

**A Review of the Lagoon Systems
ALCAN Kitimat Smelter
SCOPING REPORT
TO DEFINE
B-LAGOON PERFORMANCE
December 22nd, 1998**

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EXECUTIVE SUMMARY

In the summer of 1998, Boojum Technologies Ltd. conducted a scoping study of the B-Lagoon system in order to identify ways in which its capacity to treat waste water from the Kitimat Alcan smelter could be improved. Since the B-Lagoon system was first used for this purpose, roughly 30 years ago, its ability to remove regulated contaminants prior to discharge may be impaired in the future.

From initial field work, specific sources of contaminants to the B-Lagoon were identified and its flow conditions were constructed. Loadings for individual waste water streams are presently being determined. Most of the aluminum in water samples was found in the form of particulates and most PAHs were found in sediments, associated with particulates. Water moves through the system at a rate of about 30,000 - 120,000 cubic metres/day but, due to siltation, the residence time is only about one day. Good retention times for a working lagoon are in the order of weeks. By increasing the size or depth, or decreasing the rate of flow, the lagoon would be more efficient.

A diverse population of algae and aquatic vegetation was identified in the lagoon system. The function of the vegetation with respect to its ability to act as a filtration system for particulates, its adsorbable surface area for dissolved contaminants, and its role as organic particulates and sediment nutrients was evaluated through a literature review, covering both lagoon chemistry and the biota.

Our work indicated that species that accumulate aluminum in their roots but do not transport it to their shoots (e.g., cattails, which dominate the B-Lagoon) would improve the treatment capacity of the system. It was also determined that the very low redox level of the lagoon, caused by a hydrophobic surface film of oils used in the smelting process, should be improved either through degradation or the removal of surface slicks to enhance the ongoing, relatively well-documented PAH degradation.

While the data assessment to date is preliminary, as only selected information was evaluated during the scoping study, Boojum is able to recommend that the efficiency of the B-Lagoon system be increased by using biological polishing and targeted control of effluent point sources. Approaches to achieve this are being developed through a complete data analysis, with the main emphasis on connecting lagoon performance to fish kills during toxicity tests of the effluents.

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1.0 INTRODUCTION

Boojum Research Ltd was retained to conduct a scoping study of the B-Lagoon system, firstly to address the potential role of the vegetation with respect to aluminum removal in the lagoon and, secondly, to identify an approach that would improve the waste water treatment capacity of the lagoon system. As part of this feasibility study, two field trips were carried out by Boojum personnel, as well as reviews of both the literature pertinent to the problem and of the historical data on the system.

The B-Lagoon has been used as a waste water treatment system for the Kitimat Alcan smelter since at least 1969. Schematic 1, on the following page, shows a series of aerial photographs of the B-Lagoon system taken between 1969 and 1997. The photographs demonstrate the significant change that has occurred during that period. It appears that, sometime between 1975 and 1979, the discharge associated with the pot liner leachate pile started to be confined and, by 1985, dykes had been constructed to contain this area of the B-Lagoon. In this same period (1979 to 1985), the waste dump was also contained by a dyke, making it part of the surface water drainage basin of the B-Lagoon. The most important change shows up in the last of the photographs. In 1985, the open pond area covered about 80% of the B-Lagoon system. As the final photograph shows, most of this water had been landed in by 1997. At present, the J stream discharges into the B-Lagoon inside the dyke system and the B-Lagoon essentially supports an extensive vegetation cover.

As the pond area of the lagoon has decreased, the time that the waste water remains in the system before leaving it has similarly decreased. This, in turn, has reduced the opportunity for the considerable quantity of suspended solids in the waste water to settle out. In addition, since the vegetation cover itself produces suspended solids and has increased in area, it is now producing more suspended solids that add to those already in the waste water. The overall effect has been to impair the removal of regulated contaminants prior to discharge.

1969



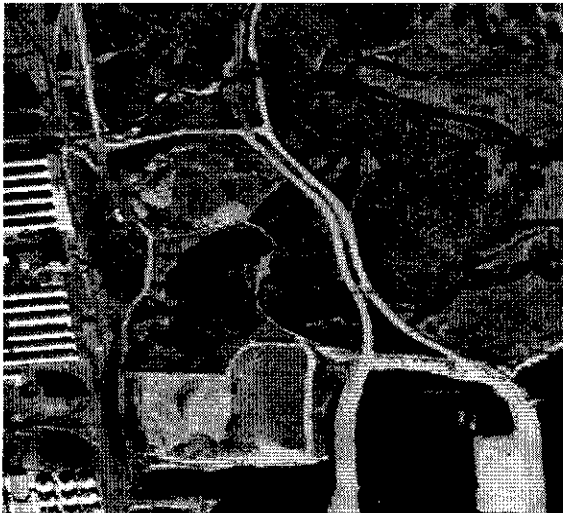
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1979



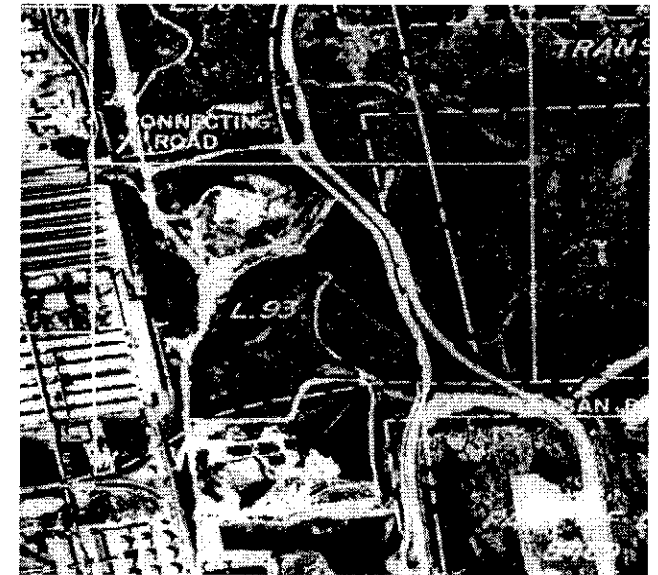
1985



1990



1997



Schematic 1: Aerial photographs of the B Lagoon system.

2.0 SUMMARY OF FINDINGS OF THE LITERATURE REVIEW

A full review of the literature is given in Appendix A of this report. It is, by necessity, complicated and technical, because the chemistry of aluminum is extremely complex. In this summary of that review, the most important findings are outlined in point form in the hope that readers are able to follow the reasoning behind the work that Boojum has carried out and that it is proposing to do, without necessarily fully understanding the processes on which Boojum's technologies rely. The details given in Appendix A are, however, essential for a complete appreciation of the work.

Despite its complexity, it is important to try to understand the chemistry of aluminum. There has been a considerable amount of research carried out on the subject which has been published. For the purposes of the work at the Kitimat site, the focus can be placed on the literature which concentrates on the biogeochemistry of aluminum, because it documents mechanisms which are relevant to the removal of aluminum from the lagoon waters to the sediments.

Aluminum is the most prevalent metal in the earth's crust (comprising about 7.1 % by weight), and it is present in almost all natural water bodies. It is a member of a group called "class A metals", which contains all of the metal ions (magnesium, calcium and potassium) which function as macro nutrients for plants. Not surprisingly, therefore, aluminum is a major constituent of fertilizer (aluminum calcium phosphate) (Archer 1985). When primary minerals are weathered, aluminum is released and precipitated as secondary minerals, largely aluminosilicates. The silicon of this compound is more rapidly lost than the aluminum when soils weather, leaving the aluminum to precipitate as oxides and hydroxides (Lindsay 1979).

The major contaminants in the effluent at the Kitimat site have been identified as ALUMINUM and POLYAROMATIC HYDROCARBONS. A summary of the findings is as follows:

- Free aluminum is found in abundance only in waters with pH levels below about 4.5. Above that level, aluminum will complex with fluoride, if it is present in high concentrations, or hydroxide if fluoride concentrations are low. Since the B-Lagoon is circumneutral (i.e., its Ph is around 7), the aluminum will complex.
- Aluminum fluoride (AlF) complexes are stable but soluble.
- Aluminum hydroxide (Al-OH) complexes are stable and will tend to form colloids and particulates.
- The longer Al-OH complexes exists, the more orderly becomes their structure and the larger the particulate size.
- Aluminum also forms stable complexes with organic molecules and particulates.
- Plants can filter out colloidal aluminum, absorb and adsorb free aluminum, and concentrate it in roots, shoots, and on plant cell walls.
- Polyaromatic hydrocarbons (PAH) have been found in B-Lagoon sediments, although their distribution is not uniform. More PAHs appear to be found in areas where sedimentation rates are highest, suggesting that PAHs may be found in conjunction with organic and inorganic particulate material in the lagoons.
- Oils used in the smelting process (Klubertec C1-101, Magnus Cal-92 and Cannola Oil) do not appear to be toxic, but they may be playing a role in reducing the redox state of the surface waters in the lagoons.

Aluminum toxicity occurs when aluminum competes with phosphorus in the metabolism of plants and animals. Organic phosphates (ATP) do not function in living

cells if aluminum is substituted for phosphorus. If phosphate (a plant nutrient) is present in excess of the aluminum, however, it can overcome some of the toxicity. Similarly, if aluminum complexes with organic material and fluoride, its toxicity will be reduced because it is no longer free to interfere with organic phosphates.

These points summarize the most important characteristics of aluminum that are relevant to the processes that are occurring in the B-Lagoon system. Recording, monitoring and analyzing these processes can lead to an understanding of the role that the vegetation is presently playing with respect to the removal of aluminum in the B-Lagoon. More importantly, that information can help identify an approach that would use these processes to improve the capacity of the B-Lagoon to treat the waste water.

3.0 THE B-Lagoon

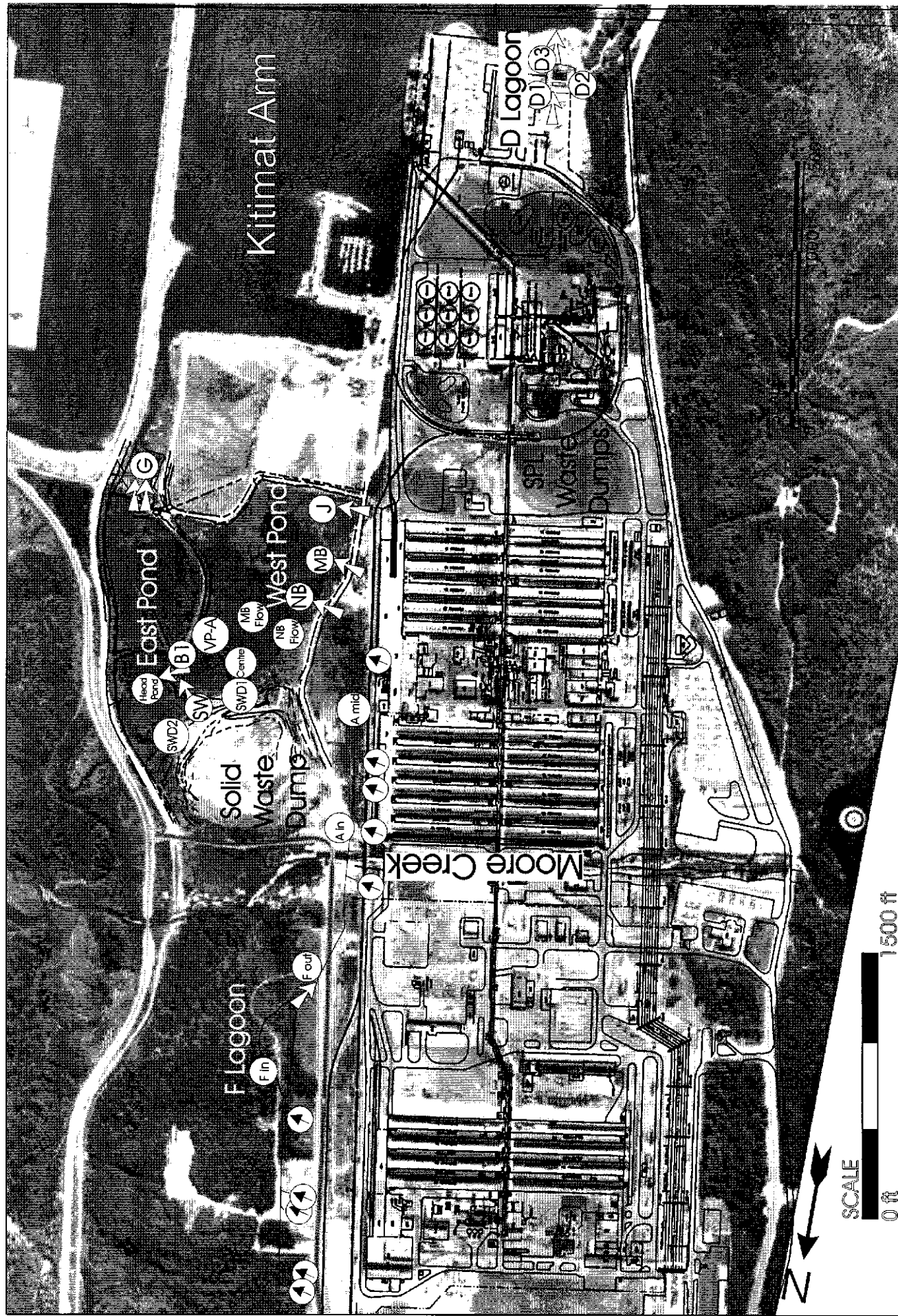
3.1 Physical Description

The B-Lagoon was surveyed by ALCAN in 1994. It is comprised of two ponds, west and east, separated by a dyke. The west pond has a surface area of 7.3 ha with a volume of 29,000 m³. It has two parts - a shallow zone to the south with a typical depth of 10 cm (filled in with sediment), and a deeper pool to the north, with a typical depth of 120 cm. The east pond has an area of 4.9 ha, with a typical volume of 32,700 m³. It, too, is divided by an internal dyke which separates a deeper upper pool from a shallow, marshy lower section. The retention time is about 1 day, giving a flow-through of approximately 43 m³ per minute.

In Map 1, a summary of the sampling locations has been reconstructed. The interpretation of the historic sampling locations may be a bit tentative, since in the various reports reviewed, the investigators did not use the same reference map to identify sampling stations. For example, in one study, the three major inflows are termed "A", "B" and "C". On Map 1, we refer to them as NB, MB and J. All three drain into the West (B1) lagoon, which exits through 3 pipes set at different elevations. Flow from the east pond (B2) is released to the Kitimat Arm via three identical Parshall flumes set at the same elevation. Neither inflow nor outflow is otherwise regulated.

3.2 The B-Lagoon Vegetation

During the brief site visit, the major plant species were noted. Macrophytic emergent plants (plants with are rooted and extend above the water, including cattails, rushes and sedges), extensive periphytic algal growth (attached filamentous algae including *Spirogyra* sp.), and submerged vascular plants (such as *Ceratophyllum* sp., *Sparganium* sp., *Polygonum* sp. and *Potamogeton* sp.) were found in the B-Lagoon. A detailed list



Map 1: Alcan Kitimat Water Sampling Locations.

of those phytoplankton species identified in the B-Lagoon is given in Appendix C. The number of species in the outflow decreased, as compared to the B-Lagoon at large. However, as most are fresh water species, this is to be expected, since seawater is added prior to the outflow.

Although the number of phytoplankton species leaving the B-2 Lagoon (east pond) was reduced, a notable improvement in their health was evident in the section of the lagoon which received seawater, as compared to section B1. The seawater resulted in more prolific growth and significantly healthier plants. Many factors can contribute to this improvement in plant health and growth.

The literature review (Appendix A) clearly demonstrates that aluminum is taken up by algae, but it also suggests that it can be toxic, especially when complexed with fluoride. Thus, it is likely that the plants in the B-Lagoon have to exhibit some degree of tolerance to aluminum and fluoride, and do not experience toxicity symptoms. Plants that accumulate and are tolerant to aluminum fall into three categories:

1. Species that accumulated aluminum in shoots (and probably in roots as well);
2. Species that accumulate aluminum in roots, but do not transport it to the shoots, and;
3. Species that are associated with the exclusion of the metal.

We prefer to use plants in the second category as an aluminum removal mechanism in the B-Lagoon. Plants in the first group could potentially pose a problem further up the food chain if lagoon plants were to be grazed, and the third category of plants are useless, as they exclude the metal. Of the preferred, second group of plants (those which accumulate in roots), our experience from previous work would indicate that cattails, which dominate the B-Lagoon (B2), very likely belong to this group.

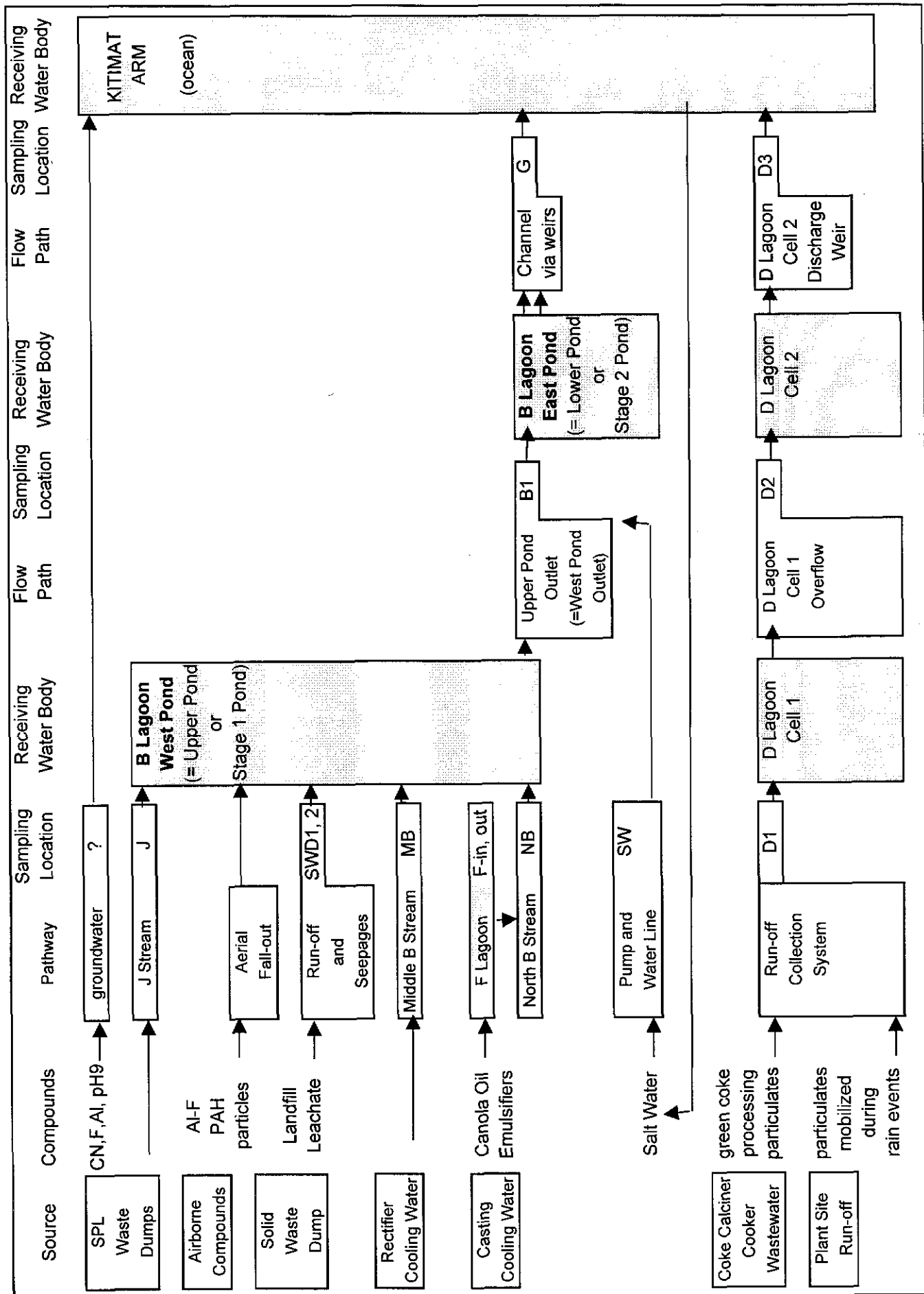
3.3 Sources of Waste Water to the Lagoon System

In Schematic 2, a flow diagram has been constructed which reflects the likely general flow conditions. It was developed based on information which could be gathered during the field trips, and may require corrections or additions. To optimize the treatment capacity of the lagoon system, the sources of the contaminants should be identified and quantified, so that a treatment strategy can be implemented. At present, loadings (concentration x flow) for the individual waste water streams are being determined.

The specific sources of contaminants to the B-Lagoon can be described as follows:

1. Particulates mobilized during rain events. A combination of rain and aerial fall-out produces either particulate or dissolved contaminants containing organic carbon. The D-Lagoon run-off contains particulate from the green coke processing.
2. Aerial fallout from site. Aluminum Fluoride and PAH, usually washed out with rain, adhering to dust particles.
3. Waste water generated from Potlining discharge. Aluminum fluoride, aluminum oxide, organic carbon and pitch.
4. Waste water generated from casting facility (cooling water). Canola oil, Magnus CAL-92 (*Ricinus* triglycerides, butyl stearate, a natural *Brassica* oil), Klubatec C1-101 (synthetic hydrocarbon oil).
5. Wastewater generated from Coke Calciner Cooker. Particulate from green coke processing.

Schematic 2: Waste Water Origins and Flow Paths: Kitimat



6. Groundwater/leachate from Potlining Pile. Composition tested as cyanide, fluoride, aluminum, with a pH of 9.
7. Groundwater/leachate from general waste pile. Composition unknown, but tested.

Waste streams 1,3,4, and 6 collect via F stream or J stream and pass through the West (B1) Lagoon system. Types 1 and 5 pass through the D-Lagoon. Water from source 7 enters the East (B2) Lagoon.

3.4 Summary of Lagoon Systems

- The B-Lagoon system is currently divided into two sub lagoons - East and West. The East lagoon receives effluent water from several parts of the smelter and mixes it with fresh water. Water from the East lagoon passes into the West lagoon and thence into the Kitimat Arm.
- Water moves through the system at a rate of about 30,000 - 120,000 cubic meters/day.
- Due to siltation, the B-Lagoon has a residence time of about 1 day.
- No information is available on effluent or freshwater loadings to the lagoon system at present, but it is being collected.
- The current lagoon system has a diverse population of algae, and aquatic (submerged and emergent) vegetation.
- The lagoon has a very low redox level due to a hydrophobic surface film, composed of oils used in the smelting process.

- Based on water chemistry data, it appears that aluminum is complexing with both fluoride and hydroxide, which alters its toxicity. The predominance of one or the other depends on the concentration at the point of entry.
- The inorganic elements of most concern in the waste water from the lagoon are aluminum and fluoride. In order to determine the causes of fish kill events (which are rare), assessments of organic compounds in combination with inorganic elements are in progress.

4.0 MONITORING DATA INTERPRETATION

For the F-Lagoon, a data set covering the period 1973-1991 was assessed for its potential to diagnose the behaviour of the lagoon. A relatively complete set of information on flow and fluoride concentrations was available within this time span. These relationships are presented in Figures 1 through 3.

Some unusually high concentrations were deleted from the data set, as they seemed to be aberrant values. All data are reported in Appendix C (AppC-Fig1 to AppC-Fig4). In Figure 1 on the following page, the concentrations of fluoride and the flow in the F-Lagoon are plotted for the years 1979 to 1991. Overall, the flow volume may have decreased somewhat since 1985, but generally flow and concentration behave in similar manners each year. The loading of fluoride resulting from these data, however, clearly indicates that, in the years since 1985, the fluoride load in the F-Lagoon has decreased (Figure 2). The questions which arise from this observation are: "How much of the fluoride has remained in the B-Lagoon system?" and "How much would be discharged with the effluent?".

Answering these questions would allow the expected fluoride mass in the sediments to be determined. A similar evaluation for aluminum would allow the aluminum expected in the B-Lagoon sediment to be assessed. This evaluation will be possible only if the F-Lagoon was entering the B-Lagoon system during the time that the effluent from B-Lagoon was being monitored.

In Figure 3, the same data are evaluated in order to determine changes during the seasons. It is evident that the fluoride discharge from the smelting activities is pretty constant, and that spring and fall rain run-offs do not produce increases. The few years when loading increased by fall, may represent events relating to smelting activities. The evaluations of all the flow and water chemistry data will lead to a solid understanding of the B-Lagoon system. This is in progress.

Fig. 1: F-Lagoon Historical Data
[F] and Flows, 1979-1991

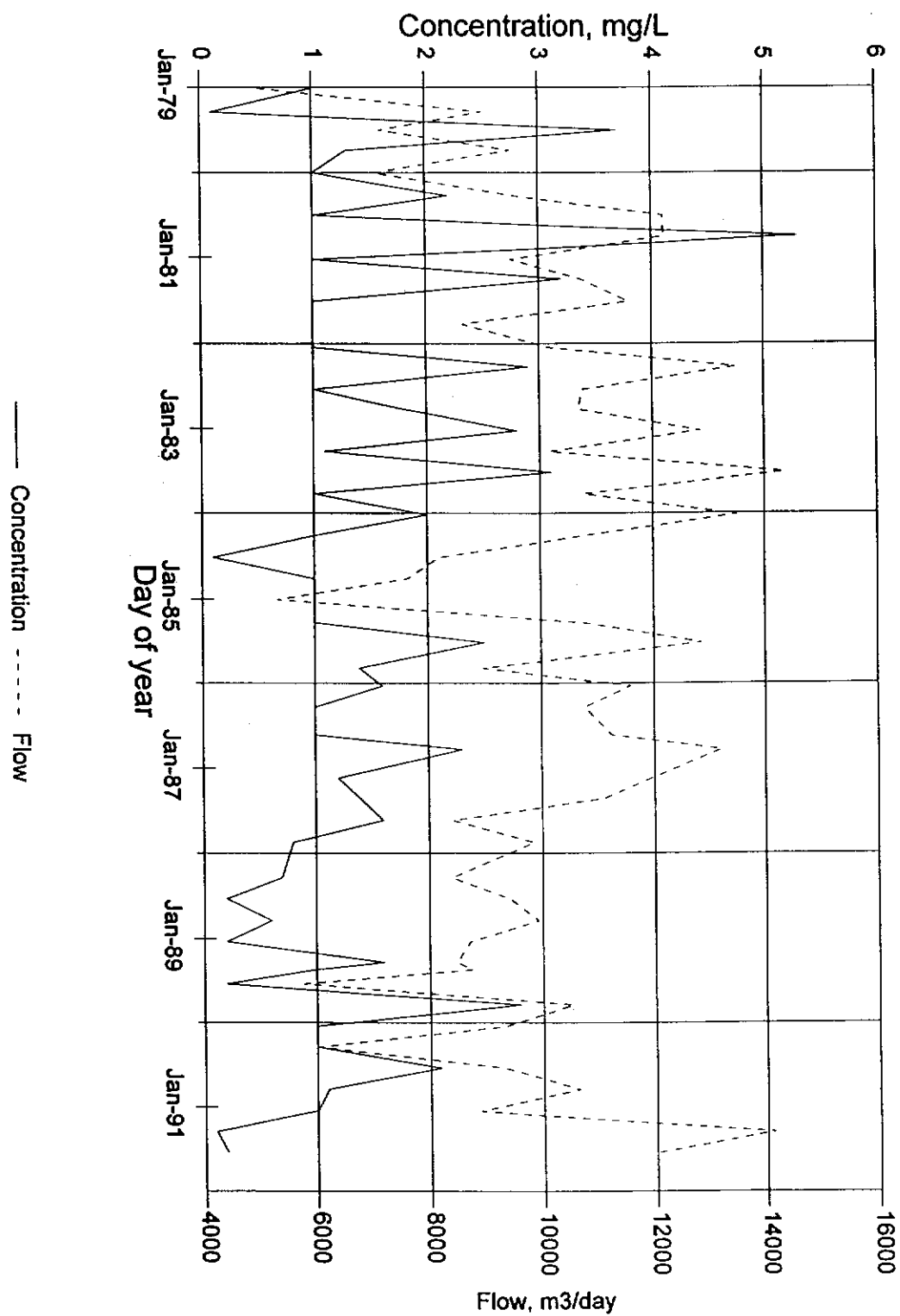


Fig. 2: F-Lagoon Historical Data
Fluoride Loading, 1979-1991

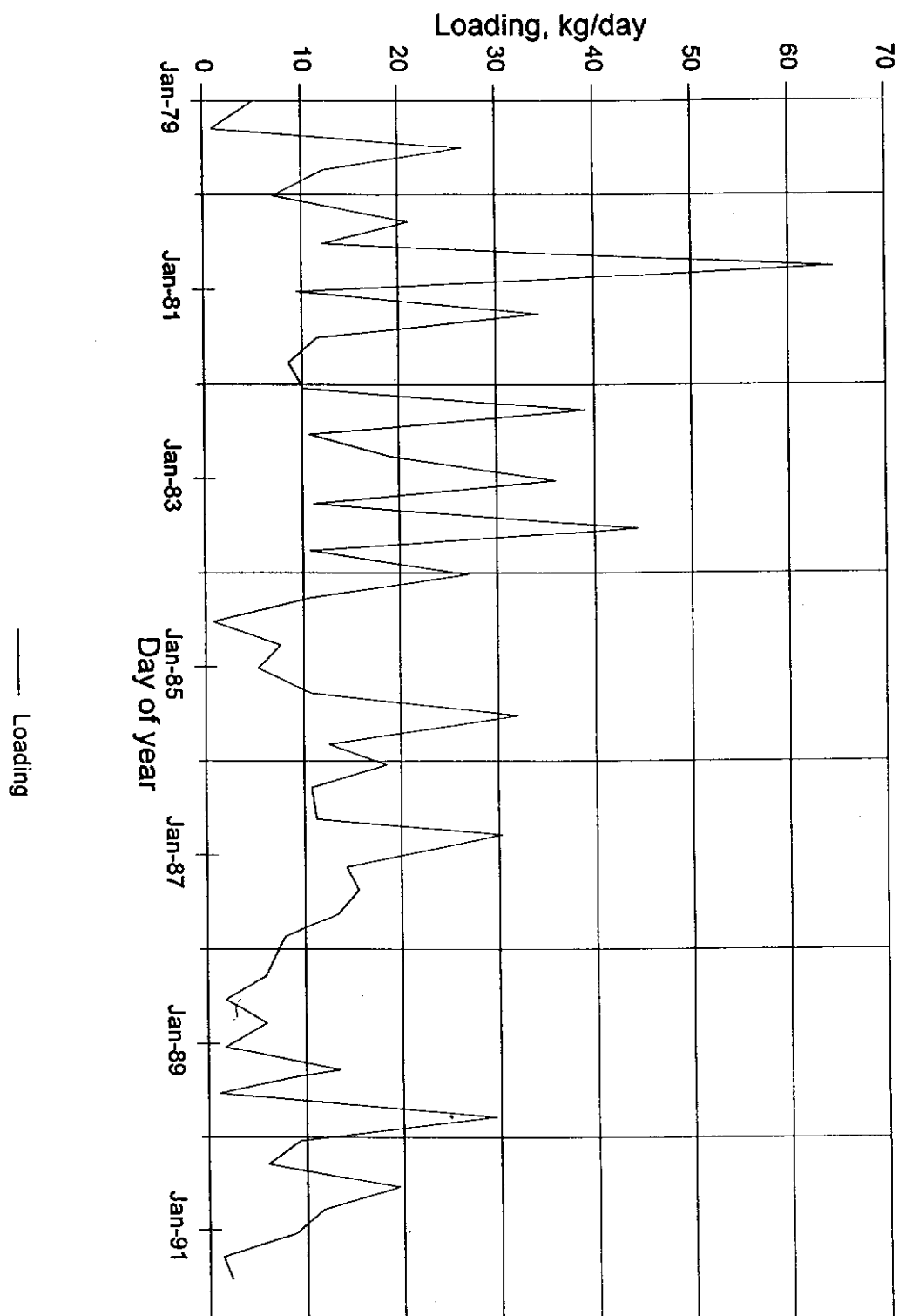
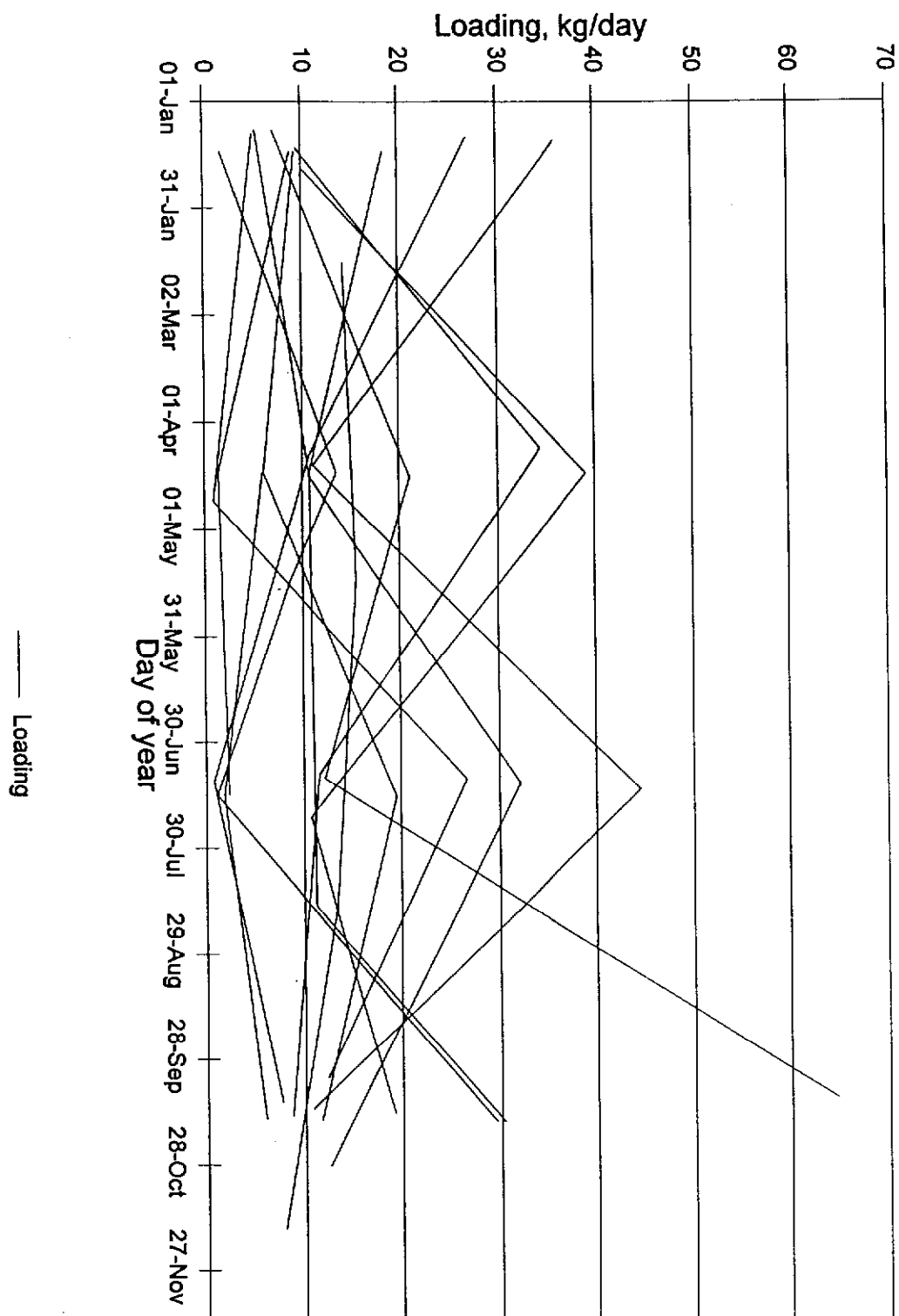


Fig. 3: F-Lagoon Historical Data
Seasonal Fluoride Loads



4.1 The 1992 Data Set

In this section, data other than the monitoring data previously discussed are examined, in order to: a) determine the potential nature of their use; b) integrate the relevant data; and c) focus the final assessment in such a manner, that the overall objective is addressed in the most cost effective and expedient manner.

In the Alcan report of August 7, 1992, (EP 102 report to EPD) solid materials from several locations were analyzed. The data on the solids do not contain concentrations of aluminum, and most elements analyzed were reported at the detection limits, which were relatively high. Fluoride was found in significant concentrations in sediment/soil. Such data sets can be used as guidelines, but focused analysis may be required at a later stage.

4.2 The 1995 Data Set

Alcan (1995 Monitoring Data)

- B (Exit from B-Lagoon, into Kitimat Arm)
- D (Exit from D-Lagoon, into Kitimat Arm)
- J (Entrance into B-Lagoon from southern end of works)
- NB (Entrance into B-Lagoon from north end of works)
- MB (Entrance into B-Lagoon from south end of works)

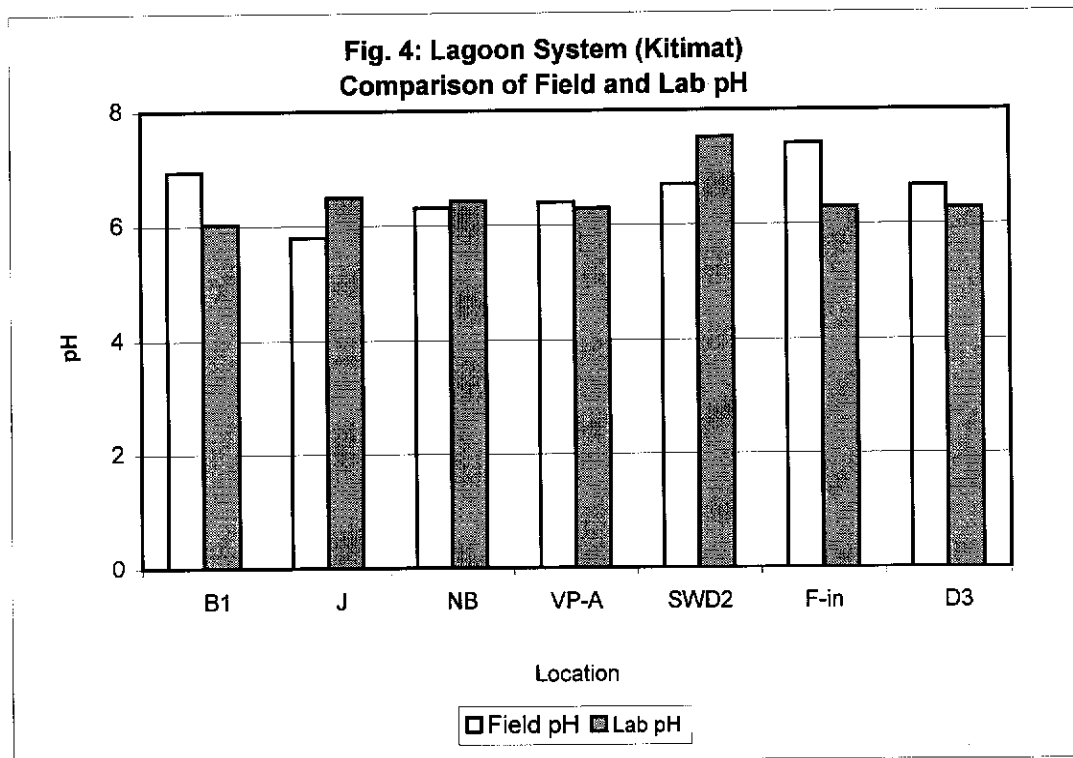
The data sets for each of the above sampling points covered two periods in 1995: the first measurements were taken between March 7-August 17 and the second ones covered September 8-December 12. Each data set contained data from both dissolved (passed through 45 μ m filter) and whole (unfiltered) water. Although the data set is incomplete at the present time, the intent of a scoping study is to demonstrate what data interpretation is able to accomplish. A complete interpretation, which takes into account the most recent data, is in progress

For effluents B, NB and J, trout and *Daphnia* toxicity tests accompanied most of the sampling dates. Such chemical data are lab-derived, however, and pH may change between the laboratory and field conditions, as exemplified in Figure 4. The detailed field data appear in Appendix C. The relevance of having the correct pH conditions in the B-Lagoon is shown by the shifts of ratios of free aluminum and/or the complexation capacity (Figures 5 and 6). Therefore, a toxicity test in which the pHs change and do not reflect the conditions in the Lagoon as it discharges, is not representative of what may take place in the field.

The pH values and conductivity measurements of this data set were extracted for further analysis. An evaluation of the pH encountered in the monitoring data noted a significant range of values. (The final pHs in toxicity experiments were used.) Effluent B ranged from a low of 6.5 to a high of 7.7, and at station NB, the pHs ranged from a low of 6.3 to a high of 7.4. Effluent J pHs ranged from 7.2 to a high of 8.4.

For effluents D and MB, anion analyses accompanied most of the water samples. Only samples from MB contained fluoride concentrations. Aluminum concentrations and fluoride concentrations were highly correlated, with a slope of 2.87. If it is assumed that the compound is AlF_4 , one would expect a slope of 2.8. This likely means that, at that time, based on this data set, this was the dominant form of aluminum. More generally, it means that monitoring a data set can allow the dominant form of aluminum to be determined. This is important in the toxicity assessment of the effluent.

From a data set collected in 1995 by Alcan, particle size was estimated by comparing aluminum concentration in water which had passed through a $0.45\ \mu\text{m}$ filter with unfiltered water to determine the percentage retained on that filter. The results of aluminum are given in Table 1.



B1 = Outflow from B lagoon west pond to east pond before seawater addition
 J = J stram at concrete weir before joining B lagoon west pond
 NB = North B stream just before discharge to B lagoon west pond
 VP-A = Vegetation patch area in B lagoon west pond near outflow
 SWD2 = Solid waste dump location 2 seepage into B lagoon west pond
 F-in = F lagoon inflow along north side
 D3 = D lagoon outflow at steel weir

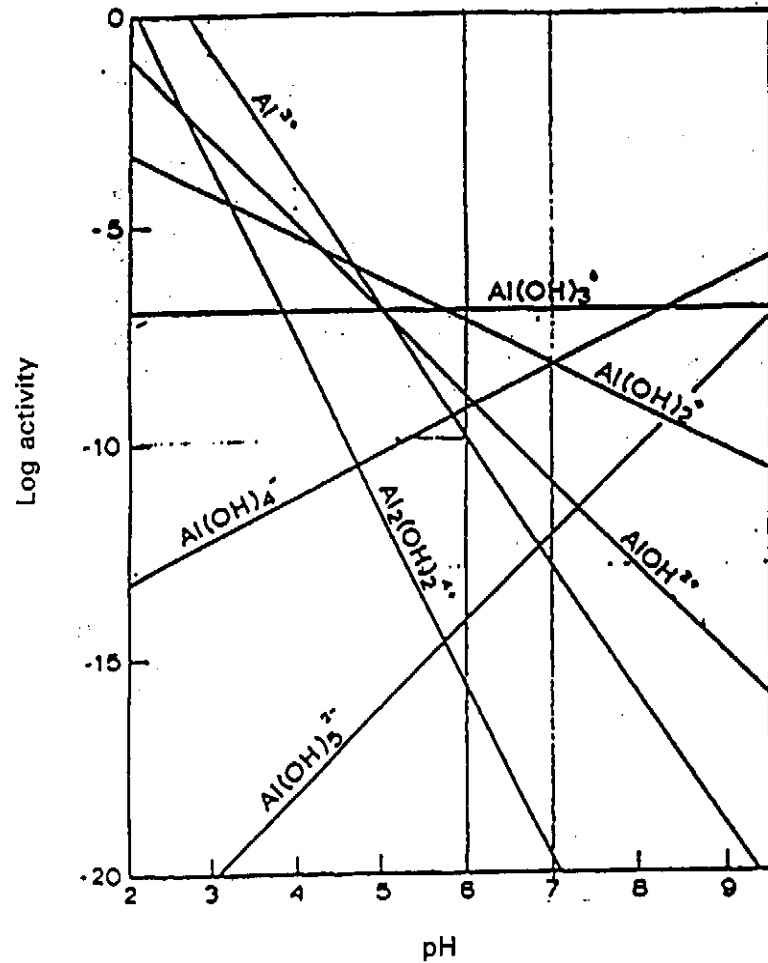


Figure 5: The activity of Al^{3+} and its hydrolysis in equilibrium with gibbsite (from Burrows, W.D., 1977)

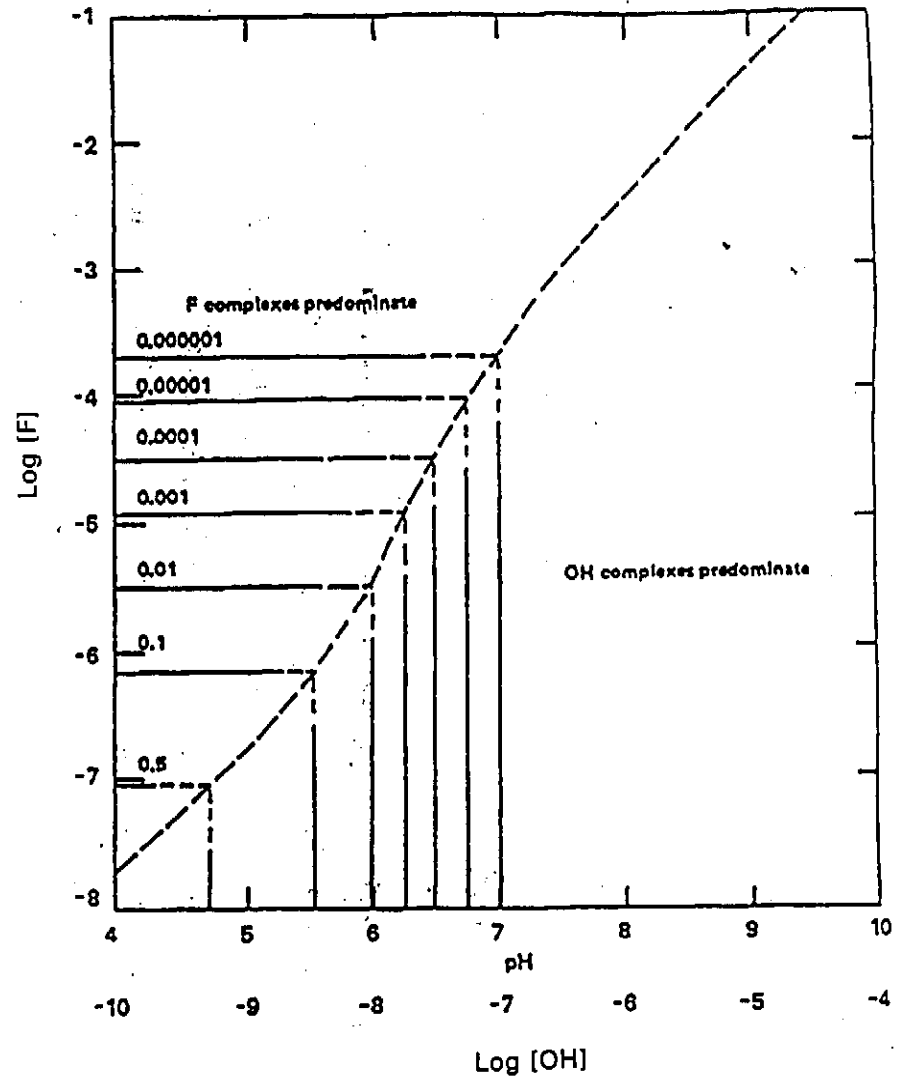


Figure 6: Ratio of free aluminum activity to total aluminum as a function of fluoride and pH (zero ionic strength). (From Hem, J.D., U.S. Geological Survey Water Supply Paper No. 1827B, 1968.)

Table 1: The Average Percentage of "Whole" Minus "Dissolved" Element

Sampling Station	G (Final outflow from B lagoon system)	D3 (D lagoon outflow at steel weir)	NB (North B stream just before discharge to B lagoon west pond)	MB (Middle B stream just before discharge to B lagoon west pond)	J (J stream at concrete weir before joining B lagoon west pond)
Al	24.0	94.3	18.2	17.2	36.3
Ba	34.9	15.7	21.4	37.2	0.0
Ca	1.8	1.1	1.4	3.9	2.1
Fe	81.8	69	72.3	80.6	45.9
Mg	2.8	7.7	5.8	6.3	3.3
Mn	4.1	22.8	7.5	6.1	49.1
Si	7.2	11.1	5.2	9.9	4.6
Na	1.6	2.4	-166.4	56.3	3.9
Sr	0.7	4.6	-3.8	3.4	3.2
Zn	20.0	26.3	-39.1	41.7	37.5

Effluent G The percentages retained on the filter were very low for all elements other than Al, Ba, Fe, and Zn. Only iron displayed very high retention (82%). Aluminum had an average 24% retention on filters.

Effluent D3 The percentages of elements retained on the 0.45 μm filter were slightly different in this effluent. The four elements that had retention greater than 20% were Al, Fe, Mn, and Zn. An average of 94% of the aluminum was retained on the filter paper at this station.

Effluent NB The elements with greater than 20% retention on the filter were Ba and Fe. Aluminum had a retention of only 18.2%.

Effluent MB Those elements that had a greater than 20% retention on filters were Ba, Fe, Na, and Zn. Again, aluminum had a retention rate of only 17.2%.

Effluent J The elements with a retention on filters greater than 20% were Al, Fe, Mn, and Zn. About 36% of the aluminum was retained.

As the monitoring stations are relatively close to the ocean, the ground water table may reflect brackish conditions. From an examination of the monitoring data, however, effluents B and D did not show the Na and Cl concentrations that would be indicative of the influence of seawater. It appeared that seawater intrusion was possible for effluent J, since Na concentrations rose to 270 mg/L and conductivity to $1400\mu\text{mhos.cm}^{-1}$. All other effluent samples had conductivities less than $150\mu\text{mhos.cm}^{-1}$.

In order to determine whether the particle fractionation is altered with time, the same data set was examined by sampling date. This revealed that, on July 9, 1995, the greatest percentage of particles with aluminum retention occurred (51%) and that on May 9, 1995, the lowest retention took place (6%) - see Table 2. The fact that some 6% to 51% of the aluminum was retained on the filter suggests that the pH range of the water is in that critical range where aluminum forms colloids, microcrystalline, and crystalline structures. Further analysis of these data suggested that, in the whole acidified (WA), the total dissolved aluminum concentration increases with increasing pH.

**Table 2: Aluminum Concentration in Effluent B from the Kitimat Smelter
The pH of the Water Samples Was Between 6.0 and 6.7**

Sampling Date	Al (mg/L)		% Particles >0.45 μm
	Total	Filtered	
9-May-95	3.95	3.72	5.80
29-May-95	0.32	0.27	15.60
10-Jun-95	1.67	1.27	24.00
21-Jun-95	0.88	0.50	43.20
9-Jul-95	0.41	0.20*	51.20
23-Jul-95	0.95	0.66	30.50
16-Aug-95	0.27	0.20*	25.90

It is important to understand and quantify the information on the cleansing function of the lagoon as a waste water treatment system. The summaries given provide useful insights into the functioning of the waste water chemistry in the B-Lagoon. The complete data set is being analyzed presently.

4.3 The 1998 Field Assessment

Water samples were collected by M. Kalin and M. Hellenius (June 30, 1998). The importance of these field measurements has been discussed before and they are appear in Appendix C in Tables AppC-Tab1 to AppC-Tab4. The chemical analyses of the water samples were carried out by the Saskatchewan Research Council (SRC).

The main objective of this sampling campaign was to determine whether aluminum is present in particulate or colloidal form in the lagoon system. The water samples were separated into three groups. One group (FA) was filtered (0.8 μm filter) and acidified with nitric acid. The second (WA) was left unfiltered but acidified, and the third group (WH) was left unfiltered and un-acidified.

The elements silver, boron, beryllium, barium, cadmium, cobalt, chromium, copper, molybdenum, nickel, phosphorus, lead, titanium, vanadium, zinc, zirconium and strontium, listed in Appendix C, (AppC-Tab3), are those which are at, or below the detection limits of the analytical methodology using ICP. These results suggest that there are no inorganic elements other than aluminum and fluoride (such as nickel, copper, cadmium and cobalt - which are well documented in aquatic toxicology) which could contribute to toxicity.

In Table AppC-Tab4, also in Appendix C, those elements with concentrations greater than the detection limits are given. The percentages of aluminum, calcium, iron, potassium, magnesium, manganese, sodium and silicone, which are in particulate form are shown in Table 3 on the following page.

Table 3: Percentage Difference of Elements above Detection Limits between Whole Acidity (WA) and Filtered Acidity (FA) Water Samples

Location	B1 (Outflow from B lagoon west pond to east pond before seawater addition)	SWD2 (Solid waste dump location 2 seepage into B lagoon west pond)	F-in (F lagoon inflow along north side)	D3 (D lagoon outflow at steel weir)	VP-A (Vegetation patch area in B lagoon west pond near outflow)	NB (North B stream just before discharge to B lagoon west pond)	J (J stream at concrete weir before joining B lagoon west pond)
Al	71	31	77	61	NM	NM	NM
Ca	0	7	0	0	0	0	0
Fe	82	84	66	72	57	65	50
K	9	3	0	3	0	25	NM
Mg	5	2	0	3	0	0	0
Mn	NM	8	NM	NM	26	25	6
Na	0	4	NM	13	NM	NM	0
Si	17	3	7	8	8	8	7

Difference (%) = $([\text{element}]_{\text{WA}} - [\text{element}]_{\text{FA}}) / [\text{element}]_{\text{WA}} * 100$

WA = Whole Acidified; FA = Filtered Acidified; NM = Not Measured

Since the monitoring data indicated that a significant fraction of aluminum is retained by a $0.45 \mu\text{m}$ filter, a larger filter pore size ($0.8 \mu\text{m}$) was used for these samples in order to determine whether the colloidal/complexed aluminum might be even larger than $0.45 \mu\text{m}$. The difference in aluminum concentrations between WA and FA gives the particulate form which is $> 0.8 \mu\text{m}$ (Table 4). The concentrations of aluminum are clearly highest from the Dump seepage and the J stream. In the open areas of the lagoon, the aluminum concentrations are below detection limits. Although this was a small survey of the B-Lagoon, it does suggest that the seepages from the Waste Dump and the J stream are likely major contributors of aluminum to the B-Lagoon. The particle size information indicates that large particles ($> 0.8 \mu\text{m}$) are present in the waste water. This, in turn, suggests that surfaces provided by the wetland vegetation are likely serving as adhesive surfaces for the particulate aluminum in the waste water.

The percentage of aluminum in particulate form ranged from 30% (Dump seepage) to $> 70\%$ in F-Lagoon, B1 (B-Lagoon system outflow) and in D-Lagoon. In the other

samples, aluminum concentrations in the WA treatment were lower than those in corresponding FA samples, suggesting that some of the aluminum in the whole samples was lost before it was acidified.

Table 4: Percentage Retention of Aluminum on 0.8 um Filter Paper

Sampling Station	Element (mg/L)			% > 0.8 um
	Al		F	
	Whole Acidified (WA)	Filtered & Acidified (FA)	Whole Water (WH)	
G (Final outflow from B lagoon system)	0.13	0.04	0.85	70.80
SWD1 (Solid waste dump location 12 seepage into B lagoon east pond)	0.59	0.41	41.00	30.50
F-in (F lagoon inflow along north side)	0.13	0.03	0.22	76.90
D3 (D lagoon outflow at steel weir)	0.08	0.02	0.20	70.30
VP-A (Vegetation patch area in B lagoon west pond near outflow)	0.005*	0.04	0.32	-6.60
NB (North B stream just before discharge to B lagoon west pond)	0.005*	0.03	0.20	-5.40
J (J stream at concrete weir before joining B lagoon west pond)	0.31	0.49	32.00	-0.60

* Detection Limit

In addition to the acidity and alkalinity determinations, the concentrations of fluoride were determined in WH (untreated and unacidified) samples submitted to SRC.

The molar ratio of aluminum to fluoride is also interesting to note (Table 5). In an earlier document, we reported that historical data for sampling station MB showed a F:Al molar ratio which suggested that the compound was AlF_4 . The data set collected during this field trip suggests that the ratio is much higher. It is clear that, in the present waste water conditions, the aluminum concentrations are significantly lower, either through process changes made in the smelter, or through the performance of the waste water lagoon, or due to the prevailing weather condition. However, the fluoride concentrations remain at historical concentrations.

Table 5: Molar Fluoride to Aluminum Concentration Ratios

Sampling Station	Element (uM)			Molar ratio
	Whole Acidified (WA)	Filtered & Acidified (FA)	Whole Water (WH)	
G (Final outflow from B lagoon system)	4.81	1.41	44.74	31.80
SWD1 (Solid waste dump location 12 seepage into B lagoon east pond)	21.85	15.19	2158.00	142.10
F-in (F lagoon inflow along north side)	4.81	1.11	11.58	10.40
D3 (D lagoon outflow at steel weir)	3.00	0.89	10.53	11.80
VP-A (Vegetation patch area in B lagoon west pond near outflow)	0.19	1.41	16.84	12.00
NB (North B stream just before discharge to B lagoon west pond)	0.19	1.19	10.53	8.90
J (J stream at concrete weir before joining B lagoon west pond)	11.48	18.15	1684.00	92.80

From this brief sampling campaign, it is evident that a systematic approach to the identification of the sources of the aluminum to the waste water lagoon would lead to a strategy which could increase the system's performance.

4.4 PAH in the B-Lagoon

A number of documents pertaining to the evaluation of polyaromatic hydrocarbon (PAH) content of Lagoon water and sediments were examined. These are listed below:

1. Alcan Kitimat Works Analytical (The PAH samples below do not appear to be summarized in any document).

19503: J - Stream, (Top 1 ft; August 5, 1992)

19505: J - Stream, (Top 1 ft; August 17, 1992)

19504: M - Stream, (Top 1 ft; August 5, 1992)

19506: M - Stream, (Top 1 ft; August 17, 1992)

2. ASC Chemical Analysis Report (7122C; December 2, 1992) report to Alcan.

3. Alcan (February 4, 1993) report to EPD summarizes PAH data (from fall and winter 1992/1993?). Only one sample (November 6, 1992; M Top) was included with the report.

4. EVS Environmental Consultants (September 14, 1993) report to Alcan (J58534) with one figure and no tables. Report details experiments on PAH degradation in Alcan sediments.

5. Miscellaneous Plant Analyses:

22594: Bullrush (leaves and stem), B-Lagoon (March 31, 1993).

22595: Bullrush (leaves and stem), Hot springs Lakes (March 31, 1993).

21978: Bullrush roots, B-Lagoon (January 10, 1993).

21979: Sedge grass leaves, B-Lagoon (January 10, 1993).

6. Miscellaneous Information:

6.1 Alcan (August 30, 1995) report on B-Lagoon Algae Survey (EE 800.1)

6.2 Material Safety Data Sheets for: Canola Oil LV134, Klubertec C1-101, Magnus Cal-92

6.3 Aquatic Toxicity test results for: Magnus Cal-92, comparison between toxicities of Canola Oil and Magnus C-92

Some general comments can be made about the information in these documents. The highest concentrations of HPAH were found in the J Stream inflow to B-Lagoon (location B), only in the surface sediments. These HPAH had not penetrated (to 7 ft).

The next highest concentrations were found at Station M, in the middle of B-Lagoon. At this point, the HPAHs had penetrated sediments (or sediments had accumulated at a greater rate here than elsewhere), because they were found in relatively high concentrations at depths as great as 13 ft.

Further into the lagoon from the J Stream, surface concentrations of HPAH decreased. This suggests that most of the HPAH entered the lagoon from the J Stream. The fact that they were found at such depths also suggests that there was/is a high degree of siltation in this lagoon. Schematic 1, where aerial photography shows the development of the B-Lagoon physical lay-out, suggests that the PAH concentration with depth may also be related to the material which appears to have been contained with a dyke (compare 1975 to 1990), close to the origin of the J Stream. If this is the case, higher concentrations of PAH may be encountered at depth in the sediments. Since the concentrations of HPAHs at all stations further into the lagoon were lower, the contaminants were probably entering with the J stream below 4F.

Indeno (1,2,3-CD) Pyrene concentrations were less than detection limits at the J stream inflow (Station B, summer data). However, they were found in significant quantities further out into the lagoon. The updated Data set (Jan 28, 1993) showed relatively high concentrations at Station B.

The data were submitted to the Saskatchewan Research Council for comment on the analytical procedures. Their comments are given in Appendix B. They indicate that such complex waste waters which have contributed to the composition of the sediments, require that an experienced analytical chemist conduct the degradation study. (Derivatives of PAHs compounds can be volatile, meaning that they would not end up in the sediment.) To test the extent to which this is significant, filter papers with particulates from the D-Lagoon were submitted to SRC to evaluate the volatile fraction on the particulates in the water.

The complexity of determining degradation is demonstrated by the analysis of particulates collected from the D-Lagoon. The results suggest that the suspended matter (TSS) in the D-Lagoon is associated with several organic compounds of the naphthalene group. For further details, see Appendix B.

5.0 BIOLOGICAL SYSTEMS AND THEIR INFLUENCE ON PAHs

Included in the review we conducted was a report by EVS. Its conclusion was that the sediments in B-Lagoon were breaking down HPAHs, and that this breakdown was enhanced by adding nutrients to the sediments. It is widely known that PAHs can be broken down in sediments by microbes. The speed with which this is accomplished is related to several criteria, including the redox state of sediments, nutrient concentrations (N, P primarily) and sediment temperature.

The redox state of the water column and the top layer of sediments should be high (e.g. oxygenated). From the field investigation of the B-Lagoon, it is evident that oxygenated conditions did not prevail at the time of the investigation, as indicated from the low Em measurements given in Table 1a, (Appendix). It would, therefore, be very important to promote oxygenation, which could be achieved if the emulsion-like material could be degraded reasonably quickly. It could also be achieved microbiologically, but would have to be addressed in detail.

A high redox state facilitates the development of heterotrophic microbial ecosystems which can start to degrade PAHs. These heterotrophic microbes also produce organic carbon sources, for use by anaerobic microbial systems. The anaerobic microbial ecosystems occur in areas where the redox state is low (little to no oxygen), and low redox ecosystems usually occur deeper in the sediments. The anaerobic sediments can re-mineralize contaminant metals, and may further breakdown complex organic carbon structures.

As the report cited above suggests, the rate of PAH degradation may be influenced by nutrient addition, and there is considerable evidence from other studies that this works. The addition of nutrients to a lagoon has a number of beneficial effects. First, it fertilizes aquatic vegetation and algae (see below). Second, it fertilizes the microbial communities. Third, the nutrients themselves can bind with contaminants, changing

their availability. At present, no information is available on the nutrient status of the waste water of the B-Lagoon, and it would be necessary to determine these nutrient concentrations.

PAHs can also be removed from sediments and water by adsorption and absorption by aquatic vegetation (Figure 7). Bullrush and Sedge data (from item #5 in the documents listed earlier) suggest that PAHs can be concentrated between 50 and 200 x concentrations in non-impacted plants. These aquatic plants can also reduce TSS and significantly alter the redox state of sediments. Cultivation of aquatic plants may enhance biofiltration, bioadsorption and bioremoval of organic and inorganic contaminants.

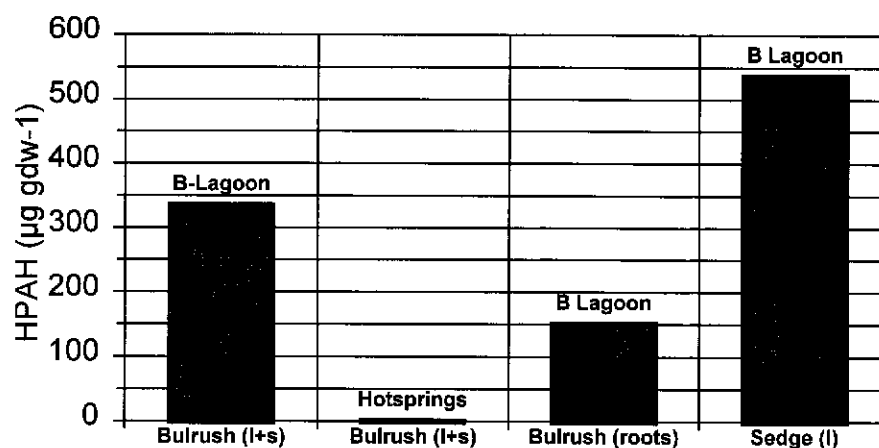


Figure 7: Total HPAH Concentration in Aquatic Vegetation from B-Lagoon and a Control Location at a Nearby Hot Springs.

Also included in the items from Alcan (Item #6 in the list in the previous section) is a report on the algal populations of the B-Lagoon system. This report concluded that there was a high degree of algal diversity, indicative of relatively clean water. The phytoplankton survey carried out on some of the samples collected during the field trip

in 1998, also indicated that, generally, a healthy algal diversity is present. The detailed data are given in Appendix C.

5.1 Summarizing PAH

The PAH data received are only for sediments and are 5 years old. This raises the question of whether this is a current problem - does the water contain PAHs? It is not known whether the "slick" on B-Lagoon, observed during the June, 1998 site visit, is composed of PAHs or simply the Magnus Cal-92, Canola Oil LV134, and/or the Klubertec C1-101, which oils seem to be non-toxic (MSDS sheets). However, their presence in the waste water may be producing the low redox state of the water and sediments. If this is the case, then their removal (degradation) becomes more important, not only from a regulatory perspective, but from an ecological perspective as well, since oxygen is required to enhance degradation.

The B-Lagoon system appears to be functioning in a manner that produces near compliance with water quality regulations. However, it also appears that the lagoons are being silted in rapidly. With a retention time of about 1 day, the lagoon is not performing optimally. Good retention times for a working lagoon are in the order of weeks. By increasing the size or depth of the lagoon, or decreasing the rate of flow of water through it, the lagoon would be made more efficient. While dredging sediments with high PAH concentrations may not be beneficial, as noted above, degradation of PAHs occurs best under aerobic conditions. Thus, removing those sediments to another location where degradation can be allowed to proceed at a faster rate, may actually enhance clean-up.

6.0 ACCOMPLISHMENTS AND RECOMMENDATIONS

- Boojum measured aluminum and PAHs with regard to particulate size.
 - Most of the aluminum encountered in water sampling was found in the form of particulates, with sizes greater than $0.45\ \mu\text{m}$.
 - Most of the PAHs encountered were found in sediments and were associated with particulates in the lagoon.
- Boojum initiated surveys of the vegetation in the lagoon system with respect to their function as:
 - filtration systems for particulates
 - adsorbable surface area for dissolved contaminants
 - biological systems to provide organic particulates and sediment nutrients.
- The process of planting floating cattail rafts, as a means of controlling hydrological and biogeochemical processes in the lagoon, was initiated.
- Initiated chemical surveys of effluents, sediments and water in the lagoon system with the intent of determining how efficient the existing lagoon system is, and how well it can be expected to handle future effluents.
- Reviewed the pertinent literature dealing with aluminum and PAHs. Such a review provides world wide access to solutions for similar problems.
- Examined the pertinent environmental data from the Alcan smelter. By summarizing the data in a number of different forms, historical trends can be determined and future directions assessed.

- Boojum recommends that the efficiency of the B-Lagoon be increased using biological polishing and targeted control of effluent point source.
- Determination of the hydrological balance for the lagoon, shunting fresh water and concentrating effluents, is recommended.
- The sedimentation of aluminum and PAHs should be enhanced, as should the processes in the sediments for their transformation and degradation.
- The redox state of the lagoon should be improved through degradation or removal of surface slicks.

We have described seven different kinds of effluents emanating from the Alcan plant. Five of the seven pass through the B-Lagoon. Chemical quantification of the sources of aluminum and loads, through determination of flows, could lead to measures that would promote removal in the ditch system, prior to reaching the B-Lagoon system.

From the data evaluated, degradation of PAH products is clearly taking place in the B-Lagoon. Therefore, it is recommended that, due to the emulsion and oily discharges, the reducing conditions of the lagoon system be restricted to the F-Lagoon. This can be achieved through evaluation of the nutrient conditions of the waste water which, to date, are not known.

A systematic sampling approach for PAH content in the more recent upper layers of sediments in the B-Lagoon would facilitate the estimation of how much degradation should have, or has, taken place in the sediments. This would facilitate an estimate of the amount of material which can be removed or has to be degraded, in order to increase the retention time of the B-Lagoon system.

APPENDIX A: A LITERATURE REVIEW OF THE CHEMISTRY OF ALUMINUM

A-1 Aluminum Chemistry in the Aquatic Environment

Aluminum is found in almost all natural water bodies. Published values for the aluminum content of natural waters in Canada vary from 0.07-1.12 mg L⁻¹ for rain and snow in S.E. Ontario in 1965, to 0.276 mg L⁻¹ for samples taken from the St. Lawrence River in Quebec. Water samples from the Slave and Mackenzie Rivers contain 1 and 1.41 mg L⁻¹, respectively, while the Nelson and Churchill Rivers in Manitoba contain 0.089 and 0.103 mg L⁻¹ respectively. These figures are cited by Burrows (1977, Table 11).

The following discussion focuses on the biogeochemistry of aluminum and the well-documented mechanisms which may lead to the removal of aluminum from the lagoon water to the sediments of the Kitimat site.

A-2 Aluminum Forms

Under somewhat acidic conditions, free aluminum can be complexed to a number of substrates, some of which form minerals and some of which are stable, soluble complexes. In wetlands, aluminum can be bound to humic acids, especially fulvic acid (Courtijn et al. 1990, Plankey and Patterson 1988). Free aluminum can also be bound to fluoride (Plankey et al. 1986; Radic and Bralic 1995). Since both fluoride and fulvic acid are present in natural waters, both play a role in the speciation and toxicity of waters with increased aluminum concentrations (Plankey and Patterson 1988). Moreover, the rate of fluoride ion consumption (complexation) is increased by the presence of fulvic acid.

A critical factor in determining the rate at which these complexes occur is the $\text{AlOH}^{2+}/\text{Al}^{3+}$ ratio. AlOH^{2+} has been shown to react with complexing ligands at a

much greater rate than Al^{3+} . Any substance that increases the AlOH^{2+} relative to Al^{3+} will, therefore, increase the rate at which aluminum is complexed by all ligands present. Soluble sulfates, carbonates, fluorides, fulvic acids and hydroxides in natural systems perform this function. On the other hand, complexing is not affected by chlorides or nitrates (Plankey and Patterson 1988). It is, therefore, reasonable to expect aluminum complexes in the B-Lagoon.

Acid deposition or runoff has an important effect on the transport and speciation of soluble aluminum. Acidification mobilizes aluminum from sparingly soluble forms in soils into aquatic ecosystems. In acidified surface waters, elevated levels of dissolved aluminum may create toxic lethal and sub-lethal conditions for biological communities, particularly fish (Burrows 1977). However, biotic impacts may be strongly influenced by the chemical speciation of aluminum. As it is important for any waste water discharge to meet criteria, such that aquatic life is protected, the form of aluminum in the discharge is of relevance to toxicity testing, carried out on the B-Lagoon effluent.

The presence of fluoride can significantly increase total soluble aluminum, or decrease highly toxic monomeric aquo- and hydroxoaluminum, depending on the location and rate mixing and reaction. Therefore aluminum fluoride complexation can potentially have either a mitigating or aggravating effect on acidic water induced aluminum toxicity. As the pH increases, the importance of fluoride decreases relative to hydroxides (see Figures 4 and 5).

The rate of AIF complexation is considerably slower in the pH range of forest soil solutions, pH 3.3-4.0, than it is above pH 4.5. There is also a strong dependence of AIF complexation on temperature. From 15°C to 0°C, the reaction half-life increases 20 x. The stability and growth of colloids and microbial proliferations has been studied by Chen and Buffle (1996) and Buffle and Chen (1996). Temperature and stirring were found to be the two most important factors controlling the growth of these inorganic/organic proliferations. These findings are relevant to the B-Lagoon as

retention time and winter conditions might affect the AlF complex formation.

The potential for mitigating or aggravating aluminum toxicity by fluoride is ultimately determined by the concentration of fluoride present in soil water and streams. Fluoride ion concentrations normally range from 10^{-4} to 10^{-10} M (Lindsay 1979; Plankey et al. 1986). Based on water samples taken in 1998 by Boojum Research, fluoride in the B1 Lagoon (west pond) ranged from 1×10^{-6} to 2.2×10^{-3} M, indicating that fluoride in the B-Lagoon is found in concentrations 10-10,000 x that of other locations. As a driving force in aluminum complexation, fluoride becomes an important anion to consider in the waste water treatment process.

Thermodynamic calculations indicate that aluminum fluoride complexes are generally the dominant inorganic aluminum species (Driscoll et al. 1980). Free aluminum and aluminum hydroxide complexes were predicted in lesser amounts and aluminum sulfate complexes were insignificant. Inorganic monomeric forms have been estimated as the major toxic forms (0.5 mg/L pH 4.4-5.2) decreasing fish survival significantly (Driscoll et al. 1980).

Basic aluminum sulfate minerals may control aluminum concentrations in waters with low pH and high sulfate (e.g. acid mine drainage). Nordstrom and Ball (1986) suggest that, for pH values less than 4.6, aluminum complexes are usually under-saturated with respect to gibbsite and kaolinite, and appear to be more related to sulfate minerals such as alunite, jurbanite, and basaluminite. Above pH 4.6, the hydrolysis of aluminum becomes dominant, and "non-conservative". This non-conservative behaviour is closely correlated with the equilibrium solubility of a microcrystalline gibbsite or amorphous aluminum hydroxide (Nordstrom and Ball 1986). Sulfate concentrations in the B1 Lagoon ranged from 2.2- 45 mg L⁻¹. Since pHs are circumneutral and sulfate concentrations are low, sulfate probably plays only a minor role in the aluminum chemistry of the B1 Lagoon.

The chemistry of aluminum in water is essentially the chemistry of aluminum hydroxide. There is a strong tendency for dissolved aluminum to form monomeric, dimeric, oligomeric, and polymeric species. As the hydration of aluminum proceeds, so too does its colloidal and mineral properties. Aluminum in a hydrated state will tend to form a stable suite of minerals ranging from:

amorphous $\text{Al}(\text{OH})_3$; bayerite $\alpha\text{-Al}(\text{OH})_3$; boehmite $\gamma\text{-AlOOH}$; norstrandite $\text{Al}(\text{OH})_3$; gibbsite $\gamma\text{-Al}(\text{OH})_3$; diascore, $\alpha\text{-AlOOH}$;

depending on the pH of the water solution.

The form and concentration of aluminum in water depends on the pH and nature of the substances dissolved in the receiving waters and, to a lesser extent, duration of exposure to the water. When an aluminum salt is added to a solution providing an OH:Al ratio of 1 to 3, a portion of the aluminum will begin to polymerize. Within 24 hours, the concentration of monomeric aluminum will have stabilized, while polymeric aluminum hydroxide is gradually converted to larger units. Gibbsite particles appear after a few days at 25° C (for ratios of OH:Al of 2-3), but complete crystallization may take a year or longer, especially at cooler temperatures (Burrows 1977). It is thus reasonable to expect that aged aluminum hydroxide in the wetlands sediments of the B-Lagoon will be found as a colloid or small particulate matter.

Solubility curves for aluminum hydroxide suggest that in a water solution in equilibrium with gibbsite, at pH of 6, the free aluminum ion concentration is about 10^{-10} molar. At a pH of 7, this concentration drops to 10^{-13} molar (Figure 4). Thus, if the total aluminum concentration found in the B-Lagoon is of the order of 45 μM , only a very small percentage of the aluminum will be found in the dissolved state. For reference, 1 mg.L^{-1} is 37 μM . The relevant question is whether aluminum is actually free aluminum, and whether removal will be dependant on adsorption of particles or complexes or settling capability. This, in turn, will be a function of the size of the particles, as Al- hydroxides or Al-fluorides prevail in the waste water.

Aluminum is capable of forming strong bonds with substances other than water (and hydroxide). Al^{3+} forms six different soluble complexes with fluoride ion. The mineral cryolite (Na_2AlF_6) is slightly soluble in water; at saturation, it provides a solution containing about 50 mg L^{-1} of aluminum, virtually all complexed by F. Complexation by fluoride is, in fact, stronger than complexation by hydroxide. Fluoride will replace hydroxide in complexes at pHs lower than about 7 (Figure 5). However, if calcium is present, fluoride and calcium will equilibrate and form CaF_2 (fluorite) (Burrows 1977; Lindsay 1979).

In summary, at circumneutral pHs, the presence of dissolved, un-complexed aluminum is vanishingly small. In the presence of high concentrations of fluoride, AlF complexes predominate. These are generally soluble, but usually non-toxic, as discussed later. If fluoride concentrations are low, i.e. $< 10^{-6} \text{ M}$, then the hydroxide complexes will predominate. These complexes, if allowed time to age, will form more stable aluminum colloids, minerals and micro-particles. These complexes, however, would probably not be large enough to be filtered by submicron filters. This again raises the important issue of the size of the particles or complexes.

Burrows (1977) suggests that there is no clear distinction between dissolved and suspended aluminum. Some filters pass microcrystalline or colloidal aluminum hydroxide, while others adsorb much of the soluble aluminum. Many investigators arbitrarily use a $0.45 \mu\text{m}$ filter to distinguish between dissolved and particulate forms, although according to Burrows (ibid), colloidal and microcrystalline forms of aluminum would pass through a $0.45 \mu\text{m}$ filter. Colloids and macromolecules refer to any inorganic or organic entity in the size range of 1 nm - $1 \mu\text{m}$. In aquatic systems, these "particles" form inherently unstable suspensions due to their propensity to undergo conformational changes; they can aggregate and finally settle to the sediment (Buffle and Leppard 1997; Leppard and Buffle 1997). This suggests that the sediments may contain different forms of Al, likely more stable than in the water, but for sure the sediments in the B-Lagoon are going to be rich in aluminum and fluoride.

Natural organic matter (NOM) has a great influence on the fate of inorganic colloids in surface waters. Fulvic acids are likely to be responsible for coating and imparting negative charges to colloids. If the adsorbed polyelectrolyte coating produces an increase in absolute surface potential, it will act to stabilize colloids in surface waters (Wilkenson et al. 1997). Colloidal organic carbon, especially chain structures, have been shown to be involved in aggregation of inorganic colloids through formation of bridges, and the importance of each process depends on the nature and concentration of organic matter in the system and, indirectly, on the productivity of the water body (ibid). Under stress conditions, it is well documented that algae extrude polysaccharides which are a form of colloidal organic matter. As the waste water conditions in the B-Lagoon could exert stress conditions for various reasons on the algae in the pond, this aggregation of inorganic colloids of aluminum and AIF could also be expected to take place.

In summary, the brief review of aluminum chemistry indicates that aluminum in the aquatic environment can be divided into three fractions :

1. Acid soluble, non-labile aluminum, which includes forms of aluminum that require acid digestion before analysis (polymeric, colloidal, and extremely stable organic and hydroxy organic complexes;
2. Non-labile (organic) aluminum, which includes organically chelated aluminum, and;
3. Labile (inorganic) aluminum, the fraction which is truly free (aquo) aluminum, and from aqueous inorganic complexes (fluoride, hydroxide and sulfate).

Depending on the dominant type of aluminum which is prevailing in the B-Lagoon, the removal process from the waste water to the sediment can be affected. The optimization of the B-Lagoon treatment capacity is, therefore, dependant on the form of the aluminum and the size of the particle.

A-3 Biological Aluminum Uptake - Biological Removal from Water in the B-Lagoon

Algae concentrate inorganic ions to amounts several thousand fold greater than in external dilute solutions by a variety of biological, chemical and physical mechanisms involving adsorption, precipitation, and metabolism-dependent processes (Gadd 1988). Inorganic metals can be concentrated by living cells, dead cells, and biochemical products like excreted metabolites, polysaccharides, and constituents of cell surfaces (Wong et al. 1984).

Aluminum can also be bound to benthic green algae such as *Ulothrix* and *Temnogrametum*. Kalin and Wheeler (1992) describe elevated aluminum concentrations found in an acid stream emanating from a coal dump in Nova Scotia. Aluminum concentrations in the water were between 25 and 100 mg L⁻¹. Algal aluminum concentrations were as high as 1% of dry weight, giving concentration factors on the order of 10 x.

A-3.1 Uptake Mechanisms

Metals bind to specific functional groups, including hydroxyl (-OH), phosphoryl (-PO₃O₂), amino (-NH₂), carboxyl (-COOH), sulfhydryl (-SH), and thiol groups (Rai et al. 1981). Biosorption of metals is often rapid, reversible, and usually complete in 5-10 minutes (Gadd 1988). Biosorption is usually not influenced by light, temperature, or the presence of metabolic inhibitors. Killed or metabolically inactive algae have been used to estimate the magnitude of biosorption. Adsorption (biosorption) can take place on cell walls at specific binding sites, onto extracellular carbohydrates, and onto inorganic particles if surface charges are compatible.

Metal ions may compete with each other for binding sites on an algal surface (Crist et al. 1981; Nakajima, et al. 1981), such as *Chlorella vulgaris*, which was sequentially exposed to a solution containing an equimolar mixture of nine metal ions at pH 5.0

(Greene et al. 1987, both). The order of selectivity in binding of the nine different ions was:



In the experiment, the binding of Ag(I) and Al(III) was essentially unaffected by the presence of all the other metal ions. In contrast, binding of the other metal ions was decreased in multi-component mixtures as compared to the binding of the same metal ion in the absence of the other metal ions. One explanation for this behaviour is that there are distinct classes of binding sites on the alga, which have preference for binding of either very hard or very soft metal ions. The hardness of a metal has to do with the electron configuration of the ion and its polarization. Al(III) ion was the hardest metal ion in the medium, and Ag(I) was the softest. Most of the other metal ions were borderline. Therefore Ag(I) and Al(III), being bound to different sites, would not compete.

Al(III) binding to non-living *Chlorella vulgaris*, *Chlorella pyrenoidosa* and *Spirulina* differs depending on pH. Different algae bind at differing capacities in acidic solutions. Some researchers have used this difference to separate aluminum and gold in acidic solutions. In acidic solutions Al(III) and Au(III) could be separated at pH 2, by sequential exposure of a solution (Greene et al. 1986 and Darnall et al. 1986).

Aluminum fluoride is a powerful inhibitor of some proteins such as nitrogenase. The first order inhibition is dependent on the aluminum fluoride species, AlF_4^- , and is linear with aluminum concentration at a pH optimum near 7.1 to 7.3 (Renner and Howard 1996). Aluminum also inhibits the ATPase activities of *Nostoc* and *Chlorella* (Husaini et al. 1996). AlCl_3 and NaF together were more toxic than either separately. Toxicity increased with increased acidity. Toxicity was reduced in the presence of EDTA and citrate (ibid). This suggests that in the B-Lagoon, toxicity from aluminum is unlikely to be encountered.

Aluminum uptake from culture media containing AlCl_3 was influenced by the presence of phosphate. Both photosynthetic systems were highly susceptible to AlF_4 . Toxicity seemed to be due to a replacement of phosphate from nucleotide binding sites of ATPases, thereby arresting the release of ATP and the translocation of ions vital for cyanobacterial growth and metabolism (Rai et al. 1996). Aluminum (10 μM) and F (50 μM) added singly or in combination have no effect on the growth of *Chlamydomonas reinhardtii* in acid or alkaline media containing organic or inorganic P. Cell surface phosphatase activity, however, is increased in the presence of aluminum. It is hypothesized that aluminum is binding to organic P, which inhibits the organic P utilization, causing phosphatase activity to compensate (Joseph et al. 1995). Phosphatase activity is inversely correlated with lake pH, suggesting that this may play an important role in natural systems with acidic pHs. As the B-Lagoon is not acid, phosphatase activity will not likely increase.

A-3.2 Aluminum Tolerance in Biota

The literature review clearly demonstrates that aluminum is taken up by algae, but it also suggests that it can be toxic, especially when complexed with fluoride. Thus, it is likely that the plants in the B-Lagoon have to exhibit some degree of tolerance to aluminum and fluoride, and do not experience toxicity symptoms. A brief look at the literature regarding accumulation and tolerance of plants to aluminum reveals that, according to Foy et al. 1978, aluminum tolerant plants have three types of responses to aluminum:

1. Species that accumulated aluminum in the shoots (and probably in roots as well);
2. Species that accumulate aluminum in the roots, but do not transport it to the shoots, and;

3. Species that are associated with the exclusion of the metal.

To utilize plants as an aluminum removal mechanism in the B-Lagoon, we prefer those plants in the second category which would accumulate aluminum in the roots, without transporting it to the shoots. Group 1 plants could potentially pose a problem further up the food chain if lagoon plants are grazed. Group 3 plants are useless for removal, as they exclude the metal. Among the first group, Chenery and Sporne (1976) examined the aluminum content of leaves of plant species from 259 families of dicotyledons and found aluminum in excess of 1000 ppm in species from 37 families, mainly primitive, rain forest types. The best known accumulator was tea, in which mature leaves are known to accumulate in excess of 20,000 ppm (Sivasubramaniam and Talibudeen 1972). *Lemna minor* (duckweed) has been found to contain as much as 1980 mg kg⁻¹ of aluminum, corresponding to a concentration factor of about 660,000 (Silvey 1967). Lycopods (ferns) have been shown to have levels exceeding 4 mg g⁻¹ (Hutchinson and Wollack 1951). Although not confirmed, it is likely in the B-Lagoon plants of this type will be found.

In the second group of plants (those which accumulate in roots), *Azalea* (Lunt and Kofranek 1970), cranberry (Medappa and Dana 1970), and *Medicago* (Ouellette and Dessureaux 1958) are noted. From our work on tailings with cattails, it is very likely that cattails, which dominate the B-Lagoon (B2), belong to this group of plants.

In the third group (those which exclude aluminum), cultivars of wheat and barley are found (Foy 1974). It is interesting to note that those cultivars that can exclude aluminum in the root zone seem to do so by preferentially taking up nitrate and releasing OH. This raises the pH of the soil around the roots, and precipitates the aluminum (Foy and Fleming 1978).

A-4 Bibliography

(contains references cited above, and others which may also be of interest).

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APPENDIX B: SRC ANALYSIS OF PAH COMPOUNDS



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July 17, 1998

TO: Margarete Kalin, Boojum

Fax: 416-861-0634

FROM: Wo Yuen

Phone: 306-933-6935

Fax: 306-933-7922

RE: Analysis of PAH compounds in Soil/Sediments

As per our phone discussion last week, the following is a brief description of the common methods used by environmental laboratories to analyse soil/sediment for PAH compounds. I also discuss some of the limitations and problems with the analytical methods as they relate to samples that have undergone some degradation in the natural environment.

The common test methods have derived from US EPA methods for priority pollutants which include PAHs. There is a common list of about 16 PAH compounds covered in the EPA methods. As you know, however, there are many more compounds that are in the PAH class. Most environmental laboratories use either the HPLC (high pressure liquid chromatography) or the GC/MS (gas chromatography/mass spectrometry) techniques. The HPLC technique is suitable for relatively clean samples with few compounds because it has less resolution than the GC/MS technique. The GC can separate more complex mixtures and with the MS can identify the compounds with more confidence. An MS can be attached to the HPLC for identifying unknown compounds, but not many labs have an HPLC/MS.

When a PAH test is requested at most labs, their procedure will do a target analysis of only the compounds in their regular list (these 16 or so compounds). This routine type analysis is set up as an automated program on their GC/MS or HPLC computer to search and identify the list. At most labs, a special request must be made to do a manual search and identification of other compounds detected in the sample (requires MS data to be collected). Extra cost may be involved at some labs. This requires the analyst to inspect the chromatogram and mass spectrum of each major peak detected and do a computer mass spectral library search to help identify the unknown compounds. This requires experience in the interpretation of mass spectral data. At the SRC Analytical Lab, when PAH test is requested, a manual search and identification is always done without additional cost. It is important to check with the lab that did the test to find out if other PAH components were included in the analysis and what the findings were.

Page 1/3

page 2/3, Boojum, 98-07-17

If PAH type compounds are present in soil or sediment, there is some degree of degradation of these compounds. There are quite detailed descriptions of the modes of degradation, both chemical and microbial, in the literature. There are many factors affecting the rates and pathways of degradation. These include bacterial/fungal/yeast species present, soil type and moisture, presence of colloidal and macromolecules, vegetation, types of PAH present (high molecular weight versus low molecular weight compounds), etc.

The first step in most degradation pathways is some mode of oxidative addition or cleavage near or at a double bond on one of the rings in the molecule. An enzymatic reaction or chemical oxygen species may be involved. These oxidized derivatives are usually more polar species and may be more soluble in water. Because the original PAH compounds are quite hydrophobic, this increase in polarity may increase the mobility of PAH species in the environment. In sediments, there is an abundance of water. If the water has dissolved macromolecules (eg. surfactants, proteins, polymers, humic or fulvic acids) or colloidal particles present, these may also facilitate the transport of PAH species. This sorption of PAH by mobile carriers may explain why the concentration of PAHs in some groundwaters is higher than predicted from the aqueous solubility model. It requires many steps before a PAH molecule is broken down completely to CO_2 .

What all this means is that in real samples, the PAHs may be made up of the original compounds, alkyl substituted PAHs, and many oxidized forms such as hydroxy-, dihydroxy-, and phenolic derivatives. Our experience is that alkyl and hydroxy forms are very common. For example, not only is naphthalene detected, but also methylnaphthalene, dimethylnaphthalene, trimethylnaphthalene, and dihydroxy-naphthalene. These breakdown species may also have toxicity, so that some knowledge of their presence is important when interpreting the data from a project site. It is important to include the degradation products in the design scheme of a project.

page 3/3, Boojum, 98-07-17

In terms of the analytical methods, it should be realized that these methods are very complex and involve many steps. The accuracy of the methods may be quite dependent on the sample itself. For example, the solvent used for the initial extraction may be very efficient in the dissolution of the original PAH compound, but not as efficient for a breakdown product. Also, the extraction technique might vary between labs. In addition, the sample may be quite heterogeneous. For these and other reasons, the agreement between labs is generally only within 25% and may be far worse depending on the sample. Each lab may have different detection limits, dependent on their specific procedure and the response of their instrumentation. When results are within 10 times the reported detection limit, the data must be viewed with caution. Consultation with an experienced analyst is usually helpful in the interpretation of these data.

Some comments on the information that you faxed to me:

The EVS biometer tests do show some CO₂ generated from the test samples. Usually, biometer tests are done in triplicate because of the variability of the process, but this was not mentioned. Also, variability in the test sample was not discussed. The tests do suggest that PAH compounds were degraded. Some information on some of the partial breakdown products would be useful.

The test results in the reports from Alcan Kitimat are presented in a poor manner in terms of analytical practice. The number of significant digits reported implies much more accuracy and precision than realistically possible. Testing for organics is rarely more precise than two or three significant digits. As an example, a result for naphthalene of 2.2225 ug/g is incorrectly represented. It should be 2.2 ug/g to reflect the degree of precision in the method. Whoever reported or reviewed these reports did not follow good analytical protocol.

All the data on PAHs only targeted on the main compounds and not on any of the degradation products. This leads me to think that the labs were not asked to look for the by-products. This may lead to incorrect conclusions in terms of the progress of the degradation at a project site. Some of the by-products may have equal or even more toxicity than the original compound and this would impact on the conclusions in a project report.

I hope this discussion will help you in designing a more complete proposal for projects involving PAH compounds.

Regards,
Wo Yen



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ANALYTICAL SERVICES LABORATORY

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Sept. 8, 1998

SRC Group #: 98-4114

Sample #: 20592

TO: Boojum Research
Yan Gan

Phone: 416-861-1086

Fax: 416-861-0634

FROM: Wo Yuen

Phone: 306-933-6935

Fax: 306-933-7922

e-mail: yuen@src.sk.ca

SUBJECT: PAH Purged from Filter Material (Alcan Project)

Each filter was weighed as received and the net weight (as received) is tabulated in the attached table. Each filter was then heated at 100C for one hour using a purge and trap technique to capture volatile PAH (polynuclear aromatic hydrocarbons) compounds. The procedure involves using a glass chamber with inlet and outlet. Air is drawn out using vacuum to remove any volatile organic compounds in the headspace of the chamber and trapping the compounds onto an adsorption tube packed with XAD-2 resin which is the recommended adsorbent for PAH. Each filter is then reweighed and the net dry weight is tabulated in the table. The weight loss upon this drying/purging procedure is calculated in this table.

Since the PAH compounds do not have a high volatility, the mass of each compound detected in the vapour phase may not represent the total mass of this compound on the filter. The total mass of PAH is only a small fraction of the weight loss. Thus, most of the weight loss is moisture.

The filter with the highest weight (after drying/purging) was used as the sample from which the adsorption tube was analyzed for PAHs following EPA Method 8270C using GC/MS. Besides the target group of PAH compounds, any other peaks that were observed were individually inspected and their mass spectra were computer library searched for the closest compound match.

page 1/2

page 2/2, Boojum/PAH, 98-09-08

Since the instrument has been calibrated for only the target group of PAHs, other PAH compounds are calculated using the response factor of naphthalene. This gives a semi-quantitative result for the other compounds. It would be exceedingly expensive to calibrate the instrument for these other compounds and may not even be possible if they cannot be purchased in the pure form.

The sample that was used for analysis was SRC #20594 (Client ID 7335). The concentration of naphthalene was found to be 16 ug/g based on the dry weight. The concentration of the naphthalene derivatives total 703 ug/g (using naphthalene response factor).

The attached portion of the chromatogram plots the components detected by the GC/MS. The mass spectrum of each peak is then compared to the computer NIST library of spectra for the closest matching compounds. The compounds written on the chromatogram are the ones with a good library match. As you can see, there are some compounds that are aromatic but not PAH such as pentamethyl benzene and hexamethyl benzene. Several of the naphthalene derivatives have a hydroxyl group which indicates that they may be oxidation products. There are also the alkyl derivatives of naphthalene.

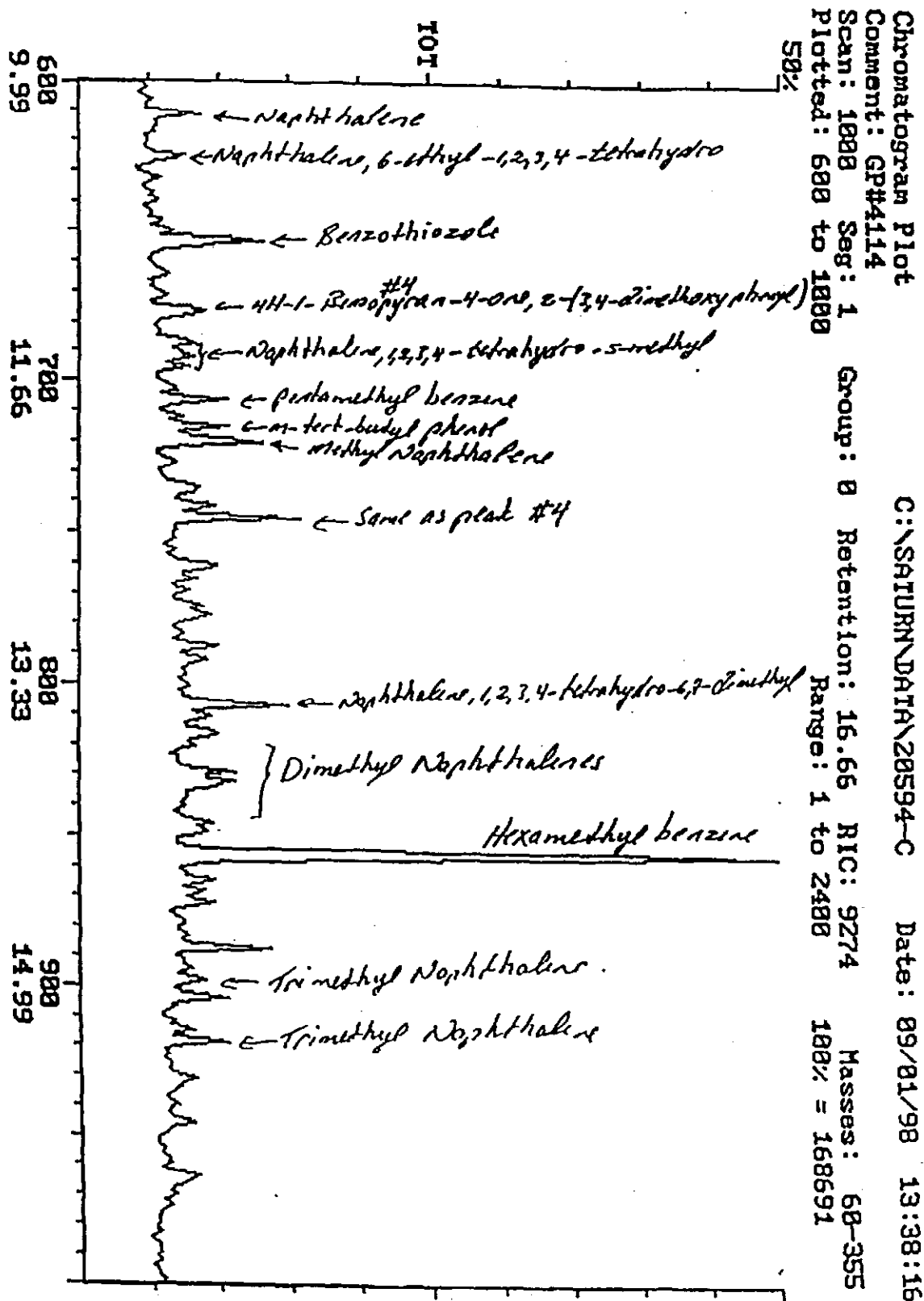
It is important that the analysis of a sample for PAHs includes a search for related PAH compounds in addition to just the target list of 12-16 compounds listed by EPA. From our experience, the target list may constitute only a small fraction of the PAH compounds present. Related PAH compounds may have toxicity effects as well.

09/08/98 TUE 16:28 FAX

SRC CHEMISTRY LAB

004

BOOJUM				
Group 98-4114				
Lab Sample	Client ID	Solids Weight (as received)	Solids Weight (after purging)	Weight Loss (mg)
20593	7334	0.00884	0.0083	0.54
20594	7335	0.0134	0.01283	0.57
20595	7336	0.01126	0.0109	0.36
20596	7337	0.01128	0.01079	0.49
20597	7338	0.00895	0.00868	0.27
20598	7339	0.00561	0.00498	0.63
20599	7340	0.00679	0.00637	0.42
20600	7341	0.00567	0.00528	0.39
20601	7342	0.0064	0.00598	0.42
20602	7343	0.00376	0.00347	0.29
20603	7344	0.00426	0.00368	0.58
20604	7345	0.00379	0.00339	0.40
20605	7346	0.00433	0.00406	0.27
20606	7347	0.00435	0.00392	0.43
20607	7348	0.00321	0.003	0.21



APPENDIX C: B-LAGOON AND F-LAGOON DATA

AppC-Table 1: Water and Sediment Characteristics in Lagoon Systems (Kitimat)

Assayer# WA/FA	Water								Sediment			
	FIELD Water pH ¹ (units)	LAB Water pH (units)	FIELD Water Temp (°C)	LAB Water Temp (°C)	FIELD Water Em ³ (mV)	LAB Water Em ⁴ (mV)	FIELD Water Cond ⁵ (uS/cm)	LAB Water Cond ⁶ (uS/cm)	FIELD Sediment pH (units)	FIELD Sediment Temp (°C)	FIELD Sediment Em ³ (mV)	FIELD Sediment Cond ⁵ (uS/cm)
Lagoon B-1												
7170/77	B1 (Outflow from B lagoon west pond to east pond before seawater addition)											
	6.94	6.02	23	21.6	133	208	800	1070	6.14	21.5	-47	50
	Floating Vegetation Pad											
	6.42		23		-70		40		4.35		-11	50
	Fast-Flowing Channel											
	6.37		23		-11		30		6.3		-12	
	Cattail Stand											
	6.4				-50		30-40		6.03		-8	30-40
	Mixed Stands, Cattails-Bullrush											
	6.4				-5		40		6		-11	
7176/83	J (J stream at concrete weir before joining B lagoon west pond)											
	5.8	6.49		21.9		160		245	5.8		-62	200
	Input Channel from J Stream, SPL Piles-B											
											-82 - -103	
7175/82	NB (North B stream just before discharge to B lagoon west pond)											
	6.3	6.42		21.8		159	30	32.1	6.01		28	30
	Close to West Pond Centre											
	6.1				20		30		5.8		38	
	Close to Inflow (fast flowing)											
	6.22		24.6		24		30		5.7		-26	
	Floating Vegetation Pad											
					-8							
	SWD1 (Solid waste dump locaion 12 seepage into B lagoon east pond)											
	6.6				-8		40				-30	
7174/81	VP-A (Vegetation patch area in B lagoon west pond near outflow)											
	6.4	6.29	23	21.9	4	160	30	30.9	6.3		-5 - -12	30
	In second emergent vegetation patch											
					-9						-4	
Lagoon B-2												
	G (Final outflow from B lagoon system)											
			23		56		900 ²					
7171/78	South Dump Seepage Stream (SWD2)											
	6.7	7.51		21.6	-7	192	1400	2530				
Lagoon F												
7172/79	F-in (F lagoon inflow along north side)											
	7.4	6.29	28.5	21.7	-9	177	40	40.5	6.58		-36	
Lagoon D												
7173/80	D3 (D lagoon outflow at steel weir)											
	6.66	6.27	23.2	21.8	45	178	400	455				

pH¹: Calibration in Morning Calibration in Afternoon ² Remote Cond reading 1300

pH 7.0 reads 7.03

pH 4.0 reads 4.00

pH 10.0 reads 9.87

pH 7.00 reads 6.00

assumed temperature to calculate Eh

Em³ Measured redox, WTW

Em⁴ Measured redox, Fisher

Cond⁵ Measured cond, YSI, uncorrected

Cond⁶ Measured cond, Orion, @ 25 C

AppC-Table 2: 1998 Alcan samples field and laboratory general chemistry.

DATE	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun
ASSAYER#	7170	7177	7171	7178	7172	7179	7173	7180	7174	7181	7175	7182	7176	7183
LOCATION	B1 (Outflow from B lagoon west pond to east pond before seawater addition)	B1 (Outflow from B lagoon west pond to east pond before seawater addition)	SWD2 (Solid waste dump location 2 seepage into B lagoon west pond)	SWD2 (Solid waste dump location 2 seepage into B lagoon west pond)	F-in (F lagoon inflow along north side)	F-in (F lagoon inflow along north side)	D3 (D lagoon outflow at steel weir)	D3 (D lagoon outflow at steel weir)	VP-A (Vegetation patch area in B lagoon west pond near outflow)	VP-A (Vegetation patch area in B lagoon west pond near outflow)	NB (North B stream just before discharge to B lagoon west pond)	NB (North B stream just before discharge to B lagoon west pond)	J (J stram at concrete weir before joining B lagoon west pond)	J (J stram at concrete weir before joining B lagoon west pond)
LAGOON														
CODE	WA	FA	WA	FA	WA	FA	WA	FA	WA	FA	WA	FA	WA	FA
F*Temp.	23	23	23	23	28.5	28.5	23.2	23.2	23	23				
F*pH	6.94	6.94	6.7	6.7	7.4	7.4	6.66	6.66	6.4	6.4	6.3	6.3	5.8	5.8
F*Cond.	800	800	1400	1400	40	40	400	400	30	30	30	30		
F*Eh	375	375	235	235	229	229	287	287	246	246				
L*Temp.	21.6	21.6	21.6	21.6	21.7	21.7	21.8	21.8	21.9	21.9	21.8	21.8	21.9	21.9
L* pH	6.02	6.02	7.51	7.51	6.29	6.29	6.27	6.27	6.29	6.29	6.42	6.42	6.49	6.49
L*Cond.	1070	1070	2530	2530	40.5	40.5	455	455	30.9	30.9	32.1	32.1	245	245
L*Eh	451	451	435	435	420	420	421	421	403	403	402	402	403	403
L*Acidity	5.4	5.4	20.4	20.4	3.7	3.7	3.8	3.8	6.7	6.7	4	4	12	12
L*Alkalinity	14.1	14.1	1379	1379	12.3	12.3	12	12	9.7	9.7	10.7	10.7	34.8	34.8

Temp. C

pH units

Cond. umhos/cm

Eh mV

Acidity mg/L

Alkalinity mg/L

23

assumed temperature to calculate Eh

FA = Filtered Acidified

WA = Whole Acidified

AppC-Table 3: 1998 Alcan Samples with elements at or below detection limits

DATE	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun	30-Jun
ASSAYER#	7170	7177	7171	7178	7172	7179	7173	7180	7174	7181	7175	7182	7176	7183
LOCATION	B1 (Outflow from B lagoon west pond to east pond before seawater addition)	B1 (Outflow from B lagoon west pond to east pond before seawater addition)	SWD2 (Solid waste dump location 2 seepage into B lagoon west pond)	SWD2 (Solid waste dump location 2 seepage into B lagoon west pond)	F-in (F lagoon inflow along north side)	F-in (F lagoon inflow along north side)	D3 (D lagoon outflow at steel weir)	D3 (D lagoon outflow at steel weir)	VP-A (Vegetation patch area in B lagoon west pond near outflow)	VP-A (Vegetation patch area in B lagoon west pond near outflow)	NB (North B stream just before discharge to B lagoon west pond)	NB (North B stream just before discharge to B lagoon west pond)	J (J stram at concrete weir before joining B lagoon west pond)	J (J stram at concrete weir before joining B lagoon west pond)
LAGOON														
CODE	WA	FA	WA	FA	WA	FA	WA	FA	WA	FA	WA	FA	WA	FA
Ag	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001
B	0.061	0.056	0.98	0.92	-0.002	-0.002	0.011	0.011	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002
Be	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001
Ba	0.014	0.013	0.01	0.009	0.019	0.015	0.015	0.014	0.018	0.016	0.015	0.015	0.019	0.016
Cd	-0.001	0.001	0.003	0.003	-0.001	0.002	0.002	0.002	0.002	0.002	-0.001	-0.001	0.002	-0.001
Co	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001
Cr	0.002	0.001	0.002	0.002	0.001	-0.001	-0.001	0.001	-0.001	-0.001	0.001	-0.001	0.001	-0.001
Cu	0.003	0.002	0.003	0.007	0.004	0.003	0.003	0.005	0.003	0.009	0.004	0.003	0.004	0.006
Mo	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001
Ni	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001
P	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05	-0.05
Pb	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002	-0.002
Ti	0.002	-0.001	0.002	-0.001	0.003	-0.001	-0.001	-0.001	-0.001	-0.001	0.002	-0.001	0.002	-0.001
V	-0.001	-0.001	0.043	0.034	-0.001	-0.001	0.002	0.002	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001
Zn	0.63	0.16	-0.005	0.009	-0.005	-0.005	0.007	0.007	-0.005	-0.005	-0.005	-0.005	0.025	0.019
Zr	-0.001	-0.001	0.003	0.003	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001	-0.001
Sr	0.17	0.16	0.058	0.056	0.028	0.027	0.08	0.078	0.023	0.023	0.024	0.024	0.03	0.03

Elements: mg/L FA = Filtered Acidified WA = Whole Acidified

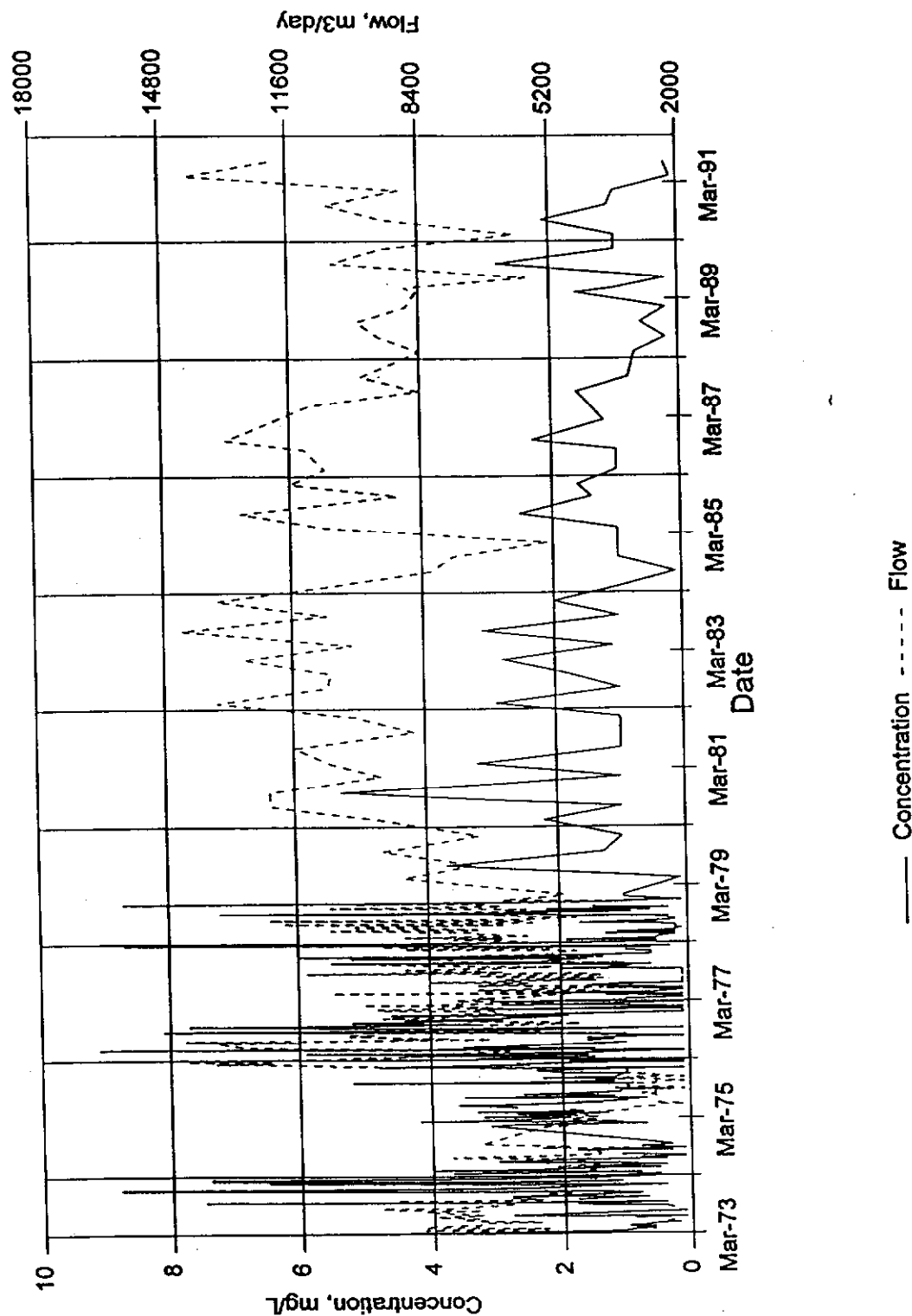
AppC-Table 4: 1998 Alcan Samples with elements above detection limits

DATE	35976	35976	35976	35976	35976	35976	35976	35976	35976	35976	35976	35976	35976	35976	
ASSAYER#	7170	7177	7171	7178	7172	7179	7173	7180	7174	7181	7175	7182	7176	7183	
LOCATION	B1 (Outflow from B lagoon west pond to east pond before seawater addition)	B1 (Outflow from B lagoon west pond to east pond before seawater addition)	SWD2 (Solid waste dump location 2 seepage into B lagoon west pond)	SWD2 (Solid waste dump location 2 seepage into B lagoon west pond)	F-in (F lagoon inflow along north side)	F-in (F lagoon inflow along north side)	D3 (D lagoon outflow at steel weir)	D3 (D lagoon outflow at steel weir)	VP-A (Vegetation patch area in B lagoon west pond near outflow)	VP-A (Vegetation patch area in B lagoon west pond near outflow)	NB (North B stream just before discharge to B lagoon west pond)	NB (North B stream just before discharge to B lagoon west pond)	J (J stram at concrete weir before joining B lagoon west pond)	J (J stram at concrete weir before joining B lagoon west pond)	
LAGOON															
CODE	WA	FA	WA	FA	WA	FA	WA	FA	WA	FA	WA	FA	WA	FA	
mg/L	Al	0.13	0.038	0.59	0.41	0.13	0.03	0.061	0.024	-0.005	0.036	-0.005	0.032	0.31	0.49
	Ca	11	11	14	13	4.4	4.4	6.6	6.6	3.7	3.7	3.9	3.9	5.6	5.6
	Fe	0.33	0.058	1.7	0.27	0.15	0.051	0.083	0.023	0.17	0.073	0.18	0.063	0.38	0.19
	K	11	10	29	28	0.4	0.4	4	3.9	0.4	0.4	0.4	0.3	0.9	1
	Mg	22	21	10	9.8	0.5	0.5	9	8.7	0.4	0.4	0.4	0.4	0.5	0.5
	Mn	0.016	0.025	1.2	1.1	0.008	0.012	0.003	0.004	0.023	0.017	0.008	0.006	0.034	0.032
	Na	180	180	740	710	2.2	2.4	83	72	1.5	1.6	1.4	1.5	54	54
	Si	1.2	1	10	9.7	1.4	1.3	1.2	1.1	1.2	1.1	1.2	1.1	1.4	1.3
	Fluoride	0.85	0.85	41	41	0.22	0.22	0.2	0.2	0.32	0.32	0.2	0.2	32	32

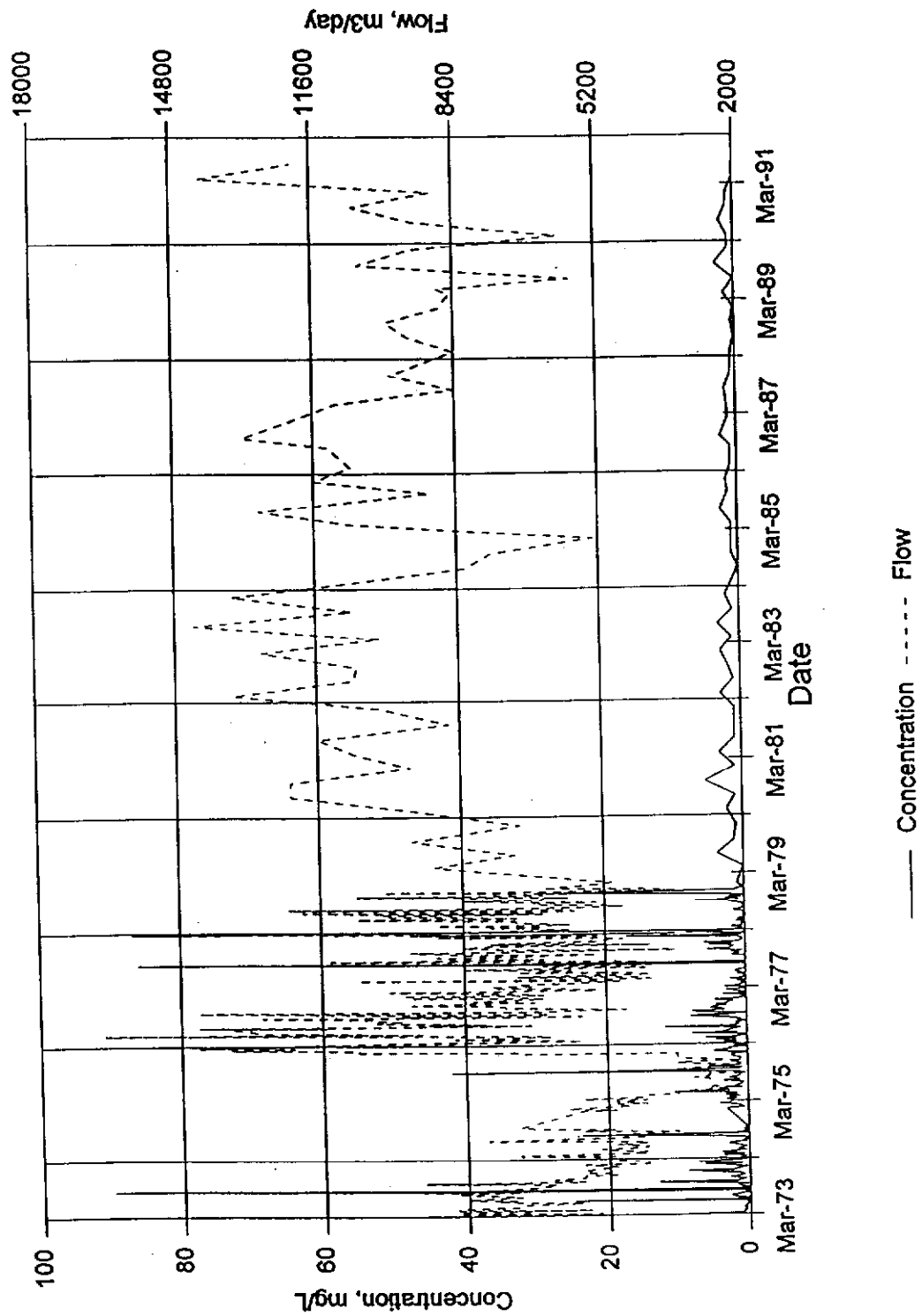
FA = Filtered Acidified

WA = Whole Acidified

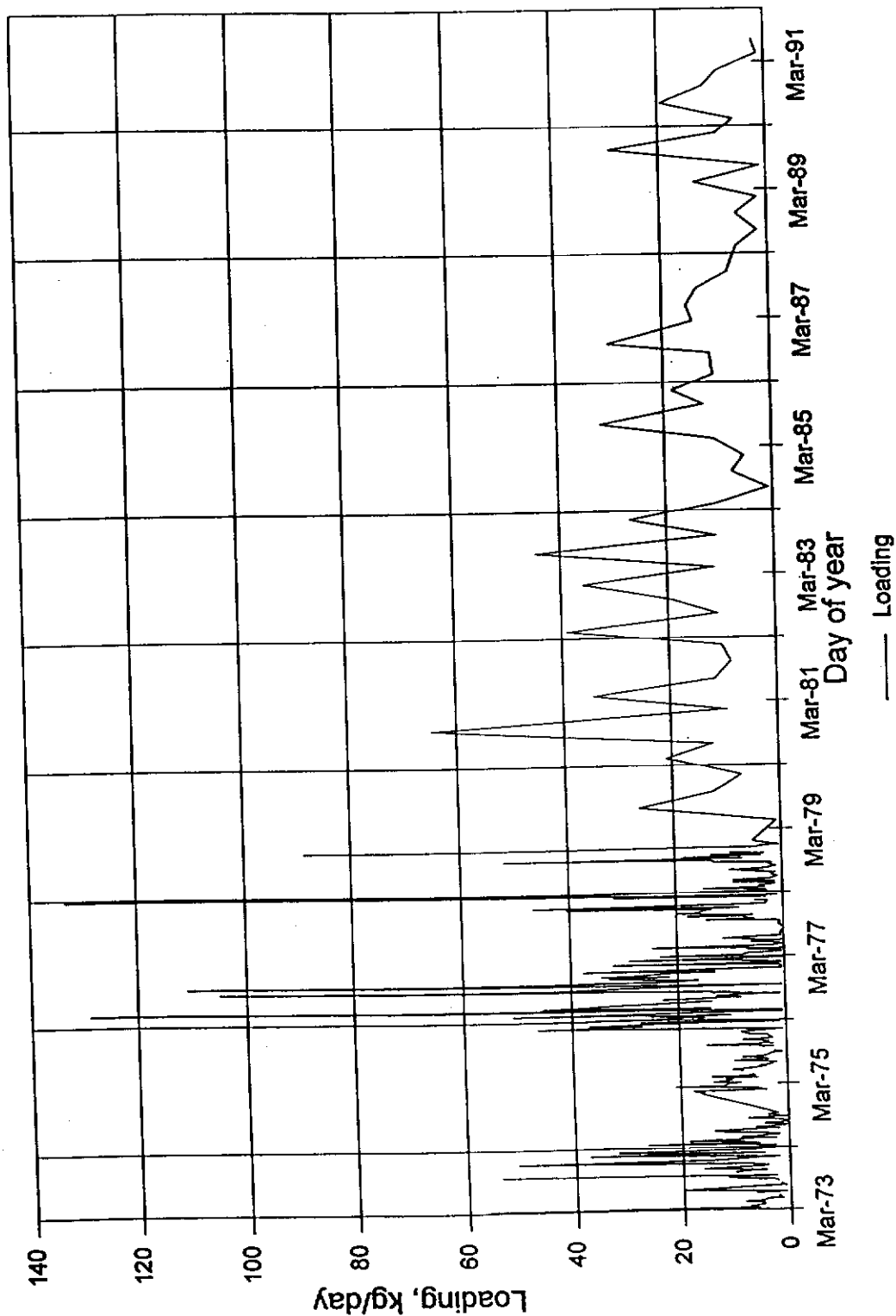
AppC-Fig. 1: F-Lagoon - Historical Data
Flow & [F] 1980-91 (0-10mg/L)



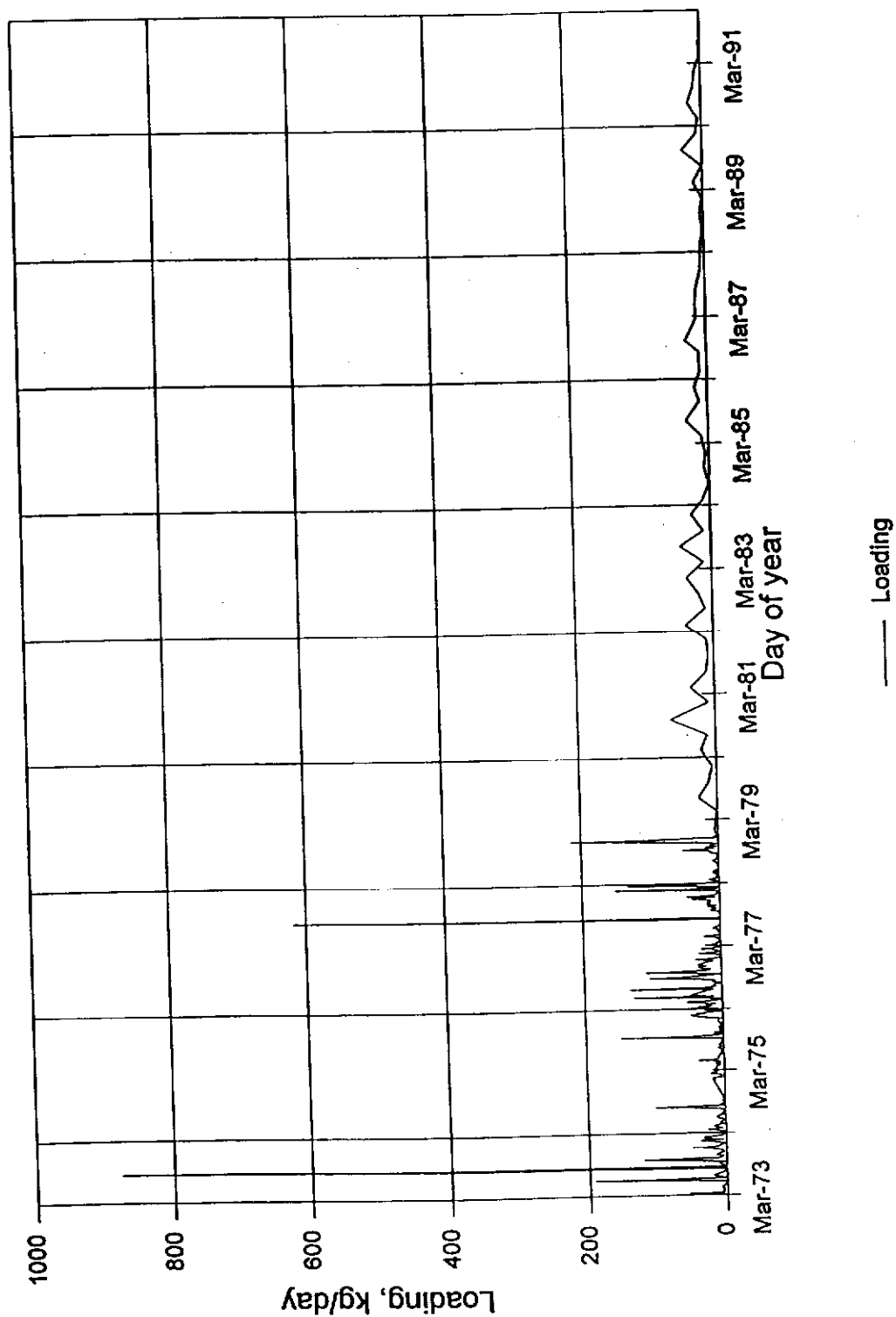
AppC-Fig.2: F-Lagoon - Historical Data
Flow & [F] 1980-91 (0-100mg/L)



AppC-Fig.3: F-Lagoon - Historical Data
Fluoride Loading, 1980-91(0-140mg/L)



AppC-Fig.4: F-Lagoon - Historical Data
Fluoride Loading, 1980-91 (0-1000mg/L)



Results of Sample Examination - Algatax Consulting

PROJECT: Alcan

British Columbia

Sample Code: A98-07

Alcan - Submerged Vegetation at B-1 Site (30/06/98)

- periphyton sample was examined for algal taxa identification
- sample dominated by filamentous green algae: *Mougeotia* spp. (3 spp. based on size)
Spirogyra sp.
- other taxa reported: *Oscillatoria* spp. (3 spp. based on size)

Dictyosphaerium pulchellum

Oocystis sp.

Scenedesmus sp.

Temnogametum sp.

Zygnema sp.

Bambusina brebissonii

Closterium spp. (3 spp.)

Cosmarium spp.

Desmidium sp.

Desmidium swartzii

Netrium sp.

Pleurotaenium sp.

Spondylosium sp.

Staurastrum pachyrhynchum

Euglena spp. (3 or 4 spp.)

Trachelomonas sp.

Cryptomonas sp. (small sp.)

Cymbella sp.

Frustulia saxonica

Pinnularia spp.

Tabellaria fenestrata

Tabellaria flocculosa

Results of Sample Examination - Algatax Consulting

PROJECT: Alcan

British Columbia

Sample Code: A98-08

Alcan - Lagoon (30/06/98) F lagoon H.K

- periphyton sample was examined for algal taxa identification
- sample dominated by filamentous green algae: *Spirogyra* sp.
- other taxa reported: *Mougeotia* sp. (medium size) *
Tennogametum sp.

Bambusina brebissonii *
Closterium spp. (3 spp.)
Cosmarium spp.
Netrium sp.
Pleurotaenium sp.
Staurastrum pachyrhynchum

Eunotia spp.
Frustulia saxonica
Nitzschia sigmoidea
Nitzschia spp.
Pinnularia spp.
Tabellaria fenestrata

Results of Sample Examination - Algatax Consulting

PROJECT: Alcan

British Columbia

Sample Code: A98-09

Alcan - Outflow (30/06/98) Duplicate B - Discharge *N.K.*

- periphyton sample was examined for algal taxa identification
- sample dominated by filamentous green algae: *Spirogyra* sp.
 - filaments 'less healthy' than in samples A98-07 and A98-08
- other taxa reported: *Oscillatoria* spp

Mougeotia sp. (medium size)

Cosmarium spp.

Desmidiium sp.

Nitzschia spp.

Pinnularia spp.

Surirella sp.

Tabellaria floccuolosa

- note: there is a considerable amount of cellular debris in sample consisting of cell wall remnants from *Mougeotia* and *Spirogyra*

Results of Sample Examination - Algatax Consulting

PROJECT: Alcan

British Columbia

Sample Code: A98-10

Alcan - B Discharge (30/06/98)

- periphyton sample was examined for algal taxa identification
- sample dominated by filamentous green algae: *Spirogyra* sp.
 - filaments 'less healthy' than in A98-07 and A98-08
- other taxa reported: *Oscillatoria* spp. (3 spp. based on size)

Dictyosphaerium pulchellum

Mougeotia sp.

Scenedesmus sp.

Temnogametum sp.

Bambusina brebissonii

Closterium sigmoidea

Closterium spp. (3 spp.)

Cosmarium spp.

Desmidium sp.

Pleurotaenium sp.

Staurastrum pachyrhynchum

Euglena spp. (2 spp.)

Phacus sp.

Cymbella sp.

Eunotia spp.

Frustulia saxonica

Nitzschia spp.

Pinnularia spp.

Stauroneis sp.

Surirella sp.

Tabellaria flocculosa

Alcan sampling location codes and descriptions, 1998.

Sampling	Sampling	
Location	Location Description	
A-in	A Lagoon inflow	on map
A-mid	A Lagoon midpoint	on map
B1	Outflow from B lagoon West Pond to East Pond before seawater addition	on map
Centre	B Lagoon West Pond centre	on map
D1	Inflow culvert to D Lagoon	on map
D2	Steel weir separating two ponds comprising D Lagoon	on map
D3	D Lagoon outflow at steel weir	on map
F-in	F Lagoon inflow along north side	on map
F out	F Lagoon outflow	on map
G	Final outflow from B Lagoon system	on map
J	J Stream at concrete weir before joining B Lagoon West Pond	on map
MB	Middle B stream just before discharge to B Lagoon West Pond	on map
MB Flow	Measurement station in flow path of Middle B stream through B Lagoon West Pond	on map
NB	North B stream just before discharge to B Lagoon West Pond	on map
NB Flow	Measurement station in flow path of North B stream through B Lagoon West Pond	on map
SW	Seawater injection point in outflow stream between West and East Pond, B Lagoon	on map
SWD1	Solid Waste Dump location 1 seepage into B Lagoon East Pond	on map
SWD2	Solid Waste Dump location 2 seepage into B Lagoon West Pond	on map
VP-A	Vegetation Patch area in B Lagoon West Pond near outflow.	only VP on map