients are homogeneous. Since the analysis on the west coast is based on only three stations, whose representativeness is open to question, the analysis is suspect.

The concern about data representativeness led to initiating a series of studies on the west coast about one year ago. These included:

- (i) establishing an event sampling network on the lower mainland,
- (ii) taking more frequent samples at the CANSAP stations, Vancouver, Port Hardy and Terrace, and
- (iii) sampling snowpacks on Vancouver Island and the lower mainland.

From the CANSAP data, we can also estimate the sulfate deposition. Allowing for a change in sampling procedure in January 1981 to eliminate an evaporation problem, we still find the sulfate deposition in the Vancouver area to be about 20 kg/ha/yr which again compares to the area of eastern Canada where there is concern. It should be noted also that Canada is pressing to set a standard of maximum deposition of 20 kg/ha/yr.

A few results from the lower mainland network sampling in 1982 can be given. Based on about one half of the 24 event samples taken, we find the pH is lower in the centre of the city of Vancouver than in the environs. In the city, the mean is about 4.8, in the mountain areas about 4.9 and in the lower Fraser Valley about 5.4. The sulfate loadings in the city appears to be over 20 kg/ha/yr, about 19 at mountain sites near Vancouver but drop to near 1.4 at Alta Lake (about 90 km north of The nitrate concentration in the Fraser Valley is about one Vancouver). We find the ammonium ion concentration much half of that in the city. higher in the Fraser Valley than in the city - probably from agricultural sources - and we feel this ammonium ion neutralizes much of the acidity in the Valley, hence the higher pH there. These results and discussions are contained in three internal reports which are available from AES Regional Office.

A preliminary analysis of the event sampling data has led to an interesting, albeit tentative, result. During the sampling period a pulp mill at Port Alice (about 40 km south of Port Hardy) operated part of the time, and was closed part of the time. The sulfate concentration at Port Hardy was found to be higher during the period the mill was in operation, leading one to suspect the mill has an influence on the depositions at Port Hardy.

The snowpack samples may be considered to have been taken along an east-west transect through Vancouver. When plotted, these results indicate a definitely higher acidity near Vancouver than at either end of the transect. A description of the methods used and the results is available in an internal report.

AES has also been involved in analysis of air trajectories and deposition modelling. Details of these efforts are also available from AES.

- Q. Was AES involved in assessment of the Clinton smelter?
- A. No.
- Q. Did you establish a background pH level for the coast region?
- A. No. The best estimate is from the Port Hardy and snowpack data. These indicate the pH in un-contaminated areas is about 5.4. We hope to have a CAPMON station to give background data but it is difficult to find a suitable location.

#### Analytical Procedures

# F. Mah Inland Waters Directorate, DOE, North Vancouver, B.C. (Editor's Summary)

At the Water Quality Laboratory of Inland Waters Directorate (IWD), we have been analyzing surface water samples for about 10 years, however we only began to analyze precipitation samples at the beginning of 1982.

Samples are analyzed according to the following priority list:

Group 1. pH, acidity (strong and total), specific conductivity Group 2.  $SO_4$ =,  $NO_3$ -,  $NO_2$ -,  $NH_4$ +, C1-Group 3. Ca+, Mg++, Na+, K+ Group 4. Extractable metals, i.e. Cd, Cu, Fe, Pb, Mn, Zn.

When a sample arrives at the laboratory, the shipper (a laboratory employee) decides if there is sufficient sample to determine extractable metals. If there is, 250 ml are extracted for metal analysis, and ions from Groups 1-3 are analyzed from the sample remaining in the original bottle.

Analysis methods used are as follows:

pH, conductivity - meters; Acidity - titration and Gran's function Chloride, sulfate nitrogen/nitrate, nitrogen/ammonia - determined colorimetrically using an auto-analyzer. Calcium, manganese - atomic absorption Sodium, potassium - automated flame photometry Extractable metals - atomic absorption spectrophotometry.

The main problem is encountered in measuring sulfate since concentrations are near the detection limit. The spectrophotometric method is used to measure extractable metals because of its efficiency.

The detection limits are as follows:

SO4, Cl	.2 mg/1
NO3/NO2 & NH3	•02
Ca ~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	•01
Mg, Cd	•005
Na, K	•12
Cu, Fe, Pb, Mn	.001

Acidity in terms of hydrogen ion concentration is measured instead of alkalinity since the former is felt to be more meaningful for acidic precipitation. Alkalinity can be related mathematically to the acidity. The Laboratory uses a rigorous bottle-washing procedure although some analysts insist it is better not to wash the bottles. Periodic testing has revealed no contamination of the washed bottles.

- Q. What is the storage time limit at the Laboratory?
- A. Acidity is measured within one day of receipt of sample; for other analyses, samples are held until a sufficient number are available to do a "run".

#### Measurements and Monitoring

# N. McQuaker Environmental Laboratory, MOE, Vancouver (Editor's Summary)

In developing a strategy for network quality assurance, we must consider the entire process. We first establish a monitoring objective, then develop a rationale to allow us to select sites to satisfy this objective. Site selection in this context is meant to include all aspects of monitoring such as siting criteria, parameters to be measured and frequency of monitoring. Next, as operational monitoring begins, we must establish quality control protocols for all components to ensure that the entire measurement process is kept in control. This will allow us to be confident that the data obtained are accurate and representative.

In quality control for chemical analysis of precipitation, the first requirement is to have a calibration procedure which is traceable to primary standards, or to a recognized procedure. Then we must ensure the measurement process is kept in control using quality control procedures, and ensure expected chemical relationships, eg. ion balance, are satisfied. Once quality control procedures for a laboratory are in place, we need an external check or an independent audit. This is best accomplished by inter-laboratory comparison studies.

The World Meteorological Organization (WMO) sponsors some of the best known studies. Some 20 laboratories were asked to analyze samples using their usual analysis procedures. The results for the principal ions in acid rain Na, K, Ca, Mg, NH<sub>4</sub>, Cl, NO<sub>3</sub> and SO<sub>4</sub> (but excluding hydrogen) were generally very favourable.

However, the comparison study analysis of pH and acidity measurements did not show such favourable results. In general, the discrepancy between expected and laboratory-reported results was unacceptably high. The pH values were determined using the conventional technique. That is, the pH meter was standardized using a buffer of <u>high</u> ionic strength and used to measure precipitation samples of <u>low</u> ionic strength. Use of a high ionic strength buffer produces a calibration bias, certainly part of the problem.

The situation is worse for acidity measurements. In addition to the calibration bias, an error results because of the difficulty of determining the titration end-point.

To this time, many questionable pH and acidity measurements have been made.

To resolve these problems, it is suggested (i) calibration of pH meters be done with a strong acid standard and measurement be made in quiescent solutions and (ii) a Gran's titration be used to assess total and strong acidity.

The recommended methods together with requisite mathematical analysis are outlined in the manuscript "The Chemical Analysis of Acid Precipitation: pH and Acidity Determinations" by N.R. McQuaker, P.D. Kluckner and D.K. Sandberg of the MOE Environmental Laboratory.

Using these methods, in an analysis of six samples, a mean precision and accuracy of + 0.01 pH units was achieved. Mean precision values for strong and total acidity determinations were 1.4 and 3.4 percent relative standard deviation respectively in the intervals 24-97 and 34-110 micro-equivalents/liter. These are considered acceptable.

To ensure quality control is maintained, the MOE Laboratory uses a ratio of 1 to 10 quality control samples and carries out an ion balance. The Laboratory is also participating in inter-laboratory studies with the Federal government and the province of Quebec.

#### Joint DFO/IPSFC Pacific Region Acid Precipitation Studies

## J. Morrison Water Quality Unit, Fisheries & Oceans Canada, Vancouver (Editor's Summary)

Joint Department of Fisheries and **Oceans** (DFO) and International Pacific Salmon Fisheries Commission (IPSFC) surface water and snowpack sampling began in 1981 under the direction of Dr. Jim Servizi (IPSFC) and Steve Samis (DFO). By the end of 1982, work was concentrated in two areas, the south central interior of B.C. and the north coast including tributaries to the Skeena River between Prince Rupert and Terrace, streams between Terrace and Houston, and streams on Graham Island in the Queen Charlotte Islands. In late winter 1983, samples will also be taken on Vancouver Island, the Sunshine Coast and the lower mainland. As well, IPSFC has done some preliminary experimental investigation of mortality of juvenile sockeye salmon in acidified waters.

In south central B.C., work on water and snow chemistry began The impetus for this came from the release in 1981 of the in 1981. Environmental Impact Statement (EIS) for the proposed Hat Creek thermal IPSFC and DFO were concerned about the buffering generating plant. capacity of areas downwind from Hat Creek, i.e. to the east and northeast at intermediate air transport distances (50-200 km). Much of the available data for the larger rivers and lakes indicated reasonable buffering capacity would be expected in systems near Hat Creek (50 km). However, few data were available for headwaters and smaller tributaries which could be more susceptible to acidification processes. Twenty-five sites (later reduced to 15) within 200 km of Hat Creek were selected for sampling. DFO was responsible for the water and snow sampling, IPSFC for the rigorous analysis, using the Gran's titration method for low alkalinity samples. Water samples were obtained in June 81, October 81, February 82, March 82 and June 82. Snow samples at 6 sites were taken in March 82 using a plexiglass corer. In the B.C. Interior lowest stream pH recorded was 6.36 and two streams had pH less than 6.5 on at least one The lowest alkalinity recorded was occasion during the sampling period. 4.72 mg/l and 8 had less than 10 mg/l on at least one occasion during the The lowest snow sample pH was 4.91, two areas had a sampling period. snow pH less than 5.0. Alkalinity and pH profiles were developed for two streams in the Thompson River system, through the snow melt period in the In the Eagle River (South Thompson drainage), stream pH spring of 82. declined from a maximum of 7.3 immediately prior to spring melt, to a minimum of 6.70 during the melt period. For the Raft River (North Thompson drainage) the corresponding figures were 7.52 and 6.60.

Water samples have been analyzed for 24 sites on the Skeena River (11 in June 82, 24 in October 82) and 10 streams on Graham Island in the Queen Charlottes (June 82). The lowest pH and alkalinity measured in the Queen Charlottes was 5.09 and 3.23 mg/1; 3 streams had a pH less than 6.5, 2 had alkalinities less than 10 mg/1. On the Skeena, the lowest

tributary pH was 4.55 and three tributaries were less than 5.0 on at least 1 occasion. Two streams appeared to be influenced by bog waters. The lowest alkalinity was 0.0; 10 of 24 streams had alkalinities less than 10 mg/1. Fish were observed swimming in these low pH waters. In January 1983, samples were again taken from these streams and the lowest pH found was 5.24. Coho and chinook salmon as well as Dolly Varden and rainbow trout were found in the streams. Further sampling is planned for spring 1983.

Preliminary sampling of 40-60 headwater tributaries on Vancouver Island and the lower mainland are scheduled for the period January-March 1983. Any extremely low alkalinity system may be priorized for weekly water chemistry sampling during the '83 spring melt period.

A report summarizing B.C. Interior sampling work to date is in preparation.

During spring melt in 1982, two Vancouver Island fish hatcheries experienced unexplained juvenile fish mortalities. Symptoms observed were disorientation, erratic swimming, cessation of feeding and increased mortality under conditions of stress. These symptoms are similar to those observed in Nova Scotia hatcheries using low pH water. One of these hatcheries is scheduled for weekly pH testing this spring.

Questions which remain to be answered are:

- (i) Are the juvenile salmon mortalities at the hatcheries attributable to the effects of a spring pH depression? Is the acidification "natural"?
- (ii) Are some salmon stocks on the north coast resistant to acidified water?
- (iii) Can fish spawn & rear in the coastal low pH streams because of interactions between metals and organic compounds in the bog waters?
- (iv) What are the pH and alkalinity characteristics of the spring melt in these systems?

The DFO/IPSFC program for fiscal year 1983-84 is now being developed. A baseline water chemistry sampling program concentrating on poorly buffered areas is envisaged.

- Q. Is your own laboratory doing the work and do you carry out a quality control program?
- A. DFO does the field work, IPSFC the laboratory analysis. No quality control procedures are in effect (Servizi).

- Q. Are the low pH values on the north coast field measurements or laboratory analysis?
- A. Lab analysis.
- Q. Are your results based on single or multiple samples?
- A. All are "one-shot" samples.
- Q. Are there bogs on the Queen Charlottes which affect acidity of streams?
- A. Field crew will investigate streams on the Charlottes when the opportunity arises.

#### The pH Tolerance Limits of B.C. Aquatic Plants

## P.D. Warrington Water Management Branch, MOE, Victoria (Author's Abstract)

Can aquatic plants be used as indicators of pH and other water parameters? What is the range of pH values and other nutrient values within which each species of aquatic plant can grow? To make a start at answering these questions three existing data sets in the Ministry of Environment have been merged and correlations of various water parameters with the presence of species of aquatic plants are being made.

of The data sets include set 1100 lakes with а presence/absence of aquatic plants noted; a set of 2300 lakes with morphometric (including bathymetric) data, pH's and oxygen and temperature profiles and a subset of the EOUIS water chemistry data set which corresponds to lakes already entered in the first named aquatic plant The quality and quantity of pH data in these files is rather file. limited and not adequate for a definitive answer to the questions above but should allow approximate ranges and means to be estimated for at least some aquatic plants.

Histograms of the frequency of occurrence of each species of aquatic plant with pH values in 0.1 pH unit increments are being constructed. A literature review and annotated bibliography on the effects of acid rain on aquatic plants is being prepared. Laboratory experiments to determine lower pH limits for several species of aquatic plants will be carried out soon.

One interesting confirmation of literature reports has come out of this work already. The literature indicates that aquatic mosses only utilize and not HCO<sup>-3</sup> as their source of  $CO_2$ can inorganic carbon for photosynthesis. This means that the upper pH limit for these plants would be about 8.2 since beyond this point there is no dissolved CO<sub>2</sub> left, it is almost all in the form of HCO-3. The histogram for the species Fontinalis antipyretica, the only aquatic moss for which data is available, shows a range of 5.9 to 8.1 and a mean pH of 7.1. Most other aquatic plants have means around 8 and ranges up to 10 since they utilize  $HCO_3$  as a carbon source.

- Q. Do you feel species can exist in low pH waters such as the bog fed streams of the north coast?
- A. A half-dozen species grow in low pH waters.

- Q. Have aquatic plant extinctions at low pH's been observed in Sweden or in eastern Canada?
- A. Limited information from the Canadian Shield area shows presence of plants down to about pH 4.0 and almost nothing below that. This is the level at which bi-carbonate cuts off. Have not noted any literature showing progressive plant extinctions with decreasing pH.

Water Quality Near Hat Creek: Vulnerability to Acidification

# Charles Newcombe Fish and Wildlife Branch, MOE, Victoria (Author's Abstract)

A study of water quality, completed in 1976, indicates that some lakes and streams in the vicinity of the proposed Hat Creek thermal power plant may be vulnerable to acidification by acid-forming compounds released into the atmosphere by the combustion of coal. Of the 166 lakes and 39 streams for which there are data, 12.6% and 56.4% respectively, have pH  $\leq$  7.0, or alkalinity  $\leq$  50.0 mg/1, or filterable residue  $\leq$  70.0 mg/1, or specific conductivity  $\leq$  119.0  $\mu$  mho/cm. Two of these water quality variables, filterable residue and specific conductivity are surrogates used in the absence of measured alkalinities. Filterable residue is significantly correlated with alkalinity as follows:

$$y = 3.44 + 0.71 x$$
,  $r = 0.96$ ,  $S_{EST} = 27.84$ 

and specific conductivity is significantly correlated with alkalinity as follows:

$$y = -4.71 + 0.49 x$$
,  $r = 0.95$ ,  $S_{EST} = 28.19$ 

The rate of acidification of water bodies is impossible to predict using information available in 1976 because the shape of the titration curves is unknown for any of the lakes or streams studied, and there is no information about the rate of acid deposition. However, it is reasonable to predict that, of all the water bodies studied, streams fed by snow melt in the spring may be most vulnerable to acidification. Mapping Lake Sensitivity to Acid Rain - The British Columbia Experience

## L.G. Swain, Aquatic Studies Branch, MOE, Victoria (Author's Abstract)

In 1981, the Aquatic Studies Branch of the British Columbia Ministry of Environment began a program whose goal was to map lakes within the Province according to their sensitivity to acid rain.

Initially the Branch was part of a Western Canada Committee responsible for recommending procedures for undertaking such a program to the West of the Manitoba/Ontario border. The major conclusions from the Committee were that parameters chosen as indicators of lake sensitivity had to be common water quality measurements in several areas of jurisdiction, had to be relatively free from potential error due to sampling and analytical techniques, and as well should provide continuity with parameters used in earlier studies in Eastern Canada. Thus the parameters initially chosen to be examined were pH, alkalinity, calcium, magnesium and aluminum.

The first step undertaken by the Committee was to determine the extent of data already available. Unlike Eastern Canada, it was decided that data for freshwater lakes should only be used since rivers in Western Canada tend to dissect a variety of large geologically heterogenous areas within any watershed.

A time limit of five years was chosen for the data to be examined, which meant only data collected in the period 1977 through 1981, would be considered. Within British Columbia, only 160 lakes had been sampled for any of the selected parameters in this period, some as seldom as once. Extensive data gaps exist along coastal British Columbia and North from  $56^{\circ}N$  latitude.

British Columbia is presently taking steps to prepare preliminary sensitivity maps, infill the data gaps, and attempt to utilize morphimetric parameters and alkalinity titration curves to predict lake sensitivity. These steps are reviewed in the paper.

- 0. Can lake acidity be related to surficial acidity?
- A. Yes. Have worked with John Wiens and found good correlation between sensitivity patterns and those to be expected from the geology.

- Q. Have you been able to complete your data bank w.r.t. aluminum?
- A. We sample many metals including aluminum co-incidentally.
- Q. Do you find aluminum values alarming?

A. No.

Ecological Land Classification and its Application in Acid Rain Sensitivity Interpretation (with specific reference to Yukon Territory)

> John P. Senyk, Lands Directorate, DOE, Victoria and Clay Rubec, Lands Directorate, DOE, Ottawa

> > (Senyk - Author's Abstract)

A variety of approaches have been used to assess terrestrial sensitivity to acid depositions. A technique that allows for ranking the sensitivity of the variety of related biological and physical resources within specific geographic areas is attractive though not completely practical at this time. Ecological Land Classification allows for the identification and characterization of ecosystems at various levels of generalization. Though biased somewhat by the physical environment, the "ecosystems" identified in the E.L.C. process have a high degree of homogeneity and continuity in terms of climate, terrain, soil, vegetation and water and fauna to some extent.

A large part of northern Canada has been mapped and characterized at the Ecodistrict level. This level of generalization has been used with varying degrees of success in assessing terrestrial sensitivity to acid deposition in eastern Canada. An initial assessment based on ecodistricts for southern Yukon was presented.

(Rubec - Editor's Summary)

In 1980 the Canadian and U.S. governments initialled a Memorandum of Intent concerning Transboundary Air Pollution. Thereafter, an Impact Assessment Working Group was established and one of its tasks was to do terrestrial sensitivity analysis and mapping. That group decided they required basic data on sensitivities of eco-systems in eastern North America from which an assessment of potential impacts could be made. This initiated a DOE Lands Directorate project to derive sensitivity maps of eastern Canada.

It soon became evident that data were lacking to complete the task. While considerable data on soils, bedrock, water, etc. were available on varying scales, no standard data base existed.

Several other groups also undertook studies to characterize sensitivity. These included:

- (i) Agriculture Canada looked at agricultural soils only and developed three classes of sensitivity based on cation exchange capacity;
- (ii) Geological Survey of Canada used data on bedrock geology to develop a four-level classification scheme and generated maps on the 1:1,000,000 scale;

- (iii) Water Quality group in Nova Scotia generated sensitivity maps for that province based on the calcium saturation index;
- (iv) Canadian Forestry Service did a preliminary analysis of vegetation sensitivity and generated maps (1:15,000,000) using three classes of sensitivity;
- (v) A group in Alberta and Saskatchewan (Shewchuk et al) generated maps (1:10,000,000) for western Canada which included soils and geological sensitivity.

At the same time Lands Directorate has gone through several phases of maps (1:1,000,000) utilizing ecological land classification. These were based on data for all of eastern Canada and employed the concept of "ecodistricts", derived from an interpretation of satellite data and using the best available information. A similar U.S. group prepared maps (1:1,000,000) for the eastern states.

Canadian and U.S. scientists agreed on simple criteria which allowed them to generate terrestrial and aquatic inputs for sensitivity maps based on a uniform system with universally available data. They developed a simple three-level sensitivity system using concepts such as pH, soil texture, presence of organic matter and bedrock data (in areas where the soil was less than 25 cm deep). Maps on a scale of 1:1,000,000 were compiled and the results stored in a computer data bank. Four regional scale maps of eastern North America were printed as part of the Phase II MOI report.

After publication of the Phase II maps, it became evident more detailed analyses using more information were needed. Phase III work was initiated and is on-going. It has resulted in a dramatic improvement of the original maps. These use soil and bedrock information but in a more refined way and take into account the percentage exposure of bedrock. More detail, where it is available, beyond ecodistrict information is provided. Southern Ontario land information is used in place of ecodistrict data and Geological Survey of Canada data south of 52° north in eastern Canada are being incorporated into the analysis. A new series of maps, to be included in the Phase III report, at the 1:1,000,000 scale and of varying reliability across the map are being generated. In all cases the <u>best available</u> data are used regardless of whether they are standardized.

In western Canada, a similar problem must be faced. It is recognized that each province will wish to go its own way. Nevertheless, it is suggested (i) since large soils and bedrock data-bases exist, they should be used first even though the information is sometimes too detailed and (ii) provinces should use standardized sensitivity criteria and generate standardized output even though variable methods are employed.

Complete data-bases on soils, etc. for the Yukon and N.W.T. are not available. For those regions, we will have to utilize to a major degree ecodistrict data and geo-climatic information. Discussion:

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- Q. Are water chemistry data for the Yukon now available? Will they be published?
- A. (Senyk) They should be published soon.

Soils and Geology Sensitivity Mapping and Related Studies in B.C.

John Wiens Surveys and Resource Mapping Branch, MOE, Victoria (Editor's Summary)

In B.C. the potential for acid rain impact is nothing like that in eastern Canada. At this stage B.C. still has time to manage development to prevent serious impacts.

In terms of soils and vegetation, precipitation is one source of acidic input. Fertilizers have to be recognized as a significant source also as has been documented for the orchards in the Okanagan Valley.

The work underway is sponsored by the Technical Committee of the Western Canada LRTAP Committee. The long-range goal is to develop sensitivity maps for all of Western Canada.

Terrestrial sensitivity refers to sensitivity of soils, rocks, wildlife, vegetation, etc. It may be interpreted (i) in terms of impact on aquatic systems, (ii) impact on forest or agricultural productivity or (iii) the potential change in soil pH, etc.

Sensitivity mapping requires a landscape stratification scheme. Such schemes include eco-district mapping, bio-physical land mapping, soil surveys, etc.

The sensitivity mapping work in B.C. includes the following:

- (i) A quick soil acidity map (1:6,000,000) of B.C. It depicts generalized existing soil acidity, hence is not a sensitivity map per se.
- (ii) A soils sensitivity map (1:6,000,000) based on five factors; soil depth, upper soil acidity, soil texture, lower-soil acidity and bedrock type. The map depicts four classes of sensitivity; low, moderately low, moderately high and high which gives general information on sensitivity. Inferences were made from bedrock type, etc. for regions where data were not available for soil acidity, texture, etc.
- (iii) Currently, a 1:2,000,000 soil sensitivity map is being developed, funded by the B.C. MOE Air Management Program. Deliberate emphasis is placed on soils. The map units being rated are described in terms of soils and parent materials. All available published and unpublished inventory information is beng used. Completion is expected by March 31, 1983.

Laboratory studies are underway to determine the actual response of soils to acidic inputs in order to check the earlier developed

criteria and to develop predictive relationships. Inventories with information on soil characteristics, such as organic matter content, cation exchange capacity, base saturation and silt and clay content, are available. An attempt is being made to find relationships between actual buffering and these characteristics. A range of soils from B.C. (200-300) were selected and titration curves were prepared for them. Buffer curves of soil pH versus incremental amounts of added acid are being generated.

- Q. Do chemically-derived sensitivities match with those derived using the five factors?
- A. A preliminary conclusion is yes.

## Acidic Deposition as a Component of Soil Deterioration

## Terry Lord, Agriculture Canada, Vancouver (Author's Abstract)

Soils in Canada are deteriorating through processes that include erosion, salinity, intensive cultivation, contamination, disturbance and acidification. Acidic deposition is one aspect of accelerated acidification; other processes are heavy use of N fertilizer, irrigation and drainage.

Podzolic soils, Dystric Brunisols, and many Gray Luvisols have a pH of less than 5.5 in the upper soil horizons. They are poorly buffered and readily acidified.

Unless soil acidity remains at suitable levels in the soil, nutrients such as Fe, Al and Mn leach out, frequently contaminating surface waters and groundwater.

In Eastern Canada, scientists at the institute of Land Resource Research and Biology Research within the Research Branch of Agriculture Canada have reported on a preliminary assessment of the effects of acid rain on agriculture (Coote et al., 1981) (Coote and Wang, 1981). They deal with the problems under four main aspects:

- the sensitivity of soils to acidification
- the distribution of acid rain
- the effects of acid rain on crop plants
- the significance of the problem to agriculture

Although little is known on the amounts and distribution of acid rain in Western Canada, the need for and the benefits of lime application to acid soils have been well documented by Hoyt, Nyberg and others. In the western plains area soil acidity causes damage to crops when the pH is below 6.1. Soils with pH 6.1-6.5 are considered to be potentially acid. The 500,000 acres (200,000 ha) of acid soils in central and southern B.C. include significant amounts of very strongly acid soils (< pH 5.0) in the Okanagan fruitlands. On the farmlands of the Lower Mainland and Vancouver Island about 200,000 acres (80,000 ha) of acid soils occupy over 80% of the cultivated land.

There are two ways to deal with soil acidity - lime the soil or grow acid tolerant crops. Either alternative may be economically unsound or impractical. Although the rapid increase in the use of fertilizers has been identified as the main cause of accelerated acidification of our soils, other causes such as sulfur dioxide emissions from gas processing plants, removal of calcium from the soil by growing crops and erosion of topsoil are of serious concern to agriculturalists.

## Vegetation Sensitivity Mapping Concept

# J.W. van Barneveld Surveys and Resource Mapping Branch, MOE, Victoria (Author's Abstract)

The Vegetation Unit of the Surveys and Resource Mapping Branch of the Ministry of Environment is probably the most recent newcomer in the area of acid rain and air quality. The unit was asked by the Air Studies Branch of the Ministry of Environment to participate in the definition of air quality guidelines for British Columbia and to collaborate on the provincial LRTAP committee.

The Ministry of Environment is concerned with maintaining quality habitat for man, animal and fish. Much of this habitat is composed of vegetation. The vegetation may be affected by air pollution in the form of:

- a) changes in actual or potential species diversity
- b) changes in productivity, (actual or capability)
- c) changes in the quality.
- a) changes in actual or potential species diversity are of primary concern to this ministry. Rare or endangered species will require stringent protection measures. Visible damage to vegetation has been identified as a criterion for determining desirable air quality guidelines for British Columbia. Sustained damage of this nature will likely lead to elimination of the affected species.
- b) changes in actual or potential productivity are of direct concern to the Ministry of Environment where it affects the ability to produce sufficient biomass for wildlife use as browse or forage (primarily). Although not of immediate concern to the Ministry of Environment, reductions in productivity may be significant from the perspective of agriculture or forestry.
- c) changes in the quality of vegetation biomass are more difficult to evaluate. A reduced protein content of the vegetation may render a winter range inadequate for survival of wildlife through the winter. Or accumulations of toxic metals may cause chronic deterioration of the health of animal populations.

The previous speaker dealt with the effects of acidification on the health of submerged plants. For the non-aquatic plants it is useful to recognize two categories:

- 1) plants rooted in the soil
- 2) plants not deriving their nutrition from the soil.

The latter category includes epiphytic plants, mosses and lichens. Epiphytes and mosses derive much of their nutrients from the rain, stemflow and crown drip. For mosses the nature of the surface moisture is further important as it provides the medium for the motile gametes to "swim" to the female structures. Lichens, a symbiosis of a fungus and an alga, derive some of their nutrition from decomposing organic material. Substances required to cause "rotting" are excreted. Released nutrients are subsequently absorbed into the fungal tissue. Immobilization of nutrients, and neutralization of the excreted substance by the chemical composition of atmospheric moisture leads to the elimination of the lichen.

The very high sensitivity of lichens to atmospheric contamination renders them useful as an "early warning" indicator. However in areas such as the northern parts of British Columbia, where lichens form an important component of the diet of Caribou, lichens must be maintained, and air quality must be in accordance with this objective.

Both categories of plants are exposed to the open atmosphere, and  $CO_2$  for photosynthetic assimilation and  $O_2$  for respiration are not usually in short supply. However, high concentrations of contaminant may cause direct damage to the various structures of the plants (including cuticle, stomata and sponge parenchyma of the leaves).

The majority of plants with which we are concerned here belong in the first category. This category derives its nutrients from the "soil solution." The adverse effects of acid rain on this solution may be:

- (i) to immobolize certain essential nutrients.
- (ii) to mobilize toxic quantities of certain minerals.
- (iii) to remove by leaching essential minerals and replace them by hydrogen ions.

The Vegetation Unit is in the initial phases of a program which should lead to the preparation of maps of vegetation sensitivity.

The concept of this sensitivity is that plants will be tolerant of changes in some pH ranges while changes at certain critical pH levels are lethal. It is the intent to define such critical acidity levels for significant species, determine the acid loading required to change each soil beyond such critical limits, and to determine how the vegetation communities will be affected by such changes.

In British Columbia, in contrast to many other areas of Canada, we have accumulated a substantial data base of soils and vegetation information and soils have been mapped for a large portion of the province. Soil titration curves are presently being prepared as indicated by Mr. Wiens.

Although there are many areas of this project that need to be investigated carefully, we anticipate that a number of approximations of vegetation sensitivity for planning and operational purposes are within our grasp.

#### NH&W Acid Rain-Related Programs

John M. Hopper, South Mainland Zone Health Services, Health & Welfare Canada, Vancouver (Editor's Summary)

The mandate of the Medical Services Branch of Health and Welfare Canada (NH&W) includes administration of the Indian health program. One responsibility of the Branch is to be aware of any factors, such as air pollution, which may affect the general health of the population. These approaches to the problem are taken:

- (i) Sources of air pollution are identified,
- (ii) Release of heavy metals which may be harmful to people are investigated, and
- (iii) It is assumed that increased acidity may lead to leaching of heavy metals.

The main air pollution sources of interest to NH&W are as follows:

Fort Nelson - Emissions of  $SO_2$  from the gas refinery, at one time large, are now reduced significantly and no complaints are heard.

Fort St. John - A great release of sour gas  $(H_2S)$  from gas well cleaning, occurred some time ago. Compensation was paid to those affected.

Prince George - Three pulp mills emit pollutants but the residents have become accustomed to the odour.

Kamloops - Although several pollution sources are found here, Pollution Control Branch figures indicate concentration levels are low.

Sparwood - Particulate matter from the mines has resulted in some subjective health effects on the residents.

Kimberley –  $SO_2$  emissions from a concentrator used to exceed the limits.

Trail - Measurements in vegetation indicated high lead levels.

Hat Creek - Had the thermal plant been built, fluorosis in cattle but not in people would be a concern.

A data-base of chemical analyses of well water in B.C. has been built up over the years.

A few findings with regard to heavy metals are:

- (i) High mercury levels were measured in the Indian population of Lake Williston and it was assumed the source was mercury used to extract gold from ore but this assumption proved incorrect. Mercury was found in fish from the lake, but the source remains a mystery.
- (ii) High cadmium levels were found in moose liver but none found in human beings. The source of the cadmium is unknown.
- (iii) Arsenic concentrations have been observed to be three times greater in salmon than in char, but these are within acceptable limits.

The above discussion relates to medium and long-range air pollution transport. One ultra short-range pollution source has been well documented to cause low birth rates, delay in healing of duodenal ulcers, cancer of the bladder, coronary heart disease, emphysema and lung cancer. It is cigarette smoking!

- 0. What elements do you look for in your well-water analyses?
- A. Heavy metals. We have noted an increase in iron and manganese over time.
- Q. Are data readily available?
- A. Yes.

#### Panel Session

Editor's Note: The workshop concluded with a panel discussion. The panel members were:

Steve Nikleva, Atmospheric Environment Service, EC - Chairman

Dr. Jim Servizi, IPSFC

Paul Whitfield, Inland Waters Directorate, EC

Dr. Malcolm Clark, Waste Management Branch, MOE

Speakers were asked to discuss the questions:

- (i) Based on your knowledge and what you have heard at the workshop today, do you perceive that a significant acid rain problem exists in B.C. and the Yukon?
- (ii) If your answer to the above is affirmative, how serious do you perceive the problem to be and what should we do about it?

The following are brief summaries of the comments of the speakers. It was hoped to record the open discussion which followed but this proved too difficult.

D.A. Faulkner

### Nikleva:

The workshop discussion covered, amazingly in one day, the whole range from emissions to effects.

A chart of mean pH in Canada shows the pH 5.0 line encompasses the area of southern Ontario and southern Quebec, i.e. the areas where acid rain is of greatest concern. The same chart indicates that, possibly, the west coast is also an area of pH less than 5.0

Similarly, a chart of sulfate depositions (1980 data) shows an annual deposition of 23.7 kg/ha at Vancouver which exceeds the 20 kg/ha guideline favoured by Canada. Beyond the lower mainland in B.C., depositions drop below the 20 mark (to 13 at Port Hardy, 12 at Prince George).

Similar deposition patterns are noted for nitrate and ammonium ion.

#### Servizi:

Only from areal deposition patterns can one judge if the amount of hydrogen ion being deposited is enough to cause a problem. The pH of rain is interesting, but doesn't indicate if you have a significant problem since the deposition depends also on precipitation amount. Researchers should be encouraged to present results in micro-equivalents of hydrogen ion per hectare.

Significant work is being done to document the soil and water sensitivity, particularly in the area south of Prince George. A small amount of work is being done in the Yukon but no real sampling program is underway.

We have no reports of impacts of acid rain on fish except possibly the fish kill at hatcheries on Vancouver Island. That is yet to be documented, hopefully with studies in spring 1983.

It is not necessary that a significant problem exists before pursuing research; with industrial growth in B.C., emissions will increase and a problem could arise. We should obtain the data necessary to deal with any problem when industrial projects are proposed. The Hat Creek thermal generating plant, which may be resurrected, is a case in point. Unless we have good documentation on sensitive areas, we are unable to predict effects using models available to us.

Worthwhile work is on-going in documenting sensitive areas. One interesting thing to come out of this, so far, is that we cannot conclude that waters in an area are of similar sensitivity by looking only at the soil and bedrock. Whitfield:

Frank Read of the Harvard Law School, in a paper "Acid Precipitation Scientific Uncertainty - Problems and Probability" (published in <u>Inter. Journal of Environmental Studies</u>) points out there is a fine line between science and management, or between science and law; it is necessary to bridge the gap. He uses an example of fish kills by aluminum leached from the soil by acid rain. Indirectly acid rain kills fish but he then comes back to the question of whether acid rain is bad, or whether it is a problem. We can go so far scientifically but then must make a value judgement. That is where a scientist encounters difficulties.

In our work in Atlantic Canada (Limnology and Oceanography, Vol. 28, p. 160-165), we applied a simplistic but widely accepted model developed by Kramer. This model suggests that if you add acid to surface waters, the sulfate concentration goes up, the pH goes down and the calcium concentration stays the same. We looked at 11 rivers in Atlantic Canada, classified as sensitive or not based on the Calcium Saturation Index. Only one or two of the 11 behaved as they should according to the model which shows we don't understand how acid precipitation affects the total chemistry of the liquid phase.

On the micro-scale, i.e when we look at small creeks, we get into a real averaging problem. We don't have the detailed, sequential data to determine trends. If we are to determine sometime in the future that acid rain is a problem, we must begin now collecting systematic data which we can analyze in those terms. At present we (IWD) are not collecting any. Precipitation and surface waters are monitored but we may be unable to link the two.

#### Clark:

Is there a significant acid rain problem in B.C.? Yes, there is a problem, at least it is a problem we cannot ignore in the future. The problem is probably minor compared to that back east.

Several charts with carefully drawn isopleths have been presented at the workshop. However, one gets the feeling that many of these are "wishful thinking" and many data gaps remain to be filled in.

We have only a few major emission sources in B.C. now. For the next few decades, about the best we can hope is that the amount of emissions will remain constant.

Two of the main areas of emissions, the lower mainland and the Kitimat area happen to correspond to the most sensitive areas in B.C. (It is not clear what is happening at Fort Nelson). Furthermore, we are uncertain of the sources south of the U.S. border and in Alaska. What is the impact of the latter on the Yukon?

No one at the workshop has mentioned plankton. It would be surprising if acid rain had no impact on those organisms. Concern was expressed about the impact on salmon and on plant species.

As we do have some major sources, we have areas sensitive to acid rain, and we are concerned about the effects on some species, it appears governments have justification to fund further studies.

For the non-chemists, a few remarks about basic chemistry may be in order.

Some chemicals considered to be alkaline (ammonia and the amines) can be oxidized to  $NO_3$ . In the short-term, they may neutralize acidity but in the long-term can contribute to acid rain. Amines from oceanic plankton can be oxidized and thus contribute to acid rain on the coast.

One should recall that pH is defined for a temperature of  $25^{\circ}$ C. The dissociation constant of water changes by more than an order of magnitude as the temperature lowers to about  $10^{\circ}$ C. One should bear this in mind when doing chemistry of lakes and streams of B.C., many fed by snow melt, and few having a temperature near  $25^{\circ}$ C.

We should also be considering the speciation of chemicals. Particularly, in the sensitive areas affected by plumes from the major sources, we should be studying the detailed chemistry, eg. we should be determining not just the total copper concentration but should measure the ionic and complexed concentrations.

If strong acid is added at a constant rate to water of starting pH 7-8, at first the pH changes slowly. However, at a pH of 5.8-6.4 the slope of the titration curve becomes quite steep and a small amount of acid will reduce the pH rapidly. It appears in B.C. we have few water bodies with pH less than 5.8 and we are probably still using the buffering capacity we have. At the critical point, however, a small amount of acid injected into these waters may cause a very serious problem.

Consider the effects of reducing the pH of some of our water bodies from 7.5 to 7.0. In some instances, this may be beneficial to plant life. However, in others the zinc is bound up as zinc silicate and a reduction of the pH to 7.0 changes the zinc to the highly toxic  $Zn^{++}$ . A similar process occurs for copper, though as hydroxide and carbonate rather than as silicate.

We need to do detailed chemistry of water bodies in B.C. For this we need field data we believe in. We tend to throw out some field data, not because it is in error but because we do not understand the differences between field (often non-equilibrium) and laboratory chemistry (equilibrium).

# List of Participants

Ed Wituschek, EC	Dr. P. Warrington, MOE
M.S. Kotturi, MOE	J.H. Wiens, MOE
L. Swain, MOE	W.E. Erlebach, EC
R. Wilson, MOE	F. Mah, EC
J.P. Senyk, EC	C. Rubec, EC
J.W. Van Barneveld, MOE	Steve Nikleva, EC
Lorrie Pella, DFO	Colin Gray, EC
J. Servizi, IPSFC	Linda Vanderhoek, MOE
D. Martens, IPSFC	Dr. N. McQuaker, MOE
R.W. Gordon, IPSFC	L. McGregor, MOE
Ron McLaren, EC	C.E. Van Alstyne, NH&W
Malcolm Clark, MOE	J.M. Hopper, NH&W
Doug K. Sandberg, MOE	Deborah Barkhouse, EC
Donald A. Faulkner, EC	Chad Thorp, EC
J.A. Morrison, DFO	David Poon, EC
T.M. Lord, Agric. Canada	Paul Beauenemin, EC
Laszlo Retfalvi, EC	Patrick Pang, EC
Steve Samis, DFO	Paul Whitfield, EC