THE DECOMMISSIONING OF BUCHANS UNIT, ASARCO

ZINC REMOVAL STRATEGY

1996 FINAL REPORT

Prepared For

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BUCHANS 1996 FINAL REPORT

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It is to be understood that Boojum Research Limited has attended at the Joint Venture Group at Buchans, Newfoundland - ASARCO Inc., and Abitibi-Price Inc., for the sole purpose of conducting environmental work at the request of Joint Venture Group at Buchans, Newfoundland - ASARCO Inc., and Abitibi-Price Inc. During the time (January 1, 1996 to December 31, 1996) that Boojum Research Limited or its agents conducted environmental work they at no time had the charge, management or control of the property and at no time did Boojum Research Limited have possession, occupation or direct control of any source of contaminant that may have been present on the subject property/site while undertaking to carry out the instructions of the Joint Venture Group at Buchans, Newfoundland - ASARCO Inc., and Abitibi-Price Inc. to conduct environmental work. Further, as a result of conducting environmental work, Boojum Research Limited is not to be considered a "person responsible" as defined under the *Environmental Protection Act*, R.S.O. 1980, c.141, as amended.

Summary

The 1996 objectives, addressing the winter problem, represented collectively one of the most complex years spent addressing decommissioning of the Buchans unit. The approach taken to solving the winter problem was two fold. One avenue was to define and quantify the pathway of zinc during the summer. The second avenue was to review the entire site with the knowledge gained during the years of investigation. Had we missed something, or were some aspects of the process misinterpreted?

In Schematic 3 (Section 9), an overview of the different aspects of science are given, including all players which can interfere or contribute to the winter problem, a phenomenon overall controlled by temperature. Firstly, the monitoring data were reviewed for Buchans with respect to seasonal trends relating to temperature (Section 1). It was evident that carbon dioxide-bicarbonate-bicarbonate chemistry is producing changes in pH in all monitoring data which result in changes in zinc concentration.

Secondly, a mass balance of the groundwater distribution using chloride for the Drainage Tunnel - OEP - OWP suggests that clean groundwater is entering the OEP, contrary to what was previously postulated (Section 2). These findings suggested that the proposed gradual decrease in zinc concentrations in the OEP had to be due to additional causes other than the depletion of zinc released from the sludge in the underground workings.

The iron mass balance in the system suggested that more iron is being collected in the sedimentation traps than could be accounted for in the ground water. The iron mass balance for the polishing ponds also suggested iron cycling. Iron oxidation and reduction have therefore set up a recycling of iron, increasing the material collected in the sedimentation traps. This was further supported by the results of the iron oxidation experiments carried out this year (Section 3.2). While iron oxidation is controlled by the temperature and oxygen supply, it is not related to the removal of

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zinc from the solution. Zinc removal is independent of the iron oxidation process and, contrary to the earlier proposal, not directly related to the formation of iron hydroxide, a reportedly very good adsorbent of zinc.

The SEM-EDX investigations of the particles collected in the sedimentation traps and the biological material supported further the elusive nature of the iron III hydroxide adsorption process. Zinc was not associated with the surface of the sedimentation trap material at magnifications of 200 - 2000 x. It was found predominantly in the biological material in Polishing Pond 17, where particle surfaces reporting up to 40 % zinc, likely a zinc carbonate. Magnification of the sedimentation material at 20,000 x revealed that crystals are surrounding the iron particles, and up to 3 % zinc was found on these surfaces. If the proposed zinc adsorption was indeed taking place, these findings did not support this zinc removal process. Connecting this with the oxidation experimental results, which suggested that iron precipitation and zinc removal was not related, further refutes the importance of the process of zinc adsorption onto iron hydroxide at this specific site.

Through a review of the old work (for example, the inorganic chemistry section in the 1991 report and the field data prior to construction of the polishing ponds), it was evident that zinc removal and iron III hydroxide formation were not related. Where did all the iron in the algae/ moss in the polishing ponds originate, given that most iron remained in the OEP during the ice-free season? On the other hand, during the summer, zinc was effectively removed by the polishing ponds (Section 3.0).

The laboratory and field fertilization experiments, the latter carefully planned according to flow and retention time, did not result in increased zinc removal. However, in the small-scale field experiment, zinc did drop out along with the phosphate added in fertilizer. Because the experiment was conducted for less than 24 hours, the large-scale field application of fertilizer in the polishing ponds for zinc removal produced negative results (Section 3.7).

The large scale experiment was also carefully planned. The flow in the ponds was modelled, along with the dosage of fertilizer related to the growth rates of the algae derived from the laboratory experiments. No zinc removal was noted. A filter paper collecting the particles from the small scale field experiment (mini limnocorral), carried out in July preceding the scaled up fertilization effort, was submitted for chemical analysis. There indeed was phosphate, as well as iron, zinc and, in addition, reasonable amounts of Mg. Zinc was precipitating in some other form, but not adsorbed onto iron- hydroxide.

The answer had to be found in the areas of particle formation, surface charges of particles and colloid formation. This was definitely supported by the experiments where bentonite and sand (rich in iron oxide) did not result in zinc removal. Thus, the surface charges of the zinc were not positive, as would be predicted if zinc has actually adsorbed onto the negatively charged bentonite. The literature on formation of environmental particles reports that iron hydroxides are smaller than 0.45 μ m (Section 3.8). These smaller particles have difficulties settling, and must aggregate into particles large enough for gravity to overcome hydrodynamic forces. The major difference between the large scale fertilization experiment and the mini-limnocorral experiment was that the latter provided less turbulent conditions, allowing smaller particles to settle.

The formation of particles in winter in OEP is hindered, since the larger particles of Fe III hydroxide do not form, and no nucleation sites are provided to collect the zinc precipitates. Interesting support for the strong hydrodynamic forces on the particles was obtained from the phytoplankton enumerations (Section 3.5). Phytoplankton productivity in OEP is virtually nil, despite apparently suitable chemical and nutritional conditions for periphyton. Physical factors, such as light limitation, the presence of the thermocline associated with a chemocline and a change in redox, may collectively prevent the growth of algae with a free-floating growth habit. While the hydrodynamic conditions of OEP are only slightly different from OWP, these differences result in relatively sterile pit water. The picoplankton results, when available, will indicate whether living organisms smaller than 2 μ m are present in OEP; these organisms may have lower light requirements than phytoplankton. If these minute organisms are present, this may indicate that organisms in this size range are too small to aggregate precipitates and settle.

All evidence suggests that particle formation in the OEP is hindered by the hydrodynamics of the OEP water column, rather than its chemistry. The question, then, is what could be done to overcome the difference in hydrodynamics in the OEP between summer and winter, a classical problem of flotation, or possibly microflotation. The degassing of the CO_2 in the open bottle treatments of the oxidation experiments is the most likely explanation for the observed decreases in the zinc at 20° C, since a precipitate could form as a result of CO_2 leaving the bottle.

The current strategy for solving the winter problem is to form a zinc precipitate particles which are relatively independent of the carbon dioxide-bicarbonate-carbonate chemical reactions and are large enough to effectively settle in OEP. Phosphate was an old candidate, discussed in detail in the 1991 report in connection with the Long Harbour sand. The 1996 fertilization experiments suggested some involvement of zinc removal with phosphate. Since iron is predominantly in the reduced form in pit bottom water, it should not complete with cations, such as zinc, calcium and magnesium, for phosphate if added to the <u>bottom</u> of OEP in molar proportions which promote the formation of calcium, magnesium and zinc phosphate. Competition for phosphate by iron was observed when fertilizer was added to the ponds to increase biological production of particle formation.

In January, 1997, George Neary performed an experiment using water collected from beneath the ice of the OEP. The best zinc removal occurred in the treatment where enough phosphate was provided to combine with all zinc and magnesium present in OEP water. Upon addition of smaller or larger amounts of phosphate, less zinc was removed. Inadequate phosphate for zinc removal may have been provided in the low treatment, while interference by nitrate in the larger fertilizer treatment may explain lower zinc removal in the high application treatment.

Since phosphate can interact with magnesium, this may in part affect the fraction of the zinc which precipitates in the pit and contributes to the annual zinc reductions at the outflow. The fraction of the settled zinc carbonate solids likely recycles each year, due to changes in solubility of this compound due to seasonal changes in inorganic carbon forms and concentrations present in the pit water column. To remove the zinc, clearly a particulate needs to be formed which can settle out, and remain as a solid at the pit bottom under the prevailing conditions.

It is were assumed that no new zinc is currently being added to the pit, and zinc remobilization from precipitate deposits is responsible for the current zinc load at the outflow, the observed annual decrease could be due to dilution of the remobilized zinc by fresh water, and the slope of such a decrease should be quite even. It could, however, also be that a precipitate is formed which is stable and settles out in the bottom of the pit. If this is the case, magnesium concentrations for OEP should decrease similarly to those for zinc. The slope of both magnesium and zinc concentration decreases in the OEP pit (Figure 1; Section 3.8) for the years 1989 to 1996 are convincingly similar, suggesting a similar removal process.

If these observations can be confirmed, then practically it provides the following options. The zinc carbonate is recycling between shifts of carbonate and bicarbonate and only removed through formation of a more stable forms such as zinc phosphate. As fertilizer added more than just phosphate (e.g., nitrate, ammonia), the precipitates have to be analyzed and further experiments conducted to ascertain the possibility of forming a zinc precipitate other than the carbonate.

Through changes in the hydrodynamics, we can bring about particle formation which should settle to the sediment. We could therefore form a stable zinc precipitate with a one-time application, as long as the application consists of the correct chemical addition. The formed precipitate will be collected by biological polishing. The same approach can be taken for the Lucky Strike, resulting in reductions of zinc in the Valley Seeps, the Drainage Tunnel; essentially, the problem could be solved. The precipitation with hydroxide should also be evaluated in relation to the stability of the zinc precipitate formed. It is likely that, if the zinc is precipitated in the carbonate form, it will eventually remobilize from the sludge.

In summary, the key breakthroughs from the investigation of the winter problem in 1996 were:

- Zinc is precipitating independently from iron III hydroxide; iron is likely recycled in the pit.
- Zinc phosphates can be formed in the winter conditions of the OEP.
- The hydrodynamics of OEP hinder particle formation which are sufficiently large to settle in the pit.
- It is likely that a significant flow of clean groundwater enters OEP, in addition to the zinc and iron-contaminated groundwater emerging from the underground workings.
- The Old Buchans Valley seeps receive water from the Lucky Strike.
- The Lucky Strike is in many ways similar to the OWP, which raises concerns regarding the buffering capacity of the groundwater entering the pit, presently not suggested, as water is leaving the gloryhole, rather then entering it, which

was a similar situation in the OWP, prior to Drainage Tunnel additions.

- Biomass production in the OEP is limited hydrodynamics and light, but not in the OWP and the Polishing ponds.
- •• The below data report now needs to be interpreted, using all the newly assembled data, to confirm or refute tentative conclusions reached to date. A large amount of data accumulated since 1988 can be utilized to ascertain a firm understanding of the site.

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1.0 MONITORING DATA

The main objective in 1996 was to address the winter problems with the absence of zinc removal in the polishing ponds. The approach taken to view the monitoring data was different then in the years prior. Data were plotted with respect to seasonal variations in zinc concentrations. The zinc removal in the polishing ponds appeared to display curves which seasonally reflected the temperature, pH and to some degree also to conductivity changes, like being opposed or similar.

The 1991 report (Section 3) dealt with the inorganic chemistry of Buchans waters on a non-site specific basis. It was concluded that Buchans waters are dominated by carbonate - bicarbonate couple. Therefore, the temperature would affect all formation of carbonaceous zinc species, due to the solubility of carbon dioxide. Zinc carbonate and zinc bicarbonate posess different behaviours, shifting from precipitating and settling to remaining dissolved. If this is the case, then pH should show similar trends seasonally in all monitoring points, which are relatively close to contaminant sources, such as the pits and the tailings. Higher concentrations should be evident both in the beginning and at the end of the year, and the lowest concentrations should be found in the summer time. The pH should be lower in the winter months and increasing slightly in the summer months.

This pattern would suggest that the carbonate-bicarbonate couple dominates in the zinc removal process related to CO_2 solubility, which is related to the temperature. If this is the case in the monitoring data, then the behaviour of OEP is more pronounced, solely due to the degassing of CO_2 from the ground water.

From this perspective, it also would follow that seasonal fluctuations should be essentially eliminated as the water is further away from the zinc source, i.e. either tailings or pits. Zinc removal through a precipitate would have settled out of the water column resulting in lower zinc concentrations and very flat shaped curves. In Schematic 1, the sequence of water entering the Buchans River is given. The monitoring point, Buchans River at Highway Bridge should be flat, i.e. show not seasonal trends. In Figure 1a and Figure 1b, the zinc concentrations and the pH values are plotted. Essentially, since 1992, which was a year with large fluctuations, the zinc concentrations are around 0.1 mg/L and the pH displays a slight trend of lower pH with lower temperatures and high pH in the summer, generally ranging from 6.2 to 7.4. The same applies for the station below the Hydro Plant (Figures 2a and 2b).

In Figures 3a and 3b, the zinc concentrations for Simms Brook show a trend with lower concentrations in the winter month increasing over the summer, but the pH values do not show a seasonal trend.

In Figures 4a and 4b, the concentrations of zinc in TP1 show an increase after the ice melts and climbing over the summer month from less than 1 mg/L to about 2 mg/L and the pH depression in the beginning of the year is pronounced. In Figures 5a and 5b, the data from TP2, show that the ice cover releases some zinc from the beaches, but the pronounced drop in zinc at the end of the season is evident.

The dramatic increase from about 1.5 mg/L to 4 mg/L in 1996 is due to raising the water level in TP2. The origin of zinc in this pond was identified previously as pore water in beach tailings, which is exemplified by the 1996 data (Figure 5a). The pH of TP2 decreases in winter and remains around neutral pH over the remainder of the year (Figure 5b). This would be expected, given that the solubility of carbon dioxide in the pond water is lower during the warm summer months.

These trends are not new, and were previously interpreted as solely due to dilution taking place during spring run off, followed by concentration of zinc due to evaporation. Although this can not be excluded, the corresponding trends in pH values are more difficult to explain due to spring run-off dilution, and are likely related to the dominant bicarbonate couple.

The Drainage Tunnel should not show any seasonal trends, given that it is measured at the outflow, and is essentially degassed ground water. Figure 6a shows essentially a steady concentrations along with a steady pH value (Figure 6b). Average zinc concentrations for the year have increased for the Drainage Tunnel, particularly in 1996 (Figure 6c) and the flow is higher in the last two years (Figure 6d). This was suggested in previous evaluations of the Lucky Strike flooding.

The seasonal trends in the OWP are given in Figure 7a for the zinc concentrations. The trend was very evident in the years prior to Drainage Tunnel discharge to the OWP. Since 1995, seasonal variations in the Drainage Tunnel loading has diminished. However, the 1996 pH values (Figure 7b) increased by about 1 unit, when the system had stabilized. Overall, the OWP zinc concentrations are increasing as expected, reflecting input from the Drainage Tunnel (Figure 7c).

In the OEP, the 1996 annual decrease in zinc concentration is lower than the year before (Figure 8a). In Figure 8b, the seasonal variation in the water are displayed and magnified by changing the scale on the graph in Figure 8c.

Finally, the Lucky Strike annual average zinc concentration continues to increase, but appears to level out with respect to the magnitude (Figure 9a). In 1996, the increase was only about 2 mg/L, in comparison to the previous year with a 6 mg/L increase. The seasonal behaviour of the Lucky Strike resembles that of the OWP with dilution or ground water input producing a significant decrease in the spring and increasing steadily as the water warms up and the pH decreases by typically 1 unit (Figure 9b and 9c). Given the similarity to the Orientals, it is therefore not surprising that the Lucky Strike also stratifies during the summer. Since an anchor was placed into the pit, the pit can be monitored and sampled also during the summer months (Figure 10).

The water was sampled during the last field trip for titration (Table 1). The acidities are much lower than the OEP suggesting that there are very few metals in the water

up to about 25 m, where the values then approach those of the OEP (Figure 11a). The acidities in the summer time in the OEP are below 50 mg/L and rise to about 160 mg/L in September, when the iron starts to remain in solution. This suggests that only the lower portion of the Lucky Strike pit receives or remains ground water containing iron. Comparing the alkalinities of the Lucky Strike and the OEP (Figure 11b), little ground water appears to be added to Lucky Strike, since the alkalinities are very low at 20 mg/L, compared to the OEP with alkalinities ranging from 200 to 300 mg/L. At present, the Lucky Strike water resembles more that of the old OWP with respect to buffer capacity, expressed by acidity/alkalinity values (Table 2).

Depth (m)	Field O ₂ mg.L ⁻¹	Field Temp °C	Field pH	Lab pH	Field Cond uS.cm ⁻¹	Lab Cond uS.cm ⁻¹	Field Em mV	Lab Em mV	Lab Acidity mg.L ⁻¹	Lab Alkalinity mg.L ⁻¹	Lab Temp °C
Surface	12.5	10.6	6.64	6.61	520	295	139	69	59	22	6.2
5	10.1	10.6	6.64	6.8	520	325	140	123	53	20	10.4
10	10	10.5	6.64	6.81	510	350	145	126	52	21	12.1
15	10.3	6.4	6.64	6.79	560	360	158	133	66	24	11.9
20	9.3	5	6.77	6.76	670	390	171	145	81	32	12
25	5.8	5.1	6.31	6.57	960	530	185	152	122	49	13
33		5.6	6.29	6.4	770	580		129	138	52	7.8

Table 1: Lucky Strike Pit Water Chemistry With Depth, September 27, 1996.

Date	pН	Acidity,m	g/L CaCO3	Iron, mg/L		Aluminum, mg/L		Zinc, mg/L		Sulphur, mg/L	
	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	i
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
Feb-93	3.76	87.8	105	0.95	1.03			26.9	30		
Mar-93	3.77	97.9	110.7	0.95	1.1			34.6	33.8		-
Apr-93	3.84	81,4	94.3	0.15	0.202	2.72	3.07	30.7	33.8	94.9	106
May-93	4.04	40.3	101.5	0.069	0.205	1.29	3.15	11.5	33.6	43.4	107
Jul-94	6.07	35.0	226.0	0.308	21.1	0.032	0.076	17.4	26.6	172	204
Jul-94	6,05	47.0	235.0	0.786	8.59	0.06	0.112	16.6	24.8	151	196
Aug-96	5.80	32.9	171.3	<0.02	<0.02	<0.025	<0.025	16.3	29.9		

Table 2: Concentrations of Selected Elements in Oriental West Pit, 1988-1996

Fig. 1a: River at Highway Bridge Zinc Concentration, 1992-1996











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Fig. 6a: Drainage Tunnel Zinc Concentration, 1992-1996







Fig. 7c: Oriental West Pit Average [Zn], 1989-1996



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Fig. 9a: Lucky Strike Glory Hole Average [Zn], 1991-1996

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Schematic 1: Generalized lay-out of sources of drainage to the Buchans River

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2.0 GROUND WATER DISTRIBUTION IN THE SYSTEM

2.1 Introduction

- Until recently, the contributions of various surface and ground water flows to the OEP and OWP which make up the flow at OEP weir could not be confirmed, due to the lay-out of the system and the lack of appropriate monitoring data.
- Sufficient information is now available to estimate the contributions of these various flows.

2.2 Brief History

- Following completion of flooding of the OEP and OWP (August, 1987), the flow volume at the outflow was approximately 10 L/s, with slight variation due to high spring run-off and lower base flows during mid winter.
- No surface water inflow, other than local run-off during precipitation events, contributed to the flow volume at the OEP weir.
- Ground water containing elevated zinc and ferrous iron concentrations was essentially the only source of flow.
- The pH of OEP water was near neutral.
- Following flooding of the OWP, no surface inflow or outflow could be seen, while the water level remained relatively constant year-round. However, variation in zinc concentrations, particularly during spring run-off when surface water zinc concentrations temporarily decreases, suggested that clean water entered the

OWP and OWP water must have been displaced from the pit in spring in order to maintain the water levels at a constant elevation. This phenomenon is depicted in Figure 12 for 1995. This phenomenon did not occur in 1996, as shown in Figure 12.

- Between 1987 and 1993, the pH of the OWP water column was low (pH 3.5), and the water column was clear and contained little suspended solids. Due to its high clarity, light penetrated the water column and thermal stratification did not establish during the ice-free season. This is shown for September 27,1992 in Figure 13.
- The surface water of the OWP was joined to the OEP's surface water by a culvert in September, 1993. Pumping of Drainage Tunnel water to the surface of OWP commenced in August, 1994.
- Following joining of the two pits and lowering of the OWP water level by approximately 0.3 to 0.6 m, major changes in the OWP's water column occurred and have since remained. The pH of the OWP water column increased to near neutral pH, while the OWP pit became and remains thermally stratified, as shown in Figure 13. OWP's stratification is similar to that which has existed in OEP since flooding (Figure 14).
- There is now a ground water source of ferrous iron source to the OWP, and ferrous iron oxidation and ferric hydroxide precipitation occurs in near surface strata of the pit.
- Drainage tunnel water entering the OWP oxygenates the surface water.

2.3 Flow Distribution Using Chloride Data

A summary of flows, chloride concentrations and mass balance is provided in Table 3.

2.3.1 Oriental West Pit

- Prior to the joining of OWP and OEP surface waters, chloride concentrations in the OWP were low, ranging from 0.8 to 1.5 mg/L.
- Drainage Tunnel water, now pumped to the OWP, contains on average 12.7 mg/L chloride.
- However, OWP water now contains 35 mg/L CI on average, a higher concentration than the Drainage Tunnel.
 - Ground water entering OWP containing an elevated Cl concentration is likely the source of this extra chloride.
 - Assuming that the ground water is from the same source as that entering OEP, then the CI concentration in OEP 7 m samples (similar to the depth of the bottom of OWP) can be used to estimate the flow of ground water required to contribute that extra chloride present in OWP in addition to the CI contributed by the Drainage Tunnel flow.

(D.T. [CI] × D.T. Flow) + (GW [CI] × GW Flow) = (OWP [CI] × OWP Out Flow)

 $(12.7 \text{ mg/L} \times 8.3 \text{ L/s}) + (144 \text{ mg/L} \times \text{X L/s}) = 35 \text{ mg/L} \times (\text{X L/s} + 8.3 \text{ L/s})$

Solving for X: Ground water flow is 1.7 L/s.

 According to the chloride concentrations, approximately 10 L/s (8.3 + 1.7 L/s) of water leaves OWP and joins OEP surface water.

2.3.2 Oriental East Pit

- The contribution of ground waters to the OEP can be estimated based on the estimated flow and chloride load from OWP and the measured flow and chloride load leaving OEP at the weir.
- The OWP contributes 354 mg of Cl per second, in 10 L/s of water, to the OEP via the culvert joining the two pits.
- Based on monitoring data, approximately 1231 mg CI leave OEP per second in a flow of 19.2 L/s. Therefore, by difference, the ground water is contributing 9.2 L/s of water, and a CI load of 877 mg/s.
- OEP bottom waters contain 149 mg/L chloride (1996 average). If all ground water entering the OEP contained this concentration of chloride, then the ground water chloride contribution to the chloride loading at OEP outflow would be 1371 mg/s, a load exceeding the above estimate (877 mg/s) by 494 mg/s.

A high chloride ground water flow of only 5.8 L/s is required to add the 870 mg/s to the chloride load at OEP outflow. The remaining 3.4 L/s (6.7 mg/s Cl) likely originates from a low chloride (2 mg/L: DDH 2367 groundwater sample) groundwater flow, perhaps emerging at the overburden-bedrock interface along the pit walls.

2.4 Verification of Estimates Using Sodium Concentration Data

- A mass balance for sodium in the OWP-OEP system is provided in Table 4. In this table, flows determined using chloride as a tracer were used, and sodium concentrations determined for equivalent locations from the same data set were used.
- Chloride is typically the element of choice as a natural tracer of surface and ground water mass balance estimates, such as that performed above, since chloride compounds rarely form and chloride is not precipitating.
- While more opportunities may exist for loss of sodium mass from a system, such as in jarosites, this element can be used to evaluated the assumption that NaCl is the source of chloride, as used in the geochemical simulations presented in Section 4.
 - The estimated Na load at OWP outflow from Drainage Tunnel and groundwater is 22 % less than the measured Na load estimated by multiplying the OWP outflow by the OWP surface sodium concentration. For OEP outflow, the estimated Na load is only 1 % less than the measured Na load (Table 4).

These comparisons provide confidence that the flow volume estimates derived from the chloride mass balance exercise may adequately represent field conditions. Therefore, it can be assumed that clean ground water contributes about 3.4 L/s to OEP.

2.5 Application of Mass Balance Model to Zinc, Iron and Sulphate Loads

2.5.1 Zinc

- A mass balance for zinc in the OWP-OEP system is provided in Table 5. In this table, flows determined using chloride as a tracer were used, and zinc concentrations determined for equivalent locations from the same data set were used.
- The estimated zinc load leaving OWP (162 mg/s) is 3% less than the measured zinc load leaving OWP (166 mg/s). This indicates that zinc removal in OWP may be negligible. However, sedimentation of zinc-bearing compounds and algal uptake of zinc have been measured in the OWP.
- The estimated zinc load leaving OEP is 10 % greater than the measured zinc load exiting OEP at the weir. This suggests that processes in OEP remove zinc prior to discharge here but not in the OWP.
- According to these estimates, the Drainage Tunnel Input (135 mg/s) is a larger contributor of zinc (166 mg/s) to the OWP-OEP system than OEP (255-162=93 mg/s).

2.5.2 Iron

- A mass balance for iron in the OWP-OEP system is presented in Table 6.
- According to this mass balance, 99 % of iron entering OWP remains in the pit as sedimented particles, while 91 % of the iron entering OEP remains in the pit as sedimented particles. While this is consistent with summer water quality data and

observations, significantly less iron removal occurs in the winter, when an ice layer covers OEP, blocking oxygen transport into OEP surface waters, which in turn slows ferrous iron oxidation and ferric hydroxide precipitation.

2.5.3 Sulphate

- A mass balance for sulphate is presented on Table 7.
- Using flows estimated from the chloride mass balance, 11 % of the sulphate entering OWP remains in the pit, while 2 % of the sulphate entering OEP remains in the pit. Sulphate removal in the pits appears to be minor. Some gypsum formation could be occurring.

2.6 Areas, Volumes and Residence Times in OWP, OEP and Polishing Ponds

- In Table 8, the areas, water volumes and flows are used to estimate residence time of water in these water bodies.
- The theoretical residence of OWP is 77 days. However, Drainage Tunnel water (8.3 L/s) joins the top 1 m of surface water of OWP, and likely exits OWP without mixing with the entire water volume. The 1.7 L/s groundwater flow also enters the top 1 m of surface water. Therefore, the residence time of the top 1 m of water may only be 5.4 days.
- The theoretical residence of OEP is 126 days. However, as in OWP, water enters OEP from OWP (10 L/s) joining OEP surface water, and does not likely mix with the entire OEP volume before exiting OEP via the weir. Meanwhile, another 9.2 L/s of groundwater joins the top 1 m of OEP surface water, and the flow through

this layer totals 19.2 L/s. Therefore, the residence time of the top 1 m of OEP surface water may be only 11.8 days.

The Polishing Ponds are relatively shallow, averaging only 0.46 m deep. The theoretical residence times of the PP10-PP13 and PP14-PP17 series of ponds are 9 and 6 days, respectively. However, a large fraction of these ponds' areas are virtually stagnant or above water, and actual residence times in these ponds are likely much shorter.

2.7 Sedimentation Rates in OWP, OEP and the Polishing Ponds

2.7.1 Sedimentation Data

- Measurements of sedimentation rates in OEP and OWP have been measured since 1990 and 1994, respectively. These data, in g·m⁻²·d⁻¹, are presented in Table 9.
- Generally, the rates are consistent from year to year, with two exceptions where very high rates were determined: OEP 20 m and OWP 7 m, but in place between October 12, 1995 to July 10, 1996. These two data were not used in calculations, as they may have been due to improper placement of the traps or erosion of iron hydroxide into the traps from the pit walls into the traps.
- The sedimentation rate data were used to estimate the total weight of sediment settling to the bottom of OWP and OEP each year (Table 10). Since many sedimentation trap incubation periods span two chronological years (e.g., October 18, 1991 to September 29, 1992), a proportional fraction of the measured sedimentation spanning two different years was allocated to the each of the two years (e.g. 21 % of the measured amount of sediment for October 18 to

December 31, 1991 and 79 % for January 1 to September 29, 1992).

- Using OEP sedimentation rates, the estimated sedimentation in OEP ranges from 41 t per year (1995) to 113 t per year (1992). The 1996 weight (27 t) is that amount up to September 26, and does not represent a full year.
- Sedimentation in OWP ranges from 4 t to 9 t per year. Sedimentation traps were not installed in OWP until 1993, following joining of the two pits when it was observed that iron hydroxide was forming due to changes in OWP's limnology.

2.7.2 Comparison of Sedimentation Rate Data With Iron Load Estimates

2.7.2.1 Oriental West Pit

- In Table 11, estimated loads of iron to OWP is presented for the ice-free season (May 1 to November 1), based on iron mass balance presented in Table 6. The estimated Fe load for the 183 day ice-free period is 1,700 kg.
- The elemental composition of particulates captured by the sedimentation traps in the OEP and OWP sedimentation traps are presented in Table 13.
- Estimates of total kg of iron sedimenting in OWP over the ice-free season, based on sedimentation rates and sediment iron assay data for 1994, 1995 and 1996 are 1,163 kg, 817 kg and 439 kg, respectively. In 1995 and 1996, iron settling rates, based on sedimentation trap data, are lower than estimates of the iron load to OWP during the ice-free season. It is possible that the actual mass of iron entering the OWP is diminishing with time. Another possibility is that smaller particles are being formed in more recent years, and settling rates have diminished.

2.7.2.2 Oriental East Pit

- Estimated loads of iron to OEP are presented in Table 12 for the ice-free season, for comparison to measured sedimentation of iron in particles according to sedimentation trap data.
- The estimated iron load to OEP between May 1 and October 31 is 4,759 kg for the 183 day period. In 1995 and 1996, the sedimentation traps collected a similar amount of iron (7,758 and 8,038 kg) in this period.
- Using sedimentation trap data and sediment sample analytical data, between 7 and 8 t of iron settle in OEP during the ice-free season. The iron load estimates are about half the mass of iron collected by the sedimentation traps for the same period. Re-suspension of settled iron may account for higher Fe load captured by the sedimentation traps than indicated by the iron mass balance.

2.7.3 Iron Loads to Polishing Ponds

- An estimate of the accumulation of iron by new algal biomass grown over the 183 day ice-free season is given in Table 14. Data on pond areas, alder substrate surface areas, algal growth rates and iron content of algal biomass are available in the 1995 Report (Tables 1b, 2b and 5b).
- It is estimated that new algal biomass grown over 183 days captures 772 kg of iron. This suggests that the algal biomass may capture iron settled from previous periods which has been resuspended from the pond sediments. In other words, iron is being recycled in the ponds.
- There is direct visual evidence of this process in the ponds. Slabs of algal

biomass covering the sediment and substrates periodically buoy to the surface due to an accumulation of air bubbles in the biomass. These floating slabs of algae are broken up by wave agitation or upon being carried over the weirs where they are smashed into smaller particles. Resuspended iron particles are likely recaptured by sieving by algal biomass.

The iron load to OEP was estimated in the Fe mass balance. A mass of 4,733 kg of Fe enters the OEP in the 182 day ice-covered season. High iron concentrations in PP17 discharge water in winter suggest that little iron is removed from the Polishing Pond system, and that a large fraction of the discharge iron remains in the ferrous form.

The ice covers over the pits and polishing ponds serve to prevent ferrous iron oxidation and ferric hydroxide precipitation.

CHLORIDE	Flow	[CI]	CI Load	Removal
	L/s	mg/L	mg/s	%
Drainage Tunnel	8.3	12.7	105	
OWP Contaminated Groundwater	1.7	144 ^v	249	
OWP Surface Outflow	10	35.3	354	
	-9.2			
OEP Surface Inflow	610	35.3	_ 200354	
OEP Contaminated Groundwater	5.84	149	870	
OEP Clean Groundwater	3.36	2	6.7	
OEP Outflow	19.2	64.1	1231	877

Table 3: Chloride Mass Balance for OWP, OEP System.

Table 4: Sodium Mass Balance for OWP, OEP System Based on Flows Derived from Chloride Mass Balance

MILIDIO		Flow	[Na]	Na Load	Removal
300101		L/s	mg/L	mg/s	%
	Drainage Tunnel	8.3	10.2	85 ———	٦
	OWP Contaminated Groundwater	1.7	114	197	V
	OWP Surface Outflow	10	22	221 28	1 22%
	OEP Surface Inflow	10	22	221 ———	
	OEP Contaminated Groundwater	5.8	120	701	
	OEP Clean Groundwater	3.4	8	26.9	
	OEP Outflow	19.2	49	941 94	8 1%

Table 5: Zinc Mass Balance for OWP, OEP System Based on Flows Derived from Chloride Mass Balance

ZINC		Flow	[Zn]	Zn Load	Removal
		L/s	mg/L	mg/s	%
	Drainage Tunnel	8.3	16.3	135	
	OWP Contaminated Groundwater	1.7	15.5	27	V V
	OWP Surface Outflow	10	16.6	. 166 <i>3</i>	162 -3% 7708 (24)
	OEP Surface Inflow	10	16.6	166	······
	OEP Contaminated Groundwater	5.8	15.2	89 ——	
r.	OEP Clean Groundwater	3.4	0.01	0.03	
	OEP Outflow	19.2	11.9	228	255 10%

IRON	Flow	[Fe]	Fe Load	Removal
	L/s	mg/L	mg/s	%
Drainage Tunnel	8.3	0.131	1.1	·
OWP Contaminated Groundwater	1.7	63.2	109	
OWP Surface Outflow	10	0.1065	1.1	110 99% 3,469kg
OEP Surface Inflow	10	0.1065	1.1	
OEP Contaminated Groundwater	5.8	51.27	300 —	
OEP Clean Groundwater	3.4	0.01	0.03	
OEP Outflow	19.2	1.46	28	301 91%

Table 6: Iron Mass Balance for OWP, OEP System Based on Flows Derived from Chloride Mass Balance

Table 7: Sulphate Mass Balance for OWP, OEP System Based on Flows Derived from Chloride Mass Balance

SULPHATE	Flow	[SO4]	SO₄ Load		Removal
	L/s	mg/L	mg/s		%
Drainage Tunnel	8.3	120	998 —		-
OWP Contaminated Groundwater	1.7	1080	1863	VV.	
OWP Surface Outflow	10	255	2552	2861	11%
OEP Surface Inflow	10	255	2552		
OEP Contaminated Groundwater	5.8	1166	6812	— T	
OEP Clean Groundwater	3.4	10	34		
OEP Outflow	19.2	479	9197	9397	2%

					Theoretical	Top 1 m
		Whole	Top 1 m		Residence	Residence
	Area	Volume	Volume	Flow	Time	Time
	<u>m²</u>	<u>m³</u>	m ³	L/s	days	days
Drainage Tunnel				8.3		
OWP	4,645	66,245	4,645	10.0	77	5.4
OEP	19,510	208,197	19,510	19.2	126	11.8
PP10-13 (40% of OEP flow)	13016	5951		7.7	9.0	
PP14-17 (60 % of OEP flow)	13142	6009		11.5	6.0	

Table 8: Areas, Volumes and Residence Times of Water in OWP, OEP and Polishing Ponds

Table 9: Summary of Sedimentation Trap Data for OEP and OWP.

r				Sedimen	tation	Rate,	g.m ⁻² .	d ⁻¹		
				OEP						OWP
			Summer	Outflow	Outflow		11 m	20 m		7 m
From	То	Days	Period?	A	В			Α	В	
20-Sep-90	22-Oct-90	32	Yes	0.62				2.1		
20-Sep-90	28-May-91	250			2.1				5.4	
22-Oct-90	28-May-91	218		4.57				4.6		
28-May-91	18-Oct-91	143	Yes	1.87				5.3		
18-Oct-91	29-Sep-92	347		3.84				19		
14-Jun-93	30-Aug-93	77	Yes		1	5.9	9.9			
30-Aug-93	11-Jul-94	315				5.1	4.5			
11-Jul-94	07-Sep-94	58	Yes					ĺ		6.22
07-Sep-94	07-Jul-95	303			Ì	3.9	3.2	12		4.89
07-Jul-95	12-Oct-95	97	Yes			5.3	4.9	6		6.16
12-Oct-95	10-Jul-96	272			· ·	4.5	4.5	60		42.7
10-Jul-96	29-Sep-96	81	Yes			4.8	5.5	9.3		7

					Orienta	al East Pit (OEP)	<u></u>					Orienta	West Pit (C	WP)		
										Proportions		Estimate		· · · · · ·			
		No. of				Average		Sediment	Cumulative	for years ***		for year	10 m S.T.		Sediment	Cumulative	Estimated
Sedimentation Tr	raps	Days in	Sed. rate,k	(g.d⁻¹.pit⁻	1	Sedimenta	tion	in period	to date	(current,		(to date)			in period	to date	for year
Placed	Retrieved	Period	20 m	4 m	11 m	kg.d [™] .pit ⁻¹	kg.m ⁻² .d ⁻¹	kg in period	kg	prev/next)	Year	kg.y ⁻¹	kg.d ⁻¹ .pit ⁻¹	kg.m ⁻² .d ⁻¹	kg	kg	kg.y⁻¹
20-Sep-90	22-Oct-90	32	40			40.1	2.06	1,283	1,283	1.00							
22-Oct-90	28-May-91	218	89			89.2	4.57	19,446	20,729	0.32 0.68	1991	54,775					
28-May-91	18-Oct-91	143	104			103.5	5.30	14,801	35,529	1.00							
18-Oct-91	29-Sep-92	347	362			361.8	18.54	125,545	161,074	0.21 0.79	1992	113,144	-				
29-Sep-92	14-Jun-93	258	:			154.5 *	,	39,873	200,947	0.36 0.64	1993	48,816					
14-Jun-93	30-Aug-93	77	6,904 *	115	193	153.8	7.88	11,839	212,786	1.00							
30-Aug-93	11-Jul-94	315	2,006	99	88	93.3	4.78	29,393	242,179	0.39 0.61	1994	56,229					4,287
11-Jul-94	07-Sep-94	58	415			414.6	21.25	24,047	266,226	1.00			28.9	6.22	1,676	1,676	
07-Sep-94	07-Jul-95	303	233	77	62	124.1	6.36	37,589	303,815	0.38 0.62	1995	40,513	22.7	4.89	6,878	8,554	9,298
07-Jul-95	12-Oct-95	97	116	103	95	104.6	5.36	10,143	313,958	1,00			28.6	6.16	2,774	11,329	
12-Oct-95	10-Jul-96	272	1,162 *	88	88	88.1	4.52	23,963	337,921	0.29 0.71	1996	27,205	198.3	6.07 @	7,670	65,266	8,055
10-Jul-96	29-Sep-96	81	181	93	107	127.0	6.51	10,290	348,211	1.00			32.6	7.00	2,641	67,907	
	equiv. to	6.0	years		Avg =	154.5 (avg used for	** above)					28.2	(avg used	in @ above))	

Table 10: Sedimentation Rate Data and Calculations for OEP and OWP, 1990 to 1996.

* High values likely due to sediment subsidence; Values not used in calculations

*** proportion of total kg of sediment collected in sed trap for a period which spanned more than one year

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OWP IRON	1994 kg in 183 days	1995 kg in 183 days	1996 kg in 183 days
OWP Fe Load in 183 days, based on Fe Mass Balance (Table 6)	1,739	1,739	1,739
Sed Trap Captured Iron Mass, May 1-Nov 1, kg Using summer sedimentation rates; Fe content of sediment	1,163	817	439

Table 11: Ice-free season (May 1 - Oct 31) Iron Load to OWP versus Measured Ice-free Season Sedimentation Rate.

Table 12: Ice-free season (May 1 - Oct 31) Iron Load to OEP versus Measured Ice-free Season Sedimentation Rate.

OEP IRON	1994	1995	1996
	kg in 183 days	kg in 183 days	kg in 183 days
OEP Fe Load in 183 days, based on Fe Mass Balance (Table 6)	4,759	4,759	4,759
Sed Trap Captured Iron Mass, May 1-Nov 1, kg Using summer sedimentation rates; Fe content of sediment		7,758	8,038

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		OWF	, % of dry	weight	OEP	% of dry	weight
		Branches	Netting	Sed Trap	Branches	Netting	Sed Trap
	Assay No.	5735	5736	5733 🗸	5729	5730	5725 🗸
1994	ug/g, Al	0.72	0.61	0.97	0.24	0.34	0.45
	Ba	0.15	0.13	0.12	0.05	0.04	0.065
	Cd	0.003	0.005	0.003	0.005	0.005	0.003
	Cu	0.08	0.11	0.18	0.03	0.04	0.026
	Fe	8.5	15	22	29	29	17
	Mn	0.04	0.06	0.06	0,09	0.09	0.056
	Pb	0,19	0.19	0.36	0.04	0.04	0.19
	Zn	0,93	1.9	1.2	4.3	4.4	1.1
	Assay No.	5737	5738	5734 ~	5731	5732	5726 [~]
1995	ug/g, Al	0.54	0.48	0.38	0.17	0.16	0.10
	Ba	0.073	0.064	0.077	0.021	0.062	0.021
	Cđ	0.010	0.012	0.003	0.012	0.013	0.003
	Cu	0.26	0.31	0.11	0.05	0.06	0.03
	Fe	24	28	16	38	38	41
	Mn	0.08	0.03	0.02	0.14	0.09	0.11
	Pb	0.16	0.17	0.17	0.02	0.03	0.02
	Zn	1.6	2.5	0.6	5.1	5.8	2.5
		Fil Algae	Fil Algae	J.			è.
1996	Assay No.	Bulk 5993	5989	5990			5988
	ug/g, Al	0.29	0.18	1.15			0.18
	Ва	0.013	0.007	0.068			0.016
	Cd	0.006	0.003	0.001			0.003
	Cu	0.16	0.11	0.04			0.03
	Fe	7.4	4	7			47
	Mn	0.02	0.01	0.02			0.10
	Pb	0.07	0.04	0.16			0.03
	Zn	1.1	0.6	0.2			1.8
	N, total	3.1					
	P, total	0.16					
	Organic C	39					
	Inorganic C	0.020					

Table 13: Elemental Composition of Periphyton Grown on Alder Branches or Nylon Netting and Sedimentation Traps in OWP and OEP, 1994, 1995 and 1996.

Table 14: Iron accumulation in polishing ponds algal biomass over 183 d ice-free season. May 1 - Oct 31

			Alga Biomass	<u></u>		1			Alga Biomass	- <u></u>	Fe
			In Period	[Fe] in	Fe Accum				In Period	[Fe] in	Mass
	Pond	Substrate	@ 1.8 g.m ⁻² .ď	Biómass	in Algae		Pond	Substrate	@ 1.8 g.m ⁻² .d	Biomass	in Algae
	Area, m ²	Area, m ²	kg	kg Fe.kg	in 183 d, kg		Area, m²	Area, m²	kg	kg Fe.kg ⁻¹	kg
	(a)	(b)	(c)	(d)			(a)	(b)	(c)	(d)	
PP10	595	1153	386	0.157	61	PP14	1867	3617	1211	0.067	81
PP11	2490	4824	1615	0.040	64	PP15	3465	6713	2247	0.04	90
PP12	4041	7828	2620	0.021	54	PP16	4038	7823	2618	0.0423	111
PP13	5890	11410	3819	0.050	190	PP17	3772.0	7307	2446	0.050	122
					368						403
					772	kg Fe	accumulat	ed by new a	llgae over 193 io	ce-free seas	on.
	Fe Load fro	om OEP in ic	e-free season (1	83 d)	443	kg Fe	(Fe Mass I	Balance, Fe	Load at OEP V	Veir).	
	Fe Load fro	om OEP in w	inter (1982 d)		4733	kg Fe	(Fe Mass I	Balance, Inp	out to OEP from	D.T. and G	v)

(a) Pond areas from Table 1b, 1995 Report.

(b) Alder substrate surface area of 50,430 m2 (Table 2b, 1995 Report) split among ponds proportional to pond areas.

(c) Growth rate of 1.829 g.m-2.d-1 for fertilized ponds from Table 2b of 1995 Report.

(d) Iron content (ICAP) of branch and netting algae collected in 1994 and 1995 used, from Table 5b of 1995 report.



Boojum Research Limited January 1997



3.0 IRON AND ZINC REMOVAL MECHANISMS

3.1 Review of Zinc Removal Processes

In the evaluation presented in the 1995 report, it is suggested that virtually no zinc is removed from the system during winter months. Adsorption of zinc on the iron oxides and hydroxides formed during the ice-free season was previously proposed as the removal mechanism. This mechanism is well known from the literature (M.Langen; Hobert and B.Hamacher; B.Muller and L.Sigg, 1990). It was therefore a natural choice for explaining the process of zinc removal in the OEP.

This adsorption mechanism would include a significant role for oxygen in the process of zinc adsorption to the iron oxides and hydroxides. Therefore, a significant quantity of oxygen is required in the pit to oxidise ferrous iron dissolved in solution, which is followed by precipitation as ferric iron hydroxide/oxide.

The process of iron oxidation is slow. The kinetics of oxidation were described by J.L.Liu and M.Kalin (1990) as an exponential curve with the varying coefficients, depending on the conditions of the AMD in which the oxidation takes place. The limitation of oxygen when the pits and ponds are covered by ice was used to explain the increase of the concentration of zinc in the outflow; there was not enough oxygen in the water to oxidize iron, preventing iron hydroxide formation and zinc adsorption. This was also a plausible explanation for observed zinc removal patterns.

However, other experimental facts were collected and have to be examined. The scanning electron microscopy and X-ray microanalyses of sedimentation trap samples have shown that the samples from the OEP itself consist largely of Fe-rich grains with high oxygen signal. This means that there was enough oxygen to form iron oxides/hydroxides and, if the proposed zinc adsorption mechanism was adequate, zinc should have been detected in the samples. The SEM-EDX work showed that zinc could

only be detected at 20,000 x magnification. This suggested that the zinc removal mechanism may not be based on adsorption to iron precipitates.

The SEM-EDX analyses detected microzones within polishing pond solid samples with very high concentrations of zinc, but comparatively little iron. This must be considered in light of 1991 observations; a lot of zinc was present in the upper part of the "meadows" close to the outflow of OEP. In this area, large amounts of ferrous iron were detected, while ferric iron was present in large quantities only in the lower part of the "meadows". The fact that zinc was concentrated in areas with little ferric iron, while lower concentrations were present in areas with higher concentrations of ferric iron, contradicts the expected distribution of iron and zinc if zinc adsorption was the primary removal mechanism. However, the pattern of zinc removal can be explained in terms of zinc carbonate precipitation, suggested from the oxidation experiments discussed in Section 3.2 below.

The ferrous iron oxidation-ferric hydroxide precipitation process and the zinc removal process do not appear to be directly related. The process of iron oxidation is not important for the removal of zinc, since this element was not adsorbed in large quantities when iron oxide/hydroxide particles are abundant, such as in OEP. The zinc removal process and iron oxidation/precipitation process take place simultaneously, but are likely independent.

Another observation was presented in the 1995 Final Report (page 13); the zinc concentration dropped rapidly in April (ice melting) but increased again starting in August, when water temperatures began to decrease. The solubility of oxygen in water was therefore increasing as the water temperature decreased. Contrary to the observed zinc concentration increase, higher dissolved oxygen concentrations should have enhanced ferric iron oxidation, and zinc adsorption, if this were the major zinc removal mechanism.

This analysis of old data leads to the conclusion that it is necessary to examine whether the proposed mechanism of zinc adsorption on iron oxides, suggested in the literature, is a significant process removing this metal from OEP water. In the 1991 report, it was determined that both zinc and iron enter the pit through the bottom primarily in the forms of soluble $Zn(HCO_3)_2$ (zinc bicarbonate) and $Fe(HCO_3)_2$ (ferrous bicarbonate). Ferrous bicarbonate hydrolyse to produce ferrous hydroxide and release carbon dioxide.

$$Fe(HCO_3)_2 + 2H_2O = Fe(OH)_2 + 2H_2O + 2CO_2$$

Taking this equation, it is possible than iron precipitates can form in the absence of oxygen, if carbon dioxide is removed from water (e.g. degassing). With zinc, the situation seems more difficult. There is the possibility that zinc bicarbonate decomposes to zinc carbonate, which in turn precipitates. This reaction is favoured if carbon dioxide were removed from solution by, for instance degassing as ground water rises to the pit surface.

 $Zn(HCO_3)_2 = ZnCO_3 + H_2O + CO_2$

However, zinc carbonate settling through the water column and entering pit bottom water, supersaturated with carbon dioxide and bicarbonate (with respect to surface water), may redissolved into solution as zinc bicarbonate.

$$ZnCO_3 + H_2O + CO_2 = Zn(HCO_3)_2$$

The production of carbon dioxide by the formation of ferrous hydroxide may maintain high carbon dioxide concentrations in water, and suppress the formation of zinc carbonates. This may explain why relatively little zinc removal takes place in the pit. Zinc carbonate formation and precipitation may take place only after the removal of significant amounts of iron and loss of carbon dioxide from the system. This analysis suggests that the presence of oxygen may not be necessary for the removal of zinc. However another factor(s), as yet not described, may also be very important, which is a reaction which is producing precipitating forms of zinc, a process which takes place only in the upper part of the pit (< 2 m) but not at depth. Some zinc removal occurs in the top layer of the OEP during the summer when surface water temperatures are high and exposed to sunlight. Sunlight could assist in iron oxidation and may also assist zinc removal. An experiment examining the effects of aeration and temperature upon zinc removal from OEP and OWP surface and bottom water samples is described in Section 3.2.

3.2 The Precipitation of Iron and Zinc: The OWP, OEP Oxidation Experiments

- An experiment was conducted examining changes in dissolved zinc and iron concentrations in samples collected from OWP and OEP surface and at depth according to time following collection and storage conditions (open bottles versus closed; 5° C, 15° C or 20° C storage temperatures).
- All zinc and iron analyses presented were performed on whole samples using the Buchans Asarco AAS equipment. The results of these two experiment are presented in Figure 15 a-f (OEP Surface), 16 a-f (OEP Bottom), 17 a-f (OWP Surface) and 18 a-f (OWP Bottom).

3.2.1 OEP Surface Water Samples

OEP surface samples were collected and analyzed for iron and zinc within 24 hours of collection. Three identical pairs of samples (open, closed bottle) were stored at room temperature (20° C), in the Asarco vault (~ 12° C) and in a fridge (5° C). These samples' zinc and iron concentrations were determined 4 and 14 days after collection (Figure 15 a - f).

- The dissolved iron concentration in these samples was less than 0.1 mg/L at the time of collection, and remained so over the 14 day experiment. The zinc concentration was 14.1 mg/L.
- After 4 days of storage, zinc concentrations remained virtually the same in all treatments. A slight decrease in the zinc concentration in the 20° C bottle stored open was observed.
- After 14 days, zinc concentrations decreased in the open bottle treatment stored at 20° C, but remained near original zinc concentrations in the remaining five treatments.
- In summary, zinc was removed from OEP surface water if the sample was stored at 20° C and open to aeration. Dissolved or suspended iron was not required for this process.

3.2.2 OEP Bottom Water Samples

- Six OEP bottom water samples were collected, stored and analyzed for zinc and iron in an identical manner as the OEP surface water samples (Figure 16 a f).
- The iron concentration in the OEP bottom water was 64 mg/L. The initial zinc concentration was 16.9 mg/L.
- After 4 days, the zinc concentration diminished in the sample stored at 20° C open to aeration. By 14 days, most of the zinc was removed from the solution.
 Zinc removal was not observed in the remaining five treatments by day 14.
- Upon storage for 4 days, iron concentrations decreased in samples stored at

20° and 12° C. Larger decreases in iron concentrations occurred at 20° C temperature, compared to 12° C.

- By day 14, iron concentrations had dropped to undetectable concentrations at 12° and 20° C in both open and closed bottles. Iron concentrations had also decreased in samples stored at 5° C, but to a lesser degree than at higher temperatures.
- In summary, zinc was removed from OEP bottom water if the sample was stored at 20° C and open to aeration, as observed for the OEP surface water sample treatment stored open at 20° C. Iron oxidation, precipitation and settling did not enhance zinc removal in the remaining five treatments. Based on the observations of iron and zinc removal in OEP surface and bottom water in this experiment, zinc removal appears to be independent of iron removal.

3.2.3 OWP Surface Water Samples

- Six OWP surface water samples were collected, stored and analyzed for zinc and iron in an identical manner as the OEP surface and bottom water samples (Figure 17 a - f).
- The iron concentration in these samples was less than detection limit. The zinc concentration at collection 16.9 mg/L.
- As observed for OEP samples, the zinc concentration in OWP surface water declined in the open sample stored at 20° C, but not in the remainder of treatments. Over 14 days, the zinc concentration diminished from 16.9 mg/L to 12.4 mg/L, a smaller decline than observed for OEP surface and bottom water samples.

3.2.4 OWP Bottom Water Samples

- Six OWP bottom water samples were collected, stored and analyzed for zinc and iron in an identical manner as the other three sets of samples (Figure 18a-f).
- The iron concentration in these samples was less than detection limit. The zinc concentration at collection 18 mg/L.
- The zinc concentration declined from 18 mg/L to 7 mg/L in the OWP bottom water sample open to aeration and stored at 20° C. This decline was much greater than observed in the same treatment of OWP surface water.

In summary, zinc removal was observed in OEP and OWP surface and bottom water samples only if the samples were stored at 20° C and were left open to the atmosphere. Zinc removal appears to be unrelated to iron removal. Instead, zinc may be present in OEP and OWP bottom water a soluble zinc bicarbonate, coexisting with high bicarbonate and dissolved carbon dioxide. When these waters flow to the surface, the water warm in the epilimnion, and carbon dioxide solubility decreases. As CO_2 is degassed from solution, soluble zinc bicarbonate decomposes to zinc carbonate, CO_2 and water.

In the equation below, CO_2 degassing from the right side of the equation favours the reaction from left to right.

 $Zn(HCO_3)_2 \rightarrow ZnCO_3 + H_2O + CO_2 \checkmark$ (dissolved) (precipitate)

 In the experiment, high temperatures reduced the solubility of CO₂. The open bottles favoured degassing, while the closed bottles prevented degassing. In the 12° C and 5° C treatments, enough dissolved CO₂ remained in solution, and zinc bicarbonate was not decomposed. This process was originally described
in the December 1991 Final Boojum Report to Asarco (Section 3, pgs 3-3 to 3-10).

3.3 Zinc Precipitation With Phosphate

- Permanent removal of zinc, presently in the form of bicarbonates and carbonates, from OEP water could be achieved by adding phosphate to form zinc phosphates.
- A precipitation experiment consisting of the addition of 10-52-10 fertilizer to four samples, 4 L in volume, of OEP water collected from a depth of 0.6 m below the ice cover. The experiment was set up on January 7, 1997 and run until January 20, 1997.
- Fertilizer was added to three samples, and the fourth was left as a control. To Treatment 1, 45 g were added, while to Treatment 2, 6.3 g, and to Treatment 3, 0.87 g were added. Treatment 4 was the control. The samples were stored in the laboratory at 20 °C. The amounts of fertilizer added were based on the molar phosphate equivalent of zinc, magnesium and calcium concentrations present in OEP bottom water. For instance, 45 g of 10-52-10 fertilizer added to 4 US gallons of OEP water contains the equivalent number of moles of phosphate as the sum of the moles of calcium, magnesium and zinc present in 4 US gallons of OEP bottom water (Tables 15 17).
- Zinc concentrations were monitored regularly over the first 50 hours, then again after 190 and 320 hours (Figure 19 a d).
- The zinc concentration in Treatment 1, the control, remained relatively constant over the first 50 hours of the experiment. Zinc concentrations declined over the

first 50 hours in Treatments 1 through 3 where fertilizer was added.

- The greatest zinc removal was measured in Treatment 2, where 6.3 g of 10-52-10 fertilizer was added. After 13 days, the zinc concentration had declined by 87 %, compared to the concentration 1 hour after set-up (Table 18). The high fertilizer addition, Treatment 1 (45 g/4 USG), removed less zinc (57 %), comparable to Treatment 3 (73 %: 0.87 g/4 USG) after 13 days.
- Unlike the earlier oxidation experiment, appreciable zinc removal in the control, Treatment 4, was not observed after 8 days, despite the fact this sample was stored open to aeration at room temperature. After 13 days, the control samples's zinc concentration had begun to decrease. At this time, the zinc concentration was 10.6 mg/L, equivalent to a 43 % decrease, compared to the concentration 1 hour after set-up of the experiment.
- The delay in zinc removal in the control sample stored open at 20°C, compared to the previous experiment's 20°C, open treatments, may have been due to the larger sample size in this experiment (4 USG) compared to the previous experiment (0.25 L). Also, for this experiment, water samples were collected from OEP from beneath the ice in January, when any very fine zinc precipitates formed in the ice-free season would have been flushed out of the pit. These fine particles may serve as flocculation nuclei, accelerating the process of zinc removal through promoting larger particle formation and settling.

	M.W. g	OEP [] used mg/L	mM/L	Equiv. PO₄ mg/L	Equiv. mg of 10-52-10 Fert per L	Equiv. g of 10-52-10 Fert per 4 USG	
Ca	40.1	502	12.5	1190	2527	38	
Mg	24.3	44.5	1.8	174	369	5.6	
Zn	65.4	16.2	0.2	24	51	0.76	(0.87 g added to #3)
NO3	62						
NH4	18						

Table 15: Experimental Design of January 7-15, 1997 Fertilizer Experiment.

Table 16: Composition of Treatments Immediately Following Fertilizer Addition.

	ADDITION					
	g of	Equiv.	Equiv.	Equiv.	Equiv.	Equiv.
	10-52-10 Fert	mM of PO ₄	mM of Ca	mM of Mg	mM of Zn	mM of NO_3
	per 4 USG	in 4 USG	in 4 USG	in 4 USG	in 4 USG	in 4 USG
Treatment 1 for Ca, Mg and Zinc	45	221	190	28	3.8	26
Treatment 2 for Mg and Zinc	6.3	31	190	28	3.8	3.7
Treatment 3 for Zinc only	0.87	4.3	190	28	3.8	0.51
Treatment 4: Control	0	0	190	28	3.8	0

Table 17: Mass Calculations for Elements Present in OEP and K₃PO₄ equivalents.

		OEP						
	M.W.	Volume	[]	Mass	Mass	Equiv. PO₄	Equiv. K ₃ PO ₄	
	g	L	mg/L	kg	Moles	Mass, kg	Mass, kg	
OEP		208,197,000						
Zn	65		14.6	3,047	46,606	4,428	8,636	
Fe	56		47.0	9,785	175,212	16,645	32,468	
Ca	40		390	81,197	2,025,869	192,458	375,406	
Mg	24		34.7	7,217	296,870	28,203	55,012	
Mn	55		9.9	2,062	37,530	3,565	6,955	
PO₄	95							
K₃PO₄	185							
					For Entire Pit			
Treatment 4: Control								
Treatment 3: Add K₃PO₄ equiv. to Zn Mass in Pit 8,636 kg K₃PO₄							kg K₃PO₄	
Treatment 2: Add K₃PO₄ equiv. to Zn and Mg Mass in Pit 63,648 kg K₃PO₄							kg K₃₽O₄	
Treatment	Freatment 1: Add K ₃ PO ₄ equiv. to Zn, Mg and Ca Mass in Pit 439,054 kg K ₃ PO ₄							

	7-Jan-97	7-Jan-97		
	[Zn],mg/L	[Zn],mg/L		
Treatment	1 hour	314 hours	%	
	Whole	Whole	Filtered	Removal
#1: 45 g per 4 USG	17.4	7.4	7.4	57
#2: 6.3 g per 4 USG	17.6	2.8	2.4	87
#3: 0.87 g per 4 USG	17.5	4.8	4.7	73
#4:Control	17.5	10.6	9.9	43

Table 18:Zinc Concentrations in 4 USG OEP (5') Samples Treated
with 10-52-10 Fertilizer.











4.0 SEM-EDX EXAMINATION OF PARTICLES

The purpose of this work is to identify the chemical and physical nature of zinc present on particles formed in the OWP-OEP Polishing Pond system. This was done through SEM-EDX investigations on particles and through sequential extractions using material collected in sedimentation traps (chemical particles).

Variation of concentration of zinc in OEP with depth in the summer shows that there is a zinc removal mechanism operating in the pit, and zinc-containing particles should collect in sedimentation traps. The EDX-SEM surface investigation of the particles in the sedimentation traps did not detect sufficient zinc on the surfaces of the particles to yield a zinc signal (0.1 %) from the surface when investigated at magnifications covering a range of 200 x to 2,000 x. The particle size in these magnifications was identified as submicron (< 1 μ m) size.

The bulk samples, however, report, on average, about 1.1 to 2.5% Zn in sedimentation traps (Table 13, Section 2). These two findings suggest that the particles containing zinc which settle in the sedimentation traps are small, but they must be numerous, as the concentrations of zinc accumulated are relatively high. Samples collected in July, 1996 were examined at a magnification of 20,000 x (data presented at the end of this section under SEM-EDX, September 15, 1996 samples). Particles sizes ranged from 0.25 to 1.0 μ m. The same samples were previously examined at 200 x to 2,000 x magnification to derive confirmation of the biological accumulation of zinc (data presented at the end of the section under EDX: Samples Collected July 10 & 12, 1995).

At the 20,000 x magnification, it could be confirmed that, indeed, these smaller particles are associated with zinc. It also was determined that there is a distinct layer of precipitate with a thickness of about 100 nm coating the larger particles. The coating was thinner on particles in samples from the bottom of the OEP (25 m deep).

The OWP had particles (at 20,000 x magnification) free of precipitate coatings, which was also the case for the particles in the Polishing Pond samples examined at this magnification.

The observations of the coatings on precipitate particles suggests that a chemical mechanism is involved in the removal of zinc which is associated with the formation of larger particles, governed by colloid formation processes. It is well known from the chemical kinetics that large particles or aggregates can only be formed when small particles are present.

The phytoplankton identified in the Buchans system cover a size range of 2 μ m to 100 μ m. No populations were detected in the OEP, but they were present in the OWP and the Polishing Ponds. This finding also adds to the conclusion that physical forces must be overwhelming to phytoplankton in the OEP since the nutrient status should support phytoplankton growth, demonstrated by the growth of periphyton (attached algae) and cattails in OEP. Since chemical and biological factors inhibiting phytoplankton growth can be ruled out, the only other factors not considered to date, but relevant to particle formation, are hydrodynamical forces.

The microscopic investigations counting phytoplankton (both in Germany and Canada) reported the presence of needle-like crystals in the single OEP sample collected close to the thermocline in September. Particles experience different hydrodynamical influences when the thermocline is deeper during the summer months. In the September samples, the needle-like form of particles suggests that particles of such shape can be formed only as a result of different hydrodynamic forces, compared to those which lead to round aggregates of colloidal particles. A needle-like crystal can be induced when the hydrodynamical forces are laminar and not turbulent, as would be the case when the thermocline deepens and dissipates towards the end of the ice-free season (Figure 14, Section 2). The gradual decrease in Polishing Pond performance may also be related to particle formation and settling, due to seasonal

changes in both temperature and pH.

The observations to date can, in part, be explained in terms of those water flow patterns which influence those processes involved in the formation of zinc-bearing particles and the settling of these precipitates. After the formation of small particles of zinc carbonate, two simultaneous processes are taking place in the OEP to remove zinc via particle formation.

- a) the further growth and/or aggregation of particles.
- b) once the particle sizes is sufficiently large, then it is possible that they can settle.

Ferric iron oxidation and iron hydroxide formation may provide sufficiently large particles to assist in the aggregation of particles containing zinc.

Some zinc particle formation and settling occurs in OEP during the ice-free season, when ground water must enter and, prior to discharge from the pit, mix with the horizontally and vertically circulating epilimnion (1-2 m thick) covering the entire surface of the pit. Particulates borne in the circulating epilimnion are subjected to both zones of laminar (middle stratum of epilimnion) and turbulent (at epilimnion-thermocline interface) flow, and quiescent zones (pit perimeter). Particle aggregation and settling are possible in these months. However, in winter, gravity and hydrodynamics (dragging of particles with water) are, unfortunately, acting in opposite directions.

For example, while small particles may be forming in winter along the flow paths between ground water input and the OEP outflow, these flow paths may be both relatively laminar and high velocity, such that particles can neither aggregate by turbulent mixing, nor settle out of the rapid flow path. Particles may remain in the moving volume of water until discharged from the pit. The association of zinc with the small particles also explains in part why the polishing ponds, where no dissolved iron is present, still remove zinc at better rates when periphyton growth rates are high, through providing turbulent and quiescent zones for particle aggregation and settling by gravity. The SEM-EDX analyses revealed that a significant amount of zinc in precipitates is associated with algal biomass in the first polishing pond, located very close to the weir of OEP (data presented at the end of this section under EDX, Samples Collected July 10 & 12, 1995; SEM/EDX, February 1996 with 1995 Samples).

The differences between the summer hydrodynamics suggest an opportunity for particle formation and removal of zinc by inducing changes in flow patterns in the OEP. Potentially, changes in the flow pattern may improve the current hydrodynamic conditions. An evaluation of the physical changes which are required can be carried out by evaluating the particles sizes present in the pit, and the orders of magnitude of changes required to augment the particle formation/precipitation process will be estimated.

SEM/EDX

Febuary 1996

with 1995 Samples

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SEM/EDX

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SEM Image, Carbon Distribution, Zinc Disribution
Figure 8a PP 14 Bubble



Figure 1

F	ig	ure	2
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Spectrum file : NCE LIVETIME(spec.)= 50 E Ø2/96 RES AREA ENERGY - 5.2 79.52 37Ø48 TOTAL AREA= 51491 Peak at .50 keV omitted? FIT INDEX= 1.92APP.CONC ERROR (WT%) ELMT .Ø76 .146 .Ø74* < 2 Sigma* SK:Ø .236* < 2 Sigma* CuK : Ø .Ø79 SiK: Ø 1.158 .Ø55 NaK : Ø .415 1.144 01K : Ø .ø95 ZnK : Ø .669 .331 PeK:Ø 16.097 . 392 MnK : Ø .106 .401 .125* < 2 Sigma* .Ø82 A1K : Ø .Ø76* < 2 Sigma* CaK : Ø .Ø22 КК: Ø .Ø79 .Ø76* < 2 Sigma* ZAF CALCULATIONS ...[3 iterations] 20.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000 Spectrum: E Ø2/96 * INITIAL START-UP * All elmts analysed ZAF %ELMT +--Error ATOM.% ELMT .Ø74 SK: Ø .712 < .148 +-CuK : Ø .834 < .471 +-.236 .146 SiK : Ø .542 2.138 +-14.251 .178 1Ø.863 NaK : Ø .311 1.334 +-1.449 +-C1K:Ø.789 .121 7.652 ZnK : Ø .852 .784 +-. 388 2.246 FeK: Ø .953 16.897 +-.411 56.636 MnK : Ø .925 < .25Ø +-.125 .914 +-A1K : Ø .439 .188 6.339 < .152 +-**.**Ø76 CaK : Ø 1.000 κκ**: Ø .969** < .152 ++ .076 TOTAL 23.516 100.000



Figure 3





Page 5

Spectrum file : NCW Ø2/96 LIVETIME(spec.)= 5ø Ψ ENERGY RES AREA 5.8 78.21 36464 TOTAL AREA= 42109 Peak at .50 keV omitted? FIT INDEX= 1.48 APP.CONC ERROR (WT%) ELMT .ø22 SK:Ø .067* < 2 Sigma* CuK : Ø .173 .204* < 2 Sigma* 1.872 .Ø87 SiK : Ø NaK : Ø .552 .Ø59 .617 CIK:Ø .Ø78 ZnK : Ø .287 .271* < 2 Sigma* .256 Fek : Ø 5.648 MoK : Ø .104* < 2 Sigma* .1Ø3 1.502 A1K : Ø .1Ø1 -.Ø58 .Ø69* < 2 Sigma* CaK : Ø .070* < 2 Sigma* K K : Ø .117 ZAF CALCULATIONS ...[3 iterations] 20.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000 Ø2/96 * INITIAL START-UP * Spectrum: ₩ All elmts analysed ELMT ZAF %ELMT +~ Error ATOM.% .067 SK:Ø.618 < .133 +-CuK : Ø .822 < .408 +-.2Ø4 .535 SiK : Ø 3.498 +-.163 28.628 1.256 +~ NaK : Ø .440 .134 12.563 .883 +-. 678 .112 5.728 C1K : Ø < .542 +-.833 ZnK : Ø .271 .899 .285 FeK : Ø 6.283 +~ 25.866 .871 .1Ø4 MnK : Ø < .209 +-. 541 2.781 +~ A1K : Ø .188 23.703 CaK : Ø .908 < .137 +~ .069 < .141 +-K K : Ø .879 .Ø7Ø TOTAL 14.702 100.000 the same star and the first and the same same shall be all the same same same



Figure 5b



Figure 5





 Spectrum file : NC13

 13
 Ø2/96

 ENERGY
 RES
 AREA

 5.9
 77.59
 37092

 TOTAL
 AREA=
 19890

 FIT
 INDEX=
 1.58

ELMT			APP.CONC	ERROR (VT:	¥)	
s K	:	Ø	.073	.Ø41*	<	2	Sigma*
FeK	:	$\tilde{\mathcal{Y}}$.419	.122			-
NaK	:	ø	.549	.Ø42			
CaK	2	ø	.252	.ø64			
CIK	5	ø	.Ø72	.Ø45*	<	2	Sigma*
ZnK	2	Ø	Ø56	.195*	<	2	Sigma*
MnK	5	ø	Ø17	.Ø84*	<	2	Sigma*
A1K		Ø	3.813	. 124			-
SiK	Ľ.	ø	4.147	.105			
κĸ	:	ø	. 493	.Ø69			

ZAF CALCULATIONS

...[3 iterations]

20.00 KV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Spectrum: 13 Ø2/96

* INITIAL START-UP *

LIVETIME(spec.)= 50

All elmts analysed, NORMALISED

ELMT		ZAF	%ELMT	+	Error	ATOM.%
8 K :	ø	. 509	< .Ø82	+	.Ø41	
FeK :	Ø	.825	3.855	+	1.125	1.979
NaK :	ø	.953	4.365	+	.337	5.444
CaK :	ø	.794	2.408	+	.614	1.722
C1K 👔	Ø	.584	< .ø89	+-	.Ø45	
ZnK :	Ø	.809	< .39Ø	+	.195	
MnK :	ø	.797	< .168	+	.Ø84	
A1K :	ø	.925	31.248	+-	1.Ø14	33.2Ø4
SiK :	Ø	.613	51.364	÷	1.302	52.423
< K :	Ø	.785	4.764	- +	.665	3.493
TOTAL			98.ØØ4			100.000



Figure 7



Spectrum file : NC17 Ø2/96 LIVETIME(spec.)= 5ø 17 ENERGY RES AREA 6.3 75.99 35655 n/m TOTAL AREA= 8843 FIT INDEX= .54 ERROR (WT%) ELMT AFF.CONC .026* < 2 Sigma* SK:0 .009 .391 .Ø95 FeK : Ø .182 .Ø24 NaK : Ø .132 CaK : Ø .Ø46 C1K : Ø -.Ø16 .ø28* < 2 Sigma* .141* < 2 Sigma* ZnK : Ø - Ø23 .Ø51* < 2 Sigma* MnK : Ø .Ø2Ø A1K : Ø .Ø75 1.356 1.631 .Ø66 SiK : Ø .22Ø К:Ø .Ø47 ZAF CALCULATIONS ...[2 iterations] 20.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000 * INITIAL START-UP * Ø2/96 Spectrum: 17 All elmts analysed, NORMALISED Error ATOM.% ZAF %ELMT +-ELMT < .052 +-SK:Ø.516 .Ø26 2.092 FeK : Ø .832 8.616 +-4.555 4.013 +-5.154 NaK : Ø .833 .536 2.975 +-CaK : Ø .81Ø 1.Ø51 2.191 .Ø28 C1K : Ø .597 < .Ø57 +-.141 ZnK : Ø .811 < .281 +-.Ø51 MinK: Ø .804 < .1Ø1 +-29.029 +-A1K : Ø .858 1.607 31.771 51.994 SiK : Ø .602 49.461 +-2.ØØ1 3.783 K:Ø.803 5.009 +-1.076 99.1Ø2 100.000 TOTAL







Figure 10



Spectrum file : NC17B 17B Ø2/96 LIVETIME(spec.)= 50 ENERGY RES AREA 5.9 81.05 40698 TOTAL AREA= 94911 Peak at 4.46 keV omitted? FIT INDEX= 4.13 ELMT APP.CONC ERROR (WT%) S K : Ø . 447 .095 .412 FeK : Ø 13.173 1,084 .065 NaK : Ø CaK : Ø 1.934 .153 C1K : Ø .100* < 2 Sigma* .148 .618 ZnK : Ø 7.998 MoK : Ø .654 .200 AIK : Ø 9.751 .208 .205 SiK : Ø 15.618 K K : Ø 3.720 .165 ZAF CALCULATIONS[4 iterations] 20.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000 Spectrum: 178 Ø2/96 * INITIAL START-UP * All elmts analysed, NORMALISED ELMT ZAF %ELMT +--Error ATOM.% SK:Ø .566 .997 +--.212 1.064 .878 11.606 FeK : Ø 18.933 +-.592 NaK : Ø .52Ø 2.632 +-3.920 .158 .855 .225 CaK : Ø 2.854 + -2.438 C1K : Ø < .200 +-.644 .100 .935 ZnK : Ø .835 12.095 +-6.334 .846 .976 +-MnK : Ø .299 .608 .434 AIK : Ø .604 20.361 +-25.836 35.363 +-SiK : Ø .558 43.099 . 464 $K K : \emptyset$.854 5.499 +-.244 4.815 TOTAL 99.711 100.000



Figure 11

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Figure 12





Spectrum file : NC17C 170 Ø2/96 LIVETIME(spec.)= 5Ø ENERGY RES AREA 5.8 80.06 39993 ----TOTAL AREA= 139680 FIT INDEX= 3.95 ELMT APP.CONC ERROR (WT%) SК: Ø .527 .112 FeK : Ø 29.749 .597 .Ø57 NaK : Ø .838 .2ø5 CaK : Ø 4.834 .696 .128 C1K : Ø 59.544 1.263 ZnK : Ø .28ø .159 MnK : Ø 1.899 5.1ø3 A1K : Ø 10.022 SiK : Ø .17Ø кк: Ø 1.232 .167 ZAF CALCULATIONS ...[3 iterations] 20.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000 Spectrum: 17C Ø2/96 * INITIAL START-UP * All elmts analysed, NORMALISED Error ATOM.% ELMT ZAF %ELMT +-.596 +-.615 .126 .847 S K : Ø 21.118 +-FeK : Ø .981 .424 17.214 .34Ø NaK : Ø 1.717 +-.118 3.400 .151 CaK : Ø .949 3.549 +-4.031 .700 .693 +-.127 C1K : Ø • 89Ø .979 46.152 +--32.141 ZnK : Ø .898 MnK : Ø .935 1.415 +-.209 1.172 A1K : Ø .396 8.975 +-.280 15.144 SiK : Ø .47Ø 14.857 +-.253 24.078 .922 .931 +-.126 1.084 $K K : \emptyset$ TOTAL 100.002 100.000



Figure 13



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EDX

Samples Collected

July 10 &12 1995

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BUCHAN	Figure 2	Figure 3	Figure 4	Figure 5	Figure 6	Figure 7	Figure8	Figure 9	Figure 10	Figure 11	Figure 12
ELEMENT	OWP	OEP	OWP	OEP	PP-10	PP-11	PP-13	PP-14	PP-14	PP-17	PP-17
	BRANCH	BRANCH	BOTTOM	32' SED	FLOATING	MOSS	BUBBLE	FLOATING	FILAMENTOUS	FILAMENTOUS	SEEP
	#2	#3	SED TRAP	TRAP	MAT		ALGAE	ALGAE	ALGAE	ALGAE	ALGAE
					ALGAE						
	10/07/95	10/07/95	10/07/95	10/07/95	12/07/95	12/07/95	12/07/95	12/07/95	12/07/95	12/07/95	12/07/95
CI	<u> </u>					8.232			5.705	2.192	
Na	6.644	13.709		13.964	15.109	10.531	7.126	12,352	7.387	15.428	15.258
S						9.398			11.63		
Zn						12.779	3.505	14.485		6.468	13.898
Fe	15.103	45.946	47.763	46.981	40.401	11.972	20.361	36.768	39.032	17.255	38.503
Cu											
Mn							2.367	2.688			
AI	13.402		11.118				10.672			11.062	
Si	58.421	26.041	24.183	21.705	30.306	19.157	47.06	25.73	24.831	43.705	24.846
Ti											
As											
Cr											
Ca						18.477	3.283	3.594	6.192	2.476	3.078
ĸ						4.065	2.65		3.377		
TOTAL	100	100	100	100	100	100	100	100	100	100	100

. . . .

Operator: Coombs Client: coombs Job: Job number 155 Label: (untitled) (26 Sep 96 13:25:28)



ti shekarata

PP13 New Stub 09/96





I

Buchans OWP Branch #2 10/7/95



Spectrum file : NCØ1 54C (211 LIVETIME(spec.)= 50 - KES AREA - A.2 83.98 36439 - Otal Appa-36438 COTAL AREA= 31369 . . **.** >>> at .50 keV omitted? FIF INDEX= 1.37 CLIME APP.CONC ERROR(WT%) CLIME Ø .005 .058* < 2 $01/3 \pm 0$.005 .058* < 2 Sigma*

				4 18 44 44	-					
Next	i.	(2)	.173	.050						
	â	(2)	øøø	,Ø79*	<	2	Sigma⊁			
×	÷	\overline{O}	.281	.27Ø*	\leq	2	Sigma∗			
.1.		.0	1.548	,174						
1.1.41	÷	Ω.	174	.204*	<	2	Sigma*			
$(1,1) \in \mathbb{R}^{n}$:	25	.Ø89	.10Ø*	<	2	Sigma*			
$\{n_{i}^{(1)}\}_{i=1}^{n}$	÷	ЯŽ	.465	.Ø82						
11 L M	2	\mathcal{D}	2.162	,Ø9Ø			÷			
	';	29	.013	.Ø68*	<	2	Sigma*			
na ay si	÷	$\langle 0 \rangle$.Ø8Ø	. 534*	<	2	Sigma*			
1	ж 2	(β)	Ø54	. Ø86 *	\langle	2	Sigma*			
en fri	1	$\langle \vec{2} \rangle$.Ø83	. Ø62*	<	2	Sigma∗			
	:	Ø	.067	.060*	\leq	2	Sigma*			
	;	$\{\zeta_i\}$	-1.544	. 879*	<	2	Sigma*Not	used	for	quantitation
1.1	2	2	.021	174×	<	2	Sigma*Not	used	for	guantitation

CAR CALCULATIONS

... 2 iterations]

10.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Reader NC01

All elmts analysed, NORMALISED

			ZAF	%ELMT	+	Error	ATOM.%	
1		(2)	. 625	< .116	-+	.Ø58		
8 . (5 ⁸⁴	ę	$\langle \hat{\mathcal{O}} \rangle$.542	4.541	÷	1.309	6.644	
1. 1	;	23	.542	< .158		.079		
1		\mathbb{R}^{N}	.827	< .539	·•	.27Ø		
[™] ∰11	4	Ø	.872	25.Ø76		2.825	15.103	
'. Alt	ĩ.	Ø	.818	< .408		.2Ø4		
	1	Ø	.844	< .201	+	.100		
en a des		Ø	.614	10.749	+	1.899	13.402	
SiK	n 9	Q^{i}	.623	48.784	+	2.020	58.421	
T 3 K	H C	Ø	.817	< .136	+	. Ø68		
\rightarrow S \leq	a D	$(\hat{\ell})$.753	<1.Ø69	- -	.534		
Cek	5	Ø	.882	< .173		.Ø86		
1.3.6	a Z	k^{0}	.866	< .124		.062		
9 E	2	\varnothing	.837	< .121		.Ø6Ø		
1076	L.,			89.15Ø			100.000	

Page 4

* INITIAL START-UP *

Buchans OWP Branch #3 10/7/95



Symptomum file : NCØ2 LIVETIME(spec.)= 5%ENERGY RES AREA 35686 5.8 80.81 TOTAL AREA= 19821 l'Halt at .50 keV omitted? FIT INDEX= .95 APP.CONC ERROR(WT%) The Park .049* < 2 Sigma* -.015 .179 .Ø42 1999 ; Ø . . . <u>(</u>1 .073 .Ø72* < 2 Sigma* 7.55 ; B .378 .232* < 2 Sigma* Start : Ø 4.ø33 .223 Ø72 .152* < 2 Sigma* 1. 1 E .079* < 2 Sigma* 25.11 t Ø -.010.øø3 .057* < 2 Sigma* . 651 Ø59 11. s 2 .Ø58* < 2 Sigma* -.967 .378* < 2 Sigma* .348 .073* < 2 Sigma* 1. 1. 1. 19 .113 .060* < 2 Sigma* .108 .Ø51 .054* < 2 Signa* . . Ø .660* < 2 Sigma*Not used for quantitation N N 1 😥 -.055 $\mathrm{ALL}^{n} \subset \mathcal{D}$.410 .165Not used for guantitation CALCULATIONS 🗆 ... 🗋 iterations] こ このの RV - TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000 * INITIAL START-UP * Spectrum: NCØ2 All elmts analysed, NORMALISED ZAF %ELMT +-Error ATOM.% 230< MQQ +-610

1 1 E S	a.	101	a tutur		Ŧ	a 30 mm 7		
1664 S	î	Ø	. 344	7.124	+	1.658	13.709	
		5	. as to Z	. 144		.Ø72		
		{	. 65 C) +7	< .465	4	.232		
			2947	58.ØØ2	·] ·	3.208	45.946	
	L	3Å	.847	< .3ø3	-+	.152		
1111	5	$\langle i \rangle$.921	< .158	·	.Ø79		
	5	<u>(</u> 2)	.422	< .114	+-	.Ø57		
81 K.	7	(2)	.536	16.534	- j	1.501	26.Ø41	
$\mathbb{T} \in \mathcal{H}$	t.	$\langle 2 \rangle$.93Ø	< .116	+	.Ø58		
-48 P	3	Ø	.800	< .756	-+	.378		
	e t	\emptyset	1.032	< .146	~ ~ ~~~	.073		
13.45	1	<u>R</u> i	.987	< .120	-j	. Ø6Ø		
	4	87	.962	< .107	- -	.Ø54		
016	1 u.a			81 . 66Ø			1@@,@@@	

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.



Buchans OWP Bottom Sed Trap 10/7/95



Whenthow file : NCØ3 $X \in \{1, \dots, n\} \subseteq \{1, \dots, n\}$ LIVETIME(spec.)= 50 ENERGY RES AREA 6.Ø 8Ø.57 **35884** TOTAL AREA= 20625 Seak at .50 keV omitted? FIT INDEX= .86 APP, CONC 94. AND ERROR (WT%) 1 : . . . Ø .052* < 2 Sigma* . Ø66 "ø47 Tet : Ø .038* < 2 Sigma* 13 Z # 4 4 54 Zeas 57 g. e $\mathbb{N} \oplus \mathbb{P}$ Nati LEE CALCULATIONS . . 2 2 iterations] 20.000 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000 * INITIAL START-UP * Spectrum: NCØ3 Gil elmts analysed,NORMALISED <u>1 191</u> %ELMT +--Error ATOM.% ZAF .Ø52 8 .739 < .1Ø4 +-.Ø38 Se : 6 .329 < .076 +-- \sim $< \phi$ < .149 +-.Ø74 .574 < .421 +-.211 1.0. ; Q. 848 61.942 +-.938 3.908 47,763 0 ann 💼 😰 -.831 < .325 +-.163 .Ø78 1973 - 1 Ø .91Ø < .156 +-6.965 +-A18 : Ø .467 2.238 11.118 15.773 +--Ste : Ø .547 1.774 24,183 11. t 🖗 .926 < .109 +-.055 < .805 +where $z = \emptyset$. .791 .402 Page 8 0 1.029 < .142 +-.071 .Ø53 Call : Ø .978 < .106 +-≥ < : Ø .951 < .105 +-.Ø52 JOTAL. 84.681 100.000

.....

0	21 14	\mathcal{O}	.110	.Ø74* < 2 Sigma*
0	:	Ø	.139	.211* < 2 Sigma*
e.	ia Ir	\emptyset	3.292	.208
	2	$\widetilde{\mathcal{O}}$,132	.163* < 2 Sigma*
-	4	$\bar{Q}\bar{q}$	Ø33	.Ø78* < 2 Sigma*
:	۸. ۲	$\tilde{\mathcal{L}}$.184	.059
	2	-24	.490	.055
	Ŀ,	$\sqrt{2}$.043	.055* < 2 Sigma*
	ý.	Ž1	502	.402* < 2 Sigma*
	ţ	2	. (#224)	.071* < 2 Sigma*
		$\hat{\mathcal{D}}$.ø36	.053* < 2 Sigma*
	2	$\tilde{\mathcal{O}}$. Ø40	.052* < 2 Sigma*
	n. V	Ø	.132	.720* < 2 Sigma*Not used for quantitation
	•	$\tilde{U}^{(i)}$.364	.169Not used for guantitation

Buchans OWP 32 Sed Trap 10/7/95



Spectrum file : NCØ4 LIVETIME(spec.)= 50 ~ 0.04 AREA ENERGY RES 35792 S.Ø **80.63** 1179. AREA= 32676 tak at .50 keV omitted? FIT INDEX= 1.26 APP.CONC ERROR (WT%) 1. . . Ž -. 349 .059* < 2 Sigma* .132 .Ø51 $\gamma_{\rm ext} = \pm i \mathcal{D}$.Ø84* < 2 Sigma* 1 5 3 2 .125 .293* < 2 Sigma* : 6 .419 3.168 .219 1919 - S. 🖉 .ø23 .222* < 2 Sigma* 5 A. 5 3 .035 .104* < 2 Sigma* .073 .Ø67* < 2 Sigma* . F : Ø .416 Ø6Ø · · · · · Ø -.095 .070* < 2 Sigma* .547* < 2 Sigma* - 37 - Ø .Ø92* < 2 Sigma* $(\mathbb{R}^{n})^{*} := \emptyset$ -.043 `st: € Ø. .Ø56 .066* < 2 Sigma* : B .063* < 2 Sigma* -.043 .965* < 2 Sigma*Not used for quantitation .133 $\phi_{i,i}(t) \in \mathbb{C}$.293 .188* < 2 Sigma*Not used for quantitation

CAF CALCULATIONS

1 2 iterations]

20.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

.....NCØ4

* INITIAL START-OP *

1.1

All elmts analysed, NORMALISED

11			ZAF	%ELMT		Error	ATOM.%	
CIK	л а	$(\tilde{2})$.737	< .117		.Ø59		
$\mathbb{N}_{n, 0} \in \mathbb{N}$	n V	$\langle \tilde{\mathcal{O}} \rangle$, 325	7.441		2.891	13.964	
8.00	4	ø	.674	< .167		.Ø84		
T. MAR	•.	$\langle \hat{C} \rangle$. 853	< .586		.293		
in the pro-	3	\mathcal{O}	.947	60.817	+	4.211	46.981	
$(-1)^{-1}$:	ŝŽ	.836	< ,444	· ·····	- 222		
· ·		9	,918	< .207	···	.104		
						a/ 7		
		$\langle \tilde{z} \rangle$.43i	< .135	-+ ··-	• 100 i		
$\mathcal{L} \in \mathcal{H}^{1}$		$\langle \hat{g} \rangle$,535	14.132	+	2.Ø48	21.705	
	1	$\langle \vec{2} \rangle$.934	< .139	+	.Ø7Ø		
1994 (N	2	$\dot{\phi}$. 792	<1.Ø94	- -	.547		
una gi	-	Ø	1.043	< .183	+	.Ø92		
	5	(7)	990	< .131		.066		
1.	-	 Vi	959	< .127		.063		
	; ; *		1. 1 444	82.390			100.000	

Page 10

Buchans PP-10 Folating Mat Algae 12/7/95



ALAR 2017 2018 2018 2018 2018 2018 2018 2018 2018	A PALCULATIONS 10.30 xV TILT=15.00 EL 10.30 xV TILT=15.00 EL	CNERCY RES CNERCY RES THAL AREA B0.29 TTINDEX 1.82 AREA 1.02 AREA
<pre>t+- Error ATOM.% t+- 2.428 15.109 t+- 2.428 15.109 t+- 4.008 40.401 t+0857 t+0855 t+0855 t+0855 t+0855 t+0851 100.000 </pre>	EV=10.00 AZIM=15.00 COSINE=1.000 * INITIAL START-UP	<pre>2 LIVETIME(spec.) = 50 2 ted? ted? #49* < 2 Sigma* 049* < 2 Sigma* 066* < 2 Sigma* 167* < 2 Sigma* 180 139* < 2 Sigma* 083* < 2 Sigma* 055* < 2 Sigma* 066* < 2 Sigma* 055* < 2 Sigma* 066* < 2 Sigma* 055* < 2 Sigma* 05* < 2 Sig</pre>



Spectrum.	file : NC	53			TUETIM	E lann		EQ
CONTRACTOR V	RES	AREA			-1461110	e rabe	C . / -	210
	10.74 10.40	39313						
ARE ARE	D= 226/	12						
	and the body							
	SG KeV	omitted?						
CALLEY X	- 45	with the second of						
	APP: CONC	ERROR (WT%)					
2011	586	. 874						
	279	.045						
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	.582	.096		14.				
C=	1.968	.314						
1.	1.630	.170						
	.015	.166%	22	Str	mat			
- 14 A B	175	- 1 2103*	< 2	Sic	mat			
1. S. S. Mar	. 264	.058*	22	Sir	UTLA #			
31 F 10	.854	. 0.66		1000	Million Co.			
- E	012	. 064*	< 2	Sic	max			
	. 241	.357*	1 2	Sic	max			
	0.67	085.	12	Sic	max			
434 V 281	1,832	104	10.000		Colles			
3 10	395	070						
	896	.796*	2 2	Sin	mainter	o-enad	Sec.	auantitation.
	118	1944	2 3	Sin	mashior	used	6.000	quantitation
	1	1.27.25	13 . Jan	Sec. 9	44526 - 1462/C	Maich	1. 541	diversion care care to
THE DALEUR	ATIONS							
000 2 ster	ations]							
STOLEN R.M.	TILT=15.0	# ELEV=10	.øø	AZI	M=15,88	COSI	NE=1	. 1211213
S () OWN #	NCS						TNET	TAL START-UP
	11111							AND DIRECT OF
al elmts	analysed,	NORMALISE	D					
100.00	ZAF	MT +	F	inne	ATOM V			
1	735 7	205 +		1017	8.232			
NAT & G	4/23 5	978 +		50	10.531	1		
đ	707 7.	4403 +-	1.5	223	0 100			
3 at 11	963 20	A25 +	3.0	288	10 770	4		
1 A .	193 16	509 +	1 7	1.6	11 020	~		
	ARA (332 +		44	11.772			
103	855	200		60				
all a a	471	116 +		50				
	581 13	287 +	1 0	123	19 157			
1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1 1	788	128 +-	***	164	+1+141			
Dellas la	777 2 .	714 +		57				Deers de
	863	169 +-		IRS.				Page 14
Mark in lat	984 18	285 +-	1.0	35	18.477			
1.1	911 3	924 +-		99	A GAE			
	5.9	154		sof	00.000			
					e man e demante			











coestrum file : NCØ7 LIVETIME(spec.) = 50 14C107 AREA 36199 ENERGY RES 5.6 83,28 COTAL AREA= 32039 saw at .50 keV omitted? TET INDEX= 1.75 i wi T APP.CONC ERROR (WT%) े । उठे .022 **.056*** < 2 Sigma* .337 : *6*4 .053 .141 . X : Ø .Ø83* < 2 Sigma* .866 .313 .nK : Ø .249 1991 i 18 4.569 : 0 -,Ø89 .202* < 2 Sigma* . . 505 .127 708 .ø93 7.576 .111 . di -.ø37 .072* < 2 Sigma* .29ø .485* < 2 Signa* $1 - \kappa \tilde{J}$ -.Ø6Ø .Ø92* < 2 Sigma* .531 leans : Ø .Ø8Ø $z \in \mathcal{D}$.Ø74 .411 .907* < 2 Sigma*Not used for quantitation 1.062.194* < 2 Sigma*Not used for quantitation .131 . . . Ø

OF CALCULATIONS

... 3 iterations]

spectrum: NCØ7

* INITIAL START-UP >

. . .

i elmts analysed,NORMALISED

1 ²		ZAF	%ELMT	+-	Error	ATOM.%	
	62	. ఉపచ	< .111		.056		
	8	.456	4.490	`+	.702	7.126	
	$\widetilde{\mathcal{O}}$.590	< .166	*	.083		
2	\odot	.837	6.280	+	2.274	3.5Ø5	*
	A	.391	31.166	* }	1.701	20.361	*
1997 - B	$\widetilde{\mathcal{D}}$.826	< .4ø4		.202		
tendel de	\mathscr{D}	.86Ø	3.563	·++- ++++	.895	2,367	
	Ø	.545	7.892	- i	1,033	10.672	
··	Ž2	. 600	36.23Ø		1,120	47.060	
The t	\mathscr{D}	.035	< .144		.072		
a ta 🍾 a	Ø	.766	< .969		.485		
$z_{i} \in \mathbb{R}^{n} \setminus \mathbb{Q}$	\bigotimes	.907	< .184	-fr	.Ø92		
11.e.M 🔮	;7)	.894	3.606	+-	.542	3.283	
h. 1	Ø	.880	2.84Ø	+-	.512	2.650	
DTAL.			96.Ø66	•		100.000	

Page 16

Buchans PP-14 Folating Algae 12/7/95



Spectrum file : NCØ8 NCØ8 ENERGY RES AREA - 5.6 81.50 36000 FOTAL AREA= 38372 Peak at .50 keV omitted? FIT INDEX= 2.06

1	1		APP.CONC	ERROR(WT%)	
D1K	5	$\langle 2 \rangle$	Ø15	.ø67* < 2	Sigma*
NæH	41 8-	\varnothing	.368	.Ø59	
	ł	\mathcal{O}	.164	.097* < 2	Sigma*
ZnK	:	(2)	3.312	.407	
ê si C	ž	Ŵ	7.914	.315	
¶K	1	$\langle \tilde{\beta} \rangle$.284	.221* < 2	Sigma*
	4	$\langle \hat{p} \rangle$.549	.133	
141	b -	$\langle \rangle$	Ø31	.074* < 2	Sigma*
5i S	::	Ø	1.534	.Ø85	
TiK	2	\tilde{Q}	.008	.Ø8Ø* < 2	Sigma*
asia.	ā.	(2)	.Ø4ø	.538* < 2	Sigma*
724	đ	S.	085	.1Ø3* < 2	Sigma*
l.est	:	ź)	. 569	.Ø92	
	17 4	Ø	.141	.076* < 2	Sigma*
Sec.	:	Ø	097	.949* < 2	Sigma*Not used for quantitation
	5	5	.356	.224* < 2	Sigma*Not used for quantitation

ZAF CALCULATIONS

...[3 iterations]

20.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Spectrum: NCØ8

* INITIAL START-UP *

All elmts analysed, NORMALISED

		ZAF	%ELMT	+-	Error	АТОМ.%		
71 H. 4	$\langle j \rangle$.736	< .135	÷	.Ø67			
siak :	$\widetilde{\mathcal{D}}$.323	6.318		1.ØØ7	12.352		
3×3	$\langle i \rangle$.659	< .194	+	.Ø97			
2:546 - 5	Ø	.871	21.067	·+ ····	2.590	14.485	*	
1e) :	(2)	.960	45.686		1.820	36.768		
S. 8	Ø	.857	< .442		.221			
MOR 1	(\tilde{c})	.925	3.286	-+	.798	2.688		
A18 (Ø	.410	< .148	+	.Ø74			
siK :	$\tilde{\mathcal{Q}}$. 529	16.Ø8Ø	-+	.89Ø	25. 73Ø		
TiK :	\tilde{C}	.916	< .161	·+··	.Ø8Ø			
AsK :	\varnothing	.796	<1.077	+	.538			Page 18
2 m 8 👔	\varnothing	1.007	< .206	• -	.1Ø3			-
Jark :	(Ž)	.984	3.205	- }-	.516	3.594		
8. 8. 4	Ø	.960	< .151		.Ø76			
1011AL			95.641			100.000		

LIVETIME(spec.)= 50

Buchans PP-14 Filamentous Algae 12/7/95



Spectrum file : NC9 NO9 FNERGY RES AREA 6.1 83.57 36585 TOTAL AREA= 37382 Heat at .50 keV omitted? FIT INDEX= 1.96 CLMT APP.CONC ERROR(WT%)

21K	3	\mathcal{G}	. 639	.083						
NaK	ii F	$\hat{\mathcal{O}}$.271	.Ø51						
	4 2	Ö	1.149	.131						
	Ţ	S.	.Ø11	.274*	<,	2	Sigma*			
$\leq \frac{m}{2} < \epsilon$:	2)	8.505	.314						
i sere	·		.Ø2Ø	.215*	Ś	2	Sigma∗			
(1,1,1)		<i></i>	.012	.117*	<	2	Sigma∗			
		15	.029	.073*	$\langle \langle$	2	Sigma∗			
		5	1.864	.Ø89						
	2	$\mathcal{G}^{(1)}$.035	.Ø8Ø*	\langle	2	Sigma*			
$\tilde{\bar{\gamma}} \otimes \tilde{\Gamma}_{1}$	i.	$\hat{\omega}$.239	.483*	<	2	Sigma*			
Criti	84 16	(\tilde{c})	.ØØ2	.Ø98*	<	2	Sigma∗			
	3	Ø	, 9 9 5	.Ø99						
1.1	:	0	.524	.Ø87						
Selden -	:	3	.102	.934*	\leq	2	Sigma*Not	used	for	quantitation
···	:	<u>(</u> 7	4 1 1	.282*	<	2	Sigma*Not	used	for	quantitation

LIVETIME(spec.)=

STRUCTIONS

...C 2 iterations]

LOUDE RY TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Spectrum: NC9

* INITIAL START-UP *

 $5\emptyset$

All elmts analysed, NORMALISED

	ZAF	%ELMT	 	Error	ATOM.%		
C18 : Ø	.731	4.925	·] - ····	.641	5.705		
NaK : Ø	.371	4.135	+	.778	7.387		
8 K : Ø	.714	9.078	+	1.Ø38	11.630		
ink : Ø	.839	< .547	+-	.274			
°eK :Ø	.905	53.076	+	1.962	39.032		
Claire 🕆 🖄	. 823	< .431	+	.215			
10000 ± 100	.875	< .234	+-	.117			
$S \in \mathcal{O}$.	.499	< .147)	.073			
Alt : Ø	.619	16.983		.813	24.831		
$1 < 1 \otimes 2$. 86Ø	< .160		.Ø80			
As⊦ : Ø	.782	< .965		.483			
Cok : Ø	.953	< .196		.098			
DaK : Ø	.929	6.Ø42	+	.602	6.192		Page 20
K K : Ø	.919	3.215		.535	3.377		
TOTAL		97.453			100.000	17	





Spactrum file : NC10 2010 ENERGY RES AREA 5.5 84.16 36449 TOTAL AREA= 28823 Paak at .50 keV omitted? FIT INDEX= 1.72

<u>s</u> m	ľ		APP.CONC	ERROR (WT%)	
[] [*	\emptyset	.136	.Ø58	
$(1,1)^{\prime}$	4	\mathcal{J}	.437	.Ø61	
1 K.	-	\mathbb{Z}	Ø16	.079* < 2	Sigma*
268	5	$\widetilde{\mathcal{O}}$.933	.293	
午會校	u a	$\hat{\mathcal{O}}$	2.265	.194	
	:	\mathcal{O}	-,Ø75	.184* < 2	? Sigma*
19 m.	÷	ŵ	. 1998	.095* < 2	Sigma*
A18.	:	\emptyset	.409	.Ø8ø	
Suk"		Ø	1.866	.Ø86	
12.00	к 2-	(0)	- . Ø56	.ø66* < 2	Sigma*
é s K	ŧ	(2)	372	.447* < 2	Sigma*
Cr.C	U b	\varnothing	.Ø29	.Ø8Ø* < 2	Sigma*
Def.	÷	ψ	. 233	.069	
i d	۲. ۲	\emptyset	,Ø99	.Ø6Ø* < 2	Sigma*
Sec. 1		Ø	.ø68	.759* < 2	Sigma*Not used for quantitation
	2	$\langle \dot{\gamma} \rangle$	133	$.184 \star < 2$	Sigma*Not used for quantitation

LIVETIME(spec.)=

BAR CALCULATIONS

...[3 iterations]

20.00 KV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Spectrum: NC10

* INITIAL START-UP *

50

All elmts analysed, NORMALISED

N.	Ţ		ZAF	%ELMT	+	Error	ATOM.%	
<u> </u>	2	(2)	.664	2.218	+	.944	2.192	
681	5	(2)	.467	10.125	- +	1.412	15.428	
$\frac{1}{2} = \sqrt{2}$	a a	\bigcirc	.581	< .157		.079		
2nH.	ĩ	Ø	.837	12.070	+-	3.790	6.468 🖈	
	:4 #	$\langle j \rangle$.892	27.5Ø9	+	2.351	17.255	
el alter	6	Ñ	. 828	< .367	-fr -n	. 184		
Name (a	2	$\langle \dot{q} \rangle$.861	< .191	·• •• •••••	.095		
	5	\odot	.521	8.519	+-	1.666	11.062	
$\oplus \{i_i\}$	12 12	Ø	.577	35.Ø45		1.617	43.705	
	ŧ	(2)	.832	< .132	- †	.066		
Ask.	2	δD	.760	< .895		.447		
$\sum_{i=1}^{m} e_i \in \mathbb{R}^d$	4 K	\mathcal{O}	.9ø3	< .16Ø	+-	.Ø8Ø		
C a K	а 4	$\langle \mathcal{I} \rangle$.891	2.833		.840	2.476	Page 22
$\mu^* = \{ \zeta \}$	t	Q	.866	< .121	fe	.060		
1014	ài.			98.318			100.000	

Figure 12





Spectrum file : NC11 NC22.2 LIVETIME(spec.) = ENERGY RES AREA - 5.9 82.10 36595 TOTAL AREA= 26835 g desk at .50 keV omitted? FIT INDEX= 1.56 APP, CONC ERROR (WT%) .042 S18 : Ø .058* < 2 Sigma* 439 1440 2 12 .Ø52 \mathbb{S} \times : \emptyset .007.Ø79* < 2 Sigma* InK : Ø 2.825 .365 Server 👔 🧭 7.369 . 293 Cen : Ø .Ø84 .186* < 2 Sigma* .Ø8Ø 1. N. 1 (2) .105* < 2 Sigma* ាន់ ៖ 🧭 .Ø65* < 2 Sigma* .064 - 1 : S 1.308 .076 . 075 1. - <u>1</u>. Ø .071* < 2 Sigma* - 19 1 B -.050 .439* < 2 Sigma* .Ø87* < 2 Sigma* CrK : Ø -.110 Dai : Ø .Ø77 .435 1 1 : 2 .121 .066* < 2 Sigma*

OF CALCULATIONS

Sector : Ø

 $\operatorname{relation}(Y) = f = \int \partial f$

.... 3 iterations]

00.00 KY TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Spectrum: NC11

* INITIAL START-UP *

.868* < 2 Sigma*Not used for quantitation

.187* < 2 Sigma*Not used for quantitation

50

All almts analysed, NORMALISED

-.361 .214

	ZAF	%ELMT	-j	Error	ATOM.%		
111 K & 4	ð .74ø	< .117	·•••	.Ø58			
NAR 6	0.325	7.966		1.005	15.258		
2 K i i	0 ,655	< .159		.079			
find a s	868, 5	29.631	+	2.666	13.898	*	
Stat 1	0.956	48.835	+~-	1.944	38.503		
0016 N 1	0.853	< .371	+	.186			
MAK : (ð . 922	< .211	+	.105			
75115 s s	8 . 4Ø9	< .13Ø	·}· ···	,Ø65			
	0.523	15.849		.916	24.846		
é hés a s	8.517	< .142	•• •• ••	.071	•		
-MeX : (3.794	< .878		, 439			
1.1 s. t. f	0 1.Ø11	< .174	- j	.Ø87			_
्य हो जिल्ला ह	ð . 984	2.802	·••· ··•	.497	3.078		Page
1 (s. 1)	ð ,961	< .132		.066			
TOTAL		96.Ø85			100.000		

24

SEM/EDX

September 15 1996

with 1996 Samples

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SEM/EDX

Report On Analysis Of Buchans Sediment Samples
Figure 1a OEP 13
Figure 1b OEP 13' Water Sample Scan
Analyses Data
Figure 2a OPE Middle
Figure 2b OPE Middle Scan
Analyses Data
Figure 3a OEP Bottom
Figure 3b OEP Bottom Scan
Analyses Data
Figure 4a OWP
Figure 4b OWP Scan
Analyses Data
Figure 5a DT
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IMAGETEK Analytical Imaging

September 15, 1996

Report on analysis of Buchans sediment samples (1996)

Sample preparation and analysis

Sediment samples from Buchans (10 in all) were examined by high resolution scanning electron microscopy (SEM) and energy dispersive X-ray microanalysis (EDX). Samples fixed in glutaraldehyde were dehydrated by taking them through an ethanol series. The sediments were then dispersed on filter paper and allowed to air dry. All samples were carbon coated prior to examination. Imaging of the samples was carried out using an Hitachi S-4500 field emission SEM (N.B. All micrographs were recorded at a magnification of 20,000x.). Each sample was also analysed by EDX with an analysed area of approx. 50µm x 50µm. A windowless detector was used allowing for the qualitative detection of light elements including carbon and oxygen. Quantative results were obtained for elements in the range Na - U.

Results & Discussion

High Resolution SEM & EDX:

All three OEP samples (13', middle, bottom) have a grain size in the range $0.25-1.0\mu$ m. A close examination of the micrographs (Fig. 1a, 2a, 3a) reveals that the grains are uniformly coated with what appear to be precipitate particles. The particles are largest in the OEP 13' sample (approx. 100nm) and smallest in the OEP Bottom sample (approx. 25nm). The results from EDX analysis of the three samples are shown in fig. 1b, 2b, 3b. All three of the samples have high Fe (40-70%) and Si (15-30%) content. OEP 13' also showed a significant amount of Zn (approx. 3%).

An example of the morphology of the OWP sample is shown in figure 4a. The sample grain size falls in the range $0.25 - 1.0 \mu m$. The grains are somewhat faceted and free of any obvious surface coating. EDX of the sample (fig.4b) indicates that the grains are aluminosilicate in composition.

The structure of sample D.T. is illustrated in Fig.5a. Examination of the specimen by SEM revealed that the grain size was finer than the other samples (in the range $0.25 - 0.5 \mu m$). Additionally, the grains appear to be coated with a smooth, essentially continuous coating. EDX (fig.5b) showed that the sample was Al/Si rich with significant amounts of Fe (20%) and Zn (4%). The coating is probably a thin adsorbed layer. Determination of the specific chemistry of this layer would require alternate analytical techniques.

SEM images for PP11, PP12, PP14 (branch, float & bubble) are shown in figures 6a - 10a respectively. All samples have a grain size in the range $0.25 - 1.0\mu m$. There are no obvious signs of surface adsorption or precipitation. EDX of the samples (fig.6b - 10b) indicate that the samples are essentially aluminosilicates with traces of Fe and no Zn.

Figure 1a



Page 1

Figure 1b							
-RAV: 0 - 20 2006: 50s Pro 221: 87s) keU eset: 50s Remaining: 43% Dead	15					
4. 							
a subject to the second se							
Щ <u>г</u> я 5 КК с п 1 л. а							
FERT:DEP 13'3.	7.480 keV 17 ch 384= 119 T.						

...

.

Page 2

Spectrum file : NCOEP13 06P 13'S.T. AREA ERGY RES 4.4 81.97 37621 COTAL AREA= 129504 5 a 5 8 8 8 8 Peak at .50 keV omitted? FIT INDEX= 5.49 APP.CONC ERROR (WT%) E PT Ø92 NaK : Ø .610 < \times : Ø -.079

.136* < 2 Sigma* .Ø11 .124* < 2 Sigma* Cost : Ø -.*00*4 .123* < 2 Sigma* 15 f. : Ø Cak : Ø .427 .142 3.372 SiK : Ø .136 . 256 418 t Ø .128 749 ≝eK : Ø – 50**.568** – ZnK : Ø 2.312 .637 \approx : Q .136 .172* < 2 Sigma*

2AF CALCULATIONS

.... 3 iterations]

20.00 KV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Spectrum: OEP 13'S.T.

* INITIAL START-UP *

wir elmts analysed,NORMALISED

. د بندر دسی ۲۰۰۰ و به ایست برد می مند در د	
-Nak : 0 ,287 3.306 +500 6.1	770
× № : Ø 1.Ø14 < .271 +136	
Cik : Ø .79Ø < .248 +− .124	
ЗК: Ø.7Ø5 <.247 +123	
CaK : Ø 1.Ø44 .636 +211 .	769
BiK : Ø .539 9.719 +392 16.	771
A1M: Ø .421 .946 +472 1.0	599
Fek: Ø .97Ø 80.902 +- 1.199 70.1	216
ZnK : Ø .857 4.189 +- 1.155 3.	1%6
100.0	TØØ

and were then that approximate search bear brain basis and and any search and the search and the search and the



Figure 2a



Page 5
el.Mî			APP.CONC	ERROR(WT%)	
气力的	ы с.	ø	1.141	.117	
1	â	$\hat{\mathscr{O}}$.093	.137* < 2	Sigma*
.11K	ř	\mathcal{D}	- ,Ø4Ø	.126* < 2	Sigma∗
$\leq -\infty$	A A	Ø	.215	.13Ø* < 2	Sigma*
1.28	È.	Q_{2}	.673	.146	
di a rK	4 11	(\tilde{o})	2.729	.14ø	
44	5	\tilde{C}^{i}	.743	.153	
	 	25	31.181	.637	
2 dais	a.	$\overline{\Omega}$	1.042	.669* < 2	Sigma*
25		Ø		.183* < 2	Sigma⊁

CALCULATIONS

.... 3 Sterations]

000 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

.

Coectnum: OEP MIDDLE

* INITIAL START-UP *

All elmts analysed,NORMALISED

61.417			ZAF	%ELMT		Error	ATOM.%
$\sum \{f_{ij}\}_{i=1}^{N}$	2	Ø	.313	7.932	+	.811	15.Ø93
11 ± 10	*	Ø	.988	< .275		.137	
	a #	\mathcal{Q}	.766	< .251	- +	.126	
t N	2.4	$\langle 2 \rangle$.687	< .26Ø	· - • •••	.130	
	3	$\langle j \rangle$	1.Ø14	1.444	··j	.312	1.576
$\pi \in \mathbb{R}$	-1 H	Ø	. 335	11.Ø89	+	.569	17.269
÷ 17.	2	$\langle j \rangle$.433	3.731		.767	6.049
$[-m] \in$	*	Ø	.949	71.483	- -	1.460	55.991
7 m M	4	(\tilde{i})	.848	<1.338	+	.669	
₽ K.	rt Li	$(\tilde{\partial}$.732	< .365	+	.183	
TOTA	۹L.			95.678			100.000

Page 6



Figure 3a



Page 8

Spectrum file : NCOEPBOT DEP BOTTOM LIVETIME(spec.) = 50 AMERGY RES AREA 4.2 82.97 36196 TOTAL AREA = 137591 Peak at .50 keV omitted? SIT INDEX= 6.16 ECMT OPP CONC EEBOR(WT%)

75 A. (13			ᆘᆟᆙᆙᆙᆙᇥᄔᄮᆝᆋᆋᇉ		
liah	a t	\mathcal{O}	1.134	.110	
st, 14	N 11	Ø	.948	.149	
CIK	5	$\langle \partial$.Ø28	.124* < 2	Sigma*
$\mathbb{W}_{1} = \mathbb{W}_{1}$	5	Ø	14	.126* < 2	Sigma*
Ú.a.N	4 3	Ø	.377	.144	
SiK	1	$\langle \vec{p} \rangle$	6.689	.173	
ALK.	5	Ø	2.184	.173	
C ek	и в	\emptyset	29.Ø1Ø	.6ø4	
čnK	ji M	Ø	.994	.617* < 2	Sigma*
- 6 <u>.</u>	4	Ø	, 398	.182	

CALCULATIONS

....C 3 iterations]

20.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Spectrum: OEP BOTTOM

* INITIAL START-UP *

ints analysed,NORMALISED

SLM			2 AF	%ELMT		Error	· ATOM.%
No. C	÷	\mathfrak{O}	.360	5.787		.563	91999
11 N.	11	Ø	.936	1.861		.292	1.890
C1E	4	\mathcal{J}	.720	< .249	+	.124	
> K	р 8	$\tilde{\mathcal{Q}}$.635	< .252	+	.126	
CaK	ы ж	Ø	.955	.727	+-	.277	. 72Ø
SiK	:	ø	.557	22.Ø94	+-	.571	31.244
A H	u z	\mathcal{D}	.488	8.237	+	.653	12.128
FæK	ĩ	Ø	.920	57.95Ø	+-	1.207	41.216
ZnK.	1	$\tilde{\mathcal{O}}$.837	<1.234	+-	.617	
$\mathbb{P}^{n} \to \mathbb{R}^{n}$	4: 8	Ø	.672	1.Ø87	+	.497	1.395
ione	L.,			97.743			100.000

Page 9

Figure 4a





Page 11

ELM)	~		APP.CONC	ERROR (V	VT :	%)	
NaK	u H	\emptyset	5.957	.161			
$\gamma_{\rm c} \lesssim$	23 14	\mathcal{O}	.933	.131			
СIК	40 1.	\mathcal{O}	001	.103*	<	2	Sigma*
S 8	0 4	\tilde{Q}	.053	.1Ø1*	\leq	2	Sigma∗
(1. A K	5	$\langle \cdot \rangle$.631	.130			
31K	4	Ø	22.828	.27Ø			
	÷	ø	23.518	.341			
이 관련	3	$\langle \tilde{Q} \rangle$.894	. 24Ø			
	;	$(\partial$	663	.464*	\leq	2	Sigma*
$p \in \mathbb{N}_{+}^{n}$	-	(i)	.208	.156*	<	2	Siqma*

ZAF CALCULATIONS

....C 3 iterations]

20.00 EV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Deathum: OWP

* INITIAL START-UP *

All elmts analysed, NORMALISED

			ZAF	%ELMT	· † - ···-	Error	ATOM.%
i aR	ő	$\langle \hat{\partial}$	1.092	7.487	-+	.203	9.012
$F = F_{i}$	i.	Ø	.772	1.658	+	.234	1.173
C1K	3	(2)	.567	< .205		103	
8 r	и 5	(\tilde{g})	.487	< .202	·+· ····	101	
1. a.e.	a e	Ŵ	.799	1.083		. 224	.748
S1K	ŝ	(2)	.589	53.235	··[.630	52.443
対抗	à	Ø	.939	34.36Ø		.499	35.241
Fek	5	\emptyset	.825	1.489	·+· ····	.399	.738
ZaK	2	Ø	.808	< .928	-+	.464	
F K	ü	ϕ	.495	< .311	- t	.156	
TOTA	i 6.,.			99.312			100.000
	H-4 3						المنتب سلمة لتجع وإجازة ليعتر فتعلم متعلم

Page 12

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Page 14

 Spectrum file : NCDT
 LIVETIME(spec.) = 50

 0.T.
 LIVETIME(spec.) = 50

 FNERGY
 RES
 AREA

 4.4
 79.35
 37093

 COTAL AREA=
 105243

 FAE at
 .50 keV omitted?

 FLMT
 APP.CONC
 ERROR(WT%)

	5	Ø	1.863	.116	
$(5, -\frac{1}{2} N_{\rm e})$	5. #	\mathcal{D}	.704	.133	
0. K	4	Ø	.Ø12	.109* < 2	Sigma*
8. 1	ŀ	\widetilde{O}	.205	.113* < 2	Sigma∗
$\{ i_{k}, j_{k} \}$	á	$\langle \hat{Z} \rangle$.548	.132	
		$\tilde{\mathbb{S}}_{i}$	8.379	.185	
	1	$\langle i \rangle$	5.375	. 2øø	
s seté		Ø	16.964	.476	
na Talahu	-	$\langle \hat{g} \rangle$	3.682	.588	
$(-1) = (-1)^{-1}$	2	Ø	.941	. 177	

CALCULATIONS

.... 4 iterations]

10.30 KV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Spectrum: D.T.

* INITIAL START-UP *

.

All elmts analysed, NORMALISED

$\pi(4,2,2)^{N_{1}}$		2 AF	%ELMT	· † · ··	Error	ATOM.%
1.1.4.1.4	$\tilde{\mathcal{Q}}$. 460	7.211	-!	. 449	11.015
2 E 1	\otimes	.874	1.434	·+	.272	1.288
	\mathcal{O}	. 550	< .219	-j	.109	
	Ø	.579	< .225	r † • ···-	.113	
	2	.998	1.Ø87	-+	.263	.952
	$\langle \phi \rangle$.539	27.681	·+	.610	34.608
A) 8 4	Ø	.545	17.566	+	.652	22.865
T ann a	Ø	.895	33.774	-	.948	21.237
2005	Ø	.834	7.861	+	1.256	4.223
í í	Ø	.615	2.725		.514	3.090
TOTAL	•		99.339			100.000

Page 15

an gan tare will been men Mile 1996 pen late tert and alog and term true type term with the cost and the type type term of the



Figure 6a

Ê



Figure 6b

Page 17

Page 18

ZAF %ELMT +- Error ATC 10 .783 2.104 +- .226 12. 10 .783 2.104 +- .238 1. 10 .579 <.210 +- .105 1. 10 .498 <.207 +- .105 1. 10 .806 1.202 +- .104 10 .806 1.202 +- 10 .875 48.950 +- 10 .874 .33.495 +- 10 .828 3.212 +- <
ZAF %ELMT Error ATC 0 1.037 10.058 .226 12. 0 .783 2.104 + .238 1. 0 .498 <.210
ZAF %ELMT + Error ATC .783 2.104 + .226 12 .783 2.104 + .238 1 .579 .210 + .105 .498 .207 + .105 .806 1.202 + .104 .806 1.202 + .104 .806 1.202 + .104 .875 48.950 + .425 .874 33.496 + .508 .828 3.212 + .425 .810 .906 + .425 .828 .3.212 + .425 .810 .3218 + .453 .996 + .159 .906 + .159 .906 + .453 .908 .318 + .159 .100
%ELMT +- Error ATC 2.104 +226 12. 2.104 +238 1. .207 +105 .207 +104 1.202 +104 .33.496 +508 34. 3.212 +425 1. .3218 +453 .318 +159 .99.022 100.
+++ +++ +++ +++ +++ +++ +++ +++ +++ ++
Error ATC 2226 1005 1220 1220 1220 1220 1220 1220 1220
Q 4 40 00 ⊢N 44 00 ⊢N 104 1
КЧ4 8403 0 ,60 00400 0 %06 00800 0

×.

* INITIAL START-UP

Soectrum:

PP11

YN,ØØ KV

TILT=15.00

ELEV=10.00 AZIM=15.00 COSINE=1.000

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4

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. !>

iterations]

CALCULATIONS

al ger

--.*090* :247

• • • • • • • • • • • • • •

 $\wedge \wedge$

NN

Sigma* Sigma*

24 88 14 ST

. 2261

 $\gamma =$

APP.CONC 777.00 1.77.00 200.7217 200.7217 200.7217 200.7217 200.7217 200.7217 200.7217

.1Ø4*

.100* 1.38 80

 $\wedge \wedge$

NN

Signa* Signa*

4.5 80 Ictal Area=

80.23 43 A= 118228

2008k at .50 207 INDEX≈23.14

.50 keV omitted?

ERROR (WT%)

3 *

foyst<mark>trum</mark> Sil

- + i] ©

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NCPP11

YOKING

70 M 20 M 20 M

AREA

43113

رتا ©

۰ ۱۱

LIVETIME(spec.



Figure 7a

				1999	
X-RAY: Live: Seal:	0 - 50s P 94s	20 keV reset: 47%	50s Dead	Remainin	gt Ûs
	S H 1				
		KKCC	ut for the second s	F F E E	7 7 1 1 1
FS= 4K MEM1:PP	12	4.5	60 ki ch	εŲ 238=	9.7 > 100 cts

Figure 7b

Page 20

spectrum file : NCPP12 LIVETIME(spec.) = 50 INERGY RES AREA ≥.4 8Ø.64 46698 14_ AREA= 1376**88** Peas at .50 keV omitted? T INDEX=28.15 APP.CONC ERROR(WT%) 6.309 tak : 🗭 .169 1.076 .139 \sim : O.013 ur t 🖄 .109* < 2 Sigma* .079 .886 · 3 .111* < 2 Sigma* - E 1 - E - 621 .137 . . . 0 24.176 .281Ø **26.083** .358 .973 1 (etc. ; 💋 . 267 ,219 $\psi_{i}(z) = \psi_{i}(z) = \psi_{i}(z)$.534* < 2 Sigma* < : \varnothing .395 .172AF CALCULATIONS * INITIAL START-UP * Seastrum: PP12 111 elmts analysed, NORMALISED n. 147 ZAF %ELMT +--Error ATOM.% 133 : <u>01.076</u> 7.309 +-.196 8.829 1. : Z .774 1.733 +--.224 1.231 2 .569 < .219 +-.109 . 8 : 0 .489 < .222 +-.111 Cak : Ø .800 1.380 +-.956 .213 .601 51.126 515 : Ø **.584** 51.714 +--.479 35.903 SIN : Ø .932 34.881 +-fed : Ø .826 1.470 +-.403 ,731 .534 258 : Ø .809 <1.Ø68 +-S & Ø .499 .986 +-.429 .884 100.000 99.474



Figure 8a



		a strumt		CALCUL	TANKA ARANGY
and a serie series (series barries and series	ХУГГОЛОВОВО АГГОЛОВИО ТСГОВОВИНИ ТСГОВОВИ ТСГОВИ ТСГОВИ ТСГОВИ ТСГОВИ ТСГОВИ ТСГОВИ ТСГОВИ ТСГОВИ ТСГОВИ ТСГОВО ТСГОВО ТСГОВОВОВО ТСГОВОВОВО ТСГОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВОВО ТССОВОВОВО ТССОВОВОВО ТССОВОВОВОВО ТССОВОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВО ТССОВОВОВОВО ТССОВОВО ТСОВОВО ТССОВОВО ТССОВО ТССОВОВО ТСОВОВО ТССОВОВО ТССОВОВО ТСОВОВО ТССОВОВО ТС	PP14 BRAN analysed,	erations] TILT=15.0	ATIONS	HIP
	□ C D 4 44 Ø 4 10 4 10 4 10 0 7 ► Ø Ø Ø C F Ø Ø Ø F F 4 4 + + 4 & 0 Ø F 4 1 0 Ø F 4 4 4 + + + + + + + + + + + + + + + + + + +	CH NORMALI SED	Ø ELEV=1Ø.Ø		0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0 0
	Error ATOM.% .357 11.862 .373 1.369 .0884 .0884 .347 1.369 .347 48.200 .761 33.940 .761 33.940 .758 2.602 .130 100.000	*	0Ø AZIM=15.ØØ COS		LIVETIME (spec
		INITIAL ST	1 NE = 1 . ØØØ		ריייייייייייייייייייייייייייייייייייי
		ART-UP *			





 Spectrum file : NCPF14FL0

 PP14 FLOAT
 LIVETIME(spec.) = 50

 ENERGY
 RES
 AREA

 - 4.6
 82.40
 38847

 TOTAL AREA=
 79035

 Peak at
 .50 keV omitted?

 FIT INDEX=15.73

ELMT	-		APP.CONC	ERROR (VT?	6)	
NaK	4 9	$\langle Z \rangle$	4.710	.138			
< c	:	\mathcal{O}	1.219	. 119			
CIK	1 0	$\langle \hat{c} \rangle$	051	.Ø87*	\leq	2	Sigma∗
3 14	3 6	Ø	.øø8	.Ø85 *	<	2	Sigma*
\mathbb{C} as \mathbb{C}	:	\odot	.431	.1Ø8			
$\leq 1 \leq k_{\rm c}$	1	\mathfrak{G}	13.320	.209			
AIK	" 73	\mathfrak{O}	14.653	.267			
₩æK	3 4	Ø	.633	.199			
ZnK	ŧ	Ø	.307	. 4Ø8*	<	2	Sigma*
$\mathbb{P}^{*} = \{0\}$	a q	$\langle i \rangle$.131	.128*	<	2	Sigma*

ZAF CALCULATIONS

...[3 iterations]

20.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Spectrum: PP14 FLOAT

* INITIAL START-UP *

All elmts analysed, NORMALISED

- 7 T		ZAF	%ELMT		Error	ATOM.%
to girl a	$\langle j \rangle$	1.054	9.347	-+	.273	11.310
14 X 1	įŹ	.783	3.256	·+	.317	2.317
21 K 3	(2)	.578	< .174	-+	.Ø87	
1 1	\mathcal{G}	. 497	< .169	14m ;174	.Ø85	
CaK #	(Z)	.801	1.126	-hm	.282	.782
SiX :	\varnothing	.571	48.790	· 4 ·· ·····	.765	48.320
高区:	Ø	. 887	34.549	+	.629	35.624
Fek :	Ø	.828	1.599	+	.503	.797
ZnK i	Ø	.810	< .816		.408	
10 K 1	Ø	.507	< .257	+	.128	
TOTAL			98.667			100.000









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Spectrum file : NCPP14BUB PP14 BUBBLE LIVETIME(spec.)= 50 ENERGY RES AREA - 4.7 79.03 36117 TOTAL AREA= 53441 Peak at .50 keV omitted? PlT INDEX= 8.73

ELMT			APP.CONC	ERROR (V	VT9	\$)	
NaK	2	Ø	2.208	.1Ø3			
K K	<u>:</u> ;	Ø	.572	.093			
$\odot1\times$	÷	(2)	.1ØØ	.Ø77*	\leq	2	Sigma≁
a e	2	(ž)	ø37	.Ø78*	\leq	2	Sigma∗
$\mathbb{C} \ll \mathbb{N}$	*	$\langle \hat{\mathcal{O}} \rangle$.115	.Ø89*	\leq	2	Sigma∗
	à	Ø	6.Ø33	.149			
esî B		$\langle 2 \rangle$	6.095	.185			
24	à	\mathcal{D}	. 351	.172			
2016		Ø	.302	.37Ø*	*	2	Sigma*
$\mathbb{R}^{n} = \mathbb{R}^{n}_{n}$	a B	Q	.090	.117*	\leq	2	Sigma*

ZAF CALCULATIONS

... 3 iterations]

10.00 kV TILT=15.00 ELEV=10.00 AZIM=15.00 COSINE=1.000

Spectrum: PP14 BUBBLE

* INITIAL START-UP *

			ZAF	%ELMT		Error	ATOM.%
Nak	i. U	<u>{</u>	1.016	9.962	-	.464	12.139
2 K	ï.	(2)	.783	3.351	- †	.545	2.401
	;	$\mathcal{G}^{\mathfrak{f}}$.582	< .154	··þ- ····	.077	
	1	i	- C22 1	< .157		.Ø78	
$C \otimes \mathbb{N}$;	$(\vec{2})$.8Ø1	< .178		.Ø89	
$St \mathbb{R}$	2.	\emptyset	.575	48.157	+	1.192	48.Ø27
Al K	A N	Ø	.856	32.662	+-	.991	33.914
Fek	;	Ø	.831	1.937	÷	.949	.971
ZnK	a	Ø	.812	< .739	+-	.37Ø	
PK	k K	\varnothing	.512	< .234	+	.117	
TOTA	Ļ.,			96.069			100.000

5.0 PARTICLE FORMATION BY PHYTOPLANKTON AND PICOPLANKTON

To purpose of this component is to identify the biological contribution of phytoplankton and picoplankton populations as initiators of particle formation. Picoplankton data we generated out of an independent contract and are arriving in time for the meeting.

The enumeration of small organisms were carried out by flow cytometry and using autofluorescence of pigments in the algal groups. This was done through systematic sampling of phytoplankton (size greater than > 2 μ m) and picoplankton (< 2 μ m). All phytoplankton and periphyton data are presented at the end of this section ("PHYTOPLANKTON AND PERIPHYTON TAXA IN 1996 BUCHANS SAMPLES AND BUCHANS CULTURING EXPERIMENT").

5.1 Phytoplankton Productivity and Diversity

Samples from different locations at Buchans were analyzed for phytoplankton density, biomass and species diversity into different classes of algae during spring, summer and fall of 1996 (Table 19 and Table 20). As expected, cell density and biomass were very low in early May, and increased in general during the summer and fall. However, one can note very specific differences in these parameters for different locations.

The Drainage Tunnel (DT) water had low cell density, biomass and species diversity at all times sampled. Phytoplankton in OWP increased its cell density, biomass and species diversity during fall and summer, while OEP supported exceptionally low cell densities and biomass at all times of the year (spring, summer and fall) as seen in Table 19. Interestingly, Tailings Pond 2 (TP2) had quite high phytoplankton population and biomass in early May. As expected, the polishing ponds (PP) supported considerable phytoplankton populations and biomass, and generally had high species diversity both in the spring and the fall. The qualitative assessment of species diversity shows high species diversity for the polishing ponds during the summer (Table 20).

According to nutrient data available for Oriental East Pit (phosphate, nitrate and ammonium), one would have expected significant phytoplankton biomass to have developed. This did not take place at any time of the year. The data indicate that the system behaves as an exceptionally oligotrophic (nutrient-poor) aquatic ecosystem. There may be several reasons for this:

- (1) phosphate may not be available for uptake by the algae due to complexing with metals (e.g., zinc);
- (2) the low Secchi disc values (around 1.4 m) indicates low water transparency in spite of the very low phytoplankton biomass, indicating that light is rapidly lost due to scattering or absorption by abiotic particles;
- (3) the very shallow chemo/thermocline (at about 1.5 m during most of the productive season).

It is very likely that the unfavourable chemistry and establishment of a very shallow epilimnion, coupled with very low water transparency, inhibits development of a significant phytoplankton productivity and biomass. Only the top meter is strongly oxygenated, light is rapidly absorbed in the top 1-2 meters and it appears likely that key nutrients, such as phosphorus, may not be available for algal transport system due to metal complexing. The conditions on Oriental West Pit appear to be much more favourable for phytoplankton productivity in addition to rapid development of aquatic mosses. The experiments conducted in the laboratory (see Sections 6.1 and 6.2) and in the field suggest that:

- Results of laboratory experiments examining the effects of nutrients upon primary productivity cannot be related to the Polishing Pond ecosystem, due to interferences by zinc, iron and manganese present in the effluent in the field, but attenuated or eliminated in effluent samples shipped to the laboratory.
- b) Geochemical reactions precipitating phosphate in the pits and Polishing
 Ponds are potentially competing with the algal population for phosphate.
- c) N:P ratios in Polishing Pond algal biomass indicate that these plants have access to sufficient P for growth, and are not nutrient-starved. While a large fraction of added phosphate appears to be relegated to the sediments by precipitation reactions, remobilization of P from the sediments could supply adequate phosphate to the Polishing Pond ecosystem. Phosphorus cycling can be addressed in the field in 1997 using a new radioactive isotope of phosphorus, ³³P, a compound analogous to ¹⁴C in terms of acceptability by agencies regulating the application of this isotope in scientific field work.

Table 19:Phytoplankton density, biomass and percent distribution into different classes.Samples were collected spring, summer and fall of 1996 at different locations
at Buchans, Newfoundland.

Date	Location ¹	Cell Density	Biomass	Diversity (%) ²			
		(x10 ⁶ ·L⁻¹)	(µg L⁻¹)	G	D	Су	Chr
	DT	0.02	1.2	80	-	-	20
	OWP	0.01	0.7	38	63	-	-
May 3	OEP	0.06	25	60	40	-	-
	PP13	0.1	10	38	6	48	8
	PP17	0.7	59	54	6	21	16
	TP2	1.8	240	8	25	5	60
Jul 11	OWP	1.9	168	40	26	6	29
	OEP	0.06	4	35	10	-	55
	DT	0.3	16	75	22	1	3
	OWP	1.1	127	39	18	27	14
Sep 29	OEP	0.1	2.5	32	12	-	56
	PP13	1.5	480	60	33	1	1
	PP17	0.6	38	50	18	7	25

¹ DT = Drainage Tunnel; OWP = Oriental West Pit; OEP = Oriental East Pit; PP13 = Polishing Pond 13; PP17 = Polishing Pond 17; TP2 = Tailings Pond 2

² Diversity expresses as percent of total algae identified; G = Green algae;
 D = diatoms; Cy = cyanobacteria; Chr = chrysophytes

Table 20:Qualitative assessment of diversity of phytoplankton as distribution into
different classes. Samples were collected during the summer 1996.

Date	Location ¹		Divers	ity (%) ²	
		G	D	Су	Chr
May 5	OWP	30	70		-
Jul 8	PP-In	40	20	20	20
-	PP-Out	10	60	10	20
Jul 11 PP-In		30	40	10	25
	PP-Out	45	35	15	5
Jul 12	PP12	70	20	5	-
	PP14	60	25	10	-

¹ OWP=Oriental West Pit; PP-In=intake water for Polishing Ponds; PP-Out=exit water from Polishing Ponds; PP12=Polishing Pond 12; PP14=Polishing Pond 14

² Diversity expresses as percent of total algae identified; G = Green algae;
 D = diatoms; Cy = cyanobacteria; Chr = chrysophytes

PHYTOPLANKTON AND PERIPHYTON TAXA PRESENT

- '

IN 1996 BUCHANS SAMPLES

AND

BUCHANS CULTURING EXPERIMENT

LIST OF PHYTOPLANKTON SAMPLES

1	A96-17	Drainage Tunnel, May 3, 1996
2	A96-30	OWP, Surface, July 9, 1996 2
3	A96-31	OEP, Surface, July 9, 1996 3
4	A96-32	OEP, May 3, 1996 4
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6	A96-34	TP-2, May 3, 1996 6
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11	A96-46	PP13, May 13, 1996 27
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19	A96-56	PP12, Seep Algae, July 12, 1996
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BUCHANS CULTURING EXPERIMENT

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List of Algal Taxon Codes for Boojum Research Samples - 1996

Cyanobacteria (Bluegreen Algae)

AN	spp	1R	Anabaena spp.
BG	fil	1R	Undentified fialmentous bluegreen sp.
ME	min	1E	Merismopedia minutus
os	lim	1R	Oscillatoria limnetica
os	sps	1R	Oscillatoria spp. (small spp.)
os	ten	1R	Oscillatoria tenuis
UN	bgf	1R	Unidentified bluegreen filament (small)
UN	blg	1E	Unidentified small spp. (e.g. Synechococcus,
			Merismopedia, Chroococcus, etc.)

Chlorophyceae (Green Algae)

AK	fal	2R	Ankistrodesmus falcatus
во	bra	2E	Botryococcus braunii
СН	spp	2E	Chlamydomonas spp.
$\mathbf{C}\mathbf{L}$	spp	2R	Chlorogonium sp.
\mathbf{CT}	spp	2E	Carteria spp.
\mathbf{DT}	pul	2E	Dictyosphaerium pulchellum
MG	spm	2R	Mougeotia sp. (medium width filament)
MG	spn	2R	Mougeotia sp. (narrow filaments)
MG	spw	2R	Mougeotia sp. (wide filaments)
MT	spp	2E	Mesotaenium sp.
00	spp	2E	Oocystis spp.
SC	spp	2E	Scenedesmus spp.
SP	sub	2E	Sphaerellopsis cylindrica
ΤМ	spp	2R	Temnogametum spp.
UL	spp	2R	Ulothrix sp.
UN	chl	2E	Unidentified small spp. (e.g. Chlorella,
			Chlamydomonas, Chlorococcum, etc.)

Euglenophyceae (Euglenoids)

EG	spp	3 E	Euglena spp.
ЪР	spp	3E	Lepocinclis sp.
TR	spp	3 E	Trachelomonas sp

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Chrysophyceae (Chrysophytes)

CK	pla	4E	Chrysolykos planctonicus
CM	spp	4E	Chromulina spp.
CS	spp	4E	Chrysosphaerella sp.
DI	mon	4E	Dinobryon monads
DI	ser	4E	Dinobryon sertularia
DI	spp	4E	Dinobryon sp.
EP	app	4E	Epipyxis sp.
KP	spp	4E	Kephyrion sp.
ОМ	\mathbf{spp}	4E	Ochromonas spp.
ΡK	spp	4E	Pseudokephyrion spp.
UN	chr	4E	Unidentified small spp. (e.g. Chromulina, Ochromonas,
			etc.)

Cryptophyceae (Cryptophytes)

CR	ero	5F	Cryptomonas erosa
CR	ova	5F	Cryptomonas ovata
CR	spp	5E	Cryptomonas spp. (small taxa)
RH	min	5E	Rhodomonas minutus
UN	cry	5E	Unidentified spp. (e.g. Chroomonas, Cryptomonas,
			Rhodomonas, etc.)

Dinophyceae (Dinoflagellates)

GM	spp	6E	Gymnodinium	spp.
PE	inc	6E	Peridinium :	inconspicuum

Bacillariophyceae (Diatoms)

MS	isl	7R	Melosira islandica
AC	spp	7R	Achnanthes spp.
AH	spp	7R	Achnanthes spp. (small taxa)
AS	for	7R	Asterionella formosa
ΕŲ	ssp	7R	Eunotia spp. (small)
FR	rhm	7D	Frustulia rhomboides
NV	spp	7D	Navicula spp.
NZ	spp	7R	Nitzschia spp.
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PN	spm	7R	Pinnularia sp. (medium frustule)
PN	spp	7R	Pinnularia spp.
SY	spl	7R	Synedra spp. (large frustule)
SY	spm	7R	Synedra spp. (medium frustule)
TA	flc	7 T	Tabellaria flocculosa
TA	fen	7 T	Tabellaris fenestrata
UN	dia	7R	Unidentified spp. (e.g. Achnanthes, Cyclotella,
			Cymbella, Eunotia, Navicula, Pinnularia,
	``		

etc.)

Buchans - Drainage Tunnel 3/05/96 (A96-17)

Sample File BR9617 DATE ANALYSED...09-12-1996

SUBSAMPLE VOLUME... 500.0 mLs

TAX	on		$\begin{array}{c} \textbf{CELLS.L}^{-1} \\ \textbf{(L}^{-1}) \end{array}$	BIOMASS (MG.M ⁻³)	COL	CELLS	LEN (µM)	WID (µM)	D # (μM)	TRANS	BIOVOL (μM^3)	COR.F
CYA	NOB	ACTER	[A									
UN 🖯	blg	1E	11404	0.0038	0	289	1.0	0.8	0	1 3	0.34	59.19
CHL	OROI	PHYTA										
UN	chl	2E	3117	0.1480	0	79	7.4	3.5	0	13	47.46	59.19
EUG	LENG	OPHYTZ	Ŧ									
EG .	qqa	ЗE	308	1.0167	0	26	41.7	12.3	0	15	3303.28	29.59
CHR	YSOI	PHYTA										
UN	chr	4E	1184	0.0486	0	30	4.9	4.0	Ð	1 3	41.05	59.19
CRY	PTO	PHYTA										
CR	app	5E	252	0.2479	0	17	19.6	9.8	0	14	985.61	29.59
 тот	CN	 Г	16264	1.4650		441						

Buchans - Drainage Tunnel 3/05/96

PHYLUM	TOT	CELLS.L ⁻¹	TOT	BIOMASS.M ⁻³	
CYANOBACTERI	[A	11404		0.004	
CHLOROPHYTA		3117		0.148	
EUGLENOPHYTZ	J –	308		1.017	
CHRYSOPHYTA		1184		0.049	
CRYPTOPHYTA		252		0.248	
PYRROPHYTA		0		0.000	
DIATOMS		0		0.000	
RHODOPHYTA		0		0.000	
TOTAL ALGAE		16264		1.465	

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SUMMARY:

Cell Density: 1.52 X 10⁴ cells/L

Biomass Estimate: 1.47 μ g/L

Buchans - OWP (surface) 9/07/96 (A96-30)

(Sample File BR9630) DATE ANALYSED...09-22-1996

SUBSAMPLE VOLUME... 125.0 mLs

TAX	ON		$\begin{array}{c} \text{CELLS.L}^{-1} \\ (\text{L}^{-1}) \end{array}$	BIOMASS (MG.M ⁻³)	COL	CELLS	LEN (µM)	WID (µM)	# D (µM)	TT :	RANS	BIOVOL (µM ³)	COR.F
CYA	NOBA	ACTE	RIA										
os	lim	1R	119799	9.4090	0	253	100.0	1.0	0	1	1	78.54	59.19
UN 🛛	blg	1E	114117	0.0896	0	241	1.5	1.0	0	1	1	0.79	59.19
CHL	OROI	HYT	A										
ரு	app	2R	789	0.1458	0	10	9.8	4.9	0	1	3	184.80	29.59
тм	qqa	2R	11838	18.0595	0	150	80.9	4.9	0	1	3	1525.56	29.59
CH	qqa	2E	40722	7.7314	0	86	7.4	7.0	0	1	1	189.86	59.19
UN	chl	2 E	573427	39.6490	0	1211	5.5	4.9	0	1	1	69.14	59.19
CHR	YSOE	PHYT	A										
EP	epp	4E	66292	1.0630	0	140	4.9	2.5	0	1	1	16.04	59.19
UN	chr	4E	374551	7.0287	0	791	3.5	3.2	0	1	1	18.77	59.19
CM	врр	4E	226814	37.1301	0	479	7.4	6.5	0	1	1	163.70	59.19
OM	qqa	4E	90441	4.6988	0	191	4.9	4.5	0	1	1	51.95	59.19
BAC	ILLA	ARIO	PHYTA										
AC	врр	7R	304470	43.0614	0	643	14.7	3.5	0	1	1	141.43	59.19
TOT	CNI	 r	1923262	168.0664		4195							

Buchans - OWP (surface) 9/07/96 (A96-30)

PHYLUM TOT	CELLS.L ⁻¹ TOT	BIOMASS.M ⁻³
CYANOBACTERIA	233917	9.499
CHLOROPHYTA	626777	65.586
EUGLENOPHYTA	0	0.000
CHRYSOPHYTA	758098	49.921
CRYPTOPHYTA	0	0.000
PYRROPHYTA	0	0.000
DIATOMS	304470	43.061
RHODOPHYTA	0	0.000
TOTAL ALGAE	1923262	168.066

SUMMARY :

Cell Density: 1.92 X 10⁶ cells/L Biomass Estimate: 168.01 µg/L

Buchans - OEP - surface 10/07/96 (A96-31)

Sample File BR9631 DATE ANALYSED...09-26-1996

SUBSAMPLE VOLUME... 26.3 mLs

TAXON	$\begin{array}{c} \text{CELLS} \cdot \text{L}^{-1} \\ (\text{L}^{-1}) \end{array}$	BIOMASS (MG.M ⁻³)	COL	CELLS	LEN (µM)	WID (µM)	D (µM)	#	TRANS	BIOVOL (µM ³)	COR.F	
CHLOROPHYTA	·											-
UN chl 2E	22548	1.5591	0	10	5.5	4.9	0	;	1 1	69.14	59.19	
CHRYSOPHYTA	L											
UN chr 4E	38332	1.4451	0	17	4.5	4.0	0		1 1	37.70	59.19	
DI spp 4E	6765	0.8334	0	3	9.8	4.9	0		1 1	123.20	59.19	
BACILLARIOF	PHYTA											
AH spp 7D	8268	0.4561	0	22	17.2	3.5	0	:	13	55.16	29.59	
												-
TOT CNT	75913	4.2936		52								

Buchans - OEP - surface 10/07/96 (A96-31)

PHYLUM	TOT	CELLS.L ⁻¹	TOT	BIOMASS.M	-3
CYANOBACTER	RIA	0		0.000	
EUGLENOPHYT	A.	22548		0.000	
CHRYSOPHYTA CRYPTOPHYTA	7	45097 0		2.278 0.000	
PYRROPHYTA		0		0.000	
RHODOPHYTA		8288 0		0.456	
TOTAL ALGAE	- S	75913		4.294	

SUMMARY:

Cell Density: 7.59 X 10⁴ cells/L

Biomass Estimate: 4.29 μ g/L

Buchans - OEP 3/05/96 (A96-32)

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Sample File BR9632 DATE ANALYSED...09-22-1996

SUBSAMPLE VOLUME... 105.0 mLs

TAXON			$\begin{array}{c} \textbf{CELLS.L}^{-1} \\ (\textbf{L}^{-1}) \end{array}$	BIOMASS (MG.M ⁻³)	COL	CELLS	S LEN (μM)	WID (µM)	D # (μM)	TRANS		BIOVOL (µM ³)	COR.F
CYF	NOB	ACTE	 RIA										
UN	blg	1E	7892	0.0186	0	14	2.0	1.5	0	1	1	2.36	59.19
CHI	lorol	PHYT	A										
MG	spw	2R	141	1.3128	0	2	78.4	12.3	0	1	4	9315.72	29.59
MΤ	$\mathbf{q}\mathbf{q}\mathbf{a}$	2E	352	9.6677	0	5	51.5	31.9	0	1	4	27440.20	29.59
MG	spn	2R	493	0.1974	0	7	41.6	3.5	0	1	4	400.24	29.59
ΩL	spp	2R	13177	2.4351	0	187	9.8	4.9	0	1	4	184.80	29.59
UN	chl	2E	10147	1.6611	0	18	7.4	6.5	0	1	l	163.70	59.19
CHF	(VSO	PHYT	A										
UN	chr	4E	9583	0.4979	0	17	4.9	4.5	0	1	1	51.95	59.19
BAC	CILL	ARIO	PHYTA										
NV	app	7D	775	0.1651	0	11	26.9	5.5	0	1	4	213.03	29.59
EU	spp	7R	6201	3.7301	0	88	31.9	4.9	Û	1	4	601.55	29.59
UN	dia	7R	11838	5.4692	0	21	24.5	4.9	0	1	1	462.01	59.19
TOT	CN	г Г	60599	25.1549		370							

Buchans - OEP 3/05/96 (A96-32)

PHYLUM	TOT	CELLS.L ⁻¹	TOT	BIOMASS.M ⁻³	
CYANOBACTER	RIA	 7892		0.019	
CHLOROPHYTA	7	24310		15.274	
EUGLENOPHYT	Α	0		0.000	
CHRYSOPHYTA	ł	9583		0.498	
CRYPTOPHYTA	ł	0		0.000	
PYRROPHYTA		0		0.000	
DIATOMS		18814		9.364	
RHODOPHYTA		0		0.000	
TOTAL ALGAP	Ē	60599		25.155	

SUMMARY:

Cell Density: 6.06 X 10⁴ cells/L

Biomass Estimate: 25.16 μ g/L

Buchans - Drainage Tunnel 3/05/96 (A96-33)

Sample File BR9633 DATE ANALYSED...09-21-1996

SUBSAMPLE VOLUME... 500.0 mLs

TAXON	$\begin{array}{c} \text{CELLS.L}^{-1} \\ \langle \text{L}^{-1} \rangle \end{array}$	BIOMASS (MG.M ⁻³)	COL	CELLS	LEN (µM)	WID (µM)	D (μM)	#	TRANS	BIOVOL (µM ³)	COR.F	
CYANOBACTERIA	A											
UN blg 1E CHLOROPHYTA	3038	0.0024	0	77	1.5	1.0	0	1	3	0.79	59.19	
UN chl 2E CHRYSOPHYTA	2091	0.1446	0	53	5.5	4.9	0	1	3	69.14	59,19	
UN chr 4E	1539	0.0289	0	39	3.5	3.2	0	1	3	18.77	59.19	
TOT CNT	6669	0.1759		169								

Buchans - Drainage Tunnel 3/05/96 (A96-33)

PHYLUM	TOT	CELLS.L ⁻¹	TOT	BIOMASS.M ⁻³	
CYANOBACT	ERIA	3038		0.002	
CHLOROPHY	TA	2091		0.145	
EUGLENOPH	YTA	0		0.000	
CHRYSOPHY	TA	1539		0.029	
CRYPTOPHY	TA	0		0.000	
PYRROPHYT	'A	0		0.000	
DIATOMS		0		0.000	
RHODOPHYT	Ά	0		0.000	
TOTAL ALG	AE	6669		0.176	
TOTAL ALG	AE	6669		0.176	

SUMMARY:

Cell Density: 6.67 X 10³ cells/L

Biomass Estimate: 0.18 μ g/L

Sample File BR9634 DATE ANALYSED...09-22-1996

SUBSAMPLE VOLUME... 105.0 mLs

ТАХ	ON		CELLS.L ⁻¹	BIOMASS	COL	CELLS	LEN (UM)	WID (VM)	D #	TR.	ANS	BIOVOL (µM ³)	COR.F
			·										
CYA	NOB	ACTER	AIA										
UN	bgf	1R	142055	11.1569	0	252	100.0	1.0	0	1	1	78.54	59.19
UN	blg	1E	112742	0.0885	0	200	1.5	1.0	0	1	1	0.79	59.19
CHI	ORO	PHYTA	ł										
TM	spp	2R	940	0.9124	0	10	51.5	4.9	0	1	3	971.16	29.59
UN	chl	2 E	133599	16.3688	0	237	6.5	6.0	0	1	1	122.52	59.19
CHE	yso	PHYTA	4										
ΕP	вpp	4E	14656	0.2750	0	26	3.5	3.2	0	1	1	18.77	59.19
UN	chr	4E	404179	7.5847	0	717	3.5	3.2	0	1	1	18.77	59.19
CM	spp	4E	81174	13.2885	0	144	7.4	6.5	0	1	1	163.70	59.19
DI	ser	4E	275654	42.6245	0	489	12.3	4.9	0	1	1	154.63	59.19
DI	mon	4 E	299329	46.2855	0	531	12.3	4.9	0	1	1	154.63	59.19
KP	spp	4E	90757	2.3285	0	161	4.0	3.5	0	1	1	25.66	59.19
OM	spp	4E	130217	4.9091	0	231	4.5	4.0	0	1	1	37.70	59.19
BAC	ILL	ARIO	PHYTA										
UN	dia	7R	27622	10.2091	0	49	19.6	4.9	0	l	1	369.61	59.19
TOT	CN	 T	1712923	156.0317		3048							

Buchans - Tailings Pond 2 (TP-2) 3/05/96 (A96-34)

PHYLUM	TOT	CELLS.L ⁻¹	TOT	BIOMASS.M	[⁻³
CYANOBACTER	RIA	254796		11.245	
CHLOROPHYTA	Ŧ	134539		17.281	
EUGLENOPHYT	ΓA	0		0.000	
CHRYSOPHYTA	1	1295967		117.296	
CRYPTOPHYTA	7	0	-	0.000	
PYRROPHYTA		0		0.000	
DIATOMS		27622		10.209	
RHODOPHYTA		0		0.000	
		• • • -		 -	
TOTAL ALGAE	3	1712923		156.032	

SUMMARY:

Cell Density: 1.71 X 10⁶ cells/L

Biomass Estimate: 156.03 μ g/L

Buchans - Tailings Pond 2 (TP 2) 3/05/96 (A96-35)

Sample File BR9635 DATE ANALYSED...09-25-1996

SUBSAMPLE VOLUME... 105.0 mLs

TAX	KON		$\begin{array}{c} \textbf{CELLS.L}^{-1} \\ (\textbf{L}^{-1}) \end{array}$	BIOMASS (MG.M ⁻³)	COL	CELLS	LEN (µM)	WID (µM)	D # (µM)	T	RANS	BIOVOL (μM^3)	COR.F
CYF	NOB	ACTE	RIA										
UN	bgf	1R	49606	3.8961	0	88	100.0	1.0	Ð	1	1	78.54	59.19
UN	blg	1E	164603	0.1293	Q	292	1.5	1.0	0	1	1	0.79	59.19
CHI	ORO	рнут	'A										
MΤ	qqa	2R	211	2.3471	Q	3	36.8	19.6	0	1	4	11103.24	29.59
$\mathbf{T}\mathbf{M}$	вpp	2R	282	0.3386	0	4	63.7	4.9	0	1	4	1201.22	29.59
UN	chl	2E	104286	12.7774	0	185	6.5	6.0	Û	1	1	122.52	59.19
CHF	rysol	рнут	A										
UN	chr	4 E	315113	8.0847	0	559	4.0	3.5	0	1	1	25.66	59.19
CM	вpp	4 E	98649	16.1492	0	175	7.4	6.5	0	1	1	163.70	59.19
DI	ser	4E	220974	51.4496	0	392	14.7	5.5	0	1	1	232.83	59.19
DI	mon	4E	312295	57.7129	0	554	14.7	4.9	0	1	1	184.80	59.19
ΚP	app	4E	103159	3.8890	0	183	4.5	4.0	0	1	1	37.70	59.19
OM	spp	4E	153893	5.8016	0	273	4.5	4.0	0	1	1	37.70	59.19
CRY	PTO	рнут	'A										
UN	cry	5E	1691	0.0000	0	3	0.0	0.0	0	1	1	0.00	59.19
BAC	LL	ARIC	PHYTA										
FR	rhm	7D	1015	3.3753	0	18	58.8	14.7	0	1	5	3326.45	29.59
TA	fl¢	7T	113	0.1787	0	2	14.7	4.9	22	1	5	1584.66	29.59
PN	app	7R	41714	66.0219	0	74	36.8	7.4	0	1	1	1582.71	59.19
NZ	spp	7R	2255	1.3819	0	4	63.7	3.5	0	1	1	612.87	59.19
UN	dia	7R	219283	81.0481	0	389	19.6	4.9	0	1	1	369.61	59.19
TOT	CN.	 r	1789142	314.5811		 3198							

Buchans - Tailings Pond 2 (TP 2) 3/05/96 (A96-35)

PHYLUM	тот	CELLS.L ⁻¹	TOT BIOMASS.M ⁻³	
CYANOBACTER	XIA	214209 104779	4.025	
EUGLENOPHYT	- TA	0	0.000	
CRYPTOPHYTA	7 7	1691	0.000	
PYRROPHYTA DIATOMS		0 264379	0.000 152.006	
RHODOPHYTA		0	0.000	
TOTAL ALGAE	2	1789142	314.581	

SUMMARY:

Cell Density: 1.78 X 10⁶ cells/L

Biomass Estimate: 314.58 μ g/L

Buchans - Pool 13 3/05/96 (A96-36)

Sample File BR9636 DATE ANALYSED...09-23-1996

SUBSAMPLE VOLUME... 105.0 mLs

ТАХ	ON		$\begin{array}{c} \texttt{CELLS.L}^{-1} \\ (\texttt{L}^{-1}) \end{array}$	BIOMASS (MG.M ⁻³)	COL	CELLS	LEN (µM)	WID (µM)	D # (μM)	TRAI	15	BIOVOL (µM ³)	COR.F
CYA	NOB.	ACTER	IA										
os	sps	1R	27058	4.7815	0	48	100.0	1.5	0	1	1	176.71	59.19
UN	blg	1E	10147	0.0531	0	18	2.5	2.0	0	1	1	5.24	59.19
СШ	юro	PHYTA											
ΥM	арр	2R	5543	2.8118	0	59	26.9	4.9	0	1	3	507.26	29.59
UN	chl	2E	15220	1.0524	Q	27	5.5	4.9	0	1	1	69.14	59.19
CHF	YSO	PHYTA											
UN	chr	4E	21985	0.4126	0	39	3.5	3.2	0	1	1	18.77	59.19
OM	врр	4E	7892	0.4100	0	14	4.9	4.5	0	1	1	51.95	59.19
BAC	ILL	ARIOP	HYTA										
UN	dia	7R	3946	0.5581	0	7	14.7	3.5	0	1	1	141.43	59.19
тот	CN	 Т	91791	10.0795		212							

Buchans - Pool 13 3/05/96 (A96-36)

PHYLUM	TOT	CELLS.L ⁻¹	TOT	BIOMASS.M ⁻³	
CYANOBACTER	AIS	37205	,	4.835	
CHLOROPHYTA	ł	20763		3.864	
EUGLENOPHYI	'A	C)	0.000	
CHRYSOPHYTA	f	29877	,	0.823	
CRYPTOPHYTA	7	C)	0.000	
PYRROPHYTA		C)	0.000	
DIATOMS		3946	5	0.558	
RHODOPHYTA		C)	0.000	
TOTAL ALGAE	2	91791		10.080	

SUMMARY:

Cell Density: 9.18 X 10⁴ cells/L

Biomass Estimate: 10.08 µg/L

Buchans - Pool 17 3/05/96 (A96-37)

Sample File BR9637 DATE ANALYSED...09-24-1996

SUBSAMPLE VOLUME... 105.0 mLs

TAXON	$\begin{array}{c} \textbf{CELLS}, \textbf{L}^{-1} \\ (\textbf{L}^{-1}) \end{array}$	BIOMASS (MG.M ⁻³)	COL	CELLS	LEN (µM)	WID (µM)	D # (µM)	TR.	ans	BIOVOL (µM ³)	COR.F
CYANOBACTE	RIA										
AN spp 1R	5073	1.5938	0	9	100.0	2.0	0	1	1	314.16	59.19
OS lim 1R	134726	10.5814	0	239	100.0	1.0	0	1	1	78.54	59.19
UN blg 1E	166858	0.3931	Û	296	2.0	1.5	0	1	1	2.36	59.19
CHLOROPHYT	A										
TM spp 2R	12402	10.8980	0	88	46.6	4.9	0	1	2	878.76	29.59
SP cyl 2E	2819	0.9940	0	5	12.3	7.4	0	1	1	352.67	59.19
00 врр 2Е	6201	2.0165	0	11	14.7	6.5	0	1	1	325.19	59.19
SC spp 2E	6201	0.9588	0	11	12.3	4.9	0	1	1	154.63	59.19
UN chl 2E	112742	13.8134	Q	200	6.5	6.0	0	1	1	122.52	59.19
EUGLENOPHY	ТА										
EG spp 3E	1691	3.1295	0	36	36.8	9.8	0	1	з	1850.54	14.80
TR spp 3E	188	1.2057	0	4	31.9	19.6	0	1	з	6416.55	14.80
CHRYSOPHYT	A										
UN chr 4E	217028	8.1818	0	385	4.5	4.0	Û	1	1	37.70	59.19
ОМ врр 4Е	25931	1.3472	Q	46	4.9	4.5	0	1	1	51.95	59.19
CRYPTOPHYT	A										
CR ova 5F	141	0.4071	Û	3	41.7	14.7	9	1	3	2888.65	14.80
BACILLARIO	Phyta										
PN spm 7R	1550	1.9601	0	11	29.4	7.4	0	1	2	1264.45	29.59
UN dia 7R	4510	1.6668	0	8	19.6	4.9	Ó	1	1	369.61	59.19
TOT CNT	698059	59.1472		1352							

Buchans - Pool 17 3/05/96 (A96-37)

PHYLUM	TOT	CELLS.L ⁻¹	TOT BIOMASS.	M_3
CYANOBACTE	ERIA	306658	12.568	3
CHLOROPHYT	ΓA	140364	28.681	L
EUGLENOPHY	TA	1879	4.335	5
CHRYSOPHYT	ſA	242959	9,529	Ð
CRYPTOPHYT	ГA	141	0.407	7
PYRROPHYTA	7	0	0.000)
DIATOMS		6060	3.627	7
RHODOPHYTZ	Ŧ	0	0.000)
TOTAL ALGA	 \Е	698059	59.147	 7

SUMMARY:

Cell Density: 6.98 X 10⁵ cells/L

Biomass Estimate: 59.15 μ g/L

Buchans - OWP 3/05/96 (A96-43)

Sample File BR9643 DATE ANALYSED...01-11-1997

SUBSAMPLE VOLUME... 52.5 mLs

TAXON	$\begin{array}{c} \textbf{CELLS.L}^{-1} \\ (\textbf{L}^{-1}) \end{array}$	BIOMASS ((MG.M ⁻³)	COL CELI	LS LEN (µM)	WID (µM)	D # (µM)	TRANS	BIOVOL (µM ³)	COR.F
CHLOROPHYTA UN chl 2E BACILLARIOP	6765 HYTA	0.2550	0	6 4.5	4.0	0	1 1	37.70	59.19
AH sps 7R	6952	0.4198	03	7 12.3	2.5	0	1 3	60.38	29.59
TOT CNT	13717	0.6748	4	3					

Buchans - OWP 3/05/96 (A96-43)

PHYLUM	тот	CELLS,L ⁻¹	TOT	BIOMASS.M ⁻³	
CYANOBACTER	 ?TA		·)	0.000	
CHLOROPHYTZ	1	6765	5	0.255	
EUGLENOPHYT	A	()	0.000	
CHRYSOPHYTA	7	()	0.000	
CRYPTOPHYTA	Į	()	0.000	
PYRROPHYTA		()	0.000	
DIATOMS		6952	2	0.420	
RHODOPHYTA		()	0.000	
TOTAL ALGAE	3	13717	7	0.675	

SUMMARY:

Cell Density: 1.37 X 10⁴ cells/L

Biomass Estimate: 0.68 μ g/L

Buchans - PP13 (regular) 29/09/96 (A96-99)

Sample File BR9699 DATE ANALYSED...11-05-1996

SUBSAMPLE VOLUME... 105.0 mLs

TAI	KON		$\begin{array}{c} \text{CELLS} \cdot \text{L}^{-1} \\ (\text{L}^{-1}) \end{array}$	BIOMASS (MG.M ⁻³)	COL	CELLS	LEN (µM)	WID (µM)	D ; (μM)	# 1	frans	BIOVOL (µM ³)	COR.F
CY	ANOBI	ACTE	RIA					•••					
AN	app	1R	4651	4.4744	0	33	100.0	3.5	0	1	. 2	962.11	29.59
BG	fil	1R	40023	3.5364	0	71	50.0	1.5	0	1	. 1	88.36	59.19
RB	lin	1R	12402	2.2918	0	22	9.8	4.9	0	1	. 1	184.80	59.19
UN	blg	1E	61444	0.1448	0	109	2.0	1.5	0	1	. 1	2.36	59.19
CHI	LORO	PHYT	A										
TM	spp	2R	133035	196.6822	0	944	78.4	4.9	0	1	. 2	1478.42	29.59
SP	cyl	2E	141	0.0458	0	1	14.7	6.5	0	1	. 2	325.19	29.59
00	spp	2E	153893	54.2731	0	273	12.3	7.4	0	1	. 1	352.67	59.19
KS	spp	2R	636427	13.9958	0	1129	7.0	2.0	0	1	1	21.99	59.19
UN	chl	2E	141491	9.7832	0	251	5.5	4.9	0	1	. 1	69.14	59.19
EU	JLEN	OPHY	ТА										
EG	spp	3E	3100	24.0830	0	22	49.0	17.4	0	1	2	7767.71	29.59
CHI	RYSOI	PHYT	A										
UN	chr	4E	120634	6.2674	0	214	4.9	4.5	0	1	. 1	51.95	59.19
CM	spp	4E	37768	4.6275	0	67	6.5	6.0	0	1	. 1	122.52	59.19
OM	spp	4E	92448	1.7349	0	164	3.5	3.2	0	1	. 1	18.77	59.19
CR.	YPTO:	PHYT	A										
CR	ero	5F	1973	2.1792	0	14	24.5	12.3	7	1	. 2	1104.51	29.59
UN	cry	5E	6765	1.3178	0	12	12.3	5.5	0	1	. 1	194.82	59.19
BA	CILL	ARIO	PHYTA										
PN	spm	7R	16207	150.9763	0	115	78.4	12.3	0	1	. 2	9315.72	29.59
NZ	вpp	7R	7892	1.3288	0	14	34.3	2.5	0	1	. 1	168.37	59.19
UN	dia	7R	42278	5.9794	0	75	14.7	3.5	0	1	. 1	141.43	59.19
TO	I CN	г Г	1512572	483.7218		3530							

Buchans - PP13 (regular - unconcentrated) 29/09/96 (A96-99)

PHYLUM TOT CELLS.L⁻¹ TOT BIOMASS.M⁻³ CYANOBACTERIA 118520 10.447
 LI0520
 10.447

 CHLOROPHYTA
 1064987
 274.780

 EUGLENOPHYTA
 3100
 24.083
 CHRYSOPHYTA 250850 12.630 8737 CRYPTOPHYTA 3.497 0.000 PYRROPHYTA 0 66377 DIATOMS 158.285 RHODOPHYTA 0 0.000 _____ TOTAL ALGAE 1512572 483.722

SUMMARY:

Cell Density: 1.51 X 10⁶ cells/L

Biomass Estimate: 483.72 µg/L

Buchans - Drainage Tunnel (regular) 29/09/96 (A96-101)

Sample File BR96C1 DATE ANALYSED...10-12-1996

SUBSAMPLE VOLUME... 105.0 mLs

TAX	ON		CELLS.L ⁻¹ (L ⁻¹)	BIOMASS (MG.M ⁻³)	COL	CELLS	LEN (µM)	WID (µM)	D # (μM)	T	RANS	BIOVOL (µM ³)	COR.F
CYA	NOBA	ACTER	IA										
UN	blg	1E	15220	0.0359	0	27	2.0	1.5	O	2	1	2.36	59.19
CHL	OROI	рнута											
sc	$_{ m spp}$	2 E	165730	10.4175	0	294	9.8	3.5	0	1	1	62.86	59.19
UN	chl	2E	23676	1.2301	Q	42	4.9	4.5	0	1	1	51.95	59.19
CHR	YSOI	рнута											
UN	chr	4E	23676	0.4443	0	42	3,5	3.2	0	1	1	18.77	59.19
BAC	ILL	ARIOP:	нута										
EU	spa	7R	20294	0.7842	Û	36	12.3	2.0	0	1	1	38.64	59.19
НA	spe	7R	42842	2.5867	0	76	12.3	2.5	0	2	1	60.38	59.19
тот		r	291437	15.4986		517							

Buchans - Drainage Tunnel (regular-unconcentrated) 29/09/96 (A96-101)

PHYLUM	TOT	CELLS.L ⁻¹	TOT	BIOMASS.M ⁻³	
CYANOBACTER	RIA	15220		0.036	
CHLOROPHYTA	Ŧ	189406		11.648	
EUGLENOPHYT	ΓA	0		0.000	
CHRYSOPHYTZ	Ĵ	23676		0.444	
CRYPTOPHYTA	J	0		0.000	
PYRROPHYTA		0		0.000	
DIATOMS		63135		3.371	
RHODOPHYTA		0		0.000	
TOTAL ALGAR	3	291437		15.499	

SUMMARY:

Cell Density: 2.91 X 10⁵ cells/L

Biomass Estimate: 15.5 μ g/L

Buchans - OWP (regular) 29/09/96 (A96-103)

Sample File BR96C3 DATE ANALYSED...12-10-1996

SUBSAMPLE VOLUME... 52.5 mLs

TA	KON		$\begin{array}{c} \text{CELLS.L}^{-1} \\ (\text{L}^{-1}) \end{array}$	BIOMASS (MG.M ⁻³)	COL	CELLS	LEN (µM)	WID (µM)	D; (μM)	# T	RANS	BIOVOL (µM ³)	COR.F
CY	ANOB	ACTI	ERIA										
os	spl	1R	14469	27.2839	0	77	100.0	4.9	0	1	3	1885.74	29.59
BG	fil	1R	80047	7.0727	0	71	50.0	1.5	0	1	1	88.36	59.19
UN	blg	1E	138672	0.3267	0	123	2.0	1.5	0	1	1	2.36	59.19
CH	LORO	PHYI	ra -										
PD	$_{\mathrm{spp}}$	2F	451	1.9150	0	8	61.3	44.1	3	1	5	4246.38	14.80
TM	spp	2R	1879	2.6044	0	10	73.5	4.9	0	1	3	1386.02	29.59
MC	spp	2R	8080	1.1427	0	43	14.7	3.5	0	1	3	141.43	29.59
sc	app	2E	48479	7.4963	0	43	12.3	4.9	0	1	1	154.63	59.19
UN	chl	2E	289746	35.5003	0	257	6.5	6.0	0	1	1	122.52	59.19
EU	GLEN(OPHY	/TA										
EG	spp	3E	752	2.6257	Q	4	44.1	12.3	0	1	3	3493.39	29.59
CHI	RYSO	PHY	ra -										
UN	chr	4E	224356	11.6562	0	199	4.9	4.5	0	1	1	51.95	59.19
CM	spp	4E	27058	3.5399	0	24	6.5	6.2	0	1	1	130.83	59.19
OM	spp	4E	135290	2.5388	Q	120	3.5	3.2	0	1	1	18.77	59.19
BAG	CILL	ARIC	PHYTA										
AH	sps	7R	23676	1.7084	Q	21	14.7	2.5	0	1	1	72.16	59.19
NZ	sps	7R	4510	0.4339	0	4	19.6	2.5	0	1	1	96.21	59.19
UN	dia	7R	65390	21.2092	0	58	17.2	4.9	0	1	1	324.35	59.19
TO	r cn	 T	1062854	127.0542		1062							

Buchans - OWP (regular - unconcentrated) 29/09/96 (A96-103)

PHYLUM	TOT	CELLS.L ⁻¹	TOT	BIOMASS.M ⁻³	
CYANOBACTER	RIA	233188		34.683	
CHLOROPHYTZ	A	348635		48.659	
EUGLENOPHY	ΓA	752		2.626	
CHRYSOPHYTA	Ą	386704		17.735	
CRYPTOPHYTA	A	0		0.000	
PYRROPHYTA		0		0.000	
DIATOMS		93576		23.351	
RHODOPHYTA		0		0.000	
TOTAL ALGAN	Ε	1062854		127.054	

SUMMARY:

Cell Density: 1.06 X 10⁶ cells/L

Biomass Estimate: 127.05 μ g/L

Buchans - PP 17 (regular) 29/09/96 (A96-105)

Sample File BR96C5 DATE ANALYSED...11-29-1996

SUBSAMPLE VOLUME... 52.5 mLs

TAJ	KON		$\begin{array}{c} \text{CELLS.L}^{-1} \\ (\text{L}^{-1}) \end{array}$	BIOMASS (MG.M ⁻³)	COL	CELLS	LEN (µM)	WID (µM)	D # (µM)	T	rans	BIOVOL (µM ³)	COR.F
CY	ANOB.	ACTE	RIA										
BG	fil	1R	25179	2.2247	0	134	50.0	1.5	0	1	3	88.36	29.59
UN	blg	1E	157838	0.3719	٥	140	2.0	1.5	0	1	1	2.36	59.19
CHI	LORO	РНҮТ	'A										
KS	spp	2R	25931	0.5295	0	23	6.5	2.0	0	1	1	20.42	59.19
00	spp	2E	9019	3.1808	0	8	12.3	7.4	0	1	1	352.67	59.19
UN	$_{chl}$	2E	125143	15.3328	0	111	6.5	6.0	0	1	1	122.52	59.19
CHE	RYSO	рнут	A										
UN	chr	4E	131908	4.9728	0	117	4.5	4.0	0	1	1	37.70	59.19
CM	spp	4E	29313	3.5915	0	26	6.5	6.0	Û	1	1	122.52	59.19
OM	spp	4E	55243	1.0367	0	49	3.5	3.2	0	1	1	18.77	59.19
BAG	CILL	ARIC	PHYTA										
PN	spm	7R	564	5.0839	0	1	75.9	12.3	0	1	1	9018.66	29.59
ΗA	spa	7R	9019	0.5446	0	8	12.3	2.5	0	1	1	60.38	59.19
UN	dia	7R	6765	0.9567	0	6	14.7	3.5	0	1	1	141.43	59.19
TO	r CN	 T	575922	37.8260		623							

Buchans - PP 17 (regular-unconcentrated) 29/09/96 (A96-105)

PHYLUM	TOT	CELLS.L ⁻¹	TOT	BIOMASS.M ⁻³	
CYANOBACTER	RIA	183017	,	2.597	
CHLOROPHYTA	Ð	160093		19.043	
EUGLENOPHY.	ГА	C)	0.000	
CHRYSOPHYT2	Ĵ	216464		9.601	
CRYPTOPHYTA	Ŧ	C)	0.000	
PYRROPHYTA		C)	0.000	
DIATOMS		16348	ļ	6.585	
RHODOPHYTA		C).	0.000	
TOTAL ALGAN	3	575922	2	37.826	

SUMMARY:

Cell Density: 5.76×10^5 cells/L

Biomass Estimate: 37.83 μ g/L

Buchans - OEP (regular) 29/09/96 (A96-107)

Sample File BR96C7 DATE ANALYSED...10-27-1996

SUBSAMPLE VOLUME... 105.0 mLs

TAXON	$\begin{array}{c} \text{CELLS.L}^{-1} \\ (\text{L}^{-1}) \end{array}$	BIOMASS (MG.M ⁻³)	COL	CELLS	LEN (µM)	WID (µM)	D # (µM)	TRANS	BIOVOL (µM ³)	COR.F	
CHLOROPHYT.	'A										-
UN chl 2E	1785	0.2922	0	19	7.4	6.5	0	1 3	163.70	29.59	
UN chl 2E	12965	0.4888	0	23	4.5	4.0	0	1 1	37.70	59.19	
CHRYSOPHYT	A										
UN chr 4E	75537	1.4175	0	134	3.5	3.2	0	1 1	18.77	59.19	
BACILLARIO	PHYTA										
UN dia 7R	1691	0.3189	0	З	19.6	3.5	0	1 1	188.57	59.19	
TOT CNT	91978	2.5174		179							-

Buchans - OEP (regular-unconcentrated) 29/09/96 (A96-107)

PHYLUM	тот	CELLS.L ⁻¹	TOT BIOMASS.	M ⁻³
CYANOBACTER CHLOROPHYTZ	RIA	0 14750	0.00 0.78	0
EUGLENOPHYT CHRYSOPHYTZ	TA A	0 75537	0.00 1.41	0 8
CRYPTOPHYTA	ł	0	0.00	0
DIATOMS		1691	0.31	9
RHODOPHYTA		U 	0.00	0
TOTAL ALGAE	2	91978	2.51	7

SUMMARY:

Cell Density: 9.2 X 10⁴ cells/L

Biomass Estimate: 2.52 μ g/L

SITE: Buchans

Sample # A96-23

Location: Buchans - PP in (00:56)

Date: 8/07/96

- 250 mLs concentrated to 20 mLs; settled 2.1 mLs for examination (at 200X and 400X)

- some floc-like material and fine debris present; very little algal matter present

Algal Taxa Present:

CLASS	TAXON	Ranking
Cyanobacteria	Oscillatoria sp. (small filament)	1
Chlorophyceae	Chlamydomonas spp. Ulothrix sp. Unidentified small green spp.	1 1 2
Euglenophyceae		
Chrysophyceae	Ochromonas spp. Unidentified small chrysophytes	2 2
Bacillariophyceae Cryptophyceae	Achnanthes sp. Eunotia fallax	2 2
Dinophyceae		

Note: - fungal hyphae evident in sample

SITE: Buchans

Sample # A96-24

Location: Buchans - PP out (00:36)

Date: 8/07/96

- 250 mLs concentrated to 20 mLs; settled 2.1 mLs for examination (at 200X and 400X)

- very dilute sample with very little algal material present; some floc-like precipitate present - similar to sample A96-23

Algal Taxa Present:

CLASS	TAXON	Ranking
Cyanobacteria	Oscillatoria sp. (small filament)	2
Chlorophyceae	Unidentified small green spp.	3
Euglenophyceae		
Chrysophyceae	Ochromonas spp. Unidentified small chrysophytes	3 2
Bacillariophyceae	Achnanthes sp. Eunotia fallax Fragilaria sp. Navicula sp. (small sp.)	1 2 1 1

Cryptophyceae

Dinophyceae

Note: - fungal hyphae evident in sample

SITE: Buchans

Sample # A96-38

Location: Buchans - MLC - i (16:54)

Date: 11/07/96

- 250 mLs concentrated to 20 mLs; concentrated 10 mLs to 2.1 mLs for examination (at 200X and 400X)

- very dilute sample with very little algal material present; also very little debris present

CLASS	TAXON	Ranking
Cyanobacteria		
Chlorophyceae	Scenedesmus acuminatus Selenastrum sp. Unidentified small green spp.	2 2 3
Euglenophyceae		
Chrysophyceae		
Bacillariophyceae		
Cryptophyceae		
Dinophyceae		

SITE: Buchans

Sample # A96-39

Location: Buchans - MLC - II (17:21)

Date: 11/07/96

- 250 mLs concentrated to 20 mLs; concentrated 10 mLs to 2.1 mLs for examination (at 200X and 400X)

- very dilute sample with very little algal material present; also very little debris present

CLASS	TAXON	Ranking
Cyanobacteria		
Chlorophyceae	Selenastrum sp. Unidentified small green spp.	1 2
Euglenophyceae		
Chrysophyceae		
Bacillariophyceae	Navicula sp. (small sp.)	1
Cryptophyceae		
Dinophyceae		

SITE: Buchans

Sample # A96-40

Location: Buchans - MLC - III (17:41)

Date: 11/07/96

- 250 mLs concentrated to 20 mLs; concentrated 10 mLs to 2.1 mLs for examination (at 200X and 400X)

- very dilute sample with very little algal material present; also very little debris present

Algal Taxa Present:

CLASS	TAXON	Ranking
Cyanobacteria	Unidentified bluegreen filament	1
Chlorophyceae	Scenedesmus acuminatus	1
	Selenastrum sp.	1
	Temnogametum sp.	З
	Ulothrix sp.	2
	Unidentified small green spp.	3
Euglenophyceae		
Chrysophyceae		
Bacillariophyceae	Achnanthes sp. Navicula sp. (small sp.)	2
Cryptophyceae		Ū
Dinophyceae		

21

SITE: Buchans

Sample # A96-41

Location: Buchans - PP - in (18:42)

Date: 11/07/96

- 250 mLs concentrated to 20 mLs; concentrated 10 mLs to 2.1 mLs for examination (at 200X and 400X)

- dilute sample with very little debris present

Algal Taxa Present:

CLASS	TAXON	Ranking
Cyanobacteria	Unidentified bluegreen filament Unidentified bluegreen spp.	1 2
Chlorophyceae	Chlamydomonas sp. Unidentified small green spp.	1
Euglenophyceae	Euglena sp.	1
Chrysophyceae	Epipyxis sp. Ochromonas spp. Unidentified small chrysophytes	1 3 2
Bacillariophyceae	Achnanthes sp. Navicula spp. (small spp.) Nitzschia sp. Pinnularia sp. (small sp.)	2 2 1 1
Cryptophyceae		

Dinophyceae

Note: - amoeboid species also present

SITE: Buchans

Sample **# A96-42**

Location: Buchans - PP out (18:16)

Date: 11/07/96

- 250 mLs concentrated to 20 mLs; concentrated 10 mLs to 2.1 mLs for examination (at 200X and 400X)

- dilute sample with very little algal material present

CLASS	TAXON	Ranking
Cyanobacteria	Unidentified bluegreen filament Unidentified small bluegreens	1 2
Chlorophyceae	Chlamydomonas spp. Scenedesmus acuminatus Selenastrum sp. Temnogametum sp. Ulothrix sp. Unidentified small green spp.	1 1 1 1 3
Euglenophyceae	Euglena sp.	1
Chrysophyceae	Unidentified small chrysophytes	2
Bacillariophyceae	Achnanthes sp. Navicula sp. (small sp.) Nitzschia sp.	1 1 1
Cryptophyceae	Chroomonas sp.	1
Dinophyceae		

SITE: Buchans

Sample **# A96-43**

Location: Oriental West Pit (OWP)

Date: 3/05/96

- 1000 mLs concentrated to 20 mLs; considerable amount of sediment and floc-like precipitate present

- too much sediment to permit enumeration; very little algae present

Algal Taxa Present:

CLASS	TAXON	Ranking
Cyanobacteria		
Chlorophyceae	Oocystis sp. Ulothrix sp.	1 2
Euglenophyceae		
Chrysophyceae		
Bacillariophyceae	Achnanthes sp. Eunotia fallax Navicula spp. Nitzschia spp. Pinnularia sp.	2 2 1 1 1
Cryptophyceae		

Dinophyceae

SITE: Buchans

Sample # A96-44

Location: Oriental West Pit (OWP)

Date: 13/05/96

- 250 mLs concentrated to 20 mLs; considerable amount of sediment and floc-like precipitate present

- considerable amount of filamentous algae; many filaments coated with precipitate; also many filaments look 'unhealthy' with distorted cell shapes

CLASS	TAXON	Ranking
Cyanobacteria		
Chlorophyceae	Microspora spp. Ulothrix sp.	5 2
Euglenophyceae		
Chrysophyceae		
Bacillariophyceae		
Cryptophyceae		
Dinophyceae		

SITE: Buchans

Sample # A96-45

Location: Oriental East Pit (OEP)

Date: 13/05/96

- 250 mLs concentrated to 20 mLs; considerable amount of floc-like precipitate present

- cells appear healthy and greater algal diversity is evident

- considerable amount of moss protonemata present (at least 2 distinct sizes); much of the protonemata is coated with floc-like precipitate
- narrow fungal hyphae also present

Algal Taxa Present:

CLASS	TAXON	Ranking
Cyanobacteria	Bluegreen filament (small sp.)	3
Chlorophyceae	Temnogametum sp.	2
Euglenophyceae		
Chrysophyceae		
Bacillariophyceae	Achnanthes sp. Nitzschia spp. Pinnularia sp. (medium)	4 3 3
Cryptophyceae		

Dinophyceae

SITE: Buchans

Sample # A96-46

Location: Pool 13 (PP 13)

Date: 13/05/96

- 250 mLs concentrated to 20 mLs; relatively little precipitate present

- moss protonemata also common; not coated with precipitate in this sample

CLASS	TAXON	Ranking
Cyanobacteria	Bluegreen filament (small spp.) (maybe Phormidium sp.)	4
Chlorophyceae	Temnogametum sp. (very healthy filaments)	5
Euglenophyceae		
Chrysophyceae		
Bacillariophyceae	Pinnularia sp. (medium)	2
Cryptophyceae		
Dinophyceae		

SITE: Buchans

Sample # A96-47

Location: Pool 17 (PP 17)

Date: 13/05/96

- 250 mLs concentrated to 20 mLs; considerable amount of sediment and floc-like precipitate present

- moss protonemata co-dominant with filamentous algae

- narrow fungal hyphae also common

CLASS	TAXON	Ranking
Cyanobacteria	Bluegreen filament (small sp.)	3
Chlorophyceae	Temnogametum sp.	4
Euglenophyceae		
Chrysophyceae		
Bacillariophyceae	Pinnularia sp. (medium) Pinnularia sp. (small)	1 1
Cryptophyceae		
Dinophyceae		

SITE: Buchans

Sample # A96-55

Location: Buchans - Pollshing Pond (PP14) - Mat "Bubble" (pH 6.93) (sample labelled A)

Date: 12/07/96

- 100 mLs "pureed" sample for Culturing Experiment

- considerable amount of floc-like sediment present; let sample settle then examined algae in supernatant

- sample dominated by moss protonemata (wide filament form)

Algal Taxa Present:

CLASS	TAXON	Ranking
Cyanobacteria	Oscillatoria sp. (small sp.)	1
Chlorophyceae	Microthamnion sp. Oocystis sp. Ulothrix sp.	2 2 3
Euglenophyceae	Euglena gracilis	2
Chrysophyceae		
Bacillariophyceae	Nitzschia spp.	3
Cryptophyceae		
Dinophyceae		

NOTE: - numerous bacteria and heterotrophic flagellates also present

SITE: Buchans

Sample # A96-56

- Location: Buchans Polishing Pond (PP 12) Seep Algae (sample labelled B)
- Date: 12/07/96
- 100 mLs "pureed" sample for Culturing Experiment
- considerable amount of floc-like sediment present; let sample settle then examined algae in supernatant (sample similar to samples A96-55 and A96-58)

(pH 6.99)

- sample dominated by moss protonemata (both wide and narrow filament forms)

CLASS	TAXON	Ranking
Cyanobacteria		
Chlorophyceae	Chlamydomonas spp. Chlorella sp. Microthamnion sp. Oocystis sp. Ulothrix sp.	2 1 2 3
Euglenophyceae	Euglena gracilis	2
Chrysophyceae		
Bacillariophyceae	Nitzschia spp.	2
Cryptophyceae		
Dinophyceae		

SITE: Buchans

Sample # A96-57

Location: Oriental West Pit (OWP) - Filamentous Algae (pH 4.83) (sample labelled C)

Date: 12/07/96

- 100 mLs "pureed" sample for Culturing Experiment

- very little debris or sediment present; essentially 'pure' sample of Ulothrix sp.

Algal Taxa Present:

CLASS	TAXON	Ranking
Cyanobacteria		
Chlorophyceae	Ulothrix sp.	5
Euglenophyceae		
Chrysophyceae		
Bacillariophyceae		
Cryptophyceae		
Dinophyceae		

NOTE: - bacteria and fungal hyphae also noted

SITE: Buchans

Sample # A96-58

Location: Buchans Polishing Pond (PP 14) - "Floating Bubble" (pH 6.98) (sampled labelled D)

Date: 12/07/96

- 100 mLs "pureed" sample for Culturing Experiment

- considerable amount of floc-like sediment present; let sample settle then examined algae in supernatant (sample similar to A96-55 and A96-56)

1

- sample dominated by moss protonemata (wide filament form)

Algal Taxa Present:

CLASS	TAXON	Ranking
Cyanobacteria		
Chiorophyceae	Chlamydomonas sp. Chlorella sp. Microthamnion sp. Oocystis sp. Ulothrix sp.	2 2 2 3
Euglenophyceae	Euglena gracilis	2
Chrysophyceae		
Bacillariophyceae	Nitzschia spp.	2
Cryptophyceae		
Dinophyceae		

NOTE: - fungal hyphae also present in sample

Summary of Macronutrients Present in Media Used for Culturing Buchans Algal Mat Samples and for <u>Dictyosphaerium</u> pulchellum

MEDIA TYPES

(concentrations given in mmolar and mg/L)

			Regular (10:1	Regular a N to P)	nd Modified Chu-1 0 Reduced Silica (Content	Field Levels (1:1	N to P)
	Inorganic N	lacronutrients	mM	mg/L	mM	mg/L	mM	mg/L
	Ammonium	(NH₄ ⁺)						
	Calcium	(Ca ²⁺)	0.17	6.81	0.17	6.81	0.085	3.41
	Magnesium	(Mg ²⁺)	0.1	2.43	0,1	2.43	0.1	2.43
	Potassium	(K⁺)	0.11	4.3	0.11	4.3	0.46	4.3
33	Sodium	(Na ⁺)	0.55	12.6	0.39	8.97	0.55	12.6
	Carbonate	(CO ₃ ²⁻)	0.19	11.4	0.19	11,4	0.19	11.4
	Chloride	(CI ⁻)	0.0089	0.32	0.0089	0.32	0.0089	0.32
	Nitrate	(NO3)	0.34	21.08	0.34	21.08	0.17	10.54
	Phosphate	(PO4 ³)	0.057	5.41	0.057	5.41	0.23	21.84
	Silicate	(SiO ₃ ²)	0.088	6,69	0.0088	0.669	0.0088	0.669
	Sulphate	(SO4 ²)	0.1	9.6	0.1	9.6	0.1	9.6

Summary of Macronutrients Present in Media Used for Culturing Buchans Algal Mat Samples and for <u>Dictyosphaerium</u> pulchellum

MEDIA TYPES (concentrations given in mmolar and mg/L)

		B.B.M. Bold's Basal Medium		B.G11 Blue-Green-11 Medium	
	Inorganic Macronutrients	mM	mg/L	mМ	mg/L
	Ammonium (NH₄ ⁺)				
	Calcium (Ca ²⁺)	0.17	6.81	0.25	10.02
	Magnesium (Mg ²⁺)	0.3	7.29	0.3	7.29
	Potassium (K ⁺)	2.7	105,56	0.34	13.29
34	Sodium (Na⁺)	3.37	77.48	18.03	414.51
	Carbonate (CO ₃ ²⁻)			0.19	11.4
	Chloride (Cl ⁻)	0.77	27.3	0.49	17.37
	Nitrate (NO ₃ ⁻)	2.94	182.28	17.65	1094.3
	Phosphate (PO ₄ ³⁻)	1.72	117.27	0.17	16.15
	Silicate (SiO ₃ ²)				
	Sulphate (SO ₄ ²⁻)	0.34	32.66	0.3	28.82

BUCHAN'S CULTURING EXPERIMENT- Sampling Day 31

Identification of Major Taxa Found in Four Different Types of Freshwater Media

Ranking System Used:	
5 = most abundant, found dominating most	3 = common
fields of view	2 = less common
4 = very abundant	1 = r are

Innoculum Taken From Sampling Container Marked: C - OWP fil.algae from 12/7/96

REGULAR CHU 10 MEDI	A	
CATEGORY	GENERA	RANK
Green algae	Scenedesmus	5
Filamentous greens	Mougeotia	5
Blue-Green filaments	Phormidium	4
	Anabaena	1
Diatoms	Pinnularia	4
	Navicula	2
	Achnanthes	3
Small Greens		1
CHU 10 WITH LESS SILIC	CA	
CATEGORY	GENERA	RANK
Green algae	Scenedesmus	5
Filamentous greens	Mougeotia	5
Blue-Green filaments	Lyngbya	4
	Anabaena	3
	Phormidium	1
Diatoms	Pinnularia	3
	Navicula	2
Moss		2
Small Greens		2
BOLD'S BASAL MEDIUN	/ (B.B.M.)	
CATEGORY	GENERA	RANK
Green algae	Scenedesmus	5
Filamentous greens	Mougeotia	3
Blue-Green filaments	Phormidium	4
	Lyngbya	2
Diatoms	Pinnularia	2
Moss		1
BLUE - GREEN 11 (B.G.	11)	
CATEGORY	GENERA	RANK
Green algae	Scenedesmus	4
Blue-Green filaments	Phormidium	4
	Lyngbya	4
	Anabaena	3

Small Greens

2
BUCHAN'S CULTURING EXPERIMENT- Sampling Day 31

Identification of Major Taxa Found in Four Different Types of Freshwater Media

3 = common
2 = less common
1 = rare

Innoculum Taken From Sampling Container Marked: D - PP14 Float Bubble from 11/7/96

REGULAR CHU 10 MEDI	A	
CATEGORY	GENERA	RANK
Green algae	Scenedesmus	1
Filamentous greens	Mougeotia	1
-	Ulothrix	5
Blue-Green filaments	Lyngbya	3
Small Greens		1

CHU 10 WITH LESS SILICA

CHU TU WITH LESS SILIC	A	
CATEGORY	GENERA	RANK
Green algae	Scenedesmus	1
Filamentous greens	Mougeotia	3
	Ulothrix	5
Small Greens		4

BOLD'S BASAL MEDIUN	л (В.В.М.)	
CATEGORY	GENERA	RANK
Green algae	Scenedesmus	4
Filamentous greens	Mougeotia	1
	Ulothrix	5
Small Greens		1

BLUE - GREEN 11 (B.G.11)		
CATEGORY	GENERA	RANK
Green algae	Scenedesmus	3
Filamentous greens	Mougeotia	4
	Ulothrix	5
Small Greens		2

BUCHAN'S CULTURING EXPERIMENT- Sampling Day 31

Identification of Major Taxa in Preserved Samples

Ranking Sy 5 = most fields 4 = very	ystem Used: t abundant, found dominating mo s of view abundant	ost	3 = common 2 = less common 1 = rare
SAMPLE			
VIAL	CATEGORY	GENERA	RANK
A1	Diatoms	Pinnularia	4
		Navicula	4
	Blue-Green Filaments	Phormidium	2
	Moss		5
	Small Greens		1
	Rod and Coccoid Bacteria		5
A2	CATEGORY	GENERA	RANK
	Diatoms	Pinnularia	3
		Navicula	3
	Blue-Green Filaments	Phormidium	3
	Moss		5
	Small Greens		1
	Rod and Coccoid Bacteria		5
A3	CATEGORY	GENERA	RANK
	Diatoms	Pinnularia	2
		Navicula	2
	Blue-Green Filaments	Phormidium	4
	Moss		5
	Small Greens		1
	Rod and Coccoid Bacteria		4

SAMPLE

CATEGORY	GENERA	RANK
Filamentous Greens	Microspora	5
	Ulothrix	1
Diatoms	Pinnularia	1
	Navicula	1
Blue-Green Filaments	Phormidium	4
Moss		5
Small Greens		1
Rod and Coccoid Bacteria		3
CATEGORY	GENERA	RANK
Filamentous Greens	Microspora	5
	Ulothrix	1
Rod and Coccoid Bacteria		4
CATEGORY	GENERA	RANK
Filamentous Greens	Microspora	5
Blue-Green Filaments	Phormidium	3
Rod and Coccoid Bacteria		4
	CATEGORY Filamentous Greens Diatoms Blue-Green Filaments Moss Small Greens Rod and Coccoid Bacteria CATEGORY Filamentous Greens Rod and Coccoid Bacteria CATEGORY Filamentous Greens Blue-Green Filaments Rod and Coccoid Bacteria	CATEGORY Filamentous GreensGENERA Microspora UlothrixDiatomsPinnularia NaviculaBlue-Green FilamentsPhormidiumMoss Small Greens Rod and Coccoid BacteriaPhormidiumCATEGORY Filamentous GreensGENERA Microspora UlothrixRod and Coccoid BacteriaMicrospora UlothrixCATEGORY Filamentous GreensGENERA Microspora UlothrixRod and Coccoid BacteriaMicrospora PhormidiumCATEGORY Filamentous GreensGENERA Microspora PhormidiumRod and Coccoid BacteriaMicrospora Phormidium

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SAMPLE VIAL

C1	CATEGORY Green algae Filamentous Greens Blue-Green Filaments Diatoms Rod and Coccoid Bacteria	GENERA Scenedesmus Microspora Lyngbya Achnanthes Pinnularia Nitzschia Navicula	RANK 1 5 3 3 3 3 3 3 3 3
C2	CATEGORY Green algae Filamentous Greens Blue-Green Filaments Diatoms Rod and Coccoid Bacteria	GENERA Scenedesmus Microspora Lyngbya Achnanthes Pinnularia Nitzschia Navicula	RANK 1 5 3 3 3 3 3 3 3 3
С3	CATEGORY Green algae Filamentous Greens Blue-Green Filaments Diatoms Rod and Coccoid Bacteria	GENERA Scenedesmus Microspora Lyngbya Phormidium Achnanthes Pinnularia Nitzschia Navicula	RANK 2 5 4 3 3 3 3 4

SAMPLE

VIAL			
D1	CATEGORY	GENERA	RANK
	Blue-Green Filaments	Lyngbya	2
		Phormidium	2
	Diatoms	Navicula	3
		Pinnularia	3
	Rod and Coccoid Bacteria		5
	Moss		5
	Fungal Hyphae		5
	CATEGORY	GENERA	RANK
D2	Blue-Green Filaments	Lyngbya	2
	Diatoms	Navicula	2
		Pinnularia	2
	Rod and Coccoid Bacteria		5
	Moss		5
	Fungal Hyphae		5
	Small Greens		1
D3	CATEGORY	GENERA	RANK
	Green Algae	Scenedesmus	1
	Blue-Green Filaments	Lyngbya	5
	Diatoms	Navicula	3
		Pinnularia	3
	Rod and Coccoid Bacteria		4
	Moss		5
	Fungal Hyphae		5

SAMPLE VIAL

F1	CATEGORY	GENERA	RANK
- I	Filamentous Greens	Ulothrix	5
	Diatoms	Achnanthes	2
	Diatonis	Pinnularia	2
	Ded and Cassaid Postatio	T mmanana	2
			J 4
	Small Greens		1
E2	CATEGORY	GENERA	RANK
	Filamentous Greens	Ulothrix	5
	Diatoms	Achnanthes	2
	Diatorno	Pinnularia	2
	Rod and Coccoid Bacteria		2
	Small Groops		- 1
	Smail Greens		•
E3	CATEGORY	GENERA	RANK
	Filamentous Greens	Ulothrix	5
	Diatoms	Achnanthes	2
		Pinnularia	2
	Rod and Coccoid Bacteria		1
	Small Greens		1
	Funcal Hyphae		4

F1	CATEGORY Filamentous Greens Blue-Green Filaments Rod and Coccoid Bacteria Small Greens Fungal Hyphae Moss Diatoms	GENERA Ulothrix Microspora Lyngbya Phormidium	RANK 2 4 2 1 5 5 3
		Pinnularia Nitzschia Navicula	3 3 3
F2	CATEGORY Filamentous Greens Diatoms	GENERA Ulothrix Microspora Achnanthes Pinnularia Nitzschia	RANK 4 5 4 4 4
	Rod and Coccoid Bacteria Fungal Hyphae Moss	Navicula	4 3 4 5
F3	CATEGORY Filamentous Greens Green algae Blue-Green Filaments Diatoms	GENERA Ulothrix Microspora Scenedesmus Lyngbya Achnanthes Pinnularia Nitzschia Navicula Eunotia	RANK 2 2 1 3 4 4 4 4 1
	Rod and Coccoid Bacteria Fungal Hyphae Moss		2 5 5

SAMPLE VIAL

G1	CATEGORY Filamentous Greens Green algae Blue-Green Filaments Diatoms	GENERA Ulothrix Microspora Scenedesmus Lyngbya Achnanthes Pinnularia Nitzschia	RANK 1 3 1 3 2 2 2 2
	Rod and Coccoid Bacteria Fungal Hyphae Moss	Eunotia	- 1 2 5 5
G2	CATEGORY Blue-Green Filaments Diatoms	GENERA Lyngbya Achnanthes Pinnularia Nitzschia Navicula	RANK 3 3 3 3 3
	Rod and Coccoid Bacteria Fungal Hyphae Moss		3 5 5
G3	CATEGORY Filamentous Greens Green algae Blue-Green Filaments Diatoms	GENERA Microspora Scenedesmus Lyngbya Achnanthes Pinnularia Nitzschia Navicula	RANK 2 4 3 3 3 3 3
	Rod and Coccoid Bacteria Fungal Hyphae Moss Small Greens		2 5 5 1

6.0 PHOSPHATE: LIMITING NUTRIENT FOR PRIMARY PRODUCTIVITY

Phosphate was identified as the limiting nutrient in the system, based on the water chemistry and previous studies. Fertilization of Polishing Pond water assisted in the productivity and growth of algae. It was inferred that this assisted zinc removal through providing more sites to collect particles. This was addressed through a series of lab and field experiments.

6.1 Nutrient Availability: Lab Experiments

6.1.1 Nitrogen and Phosphorus Solubility in Distilled and Boomerang Lake Water

Laboratory studies were performed to determine the solubility of various fertilizer formulations in distilled water and in OEP and polishing pond water.

A wide range of fertilizer formulations are available for supplying nutrients to plants and bacteria for agriculture and land reclamation. However, few fertilizers are marketed for application as a slow-release source of nutrients for aquatic environmental applications, such as supplying nitrogen and phosphorus to acidic water bodies to enhance primary productivity.

Fertilizers are typically described according to their available nitrogen, phosphorus and potassium (N-P-K) content in percent. However, there is typically ambiguity whether the P content actually refers to, for instance, P, PO_4 or P_2O_5 , while the form of nitrogen (e.g., ammonia, nitrate and/or urea) is not specified. 'Slow-release' refers to the dissolution rate in soil conditions; submerged in water, most slow release fertilizers rapidly dissolve.

The section reports on the dissolution behaviour of eleven types of fertilizer, and describes the release of nitrate, ammonia and phosphate to distilled water or acidic lake water in stirred conditions for up to 14 days.

Methods and Materials

Fertilizer Types: In total, eleven types of fertilizer were tested (see Table 21). For many of the types, the N, P and K content is given. However, whether a fertilizer contains 10% P_2O_5 or 10 % P could not always be verified from manufacturers' specifications provided on packaging. In Tables 21 and 22, manufacturers' specifications are given under "Reported N:P:K", while under "Amount of N/P added, mg/L" the best estimate of the actual amount of N or P present in the experimental solution is given.

Types 1, 2 and 3 are resin-coated fertilizer granules, designed to slowly release nutrients even in saturated conditions (Osmocote, Grace; Nutricote, Plant Products).. According to the manufacturer, Type 1 contains potassium nitrate, while Type 3 contains 21%-7%-7% N-P-K. Information on the composition of Type 2 is not available.

Fertilizer Types 4 and 5 are liquid fertilizers containing 14-4-6 and 4-18-6 N-P-K, respectively. These fertilizers were designed as foliar fertilizers for supplementing the nutrient supply to citrus trees. These types are presumed to contain 14% and 4% N as specified. Without additional information, these types are presumed to contain 4% and 18% P.

Type 6 fertilizer is molasses. While this is not specifically a fertilizer, molasses has been use to augment bacterial growth, and may be suitable for initiating remediation processes for AMD and groundwater. Therefore, information regarding the release of nitrate, ammonia and phosphate from molasses may be of utility. Type 7 is calcium nitrate, in the form of soluble white crystals. The manufacturer specifications indicate that Type 7 is composed of 15.5-0-0 N-P-K. Type 7 is presumed to contain 15.5% N.

Fertilizer types 8 and 9 are two forms of ground natural phosphate rock, used as soil supplements in agriculture as long term sources of phosphate and alkalinity. Type 8 is Code 30 phosphate rock, ground to a fine sand consistency, while Type 9 is Code 31 phosphate rock ground finely to a flour-like powder. Phosphorus content (P) of these materials were determined by ICAP by Boojum.

Fertilizer Types 10 and 11 are water soluble horticultural formulation which, according to the manufacturer, contains 15-30-15 and 10-52-10 N-P₂O₅-K, respectively. Type 11 is exactly the same fertilizer used to supplement the Buchans polishing ponds with nutrients Converting P2O5 to P, Type 10 contains 13.1.7% P and Type 11 contains 22.7 % P.

Experiment Set-up: A 100 mg sample of each solid fertilizer was added to 1 of distilled water or 1 L water sample from Boomerang Lake (an acidified water body). For fertilizer Type 3, 1000 mg were added, since this type was a blend of several solids types of different colours. For liquid fertilizers, 1 mL was added, and the equivalent dry weight was determined by drying down a 25 mL sample at 75°C.

The 1 L samples were continuously stirred using a magnetic stirrer and stir bar at room temperature. Controls were set up, consisting of distilled water or Boomerang Lake water with no added fertilizer.

The pH, conductivity and temperature were measured 1 hour, 24 hours, 1 week, 11 days and 2 weeks following set up. Nitrate, ammonium and phosphate concentrations were determined at these times using Hach reagents and hand-held colorimeters.

Results

- The results of phosphate concentration determinations are expressed as P in Table 21, and nitrate and ammonium concentrations as N are presented in Table 22.
- Measurable phosphate concentrations were detected in solutions of fertilizer types 1, 2, 3, 4, 5, 6, 8, 9, 10 and 11. as expected, phosphate was not released from type 7 (calcium nitrate).
- For types 1, 2 and 3, phosphate release to distilled water could be compared to release to Boomerang Lake water. More phosphate was measured in distilled water leachates, indicating that phosphate may be precipitated by iron and/or zinc present in Boomerang L. water.
- Actual phosphate release could be compared to the manufacturer's specification on phosphate content for types 3, 4, 5, 8, 9, 10 and 11. With the exception of type 10 (15-13.1-15), all fertilizers released less phosphate than specified.
- Relatively little phosphate was released by types 1 and 2 resin-coated slow release fertilizers. However, up to 70 % of the phosphate content of type 3 (resin coated) was released, indicating that the resin coating did not impede release in the stirred solutions.
- The fertilizer type used to provide nutrients to the Polishing Ponds (type 11) readily dissolved, providing 133 % of the specified phosphate content within 1 hour of dissolving.
- Measurable nitrogen concentrations were detected in solutions of all fertilizer types, including the phosphate rock samples (ammonia: types 8 and 9).

- For types 1, 2 and 3, nitrogen release to distilled water could be compared to release to Boomerang Lake water. Much more nitrogen was measured in Boomerang Lake water than in distilled water leachates, indicating that nitrogen compound dissolution may be enhanced by the low pH of Boomerang L. water.
- Actual nitrogen release could be compared to the manufacturer's specification on nitrogen content for types 3, 4, 5, 7, 10 and 11. In many instances, fertilizers released more nitrogen than specified.
- Relatively little nitrogen was released by type 1 resin-coated slow release fertilizer. Type 2 released up to 93 mg/L N as ammonia in Boomerang L. water. However, up to 38 and 152 % of the nitrogen content of type 3 (resin coated) was released, indicating that the resin coating did not impede release in the stirred solutions.
- The fertilizer type used to provide nutrients to the Polishing Ponds (type 11) readily dissolved, providing 256 % of the specified nitrogen content within 1 hour of dissolving.

Discussion

This experiment was required to determine whether one particular fertilizer was particularly suitable among the types available for experimentation. The type 11 fertilizer, used in Buchans to date, appears to readily dissolved and release nutrients upon addition.

6.1.2 Manipulation of N and P Concentrations and Ratios

Laboratory studies with OWP water and algae were performed to determine a fertilization rate based on the consumption rate of phosphate by the periphyton population in the Polishing Ponds.

Background concentrations of nutrients in OWP water were determined using Hach reagents and a spectrophotometer. Phosphate and nitrate were then added to set up the following type of nutrient status:

- 1) N:P ratio of 10:1, achieved by adding KNO_3 or K_2HPO_4 .
- 2) N concentration of 10 mg/L, by adding KNO₃.
- 3) N concentration of 10 mg/L and P concentration of 1 mg/L.

The results indicated that some nitrate was taken up by the algae. Ammonia release occurred in some cultures. Phosphate was rapidly depleted from the solutions, and its concentration was less than detection limits, including control samples without algae Table 23).

It was concluded that phosphate determinations are prone to interference, and meaningful results could not be obtained, unless phosphorus isotopes could be used and monitored.

6.1.3 Periphyton Growth Study in Media

Growth studies with the biological material growing in the ponds in chemically defined growth media to determine which biological group might be the dominant component of the biological activity and what differences are possibly related to the chemical composition, i.e. nutrient limitation other than phosphate. The results of this study indicated that upon transfer to laboratory conditions, those algal species dominant in the periphyton community in the field are replaced by species more suited for growth in the laboratory (see "PHYTOPLANKTON AND PERIPHYTON TAXA IN 1996 BUCHANS SAMPLES AND BUCHANS CULTURING EXPERIMENT", Section 5). Without extensive further work, field conditions cannot be emulated in the lab.

6.2 **Periphyton Communities**

The periphyton in Polishing Pond system were characterized according to growth form. At the time of observations, periphyton in the polishing ponds consists primarily of aquatic moss, with some algal biomass, growing as 'mat bubble algae' over the bottom and as 'branch algae' on alder branches of the ponds.

- As 'mat bubble algae' accumulate air bubbles (O₂, CO₂), slabs of this mat buoy up from the bottom, and become 'float bubble algae'. Sand and gravel lifted from the bottom sifts out of the mat, while iron hydroxide accumulates on the underside of the floating mat.
- 'Float bubble algae' is found as large mats in the ponds. Portions breaking away and passing over the weirs is pulverized and returns to the pond bottom, probably to reform as 'mat bubble algae'.
- In terms of nutrients, the existing mat and float bubble periphyton in the polishing ponds have nitrogen available primarily as ammonia (0.5 mg/L N as NH₄), with a small amount of N as NO₃ (0.03 to 0.05 mg/L) and trace amounts of phosphate (0.1 mg/L PO₄; see Table 24, PP11 In data).

- Small populations of 'seep algae' remain along the upstream berm of Polishing Pond 12, in areas where water is seeping from the pond bottom from the Pond 11 area. This periphyton is clearly a filamentous species with no moss present. Nutrient concentrations were not measured in the vicinity of the this algae.
- A special interest is the filamentous algae growing on the remaining section of the peribasket in OWP. Large tough ropes of filamentous algae up to 5 m long have grown in the area where the Drainage Tunnel inflow maintains a relatively constant flow pattern. This massive growth of periphyton in OWP is encouraging, as the new perigrid can now be anticipated to be readily colonized by this algae.
- The OWP 'rope periphyton' is growing in the area of the drainage Tunnel input. This flow generally maintains a unidirectional flow, which may favour the growth of this form of periphyton. In addition, the primary form of N is nitrate, present at a concentration of 0.4 mg/L N as NO₃). The ammonia concentration in the D.T. water was less than 0.1 mg/L as N (Hach, determined in field), while trace amounts of PO₄ was measured, as observed in the polishing ponds.

<u>Summary</u>

• The field data on the periphyton biomass produced in the OWP and the results of the perigrid suggest that the OWP is a suitable area to focus on increasing biological productivity (Table 25, Schematic 2, Plates 1 and 2).

6.3 Nutrient Additions in Field

6.3.1 Polishing Pond 11 Small-Scale Study

With fertilizer additions based on the rates determined in the laboratory studies, both mini limnocorrals (96 L) and in Pond 11 with monitoring phosphate concentrations in the field.

The nutrient concentrations and general water chemistry were measured for PP11 in and out on the morning of July 8, 1996. At noon, 3.7 kg of 10-52-10 fertilizer was added in a 20 L slurry. At noon on July 9, 3.7 kg were added, on July 10, 2.8 kg and on July 11, 3.7 kg.

According to Plant Products (G.Neary, p.c.) the 10% N in the 10-52-10 fertilizer is 7.8 ammonia, 0.9 % nitrate and 1.3 % urea.

Phosphate, [N] as nitrate and [N] as ammonia were determined at 2 to 4 hr intervals during daylight hours. Small amounts of precipitates regularly developed during the ammonia tests, while nitrate tests were frequently unsuccessful due to formation of yellow colour, instead of the expected pink colour formation. Overall, phosphate concentrations are likely the most reliable results. All PP11 fertilizer experiment data are presented in Table 24.

The actual flows at PP11 in and out were measured once using a water collection system, a bucket and stopwatch. The water levels over these weirs were also periodically measured. These levels were used to estimate flow, using G. Neary's equation relating head with flow.

The changes in [phosphate], [N] as nitrate and [N] as ammonia in PP11 in and PP11 out are presented in Figures 20, 21 and 22. Water samples were saved in the event

that the Hach kit results can be compared to results produced by an analytical lab.

In Figure 22, N concentrations as ammonia at the inflow and outflow of PP11 are presented. As expected, N as ammonia concentrations increased upon addition of ammonia-containing fertilizer just below the inflow of PP11. N as ammonia concentrations reached as high as 1.2 mg/L. The N as ammonia concentrations in the PP11 inflow at a location just upstream of additions remained relatively constant over the course of the experiment, ranging from 0.45 to 0.7 mg/L, and averaging about 0.5 mg/L N.

In Figure 20, phosphate concentrations in PP11 in and out are plotted. As observed for ammonia, measured phosphate concentrations also increased following addition of fertilizer to the PP11 inflow. Phosphate concentrations reached as high as 1.3 mg/L as PO₄. Background (PP11 Inflow) concentrations remained around <1 to 0.3 mg/L, averaging about 0.1 mg/L.

The Hach nitrate tests were very unreliable during the experiment. Typically, following the three minute shaking period with the Nitraver 6 (Cadmium reduction step), transfer to clean tube and addition of the Nitraver 3 reagent, the sample turned a light to deep yellow, masking the pink to red colour indicative of the presence of nitrate. Addition of the Nitraver 3 alone also resulted in the yellow colour. However, occasionally the test worked and detectable nitrate could be measured. The results of the nitrate tests are shown in Figure 21.

Nitrate concentrations, when detected, ranged from 0.03 to 0.1 mg/L N-NO₃ in the PP11 outflow samples. The test worked only once for the PP11 in samples, and a 0.03 mg/L N-NO₃ was recorded. This suggests that upon addition of the 10-52-10 fertilizer, nitrate concentrations increased in PP11.

A model of the polishing ponds has been developed. This model simulates nutrient

concentrations in the polishing ponds, taking into account the volumes of the cells, the flow volumes, the background concentrations and the additions of phosphate. The program repeats calculations in iterations of 1 hour. The program assumes complete mixing of a fertilizer addition with the receiving pond's volume within an hour; in reality, the mixing process is probably not this rapid.

The model was run for ammonia and phosphate. The expected N-NH₄ concentrations in PP10, PP11, PP12 and PP13 are shown in Figure 23 upon addition of fertilizer (starting at hour 0) at the rate applied during the experiment, and at the flow volumes measured during the experiment. In addition, the actual concentrations measured in the field are also plotted in the graph.

The model was started 456 hours (19 days) prior to the addition of the first lot of fertilizer, since ammonia was already present in the inflows to PP10 prior to the experiment, and the model needed these 19 days to reach equilibrium with respect to ammonia concentrations throughout the PP10-PP13 system.

The match between predicted ammonia concentrations (red) and the measured ammonia concentrations determined during the field experiment (blue) is remarkable. Both the magnitude of ammonia concentrations match well, as well as undulations in concentrations due to the 24 hour time spans between successive additions of fertilizer. There appears from Figure 23 that the actual ammonia concentration increases were delayed, compared to the modeled concentration increases. This is likely due to actual mixing times exceeding modeled mixing times.

Overall, it appears that PP11's behaviour is closely simulated by the model. Given that similar ammonia concentrations were measured as modeled, it appears that ammonia uptake by algae or ammonia adsorption onto organics during the field experiment may have been negligible. This also indicates that the ammonia was well mixed in the estimated pond volume. Finally, although some doubt remains regarding the accuracy of the Hach ammonia kit (precipitate formation), it appears to be working adequately.

The model was also run for phosphate in the system, for comparison to measured phosphate concentrations in PP11 during the field experiment (Figure 24). The measured phosphate concentrations (blue) were much lower than those predicted by the model (red), although undulations relating to the fertilizer additions, and delays due to mixing, can be seen in the curve. This suggest that a substantial fraction of the phosphate added to PP11 was lost by, for example, adsorption onto algae and/or precipitation with other compounds, such that the Hach phosphate kit did not detect the phosphate present in solution.

Apparent loss of phosphate mass during the field experiment was anticipated. A second static field experiment was performed during the site visit in order to examine apparent losses of nutrients from the system. This results of the Mini-Limnocorral Experiment, is described in the next section.

6.3.2 Fate of Nutrients: Mini-Limnocorral Experiment

Mini-Limnocorrals (MLCs) were set up in PP11. These consisted of plastic bags containing 96 L of PP11 water added prior to addition of the large doses of fertilizer to PP11. All MLC fertilizer experimen data are presented in Table 26.

MLC-i was set up as a control. This container did not receive any fertilizer, nor was periphyton added. A does of 0.797 g of 10-52-10 fertilizer was added to MLC-ii and MLC-iii. A sample of float bubble algae was carefully added to the surface of MLC-iii such that the mat remained afloat over the course of the experiment. Nutrient concentrations were periodically measured in each MLC. The entire algal sample was recovered at the end of the experiment in order that its dry weight could be

78

determined.

The results of ammonia determinations in the MLCs are shown in Figure 25. In the control set-up, MLC-i, ammonia concentrations remained at background (0.5-0.6 mg/L N-NH₄). In MLC-ii, where fertilizer was added, the ammonia concentration stayed relatively constant at 1.7 to 1.8 mg/L N-NH₄ over the course of the experiment. A slight decrease in the ammonia concentration, to 1.4 mg/L N-NH₄ was measured in MLC-iii, the set-up where a clump of float bubble algae was added.

In a separate test ('dose check'), an identical dose of the fertilizer was added to distilled water, and diluted to the correct fertilizer dose:96 L ratio. This sample contained 1.2 mg/L N as ammonia. Since the background N (ammonia) concentration was 0.5 mg/L, the expected N as ammonia concentration in MLC-ii and MLC-iii was 1.7 mg/L, a perfect match with measured concentrations.

These results match the PP11 Fertilizer Experiment. Ammonia added to PP11 and the MLCs remained dissolved in the solutions. Despite formation of precipitates, the Hach ammonia test was functioning well.

The 'dose check' test indicated that the fertilizer dose added to MLC-ii and MLC-iii should yield a final concentration of 3.8 mg/L PO₄. In fact, PO₄ concentrations in MLC-ii and MLC-ii were 3.5 to 3.7 mg/L at the start of the experiment and after 20 hours (Figure 26). However, the phosphate concentration decreased to 1.8 to 1.9 mg/L after 55 hours, both in water only (MLC-ii) or in the presence of periphyton (MLC-iii). This indicates that the phosphate was initially present at the expected dose at the start of the MLC experiment, but was adsorbed by organics and was removed from the system, or had combined with compounds and was not detected by the Hach kit 35 hours later in the experiment (Table 27).

The MLC experiment's phosphate results also match well with the PP11 Fertilizer

experiment. A substantial fraction (\sim 70 %) of the phosphate 'disappeared' (no longer detected by Hach test) in the MLC experiment between hours 20 and 55. In the Field Fertilizer experiment, the peak phosphate concentration was 1.3 mg/L, while the modeled (expected) concentration for that fertilizer dose was 4 mg/L, a difference where the measured concentration was 67 % lower than the expected concentration.

Unfortunately, the Hach nitrate test did not function properly for most attempts, including during measurements of the MLC experiment (Figure 27). Only one observation can be made from the very limited results, namely, that the final nitrate concentration in MLC-iii (with periphyton) was lower than the nitrate concentration in MLC-iii (no periphyton), suggesting measurable nitrate uptake by the periphyton in MLC-iii.

				Am't Fert.	Amount of	[P]	[P]	[P]	[P]	[P]	
Fertilizer	Fertilizer	Reported		added to	P added	mg/L	mg/L	mg/L	mg/L	mg/L	% of P
Sample	Desription	N:P:K	Medium	1 L, mg	mg/L	1 Hour	24 Hours	1 Week	11 days	2 Weeks	Dissolved
1	Dearborn resin coated	unknown	Distilled Water	108	unknown	0.03	0.24	0.16	0.2	0.13	N.C.
	potassium nitrate pellets		Boomerang L.	135	unknown	0.03	0.03	0.03	N.R.	N.R.	N.C.
2	Dearborn resin coated pellets	unknown	Distilled Water	109	unknown	0.03	0.1	0.23	0.1	0.13	N.C.
			Boomerang L.	146	unknown	0.03	0.03	0.03	N.R.	N.R.	N.C.
3	Dearborn resin coated pellets	21-7-7	Distilled Water	1044	73	51	29	29	29	29	70
			Boomerang L.	321	22	7	8	8	N.R.	N.R.	36
4	Harvest Plus liquid fertilizer	14-4-6	Distilled Water	462	18	12	12	13	N.R.	N.R.	71
5	Harvest Plus liquid fertilizer	4-18-6	Distilled Water	610	110	88	91	95	N.R.	N.R.	86
6	Liquid molasses	unknown	Distilled Water	1200	unknown	0,75	0.72	0.52	N.R.	N.R.	N.C.
7	Calcium nitrate crystalline	15.5-0-0	Distilled Water	95	0	0.01	0.01	0.012	N.R.	N.R.	N.C.
8	Natural phosphate rock	?-12.8-?	Distilled Water	106	14	0.62	1.2	1.3	1.1	N.R.	10
	Code 30 fine sand										
9	Natural phosphate rock	?-12.1-?	Distilled Water	89	11	0,85	0,85	0.82	0.78	N.R.	8
	Code 31 powder										

103

104

0

0

0

14

24

0

0

0

18

16

0.07

N.R.

N.R.

11

16

0.1

0.03

0.03

N.R.

N.R.

N.R.

N.R.

N.R.

12

16

0.1

0.03

0.03

N.R.

N.R.

N.R.

N.R.

N.R.

133

69

N.A.

N.A.

N.A.

Table 21: Dissolution of Phosphorus from Various Fertilizer Types in Distilled Water and Boomerang Lake Water.

Distilled Water

Distilled Water

Distilled Water

Boomerang L.

Boomerang L.

15-13.1-15

10-22.7-10

10

11

Plant Products fertilizer, powder

Plant Products fertilizer, powder

Distilled Water (Control)

Boomerang Lake (Control)

New Boomerang lake (Control)

Table 22:	Dissolution of Nitroge	en from Various Fe	rtilizer Types in Dis	stilled Water and Bo	oomerang Lake Water

.

			<u> </u>	Am't Fert.	Amount of		[N]		[N]		[N]	[N]	[[N]	
Fertilizer	Fertilizer	Reported		added to	N		mg/L		mg/L		mg/L	mg/L	m	g/L	% of N
Sample	Desription	N:P:K	Medium	1 L, mg	added, mg/L		1 Hour	2	4 Hours		1 Week	11 days	<u> 2</u> W	eeks	Dissolved
1	Dearborn resin coated	unknown	Distilled Water	108	unknown	[N] as NO ₃ <	0.02	<	0.02		0.90	1.7	1	.7	N.C.
	potassium nitrate pellets					[N] as NH₄	0.19		0.19		0.56	0.37	0	37	
			Boomerang L.	135	unknown	[N] as NO ₃ <	0,16		1.8		21				N.C,
						[N] as NH₄	0.93		1.5		1.39				
2	Dearborn resin coated pellets	unknown	Distilled Water	109	unknown	[N] as NO ₃ <	0.02		0.045	<	0.02	1.1	1	.4	N.C.
1						[N] as NH ₄	0.19		0,19		0.46	1.6	2	2.3	
			Boomerang L.	146	unknown	[N] as NO ₃ $<$	0.12		0.14		9				N.C.
						[N] as NH₄	1.3		1.6		93				
3	Dearborn resin coated pellets	21-7-7	Distilled Water	1044	219	[N] as NO ₃ $<$	0.02	<	0.02	<	0.02	< 0.02	< 0	.02	38
						[N] as NH₄	9		28		37		(55	
			Boomerang L.	321	67	[N] as NO₃ <	0.12		0.13		0.17				152
					• • • •	[N] as NH ₄	65		102		74				445
4	Harvest Plus liquid fertilizer	14-4-6	Distilled Water	462	65	[N] as NO ₃ <	0	<	0.02	<	0.02				115
						[N] as NH4	37	<u>.</u>	46		/4				
5	Harvest Plus liquid fertilizer	4-18-6	Distilled Water	610	24	[N] as NO ₃ <	0.02	<	0.02	<	0.02				38
ļ			0.00	4000			9		9.3		9.29				NC
6	Liquid molasses	unknown	Distilled Water	1200	unknown		0.02	<	0.02	<	0.02				N.C.
		45.5.0.0		05	45		N.U.		9.3		9.29				101
	Calcium nitrate crystalline	15,5-0-0	Distilled Water	95	15		11		10		10.17				101
							1.56		00.1		1.39	- 0.02			N.C
8	Natural phosphate rock,	7-12.8-7	Distilled Water	105	Unknown	$[N]$ as $NU_3 <$	0.02	~	0.02	~	0.02	< 0,02			N.C.
<u> </u>	Code 30, fine sand		Polia Alle at Markan				0.37		0.02		0.19	0.00			NC
9	Natural phosphate rock,	2-12.1-7	Distilled vvater	89	UNKNOWN	INJ as NU ₃ <	0.02		0.02	`	0.02	< 0.02 0.46			N.C.
- 10	Code 31, powder	45 10 1 15	Distilled Mater	103	15		36		0.40		3.70	0.40			95
10	Plant Products fertilizer,	10-13,1-10	Distined water	105	15	$[N]$ as NU_3	3.0		3.0		10.94				20
	powder	10 00 7 40	Distilled Mater	104	10		80		9.3		10.04				256
11	Plant Products tertilizer	10-22.7-10	Distilled vvater	104	10	[N] as NU ₃	0.0		2.0		0.20				200
¥	powder		Chine Silfer of A.M. (many		0		19		9.3		9.29				NC
	Distilled Water (Control)		Distilled vvater	0	0	INJ as NU ₃	0.00		0.10		0.09				14.0.
	Decision - Labor (Cartan)						0.40		0.37		0.37				
	Boomerang Lake (Control)		Boomerang L.	U	U		0.11		0.13		0.00				N.C.
	New Deemonal (Center)		Reemorane I				١.۷		0.12		0.00				N.C.
	New Boomerang L.(Control)		Boomerang L.	U	U	[N] as NU₃			1.6		1 11				N.O.
ł						[เล] สุราชการ			0.1		1.11				

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Boojum Research Limited January 1997

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8 2

1996 Final Report For: ASARCO INC.

		BEFORE AD	DITION OF N	UTRIENTS	TREATMENT	ADDED	TARGETED		MEASURED	CONCENTRAT	IONS
	DATE STARTED: 21/7/96	[NO ₃ OLD]	[NH ₃ OLD]	[PO4 OLD]	1: N:P 10:1	NUTRIENTS	CONCENTR	ATIONS	[NO3 NEW]	[NH₃ NEW]	[PO4 NEW]
Culture	DESCRIPTION	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	2: N, 10 mg.L-1	2/8/1996	[NO ₃ NEW]	[PO₄ NEW]	mg.L ⁻¹	mg.L ⁻¹	mg L ⁻¹
		1/8/1996	1/8/1996	1/8/1996	3: [N],[P],10, 1 mg.L ^{.1}		mg.L ⁻¹	mg.L ⁻¹	7/8/96	7/8/96	7/8/96
A1	PP14 MAT BUBBLE	0.06	0.12	0.08	N:P 10:1	N-NO ₃	0.22		0.05	0.07	0.07
A2	PP14 MAT BUBBLE	0.13	0,13	0.08	N, 10 mg.L-1	N-NO3	9.86		6.39	0.07	0.09
A3	PP14 MAT BUBBLE	0,05	0.10	0.14	[N],[P],10, 1 mg.L ⁻¹	N-NO3+P-PO4	9.89	2.21	5.77	0.07	0.12
C1	PP12 SEEP ALGAE	0.05	0.10	0.11	N:P 10:1	N-NO3	0.39		0.04	0.07	0.07
C2	PP12 SEEP ALGAE	0.06	0.20	0.18	N, 10 mg.L-1	N-NO ₃	9.7 9		8.42	0.08	0.08
C3	PP12 SEEP ALGAE	0.05	0.11	0.14	[N],[P],10, 1 mg.L ⁻¹	N-NO3+P-PO4	9,89	2.21	5.27	0.08	0.07
D1	PP14 FLOAT BUBBLE	0.22	0.12	0.09	N:P 10:1	N-NO ₃	0.29		0.05	0.11	0.07
D2	PP14 FLOAT BUBBLE	0.32	0.12	0.10	N, 10 mg.L-1	N-NO3	9.88		8.63	0.08	0.08
D3	PP14 FLOAT BUBBLE	0.23	0.11	0.13	[N],[P],10, 1 mg.L ⁻¹	N-NO3+P-PO4	9.89	2.21	6.55	0.07	0.11
F 1	PP14 MAT BUBBLE PUREE	0.05	0.10	0.25	N:P 10:1	N-NO ₃	1.04		0.04	0.07	0.07
F2	PP14 MAT BUBBLE PUREE	0.05	0.09	0.25	N, 10 mg.L-1	N-NO ₃	9.91		7.81	0.07	0.07
F3	PP14 MAT BUBBLE PUREE	0.05	0.11	0.24	[N],[P],10, 1 mg.L ^{-t}	N-NO3+P-PO4	9.88	2.21	3.09	0.07	0.10
G1	PP14 FLOAT BUBBLE PUREE	0.53	0.43	0.12	N:P 10:1	P-PO₄	0.53	0.18	0.05	0.08	0.07
G2	PP14 FLOAT BUBBLE PUREE	1.30	0.22	0.13	N, 10 mg.L-1	N-NO ₃	9.77		9.09	0.07	0.07
G3	PP14 FLOAT BUBBLE PUREE	0.53	0.37	0.10	[N],[P],10, 1 mg.L ⁻¹	N-NO3+P-PO4	9.63	2.21	4.43	0.07	0.06
B1	OWP PER!	0.38	0.70	0.14	N:P 10:1	P-PO4	0.38	0.20	0.36	3.55	0.09
B2	OWP PERI	0.34	0.67	0.13	N, 10 mg.L-1	N-NO3	9.33		9.20	3.85	0.11
B3	OWP PERI	0,53	0.68	0.29	[N],[P],10, 1 mg.L ⁻¹	N-NO3+P-PO4	9.32	2.21	10.94	3.65	0,68
E1	BOOMERANG LAKE ALGAE	0.07	2.00	0.08	N:P 10:1	P-PO4	0.07	0.33	0.07	4.29	0.11
E2	BOOMERANG LAKE ALGAE	0.05	2.00	0.08	N, 10 mg.L-1	N-NO3	8.00		6.55	5.02	0.08
E3	BOOMERANG LAKE ALGAE	0.05	1.30	0.09	[N],[P],10, 1 mg.L ⁻¹	N-NO3+P-PO4	8,69	2.21	8.11	4.34	0.11
OWP-1	ORIENTAL WEST PIT	0.47	0.10	0.08	N:P 10:1	P-PO4	0.47	0.11	0.52	0.09	0.07
OWP-2	ORIENTAL WEST PIT	0.55	0.12	0.08	N, 10 mg.L-1	N-NO ₃	9.88		10.22	0.09	0.06
OWP-3	ORIENTAL WEST PIT	0.51	0.11	0.07	[N],[P],10, 1 mg.L ⁻¹	N-NO3+P-PO4	9.89	2.21	10.22	0.08	0.55
BL1	BOOMERANG LAKE 1	0.24	0.77	0.06	N:₽ 10:1	P-PO₄	0.24	0.17	0.25	0.56	0.17
BL2	BOOMERANG LAKE 2	0.24	0.78	0.09	N, 10 mg.L-1	N-NO ₃	9.22		10.09	0.48	0.07
BL3	BOOMERANG LAKE 3	0.24	0.73	0.07	[N],[P],10, 1 mg.L ⁻¹	N-NO3+P-PO4	9.27	2.21	7.71	0.52	3.11

Table 23: Treatments and Nutrient Concentrations in Buchans and South Bay Algal Cultures.

Table 24: PP11 Nutrient Exp't Data.

						PP1 ⁻	In				<u>.</u>					W.L.		Flow	Kg Fert
				Hours		[PO4	1	[N]		[N]	pН	ΤС	Cond	Em	[02]	(CM)		(l/s)	Added
Date	Days	Hr	Min	after start				as NO3	3	as NH	4								
08-Jul-96	0	9	8	-2,98		0.1													
08 - Jul-96	0	9	16	-2.85		0.1	<	0.01	Y	0.6	6.4	18	1365	110	8.04				
08-Jul-96	0	12	7	0															3.7
08-Jul-96	0	12	27	0.33															
08-Jul-96	0	13	15	1.13															
08-Jul-96	0	13	32	1.42															
08-Jul-96	0	15	2	2.92													2.2	6.78	
08-Jul-96	0	16	55	4.80															
08-Jul-96	0	19	14	7.12															
08-Jul-96	0	22	20	10.22															
09-Jul-96	1	8	36	20.48															
09-Jul-96	1	8	53	20.77		0.1			N.M.	0.45									
09-Jul-96	1	9	0	20.88															
09-Jul- 96	1	9	15	21.13	1														
09-Jul-96	1	9	30	21.38													2	5,88	
09-Jul-96	1	11	31	23.40															
09-Jul- 96	1	11	43	23.60															3.7
09-Jul-96	1	13	46	25.65	1														
09-Jul-96	1	16	18	28.18															
09-Jul-96	1	16	48	28.68	1	0.1			N.M.	0.45	6.7	18	1346	149			2.1	6.33	
09-Jul-96	1	21	35	33.47															
10-Jul-96	2	8	42	44.58															
10-Jul-96	2	11	30	47.38															
10-Jul-96	2	11	50	47.72															2.815
10-Jul-96	2	11	52	47.75		0.1		0.05		0.5	6.9	16	1209	143			2.5	8.22	
10-Jui-96	2	15	18	51.18	1														
10-Jul-96	2	18	43	54.60	<	0.1		0.1		0.5									
10-Jui-96	2	21	30	57.38															
11-Jul-96	3	8	54	68.78		0.2	<	0.01	Y	0.5							2.4	7.73	
11-Jui-96	3	9	10	69.05															
11-Jul-96	3	9	45	69.63															
11-Jul-96	3	10	5	69.97							6.9	17	1303	138					
11-Jui-96	3	12	11	72.07															3.7
11-Jul-96	3	12	13	72.10		0.1	<	0.01		0.5									
11-Jul-96	3	12	28	72.35															
11-Jul-96	3	15	10	75.05		0.3	<	0.01		0.6									
11-Jul-96	3	15	32	75.42	1												2.3	7.25	
11-Jul-96	3	16	54	76.78															
11-Jul-96	3	17	22	77.25	1														
11-Jul-96	з	17	44	77.62															
11-Jul-96	З	18	24	78.28															
11-Jul-96	З	18	45	78.63		0.1		0.03		0.7	7,1	21	1307	109			2.2	6.78	
12-Jul-96	4	11	40	95.55	1														
12-Jul-96	4	11	40	95.55															
12-Jul-96	4	19	30	103.38															
12-Jul-96	4	19	30	103.38															
12-Jul-96	4	19	30	103.38	1														
12-Jul-96	4	19	30	103.38															
13-Jul-96	5	12	0	119.88															
13-Jul-96	5	12	0	119.88	1														
13-Jul-96	5	12	0	119.88	ŀ														
13-Jul-96	5	12	0	119.88															

Table 24: PP11 Nutrient Exp't Data.

						PP11 Out													
				Hours	ĺ	[PO4]		[N]		[Nj	pН		тс	Cond	Em		[02]	W.L
Date	Days	Hr	Min	after start				as NO3		a	IS NH4								(cm)
08-Jul-96	0	9	8	-2.98															
08-Jul-96	0	9	16	-2.85															
08-Jul-96	0	12	7	0															
08-Jul-96	0	12	27	0.33		0.1	<	0.0	1 Y		0.4		6.64	17.4	1235		102		
96-Jul-96	Ō	13	15	1.13															
96-Jul-96	0	13	32	1.42															
08-Jul-96	0	15	2	2.92		0.1	<	0.0	IY		0.5								
	0	16	55	4 80		0.3			N	м	0.5		8 6 8	18.6	1264		137		
08-10-96	n	19	14	7 12		0.0			N I	M.	0.4		0.00	10.0	, 204				
08-Jul-96	õ	22	20	10.22		0.6			N.I	м.	0.6								
09-Jul-96	1	- 8	36	20.48		0.6	<	0.0	1 Y		0.7								
09-Jul-96	1	8	53	20.77															
09-Jul-96	1	9	0	20.88															
09-Jul-96	1	9	15	21.13															
09-Jul-96	1	9	30	21.38															
09-Jul-96	1	11	31	23.40		0.6			N.I	M.	0,6								
09-Jul-96	1	11	43	23.60															
09-Jul-96	1	13	46	25.65		0.6			N.I	М.	0.7								
09-Jul-96	1	16	18	28.18		0.6			N.I	И.	0.7		6.6	17.6	1291		122		
09-Jul-96	1	16	48	28.68															
09-Jul-96	1	21	35	33.47		0.9		0.0	5 tr		0.9								
10-Jul-96	2	8	42	44.58		0.9		0.0	9		0.75								
10-Jul-96	2	11	30	47.38		0.95		0.0	3		0.85		6.58	15.6	1264		177		
10-Jui-96	2	11	50	47.72															
10-Jul-96	2	11	52	47.75					7		4		7 46	164	1307		160		
10-Jul-96	2	15	10	51.10		0.05		0.0	1				7,40	10.4	1527		102		
	د م	10 01	40	57.38		13		0. n n	7		, 0.9								
11-bil-96	2	2, B	54	68 78		1.5		0.0	,		0.8								2.3
11-10-96	3	ä	10	69.05		0.9	<	0.0	ı v		1.2								
11-Jul-96	3	9	45	69.63		0.0	1	0.0	• •		••=		6.83	17.1	1289		155		
11-Jul-96	3	10	5	69.97															-
11-Jul-96	3	12	11	72.07															1
11-Jul-96	3	12	13	72.10															
11-Jul-96	3	12	28	72.35		0.7	<	0.0	i		0.9								
11-Jul-96	з	15	10	75.05															ţ
11-Jul-96	3	15	32	75.42		1	<	0.0	I		1.1								
11-Jul-96	З	16	54	76.78															
11-Jul-96	3	17	22	77.25															
11-Jui-96	З	17	44	77.62															
11-Jul-96	3	18	24	78.28		1.05	<	0.0			0.95		6,53	20.4	1333		96		
11-Jul-96	3	18	45	78.63															
12-Jul-96	4	11	40	95.55															
12-Jul-96	4	11	40	95.55															
12-Jul-96	4	19	30	103.38															
12-Jul-96	4	19	30	103.38															
12-Jul-96	4	19	30	103.38															
12-Jul-96	4	19	30	110 00															
13-JUI-96	5 E	12	0	110 88															Ì
13-10-00-90	5	12	n	119.88															
13-Jul-96	5	12	ō	119.88															

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Days installed (Jul 13-Sep 29)	78	days
Area of perigrid netting	391	m ²
Algal fresh biomass	0.5	cm ³ per cm ²
Wet volume of algae	1.955	m ³
Periphyton dry weight:wet volume	0.1	g.cm ⁻³
Dry weight of algae	0.196	t
Growth rate	6.41	g.m ⁻² netting.d ⁻¹
Zn content in periphyton	10,900	ug.g ⁻¹ (#5993)
Zn content of periphyton biomass	2.13	kg
If perigrid scaled up 19 x	40.5	kg
Potential Zinc removal rate	0.52	kg.d ⁻¹
OWP Zinc load from D.T.	11.4	kg.d ⁻¹
Zinc Removal	4.6	% of load

Table 25	: OWP	Perigrid	Zinc Removal	Performance	and	Scale-up
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Table 26: PP11 Nutrient Exp't Data.

[MLC i			MLC II				MLC iii			
				Hours	[PO4]	[N]	[N]	[PO4]	[N]		[N]	[PO4]	[N]		[N]
Date	Days	Hr	Min	after start		as NO3	as NH4		as NO3		as NH4		as NO3		as NH4
08-Jul-96	0	9	8	-2.98											
08-Jul-96	0	9	16	-2.85	0.1	0.01	0.6								
08-Jul-96	0	12	7	0											
08-Jul-96	0	12	27	0.33											
08-Jul-96	0	13	15	1.13				3.5	0.01	Y	1.8				
08-Jul-96	0	13	32	1.42				1				3.7	0.01	Y	1.8
08-Jul-96	0	15	2	2.92											
08-Jul-96	0	16	55	4.80											
08-Jul-96	0	19	14	7.12											
08-Jul-96	0	22	20	10.22											i
09-Jul-96	1	8	36	20.48											Ì
09-Jul-96	1	8	53	20.77											
09-Jul-96	1	9	0	20.88	0.1	N.M.	0.5								
09-Jul-96	1	9	15	21.13				3.5		N.M	1.7				1
09-Jul-96	1	9	30	21.38								3.7		N.M	1.5
09-Jul-96	1	11	31	23.40											;
09-Jul-96	1	11	43	23.60				}							
09-Jul-96	1	13	46	25.65	ł										
09-Jul-96	1	16	18	28.18											
09-Jul-96	1	16	48	28.68			-								
09-Jul-96	1	21	35	33.47											
10-Jul-96	2	8	42	44.58											
10-Jul-96	2	11	30	47.38											
10-Jul-96	2	11	50	47.72											
10-J บ -96	2	11	52	47.75											
10-Jul-96	2	15	18	51.18											
10-Jul-96	2	18	43	54.60	0.2	0.09	0.5	1.9	0.14		1.7	1.8	0.12		1.4
10-Jul-96	2	21	30	57.38											
11-Jul-96	3	8	54	68.78	1						1				ľ
11-Jul-96	3	9	10	69.05											
11-Jul-96	3	9	45	69.63											
11-Jul-96	3	10	5	69.97											
11-Jul-96	3	12	11	72.07											
11-Jul-96	3	12	13	72.10											
11-Jul-96	3	12	28	72.35							Í				2
11-Jul-96	3	15	10	75.05											
11-Jul-96	3	15	32	75.42											
11-Jul-96	3	16	54	76.78	1.0		0.6	* 7							
11-Jul-96	3	17	22	77.25				1.7			1.9	4 7			
11-JUI-96	3	17	44	77.02								1.7			1.30 /
	3	10	24	70.20							ĺ				
11-JUI-96	3	18	45	78.63											
12-JUI-96	4	11	40	95.55											
12-Jul-96	4	11	40	90.55											
12-Jul-96	4	19	30	103.38											
12-Jul-96	4	19	30	103.38							ļ				
12-Jul-96	4	19	30	103.38											
12-001-96	4	19	30	110 50											
13-JUI-96	5 -	12	0	110 90											
12-00-90	ວ ະ	12	0	110.00							1				
13-00-96	5 E	12	0	110.00											
13-JUI-96	5	12	<u> </u>	119.00											ل

		# 5999	Equiv.	Equiv.
Element	M.W., g	total ug on F.P. from 0.1 L sample	mg/L	uM/L
Al	27	2.5	0.025	0.93
Ва	137	2.4	0.024	0.17
Са	40	339	3.4	85
Cd	112	6.6	0.066	0.59
Co	59	0.3	<0.003	<0.05
Cu	64	3.1	0.031	0.49
Fe	56	55.1	0.55	9.9
Mg	24	4.6	0.046	1.9
Mn	55	28.3	0.28	5.2
Na	23	17.2	0.17	7.5
Р	31	544	5.4	176
S	32	2.77	0.028	0,86
Zn	65	2300	23	352

Table 27. WILLIALITITIOCOLLAT III FILLEL FAPEL ALIAIYS	Table	27: Mini-Limnocorra	ıl iii Filter F	² aper Analy	sis
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Boojum Research Limited January 1997









Schematic 2: OWP Perigrid Construction and Possible Scale-up.



Plate 1: Overview of Perigrid structure during installation in OWP, July 13, 1996.



Plate 2: Installed Perigrid supporting periphyton population adjacent to Drainage Tunnel inflow, August 1, 1996.

Boojum Research Limited January 1997 1996 Final Report For: ASARCO INC.
7.0 POLISHING POND PERFORMANCE AND SCALE-UP

7.1 Fate of Nutrient Additions: Mass Balance Calculations

The ammonia and phosphate data collected during the PP11 Fertilizer Experiment was used to estimate a mass balance of these nutrients during the experiment. Table 27 presents the data and estimates made to perform the mass balance. Data is shaded in grey, while interpolated and calculated values are not shaded.

In Figure 28, a mass balance for ammonia is presented. The cumulative mass of N as ammonia added to PP11 (PP11 In, '+') is plotted versus hours after the experiment was started. The cumulative mass of N as ammonia is constantly increasing, as ammonia was present in PP11 inflow water. Big jumps in the cumulative mass occur every 24 hours when fertilizer was added.

The PP11 out cumulative mass of N as ammonia (squares) is based on measured N as ammonia concentrations at the outflow, multiplied by the flow measured leaving PP11.

Overall, the slope of the expected mass of ammonia entering the pond closely parallels the measured mass of ammonia leaving PP11. The mass of ammonia leaving PP11 is delayed with respect to the mass entering PP11. This is most likely due to the residence time of water in PP11. In 1995, the results of a Rhodamine tracer experiment conducted in PP11 suggested that the residence time of water in PP11 in 18 hours. In Figure 28, the slope of the PP11 out ammonia mass is delayed by approximately 17 hours with respect to the PP11 In ammonia balance, again a very close match between data sets and projections.

In Figure 29, the results of the phosphate mass balance for PP11 are presented. This presentation indicates that either phosphate is remaining in PP11, or that phosphate has reacted with other compounds in PP11 pond water such that the Hach phosphate

kit does not detect it.

7.2 Large-Scale Study in Polishing Ponds 14 to 17

A field study was conducted on August 21, 1996, between 8 am and 6 pm, examining zinc concentrations in Polishing Ponds 11 to 13 following addition of a large dose of fertilizer (Figure 30). Unfortunately, given the results of phosphate consumption by algal biomass in the laboratory experiments, the field experiment was not conducted over a sufficiently long period in order to detect zinc concentration changes induced by the phosphate addition.

7.3 Drainage Tunnel-OWP-OEP-Polishing Pond Mass Balance Modelling

The model is based on the mass equation. This model assumes that the added fertilizer dissolves and mixes immediately. For one time step (all simulations were made using 1 hour time step) for each "vessel" (OWP, OEP, PP10, PP11, PP12, PP13), the mass and the new concentration is calculated. The mass consists of the following components:

- (1) existing mass = the concentration multiplied by the volume.
- (2) mass coming in = flow in multiplied by the concentration and by time step.
- (3) mass leaving the "vessel" = flow out multiplied by the concentration and by time step.
- (4) mass consumed by algae = rate multiplied by volume and by time step.

Then the new mass is calculated:

new mass = mass existing + mass in - mass out - mass eaten

and new concentration in the "vessel"

new concentration = new mass/volume

The program does this calculation for each "vessel" in this same time step and repeats so many time steps as required by user.

As input data, the following parameters have to be prepared:

- the initial concentration in each "vessel"
- rate of consumption of the nutrient (P or N) by algae
- the volume of each "vessel"
- the flows between the "vessels"
- the time intervals and rates, when and how much fertilizer is added to each "vessel"

The results (mass, concentration) are stored in ASCII format. The examples of the input parameters and output results are given below.

Model#1 - 1994 (Figure 31)

Pool 10 - Pool 13

June 24 - September 8, PP10 addition of 350 g of fertilizer /day September 9 - September 26, PP13 addition of 350 g of fertilizer/day September 27 - October 31, PP12 addition of 350 g of fertilizer/day

Model #5 (Figure 32)

for 4 days addition of 3700 g of fertilizer/day to PP11

According to Boojum's Lab Experiment 100 g of 10-52-10 fertilizer converts to 77.03 g of PO_4 or 25.12 g of P So: 350 g = 269.6 g of PO_4 or 87.9 g of P 3700 g = 2850 g of PO_4

P MODEL	# 1			
Calculation	time:	1441 hours		
Initial conce	entration:			
	DT GW OWP OEP PP10 PP11 PP12 PP13	0.0 mg/L 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	ground wate	ər
Rate of P c	onsumption b	y algae:	0.018 mg/L	/hour
Volumes:	OWP	23,225 m³	(area 4645 i	m² x 5 m thermocline)
	OEP PP10 PP11 PP12 PP13	48,775 272 1,138 1,848 2,693	(area 19510) x 2.5)
Flows:	DT GW OWP OEP PP10 PP11 PP12 PP13	29.52 m ³ /h 39.312 29.52 68.832 26.156 26.156 26.156 26.156	= 8.2 L/s = 10.92 = 8.2 = 19.12 (8 38 % of OE	2 .2 + 10.92) P flow, 62% goes to PP14
FROM LAB	EXPERIMENT	Γ: 15% of 1	0-52-10 fertil	lizer converts to P
Addition of	P: OWP PP10 PP11 PP12 PP13	5000 g/day 50 g/day 150 g/day 250 g/day 400 g/day	approx.	30 kg of fertilizer 0.3 0.9 1.5 2.4

Figure 33 shows the results for one day. All phosphate is used by algae, so the process repeats every day.

P MODEL # 2

Calculation 1	ime:	1441 hours		
Initial conce	ntration: DT GW OWP OEP PP10 PP11 PP12 PP13	0.0 mg/L 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	ground wate	ər
Rate of P co	nsumption by	y algae:	0.009 mg/L	/hour
Volumes:	OWP OEP PP10 PP11 PP12 PP13	23225 m ³ 48775 272 1138 1848 2693	(area 4645 ((area 19510	m ² x 5 m thermocline)) x 2.5)
Flows:	DT GW OWP OEP PP10 PP11 PP12 PP13	29.52 m ³ /h 39.312 29.52 68.832 26.156 26.156 26.156 26.156 26.156	= 8.2 L/s = 10.92 = 8.2 = 19.12 (8 38 % of OE	2 .2 + 10.92) P flow, 62% goes to PP14
FROM LAB	EXPERIMENT	: 15% of 10	0-52-10 ferti	lizer converts to P
Addition of I	P: OWP	5000 g/day	approx.	30 kg of fertilizer

OWP	5000 g/day	approx.	30 kg of fertilize
PP10	50 g/day		0.3
PP11	150 g/day		0.9
PP12	250 g/day		1.5
PP13	400 g/day		2.4

Figure 34 shows the results for one day. All phosphate is used by algae, so the process repeats every day.

N MODEL # 1

Calculation time:	1441 hours	
Initial concentration: DT GW OWP OEP PP10 PP11 PP12 PP13	0.0 mg/L 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	ground water
Rate of N consumpti	on by algae:	0.041 mg/L/hour
Volumes: OWP OEP PP10 PP11 PP12 PP13	23225 m ³ 48775 272 1138 1848 2693	(area 4645 m ² x 5 m thermocline) (area 19510 x 2.5)
Flows: DT GW OWP OEP PP10 PP11 PP12 PP13	29.52 m ³ /h 39.312 29.52 68.832 26.156 26.156 26.156 26.156	= 8.2 L/s = 10.92 = 8.2 = 19.12 (8.2 + 10.92) 38 % of OEP flow, 62% goes to PP14
FROM LAB EXPERIM	ENT: 10% of 1	0-52-10 fertilizer converts to N
Addition of N (Calcu OWP PP10 PP11 PP12 PP13 From Figure 35, it ca	lated from amoun 3000 g/day 30 g/day 90 g/day 150 g/day 240 g/day	It of fertilizer added in P models 1 & 2):

N MODEL # 2

Calculation t	ime:	1441 hours	
Initial conce	ntration: DT GW OWP OEP PP10 PP11 PP12 PP13	0.0 mg/L 0.0 0.0 0.0 0.0 0.0 0.0 0.0 0.0	ground water
Rate of N co	onsumption b	y algae:	0.002 mg/L/hour
Volumes:	OWP OEP PP10 PP11 PP12 PP13	23225 m ³ 48775 272 1138 1848 2693	(area 4645 m ² x 5 m thermocline) (area 19510 x 2.5)
Flows:	DT GW OWP OEP PP10 PP11 PP12 PP13	29.52 m ³ /h 39.312 29.52 68.832 26.156 26.156 26.156 26.156	= 8.2 L/s = 10.92 = 8.2 = 19.12 (8.2 + 10.92) 38 % of OEP flow, 62% goes to PP14
FROM LAB	EXPERIMENT	: 10% of 10	0-52-10 fertilizer converts to N
Addition of I	N (Calculated OWP PP10 PP11 PP12 PP13	from amoun 3000 g/day 30 g/day 90 g/day 150 g/day 240 g/day	t of fertilizer added in P models 1 & 2):
From Figure	36, it can be	seen that al	I N is consumed in about 4-5 hours.

7.4 Polishing Pond System Performance - 1996

Long term monitoring and performance data are presented in Figures 37 - 43 and Table 29 for the following:

- OEP weir and Polishing Pond system effluent seasonal zinc loads.
- PP10 and PP13 seasonal zinc loads.
- PP14 and PP17 seasonal zinc loads.
- Polishing Pond system seasonal zinc removal performance.
- OEP weir and Polishing Pond system final effluent seasonal pH.
- OEP weir and Polishing Pond system final effluent seasonal zinc concentrations.
- OEP weir and Polishing Pond final effluent seasonal zinc concentrations, by year.
- Iron and zinc concentrations in OEP with depth, 1993 to 1996.

Table 28: Mass Balance of Phosphate and Ammonia in PP11 tertilizer Experiment, Buchans.

						PF	P11 in		W.L.		Flow	Kg Fert	Kg PO4	Kg N-NH	44 r	ng PO4	Cumulative	mg N-NH4	Cumulative	PP11 Out				mg PO4	Cumulative	mg N-NH4	Cumulative	PP in in
					Hours	(Բ	² O4]	{N]	(CM)		(l/s)	Added	Added	Added	e	- entering	mg PO4	entering	mg N-NH4	[PO4]		[N]	W.L.	exiting	mg PO4	exiting	mo N-NH4	Smoothed
Date	D	ays H	١r	Min	after start		Data	as NH	4						F	PP11	ent.PP11	PP11	ent.PP11		Data	as NH4	(cm)	PP11	exit PP11	PP11	exit PP11	
08-Ju	-96	0	9	8	-2.98		0.1						<u></u>							I			<u> </u>					
08-Ju	-96	o	9	16	-2.85		01 * Y	6.0																				
08-Ju	-96	0	12	7	0	[0.1	0.525	;		6.78					٥	0	0	0					0	a	0	0	•
08-Ju	-96	0	12	27	0,33	1	0.1	0.525	5		6.78	3.	2.570	39 0.28	86	2571204	2571203.6	292871	292871		e		1	A14	814	3254	3254	8001
08-Ju	-96	0	13	15	1.13		0.1	0.525	5		6.78					1953	2573156.2	10251	303123	0 1		0.45		1953	2766	8787	12041	30364
08-Ju	-96	ō	13	32	1.42		0.1	0.525	5		6.78					692	2573847.8	3631	306753	0.1		0.45		802	3459	2112	15153	37830
08-Ju	-96	0	15	2	2.92		0.1	0.525	5	2.2	6.78					3663	2577510.6	19230	325083	in the second			į	3663	7121	18314	22467	37030
08-Ju	-96	0	16	55	4.80		0.1	0.525	5		6.331					4293	2581803.2	22536	348519			0.5	Į.	12878	10008	21463	54030	108178
08-Ju	-96	ō	19	14	7.12		0.1	0.525	5		6.331					5280	2587083 5	27721	378241			T 4		21121	41110	21103	76061	100040
08-Ju	-96	0	22	20	10.22		0.1	0.525	5		6 331					7065	2594149 1	37005	413335					47304	83543	40204	119445	130042
09	-96	1	8	36	20.48	ļ	0.1	0.525	Ś		6 331					23400	2817549.3	122851	536186					140401	222045	42,394	080047	2/2024
09-Ju	-96	1	8	53	20.77		, i se				6.331					545	2618195.1	2008	530000	0.6		0.75	8	2975	2007780	103001	206447	340903 EE4E40
09-Ju	-95	1	9		20.88	P	0.1	0 45		******	6 331					266	2618461	1107	540000	0.0		0.75		1505	227703	4043	207/090	557005
09- ku	-96	1	9	15	21.13	ļ	0.1	0.45	, ,		6 331					570	2610030.8	2564	540200	0.0		0.75		2410	229303	13/344	203004	55/005
09-10	-96	1	9	30	21.38	1	0.1	0.45		2	5 88					520	2013030.0	1024	542033	0.0		0.75		2413	232004	42/4	295356	504341
09-34	-96	1	13	31	23 40	1	0.1	0.45	, ,	-	6 103					4431	2013000	10027	565177	0.5		0.75	2	0170	230910	3909	291321	5/101/
09-10	.96	1	11	43	23.60		0.1	0.45			6 103	3	2 5 70	30 0.29		2570820	E104910.0	200577	956710				8	20000	202302	20000	323910	624669
09-10	-00	1	12	46	25.65		0.1	0.45	, ,		5 103		2.570	59 0.20	00	2370028	5100000 A	290317	033749	0.0		0.00 44	¥	2030	200190	2000	320/00	630210
00-10		÷	16	18	28.00		0.1	0.45			6 103					5509	E004000.0	20201	070010) }	27022	202220	31020	300292	084933
09-10	LOG	÷	16	48	20.10				, 		6.103					1120	5204008,2	20040 5104	901001	A 75	S		8	33394	323614	38959	397251	752603
. 09-Ju	 L.QS	4	21	35	20.00	80000 1	869600000000 A 1	0 475	\$\$\$\$\$\$\$ \$	800 799 780	7 971					10501	5200027.9	J124 E0476	005000	0.75		U.8	ŝ	8540	334154	9109	406360	/65954
0 10-ki	1.06	,	- I A	42	44 59		0.1	0.475	,		7.271					20100	5210049	100004	1102884	48			ĺ.	112091	440044	112091	519051	893688
	1.04			20	47.00		V-1	0.475	-		7.074					23100	5247040.0	130224	1103004			444	ţ.	201098	/05/42	218248	737239	1190545
10-00	1.08	~		50	47,30		0.1	0.475	-		7.271			05 0.040		1329	3234978.2	34615	1130099		7.33 223		\$	69630	776372	62300	/99599	1265316
10-50	-90	<u>د</u>	11	50	47.72			0.475			1.21	2.01	1.80000	05 0.219	57	1900400	7211431.3	223/15	1302414	0.975		0.925		8507	/866/9	80/1	807670	1274217
10-10	lor	2	15	18	47.73 51 th	*****	09502200000 0-1				7 072					2054	7211029.9	493	1302907	0.975		0.925	\$	961	/8/841	912	808582	12/5107
10-10		5	18	43	54.60				, 		7.873					0004	7021100.0	49271	14121/5					90043	886363	98543	90/125	1305790
10-60		2	24	20	57.38	N	2022))) 0.4				7.273					3000	7231190.0	99042	1401210	0.8			ŝ	93161	9/9545	98064	1005190	1456025
10-00		2	21 0	50	07.30 69.78		u. 1	0.5			1.413					1909	7239179.3	39343	1501154		******	****	8 200000	103853	1063397	/1898	1077088	1532354
11-04	1.06	3	0	10	00.70	PR	1867 IS. 1883 IS. 1883				7.13					03437	/ 3020 10.3	106093	1009/4/	1.1		1.05		8 34 8905	1432302	333045	1410133	1836777
11-06	1-340 L.GR	3	а С	10	60.63	1 2	1.13 \ 15	0.3	2		7.49					10/9	7303090	3393	16653342						1436773	8628	1418761	1843898
11-10	0.00	~		-0	03.03			0.5			7.48					2309	7300004.3	/ / 004	16/1200	0.8		1.05		12563	1451356	16515	1435276	1559475
44.4	1-940 I AR	3	10		70.97		. 10	0.5	3		7.49	-				1348	/30/402.4	4494	16/5/00	0.8		1.05		7190	1458546	9437	1444713	1568377
11-50	1.00	3	12	11	72.07	kan	ר ז. בייגע אינע אינע	0.0 202000000			7.49	э.	2.570	39 0,28	30	20/8883	9586285./	316911	1992011	0.8		1.05		45298	1503844	59453	1504166	1924455
11-30	1-90	3	12	13	72.10	10000	*********		•••••		7.49					90	9886375.6	449	1993060	0.8		1.05	*******	∞	1504583	944	1505110	1925345
11-30	-90	3	12	20	72.35		0.2	0.53			7.49					1348	9887723,8	3707	1996768		2.33.2		*****	× 4719	1509281	6067	1511177	1932021
11-30	1-940	3	15	10	75.05	10000	**********				7.49					21540	9909553.8	43680	2040448	0.85		1		61880 **	1571161	72800	1583977	2004121 .
11-34	1-160 L 0.0	3	15	32	/5.42		0.2	0.65	• \$\$\$\$\$\$ •		7.25					1914	9911478	6221	2046669		a Mili	anin in St		© 9571	1580732	10528	1594505	2013913
11-34	⊷¥00 Loo	3	10	54	/6.78		0.2	0.65	> -		7.017					6905	9918382.6	22440	2069109	1.025		0.975		35386	1616118	33660	1628165	2050408
11-Ju	⊩916j	3	17	22	11.25		0.2	0.65	5		7.017					2358	9920740.2	7662	2076771	1.025		0.975		12083	1626201	11494	1639659	2062870
11-Ju	1-96	3	17	44	77.62		0.2	0.65	5		7.017					1852	9922592.7	6020	2082792	1.025		0.975		9494 ***	1637695	9031	1648689	2072551
11-Ju	1-96	3	18	24	78.28		0.2	0.65	5 *********	******	7.017					3368	9925960.8	10946	2093738					8 17683	1655378	15998	1554688	2090464
11-34	1-96	3	18	45	78.63	E.388	0.1			22	6.78					855	9926815.5	i 5983	2099721	1.05		0.95		8974	1564352	5119	1672807	2099810

		<u> </u>	Zinc					Iron	<u> </u>	
			(mg/L)					(mg/L)		
Depth	Apr 17,93	Apr 12,95	Oct 10,95	May 10,96	Jun 18,96	Apr-17-93	Apr-12-95	Oct-10-95	May 10,96	Jun 18,96
weir	18.4		13.1	13.5	13.8	45.8		0.1	ND	ND
2m	18.3	15.4				41.0	3.9			
3 m			16.7					1.2		F
4m	22.7				15.7	29.2				45.1
6m	23.8					53.6				
8m	24.9				14.3	54.7				51.3
10m	25.7	19.5	17.7	15.4	14.8	49.0	10.6	7.4	43.3	50.9
12m	21.1			15.4	15.9	59.8			49.9	53.1
14m	24.8			16.3	16.6	56.2			51.9	56.4
16m	26.9					70.9				
18m	27.7			16.6	17.6	76.4			53.8	58.4
20 m	28.1	20.2	19.2			188.0	6.4	30.8		

Table 29: Water Quality Data for OEP Profile Water Samples, 1993 - 1996

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Fig. 35: N Model#1, Concentration of N OWP, PP10, PP11, PP12, PP13











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8.0 GEOCHEMICAL ASSESSMENTS OF OLD BUCHANS VALLEY SEEPAGES

The primary nutrient and chemistry data used in mass balance and nutrient status assessments are presented in the attached tables.

A overview of the Buchans areas is presented in Map 1. Sampling locations in the Old Buchans Valley drainage area are presented in Map 2.

The report by R.O. Van Everdingen (December 28, 1996), "ASARCO-Buchans. The Valley Seeps, 1995/1996" is attached. The report by J. Gerits (January, 1997), "Valley Seepages at Buchans" is also attached.

	PO		PO	PO	PO	BO	PO.	BO	Pio.	DO	7
	mol ⁻¹	mal ⁻¹	r ∪4 mal ⁻¹	r ∪4 ma i -1	FU4	r∪4 ma [^1	FU4	ru ₄	FU4		1
	04 101 00	05 UL01	06 Amr 02	16 M-++ 03	1119.L		Ing.L	nig.L	mg.L	mg.L	ţ
	01-30-90	02-301-91	oo-Abi-aa	to-may-95	14-Jun-95	21 -re D-96	09-101-96	15-301-96	09-101-96	13-Aug-96	
	EPI	EĐI	EPI	EDI	MDS	MDS	Hach	Hach	MDe	MDS	
Drainago Tunnol		-31	-0.18		<0.19	-0.19	0.10	-0.1	-0.48	MD3	-
		~3.1	~0.10	-0.19	NU. 10	SU.10	-0.12	<0.1	<0.18	-0.24	
OWP Battan		-0.1	<0.10	~0.10			NU. 1	NO.1	NU. 10	<0.31	
	-0.03		~0.10	<0.10				-0.4	-0.40	<0.31	
	<0,03		\$0.10			0.40		<u.1< td=""><td><0.18</td><td><0.31</td><td></td></u.1<>	<0.18	<0.31	
	-0.02		0.09			<0.18					
	<0.03	-24	0.20		-0.40	<0.18		-0.4		<0.31	
	<0.03	<3.1			<0,18	<0.18		<0.1	<0.18		
PP11 IN						<0.18	0.1	<0.1	<0.18		
PP13 out							0.1	<0.1	<0.18		
PP17 out			·····			<0.18	0.15	<0.1	<0.18		
	1										
	N-NO ₃	N-NO ₃	N-NO ₃	N-NO ₃	N-NO ₃	N-NO ₃	N-NO ₃	N-NO ₃	N-NO3	N-NH₄	N-NH₄
	mg.L"	mg.L	mg.L	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹
	01-Jul-90	05-Jul-91	06-Apr-93	16-May-93	15-Jun-95	21-Feb-96	09-Jul-96	15-Jul-96	13-Aug-96	09-Jul-96	15-Jul-96
							Hach	Hach		4	
	1									Hach	Hach
Drainage Tunnel	EPL EPL	EPL	EPL	EPL	MDS	MDS	Field	Lab	MDS	Hach Field	Hach Lab
-		EPL 2.27	EPL 1.07	EPL	MDS 0.94	MDS 0.8	Field 0.4	Lab 0.5	MDS	Hach Field <0.1	Hach Lab 0.2
OWP Surface		EPL 2.27 <0.05	EPL 1.07 <0.03	EPL 0.14	MDS 0.94	MDS 0.8	Field 0.4 0.12	Lab 0.5 0.28	MDS 0.36	Hach Field <0.1 0.3	Hach Lab 0.2 0.3
OWP Surface OWP Bottom		EPL 2.27 <0.05	EPL 1.07 <0.03 <0.03	0.14 <0.03	MDS 0.94	MDS 0.8	Field 0.4 0.12	Lab 0.5 0.28	MDS 0.36 <0.05	Hach Field <0.1 0.3	Hach Lab 0.2 0.3
OWP Surface OWP Bottom OEP Surface	<0.01	EPL 2.27 <0.05	EPL 1.07 <0.03 <0.03 <0.03	0.14 <0.03	MDS 0.94	MDS 0.8	Field 0.4 0.12	Lab 0.5 0.28 0.2	MDS 0.36 <0.05 0.2	Hach Field <0.1 0.3	Hach Lab 0.2 0.3 0.4
OWP Surface OWP Bottom OEP Surface OEP Middle	<0.01	EPL 2.27 <0.05	EPL 1.07 <0.03 <0.03 <0.03	0.14 <0.03	MDS 0.94	MDS 0.8 <0.03	Field 0.4 0.12	Lab 0.5 0.28 0.2	MDS 0.36 <0.05 0.2	Hach Field <0.1 0.3	Hach Lab 0.2 0.3 0.4
OWP Surface OWP Bottom OEP Surface OEP Middle OEP Bottom	<0.01 <0.01	EPL 2.27 <0.05	EPL 1.07 <0.03 <0.03 <0.03 <0.03	 0.14 <0.03	MDS 0.94	MDS 0.8 <0.03 <0.03	Field 0.4 0.12	Lab 0.5 0.28 0.2	MDS 0.36 <0.05 0.2 <0.05	Hach Field <0.1 0.3	Hach Lab 0.2 0.3 0.4
OWP Surface OWP Bottom OEP Surface OEP Middle OEP Bottom OEP outflow	<0.01 <0.01 <0.01	EPL 2.27 <0.05	EPL 1.07 <0.03 <0.03 <0.03 <0.03	0.14 <0.03	MDS 0.94 0.35	MDS 0.8 <0.03 <0.03 0.23	Field 0.4 0.12	Lab 0.5 0.28 0.2 0.2	MDS 0.36 <0.05 0.2 <0.05	Hach Field <0.1 0.3	Hach Lab 0.2 0.3 0.4 0.2
OWP Surface OWP Bottom OEP Surface OEP Middle OEP Bottom OEP outflow PP11 In	<0.01 <0.01 <0.01	EPL 2.27 <0.05	EPL 1.07 <0.03 <0.03 <0.03 <0.03	0.14 <0.03	MDS 0.94 0.35	MDS 0.8 <0.03 <0.03 0.23 <0.03	Field 0.4 0.12	Lab 0.5 0.28 0.2 0.2	MDS 0.36 <0.05 0.2 <0.05	Hach Field <0.1 0.3 0.6	Hach Lab 0.2 0.3 0.4 0.2 0.2 0.5
OWP Surface OWP Bottom OEP Surface OEP Middle OEP Bottom OEP outflow PP11 In PP13 out	<0.01 <0.01 <0.01	EPL 2.27 <0.05	EPL 1.07 <0.03 <0.03 <0.03 <0.03	0.14 <0.03	MDS 0.94 0.35	MDS 0.8 <0.03 <0.03 0.23 <0.03	Field 0.4 0.12 <0.01 <0.01	Lab 0.5 0.28 0.2 0.18 0.16 0.04	MDS 0.36 <0.05 0.2 <0.05	Hach Field <0.1 0.3 0.6 0.5	Hach Lab 0.2 0.3 0.4 0.2 0.2 0.5 0.2

Table 30: PO₄, N as NO₃ and N as NH₄ Concentrations in OWP, OEP and Polishing Ponds, July 1, 1990 to August 13, 1996.

	Assay No.	pН	Cond.	Acidity	Alkalinity	Diss. Zn		Diss .Iron		Diss. Mn	Diss. Ca	Diss. Mg	Diss. Na
			uS.cm	mg.L ¹	mg L ⁻¹	mg.L ⁻¹	mg L ⁻¹	mg.L ⁻¹					
						AAS	ICAP	AAS	ICAP	ICAP	ICAP	ICAP	ICAP
Drainage Tunnel													
OWP Surface)												
OWP 7 m	1												
OEP Surface	;												
OEP 11 m	1822	6.4	1400				20		1.1	6.5	240	30	111
OEP bottom	1824	6.4	1400				24		8.6	8.3	292	37	149
OEP outflow	1825	6.9					15		<0.01	6.3	231	30	116
PP11 In	1												
PP11 out	[
PP13 Out PP17 out	[L												
								<i></i>				<u> </u>	
<u> </u>	TDS	SO.	SiO	НСО	TOC	CI	ור						
		~ 1 *			100	01							
	mg.L	g.L	mg.L	mg.L	mg.L	mg.L	4						
			ICAP										
Dialinage Tunnel	1						11						
OVVF Sunace	•												
	3												
OWP 7 m) 1												
OWP 7 m OEP Surface OEP 11 m	3 1 2	732	8.1	170		222							
OWP 7 m OEP Surface OEP 11 m OEP bottom	3 1 3 1	732 900	8.1 9 4	170 188		232							
OWP 7 m OEP Surface OEP 11 m OEP bottom OEP outflow	€ 1 € 1 1	732 900 726	8.1 9.4 6.6	170 188 157		232 256 128							
OWP 7 m OEP Surface OEP 11 m OEP bottom OEP outflow PP11 In	9 1 9 1 1	732 900 726	8.1 9.4 6.6	170 188 157		232 256 128							
OWP 7 m OEP Surface OEP 11 m OEP bottom OEP outflow PP11 In PP11 out	9 1 9 1 1 1	732 900 726	8.1 9.4 6.6	170 188 157		232 256 128							
OWP 7 m OEP Surface OEP 11 m OEP bottom OEP outflow PP11 In PP11 out PP13 out	e 1 e 1 1 v t t	732 900 726	8.1 9.4 6.6	170 188 157		232 256 128							

Table 31: Chemistry of OWP, OEP and Polishing Pond System Water Samples Collected July 1, 1990.

	Assay	ρН	Cond.	Acidity	Alkalinity	Diss. Zn		Diss .Fe	!	Diss. Mn	Diss. Ca	Diss_Mg	Diss Na
	No		uS.cm ⁻¹	mg.L ⁻¹									
						AAS	ICAP	AAS	ICAP	ICAP	ICAP	ICAP	ICAP
Drainage Tunnel	2914	5.61	483				17		<1	<1	37	5	13
OWP Surface OWP 7 m OEP Surface OEP 11 m OEP bottom	2909	3.9	733				35		2	2	85	11	4
OEP outflow PP11 In PP11 out PP13 out PP17 out	2910	6.47	2410				23		<1	11	389	40	98

Table 32: Chemistry of OWP, OEP and Polishing Pond System Water Samples Collected July 5, 1991.

	TDS	SO₄	SiO ₂	HCO ₃	TOC	CI
	mg.L ⁻¹					
			ICAP			·····
Drainage Tunnel		106	17.1	4.88		16
OWP Surface		316	12.8	1.22		1.5
OWP 7 m						
OEP Surface						
OEP 11 m						
OEP bottom						
OEP outflow		907	17.1	25.93		123
PP11 In						
PP11 out						
PP13 out						
PP17 out						

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Table 33: Chemistry of OWP, OEP and Polishing Pond System Water Samples Collected April 6, 1993.

	Assay	pН	Cond.	Acidity	Alkalinity	Diss. Zn		Diss .lron		Diss. Mn	Diss. Ca	Diss. Mg	Diss. Na
	No.		uS.cm ⁻¹	mg.L ⁻¹									
		•				AAS	ICAP	AAS	ICAP	ICAP	ICAP	ICAP	ICAP
Drainage Tunnel	4413	5.72	450	54.5	29.5		23.9		0.006	0.267	43.2	5.76	12.6
OWP Surface	4414	3.91	456	81.4			29		0.15	2	71.1	9.61	2.86
OWP 7 m	4415	3.84	495	94.3			33.8		0.202	2.22	79	10.2	2.86
OEP Surface	4416	6.02	1510	248.5	229.7		17.2		0.788	10,3	332	32.6	88.5
OEP 11 m													
OEP bottom	4417	6.09	2040	397.8	340.6		24.2		3.97	14.6	508	45.9	127
OEP outflow													
PP11 In													
PP11 out													
PP13 out													
PP17 out													

	TDS	SO₄	SiO ₂	HCO ₃	тос	CI
	mg.L ⁻¹					
			ICAP			
Drainage Tunnel	259	122	19.8	23		20.9
OWP Surface	390	267	12.8	<0.1		1.54
OWP 7 m	447	310	13.8	<0.1		1.54
OEP Surface	1650	861	16.3	170		129
OEP 11 m						
OEP bottom	2410	1260	18.9	220		196
OEP outflow						
PP11 In						
PP11 out						
PP13 out						
PP17 out						

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												1 C	
	Assay	pН	Cond.	Acidity	Alkalinity	Diss. Zn		Diss .Iron		Diss. Mn	Diss. Ca	Diss. Mg	Diss. N
	No.		uS.cm ⁻¹	mg.L ⁻¹	mg L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L				
	·					AAS	ICAP	AAS	ICAP	ICAP	ICAP	ICAP	ICAP
Drainage Tunnel													
OWP Surface	4418	4.24	315	40.3			13.2		0.69	0.834	32	4.16	1.36
OWP 7 m	4419	4.04	700	101.5			34.4		0.205	2.14	75.8	9.86	2.78
OEP Surface													
OEP 11 m					•								
OEP bottom													
PP11 out													
PP11 Out) }
PP17 out													
	TDS	SO ₄	SiO_2									· ·	
	105	SU₄	SIO ₂	HCU ₃	100								
	ing.c	ing.c		ing.c	mg.r	ing.c	╣						
Drainage Tunnel			(OF(
OWP Surface	182	125	6.2	<0.1		0.83							
OWP 7 m	450	316	13.6	<0.1		1.48							÷
OEP Surface													
OEP 11 m							1						
OEP bottom													
OEP outflow													
PP11 In													
PP11 out													
PP13 out													
PP17 out									·				
					÷								
									. *			• •	
													127 - 12
												. v	1.1

Table 34: Chemistry of OWP, OEP and Polishing Pond System Water Samples Collected May 16, 1993.

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	Assay	рН	Cond.	Acidity	Alkalinity	Diss, Zn		Diss .Iron		Diss. Mn	Diss. Ca	Diss. Mg	Diss. Na
	No.		uS.cm ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ^{.1}	mg.L ⁻¹
						AAS	ICAP	AAS	ICAP	ICAP	ICAP	ICAP	ICAP
Drainage Tunnel OWP Surface OWP 7 m	5575	6.4	192				13		0,009	0.172	41.1	3.88	9.41
OEP Surface OEP 11 m OEP bottom													
OEP outflow PP11 In PP11 out PP13 out PP17 out	5576	7.1	1080				12.2		0.024	6.29	243	21.7	58.3
												······	
	TDS	SO₄	SiO ₂	HCO3	TOC	CI							
	mg.L ⁻	mg.L	mg.L ⁻	mg.L ⁻¹	mg.L ⁻ '	mg.L°ʻ							
Drainage Tunnel OWP Surface	205	93.6	ICAP	28		10.9							
OWP 7 m OEP Surface OEP 11 m OEP bottom													
OEP outflow PP11 In	1070	535		114		70.5							
							61						

.

Table 35: Chemistry of OWP, OEP and Polishing Pond System Water Samples Collected June 14, 1995.

	Assay	pН	Cond.	Acidity	Alkalinity	Diss. Zn		Diss .Iron		Diss. Mn	Diss. Ca	Diss. Mg	Diss. Na
	No.		uS.cm ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg L ⁻¹	mg.L ⁻¹						
						AAS	ICAP	AAS	ICAP	ICAP	ICAP	ICAP	ICAP
Drainage Tunnel	5857	6.3	215	26.6	21.2		16.3		0.348	0.327	54.2	4.34	9.34
OWP Surface													
OWP 7 m													
OEP Surface													
OEP 11 m	5853	6,4	2050	227	361		16.4		63.7	13.6	489	41.7	116
OEP bottom	5852	6.4	2270	206.2	256.9		16.5		65.6	13.6	492	41.4	116
OEP outflow	5854	6.2	900	43.5	73.6		10.5		4.26	4.21	150	13.3	34.8
PP11 In													
PP11 out	5855	6.5	1292	49.8	132.3		11.9		7.93	9.1	265	23.3	62.8
PP13 out													
PP17 out	5856	6.6	1177	33.8	109.1		10.8		5.33	6.62	226	20	53.5

Table 36: Chemistry of OWP, OEP and Polishing F	Pond System Water Sar	nples Collected February	y 21, 199	96.
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.

	TDS	SO₄	SiO ₂	HCO ₃	TOC	CI
	mg.L ⁻¹	mg L ¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹
* "			ICAP			
Drainage Tunnel	254	125	17.1	26.3	3	11.6
OWP Surface						
OWP 7 m						
OEP Surface						
OEP 11 m	2320	1160	15.8	255	8.9	154
OEP bottom	2320	1160	15	249	16.9	157
OEP outflow	716	363	10.8	84.9	2.8	46.5
PP11 In						·
PP11 out	1250	624	12	154	6	86.6
PP13 out						
PP17 out	1060	534	11.4	128	5.3	73

.

	Assay	pН	Cond.	Acidity	Alkalinity	Diss. Zn		Diss .Iroi	1	Diss. Mn	Diss. Ca	Diss. Mg	Diss. Na
	No.		uS.cm ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg.L ⁻¹				
						AAS	ICAP	AAS	ICAP	ICAP	ICAP	ICAP	ICAP
Drainage Tunnel	5927	6.26	410	49.4		18.75	19.6	<d.l.< td=""><td>0.036</td><td>0.173</td><td>47</td><td>5.15</td><td>11.9</td></d.l.<>	0.036	0.173	47	5.15	11.9
OWP Surface	5928	6.6	624	44.8		16.8	16.8	<d.l.< td=""><td>0.193</td><td>1.22</td><td>83.4</td><td>8.56</td><td>19.4</td></d.l.<>	0.193	1.22	83.4	8.56	19.4
OWP7m	5935	6.26	983			18.26	18	<d.l.< td=""><td>0.634</td><td>2.43</td><td>132</td><td>12</td><td>24.1</td></d.l.<>	0.634	2.43	132	12	24.1
OEP Surface	5929	7.52	1331	49		14.15	13.1	<d.l.< td=""><td>0.197</td><td>5.01</td><td>224</td><td>20.3</td><td>52.8</td></d.l.<>	0.197	5.01	224	20.3	52.8
OEP 11 m	5936	6.59	2600	301		15	14.6	45.5	62.7	11.5	444	39.2	109
OEP bottom	5937	6.47	3010			16.55	16.2	55,35	78.1	13.2	502	44.5	123
OEP outflow	5938	7.24	1357	55.5		13.71	13	<d.l.< td=""><td>0.107</td><td>4.67</td><td>227</td><td>20.5</td><td>52.6</td></d.l.<>	0.107	4.67	227	20.5	52.6
PP11 In	5932	6.64	1235	22.8		13.35	13.1	0.11	0.194	4.88	226	21.1	54.6
PP11 out	5933,34	6.53	1333			10.5		<d.i.< td=""><td></td><td></td><td></td><td></td><td></td></d.i.<>					
PP13 out	5930	7.46	1284	8.6		4.65	3.88	<d.1.< td=""><td>0.044</td><td>1.46</td><td>222</td><td>19,8</td><td>50.8</td></d.1.<>	0.044	1.46	222	19,8	50.8
PP17 out	5931	7.22	1295	16.4		7.755	6.79	<d.l.< td=""><td>0.04</td><td>2.5</td><td>215</td><td>19.8</td><td>51.3</td></d.l.<>	0.04	2.5	215	19.8	51.3

	SO4	TDS	SiO ₂	HCO3	TOC	CI
	mg L ⁻¹	mg.L ⁻¹				
· · · · · · · · · · · · · · · · · · ·			ICAP			
Drainage Tunnel	142	300	16.3	24	2.3	15.5
OWP Surface	223	482	14.8	45	4.1	39.4
OWP 7 m	327		14.8			
OEP Surface	527	1080	13.3	113	2.8	76
OEP 11 m	999	2000	18.2	220	5,9	134
OEP bottom	1167		19.4			
OEP outflow	539	1110	13.2	118	2.7	75.4
PP11 In	537	1320	13			163?
PP11 out					5.6,4	
PP13 out	524	1010	10.8	109	4.3	65.1
PP17 out	510	1030	11.2	106	42	61

Table 37. Chemistry of OWP, OEP and Polishing Pond System Water Samples Collected July 9, 1996.

	Assay	рН	Cond.	Acidity	Alkalinity	Diss. Zn		Diss Iron		Diss. Mn	Diss. Ca	Diss. Mg	Diss. Na
	No.		uS.cm ⁻¹	mg.L ⁻¹	mg.L ⁻¹	mg,L ⁻¹	mg.L⁻¹	mg.L ⁻¹					
						AAS	ICAP	AAS	ICAP	ICAP	ICAP	ICAP	ICAP
Drainage Tunnel													
OWP Surface(5')	5977	6.49	748	32.9	63.5		16.3		<0.02	2.03	112	10.3	24.2
OWP 7 m	5978	5,73	962	171.3	42.8		29.9		<0.02	3.88	168	15.2	23.1
OEP Surface (5')	5975	6.89	1235	44.6	112.9		13.4		<0.02	5.15	224	19.6	51.7
OEP 11 m													
OEP bottom	5976	6.3	2410	71.5	301,3		13		10.1	13.2	505	41.2	116
OEP outflow													
PP11 in													
PP11 out													
PP13 out													
PP17 out													

Table 38: Chemistry of OWP, OEP and Polishing Pond System Water Samples Collected August 13, 1996.

.

	TDS	SO₄	SiO ₂	HCO ₃	тос	CI
	mg.L ⁻¹					
			ICAP			
Drainage Tunnel						
OWP Surface(5')	548	286		61. 9		31.1
OWP 7 m	763	452		41.4		25.8
OEP Surface (5')	982	488		125		51.7
OEP 11 m						
OEP bottom	2300	1170		285		141
OEP outflow						
PP11 in						
PP11 out						
PP13 out						
PP17 out						

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Boojum Research Limited January 1997



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1996 Final Report For: ASARCO INC.

ASARCO - BUCHANS

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THE VALLEY SEEPS, 1995/1996

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ASARCO - BUCHANS

THE VALLEY SEEPS, 1995/1996

INTRODUCTION

Information on discharge rates and chemical composition of the Valley Seeps at Buchans, measured during 1995 and 1996, was used to attempt the determination of a possible relationship between the seeps and the waterlevel in the Lucky Strike Pit. Because of time constraints the extent of the interpretation had to be limited in scope.

BOOJUM has checked the assumptions and uncertainties and presents the answer as bold, italic text.

DATA QUALITY

The available information presented a few uncertainties, as follows (numbers mentioned below are Assayer's numbers).

- Sample point VS-3 could not be found on the map of "Old Buchans/Valley Drainage Area", dated 11 September 1996.
 Flow through the pipe was discontinued in summer 1996. This flow became part of flow at VS-4. Location VS-3 was added to Map 2.
- 2 #5970: the listing of sample numbers and dates indicates this sample came from sample point VS-5; the analysis file BU0595.WQ1 indicated the sample represents "Total Valley S. Drainage at River"; the map suggests that the sample point likely was VS-6.

Yes, this is location VS-6 called Total Valley South Drainage at River

- 3 Values for SO₄ (or S) were not provided for three of the seep samples collected in May 1995.
 The samples were sent for ICP analysis. S is not a part of standard ICP.
- 4 Some of the values for discharge rates were estimated rather than measured; Mr.Neary suggested that some of those values may be too high.

ASSUMPTIONS

Several assumptions had to be made because of inconsistencies in the designations of sample sources.

1 - #5572 and 5966 are from the same place, VS-1 on the map, called "Mucky Ditch at Culvert" (BU0595 and BU0896)
- 2 #5574 and 5967 are from the same place, VS-2 on the map, called "4" Swimming Pool Pipe" (BU0595), and "Pipe Disch. Swimm. Pool" (BU0896)
- 3 #5573 and 5970 are from the same place, VS-6 on the map, called "Mucky Ditch at River" (BU0595), and "Total Valley S. Drainage at River" (BU0896)
- 4 #5569 and 5969 are from the same place, VS-5 on the map, called "Valley Seep 110' S.of Tun. Pumph." (BU0595), and "Valley Lower Seep" (BU0896)
- 5 #5571 and 5968 are from the same place, VS-4 on the map, called "Valley Seep 370' S.of Tun. Pumph." (BU0595), and "Valley Combined Upper Seeps" (BU0896)
- 6 #5570 is from VS-3, not on the map, called "Valley Seep 220' S. of Tun. Pumph." (BU0595)

If any of the above assumptions is erroneous, you may have to change the X-axis data labels on Figures 17 and 18, showing chemical compositions for these samples.

All of the above assumptions are correct. The seepages VS-1, VS-2, VS-3, VS-4, VS-5, VS-6, VW-1, VW-2, VW-3 are located on Map 2.

DATA GRAPHS and INTERPRETATION

- Fig. 1 amounts of precipitation from storms producing 20 mm or more water equivalent, vs. time. Melting of any snowpack has not been taken into account.
- Fig. 2 waterlevels in the Lucky Strike Pit (LSP) and the diamond drill holes (DDH's), vs. time.
 The LSP seems to have been "overfilled" by early 1995, and the waterlevel appears to have dropped more or less continuously since June 1995.
 Waterlevels in the DDH's that had initially increased during filling of the LSP declined somewhat when the waterlevel in the LSP dropped; they showed minor fluctuations, probably in response to local precipitation. This behaviour can be expected to continue. It is unlikely that complete analyses of further samples from the DDH's will provide any additional useful information.
- Fig. 3 (Zn) and flow rates for the discharge from the **Drainage Tunnel** (DT), vs. time. No clear correlation between the two parameters.
- Fig. 4 intervals between successive measurements of flow rates and (Zn) for sample points VS 1, 2, 3, 4, 5, and 6, vs. time. The intervals ranged from 7 to more than 110 days. The irregularity of the intervals and the fact that the sample points were not all measured and sampled on the same dates makes the interpretations considerably less reliable than they could have been.

Fig. 5 -	(Zn) values and flow rates for VS-1, vs. time. In some instances (Zn) increases with increasing flow rate, in others (Zn)
	decreases with increasing flow rate. Short-term variations are too large to discern any clear long-term trend (see VS-6).
Fig. 6a -	(Zn) values vs. flow rates for VS-1
8	No clear correlation between the two parameters.
Fig. 6b -	(Zn) values for VS-1 vs. LSP waterlevels
-	No clear correlation between the two parameters.
Fig. 6c -	flowrates for VS-1 vs. LSP waterlevels
	No clear correlation between the two parameters.
Fig. 7 -	(Zn) values and flow rates for VS-2, vs. time.
	(Zn) appears to increase with decreasing flow rate and to decrease with
	increasing flow rate; no long-term trend.
Fig. 8a -	(Zn) values vs. flow rates for VS-2
	No clear correlation between the two parameters.
Fig. 8b -	(Zn) values for VS-2 vs. LSP waterlevels
	No clear correlation between the two parameters.
Fig. 8c -	flowrates for VS-2 vs. LSP waterlevels
	No clear correlation between the two parameters.
Fig. 9 -	(Zn) values and flow rates for VS-3, vs. time.
C	The data record is insufficient to warrant interpretation.
Fig. 10 -	(Zn) values and flow rates for VS-4, vs. time.
	(Zn) appears to have increased somewhat with time (see VS-5).
Fig.11a -	(Zn) values vs. flow rates for VS-4
	No clear correlation between the two parameters.
Fig.11b -	(Zn) values for VS-4 vs. LSP waterlevels
	Negative correlation between the two parameters.
Fig.11c -	flowrates for VS-4 vs. LSP waterlevels
	No clear correlation between the two parameters.
Fig. 12 -	(Zn) values and flow rates for VS-5, vs. time.
	(Zn) appears to have increased with time (see VS-4).
Fig.13a -	(Zn) values vs. flow rates for VS-5
	Negative correlation between the two parameters.
Fig.13b -	(Zn) values for VS-5 vs. LSP waterlevels
	Negative correlation between the two parameters.
Fig.13c -	flowrates for VS-5 vs. LSP waterievels
	Positive correlation between the two parameters.
Fig. 14 -	(Zn) values and flow rates for VS-6, vs. time.
_	In some instances (Zn) increases with increasing flow rate, in others (Zn)
	decreases with increasing flow rate. Short-term variations are too large to
	discern any clear long-term trend (see VS-1).
Fig.15a -	(Zn) values vs. flow rates for VS-6

	No clear correlation between the two parameters.
Fig.15b -	(Zn) values for VS-6 vs. LSP waterlevels
-	No clear correlation between the two parameters.
Fig.15c -	flowrates for VS-6 vs. LSP waterlevels
	No clear correlation between the two parameters.

- Fig. 16 (Zn) values vs. time for VS-1, 2, 3, 4, 5, and 6 VS-1 shows the widest range of variation of (Zn). VS-2 shows both the lowest (Zn) values and the smallest variations in (Zn). VS-3 and VS-4 appear to be related in both (Zn) values and flow rates (VS-3 record is too short to be sure). VS-4 and VS-5 show somewhat similar variations in (Zn) values and flow rates, although (Zn) values in VS-4 are almost double those in VS-5.
- Fig. 17 Concentrations of selected elements (Ca, Cu, Mg, Mn, Zn, S) in samples from LSP and VS-1, 2, 3, 4, 5, and 6 collected on 28 May 1995 and a sample from DT collected on 14 June 1995 (see ASSUMPTIONS above). Metal concentrations in the LSP increased with depth; those in the DT discharge were lower than those in the near-surface LSP sample. Values for (S), (Ca), (Mg), and (Zn) indicate that the samples from the LSP, DT and VS-1, 3, 4, 5, and 6 had a similar origin. Values for (Cu) and (Mn) varied more than those for the other metals (likely due to increased significance of analytical precision at low concentrations). Concentrations for each element in the VS samples were lower than those for the LSP bottom sample and higher than those for the DT sample. The sample from VS-2 appears to have had a different origin.
- Fig. 18 Concentrations of selected elements (Ca, Cu, Mg, Mn, Zn, S) in samples from LSP, DT, and VS-1, 2, 3, 4, 5, and 6 collected on 13 August 1996 (see ASSUMPTIONS above).
 Metal concentrations in the LSP still increased with depth; those in the DT discharge (with the exception of (Cu)) were lower than those in the near-surface LSP sample. Values for (S), (Ca), (Mg), and (Zn) indicate that the samples from the LSP, DT and VS-1, 3, 4, 5, and 6 had a similar origin.

Values for (Cu) and (Mn) varied more than those for the other metals (likely due to increased significance of analytical precision at low concentrations). Concentrations for each element in the VS samples were lower than those for the LSP bottom sample and (with the exception of the sample from VS-1) higher than those for the DT sample. The sample from VS-2 again appears to have had a different origin.

- Fig. 19 (Zn) values and flow rates for VW-1, vs. time. (Zn) appears to increase with decreasing flow rate and to decrease with increasing flow rate; record too short to determine long-term trend.
- Fig. 20 (Zn) values and flow rates for **VW-2**, vs. time. No clear correlation between the two parameters.

- Fig. 21 -(Zn) values and flow rates for VW-3, vs. time. In some instances (Zn) increases with increasing flow rate, in others (Zn) decreases with increasing flow rate. Short-term variations are too large to discern any clear long-term trend. Fig.22a -(Zn) values vs. flow rates for VW-3 No clear correlation between the two parameters. (Zn) values for VW-3 vs. LSP waterlevels Fig.22b -No clear correlation between the two parameters. flowrates for VW-3 vs. LSP waterlevels Fig.22c -Minor positive correlation between the two parameters. Fig. 23 -Zn contents vs. time for VW-1, 2 and 3
 - VW-3 shows the widest range of variation for (Zn). There appears to be some correlation between (Zn) for VW-1 and VW-2, but inconsistent sample dates make the relationship uncertain.

The behaviour of the Zn concentrations in the discharge from the Valley Seeps can probably be explained in principle as follows.

- (1) After a prolonged dry period, increased infiltration from precipitation (or snowmelt) may push out water with higher metal concentrations, due to a preceding extended residence time, resulting in increased flow rates and increased metal concentrations.
- (2) If infiltration continues, metal concentrations will gradually drop due to dilution.
- (3) When infiltration stops, flow rates will gradually decrease, whereas metal concentrations will gradually increase due to lack of dilution, and longer residence times.

It should be noted that the "monitoring data" for the Valley Seeps cannot be used to give a clear indication of the diluting effects of local precipitation, unless the concentration of at least one other metal (e.g. Ca or Mg) is also determined for each sample. If at all possible, discharge rates should be measured rather than estimated.

The magnitude of the metal loadings from some of the Valley Seeps appears to have become sufficiently large to warrant continuing monitoring of the main seepages.

Robert O. van Everdingen 28 December 1996















■- Zinc -⊕- Flow



Fig. 11b; VALLEY SOUTH, VS-4 [Zn] versus LS Waterlevel





-∎- Zinc -⊟- Flow





- Zinc - - Flow









- VS-4 - XS-5 - A- VS-6

Fig. 17: LSP, DT and VALLEY S. SEEPS Concent. of Selected Elem., May 28,95 10000₃ 1000 100= Concentration, mg/L 101 0.1 0.01 0.001 VS-3 V\$-5 VS-1 LSP-#5/5' LSP-#5/94' VS-4 **VS-6** VS-2 LSP-#5/65' DT-6/'95 Source - Cu -≫- Mg - Ca — → Mn → → Zn -A- SO4 Fig. 18: LSP, DT and VALLEY S. SEEPS Concent. of Selected Elem., Aug 13,96 10000= 1000_Ξ 100₌ Concentration, mg/L 10 0.1 0.01 0.001-VS-6 VS-1 vs-4 LSP-#5/94' LSP-#5/5' VS-5 VS-2 LSP-#5/65' DT Source --+-- Cu ---── Mg 🖬 – Ca 🖅 Mn -× Zn 🚽 SO4











Valley Seepages at Buchans

Dr. Jan Gerits University of Toronto (January 1997)

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-	Discharge Rates

1.0 INTRODUCTION

After termination of the mining activities at Buchans in 1984, the mine workings were flooded. This resulted in a rise of the water levels in the Lucky Strike (LS), the Oriental West (OWP) and the Oriental East (OEP) pits. Initially the discharge from the Drainage Tunnel (DT) showed an increase with the rise of the water level in the Lucky Strike pit. After installation of a concrete plug in the Drainage Tunnel (1988) the discharge dropped to about 80% of the discharge before the installation of the plug. Pumping of the discharge from the Drainage Tunnel (DT) to the Oriental West pit (OWP) started on September 27, 1994. During the period between August 2, 1992 and November 18, 1994 water from Tailings Pond #1 (TP1) was siphoned into the Lucky Strike pit. This caused a rapid rise of the water level in the Lucky Strike pit which finally approached a more 'natural' elevation (approx. 272.5 m) in July 1995. Associated with the flooding of the mine workings are a number seepages occurring East of the Lucky Strike pit. These seepages are the focus of this study.

At present it is not clear if the seepages and their associated Zn loadings to the Buchans River, are *mainly* caused by flooding the Lucky Strike pit or if they are due to a *combination* of several factors, including changes in groundwater table elevations and groundwater flow patterns associated with the local geologic structure and aquifer characteristics. To investigate the origin or the source of the seepages, a separate hydrological and geochemical approach were chosen. This report represents the geochemical study approach.

Since the beginning of 1995, discharge, pH, conductivity and Zn concentrations of several seepages (map location and elevation) have been monitored periodically (G.N. Neary). Three of the seepages occur in the sandfill deposits, NE of the Lucky Strike pit: VW1 (N6600'/E7800', 252.7 m), the combined sandpit seeps; VW2 (N6550'/E8150', 239.6 m), the seepage from the bank near the DT pumphouse; VW3 (N6650'/E8300', 239.6 m), the total drainage from the West discharging into the Buchans River.

Three other, isolated seepages occur SE of the Drainage Tunnel, at the bank close to the "swimming pool" road, S of the DT pumphouse: VS4 (N6193'/E8080', 248.1 m), the combined

upper seeps; VS5 (N6400'/E8200', 243.8 m), the combined lower seeps; VS4-5, between VS4 and VS5, 220' S of the DT pumphouse. Seepage from the area E of the Mucky Ditch and the "swimming pool" road is sampled at VS2 (N6166'/E8246', 249.6 m) at a pipe near the swimming pool pump box.

The discharge from the Mucky Ditch is measured at VS1 (N6070'/E8130', 255.7 m). The total drainage from the South is sampled at VS6 (N6448'/E8551', 239.0 m), downstream from VS1 in the Mucky Ditch near Buchans River.

In addition to monitoring the valley seepages, water levels have been measured frequently (G.N. Neary) in the Lucky Strike pit and in several drill holes (DH) close to the flooded Lucky Strike pit: **DH #3325** (N4750'/E5500', 239.0 m); **DH #3341** (N5765'/E4500', 284.1 m); **DH #3342** (N6250'/E4500', 286.8 m); **DH #3343** (N7500'/E4500', 289.9 m) and **DH #3344** (N5270'/E3000', 281.3 m).

2.0 MONITORING DATA

2.1 Hydrology

A comparison between the water levels in several drill holes and the water levels in the LS pit is shown in Fig. 1 for the period between April 4, 1995 and September 23, 1996. The groundwater elevations in the drill holes increase linearly with the rise of the water level in the LS pit. This linear correlation appears to be better for DH #3325 compared to the other drill holes for which the data show considerably more variation. Considering this variation in data it is difficult to attribute any significance to differences in the slope of the linear correlation between water levels in the LS pit and the drill holes. Drill holes #3341, #3342 and #3343 are located at an increasing distance, N from the LS pit. Drill hole #3325 (SE) is located at a larger distance from the LS pit than drill hole #3341 (N). Apparently there is no simple relation between groundwater elevation and distance from the LS pit. Groundwater elevations in the drill holes are always higher than the water levels in the LS pit.

Daily precipitation at Buchans (Environment Canada) and water levels in the drill holes and the LS pit are plotted in Figs. 2A (rainfall) and 2B (rainfall + snowfall) for the period between January 1, 1995 and November 1, 1996. As expected, there exists no clear relation between the precipitation record and the fluctuations of the water levels in the drill holes and the LS pit. Even snowmelt runoff does not appear to have a significant effect on the water levels in the drill holes and LS pit.

Similar to Figs. 2A and 2B, daily precipitation and periodically measured discharge rates (Q) from seepages are shown in Figs. 3A and 3B (VW1 and VW2), Figs. 4A and 4B (VS2 and VS4) and Figs. 5A and 5B (VS4 and VS5). Despite the short monitoring period, the discharge from seepages in the sandfill deposits (Figs. 3) shows a rapid response to the daily precipitation. This close relation between precipitation and seepage rate (Q) may be attributed to the porous nature of the overburden. The discharge rates of the other seepages (Figs. 4 and Figs. 5) do not appear to be closely related to the daily precipitation record, even if one assumes a lag time in seepage response. A better relation, notably for VS4 in 1995, appears to exist between seepage rate and snowmelt runoff. However, this relation is less clear for the other seepages (VS2 and VS5) and during 1996. Obviously, the distinction of a pattern in seepage rate, related to precipitation and snowmelt events, also depends on the monitoring intensity of the seepages.

Seepage rates (Q) and water levels in the drill holes and the LS pit is shown in Figs. 6A-E. From these figures it is evident that changes in seepage rates are much larger and more frequent than fluctuations in water levels. There appears to be no relation between water levels and seepage rates.

The absence of *any* relation between seepage rates and water levels in the drill holes and the LS pit (Figs. 6) suggests that the seepages are largely fed by meteoric water (rainfall and snowmelt) rather than phreatic water. A somewhat better relation, although not evident at all seeps, exists between seepage rates and precipitation or snowmelt runoff (Figs. 3-5). The absence of a clear relation may be caused by a low monitoring intensity or differences in catchment size of the seeps. Presently, phreatic water (drill holes) seems to be the major source of the water in the LS pit.

2.2 Chemistry

The Zn concentrations in the seepages which discharge into the Buchans River, are of major concern. The Zn concentrations in several seepages are shown in Fig. 7. Excluding the sites where total drainage is collected (VW3, VS1 and VS6), the highest Zn concentrations occur in seepages at VS4 (40-70 ppm) and VS5 (20-40 ppm). The lowest Zn concentrations (1-5 ppb) occur in the seepages from the sandfill deposits (VW1 and VW2). The temporal variation in Zn loadings at site VS4 (Fig. 8) appears to be more pronounced but similar to the temporal variation in seepage rates (Figs. 5). The contrary applies to the temporal variation in Zn loadings at site VS5. This can be attributed to a dilution effect: the Zn concentrations in seepage at VS5 decline with increasing seepage rates (Fig. 9). The data of site VS4 show a considerable scatter and no correlation between Zn concentration and seepage rate. At all seepage sites, Zn loading increases linearly with seepage rate (Fig. 10). The rate of increase is largest for site VS4 and lowest for sites VS2, VW1 and VW2. This suggests that all seepage sites have a constant Zn source but the contribution of that (same) source varies among the different seepage sites. The contribution of the Zn source to the seepages is largest at site VS4 (approx. 50 mg Zn per It seepage).

The seepages could originate from the LS pit, phreatic or meteoric water. Based on the hydrological data discussed previously, meteoric water would be the major source of the seepages. Meteoric water would acquire Zn by reaction with waste rock or local ore deposits in the vadose zone. Larger contributions of meteoric water would produce larger seepage rates and aquire more Zn (increased weathering rates ?) and result in larger Zn loadings (e.g. Fig. 10). A similar scenario could also apply to water from the LS pit and the drill holes (phreatic water) or mixtures of different waters. However, with the available hydrological and chemical monitoring data it is very difficult to determine the sources of the seepages. One approach to determine the sources of the seepages is to derive the chemical composition of the seepages by geochemical modelling using different potential sources of water in contact with the bedrock or overburden. This approach is demonstrated below.

3.0 GEOCHEMISTRY

3.1 Water Analyses and Mineralogy

Chemical analyses of selected water samples from drill holes, seepage sites, LS pit, DT, rain and the Sandfill Spring (SS) are listed in Tables 1 and 2. Except for the Sandfill Spring and rainwater, the analyses in Table 1 apply to samples collected in 1995 and 1996. The chemical analysis of rainwater (NW Atlantic) was taken from Table 3.1 in Berner and Berner (1996). The analyses of water samples from the drill holes (Table 2) date from 1991 and were published in a previous report (December 1991). Water samples from the LS pit were taken at three different depths (5, 65 and 94 feet). The following discussion of the chemical data from Tables 1 and 2 will be concentrated on water samples from DH #2243a (closest balance of cations and anions), VS4, VS4-5 and VS5 (most representative seepages), LS, DT and rain.

Except for the water samples from the LS pit (LS5 and LS65) and DH #3342a, the concentration of chloride in rainwater (salt spray) is smaller than that in the other samples (LS94, DT, VS4, VS5 and VS4-5). Assuming that chloride behaves conservatively, this implies that only groundwater (DH #3342a) and water from the upper part of the LS pit can be derived from the reaction of rainwater (meteoric) with bedrock, ore deposit or overburden. The formation of all other waters from meteoric water requires *additional* evaporative concentration (of rainwater) to attain higher Cl concentrations since Cl containing minerals (e.g. halite) do not occur in the geologic formations and overburden at Buchans (Swanson et al., 1981). The same applies to the formation of seepage waters from water of the LS pit (LS5 or LS65) and groundwater (DH #3342a). Concentration of meteoric water or a mixture of phreatic and meteoric water often occurs as a result of capillary movement and evaporation during repeated wetting and drying of the vadose zone (e.g. Smith and Drever, 1976).

The seepage waters (VS4, VS4-5 and VS5) and the deeper water in the LS pit are often characterized by a low pH, and high sulphate, iron and zinc concentrations caused by the oxidation of sulfides in the ores (e.g. sphalerite and pyrite). Without further evidence from geochemical modelling it is not clear if these high concentrations could also be due to evaporative concentration of the water. The concentrations of the same elements are much lower in the groundwater sampled in the drill holes (e.g. DH #3342a).

The predominant minerals in the ore deposits at Buchans are sphalerite, galena and barite. Other abundant minerals include pyrite and chalcopyrite. Minor metal containing minerals are chalcocite, bornite, pyrrotite and cerussite. The most important rock-forming minerals at Buchans are K-feldspar, plagioclase, illite, montmorillonite, chlorite, quartz and calcite (Swanson et al., 1981).

3.2 Modelling Approach

Waters or mixture of waters considered to be potential sources of the seepages include: water from the LS pit (three different depths), groundwater (DH #3342a) and rainwater. Using PHREEQC (Parkhurst, 1995), the composition of the potential source water (or mixture of source waters) was compared with that of the seepage waters and DT water by an 'inverse modelling' procedure (explained below). Assuming specific phase transformations of minerals and gases (required input), the model calculates the quantity of the suggested phase transformations, the mixing proportions and the evaporation that account for the differences in the composition between the seepage water and the source water(s).

A detailed example of an 'inverse modelling' simulation run (input and output files) is shown in the Appendix. In the example the phase transformation, mixing proportions and amount of evaporation that account for the difference in chemical composition between an unknown mixture of rain and LS5 water (source) and seepage water (VS4), are determined.

Considering that not all samples have anion/cation analysis, only 8 parameters were used to define the chemical composition of the water samples (solutions 1-3). The uncertainty value defines the maximum fraction by which the input concentrations are allowed to vary during the simulation run. Lower uncertainty values impose greater constraints. Next, the specific phase transformations are defined (dissolution or precipitation). Balances are specific uncertainty constraints applied to a particular input concentration. Here chloride is used and allowed to vary only by 10% from its specified input concentration. As chloride behaves conservatively the higher imposed constraint 'steers' the mixing and evaporation process. Finally, additional thermodynamic data are given for phases not defined in the thermodynamic database of the program.

The output file shows first the calculated solution characteristics of each input solution. After this it lists the original (first column), the required adjustments (second column) and the adjusted (third column) analytical data for the three input solutions. The adjustments must be within the defined uncertainty and balances defined in the input file. Next, the calculated mixing proportions of the first two solutions (seepage water sources) are listed. Finally, the required mole transfers of the previously defined phases are listed: negative values indicate precipitation, positive values indicate dissolution.

The program calculates first a model with a minimal number of phase transformations (minimal model) before it explores other models with more phase transformations. The number of models found is obviously constrained by the earlier defined uncertainty value and balances.

3.3 Modelling Results

Successful modelling results (minimal model) are shown in Table 3. Unsuccessful modelling results included runs with only one source water (LS, DH # 3342a and rain) and runs with water from DH #3342a (improper ion balance of input solution).

The data in Table 3 show that the composition of seepage and DT waters (solution 3) can be simulated by different mixtures of rain and LS water subjected to various amounts of evaporation, degassing (CO₂ (g)) and/or calcite precipitation. Only two models involving DT water (1995) were unsuccessful; they are listed for completeness of the data set.

The formation of seepage waters from rain and LS waters (minimal model) does not require any other mineral phase transformation than those listed in Table 3 ! Other models (results not shown in Table 3), involved only minor mineral transformations of mostly rock-

forming minerals (e.g. K-feldspar). This implies that the Zn loadings from the seepages are *exclusively* derived from the LS waters. The variation of the Zn concentrations in the seepages is mainly determined by the dilution of LS waters with rainwater (similar to a varying degree of evaporation of their mixture). This dilution effect increases from site VS4, to sites VS4-5 and VS5 and varies at different times (1995 and 1996). The dilution effect appears to be less for the DT water, however, the evaporation is also considerably less than that for the seepages.

Considering the listed (minimum) values for the applied uncertainty (15-25%), the number of input solution parameters used (8) and the complexity of the simulation scenario (mixing *and* evaporation), the 'inverse modelling' results are very good. The mineral transformations are relatively simple and involve predominantly precipitation of calcite.

4.0 CONCLUSIONS

1. The chemical composition of waters from the seepages and the DT can be formed by mixing rainwater and LS waters, followed by evaporation, degassing and only calcite precipitation.

2. The processes of mixing and evaporation of the different source waters for the seepages in the field is most likely due to capillary movement and evaporation during repeated wetting and drying of the vadose zone.

3. The differences in the chemical composition of the water from the various seepage sites appear to be governed by dilution of LS water with meteoric water (rain or snowmelt runoff). This is confirmed by some of the patterns observed in the response of seepage rates to particular hydrological events (e.g. precipitation and snowmelt runoff).

4. Differences in the chemical composition of the water from the various seepage sites (dilution) could also be related to differences in soil or aquifer characteristics (e.g. porosity) and the size of the catchment area (meteoric water) of each seepage.

5. The dissolved Zn concentration in seepage and DT waters appears to be entirely derived from (concentrated) LS waters. No additional dissolution of sphalerite in the aquifer or vadose zone seems to be necessary.

6. The composition of seepage and DT waters could not be simulated with a mixture of rain and groundwater (e.g. DH #3342). This is probably only due to the poor quality of the groundwater composition data. As the LS pit is largely fed by groundwater, it must be possible to 'simulate' the chemical composition of the LS water from that of the groundwater. Hence it is expected that the composition of the seepage and DT waters can also be 'derived' from a mixture of rain and groundwater.




















Discharge Rates from Seepage VW1 versus Time, January 1, 1995 - November 1, 1996



Discharge Rates from Seepage VW2 versus Time, January 1, 1995 - November 1, 1996





Discharge Rates from Seepage VS4 versus Time, January 1, 1995 - November 1, 1996













Table 1: Concentration of Selected Elements for Lucky Strike, Drainage Tunnel,

Code		LS5	LS5	LS65	LS65	LS94	LS94	DT V	DT	Vs1	Vs1	, √vs2	Vs2	Vs4	Vs4	Vs5	Vs5	Vs6	Vs6	Vs4-5	SS	Rain
No.		5566	5972	5567	5973	5568	5974	95575	5971	5572	5966	5574	5967	- 5571.	5968	\$5569	5969	5573	5970	5570	2912	
Date		19-5-95	13-8-96	19-4-95	13-8-96	19-4-95	13_8_96	14-6-95	13_8_96	28-5-95	13-8-06	28-5-05	13.8.96	28-5-05	13 8 06	28 5 05	13 8 06	28 5 05	12 9 06	28 5 05	5 7 01	
Dato		10 0 00	10 0 00	10 + 00	10-0-00	10 1 00	10 0 00	14 0 30	10 0 00	20 3 33	10-0-30	20-0-00	10-0-30	20-0-00	10-0-00	20-0-90	10-0-90	20-0-90	10-0-90	20-3-93	5-7-51	
рН		67	6.2	67	6.1	6.6	6.1	6.4	5.9	216 E.	5.1		5.9	3 4.7	4.3	6.2	5.3	- 14 3.5 1	4.6	5.9	5.9	4.9
Cond	uS/cm	. 355	470	047580	559	21000	880	314	386		37		357	4.728	822	456	679		638	564	123	
<u></u>	ma a /l	1	20		- 22	10 A 17 14	0.0		44.0				55.0		00.0		10.0					
SO4	mg/i	142.0	214.0		258.0	3684 D	9.Z	10.9	14.8		3.0		50.3	282.0	28.6	29/2	49.8	tos distant.	30.5	19.6 19.6	2.0	5.5
NO3	mg/l	- 10.4	0.3	5 C Z	0.4	ANR 0.3	0.3	4.2	3.5	1. 11. 1	0.0		4.1	1 4 5	3.5		19	Contraction of the	217.0	1000	3.5	0.3
HCO3	mg/l	16:0	15.0	32.4	23.9	60.0	45.9	28.0	27.1	11.	· · ·		18.7	0.10		09	1.6	11- L	<u> </u>	14	6.1	0.0
Na	mg/l	40	4.1	212576	4.9	15.6	11.8	4.00	11.6	6.0		51.9	35.3	26.4	20.3	25.7	35.5	216	19.9	293	5.0	3.0
Ca Ma	mg/i		68.7 7 A	1000 Co 44	88.7	1/AU	153.0		49.3	326.6	3.0	$\mathbb{N}^{\mathbb{N}}$	34.0	76.1	101.0		81.7	51.8	57.8	61.55.4	17.0	0.2
K	ma/l		10		0.5	12 1 4	10.3		1.0	10	0.4		2.9	120	28		25	1000 A	10.0		15.0	0.3
<u> </u>									<u> </u>			Difference in the second	<u> </u>		2.0		2.0		1.0		15.0	0.2
Al	mg/l	0.06				÷ 0.05				1.03	0.07	0.06		137	2.32	0.17	0.13	0.58	0.49	0.14	2.00	
Fe	mg/i	0.02				2.2.2		0.01		1.54	0.27							- 0.10		0.03		
Min	mg/i	20.36	0.56	0.63	0.75	2.01	1.82	2 DH7;	0.19	0.4/	0.04	0.03		4.78	8.31	0.361	0.75	1.84	2.85	0.40		
Ba	ma/l	0.04	0.04		0.04	0.02	0.02	0.02	0.02	0.05	0.10	0.10	0.07	\$ 0.03	0.02	S 0 02	0.04	20.0	0.06	Sector 2		
Cd	mg/l	0.07	0.13	0.12	0.17	0.21	0.22	0.04	0.06	0.06	0.10		0.01	0 07	0.10	840 DC	0.04	10.06	0.05	44.0.06		
Cu	mg/l	0.11	0.03	- O.Z.	0.43	079	0.77	2.0.03	0.08	0.42	0.03	a and	0.01	0.30	0.54	2.0.0.2	0.07	40.31	0.26	0.02		··
Pb	mg/l	0.06	0.04		0.04	0.25	0.12			41,14	0.30							0.66	0.50	(1-(1))		
Sr	mg/l		24.0		0.28		0.56	87. (328. *)	10 0	0.070	0.6						0.28		24.0	01010		
2.11	mgn		24.3		35.0		34.0		10.9	<u>GARDAR</u>	0.0	169 - 30 H2	2.3		00.∠	1082503	30.2		31.0	Anna Star Bart Bart		
Na:Cl	<u> </u>	1011220	1.44		1.47	NAME OF	1.28		0.78	26031-720703			0.64	Law 23	0.71		0.71		0.65	6. 33 2 M	2,50	0.55
				×																		
Cat	me/l		5.0		6.5	12.6	11.2		4.0	28			3.6	8 199	9.6		7.9		5.6		1.9	0.2
An	me/I		4.8		5.9		10.7	23	4.0				3.9	72	9.2		8.1		5.4		0.3	0.2
1	1	1	1	1	1	1	1	1	ł	1		1	1	1		1	ł	1	ł		E	1

Seepages VS1, VS2, VS4, VS5, VS6 and Sandfill Spring

Table 2:Concentration of Selected Elements for DDH3325, DDH3341, DDH3342,

DDH3344 and Sandfill Spring

	L	#3325a	#3341a	#3342a	#3342c	#3344b	SS	👾 Rain			#3325a	#3341a	#3342a	#3342c	#3344b	SS	- Rain
рН		7.9	7.6	6.8	6.9	6.8	5.9		рН		7.9	7.6	- 618	6.9	6.8	5.9	49
Eh	Volt	-0.050	-0.003	0.009	-0.089	-0.228			Eh	Volt	-0.050	-0.003	01(0)091	-0.089	-0.228		
CI	ppm		3.0	** 2.0	2.0	4.7	2.0	5.5	CI	mmol/1		0.08	0.06	0.06	0.13	0.06	1. 10 1 G
SO4	ppm	201.9	16.8	5.1	5.0	2.0	3.6	et 1 2	SO4	mmol/l	2.10	0.17	0.05	0.05	0.02	0.04	- 0 C4
HCO3	ppm	24.4	89.1	18.3	100.1	717.3	6.1		HCO3	mmol/l	0.40	1.46	20,30	1.64	11.76	0.10	
Na	ppm	29.8	4.3	sta 217-	4.0	12.0	5.0	1223.0	Na	mmol/l	1.30	0.19	0.02	0.17	0.52	0.22	22033
Ca	ppm	63.6	44.5	連続 95	15.0	100.0	17.0	11.2012	Ca	mmol/l	1.59	1.11	1024	0.37	2.50	0.42	
Mg	ppm	7.3	2.8	6 .7		3.0	3.0		Mg	mmol/l	0.30	0.12	(1.).		0.12	0.12	
K	ppm	2.0	1.0			1.0	15.0	#402	K	mmol/i	0.05	0.03			0.03	0.38	
AI	ppm		0.03	0.04			2.00		Al	mmol/l		0.001	0.001			0.074	
Fe	ppm		0.20	0.20		11.00			Fe	mmol/l		0.004	0.004		0.197		
Mn	ppm	0.52	0.07	0.03				The second	Mn	mmol/l	0.009	0.001	0.001				
SiO2	ppm	1.50	20.60	49	10.70	30.00		With Call	SiO2	mmol/l	0.025	0.343	205120	0.178	0.500		
Ва	ppm	0.15	0.37	042		2.00	<u></u>		Ba	mmol/i	0.001	0.003	(aus)		0.015		
Cu	ppm	0.06							Cu	mmol/l	0.001						
Sr -	ppm	0.37	0.07	S (1010)					Sr	mmol/l	0.004	0.001	SC 2 2 (9 (3 (9)				
Zn	ppm	0.11	0.05			0.64			Zn	mmol/l	0.002	0.001			0.010		
Na:Cl			1.43		2.00	2.55	2.50	255	Na:Cl	mmol/1		2.21		3.08	3.94	3.85	
Cat	me/l	5.16	2.69	0/63	0.92	6.21	1.90	2017	Cat	mmol/l	5.16	2.69	0.00	0.92	6.21	1.90	n Shirin
An	me/l	4.60	1.92	0.47	1.80	11.94	0.30	0 19	An	mmol/l	4.60	1.92	0.47	1.80	11.94	0.30	1010

Table 3:	Modelling Results	
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Year	Solution	Solution	Sol.1:Sol.2	Solution	Uncertainty	Models	H2O	CaCO3	CO2(g)
	1	2	(mixing)	3			Mol	Mol	Moi
95	rain	LS5	3.0:1	Vs4	0.25	3	-3 82E+02	-1 61F-04	-3 56E-04
96	rain	LS5	2 1:1	Vs4	0 15	2	-2 89E+02	-1 18F-04	-3 80F-04
95	rain	LS65	4.8:1	Vs4	0.20	3	-3.08E+02	-1 97F-04	-4 01F-04
96	rain	LS65	2.9:1	Vs4	0.15	1	-2 86F+02	-1 28E-04	-4.98E-04
95	rain	LS94	9.9:1	Vs4	0.20	1	-3.05E+02	-1.45E-04	-3.44F-04
96	rain	LS94	5.1:1	Vs4	0.15	1	-2.61E+02	-1.46E-04	-5.55E-04
95	rain	LS5	4.2:1	Vs5	0.15	3	-2 88E+02	-9 30E-05	-2 44F-04
96	rain	LS5	6.4:1	Vs5	0.15	8	-4 87E+02	-2 00E-05	-2 77E-04
95	rain	LS65	7.4:1	Vs5	0.20	3	-2 81F+02	-1.03E-04	-2 65E-04
96	rain	LS65	8.3:1	Vs5	0.15	6	-4.78E+02	-2.70E-04	-3.52E-04
95	rain	LS94	12.7:1	Vs5	0.20	1	-2.37E+02	-7.50E-05	-2.25E-04
96	rain	LS94	12.8:1	Vs5	0.15	5	-4.24E+02	-4.70E-05	-4.01E-04
95	rain	LS5	4.2:1	Vs4-5	0.15	4	-3 81E+02	-1.00E-04	-2 75E-04
95	rain	LS65	9.0:1	Vs4-5	0.15	4	-3.75E+02	-1.04E-04	-2 87F-04
95	rain	LS94	12.7:1	Vs4-5	0.20	1	-2.37E+02	-7.50E-05	-2.25E-04
95	rain	LS5	na	דת	0.25	0	na	na	na
96	rain	LS5	2.5.1	DT	0.25	4	-1 18E+02	0.00E+00	-6 00E-04
95	rain	LS65	na	DT	0.25	$\frac{1}{0}$	na	na	000E-00
96	rain	LS65	3.3:1	DT	0.20	5	-1.07E+02	0.00E+00	-3.60E-05
95	rain	LS94	4.0:1	DT	0.25	5	-2 50E+01	0.00E+00	4 90E-05
96	rain	LS94	5.2:1	DT	0.15	- õ	-6 80E+01	0.00E+00	6 60E-05

5.0 EXAMPLE OF "INVERSE MODELLING" SIMULATION RUN

```
Reading input data for simulation 1.
TITLE
     --Inverse modeling of Rain + LS5 + evaporation --> Vs4 (1995)
     SOLUTION 1 Rain
            units
                   mg/L
            Πq
                    4.9
            Ca
                    0.2
            Mg
                    0.3
                    3.0
            Ňа
            к
                    0.2
            S(6)
                    1.2
            Cl
                    5.5
            C(4)
                    0.0
                         as HCO3
            Zn
                    0.0
     SOLUTION 2 LS5
            units
                    mg/L
                    6.7
            pН
            Ca
                    51.6
            Mg
                    5.4
            Na
                    4.0
            Κ
                    1.4
            S(6)
                   142.0
            Cl
                    3.2
            C(4)
                    16.0
                           as HCO3
            Zn
                    14.1
     SOLUTION 3 Vs4
            units
                   mg/L
            рН
                    4.7
                    76.1
            Ca
            Mg
                   16.1
            Na
                   26.4
            ĸ
                    2.6
            S(6)
                   288.0
                   41.4
            Cl
            C(4)
                   0.0
                          as HCO3
            Zn
                    46.3
     INVERSE_MODELING
            solutions 1 2 3
            uncertainties .25
            phases
                    Sphalerite
                                  dis
                    Pyrite
                   Chalcopyrite
                   H20
                                  pre
                   Calcite
                                  pre
                   CO2 (g)
                   Plagioclase
                                  dis
                   K-feldspar
                                  dis
                   Illite
                                  pre
                   Chlorite(14A)
                                  pre
                   Ca-Montmorillonite
                                        pre
```

```
balances
                   C1
                         0.10
     PHASES
     H2O
            H2O = H2O
            log_k 0.0
     chalcopyrite
            CuFeS2 + 2H + = Cu + 2 + Fe + 2 + 2HS -
            log k -35.27
            delta h 35.48 kcal
     plagioclase
            Na0.62Ca0.37Al1.38Si2.62508 + 5.5 H+ + 2.5H2O = 0.62Na+ +
            0.37Ca+2 + 1.38Al+3 + 2.625H4SiO4
            log k 0.0
     END
_____
Beginning of initial solution calculations.
_____
Initial solution 1.
                     Rain
                     Molality
     Elements
                                   Moles
     Са
                     4.990e-06
                               4.990e-06
     Cl
                     1.551e-04
                               1.551e-04
     К
                     5.115e-06
                              5.115e-06
                              1.234e-05
                     1.234e-05
     Mq
     Na
                     1.305e-04
                               1.305e-04
                     1.249e-05 1.249e-05
     S(6)
                          pH = 4.900
                               4.000
                          pe =
            Activity of water = 1.000
               Ionic strength = 2.112e-04
           Mass of water (kg) =
                                 1.000e+00
      Total alkalinity (eq/kg) = -1.281e-05
         Total carbon (mol/kg) = 0.000e+00
           Total CO2 (mol/kg) = 0.000e+00
          Temperature (deg C) = 25.000
      Electrical balance (eq) = 2.959e-06
                   Iterations = 3
                     Total H = 1.110124e+02
                     Total O = 5.550627e+01
                                                              Log
                                            Log
                                                    Log
                                Activity Molality Activity
                                                              Gamma
     Species
                     Molality
     H+
                     1,280e-05 1.259e-05
                                           -4.893
                                                    -4.900
                                                              ~0.007
                                           -9.092
                                                    -9.100
                                                             ~0.007
     OH-
                     8.087e-10
                                7.952e-10
     H2O
                                1.000e+00
                                            0.000
                                                     0.000
                                                              0.000
                     5.551e+01
               4.990e-06
Ca
                     4.979e-06 4.658e-06 -5.303
                                                    -5.332
                                                              -0.029
     Ca+2
```

CaSO4

1.080e-08

1.080e-08

-7.966

-7.966

0.000

	CaOH+	6.244e-1	4 6	5. 14 0e-14	-13.205	-13.212	-0.007
Cl		1.55le-04					
	Cl-	1.551e-0	4	1.526e-04	-3.809	-3.817	-0.007
H(0)		2.244e-21					
	H2	1.122e-2	1 :	1.122e-21	-20.950	-20.950	0.000
к		5.115e-06					
	K+	5.114e-0	6 '	5.029e-06	-5.291	-5.298	-0.007
	KS04-	4 2096-1	- 0 4	1396-10	-9 376	-9383	-0.007
	KOH KOH	1 3850-1	5 1	1.3850-15	-14 859	-14 859	0 000
Mer	ROIL	1 2346-05		1.9030 15	14.000	14.000	0.000
мg	Mer 1 O	1 2210 0	۲ 1	1520-05	4 910	-1 020	-0.029
	Mg+2 M-CO4	1.251e-0	0 7 0 1	130- 00	-4.910	-4.939	-0.029
	MgSU4 MmOU	3.1380-0	6 J	3.138e-08	-7.503	-7.503	0.000
NI-	MGOH+	3.3//e-1	4 3	3.321e-12	-11.4/1	-11.4/9	-0.007
Na		1.305e-04					
	Na+	1.305e-0	4]	L.283e-04	-3.884	-3.892	-0.007
	NaSO4-	7.602e-0	97	7.476e-09	-8.119	-8.126	-0.007
	NaOH	6.734e-1	4 6	5.734e-14	-13.172	-13.172	0.000
0(0)		0.000e+00					
	02	0.000e+0	0 0).000e+00	-50.480	-50.480	0.000
S(6)		1.249e-05					
	SO4-2	1.243e-0	51	.162e-05	-4.906	-4.935	-0.029
	MgSO4	3.138e-0	8 3	3.138e-08	-7.503	-7.503	0.000
	HSO4 -	1.447e-0	8 1	423e-08	-7.840	-7.847	-0.007
	CaSO4	1.080e-0	8 1	.080e-08	-7.966	-7.966	0.000
	NaSO4-	7,602e-0	97	476e-09	-8.119	-8.126	-0.007
	KS04 -	4.209e-1	0 4	.139e-10	-9.376	-9.383	-0.007
					2.2.0	2.000	
	Phase	SI log	IAP	log KT			
	Anhydrite	-5.91 -1	0.27	-4.36	CaSO4		
	Gypsum	-5.69 -1	0.27	-4.58	CaSO4:2H2O		
	H2 (g)	-17.80 -1	7.80	0.00	Н2		
	H20	0.00	0.00	0.00	Н2О		
	02 (q)	-47.52 3	5.60	83.12	02		
Initi	al solution	2. LS5					
	Blementer	M-1-1-1-	_	No. 1 -			
	Elements	MOTATIC	(Mores			
	C(4)	2.623e-04	1 2	.623e-04			
	Ca	1.288e-0	 1	288e-03			
	CI	9 0286-0	; <u> </u>	0280-05			
	к ст	3 5816-03		5810-05			
	Ma	2 2220 0		.301e-03			
	Ne	2.2226-04	• ~	.2228-04			
	Na C(C)	1.7400-04	ь <u>т</u>	.7400-04			
	5(6)	1.479e-0.	5 1	.479e-03			
	Zn	2.157e-04	. 2	.157e-04			
		На	=	6.700			
		De De	=	4.000			
	Ъc	tivity of water	_	1.000			
	<i>4</i> ,	Tonic strength	_	 5 7930-03			
	Mae	a of water (ka)	-	1 0000+00			
	Total all	alinity (ac/ba)	_	1 8020-04			
	TACAT GTV	arrar (cd/vd)		エ・ロラムビー 04			

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Total CO2 (mol/kg)	=	2.623e-04
Temperature (deg C)	_ =	25.000
Electrical balance (eq)	=	4.246e-04
Iterations	=	8
Total H	=	1.110126e+02
Total O	=	5,551284e+01

					Log	Log	Log
	Species	Molal	ity	Activity	Molality	Activity	Gamma
	Чь	2 1474	-07	1 9950-07	-6 668	-6 700	-0.032
	лт ОЧ-	5 4476	- 09	5 0170-08	-7 264	-7 300	-0.036
		5.4476	- 00	9,017e-00	-7.204	0.000	0.000
C(A)	H20	2 6226-04	-+01	9.99998-01	0.000	0.000	0.000
C(4)	11002	1 0102	04	1 6720 04	-2 742	-3 777	-0 034
	ACO3-	1.0106	-04 . or	1.072e-04	- 3 . / 4 2	-3.777	0.001
	CO2	7,4926	:-05	7.5020-05	-4.125	-4,125	0.001
	ZNHCO3+	3.0236	-05	2.787e-06	-5.520	-5.555	-0.035
	CaHCO3+	1.9096	-06	1.764e-06	-5.719	-5.754	-0.034
	znc03	1.0376	-06	1.0380-06	-5.984	-5.984	0.001
	MgHCO3+	2.9766	9-07	2.744e-07	-6.526	-6.562	-0.035
	CaCO3	5.452€	-08	5.459e-08	-7.263	-7.263	0.001
	CO3-2	5.3896	-08	3.931e-08	-7.269	-7.406	-0.137
	NaHCO3	1.5010	-08	1.503e-08	-7.824	-7.823	0.001
	MgCO3	5.253€	-09	5.260e-09	-8.280	-8.279	0.001
	Zn (CO3) 2-2	1.207e	-09	8.724e-10	-8.918	-9.059	-0.141
	NaCO3-	1.2690	-10	1.170e-10	-9.897	-9.932	-0.035
Ca		1.288e-03					
	Ca+2	1.1346	-03	8.267e-04	-2.945	-3.083	-0.137
	CaSO4	1.517e	-04	1.519e-04	-3.819	-3.819	0.001
	CaHCO3+	1.909€	-06	1.764e-06	-5.719	-5,754	-0.034
	CaCO3	5.452e	-08	5.459e-08	-7.263	-7.263	0.001
	CaOH+	7.457€	-10	6.876e-10	-9.127	-9.163	-0.035
Cl		9.028e-05					
	Cl-	9.025€	-05	8.313e-05	-4.045	-4.080	-0.036
	ZnCl+	3.212€	-08	2.962e-08	-7.493	-7.528	-0.035
	ZnCl2	2.575e	-12	2.579e-12	-11.589	-11.589	0.001
	ZnCl3-	2.609e	-16	2.405e-16	-15.584	-15.619	-0.035
	ZnCl4-2	1.386e	-20	1.002e-20	-19.858	-19.999	-0.141
H(0)		5.629e-25					
	H2	2.815e	-25	2.818e-25	-24.551	-24.550	0.001
К		3.581e-05					
	K+	3.558e	-05	3.278e-05	-4.449	-4.484	-0.036
	KSO4 -	2.317e	-07	2.136e-07	-6.635	-6.670	-0.035
	кон	5.688e	-13	5.695e-13	-12.245	-12.244	0.001
Ma		2.222e-04					
5	Ma+2	1.916e	-04	1.402e-04	-3.718	-3.853	-0.136
	MaSO4	3.023e	~05	3.027e-05	-4.520	-4.519	0.001
	MaHCO3+	2 9766	-07	744e = 07	-6 526	-6 562	-0.035
	Macos	5 2530	-09	5 2600-09	-8 280	-8 279	0.000
	MgC03	2.2550	-09 -	5.200e-09	-0.20V	-0.272 9 EQ2	0.001
N I	MyOn+	2.768e	-09 .	4.0048-09	-0.000	-0.020	-0.035
иd	No	1.7408-04	0 4			2 200	0 075
	Na+	1,732e	-04	1.5988-04	-3./01	-3./90	-0.035
	NaS04-	7.999e	-07	7.376e-07	-6.097	-6.132	-0.035
	NaHCO3	1.501e	-08 :	1.503e-08	-7.824	-7.823	0.001

	NaCO3-	1.269e-10	1.170e-10	-9.897	-9.932	-0.035
	NaOH	5.285e-12	5.292e-12	-11.277	-11.276	0.001
O(0)		0.000e+00				
0(0)	02	0.0000100	0.0000.00	- 42 291	-43 280	0 001
0 (7)	02	0.00000+00	0.0000+00	-43.201	-43.200	0.001
S(6)		1.4790-03				
	SO4-2	1.266e-03	9.207e-04	-2.897	-3.036	-0.138
	CaSO4	1.517e-04	1.519e-04	-3.819	-3.819	0.001
	MgSO4	3.023e-05	3.027e-05	-4.520	-4.519	0.001
	ZnSO4	2.853e-05	2.857e-05	-4.545	-4.544	0.001
	NaSO4-	7.999e-07	7.376e-07	-6.097	-6.132	-0.035
	2n(SO4)2-2	2 9586-07	2 138e-07	-6 529	-6 670	-0.141
		2,3170-07	2.1360-07	6 6 2 5	-6 670	-0.035
	N304-	2.31/6-07	2.1366-07	-0.035	-0.070	-0.035
_	HSU4 -	1.937e-08	1.7868-08	-7.713	-7.748	-0.035
Zn		2.157e-04				
	Zn+2	1.820e-04	1.324e-04	-3.740	-3.878	-0.138
	ZnSO4	2.853e-05	2.857e-05	-4.545	-4.544	0.001
	ZnHCO3+	3.023e-06	2.787e-06	-5.520	-5.555	-0.035
	ZnCO3	1.037e-06	1.038e-06	-5.984	-5.984	0.001
	ZnOH+	7 8896-07	7 2740-07	-6 103	-6 138	-0 035
	$\frac{2m(s_{0,4})}{2m(s_{0,4})}$	2.9580-07	2 1290.07	6 529	6.200	0.000
	$211(304) \ge 2$	2.9586-07	2.1360-07	-0.329	-0.070	-0.141
	Zn (OH) Z	4.1800-08	4.1860-08	-7.379	-7.378	0.001
	ZnCl+	3.212e-08	2.962e-08	-7,493	-7.528	-0.035
	Zn (CO3) 2-2	1.207e-09	8.724e-10	-8.918	-9.059	-0.141
	ZnCl2	2.575e-12	2.579e-12	-11.589	-11.589	0.001
	Zn (OH) 3 -	7.194e-13	6.633e-13	-12.143	-12.178	-0.035
	ZnCl3-	2.609e-16	2.405e-16	-15.584	-15.619	-0.035
	Zn (OH) 4 - 2	7.289e-19	5.269e-19	-18,137	-18.278	-0.141
	ZnC14-2	1 386e-20	1 002e-20	-19 858	-19 999	-0 141
		1.5000 20	1,0020 20	£2.000		0.141
	Phase	SI log IA	AP Log KT			
	Annyarite	-1.76 -6.1	L2 -4.36	CaSO4		
	Aragonite	-2.15 -10.4	19 -8.34	CaCO3		
	Calcite	-2.01 -10.4	49 -8,48	CaCO3		
	CO2 (g)	~2.66 -20.8	31 -18.15	CO2		
	Dolomite	-4.66 -21.7	75 -17.09	CaMg (CO3)2		
	Gypsum	~1.54 -6.1	.2 -4.58	CaSO4:2H2O		
	H2 (q)	-21.40 -21.4	0.00	H2		
	H2O	0.00 0.0		H20		
	02(a)	-40 32 42 9	20 92 12	02		
	Cz(g) Smitheonito	1 00 11 0		02 8002		
		-1.28 -11.2	8 -10.00			
	2n (OH) 2 (e)	-1.98 9.5	2 11.50	Zn (OH) 2		
Initia	al solution	3. Vs4				
	Elements	Molality	Moles			
	Ca	1.900e-03	1.900e-03			
	Cl	1.168e-03	1.168e-03			
	ĸ	6,653e-05	6 653e-05			
	Mar	6 6260-01	6 6260-04			
	・*ジ N つ	1 1400 00	1 1400 07			
	Na 0 (c)	1,1498-03	1.1496-03			
	5(6) -	2.9998-03	2.999e-03			
	zn	7.086e-04	7.086e-04			

pH	=	4.700
pe	=	4.000
Activity of water	=	1.000
Ionic strength	-	1.136e-02
Mass of water (kg)	=	1.000e+00
Total alkalinity (eq/kg)	=	-2.530e-05
Total carbon (mol/kg)	=	0.000e+00
Total CO2 (mol/kg)	=	0.000e+00
Temperature (deg C)	=	25.000
Electrical balance (eq)	=	6.151e-04
Iterations	=	4
Total H	=	1.110125e+02
Total O	Ħ	5.551821e+01

				Log	Log	Log
	Species	Molality	Activity	Molality	Activity	Gamma
	H+	2.195e-05	1.995e-05	-4.659	-4.700	-0.041
	OH-	5,609e-10	5.017e-10	-9.251	-9.300	-0.049
	H2O	5.551e+01	9.999e-01	0.000	0.000	0.000
Ca		1.900e-03				
	Ca+2	1,578e-03	1.034e-03	-2.802	-2.985	-0.183
	CaSO4	3.214e-04	3.223e-04	-3,493	-3.492	0.001
	CaOH+	9.596e-12	8.602e-12	-11.018	-11.065	-0.047
Cl		1.168e-03				
	Cl-	1.167e-03	1.044e-03	-2.933	-2.981	-0.048
	ZnCl+	1.164e-06	1.044e-06	-5.934	-5.981	-0.047
	ZnCl2	1.138e-09	l.141e-09	-8.944	-8.943	0.001
	ZnCl3-	1.492e-12	1.337e-12	-11.826	-11.874	-0.047
	ZnCl4-2	1.084e-15	6.999e-16	-14.965	-15.155	-0.190
Н(О)		5.622e-21				
	H2	2.811e-21	2.818e-21	-20.551	-20.550	0.001
к		6.653e-05				
	K+	6.580e-05	5.887e-05	-4.182	-4.230	-0.048
	KSO4	7.260e-07	6.508e-07	-6.139	-6.187	-0.047
	кон	1.020e-14	1.023e-14	-13.991	-13.990	0.001
Mq		6.626e-04				
	Mq+2	5.339e-04	3.524e-04	~3.273	-3.453	-0.180
	MqSO4	1.287e-04	1.290e-04	-3.891	-3.889	0.001
	MqOH+	7.153e-11	6.412e-11	-10.146	-10.193	-0.047
Na	-	1.149e-03				
	Na+	1.140e-03	1.023e-03	~2.943	-2.990	-0.047
	NaSO4-	8.933e-06	8.008e-06	-5.049	-5.096	-0.047
	NaOH	3.379e-13	3.388e-13	-12.471	-12.470	0.001
0(0)		0.000e+00				
	02	0.000e+00	0.000e+00	-51.281	-51.280	0.001
S(6)		2.999e-03				
	SO4-2	2.395e-03	1.562e-03	-2.621	-2.806	-0.186
	CaSO4	3.214e-04	3.223e-04	-3.493	-3.492	0.001
	ZnSO4	1.356e-04	1.360e-04	-3.868	-3.867	0.001
	MgSO4	1.287e-04	1.290e-04	-3.891	-3.889	0.001
	NaSO4-	8.933e-06	8.008e-06	-5.049	-5.096	-0.047
	HSO4 -	3.379e-06	3.029e-06	-5.471	-5.519	-0.047
	7n(904)2-2	2 6728-06	1 726e-06	-5.573	-5.763	-0.190

	KSO4 -	7.260e-07	6.508e-07	-6.139	-6.187	-0.047
Zn		7.086e-04				
	Zn+2	5.692e-04	3.714e-04	-3.245	-3.430	-0.185
	ZnSO4	1.356e-04	1.360e-04	-3.868	-3.867	0.001
	Zn (SO4) 2-2	2.672e-06	1.726e-06	-5.573	-5.763	-0.190
	ZnCl+	1.164e-06	1.044e-06	-5.934	-5.981	-0.047
	ZnOH+	2.277e-08	2.041e-08	-7.643	-7.690	-0.047
	ZnCl2	1.138e-09	1.141e-09	-8.944	-8.943	0.001
	Zn (OH) 2	1.171e-11	1.174e-11	-10.931	-10.930	0.001
	ZnCl3-	1.492e-12	1.337e-12	-11.826	-11.874	-0.047
	ZnCl4-2	1.084e-15	6.999e-16	-14.965	-15.155	-0.190
	Zn (OH) 3~	2.076e-18	1.861e-18	-17.683	-17.730	-0.047
	Zn (OH) 4~2	2.288e-26	1.478e-26	-25.640	-25.830	-0.190
	Phase	SI log I	AP log KT			
	Anhydrite	-1.43 -5.	79 -4.36	CaSO4		
	Gypsum	-1.21 -5.	79 -4.58	CaSO4:2H2O		
	H2 (g)	-17.40 -17.	40 0.00	H2		
	H2O	0.00 0.	00 0.00	H2O		
	02 (g)	-48.32 34.	80 83.12	02		
	Zn(OH)2(e)	-5.53 5.	97 11.50	Zn (OH) 2		

Beginning of inverse modeling calculations.

Solution 1: Rain					
pH	4.900e+00	+	0.000e+00	=	4.900e+00
A1	0.000e+00	+	0.000e+00	Ξ	0.000e+00
Alkalinity	-1.281e-05	+	0.000e+00	=	-1.281e-05
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	0.000e+00	÷	0.000e+00	=	0.000e+00
Ca	4.990e-06	+	0.000e+00	=	4.990e-06
Cl	1.551e-04	+	0.000e+00	=	1.551e-04
Cu(1)	0.000e+00	+	0.000e+00	=	0.000e+00
Cu(2)	0.000e+00	+	0.000e+00	=	0.000e+00
Fe(2)	0.000e+00	+	0.000e+00	=	0.000e+00
Fe(3)	0.000e+00	+	0.000e+00	=	0.000e+00
H(0)	0.000e+00	÷	0.000e+00	=	0.000e+00
K	5.1 15e-06	+	0.000e+00	=	5.115e-06
Mg	1.234e-05	+	0.000e+00	=	1.234e-05
Na	1.305e-04	+	-2,959e-06	=	1.275e-04
O(0)	0.000e+00	÷	0.000e+00	=	0.000e+00
S(-2)	0.000e+00	+	0.000e+00	Ξ	0.000e+00
S(6)	1.249e-05	+	0.000e+00	=	1.249e-05
Si	0.000e+00	+	0.000e+00	=	0.000e+00
Zn	0.000e+00	+	0.000e+00	=	0.000e+00
Solution 2: LS5					
pH	6.700e+00	+	0.000e+00	=	6.700e+00
Al	0.000e+00	+	0.000e+00	==	0.000e+00
Alkalinity	1.892e-04	+	0.000e+00	=	1.892e-04
C (-4)	0.000e+00	+	0.000e+00	=	0.000e+00

C(4)	2.623e-04	+	0.000e+00	=	2.623e-04	
Ca	1.288e-03	+	-2.569e-04	=	1.031e-03	
Cl	9.028e-05	+	0.000e+00	=	9.028e-05	
Cu(1)	0.000e+00	+	0.000e+00		0.000e+00	
Cu (2)	0.000e+00	+	0.000e+00	=	0.000e+00	
Fe(2)	0.000e+00	+	0.000e+00	=	0.000e+00	
Fe(3)	0.000e+00	. +	0.000e+00	=	0.000e+00	
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00	
ĸ	3.581e-05	+	-8.953e-06	=	2.686e-05	
Ma	2.222e-04	+	0.000e+00	=	2.222e-04	
Na	1.740e-04	+	0.000e+00	=	1.740e-04	
0(0)	0.000e+00	+	0.000e+00	=	0.000e+00	
S(-2)	0.000e+00	+	0.000e+00	=	0.000e+00	
S(6)	1.479e-03	+	4.804e-06	=	1.483e-03	
Si	0.000e+00	+	0.000e+00	Ŧ	0.000e+00	
Zn	2.157e-04	+	5.394e-05	-	2.697e-04	
Solution 3: Vs4						
Hq	4.700e+00	+	0.000e+00	=	4.700e+00	
Āl	0.000e+00	÷	0.000e+00	=	0.000e+00	
Alkalinity	-2.530e-05	+	0.000e+00	=	-2.530e-05	
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00	
C(4)	0.000e+00	+	0.000e+00	=	0.000e+00	
Ca	1.900e-03	+	0.000e+00	=	1.900e-03	
Cl	1.168e-03	+	-7.366e-05	=	1.095e-03	
Cu(1)	0.000e+00	+	0.000e+00	=	0.000e+00	
Cu(2)	0.000e+00	+	0.000e+00	=	0.000e+00	
Fe(2)	0.000e+00	+	0.000e+00	=	0.000e+00	
Fe(3)	0.000e+00	+	0.000e+00	=	0.000e+00	
H(0)	0.000e+00	+	0.000e+00	-	0.000e+00	
ĸ	6.653e-05	+	1.663e-05	X	8.316e-05	
Mg	6.626e-04	+	-1.518e-04	Z =	5.107e-04	
Ňa	1.149e-03	+	-5.230e-05	=	1.097e-03	
0(0)	0.000e+00	+	0.000e+00	~	0.000e+00	
S(-2)	0.000e+00	+	0.000e+00	=	0.000e+00	
S(6)	2.999e-03	+	-2.428e-06	-	2.997e-03	
Si	0.000e+00	+	0.000e+00	=	0.000e+00	
Zn	7.086e-04	+	-1.772e-04	=	5.315e-04	
Solution fractions	:		Minimum		Maximum	
Solution 1	5.909e+00		0.000e+00		0.000e+00	
Solution 2	1.971e+00		0.000e+00		0.000e+00	
Solution 3	1.000e+00		0.000e+00		0.000e+00	
Phase mole transfe:	rs:		Minimum		Maximum	
H20	-3.819e+02		0.000e+00		0.000e+00	H2O
Calcite	-1.612e-04		0.000e+00		0.000e+00	CaCO3
CO2 (g)	-3.556e-04		0.000e+00		0.000e+00	CO2
_ · · -						_
Sum of residuals:			9.808e+00		0	
Maximum fractional	error in elem	ment	concentrat:	ion:	2.500e-0	1

I

Model contains minimum number of phases.

Solution 1: Rain					
PH	4.900e+00	÷	0.000e+00	=	4.900e+00
Al	0.000e+00	+	0.000e+00	=	0.000e+00
Alkalinity	-1.281e-05	+	0.000e+00	=	-1.281e-05
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	0.000e+00	+	0.000e+00	=	0.000e+00
Ca	4.990e-06	+	0.000e+00	=	4.990e-06
Cl	1.551e-04	+	0.000e+00	=	1.551e-04
Cu(1)	0.000e+00	+	0.000e+00	=	0.000e+00
Cu(2)	0.000e+00	+	0.000e+00	=	0.000e+00
Fe(2)	0.000e+00	+	0.000e+00	=	0.000e+00
Fe(3)	0.000e+00	+	0.000e+00	=	0.000e+00
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00
ĸ	5.115e-06	+	0.000e+00	=	5.115e-06
Ma	1.234e-05	-	0.000e+00	=	1.234e-05
Na	1.305e~04	+	-2.959e-06	=	1.275e-04
O(0)	0 000e+00		0.000e+00	-	0 000e+00
S(-2)		1 -	0.0000+00	_	0 0000+00
G (6)	1 2490-05	т ,	0.0000+00	_	1 2490-05
5(0)	0.0000400	म ।	0.0000+00	_	0 0000+00
21	0.00000400	.	0.00000000	_	0.00000+00
211	0.00000400	+	0.0000400	=	0.00000000
Solution 2: LSS	6 800- 00				6 600 . 00
рн	6.700e+00	+	0.000e+00	=	6.700e+00
AL 	0.000e+00	+	0.000e+00	=	0.000e+00
Alkalinity	1.892e-04	+	0.000e+00	=	1.892e-04
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	2.623e-04	+	0.000e+00	=	2.623e-04
Ca	1.288e-03	+	-2.205e-04	=	1.067e-03
Cl	9.028e-05	+	0.000e+00	=	9.028e-05
Cu (1)	0.000e+00	+	0.000e+00	=	0.000e+00
Cu(2)	0.000e+00	+	0.000e+00		0.000e+00
Fe(2)	0.000e+00	+	0.000e+00	=	0.000e+00
Fe(3)	0.000e+00	+	0.000e+00	=	0.000e+00
н(о)	0.000e+00	÷	0.000e+00	=	0.000e+00
K	3.581e-05	+	0.000e+00	=	3.581e-05
Mg	2.222e-04	+	0.000e+00	=	2.222e-04
Na	1.740e-04	+	0.000e+00	=	1.740e-04
0(0)	0.000e+00	+	0.000e+00	Ŧ	0.000e+00
S(-2)	0.000e+00	+	0.000e+00	=	0.000e+00
S(6)	1.479e-03	+	0.000e+00	=	1.479e-03
Si	0.000e+00	+	0.000e+00	=	0.000e+00
Zn	2.157e-04	+	8.214e-06	=	2.240e-04
Solution 3: Vs4					
рH	4.700e+00	+	0.000e+00	=	4.700e+00
Al	0.000e+00	+	0.000e+00	=	0.000e+00
Alkalinity	-2.530e-05	+	0.000e+00	=	-2.530e-05
C(-4)	0.000e+00	+	0.000e+00	=	0.000e+00
C(4)	0.000e+00	+	0.000e+00	-	0.000e+00
Ca	1.900e-03	+	4.749e-04	=	2.375e-03
Cl	1.168e-03	+	0.000e+00	=	1,168e-03
Cu(1)	0.000e+00	+	0.000e+00	=	0.000e+00
Cu(2)	0.000e+00	+	0.000@+00	=	0.000e+00

Fe(2)	0.000e+00	+	0.000e+00	=	0.000e+00	
Fe(3)	0.000e+00	+	0.000e+00	=	0.000e+00	
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00	
K	6.653e-05	+	0.000e+00	=	6.653e-05	
Ma	6.626e-04	+	-6.839e-05	=	5.942e-04	
Na	1.149e-03	+	9.813e-05	=	1.247e-03	
0(0)	0.000e+00	+	0.000e+00	=	0.000e+00	
S(-2)	0.000e+00	+	0.000e+00		0.000e+00	
S(6)	2.999e-03	+	5.860e-04		3.585e-03	
Si	0.000e+00	4	0.000e+00	<u>~</u>	0.000e+00	
2n	7 0868-04	+	-1 772e-04	=	5.315e-04	
211	7.0000-04		1.7720 01		0.0100 00	
Solution fractic	nns.		Minimum		Maximum	
Solution 1	6 150e+00		0 000e+00		0.000e+00	
Solution 2	2 373e+00		0.0000+00		0.000e+00	
Solution 3	1 0000+00		0 000e+00		0.000e+00	
Solution 5	1.0000400		0.0000100		0.00000100	
Phase mole trans	ferg.		Minimum		Maximum	
Phase more crane	-4 1760+02				0 0000+00	H2O
Caldite	-2 1840-04		0.00000100		0 0000+00	CaCO3
			0.00000000		0.0000+00	CO2
coz(g)	-4.0400-04		0.000000000			002
pragrocrase	8.0180-05		0.00000000		0.00000+00	KV164308
K-reidspar	-2.8480-05		0.00000+00		0.00000000	INIS1300
IIIIce	-3.5/30-05		0.00000400		6 0Plat	0
Sum of residuals	;: 			ion	0.0010+0	10
Maximum fraction	lat error in ele	men	c concentrat	TOUT	: 2.500e-0	/1
Colution 1. Dair	<u>_</u>			====		
Solution 1: Rain		:===			4 9000+00	
Solution 1: Rain	4.900e+00		0.000e+00	====	4.900e+00	
Solution 1: Rain pH Al	4.900e+00 0.000e+00	 + +	0.000e+00 0.000e+00 0.000e+00	====	4.900e+00 0.000e+00 -1.281e=05	
Solution 1: Rain pH Al Alkalinity	4.900e+00 0.000e+00 -1.281e-05	+ + +	0.000e+00 0.000e+00 0.000e+00 0.000e+00	= = = = = = = = = = = = = = = = = = = =	4.900e+00 0.000e+00 -1.281e-05	
Solution 1: Rain pH Al Alkalinity C(-4)	4.900e+00 0.000e+00 -1.281e-05 0.000e+00	+ + + + +	0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00	= = = = = = = = = = = = = = = = = = = =	4.900e+00 0.000e+00 -1.281e-05 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4)	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00	+++++++	0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00	= = = = = = = = = = = = = = = = = = = =	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06	+ + + + +	0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04	+ + + + + +	0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1)	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00	+ + + + + + + +	0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2)	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00		0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Pr(2)	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00	·=== + + + + + + + + + + + + + + + + + +	0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(3) T(6)	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00	· = = = = + + + + + + + + + + + + + + +	0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(3) H(0)	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00	== + + + + + + + + + + + + + + + + + +	0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(3) H(0) K	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06	= = + + + + + + + + + + + + + + + + + +	0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(3) H(0) K Mg	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05		0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(3) H(0) K Mg Na	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.305e-04		0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.275e-04	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(3) H(0) K Mg Na O(0)	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.305e-04 0.000e+00		0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.275e-04 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(3) H(0) K Mg Na O(0) S(-2)	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.305e-04 0.000e+00 0.000e+00		0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.275e-04 0.000e+00 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(3) H(0) K Mg Na O(0) S(-2) S(6)	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.305e-04 0.000e+00 0.000e+00 1.249e-05		0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.275e-04 0.000e+00 0.000e+00 1.249e-05	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(3) H(0) K Mg Na O(0) S(-2) S(6) Si	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.305e-04 0.000e+00 0.000e+00 1.249e-05 0.000e+00		0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.275e-04 0.000e+00 0.000e+00 1.249e-05 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(3) H(0) K Mg Na O(0) S(-2) S(6) Si Zn	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.305e-04 0.000e+00 0.000e+00 1.249e-05 0.000e+00		0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.275e-04 0.000e+00 0.000e+00 1.249e-05 0.000e+00 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(2) Fe(3) H(0) K Mg Na O(0) S(-2) S(6) Si Zn	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.305e-04 0.000e+00 0.000e+00 1.249e-05 0.000e+00 0.000e+00		0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.275e-04 0.000e+00 0.000e+00 1.249e-05 0.000e+00 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(2) Fe(3) H(0) K Mg Na O(0) S(-2) S(6) Si Zn Solution 2: LS5	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.305e-04 0.000e+00 0.000e+00 1.249e-05 0.000e+00		0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.275e-04 0.000e+00 0.000e+00 1.249e-05 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(2) Fe(3) H(0) K Mg Na O(0) S(-2) S(6) Si Zn Solution 2: LS5 pH	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.305e-04 0.000e+00		0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.275e-04 0.000e+00 0.000e+00 1.249e-05 0.000e+00 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(3) H(0) K Mg Na O(0) S(-2) S(6) Si Zn Solution 2: LS5 pH Al	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.305e-04 0.000e+00 0.000e+00 1.249e-05 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00		0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.275e-04 0.000e+00 0.000e+00 1.249e-05 0.000e+00 0.000e+00	
Solution 1: Rain pH Al Alkalinity C(-4) C(4) Ca Cl Cu(1) Cu(2) Fe(2) Fe(3) H(0) K Mg Na O(0) S(-2) S(6) Si Zn Solution 2: LS5 pH Al Alkalinity	4.900e+00 0.000e+00 -1.281e-05 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.305e-04 0.000e+00 1.249e-05 0.000e+00 0.000e+00 1.249e-05 0.000e+00 1.249e-05 0.000e+00 1.249e-05 0.000e+00 1.249e-05 0.000e+00 1.249e-05 0.000e+00 1.249e-05 0.000e+00 0.000e+00 1.249e-05 0.000e+00		0.000e+00 0.000e+00		4.900e+00 0.000e+00 -1.281e-05 0.000e+00 4.990e-06 1.551e-04 0.000e+00 0.000e+00 0.000e+00 0.000e+00 0.000e+00 5.115e-06 1.234e-05 1.275e-04 0.000e+00 0.000e+00 1.249e-05 0.000e+00 0.000e+00 1.249e-05	

C(4)	2.623e-04	+	0.000e+00	=	2.623e-04	
Ca	1.288e-03	· +	-1.762e-04	=	1.112e-03	
C1	9.028e-05	+	0.000e+00	=	9.028e-05	
Cu (1)	0.000e+00	+	0.000e+00	=	0.000e+00	
Cu (2)	0 000e+00	+	0.000e+00	=	0.000e+00	
$E_{\alpha}(2)$	0.0000+00	, +	0.000e+00	=	0.000e+00	
FC(2)	0.00000+00	, _	0.00000.00	_	0 0000+00	
re(3)	0.0000+00	т т		_	0 000e+00	
H(U)	2 5910-05	- -	0.0000+00	_	3 5810-05	
	3.301e-03	+	0.00000000	_	2,2220-04	
Mg	2.2228-04	+	0.00000000	-	2.2220-04	
	1.7408-04	+	0.0000+00	=	1.7408-04	
0(0)	0.000e+00	+	0.000e+00	=	0.000e+00	
S(-2)	0.000e+00	+	0.000e+00	=	0.00000+00	
S(6)	1.479e-03	+	9.001e-05	=	1.569e-03	
Si	0.000e+00	+	0.000e+00	=	0.000e+00	
Zn	2.157e-04	+	5.394e-05	=	2.697e-04	
Solution 3. Vs4						
DH	4.700e+00	+	0.000e+00	-	4.700e+00	
 A]	0.000e+00	+	0.000e+00	=	0.000e+00	
Alkalinity	-2.530e-05	+	0.000e+00		-2.530e-05	
C(-4)	0.0000+00	+	0.000e+00	=	0.000e+00	
C(4)	0.00000+00	т -	0.0000+00	_	0 0000+00	
C(4)	1 9000-03	т 	0.0000+00	_	1 900e-03	
Ca Cl	1.9000-03	+	0.00000000	_	1 1680-03	
	1.1000-00	Ť	0.00000+00	=	1,1000-00	
Cu(1)	0.000e+00	+	0.00000+00	=	0.00000000	
$\operatorname{Cu}(2)$	0.000e+00	+	0.000e+00	-	0.00000000	
Fe(2)	0.000e+00	+	0.000e+00	=	0.000e+00	
Fe(3)	0.000e+00	+	0.000e+00	=	0.00000000	
H(0)	0.000e+00	+	0.000e+00	=	0.000e+00	
ĸ	6.653e-05	+	1.663e-05	=	8.316e-05	
Mg	6.626e-04	+	2.765e-05	=	6.902e-04	
Na	1.149e-03	+	1.012e-05	=	1.159e-03	
0(0)	0.000e+00	+	0.000e+00	=	0.000e+00	
S(-2)	0.000e+00	+	0.000e+00	=	0.000 e +00	
S(6)	2.999e-03	+	1.714e-04	=	3.171e-03	
Si	0.000e+00	+	0.000e+00	=	0.000e+00	
Zn	7.086e-04	+	-1.772e-04	=	5.315e-04	
Colution frontiona			Minimum		Maximum	
Solution Haccions	; C 3840100				0 0000+00	
Solution 1	6.384e+00		0.00000000		0.00000+00	
Solution 2	1.9/1e+00		0.000e+00		0.00000000	
Solution 3	1.000e+00		0.000e+00		0.000e+00	
Phase mole transfe	rs:		Minimum		Maximum	
H2O	-4.082e+02		0.000e+00		0.000e+00	Н2О
Calcite	-3,238e-04		0.000e+00		0.000e+00	CaCO3
CO2 (a)	-1.931e-04		0.000e+00		0.000e+00	CO2
nlagioglase	3 0140-06		0.0000+00		0.000e+00	
Prayrocrase TJJ:+~	-3 3/Ea-05				0 0000+00	
Chlorito (147)	3 6200-05		0.0000400		0 0000+00	
CHIOLICE (14A)	3.0398-03		0.00000000		0.0000100	
Sum of residuals:					6.539e+0	00
Maximum fractional	error in ele	men	t concentrat:	ion:	2.500e-0)1

Summary of inverse modeling: Number of models found: 3 Number of minimal models found: 1 Number of infeasible sets of phases saved: 10 Number of calls to cl1: 269 End of simulation. Reading input data for simulation 2. End of run.

9.0 CONCLUSIONS AND RECOMMENDATIONS

9.1 Conclusions

The marginal performance of the polishing ponds during the winter months and the repeated good zinc removal (Figures 37 to 43; Section 7) during summer months prompted a re-evaluation of the zinc removal process. The assumption was made that, if the removal process is understood, it can then be controlled or promoted. In Schematic 3, all disciplines utilized, or potential areas which may be affecting performance, are given.

The nutrient limiting plant growth in the system, phosphate, has been identified. In April, 1996, geochemical simulations suggested that additions of phosphate would result in zinc phosphate formation, but the reactions are rather slow and biological activity could potentially remove the phosphate prior to any chemical reactions. This appeared to be confirmed by laboratory growth experiments where phosphate, added to periphyton cultures, was rapidly removed from solution.

A small field trial in Polishing Pond 11 produced important results regarding the fate of phosphate following addition to the system. Concentrations of phosphate could be predicted based on the flow in the pond. In mini-limnocorrals, where a relatively large mass of periphyton was incubated in a closed volume of pond water over 3 days, most of the added phosphate was not detectable in this solution. This confirmed the results of the geochemical simulations which suggested that zinc-phosphate should slowly form and precipitate. The results of analysis of the filter paper used to filter the mini-limnocorral solution (Table 27, Section 6) confirms that a considerable quantity of zinc and phosphate had precipitated in this solution.

If some phosphate remobilizes from zinc phosphate settled to the bottom of polishing ponds, primary productivity in these ponds should increase, as indicated by from the results of phytoplankton counts for OWP and Polishing Pond 17 (Table 19 and 20; Section 5). These data on small-celled phytoplankton also revealed that virtually no phytoplankton growth is present the OEP, even though the TOC values were relatively high in OEP bottom water samples (Table 36; Section 8.1). This could be explained if picoplankton growth was present in this pit, information which are still outstanding at this time. It was concluded that, based on available phytoplankton data, physical factors in OEP inhibit growth, as these organisms are subjected to poor/ lethal growing conditions, including low light availability, variable water chemistry in surface water, and turbulent flow in the epilimnion as it mixes with hypolimnion water along the thermocline stratum in summer. Turbulent flow in summer months was suggested from observations of round/globular particles during the growing season but more elongated, crystalline particles towards the end of the growing season.

If we assume that particle formation can be assisted by the production of phytoplankton particles and that zinc, adsorbed onto iron hydroxide particles, will be captured by periphyton biomass surfaces in the polishing ponds, then performance data for the polishing ponds during the summer can be reasonably well explained. However, the iron precipitation experiments, discussed in Section 3.0, clearly indicate that zinc precipitation and iron precipitation are independent processes. A review of the chemistry of the removal process, outlined in previous reports, suggested that zinc carbonate is formed. This has been confirmed by the assay data indicating zinc accumulation in polishing pond algae and moss biomass, and by the SEM/EDX observations on the material from the sedimentation traps (Section 4.0).

The monitoring data were reanalyzed on the premise that, if there is an independent zinc removal process involving zinc carbonate precipitation, then variation in zinc removal with the seasons should be observed. This has been confirmed for effluents close to the waste source (Section 1.0). With this new removal process in mind, the main objective was then to determine the specific mechanism of zinc carbonate formation and precipitation, particularly in relation to seasonal variations in
temperature, flow patterns and gas exchange between the water bodies and the atmosphere.

The SEM/EDX clearly suggested that small crystals accumulate around the iron particles. Surface science parameters for particle formation and settling were reviewed. In Figure 44, the buoyancy and sedimentation coefficients are given for selected bio-organic and inorganic particles, including those species known to be present in the OEP or OWP water.

A field experiment testing iron oxide-rich local sand, as well as bentonite, confirmed that zinc was not adsorbed, as the negatively-charged surface of the bentonite did not reduce zinc concentrations. Thus, additions of oxides and/or bentonite would not assist the settling of the particles.

In Figure 44, the distribution of various major compounds, typically found in surface waters is presented according to particle size. This figure reveals that the arbitrary cut off size, 0.45 μ m, typically used to distinguish dissolved compounds from particulate, is inappropriate for present purposes, since both iron hydroxide and inorganic precipitates of zinc carbonate can be less than 0.45 μ m in size. SEM examinations at 20,000 x magnification suggested that the coat of zinc carbonate is about 100 nm on particles 0.25 to 1 μ m in size. These size ranges also explained the last experiment (conducted in January by G. Neary), where fertilizer-treated OEP water samples, filtered through 0.45 μ m filters contained similar zinc concentrations as whole samples (Table 18, Section 3). In this experiment, where fertilizer was added such that phosphate molar concentration was the same as the molar concentration of Ca+Mg+Zn, Mg+Zn or just Zn, 73 % to 87 % of the zinc was removed in the Zn or Mg+Zn treatments, respectively. These results suggested that indeed zinc phosphate may be formed. The precipitate is presently being subjected to SEM/EDX for determination of the composition of the particles/ precipitates.

Assuming that all the above observations solidly back zinc carbonate precipitation as the removal process, then a completely different picture emerges for the biological polishing approach. The biological components and the physical components of the system are integral to the zinc removal process, in that zinc carbonate can only form when CO_2 can degas from surfacing ground water, and particles can only settle when the hydrodynamic conditions permit, such as in the vicinity of periphyton biomass in quiet parts of the polishing ponds, and on iron hydroxide particles large enough to settle despite flow conditions.

In Schematic 4, an overview of the ongoing processes are summarized, including the basics of the 'iron wheel' and the carbon dioxide-bicarbonate-carbonate reaction series. The findings of the geochemical simulations suggest that the Valley seeps are composed of Lucky Strike water which has evaporated and then degassed, again demonstrating the dominance of inorganic carbon species as a controlling factor in the precipitation zinc carbonate. The solubilities of carbon dioxide are given in Table 39, for connection of the behaviour of the biological polishing system to temperature and, in turn, to the formation of a zinc carbonate. In Figures 46, 47 and 48, other aspects of the carbon dioxide-bicarbonate-carbonate series, controlling the zinc removal process, are presented. Inorganic carbon chemistry has to be fully integrated before a complete understanding of the removal mechanism is reached.

Since the Buchans water chemistry is dominated by the inorganic carbon reaction series, other elements competing with zinc for carbonate, as well as phosphate, will also come into play. The concentrations of Ca, Fe, Mg and Mn in OEP and OWP, all potential forming carbonates and phosphates, are plotted for the surface and bottom waters of both glory holes. All available ICP data for these elements, collected since decommissioning activities started, are presented. In OEP, a decrease in the Ca concentration over the years is noted in the surface water, but not for bottom water. Fe, Mn and Mg remained at relatively constant concentrations in both surface and bottom waters. However if the scale is changed, a subtle decrease in Mg

concentrations in the surface water since 1989 is noted for OEP (Fig 50c), from 40 mg/L to 20 mg/L. In bottom water, the Mg concentration is constant at around 45 mg/L. Iron concentration have been somewhat erratic over time. In the OWP, a similar decrease in Ca concentrations is noted (Figure 51a and 51b) for the bottom water, but not surface water, while Fe, Mg and Mn have remained at constant concentrations.

Although this type of analysis remains to be completed for other elements, these observations suggest that different sources of water are entering the gloryholes at different locations, and that some elements could be precipitating, as observed for zinc. In Figure 52, the comparison of the slope of the Zn curve to that of Mg suggests that, indeed, these two elements may be removed by the very similar processes. In Table 40, Ca, Fe, Mg and Mn concentration data in water and captured by filter papers are summarized for both OEP and OWP. Although this is a crude 'shotgun' approach (the information drawn from Paradox database without quantification and verification of the conversion from concentrations on filter paper to amount filtered), given that the elements are reported in the filter paper analyses, these elements must be forming aggregates of particles larger than 0.45 μ m.

In Figure 49a and 49b, the same elements which are suspected to be part of the zinc precipitation process are plotted for the periphyton and sedimentation trap material. Data presented in this manner suggest that Mg and Zn are strongly associated in OWP, but this association is essentially absent in solids collected from the Polishing Ponds. Note that the data were only available for the Polishing Ponds 1 to 6, since analytical costs have been minimized since scale-up of the polishing pond system. From these preliminary analyses, it is suggested that, in different parts of the system, different elements play a role in controlling the zinc precipitation process.

One further new aspect shedding additional light on long-term conditions in OEP is drawn from the conclusion of freshwater input to OEP, based on the mass balance

calculations for chloride (Section 2). The flow model developed for the polishing ponds (Section 7) was extended to be used for the Drainage Tunnel and the OEP. Preliminary model calculations are given in Figures 53 a to 53 d, each utilizing different zinc input concentrations/changes with time, with and without zinc removal by sedimentation, for comparison to the measured zinc concentration trend in OEP outflow water.

In Figure 53c, the zinc concentration decreases calculated by the model and the measured decreases are in close agreement. In this scenario, zinc-containing solids, as captured in the sedimentation traps, is recycling or, as suggested in Figure 53d (Case 5), the initial concentrations was lower in the pit and the groundwater concentration is at 45 mg/L zinc. Although not all reasonable scenarios have been tested, it is likely that a considerable amounts of iron and zinc precipitating and settling in OEP are recycling. If recycling can be prevented, there may be an end to long-term treatment.

Given these radical new findings, and the overwhelming amount of data available for confirmation of these key conclusions, further analysis of the compiled data in the present report will be required. However, there is no doubt that the zinc removal process was incorrectly identified as coprecipitation with iron hydroxide and that fresh water is entering the OEP. Freshwater input may even be responsible for the observed long-term decrease in zinc concentrations, in view of the fact that iron and zinc may be recycled. Although the magnitude of this recycled fraction is not known, and the data have to be analyzed in more detail, it provides a new treatment alternative which was not recognized before.

The results of the phosphate addition experiments completed late January, 1997 using OEP water, as well as the particle size and hydrodynamic considerations, provide for the possibility of a one or two-time treatment with phosphate, and possible addition of organics as a sealant promoter of organic phosphate cycling.

If it can be confirmed that portions of zinc and iron are recycling in the OEP, that the contribution from the underground is diminishing, and that zinc-free fresh water is entering the OEP, then with a one time removal of the iron and zinc, in form of the iron phosphate/zinc phosphate, a final decommissioning solution would be provided. The particles have to be settled and chemoclines have to be destroyed. A healthy pond would replace the problem of the OEP, providing continuous polishing for the ground water zinc contribution. The elegant component of the 1996 results is the fact that, if this can be confirmed, the observations on the Valley seeps, the Lucky Strike and the Drainage Tunnel are all part of the same solution and would essentially solve the problems presented by all contaminant sources in the Buchans area.

9.2 Recommendations

1) Data Interpretation

The 1996 work has resulted in a completely new view of the Buchans situation. These new scenarios have to be evaluated in detail. The present report is considered a data report, assembling all the information gathered this year, but also represents a review of previous years' work. Normally, after all data are assembled, a systematic analysis and interpretation of the data is carried out. The 1996 objectives involved such an extensive scope of work that many aspects have not been analyzed yet and oversights of the seemingly contradictory behaviour of the chemistry cannot yet be eliminated. Therefore, Task 1 will confirm, using all available data, the new scenario.

Furthermore, organization of the available data is urgently needed, as there are 1,195 chemical analysis, of which there are 717 water chemistry analyses, 106 biomass sample analyses, 137 filter paper analyses and 235 solids analyses.

Digitized maps of the Buchans area have been completed, which can be used to generate detailed site maps providing coordinates for any sampling point.

After the data are fully interpreted, the following activities can be identified:

Final experiments and measurement to be done in winter, 1997.

- Field Studies
 - under ice experiments phosphate reactions in ambient conditions
 - Monitoring under ice LS, OWP, OEP, Polishing Ponds: iron, zinc, phosphate.
 - sourcing non-acidifying, non-Ca, Mg, Na fast release phosphate source,
 e.g. potassium phosphate.
- geochemical modelling of any changes or additions based on the existing model with O₂, CO₂ degassing; new PHEQUE version
 - are carbonates truly formed?
- Phosphate addition to OEP in winter major considerations?
- Phosphate addition to Drainage Tunnel pump house a consideration?
- Lucky Strike Gloryhole Action plan?

Organize the data and validate entry and units for all data points, analyze the data set for complete set of elements which are part of the precipitation process. Test the decreases (surface and bottom) for all water bodies and all elements, i.e. Drainage Tunnel, Lucky Strike, Valley Seeps, Tailings Ponds as well as OEP and OWP.

Task 2: Phosphate Cycling in System

To arrive at these new perspectives, Dr. Hellebust (Dept. of Botany, U of Toronto) was consulted. He had periodically contributed to the biological aspects of the site for the past 10 years ago. He has agreed to evaluate the possibility to use radioactive phosphate in tracing the fate of phosphate. This clearly is a key component in zinc removal and for the biological integrity of the polishing system. The picoplankton data which are coming, together with the identifications of the precipitates from the January experiments, will be evaluated and biological productivities projected for each polishing area, taking the present physical /chemical limitations into account.

The fate and stability of phosphate for zinc removal in the context of primary productivity in the Buchans waters. Development of a field test protocol to differentiate between biological and chemical phosphate fate. Sediment release of precipitated phosphate to provide long term phosphate fertilisation.

To determine the long term fate of the particles, their biological components are being identified. This is proposed to be carried out as an M.Sc. thesis using epifluorescence microscopy, which can identify living forms on solids particles. It can be expected that phosphate particles will be microbially transformed in the long term, since it contains one of the key limiting nutrients. In the first year, the colonisation (coating observed in SEM investigation) will be delineated.

Task 3: Factors Controlling Particle Formation

It is proposed that a surface scientist (Dr. Mikahailovski) should engaged. He has already provided perspectives on particle formation and particle sizes and their relevance in forming colloids, aggregates and hence their ability to settle out of the water column. During 1996, he has assisted in reviewing the Buchans data and has pointed out one of the key facts; only particles large enough to respond to gravitational forces would end up in the sedimentation traps. His insight into the physics and colloid chemistry added new dimensions to the sequential extractions of sedimentation trap materials (not discussed in this report; M.Sc. thesis, U of T) and oxygen availability in the OEP. A microelectrophoresis apparatus for the determination of particle sizes and charges has been located at the University of Toronto and zeta-potentials of various particles and their aggregates/colloids will be determined. With this information, the hydrodynamical changes required in the pits can be estimated. Upon this assessment, it will be possible to determine whether improvements in the particle settling characteristics can be achieved.

Task 4: Inorganic Carbon Solution Chemistry; Partial Pressure and Degassing

The new geochemist, using a version of PHREQUE which integrates gases, has provided insight into the processes which may be responsible for observed solution chemistry. Evaporation as a concentrating process for zinc in the overburden was identified. Based on chloride concentrations, using sea spray numbers and the drill hole water quality as background data, combined with degassing, produced Valley seep concentrations from Lucky strike water. The concentration process through evaporation has to be evaluated and possibly tested. Many of these aspects, given the new scenario, have to evaluated in detail, time not permitting to date. One key aspect which needs to be addressed is whether there is the potential for Lucky Strike pit's limnology to resemble that of OWP prior to Drainage Tunnel discharge, i.e. turn acid. While there was some past effort extended (some years ago) to identify the source of bicarbonate, information regarding this source in of increasing importance for the Lucky Strike, since this water is reaching the Drainage Tunnel and the Valley seeps.

Gas	$K \times 10^{-7}$ $K = P/X$ P = partial pressure mm. of Hg X = mole fraction									
References	$t = 0^{\circ}$	10°	20°	30°	38°	40°	50°	60°	70°	80°
Argon 1, 8, 14, 15, 17	1.65	2.18	2.58	3.02	3.41	3.49	3.76	3.92	4.12	4.25
Carbon dioxide 6, 7, 9, 12 Helium 3 8 12 14	.0555 10.0	.0788 10.5	10.9	.139	.168	.173 10.9	.217	.208 10.3	9.88	
15, 18, 21 Hydrogen 6, 12	4.42	4.82	5.20	5.51	5.72	5.78	5.82	5.80	5.77	5.73
Krypton 2, 14, 15 Neon	0.853 7.68	1.20 8.49	1.52 9.14	1.85 9.45	2.13 9.76	2.18 9.80	2.43 10.0	2.66	2.83	2.94
(2), 8 Nitrogen 12, 16, 20, 22 , 23 24	4.09	4.87	5.75	6.68	7.51	7.60	8.20	8.70	9.20	
Oxygen 6, 10, 12, 13	1.91	2.48	2.95	3.52	4.04	4.14	4.5 0	4.84	5.13	5.28

2.0

Table 39: Solubilities of Various Gases in Water. Henry's Law Constant K.

	ORIE	NTAL EA	ST PIT			
WATER SAMPLES						
	Ca	Fe	Mg	Mn		
Min	224	0.01	19.6	4.67		
Max	547	88.9	57.0	17.0		
Avg	387	18.0	38.5	10.6		
N	76	80	76	80		
FILTER PAPERS						
	Ca	Fe	Mg	Mn		
Min	0.11	0.24	0.02	0.00		
Мах	15.0	3.53	0.58	5.75		
Avg	1.33	2.09	0.12	0.38		
N	16	16	16	16		
	ORII	ENTAL W	EST PIT			
WATER SAMPLES						
	Ca	Fe	Mg	Mn		
Min	31.0	0.02	4.00	0.18		
Мах	170	21.1	17	5.11		
Avg	90.5	1.91	10.5	2.34		
N	65	72	65	72		
FILTER PAPERS						
	Ca	Fe	Mg	Mn		
Min	0.14	0.22	0.04	0.002		
Max	0.50	0.50	0.50	0.50		
Avg	0.37	0.39	0.27	0.25		
N	4	4	4	4		

Table 40: OWP and OEP statistics for selected elements.



Figure 44: Semilogarithmic plot of buoyancy density and sedimentation coefficient of selected bio-organic and inorganic particles found in natural water. Species found in Buchans OWP and OEP are marked with '+'. From Ciaccio, 1971.



Figure 45: Nature and size domain of the important particles of aquatic systems.











Figure 48: Carbon components in sea water of CI =19.00 ‰ at 20°C as a function of pH and the partial pressure of carbon dioxide.

Fig. 49a: Periphyton and Sed Trap Data Magnesium:Zinc Ratio







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Fig.50a: OEP Surface Water 1988 - 1996



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Fig. 51a: OWP Surface Water 1988 - 1996



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Fig. 53a: OEP Zinc Model Case 1:



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Fig. 53c: OEP Zinc Model Case 3:



Fig. 53e: OEP Zinc Model Case 5:



Model	Measured Surface Zn

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Schematic 3: Physical, Chemical and Biological Factors Affecting Winter Zinc Removal Performance in the OWP-OEP-Polishing Ponds System.



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