

**A Review of the Lagoon Systems
ALCAN Kitimat Smelter
FINAL REPORT
September 21, 1998**

TABLE OF CONTENTS

1.0	INTRODUCTION AND PROBLEM DEFINITION	1
1.1	Aluminum Chemistry in the Aquatic Environment	3
1.1.1	Aluminum forms	3
1.1.2	Biological aluminum uptake - biological removal from water in the B Lagoon.	10
1.1.2.1	uptake mechanisms	10
1.1.2.2	aluminum tolerance in biota	12
2.0	B LAGOON SITE DESCRIPTION	15
2.1	Physical Description of the Lagoon	15
2.2	B Lagoon Vegetation	18
2.3	Sources of Waste Water to the Lagoon System	18
3.0	MONITORING DATA INTERPRETATION	20
3.1	1992 Dataset	24
3.2	1995 Dataset	24
3.3	Boojum Technologies 1998 Dataset	28
3.4	PAH in the B Lagoon	35
4.0	BIOLOGICAL SYSTEMS AND THEIR INFLUENCE ON PAHs	38
5.0	BRIEF SUMMARY	41
5.1	Aluminum	41
5.2	PAH	42
6.0	RECOMMENDATIONS	43
7.0	BIBLIOGRAPHY	44

TABLE OF CONTENTS (continued)

8.0 APPENDICES

8.1 Appendix A: SRC Analysis of PAH Compounds

8.2 Appendix B: Phytoplankton Data

8.3 Appendix C: F Lagoon F Concentrations, Flows, Loads

LIST OF TABLES

Table 1:	The average concentration of "whole" element minus the "dissolved" average concentration divided by the average "whole" element concentration x 100	27
Table 2:	Aluminum concentrations in Effluent B from the Kitimat Smelter. The pH of the water samples was between 6.0 and 6.7	28
Table 3a:	Water and sediment characteristics in Lagoon Systems (Kitimat) . .	29
Table 3b:	198 Alcan samples field and laboratory general chemistry	30
Table 4:	1998 Alcan samples with elements at or below detection limits . .	31
Table 5:	1998 Alcan samples with elements above detection limits	32
Table 6:	% Retention of aluminum on 0.8 μm filter paper	34
Table 7:	Molar fluoride to aluminum concentration ratios	34

LIST OF FIGURES

Figure 1:	The activity of Al^{3+} and its hydrolysis species in equilibrium with gibbsite	5
Figure 2:	Ratio of free aluminum to total aluminum as a function of fluoride and pH (zero ionic strength)	5
Figure 3:	F Lagoon historical fluoride concentrations and flows from 1979 to 1991	21
Figure 4:	F Lagoon historical fluoride loads from 1979 to 1991	22
Figure 5:	F Lagoon historical seasonal fluoride loads from 1979 to 1991 . . .	23
Figure 6:	Total HPAH concentration in aquatic vegetation from B Lagoon and a control location at a nearby hot springs	39

LIST OF SCHEMATICS

Schematic 1:	Aerial photographs of the B Lagoon system: 1969, 1975, 1979, 1985, 1990 and 1997	2
Schematic 2:	Waste water origins and flow plaths: Kitimat	17

LIST OF MAPS

Map 1:	Alcan Kitimat water sampling locations	16
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1.0 INTRODUCTION AND PROBLEM DEFINITION

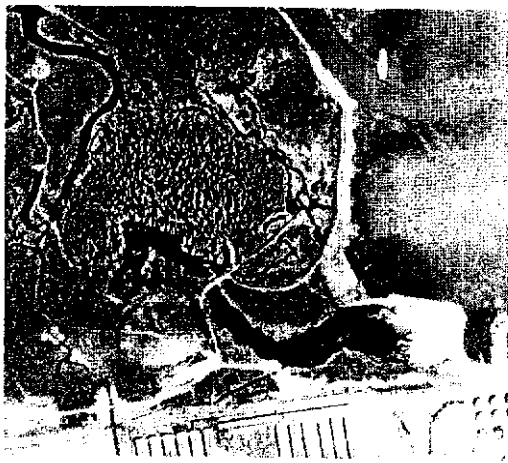
The B Lagoon has been used since at least 1969 as a waste water treatment system for the Kitimat Alcan smelter. In Schematic 1, an overview is given of the distribution of solids and the spatial arrangement of the system covering a period from 1969 to 1997. It appears that, between 1975 and 1979, the discharge in association with the pot liner leachate pile started to be confined and, in 1985, this area of the B Lagoon was contained into dikes. At present, the J stream discharges into the B Lagoon on the inside of the dyke. Also, between 1979 and 1985, the waste rock dump was contained by a dyke and became part of the surface water drainage basin of the B Lagoon. In 1985 the open pond area was covering about 80% of the B Lagoon system but by 1997 most of the lagoon is landed in. The B Lagoon essentially supports an extensive vegetation cover.

As the waste water carries a considerable quantity of suspended solids in addition to that produced by the vegetation inside the lagoon. This will continuously reduce the residence time of the water, reducing the effectiveness of settling of suspended solids and thereby impairing the removal of regulated contaminants prior to discharge.

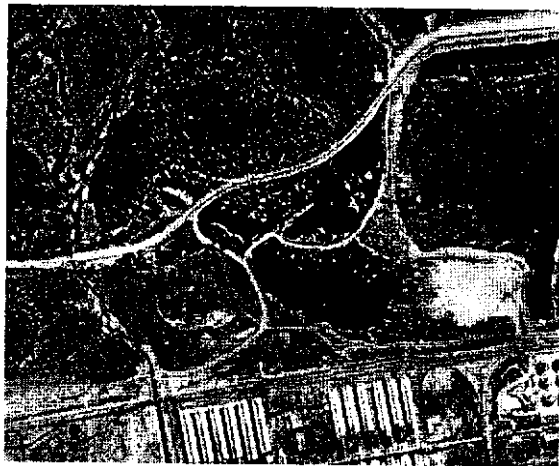
Boojum Research Ltd was retained to conduct a feasibility study on the B Lagoon system. The feasibility study was to address first, the potential role of the vegetation with respect to Al removal in the lagoon. Second, the study was to identify an approach to either improve or optimize the waste water treatment capacity of the lagoon system.

Two field trips were carried out by Boojum personnel, a literature review was carried out and historical data from the system were reviewed.

1969



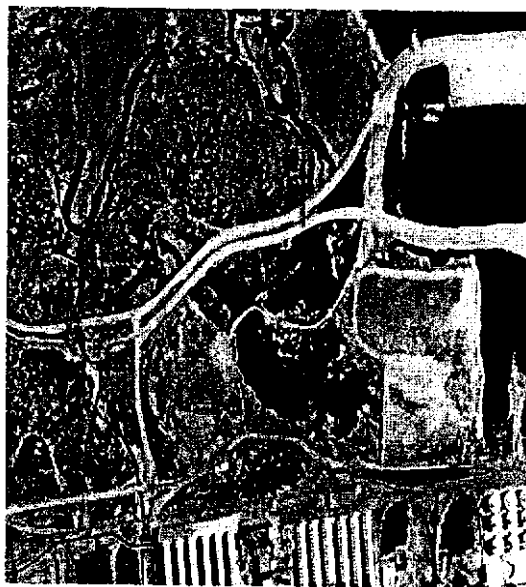
1975



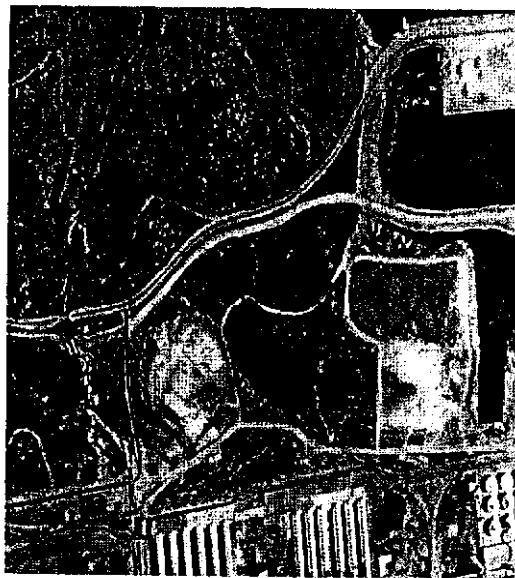
1979



1985



1990



1997



Schematic 1: Aerial photographs of the B Lagoon system.

1.1 Aluminum Chemistry in the Aquatic Environment

Aluminum is the most prevalent metal in the earth's crust, comprising about 7.1% by weight. It is a member of the class A metals, a group which contains all of the metal ions which function as macronutrients for plants (Mg, Ca, and K). It can be found as a major constituent of fertilizer (aluminum calcium phosphate) (Archer 1985). During weathering, aluminum is released from primary minerals and is precipitated as secondary minerals, largely as aluminosilicates. As soils weather, silicon is more rapidly lost than aluminum, leaving it to precipitate as oxides and hydroxides (Lindsay 1979).

Aluminum is found in almost all natural water bodies. Published values for aluminum content of natural waters in Canada vary from 0.07 to 1.12 mg L⁻¹ for rain and snow in S.E. Ontario (1965); 0.276 mg L⁻¹ for samples from the St. Lawrence River in Quebec. Samples from the Slave and Mackenzie Rivers contain 1 and 1.41 mg L⁻¹, respectively. Samples from the Nelson and Churchill Rivers in Manitoba contain 0.089 and 0.103 mg L⁻¹, respectively (cited in Burrows 1977, Table 11- 9 pages).

The review of the literature is focused on the biogeochemistry of aluminum, and well documented mechanisms which may lead to the removal of aluminum from the lagoon water to the sediments.

1.1.1 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 speciation and toxicity of waters with increased aluminum concentrations (Plankey and Patterson 1988). 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 increase the rate at which aluminum is complexed by all ligands present. Therefore, soluble sulfates, carbonates, fluorides, fulvic acids, and hydroxides in natural systems will increase the rate at which aluminum is complexed. It is therefore reasonable to expect aluminum complexes in the B Lagoon. The complexing is not affected by chlorides or nitrates (Plankey and Patterson 1988).

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 Al 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 1 and 2).

The rate of AlF complexation is considerably slower in the pH range of forest soil solutions pH 3.3 to 4.0, than it is above pH 4.5. There is also a strong dependence of

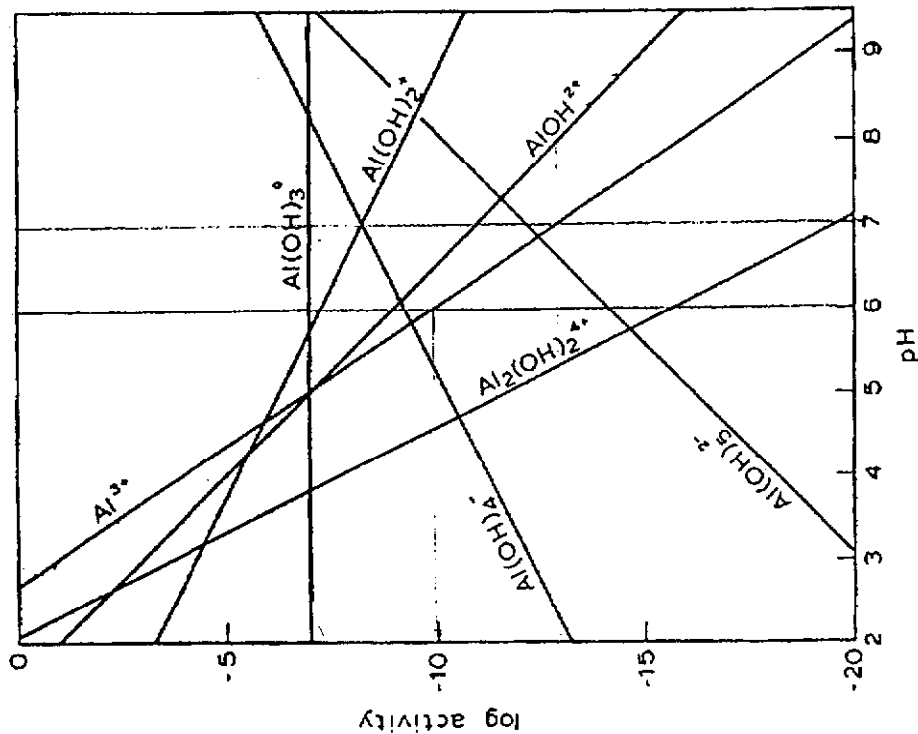


Figure 1: The activity of Al^{3+} and its hydrolysis species in equilibrium with gibbsite (from Burrows, W.D, 1977).

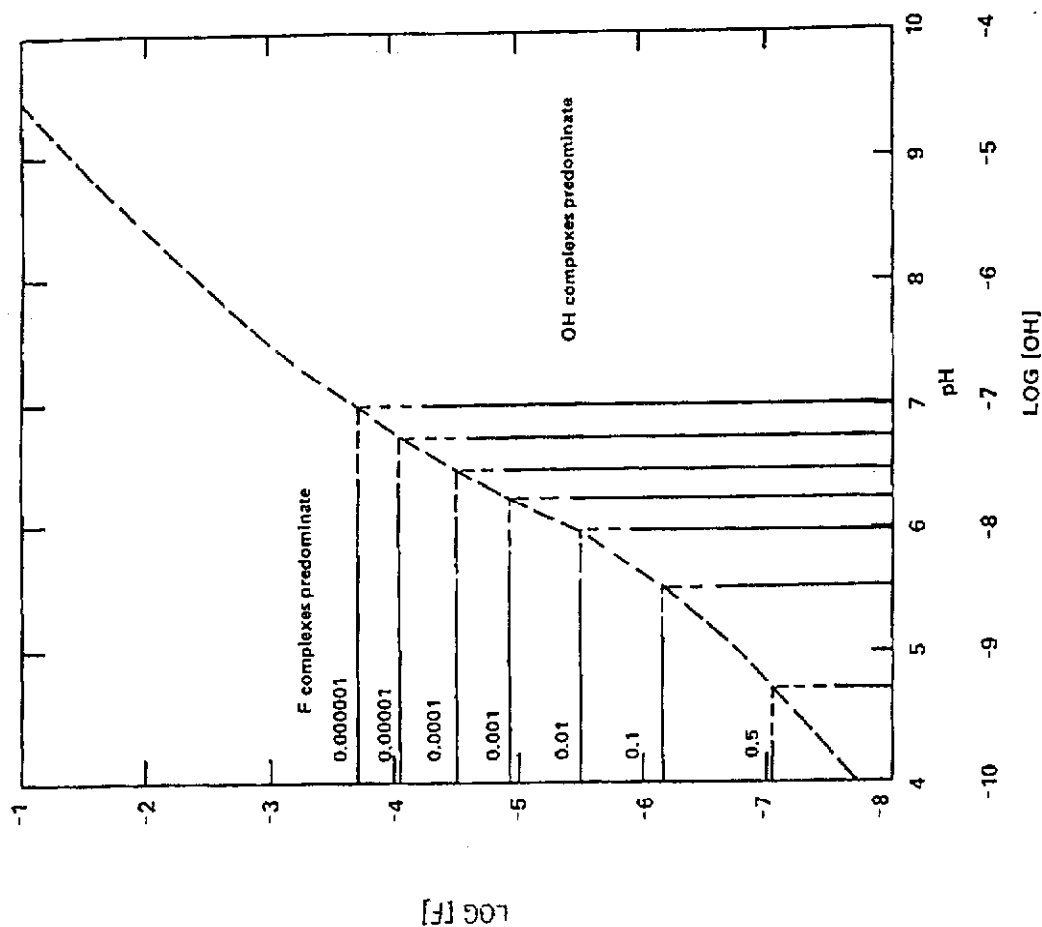


Figure 2: Ratio of free aluminum activity to total aluminum as a function of fluoride and pH (zero ionic strength).
(From Hem, J.D., U.S. Geological Surv. Water Supply Pap. No. 1827B, 1968.)

AlF 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) decreased 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 to 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 $\gamma\text{-Al}(\text{OH})_3$; diaspore, $\alpha\text{-AlOOH}$;

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 (see Burrows 1977). It is thus reasonable to expect that aged aluminum hydroxide in 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 1). Thus, if the total aluminum concentration found in the B Lagoon on 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 $37 \text{ }\mu\text{M}$). The question which is relevant is whether Al is actually free Al, 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 are prevailing 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 2). 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 $0.45 \text{ }\mu\text{m}$ filter to distinguish between dissolved and particulate forms, although according to Burrows (ibid), colloidal and microcrystalline forms of aluminum would pass through a $0.45 \text{ }\mu\text{m}$ filter. Colloids and macromolecules refer to any

inorganic or organic entity in the size range from 1 nm to 1 μ 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 Al and F.

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 (ibid). 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 Al and AlF 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 Al and the size of the particle.

1.1.2 Biological aluminum uptake - biological removal from water in the B Lagoon

Algae concentrate inorganic ions to amounts several thousandfold 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 *Temnogametum*. 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.

1.1.2.1 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:

$\text{Al (III)} \sim \text{Ag(I)} \gg \text{Cu(II)} > \text{-Ni(II)} \text{ Pb(II)} > \text{Zn (II)} = \text{Co(II)} > \text{- Cr(III)}$

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. (See 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 *Chorella* (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 al 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 increase likely.

1.1.2.2 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).

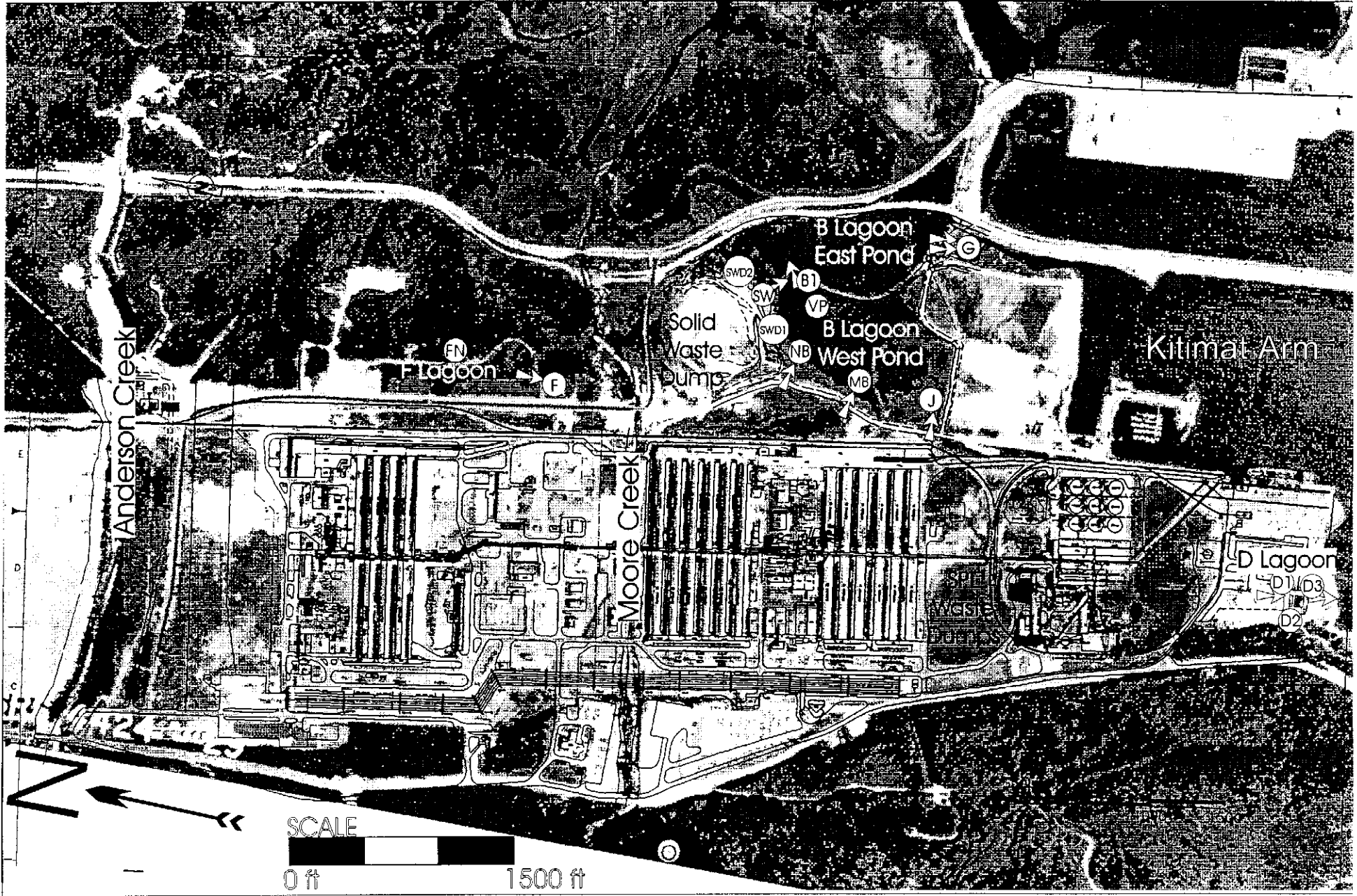
2.0 B LAGOON SITE DESCRIPTION

2.1 Physical Description of the Lagoon

The B Lagoon was surveyed by ALCAN in 1994. It is comprised of two ponds, west and east, separated by a dike. 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 into two parts, separated by an internal dike. The dike separates a deeper upper pool from the shallow, marshy lower section. The retention time is about 1 day, giving a flow-through of approximately 43 m³ per minute.

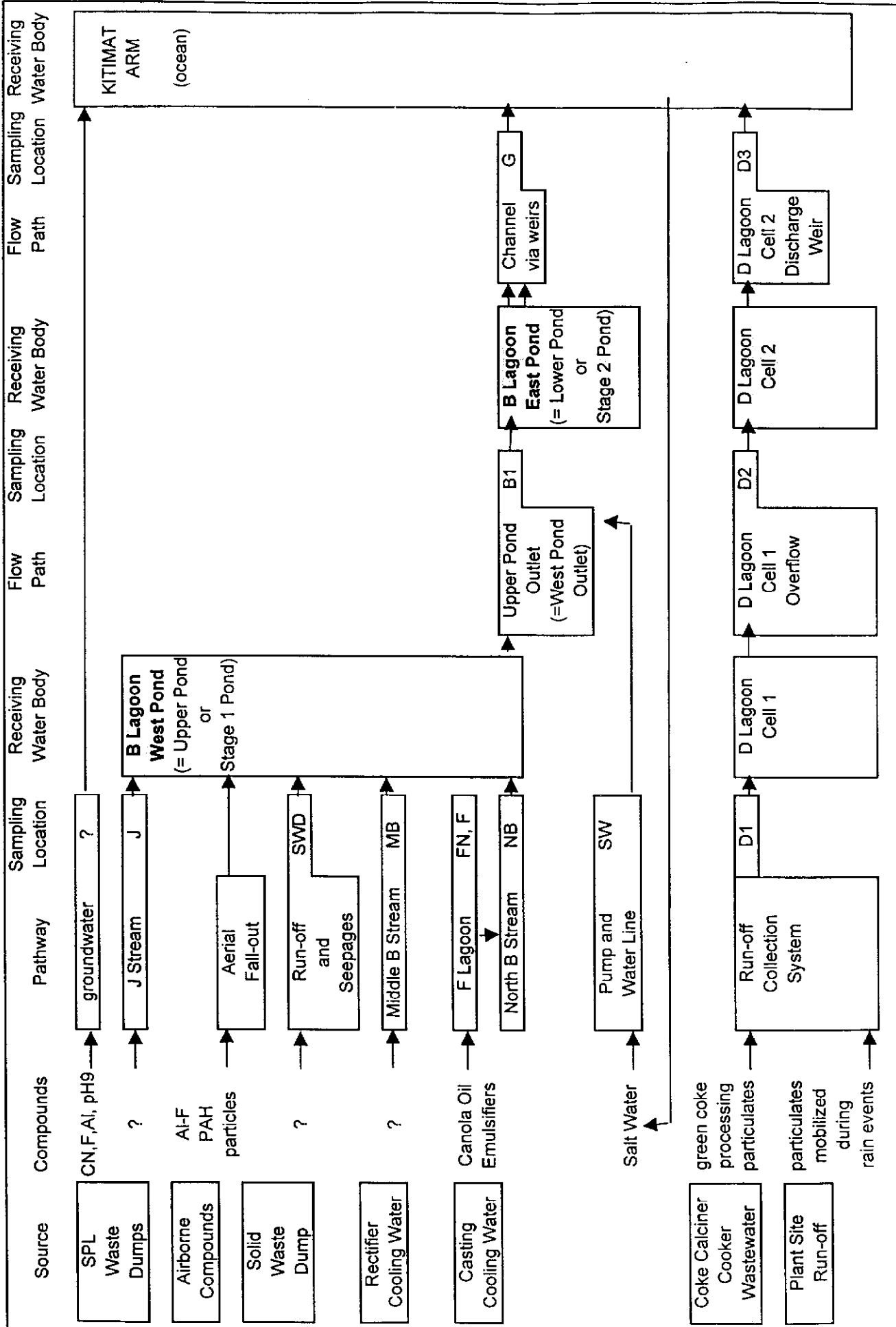
In Map 1, a summary of the sampling locations has been constructed. The interpretation of the historic sampling locations may be a bit tentative, as in the various reports, the investigators did not refer to the sampling stations based on the same reference map. For example in one study the three major inflows, termed "A", "B" and "C". On Map 1 we refer to them as NB, MB and J. All three inflows drain into the West (B1) lagoon. Flow leaves the West (B1) lagoon in 3 pipes (2 24 in and 1 36 in) 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.

In Schematic 2, a flow diagram has been constructed which is likely reflects the general flow conditions. The schematic was developed based on the information which could be gathered during the field trip 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, such that treatment strategy can be implemented. At present, loadings (concentration x flow) for the individual waste water streams are not available, or might be available but have not been summarized.



Map 1: Alcan Kitimat Water Sampling Locations.

Schematic 2: Waste Water Origins and Flow Paths: Kitimat



2.2 B Lagoon Vegetation

During the brief site visit, the major plant species were noted. Those are macrophytic emergent plants (rooted plants extending 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 of those phytoplankton species identified in the B Lagoon is given in Appendix 6.3. The number of species decreased in the outflow as compared to the B Lagoon at large. However, as most of the species are fresh water species, this is expected, due to the addition of the seawater prior to the outflow.

Although a reduction in phytoplankton species leaves the B-2 Lagoon (east pond), a notable difference in the degree of 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 the improvement in plant health and growth.

2.3 Sources of Waste Water to the Lagoon System

1. Particulates mobilized during rain events
 - Combination of rain and aerial fall-out - produces either particulate or dissolved contaminants containing organic carbon, D Lagoon run-off contains particulate from green coke processing.
2. Aerial Fall out from site.
 - Aluminum Fluoride, 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.
6. Groundwater/leachate from Potlining Pile
 - CN, F, Al, pH 9, composition tested
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 East (B2) Lagoon. Seawater is added to detoxify the final effluent in the East (B2) Lagoon.

3.0 MONITORING DATA INTERPRETATION

For the F Lagoon, a data set was made available which covered the period of 1973 to 1991.

A relatively complete data set is available for flow and fluoride concentrations. These data are presented in Figures 3 through 5.

From the data set, some unusually high concentrations were deleted as they seemed to be aberrant values. All data are reported in the appendix. In Figure 3, the concentrations of F 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 for each year. The loading of F resulting from these data clearly indicate, however, that in the years since 1985 the F load in the F lagoon has decreased (Figure 4). The questions which arises from such an evaluation are, how much of the F loading has remained in the B Lagoon system, and how much would be discharged with the effluent. This data evaluation would allow the determination of the expected F mass in the sediments. A similar evaluation for Al would facilitate an assessment of aluminium expected in the B Lagoon sediment. This evaluation is, of course, only possible if, during the same time span, the F Lagoon was entering the B Lagoon system, and that the effluent from B Lagoon was monitored.

In Figure 5, the same data are evaluated with respect to changes during the seasons. It is evident that the F discharge from the smelting activities are pretty constant, and that spring and fall run off does not regularly produce increases. The few years where loading increased by fall likely represent events relating to smelting activities.

Fig. 3: F Lagoon Historical Data
[F] and Flows, 1979-1991

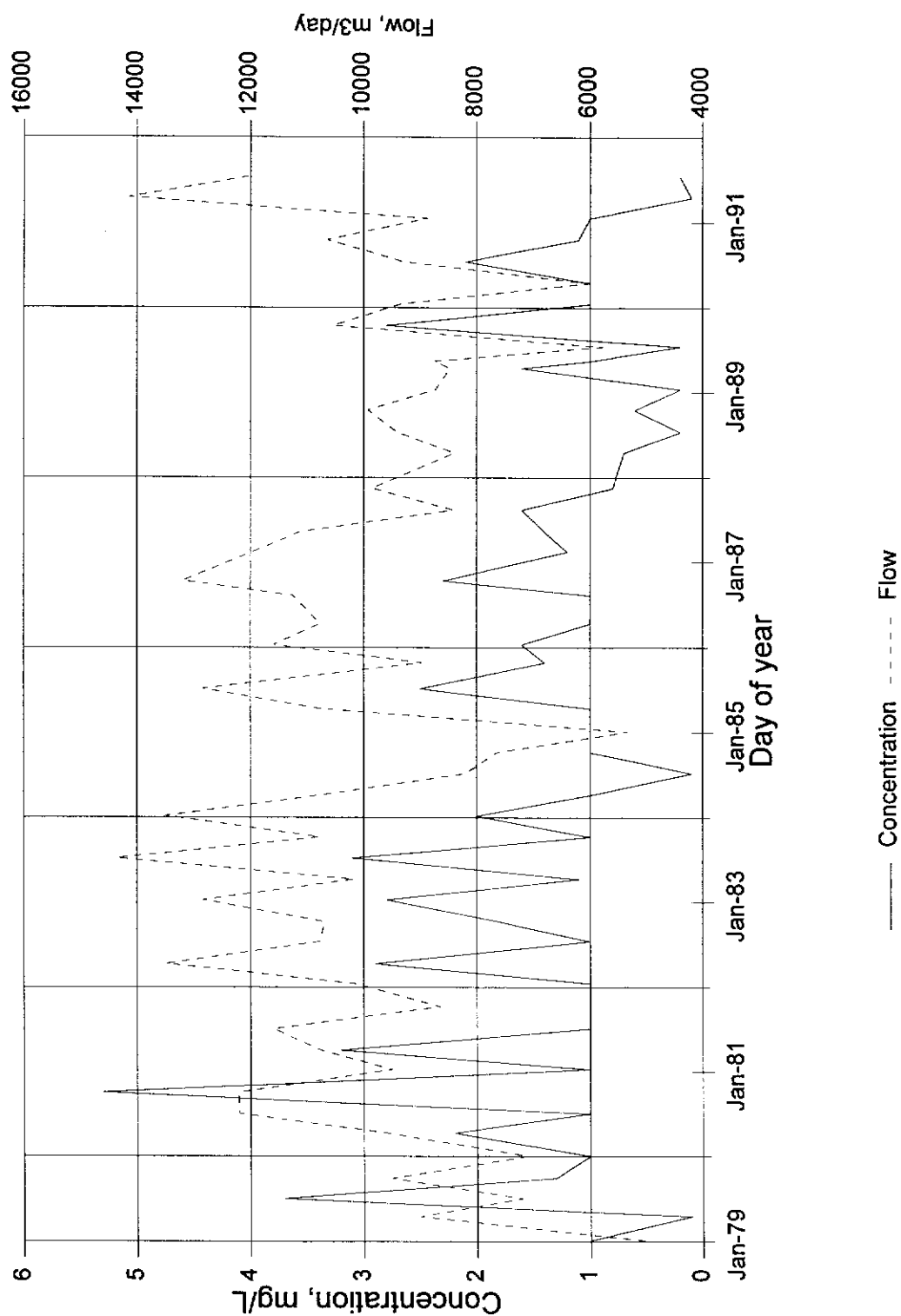


Fig. 4: F Lagoon Historical Data
Fluoride Loading, 1979-1991

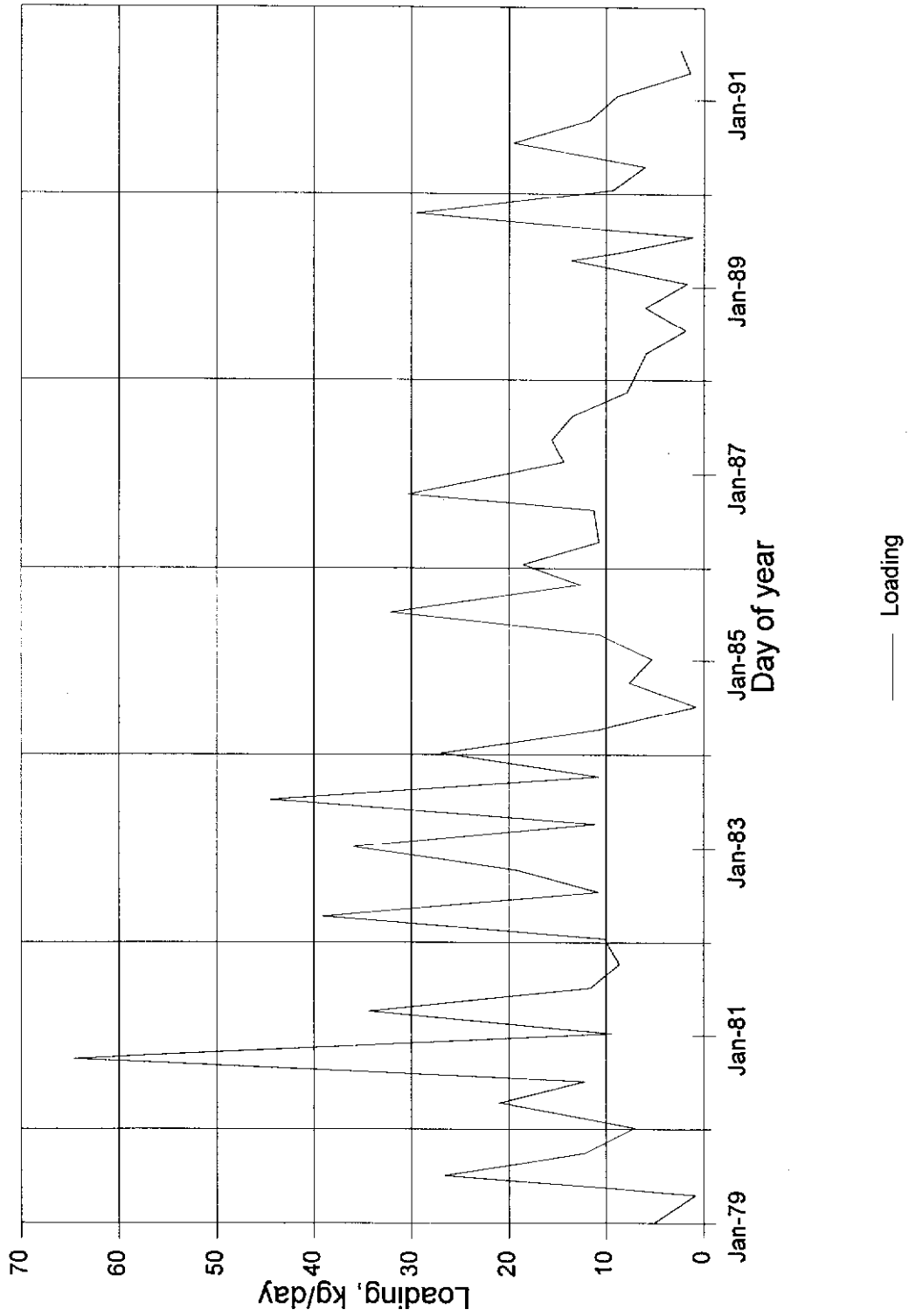
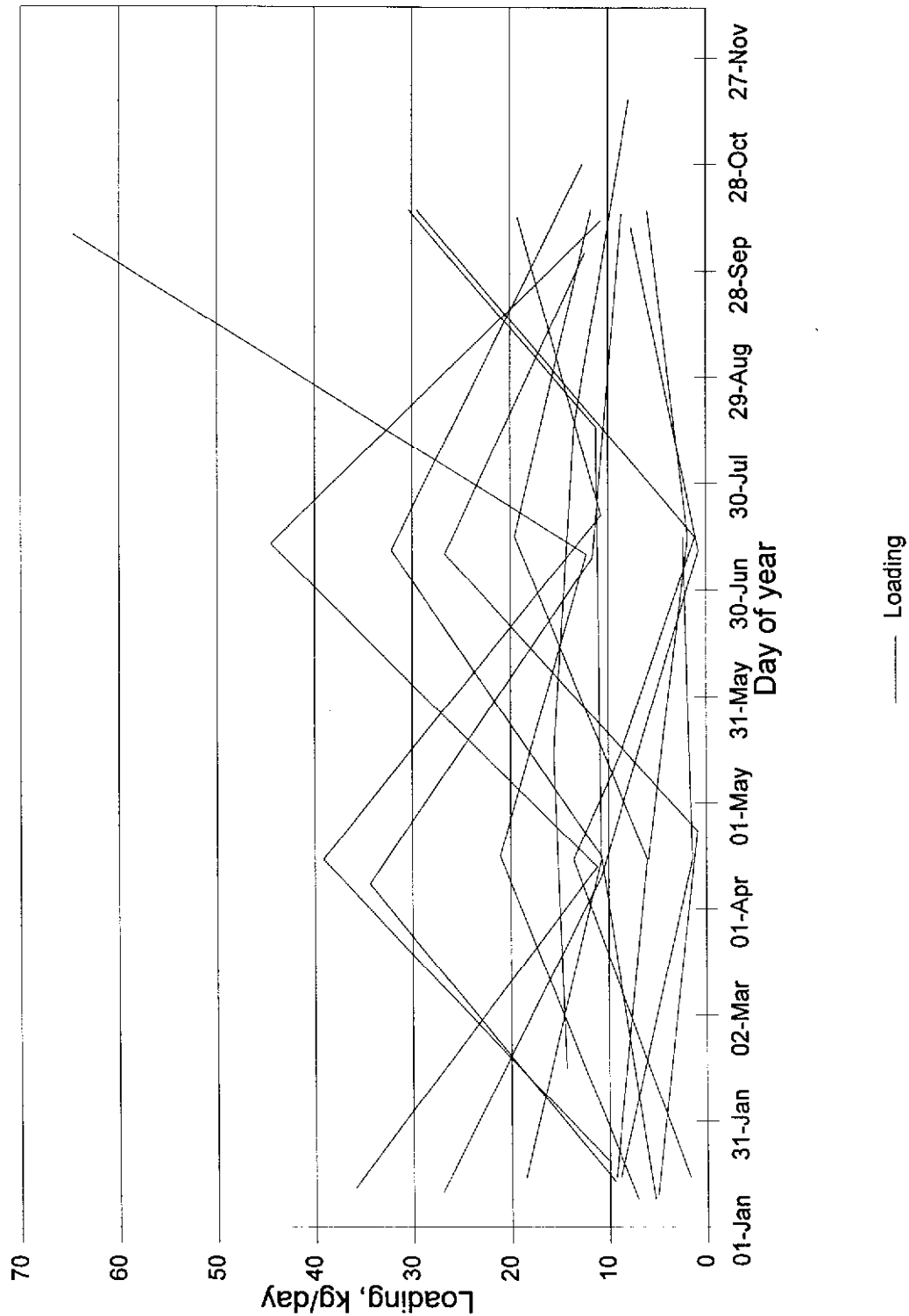


Fig. 5: Lagoon F - Historical Data
Fluoride Loading, 1979-1991



3.1 1992 Dataset

Alcan (August 7, 1992; EP 102) report to EPD

This report summarizes ALCAN Sample Numbers

17761: B Main, 1A top	(contains metal data)
17762: B Main Discharge, 1A top, suppl.	(contains metal data)
17765: Main Lagoon, 1E top, suppl.	(contains metal data)
17766: Main Lagoon, 1M top, suppl.	(contains metal data)
17773: 1 Stream inflow; 1B top	(contains metal and PAH data)
17776: L1&2 Courtyard Inflow	(contains metal data)

The data set does 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.

3.2 1995 Dataset

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)

Datasets for each of the above sampling points were received. The datasets covered two measuring periods in 1995. Period 1 covered from March 7 to August 17. Period 2 covered from September 8 to December 12. Each dataset contained data from both dissolved (passed through 45µm filter) and whole (unfiltered water). The data set was provided incomplete, but this was only discovered after the data were summarized, and thus the observations derived from the data are based only on half of the available

data. The second half of the dataset have not been included, although it was made available at a later date. The intent of the feasibility study is only to demonstrate what the possibilities are when monitoring data are interpreted. The data interpretation should be carried out including the most recent data, which are not available. The data interpretation below is given as an example of the type of information which can be derived from monitoring data.

For effluents B, NB and J, trout and *Daphnia* toxicity tests accompanied most of the sampling dates. However, these data are mostly lab-derived and pH may change between the laboratory and the field conditions, as exemplified by the measurements made by Boojum Research during the field investigation (Tables 1a and 1b). The relevance of the correct conditions in the B Lagoon with respect to pH is exemplified by the shifts of ratios of free aluminum and or the complexation capacity (Figures 1 and 2). Therefore, a toxicity test in which the pH changes, and does 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 were extracted for further analysis. Evaluating the pH ranges encountered in the monitoring data a significant range can be noted.

The pHs (the final pH in toxicity experiments were used) ranged in Effluent B from a low of 6.5 to a high of 7.7. 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 the dominant form of aluminum can be derived based on the monitoring data.

Effluent B: A comparison is made of the aluminum which passes through a 0.45 μm filter to determine the percentage of element retained on a 0.45 μm filter. This was possible for a data set collected in 1995. The percentage of elements retained by filtration is very low for all elements other than Al, Ba, Fe, and Zn. Of the elements with significant retention, only iron (82%) was very high (Table 1). Aluminum had an average 24% retention on filters in effluent B.

Effluent D: The % of element retained on 0.45 μm filter was slightly different from Effluent B. The four elements that had retention greater than 20% were Al, Fe, Mn, and Zn (Table 1). 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 filters were Ba and Fe (Table 1). Aluminum had only a 18.2% retention. Effluent MB. Those elements that had a greater than 20% retention on filters were Ba, Fe, Na, and Zn. Again, aluminum had only a 17.2% retention (Table 1).

Effluent J: Those elements that had a greater than 20% retention on filters were Al, Fe, Mn, and Zn. About 36% of the aluminum was retained on the filter paper (Table 1).

Table 1: The average concentration of "whole" element minus the "dissolved" average concentration divided by the average "whole" element concentration (x 100) .

	Effl. B	Effl. D	Effl. NB	Effl. MB	Effl. J
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	69.0	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

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, Effluents B and D do not show Na and Cl concentrations indicative of seawater influences. However, for Effluent J, it appears that seawater intrusion is possible. Na concentrations rise to 270 mg/L and conductivity rises to $1400 \mu\text{mhos} \cdot \text{cm}^{-1}$. All other effluent samples have conductivities less than $150 \mu\text{mhos} \cdot \text{cm}^{-1}$.

In order to determine whether the particle fractionation is altered with time, the same data set was examined by sampling date. This examination reveals that, on sampling date July 10, 1995, the greatest % retention (51%) occurred and that on May 10, 1995, the lowest retention, 6%, occurred (Table 2). The fact that some 6% to 51% of the aluminum is retained on the filter suggests that the pH range of the water is in that critical range where the aluminum is forming colloids, microcrystalline, and crystalline structures. Further analysis of these data suggests that, as expected from the literature review, the "WA" aluminum concentration increases with increasing pH.

This interpretation is only given as an example of the information which can be extracted on the functioning of the lagoon as a waste water treatment system. It

would be useful to carry out such analyses on the more recent and complete data set.

Table 2: Aluminum concentrations in Effluent B from the Kitimat Smelter. The pH of the water samples was between 6.0 and 6.7.

Sampling Date	Total Metal [mg L ⁻¹]	Filtered Metal [mg L ⁻¹]	% Particles > 0.45µm
5-10-95	3.95	3.72	5.8
5-30-95	0.32	0.27	15.6
6-11-95	1.67	1.27	24.0
6-22-95	0.88	0.50	43.2
7-10-95	0.41	0.2*	51.2
7-24-95	0.95	0.66	30.5
8-17-95	0.27	0.2*	25.9

* detection limit

The above summaries give some tantalizing insights into the functioning of the waste water chemistry in the B Lagoon. It would be pertinent to analyze all the available data, starting from 1979 to present. The behaviour and the function of the B Lagoon as a waste treatment system can be derived from the monitoring data.

3.3 Boojum Technology 1998 Dataset

Water samples were recently collected by M. Kalin and M. Hellenius (June 30, 1998). Measurements collected in the field are presented in Table 3a. The chemical analyses were carried out by SRC (Saskatchewan Research Council).

Table 3a: Water and Sediment Characteristics in Lagoon Systems (Kitimat)

Assayer# WA/FA		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	B Lagoon West Pond Outflow (B1)	6.94	6.02	23	21.6	133	208	800	1070	6.14	21.5	-47	50
	Floating Vegetation Pad, (VP)	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	Input Channel from J Stream, SPL Piles-A (J)	5.8	6.49		21.9		160		245	5.8		-62	200
	Input Channel from J Stream, SPL Piles-B											-82 - -103	
7175/82	Input Channel from NB stream (NB)	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							
	At Seepage on shore from waste pile(SWD1)	6.6				-8		40				-30	
7174/81	In emergent vegetation patch (VP-A)	6.4	6.29	23	21.9	4	160	30	30.9	6.3		-5 - -12	30
	In emergent vegetation patch (VP-B)					-9						-4	
	At edge of emergent sedges	5.4				6				5.73		11	70
Lagoon B-2													
	Final Outflow to Habitat (G)			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	North end shore (FN)	7.4	6.29	28.5	21.7	-9	177	40	40.5	6.58		-36	
Lagoon D													
7173/80	shore, discharge (D3)	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

Em³ Measured redox, WTW

Em⁴ Measured redox, Fisher

Cond⁵ Measured cond, YSI, uncorrected

Cond⁶ Measured cond, Orion, @ 25 C

23 assumed temperature to calculate Eh

Table 3b: 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	B1	SWD-2	SWD-2	FN	FN	D3	D3	VP-A	VP-A	NB	NB	J	J
LAGOON	B Lagoon	B Lagoon	B Lagoon	B Lagoon	F Lagoon	F Lagoon	D Lagoon	D Lagoon	B Lagoon	B Lagoon	B Lagoon	B Lagoon	B Lagoon	B Lagoon
	West Pond	West Pond	East Pond	East Pond	North	North	Outflow	Outflow	West Pond	West Pond	West Pond	West Pond	West Pond	West Pond
	Outflow	Outflow	Dump	Dump	End	End	Disch.	Disch.	Vegetat.	Vegetat.	NB Input	NB Input	J Input	J Input
			Seepage	Seepage	shore	shore	shore	shore	Patch	Patch	Channel	Channel	Channel	Channel
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
assumed temperature to calculate Eh

Eh mV

Acidity mg/L

Alkalinity mg/L

Elements mg/L

Table 4: 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	B1	SWD-2	SWD-2	FN	FN	D3	D3	VP-A	VP-A	NB	NB	J	J
LAGOON	B Lagoon	B Lagoon	B Lagoon	B Lagoon	F Lagoon	F Lagoon	D Lagoon	D Lagoon	B Lagoon	B Lagoon	B Lagoon	B Lagoon	B Lagoon	B Lagoon
	West Pond	West Pond	East Pond	East Pond	North	North	Outflow	Outflow	West Pond	West Pond	West Pond	West Pond	West Pond	West Pond
	Outflow	Outflow	Dump	Dump	End	End	Disch.	Disch.	Vegetat.	Vegetat.	NB Input	NB Input	J Input	J Input
			Seepage	Seepage	shore	shore	shore	shore	Patch	Patch	Channel	Channel	Channel	Channel
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

Temp. C

pH units

Cond. umhos/cm
assumed temperature to calculate Eh

Eh mV

Acidity mg/L

Alkalinity mg/L

Elements mg/L

[illegible]

The main objective of this sampling was to determine if Al is present in particulate or colloidal form in the lagoon system. The water samples were separated into three groups. One group was filtered ($0.8\ \mu\text{m}$ filter) and acidified with nitric acid (FA). The second group was left unfiltered but acidified (WA), and the third group was left unfiltered and un-acidified (WH). Using the WH sample, the pH, conductivity, Em, acidity and alkalinity were determined in the Boojum laboratory. The locations of these sampling locations are given in Map 1. The data for these parameters are given in Table 3b, where the field measurements are compared to those made in the laboratory.

In Table 4 the chemical analyses is summarized for all those elements which are at or below the detection limits of the analytical methodology using ICP. Table 5 presents those elements whose concentrations were greater than the detection limits.

As the monitoring data indicated that a significant fraction of Al is already 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 Al 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 6). The concentrations of Al are clearly highest from the Dump seepage and the J stream. In the open areas of the lagoon, the Al concentrations are below detection limits. Although this was a small survey of the B Lagoon, it does suggest that the seepages from the Solid Waste Dump and the J stream are likely the major contributors of Al to the B Lagoon. The particles size information indicates that large particles ($> 0.8\ \mu\text{m}$) are present in the waste water. This suggests that surfaces provided by the wetland vegetation are likely serving as adhesive surfaces for the particulate Al in the waste water.

Table 6: % Retention of aluminum on 0.8 μ m filter paper.

Description	WA	FA	WH	% > 0.8 μ m
	Al (mg/L)	Al (mg/L)	F (mg/L)	
B1 Lagoon Outflow	0.13	0.038	0.85	70.8
B2 Lagoon S. Dump Seepage	0.59	0.41	41	30.5
F Lagoon N. shore	0.13	0.03	0.22	76.9
D Lagoon Shore Discharge	0.081	0.024	0.2	70.3
B1 Lagoon Vegetation Patch	0.005*	0.038	0.32	-6.6
B1 Lagoon Input Channel NB	0.005*	0.032	0.2	-5.4
B1 Lagoon Input Channel J	0.31	0.49	32	-0.6

* detection limit

The percentage of aluminum in a 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.

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

Table 7: Molar fluoride to aluminum concentration ratios.

	WA	FA	WH	M o l a r Ratio
Description	Al(uM)	Al(uM)	F (uM)	F/Al
B1 Lagoon Outflow	4.81	1.41	44.74	31.8
B2 Lagoon S. Dump Seepage	21.85	15.19	2158	142.1
F Lagoon N. shore	4.81	1.11	11.58	10.4
D Lagoon Shore Discharge	3.00	0.89	10.53	11.8
B1 Lagoon Vegetation Patch	0.19	1.41	16.84	12.0
B1 Lagoon Input Channel NB	0.19	1.19	10.53	8.9
B1 Lagoon Input Channel J	11.48	18.15	1684	92.8

The molar ratio of aluminum to fluoride is also interesting to note. 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 dataset collected during this field trip suggests that the ratio is much higher. It is obvious 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. However, the fluoride concentrations are remaining at historical concentrations. From this brief sampling campaign, it is evident that a systematic approach to the identification of the sources of the Al to the waste water lagoon would lead to a strategy which could increase the system's performance.

3.4 PAH in the B Lagoon

Boojum Technologies received a number of ALCAN documents pertaining to the evaluation of polyaromatic hydrocarbon (PAH) content of lagoon water and sediments. These data summaries are listed below:

1. Alcan Kitimat Works Analytical 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 (Nov 06, 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), Hotsprings 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 these results. The highest concentration of HPAH were found in J stream inflow to B Lagoon (loc B). These HPAH were found only in the surface sediments and have not penetrated (to 7 ft). Station 1A (outflow) was not included in the dataset.

The next highest concentrations were found at Stn. 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 at depth (significant concentrations at depths as great as 13 ft).

Further from J stream into the lagoon, Stn. E and then G, 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. From Schematic1, where aerial photography was used to evaluate the development of the B-Lagoon physical lay-out, the PAH concentration with depth may also be related to the material which appears to have been contained with a dyke, 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 station 4F were low, the contaminants were probably entering 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 dataset (Jan 28,93) showed significant concentrations at Station B.

The data were submitted for comment on the analytical procedures, which are the foundation to all interpretation. The comments on the data are given in Appendix 6.2. It is quite clear that, working in such complex waste waters and the resulting sediments, a degradation study has to include an experienced analytical chemist. We would recommend SRC as analytical laboratory.

The complexity of determining degradation is demonstrated by the analysis of suspended solids collected from the D Lagoon. Generally, PAH compounds do not have a high volatility but they may be associated with suspended fraction in the water. The filter papers were purged and reweighed. 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 6.2.

4.0 BIOLOGICAL SYSTEMS AND THEIR INFLUENCE ON PAHs

Included in the items from ALCAN was a report by EVS (#4). 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 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 do not prevail in the B Lagoon as indicated from the low Em measurements given in Table 3a. It would therefore be very important to promote oxygenation, which could be achieved if the emulsion-like material could be degraded reasonably fast. This may well be possible microbiologically, but has 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 usable by anaerobic microbial systems. These anaerobic microbial ecosystems occur in areas where redox state is low (little to no oxygen). These low redox ecosystems usually occur deeper in the sediments. The anaerobic sediments can remineralize contaminant metals, and may further breakdown complex organic carbon structures.

The rate of PAH degradation may be influenced by nutrient addition. 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 the nutrient concentrations.

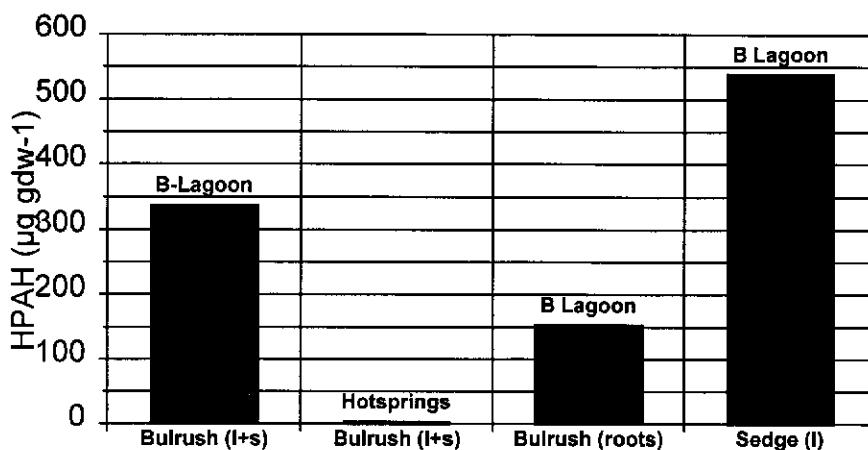


Figure 6: Total HPAH concentration in aquatic vegetation from B Lagoon and a control location at a nearby hotsprings.

The preliminary report cited above suggests that this may be the case, and there is considerable evidence from other studies that this works. 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.

PAHs can also be removed from sediments and water by adsorption and absorption by aquatic vegetation (Figure 6). Bullrush and Sedge data (item #5) 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 redox state of sediments. Cultivation of aquatic plants may enhance biofiltration, bioadsorption and bioremoval of organic and inorganic contaminants.

Item #6 is a report done for Alcan on the algal populations of the B Lagoon system. The conclusion of this report was that there was a high degree of algal diversity,

which was 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 6.3.

5.0 BRIEF SUMMARY

5.1 Aluminum

- ▶ Aluminum chemistry is complex. Free aluminum ion is found in abundance only in waters with pHs below about 4.5. Above, this pH, if fluoride is present in high concentrations, it will complex with Al between pH 4.5 and 7. If fluoride is not present in great concentrations, hydroxide will complex with Al in the pH region above pH 4.
- ▶ AlF complexes are stable, but soluble
- ▶ Al-OH complexes in the pH region between 6 and 7 are stable, and will equilibrate towards colloids, amorphous aluminum and Gibbsite.
- ▶ The longer the Al-OH complexes are allowed to sit, the more orderly becomes there structure, and the larger the particle size of the precipitates.
- ▶ Al also forms stable complexes with fulvic acid and other natural organic molecules (NOM)
- ▶ Outside of smelters, aluminum is usually found in stable silicate minerals. When acid water runs over aluminum silicates, the silicate-minerals are dissolved, releasing the aluminum.
- ▶ Plants (algae and higher plants) can filter out colloidal aluminum, adsorb free aluminum onto plant surfaces, take up high concentrations of aluminum, and generally remove aluminum from surface waters, interstitial waters, and sediments.
- ▶ The primary toxicity of aluminum comes from its competition with phosphorus in the metabolism of plants and animals. Organic phosphates such as ATP are rendered useless if aluminum substitutes for the phosphorus. Excess phosphate over aluminum can overcome some of the toxicity of aluminum.
- ▶ Complexing of aluminum with organic acids and fluoride will reduce toxicity, because aluminum is no longer free to interfere with organic phosphates.

- ▶ Fluoride was found in significant concentrations in sediment/soil, although its form was not determined. High concentrations were found at Station B, but were about 80% lower at station 1A.

5.2 PAH

- ▶ The PAH data received are only for sediments and are 5 years old. Is this a current problem? Does the water contain PAHs? Is the "slick" observed during the June, 1998 site visit on B Lagoon composed of PAHs or just the Magnus Cal-92, Canola Oil LV134, and or the Klubertec C1-101? These 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 appears that the lagoons are being rapidly silted in. With a retention time of about 1 day, the lagoon is not performing optimally. Good retention times for a working lagoon are on the order of weeks. By increasing the size or depth of the lagoon, or decreasing the flow of water through it, the lagoon may be made more efficient. Dredging sediments with high PAH concentrations may not be beneficial. However, as noted above, degradation of PAHs occurs best under aerobic conditions. Thus, removing sediments to another location where degradation can be allowed to proceed at a faster rate may actually enhance clean-up.

6.0 RECOMMENDATIONS

Information regarding the removal of aluminum, based on the literature review, indicates that considerable control can be brought to increasing the B Lagoon performance using biological polishing and targeted control on point sources of the aluminum input to the B Lagoon system.

We have described seven different kinds of effluents emanating from the Alcan plant. Five of the seven effluents pass through the B Lagoon. Chemical quantification of sources of Al and loads, through determination of flows, would be very usefull. This could lead to measures to 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 the reducing conditions of the lagoon system, due to the emulsion and oily discharges, is restricted to the F Lagoon. This can be acheived through evalution 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/ has to be degraded in order to increase the retention time of the B Lagoon system.

7.0 BIBLIOGRAPHY

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8.0 APPENDICES

8.1 Appendix A: SRC Analysis of PAH Compounds

8.2 Appendix B: Phytoplankton Data

8.3 Appendix C: F Lagoon F Concentrations, Flows, Loads



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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 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 CO₂.

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

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FROM: Wo Yuen

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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.

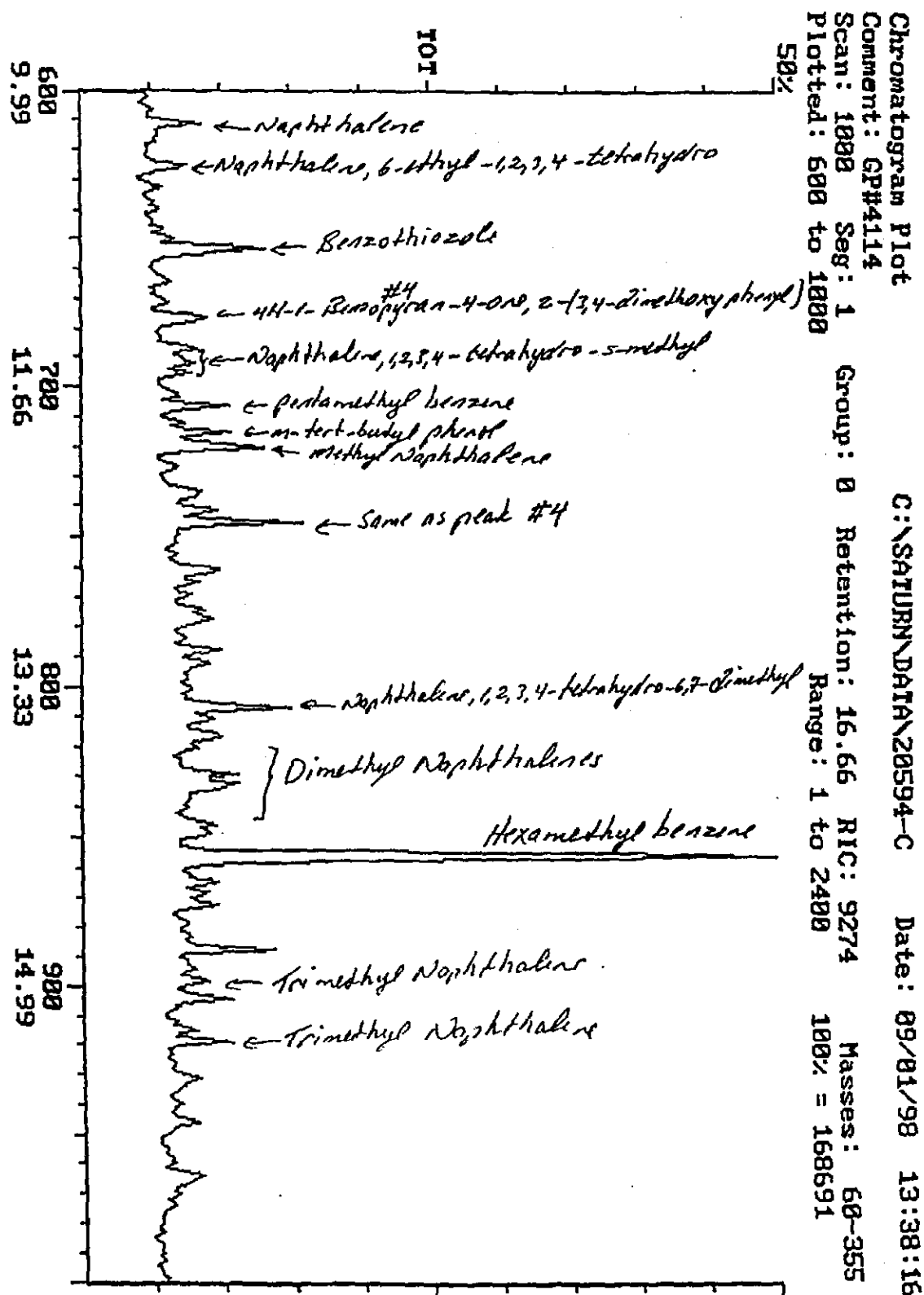
The sample that was used for analysis was SRC #20594 (Client ID 7335). The concentration of naphthalene was found to be 16 ug/g based on the dry weight. The concentration of the naphthalene derivatives total 703 ug/g (using naphthalene response factor).

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.

BOOJUM		Group 98-4114		
Lab Sample	Client ID	Solids Weight	Solids Weight	Weight Loss
		(as received)	(after purging)	(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

TSS →



8.2 Appendix B: Phytoplankton Data

Results of Sample Examination - Algatax Consulting

PROJECT: Alcan Mine Site, 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) *
Temnogametum 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 Mine Site, 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 Mine Site, 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.

Eumotia spp.

Frustulia saxonica

Nitzschia spp.

Pinnularia spp.

Stauroneis sp.

Surirella sp.

Tabellaria flocculosa

Results of Sample Examination - Algatax Consulting

PROJECT: Alcan Mine Site, British Columbia

Sample Code: A98-09

Alcan - Outflow (30/06/98) Duplicate B-Discharge H.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.

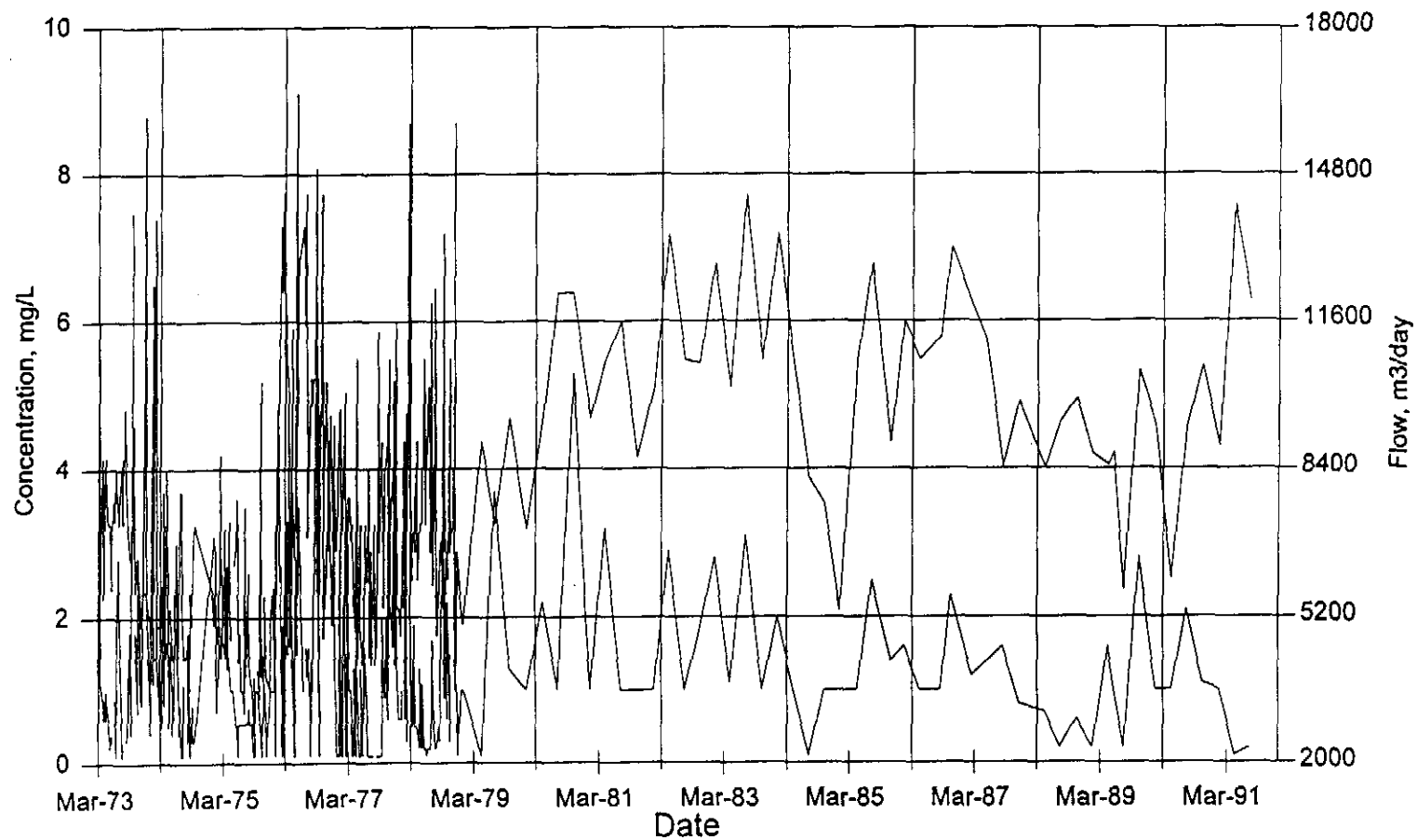
Surirella sp.

Tabellaria floccuolosa

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

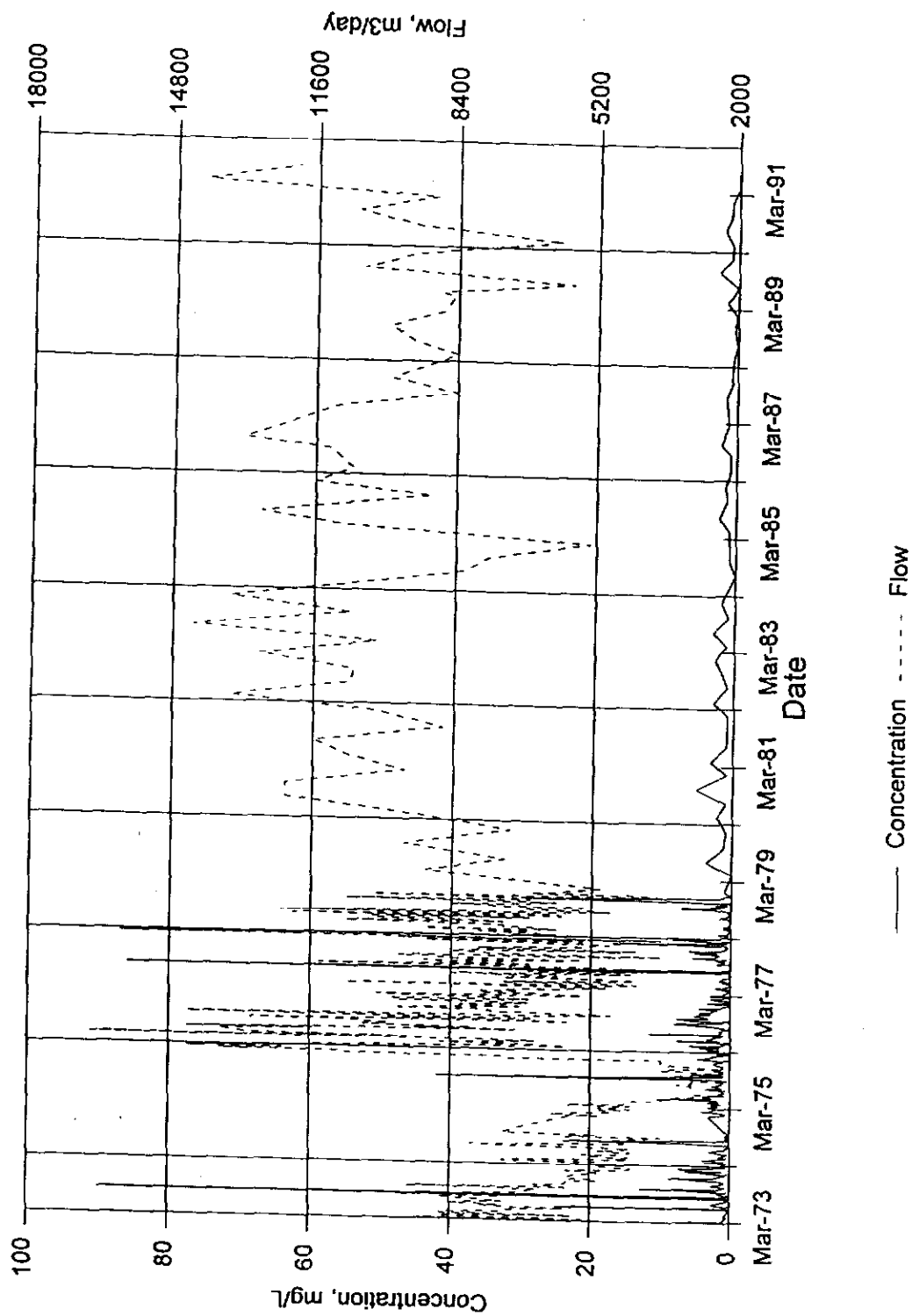
8.3 Appendix C: F Lagoon F Concentrations, Flows, Loads

App-Fig. 1: Lagoon F - Historical data
Flow & [F], 1980-1991

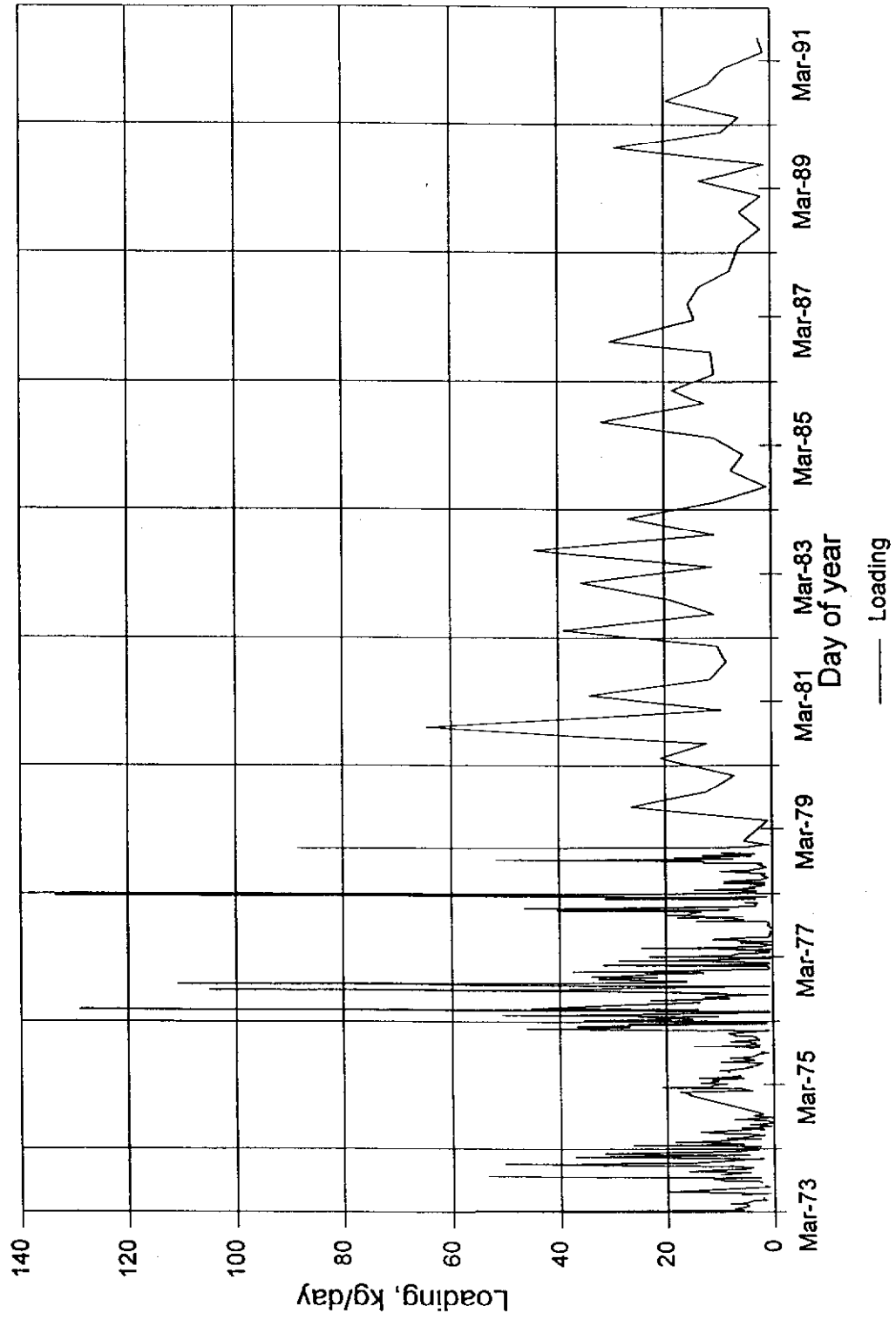


— Concentration — Flow

App-Fig. 2: Lagoon F - Historical Data
Flow & [F], 1980-1991



App-Fig. 3: Lagoon F - Historical data
Fluoride Loading, 1980-1991



App-Fig. 4: Lagoon F-Historical Data
Fluoride Loading, 1980-1991

