Boojum
RESEARCH LIMITED

THE APPLICATION
OF
ECOLOGICAL ENGINEERING
FOR CLOSE-OUT AT BUCHANS

FINAL REPORT

Prepared for Mr. George Neary

Joint Venture Group at Buchans NFLD.

ASARCO INC. - Abitibi-Price Inc.

By: Margarete Kalin

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EXECUTIVE SUMMARY

Since 1988 Ecological Engineering work has been carried out in Buchans Newfoundland with the objective to develop a decommissioning solution to the effluents from the mining operation. Hydrological, geochemical and biological research has been brought ytogether to recommend the first implementation steps of the decommissioning measures.

In principle, two Ecological Engineering processes were tested for implementation in the close-out for the Buchans effluents, the ARUM Process and Biological Polishing.

ARUM is sediment-based, microbially-driven, acid-reducing, and alkalinity-generating process, which to run optimally, requires an appropriate combination of organic amendments as a food source to the microbes. Tests, carried out in limnocorrals and curtained-off enclosures in the OEP and the OWP, used peat and sawdust as organic amendments. Decomposition of these materials in both pits and in limnocorrals indicated that sawdust provided only a small fraction of foodstuffs to the process; peat was a better substrate. However, through laboratory studies, more degradable carbohydrate sources were identified. These results were translated to the field by constructing sediments in the OWP with a mixture of potato waste and peat. These sediments generate alkalinity, increase the pH, and remove the zinc in limnocorrals as long as reducing conditions are maintained. Reducing conditions were simulated with a plastic cover, which was placed on the limnocorrals in 1992.

The effectiveness of the ARUM sediments placed behind curtains in the OWP, however, is impossible to determine, since natural zinc reductions take place in the pit. Each year, the zinc concentrations drop naturally by about 5 mg/L. Full scale ARUM implementation and the addition of phosphate to the pit will increase this zinc reduction rate. The key conclusion suggested by data is that no new contamination will be added to the OWP. Therefore, once the residual contaminated acidic water is treated with an ARUM sediment or phosphate rock, the OWP will no longer require treatment.

Although extensive efforts were expended in 1992 to identify the exact location of the ground water entry to the OEP, it was not possible to find any specific locus. This precludes the use of ARUM, as the water would flow through the sediment, physically disturbing the microbial communities.

The source of the zinc in the OEP has been identified as precipitates which formed at the time of mine flooding. The downward trend in effluent concentrations suggests, and the neutral pH and low oxygen content of the ground water indicate strongly that acid generation in the underground workings has ceased. Therefore, in the long-term, the OEP effluents are expected to reach background zinc concentrations around 1 to 2 mg/L. This background concentration is due to the chemical equilibrium between CO, in the ground water and the zinc which has precipitated as zinc-carbonate.

The reduction of zinc in the OEP effluent is further controlled by iron precipitation which takes place in the upper **4** m of the pit. Reduced iron present in the bottom of the pit oxidizes as the thermocline establishes after spring melt. Through co-precipitation, zinc settles to the bottom of the pit. It is proposed that this natural process might be optimized by using Drainage Tunnel water to oxygenate the OEP water column. Oxygenation would precipitate more iron, thus co-precipitating more zinc. There is no indication that the alkalinity of the ground water is changing, and due to the reducing conditions at the bottom of the pit, iron concentrations are increasing. With more iron at the bottom of the pit, increased removal of zinc *is* expected.

During winter 1993 it is recommended that a water sampling program be carried out to confirm the chemical conditions which lead to zinc reductions in both in the OWP and the OEP.

Effluent from Tailings Pond 2 was also addressed with respect to decommissioning. It was concluded through investigations of the acid generation processes in the tailings beaches, that porewater movement is minimal, suggesting that any acid generation yoccurring in the beaches will remain there. Zinc reductions seen over the last few years in the pond can be accounted for by the zinc loading leaving the pond. Therefore, it was concluded that annual zinc loading to TP-2 from tailings beaches is minimal and essentially has ceased. No long-term treatment for this effluent is required and through biological polishing and/or phosphate additions it will be possible to reduce the zinc concentrations further.

Biological polishing is a process in which zinc is relegated to the sediment mediated by algae and moss. Biomass growing on alder, through a combination of adsorption, co-precipitation with iron, precipitation of zinc-carbonate (due to photosynthetic activity), and uptake into the biomass, removes zinc from the effluent. The performance of this process has been tested in a series of ponds in which biomass growth and zinc removal were quantified. A model to determine the relationship of zinc removal with retention time, flow, and biological activity has been developed based on data collected in 1991 and 1992.

Fertilizer applications increase biological polishing performance and assist directly in the zinc removal process. Phosphate in the fertilizer reacts with zinc forming zinc-phosphate, which is a stable precipitate. Thus, biological polishing is a process of zinc removal which combines several mechanisms. The size of the biological polishing pond to be implemented will depend on how quickly, and by how much the compliance schedule requires reductions in the zinc loading to the Buchans River.

After the 5th year of investigations of the Buchans mining effluents it can be concluded that the Ecological Engineering approach has lead to the finding that, conventional treatment plants are not required TP-2, the OWP, or for the OEP. Compliance can be achieved through the enhancement of natural water cleansing processes, such as biological polishing. The work to date has determined that the Drainage Tunnel is the only effluent area where acid generation is taking place. The conditions for Lucky Strike have to await further force flooding, and TP-1 has to addressed. The Ecological Engineering approach to decommissioning of the two Oriental pits suggests that conditions can be achieved to discharge clean water to the environment.

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1. INTRODUCTION

A feasibility study carried out in 1988 resulted in the overall formulation of an Ecological Engineering decommissioning approach. Experiments were set up in 1989 to remove zinc with algae, which is referred to as biological polishing. Tests were set up in the same year in limnocorrals in order to find the appropriate combination of organic materials to construct sediments in which microbial activities would generate alkalinity and precipitate metal sulphides. The microbially-driven metal removal process is referred to as ARUM (Acid Reduction Using Microbiology).

The geochemical interactions of ground water with contaminant sources (waste rock, tailings and underground workings) were studied to determine sources (location and type) of the contaminants in the effluent and their long-term fate.

Generally, downward trends in zinc concentrations of the effluents were noted. In the OEP, this had been attributed to the depletion of precipitates available for dissolution by ground water. These precipitates were formed during the flooding of the underground workings, where acid generation had been reported. Dissolution of zinc takes place due to a chemical equilibrium between zinc and carbon dioxide. For details see page 3-6 in the 1991 report and Figure 17a and 17b in this report.

In Tailings Pond 2, decreasing zinc concentrations were allegedly due to the depletion of the contaminants in the acid-generating beaches. A further reduction in zinc concentrations to a plateau at a level of 1 to 2 mg/L was expected.

In 1991, through the evaluation of the chemistry of the Buchans effluents, it was suggested that the OEP and TP-2 effluents should have a background zinc concentration of 1 to 2 mg/L, due to the fact that the precipitate formed is zinc-carbonate which will redissolve in relation to the carbon dioxide concentrations in the water. If zinc is removed through liming, in time, the zinc-hydroxide will form zinc-carbonate and maintain the background concentration of zinc. Details on the chemical reactions were given in the 1991 report.

In 1992, therefore, it was necessary to address the removal of the zinc-carbonate, possibly by forming zinc-phosphate. Phosphate rock was tested to determine if zinc-phosphate could be formed instead of zinc-carbonate in the effluents of the OEP. The phosphate rock applications would serve a dual purpose. Phosphate which did not react with zinc could serve as fertilizer. Fertilization of the algal polishing ponds 1-6 produced good results in 1991, establishing some, and confirming other, design parameters for a biological polishing system for the OEP effluent.

The berms of the new polishing ponds will be constructed in the same manner as those berms surrounding the test ponds, using the excavated peat from the meadows. Since construction of the berms in 1989, no vegetation has become established, and erosion is evident. The new polishing ponds would likely need some stabilization. Therefore, experiments were initiated to establish indigenous vegetation on the exposed berms.

As the geochemistry and hydrology of the site were elucidated throughout the years, and the test work on biological polishing and ARUM proceeded, a compliance schedule was developed. It was based, in part, on the results of the research carried out to date. The focus of this report is to analyze the site characteristics and the research results to ascertain which measures can be taken to achieve performance with respect to the compliance schedule. It addresses the required maintenance of the biological polishing system receiving the OEP effluent, Tailings Pond 2, and the ARUM sediment in the OWP.

2. LONG-TERM TRENDS IN EFFLUENTS

With the large set of monitoring data on concentrations of copper and zinc in the effluents it is possible to determine relatively reliable rates at which decreases in concentrations take place. Copper concentrations are generally very low, only slightly above the analytical detection limit, and they have not been used for interpretation.

In Table 1, the initial rates of zinc decrease (slope) in the OEP, OWP and the tailings pond are shown. These initial rates (slopes) are derived from the monitoring data. The comment in the table defines the database. These initial rates of zinc decrease are also presented for the biological polishing pools, phosphate treatment and retention time or zinc-carbonate precipitation. The zinc reduction rate due to retention time or zinc-carbonate precipitation is high enough that if the effluents were contained, zinc concentration would decrease at the rate of 1.4 mg/L/month, at the present zinc concentration of 20 mg/L. A natural solution to decommissioning, i.e. Ecological Engineering, would increase the rates at which contaminant removal is occurring. For the case of Buchans, it consists of replacement of $ZnCO_3$ with $Zn_3(PO_4)_2$ and enhancement of these precipitation processes with biological polishing. Therefore, within the Ecological Engineering treatment system, be it phosphate or biological polishing, removal rates should be increased, which indeed is the case (Table 1).

Table 1: Rates of reductions in Zinc

	Zn Rate mg/L/month	Comment
OWP Center	-0.36	Based on average values for 6 years (1987-1992)
OEP Outflow	-1.22	Based on average values for 4 years (1987-1990)
OEP Bottom	-0.97	Based on values for 3 years (see table 3)
TP2 Outflow	-0.04	Based on average values for 7 years (1986-1992)
PO4 Treatment	-12.97	Based on phosphate box experiment (table C2)
Biopol	-18.93	Based on 7 sets of measurements (4 to 60 days)
Retention Time/ Carbonate	-1.39	Based on 3 sets of measurements (0.6,1,1.6 years)

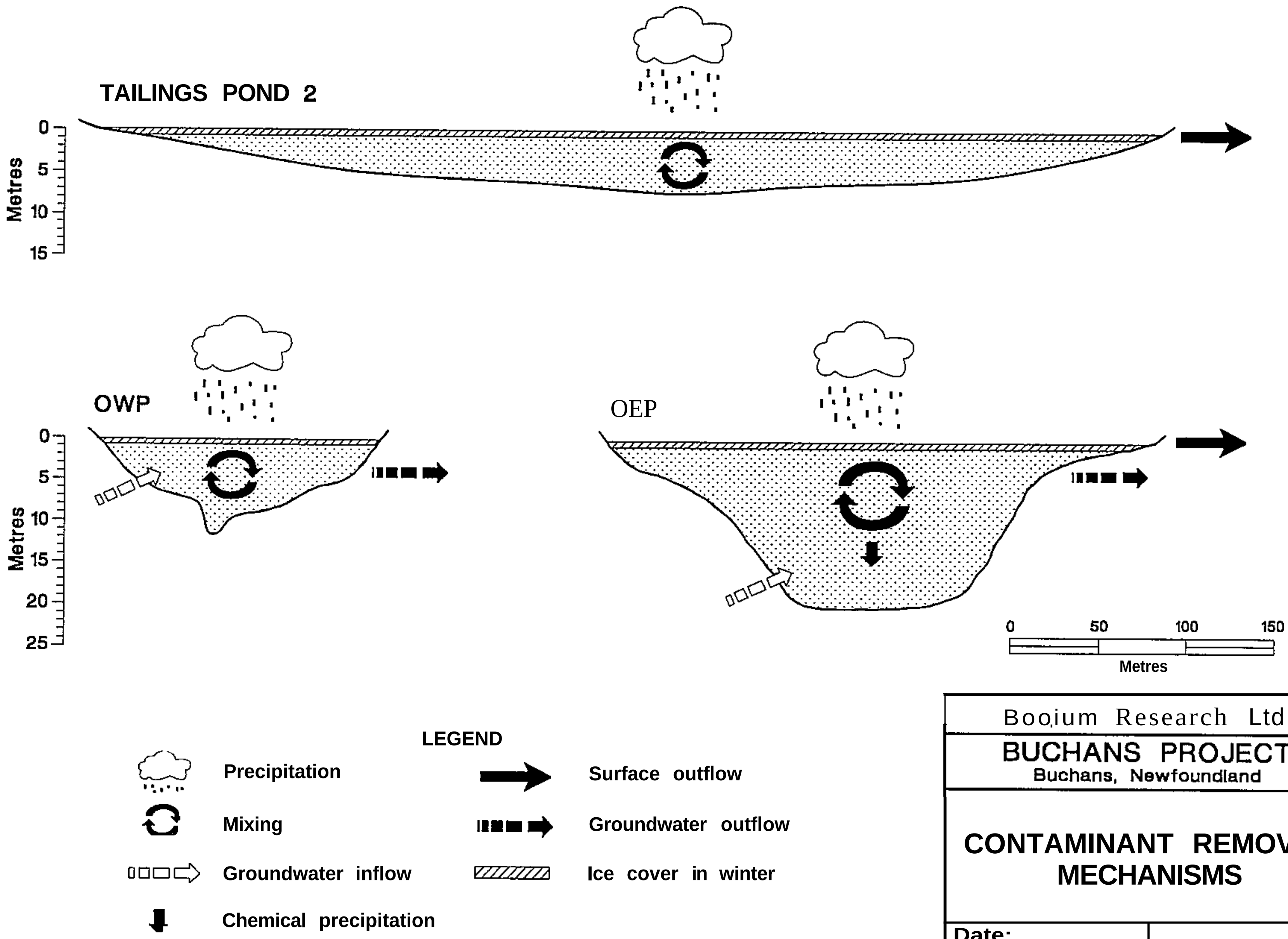
In the experimental work with biological polishing, phosphate and retention/ carbonate removal rates are mediated by different chemical processes. Chemical removal rates change with the zinc concentrations. In order to compare the rates of chemical removal in the OEP with and without the Ecol. Eng. measures (phosphate and biological polishing), it is essential that rates be derived for comparable time units, and represent only the beginning of the chemical process or the initial rate. The variety of time intervals available for regression suggested that a monthly interval would be the most appropriate time unit. For the OEP reduction slope, the regression was derived for the years 1987 to l990. Over these years, the regression indicated a negative slope of 1.2 mg/L/month. This slope is very similar to the regression based on the retention time/ carbonate experiments. In fact, it gives further confirmation that the proposed removal processes have been correctly identified. Due to the continues input of zinc to the OEP, this removal rate is not reflected in the monitoring data.

The zinc concentration decreases provide a moving target for the design of the treatment system, on one hand, and, on the other hand, can be used to predict the minimum requirement for treatment, i.e. that system which has to treat background concentrations. If we can predict with a reasonable degree of certainty that in year x the concentrations of zinc will reach 1 to 2 mg/L in the effluent, then the design of the treatment system can take this time component into account.

The removal rates derived from the slopes representing the chemical processes in Table 1 differ between the top and the bottom of the OEP, the OWP and of course for TP-2. This suggests that in these water bodies, the removal processes differ. For example if in all water bodies the retention time/carbonate were responsible for the removal process the rates would all be similar.

The removal rates in the effluents are governed not only by the geochemistry, but also the hydrology of the water body of concern. In identifying both the chemical and the hydrological mechanism which is most likely responsible for the contaminant reductions, it will be possible to determine the most successful method to assist the naturally-occurring reduction to achieve compliance.

It is necessary to identify the mechanism which lead to removal and/or reduction. The mechanisms are discussed below for the TP2, OWP and the OEP, and are presented in Schematic 1 as an overview.



Boojum Research Ltd.

BUCHANS PROJECT
Buchans, Newfoundland

CONTAMINANT REMOVAL MECHANISMS

Date: Dec./92
Schematic: 1

2.1 Tailings Pond 2

The investigations in 1991 lead to the recognition that most of the TP-2 tailings beaches are depleted of metals. The only potential source of contamination, the pore water in Beach 1, was identified. It was proposed that phosphate rock be used to decrease the permeability of the tailings, thereby reducing contaminant release. Although phosphate rock in the tailings precipitated iron and the proposed approach has merit, it was noted when pits were dug into the tailings that the water level in the tailings pits and the pond related very well to the evaporation data collected by G. Neary throughout the summer months of 1992. The results of phosphate rock testing in tailings pits are given in Appendix C.

In Figure 1, the water levels in TP-2, measured along the transect of the tailings pits, are compared to the water levels in the pits. Map 1 gives the location of the two holes in Tailings Beach 1. Evaporation was 147 % in June, and 102 % in July. If the water level in the holes (pits) responds in the same manner as the water level in TP-2, then a decrease in water level would be expected in June and July. Although this is the case up to the beginning of July, pond level and hole (pit) level do not correspond for the remainder of the observation period. This indirectly suggests that the permeability of the tailings inhibits any immediate connection between the tailings pore water and pond water.

As the outflow volume of TP-2 is controlled by the decant tower, the outflow volume and the pond level correspond extremely well (Figure 2). Inputs of water other then precipitation to the pond are likely minimal. Reductions in zinc concentrations in TP-2 could therefore be a function strictly of the water leaving TP-2.

If we assume that the pond has no new zinc source then we can calculate the expected zinc concentrations based on the annual volume of water leaving TP-2. The expected concentrations are plotted along with the measured concentrations in the pond from 1986 to 1992 in Figure 3. In the period from 1986 to 1989 the fit of these two curves was not as close as in the last three years (1990 to 1992), as the beaches were not yet depleted and provided a small zinc input. Measured concentrations were slightly higher than those calculated (exception 1987). The fit of the two curves, expected and actual, however, was perfect for the last three years. It is therefore concluded that the mechanism of zinc reduction in TP-2 is chiefly due to loss of zinc through the ouflow.

Fig. **1**: Comparison of water levels in
TP2, PIT 1 and PIT 3 (1992)

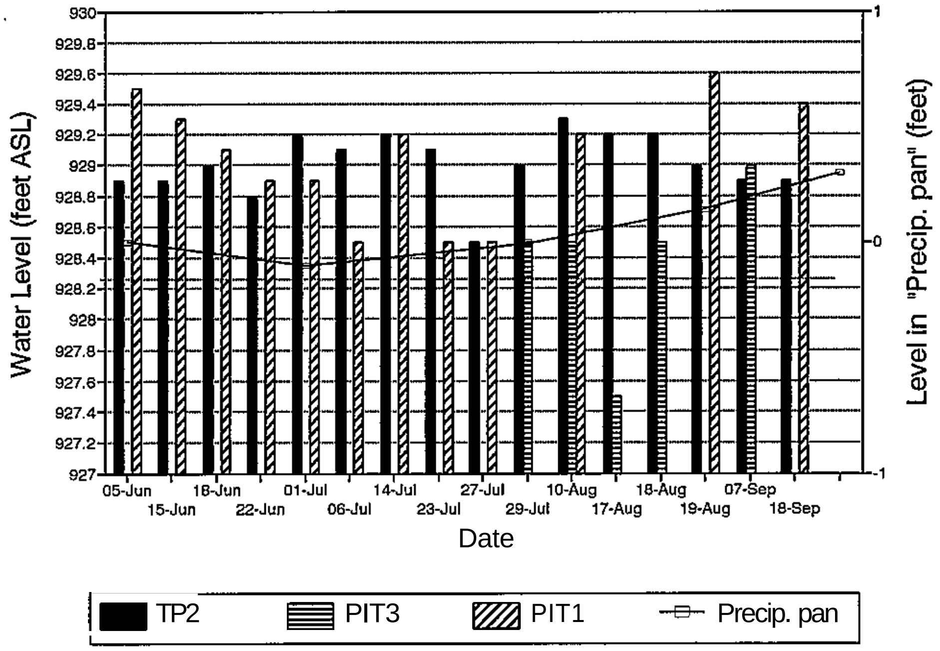


Fig. 2: Water level with outflow volume
Tailings Pond 2

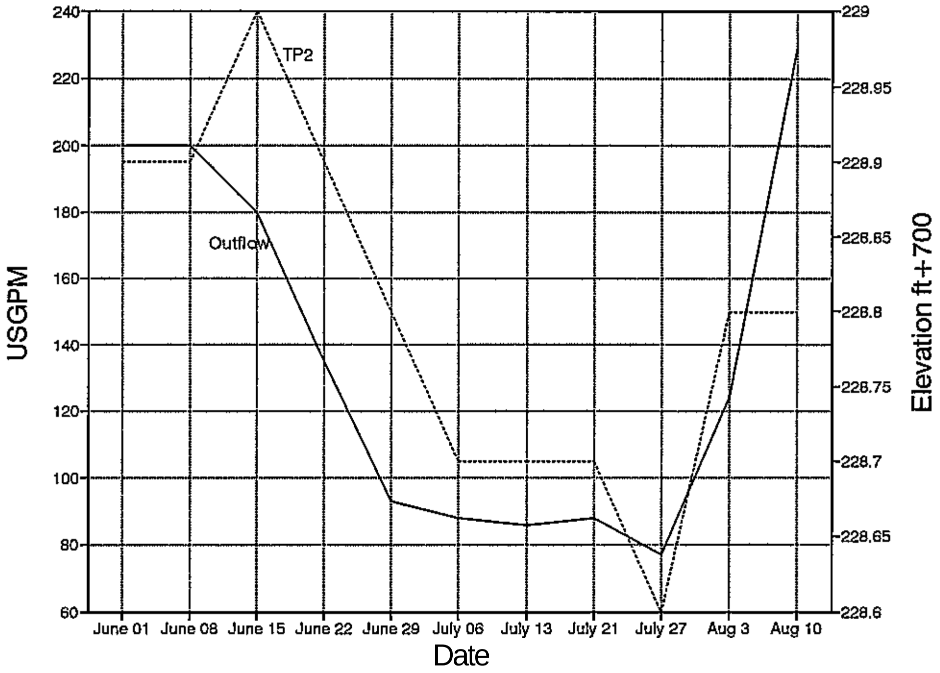
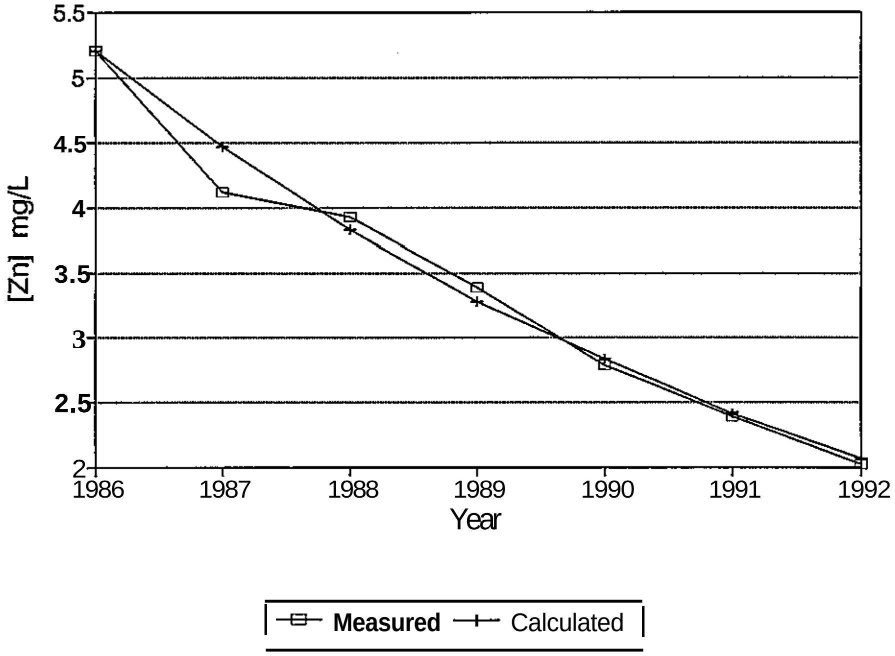
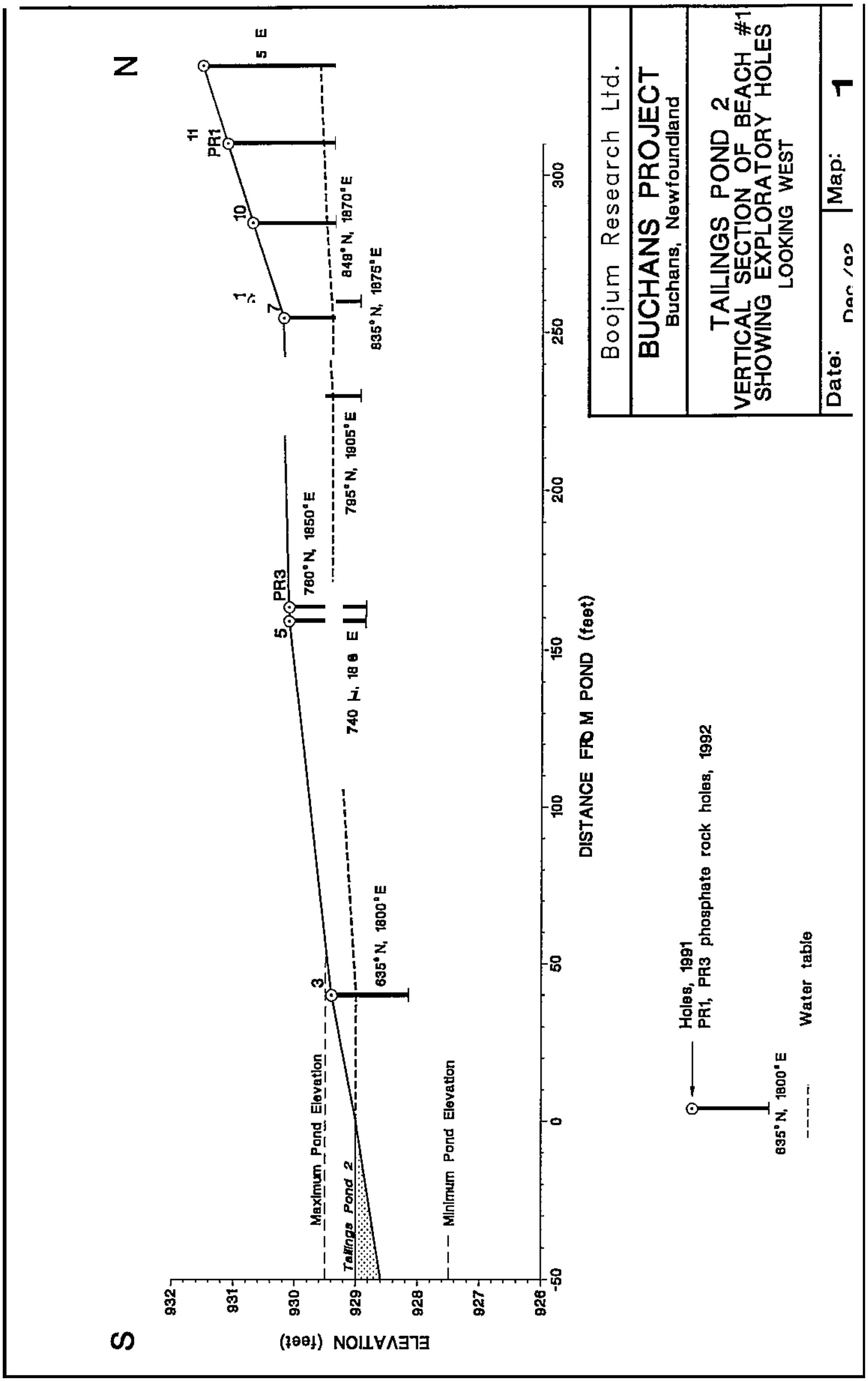


Fig. 3: Measured and calculated [Zn]
Tailings Pond *2*



Boojum Research Ltd.
BUCHANS PROJECT
Buchans, Newfoundland
TAILINGS POND 2
VERTICAL SECTION OF BEACH #1
SHOWING EXPLORATORY HOLES
LOOKING WEST
Date: Dec /92
Map: 1
S
N
ELEVATION (feet)
932
931
930
929
928
927
926
DISTANCE FROM POND (feet)
-50
0
50
100
150
200
250
300
Maximum Pond Elevation
Minimum Pond Elevation
Tailings Pond 2
3
635° N, 1800° E
5
PR3
780° N, 1850° E
740 [illegible] 186 E
795° N, 1905° E
7
835° N, 1875° E
10
848° N, 1870° E
11
PR1
5 E
635° N, 1800° E
Holes, 1991
PR1, PR3 phosphate rock holes, 1992
Water table

2.2 Oriental West Pit

Based on the investigations leading up to 1991, it was concluded that a connection between OWP and OEP was, at best, minor, due to the significant differences in chemistry of the two waters. Therefore it had to be assumed that contaminant sources to the two pits were different. That the sources of contaminants are different between the OEP and the OWP is also indicated by the different rates of zinc reduction between the OWP with -0.36 mg/L/month and the OEP with -1.22 mg/L/month (Table 1).

The water level in the OWP has remained steady for the last four years (Figure **4).** The water level in the OWP varied less than one half foot over the last **4** years, regardless of spring or fall runoff. In Figure 5, the zinc concentrations are plotted by month for the same four years. The repeated decrease in zinc concentrations to the same concentration of 2 mg/L between April and May each year, suggests that water with a background zinc concentration enters the pit (assuming that sampling depth has remained constant). The cooler ice melt water is overlying the contaminated pit water just before the pit starts to turn over in spring. The mixing process in the OWP pit is indicated by the same rate of zinc concentration increase each year in May and June. In Figure 5 the patterns of recovery are plotted for each year. The annual decrease in zinc concentration always occurs during the same time of the year, namely spring. The slope of the recovery to the new annual zinc concentration is essentially the same for each year. This would suggest that the amount of cleaner water added each year is very similar and that it enters the pit at a constant rate. Each year, the summer concentrations are decreased by the same amount (5 mg/L). Therefore, the next winter turnover starts with a lower total load of zinc remaining in the pit.

Presenting the same data along with the pH measurements for the same sampling dates (Figure ***6),*** it can be noted that, the low zinc concentrations in April and May are always associated with higher pH values. This higher pH can only be due to ground water input.

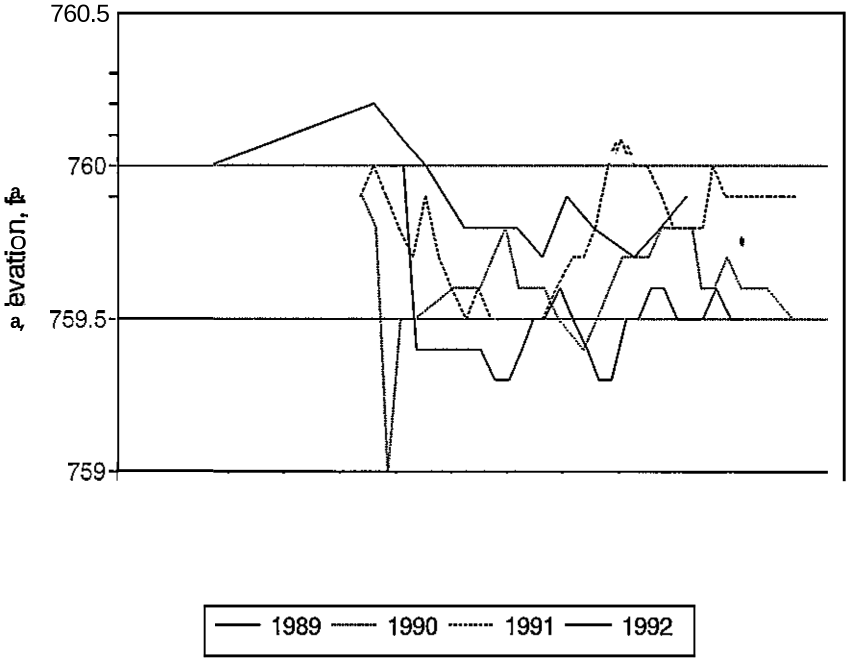
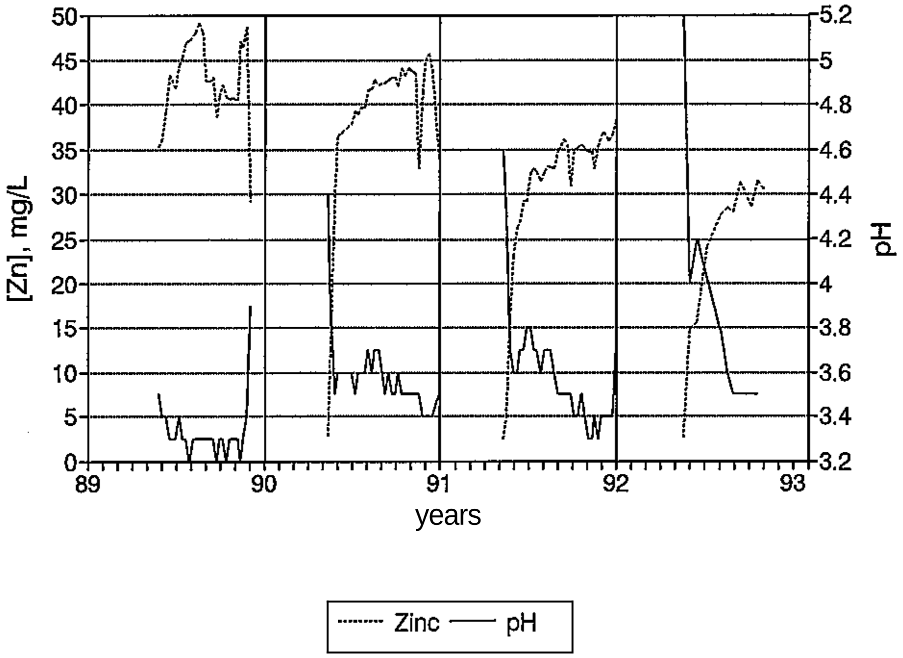


Fig. 5: Zinc ntration 1989-1992
Oriental West Pit

Fig. 6: Zinc concentration and pH
Oriental West Pit



The mechanism of zinc reduction in the OWP is due to an annually similar input of ground water which enters the pit below the pit water level, but not from the bottom. The reduction in zinc concentrations from year to year is therefore due to removal of some of the zinc with ground water which enters and leaves the pit. The amount of ground water entering and leaving the pit is very constant and relatively small, representing a decrease of 5 mg/L per year (Schematic 1).

The zinc reduction mechanism suggests that no significant new annual zinc loading enters the OWP. This can be further substantiated through comparison of the bottom and surface concentrations in water samples from the OWP. In Table 2, the available samples, both surface and bottom, are tabulated for selected elements. In May samples, both for 1991 and 1992, the differences in elemental concentrations between bottom and surface are very striking and suggest a dilution factor of 2 or 3. Elements in the bottom water have remained within the same concentration range over the last few years. In general, over the years, elemental concentrations in the bottom water have also dropped slightly due to spring runoff **and/or** ground water input. Acidities, iron, and sulphur concentrations suggest no new acid generation. Therefore, if the OWP is left in its present state, and not backfilled (as has been proposed), several advantages can be gained. The present seepage rates to the Buchans river, and those in the vicinity of the waste rock pile are expected to remain the same. As no new contamination is generated in the pit, the water body can be utilized for the treatment of the Drainage Tunnel water. In summary, the data indicate that for both TP-2 and OWP, no new contaminant loading takes place and background zinc concentrations of 1 to 2 mg/L can be expected.

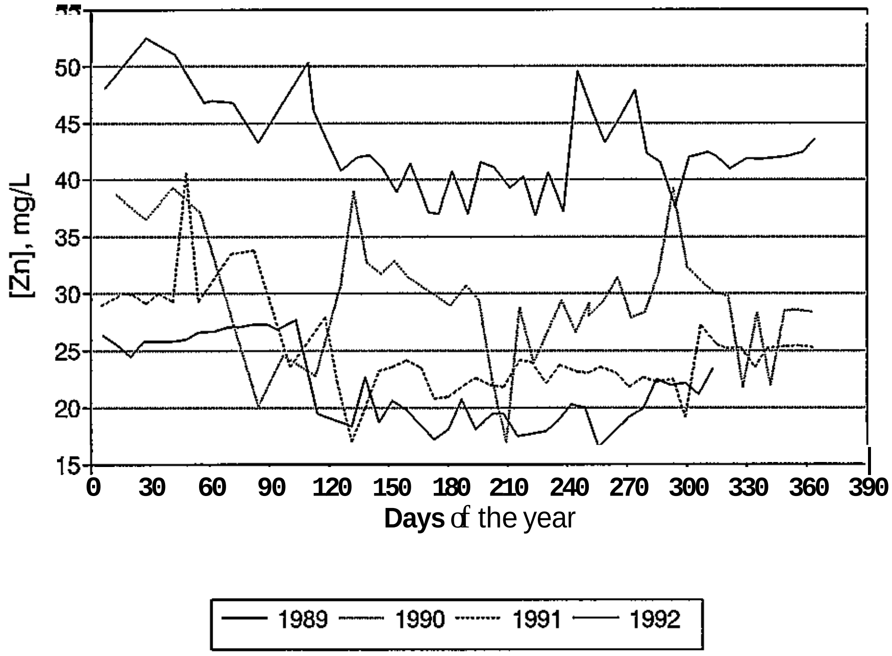
Table 2: Elements Distribution in Oriental West Pit

Date	pH	Acidity		Iron (Fe)		Aluminum (Al)		Zinc (Zn)		Sulphur (S)	
	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Jul-88				1.3	3.6	3.8	4.9	53	75	170	230
Jul-88				1.4	2.7	3.9	4.7	54	70	176	220
Dec-88					0.05		<0.01		55		195
Mar-89				0.1		3.6		48		169	
Jun-89				1.2		4.4		>10			
Aug-89					0.7		4.1		53		291
Sep-89				1.2		4.7		58		362	
Jul-90				1.2		3.8		39		120	
May-91	3.55	67	167	1.3	2.1	2.44	4.96	23.5	52.3	73.3	146
Aug-91	3.94	118	122	<1	1	7	6	33	33	107	107
Oct-91	3.72			1.5	1.3	7.4	7.2	39	37.3	119	105
May-92	3.55	38	138	0.9	3.2	1.6	4.2	15.4	50	52.4	144
May-92	3.7	37	110	0.8	1.4	1.45	6.35	12.4	35.1	47.3	114
Jul-92	4.13		57		<1		2.15		21.7		73.1
Jul-92	3.92	61.5	70	0.07	0.03	2.17	1.62	20.9	23.6	75.3	76.8
Sep-92	3.62		70.5	<1	<1	3	3	31.3	31.6	98	97

2.3 Oriental East Pit

This water body is somewhat more complex due to two conditions. First, a contaminant removal process is taking place through the formation of iron-precipitate which co-precipitates zinc. Second, a thermocline has resulted in the formation of a chemocline. This chemocline and thermocline separate the surface 4 meters from the water below 4 m. The thermocline separates water with different temperatures, and the chemocline separates water with different chemical compositions. Based on slopes calculated using annual averages (Table 1), the zinc concentration has been decreasing in the OEP since 1987 by about 1.22 mg/L/month. However, the trends from June 1989 (day 180) onward to the end of each year up to 1992, indicate a positive slope, showing on the average, an increase of about 0.38 mg/L/month over the summer season. This behaviour is connected to the annual thermocline development which gradually brings the zinc from the completely mixed pit to the surface layer.

Fig. 7: Zinc concentration
Oriental East Pit



Thermocline temperature data are presented by month of the year over the last 2 years in Figure 8a and for the same months over 4 years in Figure 8b. The thermocline which is at 4m during the summer is absent by October, when the entire pit has a temperature of between 6 and 8 degrees. Temperature profiles measured in March 1989 and April 1992 along the J transect of the pit (Map 2) indicated that the near surface water cools underneath the ice, but the water at the bottom of the pit remains between 5° and 9" C (Figures 8c,d). If ground water in the drill holes and Drainage Tunnel has a temperature ranging from 6° to 9° C, then the water temperatures below the summer thermocline in Oriental East Pit are probably caused by an intrusion of ground water. In Figure 9, the temperature of the OEP outflow water is plotted seasonally along with the steady Drainage Tunnel temperatures (5 - 7 °C). It is evident that, since 1989 temperature in the OEP has also decreased slightly.

As the pit slowly filled over a period of 2 years and 2 months, it would have warmed up considerably with the backfilling of the aquifer, especially over the summer. In addition, the pit was force flooded with warmer, oxygenated water. From 1988 onward, the thermocline in the top 4m started to separate surface water from bottom water. The bottom of the pit, however, received colder ground water at a volume and rate considered equivalent to the outflow rate of 10 L/s. Thus, gradually over the last two years, the depth of the thermocline and the length of time over which the pit is completely mixed has increased. The increasing similarity between bottom and surface temperatures would allow the ground water inflow to mix the water body more thoroughly during the ice covered period.

Concentrations of iron have been increasing below the thermocline for a couple of years. This means that there will be higher concentrations of iron available to precipitate as hydroxide and coprecipitate zinc-carbonate once the ice cover has melted. Thus, a further reduction of zinc leaving the OEP outflow is expected in 1993. At the bottom of the pit, water with a low oxygen concentration and low Eh provides the reducing conditions which facilitate the reversion of ferric-hydroxide back into

Fig. 8a: OEP Centre Profiles
Temperature

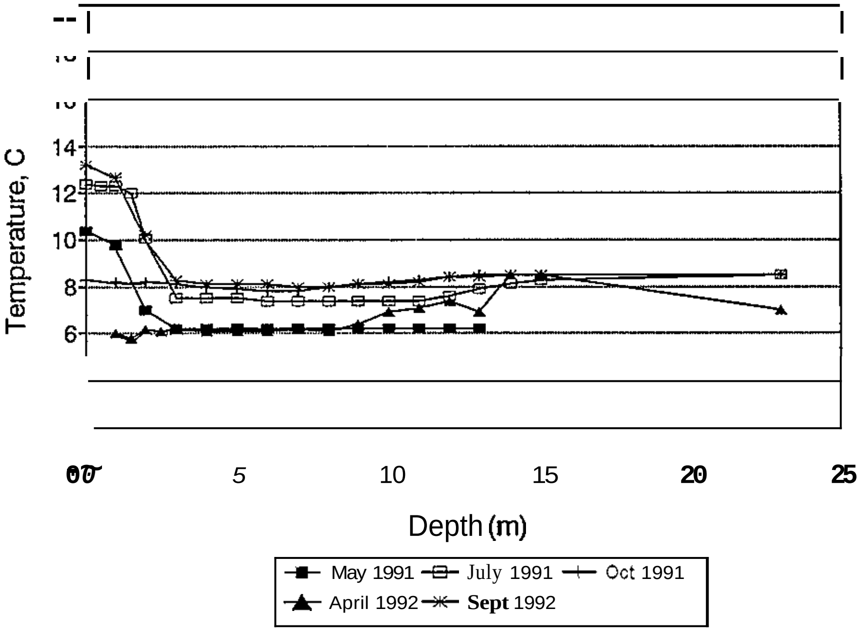


Fig. 8b: OEP Centre Profiles
Temperature

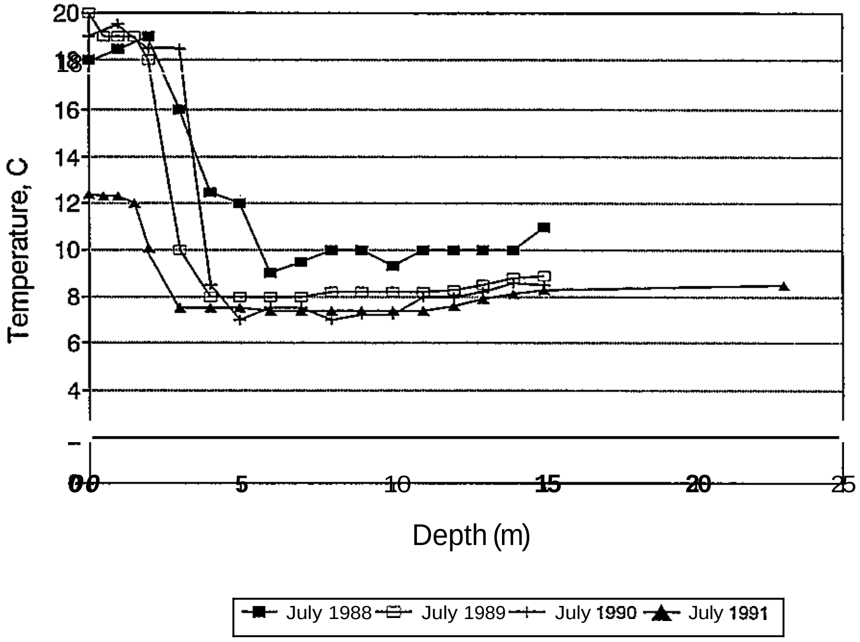


Fig. 8c: OEP Temperature Profile
March 1989, J Series

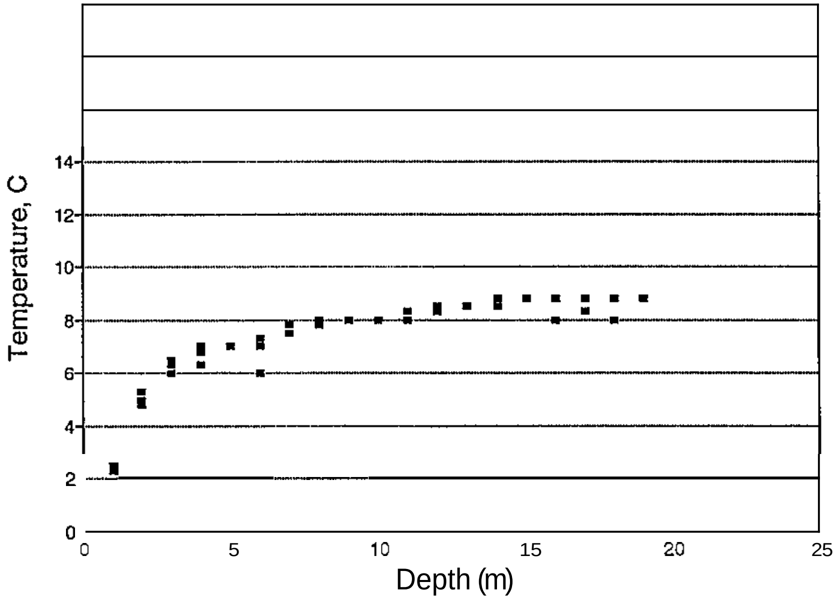
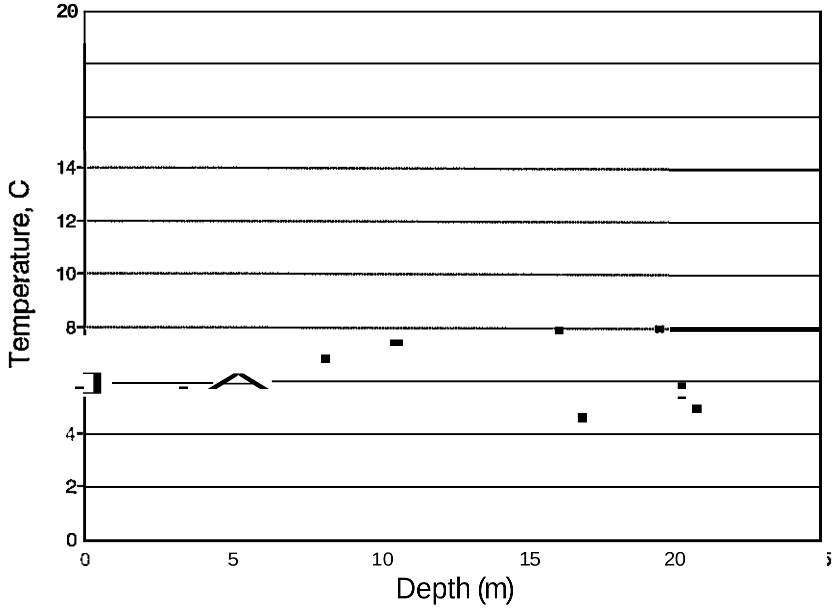
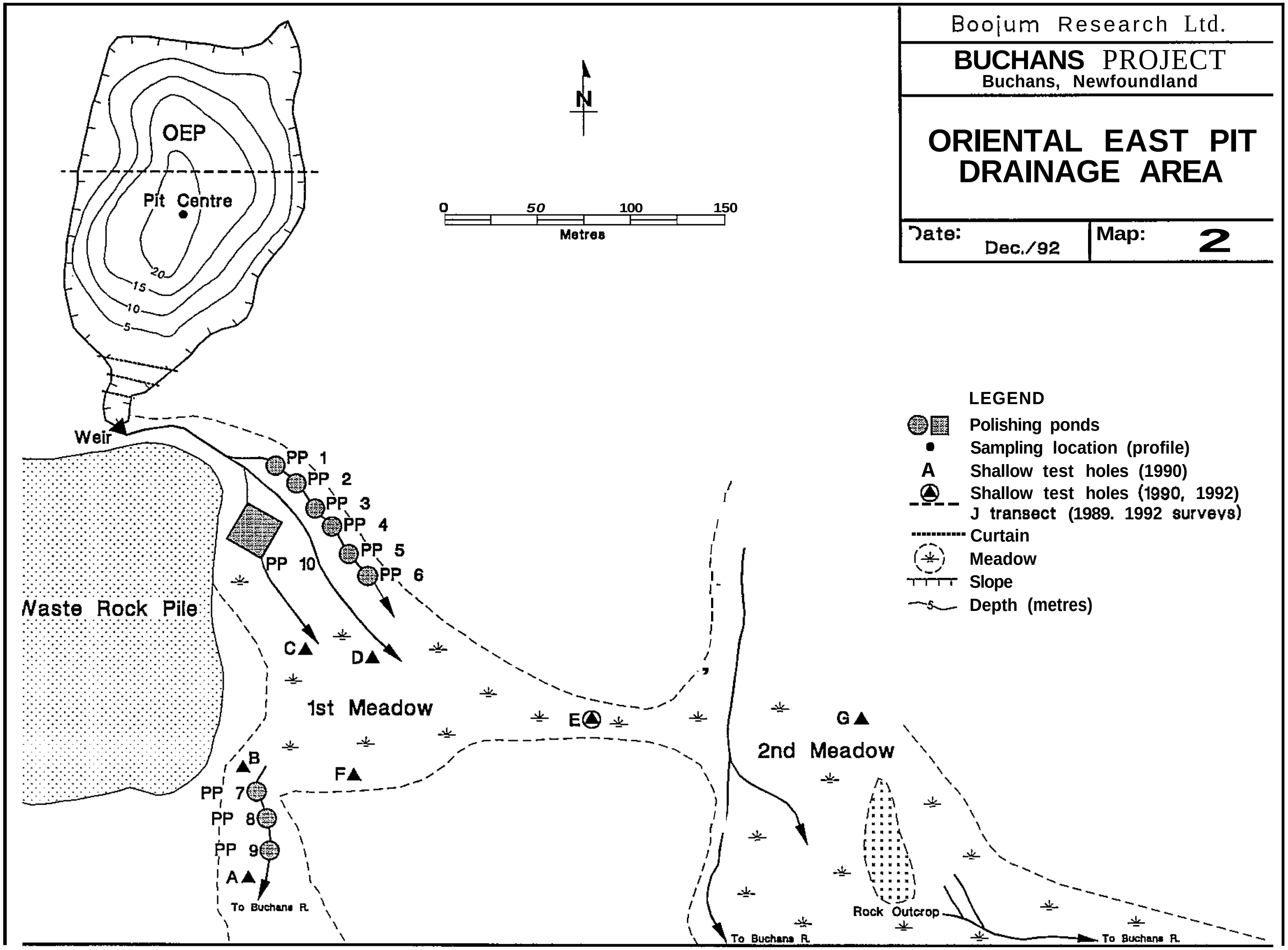


Fig. 8d: OEP Temperature Profiles
April 1992 J Series





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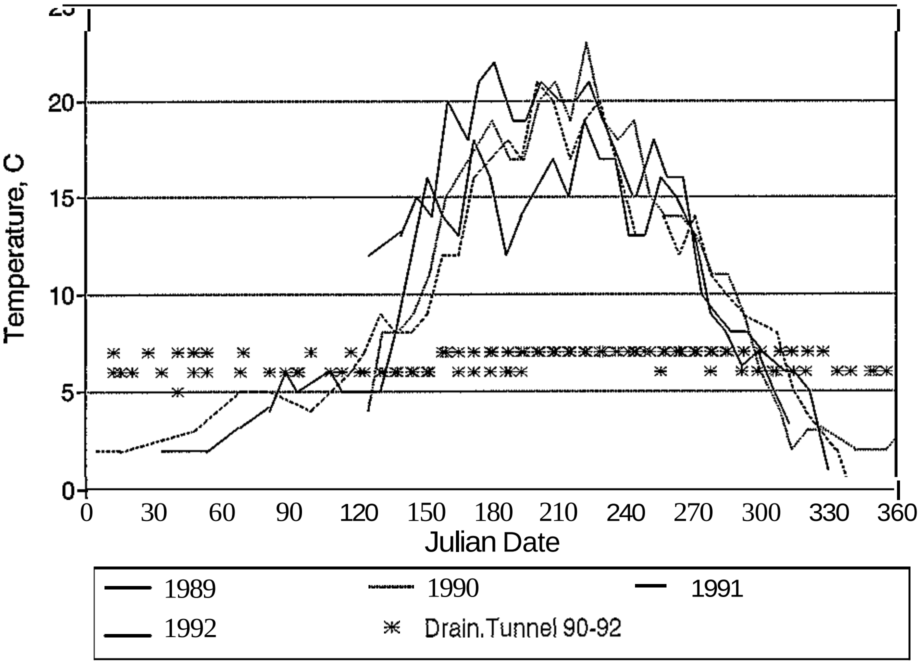
Buchans, Newfoundland

ORIENTAL EAST PIT DRAINAGE AREA

Date: Dec./92 **Map:** 2

Fig. 9: OEP Outflow Water Temperature
1989- 1992



ferrous-hydroxide, which is soluble at the prevailing pH. The end result is that dissolved iron concentrations rise at the pit bottom.

Increased iron precipitation is occurring as indicated by the data collected from the sedimentation traps. The sedimentation rates based on the material trapped at the bottom of the pit increased from a range of 0.05 tonnes/day in 1991 to 0.35 tonnes/day in 1992.

The differences in water chemistry between surface and bottom samples are presented in Table 3. The differences are striking and very consistent. At the time when the spring flush occurs, and the pit turns over, water from the bottom is moved through the pit and diluted by melt water (note early spring samples in Table 3). Water with characteristics of bottom samples leaves the pit during the winter months.

Table 3: Elements Distribution in Oriental East Pit

Date	pH	Iron (Fe)		Aluminum (Al)		Zinc (Zn)		Sulphur (S)	
	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom	Surface	Bottom
Jul-88		0.08	58	0.3	0.3	47	61	398	508
Dec-88					0.09		33		443
Mar-89		0.01		0.01		31		380	
Jun-89		0.6	21.8	<0.2	<0.2	>10	>10		
Aug-89			36		0.01		45		875
Sep-89		0.01		0.03		37		825	
Oct-89		2.8		0.3	0.1	37	38	366	386
Oct-89		8.7		0.3		36		373	
Jun-90		0.02		0.08		29		432	
Jun-90		0.02		0.04		27		427	
Jul-90	6.4	6.1	56	<0.01	<0.01	30	40	312	383
Jul-90	6.9		42		<0.01		38		378
Jul-90	6.05	4.4	68	0.03	0.1	30	41	329	400
Jul-90	6.07	0.3	46	0.06	0.1	28	39	339	407
May-91	6.77	2.2	61.2	0.31	0.05	24	35.1	277	419
Aug-91	6.28	1	60	8	12	19	30	303	415
Oct-91	6.28	1.5	88.9	9.9	12.4	20	33.2	297	479
May-92	6.04	10.2	86.7	<0.1	<0.1	21.8	30.5	300	418
Aug-92		<0.005		<0.03		14.1		280	
Sep-92		<1	79	<1	<1	20.5	30.2	330	446

This can be further substantiated by an examination of the seasonal trends in temperature and pH of the water leaving the OEP. The bottom water ranges in pH between 6.90 and 6.04 (Table 3). The pH of the outflow between January and April has the same range (Figure 10). During the summer, the pH of the OEP outflow gradually increases to a range of 6.8 to 7.2. During the summer when a thermocline has developed more water from the surface leaves the pit. The mechanism of zinc reduction in the OEP is therefore driven by: a) the thermocline development; b) precipitation with iron; and c) a constant ground water input.

The ground water is travelling through the ore zone in which the supply of precipitates produces a slow decrease. In the years 1988 and 1989 the decrease in zinc

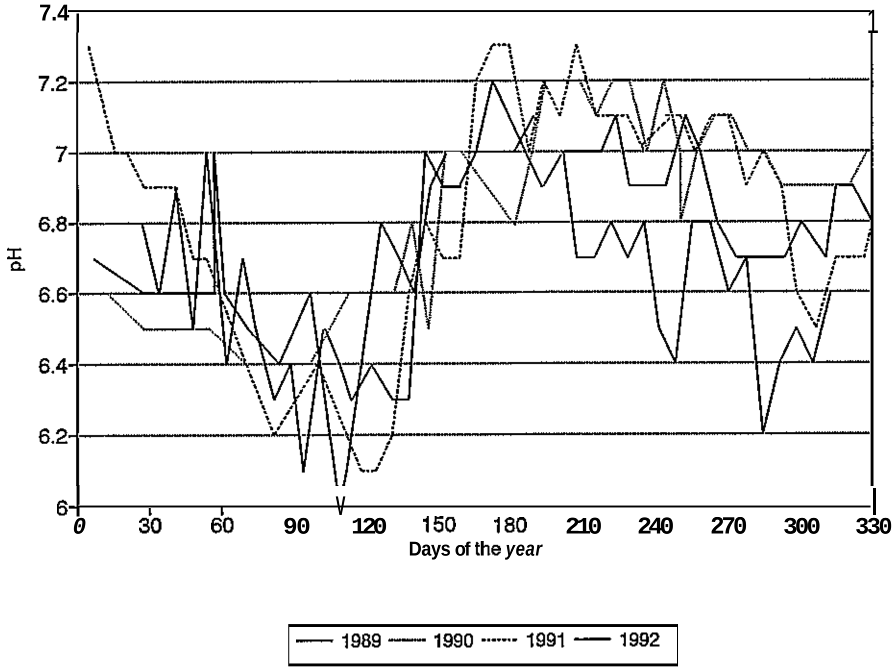
Table 4: Acidity and Alkalinity

Date	Acidity	Alkalinity
04-Oct-89	61	33
27-Jul-90		160
18-OCt-90		50
28-May-91	40	134
05-Jul-91		163
23-Aug-91	94	221
05-Jun-92	96	167.5
24-Aug-92	41	183
28-Sep-92	45	193.5

concentrations was higher. This was because the original water contained zinc which was dissolved from the pit walls, and the pit itself filled up with water with lower zinc concentration. This explains the steeper decreases in zinc concentrations in the early years. The thermocline started to establish itself at **4** m and the warmer water was being moved out of the pit and replaced by colder ground water. It can be expected that the pit will be mixed from now on each winter and the zinc reductions noted over the last two years are representative of the long-term trend.

It is also reasonable to assume that AMD generation has stopped in the underground workings, due to flooding with ground water with a low oxygen content and high alkalinity (Table **4). As** long as the ground water continues to bring in alkalinity, the situation in the OEP will not change. Although data on alkalinity and acidity are scarce, they are summarized in Table **4.** No obvious trend is noted. In 1989 drill core records were examined in the vicinity of the Oriental pits and calcite was found to be present in the drill cores. The total amount of calcite, however, could not be quantified. Its presence at least indicates a natural supply of alkalinity.

Fig. 10: OEP Outflow pH
1989-1992



To assess if this assumption is reasonable (i.e. that **AMD** is no longer being generated in the underground workings), the Drainage Tunnel monitoring data were used. In the Drainage Tunnel, the walls are exposed and the mine slimes are pyritic. The result is a steady zinc concentration in the effluent over the last three years, along with expected seasonal pH fluctutations (Figures 11 a and 11b).

Given the absence of further acid generation in the underground working then the estimates of zinc depletion in the underground can be calculated based on the data available for the OEP.

To arrive at estimates of zinc depletion in the underground workings from the precipitate formed at the time of flooding it is assumed that the only mechanism of removal of zinc in the OEP is that of zinc precipitation. It was **s** measured with the sedimentation traps in the pit in 1991 and 1992. This assumption leads to a conservative estimate due to the expected increases in iron concentrations in the bottom of the OEP. However the precipitation rate can be confirmed with further measurements in 1993.

Fig. 11a: Zinc concentration 1990-1992
D Tunnel

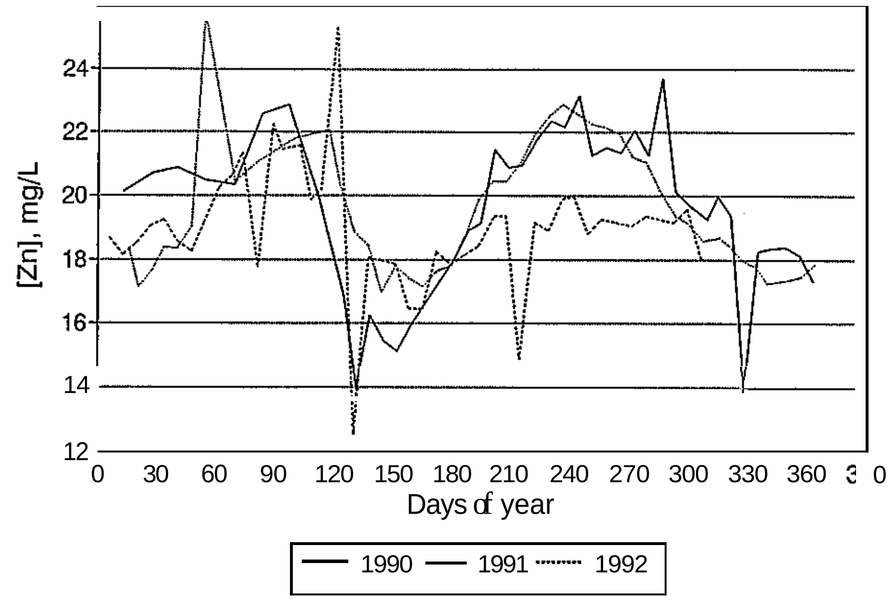
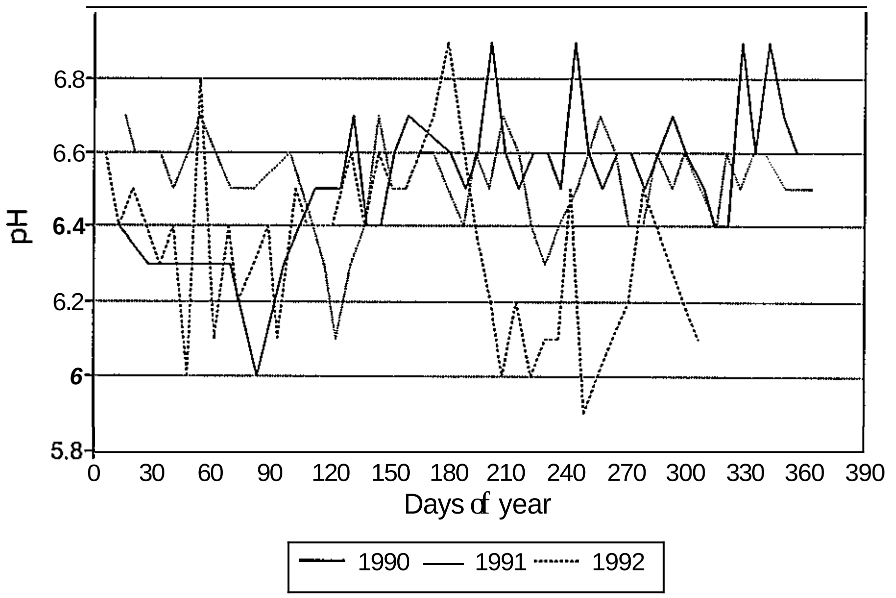


Fig. 11b: pH 1990-1992
Drainage **Tunnel**



Zinc loadings which have left the OEP to the first meadow in 1988 to 1991 were used to derive those loadings which we expect the polishing pond to treat in the future.

It is reasonable to assume that the zinc concentrations at the bottom of the OEP are those concentrations entering the pit (Table 3). We further assume that the bottom concentrations times the total volume of pit is representative of the original mass of zinc in the pit (1988). The flow rates out of the pit times the zinc concentration is the actual load of zinc leaving. It is also reasonable to assume that the flow entering the pit for the years 1988 to 1992 is the same as the flow leaving the pit.

The zinc decrease in the incoming water, i.e. that entering or incoming concentration to the pit is calculated as follows:

$$\text{INCOME(yr)} = \text{TOTAL(yr+1)} - [\text{TOTAL(yr)} - \text{OUTFLOW(yr)} - \text{PPT(yr)}].$$

The expression in brackets describes the amount of zinc which stays in the pit. This amount is a result of that zinc leaving the pit OUTFLOW (yr) and that zinc which is removed as precipitate to the bottom of the pit PPT (yr) and the amount which was there in the previous year TOTAL (yr).

Given that we have monitoring data from 1987 to 1992 and loadings removed by the precipitation process in the pit, we can mathematically derive TOTAL (yr+1) and calculate INCOME (yr). This will allow us to estimate the reduction in the zinc loading leaving the pit (Table 5a, page 26). Thus, the predictions are based on actual data - the rates of removal of zinc measured in the sedimentation traps, measured outflow loadings, and measured concentrations at the bottom of the pit.

If we assume that the iron-hydroxide precipitation rate and the zinc co-precipitation rate, will continue at the 1992 level of 948 kg per year, then the zinc concentration in the outflow will be reduced significantly by 1995. However, it is likely that the concentrations leaving the pit will drop even faster, since the amount of iron which remains in the pit through precipitation will increase with time. The zinc precipitation was calculated based on the zinc concentrations in the material collected in the sedimentation traps. Utilizing these calculations, the decreases in zinc loadings can be predicted. In 1995 the zinc loading from the OEP will be significantly reduced, from a total loading of 8 tonnes in 1992 to about 2.5 tonnes.

Iron-hydroxide, formed in the upper part of the pit, redissolves as it enters reducing conditions below the thermocline. Zinc co-precipitates as zinc-carbonate and remains in the bottom sludges. Thus, the pit will serve as a zinc precipitation pond.

With an understanding of the mechanisms which contribute to the reductions in all three water bodies, OWP, OEP, and the TP2, predictions can be made on future zinc concentrations. These predictions assume that no major changes take place in the hydrological conditions of the water bodies. The predictions are presented in Table 5a for the OEP and in Table 5b for OWP and for TP-2. For the OWP, zinc reductions were calculated from slopes which were derived during the summer months, i.e. without taking the spring decreases into account. It suggests that by 1995, only half of the present loading in the pit in 1992 will remain. The zinc load will have dropped from 1.7 tonnes to 0.8 tonnes. The calculations for TP-2 suggest that we will reach the background concentration of 1 mg/L of zinc, by the year 1994 (Figure 3 and Table 5b).

The compliance schedule dictates that the zinc loading to the Buchans River is to be reduced by 1994. The above analysis of the monitoring data indicates that zinc loadings will be significantly reduced to an annual loading of 6.5 tonnes by 1994, and by 1995, the total loading will be reduced to 4.3 tonnes of zinc from all these sources.

To confirm the above deductions, it is recommended that bottom and surface samples be collected from both the OEP and the OWP throughout the winter months of 1992/93. Optimally, these would be submitted for ICP analysis. Minimally, iron and zinc concentrations should be determined.

Table 5a: **OEP** Zinc Balance and Predictions

Year	Total Bottom kg/year	Outflow kg/year	PPT kg/year	Income kg/year
1987		12647		
1988	12700	20310	474	16724
1989	8640	14721	474	14571
1990	8016	11861	474	11141
1991	6822	9991	948	10436
1992	6319	8121	948	8566
1993	5816	6251	948	6696
1994	5313	4381	948	4826
1995	4810	2511	948	2956
1996	4307	641	948	1086
1997	3804		948	

Table 5b: OWP and TP2 Zinc Loading and Predictions

Year	OWP kg/year	TP2 kg/year
1987	3144	4117
1988	2902	3925
1989	2757	39
1990	2564	2787
1991	2051	2387
1992	1716	2020
1993	1434	1500
1994	1152	1000
1995	869	
1996	587	
1997	305	

3. BIOLOGICAL PROCESSES

3.1 Biological Polishing

Zinc reductions have been quantified in the experimental pools, 1-6. With the available data set now covering three growing seasons, it is possible to formulate an understanding of the system. The biological polishing system for the Buchans effluents can be summarized as follows.

The iron precipitate-laden OEP effluent carries zinc both dissolved and in the form of a co-precipitate. The precipitates adhere to the algal/moss mat which grows on the surfaces provided by the brush. As residence time in the pools is increased, photosynthesis causes an increase in pond water pH, and dissolved zinc precipitates as zinc-carbonate. A small proportion of the dissolved zinc is adsorbed onto algal/moss surfaces. After sufficient growth and precipitate accumulation has taken place, the mat, laden with precipitates sloughs off and settles to the bottom of the polishing pond.

Details on the removal process are summarized in the paper by Kalin and Wheeler (1992) which is given in Appendix A. If one of the components of the removal process is the accumulation of precipitates on the biological polishing surfaces, then it follows that the formation of precipitates is a key factor in the process.

Growth of the biological polishing agent is providing surface area which is mainly renewed during the summer months. Hence the system will perform during the winter months, but at that time the process works only with the existing surface areas, no new surface area is added. However, the data indicate that during the summer months photosynthetic activity of the algae greatly enhances precipitate formation and hence biological polishing.

In Figure 12 the growth of the mats (Periphyton Precipitate Complexes - PPC) is given, covering also the winter months for the first time. Growth was assessed with peritraps which remained in the ponds over the winter months (see 1991 report for description of peritraps). Large increases in growth rates were noted for September. This is due to fertilization of the ponds which was carried out to confirm the findings from the previous year. With respect to maintenance of the biological polishing, nutrients assist in the development of surface area, and can be used to obtain increased performance, if required.

In the TP-2, where it is also proposed to utilize biological polishing, a lower performance should be expected, since there is much less precipitate formation, because zinc concentrations are controlled by the solubility of the CO, from the air into TP-2 water. The algal biomass from the TP-2 enclosure, which was set up in 1991, was collected several times during 1992. Comparisons of the biomass obtained with biomass collected from the polishing ponds suggests that the amount of TP-2 biomass was similar to that found in the first year in the ponds (1990; Figure 13).

A large increase was obtained in the last sampling interval of the year after fertilizer was added in July. Later in the year, the algae in TP-2 were covered with a grey precipitate. It was suspected that the algal surfaces were accumulating fines which resembled tailings. In Figure 14, the elemental composition of the enclosure water is compared to that of the algal complex (PPC) and that of a tailings sample collected at the beach. The tailings and the PPC have a very similar composition, suggesting that, indeed, the algae collected tailings fines. Together with the long retention time in the TP-2 of 4.5 years, which facilitates the formation of zinc-carbonate, biological polishing will provide a sink for the zinc and the tailings fines. The growth which was achieved through the addition of the fertilizer to the enclosure in TP-2 is shown in Figure 15.

From the preceding discussion it can be stated that, in principle, biological polishing of "precipitates" applies to both effluents, the OEP being dominated by precipitates formed by iron and in the tailings pond being dominated by tailings fines. For both the

Fig. 12: Buchans Peritraps
PPC Growth (Oct 1991-Sep 1992)

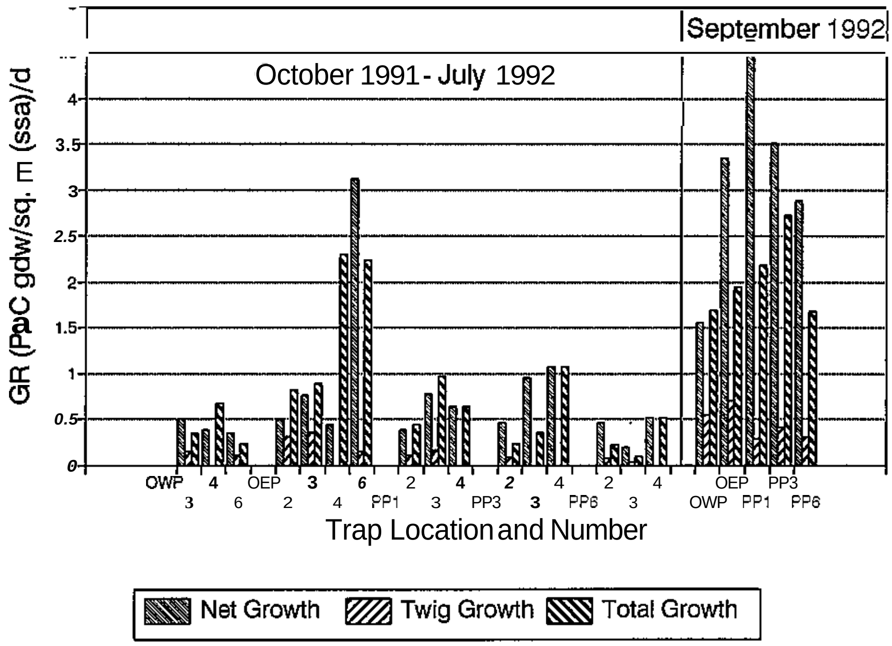


Fig. 13: Historical PPC Growth
Polishing Ponds and TP2

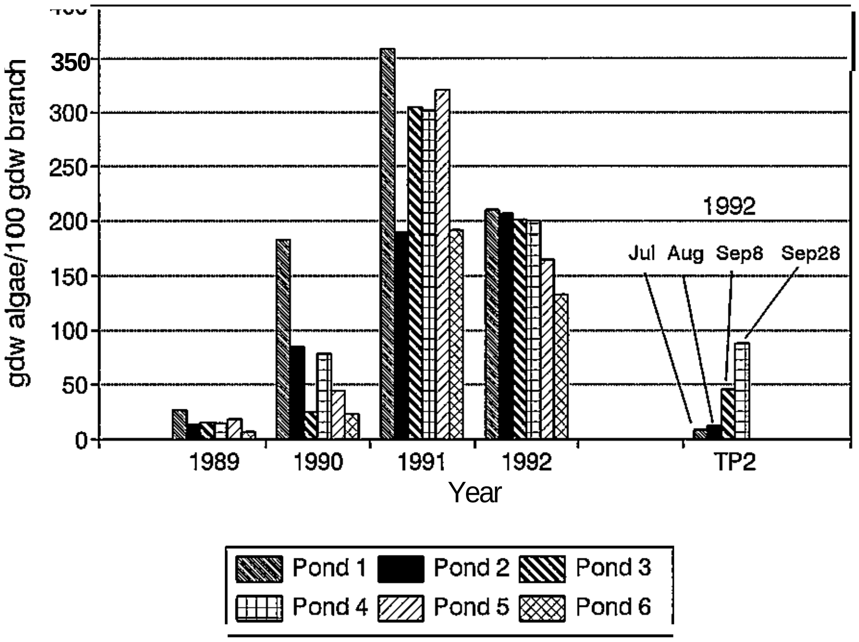


Fig 14: Elemental Scans, TP-2
Water, PPCs, and Tailings

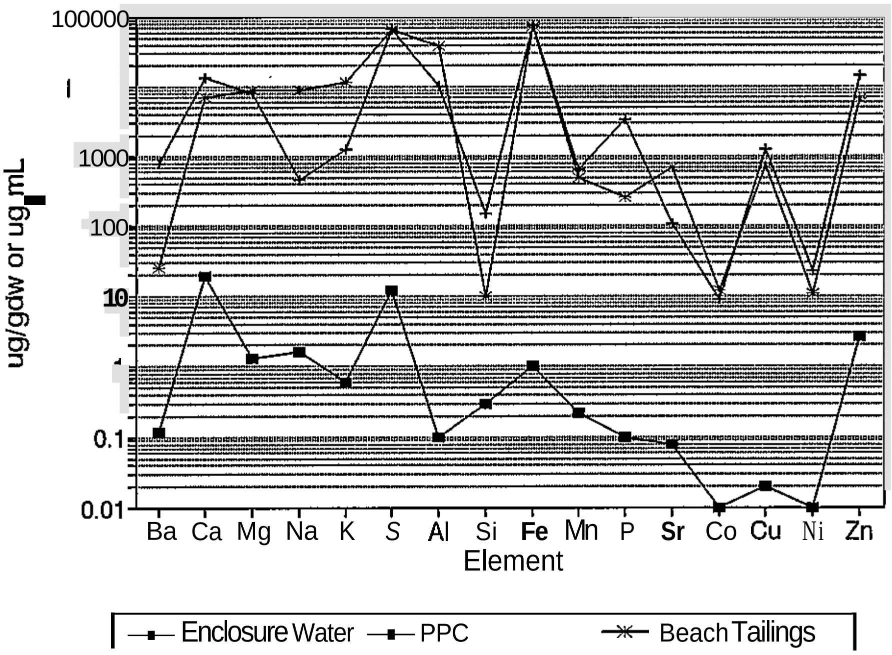
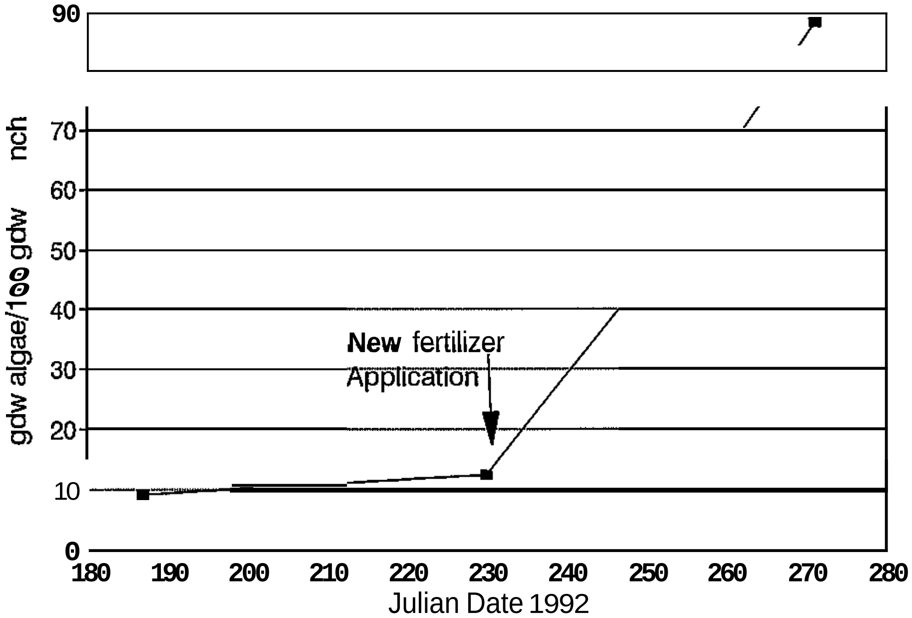


Fig. 15: Tailings Pond 2
Algae on Branches



effluents, PPC "sticky" surfaces trap precipitates of a different nature. The fractionation with respect to the function of the PPC surface is estimated as 71 % tailings or iron precipitate accumulation on the surface and 29 % biologically-mediated precipitation ladsorption and uptake of zinc onto the algae.

In Table 1 zinc removal rates were calculated to be 18.9 mg of zinc/L/month based on zinc reductions observed between pool 1 to 6. This represents an increased rate over last year, since the 1992 performance was improved. The data used to derive the regression are plotted for 1991 and 1992 in Figure 16, correlating zinc concentrations with retention time in the pools. The removal rates in Table 1 are those based on chemical and biological processes. The biological polishing rate was the highest of any process. Since, in this removal process, all other removal processes are working together, this result was expected. This biological polishing is the summation of phosphate (fertilizer), zinc-carbonate (enhanced through photosynthesis), and adsorption onto the surfaces as well as co-precipitation with iron. Retention time or zinc-carbonate precipitation alone produced a reduction rate of 1.3 mg Zn/L/month. This reduction rate is based on the carbonate precipitation which occurred during storage of the samples in the laboratory (data presented in the 1991 report, Figure 3-3). Phosphate treatment resulted in a reduction rate of 12.9 mg Zn/L/month. Details on the calculations for the phosphate rate are given in appendix C.

In summary, by increasing the retention time, increasing the pH (through biological activity and fertilizing) it is evident that all processes work together. As they are all interconnected, it is difficult to account for each individual contribution.

In Table 6a the results of the first round of the biological polishing model calculations are presented for the loadings of 1992. This version essentially considers current conditions as a worst case scenario. Assuming 20 mg/L zinc and a flow of 12.8 L/s with a retention time of 14 days, the pond size required would be 4.2 ha. This would cover all of the First Meadow (2.9 ha) and part of the Second Meadow (5.6 ha). If we

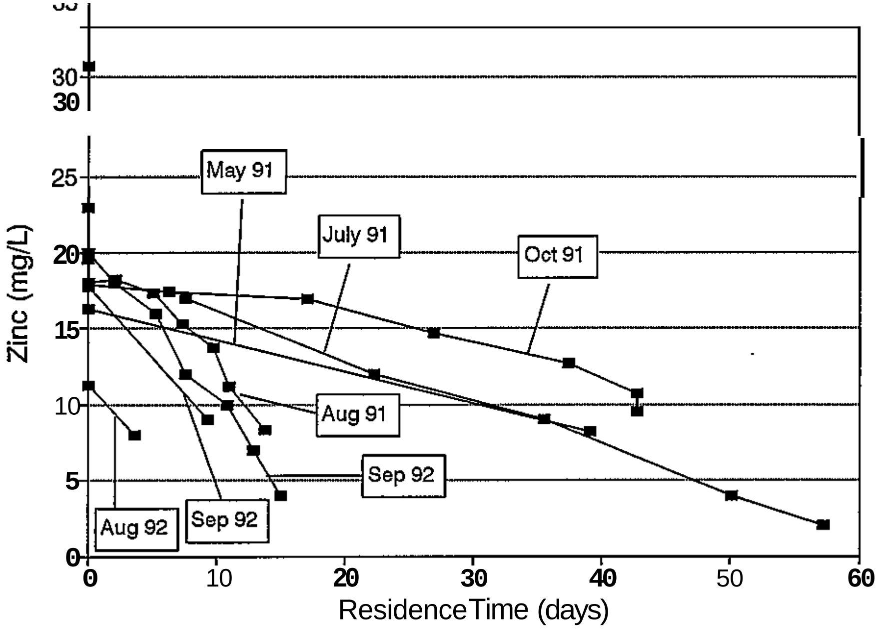


Fig. 16: Zinc Decreases
Polishing Ponds

take background concentrations projected to be around 2 mg/L, the extrapolated pond size would cover an area of 0.4 ha. The highlighted areas in Table 6a and 6b also indicate the number of alder "trees" and the zinc loading which is expected to be removed. The new pond, Pond 10, which was constructed in 1992, should be used to confirm the predictions. It is depicted in Plate 1. With the 1992 zinc concentrations, the flow into the pond should be reduced to 0.3 L/s which should result in Pond 10 removing 68 % of the annual loading to Pond 10, which is 1.8 % of the total outflow from the OEP.

If we consider the natural reductions in the OEP and assume an outflow with a zinc concentration of 2 mg/L, Pond 10 would, at the same flow rate (0.3 L/s), remove more than 100 % of the annual loading. Therefore, we adjusted the flow rate to achieve a 78 % removal of the annual zinc load (i.e. final effluent <0.5 mg/L). At that removal rate, the flow into the pond can be increased to 2.3 *Us*. This would represent a treatment of about 16 % of the total outflow from the OEP.

Table 6a and 6b, as indicated before, are a first cut of the model which we are completing by March 1993 under the CANMET supported contract. For the model, the data and parameters which are used on each line will be referenced. Although the entire model description is not completed at this time the essential framework for the decision-making process is provided.

Table 6a: Polishing Pond Extrapolations
(Residence Time - 14 days, OEP [Zn] - 20 mg/L)

1	DENSITY OF PPC IN LAB AND FIELD	3	kgfw/cu. m
2	DRY TO FRESH WEIGHT	0.61	kgdw/kgfw
3	GROWTHRATE	0.0126	/d
4	AVG PPC ZN (1992)	62	g/kg
5	VOLUME OF POND 10	320	cu. m
6	MINIMUM REQUIRED RESIDENCE TIME	14	d
6a	OEPFLOW	12.875	L/s
6b	OEP ZN CONCENTRATION	20	g/cu.m
6c	OEP Zn LOADING (1992)	8121	kg/yr
6d	OEP Zn LOADING (1992)	22.2	Kg/d
7	Periphyton Zn removal Capacity	1.4	g Zn/cu. m of pond/d
8	Periphyton Zn removal from system	347.4	g Zn/system/d
9	Periphyton Zn removal from system	62.5	kg Zn/system/yr
10	Average Zn loading Pool 1-6 (1992)	166.7	kg/yr
11	Average Zn leaving Pool 1-6 (1992)	88.8	kg/yr
12	Average Zn remaining in Pools 1-6 (1992)	77.9	kg/yr
13	Zinc removal rate	320.4	g Zn/cu. m/yr
14	Zinc removal rate	114.5	g Zn/tree/yr
15	Trees required to remove Zn load	70,916	
16	Projected pond volume	25,342	cubic meters
17	Projected pond area	42,236	sq. meters
18	Maximum flow into pond	0.3	L/s
19	Maximum Zn loading to pond 10	0.4	kg Zn/d
20	Maximum Zn loading to Pond 10	150	kg Zn/yr
21	Percentage of total flow treated	1.8	% of total flow
22	Pond 10 Zn removal	102.5	kg Zn removed per year
23	Percentage of Pond 1a Zn load	68.36	% of loading

Table 6b: Polishing Pond Extrapolations
(Residence Time - 1.6 days, OEP [Zn] - 2 mg/L)

1	DENSITY OF PPC IN LAB AND FIELD	3	kgfw/cu. m
2	DRY TO FRESH WEIGHT	0.61	kgdw/kgfw
3	GROWTHRATE	0.0126	/d
4	AVG PPC ZN (1992)	62	g/kg
5	VOLUME OF POND 10	320	cu. m
6	MINIMUM REQUIRED RESIDENCE TIME	1.6	d
6a	OEPFLOW	12.875	L/s
6b	OEP ZN CONCENTRATION	2	g/cu.m
6c	OEP Zn LOADING (1992)	812	kg/yr
6d	OEP Zn LOADING (1992)	2.2	Kg/d
7	Periphyton Zn removal Capacity	1.4	g Zn/cu. m of pond/d
8	Periphyton Zn removal from system	347.4	g Zn/system/d
9	Periphyton Zn removal from system	62.5	kg Zn/system/yr
10	Average Zn loading Pool 1-6 (1992)	166.7	kg/yr
11	Average Zn leaving Pool 1-6 (1992)	88.8	kg/yr
12	Average Zn remaining in Pools 1-6 (1992)	77.9	kg/yr
13	Zinc removal rate	320.4	g Zn/cu. m/yr
14	Zinc removal rate	114.5	g Zn/tree/yr
15	Trees required to remove Zn load	7,092	
16	Projected pond volume	2,534	cubic meters
17	Projected pond area	4,224	sq. meters
18	Maximum flow into pond	2.3	L/s
19	Maximum Zn loading to pond 10	0.4	kg Zn/d
20	Maximum Zn loading to Pond 10	131	kg Zn/yr
21	Percentage of total flow treated	16.2	% of total flow
22	Pond 10 Zn removal	102.5	kg Zn removed per year
23	Percentage of Pond 10 Zn load	78.13	% of loading

Table 6c: Tailings Pond 2 Extrapolations

	TP-2 SCALEUP		
1	JELLY ACCUMULATION	0.45	kgdw/kg branches
	Polpond jelly accumulation 1992	1.86	kgdw/kg branches
	Polpond jelly accumulation 1991	2.77	kgdw/kg branches
2	TOTAL ZINC CONC. IN JELLIES	12	g Zn/kgdw
2a	DISSOLVED ZINC IN JELLIES	4.9	g Zn/kgdw
3	AVG. STANDARD TREE MASS	0.96	kg/tree
4	AVG. MASS OF TWIGS/LVS/FRUITS	0.349	kg/tree
5	# OF TREES IN ENCLOSURE	4000	
6	AVG DISS. ZN CONCENTRATION (1992)	2	g/cu. m
7	AVG FLOW (1992)	659	cu.m/d
8	AVG ZN LOADING	481	kg/yr
9	VOLUME OF ENCLOSURE	1600	cu. m
10	VOLUME OF TP-2	1,050,000	cu. m
11	Total PPC biomass	628.2	kgdw
12	Total Sequestered Zn	7.5	kg Zn
13	Total Zn loading removed	1.57	%
3a	Dissolved Zn loading removed	0.45	%
14	Enclosure volume to pond volume ratio	0.15	%
15	% of TP2 volume for 100% removal	9.7	%
16	Current pond volume for 100% removal	102,105	cu. m
17	Biomass multiplier for 1993	4	1991 polpond jelly weights were 4 x the jelly weights of 1990
18	Projected volume needed in 1993	25,526	cu.m

Plate 1: Pond 10 as seen from the Waste Rock Pile

In Table 6c the same type of calculations are made for TP-2. From the data obtained in the enclosure in 1992, it can be calculated that about 0.9% of the zinc loading leaving TP-2 was removed in 1992. This amount of zinc was removed with a biological polishing agent in an enclosure which occupied only 0.15 % of the pond volume (Lines 13 and 14 of Table 6c). In order to transfer 100 % of the zinc load from the pond water to the algae, a biological polishing volume would have to fill 16 % of the tailings pond.

In Table 7a to 7c the calculations of the fertilizer requirements are presented. Fertilizer requirements can be determined in two ways. One approach is to use the concentrations of phosphorus which should be present in healthy biomass. The second approach is based on the water concentrations of phosphorus which are necessary to bring about a eutrophic (highly productive) algal biomass. The calculations are made assuming that we want to support growth in the Pond 10 of about 7 kgdw/d for the two scenarios with the OEP outflow at 20 mg Zn/L and 2 mg Zn/L. The biomass quantity under both scenarios is the same, but under the lower loading, more water is run through the pond. In this case about 110 kg of fertilizer are required for a 180 day growing season. If we calculate the fertilizer requirements based on the concentration of phosphorus in the water, the scenario with the enhanced flow through (lower loading), will require more fertilizer. In this case, the amount ranges from 30 kg for the low flow and 266 kg for the high flow (Table 7a and 7b). In both cases, the quantity of fertilizer required to grow enough biomass to treat the entire yearly Zn loading from the OEP is 1.5 tonnes, as the fertilization is based on phosphorus concentrations, not on zinc concentration. For TP-2 the same calculations are presented in Table 7c and the requirements are either **4** tonnes or 17.5 tonnes. A reasonable requirement of fertilizer is between the two approaches taken for the calculation, i.e. water concentrations and biomass concentrations of phosphorus.

Table 7a: Fertilizer Requirements for Polishing Pond 10
(Residence Time - 14 days, OEP [Zn] - 20 mg/L)

FERTILIZER REQUIREMENTS: PIANT-BASED			
24	Biomass production to remove load	7	kgdw/d
25	HEALTHY PIANTS REQUIRE APPX 0.5	0.01	P
26	Phosphorus requirement for biomass	36.89	g P/d
27	**P CONTENT OF NUTRICOTE (19:6:12)**	**0.06**	**P**
28	Fertilizer requirement	110.68	kg fertilizer over 180 d growing season
FERTILIZER REQUIREMENTS: WATER-BASED			
30	Flow through Pond 10	15.9	Umin
31	Need about **4** mg/L for eutrophic pond	30.5	g P/day
32	**Using a 6% P fertilizer**	**169.3**	**g fertilizer per day**
33	Fertilizer requirement	30.5	kg fertilizer over 180 d growing season

Table **7b:** Fertilizer Requirements for Polishing Pond 10
(Residence Time - 1.6 days, OEP [Zn] - 2 mg/L)

FERTILIZER REQUIREMENTS: PLANT-BASED			
24	Biomass production to remove load	7	kgdw/d
25	HEALTHY PLANTS REQUIRE APPX 0.5	0.01	P
26	Phosphorus requirement for biomass	36.89	g P/d
27	**P CONTENT OF NUTRICOTE (19:6:12)**	**0.06**	**P**
28	Fertilizer requirement	110.68	kg fertilizer over 180 d growing season
FERTILIZER REQUIREMENTS: WATER-BASED			
30	Flow through Pond 10	138.9	L/min
31	Need about **4** mg/L for eutrophic pond	266.7	g P/day
32	Using a 6% P fertilizer	1481.5	g fertilizer per day
33	Fertilizer requirement	266.7	kg fertilizer over 180 d growing season

Table 7c: Tailings Pond 2 Fertilizer Calculations

	PIANT-BASED FERTILIZER REQUIREMENT		
19	Projected PPC mass required	40,089	kg PPC mass
20	P LEVEL IN WELL-GROWING BIOMAS	0.005	gdw/gdw
21	**P required**	**200**	**kg**
22	Fertilizer required (12:8:12)	2,506	kg
	WATER BASED FERTILIZER REQUIREMENT		
23	Water PO4 level to 4 mg/L	4	g/cu.m
24	**total P required**	**1400**	**kg**
25	total fertilizer required (12:8:12)	17500	kg

3.2 Vegetation Stabilization of Polishing Pond Berms and the Tailings Beaches

The overall objective of vegetation stabilization is to create conditions for effluent treatment, which, in the long term, will not require any maintenance. Thus, the polishing pools in the First Meadow, what ever size they may eventually be, should be covered by a vegetation layer, which preferably is indigenous to the area. From a regulatory point of view, it is considered prudent to recover or to restore the habitat in which the treatment is to take place. Thus, experiments were started to establish sedges, cattails, and moss on the berms of the pools in the First Meadow (Plate 2).

To maintain a grass cover on the beaches of the tailings pond would require continued maintenance effort. Non-native vegetation also has the potential to encourage destructive grazing by geese (as seen on Tailings Pond 1).

To establish a vegetation cover with indigenous species that might be less palatable to geese and which would require little or no maintenance, experiments were also carried out on the tailings (Plate 3). The details of the work are reported below.

A species of sedge, *Scirpus atrocinctus*, is the most abundant, and one of a very few species, which has colonized some areas of the exposed beaches of Tailings Pond 2. In addition, this species is found in the First Meadow, and over a large area adjacent to Lake 1.

This species has apparently germinated and established on the exposed tailings beach, even where acid generation has taken place. At other locations, this species is an important colonizer. Understanding the conditions for germination and establishment of this species should facilitate revegetation of exposed tailings beaches and berms containing polishing ponds. This will result in reduced erosion of these areas, and may even increase run-off.

Plate 2: Vegetation experiment on polishing pond berms. Note green vertical rows where fertilizer was added.

Plate 3: Vegetation experiment on the tailings beach. Green patch in centre shows conditions necessary for moss germination and growth.

The overall objective is to devise a simple, inexpensive technique of establishing a permanent vegetation cover on the tailings and future ditch banks to minimize erosion. *Scirpus atrocinctus* may be the appropriate candidate species for the Buchans area.

The first two milestones towards development of this technique were:

1) Verify that *Scirpus* seeds collected in autumn were viable, and identify the key conditions required for germination.
2) Identify the key conditions for germination and plant establishment under field conditions.

3.2.1. Lab Germination Experiments

Laboratory experiments were set up to examine the relationship between germination and time of seed collection, storage temperature, and etching of seed coats with acid (scarification). These steps were taken into consideration, as species of sedge have been reported to be difficult to germinate, and because the above factors are likely important.

The first lab experiment examined germination of seeds collected on October 12, 1991, and stored at room (21° C), fridge (8° C) and freezer (-20° C) temperatures. Seeds were soaked in concentrated (60 %) sulphuric acid for 0.5, **2** and 5 minutes, then thoroughly rinsed with distilled water. Seeds were planted on 0.8 % agar, and placed 50 cm below four standard fluorescent lights.

After 16 days incubation, the highest germination rate was 6.9 %. The seeds in this treatment had been stored in a freezer, and soaked in sulphuric acid for 2 min before planting. Because of this poor germination rate, as well as slow development of the seedlings in the following weeks, the experiment was, in part, repeated using seeds stored in the freezer, while a control (no scarification) was included.

In this second experiment, better germination percentages were observed, especially in the 0.5 minute scarified seeds, where 32 % germinated. However, there were large variations among replicates of the remaining treatments, and germination could not be clearly attributed to specific factor.

A final experiment was set up, where seeds, collected on six dates, were subjected to four concentrations of sulphuric acid for four different lengths of time. In addition, three sets of one seed collection (October 12, 1991), stored at room, fridge and freezer temperatures, were also subjected to the combinations of scarification (concentration x time). In all, 136 treatments were set up.

Germination was monitored twice weekly for three weeks. Germination was much poorer here than in the second experiment (<5 %), and no pattern of germination was evident across the treatments. Before terminating the experiment, one last step was taken. All petri plates were placed outdoors under bright sunshine for 6 hours, then replaced under fluorescent lighting.

During examination of the plates the following day, it was noted that any seedlings which had already germinated prior to placement outdoors were killed by the high light intensity and heat. However, during examination of the plates three days later, widespread germination, up to 97 %, was observed across most treatments. Seeds pretreated with sulphuric acid typically had lower percent germination, while most seeds stored at refrigerator temperature germinated without the scarification treatment.

In retrospect, each of the three experiments were set up at different locations in the growth facility. The minor variations in light intensity which probably existed between experiments may have accounted for variation in germination percentages between treatments and experiments.

Overall, the final experiment demonstrated that:

a) virtually all seeds of *Scirpus atrocinctus* collected in September through November, 1991 were viable.

b) a temperature of 8° C in the refrigerator may be the best storage temperature.

c) Pretreatment of seeds with acid for etching the seed coat is not necessary

d) High light intensity and/or temperature are/is required for high percentage germination.

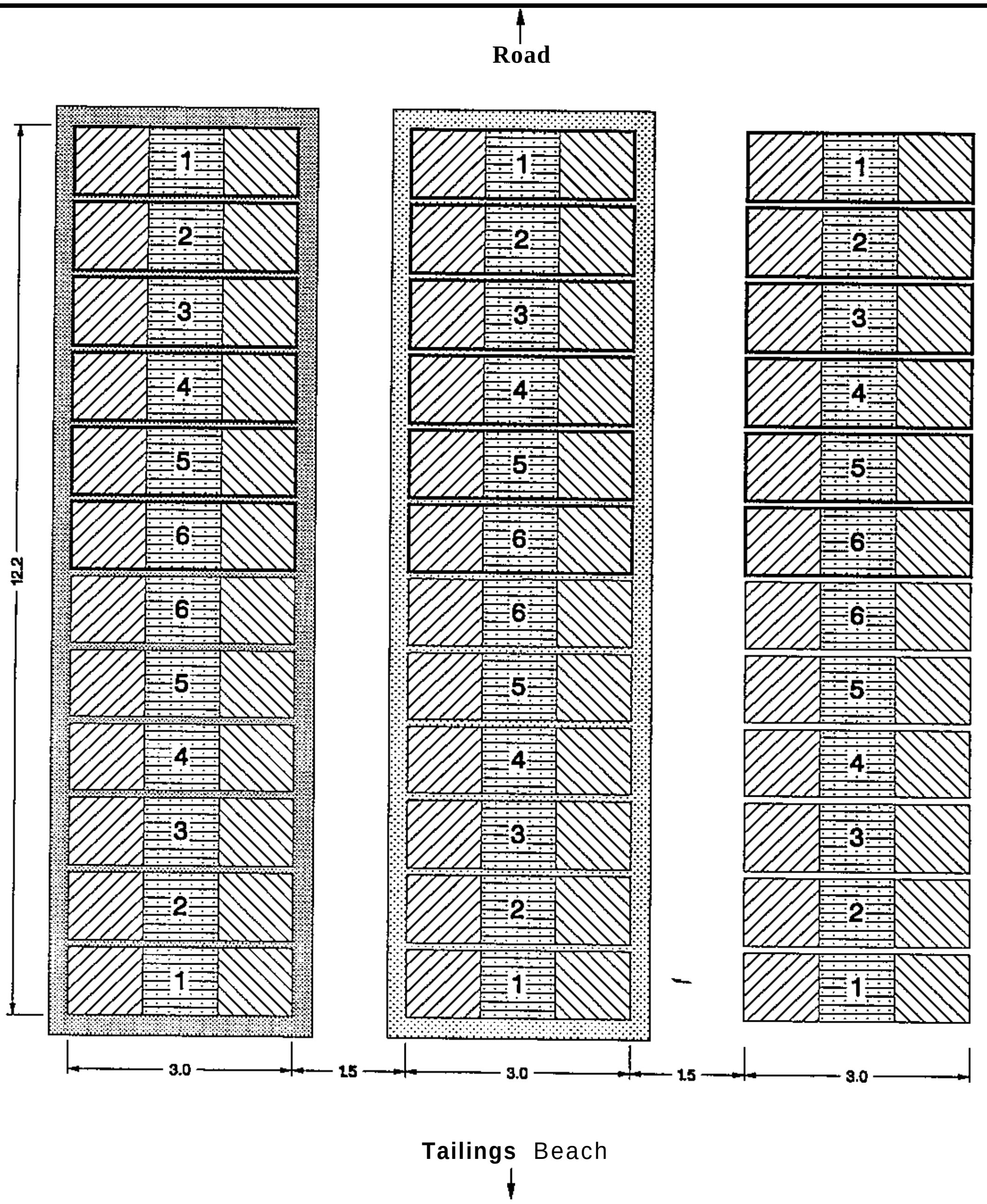
3.2.2. Tailings Beach Experiment

A field experiment was set up on the tailings beach of Tailings Pond 2 and seeded with *Scirpus* (see Schematic *2).* This multifactorial experiment tested the germination of *Scirpus* and other plants on the tailings beach. Factors which were tested included:

1) Moisture Retention. Moisture retention was modified by covering the beds with plastic sheeting. Two beds were covered; on one bed the plastic remained for the entire summer, while on a second bed it was removed after a short period. In a third plot no cover was placed.

2) Tailings Conditioners. This factor tested the usefulness of peat, sawdust and unamended tailings as medium for growth.

3) Chemical Amendments. This factor tested the effect of nutrients, such as phosphate rock and Nutricote (slow-release fertilizer), and neutralization with limestone on germination and growth of plants.



ORGANIC TREATMENT

- ▨ Tailings
- ▤ Peat
- ▧ Sawdust

CHEMICAL TREATMENT

- 1 Phosphate rock
- 2 Limestone
- 3 Nutricote
- 4 Limestone and nutricote
- 5 Phosphate rock and nutricote
- 6 Control

- ▭ Plot seeded with Scirpus
- ☐ Unseeded plot
- ▓ Plastic cover (long term)
- ░ Plastic cover (short term)

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Buchans, Newfoundland

Date: Dec./92	Schematic: 2

Methods: The tailings plots were originally raked to provide a roughened surface for seed and amendment penetration. About 0.12 m^3 of peat and sawdust were applied to the surface of 0.8 x 3 m plots. Control plots received just raking. Phosphate rock plots received about 200 mL of Long Harbour phosphate sand. Limestone treated plots received about 100 mL of limestone per plot, and Nutricote plots received 100 mL Nutricote per plot. Two plots in each moisture regime received both limestone and Nutricote, and phosphate rock and Nutricote.

The upper moisture plots (high beach) were seeded with local *Scirpus* seeds. For this, 2 kg of local *Scirpus* seed heads were collected locally, broken up and slurried with about 5 L of water. The slurry was applied to the appropriate plots. Approximately **56** g of seed/ seed head material was applied to each plot.

The lower plots (lower beach) were not seeded. These plots received an identical set of treatments, but any vegetation germination and growth would have to come from natural recruitment.

Results: After **4** months, the field plots were evaluated. In the plots with no plastic sheeting, both upper (seeded) and lower (unseeded) plots contained little vegetation. The best treatments were with peat and sawdust, and Nutricote. The best vegetation was not *Scirpus,* but grass and moss which covered a small proportion of the treated areas.

In the plots with a temporary plastic cover, the seeded (upper) plots contained only moss in the limestone and Nutricote treatments. In the lower moisture plots, moss again dominated the vegetation, but appeared in only those treatments with Nutricote.

The major vegetation response occurred under the long-term plastic cover. Here, *Scirpus* germinated and grew in the one plot with peat, limestone and Nutricote. Again, moss was the predominant plant growing in other plots, especially those treated with Nutricote (Plate 3).

Conclusions: *Scirpus* has been observed to colonize the tailings beaches naturally. However, this experiment demonstrated that specific conditions must be met before widespread establishment of a plant cover can be achieved. Currently, it appears that sedge can be grown from seed if the tailings surface is modified though increasing moisture retention and reducing erosion, by adding peat as a tailings conditioner, by applying limestone to buffer the tailings and by adding Nutricote as nitrogen, phosphorus, and potassium source.

Moss can be cultivated on the tailings beaches by simply providing a long-term, slow-release nitrogen, phosphorus, and potassium source.

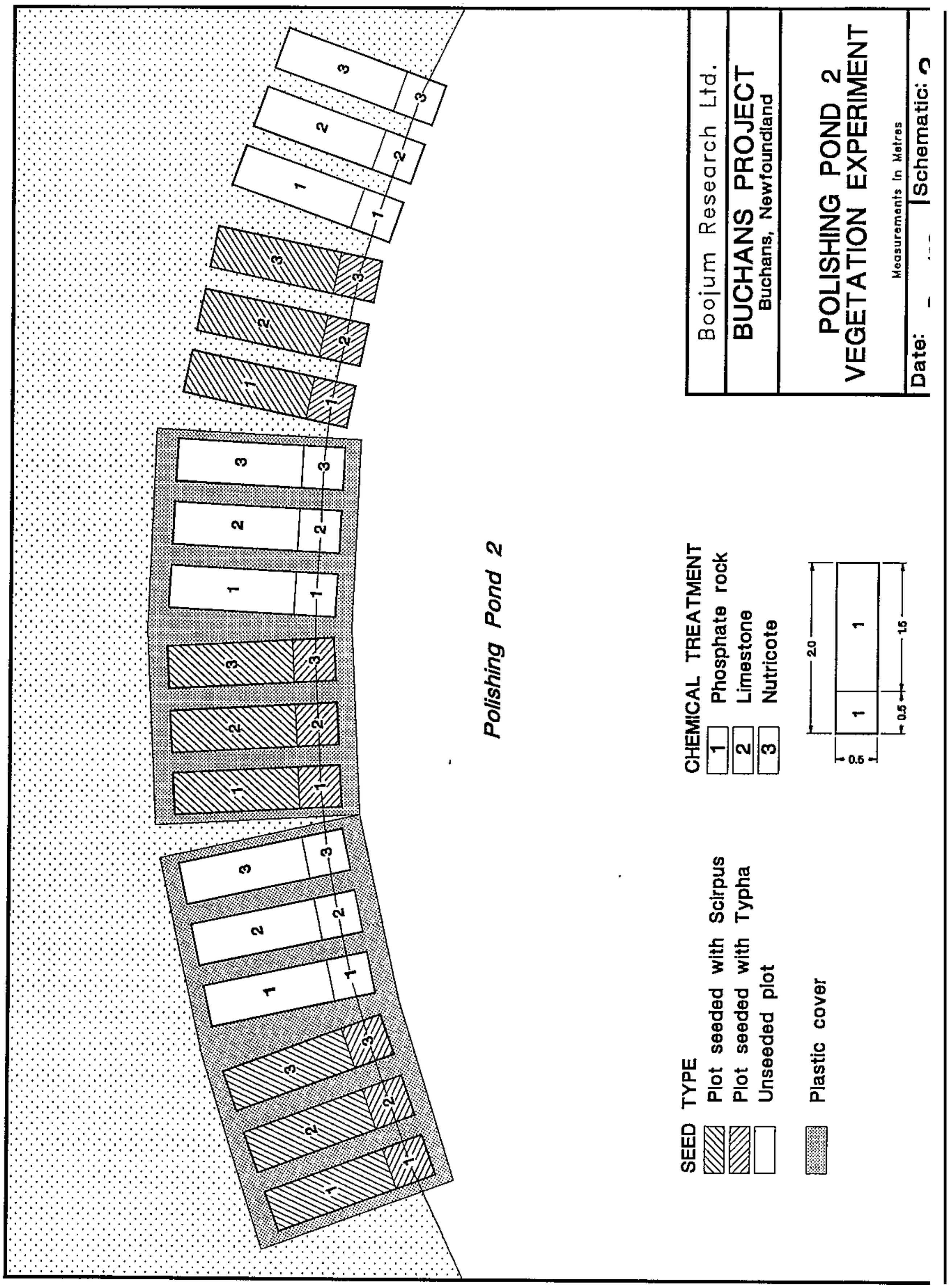
Grass can be cultivated by applying limestone as a buffer, peat or sawdust as a tailings conditioner, and Nutricote as a slow-release nitrogen, phosphorus, and potassium source.

3.2.3. Polishing Pond Berms

A second field experiment was set up on the banks of Polishing Pond 2 below the OEP outflow (Schematic 3). This multifactorial experiment tested various physical and chemical factors on the germination and growth of both *Scirpus* (embankment) and *Typha* (water line).

Methods: In this experiment, the primary factor tested was moisture retention. This was accomplished by covering two of three plots with plastic sheeting. The plastic sheets were in place for seven weeks. The plots were set up vertically on the banks, through a moisture gradient which reached from the water line to 2 meters above water level.

The second factor was nutrients. One of 3 plots received phosphate rock as a phosphate source, one received Nutricote as a slow-release plant fertilizer, and one was left as a control. Both seeded and non-seeded plots were set up.



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POLISHING POND 2
VEGETATION EXPERIMENT

Measurements in Metres

Date:

Schematic 2

Scirpus seed heads had been collected locally in the previous fall (October, 1991). About 500 g of dried seed heads were slurried with 5 L of water, and distributed over the top 1.5 m of each of the "seeded" plots (37g of seeds per m^2).

Typha seed heads were also collected locally. In this case about 3 seed heads were slurried with detergent and 5 L of water. The seeds were distributed over the lower 0.5 m of each "seeded" treatment plot. About one third of a seed head was applied to each plot.

The phosphate rock plots received about 250 mL of Long Harbour phosphate sand (250 mL/m^2). The Nutricote plots received 200 mL/m^2.

Results: *Scirpus* grew well in seeded plots. Coverage sometimes reached as high 90% of the plot in areas fertilized with Nutricote. The next best growth was in plots with phosphate rock, followed by control plots.

Typha also grew well along the bottom of the plots, although many of the plants were eaten by moose. Again, the best growth occurred in the Nutricote plots, followed by the phosphate rock plots, followed by the control plots. Plastic covers did not seem to influence germination and growth.

Along with the planted *Scirpus* and *Typha,* three kinds of grasses, a *Juncus* species, moss, another sedge, and one *Tarnarix* plant also grew in the plots. Again, the highest plant densities were in the Nutricote fertilized plots.

Conclusions: Vegetating polishing pond berms with *Scirpus* appears to be a relatively simple procedure. While very little vegetation has appeared on the polishing pond berms over the last three years, this appears to be due to a lack of nutrients. Application of seeds and provision of proper nutrient conditions will allow us to develop dense vegetation covers on the berms, thereby minimizing erosion.

3.3 Polishing Pond Sediments

Zinc removed from the water via biological polishing is transferred to the sediments. The question therefore arises -what is the long-term fate of metals in these sediments, at the bottom of the polishing ponds. To address this question, sediment layers excavated in the First Meadow were analyzed. In Map 2 the locations of the sampled profiles are given. In 1992, a second sample was taken at station E, the location at which the highest metal precipitate layer was expected. A series of four leaching experiments were carried out. Detailed descriptions of the experiments, and with the results are given in Appendix B.

Deposition of the precipitates together with organic material to the sediments adds a new component to the metal removal process, namely soil particulates. Soil profiles have varying amounts of organic matter. Organic matter controls to a large degree sorptive and desorptive processes. If we carry out leaching experiments with distilled water then we would expect desorption to take place, i.e. zinc and copper should be released from the sediment. On the other hand, if the organic component in the soil is high, desorption should be lower. In all experiments this is what was found. Zinc was released from the soil/ precipitate and the highest desorption occurred from material which had precipitated under acidic conditions (locations A and B at a depth of 15 cm). Adsorption was also tested through experiments, but here, the leaching water used was from OEP or OWP. Again, organic content of the soil could be related to the amount which was adsorbed. Details are given in Appendix B.

These experiments suggest that as long as vegetation covers the sediments, be they floating or rooted, organic matter will be deposited over the metal-rich sediments and zinc will remain in the sediment.

One may conclude that for sediments in the polishing ponds which are dominated by carbonate precipitates, sorption will have to be controlled by a vegetation cover which is rich in organic matter, but not necessarily anaerobic.

The removal processes which take place in the water with the algae are controlled by the chemistry, and likewise, chemistry will determine their behaviour in the sediments. Thus a summary of conditions under which precipitates form and redissolve is presented.

The predominance diagram for zinc describes the dynamic relationship between precipitation and solubilization processes in the OEP and its outflow ponds (Figure 17a). Between pH 6 and 8.5, zinc may precipitate as its phosphate, hydroxide or carbonate. There are four lines to show the boundaries between zinc precipitation and solubilization states. In the diagram, the region above each line is the area in which zinc precipitates. Below the line is the area where zinc dissolves in water. For instance, when [Zn] is higher than 20,000 mgIL at pH=6 or 0.2 mgIL at pH=8.5, it precipitates as zinc-hydroxide. If phosphate sands were spread in OEP water, resulting in a total orthophosphate concentration of 5 mgIL (or P = 1.7 mg/L), soluble [Zn] should decrease to below 10 mgIL at pH 7.

Zinc may also precipitate as zinc-carbonate. Generally, zinc-carbonate is in equilibrium with CO, in the air. Its concentration is bounded by 5000 mgIL at pH = 6 and 0.5 mgIL at pH = 8. But considering that OEP water contains high concentrations of carbonate (total inorganic carbon = 100 mg/L), soluble zinc concentrations will be even lower.

In the polishing ponds, then, zinc may precipitate as zinc-carbonate or zinc-phosphate (with added phosphate sands). The overall precipitation or removal process in the ponds is controlled by pH, temperature, phosphate concentrations, partial pressure of CO, in the atmosphere and total inorganic carbon in water. The precipitate desorption processes in the sediments are influenced by the presence of organic matter and the conditions under which they accumulated.

Fig. 17a: Predominance Diagram
P(CO2) = 3.16e-4 atm, Tot [PO4] = 5 ppm

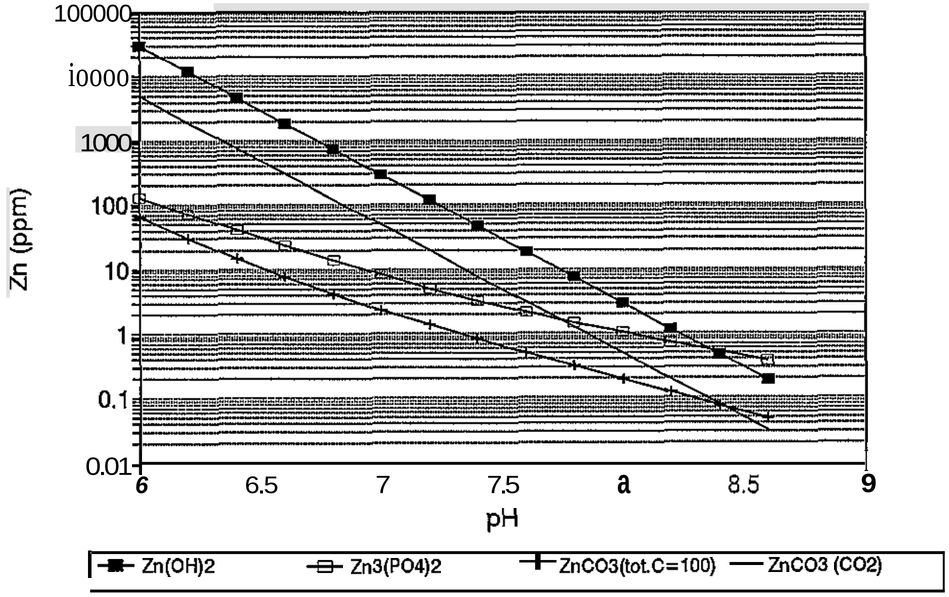
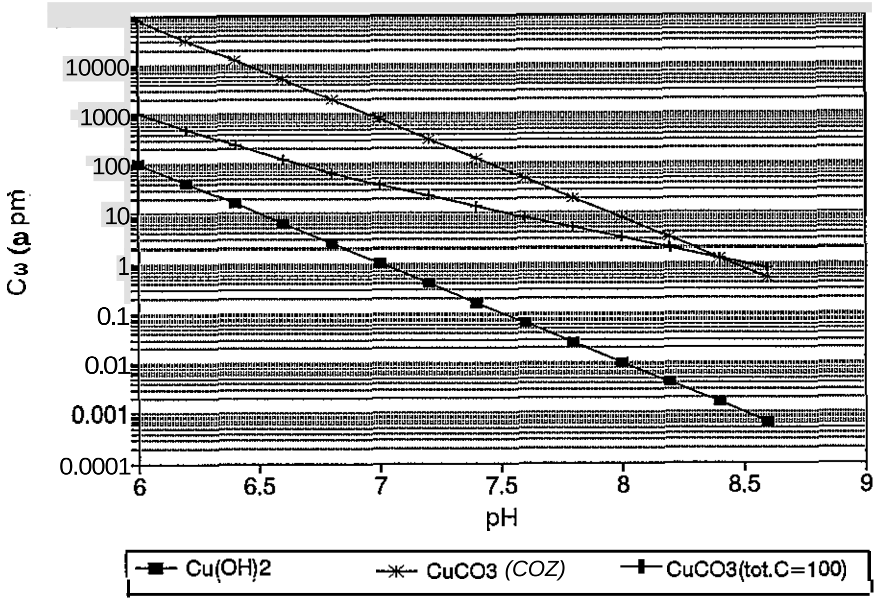


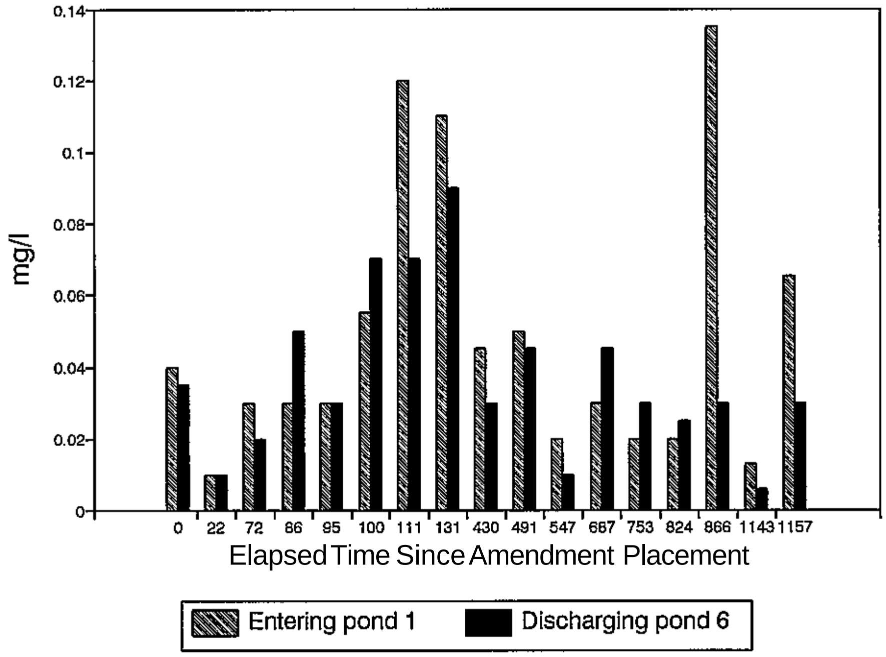
Fig. 17b: Predominance Diagram
P(CO2) = 3.16e-4 atm



When pools 1 to 6 were constructed in 1989, dissolved copper concentrations inexplicably increased. However, in 1992, when pool 10 was constructed, the same phenomenon was observed. During the soil leaching experiment this problem was also addressed. Copper is desorbed from the soil after it is disturbed, and before its equilibrium is re-established, it will leach into the water. From the predominance diagram for copper (Figure 17b), solubilities of copper-carbonate are such that a slight pH drop, which is inevitable with soil disturbance, will re-solubilize copper (Figure 17b).

Copper concentration changes in the six ponds since 1989 are shown in Figure 18. Copper concentrations fluctuate around 0.1 mg/L. However, when the inflow [Cu”] is higher than 0.1 mg/L, outflow concentrations decreased. When the inflow [Cu^{+2}] is lower than 0.1 mg/L the concentrations remained the same. This can be explained by the predominance diagram, showing both $Cu(OH)_2$ and $CuCO_3$ solubility curves (Figure 17b). Since $Cu(OH)_2$ has a lower solubility, it is the major precipitate which controls copper concentrations in nature. Around pH 7.5, Cu^{2+} concentration is about 0.1 mg/L. This is the condition which prevails in the polishing pond. If algae in polishing ponds raise the pH of the water higher than 8.4, copper concentrations will drop to 1µg/L.

Fig. 18: [Cu] in Polishing Ponds
Pond 1 - 6 Dissolved Copper



3.4 ARUM - Oxidation and Reduction

The purpose of the experiments carried out on ARUM in 1992 was to elucidate the controlling factors of alkalinity generation in limnocorrals in OEP and OWP. Description of these experiments, which were mainly carried out in the Boojum laboratories,and the results obtained are presented in detail in Appendix D.

Complementary experiments to the laboratory work were carried out in the field through organic matter additions to the limnocorrals. To simulate the proposed cattail cover over the water body the limnocorrals were covered with plastic.

It was concluded that ARUM sediment activity is controlled by a fine balance of microbial activity and the maintenance of reducing conditions. Microbial activity is dependant on the availability of easily degradable carbohydrates, such as supplied by potato waste. The work on decomposition of organic materials was completed. The results indicate that decomposition takes place under acidic, reducing conditions in the sediment. The most promising amendment material was peat and the least promising was sawdust. Detailed results are summarized in Appendix E.

Two curtains with ARUM sediment were installed in OWP. Work on the floating cattail covers was continued. One year after the first curtain was installed, pH increased slightly in the water overlying the sediment. This increase was attributed to the ARUM sediment. A second curtain was constructed, this time with improved amendments, mixing peat and potato waste.

Although it might have been possible that the pit at large benefited from the installation of the curtain, with the new and final interpretation of the observed zinc decreases, significant effects of the ARUM sediment are difficult to demonstrate.

Table 8: Bottom surveys in the OWP

Date	Behind the New Curtain					
	Depth m	pH	Temp C	Cond. uS/cm	Eh mV	Oxygen mg/L
31/5/92	4	4.47		572	4	-
27/9/92	2	5.27	14.2	463	-	<7.0
27/9/92	2	5.66	14.1	563	-	<7.0
27/9/92	2	5.82	14.1	490	-	<7.0
27/9/92	1	4.09	14.5	457	-	<7.8
	Behind the Old Curtain					
2/06/92	4	5.24	19.1	450	216	-
27/09/92	-	6.46	14.2	438	-	7.5
27/09/92	-	6.15	14.1	439	-	8.4
27/09/92	-	5.8	14.3	768	-	8
27/09/92	-	4.9	14.3	474	-	<8.2
27/09/92	3.5	3.9	14.2	563	-	<8.5

This, however, does not mean that ARUM sediments have no effect or are not working. In Table 8 a sediment survey of pH and Eh is presented for both curtains. Essentially, all Eh values are negative, and pH values are significantly elevated above that of the pit at large (pH 3.5). ARUM sediments demonstrably generate alkalinity and increase the pH. The exchange between the pit water at large and the ARUM sediments has not been quantified and is most likely driven by slow process of diffusion.

Given the conditions in the OWP where natural decreases of zinc occur, it is not possible to separate the two effects, ARUM and natural decrease.

It can be concluded from the work on the ARUM sediment that ARUM is effective in providing reducing conditions at the bottom of the pit. The measures taken in the pit have brought about increases in the phytoplankton community from two species in 1988 to six species in 1992.

4. CONCLUSIONS AND RECOMMENDATIONS

Firm conclusions about the proper path to compliance can only be made if the source(s) of contaminants and the processes which generate them are well known. We are now in such a position. Compliance can be achieved on all effluents from the TP-2, OEP, and OWP. Natural reductions, combined with natural chemical precipitation will significantly reduce current loadings to the Buchans river.

For the effluent of the OEP, biological polishing will be the principal treatment method. The size of the polishing pond required will depend on the effluent concentration, and the degree to which the system will be over designed. On completion and refinement of the biological polishing model, detailed options can be developed for a given size of treatment pond.

Conclusions regarding the OWP and OEP are very different. If the OWP is left with a complete ARUM sediment at the bottom, it is certain that acidity will slowly be consumed and clean water will leave via ground water to the Buchans River. The zinc concentrations, which are expected to enter with the ground water, will likely be at background concentrations of 1-2 mg/L. With the water quality improvements which can be expected in the pit in the near future, and the continued growth of cattails, a complete ARUM sediment will provide long-term protection of the Buchans river. Increasing the cattail cover in the pit would provide further assurance of this. Although the effects of ARUM sediment on the water can not be different from the overall hydrological effects, the sediment is generating alkalinity.

From the results of the biological polishing scale-up experiments carried out in TP-2, and the chemical experiments carried out in the OEP, two processes can be used to remove zinc. These two processes are phosphate treatment and biological polishing. Phosphate fertilizer will assist both processes in removing zinc. It is recommended, in view of the zinc-carbonate equilibrium, that fertilization of the entire pond be considered. This would reduce soluble zinc levels, by forming zinc-phosphate. Excess phosphate would be taken up by the algae. Since no further annual zinc loadings to the pond are expected, fertilization of the pond should only be required for a limited period of time.

In conclusion, Ecological Engineering will provide an effective long-term solution to the decommissioning of the contaminant sources from the OEP, OWP, and TP-2. It is recommended that during the ice-covered season, bottom and surface samples are collected from the OEP and OWP, to confirm the projections presented in this report.

APPENDIX A: PERIPHYTON GROWTH AND ZINC SEQUESTRATION

ABSTRACT

Periphyton populations composed mostly of green, filamentous algae have been found in mining waste water together with large quantities of metal precipitates. These populations, because of the close interaction between precipitate and periphyton, have been termed periphyton-precipitate complexes (PPCs). These complexes can be over 80% precipitate, with zinc concentrations as high as 8%.

While growth of the periphyton and precipitate content of the complex are related to water chemistry, some commonalities have been found between PPCs growing in different waters from different mine sites. The elemental composition of precipitate is also similar to that of PPCs, suggesting that periphyton may play a role as precipitation traps sieves. This paper discusses the relationship between zinc, precipitates and periphyton growth, primarily from mining sites in northern Ontario and central Newfoundland.

INTRODUCTION

Attached, or periphytic algae grow in mine effluent ponds and streams, characterized by extremes in pH and elevated metal and suspended solids concentrations (3, 5, 6, 10, 12, 13, 16). Reviews on metal/algae interactions (11, 12, 16) indicate that tolerance is achieved by several different means. Dissolved metals can be either bound to the cell walls, charged carbohydrates, or taken up into the cell and sequestered in specific organelles. All of these processes lead to high concentrations of metals in or on the algal biomass (3, 11).

Metal precipitates present as suspended solids can also attach to periphyton populations either to extracelluar carbohydrates or onto cell walls **(4,** 9, 15) resulting in Periphyton-Precipitate Complexes (PPCs) with high solids content and a small proportion of biomass. Precipitates, especially iron hydroxide, and iron hydroxide coprecipitated with zinc have been found on cell bacterial surfaces (1). This may also correlate with encrustation of iron and manganese found in a number of filamentous algae at sites contaminated by mine water (14). The periphyton populations inhabiting acidic effluents are multi-species complexes dominate by filamentous, benthic algae, which are associated with mosses and diatoms. Cyanophytes and charophytes dominated periphyton in ponds and ditches containing more alkaline waters.

Growth rates of PPCs have been quantified in the field at two sites by Kalin and Wheeler (7,8). It was found that in Newfoundland, in circumneutral pit water, PPCs "grew" at rates up to 4.6 gdw (sq. m of surface area).' d^{-1}. In NW Ontario, PPCs in an acidic lake grew at rates of only 1.4 gdw (sq. m of surface area).' d^{-1}. Quantifying growth of the periphyton portion of the PPC, without accompanying precipitates proved difficult.

This paper describes the relationship between metal precipitates and periphyton growing at two mine sites. Comparisons are made between the composition of PPCs and precipitates, as well as the growth of PPC and deposition rates of precipitates. **A** basic understanding of these relationships is essential to the development of biological polishing as a water cleansing process.

METHODS AND MATERIALS

Site and Algal Population Description

The first 'of two intensively-studied mine sites were located on Confederation Lake in northwest Ontario (Figures 1 and 2). The site included several water bodies which contained extensive periphyton populations. Large amounts of alkaliphile cyanobacteria (*Oscillatoria*) occurred near the outflow of Decant Pond. Extensive populations of a *Ulothrix* spp.- dominated community were found on the beach end of Decant Pond and in an acidic lake (Boomerang Lake). Another population of *Ulothrix* spp. was found in Mill Pond (Table 1).

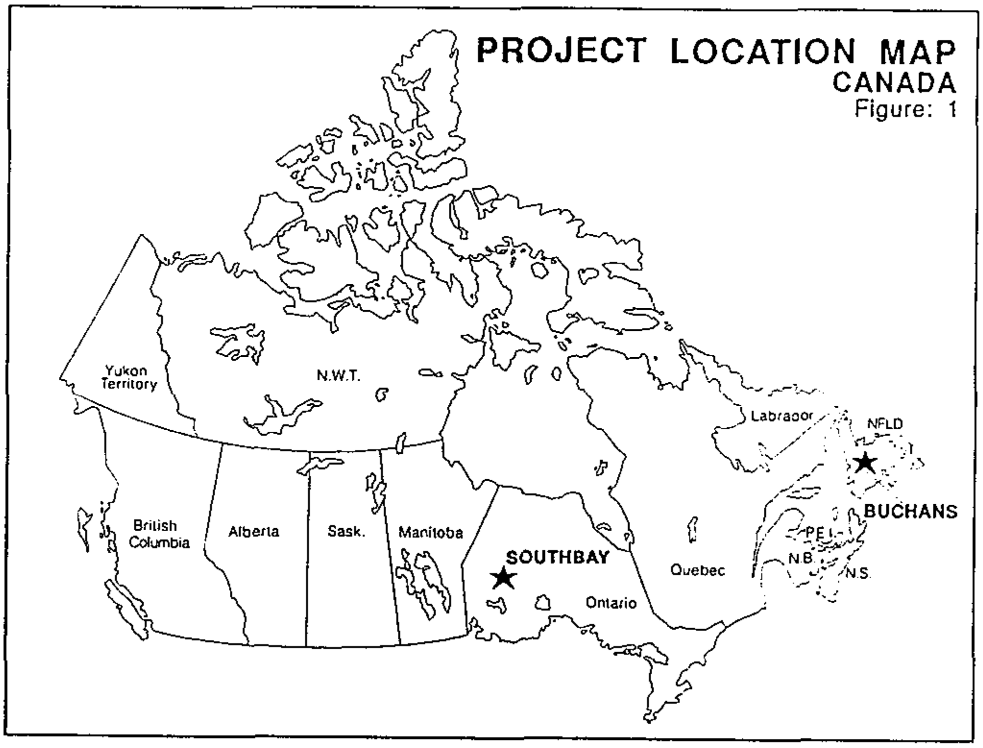


Figure 1: Location of study sites.

The second intensively studied site is the Buchans mine in central Newfoundland (Figures 1 and 3). In the Oriental East Pit and its effluent stream and polishing pond system, a *Microspora*-and moss-dominated community was proliferating (OEP). A *Ulothrix* community dominated the algal flora in the Oriental West Pit (OWP). Populations of a *Ulothrix/Microspora* -dominated community were growing in Second Meadow seepages (MDW), and in the Drainage Tunnel (DT) effluent water, another *Ulothrix/Microspora* -dominated population flourished (Table 1).

In the effluent of the Oriental East Pit, a series of six, serial experimental ponds were constructed in 1988. Each pond had a volume of approximately 40 cubic meters. Alder branches were placed in each pond to act as surface area (appx. $3.8 m^2/m^3$) for the growth of PPCs. Flow through the ponds was controlled, to provide an overall residence time between 16 and 79 days.

Field Sampling

PPCs were intensively studied over the summer of 1991 during site visits to the two mines. The habitat, i.e. pond, stream or lake shore was recorded, and pH and electrical conductivity were determined in the field. PPC and water samples were kept cool in plastic bags and bottles until processed in the laboratory.

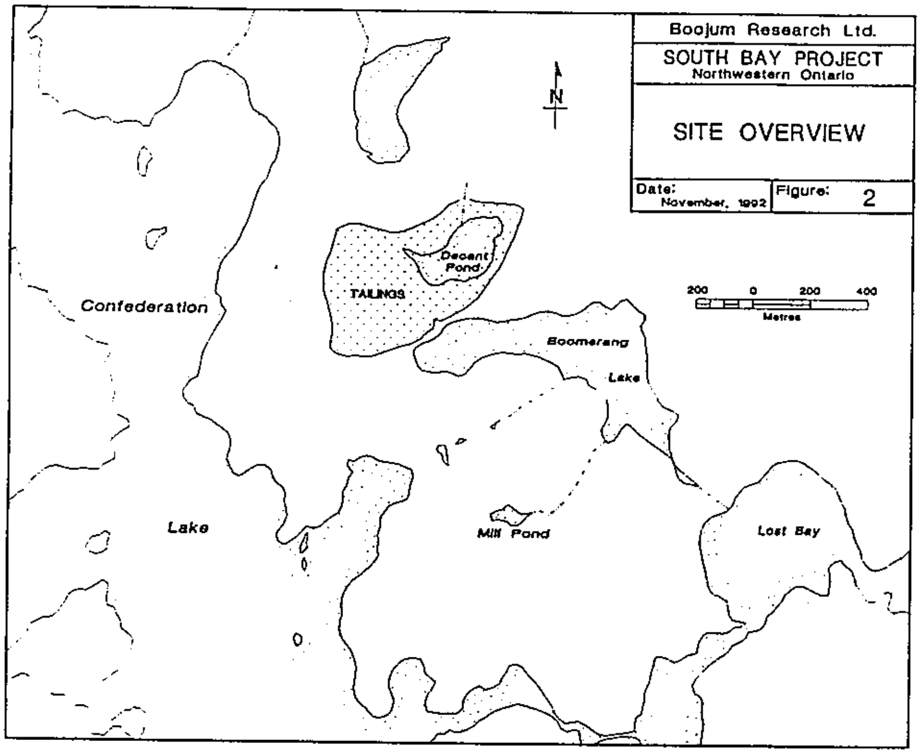


Figure **2:** Location of study **sites at** South Bay.

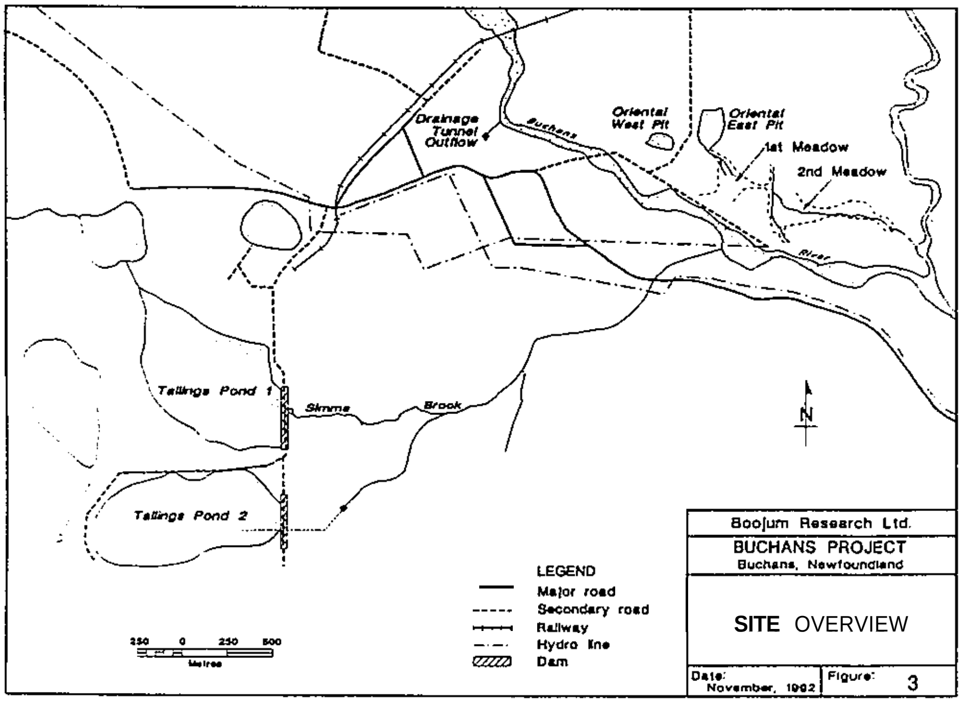


Figure 3: Location of study sites at Buchans.

TABLE 1: Description of Waste Water Sites

MINE SITE	HABITAT	pH	[Zn] mg/L	[Al] mg/L	[Fe] mg/L	[Cu] mg/L
NW Ontario	Boomerang Lake	3.2-3.5	7-11	2.1	4.5	0.1
NW Ontario	Decant Pond	3.2-4.5	1-2	0.1	0.6	0.1
NW Ontario	Decant Pond	5-7	2-6	4	1*	0.04
NW Ontario	Mill Pond	3.2-3.5	150-450	16	32	15.8
Newfoundland	Oriental East Pit	6.1-7.3	20-25	10	1*	1*
Newfoundland	Meadow seepage	6.5	7	4	1*	0.1*
Newfoundland	Drainage Tunnel	6.4-6.7	16-25	1*	1*	0.1*
Newfoundland	Polishing Ponds	6.5-7.5	4-18	4-8	2	1*
Newfoundland	Oriental West Pit	3.3-3.8	26-36	4-6	1	1*

* indicates sample at or below detection limit

PPC growth rates were quantified both locations using a combination c constructed, artificial substrates and natural. alder or black spruce branches. The artificia structures, called "peritraps" measured both growth and sloughing rates. The traps consisted of an artificial netting structure which housed alder or spruce branches. A plastic bag below the netting collected any PPC material falling from the netting or substrates. PPC growth rates could therefore be determined on both netting and branches. PPC mass was cleaned off the nets and branches, dried and weighed. Total growth was determined by adding PPC weights on nets and branches to that which had fallen into the bag. The cleaned traps were replaced for regrowth three times during the growing season. Peritraps were installed in Boomerang Lake and Decant Pond at South Bay, and in the OWP, OEP, and the polishing pond system at Buchans.

Precipitation rates were quantified at the South Bay site, in Boomerang Lake at 4 locations, including the outfall (2 m depth), the inflow area from Mill Pond (2 m), and in two deeper locations in the lake (4 and 5 m; Figure 2). Precipitation rates were also measured near the outfall in Decant Pond in 2 meters of water. At Buchans, precipitation rates were quantified at 4 locations in the Oriental East Pit, two near the outfall in 2.7 m of water and 2 in the centre of the pit in 20 m of water. The traps were a collection of 5 vertically-mounted tubes, 5 cm diam. and 50 cm in length (2). They were held vertically by a plate and harness, and lowered into the water to specific depths. The traps were hauled to the surface, and allowed to sit for 24 h. The material in the bottom of the tubes was collected, dried, and weighed. Precipitation rates per square meter of lake or pit bottom were calculated from the dry mass collected from the traps over several time intervals.

Specific comparisons between PPC composition and surrounding water can only be made using PPC populations of a similar biotic composition. Thus, *Ulothrix*-PPCs and surrounding water (Decant Pond, Mill Pond, and Boomerang Lake) were compared without precipitate correction with respect to their elemental composition (Figure 4a). For these comparisons, individual PPC samples were compared.

The distribution of elements and their concentrations in the waste water were similar to those found in PPCs, with the exception of iron, copper, and zinc. This was expected as the origin of the metals was either tailings or mill site. Sulphur, calcium, and zinc (Mill Pond only) were present in concentrations >100 mg L^{-1}. Those elements with concentrations greater than 10 mg L^{-1} were magnesium, aluminum, silicon, iron (except Boomerang Lake), and copper (Mill Pond only).

In PPCs growing in the waters, the most accumulated element was iron (> 100,000 μg gdw^{-1}), but in the next highest concentration range (>10,000 μg gdw^{-1}) sulphur, manganese (Decant Pond only), and zinc (Decant Pond only) were present. The next highest concentration range (>1,000 μg gdw^{-1}) contained the elements calcium, aluminum, copper (Decant Pond only) and phosphorus. Potassium and sodium, as essential plant nutrients, can be expected to be present in high concentrations.

At Buchans, there were also 3 sites which contained similar periphyton populations composed of *Ulothrix* and *Microspora* (Table 2). Elemental distributions are shown for specific samples of populations in the Drainage Tunnel, the Oriental West Pit, and the Meadow seepages.

Figure 4b compares the concentrations of major elements in Buchans water with those found in corresponding PPCs. Only calcium and sulphur in the OWP and Meadow sites were found in concentrations greater than 100 mg L^{-1}. Of the elements, present in concentrations greater than 10 mg L^{-1}, only zinc was of concern. Iron concentrations at these sites were low, c 10 mg L^{-1}.

The PPCs found growing at these locations had somewhat different elemental distributions. Those elements found in concentrations greater than 10,000 μg gdw^{-1}, were calcium, sulphur, iron, and zinc (only for the Meadow Seep). For the Drainage Tunnel and OWP, only aluminum and iron greater than 10,000 μg gdw^{-1}. Zinc concentrations in the Drainage Tunnel and OWP PPCs were 2000 to 5000 μg gdw^{-1}.

Precipitation Rates

The calculated average precipitate deposition rate in Boomerang Lake was around 2.2 gdw m^{-2} d^{-1} over the summer 1991 (Figure 5a). In Decant Pond, the average metal precipitation rate was 0.6 gdw m^{-2} d^{-1}. In the Oriental East Pit at Buchans, one of the shallow traps caught 2.0 gdw m^{-2} d^{-1} over the winter, and 1.9 gdw m^{-2} d^{-1} over the following summer (Figure 5b). The deeper traps caught just over twice that amount, averaging about 5.0 g m^{-2} d^{-1} over the winter, and 5.3 gdw m^{-2} d^{-1} over the summer. Since the deepest traps in Boomerang Lake were in 4-5 m of water, precipitation rates were probably more comparable to the shallow traps in Buchans (2.7 m).

Table 2: PPC Composition

LOCATION	TAXA	DW/FW	Algae	Fe	$Fe(OH)_3$	S	(SO_4)	Zn	$Zn(OH)_2$	Mn	Al	Ca	$CaCO_3$	Cu	Other
			%	%		%		%		%	%	%		%	%
Decant Pond	Oscillatoria	0.28	29.5	17.8	34.9	2.5	7.5	3.3	5.1	1.1	3.9	1.4	3.6	1.1	13.3
Decant Pond	Ulothrix	0.309	93.0	3.2	6.3	1.0	3	1.8	2.8	2.1	0.3	1.0	2.6	0.1	-10.1
Mill Pond	Uiothrix	0.264	14.0	28.9	56.6	2.6	7.8	0.2	0.3	-	0.6	0.6	1.5	0.2	18.9
Boom. Lake	Ulothrix	n.d.	35.4	20.1	39.4	1.8	5.4	0.3	0.5	.	0.4	0.5	1.3	-	17.7
Drainage Tunnel	Ulothrix/Microspora	0.376	34.0	3.1	6.1	0.6	1.8	0.7	1.1	-	2.1	0.5	1.3	0.2	53.5
Meadow	Ulothrix/Microspora	0.282	70.9	4.4	8.6	1.4	4.2	2.2	3.4	0.2	0.6	2.1	5.4	-	6.7
Oriental West Pit	Ulothrix/Microspora	n.d.	20.5	5.6	11.0	0.8	2.4	0.3	0.5	-	1.2	1.7	4.3	.	60.1
Polishing Ponds	Microspora	n.d.	18.7	10.9	21.4	0.5	1.5	8.2	12.7	1.4	1.2	1.6	4.1	-	39.0
Oriental East Pit	Microspora	0.206	35.3	25.8	50.6	0.4	1.2	3.6	5.8	0.2	0.5	1.3	3.3	-	3.3

. denotes percentage smaller than 0.1

n.d. . not determined

Specific comparisons between PPC composition and surrounding water can only be made using PPC populations of a similar biotic composition. Thus, *Ulothrix*-PPCs and surrounding water (Decant Pond, Mill Pond, and Boomerang Lake) were compared without precipitate correction with respect to their elemental composition (Figure 4a). For these comparisons, individual PPC samples were compared.

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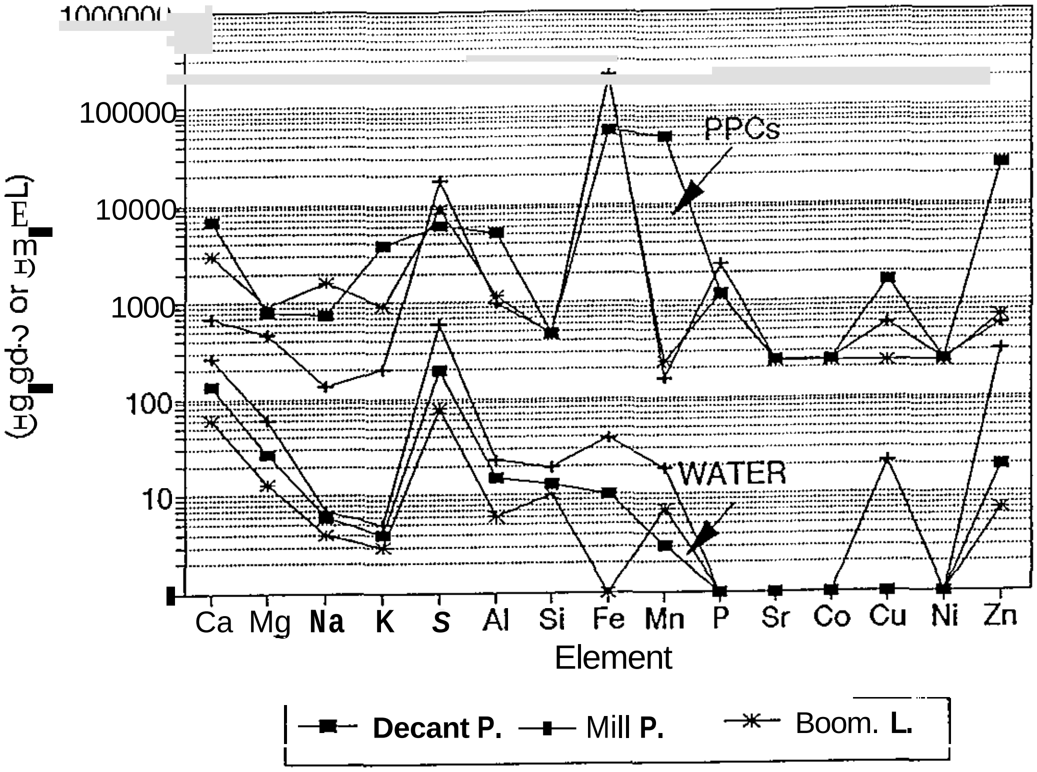

Figure 4a: Elemental scans of *Ulothrix* **PPCs** and surrounding water.

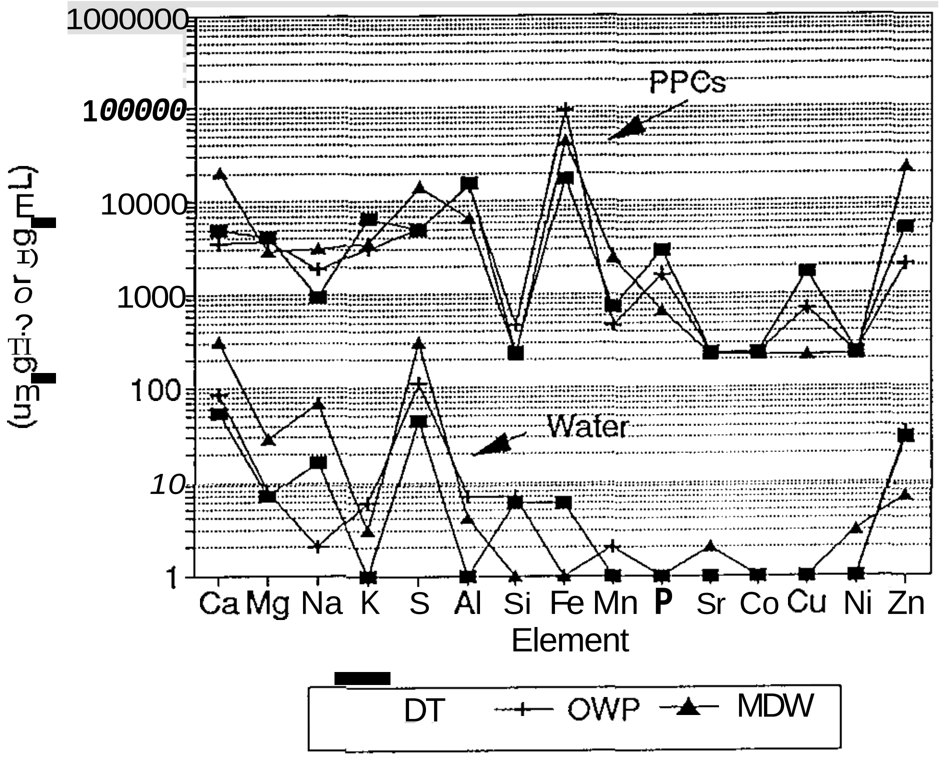

Figure 4b: Elemental scans of Ulothrix/Microspora **PPCs** and surrounding water.

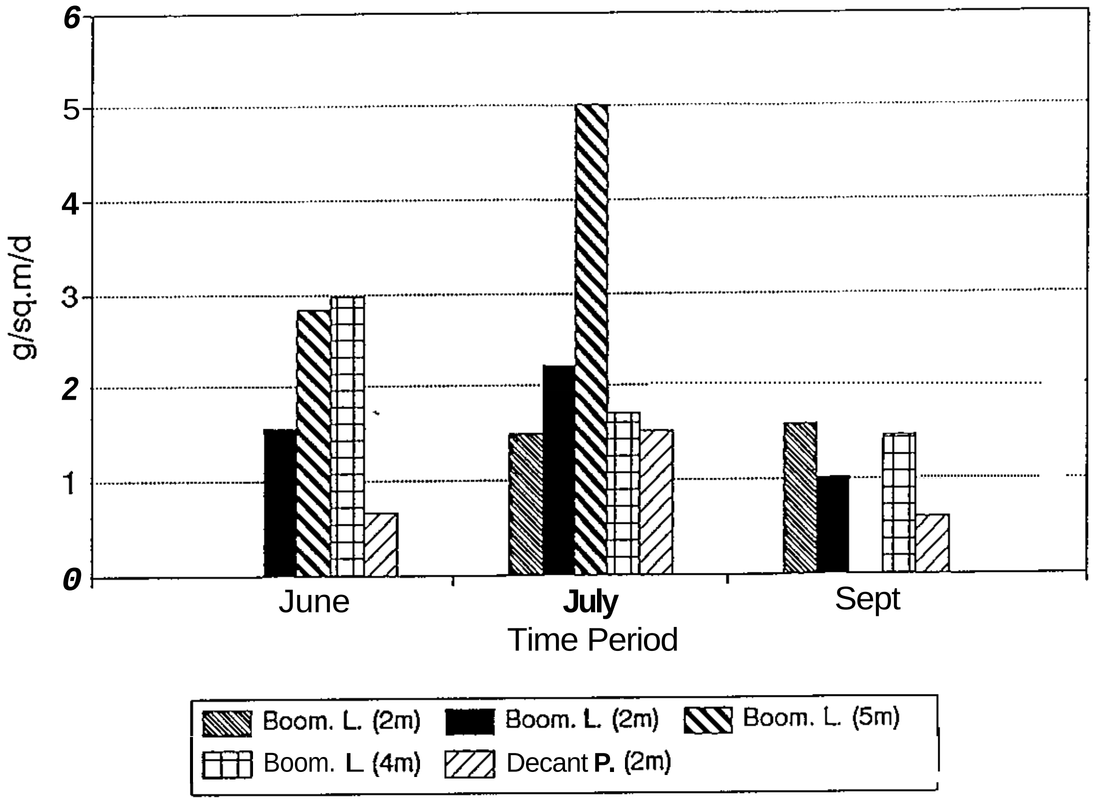

Figure 5a: Precipitation rates in Boomerang Lake and Decant Pond, 1991.

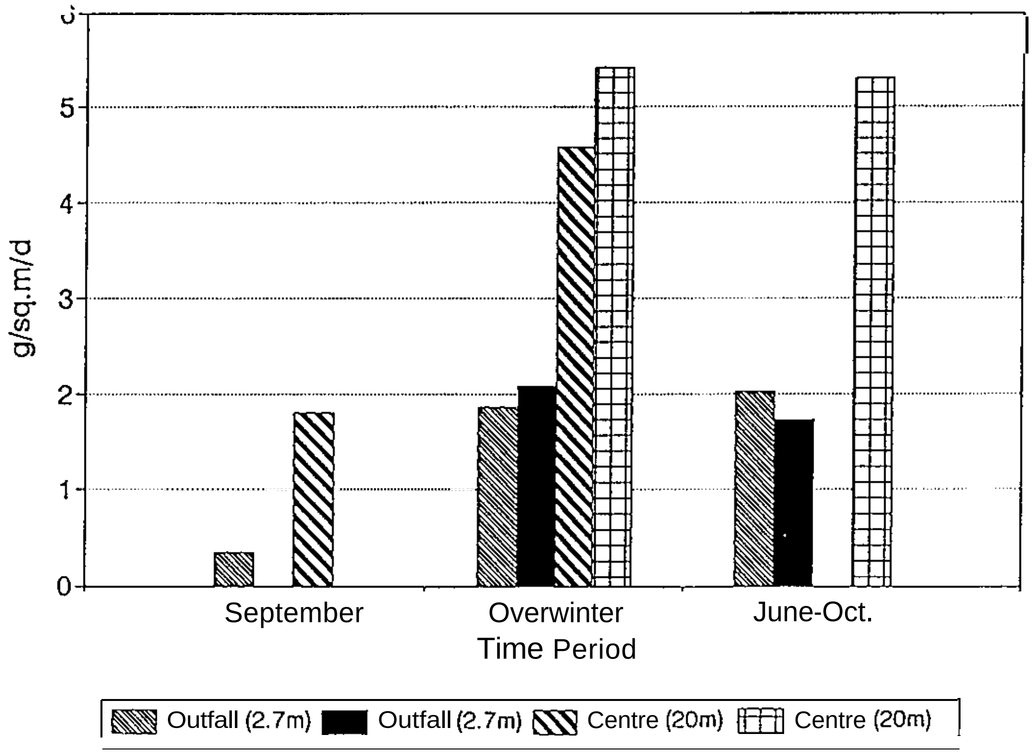

Figure 5b: Precipitation rates in the Oriental East Pit, 1990/1991.

PPC Growth Rates

At the South Bay site, 13 peritraps were set up at each of two locations in Boomerang Lake in early May. At Buchans, 5 peritraps were placed in each polishing pond at the end of May, with 6 in each of the pits. PPC growth rates over 3 periods in the summer were compared within mine sites (Boomerang Lake, and Decant Pond; OWP, OEP, PP1, and PP6) and between sites (Buchans, South Bay).

Growth rates of PPCs at South Bay and Buchans were calculated based on linear growth, i.e. the mass collected after a given submergence time per unit surface area. Growth rates of PPCs varied depending on site and time of year. In Newfoundland, in the OEP, for example, PPCs grew at rates up to 4.6 gdw (sq. m of surface area)$^{-1}$ d^{-1}. In NW Ontario, PPCs in Boomerang Lake grew at rates of only 1.4 gdw (sq m of surface area)" d^{-1}. However, in order to compare algal growth at different sites, the precipitate content of the PPCs at each site had to be taken into account. Using the LOI correction for biomass described in the methods, the mean LOI-corrected periphyton growth rates for the summer of **1991** are shown in Figure ***6.*** Due to the large precipitate component, the maximum periphyton growth rates are only about 0.75 gdw (sq. m of surface area)$^{-1}$ d^{-1}. With the exceptian of periphyton growth in the Oriental West Pit, and June samples from the polishing ponds, most of the growth rates are similar. The peritraps in Decant Pond were set up near the oufflow and experienced water with a relatively high pH. Thus, the water bodies with high pHs (Decant Pond, OEP, PP1, and PP6) showed relatively high growth rates, with the exception of June and July data for PP1 , and June data for PP6. However, among the acidic sites (all had pHs around 3.5), Boomerang Lake samples showed consistently higher growth rates than those in OWP.

PPC Growth and Precipitate Deposition

The growth of PPCs in South Bay and Buchans were compared to precipitate "growth" rates as measured by precipitate deposition rates. Comparisons were made for those periods when precipitate rates and PPC growth rates overlapped, and where precipitation traps were in close proximity to peritraps. The peritrap data were analyzed as if they were precipitate traps, i.e. growth rates were calculated based on the area of lake (or pit) bottom, rather than on a surface area basis. Data are presented in Table 3.

During peak growing periods, PPC mass "outgrew" precipitate deposition rates (Boomerang Lake July - 2.75 gdw m^{-2} d-1 PPC growth vs. 1.65 gdw m^{-2} d^{-1} precipitate deposition rates), but at other times, rates were generally equal. The percentage precipitate was calculated to indicate which process dominated the "growth rate" of the PPC. Thus, in Boomerang Lake in June, 105% of the "growth" rate could be accounted for by precipitate deposition.

Another way of analyzing the contribution of the periphyton to the precipitate deposition process was to compare the composition of precipitate collected in precipitate traps and the composition of the PPCs collected in peritraps. These data are shown in Table 4. At South Bay, the LOI of PPCs was nearly identical with those of the precipitates (45.8 vs. 42.5%, respectively). The composition of the PPCs in Boomerang Lake were also nearly identical to the composition of the precipitate, for at least iron, aluminum, and

TABLE 3: Comparison of PPC "Growth" Rates With Precipitate Deposition Rate

Treatment	June	July	Aug-Sep
	g/sq. m/day		
NW Ontario - Boomerang Lake			
Precipitate	1.60	1.65	1.60
PPC	1.52	2.75	1.45
% Ppte	105	60	110
Newfoundland - Oriental East Pit			
Precipitate*	1.9	1.9	1.9
PPC	1.77	3.33	3.3
% Ppte	107	57	58

* used over summer data (May-October)

TABLE 4: Elemental Composition of Precipitate and Periphyton Precipitate Complexes

	LOI	Al	Fe	Zn	(n)
	%	ppm	ppm	ppm	
Newfoundland - Oriental East Pit					
Precipitate	26.3	7699	299127	56267	4
PPC	36.6	5433	277716	40945	11
NW Ontario - Boomerang Lake					
Precipitate	42.5	3406	174771	618	2
PPC	45.8	2808	182490	619	13

zinc. At Buchans, however, Oriental East Pit precipitates appeared to be significantly enriched with metals over PPCs.

As an example of biological polishing capacity, zinc removal rates in the Buchans polishing ponds were calculated for selected days during the summer of 1991. Data on PPC mass, zinc concentrations in water and PPCs, and flow rates on Aug 25, 1991 were analyzed (Figure 7). Under conditions of: 1) 16 day residence time; 2) 15.5 mg L^{-1} Zn in the inflow stream, and 3) 6.75 pH, 88% of the dissolved zinc was removed from the incoming water stream.

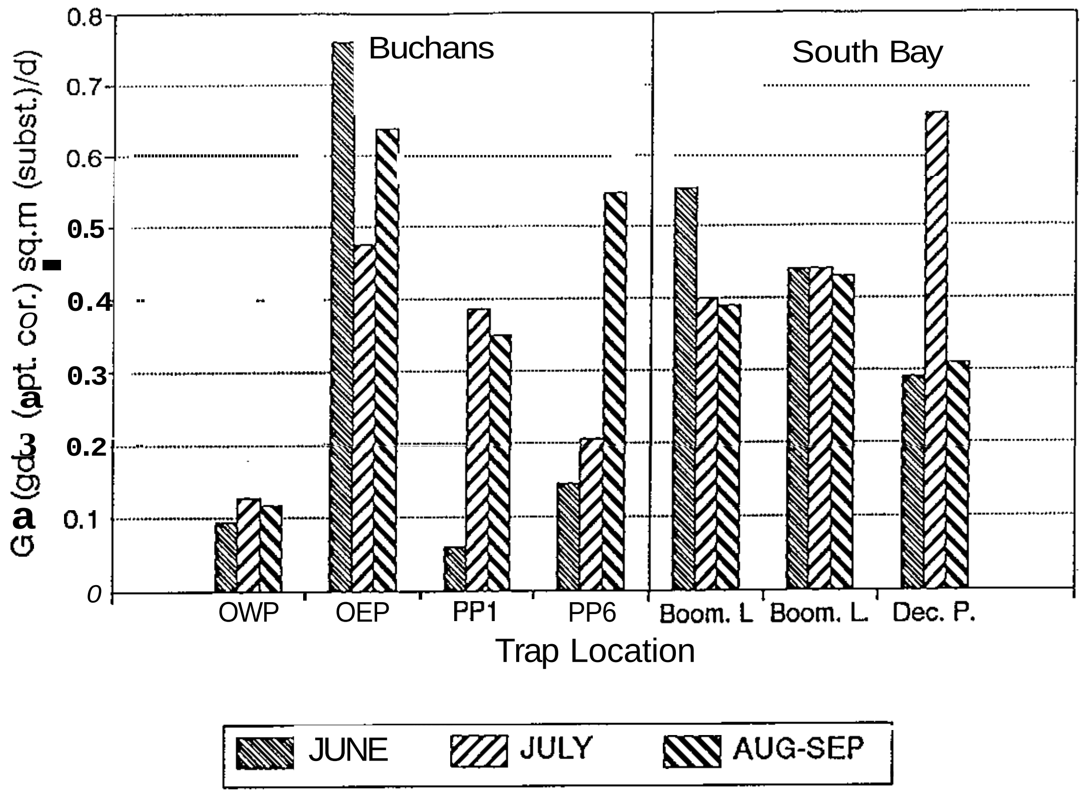

Figure 6: Periphyton growth rates on Peritraps in South Bay and Buchans waste waters.

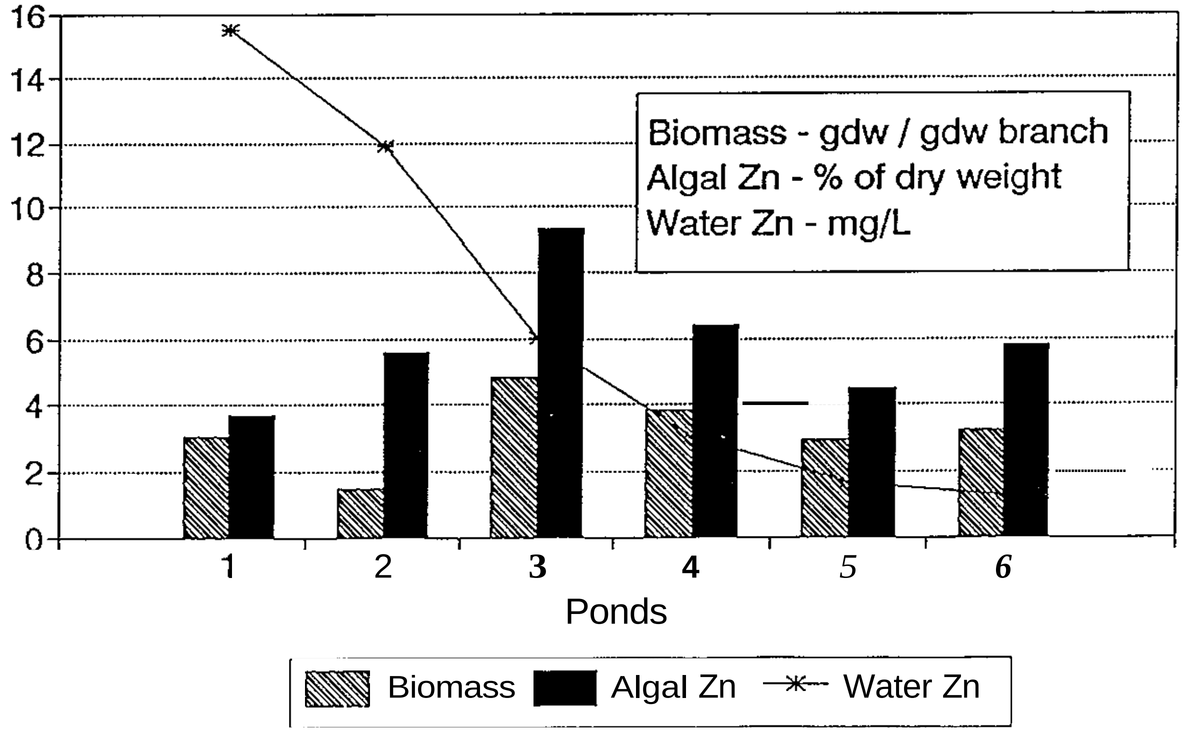

Figure 7: Biological polishing of zinc in Buchans polishing ponds, August 25, 1990.

DISCUSSION

Our data suggest that algae can grow well in mine seepages, ponds, and lakes over a range of pHs, and metal concentrations. Metal precipitates, and dissolved metals can be found in association with algae at these sites. During peak growing periods, PPC mass can "outgrow" precipitate deposition rates, but at other times, rates are generally equal. This suggests that precipitate deposition rates dominate the PPC growth rates, and that already formed precipitates are simply being sieved from the water. This is further confirmed by analyzing the composition of the PPCs and precipitates.

Newman et al. (9) correlated the composition of *aufwuchs* with the composition of precipitate. Their finding, that negative correlations between cell density and elemental concentrations indicated that the role of metal hydroxides was more important than periphyton accumulation in explaining the metal concentrations found in *aufwuchs.*

Periphyton surfaces and associated polysaccharides are providing a "sticky" surface which appears to "sieve" precipitates from the water. Where precipitates are not in high concentrations, periphyton appear to be providing surface area for the direct binding of zinc, and other metals onto algal surfaces. Thus, at high concentrations of precipitate, the composition of the precipitate and PPC are nearly identical, and the PPC is a "sticky sieve". At low concentrations of precipitate or with only dissolved metals present, the periphyton are providing a surface on which metals can be bound.

Regardless of the role that periphyton plays, a significant fraction of the zinc, and other metal loadings can be removed from waste streams, especially at higher pHs.

ACKNOWLEDGEMENTS

We wish to acknowledge partial support for this work by the joint venture group at Buchans. Newfoundland - ASARCO Inc. and Abitibi-Price Inc. Particular thanks are given to the General Manager/Consultant for ASARCO at Buchans, Mr. G. Neary. BP Resources, Development Corp. of Cape Breton, and CANMET also provided financial support, through CANMET contracts, DSS File #034SQ.23440-1-9009, DSS File # 034SQ.23440-1-9011, and DSS File #034SQ.23440-1-9010.

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APPENDIX B: OEP Meadow Soil Experiments

In 1990 Buchans soil samples were collected from several locations in the First and Second Meadows (sample area codes are shown in Map 2). The objective was to determine the zinc distribution in the soil as a function of soil horizon (depth). The soil elemental analyses are described in the 1990 Buchans Report.

Major elements in the meadow soils are Al, Ba, Fe, S, Ca, K, Na, Mg and Zn (>10 mg/g). Among them Al, Na, Mg and K are more concentrated in the lower soil layers. These elements form the basic components of natural soil. Ba, Fe, S and Zn are mainly concentrated in the top soil layer, and were probably brought in as precipitates after OEP overflowed. Calcium is concentrated in the bottom soil layers of A, B, D and G areas, but in the top soil layers of areas C, E, and F. The amount of Cu is relatively low (1.5 mg/g to 0.02 mg/g), and is concentrated in the top soil layers. All the top soil layers contain high quantities of organic matter (LOI = 48.86% - 83.01%).

Soil from station E was also collected in 1992. If the ICP analysis of soil from station E in 1992 and 1990 are compared (Table B1, ICP File 3785-3788), % LOI of the top soil layer increased from 49.9 % to 82.1 %. Manganese, zinc, and sulphur concentrations increased as well; for Mn and Zn, the increase was more obvious in the top soil layer, only sulphur increased significantly in the bottom soil layer. Aluminum and iron concentrations remained similar. Barium, sodium, potassium, calcium and magnesium all decreased.

Since iron and zinc are the major precipitates from OEP water, by taking the average concentrations in the top and bottom soil layers from C, D, E and F and comparing them with those in a clean Buchans peat sample, we can estimate the total amounts of iron and zinc caught by the First Meadow in the period of 1987 - 1990.

Comparison of Iron, Copper and Zinc Concentrations (mg/g) in Meadow Soil and Peat

	C top	C bot.	D top	D bot.	E top	E bot.	F top	F bot.	avg.	peat
Fe	47.6	15.4	15.4	13.3	80.5	17.5	98	12.6	37.5	5.6
Cu	0.3	0.02	0.4	0.02	0.2	0.02	0.4	0.02	0.17	0
Zn	15.8	0.3	0.5	0.1	21.6	0.3	44.6	0.5	10.5	0.03

The First Meadow area is 29,000 m^2; assuming the average soil depth affected by OEP water is 15 cm, and the average soil density is 1.1 g/mL, then annual loadings of the three metals in the First Meadow are:

1/3*29000*0.15*1.1*32 kg (about 51 tonnes) of Fe
1/3*29000*0.15*1.1*10.5 kg (about 17 tonnes) of Zn
1/3*29000*0.15*1.1*0.17 kg (about 0.3 tonne) of Cu

Using a depth of 15 cm results in an accumulation of 17 tonnes of zinc. This is a reasonable depth of precipitate and compares reasonably well with one third of the loading derived from Table 5 of 25.8 tonnes of zinc.

Since all the water from the OEP must flow through or near station E, it is not surprising that soil at station E contains the highest iron and zinc concentrations, compared samples from stations C, D, and F. The concentrations at station E may serve to estimate the worst case contamination in the First Meadow. From 1990 to 1992 zinc concentration in the top soil layer at E increased from 21.6 mg/g to 30.2 mg/g. This represents an annual increase of 4.3 mg Zn/g.

A surface water sample was also collected from station E in the spring of 1992. Since the water at station E comes mainly from the outflow of the OEP and passes through the First Meadow, analysis of the water should represent biologically "polished" water. Metal content should be similar to that which will found at the outflow of Pond 10 when operational.

Comparison of Station E surface water with OEP outflow water.

	Meadow E water	OEP outflow
Fe mg/L	< 0.1	10.2
Zn mg/L	12.1	21.8

The above data indicate that although the First Meadow has been contaminated for five years, and there is very high concentration of zinc in the top soil at station E, zinc and iron concentrations still decrease considerably by passing through the First Meadow alone. Iron concentrations drop after oxidation and formation of ferric-hydroxide. Zinc drops are due to the formation of zinc-carbonate. Both reactions need time. With a longer retention time in the First Meadow, water quality can be improved further.

Leaching experiments were performed on meadow sediments to determine:

(1) the condition of the remaining zinc in the sediments of the potential new polishing ponds.

(2) the possibility of zinc redissolution from meadow sediments.

A series of four soil leaching experiments were carried out in the lab.

(1) Ten grams of air-dried soil from different areas (collected in 1990) were mixed with 50 mL distilled water. The pH and zinc concentrations were measured after 55 days (Table B2).

(2) Ten grams of air-dried soil (1990) from some areas were mixed with 50 mL OWP water, pH and zinc concentrations were measured after 36 days (Table B3).

(3) A 3.3 g sample of soil (wet, subsample from experiment 1) was further mixed with 15 mL of OEP, OWP, and distilled water, separately. The slurries were shaken for 1 min and allowed to stand overnight. The pH and Zn concentrations were measured the next day. The deepest soil layer samples were shaken further with OWP water for 12 h and allowed to sit for 6 to 9 days before the pH and zinc concentrations were measured (Table B4).

(4) Ten grams of new (1992) soil from station E (fresh weight) was mixed with 50 mL of distilled water, 50 mL of OEP water, and 50 mL of OWP water, separately. The pH and zinc concentrations were measured after 152 days (Table B5).

In the soil -water system there are two possible reactions: adsorption and dissolution. Soil is comprised of large .quantities of colloidal particles and organic matter which can adsorb metal ions. In the system, there is an equilibrium between free metal ion (in water) and complexed metal ion (on the soil surface). The equilibrium is determined by metal concentration in the water and the soil particle surface. The dissolution reaction is determined by water pH and the original metal concentration in soil.

When the zinc concentration increased in the soil slurry, the dissolution reaction was considered to be the major reaction. When the zinc concentration decreased in the soil slurry, adsorption was considered to be the principle reaction.

Metal dissolution (desorption) ability in soil was calculated as:

$$([Zn]_{eq} - [Zn]_{orig})^{*}\ mL(water)/grams(soil)/[Zn]_{soil} \qquad (1)$$

The adsorption ability of soil was calculated using the following equation:

$$([Zn]_{eq} - [Zn]_{orig})^{*}\ mL(water)/grams(soil) \qquad (2)$$

A negative value means that zinc is adsorbed by the soil.

All four experiments show that soil released zinc in distilled water, but adsorbed zinc in most situations with OEP and OWP water. Equation (1) was used to analyze the data in the distilled water experiments, and Equation 2 was used when OEP/OWP water was slurried with the soil samples.

Stations A and B have soil (below 15 cm) which has a high probability of releasing zinc. These soils are contaminated by waste rock pile effluent. Most components in the soil

B4).

(4) Ten grams of new (1992) soil from station E (fresh weight) was mixed with 50 mL of distilled water, 50 mL of OEP water, and 50 mL of OWP water, separately. The pH and zinc concentration were measured after 152 days (Table B5).

In the soil - water system there are two possible reactions: adsorption and dissolution. Soil is comprised of large quantities of colloidal particles and organic matter which can adsorb metal ions. In the system, there is an equilibrium between free metal ion (in water) and complexed metal ion (on the soil surface). The equilibrium is determined by metal concentration in the water and the soil particle surface. The dissolution reaction is determined by water pH and the original metal concentration in soil.

When zinc concentration increased in the soil slurry, the dissolution reaction was considered to be the major reaction. When zinc concentration decreased in the soil slurry, adsorption was considered to be the principle reaction.

Metal dissolution (desorption) ability in soil was calculated as:

$$([Zn], - [Zn]_{orig})^{*}\ mL(water)/grams(soil)/[Zn]_{soil} \qquad (1)$$

The adsorption ability of soil was calculated using the following equation:

$$([Zn]_{eq} - [Zn]_{orig})^{*}\ mL(water)/grams(soil) \qquad (2)$$

A negative value means that zinc adsorbed by the soil.

All four experiments show that soil released zinc in distilled water, but adsorbed zinc in most situations with OEP and OWP water. Equation (1) was used to analyze the data in the distilled water experiments, and Equation 2 was used when OEP/OWP water was slurried with the soil samples.

Stations A and B have soil (below 15 cm) which has a high probability of releasing zinc. These soils are contaminated by the waste rock pile. Most components in the soil are inorganic minerals. The probability of zinc release from the bottom soil layers is even higher. Zinc release decreased with time.

Soil from C, D, E and F contained more organic material. Since the top soil contained more zinc, top soil slurries contained higher zinc concentrations. However, the calculation shows that zinc dissolution ability is low in the top soil. Zinc release increased slightly with tim.

Meadow soil showed zinc adsorption ability with OEP and OWP waters. All the top soil layers showed relatively higher zinc adsorption abilities. The values are almost the same in all soil samples. The differences only appeared when lower soil horizons were analyzed. With A and D soil samples, the adsorption ability quickly decreased with depth. In soils C, E, F and G the adsorption ability remained similar throughout the whole profile. This is in circum-neutral water. Therefore, the low pH slurry probably contains more ferrous-carbonate and less zinc-carbonate; while high pH slurry contains more zinc-carbonate and less iron-carbonate.

Since most of zinc has been precipitated recently, zinc is mostly concentrated in the top soil layers. Therefore, there is less zinc in the lower layers of the soil. Soil leaching experiments show that the adsorption ability is almost the same from the surface to the bottom of the soil profile, so we can expect the bottom soil from the new polishing pond to adsorb instead of release zinc. Since the excavated top soil layers contain large amount of organic material, the probability of metal dissolution is low. If organic material decomposition can be delayed, zinc may have a long retention time in the soil.

Table **B1**: Analysis of Meadow E Soil (ug/g)

ug/g	1990		1992			
	0-13 cm	25-50 cm	0-7 cm	7-16 cm	16-25 cm	25-37 cm
Al	23850	68900	14630	14531	45709	50959
Ba	14682	1123	254	232	373	232
Ca	14910	6390	13137	12653	3523	2768
Fe	80500	17500	84693	9095	28244	13302
K	5810	18260	4279	2966	20259	28071
Mn	770	308	11147	512	290	329
Na	9620	27380	5275	3460	12375	19562
S	7000	1000	4976	6623	1497	30027
Zn	21631	278	30155	5595	971	791
LOI%	49.85	16.71	82.1	75.3	13.3	8.67

Table B2: Zn Desorption Ability of Buchans Soil (with distilled water)

		Expt I		Expt III	
	Depth/cm	pH	Zn %	pH	Zn %
		18 - 19 days		1 day	
A 9C	0-7	4.05	0.01	5.86	0.001
	7-15			6.22	0.000
	15-30	4.42	0.03	4.80	0.003
	30-43			4.47	0.009
	43-50	5.34	0.02	4.92	0.047
		18 - 19 days		1 day	
B 7N	0-3	3.96	0.01	5.31	0.005
	3-15			4.56	0.009
	15-25	3.81	0.36	4.18	0.049
	25-30			4.29	0.037
	30-35	4.89	0.06	4.42	0.066
		12 days		dis. H2O	
C M6	0-5	6.56	0.002	6.43	0.002
	5-25			6.37	0.000
	25-40	4.84	0.002	5.04	0.001
	40-45	6.05	0.03	5.59	0.005
		12 days		dis. H2O	
D Wcreek	0-6	4.63	0.02	5.99	0.006
	6-15			5.06	0.000
	15-30	4.91	0.01	5.21	0.006
	30-50	5.46	0.003	5.91	0.000
		55 days		dis. H2O	
E Wend	0-13	7.08	0.002	7.15	0.000
	13-19	6.23	0.000	6.29	0.000
	19-24	5.69	0.001	5.61	0.000
	24-50	5.46	0.04	5.72	0.003
		12 days		dis. H2O	
F Trans.	0-5	6.52	0.001	6.82	0.001
	5-10			7.18	0.000
	10-25	5.71	0.000	6.05	0.000
	25-40	5.63	0.01	6.77	0.002
		12 days		dis. H2O	
G meadow	0-10	4.27	0.002	6.77	0.002
	10-30	5.24	0.01	6.17	0.000
	30-50	5.21	0.01	5.38	0.012

E Wend	Expt IV	
Depth cm	pH	Zn %
0-7	6.76	0.0003
7-16	6.14	0.0002
16-25	6.17	0.0020
25-37	6.21	0.0063
	19 days later	
0-7	6.82	0.0001
7-16	6.18	0.0005
16-25	6.25	0.0015
25-37	6.43	0.0073
	28 days later	
0-7		0.0002
7-16		0.0001
16-25		0.0012
25-37		0.0063
	152 days later	
0-7	6.39	0.0016
7-16	6.56	0.0021
16-25	6.57	0.0067
25-37	6.56	0.0136

Table B3: Soil Experiment I & II Data
Zinc Adsorption Ability (mg/g) of Soil

		OWP H2O		OWP H2O	
		pH	Zn mg/L	pH	Zn mg/L
	original	3.27	41.5	3.27	41.5
		1 - 2 days		24 days	36 days
	Depth cm	pH	Zn mg/g	Zn mg/g	Zn mg/g
A 9C	0-7	3.93	-0.195	-0.203	-0.202
	15-30	4.13	-0.120	-0.172	-0.167
	43-50	4.46	-0.005	-0.100	-0.104
B 7N	0-3	3.77	-0.195	-0.203	-0.196
	15-25	3.71	-0.033	-0.112	-0.093
	30-35	3.94	-0.108	-0.100	-0.031
F Trans.	0-5	6.39	-0.158	-0.195	-0.194
	10-25	5.77	-0.170	-0.156	-0.169
	25-40				
G meadow	0-10				
	10-30				
	30-50	4.85	-0.195	-0.167	-0.187

Table B4: Soil Experiment III Data
Zinc Adsorption (mg/g) of Soil

		OEP H2O		OWP H2O	
		pH	Zn mg/L	pH	Zn mg/L
	original	6.5	5	3.27	41.5
	Depth cm	pH	Zn mg/g	pH	Zn mg/g
A 9C	0-7	5.68	-0.019	5.68	-0.185
	7-15	5.87	-0.022	5.63	-0.020
	15-30	4.35	0.032	3.95	-0.070
	30-43	4.46	0.026	3.97	-0.070
	43-50	6.52	-0.007	3.92	-0.061
	7 days			5.72	-0.020
B 7N	0-3	5.32	-0.018	4.97	-0.181
	3-15	4.52	-0.016	4.33	-0.180
	15-25	4.27	0.065	3.81	-0.070
	25-30	4.29	0.061	3.78	-0.057
	30-35	6.02	0.026	3.89	-0.066
	7 days			4.31	-0.004
C M6	0-5	6.86	0.010	6.55	-0.152
	5-25	6.22	-0.021	5.67	-0.177
	25-40	5.65	-0.005	4.65	-0.117
	40-45	6.04	-0.012	4.51	-0.016
	8 days			4.75	0.003
D Wcreek	0-6	5.62	-0.023	5.35	-0.174
	6-15	5.37	-0.012	4.11	-0.063
	15-30	5.26	-0.015	4.34	-0.084
	30-50	5.98	-0.016	4.72	-0.137
	6 days			4.84	-0.001
E Wend	0-13	6.94	0.002	6.71	-0.162
	13-19	6.17	-0.019	5.00	-0.180
	19-24	5.68	-0.009	4.80	-0.061
	24-50	6.08	-0.021	5.13	-0.173
	9 days			5.00	0.012
F Trans.	0-5	6.78	0.019	6.66	-0.125
	5-10	6.95	-0.020	6.63	-0.186
	10-25	6.35	0.010	5.19	-0.154
	25-40	6.81	-0.021	4.93	-0.182
	7 days			5.35	0.035
G meadow	0-10	6.81	-0.022	5.71	-0.186
	10-30	5.53	-0.017	4.85	-0.157
	30-50	4.69	-0.015	4.49	-0.125
	9 days			5.06	-0.077

Table B5: Soil Experiment IV Data
Zinc Adsorption Ability (mg/g) in Soil E

	OEP H2O		OWP H2O	
Depth cm	pH	Zn mg/g	pH	Zn mg/g
no soil	6.53	11.9	3.96	15.7
0-7	6.69	-0.052	6.35	-0.071
7-16	6.33	-0.056	5.98	-0.076
16-25	6.32	-0.058	5.99	-0.075
25-37	6.41	-0.053	6.05	-0.067
19 days later				
0-7	6.85	-0.054	6.78	-0.072
7-16	6.33	-0.053	6.20	-0.069
16-25	6.11	-0.053	5.92	-0.072
25-37	6.22	-0.053	6.08	-0.064
28 days later				
0-7		-0.056		-0.072
7-16		-0.053		-0.064
16-25		-0.055		-0.064
25-37		-0.055		-0.055
152 days later				
0-7	6.94	-0.058	6.40	0.022
7-16	6.26	0.016	6.20	0.054
16-25	6.37	-0.054	6.34	-0.019
25-37	6.37	-0.054	6.42	-0.042

APPENDIX C: Phosphate Rock Experiments

OEP Long Harbour Phosphate Box Experiment

OEP water pH is circum-neutral. Water below the thermocline contains only ferrous iron in concentrations between 80 and 90 mg/L. The water above the thermocline is well oxygenated, oxidizing the ferrous iron to ferric and precipitating the ferric iron. The result is that dissolved iron concentrations are much lower above the thermocline than below. During the winter when the whole pit surface is sealed by ice and snow, ferrous oxidation is greatly inhibited, and most of iron is accumulated as ferrous ion. This situation is protracted until spring. Therefore, OEP water in the spring contains higher iron concentration than any other time of the year. This is shown in the table below.

Table C1: Iron Concentration (mg/L) in 1992 OEP Water

ICP File	Time	Surface	7 m	15 m	Bottom
3792-3793'	May 28	10.2			86.7
4169-4172	Sept. 28	<1	56	77	79

The titration curves of OEP water (Figure C1) show that acidity is higher at the bottom than at the surfacer, which is the case both in the spring and in the fall. This is due to the higher concentrations of iron in the bottom water.

The phosphate box water data are summarized in Table C1. Generally, at each measuring date, when both inflow and outflow are sampled, the differences in zinc concentrations range between 6 to 11 mg/L. The rate of reduction presented in Table 1 is derived from data measured during the phosphate rock box experiments. These data are presented in Table C2.

The zinc reduction rate was calculated assuming no flow, as the box was leaking. The starting concentration of zinc was taken on June 15th as 26.55 mg/L (WH, Table

Table C2: Buchans Phosphate Box Experiment Data

REMARK	LOCATION	TEST	Zn	PO4	Fe
MAY 31					
WH	OEP OUTFLO	FIELD	22.05		
FA			21.65		
JUNE 1					
WH	OEP BOTTOM	FIELD	30.65		
FA			29.45		
JUNE 2 - JUNE 3					
WH	BOX OUTFLO	8:30 FIELD	15.0	4.5	
		5:00 FIELD	12.5	25.0	
		9:00 FIELD	13.0	27.0	
JUNE 6					
WA	BOX DISCHAR	G.N.	15.85		
FA			14.4		
JUNE 15					
WH	OEP OUTFLO	G.N.	26.55		
FA			11.6		
WH	BOX DISCHAR		19.15		
FA			11.75		
JUNE 18					
WA	BOX INFLOW	LAB	16.25	0	
FA			13.75	0	
WA	BOX DISCHAR		8.75	0	
FA			10	0	
JUNE 22					
WA	OEP OUTFLO	G.N.	17.15		
WA	BOX DISCHAR		11.15		
FA			10.96		
JUNE 29					
WH	ENCLO.SURF.	LAB	20	0	
	ENCLO.BOTM.		17.5-13.5	0	
	BOX SURF.		8.75	0	0.1
	BOX BOTTOM		10-7.5	0	0.1
	OEP OUTFLO	G.N.	18.1		
WA	OEP OUTFLO	(M.K.)lab.	12.5		4.6
FA		(M.K.)lab.	12.5		3.1
WA	BOX	(M.K.)lab.	10		1.3
FA		(M.K.)lab.	4.2		1.4
JULY 6					
	OEP OUTFLO	G.N.	20.64		
WA	OEP OUTFLO	(M.K.)lab.	12.5		10.1
FA		(M.K.)lab.	12.5		4.7
WA	BOX	(M.K.)lab.	5.0		1.3
FA		(M.K.)lab.	4.2		1.4
JULY 13					
	OEP OUTFLO	G.N.	18.06		
WA	OEP OUTFLO	(M.K.)lab.	12.5		3.1
FA		(M.K.)lab.	12.5		2.3
WA	BOX	(M.K.)lab.	5.0		1.1
FA		(M.K.)lab.	4.2		1.7
JULY 17					
WH	OEP OUTFLO	(M.K.)lab.	17.5	3.1	0.46
	ENCLOSURE	(M.K.)lab.	16.6	14	0.56
	BOX INFLOW	(M.K.)lab.	17.3	3.2	0.23
	BOX INFLOW#	(M.K.)lab.	14.0	4.4	0.2
	BOX INFLOW#	(M.K.)lab.	6.5	3.3	0.14
SEPTEMBER 8					
WH	OEP OUTFLO	LAB	15.0	0.2	0.08
	OEP PR LAYE		12.3	0.1	0.08
	BOX CELL #1		12.3	0.1	0.1
	BOX CELL #2		11.5	0.15	0.08
	BOX CELL #3		5.7	0.2	0.07
	BOX DISCHAR		8.4	0.15	0.02
SEPTEMBER 28					
WH	OEP CENTRE	FIELD	19.66		
	ENCLOSURE		17.95		
	BOX CELL #1		17.07		
	BOX CELL #2		11.38		
	BOX CELL #3		6.12		

C2). The zinc reduction rate was calculated by linear regression of successive zinc concentrations measured over the experiment. The final zinc concentration of 6.1 mg/L was measured on September 28th 1992.

Ferric ion is the major competitor to zinc in reactions with phosphate. Without phosphate addition, OEP water turned orange and large quantities of iron were precipitated. The orange colour is due to the iron-hydroxide precipitate which contrasts with the greyish precipitate of $FePO_4$. After phosphate addition, the water became clear and no further orange precipitates were formed. Since most of the phosphate reacted with the iron, zinc concentrations were not reduced significantly (Table C2).

Tailings Pond 2 Phosphate Rock Experiments

Phosphate rock was tested in tailings pond ditches to precipitate iron, and make impermeable barriers, reducing water movement through the tailings. In May 1992, two pits were dug on the TP-2 beach. They measured 2 by 2 m by 1 m deep. The water height in the pits was about 25 cm. Pit #1 was used as a control. Approximately 250 kg of phosphate gravel were spread on the walls of Pit #2. Water samples from these two pits were collected and titrated periodically during the summer (see Figure C2). The water level in the pits slowly decreased during the summer, and when it no longer contacted the phosphate rock, the experiment was stopped. In July (27th), a new pit was dug (5.5 x 3 x 1 m deep; with 10 cm water), and 1800 kg of phosphate sand were spread on the pit walls. After 64 days, water and precipitates from the old phosphate pit (#2), the new pit, and the control pit (#1) were collected. The water titration curves are shown in Figure C3.

Figure C2 demonstrates that on June 1, shortly after pit #2 was dug, pit #2 water contained more iron than the control pit, pit #2 water acidity was higher; but pH was high due to the presence of phosphate sand. By June 18, both pits' acidity had increased, but pit #1's acidity had increased much more than pit #2's acidity, and the phosphate pit (#2) now had the lower acidity. The pit #1 titration curve shows that there were some ferric ions present, but considerable aluminum and ferrous ions. The titration curve of pit #2 water shows that the major ion present was ferrous iron.

Figure C3 establishes that after three months, water in the old phosphate pit (pit #2) still had lower acidity than the control pit (#1). The titration curve of the new pit shows that the majority of the metal ions were removed by phosphate sand after 64 days.

Precipitates and sediment from the three pits were oven dried at 35 C for 5 days. Two grams of each sample were mixed with 50 mL of 0.1N H_2SO_4 solution, stirred for 24 h. The colour of control pit sediment slurry was greenish grey; the colours of the two phosphate precipitates were orange. The acidic slurries were then filtered. The filtered solutions of the control and old phosphate slurry (pit #2) were greenish grey in colour; the new pit phosphate slurry was orange. The titration curves of three solutions shown in Figure C-4 are compared with the original 0.1N H2SO4 solution.

Figure C4 indicates that all three precipitate solutions have slightly higher pHs than sulphuric acid. Their titration curves are shifted to the left of the acid curve. These differences are caused by the hydroxide or carbonate components in the solids. When they dissolve in acid, hydrogen ions are consumed as reactants. The flat parts of the titration curves indicate the dissolved components in the solid. The slopes of the three titration curves from pH=4 to pH=6 are very similar, which means all three solids contain Al+3 and Fe+2, which redissolved in the acid. Only precipitates from the new phosphate pit had a region of lower slope at pH=3, which was caused by the presence ferric ion. This is consistent with the precipitate's orange colour. Although the old phosphate pit precipitate had an orange colour, its solution did not show the existence of any appreciable quantity of Fe+3. Lab phosphate and total iron (Fe^{+3} & Fe^{+2}) results are summarized in the table C-3. These experiments lead to the conclusion that phosphate rock would serve the predicted function in increasing alkalinity, and removing iron and zinc. Thus, it is a desirable product to use in tailings reclamation, either as a layer integrated into the tailings or as a fertilizer.

Table C3: Lab Phosphate and Iron

Acid Dissolved	New PO_4 Pit ppt.	Old PO_4 Pit #2 ppt.	Control Pit #1 sediment
PO_4 ug/g	3647.5	35845.0	134.6
tot. Fe ug/g	39063	3800	20813
ppt contains PO_4 ug/g	9438	63129	1060
ppt contains tot. Fe ug/g	142000	82000	43400
	New PO_4 pit water	old PO_4 pit water	control pit water
PO_4 mg/L	0.29	0.53	0.91
tot. Fe mg/L	198.7	6702.9	6523.4

The Table above shows that although precipitates in the old PO_4 pit (#2) contain quite a high concentration of iron, the acid-soluble iron is quite low. This indicates that aging has changed the physical characteristics of ferric-hydroxide; it becomes difficult to redissolve in water, even in acidic solutions.

Fig. C1: OEP Water Titration
Samples of May 28 and Sept.28, 1992

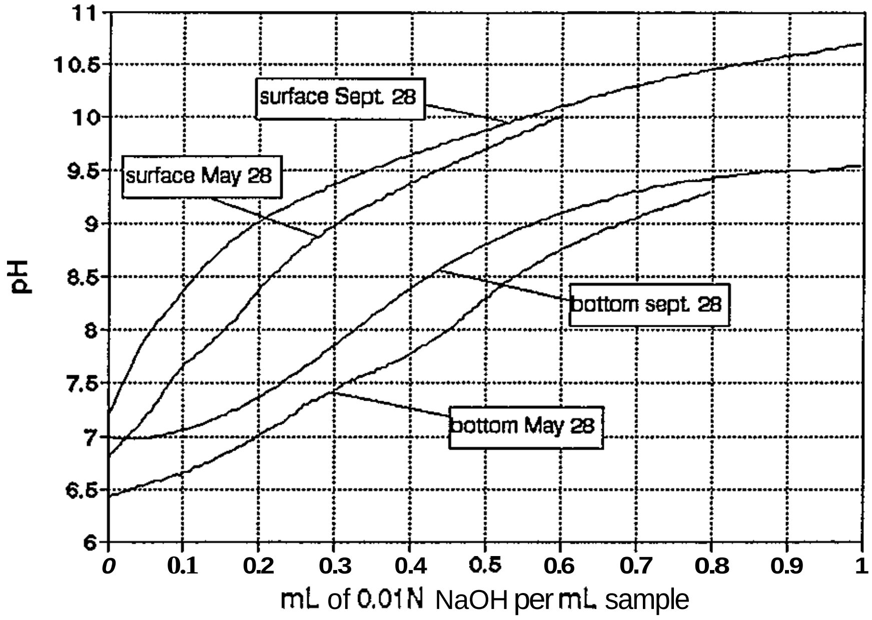


Fig. C2: TP-2 Beach Pit Experiment
1-June 1, 2-June 18

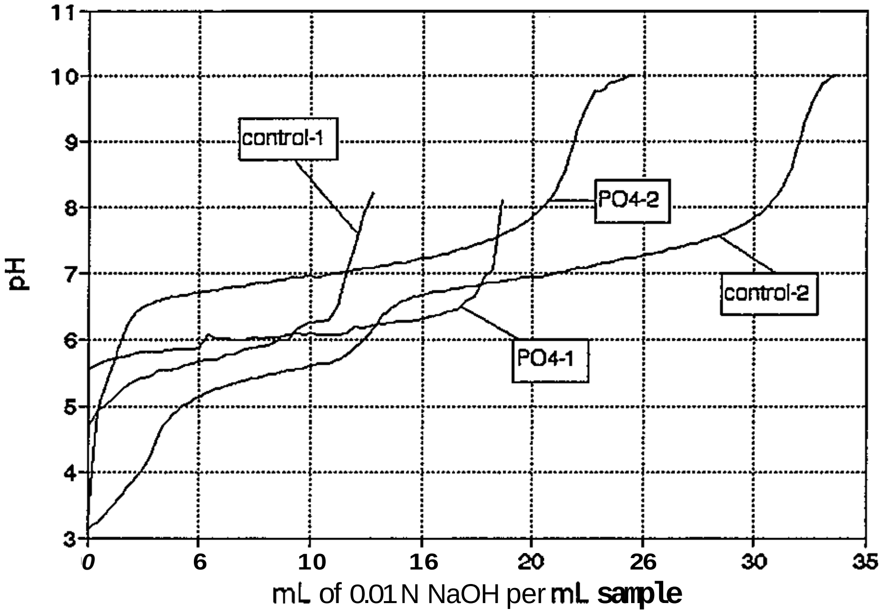


Fig. C3: TP-2 Beach Pit Experiment
Water Sample on Sept 28, 1992

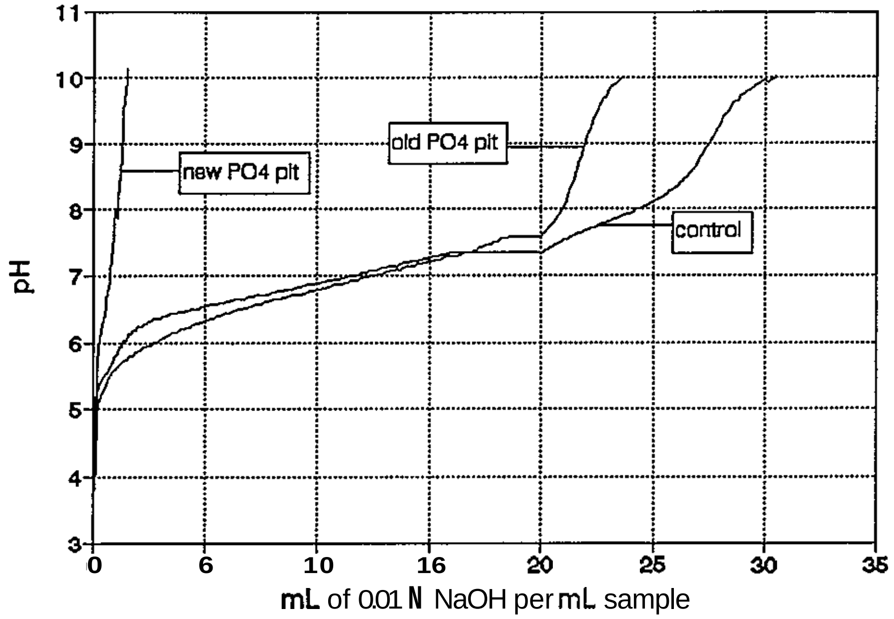
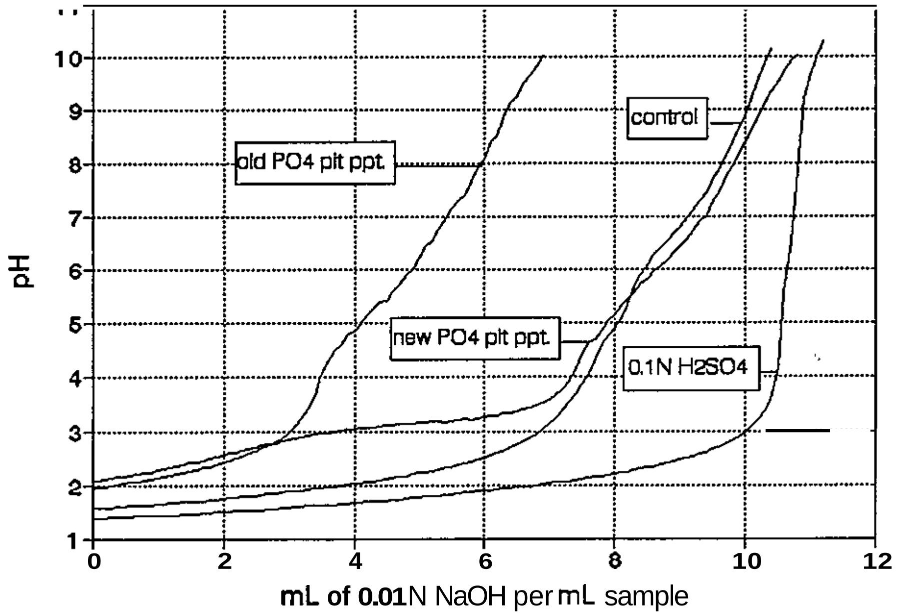


Fig. C4: TP-2 Beach Pit Precipitate
Sept 28, 1992



APPENDIX D: ARUM Jar Experiments

In order to more efficiently monitor **ARUM** process change and find better amendment to accelerate microbial activity, jar experiments have been running since September 5, 1991. Descriptions of the experiment and some early results are in the 1991 report. The experiment continued until May 1992. The final results are described in Table D1.

The first experiment (#1) results show that both glucose and Osmocote (slow-release fertilizer) fail to stimulate the activity of sulphate- reducing bacteria **(SRB).**

Jars 1 & 2 were used as controls for LC1 water and sawdust, i.e. they did not receive either glucose or Osmocote. If these data are compared to data in jars 3 & 4 and jars 19 & 20, it can be seen that both glucose and osmocote did not raise pH, and zinc concentrations were relatively high. These results can be explained by the fact that hydroxyl groups in glucose and ammonium ions in Osmmocote can complex with zinc. When the concentration of glucose and ammonium is high, then, zinc from previous precipitates may redissolve and increase zinc concentration in water.

Jars 5 & 6 may be used as LC2 water controls (Table D1). In this series the effect of Osmocote and glucose is not very distinct. Jars 7 & 17 showed higher zinc concentrations than controls. Jars 8 & 18 showed lower zinc concentrations than controls. Peat amendment in LC2 appeared to be a better microbial activity stimulant than sawdust. When glucose and osmocote were added to the jars, there was probably a competition between microbial activity and complex formation. Zinc concentrations in the water would then have been the result of that competition. If all of the LC2 jars are compared with the LC1 jars, it can be seen that LC2 jars with peat had relatively higher pH, lower Eh, lower conductivity and lower sulphate concentrations than LC1 jars, indicating that more microbial activity was taking place in the LC2 jars. Whereas, the LC2 jars have more microbial activity, most of them have higher zinc concentration than LC1 jars, indicating that there is a possibility that sulphur may re-oxidize in these jars. Eh values in all LC2 jars were +350 - +400 mV. This means that reducing conditions had been replaced by oxidative processes.

The second series of ARUM experiments carried out (#2) all jars contained alfalfa as one of the amendments (Table D2). Zinc concentrations decreased in all jars. But, the high sulphate concentrations indicate that the zinc decrease was not attributable to sulphur reducing bacteria.

The effect of alfalfa on jar water quality is dominated by the effect of organic nitrogen compounds: amine and its derivatives. These are organic alkaline compounds. They can raise water pH and reduce Eh value.

In this series the re-oxidation phenomenon is more obvious. Jars 9 to 13 all have low Ehs and low zinc concentrations. But, jars 14 to 16 have high Eh and zinc values. The pHs of the water in these jars are even lower than the original water. Titration curves (Figure D1) show that the pH decrease was caused by ferrous oxidation. The re-oxidized iron was probably from previous precipitates in the sediments. The prevention and control of this re-oxidation process needs more study.

Potato Waste Experiments

Potato waste experimental jars 5 & 6 can be used as controls to jars 3 & 4 (Table D3). Jars 11 & 12 can likewise be used as controls to jars 7 to 10. All jars with potato waste have relatively high pH, low Eh, low conductivity, low zinc, and low sulphate concentrations. These characteristics are indicative of SRB activity. Jars 1 & 2 with 40 grams potato waste raised the water pH to 7. This means that large quantities of potato waste can promote SRB activity. The appropriate amount of potato waste, however, for a given situation, has yet to be determined.

By comparing the water characteristics of jars 3-6 with jars 7-12 (Table D3), it can be shown that LC2 peat can raise water pH, but not reduce zinc as efficiently as the old or new peat. LC2 peat contains some original SRB, thereby promoting microbial activity very quickly. On the other hand, LC2 peat is also mixed with previous zinc precipitates, which may be partly dissolved during decomposition. The precipitate also diminishes the peat's metal adsorption ability. There is no difference between old (one year decomposition) or new peat in these jars. Generally, peat is not as good as potato waste when it comes to enhancing microbial activity.

The ARUM jar experimental results indicate that:

1. potato waste is the best substrate to date for microbial activity.
2. In the ARUM system there is a reducing-oxidizing cycle.

Field limnocorral monitoring

The lab experimental results can explain the situation in the field limnocorrals. If the temperature and zinc concentrations in the limnocorrals are compared (Figure D2a,b,c,d, D3a,b,c,d), it can be seen that the fluctuations in [Zn] are mainly affected by seasonal changes in weather. With higher temperature, bacteria were more active, and hence, zinc concentrations dropped; with lower temperature, zinc concentrations increased. Since in the control limnocorral zinc concentration has been almost constant over the last three years (some changes may have been caused by measurement error). The fluctuations in zinc concentration may be explained by two reaction trends. One trend **is** brought about by microbial activity, which tends to reduce sulphate into sulphide and precipitate zinc. The other trend is brought about by oxidation which oxidizes sulphide, and releases zinc from precipitates. When microbial activity is strong (as in the first 200 - 300 days in LC1 & LC2 and first 540 - 650 days of LC4 & LC5) zinc concentrations are not affected by temperature change. As time passed, microbial activity was eliminated and temperature effects gradually appeared. This was more obvious in LC1 & LC2. After each high temperature (reducing conditions) - low temperature (oxidization) cycle, zinc concentrations increased again. This indicates that microbial activity had not fully recovered. Peat was a better substrate for bacteria, **so** in LC2 and LC5 the microbial activity was higher and zinc concentration lower for quite a long time. With time, however, even the zinc concentrations in **LC2** and LC5 rose.

The above experiment and the behaviour of the limnocorrals shows that there are two ways to maintain the ARUM process. One approach is to create an anaerobic environment which suppresses the oxidation reactions. Another way is to stimulate more microbial activity. Bacterial activity needs sulphate and organic carbon. In June of this year sulphate and sulphide concentrations were measured in all the limnocorrals. The results (Table D4) showed that sulphate is not limited in the system. Therefore, more substrate (potato waste) was added to the limnocorrals and floating caps were suggested to enhance the anaerobic environment. Within 30 to 60 days, zinc concentrations dropped in all treatments in the limnocorrals. Thus, a fine balance has to be maintained between microbial activity and reducing conditions for ARUM.

Table D1: Buchans Glucose ARUM Experiment #1 (OWP Water)

No	Treatment	pH	Eh/mV	Cond.	Zn/ppm	SO4/ppm
1	LC1/sawdust	3.36	437	710	2.3	550
2	LC1/sawdust	3.32	438	700	5.38	600
3	LC1/sawdust/glucose	3.42	434	690	6.53	650
4	LC1/sawdust/glucose	3.41	444	690	6.53	700
19	LC1/sawdust/osmocote	3.47	445	650	10.3	500
20	LC1/sawdust/osmocote	3.47	456	590	17.6	400
5	LC2/peat	4.46	391	500	11.53	450
6	LC2/peat	4.48	387	550	11.53	600
7	LC2/peat/glucose	4.61	382	500	12.3	350
8	LC2/peat/glucose	4.66	379	450	5	400
17	LC2/peat/osmocote	4.47	361	540	22.3	400
18	LC2/peat/osmocote	4.76	358	400	7.3	100

Table D2: Buchans Alfalfa ARUM Experiment #2 (OEP Water)

No	Treatment	pH	Eh/mV	Cond.	Zn/ppm	SO4/ppm
9	LC4/sawdust/alfalfa	6.84	95	1500	0	1000
10	LC4/sawdust/alfalfa	6.96	146	1710	0.07	1150
11	LC4/alfalfa/glucose	7.45	141	1550	0	1000
12	LC4/alfalfa/glucose	7.36	21	1650	0	1100
13	LC5/peat/alfalfa	6.84	62	1100	0.07	800
14	LC5/peat/alfalfa	2.76	431	1780	3.3	1050
15	LC5/alfalfa/glucose	4.08	376	1500	12.3	850
16	LC5/alfalfa/glucose	3.71	419	1400	6.92	850

Table D3: Buchans Potato Waste ARUM Experiment (OWP Water)

No	Treatment	pH	Eh /mV	Cond.	Zn/ppm	SO4/ppm
1	40g P.W.	7.43	-308	1900	0.07	0
2	40g P.W.	7.11	-276	1400	0.15	10
3	LC2 peat/1g P.W.	5.54	-29	420	2.07	280
4	LC2 peat/1g P.W.	5.04	22	425	1.84	320
5	LC2 peat	4.38	107	570	15.3	410
6	LC2 peat	4.33	159	610	23.8	520
7	(N)peat/1g P.W.	3.77	74	310	0.3	160
8	(N)peat/1g P.W.	3.95	179	375	0.76	180
9	(O)peat/1g P.W.	3.79	202	380	1.15	190
10	(O)peat/1g P.W.	3.71	143	370	0.53	190
11	(O)peat	3.17	251	780	19.2	330
12	(O)peat	3.14	269	790	18	340

Table D4: Limnocoral Oxidation Reduction Data

	LC1 top	LC1 bottom	LC2 top	LC2 bottom	LC3 top	LC3 bottom	LC4 top	LC4 bottom	LC5 top	LC5 bottom	LC6 top	LC6 bottom
JUNE 1												
pH			7.68	6.97	4.69	3.67			7.5	6.95	7.12	6.51
ACIDITY			4	26	20	108			15	52.5	40	200
ALKALINITY			4.5	7					167.5	156.5	135	206
Al			co.1	0.1	<1	<1			<0.1	co.1	<1	<1
Cu			<0.01	<0.01	<1	<1			0.01	0.03	<1	<1
Fe			<0.1	2.2	<1	1			3.8	3	<1	35
Mn			0.96	2.15	<1	3			6.71	7.13	9	12
S			37.1	80	15	122			145	152	236	324
Zn			0.98	0.89	4	42			2.57	1.26	16	24
JULY 16												
pH	6.23		4.25		4.01		7.56		7.94		7.09	
ACIDITY	7		40		57.5		40		7.5		43.5	
ALKALINITY	I						22.5		17		19	
Al	<1		1.74		2.26		<1		<1		<1	
Cu	<1		<1		<1		<1		<1		<1	
Fe	<1		1.74		<1		<1		<1		<1	
Mn	1.39		1.61		1.5		11.9		5.95		11.7	
S	56.2		65.1		67.3		308		121		288	
Zn	1.11		15.8		22.8		19		1.8		18.8	
SEPTEMBER 27												
pH	6.66		6.4				7.42		7.24		7.37	
ACIDITY							58.5		40		55	
ALKALINITY							211.5		256.9		187.1	
Al	<1		<1				<1		<1		c l	
Cu	0.01		0.01				0.02		<0.01		0.01	
Fe	<1		<1				<1		<1		<1	
Mn	2						12		6		12	
S	131						318		49		324	
Zn	[illegible]		0.68				16.6		0.98		19.1	

Fig. D1: Glucose Jar Titration
from Sept.5,1991 to Mar.20,1992

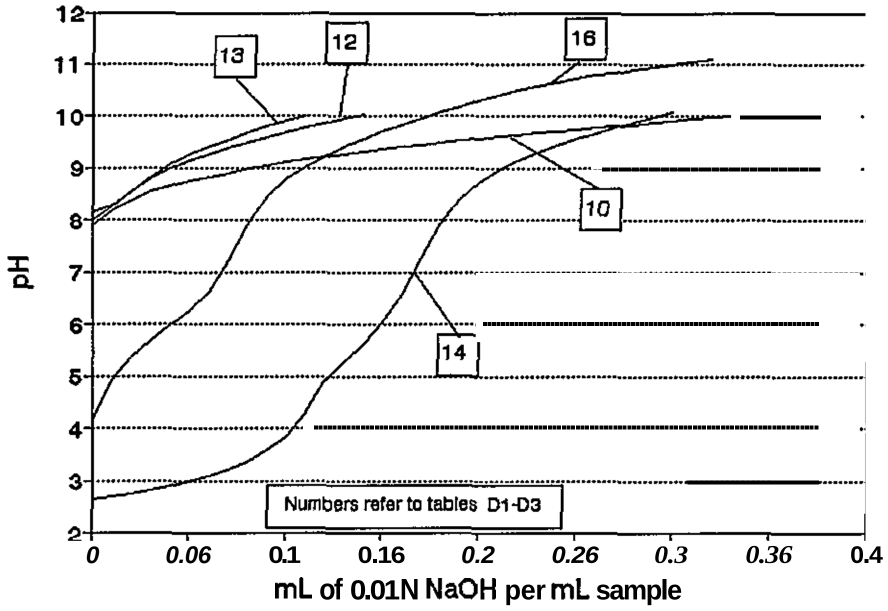


Fig. D2a: Limno 123 Temperature
Sawdust, Peat, Control

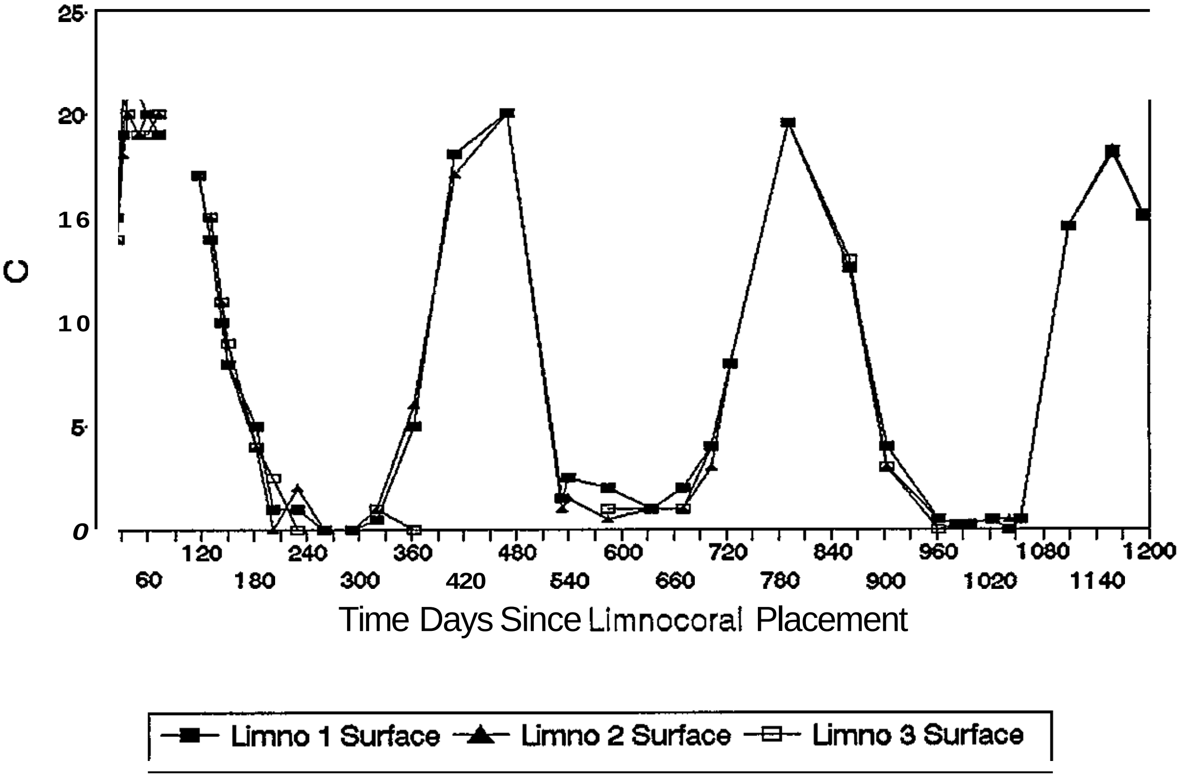


Fig. D2b: Limno 123 Temperature
Sawdust, Peat, Control

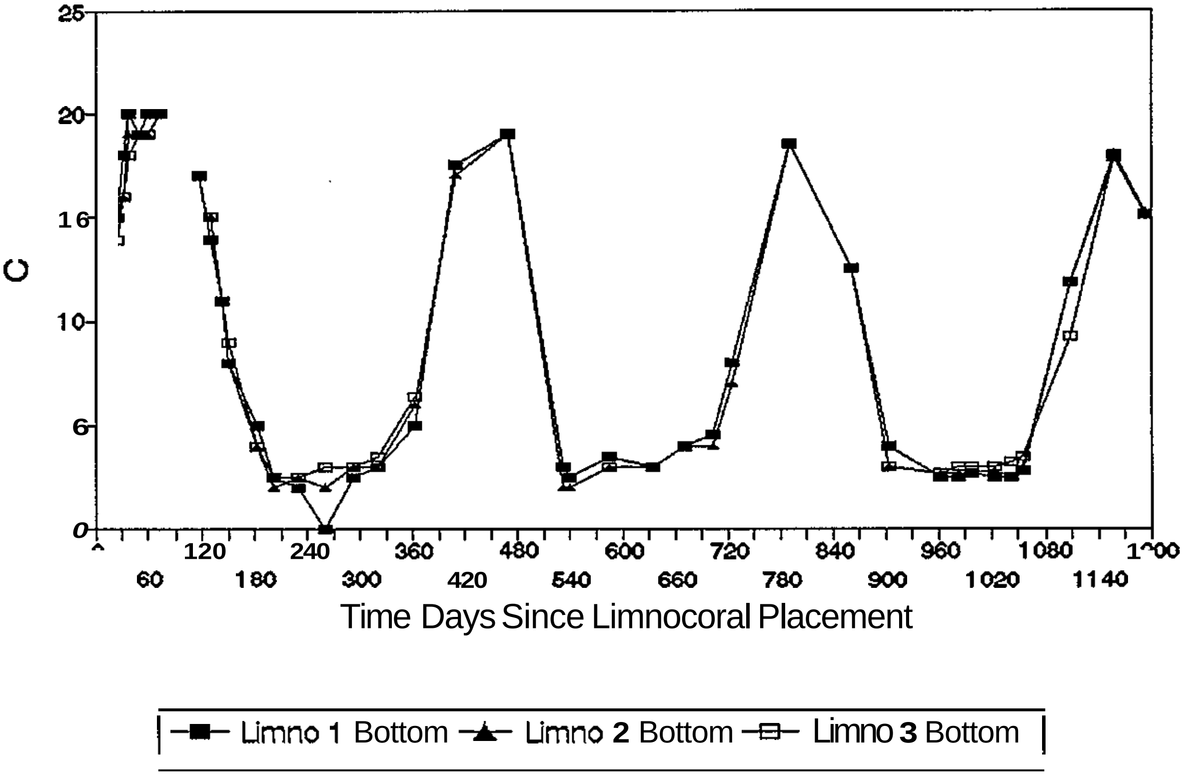


Fig. D2c: Limno 123 Zinc
Sawdust, Peat, Control

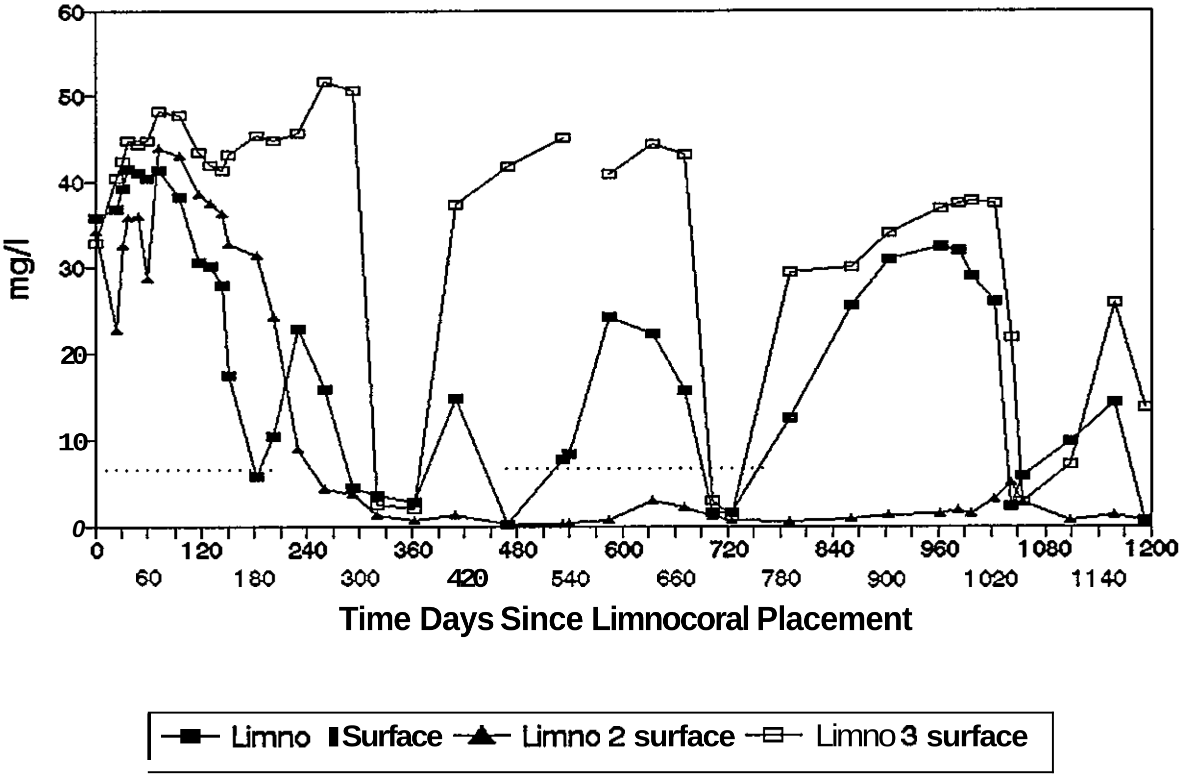


Fig. D2d: Limno 123 Zinc
Sawdust, Peat, Control

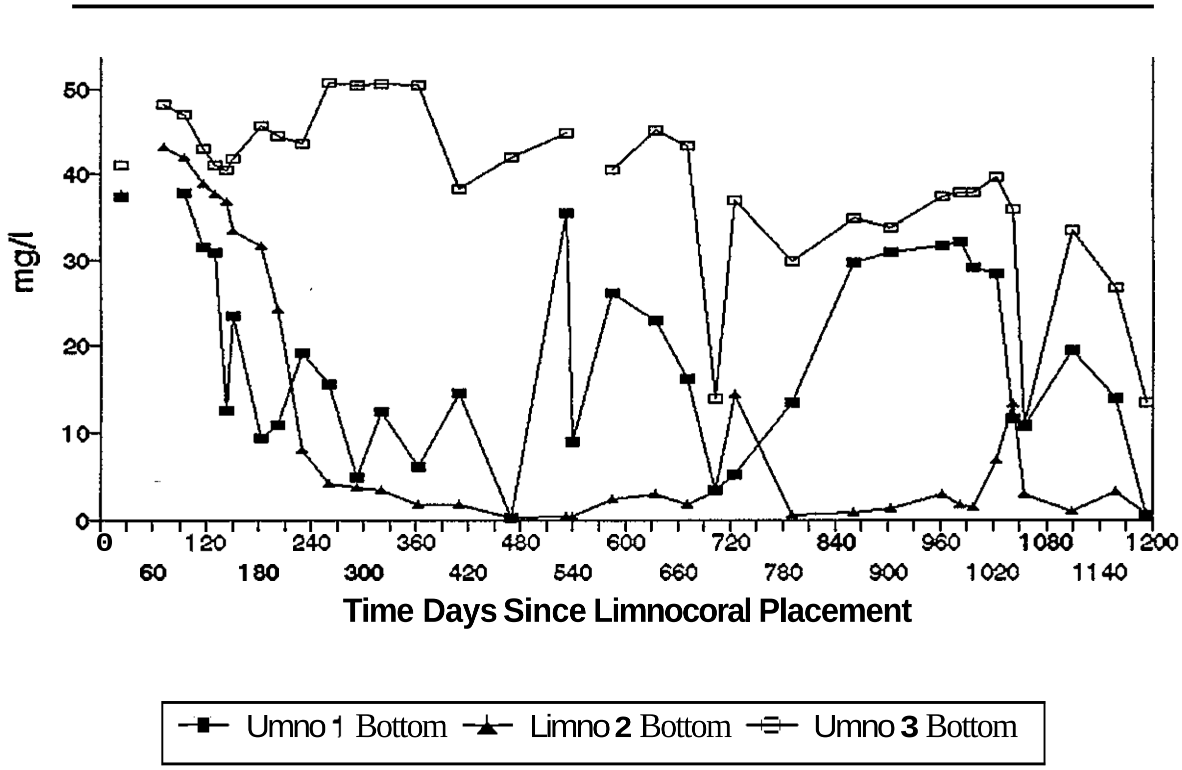


Fig. D3a: Limno 456 Temperature
Sawdust, Peat, Control

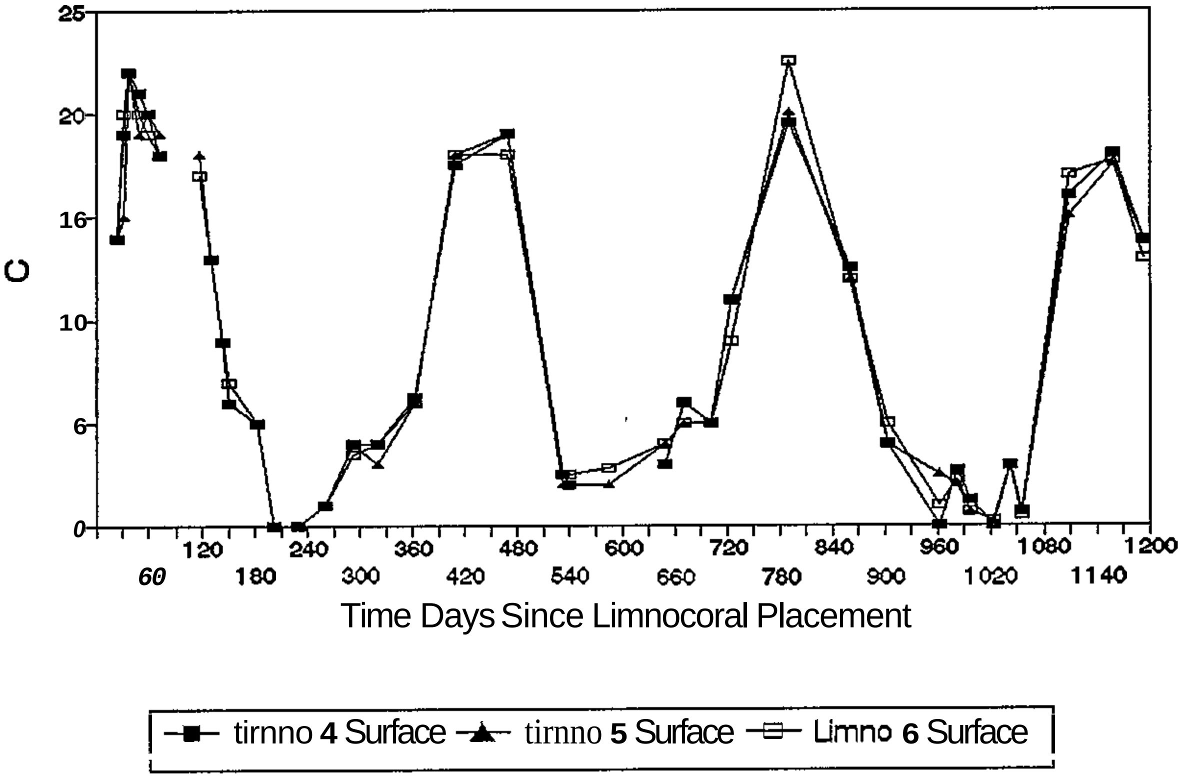


Fig. D3b: Limno 456 Temperature
Sawdust, Peat, Control

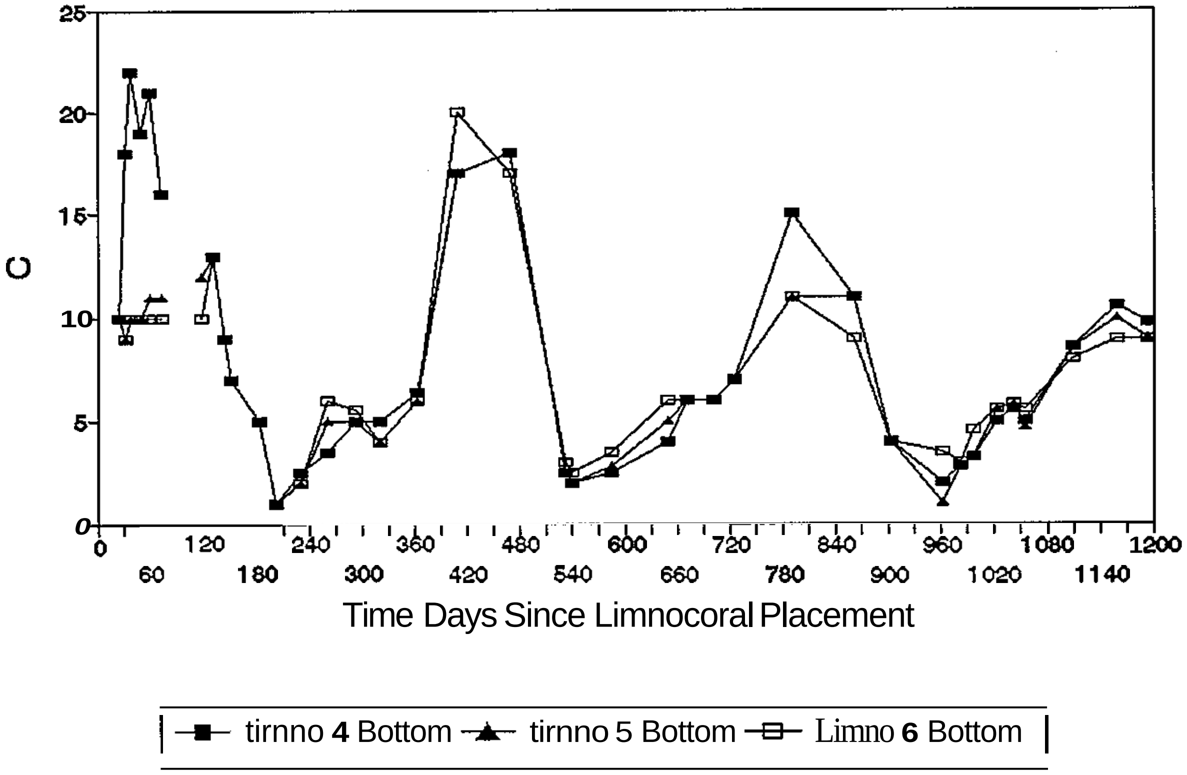


Fig. D3c: Limno 456 Zinc
Sawdust, Peat, Control

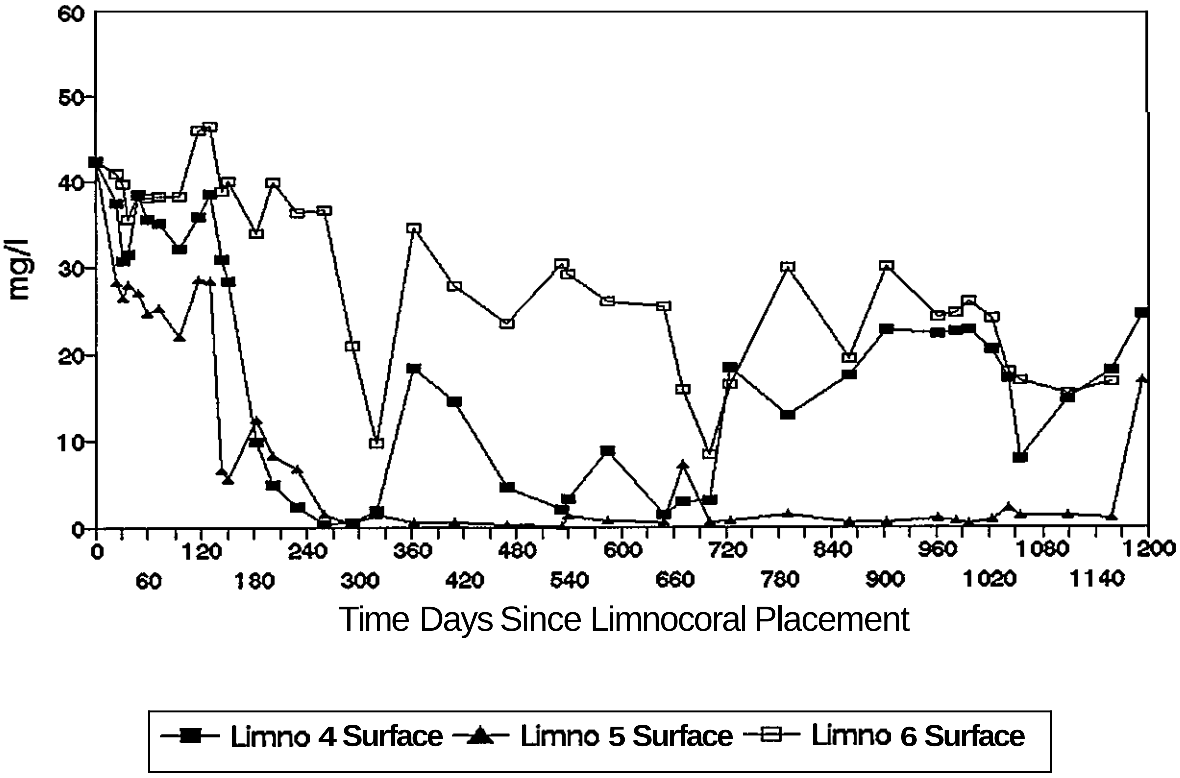
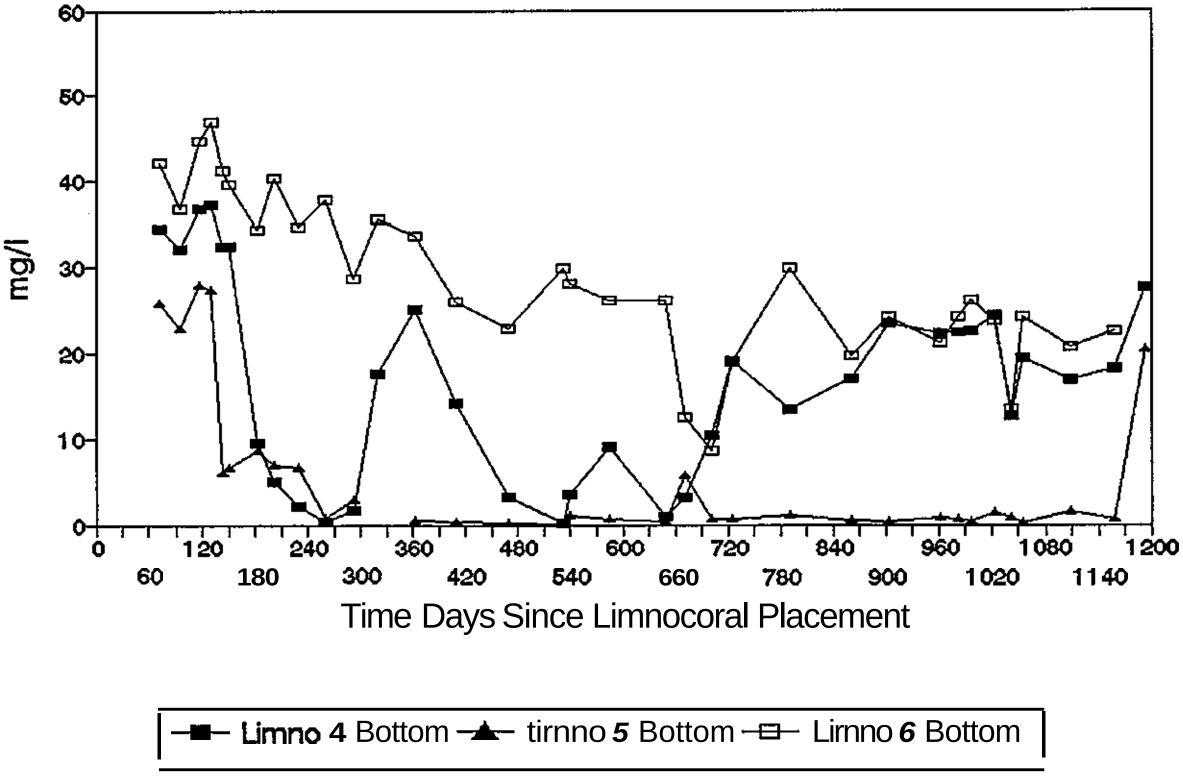


Fig. D3d: Limno 456 Zinc
Sawdust, Peat, Control



APPENDIX E - ARUM - Acid Reduction Using Microbiology

Abstract

The ability of iron-oxidising bacteria (e.g. Thiobacillus spp) to solubilise metals has been exploited in leaching processes by the mining industry. The same oxidation processes however, are the principal cause of a major environmental problem, the generation of acid rock drainage (ARD) and acid mine drainage (AMD) from pyrite-rich waste materials.

Remineralization of metals in AMD takes place in the sediments of oceans, lakes and wetlands through the activities of other types of bacteria. The main objective of the ARUM process is to optimize this mineralization in sediments created in mining waste management areas.

The most important parameter driving ARUM (or the remineralization process) is the flux of organic carbon from the water column to the microbial communities in the sediment. Various organic materials have been tested as sources of carbon for ARUM in AMD from base metal and coal operations. Carbon availability from materials such as peat, sawdust or Typha leaves depends on decomposition which is extremely limited in acidic, anoxic conditions where ARUM can occur. Weight loss from decomposition bags and sequential nutritional analysis were used to assess decomposition of test organic materials after prolonged exposure (up to two years) in AMD in ponds, lake enclosures (limnocorrals) or constructed ARUM test cells. The results indicate that decomposition does occur in the reducing conditions associated with ARUM and that all of the material tested, peat is the most promising and sawdust the least promising ARUM substrate.

Introduction

Mining wastes, tailings and waste rock, containing metals and reduced forms of sulfur are subject to oxidation on exposure to air. This leads to generation of sulfuric acid laden with metals and is referred to as acid mine drainage (AMD) or acid rock drainage (ARD). These effluents represent major environmental liabilities, particularly at the time the ore body is exhausted and mining ceases. Treatment through neutralization with lime is required which results in large volumes of hydroxide sludges. Acid generation is essentially a microbially aided weathering process and can be expected to continue for perpetuity.

Waste managements areas of mining operations generally contain large AMD collection ponds, where access of oxygen to the acid generating waste materials is not restricted. It is proposed that through the development of a microbially active sediment in such collection ponds, improvements in the AMD can be achieved. The processes which occur in the microbially active sediment are referred to collectively as ARUM, Acid Reduction Using Microbiology. Key aspects of the studies which were carried out towards the development the ARUM process are summarized in this paper.

In AMD, sulfate and dissolved metal ions, particularly iron, are abundant. In reducing conditions and provided that sources of carbon and other nutrients are available, iron reducing bacteria can reduce Fe(III) to Fe(II) and sulfate reducing bacteria can reduce sulfate to sulfide with the generation of alkalinity. If both substrates (Fe(III) and sulfate) are available, Fe(III) will be used up first (1). Most attention has been directed at sulphate reduction and this is potentially the most important source of alkalinity generation (2). Only recently has iron reduction by bacteria been characterised and the relative importance of these processes is only now being addressed (3). With alkalinity generation, as the pH rises, the sulfide will precipitate divalent metal cations such as Cu^{2+}, Fe^{2+}, Ni^{2+} and Zn^{2+} as metal sulfides. Thus metal concentrations in AMD can be reduced.

The alkalinity generating processes generally utilize organic acids as a carbon source. These can be provided from the decomposition products of plant materials. AMD itself is generally very low in soluble carbon. Therefore the provision of a continuous supply of decomposable organic material is a key factor in building an ARUM sediment.

Wetlands have been employed as a means to ameliorate AMD. Success of such wetlands is very variable (4,5). Cattails (Typha spp.) can thrive in AMD and wetlands to treat AMD are generally dominated by cattails. However, cattails do not accumulate high concentrations of metals in their biomass (6). The substrates of cattail dominated wetlands can harbour the alkalinity generating activities outlined above. Cattail wetlands remove significant metal loadings through alkalinity generating processes occurring in anaerobic conditions in the sediments. However carbon supplies are needed for the alkalinity generating processes in the ARUM sediment. Floating cattail mats can produce carbon through root exudation of recent photosynthate and from the decomposition of plant materials. Decomposition rates in cattail stands on acid generating tailings in northern Canadian conditions (7) are comparable to those for other temperate bog systems (8). Therefore these weedy acid tolerant species have the potential to provide considerable quantities of substrate (e.g. volatile fatty acids) for the alkalinity generating bacteria. If configured over the ARUM sediment as a floating mat, further wave action and oxygen penetration to the sediment is reduced.

Figure 1 Site locations of ARUM field experiments

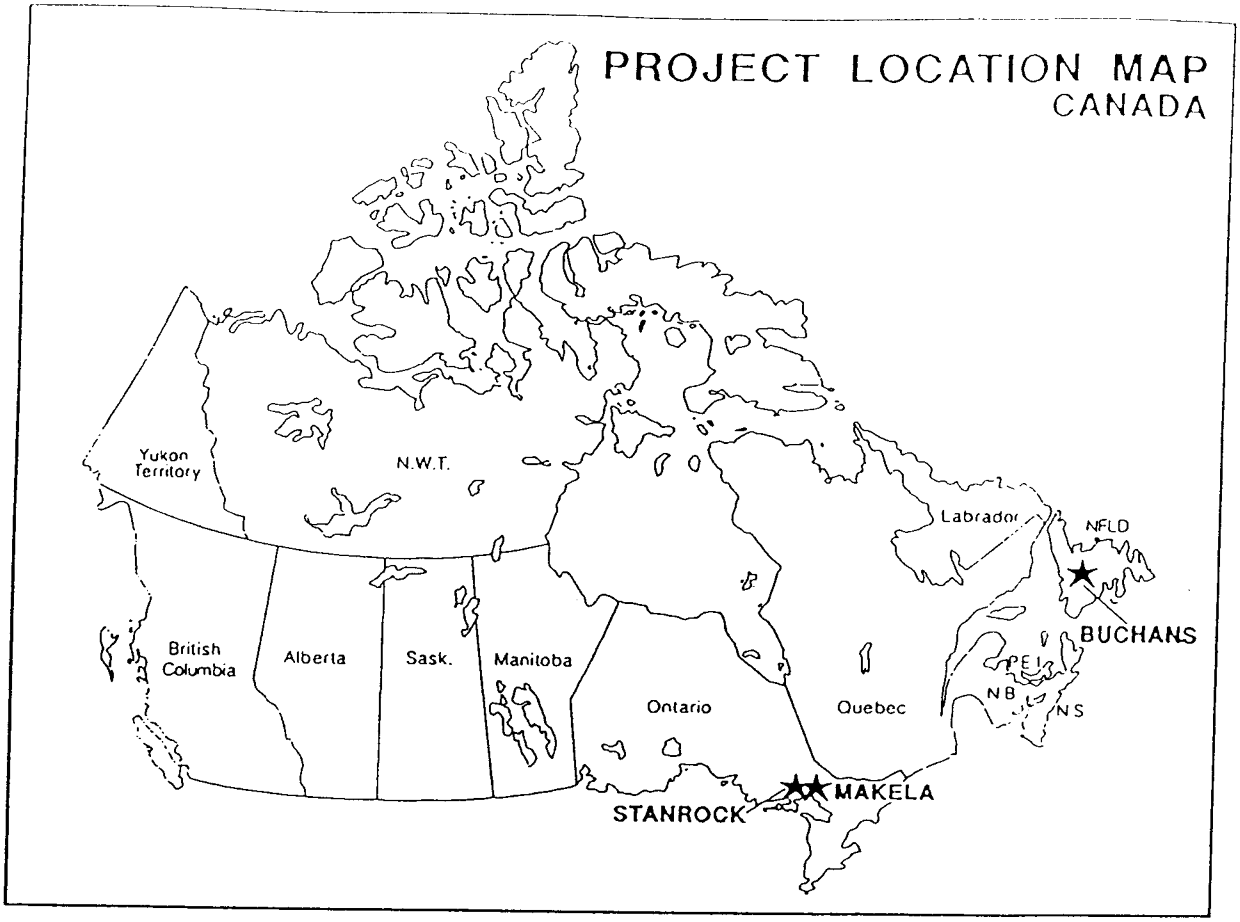


Table 1 ARUM field experiments. Acidity, pockets of elevated pH and microbiology

Site	Acidity mg/L CaCO3	pH orig	pH elev	Elevated pH pockets days	Microbiology SR	IRB	AM	DN
STANROCK								
Straw Pond	3080	2.1	5.5	365	+	+	+	ND
MAKELA								
Cell 3	520	3.0	3.5	350	+	+	+	+
BUCHANS								
Pit A	120	3.5			ND	ND	ND	ND
Pit A peat limnocorral		3.5	4.8	290	+	+	+	ND
Pit A sawdust limnocorral		3.5	4.5	140	+	+	+	ND
Pit B	100	6.5			ND	ND	ND	ND
Pit B peat limnocorral		*3.2	4.7	143	ND	ND	ND	ND
Pit B sawdust limnocorral		6.5	6.8	150	ND	ND	ND	ND

ND not determined; SRB sulfate reducing bacteria; IRB iron reducing bacteria
AM ammonifying bacteria; DN denitrifying bacteria
* pH dropped after addition of amendment

In order to initiate an ARUM sediment in waste water collection ponds, it is necessary to utilize organic materials which are available in large quantities and in relatively close proximity to the mine sites such as sawdust and peat. A large fraction (40-70 %) of these materials is lignocellulose which decomposes slowly. Decomposition of these highly refractory organic materials under acidic conditions may present the limiting component in the ARUM sediment development.

The present studies commenced following observations on test pools at Levack, Ontario amended with organic matter in a stream of AMD. Pockets of elevated pH were found. Samples were sent to CANMET and found to contain populations of sulfate reducing bacteria. Such observations led to the concept of ARUM in engineered ecosystems to provide a long term treatment of AMD. Further development of ARUM in the laboratory and field are summarised elsewhere (9-11). The work reported here summarises the types of AMD effluents in which development of an ARUM sediment is being tested. The supply of organic carbon measured by decomposition of various organic materials is investigated in AMD where reducing (alkalinity generating) conditions have or have not been established.

Materials and Methods

Experimental systems have been set up in the field at various locations in Canada (Figure 1) to develop an ARUM sediment. The chemistry of the AMD to be treated at each site is summarised in Table I. Acidities range from 100 to 3080 mg/L equivalents of $CaCO_3$. Organic materials (cattail litter, peat, straw, alfalfa hay and sawdust were either suspended in AMD or placed on organic materials serving as ARUM substrate. At all the experimental sites, changes in water chemistry were monitored. Microbiological methods used are as described elsewhere (9,11). Sulfate reducing bacteria were enumerated with Rapidchek test kits (Conoco).

Experiments on decomposition were set up at Buchans, Newfoundland in two open Pits (A and B) form an inactive lead-copper-zinc mine (Asarco), in seepage from the Copper Cliff, Ontario tailings at the Makela pumping station from Inco's nickel mining and in a seepage in Elliot Lake from the inactive Stanrock operation of Denison Mines.

At Buchans, limnocorrals were constructed in May 1989 in two flooded pits. These experiments are described in more detail elsewhere (10). The limnocorrals are columns of plastic sheeting (Fabrene) of 4 m diameter and 2 to 3.5 m depth were anchored to the pit floor with rocks. Buoyancy was maintained with polystyrene floats around the circumference at the water surface. Either peat or sawdust was added to the limnocorral water column at set up. The following summer, bags of window-screen containing 1 kg, 3 kg or 5 kg of the cattail litter, alfalfa, straw, sawdust or peat were placed in both peat and sawdust amended limnocorrals and in the open pits. These materials were chosen to test a wide range of organic materials for their suitability as substrates for ARUM. The bags were suspended from booms suspended from the floating collar of the limnocorral or from styrofoam floats in the open pits.

At Makela, a series of cells were constructed with flow control. The first cell is used for iron precipitation, the second for complete acidification of the AMD and the third and forth cells for ARUM sediment development. The decomposition bags containing each one of the five organic materials were placed in Cell 3. The Makela system generally experienced a flow rate of 1 l/minute. Floating cattails were established on Cell 3 and Cell 4 to assist the development of the ARUM sediment.

At Stanrock, a complete set of decomposition bags was placed on the surface of straw amendment in a shallow pond (Straw Pond) through which tailings drainage flows.

Between the placement of the decomposition bags and the first sampling date, ARUM was established above the sediment in the Makela cells, some of the limnocorrals but only for a short period in the uranium seepage. By the second sampling date (two years) reducing conditions and ARUM (populations of sulfate reducing bacteria, H_2S smell) activity were found throughout the water column in Cell 3 and in the active limnocorrals.

Bags were retrieved one year and two years after placement. The materials were air dried, weighed and subsamples were subjected to sequential nutritional analysis by the method of Goering and Van Soest (12). Acetone soluble fractions (waxes, fatty acids) and HCl soluble fractions (sugars, amino acids, hemicellulose, metal ions) were quantified. To determine the inorganic fraction which might have accumulated due to metal precipitation and adsorption, loss on ignition (LOI) was determined by heating one gram of ground organic matter at 480°C for one hour in a muffle furnace and remeasuring the sample dry weight.

Results and Discussion

The development of ARUM activity at the study sites is summarised in Table I. In general, a period of 1 to two years was required before an increase in pH was registered, which generally occurred only in isolated pockets of the organic material. The delay in ARUM is attributable to 1) the long time required to generate reducing conditions (requires the microbial-mediated decomposition of organic materials and the consumption of oxygen due to respiration by these microorganisms) and 2) the development of microbial consortia able to generate alkalinity in these conditions. Following commencement of ARUM (pockets of elevated pH) samples of materials were found to contain populations of sulfate reducers, iron reducers, ammonifiers and denitrifiers, all bacteria associated with alkalinity generating processes. Although a variety of organic materials was used in these studies microbial colonization did not differ with respect to the material. Identification of microbial consortia was restricted to presence /absence determination, which does not reflect metabolic activity.

Although weight loss of organic matter derived from bags with a known weight is a standard method of assessing decomposition rates, results require careful interpretation. Results for the Buchans bags after one and two years of exposure are shown in Table II. After one year, the peat bags had lost more than 70 % of the original weight. Much of this large weight loss is certainly attributable to loss through the mesh of the bag. With coarser materials (straw, cattails and alfalfa) a smaller fraction is attributable to physical loss. Most bags lost about 50 % of their weight or greater during the first year of exposure. Assuming that physical weight loss will be the same for all bags of each amendment, the weight reductions in various incubation conditions can be compared.

Losses were greater for all materials in the peat limnocorrals which had an active ARUM sediment (reducing) compared to the sawdust limnocorrals which provided mostly oxidizing conditions. This indicates greater decomposition and therefore a potentially greater supply of substrates for ARUM bacteria. Weight losses in bags suspended in the open pit were generally similar to those in the peat limnocorrals. However these values are undoubtedly inflated due to losses of undecomposed material through the mesh by wave action. Weight losses in Pit B were higher than for Pit A for all materials except peat and straw. The greater losses in this pit are certainly related to the higher pH (pH 7) in this pit than in Pit A (pH 3.5) providing conditions more favourable for decomposition. Weight losses at Makela were generally less than at Buchans. In part it is likely due to the AMD characteristics at Makela which has higher acidity and lower pH than the AMD in Buchans (Table I). Very little if any weight loss was apparent after two years at Stanrock. This as attributable to the greater acidity (3080 mg/L equiv. $CaCO_3$). It should be pointed out that the Stanrock bags were covered with a heavy encrustation of iron (III) hydroxide at the time of sampling which may affect decomposition processes. Such precipitate covers may ARUM was very localized at this site.

Sequential analysis data for peat and sawdust sampled from the bag materials are summarised in Table III. The extractions segregate essentially refractory organic pools (remaining after HCl extraction) from those which are biodegradable or available as carbon sources (acetone and HCl extractions).

Acetone extractable materials (waxes, fatty acids) of both peat and sawdust declined on exposure to AMD in both pits at Buchans, at Stanrock and in the peat at Makela. There was no decline between the one and two year samples indicating that some factor, probably plant cuticles (surface waxy deposits) was lost in the first year of exposure. Part of the acetone soluble fraction is undoubtedly fatty acids which are products of decomposition and substrates for alkalinity generating bacteria. The reduction of this fraction was similar for the two Buchans pits. Within each pit there were no clear differences between the three locations. HCl extractable materials for both peat and sawdust exhibited a decline in Pit A and an increase in Pit B and also at Stanrock. A decline indicates that some store of material is being used up. An increase indicates that more materials are entering the pool than leaving. Perhaps greater cellulose decomposition is occurring in Pit B than in Pit A relative to the utilization of products of that decomposition. We established that cellulase activity was present in both pits using a remazol blue-stained cellulose strip assay (13). Unfortunately we were unable to quantify that activity. The LOI data (not shown) indicates that for Pit A most of the HCl extractable fraction is organic material and not metal ions or displaced sediment. However, for Pit B, the LOI values are lower and the apparent increases in HCl extractable material may be due to accumulation of precipitates of metal salts.

In the Buchans peat limnocorrals and the Makela test cell, the decomposition bags were located in reducing conditions at the time of sampling. Decomposition rates decline rapidly as oxygen is consumed. Until recently it has been assumed that lignocellulose which comprises 40-70 % of the plant materials used in this study is not decomposed (14). However recent studies with long term incubations of 14-C labelled lignocellulose containing materials indicate that decomposition does occur albeit at low rates in anaerobic lake sediments (15). The weight loss and sequential analysis data clearly indicate that decomposition was occurring in the test conditions. The greater rates apparent in conditions where ARUM was active (Buchans peat limnocorrals and Makela test cells) suggest that even in reducing conditions, the materials can supply substrates for alkalinity generating bacteria. At Stanrock, where the conditions are extreme, low rates of decomposition may be limiting ARUM. Peat is the most promising material as it clearly supports ARUM in the limnocorrals and also accumulates substantial amounts of

Table 2 Weight loss of materials in decomposition bags after one and two years of exposure to AMD
Losses are corrected for LOI values of materials before and after exposure

	Weight loss (%)									
	Peat		Sawdust		Straw		Cattail		Alfalfa	
Site	1 y	2 y	1 y	2 y	1 y	2 y	1 y	2 y	1 y	2 y
BUCHANS										
Pit A	92	ND	74	ND	64	ND	79	80	75	72
Pit A peat limnocorral	78	ND	49	ND	67	ND	70	84	76	61
Pit A sawdust limnocorral	75	ND	45	ND	59	ND	70	64	58	81
Pit B	94	ND	76	ND	88	ND	59	47	67	68
Pit B peat limnocorral	78	ND	57	ND	69	ND	79	66	69	72
Pit B sawdust limnocorral	77	ND	38	ND	36	ND	68	58	63	69
MAKELA										
Cell 3	72	87	16	26	21	ND	49	42	32	31
STANROCK										
Straw Pond	ND	ND	ND	ND	ND	ND	ND	15	ND	-13

ND not determined

Table 3 Sequential nutritional analysis of decomposition bag samples
Figures represent % dry weight of a sample soluble in acetone or HCl

Source	Peat						Sawdust					
	At placement		1 year		2 years		At placement		1 year		2 years	
	Acetone %	HCl %	Acetone %	HCl %	Acetone %	HCl %	Acetone %	HCl %	Acetone %	HCl 0	Acetone %	HCl %
BUCHANS												
Pit A	3.4	40	0.4	43	2.1	32	3.2	28	3.1	27	1.9	27
Pit A-peat limnocorral	3.4	40	3.0	38	2.0	37	3.2	28	2.7	26	ND	ND
Pit A-sawdust limnocorral	3.4	40	1.9	40	3.4	32	3.2	28	3.0	25	1.9	23
Pit B	3.4	40	2.0	47	1.7	44	3.2	28	2.9	28	1.7	30
Pit B-peat limnocorral	3.4	40	1.8	50	3.6	44	3.2	28	4.9	27	ND	ND
Pit B-sawdust limnocorral	3.4	40	1.0	44	3.4	44	3.2	28	4.2	27	2.9	31
MAKELA												
Cell 3	3.4	40	5.6	41	ND	ND	3.2	28	2.0	23	ND	ND
STANROCK												
Straw Pond	3.4	40	ND	ND	2.6	50	3.2	28	ND	ND	1.5	29

ND not determined

metals. Sawdust by contrast decomposes slowly (little weight loss) and accumulates little metal precipitate. This is confirmed by the poor performance, with respect to ARUM, of the sawdust limnocorrals.

Acknowledgements

We wish to acknowledge financial support for this work by the joint venture group at Buchans (ASARCO Inc. and Abitibi Price Inc.), Shell Internationale Maatschappij BV and by the MEND program (a joint initiative of the Canadian mining industry and federal government).

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