LAKE ACIDIFICATION POTENTIAL IN THE ALBERTA OIL SANDS ENVIRONMENTAL RESEARCH PROGRAM STUDY AREA

by

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for

ALBERTA OIL SANDS ENVIRONMENTAL
RESEARCH PROGRAM

HY 2.2

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The Hon. J.W. (Jack) Cookson
Minister of the Environment
222 Legislative Building
Edmonton, Alberta

and

The Hon. John Fraser
Minister of the Environment
Environment Canada
Ottawa, Ontario

Sirs:

Enclosed is the report "Lake Acidification Potential in the Alberta Oil Sands Environmental Research Program Study Area".

This report was prepared for the Alberta Oil Sands Environmental Research Program, through its Hydrology Technical Research Committee (now the Water System), under the Canada-Alberta Agreement of February 1975 (amended September 1977).

Respectfully,

W. Solodzuk, P. Eng.
Chairman, Steering Committee, AOSERP
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LAKE ACIDIFICATION POTENTIAL IN THE ALBERTA OIL SANDS ENVIRONMENTAL RESEARCH PROGRAM STUDY AREA

DESCRIPTIVE SUMMARY

BACKGROUND

Numerous lakes in Scandinavia and eastern North America have been damaged by acidic precipitation induced by anthropogenic oxides of sulphur and nitrogen. On first approximation, lakes near present oil sands operations would not be susceptible to acidification due to buffering provided by their sedimentary setting. However, due to the planned increases in oil sands developments along with increased regional outputs of oxides of sulphur and nitrogen, a definitive study with the objective of assessing the susceptibility of nearby lakes to acidification was desired. Accordingly this study was initiated in 1976.

ASSESSMENT

The report has been reviewed by scientists and engineers in Alberta Environment, Environment Canada, and the oil sands industry. Comments by the reviewers were addressed by the author and it is our impression that an adequate estimation of the susceptibility of most lakes within 100 km of present oil sands developments has been accomplished from limnological considerations. However, it should be noted that a complete assessment of acidification potential would have to involve present and projected air quality considerations such as deposition patterns. Also, a detailed consideration of the surficial geology would have to be conducted. The content of the report does not necessarily reflect views of Alberta Environment, Environment Canada nor the oil sands industry. The Alberta Oil Sands Environmental

Research Program accepts the report "Lake Acidification Potential in the Alberta Oil Sands Environmental Research Program Study Area" as an important document to receive wide distribution and thanks the author for his contribution.

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

ABSTRACT

Twenty lakes in the AOSERP study area, surrounding the area of current oil sands processing operations, were surveyed in October 1976 to determine their susceptibility to pH change resulting from atmospheric acid additions. Major element chemistry and nutrient concentrations were measured in the water and suspended particulates. Models using the survey information are presented for prediction of the change in pH of these lakes under various acid loading rates.

Most of the lakes in the region have high alkalinities and high resistance to pH change. The only lakes which might be susceptible to serious pH alteration under high acid load are those in the Birch Mountain area. However, the simple steady state model developed in this report suggests that the more poorly buffered lakes sampled in the Birch Mountain region will only be seriously affected if the pH of rain averages below 4.0. It is not likely that pH in rain in this area will get this low since Sudbury, Ontario, with a much greater output of sulphuric acid, has rains averaging 4.0 to 4.5 in pH.

ACKNOWLEDGEMENTS

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1. INTRODUCTION

The acidification of aquatic ecosystems by industrial emission of primarily sulphur dioxide (SO_2) has been described for several areas of the earth. This effect is most severe in Scandinavia (Gjessing et al. 1976; Leivestad et al. 1976), the eastern United States (Likens and Bormann 1974; Likens 1976), and the Sudbury and LaCloche Mountain areas of Canada (Kramer 1976; Beamish 1974; Beamish and Harvey 1972). Surface waters have decreased to pH 5 or less in these areas. Fish and invertebrate populations have been lost or suffered reduced growth, production and composition of phytoplankton communities have been altered, and heavy metal concentrations have increased.

In spite of the clear record of the effects of acidification, the mechanisms for these effects have not yet been sorted out. Several chemical changes occur in surface waters in response to acid deposition in addition to changing pH. Alteration of the distribution of inorganic carbon among the soluble species of carbonate, bicarbonate and carbonic acid, with possible alteration of the concentration of dissolved free carbon dioxide (CO_2), must accompany acid addition. The concentration of free CO_2 has been shown to effect the survival of rainbow trout in acid waters (Lloyd and Jordan 1964). Changes in calcium concentrations resulting from acidification may also be important in fish survival (Beamish 1976). Increased concentrations of heavy metals often accompany acidification by industrial emissions. In most cases these increases result from addition of industrially emitted heavy metals and are well correlated in composition to particular sources (Gorham 1976; Hutchinson and Whitby 1976). Little is known about the solubilization of natural heavy metals in lakes due to increased acidity. This problem is presently being examined (Schindler et al. in prep.). Solubilization of heavy metals in soils by acid rain has been demonstrated, however, (Barrows 1966; Nilsson 1972) and this effect may add to the heavy metal input to lakes. The difficulty in defining mechanisms for effect on aquatic organisms results from the concurrence of the multiple chemical responses described above.

Because of the present and anticipated emission of oxides of sulphur (SO_2) and nitrogen (NO_x) from the processing of mined oil sands in Alberta, there is potential for acidification of lakes surrounding the processing site. Table 1 gives estimates of the magnitude of the emissions from oil sands processing as well as estimates for Sudbury, Ontario where considerable acidification effects have been observed. Estimates for oil sands processing to 1985 are about 20% of the Sudbury output.

In order to determine the sensitivity of lakes in the Alberta Oil Sands Environmental Research Program (AOSERP) study area and surrounding areas to this potential acid addition, 20 lakes, lying in all directions from Mildred Lake to a distance of 100 km, were surveyed during the period 6 to 10 October 1976. Of major importance was the estimation of the buffering capacity of the lakes (see following section) and the establishment of baseline information against which results of future studies may be compared for assessment of the effects of acid addition. To this end, measurements were made of pH, alkalinity, and major ion and nutrient constituents for these lakes. In some cases, these data can be compared to data gathered by other AOSERP investigators. Using these collected data and other data available from AOSERP, a model for the possible change of pH with acid addition has been developed.

Table 1. Atmospheric emissions of sulphur dioxide, SO_2, and nitrogen oxides, NO_x (10^6 g/d).

Site	SO_2	NO_x (as NO)
GCOS[a]	225	20
Syncrude (est. 1980)[a]	293	107
Sudbury (381 m stack)[b]	3000	-

[a] From An Inventory System for Atmospheric Emissions in the Athabasca Oil Sands Area, August 1977; SNC Tottrup Services Ltd.

[b] From Conroy (1974).

2. STUDY AREA

The 20 lakes chosen for sampling in this study are shown by letter in Figure 1. The named lakes are identified there and in Table 2. In addition to these 20 lakes, other lakes sampled by other investigators are listed in Appendix 8.1, Table 6. These lakes were chosen for sampling by their wide geographic distribution around the oil sands development area. Other factors were in some cases the existence of morphometric data, other chemical data for comparison, and recreational (Gregoire Lake) and economic importance (Gardiner-Namur lakes). Distance from the oil sands development area was limited by the speed and range of the available helicopter.

The areas of the lakes ranged from ≈0.5 km^2 to ≈20 km^2 (approximated from maps of the area by planimetry). Maximum depths of lakes sampled ranged from ≈1 m to >20 m. The drainage areas for three lakes for which areal data were available, McClelland, Gregoire, and Kearl lakes, are, respectively, six, eight, and 12 times the surface area of the lakes.

The surficial geology of the study area has been described by Turchenek and Lindsay (1978) as glaciolacustrine, glaciofluvial, and morainal materials. Calcium carbonate was present, where measured from 0.2 to 6.8% by weight. Allen and Jackson (1978) give inorganic carbon concentration equivalents of 0.5 to 10% calcium carbonate in Athabasca River sediments which should be a good integration of the general character of the eroddd materials in the study area.

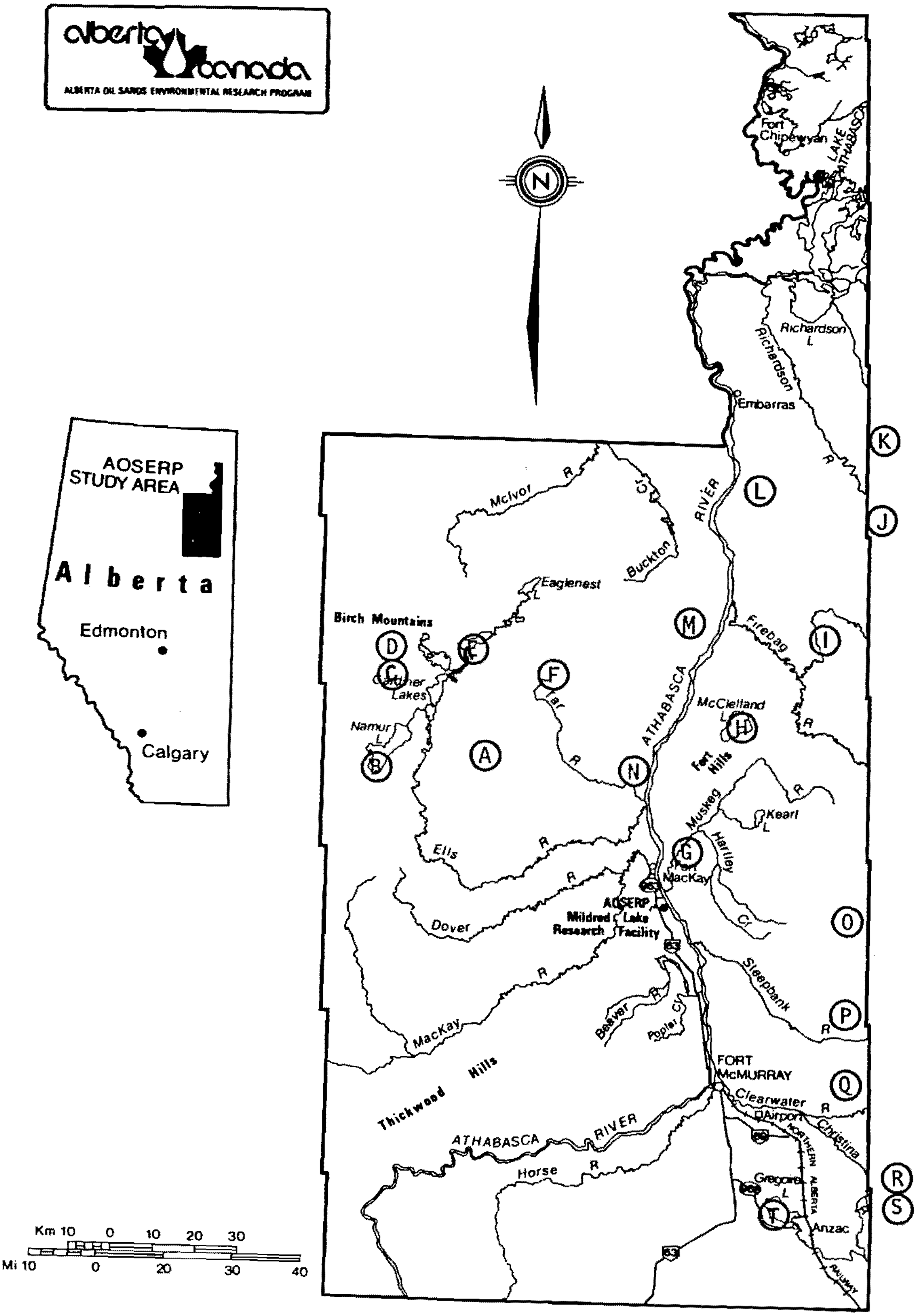

Figure 1. The AOSERP study area showing the positions of the lakes sampled in this study.

Table 2. Lakes included in study.

Letter	Name	Other AOSERP data available
A		
B	Namur Lake	x
C		
D		
E		
F		
G		
H	McClelland Lake	x
I	Audet Lake	
J		
K	Laroque Lake	
L	Pearson Lake	
M		
N		
O		
P		
Q		
R	Campbell Lake	
S	Gordon Lake	
T	Gregoire Lake	x
	Gardiner Lake	x
	Kearl Lake	x

3. METHODS

The lakes were sampled from a float-equipped helicopter in the period 6 to 10 October 1976. This time period was chosen because the lakes could be expected to be nearly or completely homogeneously mixed by fall cooling and turnover. The temperature of most lakes was below 10°C (Table 5) and the shallow mean depths suggested that this was the case. The advantage of sampling at this time is that a single sample gives a better idea of the mean values for the lakes. Proper integration of samples taken at several depths in a stratified lake requires accurate knowledge of the lake morphometry. These data are available for only a few lakes and are time consuming and expensive to get for others.

The usual sampling procedure was to land near the center of the lake, make an estimate of the depth with an echo sounder, and take a sediment sample with a small version of a Shipek grab sampler. Surface (0.25 m) water temperature was measured by mercury thermometer, and secchi disk transparency and colour estimated. A 1 L water sample was taken in a linear polyethylene bottle for chemical analyses and 20 cc drawn by glass syringe for DIC determination. Sampling depth was 0.25 m. The procedure took about 10 min for a crew of two.

On return to the field camp, pH and temperature were measured immediately and the 1 L samples filtered through one or several Whatman ^{R}GF/C glass fiber filters for particulate analysis. Filters were frozen for transport to the laboratory. Other samples were refrigerated for storage and transport.

pH was measured with a Radiometer pH meter calibrated to several standard buffers and a temperature compensator. Alkalinity was determined by titration and Gran plots as described by Stumm and Morgan (1970). Sulphuric acid was used as the titrant. Sediments were titrated similarly. A small weighted amount of dry (110°C) homogenized sediment was added to the titrating flash which was then filled with alkalinity free (Super Q^R) water. All other chemical analyses were determined by the chemistry group of the Limnology Section of the Freshwater Institute in Winnipeg. A full description of their methods can be found in their special publication by Stainton et al. (1977).

4. RESULTS

The results of the field and laboratory measurements are summarized in Appendix 8.1, Tables 5 to 10. The pH ranged from near seven in lakes in the Gardiner-Namur lake region at the farthest extent of the northwest transect, to 8.0 to 8.5 in the more highly alkaline lakes along the Athabasca River. The distribution of pH is shown in Figure 2, with distributions of pH from acid-affected areas of the world. The range in alkalinity was from ≈340 µeq/L in the Gardiner-Namur lake region to over 3000 µeq/L along the river. As the alkalinity in this range of pH is principally supplied by bicarbonate ion, the total dissolved inorganic carbon (DIC) should and does agree well with the measured alkalinity.

If the lakes were fully in equilibrium with atmospheric carbon dioxide (CO_2) there would be a predictable relationship between pH, alkalinity, and DIC (see Section 5.1). This often is not the case in natural waters, however, due probably to sediment-produced CO_2. Table 5 shows dissolved CO_2 (H_2CO_3) values for the 20 lakes as calculated from DIC and pH, and the supersaturation relative to equilibrium with the atmosphere. At the time the measurements presented here were made, supersaturation could, in addition, be caused by changes in mixing depth entraining waters high in DIC. The mean supersaturation for the 20 lakes was 2.86 times the atmospheric equilibrium value.

Figure 3 shows a linear relationship between calcium concentration and alkalinity with a slope very near to 0.67 mol calcium per equivalent of alkalinity. Another linear relationship, between calcium and magnesium, is shown in Figure 4. Here the slope is 2 mol calcium per 1 mol magnesium. These relationships strongly suggest that the alkalinity is a result of the dissolution of carbonate material with the composition $Ca_2Mg(CO_3)_3$. It is interesting to note that in both Figures 3 and 4 there is a greater variance from the line at high concentrations. The variant lakes show excess magnesium relative to Ca_2Mg. This could be due to a difference in the composition of the material being weathered or to precipitation of calcite. Summer conditions of high temperature

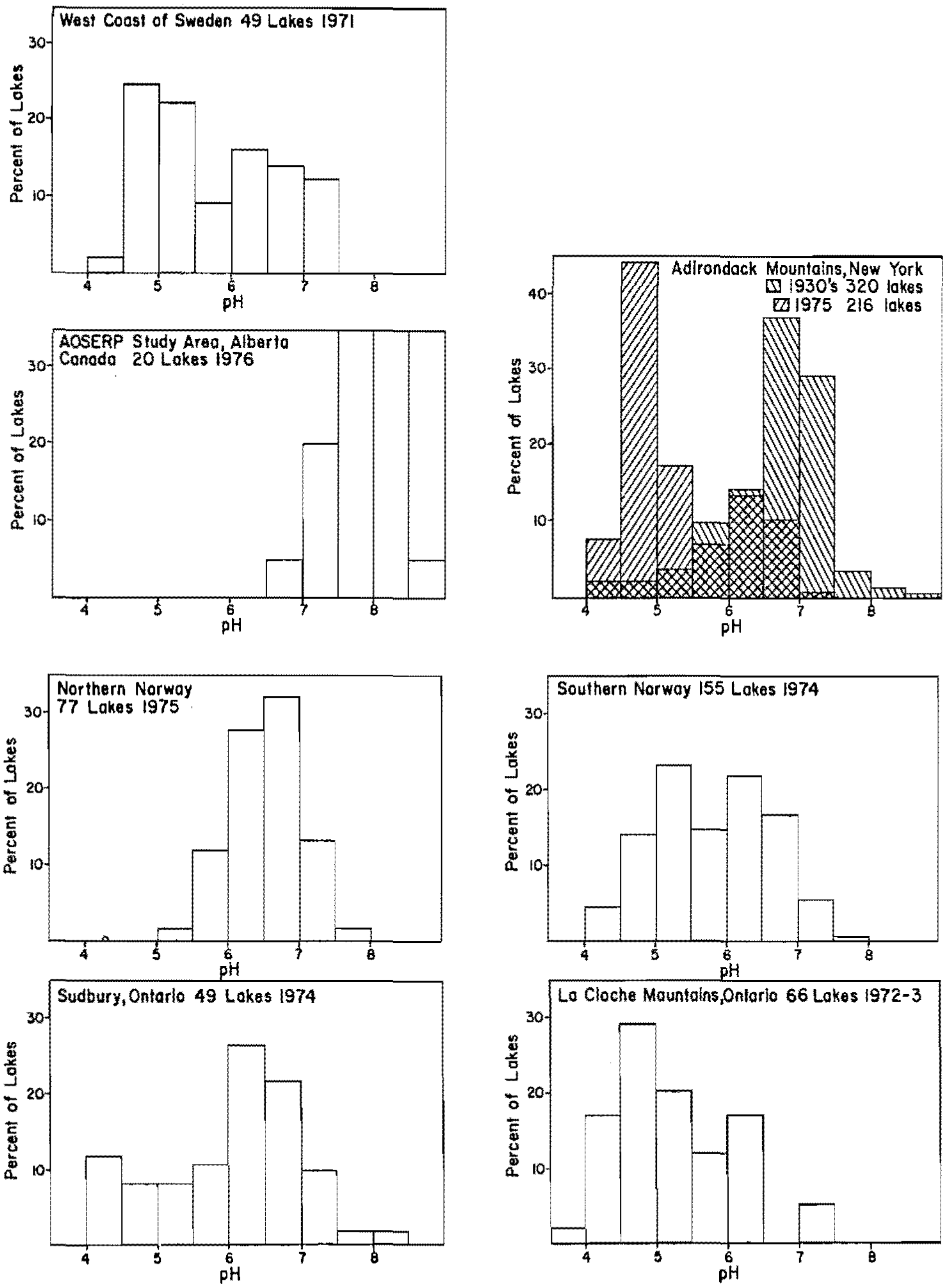

Figure 2. The distribution of pH in lakes in the AOSERP study area and in acid-affected areas of the world (parts redrawn from Wright and Gjessing 1976).

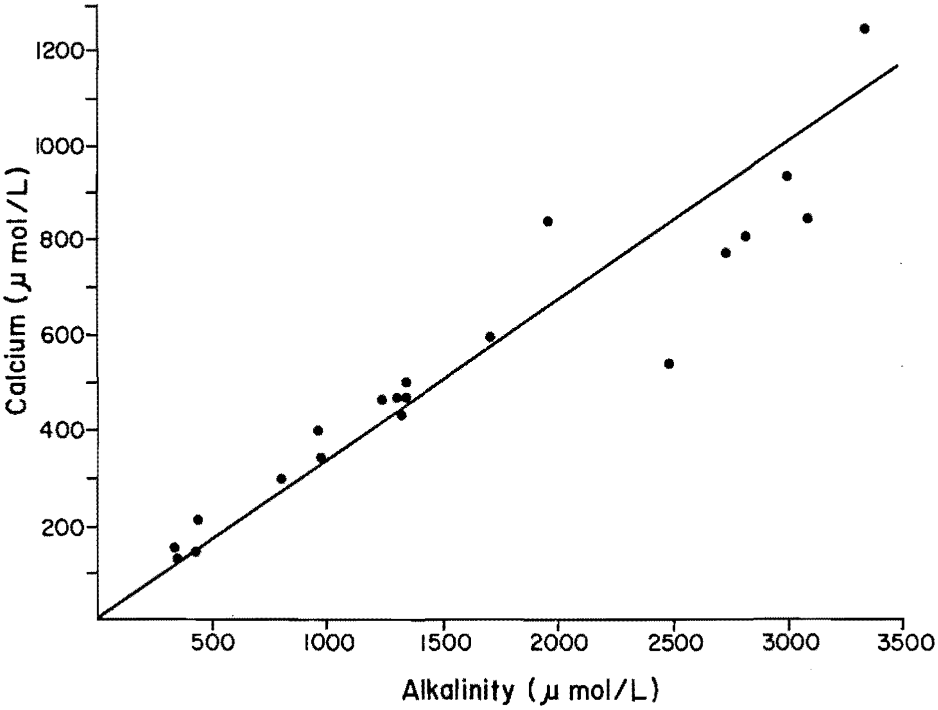

Figure 3. Calcium vs. alkalinity for lakes in the AOSERP study area. The line represents 0.67 mol calcium per equivalent of alkalinity.

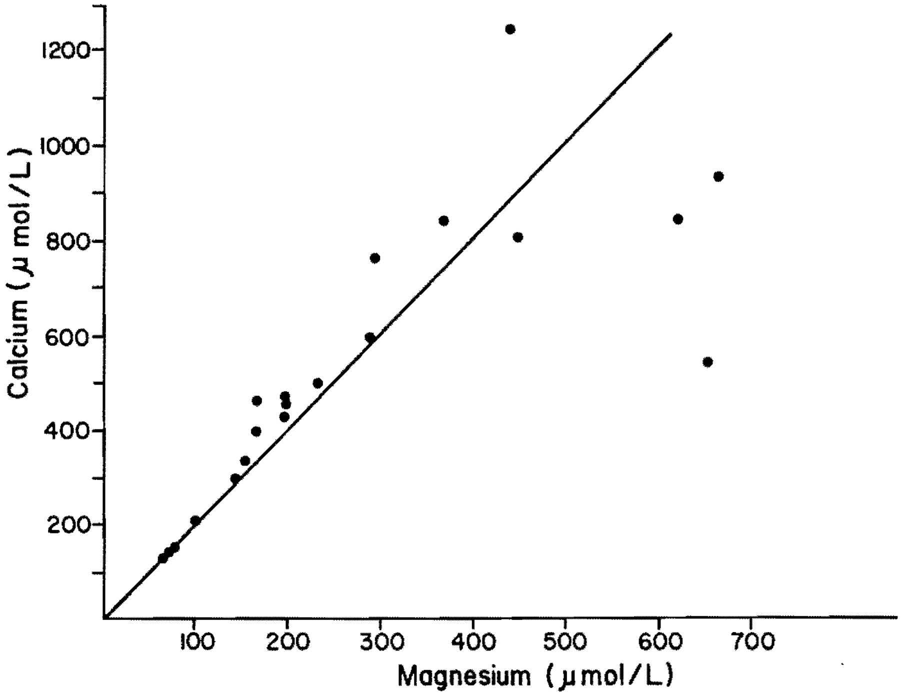

Figure 4. Calcium vs. magnesium for lakes in the AOSERP study area. The line represents 2 mol calcium per 1 mol magneiusm.

and lowered CO_2 concentration because of temperature and algal growth favour the precipitation of calcite.

Sediment buffering capacity turned out to very difficult to measure or interpret. Some of the sediments, those high in organic content, showed no buffering capacity above pH 4.5. These sediments, when wetted with distilled water, produced pH's of less than 4.5. This was probably due to the presence of organic acids. In sediments low in organic matter, mostly sandy, pH's of wetted materials were variable and titration curves were somewhat irregular. In no case, however, did the buffering capacity of the sediments, calculated to a depth of 0.5 m, exceed the alkalinity of 2 m of water overlying them. This could mean that the buffering capacity of a lake with a mean depth of 2 m is twice what one would calculate from the water measurements. This is probably not the case in most of the shallower lakes as they have highly organic bottoms. In addition, the buffering capacity of the water is replaced by inflow at the rate of greater than 1 m/yr and possibly at a much greater rate in some lakes, whereas sedimentation rate of buffering sediments is not likely to be more than 1 cm/yr and probably much less. In view of the generally high buffering capacities in the AOSERP study area, lake sediments likely do not play an important role in controlling pH.

Part of the difficulty in measuring sediment buffering capacity may result from slow rates in the buffering reactions. Waters with low alkalinity have the capacity to dissolve carbonates but the dissolution may proceed slowly at pH in the range of 5 to 7. Titrations of sediments may have to be done over long time periods. In the lake, of course, time is not a problem and low alkalinity water should eventually leach the sediments of soluble carbonate material leaving only ion exchange reactions as a possible buffer mechanism. Another possible source of buffering in lakes has recently been presented (Schindler et al. in prep.). They suggest the reduction of sulphate ($SO_4^=$) to sulphide ($S^=$) and subsequent precipitation as iron sulphide as a mechanism in anoxic waters or sediments.

5. DISCUSSION

5.1 BUFFERING CAPACITY OF LAKES

The buffering capacity of lakes can be defined as their ability to resist a change in pH while undergoing acid addition. Natural buffering capacity in freshwater is mainly provided by the various dissolved species of some carbonates, usually calcium and/or magnesium carbonate. For a lake with no carbonate in sediments the equations describing the buffering system would be:

$$\frac{[H^+]\ [HCO_3^-]}{[H_2CO_3]} = K_1 \qquad (1)$$

$$\frac{[H^+]\ [CO_3^=]^2}{[HCO_3^-]} = K_2 \qquad (2)$$

$$[H^+]\ [OH^-] = K_w \qquad (3)$$

All terms in brackets are concentration in molar units.
H^+ is hydrogen ion, HCO_3^- is bicarbonate ion, $CO_3^=$ is carbonate ion. OH^- is hydroxyl ion, and H_2CO_3 is carbonic acid.

$[H_2CO_3]$ is controlled by the rate of production or use of CO_2 in the lake and the rate of gas exchange with the atmosphere. If the rate of gas exchange is great with respect to the production or use of CO_2 in the lake, the concentration of H_2CO_3 will be fixed by that of the atmosphere at ≃13 µmol/L (20°C). Many lakes are net producers of CO_2 and are not in equilibrium with the atmosphere. Common values of H_2CO_3 calculated from pH and total dissolved inorganic carbon (DIC) in Canadian Shield lakes are two to three times atmospheric equilibrium or 20 to 30 µmol/L (Schindler, unpublished data). For the case where a carbonate mineral is present in the sediments of the lake its solubility equation can be added to the system (for calcium carbonate): $[Ca^{++}]\ [CO_3^=] = K_{sp}$. The presence of large amounts of calcium carbonate in the sediment will result in pH of about 8.4 if the lake is in equilibrium with respect to CO_2 in the atmosphere and at 20°C. If the CO_2 content in the lake exceeds that of the atmosphere the pH will be slightly lower. Temperature will also affect the pH slightly. This system will be very well buffered against pH change as the alkalinity of the water will be high and acid addition will be compensated by carbonate dissolution. The calcium concentration in the water will be raised by acid addition, however. In any case, this kind of lake is the least likely to suffer a change in pH due to acid rain.

Using equations (1), (2), and (3), one can predict the alteration of pH by acid addition to a given volume of water. As there are five unknown quantities in these equations, two quantities must be set by measurement in order to define the system. The most easily measured quantities are pH, H_2CO_3 (or partial pressure of CO_2, pCO_2), total dissolved inorganic carbon (DIC, the sum of H_2CO_3 + HCO_3^- + $CO_3^=$), or alkalinity (ALK, the sum HCO_3^- + $2CO_3^=$ + OH^-). It should be noted that in highly saline waters other chemical components, such as the borate ion ($B(OH)_4^-$), contribute to alkalinity. This is not usually the case in freshwater systems. Figure 5 shows the relationship between alkalinity and pH with a constant value of H_2CO_3. The amount of acid that is required to change from one pH to another can be calculated as the sum of the change in alkalinity plus the change in hydrogen ion concentration. Above pH ≈6 the hydrogen ion contribution is negligable. Below pH ≈5.3 alkalinity contribution is unimportant.

5.2 MODELLING ACIDIFICATION OF LAKES

One approach to modelling the effect of acid rain on the pH of a lake is to estimate the long term (steady state) effect of a given acid input. A prediction of this long term condition is of major importance as there is no present prospect for the reduction of world SO_2 emissions. A somewhat different model can be made to estimate the rate of pH change with time, that is the speed with which the "equilibrium" condition will be reached. This model is of use more in short term planning with respect to lake use and possibly in directing amelioration or emission reduction programs.

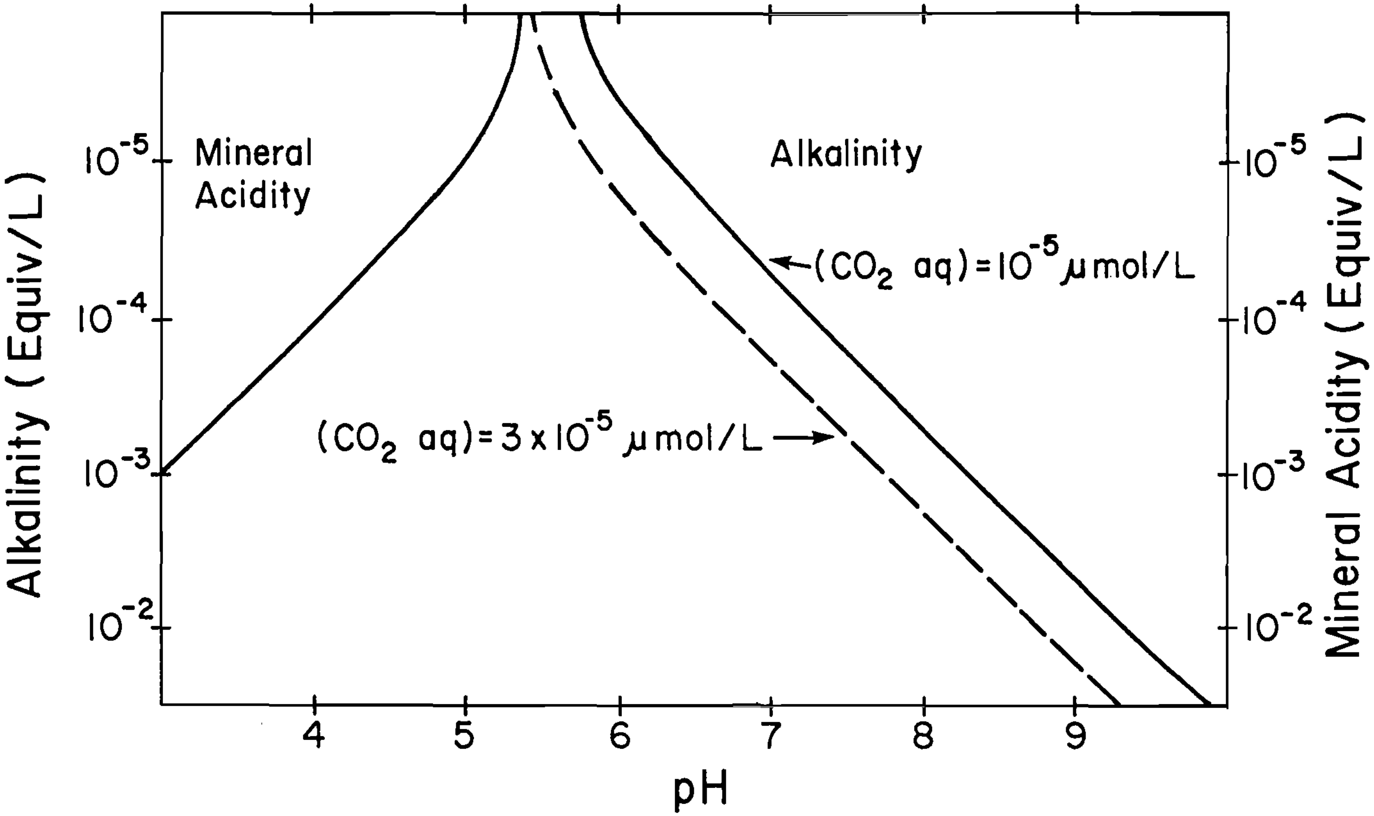

Figure 5. The relationship between alkalinity, mineral acidity, and pH (after Stumm and Morgan 1970).

A very general model for the steady condition of a lake subjected to a given level of acid input from atmospheric sources (precipitation and dryfall) can be produced using only the quantities of alkalinity of the lake, average acid input, and the efficiency of the watershed in returning rainfall as lake outflow. The pH of freshwater systems is determined primarily by the carbonate alkalinity and the partial pressure of carbon dioxide (as previously discussed). If it is possible to predict these quantities for a lake affected by acid input then the future pH can be calculated. The partial pressure of CO_2 is determined by the CO_2 production or use in the lake and its flux across the water-air interface. The first order approximation for the partial pressure of CO_2 in the lake is that it remains constant. The rate constant for flux across the water-air interface is determined by physical parameters such as wind speed and surface roughness which would not be expected to change. There is an effect of pH on the gas exchange of CO_2 known as chemical enhancement but this is not important at pH's of less than 8.5. The production or use of CO_2 in the lake is controlled respectively by the algal acitivity and the microbial degradation. Although it is conceivable that acid input would alter the rates of these biological activities, no definite effect has yet been demonstrated.

If it is assumed that alkalinity is a conservative quantity in the lake, that is, that no carbonate is precipitated or dissolved from the sediments (lake capable of this will not easily be affected by acid input anyway), then the alkalinity input to the lake can be represented by the product of the alkalinity concentration and the outflow. Because the outflows of lakes in general are not available or easily measured, it is advantageous to substitute for this quantity the product of rainfall in m/yr, the efficiency of rainfall being returned as outflow and the area of the drainage basin. Rainfall is a generally available quantity and drainage areas can usually be approximated from areal photographs and/or topographic maps. The efficiency of the basin in returning rainfall as outflow is determined by the evaporation at the lake surface and the evapotranspiration of the terrestrial function of the basin. Newbury et al. (1979)

recently showed that, for the shield area of northwestern Ontario, the evaporate losses from lake surface and terrestrial fractions of a drainage basin are nearly equal. The ratio they determined for annual precipitation to outflow for 53 lake years was 0.34 covering a precipitaton range of 49.6 to 96.7 cm/yr, lake sizes of 1.7 to 54.3 ha and drainage basins of 8.9 to 725 ha. Further examination of their data, however, suggests that forest evapotranspiration if about 0.5 of the rainfall while evaporation from the lake surface may be equal to or greater than precipitation. As lakes do not in general occupy more than 20% of their drainage basins, a figure between 0.35 and 0.5 would be a good approximation.

Using the above approximations leads to an equation for the input (outflow) of alkalinity from any lake as:

$$[\mathrm{Alk}] \times \mathrm{Rainfall} \times 0.4 \times A + [\mathrm{H}^+] \times \mathrm{Rainfall} \times A \qquad (4)$$

Where [Alk] is the alkalinity in eq/L in the lake, Rainfall is in m/yr, A is the area of the drainage in m^2, and $[H^+]$ is the hydrogen ion concentration in rain. This equation gives the total input of alkalinity as the outflow of alkalinity plus the amount already titrated by hydrogen ion from the rain. In areas with lakes of high alkalinity or areas unaffected by acid rain, the correction for hydrogen ion is small. If this total alkalinity is taken as the "natural" input to the lake the future input can be calculated by subtracting future H^+ loading from this "natural" loading. This in units of eq/m^2/yr is: $\frac{\Sigma \mathrm{Alk}}{A} - [\mathrm{H}^+] \times \mathrm{Rainfall}$. If the present $[H^+]$ loading was small this is equivalent to $[\mathrm{Alk}] \times \mathrm{Rainfall} \times 0.4 - [\mathrm{H}^+] \times \mathrm{Rainfall}$ (5)
Where $[H^+]$ is the hydrogen ion concentration of future acid rain and [Alk] is the present alkalinity. This equaiton, divided by the outflow equivalent of (Rainfall x 0.4), gives the future alkalinity concentration of the outflow or lake as: $[\mathrm{Alk}]$ present $- [\mathrm{H}^+]$ future rain/0.4 (6)
This is the predicted steady state alkalinity given a constant pH in rainfall. One further requirement is that the supply of "natural" alkalinity from the basin is not altered by the pH of the rain, only titrated by it.

Knowing the future alkalinity of the lake and assuming that the partial pressure of CO_2 will still be held to a near equilibrium value by gas exchange with the atmosphere, the future pH of a lake subjected to acid rain can be calculated. Table 3 gives the calculated present alkalinity of a lake required so that a future acid rain will result in complete titration of the buffer capacity giving the lake a pH of ≈5.5 and rendering it highly susceptible to further acidification.

The results of the model presented in Table 3 can be compared to the calcite saturation index CSI (also in Table 3) which has been presented by Conroy (1974) as an indicator of sensitivity of lakes to acidification. The CSI equivalent of alkalinity can be calculated if one uses the equivalence of 0.4 mol of calcium per 1 mol of alkalinity (see Figure 3). Conroy suggests that continued acid loading may affect lakes with CSI values as low as 3 in the future, and lakes with values above 5 to be highly susceptible. In terms of alkalinity, a CSI of 5 translates to lakes of "natural" alkalinity of less than ≈80 µmol/L which would be left with no buffering capacity by rain of pH ≈4.7. For continued exposure to rain of pH ≈3.8, lakes of "natural" alkalinity of ≈350 µmol/L and a CSI of ≈3 would be affected.

A model to predict the rate at which the new "steady state" condition of the lake will be reached requires much more specific information about the lake, and time course of pH in rain. If the pH of the rainfall were constant with time the rate of approach of the lake to a new alkalinity level would be determined by the residence time, τ, of the water in the lake, $\frac{\text{volume of the lake.}}{\text{outflow}}$ The exact expression would be exponential with a rate constant of $\frac{1}{\tau}$:

$$A = (A_O - A_F) \exp(-t/\tau) + A_F \qquad (7)$$

Where A is alkalinity at any time, τ, A_O is original alkalinity, and A_F is the future alkalinity as determined by the steady state model. The pH at any time, τ, can be calculated from the alkalinity if the

Table 3. Alkalinity and CSI[a] required to balance[b] low pH rain to a lake as presented in the steady state model.

pH (rain)	Alkalinity	CSI
5.5	9.4	8.0
5.0	30	6.5
4.5	94	4.7
4.0	300	3.4
3.5	940	2.0
3.0	3000	0.5

[a] Calcium Saturation Index as presented by Conroy (1974). For discussion see text.

[b] These combinations result in a full titration of the alkalinity to pH 5.65 in equilibrium with atmospheric carbon dioxide.

partial pressure of CO_2 in the water is known or assumed constant. If the pH of the rainfall is other than constant, the emissions become more complex and the system may be more easily modelled by a numerical model using a finite difference approach in time.

The greatest weakness in both the time dependent and the steady state model is the uncertainty in the response of the terrestrail system to acid rain. In the models presented, it has been assumed that the buffering capacity available in the drainage basin is constant with time and either used up by acid rain or flushed into the lake as alkalinity. It is likely that additional buffering capacity would be made available by more acid rain. It is also possible that the terrestrial reserve might eventually be depleted. The answers for these uncertaintiesare beyond the scope of this discussion.

For an example of the model predictions we can take Gregoire Lake, for which bathymetric data are available allowing an estimate of outflow and residence time to be made. The lake area is 3400 ha and the mean depth 4.2 m giving a volume of 1.43×10^8 m^3. The area of the drainage basin is 2.64×10^8 m^2 which, using 0.4 times a rainfall of 0.435 m/yr, gives 4.6×10^7 m^3/yr as outflow and a residence of 3.11 yr. The measured alkalinity of Gregoire Lake is 10^{-3} eq/L with a present pH of ≈8. Using equation (6), the steady state model and a pH in rain of 4.0, one predicts a new alkalinity of 0.75×10^{-3} eq/L. This translates to a pH of 8.18 if CO_2 is in equilibrium with the atmosphere of pH 7.88 if the CO_2 is twice the atmosphere equilibrium as is suggested by the present pH and alkalinity values. These pH's are within the present variance of pH in the lake and the alkalinity is only slightly outside the present variance. The new alkalinity would be approached with a time constant of 0.32/yr. The progress of alkalinity and pH is shown in Table 4.

Table 4. Predicted[a] changes in alkalinity and pH in Gregoire Lake hypothetically starting at alkalinity equalling 1000 meq/L and pH equalling 8.3 and subjected to rainfall of pH 4.0.

Year	Alkalinity (µeq/L)	pH
0	1000	8.3
1	932	8.27
2	882	8.25
3	846	8.23
4	820	8.21
5	800	8.20
7	777	8.19
10	760	8.18
15	752	8.18

[a] See text for a full description of the model.

6. CONCLUSIONS

The sensitivity of lakes in the AOSERP study area to acid loading from the atmosphere is dependent on the amount of carbonaceous material in the lake. The dissolved species in the carbonate system provide assimilatory capacity (buffer capacity) for H^+ ion through equilibrium with HCO_3^-, $CO_3^=$, OH^-, H_2CO_3, and $CaCO_3$. The simple steady state model developed in this report suggests that the most poorly buffered lakes sampled (Birch Mountain region) will only be seriously affected if the pH of rain averages below 4.0. It is not likely that pH in rain in this area will get this low since Sudbury, Ontario, with a much greater output of sulphur acid, has rains averaging 4.0 to 4.5 in pH (Dillon et al. 1977). Estimates for sulphur emissions from Athabasca Oil Sands development to 1985 do not exceed 25% of those presently experienced in Sudbury. Lakes in calcareous regions near Sudbury, exposed to the same acid loadings as strongly affected lakes, show pH values in the range of 7 to 8.5 (Conroy 1974). Sediments in lakes of lower alkalinity, and thus higher sensitivity to acid addition, are not likely to add significantly to the buffering capacity of the lakes except possibly through sulphate reduction. Because of the generally high alkalinities and the presence of carbonate materials in soils in much of the area, it is unlikely that any significant alteration of pH in lakes of the AOSERP study area will result from the projected level of sulphur emissions.

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8. APPENDIX

8.1 DATA TABLES

Table 7. Cations in lakes in the AOSERP study area, 6 to 10 October 1976 (all concentrations in mg/L).

Lake	Ca	Mg	Na	K	Mn	Fe
A	33.5	8.73	5.16	1.99	0.01	0.05
B	8.31	2.40	2.01	0.82	0.01	0.05
C	5.13	1.56	2.33	0.33	0.01	1.05
D	5.93	1.84	3.05	0.71	0.11	1.01
E	13.5	3.72	2.60	0.63	0.01	0.05
F	11.9	3.55	1.05	0.27	0.01	0.05
G	49.8	10.6	7.05	0.51	0.01	0.14
H	21.5	15.7	4.58	3.05	0.01	0.05
I	37.2	15.9	6.45	2.28	0.01	0.05
J	18.5	4.01	1.05	0.59	0.01	0.05
K	17.1	4.76	3.03	2.49	0.01	0.05
L	23.8	6.84	1.77	0.48	0.01	0.05
M	33.6	14.9	21.2	5.59	0.06	0.05
N	32.2	10.8	49.5	3.53	0.01	0.09
O	18.6	4.76	2.47	0.19	0.01	0.05
P	5.75	1.70	3.06	0.40	0.01	0.05
Q	19.9	5.61	1.60	0.65	0.01	0.05
R	18.5	4.81	1.74	0.79	0.01	0.05
S	30.7	7.02	12.7	1.05	0.01	0.05
T	15.9	3.91	2.19	0.86	0.01	0.05

Table 8. Anions in lakes in the AOSERP study area, 6 to 10 October 1976 (all concentrations in mg/L).

Lake	$SO_4^{=}$	Cl^-	Si
A	31.5	0.2	5.66
B	6.8	0.6	0.088
C	6.8	0.2	2.37
D	12.4	0.4	0.101
E	7.2	0.2	0.528
F	4.2	0.4	0.104
G	6.0	3.2	1.53
H	2.6	0.4	5.07
I	4.0	7.8	3.24
J	0.6	0.4	2.81
K	1.0	0.8	2.75
L	1.4	2.2	3.80
M	34.0	5.8	10.7
N	58.0	25.2	2.91
O	4.8	0.4	0.532
P	5.4	0.4	0.514
Q	4.2	0.6	0.181
R	4.0	0.4	1.76
S	5.6	3.4	2.56
T	9.4	0.8	1.19

Table 9. Nutrient data for lakes in the AOSERP study area, 6 to 10 October 1976 (all concentrations in ug/L).

Lake	Sechi (m)	NH_3-N	NO_2-N	NO_3-N	TDN	PO_4-P	TDP
A	1.25	20	2	142	1120	153	186
B	3.5	20	1	5	390	7	15
C	1.0	20	4	11	760	19	48
D	0.3	60	6	406	1680	21	65
E	2.5	20	1	5	530	3	15
F	1.4	40	1	5	530	2	16
G	1.7	30	1	5	780	4	16
H	2	40	1	5	870	2	9
I	2.5	40	1	5	930	3	12
J	5	30	1	5	380	1	6
K	4	20	1	5	420	2	11
L	3.5	20	1	5	290	2	11
M	0.5	20	1	5	1280	3	27
N	0.5	90	3	9	1660	14	53
O	0.8	10	1	5	680	2	14
P	0.7	40	1	5	1250	3	15
Q	2.5	10	1	5	1020	2	11
R	2.5	20	1	5	1060	3	16
S	0.3	40	8	5	1460	6	24
T	1.3	10	1	5	560	3	16

Table 10. Particulate data for lakes in the AOSERP study area, 6 to 10 October 1976 (all concentrations in µg/L).

Lake	Suspended C	Suspended N	Suspended P	Chlorophyll a
A	2 690	365	53	45.5
B	490	73	12	6.7
C	400	54	11	2.0
D	6 690	700	130	33.2
E	900	118	15	14.8
F	800	122	12	8.4
G	870	149	19	17.3
H	720	84	8	3.6
I	860	112	10	4.8
J	690	81	5	2.5
K	780	106	13	7.3
L	630	100	11	5.1
M	4 290	743	88	48.5
N	2 230	350	54	32.4
O	2 040	285	32	17.0
P	4 850	531	43	22.3
Q	920	121	11	5.7
R	770	98	11	2.4
S	26 070	2153	155	329
T	810	120	17	6.7

9. AOSERP RESEARCH REPORTS

1.		AOSERP First Annual Report, 1975
2.	AF 4.1.1	Walleye and Goldeye Fisheries Investigations in the Peace-Athabasca Delta--1975
3.	HE 1.1.1	Structure of a Traditional Baseline Data System
4.	VE 2.2	A Preliminary Vegetation Survey of the Alberta Oil Sands Environmental Research Program Study Area
5.	HY 3.1	The Evaluation of Wastewaters from an Oil Sand Extraction Plant
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7.	AF 3.1.1	A Synopsis of the Physical and Biological Limnology and Fisheries Programs whithin the Alberta Oil Sands Area
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9.	ME 3.3	Preliminary Investigations into the Magnitude of Fog Occurrence and Associated Problems in the Oil Sands Area
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13.	ME 2.3.1	Plume Dispersion Measurements from an Oil Sands Extraction Plant, March 1976
14.		
15.	ME 3.4	A Climatology of Low Level Air Trajectories in the Alberta Oil Sands Area
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21.		AOSERP Second Annual Report, 1976-77
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25.	ME 3.5.1	Review of Pollutant Transformation Processes Relevant to the Alberta Oil Sands Area

26.	AF 4.5.1	Interim Report on an Intensive Study of the Fish Fauna of the Muskeg River Watershed of Northeastern Alberta
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29.	ME 2.2	An Inventory System for Atmospheric Emissions in the AOSERP Study Area
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32.		AOSERP Third Annual Report, 1977-78
33.	TF 1.2	Relationships Between Habitats, Forages, and Carrying Capacity of Moose Range in northern Alberta. Part I: Moose Preferences for Habitat Strata and Forages.
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50.	ME 3.6	Literature Review on Pollution Deposition Processes
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65.	LS 21.6.2	A Review of the Baseline Data Relevant to the Impacts of Oil Sands Development on Black Bears in the AOSERP Study Area
66.	AS 4.3.2	An Assessment of the Models LIRAQ and ADPIC for Application to the Athabasca Oil Sands Area
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68.	AS 1.5.3 AS 3.5.2	Air System Summer Field Study in the AOSERP Study Area, June 1977
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74.	AS 4.5	Air Quality Modelling and User Needs

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