Boojum
RESEARCH LIMITED

BIOLOGICAL POLISHING

PHASE IV:
MODEL VERIFICATION AND SCALE-UP

FINAL REPORT

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DSS FILE #: 15SQ.23440-3-9213

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SCIENTIFIC AUTHORITY: Dr. D. Koren

July 30, 1994

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FIG-5	WQS	24755	49	8/12/94	10:39p	A
FIG-6	WQS	17291	34	8/13/94	9:18a	A
FIG-7	WQS	56794	111	8/20/94	2:36p	A
FIG11-12	WQS	18532	37	8/20/94	5:30p	A
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EXECUTIVE SUMMARY

Four years of research on the utilisation of attached algae in polishing ponds has resulted in the formulation of a biological polishing model. A preliminary model was completed in early 1993. The design parameters were used to scale-up the application of the biological polishing process from ponds with a volume of about 300 m^3 to ponds with a volume of 6,000 m^3.

Predictions on the performance of the process were made, relating retention time to percent zinc removal. During winter conditions, a 2.2 % decrease in zinc concentrations was predicted for each additional day of retention and, therefore, a 45 day retention time is required for 100 % removal. In summer months, a 5.2 % decrease in zinc was predicted for each additional day of retention time. By the end of 1993, the scaled-up ponds were operating with low retention times of 1 to 3 days. The % zinc decrease for the months of October to November, 1993, ranged from 2 % to 27 %. In the summer of 1994, the system was performing as predicted, with 70 % zinc removal during a retention time of 22 days.

The preliminary biological polishing model was refined with the intention to identify the key operating parameters of the process. The box model considers bioaccumulation of the contaminants by algae the only contaminant sink. Field measurements for two systems, the scaled-up ponds with a circumneutral pH and zinc concentrations of about 20 $mg.l^{-1}$, and an acidic lake (1,000,000 m^3) with 10 $mg.l^{-1}$ of zinc, are evaluated using the box model. The box model predicts for the circumneutral ponds that other sinks for zinc are present. For the acidic lake, an increase in zinc concentrations is predicted, if bioaccumulation of zinc in the algae is the only zinc removal mechanism.

A second approach to modelling considers metal cycling and evaluates the two systems as continuous time reactors. Inputs for the model are measured and quantified as rates of cycling of contaminant species, in tonnes per year. With this refinement, iron cycling is identified as a key factor which can affect the water quality and, therefore, the zinc removal processes. This refined model does describe the process better, but requires the quantification of growth rates, sedimentation rates, recycling rates in addition to contaminant loading rates.

Sedimentation rates have been quantified in order to produce input parameters for modelling the biological polishing process as a continuous time reactor. Sedimentation rates ($g.m^{-2}.d^{-1}$) of precipitates, primarily comprised of iron hydroxide are in the same order of magnitude for both the acidic and circumneutral ponds, with 1 to 4 $g.m^{-2}.d^{-1}$, and 0.5 to 8 $g.m^{-2}.d^{-1}$, respectively. Zinc removal, through co-precipitation of with iron hydroxide, is an important factor in the biological polishing process. The amount of zinc co-precipitated appears to be related to the conditions under which the iron hydroxide is formed.

A literature review, presented in this report, focuses on the oxidation and reduction of iron, the redox boundary, and adsorption and complexation of iron in sediments. Some

of the most important findings with respect to the biological polishing process are summarized. Due to seasonally changing redox boundary in the sediment, the flux of reduced iron from sediment to overlying water might be significant. Iron reduction is microbially-mediated, and iron oxyhydroxides accumulated on the sediment surface are an abundant source of iron for iron reduction. Iron oxidation and iron reduction are important processes controlling the water characteristics, as iron oxidation is associated with the production of H^+, and reduction with the production of OH^- ions. Bacteria are able to couple the oxidation of organic substrates to the reduction of iron. Organic-rich, chemically reducing (low Eh) sediments will produce those substrates sustaining microbial iron reduction in polishing pond sediments.

The sediments from the acidic lake and the circumneutral polishing ponds were assessed both in the laboratory and in the field. Concentrations of elements in sediment pore waters were determined using pore water peepers. Reduced iron concentrations in sediment pore water ranged from 10.5 mg.l^{-1} to as high as 115 mg.l^{-1} for both systems. The highest iron concentration measure exceed pore water iron concentrations of 70 mg.l^{-1} reported for non iron-enriched sediments.

Phosphate availability and iron cycling in sediment are closely coupled and, hence, phosphate can be the limiting nutrient in biological polishing systems. Phosphate additions to the sediments in the acidic lake were made using natural phosphate rock, a type of fertilizer suitable for acidic soils. It was proposed that, through addition of phosphate rock to the sediment, several objectives could be achieved which would, collectively, prevent deterioration of this lake currently receiving acidic seepage from the mine site and tailings.

Most importantly, the cycling of iron at the sediment-water interface may be curtailed following the formation of iron-phosphate colloids. If these colloids dissolve in the deeper portion of the sediment, some phosphate may be released. Upon supplying phosphate at the sediment surface, both bacterial activity and, possibly, periphytic algal growth, could be induced at the sediment-water interface. If the sediment-water interface could be covered by aquatic vegetation, an interface would be created between the sediment and the oxygenated water. A vegetation cover could be beneficial with respect to the recycling of iron hydroxides from the surface of the sediments.

The results of these additions are difficult to assess, although it is suspected that both microbial activity in the sediment and periphytic algal growth over the sediment have been stimulated. The acidic lake sediment characteristics are spatially heterogenous, with iron concentrations as high as 45 % in those areas where seepages enter the lake. Organic-rich sediments with high zinc concentrations are located in those areas where substrates were provided of periphytic algal growth. Although the continuous time reactor model indicates an trend of increasing zinc concentrations each year, this trend has not been observed in these areas where biological polishing has been implemented. Studies are under way to expand the area of biological polishing in the 1,000,000 m^3 acidic lake.

SUMMAIRE

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF FIGURES (Cont'd)

LIST OF MAPS

LIST OF SCHEMATICS

LIST OF APPENDICES

1.0 INTRODUCTION

Decommissioning of inactive mine sites presents an economic and environmental challenge. Ecological Engineering processes are being developed to assist the mining industry in finding solutions to the decommissioning challenge.

Biological Polishing, one of the Ecological Engineering processes, has been quantified with data collected from three different acid-generating mine sites as follows: (1) an abandoned coal seepage in Cape Breton, N.S.; (2) the Buchans Mine in central Newfoundland; and (3) effluents from acid-generating tailings at the South Bay Mine in northwestern Ontario.

Biological polishing can assist in the improvement of AMD seepages by the following processes:

(1) the provision of nucleation/precipitation sites for metals on attached algae, or periphyton, surfaces;

(2) the provision of living covers over metal-laden sediments; and

(3) the provision of extracellular polysaccharides for complexation of metals.

Process development started in 1990 with a literature review on periphyton growth conditions and geochemical considerations of the contaminant removal process. It was concluded that species of the order *Ulothrichales* dominated algal complexes in acid conditions, and *Oscillatoria* species dominated complexes in neutral or alkaline conditions. These algal complexes represent the surfaces on which biological polishing takes place and are referred to as polishing agents. The algal complexes have the ability to create conditions on their surfaces which facilitate metal precipitation, adsorption and absorption.

A report, entitled "Periphyton Communities as Biological Polishing Agents in Mine Waste Waters and The Precipitation Process in Tailings. Final Report." (CANMET DSS Contract # 23440-0-9182/01SQ, 1991), was issued focusing on the approach for

developing the process.

In 1991, field work was carried out at three different sites where the algal complexes were growing, covering acid to circumneutral pH mine effluents. Photosynthetic rates were determined both in controlled laboratory experiments and in field conditions. Metal concentrations were quantified in the algal biomass, and the algal communities' overall growth rates were determined, taking seasonal variations into account. The results of this work facilitated the determination of biological polishing capacity, or contaminant removal effectiveness, which is summarized in a report entitled, "Algal Bio-polishing of Zinc. Final Report." (CANMET DSS Contract # 23440-1-9009/01SQ).

In 1992, field experiments of various scales were carried out. At the old Buchans Mine in central Newfoundland, circumneutral effluent with elevated zinc levels leaving an open pit was diverted through six pools constructed in series. A mass balance of zinc entering and leaving the pools, along with the amount of zinc concentrated in the algal biomass, was determined. Algal growth and sloughing were quantified using peritraps. Peritraps are devices where growth substrate branches are held in nylon netting frames, to which slow release fertilizer can be added. The algal biomass growing on the branches is sampled periodically.

Peritraps were also installed to quantify growth and determine the effects of fertilization in acidic water at the South Bay site in northwestern Ontario. Tailings from this base metal mine have acidified a lake, which is used as a polishing pond. Boomerang Lake $(1,000,000 \ m^3)$ received 41 truck loads of cut brush in 1992, based on biological polishing measurements made on brush cuttings placed in the lake since 1989. The brush cuttings provide surface area for algal biomass growth. In Boomerang Lake, *Ulothrix* spp. dominated algal complexes represent the polishing agents. Biological polishing was quantified in the same manner in the old Decant Pond (pH 6) on the South Bay tailings using *Oscillatoria* spp. as the polishing agent for zinc removal.

An acidic seepage emerging from a coal dump in Cape Breton was included in the research program to determine the capacity of biological polishing in coal seepage. Geochemical conditions of the waste water which allow for the formation of iron-precipitates were identified as a very important factor in the biological polishing process. Slow-release fertilizer was found to be useful in increasing growth rates of the algae. A report, entitled "A Study of Algae-Precipitate Interactions." (DSS Contract # 23440-1-9011/SQ, 1992), gives the details of the work.

In 1992, a site-specific application model was developed based on the data which had been derived from data for the six experimental ponds in operation at Buchans. A model was also developed for biological polishing at the coal seepage in Cape Breton and for the acidified lake receiving tailings seepage at South Bay. In field experiments, it was found that part of the biological polishing process was due to collection of precipitates on algal biomass which formed in the water bodies. The precipitate formation was, therefore, considered an essential component of the contaminant removal process. Sedimentation of precipitates was quantified in the open pit at Buchans and in Boomerang Lake at South Bay. The results of this phase of the research are summarized in a report, entitled "Biological Polishing In Acid Mine Drainage: Contaminant Removal Capacity and Application Model. Final Report." (DSS Contract # 23440-2-9216).

This report summarizes improvements to the model and elucidates on relevant factors which affect the biological polishing process.

In 1993, it was possible to test the model predictions in large ponds constructed at Buchans, covering about 1.3 ha with a volume of 5,951 m^3. The ponds are operated based on the performance data generated from the model. Critical model parameters are evaluated and are presented in Section 2 along with a refinement of the application model.

The biological polishing capacity of these polishing ponds, filled with brush cuttings, is quantified based on growth per "unit brush". Alternative algal growth measurement units were tested in 1993. The growth results using these alternative units are incorporated into the biological polishing model presented in Section 2.

Sedimentation rates of iron hydroxide, measured since 1992 in both Buchans and South Bay, were found to be high. It was concluded that sediment iron chemistry needed to be evaluated in detail. The oxidation of reduced iron is a significant factor in acidification of water and, in turn, water pH is an important factor affecting the biological polishing process. A literature review on iron cycling in sediments is presented in Section 3.

A possible avenue to curtail acidification, caused by the hydrolysis of ferric iron, is to reduce the quantity of iron available for cycling between the water (ferric ions, ferric hydroxide) and the sediments (ferrous ions). If phosphate, released from natural phosphate rock added to the sediments, is available at the sediment-water interface, it might facilitate the formation of iron phosphate, a compound much less soluble than iron hydroxide. This compound would fix iron in the sediments, thereby reducing the amount of iron available for cycling. Surplus phosphate released from the sediments would serve as a fertilizer for the biological polishing process. Finally, through additions of natural phosphate rock to the lake sediments, it might be possible to establish a vegetation cover over the sediments which would further reduce contact of sediments with oxygenated lake water.

Laboratory and field tests were initiated to further address iron cycling between water and sediments. This included determination of iron hydroxide precipitation/ sedimentation rates and examination of natural phosphate rock as a means to fix iron in sediments. In Section 4, the results of the field and laboratory experiments are presented.

2.0   BIOLOGICAL POLISHING SCALE-UP AT BUCHANS

In 1989, six ponds were constructed in series at the Buchans mine site in Newfoundland (Map 1). A fraction of discharge from the Oriental East Gloryhole, a flooded pit, was directed through the ponds and the flow was quantified. Brush was placed as a growth substrate for the algae, and performance (% zinc removal per day retention time) of the system was derived. Fertilizer was found to increase algal growth and hence, improve the zinc removal. The summer season of 1993 represented the fourth year when samples were collected, to describe the biological polishing capacity of the system.

In 1992, Polishing Pond 10 was constructed, with a volume, 319 m^3, very similar to Polishing Ponds 1 to 6 (243 m^3). Based on the performance of this pond, construction of Polishing Ponds 11, 12 and 13 proceeded, creating a total polishing pond volume of 6,000 m^3. Construction of the large Polishing Ponds (PP) was completed by the end of 1993.

2.1   Overall Performance of Polishing Ponds 1 To 6

Using all data available from PP1 to PP6, the percentage zinc removal is plotted against retention time (in days) in the pond system. Retention time can be used as a design criterion to evaluate PP10, a pond which has the same volume, but not configured as a series of ponds as are PP1 to PP6.

From a regression analysis, a zinc concentration decrease of 2.2 % can be expected with each additional day of retention time. To achieve 100 % zinc removal, a projected retention time of 45 days would be required. For PP1 to PP6, this retention time is achieved if the inflow is maintained at 0.06 L.s^{-1}. A flow of 0.08 L.s^{-1} for PP10 would provide the same retention time.

Map 1: Buchans Polishing Ponds

Polishing Pond 1
Polishing Pond 2
Polishing Pond 3
Polishing Pond 4
Polishing Pond 5
Polishing Pond 6
Polishing Pond 10
Polishing Pond 11
Polishing Pond 12
Polishing Pond 13

WASTE ROCK PILE

0 m   100 m
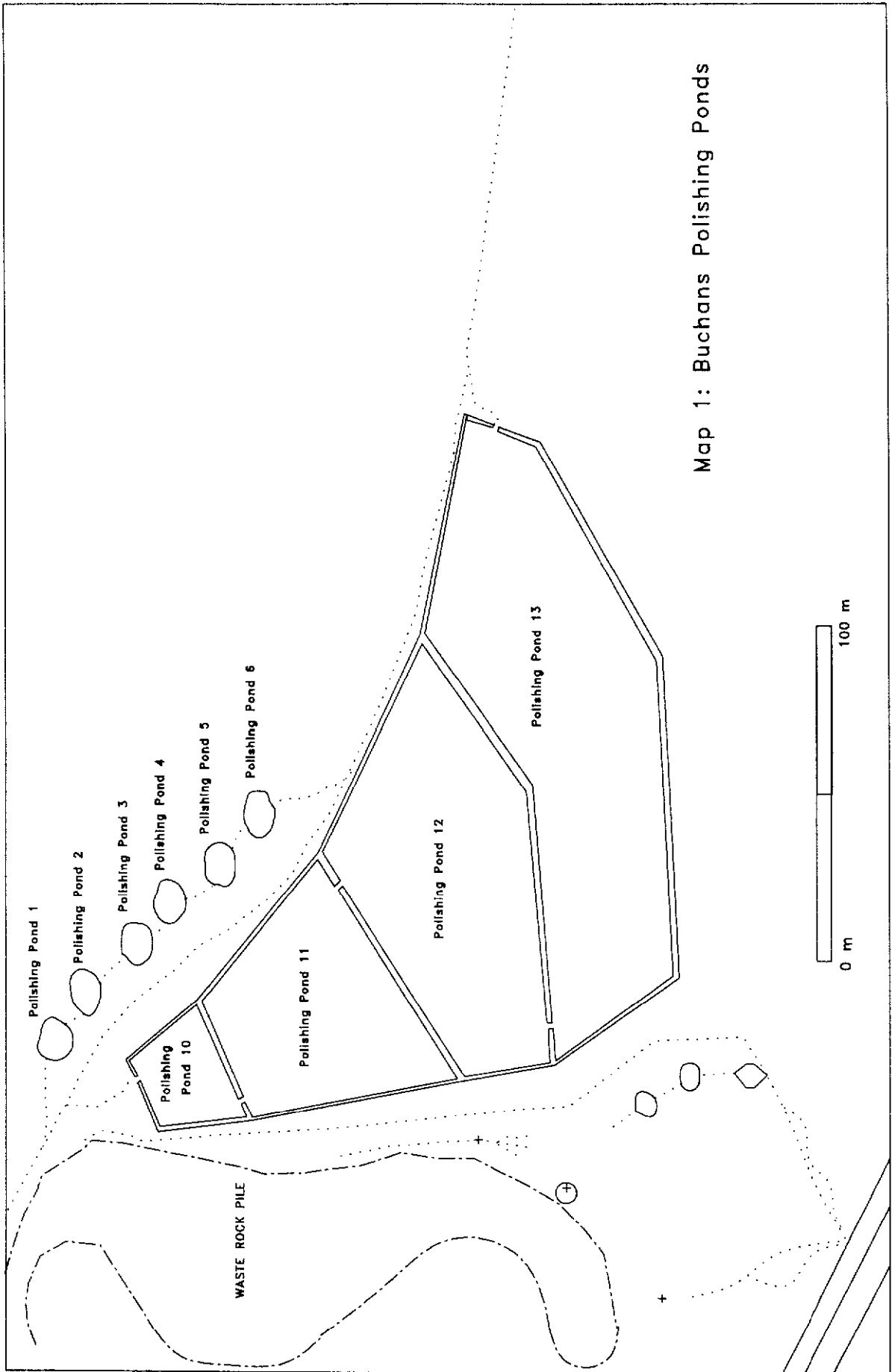
Fig.1: % [Zn] Decrease in PP 1 to 6
with Retention Time
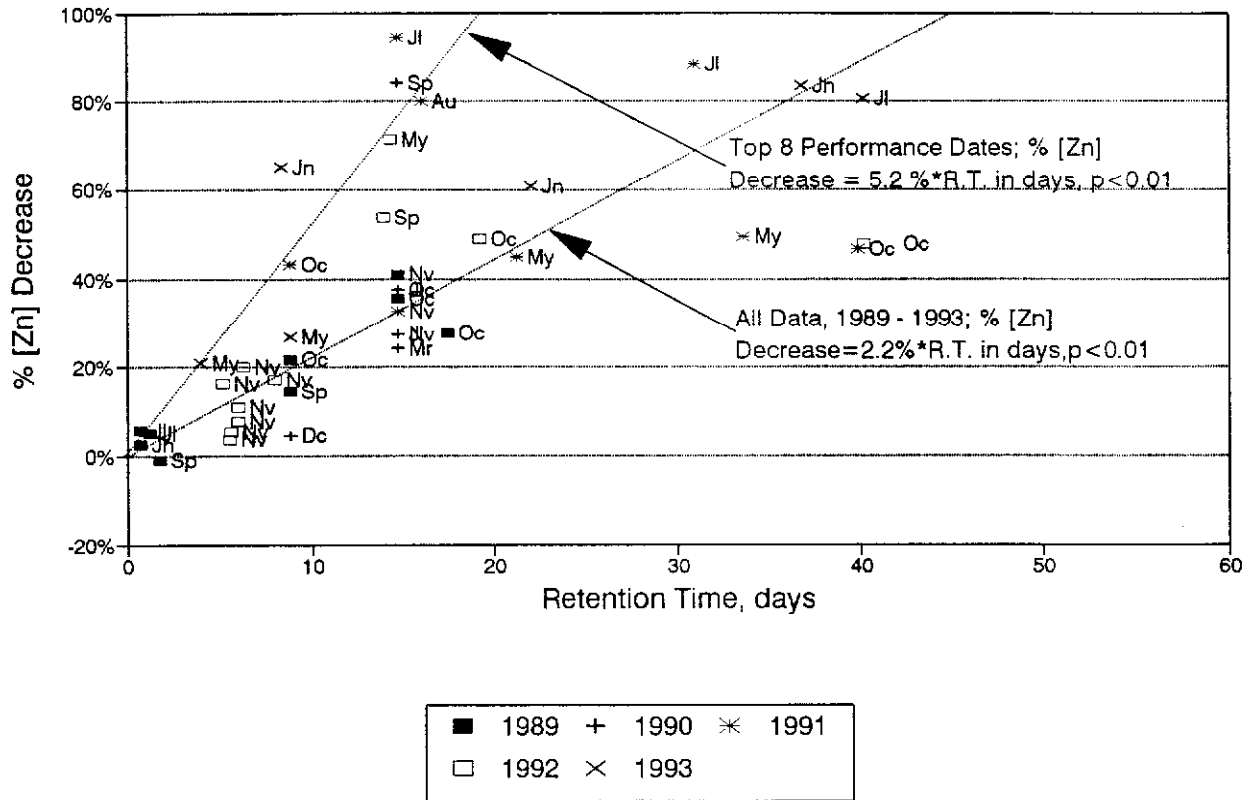
In Figure 1, each data point is differentiated according to year and month (e.g. Jn = June) of collection. Data for 1989, the first year of test system operation, are included in the calculation of the regression line. In the first year, zinc removal has to be considered to be mainly as non-biological, as virtually no algal growth was then present. In the years following 1989, all % zinc removal data are well above the 2.2 % regression line. As expected, good zinc removal performance occurs in the summer months when the algal population was actively growing. In contrast, the many data points below the regression line are mostly November and December data. Therefore, percent zinc concentration decreases represented by the 2.2 % regression line are either winter performance or non-biological removal processes.

A second regression line, using the top 8 performance period data, is given in Figure 1. The slope of top performance regression line represents a 5.2 % zinc concentration decrease for each day of retention time.

Based on the performance of PP1 to PP6, it can be concluded that winter performance will be a function of the 2.2 % regression line, where zinc removal is primarily due to non-biological processes limited by retention time. Summer performance will be a function of the 5.2% regression line, where zinc removal is enhanced by algal growth and zinc uptake.

PP10 data for 1992 and 1993 are plotted in Figure 2, and the 2.2% and 5.2% regression lines, derived from PP1 to PP6, are included so to provide the framework for performance evaluation.

Since construction of PP10 was completed in late 1992, good performance was expected in 1993. Very little data was collected in 1992, the period before algae had colonized the substrate. Also, in this period the flow rate through the pond was initially set high in order to test the stability of the berms. Therefore, with little algae present and the low retention time, zinc removal was negligible.

Fig. 2: % [Zn] Decrease in PP 10
1st Yr Performance:6-10-92 to 28-11-93
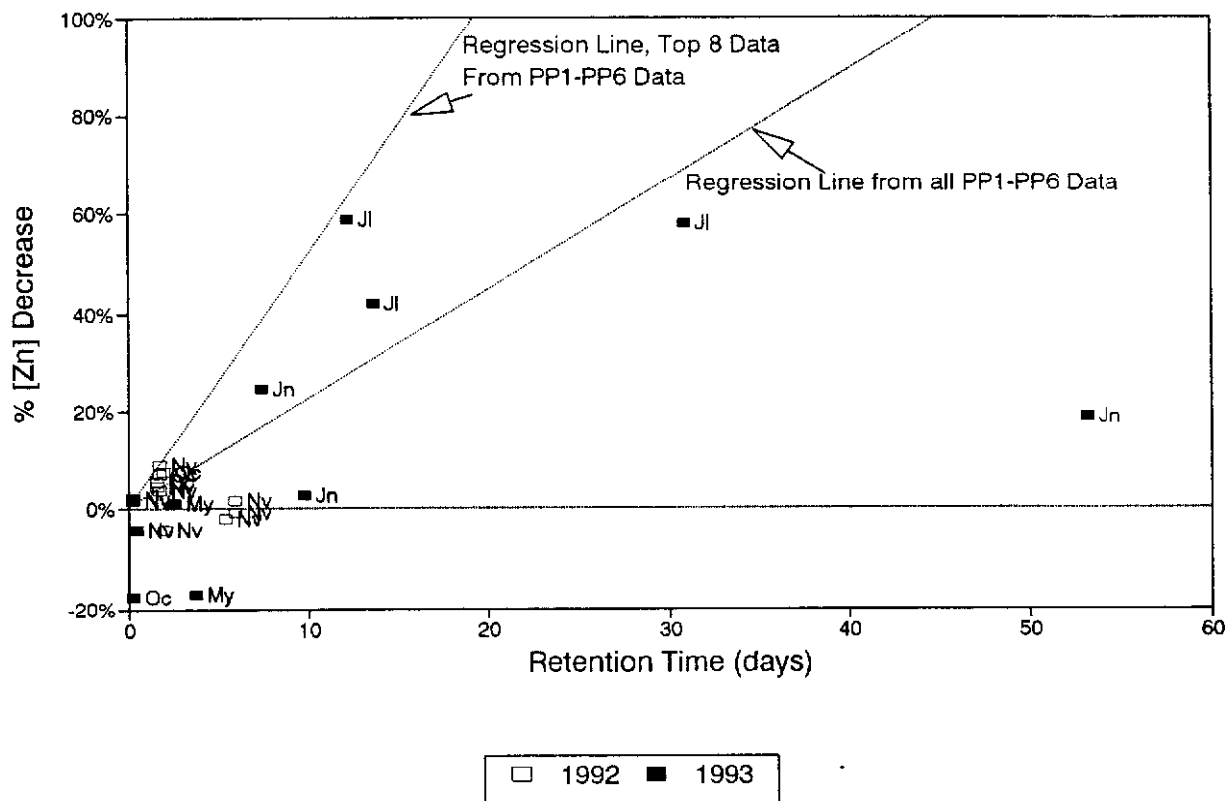
The zinc removal data collected in the summer of 1993 fall between the regression lines, indicating that the larger pond performs in the same manner as the PP1 to PP6 arranged in series. These were encouraging data, supporting the scale-up of the biological polishing system. Construction of Polishing Ponds 11, 12 and 13 during 1993 increased to system's volume to 6,000 m^3.

2.2 Projected Performance of Polishing Ponds

The mechanisms responsible for the observed zinc removal in the biological polishing process have been identified to involve: 1) settling of zinc-bearing suspended solids; 2) adhesion of suspended solids onto algal biomass surfaces; 3) adsorption of dissolved zinc onto algal cell walls; and 4) photosynthetically induced pH increases, with subsequent precipitation of zinc carbonates.

Given these different mechanisms which can take place simultaneously, the evaluation of the most important factor controlling process performance is very complex as several physical, chemical and biological variables are involved.

Removal of zinc by algal biomass via filtration and adsorption are only two of four main mechanisms which are operating. It was estimated that 70 % of zinc removal in the biological polishing ponds may occur as the result of co-precipitation followed by collection of the precipitate onto algal biomass.

Precipitate formation is, however, also mediated by algal photosynthesis which promotes the precipitation of zinc carbonates with increased pH. This can be demonstrated when changes in acidity and alkalinity take place in the water passing through the experimental pools. Data from pools 1 to 6 evidence such changes both in 1992 and 1993 (Figures 3a to d). The same process takes place in Polishing Ponds 10 through 13.

Fig. 3a: Polishing Ponds Acidities
May 28, 1992
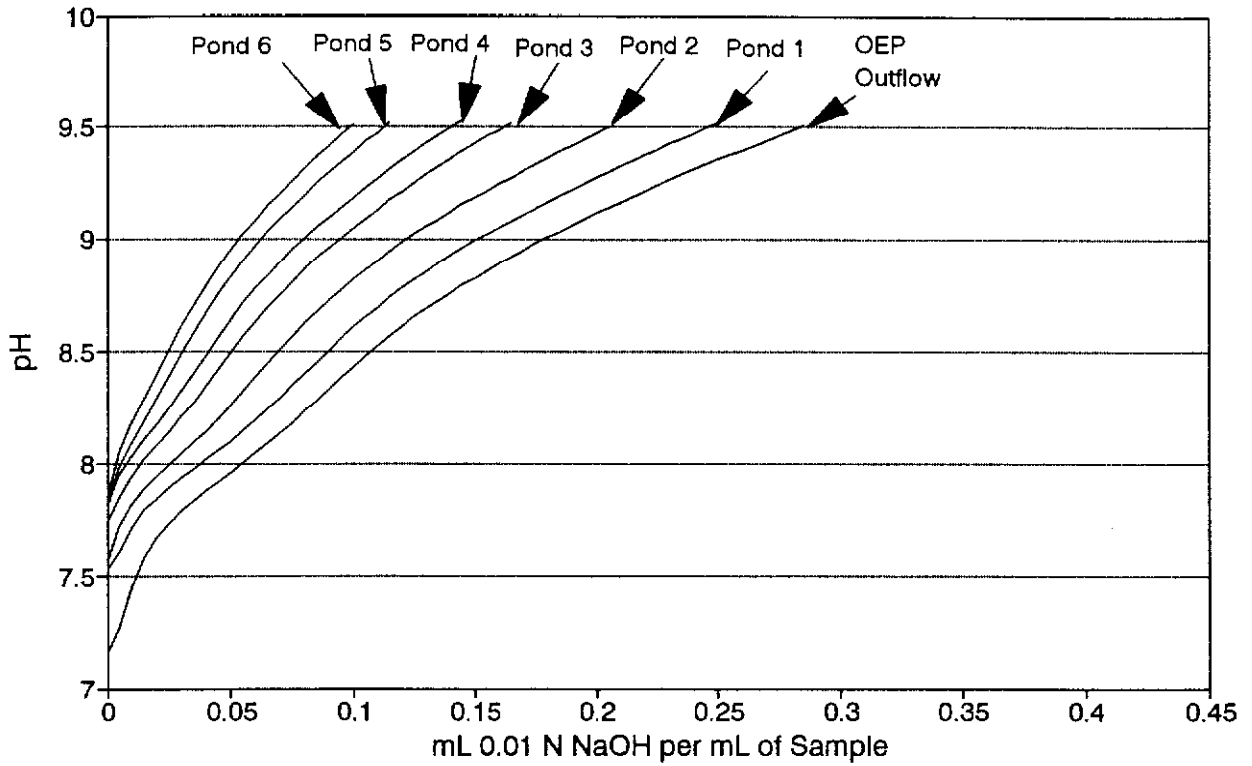
Fig. 3b: Polishing Ponds Acidities
August 29, 1993
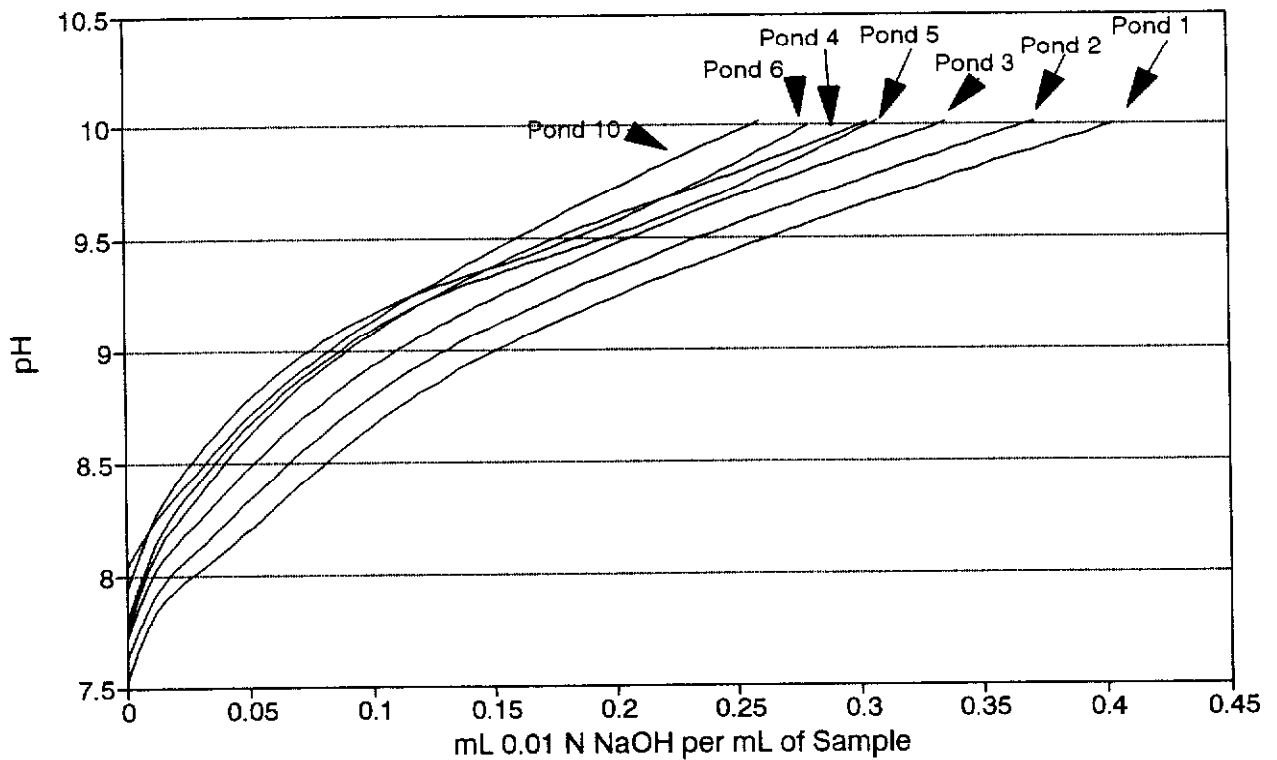
Fig. 3c: Polishing Ponds Alkalinities
May 28, 1992
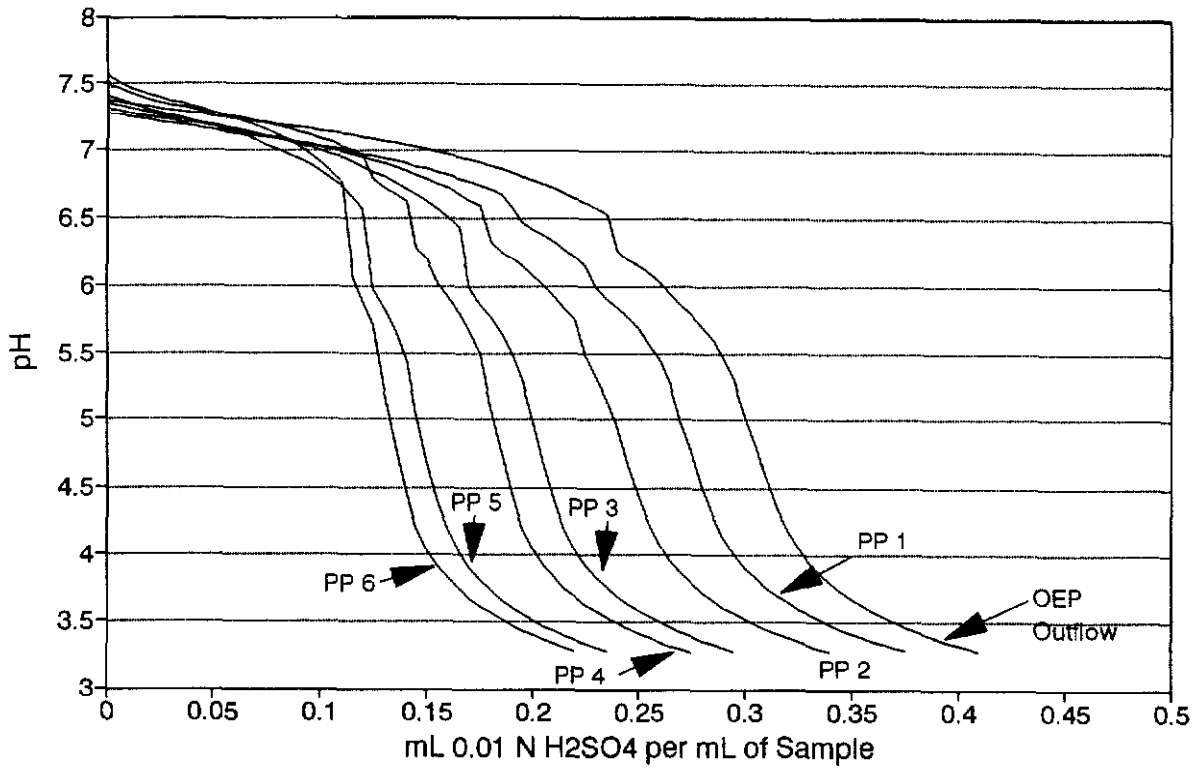
Fig. 3d: Polishing Ponds Alkalinities
August 29, 1993
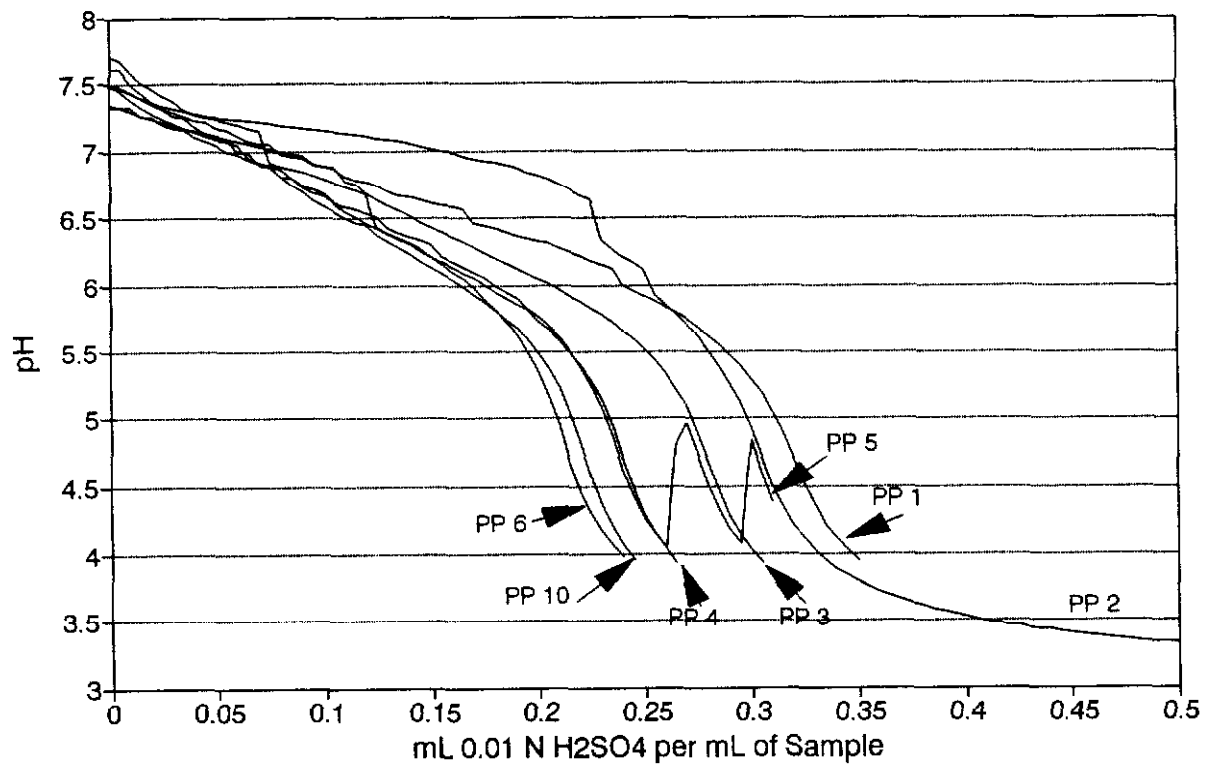
Two approaches have been selected in order to arrive at the key operating parameters. The first approach examined the overall performance of PP1 to PP6, in terms of zinc removal, according to flow rates and subsequent retention times. Assuming that the same physical, chemical and biological processes will operate in a scaled-up Biological Polishing system, the dimensions of the ponds and the flow will determine the retention times and the expected performance can be projected.

The second approach to arrive at process performance uses algal growth rates and biomass zinc concentrations. These values can be used to estimate removal rates by the algal population for comparison with zinc loadings.

The two approaches assume that performance of the process is either purely a function of retention time (First Approach), or only biological in nature (Second Approach), neither of which being exclusively the case.

Thus, it is not surprising to find that, when percent zinc removal is calculated for the newly constructed scaled-up ponds, some zinc removal is taking place despite an extremely low retention time of 1 to 2 days and low algal biomass grown to date (Table 1). The calculations based on PP1 to PP6 data indicated a minimum retention time of 14 days for 68 % zinc removal. The new scaled-up polishing ponds (PP11, PP12, and PP13) show as much as 27 % zinc decrease with a retention time of less than 3 days.

Construction of Polishing Ponds 11, 12 and 13 was completed only in late fall, 1993. Alder brush, provided as a substrate for algal growth, was then placed on top of the ice cover in November, 1993. Since all of the flooded pit discharge had been passing through PP10 to PP13 (9.5 to 14.5 l.s^{-1}), retention times were very low in each pond, ranging from 0.91 to 3.29 days (Table 1). Adsorption of zinc onto any organics in the ponds is certainly an additional process which assists in zinc removal, independent of the biological polishing.

Table 1: Polishing Ponds 11 to 13, 1993 start-up.

Date	Polishing Pond	Flow USGPM	Flow L/s	Inflow [Zn]	[Zn], mg/L In outflow	[Zn], mg/L decrease	% [Zn] Decrease	Volume (m3)	Retention Time, days
23-Oct-93	11	180	11.36	19.15	17.3	1.85	9.7%	1138	1.16
	12	180	11.36	17.3	15.45	1.85	10.7%	1848	1.88
	13	180	11.36	15.45	11.25	4.2	27.2%	2693	2.74
30-Oct-93	11	220	13.88	22.85	18.855	3.995	17.5%	1138	0.95
	12	220	13.88	18.86	17.25	1.605	8.5%	1848	1.54
	13	220	13.88	17.25	12.6	4.65	27.0%	2693	2.25
08-Nov-93	11	230	14.51	19.5	18.95	0.55	2.8%	1138	0.91
	12	230	14.51	18.95	17	1.95	10.3%	1848	1.47
	13	230	14.51	17	15.45	1.55	9.1%	2693	2.15
14-Nov-93	11	200	12.62	19.65	18.8	0.85	4.3%	1138	1.04
	12	200	12.62	18.8	18.05	0.75	4.0%	1848	1.70
	13	200	12.62	18.05	16.95	1.1	6.1%	2693	2.47
21-Nov-93	11	225	14.20	18.45	16.355	2.095	11.4%	1138	0.93
	12	225	14.20	16.36	17.3	-0.945	-5.8%	1848	1.51
	13	225	14.20	17.32	17.65	-0.33	-1.9%	2693	2.20
28-Nov-93	11	150	9.46	20.25	19.8	0.45	2.2%	1138	1.39
	12	150	9.46	19.8	20.15	-0.35	-1.8%	1848	2.26
	13	150	9.46	20.15	19.25	0.9	4.5%	2693	3.29

Using the two regression lines calculated in the section above, the projected performance of Polishing Ponds 10 through 13 can be estimated according to the first approach. Based on 2.2% zinc removal with each day of retention time (winter), 99 % zinc removal is estimated for the scaled-up PP10 to PP13, if the inflow is set at 1.55 l.s^{-1}, providing a retention time of 45 days (Table 2a).

Based on 5.2 % zinc removal per day (summer), 98% zinc removal is estimated at an inflow of 3.7 l.s^{-1} (19 day retention time; Table 2b). The overall relationship between percent zinc removal, flow and retention time, estimated by the two regression lines, is shown in Figure 4a.

Table 2: Projected performance of Polishing Ponds 10, 11, 12 and 13.

2A: PROJECTED PERFORMANCE ACCORDING TO PP 1 TO 6 DATA			
	All Performance Data	Performance of Top 8 Dates	Units
Inflow set at	1.55	3.7	L/s
Total Pond System Volume	5998	5998	m^3
Residence time in system	45	19	days
Percent Zn removal, accordng to PP1-PP6 data	99	98	Percent

Fig. 4a: Projected Zn Removal
Performance Data to Date

Top 8 data, 5.2 % Decrease per Day R.T.

Retention Time, Days

All data, 2.2 % Decrease per Day R.T.

— Percent Removal   --⊟-- Retention Time(d)

2B: PROJECTED PERFORMANCE: PP10 ALGAL GROWTH AND ZN CONTENT			
	1992 Projection	1993 Projection	Units
Growth rate (Avg 1993 Netting,Branch data)		0.745	g/m^2/day (100 d growing season)
	0.5 - 1.0	0.204	g/m^2/day over 1 year (no growth in winter)
Zinc content in PP10 algae ((1993 data)	62	115	g/kg dry wt
Alder surface area in ponds (2.8 trees/m^3)	900	17130	m^2 of trees
Zinc removed per day in polishing pond	0.007 (PP10,320 m3)	0.40 (PP10-13,5998 m3)	kg/day
1993 Avg [Zn] in OEP discharge	20	20	mg/L

Fig. 4b: Projected Zinc Removal
Algal Growth and Zinc Content to Date

45 Day Retention Time at 1.55 L/s

15 % Removal at 1.55 L/s

— Percent Removal   --⊟-- Retention Time (d)
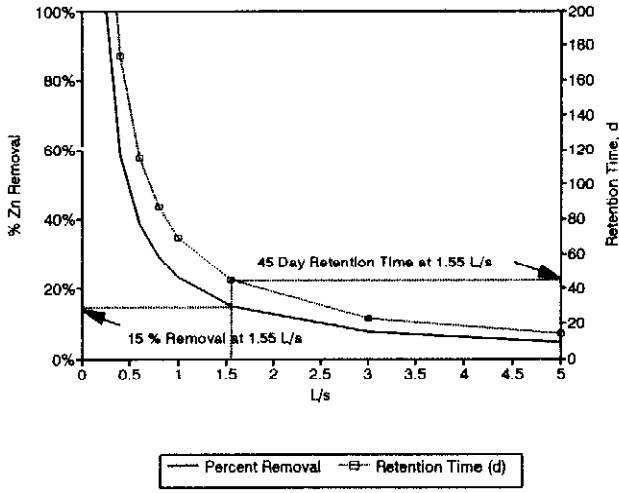
The second approach to projecting performance of the scaled-up Polishing Ponds is based strictly on algal growth rates and algal zinc content, which collectively determine the amount of new algal biomass, and subsequently the amount of zinc which can be removed, in a polishing system of a given volume per day.

Using 1992 algal growth rate data and zinc concentrations in algal biomass, it was projected in the 1992 report that algal biomass growing on alder trees could remove 115 g Zn per tree per year, or in alternative units, 121 g Zn per m^2 of tree per year (1 tree = 0.95 m^2). Using the growth data accumulated on alder branches placed in PP10, the average 1993 growth rate is estimated at 0.745 g per m^2 of substrate (tree or netting) per day (Table 2b). Assuming a growing season of 100 days, this average growth rate for the year is 0.204 g per m^2 of substrate per day (0.745 $g.m^2.d^{-1}$ * [100 d ÷ 365 d]).

These growth rates fall within the range of growth rates determined in the period October 1991 through July 1992 for the experimental ponds, PP1 to PP6. Growth rates ranged from 0.1 to 3.1 g per m^2 of substrate per day. In 1993, fertilizer (Plant Prod 10-52-10) was regularly added to Polishing Pond 10 between June 25 and July 12, 1993. Higher growth rates were anticipated as was noted in PP1 to PP6 where fertilizer was added to the peritraps. Growth rates had increased by September, 1992, to 1.5 to 4.7 $g.m^2.d^{-1}$.

In Table 3, the elemental composition of the algae is summarized. Generally, healthy plants contain on a dry weight basis 0.1 to 0.8 % phosphorus. The phosphorus content of the PP algae, 0.6 to 2.5 %, is well within this healthy range. Comparing the elemental compositions of the algae grown on netting supplemented with slow release fertilizer packets (PP6, PP10) and that growing the branches in the pond supplemented with liquid fertilizer (PP6), no consistent differences can be noted. Overall, brush cuttings and plastic netting support algal populations of similar elemental composition.

Table 3: Elemental concentrations in 1993 Polishing Pond algae.

% Dry wt.	PP 6 Algae on Perinet netting	PP 6 Algae on branches	PP 10 Algae on Perinet netting
Al	0.28	0.78	1.65
Ca	19.3	7.65	4.26
Fe	2.07	9.52	3.51
Mn	1.34	3.52	1.7
P	0.63	2.49	1.51
Zn	2.73	4.76	11.5
% L.O.I.	34	31	31

In Table 2b, the adjusted algal growth rate (0.204 $g.m^2.d^{-1}$) is used in combination with the 1993 zinc content in Polishing Pond 10 algae (115 $kg.kg$ dry wt of algae^{-1}), and the number of trees in Polishing Ponds 10 through 13 required to achieve an average density of 2.8 trees per m^3 of pond (17,130 trees), to estimate zinc removal in the system per day. Using these values, 0.40 kg of zinc would be captured by the algal biomass growing each day in the scaled-up Polishing Pond system.

Using 20 $mg.L^{-1}$ zinc as the average zinc concentration in flooded pit discharge, it can be seen in Figure 4b that this Polishing Pond system could remove only 15 % of the zinc if the inflow was kept at 1.55 $L.s^{-1}$, or effectively, a retention time of 45 days. From these considerations, the use of the growth rate of, and the zinc content in, the algal biomass (Second Approach) to project percent zinc removal performance gives a very low estimate, compared to the Second Approach, where zinc concentrations changes (due to the operation of all zinc removal processes) are related to flow rates and the retention time (Table 2a and Figure 4a).

In Table 3, the elemental composition of the algae in PP10 is summarized. Generally, healthy plants contain on a dry weight basis 0.1 to 0.8 % phosphorus. The phosphorus content of the PP10 algae, 0.6 to 2.5 %, is well within this healthy range. Comparing

the elemental compositions of the algae grown on netting supplemented with slow release fertilizer packets (PP6, PP10) and that growing the branches in the pond supplemented with liquid fertilizer (PP6), no consistent differences can be noted. Overall, brush cuttings and plastic netting support algal populations, and result in similar elemental composition. The remarkably high zinc concentration in the biomass, 11 %, is noteworthy.

2.3 Substrate Standardization

In 1993, a more easily standardized method of quantifying algal growth was applied, compared to the original unit, algal growth per surface area of tree branch. Units of plastic netting (Dupont tubular webbing) of known surface areas, termed perinets, were suspended in neutral pH Buchans polishing ponds and in the Boomerang Lake, South Bay (pH 3.2), and algal biomass was quantified after a given number of days. Each perinet unit contained a packet of slow release fertilizer. Details of the data collected are given in Appendix 1 and 2.

The Buchans polishing ponds perinets produced 0.806 $g.m^{-2}$ $netting.d^{-1}$ on average, with a minimum of 0.269 $g.m^{-2}.d^{-1}$ and a maximum of 1.781 $g.m^{-2}.d^{-1}$ (Table 4a). These growth rates are comparable to the average 1993 growth rates derived from the biomass collected from the branches in the Buchans polishing ponds (1.248 $g.m^{-2}.d^{-1}$ on average; Table 4a). Therefore, the nutrients supplied by the packets of slow release fertilizer did not appreciably increase the algal growth rate on the perinets, compared to growth on the branches. With addition of nutrients (July, 1993), the neutral pH polishing ponds contained adequate nutrients for good algal growth.

In contrast, the slow release fertilizer stimulated growth of periphytic algae on the perinets in Boomerang Lake (0.296 $g.m^{-2}.d^{-1}$), compared to biomass growing on brush cuttings branches (0.017 $g.m^{-2}.d^{-1}$; Table 4b). This lake is relatively nutrient poor.

Table 4a: Summary of 1993 Periphyton Growth Rates - Buchans Polishing Ponds

SUBSTRATE	n	Min.	Max.	Avg.	Std. Dev.
Perinets, g/m2/day	12	0.269	1.781	0.806	0.451
LOI, %	9	21	35	30	5
Branches, g/m2/day	3	0.769	1.949	1.248	0.507
LOI, %	3	18	31	25	5

Table 4b: Summary of 1993 Periphyton Growth Rates - Boomerang Lake

SUBSTRATE	n	Min.	Max.	Avg.	Std. Dev.
Perinets, g/m2/day	18	0.134	0.675	0.296	0.138
LOI, %	11	31	43	38	3
Branches, g/m2/day	15	0.006	0.039	0.017	0.009
LOI, %	15	18	46	33	7

Overall, it appears that brush cuttings are not preferred by the algal population over nylon netting as a growth substrate, and that netting could serve well as a substitute for brush cuttings, where required.

2.4   Model Improvements and Verification

The purpose of the earlier model reported in 1993 was to account for the observed decrease in metal concentrations in lakes and ponds in which periphytic algae have established. The model is based on empirical studies of periphytic growth and metal bioaccumulation, and is intended for use in polishing pond design. This section summarizes the previous biological polishing models developed for two sites, one at South Bay, Ontario, and one at Buchans, Newfoundland.

Two approaches have been selected to identify the key operating parameters of the process which were discussed in the previous sections for the Buchans effluent. They are here described in the form of the model, which is aimed to provide, ultimately, a tool to evaluate the process.

It should be emphasized that the final aim of modelling is to construct a biological polishing model which interrelates the various hydrological, biological, and geochemical cycles within the reactor system. As will be discussed in the following sections of this report, sediment chemistry is extremely important, especially iron cycling and, thus, for understanding the mass balance within a reactor system. Drawing on results obtained from the quantification of sedimentation rates and the composition of the collected precipitate, a lake/pond model is presented which can explain better the recent data from the field sites.

2.4.1 Summary of Biological Polishing Models

The application models for South Bay and Buchans are best described as algorithms for estimating the amount of metal contaminant sequestered by algae. Two main modelling approaches have been taken:

Overall Performance Model: In this approach, the metal removal for a reactor system is plotted against residence time. The amount of metal sequestered is assumed to depend only on residence time, determined by the volume of, and flow rate through, the system.

Algae Growth Model: In this model, the metal removal is quantified by assessing algal growth rates and biomass metal concentration. Model variables are measured both in the field and laboratory, and are logically related in a sequence of steps. The amount of metal removed by the periphyton is calculated by the following procedure:

1. Measure the density of the periphyton-precipitate complex (PPC) on trees and branches serving as substrate.

2. Estimate the growth rate of periphyton by using growth rate data from the field and laboratory.

3. Measure the density of metal within the PPCs.

4. Calculate the amount of metal sequestered by the algae by multiplying the growth rate by the metal concentrations in PPCs.

The metal removal rates within the reactor systems can also be measured directly by the following procedure:

(i)   Measure the input metal loadings.

(ii)   Measure the output loadings (i.e. the amount of metal leaving the lake/pond).

(iii)   Calculate the net loading, i.e., the difference between (i) and (ii).

If algal bioaccumulation is the only metal sink in the reactor, then the amount of metal sequestered by the periphyton calculated in '4' above ought to equal the amount of metal actually deposited to the system as determined in (iii). This is, therefore, an important verification of the model. Before summarizing the results from South Bay and Buchans in terms of the algal growth model, the model is cast into algebraic form - in a so-called "box model".

In the simplest case, spatial variation is ignored and, instead, the system is idealized as a single box. Here, the first version of the 1993 polishing model is summarized; later, the additions which will be made to this model will be introduced. Schematic 1 shows the inflow rate, and outflow rate of species "i" to the box, and the removal rate of a species "i" within the box:

Schematic 1:   1993 Biological Polishing Box Model (simplest case).

$$R^i$$

$$R^i_{in} \qquad R^i_{bioacc} \qquad R^i_{out}$$
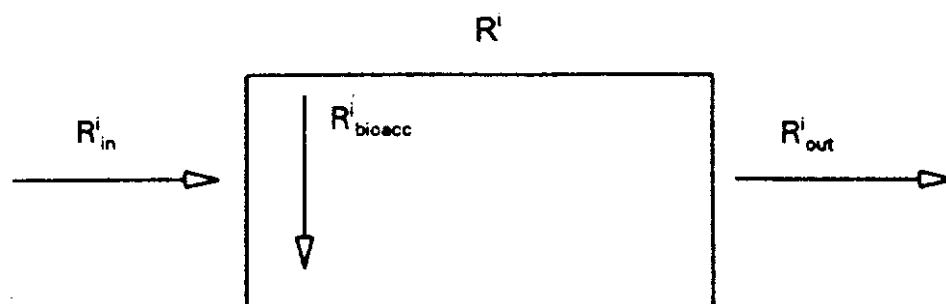
R^i_{in} = inflow rate of species i, Mass per unit Time $(M.T^{-1})$ (1)

R^i_{out} = outflow rate of species i $(M.T^{-1})$

R^i_{bioacc} = rate at which algae bioaccumulate species i $(M.T^{-1})$

R^i = rate of change of species i in lake/pond water $(M.T^{-1})$

Applying conservation of mass to the box gives the rate balance condition:

$$R^i = R^i_{in} - R^i_{out} - R^i_{bioacc} \qquad (2)$$

This equation simply states that the rate at which a species accumulates in the lake/pond water must equal the rate at which it flows in, minus the rate at which it flows out, minus the rate at which it is sequestered by the algae. The term accounting for bioaccumulation, R^i_{bioacc}, is calculated according to the procedure outlined above. Notice, at this stage, no account is made of metal cycling to and from the sediments.

2.4.2 Field Measurements

The above algae bioaccumulation model is now compared to the 1993 rate data for Boomerang Lake and the Buchans polishing ponds.

Boomerang Lake: The metal concentrations in Boomerang Lake have not increased markedly for a number of years. Table 5 summarizes the results for Boomerang Lake on the basis of the model presented. It is clear that the model does not account particularly well for Fe dynamics in Boomerang Lake, although it does not do badly for Zn and Al.

Table 5:   Boomerang Lake, South Bay, Ontario (1993).

Metal i	$R^i_{in} - R^i_{out}$ $(t.yr^{-1})$	R^i_{bioacc} $(t.yr^{-1})$	R^i $(t.yr^{-1})$
Fe	2.0	80	- 78
Zn	1.2	0.15	+1.05
Al	57.3 0.075	0.4	-0.325
SO_4	126.8 - 75.5 (t.yr⁻¹)	n a	51.3 t yr⁻¹

See Table 7

On the basis of Table 5, the [Fe] would be decreasing, [Zn] would be increasing, and [Al] would be decreasing in Boomerang Lake. Given the difficulty of estimating loadings and bioaccumulation, only the mass balance for Fe indicates trouble for the model.

The discrepancy between the model R^i and field observations suggests that some additional source of Fe must exist in Boomerang Lake. In this report it is proposed that Fe cycling from the sediments is vitally important in accounting for the Fe dynamics in Boomerang Lake. It is posited that Fe is re-cycled within lake, so that both a new source (diffusion from the sediments) and sink (sedimentation) should be added to the model.

Buchans: For the Buchans polishing ponds, the model gives slightly better results for Zn. Given the error in estimating loadings, growth rates, and algal metal concentration, the results are encouraging.

Table 6:   Polishing Ponds, Buchans, Newfoundland (1993).

Metal i	$R^i_{in}-R^i_{out}$ (kg.yr^{-1})	R^i_{bioacc} (kg.yr^{-1})	R^i (kg.yr^{-1})
Zn	78	50	+28
Fe	32	88	-56
Al	< 1	10.6	-10.6

As in Boomerang Lake, in the Buchans polishing ponds some additional sources and sinks of Zn must be present since the algae alone cannot remove all of the Zn deposited in the ponds each year.

2.5 Iron Cycling: Additional Field Data for the System Model

In this section, some additions are made to the biological polishing models developed for Boomerang Lake at South Bay, Ontario, and for the polishing ponds constructed at Buchans, Newfoundland. The contaminant dynamics are framed in terms of rates, and the key equation is conservation of mass in a reactor system. The conceptual model is best summarized in Schematic 2 below:

Schematic 2: Biological Polishing Model with metal cycling.
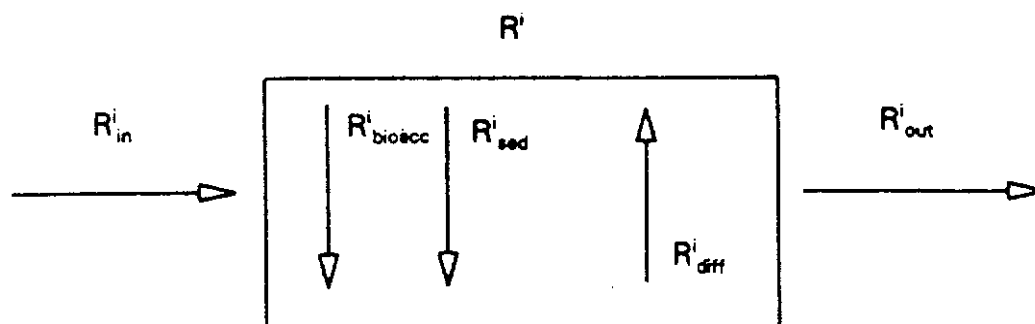
$$R^i = R^i_{in} - R^i_{out} - R^i_{bioacc} - R^i_{sed} + R^i_{diff} \tag{3}$$

Here

R^i_{in} = rate of inflow of aqueous species i, Mass per unit Time $(M.T^{-1})$

R^i_{out} = rate of outflow of aqueous species i $(M.T^{-1})$

R^i_{bioacc} = rate of bioaccumulation of species i $(M.T^{-1})$

R^i_{sed} = rate at which species settles to sediment i $(M.T^{-1})$

R^i_{diff} = rate at which species in sediment is re-suspended into water column i $(M.T^{-1})$

R^i = rate of change of species in the lake/pond water i $(M.T^{-1})$

Notice that cycling is now included in the model through the terms R^i_{sed} and R^i_{diff}. As discussed in the preceding sections, cycling - especially Fe cycling - has an important influence on the dynamics of all contaminants in the system. The same basic model applies to both Boomerang Lake and to Buchans' polishing ponds; however, the actual values for the various rates will be different.

2.5.1 Field Measurements

Boomerang Lake: Average annual rates for the various terms going into the overall mass balance of species i were calculated based on the field and literature data. These are summarized in Table 7.

Table 7: Mass Balance for Boomerang Lake (1993-1994).

Species i	R^i_{in} (t.yr^{-1})	R^i_{out} (t.yr^{-1})	R^i_{bioacc} (t.yr^{-1}	R^i_{sed} (t.yr^{-1})	R^i_{diff} (t.yr^{-1})	R^i (t.yr^{-1})
Fe	5.0	0.61	80	29	58	-44
Zn	18.7	2.5	0.144	1.3	-10	-4.7
SO$_4^-$	126.8	75.5	na	15	937	973

The data presented suggest that the biological polishing model, based on algal sequestration, is encouraging but needs further development. For example, according to the model, in Boomerang Lake the Fe concentration should be decreasing by 44 mg.l^{-1}.yr^{-1}, and the Zn concentration by 4.7 mg.l^{-1}.yr^{-1} (the volume of Boomerang Lake is approximately 10^6m^3). Under the assumption that R^{SO4}_{bioacc} is negligible, the SO$_4^-$ concentration should be increasing by 973 mg.l^{-1}.yr^{-1}.

These numbers require some explanation. To begin with, R^i_{in} and R^i_{out} are estimated from hydrological assessments of the site. Typically, loadings to a lake from a drainage basin are diffuse and cannot be precisely quantified. The values presented are representative of best estimates. Since R^i_{sed} is relatively straightforward to measure

using sedimentation traps, the values presented are sound. On the other hand, R'_{bioacc} is difficult to estimate. The bioaccumulation rate is calculated by measuring metal concentrations in the periphyton, estimating the periphyton growth rate, and by estimating the total number of trees in the lake. Estimating the number of trees (hence total surface area on which algae grow) is difficult as the branches were delivered as truck loads of cut brush. It may well be that R^{Fe}_{bioacc} and R^{Zn}_{bioacc} are overestimated in our calculations.

Finally R'_{diff} is calculated from pore water peeper data collected in 1993 and considerations of diffusion based on Fick's Law. These parameters are probably close to their actual value. Because the diffusion fluxes are maximum values, our model suggests another mechanism for transferring species from the sediment to the water column operates. Although the rates presented may differ somewhat from actual values, it is more likely that additional mechanisms within the Boomerang Lake system are responsible for the weak fit between model and data. In brief, the model needs additional sources and sinks. One possible candidate is physical re-suspension of iron hydroxide as a result of perturbation of sediment back into the water column by the action of currents in the lake.

Buchans: The sources and sinks of Zn for the Buchans polishing ponds are summarized in Table 8.

Table 8: Mass Balance for Buchans Polishing Ponds.

Species i	R'_{in} (kg.yr^{-1})	R'_{out} (kg.yr^{-1})	R'_{bioacc} (kg.yr^{-1})	R'_{sed} (kg.yr^{-1})	R'_{diff} (kg.yr^{-1})	R' (kg.yr^{-1})
Zn	166.7	88.8	50.3	na	-0.032	28
Fe	32.4	2.06	88	na	0.62	-57
Al	0.29	0.29	10.6	na	0.067	-10.5

On the basis of the model, R^{Zn} = 28 kg.yr^{-1}, predicting an increase in zinc concentration in the ponds over the last year of 116 mg.l^{-1} (volume of ponds is taken as 240 m^3). Clearly, some explanation is required. R^{Zn}_{diff} is calculated using Fick's Law in the same way sediment fluxes were calculated in Boomerang Lake, and represents the maximum diffusion flux from the sediments. R^{Zn}_{bioacc} is calculated indirectly by measuring density of Zn in periphyton, estimating the growth rate of the algae, and by estimating the number of alder branches in the ponds. The estimation of number of branches (hence growing surface) is subject to error. Finally, no account has been made of either R^{Zn}_{sed} or of re-cycling from the sediments to date. These terms are important for overall mass balance, and will be determined in future work.

2.6 Continuous Time Reactor Models

The values given in Table 7 and Table 8 are average rates over a year and do not consider differences which take place in the different seasons, when the lakes or the ponds are covered with ice. In reality, the dynamics of contaminants in a lake operate continuously, and should be described in terms of differential equations.

Applying conservation of mass to species i at each instant t gives a mass balance condition valid at all times t:

$$R^i(t) = R^i_{in}(t) - R^i_{out}(t) - R^i_{bioacc}(t) - R^i_{sed}(t) + R^i_{diff}(t) + R^i_{resusp}(t) \qquad (4)$$

Here

$R^i(t)$ = rate of change of species i in the lake/pond water (M.T^{-1})

The other terms are interpreted similarly.

Notice that cycling is now included in the model through the terms $R^i_{sed}(t)$ and $R^i_{diff}(t)$. As discussed in the preceding sections, cycling - especially Fe cycling - has an important influence on the dynamics of all contaminants in the systems. The same basic model will apply to both Boomerang Lake and to Buchans polishing ponds. However, the actual values for the various rates will be different.

The total mass of species i in the lake/pond water at time t is represented as:

$$M^i(t) = VC^i(t) \tag{4}$$

where

V   = volume of the lake/pond (L^3).

$C^i(t)$ = concentration of species i in the lake/pond water ($M.L^{-3}$)

The instantaneous rate of change of species i, $R^i(t)$, is the derivative of $M^i(t)$:

$$R^i(t) = \frac{dM^i(t)}{dt} = V\frac{dC^i(t)}{dt} \tag{5}$$

Depending on how the various terms in Equation 4 are represented mathematically, different rate equations result. Here a tentative model is presented for the dynamics of species i in a reactor system:

$$\frac{dC^i(t)}{dt} = k_{ex}(t)C^i_{in}(t) - k_{ex(t)}C^i_{out}(t) - \frac{C^i(t)\, n\, A_{tree}}{C^i(t)+K_m}\frac{da(t)}{dt} - v_{set}A_{i,b}C^i(t) + A_{i,b}J_{diff}(t) \tag{6}$$

$$\frac{da(t)}{dt} = (G_p - D_p)a(t) \tag{7}$$

Here

$C^i(t)$ = concentration of species i in lake/pond water ($M.L^{-3}$)

$a(t)$ = density of periphyton on branches ($M.L^{-2}$)

$kex(t)$ = $Q(t)/V$ where $Q(t)$ is inflow rate of water ($L^3.T^{-1}$)

K_m = Half-saturation constant ($M.L^{-3}$)

n   = number of trees in the system

A_{tree} = surface area of a standard tree (L_2)

$A_{i,b}$ = Area of lake/pond bottom (L^2)

v_{set} = Settling velocity of precipitated species in water column ($L.T^{-1}$)

$C^i_{prec(t)}$ = Concentration of precipitated species in water column ($M.L^{-3}$)

$J_{diff}(t)$ = Fick diffusion ($M.L^{-2}.T^{-1}$)

The dynamics of all the species in the system is then represented by a coupled set of differential equations, one balanced equation for each species.

In building lake/pond models, it is important to carefully measure all variables appearing in the model in order to calibrate and ultimately verify the model. The concentrations of various contaminants should be measured throughout the year at regular intervals, as should the various kinetic coefficients, and system parameters such as $k_{ex}(t)$, $A_{l.b.}$, and v_{set}. Once all these are measured, the time variation predicted by the model can be compared to the data.

In summary, continuous time models are a refinement on models based on yearly or seasonal averages. The main challenge remains to arrive at measured loading rates, growth rates, sedimentation rates, and re-cycling rates, and to test model predictions against these.

3.0 SEDIMENT CHEMISTRY: IRON CYCLING

3.1 Iron Chemistry and Cycling in the Aquatic Environment

Iron is an abundant element. Sedimentary rocks, overall, comprise 5 to 6 % iron (Stumm and Sulzberger, 1992). Chemically, iron is very reactive and, through redox reactions, probably had a major role in establishing the oxygen content of the atmosphere on earth. This element is required by all organisms in trace quantities and is used by some microorganisms in energy-releasing electron transfers. Iron can exist in the oxidation states Fe^0, Fe^{2+} and Fe^{3+}. Fe^0 rarely occurs in nature since it is readily oxidised to Fe^{2+} in most environments.

The oxidation of Fe^{2+}, the reduction of Fe^{3+} and subsequent chemical reactions are very important in determining iron concentration and mobility between environmental compartments. Iron oxidation is important in the formation of minerals including soil components. This process is also important in acid generation which takes place in mining wastes, and is also very relevant in metal recovery processes by leaching.

This literature review emphasizes the microbial aspects of the iron cycle between sediments and water, as this is relevant to processes which could ameliorate or enhance acidic conditions.

The surface chemistry of the solid phases of iron compounds enables them to act as semiconductors, which can participate in photoredox reactions. The reactivity of the surfaces and the large surface area of iron solid phases (such as oxyhydroxides or geothite which predominate in most ecosystems), play a major role in adsorption of a wide diversity of solutes. Hence the iron cycle is interdependent with that of many elements, organics and oxyanions such as phosphate.

Many of the reactions involving iron are mediated by, or catalysed directly or indirectly by, microorganisms (Ehrlich, 1990; Ghiorse, 1988; Lovley, 1991, 1993). Microbial ecology and physiology are therefore essential components in controlling iron cycling in ecosystems.

Iron reduction will increase the dissolved iron concentration in the sediments, but this process may assist in ameliorating AMD. This process results in a net consumption of protons (Stumm and Morgan, 1981; Mills et al., 1989) and an increase in pH, which will result in the precipitation of metals as hydroxides (aluminum) or sulphides (zinc, nickel, iron, copper). A similar phenomenon is associated with sulphate reduction, which is fuelled by sulphate, another ion abundant in AMD.

Sulphate reduction is inhibited by Fe^{3+} reduction (Chapelle and Lovley, 1992) but is likely to occur deeper in sediments where the Fe^{3+} does not penetrate. The significance of abiotic reduction of Fe^{3+} is not clear, but it is worth noting that photo-reduction of iron can substantially increase the dissolved Fe^{2+} concentration in streams

(McKnight et al., 1988) or wetlands (Wieder, 1992) receiving AMD.

The enhancement of reducing conditions may provide a means of ameliorating AMD. Wetlands have been designed to enhance bacterial sulphate reduction (EPA, 1993) and the importance of iron reduction in constructed wetlands for AMD is now being realised (Wieder, 1992).

Pond systems have been designed to promote reducing conditions for AMD treatment (Kalin, 1993). Such systems incorporate oxidation and reduction cells, both of which help ameliorate AMD. The oxidation cells are designed to remove iron by oxidation, hydrolysis and precipitation, and other metals by co-precipitation. In the reducing cells, additions of readily decomposable organic materials rapidly produce reducing conditions (through fermentation reactions), which support iron and sulphate reduction processes.

Recently, progress has been made in modelling the overall iron cycling in lake ecosystems (Stumm and Sulzberger, 1992; Barry et al., 1994; Deng and Stumm, 1994). In general, the stratum of water above the thermocline is oxic and well mixed, providing favourable conditions for abiotic oxidation, hydrolysis and precipitation as Fe^{3+} oxyhydroxide colloids of any iron entering the system.

In lake sediments, or below lake thermoclines, oxygen concentrations decline rapidly with depth and reducing conditions predominate, favouring the reductive dissolution of

Fe^{3+} oxyhydroxides.

Iron Oxidation: In most water bodies and soils, oxidising conditions predominate. If the pH exceeds 5, any Fe^{2+} present is readily oxidised abiotically to Fe^{3+}. At pH < 5, chemically-mediated oxidation rates are slow. However, it is now well established that at low pH (< 3), bacteria mediate the oxidation of Fe^{2+} as a source of energy, where Fe^{2+} is the electron donor for respiration. The bacterially-mediated oxidation is a very important process in acid generation in mining wastes and also in bioleach processes for the recovery of metals. The oxidation of pyrite ores in particular has been extensively studied, owing to this process's economic importance. However, the microbial ecology of iron oxidation, the mechanism of this process and its role in natural ecosystems is still poorly understood.

Fe^{3+} is readily hydrolysed and precipitated as Fe^{3+} oxyhydroxides when the pH exceeds 5. Fe^{3+} may also be removed from solution by adsorption, ion exchange and complexation processes. The role of bacteria in Fe^{2+} oxidation at pH > 5 is uncertain because of the ease of abiotic oxidation in such conditions. *Gallionella spp.* can carry out this reaction at near neutral pH but requires a low redox potential. It is reported to be active at the boundary of oxidising and reducing conditions in sediments. Since bacteria are undoubtedly associated with surfaces where most oxidation occurs, it is likely that, even if not directly involved in the oxidation process, they will have a significant effect on the processing and transport of products of oxidation. For example, Fe^{3+} oxyhydroxides have been shown to accumulate on the surfaces of bacteria in near

neutral lakes (Ferris et al., 1989a, b).

Fe^{2+} oxidation by O_2 is influenced by many factors (Stumm and Sulzberger, 1992; Barry et al., 1994). Oxidation is favoured by the hydrolysis of Fe^{2+} compounds. The OH^- ligands present in such moieties increase reducing power substantially (Luther, 1990). Above pH 5, oxidation shows a second order dependence on OH^- concentration (Stumm and Lee, 1961), whereas at pH 3 to 5, the dependence is first order, and at pH < 3, zero order. In other words, the reaction is much slower in acidic conditions (Wehrli, 1990). At low pH (< 3), oxidation of pyrite is mediated by Fe^{3+} and catalysed by bacteria, such as *Thiobacillus ferrooxidans*.

The oxidation of Fe^{2+} in relation to the overall functioning of the aquatic environment is still poorly understood, but is likely a very important process in those sediments enriched with iron such as water bodies receiving AMD. The rate of Fe^{2+} oxidation may be increased by the presence of amorphous Fe^{3+} precipitates, organic ligands and reactive chemical species which may be photochemically or biotically generated, for instance H_2O_2 and O_3 (Stumm and Sulzberger, 1992).

Iron Reduction: When reducing conditions prevail in sediments, Fe^{3+} is reduced to Fe^{2+}. Where H_2S is present as a product of bacterial sulphate reduction (a process requiring reducing conditions and sufficient sulphate and hydrogen concentrations), Fe^{2+} is precipitated as iron sulphide. Iron reduction is also directly mediated by bacteria, either as a minor side reaction or with iron as the electron acceptor for respiration

(Lovley 1991, 1993). This process utilises Fe^{3+} hydroxides. The reduced Fe^{2+} is soluble in the sediment where the pH is generally higher than 5. Therefore, the net effect of this process is the dissolution of solid Fe^{3+} oxyhydroxides. The importance of this bacterially-mediated iron reduction has only recently been realised (Jones et al., 1983; Lovley 1991, 1993). It has been substantiated by the isolation and characterisation of bacteria able to couple oxidation of organic substrates to Fe^{3+} reduction as a source of energy (Lovley and Phillips, 1988; Semple and Westlake, 1987).

Microbial Fe^{3+} reduction provides a very important mechanism for the oxidation of natural or contaminant organic compounds in aquatic environments. Lignocellulose and carbohydrates are not used directly by Fe^{3+} reducing bacteria. Rather, they utilize products of microbially-mediated fermentations of organic matter which occur when oxygen has been used up. These products include short-chain fatty acids, alcohols, simple phenolics and hydrogen. Acetic acid, phenolics and hydrogen are oxidised completely to CO_2 by *Geobacter metalloreductans* (utilises short-chain fatty acids or aromatics) or *Shewanella putrefaciens* (utilizes H_2 or formate; Lovley, 1991). There are undoubtedly many other bacteria which can carry out oxidation of organics coupled to Fe^{3+} reduction in sediments, but few have been isolated and characterized to date.

It has been shown that iron reduction may not take place unless bacteria are present, a low redox potential prevails and suitable electron donors and acceptors are available. A further requirement is direct contact between the electron acceptor and the reducing

organism (Lovley et al., 1991). In addition to bacterial mediation, Fe^{3+} reduction may be carried out through the abiotic reductive dissolution of Fe^{3+} oxyhydroxides, with or without photocatalysis (Stumm and Sulzberger. 1992; Deng and Stumm, 1994).

Biofilms: Conditions pertaining in the sediment as a whole are reflected on a smaller scale in biofilms. In sediments and soils, most surfaces are covered with organic matter. Often, this layer is comprised of carbohydrates derived from bacteria and other microorganisms. The properties of these 'biogels' are dominated by the presence of gradients. The bacteria are located at the bottom of the biofilm, attached to the substrate but furthest away from the aqueous medium. Therefore, the bacteria may be exposed to very different conditions from the external milieu, whether that be considered the open water or a single pore in the soil or sediment.

The structure and functioning of biofilms in relation to iron and sulphur cycling have been studied by Kuhl and Jorgensen (1992) and others, using microelectrodes to measure the concentrations of, for example, sulphate and oxygen. These studies indicate that there are sharp gradients within the biofilm, and that conditions within the biofilm change in response to changes within the medium outside the biofilm.

It is clear that the measurement of conditions in the bulk medium will not give an indication of reactions occurring on surfaces within biofilms. Another important consideration with respect to biofilms is that changes occurring within the biofilm may not result in changes in the medium. Recycling of iron may occur within the biofilm as

given in Schematic 3, modified after Characklis et al. (1990). The location and functioning of biofilms will change continuously, due to the accumulation of precipitates and depletion of substrates. The functioning of biofilms in ecosystems is not clearly elucidated but is, in all likelihood, of great importance in determining overall concentrations of many ions in the pore water of sediments.
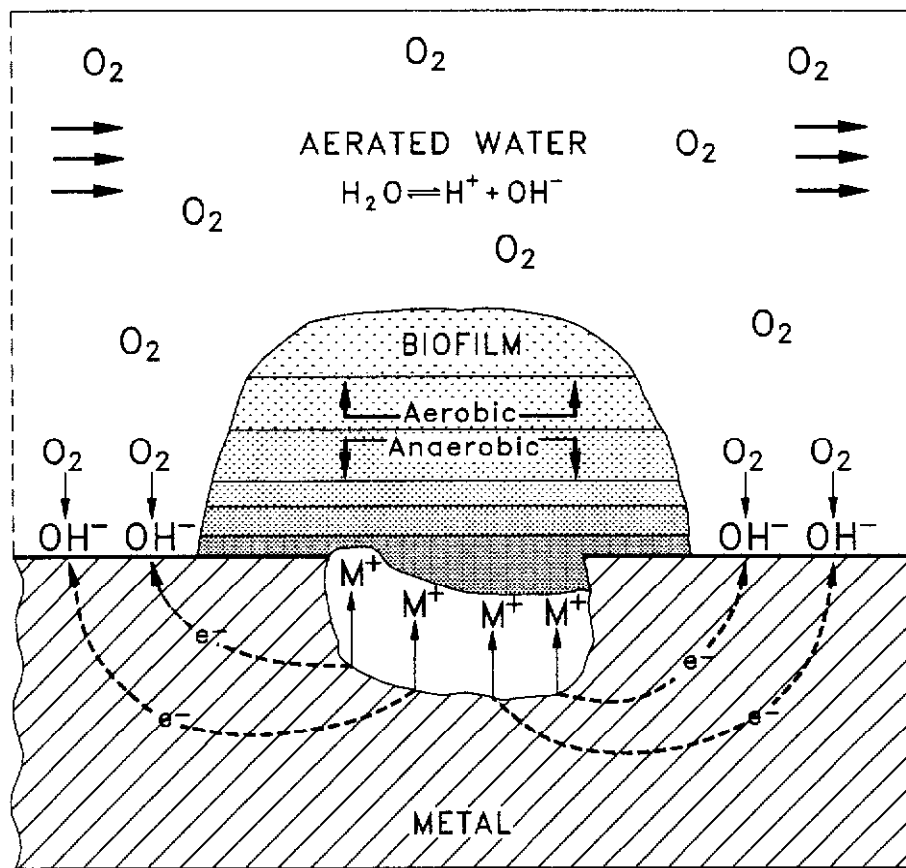
SCHEMATIC 3: CROSS-SECTION OF BIOFILM
(after Little et al., 1990)

Iron Adsorption: In addition to the direct effects of redox conditions and pH on the form of iron and its abundance in the sediment, iron concentrations are appreciably affected by 'sorption' processes such as ion exchange and complexation.

Most surfaces of sediments and suspended particulates, and all surface of algae (phytoplankton and periphyton) are coated with organic materials. These surfaces possess ion exchange sites. For instance, peat is reported to act as a cation exchange surface for protons (Wieder, 1990).

The cation exchange surface will equilibrate relatively rapidly, but changes in conditions, such as pH, redox potential and concentrations of other ions, will influence the cation exchange capacity. Therefore, the amount of iron or other cations bound in this manner will vary in different parts of the sediment. Adsorption processes are probably of importance in iron removal in the early stages of constructed wetland development for treatment of AMD (Wieder, 1992). Incorporation within, or on, surfaces (co-precipitation) may be an important means of removing heavy metals from AMD (Singh and Subramanian, 1984).

Adsorption of ions to surfaces of living organisms (biosorption) is also important in iron cycling. Iron hydroxides and sulphides are among a variety of compounds, identified by electron microscopy coupled to EDX, and X-ray diffraction, which accumulate on bacterial surfaces in aquatic environments. Such surfaces may be important nucleation sites for authigenic mineral formation (Ferris et al., 1987, 1989a).

Redox Boundaries: The importance of redox boundaries as barriers to, or active sites of, processes is well established (Davison, 1985). Because of the mixing and rapid diffusion of oxygen in the water column, oxygen is generally present throughout

and oxidising conditions predominate. In contrast, oxygen diffusion is slow in sediments, anoxic conditions develop rapidly with depth and reducing conditions predominate. As a result, a sharp redox boundary forms just beneath the sediment surface.

Iron-rich colloids near the redox boundary, in one case, have been shown to have a diameter range of 0.04 to 0.4 μm (Buffle et al., 1989). It is important to note that such colloids may pass through most filters prior to chemical analysis of waters and, therefore, dissolved iron concentration determinations may be overestimates. The colloids formed in the natural environment are very difficult to study because of handling difficulties. The properties of colloids formed in laboratory conditions, such as their rate of formation and dissolution, vary considerably according to the chemical and physical environment in which they are formed (Deng and Stumm, 1994). The presence of clay minerals, aluminum oxides, living bacteria or light may enhance the rate of formation. Clays may also enhance the dissolution of the colloids.

The redox boundary is a very active zone for cycling of iron, other elements and organics. When reducing conditions prevail, reductive dissolution of colloids of Fe^{3+} hydroxide will take place, with the consequent release of co-precipitated cations, oxyanions and organic moieties (Stumm and Stukberger, 1992). As colloids dissociate, Fe^{2+} may diffuse upwards in the sediment were it will rapidly re-oxidise when passing the redox boundary, or it may diffuse downwards where changes in the chemical environment (ion concentration gradients) will result in precipitation of, for example, FeS and $Fe_3(PO_4)_2 \cdot 8H_2O$. The same reactions can occur at the sharp redox gradients

found in biofilms and individual sediment pores.

The kinetics of colloid formation and dissolution can have a profound effect on concentrations of nutrients and heavy metals in the water column as, for example, phosphate ion incorporation into colloids (Deng and Stumm, 1994).

Over time, conditions at any location in the sediment may change, becoming more reducing or oxidising. Changes may be diurnal, seasonal or occur over even longer periods, or may be a function of changes in weather or hydrology. Diurnal changes will occur as a result of chemical photooxidation/ reduction processes, and either directly or indirectly as a result of the activity of photosynthetic organisms.

Iron Cycling in Sediments: Sediments are not merely depositories for materials removed from the water column above. They can also provide a significant source of elements to the water column. The flux to and from the sediments is very important in determining the overall composition of lake water. Iron reduction affects the composition of sediment pore waters and thereby plays a role in controlling the flux to the water column.

In sediments, transport of dissolved materials depends on the process of diffusion, the movement of molecules along concentration gradients from regions of higher concentrations to lower concentrations (Davison, 1985). Dissolved molecules must negotiate between the particles. This increases the length of the diffusion pathway to

such an extent that the rate of molecular oxygen diffusion is 100 to 1000 fold slower in sediment than in open water. It is reported that organic matter in the water column sinks to the sediment surface more rapidly than molecular oxygen can diffuse through the sediment-water interface. Oxygen demand during decomposition of organic particles usually exceeds the oxygen supplied by diffusion into the sediment, and molecular oxygen is maintained at a very low concentration just below the sediment-water interface.

Reducing conditions therefore predominate here. In some circumstances, such as in periods following establishment of ice covers (Ellis-Evans and Lemon, 1989), thermoclines (Hamilton-Taylor and Morris, 1985; Stauffer and Armstrong, 1986) or eutrophic conditions (Buffle et al., 1989), reducing conditions may extend into the water column. This also takes place when chemoclines are established, which is frequently the case in man-made lakes.

In sediments containing decomposable organic matter, redox reactions will occur in a predictable sequence following molecular oxygen depletion (Stumm and Morgan, 1981). Most of the reactions are mediated by microorganisms which utilise organic substrates as sources of respiratory energy. This sequence is determined by the electron activity of the redox reaction and occur with decreasing electron activity.

Oxygen is consumed first. Denitrification (reduction of NO_3 to N_2O and N_2) will then proceed until NO_3 is consumed. Iron reduction will occur after denitrification but before

sulphate reduction and methanogenesis. Because of the slow diffusion of substrates into and within the sediment, this sequence of reactions can be demonstrated through the concentrations of electron donors and acceptors. The flux of materials within, to and from sediments may be modified by upward flow of pore water caused by hydrostatic pressure of ground water and also by mixing processes (bioturbation and water turbulence) at the sediment surface.

Some authors have emphasised the importance of hydrogen concentration rather than redox potential in determining which reaction will take place (Lovley, 1991). The sequence is the same but, for example, sulphate reduction requires a higher hydrogen concentration than iron reduction. Therefore, bacterially-mediated iron reduction will out-compete sulphate reduction (Chapelle and Lovley, 1992).

Dissolved Fe^{2+}, resulting from Fe^{3+} reduction, may slowly diffuse into more reducing or more oxidising conditions. In the former, the Fe^{2+} may enter the sulphate reduction zone, where it will react with the product of sulphate reduction, S^-, to form sulphide precipitates. If sulphate is absent, Fe^{2+} may accumulate with depth. Fe^{2+} will also diffuse upwards and eventually encounter oxidising conditions, where it will be re-oxidised to Fe^{3+} and most likely precipitate as a hydroxide.

Over time, iron hydroxides will be buried and exposed to more reducing conditions. At any given location near the water-sediment interface, active cycling of iron is likely to occur. Above the 'redox' boundary, where oxidising conditions are maintained, Fe^{3+} will

remain in the water as a dissolved or particulate compound. Below the boundary, Fe^{2+} will remain in solution (concentration dependant on diffusion processes) or be fixed as a sulphide precipitate.

3.2 Elemental Concentrations in Sediment Pore Waters

During formation of Fe^{3+} hydroxides, a significant quantity of contaminants, for example zinc, is being co-precipitated. Fe^{3+} hydroxides captured by algal biomass is relegated to the sediment upon sedimentation of the algal biomass. Therefore, the sediments in the Buchans polishing pools and in Boomerang Lake, used as a polishing pond, will contain very high iron concentrations. Iron cycling between the overlying water and the sediment is undoubtedly a key factor in the performance of biological polishing.

As the concentration of dissolved iron in sediment pore water will, in part, determine the rate of iron flux from the sediments to the overlying water, the pore water composition in these sediments is of overall importance to the water chemistry and the biological polishing process. Sediment interstitial solution samplers, or "pore water peepers", modified after Carignan (1984), were installed in the sediments of Boomerang Lake (Map 2) and in the polishing pools 1 to 6 in Buchans (Map 1).

The goal of these measurements using the pore water peepers is to determine the concentrations of specific compounds in the interstitial water which are mobile, or free to diffuse along concentration gradients within the sediment.

Boojum Research Ltd.

SOUTHBAY PROJECT
Northwestern Ontario

BOOMERANG LAKE
SAMPLING LOCATION MAP
SHOWING PHOSPHATE ROCK
DISTRIBUTION AND
SOURCES OF CONTAMINATED RUNOFF

| Date: Nov/92 | Revised: Jul/94 | Map 2 |

Metres
0   50   100   150   200   250

0   150   300   450   600
Feet

9.3 t Code 30 (1993)

5.5 t Code 31 (1992)

15.7 t Code 132 (1993)

B4

BOOMERANG LAKE

B5

B6

15.6 t Code 30, 7.9 t Code 132 (1993)

16 5 t Code 132 (1994)

W/L 1351 ± (OCT. 1986)

0.5 t Code 31 (1992)

3.9 t Code 132
3.9 t Code 30 (1993)

Backfill Bay

B8   B7

150 kg Code 31 (1992)

HAROLD'S DAM

B3

3 t Code 31 (1992)

B12

B11

B2

B1

LEGEND
• Water sampling location
■ Pore Water Peeper Locations
→ Source of contaminated runoff
▦ 1992 phosphate rock distribution (Code 31)
▦ 1993 phosphate rock distribution (Code 30/132)
▦ 1994 phosphate rock distribution (Code 132)
--- Log boom

MILL POND
W/L 1384·25 ±

The pore water peepers were equipped with 0.45 μm membranes and filled with distilled water, which allows only "dissolved" elements to diffuse in or out of the instrument's chamber according to concentration gradients. The membrane also screens against entry of compounds bound to larger colloidal or particulate components of the sediment. The selection of a non-biodegradable membrane material, polysulfone, is described by Carignan (1984). For Fe^{3+}, the reported size of colloids is significantly smaller (0.04 to 0.4 μm) according to Buffle et al. (1989) and, thus, a fraction of pore water dissolved iron concentrations determined in the pore water peeper solutions may actually be colloidal iron.

Since the 50 cm long devices are implanted at an angle to a depth of 30 cm below the sediment surface, the chemistry of the sample gives an indication of the 'average' conditions in the top 30 cm of sediment. The conditions in the sediment to that depth may vary considerably within this zone (Davison 1985).

Pore water peepers were inserted in the B11 and Backfill Bay areas of Boomerang Lake (Map 2). In the fall of 1993, phosphate rock (principally apatite, a calcium phosphate mineral) was added to areas of the lake to precipitate iron as a ferric phosphate at the surface of the sediment. The phosphate rock will dissolve slowly when exposed to low pH. The rock was placed in areas of the lake, such as Backfill Bay, where AMD seepages are known to enter through the sediment into the lake. These locations are indicated on Map 2 with arrows. Pore water peepers were located in one such area and also in an area without phosphate rock (B11).

The chemistry of pore water samples collected in October 1993, one month after addition of phosphate rock and insertion of the pore water peepers, is summarised in Table 9.

A comparison of the data for the Backfill Bay pore water with that of the water column above indicates that the pore water in the sediment has much higher concentrations of ions, as expected. The pH of the pore waters was 6.6 to 6.7. This, together with the low Eh value, indicate that reducing conditions are present. The presence of fairly high iron concentrations at this pH and Eh indicates that ferrous iron is being mobilized, as discussed in the literature review, from previously precipitated Fe^{3+} hydroxides below the 'redox boundary'.

The presence of phosphate in pore water peeper solutions is the direct result of local phosphate rock dissolution. An alternate source of pore water phosphate, given the sediment pH, could be the reductive dissolution of Fe^{3+} hydroxides containing previously precipitated phosphates. Such a mechanism for controlling phosphate availability is indicated by Deng and Stumm (1994), as discussed previously.

Comparing the pore water concentrations in sediments at locations in Boomerang Lake where no phosphate rock was added (B11) to those where phosphate rock was added (Backfill Bay) differences are evident.

Table 9: Pore Water Peeper Chemistry

Parameter	South Bay Backfill Bay (+ phosphate)				B11 (-phosphate)				Buchans *Polishing Ponds		
	BB pre P	BB bottom	BB PWP #1	BB PWP #2	B11 pre P	B11 bottom	B11 PWP #3	B11 PWP #4	PP1 PWP1	PP1 PWP2	PP2 PWP
Temperature, C	12.9	3.9	5.4	5.3	12.5	3.5	5.1	4.9	13.2	13.5	14.7
pH	3.21	3.21	6.63	6.72	3.15	3.30	6.91	6.87	6.24	6.47	6.45
Conductivity (umhos/cm)	689	701	2770	4150	652	692	372	334	1447	1516	1718
Em (mV)	484	446	-110	-116	477	327	-20	-28	108	121	118
Acidity (mg/L CaCO3 equ.)	nd	86	192	193	85	83	59	84	25	36	nd
Alkalinity (mg/L CaCO3 eq.)	n.a.	n.a.	215	270	n.a.	n.a.	42	47	122	331	nd
Diss. Elements, in mg/L Al	1.8	2.1	0.9	0.5	1.7	2.0	0.2	0.2	0.6	0.5	16.1
Ca	57	60	213	365	57	59	39	35	350	315	353
Cu	0.10	0.17	0.03	0.04	0.10	0.16	0.32	0.32	0.04	0.02	0.18
Fe	2.2	1.7	67.6	62.2	1.9	2.2	10.5	18.5	64.4	115.5	71.8
K	2.3	2.4	28.9	33.1	2.9	1.9	3.8	3.6	2.2	2.7	2.9
Mg	11	11	42	73	11	11	6	6	32	32	33
Mn	5.8	5.8	10.1	12.9	5.8	5.8	2.2	1.9	7.2	7.3	9.2
Na	2.4	2.4	320.0	461.0	2.5	2.4	6.1	3.0	<0.05	<0.05	<0.05
P	<0.06	<0.06	0.30	0.18	<0.06	<0.06	<0.06	<0.06	0.20	<0.06	<0.06
S	81	85	400	648	82	84	35	28	nd	nd	nd
Zn	9.2	11.3	1.6	0.3	9.3	10.3	0.4	0.4	2.9	1.1	22.3

nd - not determined   * Total of filtered acidified and filtrate

na - not applicable(e.g. pH < 4.5)

B11 pore water samples have a lower conductivity (334 to 372 μS.cm^{-1}) in contrast to 2770 to 4150 μS.cm^{-1} in the Backfill Bay sediment. Addition of phosphate may have in fact stimulated reducing conditions, as the Eh in Backfill Bay sediment ranges from -110 to -116 mV, compared to B11 where the pore water measures only -20 to -28 mV. At the sediment-water interface of Boomerang Lake, the Eh is generally between 400 and 500 mV. That iron reduction is enhanced is also inferred from the high acidities and alkalinities reported. However, comparing the pore water composition between Boomerang Lake and that of the Buchans polishing ponds, the effects of phosphate rock on the sediment pore water chemistry is not readily discernable.

It was argued that, based on the higher concentrations of iron present in the Backfill Bay sediment pore waters, in the presence of phosphate rock iron reduction is stimulated. However, in the polishing pond sediments at Buchans, where phosphate rock was not added, even higher iron concentrations are reported, with 64 to 115 mg.l^{-1}.

Sediment pore water concentrations of iron in the anoxic sediments can reach as high as 70 mg.l^{-1}, but in the oxic sediment pore water, concentrations are generally less than 3 mg.L^{-1} (Baudo et al., 1990). Although the range of the iron concentrations is not significantly higher than reported for river sediments, further data should be collected since, in one of the Buchans pore waters, the mobile zinc concentration was 22 mg.l^{-1}. This zinc concentration is higher that all other pore water zinc concentrations, which ranged between less than 1 mg.l^{-1} and 2.9 mg.l^{-1} (Table 9).

When wetted, phosphate rock will undergo a swelling process like clay, accumulating sodium in the process. The elevated sodium concentrations in the Backfill Bay pore water peepers reflect this migration of sodium towards the phosphate rock overlying the sediments surrounding the pore water peepers.

Overall it is not possible, based on this limited data set, to derive a clear picture of the effects of phosphate rock on the chemistry of the sediment waters. The presence of phosphate in the pore waters at Backfill Bay indicates that some dissolution of phosphate rock has occurred.

3.3 Sedimentation Traps

Sedimentation rates have been determined both in Boomerang Lake (South Bay) and in the Buchans flooded pit since 1990. Sedimentation traps were positioned at the lake bottom at B2, B4, B5 and B11 in Boomerang Lake. Traps were suspended at the depth of the thermocline (4 m) and at a 12 m depth in the flooded pit. The precipitate accumulated in these traps was quantified after various periods between 1990 and 1994.

In 1992, the estimated iron input to Boomerang Lake was ?⁻ surface water inflows and the iron concentrations determi 1991 and 1994, the average sedimentation rate in Boomer (Table 10), an amount equivalent to 24.3 t.yr^{-1} of iron (17.4 ℅

Table 10: Boomerang Lake Sediment Trap Data for 1991 to 1994

Period From	To	Days in period	Cum. days in period	Avg. t Sed. in lake during period	Cum. t Sed. in lake during period	Avg. g/m2/d sed. in lake during period
15-May-91	23-Jun-91	39	39	21.86	21.9	2.35
23-Jun-91	23-Jul-91	30	69	18.50	40.4	2.58
23-Jul-91	25-Sep-91	64	133	19.72	60.1	1.29
25-Sep-91	13-Jul-92	292	425	73.30	133.4	1.05
13-Jul-92	17-Oct-92	96	521	87.04	220.4	3.80
17-Oct-92	17-Jun-93	243	764	116.36	336.8	2.00
17-Jun-93	12-Sep-93	87	851	57.47	394.2	2.77
12-Sep-93	11-Oct-93	29	880	4.76	399.0	0.69
11-Oct-93	17-Jun-94	249	1129	~~32.47~~ *13·28*	431.5	~~0.55~~ *0.22*

+ Aug 94

		Average Sedimentation			139.5 t/lake/yr	1.90 g/m2/d
		* @ 17.4 % Iron in trap sediment			24.3 t/lake/yr	0.33 g/m2/d
		* @ 0.77 % Zinc in trap sediment			1.1 t/lake/yr	0.01 g/m2/d
		* @ 8.89 % SO4 in trap sediment			12.4 t/lake/yr	0.17 g/m2/d
		* @ 0.37 % Al in trap sediment			0.5 t/lake/yr	0.01 g/m2/d

* Average concentrations from assay #'s 4293-4295 (1992)

2

This quantity of iron is nine times the 1992 estimate of iron input to the lake.

Iron input to Boomerang lake was re-evaluated during the modelling work described above, considering not only the surface water concentrations in the drainage basin, but adding a ground water component to the annual loading. From this re-evaluation, the iron input to Boomerang lake can be expected to be 5 t.yr^{-1}. With this value, the average sedimentation rate indicates that five times as much iron is settling in Boomerang Lake as in entering in surface and ground waters.

Given the much greater quantity of iron collecting as precipitate each year compared to the iron loading from the drainage basin, the origin of this additional 19 tonnes of iron is in question. It was proposed that, since the lake is shallow and long, it was possible that settled solids could be re-suspended over the course of the year, and the sedimentation traps were capturing these re-suspended particles as well as new (allochthonous) iron input to the lake.

If re-suspension of iron hydroxide from the sediment is taking place due to wind-driven currents in the lake, then the rates should differ between summer and winter. Sedimentation rates in Boomerang Lake are typically lower in the fall and winter periods than in spring and summer (Figure 5). With reduced inflow during winter, input of iron is lower and, with the ice cover present in these months, lake circulation is minimal. During the ice-free season, sedimentation rates in Boomerang Lake have ranged from 1.3 $g.m^{-2}.d^{-1}$ to 3.8 $g.m^{-2}.d^{-1}$. Although this would appear to be a reasonable explanation of the iron loadings, there were two occasions in 1992 where sedimentation rates were exceptionally high, which could be biasing the observed trend. Traps have been installed at various depths in Boomerang Lake in 1994 to examine the relationship between depth of water and measured sedimentation rates.

The sedimentation rates in the Boomerang Lake, an acidic water body, are comparable to those rates obtained in the flooded pit in Buchans, where the sedimentation rate ranges from 0.5 to 7.9 $g.m^{-2}.d^{-1}$ (Figure 6). In this pit, upwelling Fe^{2+}-rich ground water oxygenates near the surface and Fe^{3+} hydroxide precipitates then settles to the bottom.

Fig.5: South Bay Sedimentation Rates
Boomerang Lake - Sed Trap Data
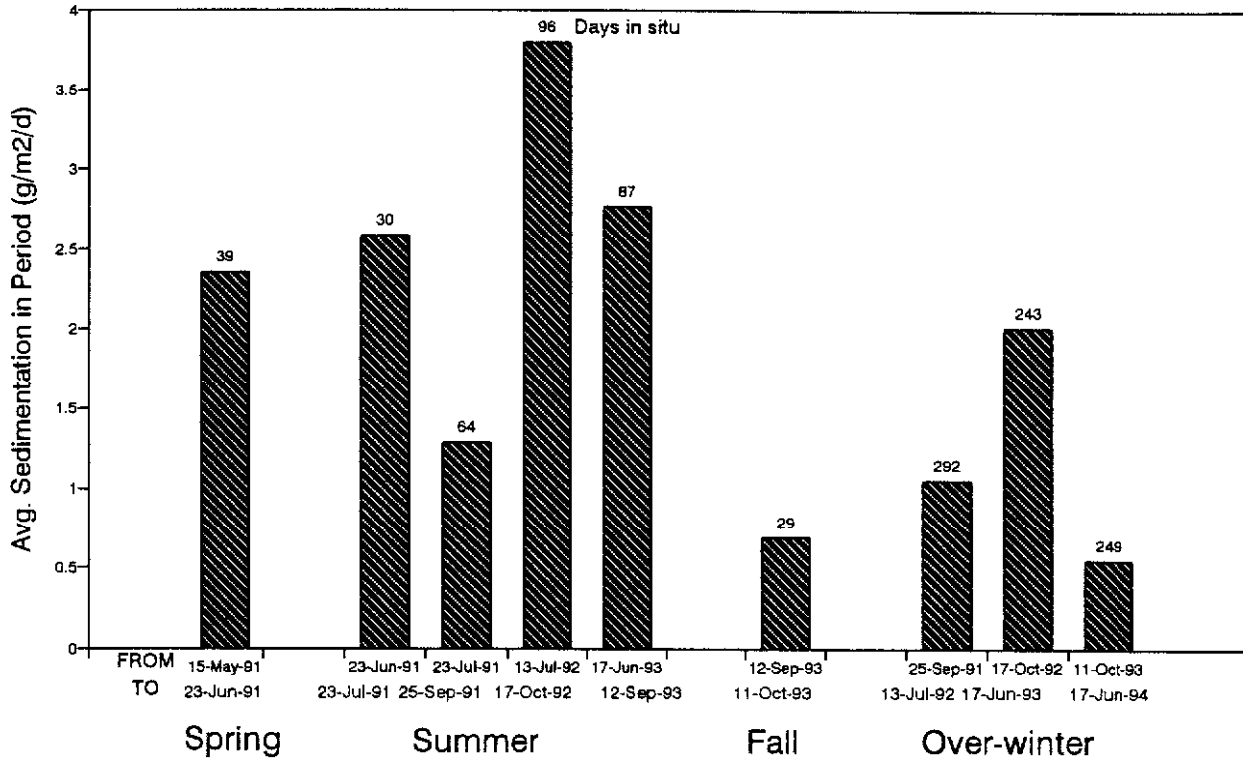
Fig. 6: Buchans Sedimentation Rates
Oriental East Pit Sed Trap Data
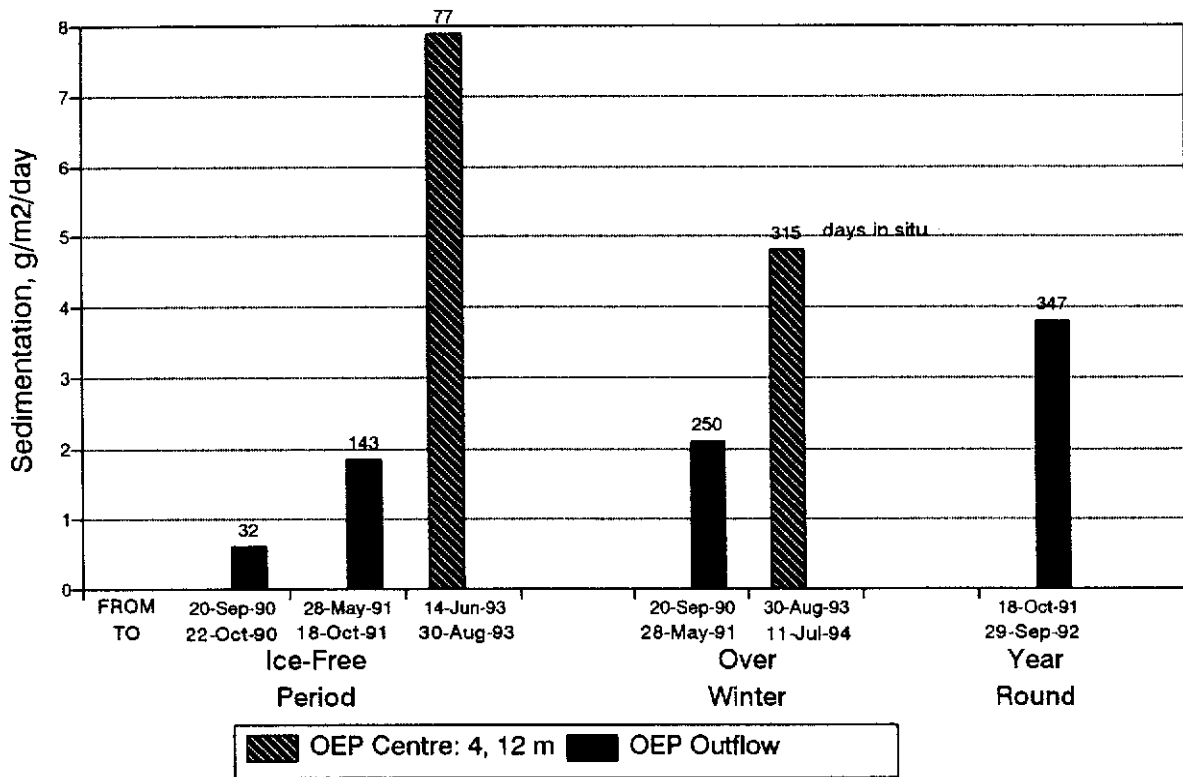
During the ice-free season, water is this flooded pit is very turbid, compared with Boomerang Lake, where bottom features can be seen in 4 m of water. That these two water bodies, with different chemistries and sources of iron, have very similar sedimentation rates is more than of passing interest for the biological polishing process. Similar sedimentation rates suggest that similar processes are taking place with respect to suspended solids formation.

Two processes could be responsible for re-suspension of the iron in Boomerang Lake. Wind-driven currents in Boomerang Lake during the ice-free season may regularly cause vertical currents of sufficient velocity to re-suspend fine ferric hydroxide particulates from top layer of sediments.

A second mechanism would involve several stages, including bacterial reduction of Fe^{3+} (in solid precipitates) to dissolved Fe^{2+} in anoxic, circumneutral pH sediment, promoting high dissolved Fe^{2+} concentrations in the sediment pore water relative to the overlying water. This concentration gradient from the sediment pore water to the overlying lake water would promote diffusion of the Fe^{2+} out of the sediment into the water column. If this flux of reduced iron is taking place, then it can be expected that, due to the re-oxidation of iron and precipitation of ferric hydroxide, iron would re-sediment. This process would serve to re-acidity the lake at a rate controlled by Fe^{2+} flux from the sediment.

There is no question regarding the process occurring in the flooded pit, the oxidation of reduced iron and formation and settling of iron hydroxide. However, for Boomerang Lake, the good water clarity could only be explained if there is indication that the iron hydroxide particle sizes formed in Boomerang Lake were larger, and subsequently settled much more rapidly, that iron hydroxide particles in the Buchans flooded pit.

From the literature review, it is suggested that the size and density of the iron hydroxide particle is affected by the conditions in which it is formed, including pH, other ions' concentrations and the characteristics and concentrations of suspended organic particles. Although direct evidence of particle size differences between Boomerang Lake and Buchans flooded pit is not available, in Boomerang Lake, there is a substantial phytoplankton (algae) population which could be providing surface area for adsorption of iron hydroxide and promoting the development of large particles with faster settling rates. Because of poor light penetration, the flooded pit has only a minor phytoplankton population which is restricted to the surface layer of water, and precipitates may remain as smaller particles with slower settling rates. Iron hydroxide particles in the Boomerang Lake sedimentation traps, on branches and on the lake sediments are also more 'crystalline'. Higher density, crystalline precipitates have higher settling rates than large, hydrated precipitates.

The implications of precipitate formation and sedimentation rates represent a new factor influencing the effectiveness of the biological polishing process. For instance, if precipitates more rapidly form and settle to the lake bottom in acid conditions, such as

in Boomerang Lake, than in neutral conditions (Buchans flooded pit), then less time is available for co-precipitation and removal of contaminants in acid conditions.

4.0 PHOSPHATE ADDITIONS TO SEDIMENTS

It has been long established that the concentrations of dissolved phosphate in lakes are closely tied to those of iron (Mortimer, 1941). In oxic conditions, much of the phosphate is adsorbed to Fe^{3+} oxyhydroxides.

The adsorption of phosphate by the Fe^{3+} oxyhydroxides followed by settlement to the sediment surface operates as a phosphate sink and a barrier to release of phosphate from the sediment. This can prevents the development of algal blooms, which otherwise depend on phosphate release from sediments (Hearn et al., 1983; Cornwell, 1987; Ellis-Evans and Lemon, 1989; Stauffer and Armstrong, 1986; Buffle et al., 1989; Leppard et al., 1989).

Phosphate contained within suspended colloids (Buffle et al., 1989) may be an important pool of phosphate in the water column. Availability of phosphate for algae and other organisms may be dependant on reductive dissolution of such colloids. In anoxic conditions, where the Fe^{3+} oxyhydroxide colloids dissolve, high pore water concentrations of Fe^{2+} and phosphate result. When these ions become supersaturated, vivianite ($Fe_3(PO_4)_2.8H_2O$) precipitates. These relationships have been reported in several studies (Emerson and Widmer, 1978; Hearn et al., 1983; Cornwell, 1987).

The study of Gachter et al. (1988) provides another explanation for the release of phosphate in anoxic conditions. These workers show that, for several lakes, there was

a partial uncoupling of Fe^{2+} and phosphate release and that, where examined in detail, the phosphate was released from bacterial biomass. In addition to phosphate, a variety of metal cations may co-precipitate with Fe^{3+} oxyhydroxides after formation of surface complexes (Dzombak and Morel, 1990). In reducing conditions, a laboratory-synthesized Fe^{3+} oxyhydroxide with co-precipitated heavy metals dissolved upon reduction of iron catalysed by a *Clostridium* spp. These bacterial activities resulted in the release of cadmium, nickel and zinc ions (Francis and Dodge, 1990).

The sediments of Boomerang Lake are very enriched with Fe^{3+} oxyhydroxides, and phosphate can be expected to be a key limiting nutrient. Enhanced algal growth rates on perinets equipped with packets of slow-release fertilizer indicate that algal productivity is limited by the low nutrient concentrations in Boomerang Lake. It was therefore proposed that, through addition of phosphate to the sediment, several objectives could be achieved which would, collectively, prevent deterioration of this lake currently receiving acidic seepage from the mine site and tailings.

Most importantly, the cycling of iron at the sediment-water interface may be curtailed following the formation of iron-phosphate colloids. If these colloids dissolve in the deeper portion of the sediment, some phosphate may be released. Upon supplying phosphate at the sediment surface, both bacterial activity and, possibly, periphytic algal growth, could be induced at the sediment-water interface. If the sediment-water interface could be covered by aquatic vegetation, an interface would be created between the sediment and the oxygenated water. A vegetation cover could be

beneficial with respect to the recycling of iron hydroxides from the surface of the sediments.

Experiments with different formulations of phosphate rock, primarily differing in grain size, were carried out in the laboratory and in Boomerang Lake. The type of phosphate rock added was North Carolina natural phosphate from Texasgulf, which is normally used as a fertilizer in acid soils. The sedimentary phosphate rock deposit in North Carolina is reported to possessing exceedingly high chemical reactivity in comparison to other phosphate deposits (Barnes and Kamprath, 1975).

4.1 Methods

Water Chemistry Methods: Redox potential, Em, was measured using a Corning Model 103 meter with Fisher Eh electrodes. The pH measurements were made with a WTW pH 196T meter and conductivity determinations with a YSI Model 33 or Orion 140 meter.

Phosphate and iron in the supernatant water were determined by colorimetric tests. Acidity was determined by titration with 0.01 N NaOH with a Brinkman Metrohm autotitrator Model 702SM. Elemental composition of filtered acidified samples was determined by Induction Coupled Atomic Plasma Spectroscopy at a certified laboratory. Samples were pre-filtered through 0.45 μm cellulose acetate filters and acidified with nitric acid.

Boomerang Lake Phosphate Rock Application: Phosphate rock was supplied in two formulations; Code 31, a fine powder containing 30 % P_2O_5; Code 132, a calcined fine sand containing 32.9 % P_2O_5; and Code 30, fine sand similar to Code 132 but not calcined, containing 30.3 % P_2O_5. The material was supplied in 27 kg bags from Texasgulf and distributed from a moving barge by slashing and dumping the bags in the lake.

In 1992, field experiments were started with the first application of phosphate rock. Phosphate rock applications were also performed in 1993 and 1994. The areas in Boomerang Lake where the various codes of phosphate rock were distributed are shown in Map 2.

Sediment sampling: All sediment sampling was carried out with an Eckman grab sampler. The samples comprise the top 10 cm of sediment. Sediment samples were collected from Boomerang Lake in September and October 1993 for laboratory experiments examining the effect of phosphate rock on the chemistry of the sediment and the overlying water column.

The September, 1993 samples were collected prior to the 1993 phosphate rock application and the October, 1993 samples were collected 30 days following the addition of phosphate rock in the field.

<u>Sediment-Static Laboratory Experiment:</u>   A single 2 litre jar was set up for each sediment collected from stations B1, B2, B4, B5, B7, B9, B10, B11 and Backfill Bay in September, 1993 (Map 2). It was noted, during the first set of measurements made on the supernatant and the sediments, that there was notable variation between sampling locations. Therefore, larger samples were collected from selected locations in October, 1993, in order that replicate jars sediment from each sampling location could be set up. Three jars were set up for each sediment sample collected in October 1993 from B5, B9, B10 and Backfill Bay, representing locations with and without phosphate rock.

After homogenizing the sediment in the lab, the samples were place in 2 litre jars. The sediments were then covered with 200 ml of Boomerang Lake water. The jars were sealed and kept at room temperature. Em, pH and conductivities were measured four times (October 27, November 30 1993; February 17, June 6, 1994) for each sample.

After 2 months, the total iron and phosphate concentrations were measured in the supernatant water overlying the sediments. The surface sediment layer in each jars was sampled, since the surface would be the zone where reactions are expected to take place. The material was dried and submitted for 18 element ICP analysis after wet oxidation with nitric and perchloric acid.   Percent Loss on Ignition (% L.O.I.) determinations were made on a sub-sample at 480° C.

<u>Sediment-Aeration Experiment:</u> Sediment samples were collected at South Bay on July 10, 1994 in South Bay from two locations in Confederation Lake (CS13a, CS13b) and four locations in Mud Lake (ML-C, ML-CS, ML-PW, ML-I). Four sediment samples were collected in Buchans, Newfoundland from Polishing Ponds P1, P6, P10 and P13. These samples were homogenized in the lab, then allowed to settle in 2 litre jars for two hours. Following this period, 100 ml of sediment from each sample were placed in a 250 ml Erlenmeyer flask, then 150 ml of each sediment's supernatant was added to the respective sediment sample in the Erlenmeyer flask. The pH, Em, conductivity, acidity and alkalinity of each sediment supernatant were then determined.

Using aquarium pumps, the sediment samples in Erlenmeyers were aerated for 143 hours over a 264 hour period. During aeration, the pH, Em and conductivity were periodically measured. The acidity and alkalinity of the supernatant in each flask was determined with a Brinkman autotitrator at the beginning and the end of the aeration period.

4.2   Sediment - Static Laboratory Experiment

All the measurements made in the sediment jars of pH, Em and conductivity are summarized for the 10 month experimental period in Appendix 3. The pH values were determined on four occasions over a 6 month period (Table 11).

Table 11: Boomerang Lake sediment pH following storage in lab.

Date of Measurement	Sample Location	Date Collected	Phosphate Rock Treatment	pH Measurement # #1	#2	#3	Geo. Mean
October 27, 1993	B1	Sept 11	no PR	4.24			4.24
	B2	Sept 11	no PR	4.81			4.81
	B4	Sept 11	no PR	4.85			4.85
	B 5	Sept 11	no PR	4.12	4.68		4.32
		Oct 11	no PR	4.21	4.11	4.32	4.20
		Oct 11	with PR	4.34	4.52	4.68	4.49
	B7	Oct 11	no PR	6.05			6.05
	B9	Sept.11	no PR	3.08	3.91		3.32
		Oct.11	no PR	3.51	3.03	2.83	3.04
		Oct.11	with PR	11.16	5.69	6.04	6.01
	B 10	Sept11	no PR	3.29	3.98		3.51
		Oct 11	no PR	3.95	3.98	3.93	3.95
		Oct 11	with PR	5.10	4.65	5.18	4.91
	B11	Oct 11	no PR	4.69			4.69
	Backfill Bay	Sept 11	no PR	3.28	3.87		3.48
		Oct 11	no PR	5.11	4.81	4.93	4.93
		Oct 11	with PR	11.25	9.98	6.61	7.09
November 30, 1993	B1	Sept 11	no PR	3.47			3.47
	B2	Sept 11	no PR	3.72			3.72
	B4	Sept 11	no PR	3.53			3.53
	B 5	Sept 11	no PR	5.11			5.11
		Oct 11	no PR	3.72	3.62	3.72	3.68
		Oct 11	with PR	3.69	4.24	3.59	3.76
	B7	Sept 11	no PR	5.33			5.33
	B9	Sept.11	no PR	3.91			3.91
		Oct.11	no PR	3.52	3.36	2.93	3.20
		Oct.11	with PR	10.35	6.33	6.37	6.53
	B 10	Sept11	no PR	4.36			4.36
		Oct 11	no PR	3.75	3.62	3.57	3.64
		Oct 11	with PR	4.56	3.82	4.96	4.20
	B11	Sept 11	no PR	3.65			3.65
	Backfill Bay	Sept 11	no PR	3.12			3.12
		Oct 11	no PR	3.52	3.58	3.51	3.54
		Oct 11	with PR	9.47	8.87	7.26	7.72
February 17, 1994	B1	Sept 11	no PR	7.42			7.42
	B2	Sept 11	no PR	3.5			3.5
	B4	Sept 11	no PR	3.51			3.51
	B 5	Sept 11	no PR	6.83			6.83
		Oct 11	no PR	3.47	3.60	3.63	3.56
		Oct 11	with PR	3.65	3.80	3.75	3.73
	B7	Sept 11	no PR	4.47			4.47
	B9	Sept.11	no PR	3.48			3.48
		Oct.11	no PR	3.53	3.31	2.66	3.00
		Oct.11	with PR	10.00	3.15	4.19	3.59
	B 10	Sept.11	no PR	3.12			3.12
		Oct 11	no PR	3.21	3.22	3.18	3.20
		Oct 11	with PR	3.32	3.39	3.57	3.41
	B11	Sept 11	no PR	3.74			3.74
	Backfill Bay	Sept 11	no PR	3.14			3.14
		Oct 11	no PR	4.23	4.00	4.48	4.19
		Oct 11	with PR	7.45	7.50	7.78	7.55
June 6, 1994	B1	Sept 11	no PR	4.49			4.49
	B2	Sept 11	no PR	3.7			3.7
	B4	Sept 11	no PR	3.83			3.83
	B 5	Sept 11	no PR	6.56			6.56
		Oct 11	no PR	3.15			3.15
		Oct 11	with PR	3.69			3.69
	B7	Sept 11	no PR	3.98			3.98
	B9	Sept.11	no PR	3.40			3.4
		Oct.11	no PR	2.96			2.96
		Oct.11	with PR	6.03			6.03
	B 10	Sept11	no PR	3.08			3.08
		Oct 11	no PR	2.83			2.83
		Oct 11	with PR	3.15			3.15
	B11	Sept 11	no PR	3.67			3.67
	Backfill Bay	Sept 11	no PR	3.43			3.43
		Oct 11	no PR	4.04			4.04
		Oct 11	with PR	7.19			7.19

In most sediment samples collected from areas which received a phosphate rock application (B9, B10, Backfill Bay), the pH of the supernatant water was typically higher than in corresponding samples which did not receive phosphate rock collected in the same vicinity. However, the supernatant pHs of sediment samples collected from the B5 area, inside and outside of the phosphate rock application area, were very similar. Sediments which did not receive phosphate rock had a low pH or remained, throughout the measurement period, at a relatively neutral pH. Overall, the pH values in the supernatant waters were generally decreasing as the experiment progressed. This reflects the oxidation rate of reduced iron which diffuses from the sediment. Although the phosphate rock sediment jars generally produced a supernatant water which was neutral, this was also the case for sediments which had not received phosphate rock. Therefore pH alone is not a good indicator of the effects of phosphate rock on sediments.

It appeared that the changes in pH in the supernatant should be related to some component of the sediments. The data concerning the elemental composition of the sediments were carefully examined and are presented in the next section, together with sediment characteristics of Boomerang Lake at large. One relationship became evident from the examination of the data, the change in pH during the static laboratory experiment and the total iron content in the sediments. In Figure 7, the total iron concentrations in the sediments from the various locations are plotted against the pH changes in the supernatants during the period of measurement.

Fig. 7: pH Changes vs Sediment [Fe]
Boomerang Lake Sediment Jars
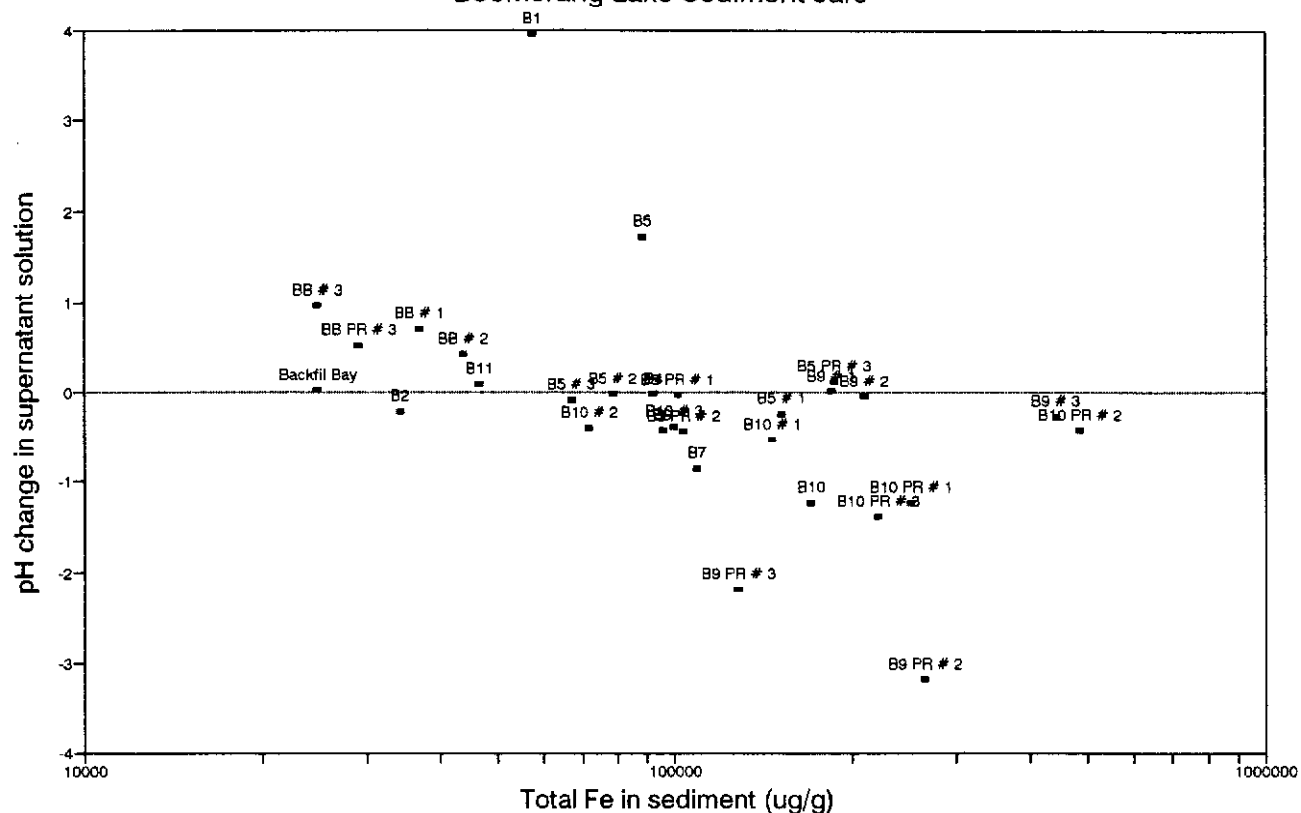
The pH of supernatant solutions typically decreased during the measurement period in sediments containing iron concentrations greater than 10 % (100,000 μg.g^{-1}), while the supernatant pH increased during the period in sediments with iron concentrations less than 10 %.

The iron concentrations in the supernatant solutions measured on December 11, 1993 and May 10, 1994 are summarized in Table 12. Iron concentrations in the supernatants remained less than 2 mg.l^{-1} in samples from B1, B2, B4, B7, and B11. Iron concentrations were typically less than 2 mg.l^{-1} in samples from B5, with the exception of one sample collected within the phosphate rock application area, where the iron concentrations in the supernatant was 127 mg.l^{-1} on December 11, 1993.

Table 12: Concentrations of phosphate and iron in supernatants over sediments in jars.

Sample Location	Date Collected	Phosphate Rock Treatment	11-Dec-93 [Fe] (mg/l)	10-May-94 [Fe] (mg/l)	11-May-94 [PO4] (mg/l)
B1	11-Sep-93	no PR	0.39	0.33	0.01
B2	11-Sep-93	no PR	1.09	0.57	0.01
B4	11-Sep-93	no PR	0.83	1.03	0.01
B5	11-Sep-93	no PR	0.16	0.83	0.01
	11-Oct-93	no PR	0.89	1.49	0.01
	11-Oct-93	no PR	0.83	0.2	0.01
	11-Oct-93	no PR	0.93	0.03	0.01
	11-Oct-93	with PR	1.23	0.03	0.02
	11-Oct-93	with PR	0.66	0.13	0.02
	11-Oct-93	with PR	127	0.83	0.02
B7	11-Sep-93	no PR	0.03	0.47	0.01
B9	11-Sep-93	no PR	1532	1699	0.02
	11-Oct-93	no PR	1565	0.2	0.03
	11-Oct-93	no PR	1665	1932	0.03
	11-Oct-93	no PR	1699	299	0.02
	11-Oct-93	with PR	1.03	0.16	0.01
	11-Oct-93	with PR	1332	0.16	0.01
	11-Oct-93	with PR	799	549	0.01
B10	11-Sep-93	no PR	1065	1932	0.01
	11-Oct-93	no PR	2599	265	0.01
	11-Oct-93	no PR	32	1.49	0.01
	11-Oct-93	no PR	49	132	0.01
	11-Oct-93	with PR	65	99	0.05
	11-Oct-93	with PR	465	1732	0.05
	11-Oct-93	with PR	79	399	0.01
B11	11-Sep-94	no PR	0.66	0.07	0.01
Backfil Bay	11-Sep-93	no PR	33	49	0.01
	11-Oct-93	no PR	0.66	0.27	0.02
	11-Oct-93	no PR	0.89	0.07	0.05
	11-Oct-93	no PR	19	1	0.01
	11-Oct-93	with PR	0.16	0.57	0.2
	11-Oct-93	with PR	0.09	0.1	1.9
	11-Oct-93	with PR	1.23	0.37	0.1

Supernatants overlying sediment samples collected from the B9 and B10 areas contained up to 2,600 mg.l^{-1} iron on the two sampling dates, while Backfill Bay sample supernatants contained up to 49 mg.l^{-1} sediment. These same sediment samples typically contained higher total iron contents (> 10 %; Figure 7) and the pHs were as low as 2.66 (Table 11). The supernatant water iron concentrations therefore corroborate with the relationship between pH changes and the total iron content.

The phosphate concentrations in the supernatants are very consistent, ranging from 0.01 mg.l^{-1} to 0.5 mg.l^{-1} with one exception, 1.9 mg.l^{-1}. As with pH, supernatant phosphate concentrations are not indicative of the effects of phosphate rock applied to the sediments.

As was noted with earlier work on sediments, laboratory data is difficult to interpret, given that conditions in the laboratory cannot simulate sediment conditions in the field. The experimental design of the static experiment represented a shallow layer of water covering the sediments, allowing oxidizing conditions the prevail above the sediment. Theoretically, these conditions should provide data indicating the effects of adding phosphate rock but, in fact, this was not the case.

One of the chemical parameters measured in the jars was Eh. Comparing data for this parameter between sediments with and without phosphate rock applications, one possible effect is indicated. In Figures 8a and Figure 8b, the Em data are reported for the four times measurements were made. Of the 13 samples without phosphate rock, negative Em values were measured in only two sediment samples during the first three measurements (Figure 8a). Of the four samples with phosphate rock, negative Em values were measured in two of the samples (Figure 8b). These trends suggest that the decomposition of organics in the sediments is promoted by the presence of phosphate rock. That the sediments are microbially active and consuming oxygen is indicated from data collected on the last measurement date (June 6, 1994), when all sediment samples' Em were negative.

Fig. 8a: Em of Boomerang Lake Sediments
without Phosphate Rock Addition
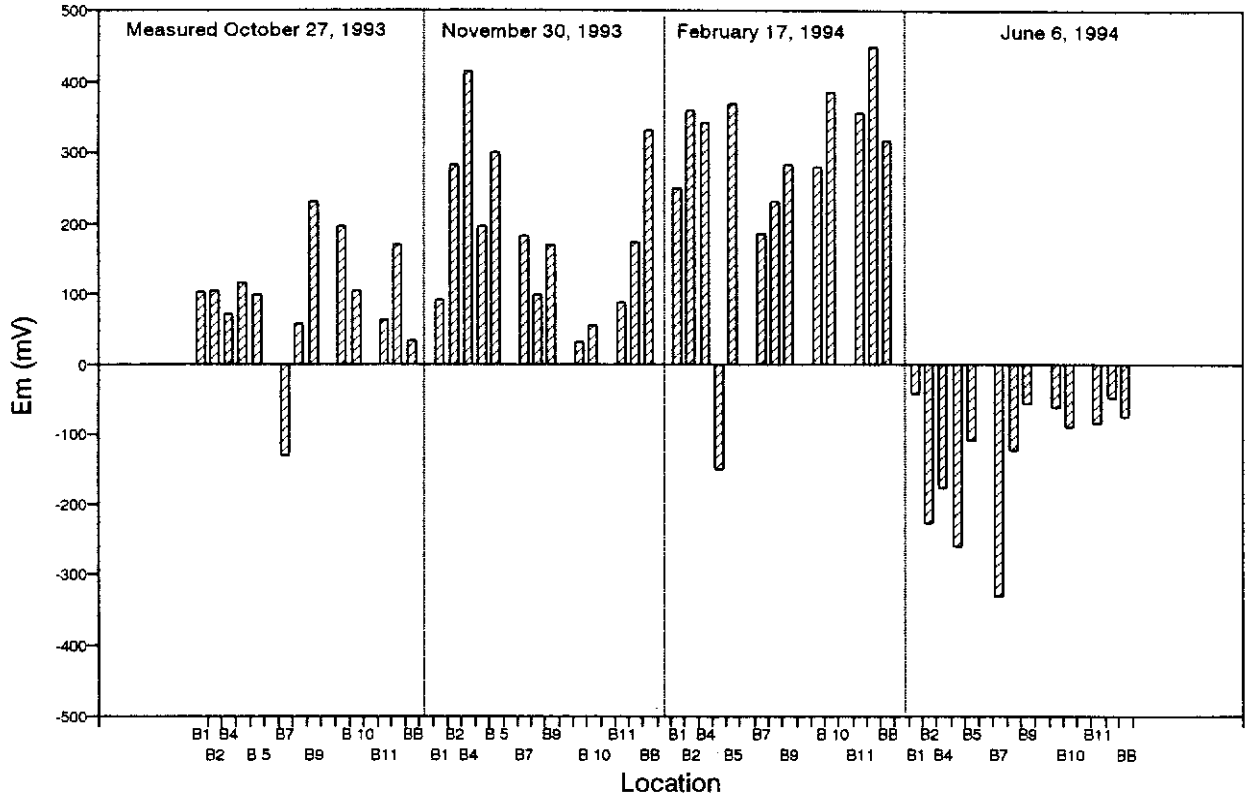
Fig. 8b: Em of Boomerang Lake Sediments
With Phosphate Rock Addition
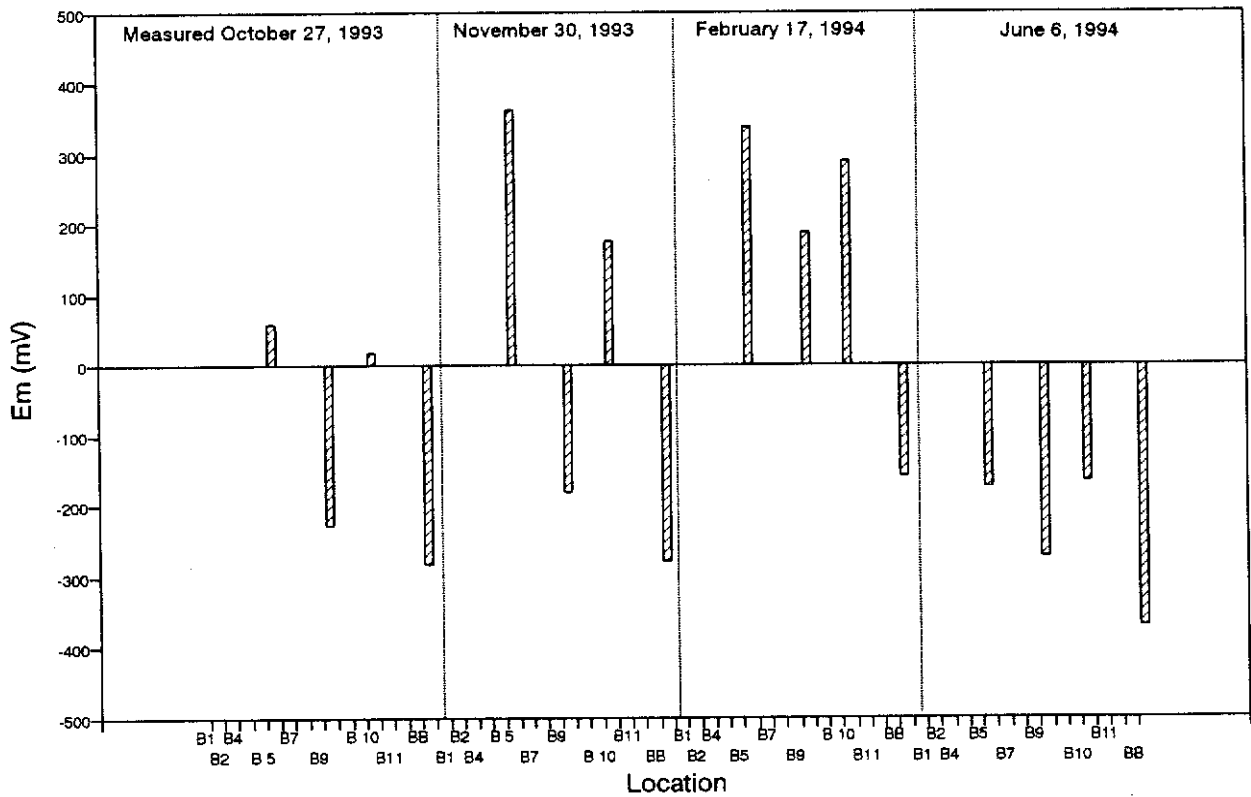
In summary, the data collected during the static sediment experiments clearly indicate only one important aspect with respect to the amelioration of acidification from sediments. When the concentration of iron is greater than 10 %, the potential for acidification exists. Therefore, sediments with and without phosphate rock applications have to be evaluated for their buffering capacity in the future.

The propensity of anoxic sediments to acidify during oxidation can be evaluated using vigorous aeration of sediment samples in the laboratory. This method was tested using a fresh set of sediment samples collected in July, 1994 from both the South Bay site and the Buchans Polishing Ponds. The South Bay samples are sediments underlying regions of lakes which receive acid mine drainage seepages.

In Figures 9a and 9b the pH values obtained during the oxidation experiment are plotted for the duration of the experiment. The pH of the ten sediment slurries did not appreciably decrease during aeration for 143 hours over the 264 hour period of the experiment.

Comparing the acidity of the supernatants, where available, before and after aeration (Table 13), only the acidity of ML-PW sediment increased. This sample was collected from an experimental area amended with potato waste to stimulate microbial activity. During aeration, the conductivity also increased, a result of decomposition of organics.

Fig. 9a: Sediment Oxidation Exp't
South Bay Samples: pH

Legend: CS13a, CS13b, ML-C, ML-CS, ML-PW, ML-I
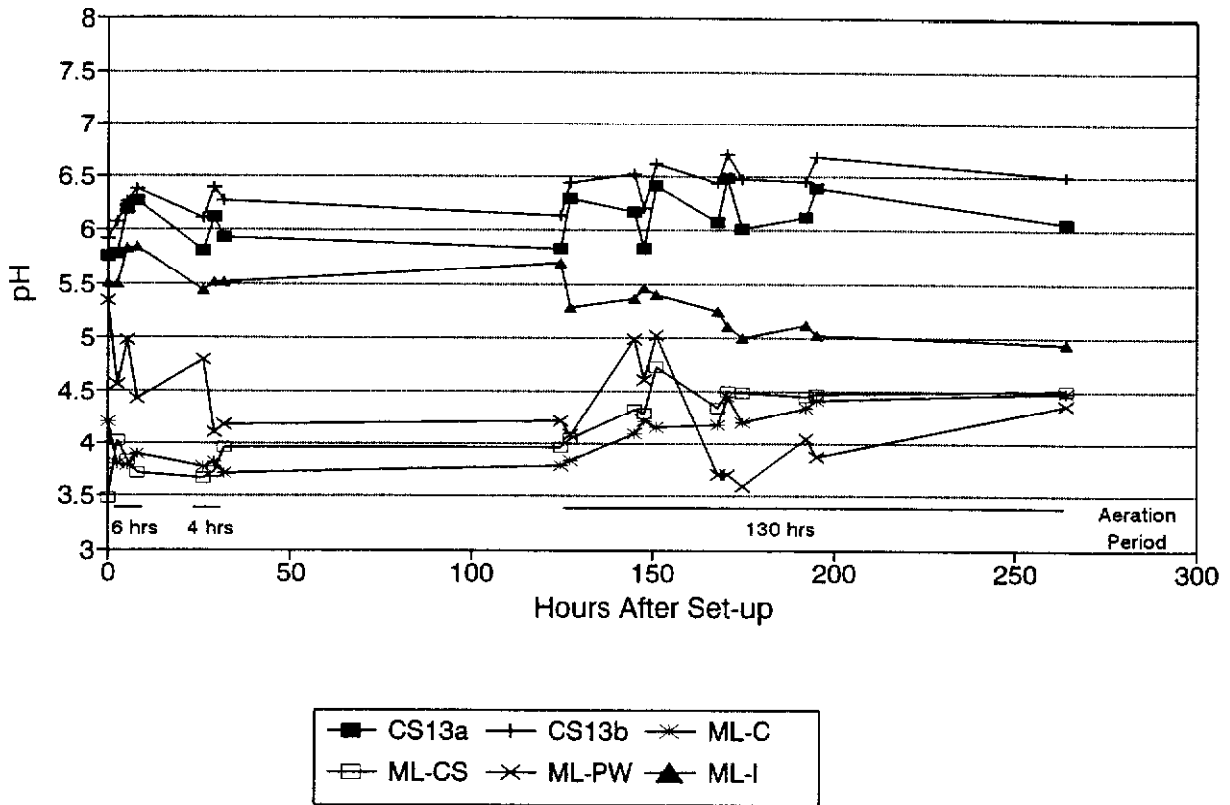
Fig. 9b: Sediment Oxidation Exp't
Buchans Samples: pH

Legend: PP6, PP13, PP1, PP10
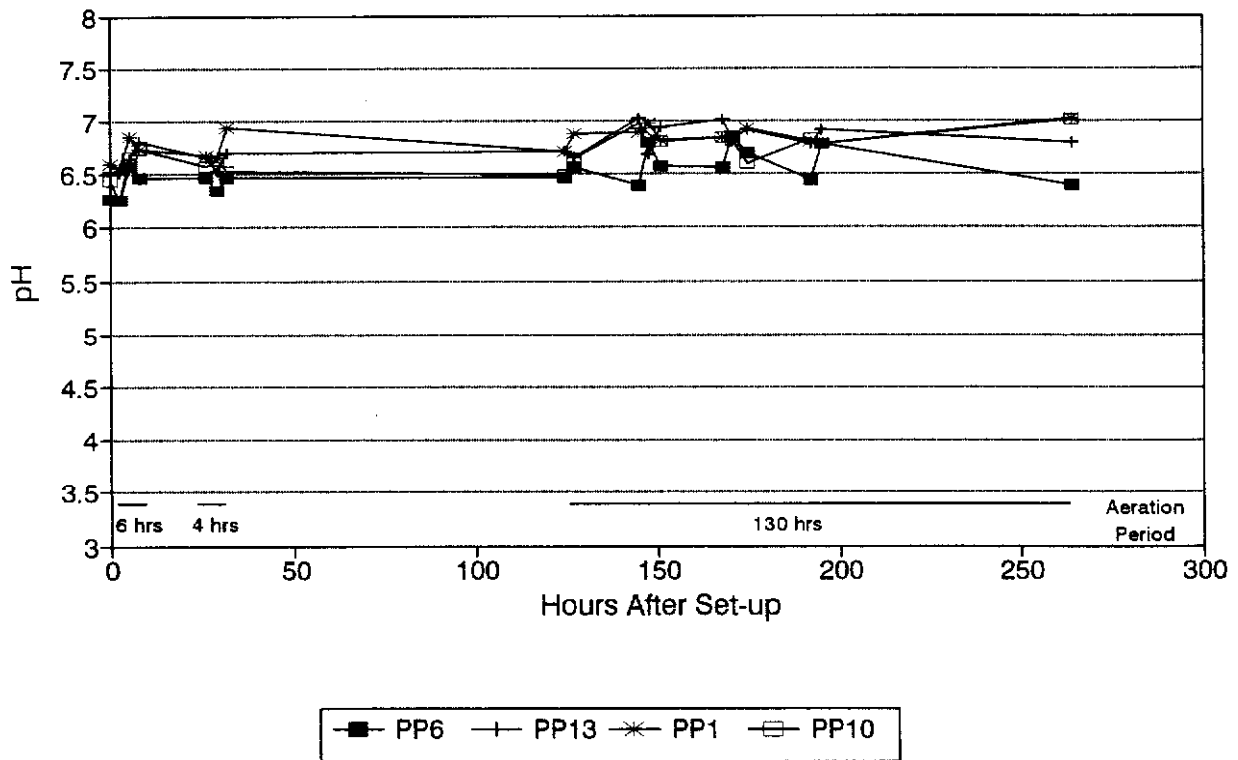
Table 13: Sediment aeration experiment. Initial and final chemistry following 143 hours of aeration.

	CS13a	CS13b	ML-C	ML-CS	ML-PW	ML-I	PP1	PP6	PP10	PP13
Initial pH	5.75	5.92	4.2	3.48	5.34	5.51	6.6	6.27	6.44	6.52
Final pH	6.06	6.5	4.49	4.51	4.37	4.94	7.02	6.4	7.01	6.8
Initial Em (mV)	192	191	219	319	-74	15	-125	270	-89	115
Final Em (mV)	169	160	230	215	332	220	88	110	-250	190
Initial Cond (uS/cm)	997	1396	1968	2160	2800	474	1502	1483	1722	1388
Final Cond (uS/cm)	1100	1460	2350	2270	4740	880	1290	1280	1490	1200
Initial Acidity (mg/l)	199	231	1223	776	2323	28	NR	NR	NR	NR
Final Acidity (mg/l)	165	84	519	334	4253	21	NR	NR	NR	NR
Initial Alkalinity (mg/l)	27	8	Nil	Nil	21	6	175	74	134	181
Final Alkalinity (mg/l)	8	39	Nil	Nil	Nil	4	74	60	127	87

The results of the vigorous aeration of the iron-enriched sediments examined suggest that, if the sediments were exposed to air, they would not represent an immediate source of hydrogen ions. With oxidation of reduced iron in the polishing pond sediments, adequate buffering is present in these sediments to neutralize any acid generated. This method will now be used to assess the sediments in Boomerang Lake with and without phosphate rock applications.

4.3 Phosphate Rock Additions to Boomerang Lake

In 1993, 50 tonnes of phosphate rock (Code 30 and code 132) were added to the sediments in the lake in the areas indicated in Map 2. This application followed a six tonne addition to the B9 area, completed in 1992, which resulted in increased pH values at the lake bottom. The phosphate treatments are expected to precipitate iron, manganese and aluminium, and to co-precipitate zinc. In Table 14, the elemental concentrations are given for Boomerang Lake for the 1993 phosphate rock application. Unfortunately, no differences are noted in concentrations of iron, manganese, aluminium and zinc. Following the 1992 application of phosphate rock, definite changes in water chemistry was reported following phosphate rock application.

Water was collected from Boomerang Lake within days after the phosphate application in 1992 but, in 1993, water was collected 1.5 months after application. Also, in 1992, a different code of phosphate rock was used, the calcined, fine ground Code 132.

Table 14: Boomerang Lake-water chemistry before and after addition of phosphate rock

Location	B1 surface pre PR	B1 surface 30d post	B5 surface pre PR	B5 surface 30d post	B5 bottom 30d post	B7 surface pre PR	B7 bottom pre PR	B7 surface post PR	B11 surface pre PR	B11 bottom pre PR	B11 surface post PR	B11 surface 30d post	B11 bottom 30d post	Back Bay surface pre PR	Back Bay surface post PR	Back Bay surface 30d post	Back Bay bottom 30d post
Date sampled	11-Sep-9	10-Oct-93	11-Sep-9	10-Oct-93	10-Oct-93	11-Sep-9	11-Sep-9	16-Sep-9	11-Sep-9	11-Sep-9	16-Sep-9	10-Oct-93	10-Oct-93	11-Sep-9	16-Sep-9	10-Oct-93	10-Oct-93
Temperature	12.9	4.2	12.7	3.9	3.2	13.1	13	13.6	12.6	12.5	13.7	4	3.5	12.9	12.4	4.2	3.9
pH	3.33	3.21	3.13	3.18	3.19	3.06	3.05	3.25	3.2	3.15	3.28	3.25	3.25	3.21	3.34	3.19	3.21
Cond. (umhos/cm)	687	695	690	701	700	693	695	673	690	652	710	698	692	689	652	697	701
Em (mV)	461	333	492	446	425	503	508	411	491	477	398	323	327	484	482	389	446
Element (mg/L)																	
Al	1.76	1.96	1.81	1.85	1.81	1.71	1.78	1.71	1.66	1.69	1.67	1.99	2.03	1.77	1.76	1.87	2.11
Ca	59	58	58	59	58	59	58	57	57	57	58	59	59	58	59	58	60
Cu	0.096	0.126	0.106	0.107	0.102	0.095	0.1	0.1	0.093	0.095	0.106	0.12	0.158	0.106	0.11	0.106	0.172
Fe	1.99	2.15	2.43	2.35	2.34	2.7	2.44	2.27	1.94	1.94	8.25	2.23	2.18	2.17	2.24	2.84	1.71
K	3.2	1.7	2.5	2.3	2.1	3.1	2.6	2.4	2.2	2.9	1.8	3	1.9	2.3	2.4	2.8	2.4
Mg	11.6	10.5	11.6	10.7	10.5	11.6	11.5	11	11.2	11.2	11.4	10.6	10.6	11.2	11.4	10.6	10.9
Mn	5.95	5.72	5.91	5.54	5.45	5.83	5.88	5.65	5.66	5.75	5.81	5.83	5.83	5.79	5.77	5.66	5.8
Na	2.45	2.41	2.59	2.46	2.34	2.48	2.4	2.81	2.48	2.45	2.73	2.42	2.35	2.43	3.8	2.51	2.42
P	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	0.06	<0.06	0.07	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06	<0.06
SO4	255	249	252	249	246	255	255	246	243	246	264	255	252	288	255	252	255
Si	9.2	9.2	9.2	9.2	9.1	9.2	9.2	9	8.9	9	9.1	9.2	9.4	8.9	9.1	9.2	9.3
Zn	9.5	9.7	9.4	9.5	9.4	9.3	9.3	9.1	9.1	9.3	10.2	10	10.3	9.2	10.1	9.8	11.3

It was planned to apply the same code in 1993 as in 1992 but, unfortunately, this material could not be bagged for a hand delivery. A second problem which might explain the absence of differences in elemental composition after, compared to before, phosphate rock application is that the application rate was changed. It was planned that 100 t were to be applied but, due to delay in shipping, only 50 t were distributed, a 50 % reduction in the application rate. In summary, the different phosphate rock type and the reduced application rate in 1993 may have, overall, been inadequate to achieve measurable water quality changes.

In Figure 10a, the annual average values of pH, Zn and sulphate in Boomerang Lake are presented. From these averages, a steady decrease in the pH and an increase in sulphate and zinc concentrations are noted. Iron and acidity are plotted for the same period in Figure 10b. Between 1970 and 1993, iron had increased from less than 0.5 mg.l^{-1} to about 2.5 mg.l^{-1}, while acidity has increased from negligible values to as high as 150 mg.l^{-1} CaCO$_3$ equivalent (Figure 10b). This trend since 1970 was reason for concern and lead to the investigation of the conditions in Boomerang Lake with respect to iron sediment chemistry, addressed in this study. The work on phosphate rock was initiated to counteract the trend. This long-term trend is clearly not desirable for the polishing process, as the deterioration of the water quality will affect the growth conditions for the algae.

Fig. 10a: Boomerang Lake Annual Average
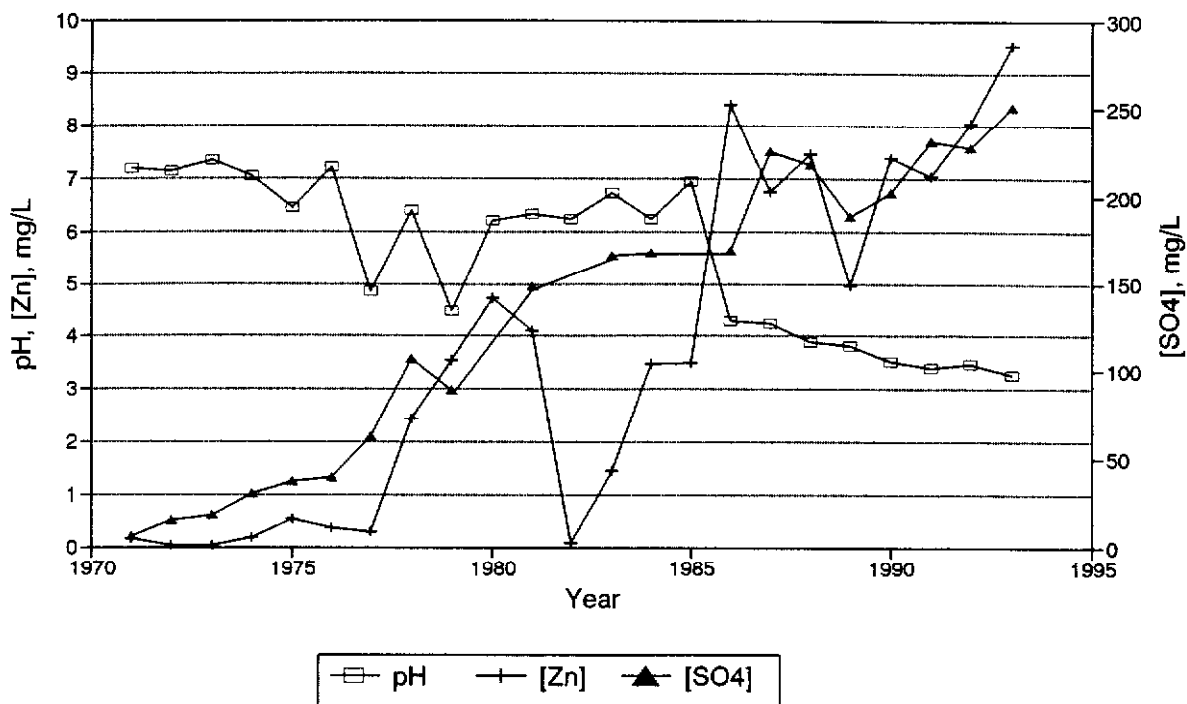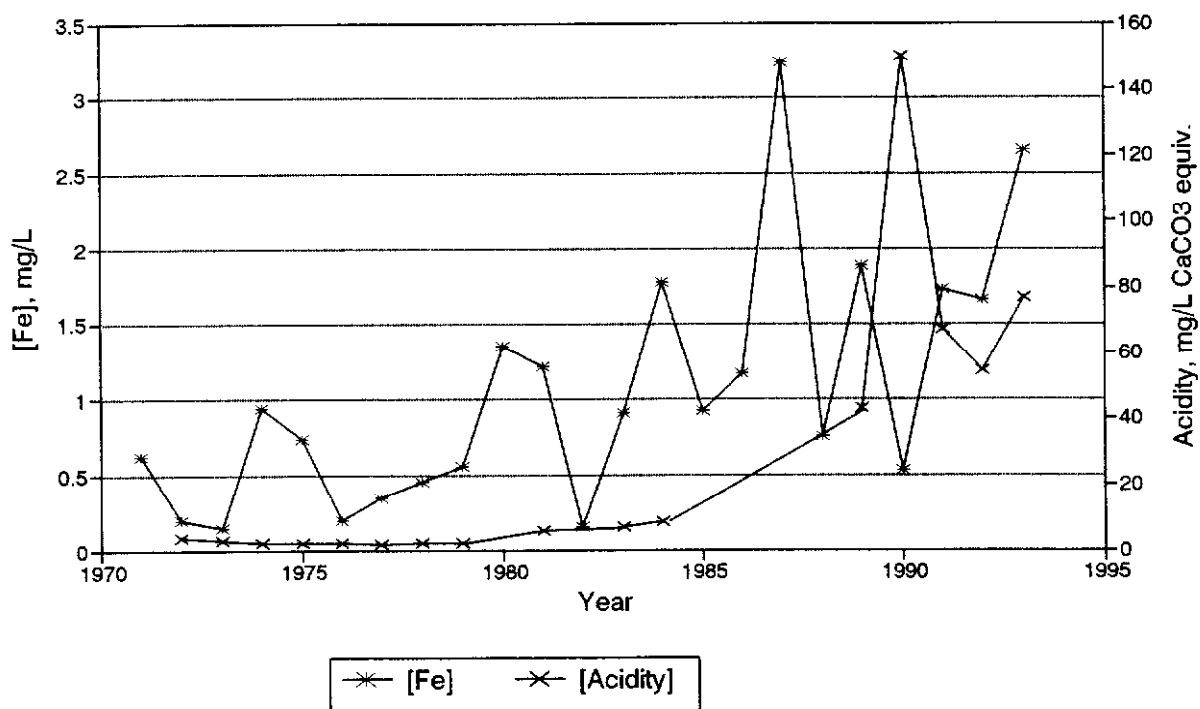pH,[Zn], and [Sulphate]

Fig. 10b: Boomerang Lake Annual Average
[Fe] and [Acidity]

All the available data for Boomerang Lake were evaluated in more detail. The 1991, 1992 and 1993 annual average iron concentrations were 1.7, 1.7 and 2.7 mg.l^{-1}, respectively, with standard deviations of 1.2, 0.6 and 0.3 mg.l^{-1}, respectively (n = 16, 15, 13). For these same years, the annual average zinc concentrations were 7.0, 8.0 and 9.6 mg.l^{-1}, with standard deviations of 1.3, 0.8 and 0.4 mg.l^{-1}, respectively (n = 15, 15, 14). For sulphate, the 1991, 1992 and 1993 annual average concentrations were 232, 227 and 250 mg.l^{-1} respectively, with standard deviations of 18, 23 and 7 mg.l^{-1}, respectively (n = 15, 12, 14). Since the number of samples per year in these three years are comparable, the conclusion that contaminant concentrations have remained constant in the last three years is valid.

Multiple samples from Boomerang Lake have typically been collected on only three on three to five occasions each year. More frequent sampling of the lake could reveal seasonal fluctuations which could not have been detected during the past monitoring schedule.

Using the detailed data available since 1987 for sampling stations B1 and B11 near the outflow of Boomerang Lake suggest that the trend of increasing concentration may have ceased in 1990 (Figures 11 and 12). The value of pH and the concentrations of Al, Fe and Mn (the elements contributing to acidity) have remained relatively constant since 1990. There is no evidence of a trend of decreasing contaminant concentrations. As the turnover time of Boomerang Lake is three years, this data spans two complete turnovers.
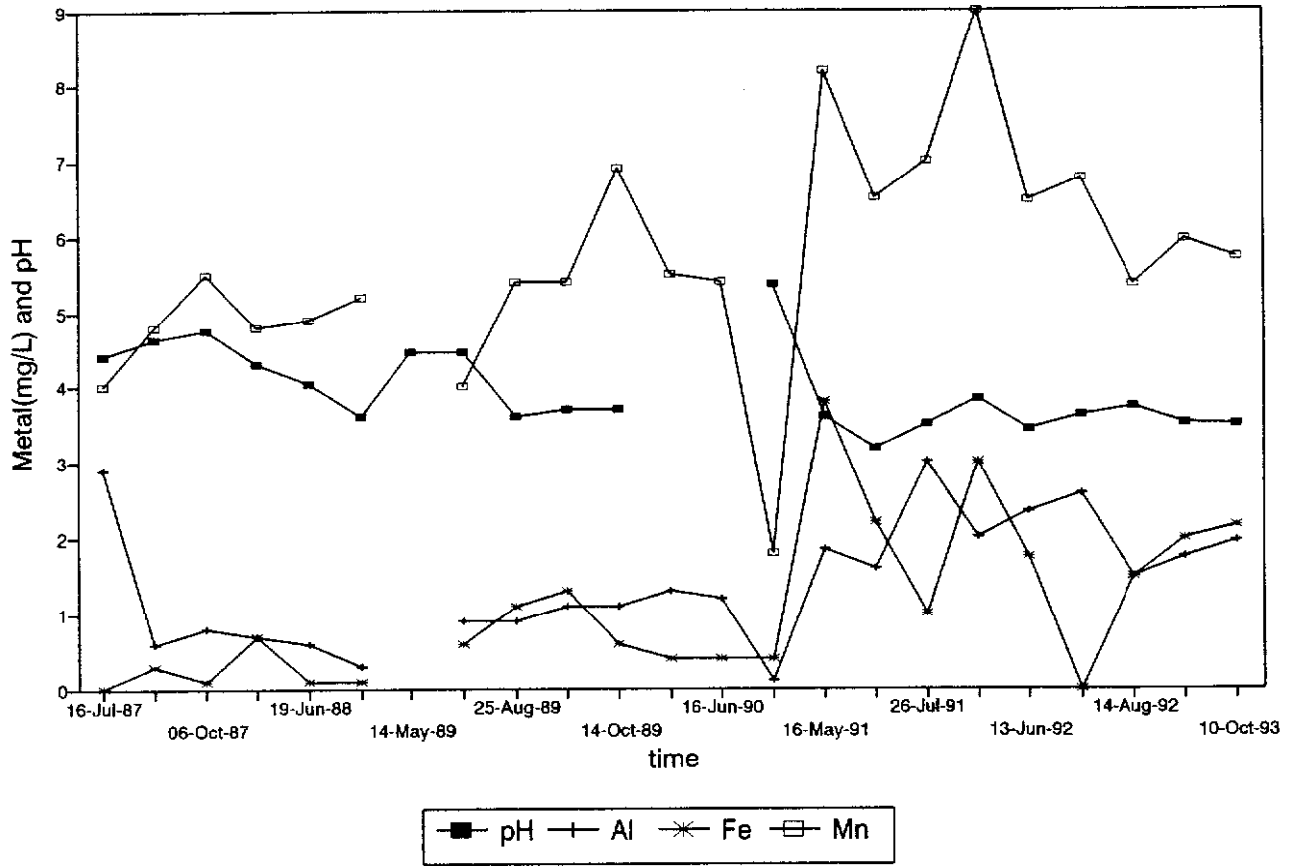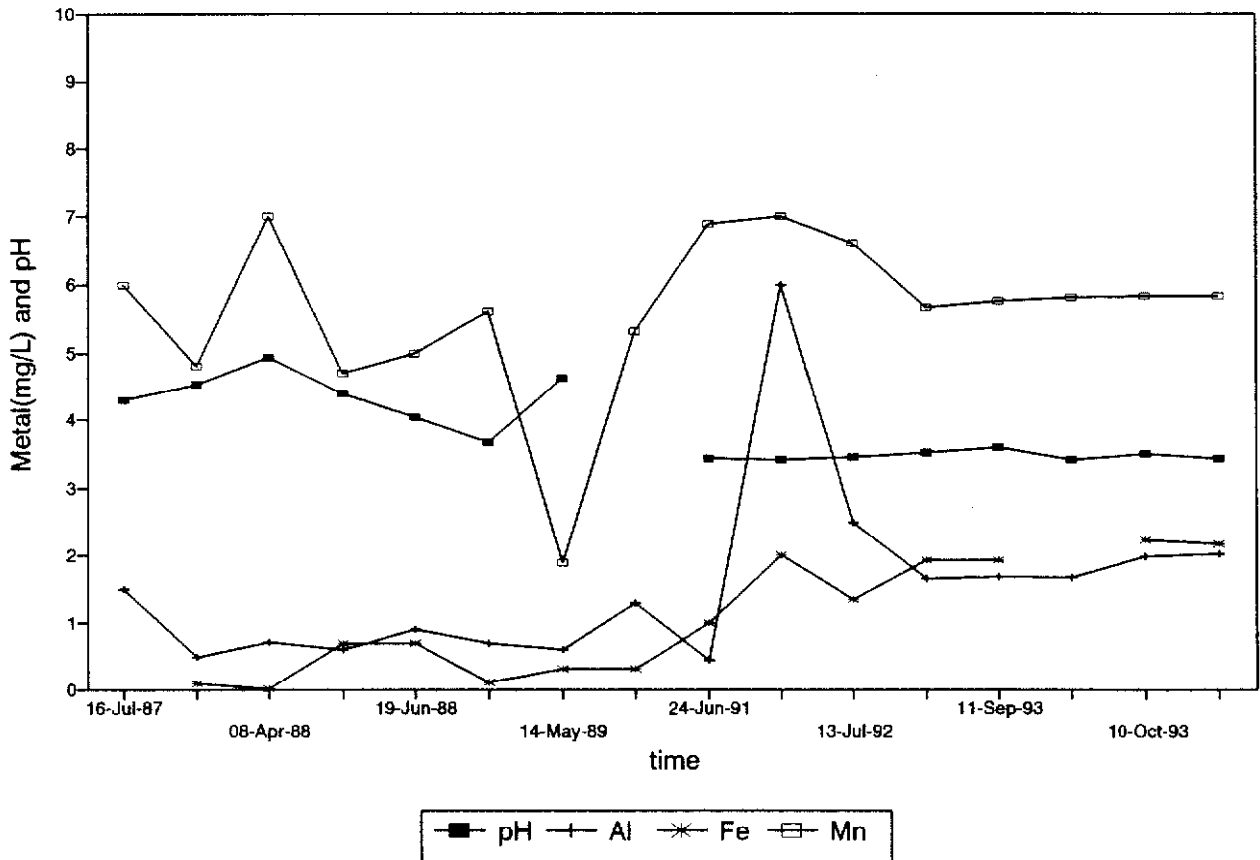
Fig. 11: B1 Area Water Quality

Legend: pH, Al, Fe, Mn

Fig. 12: B11 Area Water Quality

Legend: pH, Al, Fe, Mn

Boomerang Lake is a shallow lake and therefore its water volume completely mixes during the ice-free season. Loading of the contaminants and the treatment processes do not occur at the same locations in the lake. Seepages from the tailings, the areas of contaminant loading, are located at the opposite end of the lake with respect to sampling stations B1 and B11. Unfortunately, the sampling frequency of stations close to where the seepages are entering is lower, and comparable water quality data are not available. The absence of the increasing concentrations trends at sampling stations B1 and B11, close to the outflow area of Boomerang Lake, can potentially be a result of the biological polishing conditions concentrated near the outflow of Boomerang Lake.

The areas where the seepages enter Boomerang Lake can be expected to show larger seasonal fluctuations in concentrations of elements, since the flows would seasonally vary, producing higher concentrations during spring run-off in the vicinity of seepage entry compared to the outflow area.

Given the long-term deterioration of the water quality in Boomerang Lake until 1990, the period of relatively consistent contaminant concentrations in the last three years, and the input of contaminants from localized seepage entry, there is potentially a wide variation in sediment characteristics over the area of the lake bottom. The sediments in the area where biological polishing is active should be enriched in organics and zinc, while sediments in those areas where the seepages are entering should be enriched with iron. This potential variation in sediment characteristics with location greatly complicates the comparison of the characteristics of sediment which received a

phosphate rock addition with those of original sediments.

Sediments from Boomerang Lake were collected intermittently from different locations since l986. The % Loss On Ignition (an estimate of organic matter content; % L.O.I.), and the total concentrations of P, Al, Fe and Zn are plotted for all locations where samples have been collected in the lake (Figures 13 to 17, respectively).

The distribution of these elements throughout Boomerang Lake demonstrate that, indeed, large differences are present with respect to sampling location in the lake. The sediments used in the static laboratory experiment are integrated into this larger data set; those samples used in the laboratory which received phosphate rock are marked "P", while those which did not receive phosphate rock are marked "C".

The organic matter content in all sediment samples analyzed ranges from 1% to 46% (Figure 13). The phosphate rock was distributed in both areas with high organic content (B5 area) and low organic content (B9, B10, Backfill Bay).

Given that phosphate rock was applied in certain area, phosphorus concentrations in sediments from these locations should be measurably higher. While no difference in phosphorus concentrations are evident in the B6 area (Figure 14), there is clear indication of increased phosphorus concentrations following phosphate rock application in the B9, B10 and Backfill Bay areas.

Fig. 13: Boomerang Lake Sediments
% L.O.I.

Location, Date Sampled
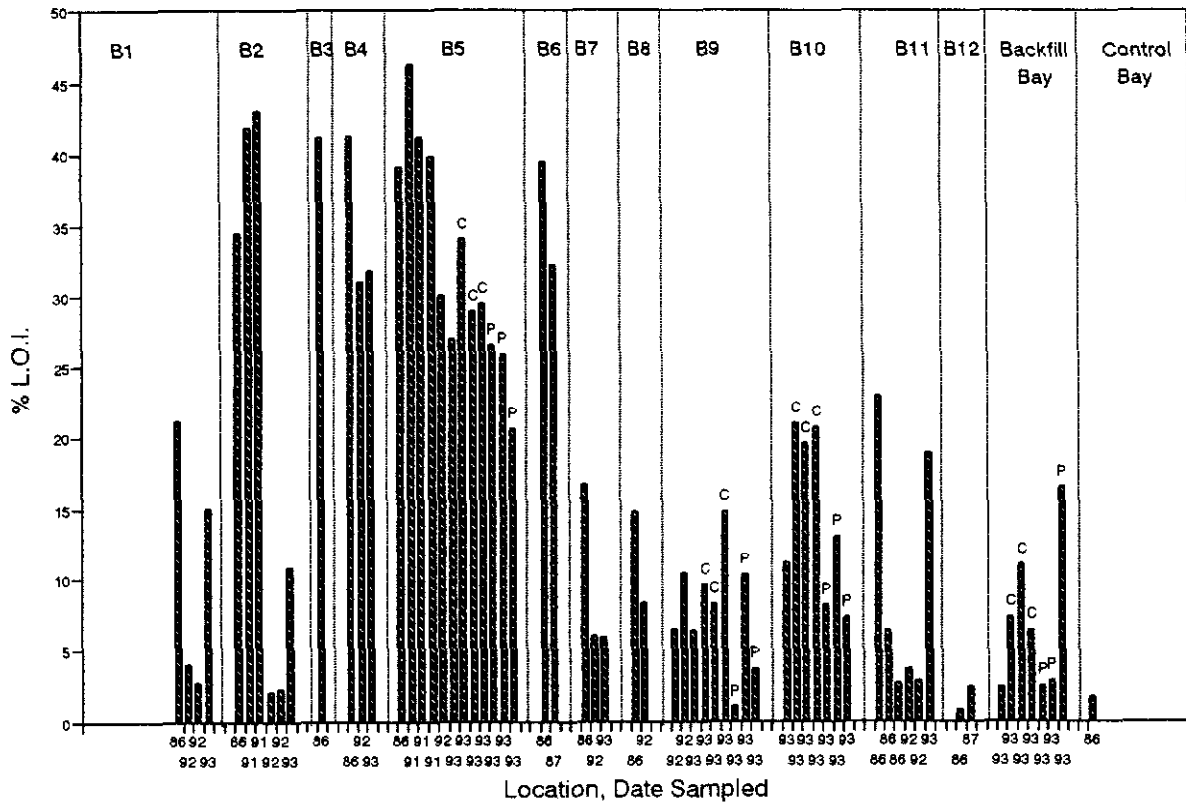
Fig. 14: Boomerang Lake Sediments
[P], ug/g

Location, Date Sampled
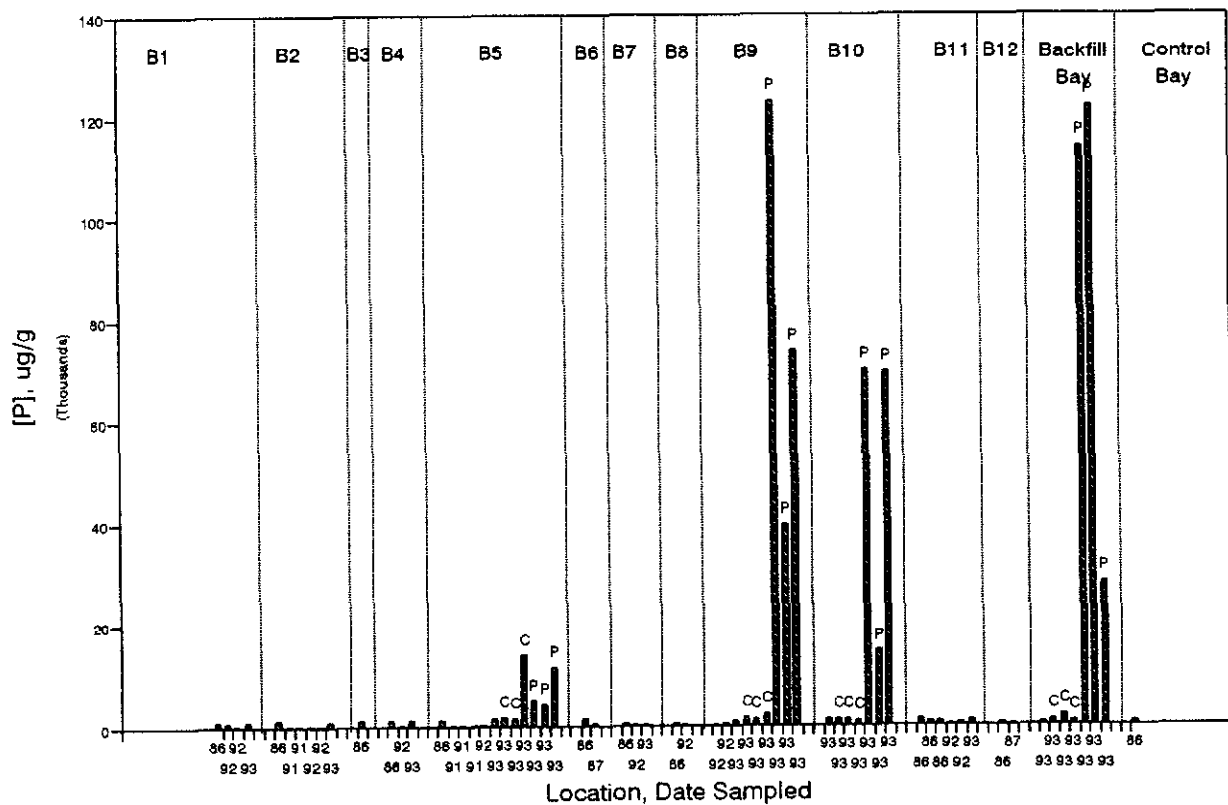
Overall, the average phosphorus content in all sediments from areas which did not receive phosphate rock is 0.1 ± 0.2 % (n = 49 samples), while in the phosphate rock-amended areas, the average phosphorus content in sediment samples is 4.2 ± 4.5 % (n = 16).

Unfortunately, following phosphate rock application, the appearance of sediment with and without phosphate rock is very similar and sediments are not easily differentiated during sampling. Phosphate rock-amended sediment samples contained as much as 12.3 % phosphorus, almost the same phosphorus content of pure phosphate rock (12.9 % P). These samples, comprised almost of pure phosphate rock, indicate that the phosphate rock distribution technique did not achieve an even layer over the sediment.

Given the uneven distribution of phosphate rock with respect to the locations in the lake, it is not possible to determine enrichment of precipitation products due to the placement of phosphate rock in the sediments. This is exemplified by the distribution of Al, presented in Figure 15. Two sediment Al concentration ranges are present in Boomerang Lake, one range generally less then 1 % Al, and the other range between 2.5% and 4.5 %. The locations of sediment samples with Al concentrations falling in the low or high range are not related the locations where phosphate rock was distributed. For example, sediments collected in the outflow area (B1 and B2) which received phosphate rock contain high Al concentrations, similar to sediments in Control Bay, an area neither affected by biological polishing or phosphate rock applications.

Fig. 15: Boomerang Lake Sediments
[Al], ug/g

Location, Date Sampled
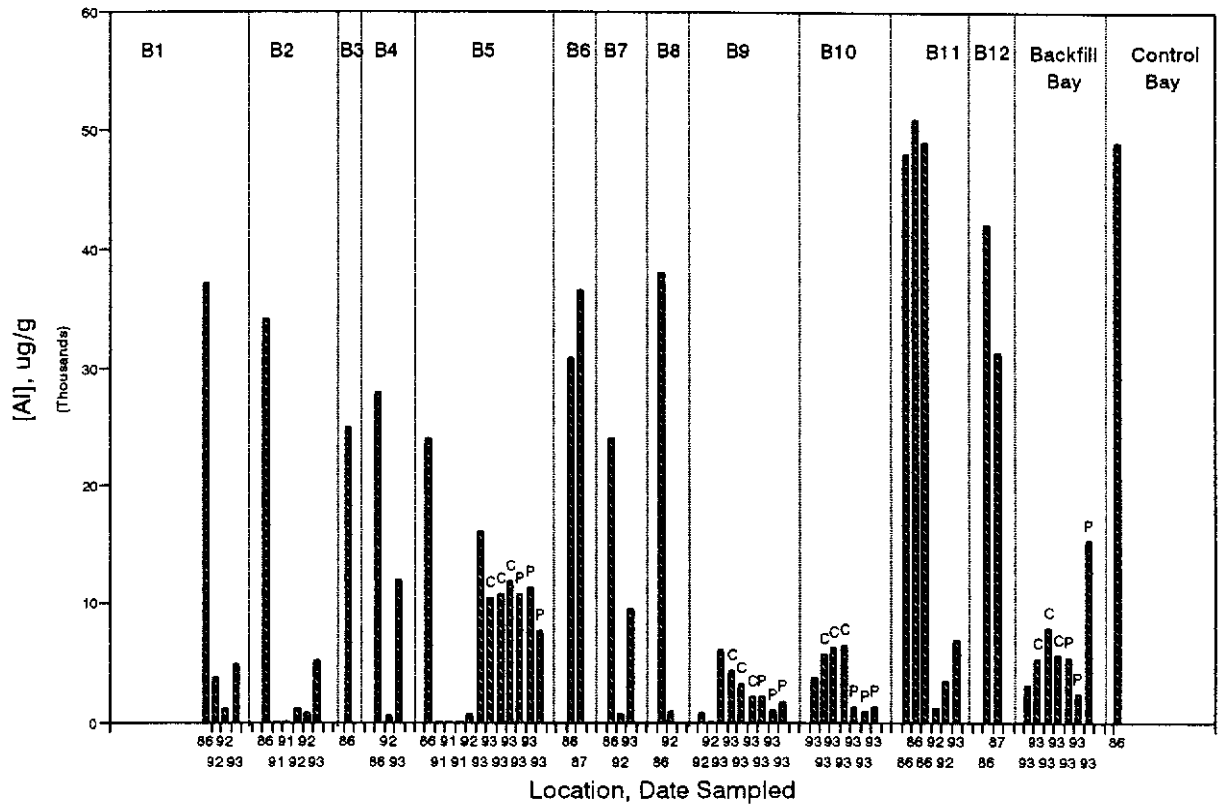
Fig. 16: Boomerang Lake Sediments
[Fe], ug/g

Location, Date Sampled
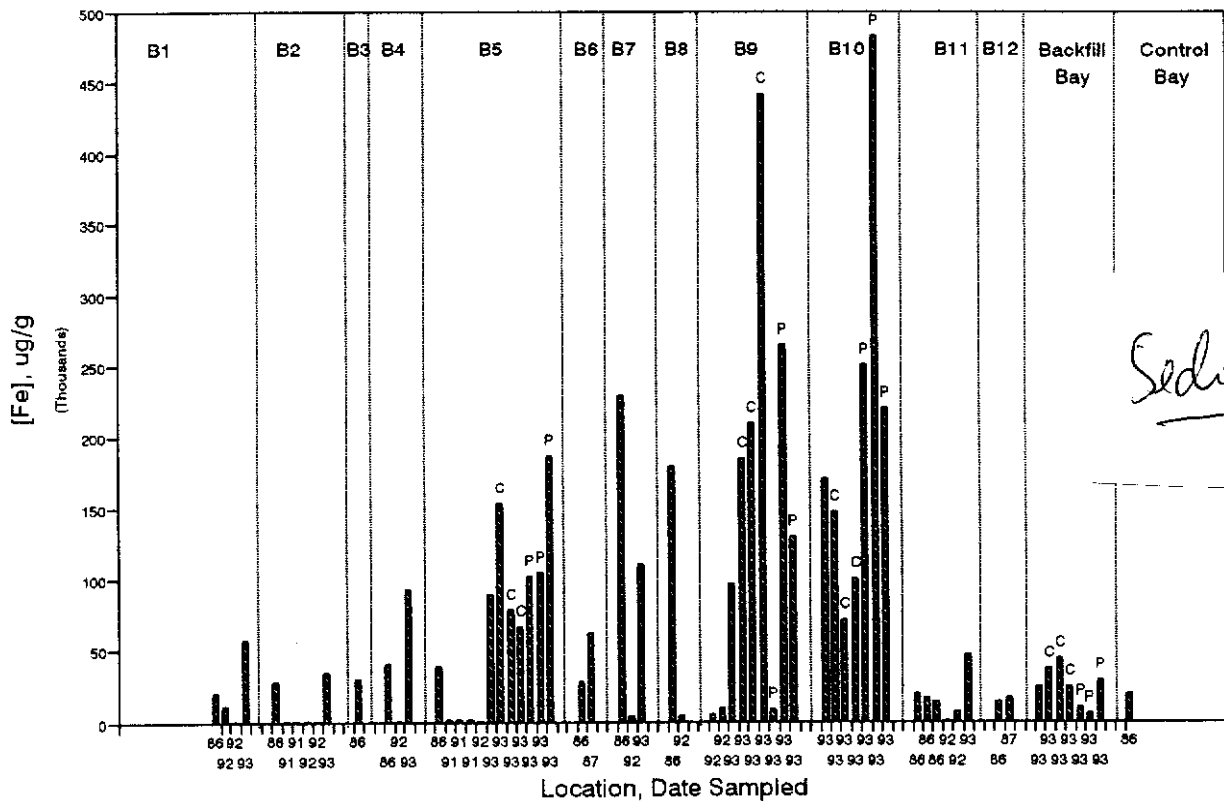
The distribution of the iron in Boomerang Lake sediments clearly indicates that iron in seepages entering near B9 and B10 is being deposited in these areas' sediments (Figure 16). Sediment iron concentrations can be as high as 45 % in the B10 area. Surface sediments in this area are comprised of crystalline-appearing dense iron hydroxide lumps. These locations will require more detailed assessment with respect to the effects of phosphate rock in the future.

The distribution of sediment zinc concentrations is presented in Figure 17. The sediment zinc concentrations are directly related to the organic content of the sediments, as indicated by the % L.O.I. values in these sediment (Figure 13). This evidence, albeit indirect, that organic matter is involved in the retention of zinc by sediments, a key component of the biological polishing process as presently understood.

The algal community is contributing substantial quantities of zinc-loaded organic matter to Boomerang Lake sediments. The current water quality at Boomerang Lake outflow, constant since 1990 following a period of deteriorating water quality since 1970, may be attributable to the biological polishing process promoted in Boomerang lake by addition of growth substrate. However, the effects of the phosphate rock additions are not evident based on the data collected to date.

A visual survey of the sediment surface of Boomerang Lake, performed in July, 1994, revealed that rooted aquatic mosses have established over areas of the lake bottom.

Fig. 17: Boomerang Lake Sediments
[Zn], ug/g
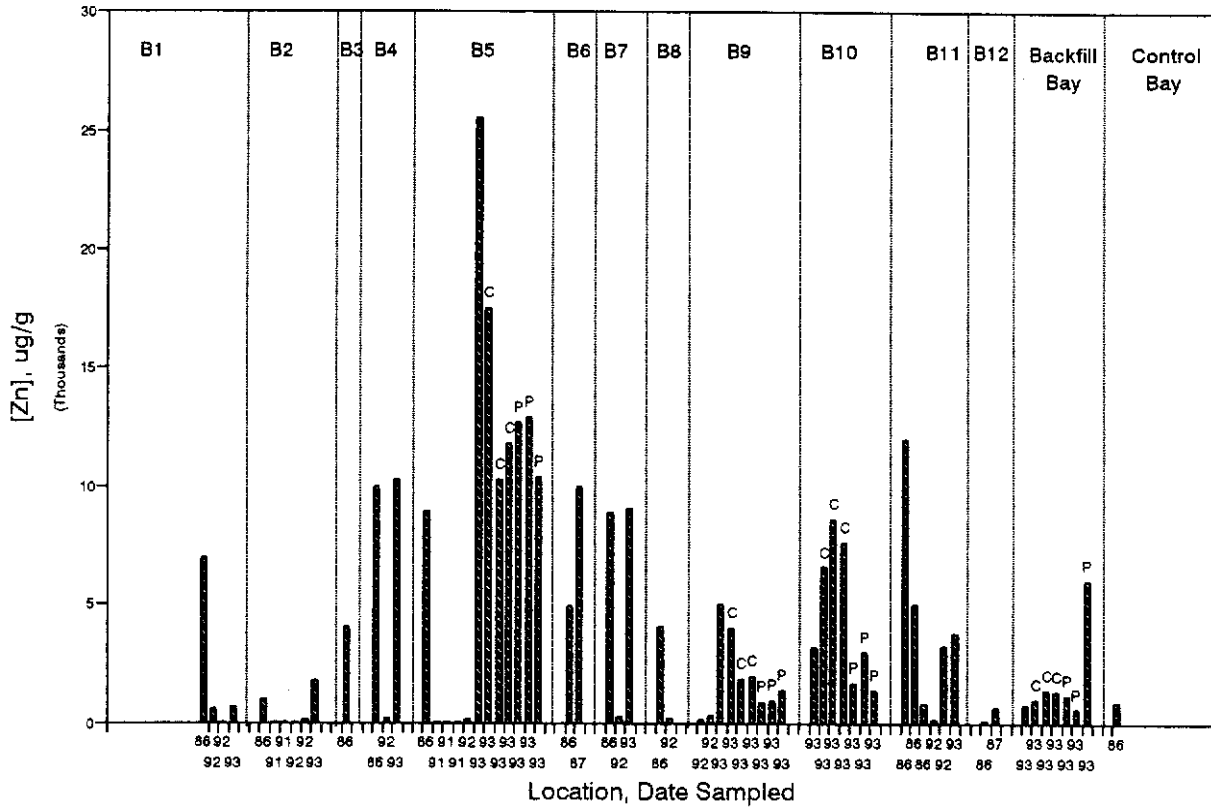
Since this is the first survey for the aquatic moss, it too cannot be attributed to

phosphate rock addition. Further assessment of the effects of phosphate rock addition

will be performed when water quality data, following the 1994 phosphate rock addition,

is available.

5.0   CONCLUSIONS

- Two approaches to modelling the biological polishing process have been developed. The box model is a useful tool for predicting zinc removal performance based on retention time. The preliminary simple box model was predicting the performance of the newly constructed ponds (6000 m^3) reliably.

- The second approach to modelling the process is a continuous time reactor model. It identifies components of the process such as growth rates and sedimentation rates which affect the process performance.

- The biological polishing unit for algal growth (biomass grown on branches) can be replaced with biomass per unit netting. In both the acidic and circumneutral polishing ponds, the mass grown per day was similar to that quantified on branches.

- A literature review of iron cycling in sediments indicated that a very important factor in passive polishing systems is the cycling of iron. Iron oxidation and microbially-mediated iron reduction in sediments of polishing ponds affect the water chemistry and the biological polishing process. The chemical conditions under which the iron hydroxide is formed results in different quantities of contaminant removal.

- Sedimentation rates of iron hydroxide have been quantified. The sedimentation rates in the circumneutral and acidic systems were similar, ranging between 0.5 $g.m^{-2}.d^{-1}$ to 8 $g.m^{-2}.d^{-1}$.

- The effects on phosphate additions to sediments are difficult to quantify, both in the laboratory and in the field. The additions possibly stimulate microbial activity in the sediment which, in turn, induces reducing conditions.

- Sediments enriched with iron hydroxide have a tendency, over a 10 month period, to acidify when kept in laboratory conditions, suggesting a slow rate of iron hydroxide oxidation. When sediments are aerated vigorously over a period of 10 days, no acidification was taking place. It is concluded that the iron hydroxide-enriched sediments are overall stable. However pore water concentrations of reduced iron were found to be higher (115 $mg.l^{-1}$) than that reported in the literature (70 $mg.l^{-1}$).

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7.0   APPENDIX

Appendix 1a: 1993 Summary of Periphyton Accumulation - SOUTH BAY

Sample Location	Treatment	Time in Situ (d)	Dry Wt (g)	Area (m2)	Accum. g/m2/da	L.O.I. %	Branch Wt (g)
BOOMERANG L.							
B1-a	Peri-Net - NPK Osmocote	87	1.52	0.1302	0.134		
B1-b	Peri-Net - NPK Osmocote	87	1.72	0.1302	0.152		
B1-c	Peri-Net - NPK Osmocote	87	1.84	0.1302	0.162	38.0	
B1-d	Peri-Net - NPK Osmocote	87	2.32	0.1302	0.205	42.6	
B11-a	Peri-Net - NPK Osmocote	87	2.29	0.1302	0.202		
B11-b	Peri-Net - NPK Osmocote	87	2.39	0.1302	0.211		
B11-c	Peri-Net - NPK Osmocote	87	2.10	0.1302	0.185	37.0	
B11-d	Peri-Net - NPK Osmocote	87	2.51	0.1302	0.222	39.7	
B11-e	Peri-Net - NPK Osmocote	87	1.62	0.1302	0.143		
B4-a	Peri-Net - NPK Osmocote	87	4.29	0.1302	0.379		
B4-b	Peri-Net - NPK Osmocote	87	3.78	0.1302	0.334	31.0	
B4-c	Peri-Net - NPK Osmocote	87	4.10	0.1302	0.362	38.0	
B4-d	Peri-Net - NPK Osmocote	87	3.48	0.1302	0.307		
B7-a	Peri-Net - NPK Osmocote	87	4.58	0.1302	0.404	34.4	
B7-b	Peri-Net - NPK Osmocote	87	4.92	0.1302	0.434	37.9	
B7-c	Peri-Net - NPK Osmocote	87	7.65	0.1302	0.675	36.6	
B7-d	Peri-Net - NPK Osmocote	87	4.33	0.1302	0.382	38.8	
B7-e	Peri-Net - NPK Osmocote	87	4.93	0.1302	0.435	39.8	
B1 Peri # 1	Jelly - On Young branch	2050	6.80	0.1486	0.022	37.0	16.7
B1 Peri # 2	Jelly - On Young branch	2050	6.35	0.1148	0.027	32.0	12.9
B1 peri # 3	Jelly - On Young branch	2050	4.00	0.2074	0.009	40.0	23.3
B1 Peri # 1a	Jelly - On Old Branch	2416	9.10	0.2554	0.015	36.0	28.7
B1 Peri # 2a	Jelly - On Old Branch	2416	7.15	0.3524	0.008	46.0	39.6
B1 Peri # 3a	Jelly - On Old Branch	2416	7.20	0.3186	0.009	39.0	35.8
B10 Peri # 1	Jelly - On Young branch	2050	15.85	0.7788	0.010	18.0	87.5
B10 Peri # 2	Jelly - On Young branch	2050	17.35	0.4632	0.018	20.0	52.1
B10 Peri # 3	Jelly - On Young branch	2050	7.10	0.5785	0.006	29.0	65.0
B11 Peri # 1	Jelly - On Young branch	2050	4.70	0.1669	0.014	38.0	18.8
B11 Peri # 2	Jelly - On Young branch	2050	14.50	0.1833	0.039	29.0	20.6
B11 Peri # 3	Jelly - On Young branch	2050	8.00	0.1976	0.020	38.0	22.2
B11 Peri # 1a	Jelly - On Old Branch	2416	11.50	0.2866	0.017	31.0	32.2
B11 Peri # 2a	Jelly - On Old Branch	2416	16.80	0.2456	0.028	28.0	27.6
B11 Peri # 3a	Jelly - On Old Branch	2416	6.40	0.2051	0.013	32.0	23.1
DECANT POND							
Sed trap	Jelly - On horiz. plate	455	4.15	0.1225	0.074	35.0	

Appendix 1b: 1993 Summary of Precipitation Rates - SOUTH BAY

Sample Location	Description	Time in Situ (d)	Accum. g/m2/da	L.O.I. %
BOOMERANG L.				
B1	Sed trap - precipitate	243	0.429	50.55
B11	Sed trap - precipitate	243	0.234	54.72
B5	Sed trap - precipitate	243	0.218	30.68
B4	Sed trap - precipitate	243	7.137	32.34
B1	Sed trap - precipitate	87	1.510	-
B11	Sed trap - precipitate	87	1.862	-
B5	Sed trap - precipitate	87	3.899	-
B4	Sed trap - precipitate	87	3.758	-
B2	Sed trap - precipitate	29	0.520	-
B4	Sed trap - precipitate	29	0.560	-
B5	Sed trap - precipitate	29	1.192	-
B11	Sed trap - precipitate	29	0.478	-
DECANT POND				
Centre	Sed trap - precipitate	455	0.297	-

Appendix 2a: 1993 Summary of Periphyton Accumulation - BUCHANS

Sample Location	Treatment		Time in Situ (d)	Percent Cover	Dry Wt (g)	Area (m2)	Accum. g/m2/day	L.O.I. %	Branch Wt (g)
FIRST MEADOW									
PP 10	Peri-Net -	# 10 Fertilizer	41	20%	2.205	0.1302	0.413	31.1	
PP 10	Peri-Net -	P 10 # 11	41	25%	9.508	0.1302	1.781	21	
PP 6	Peri-Net -	P 6 1of 6	41	80%	5.4321	0.1302	1.018	34.33	
PP 6	Peri-Net -	P 6 2 of 6	41	22%	1.5972	0.1302	0.299		
PP 6	Peri-Net -	P 6 6 of 6	41	70%	5.49	0.1302	1.028	22.77	
PP 1	Peri-Net -	P 1 5 of 6	41	82%	3.0052	0.1302	0.563	32.49	
Pp 1	Peri-Net -	P 1 3of 6	41	32%	1.435	0.1302	0.269		
PP 1	Peri-Net -	P 1 4 of 6	41	35%	1.76	0.1302	0.330		
PP 10	Peri-Net -	P10 #1	41	40%	6.0816	0.1302	1.139	30.22	
PP 10	Peri-Net -	P10 #3 Fert	41	5%	6.4831	0.1302	1.214	28.77	
PP 10	Peri-Net -	P10 # 7	41	2%	2.9429	0.1302	0.551	34.5	
PP 10	Peri-Net -	P10 # 2	41	25%	5.6653	0.1302	1.061	32.26	
PP 6	Jelly -	PP # 6 Algae	1459	100%	22	0.0147	1.027	30.68	5.4
PP 10	Jelly -	PP 10 Algae	302	100%	30.1	0.0511	1.949	26.58	18.8
PP 1	Jelly -	PP 1 Algae	1459	100%	71.7	0.0639	0.769	17.8	23.5

Appendix 2b: 1993 Summary of Precipitation Rates - BUCHANS

Sample Location	Description		Time in Situ (d)	Accum. g/m2/d	L.O.I. %
OEP					
13 ft	Sed trap -	precipitate	77	5.87	
35 ft	Sed trap -	precipitate	77	9.89	
71 ft	Sed trap -	precipitate	77	354	
TP-2					
15 ft	Sed trap -	precipitate	80	0.21	

Appendix 3:   Boomerang Lake Sediments pH. Em and Conductivity

Date of Measurement	Sample Location	Date Collected	Phosphate Rock Treatment	pH Measurement # #1	#2	#3	Geo. Mean	Em (mV) Measurement # #1	#2	#3	Mean	Conductivity (uS/cm) Measurement # #1	#2	#3	Mean
October 27, 1993	B1	Sept 11	no PR	4.24			4.24	101			101	608			608
	B2	Sept 11	no PR	4.81			4.81	103			103	1300			1300
	B4	Sept 11	no PR	4.85			4.85	71			71	1392			1392
	B 5	Sept 11	no PR	4.12	4.68		4.32	174	53		114	174	671		423
		Oct 11	no PR	4.21	4.11	4.32	4.20	113	77	103	98	1093	990	837	973
		Oct 11	with PR	4.34	4.52	4.68	4.49	56	59	61	59	1168	1019	1442	1210
	B7	Oct 11	no PR	6.05			6.05	-132			-132	487			487
	B9	Sept.11	no PR	3.08	3.91		3.32	57			57	406	776		591
		Oct.11	no PR	3.51	3.03	2.83	3.04	178	218	291	229	1253	1157	1940	1450
		Oct.11	with PR	11.16	5.69	6.04	6.01	-406	-139	-144	-230	1475	2870	2440	2262
	B 10	Sept11	no PR	3.29	3.98		3.51	300	91		196	300	1529		915
		Oct 11	no PR	3.95	3.98	3.93	3.95	96	104	107	102	1193	997	1130	1107
		Oct 11	with PR	5.10	4.65	5.18	4.91	22	66	-38	17	3350	2480	2600	2810
	B11	Oct 11	no PR	4.69			4.69	62			62	1249			1249
	Backfill Bay	Sept 11	no PR	3.28	3.87		3.48	231	108		170	231	1161		696
		Oct 11	no PR	5.11	4.81	4.93	4.93	36	37	28	34	975	1106	1000	1027
		Oct 11	with PR	11.25	9.98	6.61	7.09	-319	-279	-251	-283	3440	996	2010	2149
November 30, 1993	B1	Sept 11	no PR	3.47			3.47	91			91	904			904
	B2	Sept 11	no PR	3.72			3.72	281			281	1375			1375
	B4	Sept 11	no PR	3.53			3.53	416			416	1432			1432
	B 5	Sept 11	no PR	5.11			5.11	195			195	528			528
		Oct 11	no PR	3.72	3.62	3.72	3.68	236	392	268	299	1310	1061	1066	1146
		Oct 11	with PR	3.69	4.24	3.59	3.76	386	342	355	361	1247	1325	2630	1734
	B7	Sept 11	no PR	5.33			5.33	182			182	1162			1162
	B9	Sept.11	no PR	3.91			3.91	98			98	2960			2960
		Oct.11	no PR	3.52	3.36	2.93	3.20	108	125	271	168	3720	4210	4120	4017
		Oct.11	with PR	10.35	6.33	6.37	6.53	-125	-229	-195	-183	3720	5640	5830	5063
	B 10	Sept11	no PR	4.36			4.36	32			32	3450			3450
		Oct 11	no PR	3.75	3.62	3.57	3.64	72	53	37	54	1730	1410	1560	1567
		Oct 11	with PR	4.56	3.82	4.96	4.20	348	134	42	175	3540	3290	3350	3393
	B11	Sept 11	no PR	3.65			3.65	87			87	1380			1380
	Backfill Bay	Sept 11	no PR	3.12			3.12	172			172	1710			1710
		Oct 11	no PR	3.52	3.58	3.51	3.54	416	199	376	330	1157	1572	1456	1395
		Oct 11	with PR	9.47	8.87	7.26	7.72	-366	-228	-243	-279	3410	2820	3010	3080
February 17, 1994	B1	Sept 11	no PR	7.42			7.42	250			250	271			271
	B2	Sept 11	no PR	3.5			3.5	360			360	1160			1160
	B4	Sept 11	no PR	3.51			3.51	340			340	1129			1129
	B 5	Sept 11	no PR	6.83			6.83	-151			-151	356			356
		Oct 11	no PR	3.47	3.60	3.63	3.56	320	398	388	369	1135	840	874	950
		Oct 11	with PR	3.65	3.80	3.75	3.73	390	375	244	336	1220	1256	2900	1792
	B7	Sept 11	no PR	4.47			4.47	184			184	1450			1450
	B9	Sept.11	no PR	3.48			3.48	230			230	4000			4000
		Oct.11	no PR	3.53	3.31	2.66	3.00	251	259	335	282	3710	4560	7450	5240
		Oct.11	with PR	10.00	3.15	4.19	3.59	61	307	192	187	3560	6770	4120	4817
	B 10	Sept.11	no PR	3.12			3.12	278			278	2730			2730
		Oct 11	no PR	3.21	3.22	3.18	3.20	347	450	360	386	1830	1410	1580	1607
		Oct 11	with PR	3.32	3.39	3.57	3.41	327	270	270	289	3680	4470	3870	4007
	B11	Sept 11	no PR	3.74			3.74	357			357	917			917
	Backfill Bay	Sept 11	no PR	3.14			3.14	450			450	1248			1248
		Oct 11	no PR	4.23	4.00	4.48	4.19	276	339	330	315	725	837	706	756
		Oct 11	with PR	7.45	7.50	7.78	7.55	-120	-143	-212	-158	3860	2840	1970	2890
June 6, 1994	B1	Sept 11	no PR	4.49			4.49	-42			-42	182			182
	B2	Sept 11	no PR	3.7			3.7	-227			-227	780			780
	B4	Sept 11	no PR	3.83			3.83	-177			-177	690			690
	B 5	Sept 11	no PR	6.56			6.56	-260			-260	152			152
		Oct 11	no PR	3.15			3.15	-110			-110				
		Oct 11	with PR	3.69			3.69	-176			-176	1070			1070
	B7	Sept 11	no PR	3.98			3.98	-332			-332	1210			1210
	B9	Sept.11	no PR	3.40			3.4	-124			-124	3400			3400
		Oct.11	no PR	2.96			2.96	-57			-57	4640			4640
		Oct.11	with PR	6.03			6.03	-274			-274	3650			3650
	B 10	Sept11	no PR	3.08			3.08	-62			-62	2770			2770
		Oct 11	no PR	2.83			2.83	-90			-90	1170			1170
		Oct 11	with PR	3.15			3.15	-165			-165	3670			3670
	B11	Sept 11	no PR	3.67			3.67	-85			-85	770			770
	Backfill Bay	Sept 11	no PR	3.43			3.43	-47			-47	1020			1020
		Oct 11	no PR	4.04			4.04	-75			-75	520			520
		Oct 11	with PR	7.19			7.19	-371			-371	3950			3950