CHEMISTRY, TRANSPORT AND FATE OF
ALUMINUM IN DILUTE ACIDIFIED LAKE
SYSTEMS

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Aluminum in Dilute Acidified Lake Systems

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Abstract

Elevated levels of aluminum have been observed in acidic surface waters. Aluminum is of interest because of its role as a toxicant to aquatic organisms, a pH buffer, and an adsorbent of orthophosphate and organic carbon. In this study we evaluated the spatial and temporal fluctuations in aluminum chemistry and aluminum transport in an acidic drainage lake.

Elevated levels of nitrate, hydrogen ion and aluminum were largely introduced during snowmelt by drainage water to Dart Lake. During low flow periods, microbially mediated depletions of nitrate served to neutralize hydrogen ion and aluminum base neutralizing capacity. Thus, nitrate transformations were extremely important in regulating short-term changes in pH and inorganic forms of aluminum in Dart Lake. These transformations resulted in changes in the inorganic speciation of aluminum. During low pH conditions associated with snowmelt, Al^{3+} was the major form of inorganic aluminum. However, during higher pH conditions, observed in the summer, fluoride and hydroxide forms of aluminum predominated.

Although concentrations of organically complexed aluminum were high in Dart Lake, we know very little about the character and transformations of these solutes. Organically complexed aluminum was correlated to the dissolved organic carbon concentration. Alumino-organic solutes were introduced to the lake from both drainage inputs and sediments. Moreover these materials do not appear to be conservative within acidic lake systems.

On an annual basis Dart Lake was a net aluminum sink. However, the magnitude of various aluminum fluxes exhibited significant temporal variation. During spring snowmelt Dart Lake was highly undersaturated with respect to readily forming mineral phases and aluminum had a relatively low affinity for particulate matter. Consequently aluminum was conservative; aluminum that entered the lake was essentially transported out the outlet. During stratification, waters were supersaturated with respect to readily forming mineral phases, aluminum demonstrated a relatively high affinity for particles, and was generally non-conservative. Within the lake, aqueous aluminum was converted to particulate aluminum and these substances were deposited to lake sediments. The non-conservative nature of aluminum would appear to have significant implications for aquatic organisms.

Introduction

Atmospheric deposition of acidic substances appears to influence bio-geochemical cycling in ecosystems with soils derived from difficult to weather minerals (Braekke, 1976; Hutchinson and Havas, 1980). For example, Cronan and Schofield (1979) have hypothesized that acidic deposition alters the process of podzol development. Rather than being retained in soils, aluminum is solubilized by mineral acid inputs and transported to the aquatic environment.

Elevated levels of aqueous aluminum are significant for aquatic ecosystems in several respects:

1. Aluminum may be deleterious to fish (Baker and Schofield, 1982) and other aquatic organisms (Hall et al., 1984) in low ionic strength waters. Aluminum forms soluble complexes with hydroxide, fluoride, sulfate and organic ligands (Roberson and Hem, 1969; Lind and Hem 1975). Hydroxy-aluminum monomers appear to be particularly important to fish toxicity (Baker and Schofield, 1982). Because pH, natural organic and inorganic (e.g. F^-) ligands significantly influence aluminum speciation, they also influence hydroxy-aluminum toxicity (Driscoll et al., 1980; Baker and Schofield, 1982).

2. Aluminum is a hydrolyzing metal and therefore elevated concentrations influence the pH buffering of acidic waters (Dickson, 1978; Johannesson, 1980; Henriksen and Seip, 1980; Driscoll and Bisogni, 1984).

3. Hydrous aluminum oxides, formed by the hydrolysis and precipitation of aluminum, may serve as an adsorbent and scavenge substances from the water column. By this mechanism aluminum may alter the cycling of sorbable solutes such as orthophosphate (Dickson, 1978), trace metals (Hohl and Stumm, 1976) and dissolved organic carbon (Dickson, 1978; Davis, 1982) in acidic lake ecosystems.

Considerable information is available through synoptic surveys on total aluminum levels in acidic surface waters (Schofield, 1976; Hutchinson et al., 1978; Dickson, 1978; Wright and Snekvik, 1978; Vangenechten and Vanderborght, 1980; Hultberg and Johansson, 1981). Much less information is available on the speciation of aluminum in surface waters. Reported here are results from a study on the chemistry and transport of aluminum in an acidic drainage lake in the Adirondack region of New York State.

Materials and Methods

Study Site and Field Program

The study site, Dart Lake (43°47'N, 74°51'W), is located in the drainage basin that forms the North Branch of the Moose River in the Adirondack State Park, New York State. The watershed, which occupies 107 Km^2, is forested except in regions of exposed bedrock. The major vegetation is secondary-growth hardwoods including American beech (Fagus grandifolia), yellow birch (Betula alleghaniensis), sugar maple (Acer saccharum) and red maple (Acer rubrum). Bedrock geology is characteristically crystalline granitic gneiss (Isachsen and Fisher, 1970) which is generally resistant to chemical weathering.

Dart Lake has a surface area of 0.144 Km^2, a major inlet and a single outlet (Figure 1). The lake bathymetry is characterized by two significant depressions both reaching a maximum depth of 15 m. The mean depth of Dart Lake is 7.1 m.

The quantity of precipitation entering the watershed was measured daily and incident radiation was monitored continuously (29 April - 21 Nov '82) adjacent to the lake. To monitor discharge, staff gages were installed at the inlet and outlet, and stream height was measured on sampling dates. Stream velocity was measured, flows were calculated on 9 dates and a stage-discharge relationship was developed. To provide an estimate of the water flux through

Dart Lake, correlations between our instantaneous discharge measurements/calculations and that of the continuous discharge recorded at the nearby Independence River site (at Donnatsberg) and a site on the Hudson River (Newcomb) were used. Correlations of flow per watershed area were similar to either one or both continuous discharge sites throughout the study period and thus the estimated continuous flow for Dart Lake is believed to be representative of actual flow conditions.

In our study, samples were collected for water quality analysis approximately every two weeks at the inlet, outlet and from seven depths at a pelagic sampling station. Water column samples were collected with a battery-operated submersible pump. Temperature and light were measured in-situ with a thermister and light meter, respectively. We measured pH and dissolved inorganic carbon (DIC), fixed samples for dissolved oxygen (DO), ampulated samples for dissolved organic carbon (DOC) determination and extracted samples for mononuclear aluminum, shortly after collection.

While it is reasonably well established that pH, DIC, D.O. and DOC are prone to change, we feel it is important to emphasize that mononuclear aluminum concentrations may also fluctuate during sample storage. Natural solutions are generally supersaturated with respect to atmospheric CO_2. Carbon dioxide exolution will cause an increase in solution pH and a decrease in mononuclear aluminum levels. To illustrate the extent to which this might occur we made some hypothetical thermodynamic calculations (see the computative methods section of this report) using data of a sample collected from the hypolimnion of Dart Lake (Figure 2). In situ, this sample was highly supersaturated with respect to atmospheric CO_2 (log pCO_2 = 2.25). As we simulated the exolution of CO_2 by reducing pCO_2 to

atmospheric levels, pH values increased and inorganic aluminum concentration decreased (Figure 2a). Aluminum transformations are very temperature sensitive. We also simulated the change in aluminum concentration as the temperature of the hypolimnitic Dart Lake sample increase from the in-lake value (5.5°C) to typical laboratory conditions (up to 25°C; Figure 2b). It is apparent that changes associated with sample storage can dramatically affect aluminum levels. Therefore we extracted samples for mononuclear aluminum as shortly after collection as possible.

To monitor the gross flux of particulate material from the water column, we placed triplicate sediment traps (aspect ratio of 11.7; Bloesch and Burns, 1980) adjacent to our water column sampling site at depths of 6 and 14 m. Sediment trap samples were collected approximately every two weeks. As part of another research project, six sediment cores were obtained from Dart Lake with a 5-cm diameter gravity coring device. Sediments were sectioned on site and placed in water-tight bags for storage. (Because results of the sediment study supplement the results of this research they will be discussed in this report. For further details on the sediment investigation see White (1984)).

Analytical Methods

Water samples were measured for pH potentiometrically by glass electrode. Dissolved oxygen was measured on field-fixed samples by Winkler titration (Standard Methods, 1980). Free fluoride was determined by direct measurement with a fluoride ion selective electrode, while total fluoride was analyzed by using a total ionic strength adjustor and buffer (TISAB II: Orion, 1976). Dissolved inorganic carbon was analyzed by sample acidification and extraction of CO_2 into helium (Stainton, 1973). Dissolved organic carbon was measured using persulfate oxidation (Menzel and Vaccaro, 1964) followed by syringe stripping of CO_2 (Stainton, 1973).

A gas partitioner was used to detect CO_2 for both DIC and DOC determinations.
Basic cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) were measured by atomic absorption spectro-
photometry (AAS). Sulfate, nitrate, chloride and dissolved silica were measured
colorimetrically using the methylthymol blue (Lazrus et al., 1968), hydrazine
reduction (Kamphke et al., 1967), thiocyanate (Zall et al., 1956) and the
heteropoly blue (Standard Methods, 1980) methods, respectively, on an autoanalyzer.
The colorimetric analyses of sulfate, nitrate and dissolved silica are prone to
interference by organic solutes. However, DOC levels in Dart Lake were low,
and little background color was observed when checked by the colorimeter.
Moreover, we compared the colorimetric procedures for anion analysis with
ion chromatography, which does not have an organic carbon interference, and
observed no statistically significant difference between measured values on
Dart Lake samples.

In our study, three separate measurements of aluminum were made. 1) Total
aluminum (TAl) was determined by acidifying samples to a pH value of 1 for 1 hour,
chelating aluminum with 8-hydroxyquinoline and extracting the complex in methyl
isobutyl ketone (MIBK), using the procedure of Barnes (1976). Detection of
aluminum was made by AAS using graphite furnace atomization. 2) Monomeric alumi-
num (MAl) was directly chelated by 8-hydroxyquinoline, followed by rapid extrac-
tion in MIBK (Barnes, 1976) in the field. These extracts were analyzed in the
laboratory by AAS with graphite furnace. 3) Monomeric aluminum was separated into
two fractions using a column of strongly acidic cation exchange resin. We term
the aluminum that passes through the column and is detected using the procedure
for mononuclear aluminum, non-labile monomeric aluminum.

With these three measurements, three separate aluminum fractions were determined. 1) Non-labile monomeric aluminum was measured directly and is an estimate of mononuclear aluminum that is organically complexed (OMA1). 2) Labile monomeric aluminum is the difference between MA1 and OMA1. This fraction is thought to be an estimate of inorganic monomeric aluminum (IMA1) and would include aquo aluminum as well as hydroxide, fluoride and sulfate complexes of mononuclear aluminum. 3) Acid soluble aluminum (ASA1) is the difference between TA1 and MA1. This fraction represents aluminum which requires acid dissolution for detection and would include relatively easy to dissolve particulate aluminum and strongly bound alumino-organic substances. Further details on the fractionation procedure used for the determination of aqueous aluminum are available elsewhere (Driscoll, 1984; Appendix 1).

Selected samples, collected from drainage waters of the North Branch of the Moose River, were processed using the cation exchange column to remove any IMA1 and titrated to characterize the proton dissociation of organic solutes. These data were fit to a monoprotic proton dissociation model using a modified Gran plot analysis (Driscoll and Bisogni, 1984). A statistically significant empirical relationship was observed between DOC concentration and mols of proton dissociation sites per liter (C_T = 0.025 DOC + 8.0; where C_T is the proton dissociation sites on organic solutes in $\mu mol \cdot l^{-1}$ and DOC is in $\mu mol \cdot l^{-1}$; n = 13, r^2 = 0.69 p < 0.01). A relatively consistent fit to a proton dissociation constant was also obtained (pKa = 4.53 ± 0.25). Our detailed observations of DOC were applied to this model to estimate the base neutralizing capacity (BNC) of organic solutes and organic anion concentration of water samples.

Sediment trap samples were measured for total, volatile and fixed suspended solids using the gravimetric procedure outlined in Standard Methods (1980). Also the quantity of particulate aluminum deposited in sediment traps was measured by a brief acid (pH = 1 for 1 hr) extraction followed by direct determination of aluminum by AAS with graphite furnace.

Sediment samples were measured for total solids content (Standard Methods, 1980). In addition wet sediments were extracted sequentially for "exchangeable aluminum", "oxide-bound aluminum", "organic-bound aluminum" and residual aluminum using the procedure of Tessier et al. (1979). Note that while these fractions are operationally defined, they do provide some information on the form of particulate aluminum.

Computational Methods

Thermodynamic calculations used in this study were made with a modified version of the chemical equilibrium model MINEQL (Westall et al., 1976). Thermochemical data of aluminum equilibria used in our calculations are summarized elsewhere (Johnson et al., 1981; Driscoll, 1984). Thermodynamic calculations were corrected for temperature. Ionic strength corrections were made using the Davies equation (Stumm and Morgan, 1981).

To evaluate the distribution of IMAl we calculated aquo aluminum (Al^{3+}), hydroxide bound aluminum (Al-OH), fluoride bound aluminum (Al-F), sulfate bound aluminum (Al-SO$_4$) concentrations and aluminum base neutralizing capacity (Al-BNC) (Table 1). We define hydrogen ion and aluminum base neutralizing capacity (H-Al-BNC) as the amount of strong base required to increase the pH of a liter of aluminum solution to 8.3.

We computed mineral saturation indices (SI) for Dart Lake solutions, to
assess the potential for equilibrium with mineral phases

$$SI = \log IAP / K$$

where: SI is the saturation index for the mineral phase of interest,

IAP is the ion activity product of the solution, and

K is the thermodynamic solubility constant for the mineral
phase of interest.

Positive, negative, and zero SI values suggest that a solution is oversaturated,
undersaturated or in equilibrium, respectively, with the mineral phase of interest.
While it is possible to use any number of minerals for this analysis, past re-
search by Johnson et al. (1981) and Driscoll et al. (1984) suggest that solution
IAP values closely follow aluminum trihydroxide $(Al(OH)_3)$ solubility. Therefore,
we have chosen to use the relatively soluble phase microcrystalline gibbsite
$(p^*Kso = 9.35$; Hem and Roberson, 1967) as a reference mineral in our SI cal-
culations.

A number of pool and flux calculations were made in this study including
(1) the flux of solutes entering and leaving Dart Lake, 2) water column pools
of solutes, 3) sediment pools of metals, 4) gross deposition of particulate
substances, 5) aqueous-particulate distribution coefficients of metals (Kd),
6) upward transport of solutes, 7) net deposition of substances based on
material balance calculations and 8) net deposition of substances based on
sediment composition and sedimentation rate. Details on how these calculations
are made are beyond the scope on this report but are summarized elsewhere
(Schafran, 1984; White 1984).

Results

Aluminum Chemistry of Dart Lake

Dart Lake solutions may be characterized as acidic, low ionic strength waters in which Ca^{2+} is the dominant cation while SO_4^{2-} is the dominant anion (Table 2). We obtained a relatively close electroneutrality balance, which provides some independent confirmation of the procedures and assumptions used in the study. A discussion of the general water chemistry of Dart Lake is beyond the scope of this report but is available elsewhere (Schafran and Driscoll, 1984).

Although H_2CO_3 was the major component of BNC, levels of hydrogen and aluminum BNC (H-Al-BNC) are generally of more interest in acidic lakes because of their ecological significance (Baker and Schofield, 1982; Hall et al., 1984). Variations in H-Al-BNC were strongly correlated with variations in NO_3^- concentration (H-Al-BNC = 0.94 NO_3^- + 2.4; $\mu eq \cdot l^{-1}$, $r^2 = 0.54$, $p < 0.0001$). Note that this empirical correlation is linear with a slope close to one and an intercept near the origin. H-Al-BNC was positively correlated with organic anion concentrations (H-Al-BNC = 33.1 ($RCOO^-$) - 481.5; where $RCOO^-$ represents the organic anion concentration in $\mu eq \cdot l^{-1}$, $r^2 = 0.13$, $p < 0.0001$) and no statistically significant relationship was observed with SO_4^{2-} or Cl^-.

It is well known that processes which produce NO_3^- such as deprotonation of HNO_3, algal respiration, and nitrification result in proton release while reactions in which nitrate is depleted such as denitrification or algal assimilation of nitrate result in proton neutralization (Table 3). Water quality observations in Dart Lake indicate that biogeochemical processes result in temporal and spatial variations in NO_3^- which in turn influence pH and IMAl concentrations (Figures 3a, 3b, 3c). During the autumn, NO_3^-, pH and IMAl

exhibited an orthograde distribution. After ice-development, NO_3^- and

IMA1 levels increased and pH values decreased in the upper waters, presumably

due to freeze-concentration at the ice-water interface or minor snowmelts.

Concentrations of NO_3^- and IMA1 decreased while pH values increased with

increasing lake depth. Although the lake was aerobic throughout the study

period (D.O. > 41 $\mu mol \cdot l^{-1}$; minimum value observed, 14 m on 10/1/82),we

attribute these transformations to sediment reduction of NO_3^-. During snow-

melt, large inputs of acidic water elevated in NO_3^- were introduced to Dart

Lake. Inlet concentrations of H-Al-BNC and NO_3^- were significantly greater

during snowmelt (4/1-5/1/1982, 8.9 ± 6.9 $m^3 \cdot s^{-1}$, H-Al-BNC = 52 ± 11, NO_3^- =

51 ± 11) than during either summer-autumn (6/15-11/1, 1.7 ± 1.7 $m^3 \cdot s^{-1}$,

H-Al-BNC = 18 ± 5; p < 0.05 student t test, NO_3^- = 24 ± 5, p < 0.05) or

winter (11/1-3/1, 1.5 ± 1.0 $m^3 \cdot s^{-1}$, H-Al-BNC = 23 ± 6, p < 0.05, NO_3^- =

26 ± 6, p < 0.1) base flow periods (Figure 4). Johannes et al. (1980)

reported that NO_3^- storage in snowpack from the Adirondack region was generally

greater than SO_4^{2-}. Likewise, Galloway et al. (1980) have attributed the de-

crease in alkalinity that occurs in Adirondack lake outlets during snowmelt

to a reduction in the release of basic cations from soil and the addition of

HNO_3 from snowpack. Our observations would appear to be consistent with these

studies. Unlike NO_3^-, there were no statistically significant differences between

the concentrations of SO_4^{2-}, Cl^- (not shown) and organic anions during snowmelt

and during base flow periods (Figure 4).

During summer stratification pH increased, and NO_3^- and IMA1 were depleted

in the upper and lower waters of Dart Lake, resulting in heterograde distributions.

We attribute the epilimnitic NO_3^- depletion to algal assimilation or denitrifi-

cation in the littoral sediments and the hypolimnetic depletion to sediment deni-

trification. Note that in the extreme lower waters (below 12m) during strati-

fication, transformations of Fe, Mn, NH_4^+, DOC and Ca^{2+} also contributed to the

changes in H-Al-BNC. However, because this region represents a relatively small percentage of the total lake volume ($\sim$ 5%), NO_3^- depletions appear to be the most significant mechanism of H-Al-BNC neutralization on a whole-lake basis. For further details on the role of nitrate in regulating BNC see Driscoll and Schafran (1984; Appendix 2).

Like other studies of acidic surface waters (Johnson et al., 1981; Driscoll et al. 1984, we observed that the inorganic aluminum chemistry was rather well described by $Al(OH)_3$ solubility. The IAP of Dart Lake solutions was generally similar to the theoretical solubility of microcrystalline gibbsite (SI = 0.17 ± 0.28). Johnson et al. (1981) and Driscoll et al. (1984) reported that HBEF and Adirondack waters were somewhat undersaturated with respect to the solubility of microcrystalline gibbsite (SI = -0.69 ± 0.36 and -0.85 ± 0.45, respectively). The higher SI values for Dart Lake may be due to real differences in solution composition or the fact that we extracted our samples for monomeric aluminum in the field.

While the removal of aluminum was nearly stoichiometric with depletions of NO_3^- and IAP values were well described by microcrystalline gibbsite solubility, there were well defined patterns of disequilibrium in Dart Lake (Figure 5). During snowmelt, the inlet and outlet streams and the entire water column were highly undersaturated (negative SI values). The short retention time of water in the soil and relatively slow rates of mineral dissolution undoubtedly contributed to these low SI values. Moreover, conditions of high supersaturation, in the hypolimnion during winter and summer stratification and the epilimnion during summer stratification, coincided with periods of NO_3^- depletion. The removal of aluminum during NO_3^- depletions indicate that heterogeneous phase transformations of aluminum proceed at relatively slow rates.

In Dart Lake IMAl was distributed among a number of inorganic forms. Mean values of the concentrations of various aluminum forms as well as the relative distribution as total and monomeric aluminum are summarized in Table 4. Fluoride and organic complexes were the predominant forms of aluminum. Al^{3+} and Al-OH were present at lower but significant levels, while Al-SO_4 was insignificant. The concentrations and relative distribution of aluminum in Dart Lake were similar to those values reported by Johnson et al. (1981) for the HBEF and by Driscoll et al. (1984) for Adirondack surface waters.

As one would expect, the distribution of IMAl changed markedly with variations in pH (Figure 6). At low pH values, Al^{3+} was the predominant form of IMAl, but concentrations declined at higher pH values. Levels of Al-F were also highest at low pH values and the magnitude of the complex under these conditions was regulated by the level of total fluoride in solution. Concentrations of Al-F also decreased with increasing pH. Al-OH values were low at acidic pH values, increased to a maximum value approximately at pH 5.1 and decreased at higher pH values. The pH dependence of Al-F and Al-OH is less pronounced than Al^{3+}. Thus at higher pH values (pH $>$ 5.1) Al-F and to a lesser extent Al-OH predominated IMAl. Concentrations of Al-SO_4 also generally decreased with increasing pH.

In Dart Lake a substantial portion of mononuclear aluminum appeared to be complexed with organic ligands. We observed a weak but statistically significant empirical relationship between OMAl and DOC (OMAl = 0.018 DOC + 1.84; in $\mu mol \cdot l^{-1}$, r^2 = 0.14, p < 0.0001). Similar empirical relationships have been reported by Driscoll et al. (1984) for Adirondack lakes and streams and by Driscoll (1984) for HBEF streams. The correlation between OMAl and DOC was considerably weaker for Dart Lake than these other systems and may be attributed in part to the

limited range of DOC (220 - 420 $\mu mol \cdot l^{-1}$). Also DOC is a relatively coarse parameter because it encompasses a great variety of organic solutes which vary greatly in their capacity to complex aluminum.

DOC levels were relatively constant in the inlet and outlet streams while OMAl levels were more variable (Figure 4). Concentrations of both parameters increased slightly from autumn through the winter season. After snowmelt DOC and OMAl concentrations declined through the summer until September and increased again in autumn. An exception to these relatively smooth trends occurred during a major rainfall event (6.1 cm on 2 June 1982). pH decreased, and IMAl and DOC (and organic anion) concentrations increased in the inlet stream in response to the storm, while no increase was observed for SO_4^{2-}, NO_3^- or Cl^- (Figure 4). Therefore we presume that organic anions were associated with this increase in H-Al-BNC. OMAl levels in the inlet stream also increased in response to the rainfall event.

Within Dart Lake there were spatial and temporal trends in DOC and OMAl (Figure 7a, b). Elevated concentrations of DOC and OMAl were introduced to Dart Lake during snowmelt. After spring turnover both DOC and OMAl were substantially depleted from the epilimnitic waters. Low DOC water migrated with the thermocline to increasing lake depths during the summer season. In the hypolimnion, DOC and particularly OMAl concentrations increased dramatically during summer stratification. By September considerable OMAl was introduced to the epilimnion probably through a combination of entrainment of hypolimntic OMAl and increased concentrations in the inlet stream (Figure 4). OMAl was rapidly depleted form the epilimnion after this event.

The aluminum content of the surficial sediments in Dart Lake was high and generally declined with increasing depth (Figure 8). Sediment aluminum was largely in an oxide bound form and to a lesser extent an organic bound form. The content of residual aluminum was smaller but present in significant quantities and the exchangeable aluminum content of Dart Lake sediments was low. The oxide bound and exchangeable aluminum content of sediments increased with increasing depth while the organic bound aluminum content was highest at the water-sediment interface, declined to a minimum at a 5 cm depth and gradually increased with greater sediment depth.

Studies of the aluminum content of acidic lake sediments have produced inconsistent conclusions. Some investigators report, as observed in Dart Lake, increased aluminum levels in the upper strata (Dickson, 1980; Heit et al., 1981). Other researchers have reported aluminum depletions in the upper sediments (Norton and Hess, 1980), while still others report no change in aluminum content with depth (Galloway and Likens, 1980; Heit et al., 1981). The aluminum content and depth trends that Heit et al. (1981) report for nearby Woods Lake are nearly identical to our results for Dart Lake.

It is difficult to extrapolate sediment chemistry to in-lake processes. Moreover, the sediment aluminum fractions are operationally defined and there may be some overlap associated with the various extractions. Nevertheless, the sediment distribution between organic and inorganic forms of aluminum was very similar to our water column observations (Table 3). The rather significant amounts of both oxide and organic bound aluminum provide evidence that IMAl and OMAl are deposited from the water column. The systematic decline in organic bound aluminum with recent sediment depth (< 5 cm) might be attributed to microbial oxidation. A by-product of the oxidation of organic bound aluminum

would then presumably be oxide bound or residual aluminum. However, this process is counter to our observed decline in oxide bound aluminum with increasing sediment depth. It is more likely that deposition of OMAl to the sediments has increased in recent years or that organic bound aluminum is ₁solubilized in the sediment, diffuses into the water column, is converted to a particulate phase and redeposited to the surface sediments. This latter process would be consistent with our water column observations.

Aluminum Transport and Cycling in Dart Lake

We have computed input/output budgets for various forms of aluminum, NO_3^-, SO_4^{2-}, DOC and Cl^- for Dart Lake (Table 4). It would seem that the lake was a net nitrate sink, which resulted in BNC neutralization and net retention of IMAl. Moreover, on an annual basis Dart Lake retained OMAl, was conservative with respect to Cl^-, ASAl and SO_4^{2-} and was a net source of DOC. While these calculations are useful excercises they provide limited information on processes that are important to aluminum cycling.

We have formulated a conceptual model of reactive aluminum cycling within an acidic lake (Figure 9). Reactive aluminum is considered to be aluminum that readily moves between aqueous and particulate phases; this designation would not include highly crystalline substances. Within the lake there are various aqueous pools (IMAl, OMAl, ASAl) and sediment pools (exchangeable Al, oxide bound Al, organic bound Al and residual Al) that have been previously discussed. Inputs of aluminum to the lake include direct atmospheric deposition, seepage, and drainage flux. Within the lake particulate aluminum may be, deposited to the sediments (gross deposition), solubilized in sediments and diffuse upward into the water column (gross upward flux) or may be transported from the lake with seepage or drainage water.

Using the format of this conceptual model we have estimated the average annual pools and fluxes of aluminum for Dart Lake (Figure 10). Unfortunately we do not have estimates of seepage flux to and from the lake. Neglecting seepage, stream inputs and export would appear to quantitatively be the most important flux of all forms of aluminum in Dart Lake. The aluminum content in bulk atmospheric deposition is low (Johannes, 1984) and therefore direct atmospheric inputs of aluminum to the lake surface were probably insignificant. Because solute transport to and from the lake were largely dictated by water flow, there were pronounced variations in the drainage inputs of aluminum over the annual cycle (Figure 11). Note that 62, 44 and 46% of the annual IMAl, OMAl and ASAl inputs to the lake occurred during the spring high flow period (15 March – 15 June 1982).

We also observed pronounced temporal trends in the gross deposition of particulate aluminum to sediment traps positioned at upper (6 m) and lower (14 m) water depths (Figure 12). Gross deposition of particulate aluminum to the lower water sediment traps always exceeded upper water values due to the greater settling depth of the former. During the winter months the gross deposition of aluminum was low in the upper waters and considerably greater in the hypolimnitic waters. This observation is qualitatively consistent with our observation of high SI values in the hypolimnion during this period (Figure 5). During the high flow period (15 March – 15 June) upper and lower water values of sedimenting aluminum were quite similar, probably due to the turbulence associated with the high flux of water during this period. Also considering high aluminum inputs to the lake the gross downward flux of particulate aluminum was surprisingly low. The concentrations

of ASA1 in the inflowing stream during snowmelt were not statistically different than during base flow suggesting that the concentration of particulate aluminum did not increase with increasing water flow. Moreover, Dart Lake was highly understaturated with respect to the solubility of microcrystalline gibbsite during this period, so in-lake formation of particulate aluminum was probably minimal. During summer stratification gross deposition of particulate aluminum was high for both the upper and lower waters, which again is qualitatively consistent with our high SI values. Aluminum deposited within sediment was strongly correlated with total particulate deposition (Table 5) suggesting that vertical transport of aluminum and total particulate matter are interrelated in Dart Lake.

We can not identify a specific process of particulate aluminum formation in this study. Mechanisms by which in-lake formation of particulate aluminum may occur include direct chemical precipitation, coprecipitation and adsorption on particulate matter. The precipitation or coprecipitation of metals in nature generally occurs by homogenous nucleation (Corey, 1981). Foreign particulate matter serve to catalyze the precipitation process by lowering the activation energy required for precipitation. Thus, regardless of the mechanism of in-lake removal of aqueous aluminum, particles would appear to play an essential role. Our SI calculations indicate that direct precipitation of aluminum is thermodynamically feasible in Dart Lake (Figure 5). We have also computed aluminum distribution coefficients (Kd; mol Al gm particulate matter $^{-1}$·(mol aqueous Al·cm^{-3})$^{-1}$) which are a measure of the affinity of aluminum for particulate matter (Figure 13). In-lake distribution coefficients for aluminum were generally consistent throughout the study period. An exception to this occurred during

snowmelt when Kd values decreased, particularly in the upper water, probably due to the low pH conditions. Kd values were highest during summer stratification and upper water values were considerably greater than full water column values. This difference indicates that epilimnitic particles had a higher affinity for aluminum than hypolimnitic particles which again is qualitatively consistent with our SI calculations. In the epilimnion, high SI values persisted for only a few weeks indicating relatively rapid removal of aluminum. In the hypolimnion, elevated SI values were observed for several months indicating that mechanisms of aluminum removal were not as efficient as the epilimnion.

Using the heat-budget approach of Powell and Jassby (1975) we computed the diffusivity and, from concentration gradients, estimated the upward flux of aluminum during summer stratification in Dart Lake. To illustrate the relative significance of the upward flux of aluminum, both upward and downward gross flux as well as the net vertical flux (the difference between upward and downward gross flux) of aluminum is indicated in Figure 14 for both 6 and 14 m depths at monthly intervals during the summer stratification period. (Values of upward flux are not available for October and November because the thermocline migrated below the 6 meter depth and therefore was within the well mixed upper waters). Note that the upward flux of aluminum generally increased during the stratification period. However, this mechanism of vertical aluminum transport was insignificant when compared to the downward flux of aluminum. Although estimates of the upward flux of aluminum are not available for turnover or winter stratification periods, it would appear that the vertical transport of aluminum in Dart Lake is characterized by a very pronounced downward component.

Over an annual cycle aluminum as retained in Dart Lake. Using surficial sediment pools and observed sedimentation rates (0.35 cm yr^{-1} Heit et al., 1981; Charles, 1983), and mass balance calculations, we made two independent estimates of the annual deposition of aluminum in Dart Lake (Table 6). Moreover, the sediment trap monitoring program provides an estimate of the gross deposition of particulate aluminum. In view of the evidence that upward transport of aluminum is minor it is probably not unreasonable to assume that gross and net deposition rates of aluminum should be similar. While these estimates of aluminum deposition were obtained from independent approaches they are in relatively close agreement (Table 6) and suggest that our estimates of aluminum transport within Dart Lake may be reasonable.

General Discussion

It is apparent that there were pronounced temporal and spatial changes in the water chemistry of Dart Lake. Such variations pose a problem to interpreting data from synoptic surveys. Depending on time of year and region of the lake where the sample is collected, the water quality could vary markedly. For example most surveys are conducted in the summer and samples are collected from the epilimnion. On the basis of our observations such as sampling would be a poor representation of "typical" lake conditions. Even if surveys are accomplished over a few weeks and are only designed to provide information on relative variations in water quality, short term events like precipitation, wind entrainment, and biological transformations may substantially change lake water chemistry. Therefore any interpretation of data collected from surveys of acidic waters should be made with an understanding of spatial and temporal fluctuations in water quality that may occur.

When evaluating effects of elevated levels of aqueous aluminum consideration should also be given to temporal variations that occur within acidic lake ecosystems. Using our conceptual model we have computed aluminum pools and fluxes for snowmelt (3/28 - 6/29; Figure 15) and summer base-flow conditions (7/28 - 10/29; Figure 16). There were profound differences in the chemistry and transport of aluminum for these two periods. During high flow conditions the lake was accumulating aluminum and aluminum was generally conservative in the lake system. Most of the drainage flux of aluminum during high flow was exported from the lake outlet. During summer stratification the emphasis of aluminum transport shifted from predominantly a horizontal flux to a substantial vertical flux. Microbially mediated depletions of nitrate increased pH values and induced in-lake formation of particulate aluminum which was to a large extent retained in the lake. During this period a very high fraction of the fixed solids deposited from the water column may be attributed to particulate aluminum (Figure 17).

Elevated levels of aluminum may effect aquatic organisms by 1) acting as a toxicant or 2) modifying the cycling of ecologically important substances like phosphorus and organic carbon. Obviously snowmelt, with its associated high concentration of aluminum, is a critical period for aquatic organisms inhabiting acidic lakes. But less obvious and maybe of comparable importance are the stratification periods. During these periods considerable aluminum is converted from aqueous to particulate phases and solutes like DOC and orthophosphate are probably removed from solution as a consequence. For example the removal of DOC from the epilimnion of Dart Lake during the summer might be attributed to coprecipitation with aluminum. Such a process is potentially significant for acidic lake ecosystems because organic anions contribute to already low levels

of acid neutralizing capacity (ANC) (Johannessen 1980; Driscoll and Bisogni, 1984). Organic anions can also complex aluminum and mitigate toxicity (Baker and Schofield, 1982). Therefore, any process that results in DOC or organic anion removal probably acts to diminish the water quality of acidic lakes.

While it is reasonably well established that aluminum can remove ortho-phosphate from solution (Dickson, 1978) it may also act as a coagulant and directly facilitate the removal of algae and other forms of particulate phosphorus from the water column. Sorption and coagulation processes of phosphorus removal, would be most pronounced during the summer season when this element is in greatest demand by acidic lake ecosystems. Like DOC, any removal of phosphorus would probably diminish water quality. In acidic lakes, like Dart Lake, algal assimilation of nitrate is a significant mechanism of H-Al-BNC removal (Driscoll and Schafran 1984, Appendix 2). Thus, any reduction in the algal growth limiting nutrient phosphorus, would retard this process.

Baker and Schofield (1982) have suggested that hydroxyl complexes of mono-meric aluminum are particularly toxic to fish. Fish mortality has been correlated to elevated SI values (Baker and Schofield, 1982) and the sorption of aluminum to gill surfaces has been observed during mortality (Muniz and Leivestad, 1980). Within acidic lakes, like Dart Lake, high SI values are common during stratifica-tion, particularly in the hypolimnion. Our large Kd values suggest that aluminum has a high affinity for particulate surfaces; an observation that can undoubtedly be extrapolated to biological surfaces. Grahn (1980) reported that a fish kill of Cisco (Coregonus albula) occurred in two Swedish lakes when large inputs of aluminum associated with a rainfall event, were followed by increases in pH mediated by phytoplankton activity. Grahn (1980) hypothesized that formation of hydroxy-aluminum and sorption to gill surfaces contributed to this fish kill.

It is apparent that the extent to which aluminum is conservative within acidic lake ecosystems varies considerably over the annual cycle. During summer and winter stratification, considerable aqueous aluminum is converted to particulate aluminum which is deposited to lake sediments. This non-conservative nature of aluminum has significant implications for the biogeochemistry of acidic lake ecosystems.

Conclusions

From this study we conclude that:

1) there were significant temporal and spatial variations in the chemistry and transport of aluminum in Dart Lake,

2) hydrogen ion and aluminum base neutralizing capacity were strongly correlated with nitrate concentration,

3) during snowmelt, considerable quantities of nitrate, hydrogen ion and aluminum entered Dart Lake through drainage inputs and passed through the lake with limited retention,

4) during both summer and winter stratification microbially mediated depletions of nitrate resulted in removal of inorganic aluminum

5) fluoride and organic complexes were the predominant form of aluminum in Dart Lake and

6) there appears to be both allochtonous and autochtonous sources of alumino-organic solutes in Dart Lake.

Acknowledgements

Table 1 Inorganic Aluminum Forms

Aquo aluminum $=$ $[Al^{3+}]$

Hydroxide bound aluminum $=$ Al-OH $=$ $[Al(OH)^{2+}]$ + $[Al(OH)_2^+]$ + $[Al(OH)_4^-]$

Fluoride bound aluminum $=$ Al-F $=$ $[AlF^{2+}]$ + $[AlF_2^+]$ + $[AlF_3]$ + $[AlF_4^-]$ + $[AlF_5^{2-}]$ + $[AlF_6^{3-}]$

Sulfate bound aluminum $=$ Al-SO$_4$ $=$ $[AlSO_4^+]$ + $[Al(SO_4)_2^-]$

Aluminum base nuetralizing capacity $=$ Al-BNC $=$ $3[Al^{3+}]$ + $3[Al\cdot F]$ + $3[AlSO_4]$ + $2[Al(OH)^{2+}]$ +

$$[Al(OH)_2^+] - [Al(OH)_4^-]$$

Hydrogen ion-aluminum base $=$ H-Al-BNC $=$ $[H^+]$ + Al-BNC - $[OH^-]$
neutralizing capacity

Table 2 Average Chemical Composition (μeq·l^{-1}) of

Dart Lake 10/1981 - 11/1982 (n = 172)

	Mean	Standard Deviation
Base Neutralizing Capacity **(to reference pH = 8.3)**		
hydrogen ion	7.4	3.7
aluminum	19.6	8.2
carbonic acid	62.0	58.9
organic acids	3.0	1.2
total	92.0	59.0
Basic Cations		
calcium	99.5	4.6
magnesium	28.9	2.2
sodium	28.3	4.9
potassium	13.0	1.1
total	169.7	10.0
Anions		
sulfate	137.6	11.0
nitrate	24.4	8.6
chloride	13.5	3.4
organic anions	12.2	0.4
bicarbonate	7.2	11.9
free fluoride	0.9	0.7
total	195.8	25.6
Sum of Cations[1]	196.7	13.9
Sum of Anions	195.8	25.6

[1]Cationic equivalence were computed to be hydrogen ion and aluminum BNC plus basic cations.

Table 3 Mean Concentration and Standard Deviation of Aluminum
(in $\mu mol \cdot l^{-1}$) and Relative Distribution as Total and Monomeric Aluminum

Aluminum Form	Concentration	Relative Distribution as TAl	Relative Distribution as MAl
Total Aluminum (TAl)	14.8 ± 4.4	—	—
Monomeric Aluminum (MAl)	11.5 ± 3.7	0.78	—
Inorganic Monomeric Aluminum	8.0 ± 3.2	0.54	0.70
Al^{3+}	1.9 ± 1.7	0.13	0.17
Al-F	3.6 ± 0.7	0.24	0.31
Al-OH	2.5 ± 1.3	0.17	0.22
$Al-SO_4$	0.1 ± 0.1	0.01	0.01
Organic Monomeric Aluminum	3.5 ± 1.8	0.24	0.30
Acid Soluble Aluminum	3.3 ± 3.1	0.22	—

Table 4 Annual Flux and Retention of Solutes
for Dart Lake 1981-1982

Parameter	Input[1] $(mol \cdot ha^{-1} \cdot yr^{-1})$	Output $(mol \cdot ha^{-1} \cdot yr^{-1})$	Retention Coefficient[1]
TAl	114.3	110.9	0.064
IAMl	65.2	62.0	0.085
OMAl	28.3	27.4	0.066
ASAl	20.8	21.5	-0.001
NO_3^-	221	213	0.070
SO_4^{2-}	489	509	-0.008
Cl^-	96.5	100.2	-0.005
DOC	1976	2096	-0.026

1. Solute input was calculated by assuming that solute concentration in non-inlet water ($\sim$ 3% of the input discharge) was similar to observed values in inlet water.

Table 6   Relationships Between Gross Deposition of
Aluminum[1] (Dg-Al)[1] and Total Solids Deposition (DG – TS)[2]

6 Meter Depth	r^2	p <
Dg – Al = 0.056 (Dg – TS) – 5.9;	0.44	0.0001
14 Meter Depth		
Dg – Al = 0.032 (Dg – TS) – 0.7;	0.72	0.0001
Total		
Dg – Al = 0.036 (Dg – TS) – 1.4;	0.69	0.0001

[1] $mg \cdot Al \cdot m^{-2} \cdot d^{-1}$

[2] $mg \cdot m^{-2} \cdot d^{-1}$

Table 7 Net Deposition of Aluminum ($mmol \cdot m^{-2} \cdot yr^{-1}$) in Dart Lake 1981-1982

Method of Computation

Aluminum Form	Mass Balance[1]	Recent Sediment[2]	Sediment Trap[3]
Total	95	200	230
Inorganic	32	150	–
Organic	25	50	–
Acid Soluble	40	–	–

1. See Table 5

2. Computed assuming a sedimentation rate of 0.35 cm yr^{-1}

3. Computed by multiplying the 0-6 m surface area (63 ha) by the sedimentation rate observed in the 6 m sediment trap and the 6-15 m surface area (81 ha) by the sedimentation rate observed in the 14 m sediment trap.

Figure Titles

1. A morphometric map of the study site Dart Lake. Water samples were collected at the inlet, outlet and a single deep water station.

2. Hypothetical calculations illustrating the potential effects of changes in (a) the partial pressure of CO_2 from ambient to atmospheric levels and (b) the temperature from ambient to typical laboratory levels on hypolimnitic Dart Lake solutions. The calculations were made for a sample with an in-situ temperature of 5.5 °C and pH = 5.41, dissolved inorganic carbon = 3.6×10^{-4} M, IMAl = 6.3×10^{-6} M, fluoride = 4.0×10^{-6} M and sulfate = 5.5×10^{-5} M collected on 10/1/82 from a depth of 14 m in Dart Lake with the chemical equilibrium model MINEQL (Westall et al., 1976).

3. Isopleths of (a) nitrate, (b) pH and (c) inorganic monomeric aluminum (IMAl) within Dart Lake for the study period. Samples were collected at 0, 2, 4, 6, 9, 12, and 14 meters. Sampling dates are indicated by Δ.

4. Values of (a) pH,(b) inorganic monomeric aluminum (IMAl), (c) nitrate, (d) sulfate, (e) dissolved organic carbon (DOC) and (f) organic monomeric aluminum (OMAl) for the inlet and outlet streams of Dart Lake over the study period.

5. An isopleth of the saturation index (SI) of Dart Lake water with respect to the solubility of microcrystalline gibbsite (Roberson and Hem, 1969).

6. The concentration of (a) inorganic monomeric aluminum (IMAl) and (b) aquo aluminum (Al^{3+}), (c) fluoride bound aluminum (Al-F), (d) hydroxide bound aluminum (Al-OH) and (e) sulfate bound aluminum (Al-SO_4) which comprise IMAl in Dart Lake.

7. Isopleths of (a) dissolved organic carbon (DOC) and (b) organic monomeric aluminum (OMA1) for Dart Lake.

8. The distribution of sediment fractions of aluminum for Dart Lake. The fractions include (a) exchangeable aluminum, (b) oxide associated aluminum, (c) aluminum associated with organic matter and (d) residual aluminum.

9. Conceptual model of aluminum pools and transport for an acidic drainage lake.

10. Average annual pools and fluxes of aluminum for Dart Lake.

11. Input and output of aluminum associated with drainage flow of Dart Lake.

12. The deposition of particulate aluminum collected in upper (6m) and lower (14m) water sediment traps in Dart Lake. Error bars indicate standard deviation of triplicate sample.

13. In-lake distribution coefficients (Kd) computed for upper (6m) and lower (14m) water sediment trap samples in Dart Lake. Aluminum distribution coefficients are a measure of the affinity of aqueous aluminum for particulate matter (mol Al gm particulate matter^{-1}·(mol aqueous Al·Cm^{-3})$^{-1}$.

14. A comparison of downward (as monitored with sediment traps) and upward (as determined with values of vertical diffusivity and concentration gradients) flux of aluminum for the summer stratification period in Dart Lake. The net vertical flux is tabulated as the difference between downward and upward fluxes.

15. Fluxes and pools of aluminum in Dart Lake during high flow conditions (3/28/1982 – 6/29/1982).

16. Fluxes and pools of aluminum in Dart Lake during low flow summer conditions (7/28/1982 – 10/29/1982).
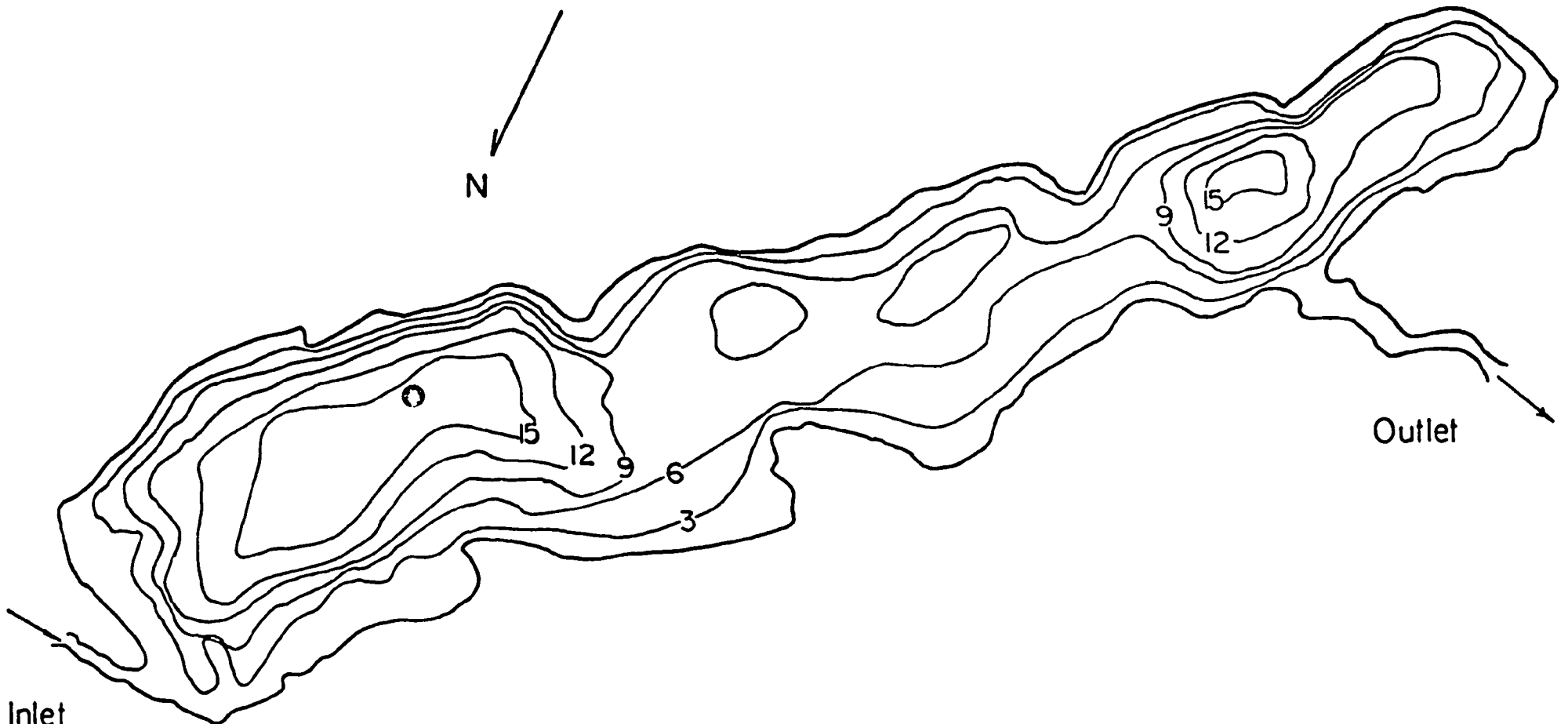
DART LAKE
74°52'W, 43°48'N
Surface Area 144ha
Volume 1.02×10^10 ℓ

Figure 1

N

Inlet

Outlet

15
12
9
6
3

9 15
12

O – Water Column and Sediment Trap
Sampling Station

Contours are in 3 meter intervals

Figure 2

a) NO₃⁻ ISOPLETH (μeq l⁻¹)
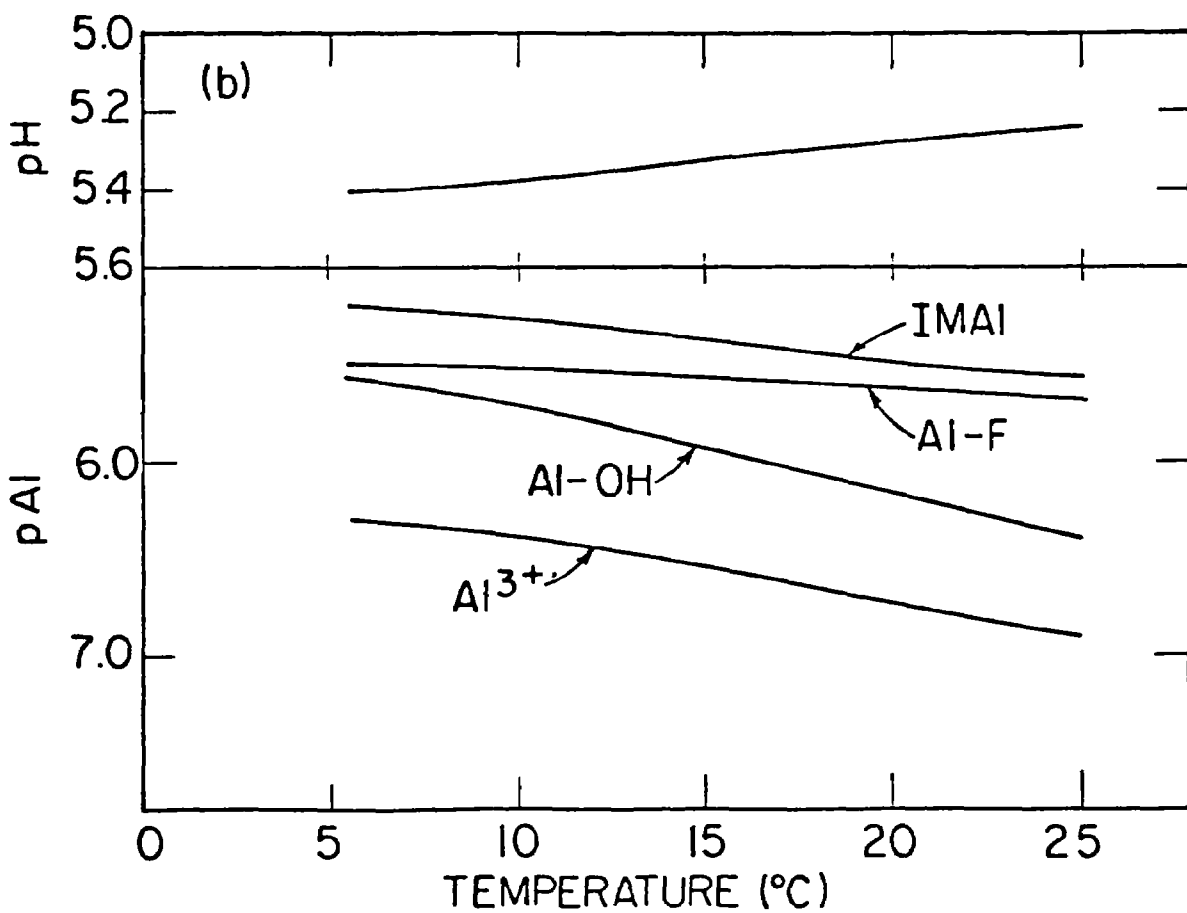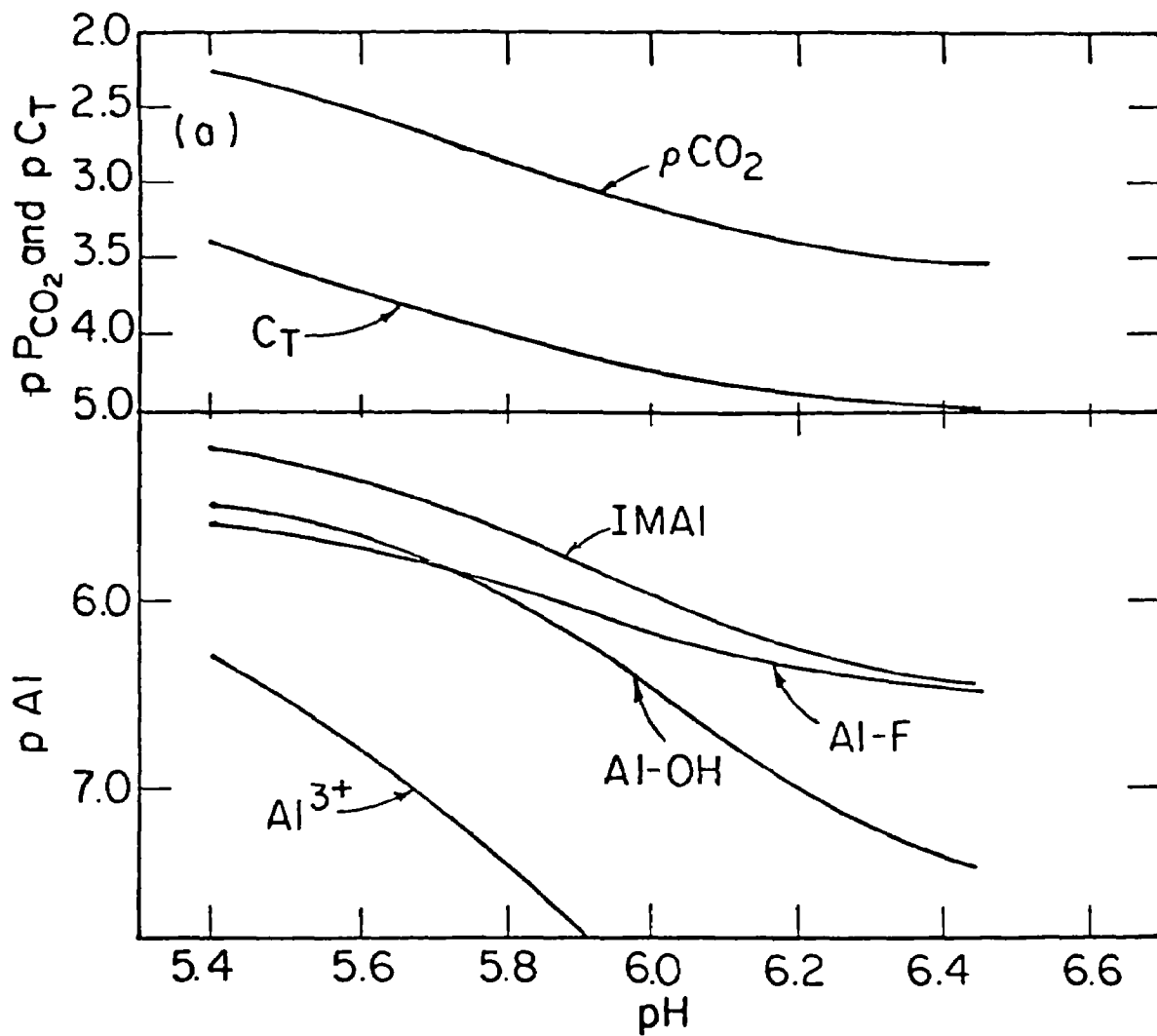
b) H-BNC ISOPLETH (μeq l⁻¹)
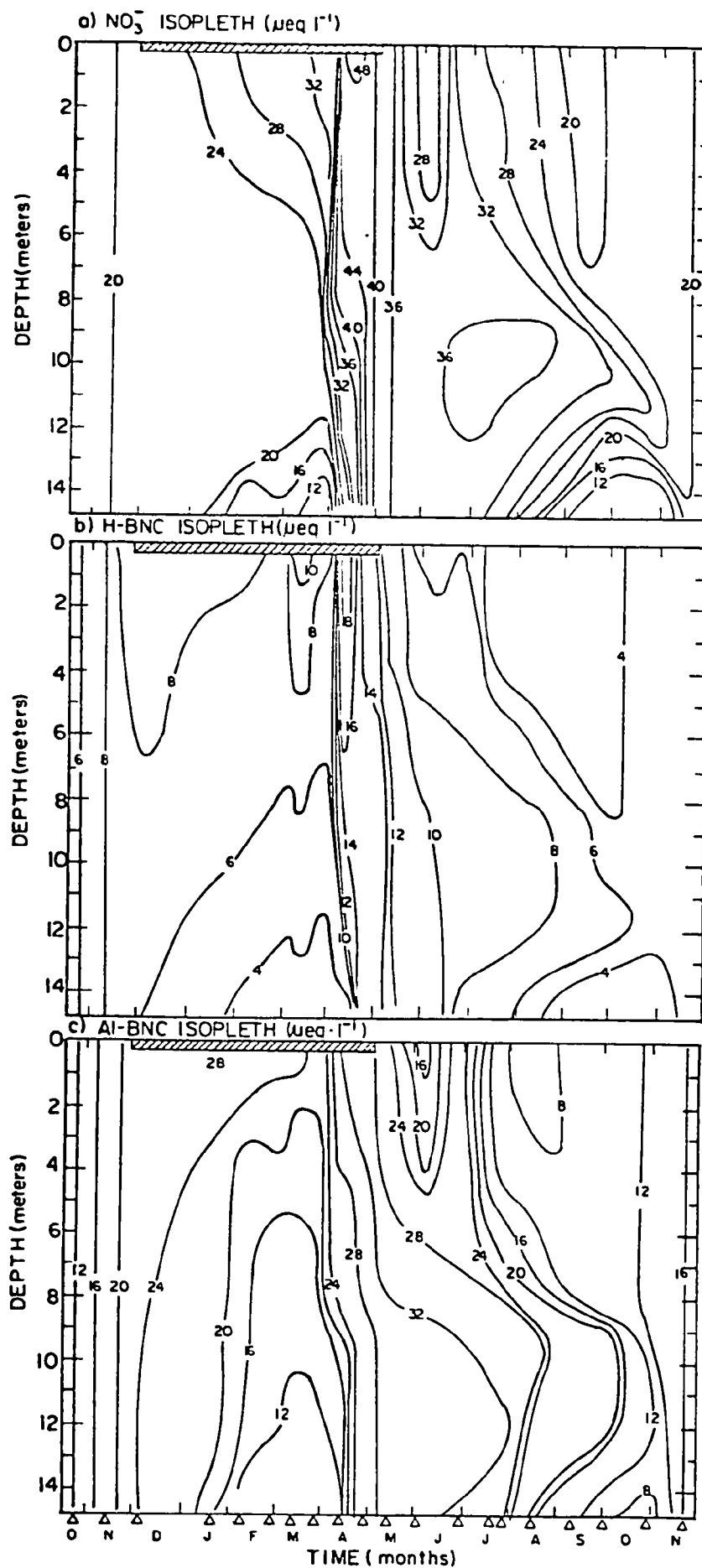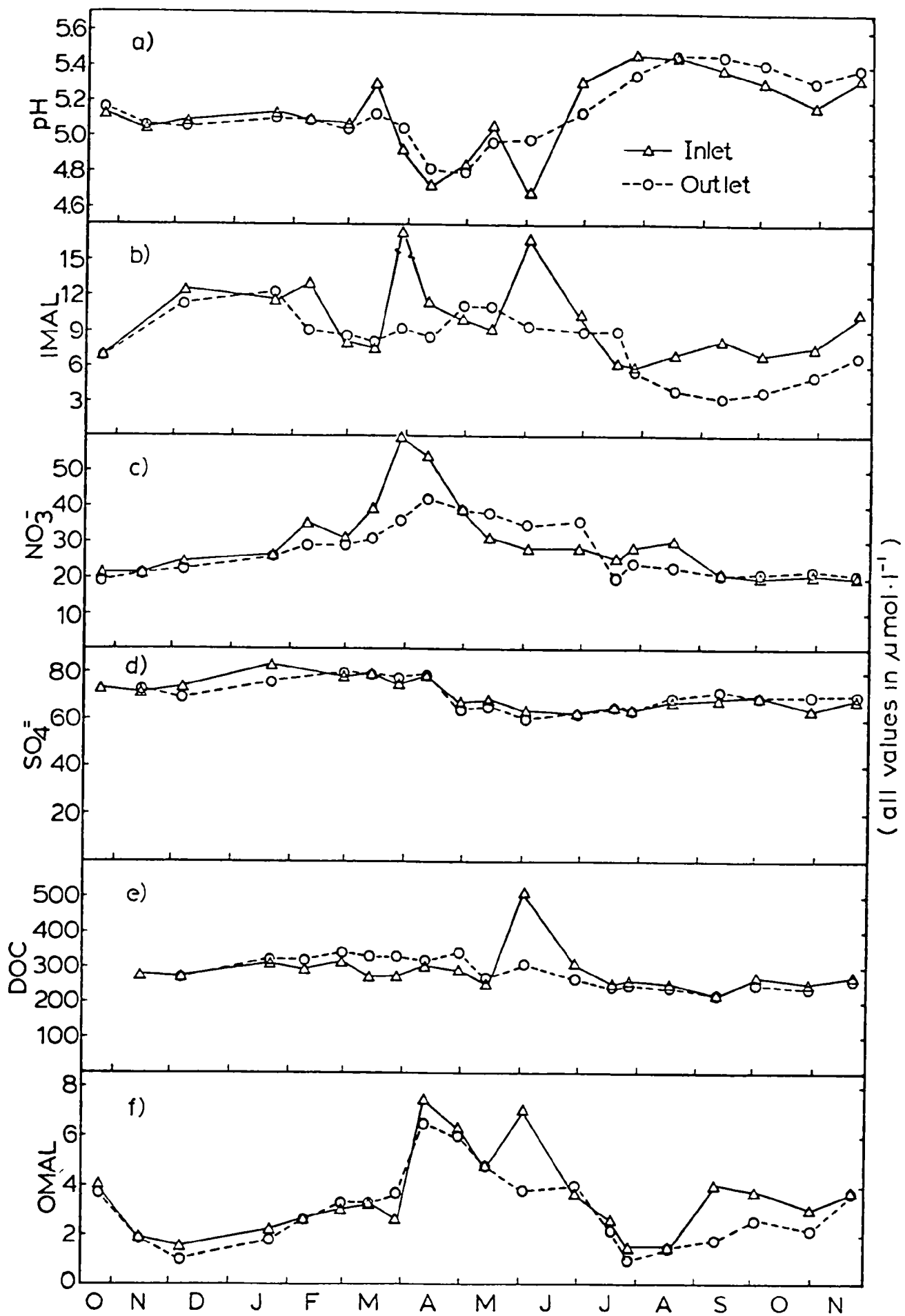
c) Al-BNC ISOPLETH (μeq·l⁻¹)

DEPTH (meters)

TIME (months)

Figure 3

Figure 4

Figure 5

Figure 6

a) Dissolved Organic Carbon (mmol C l⁻¹)

ice cover

DEPTH (meters)

O N D J F M A M J J A S O N

b) Organic Monomeric Aluminum (µmol·l⁻¹)

ice cover

DEPTH (meters)

O N D J F M A M J J A S O N
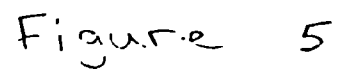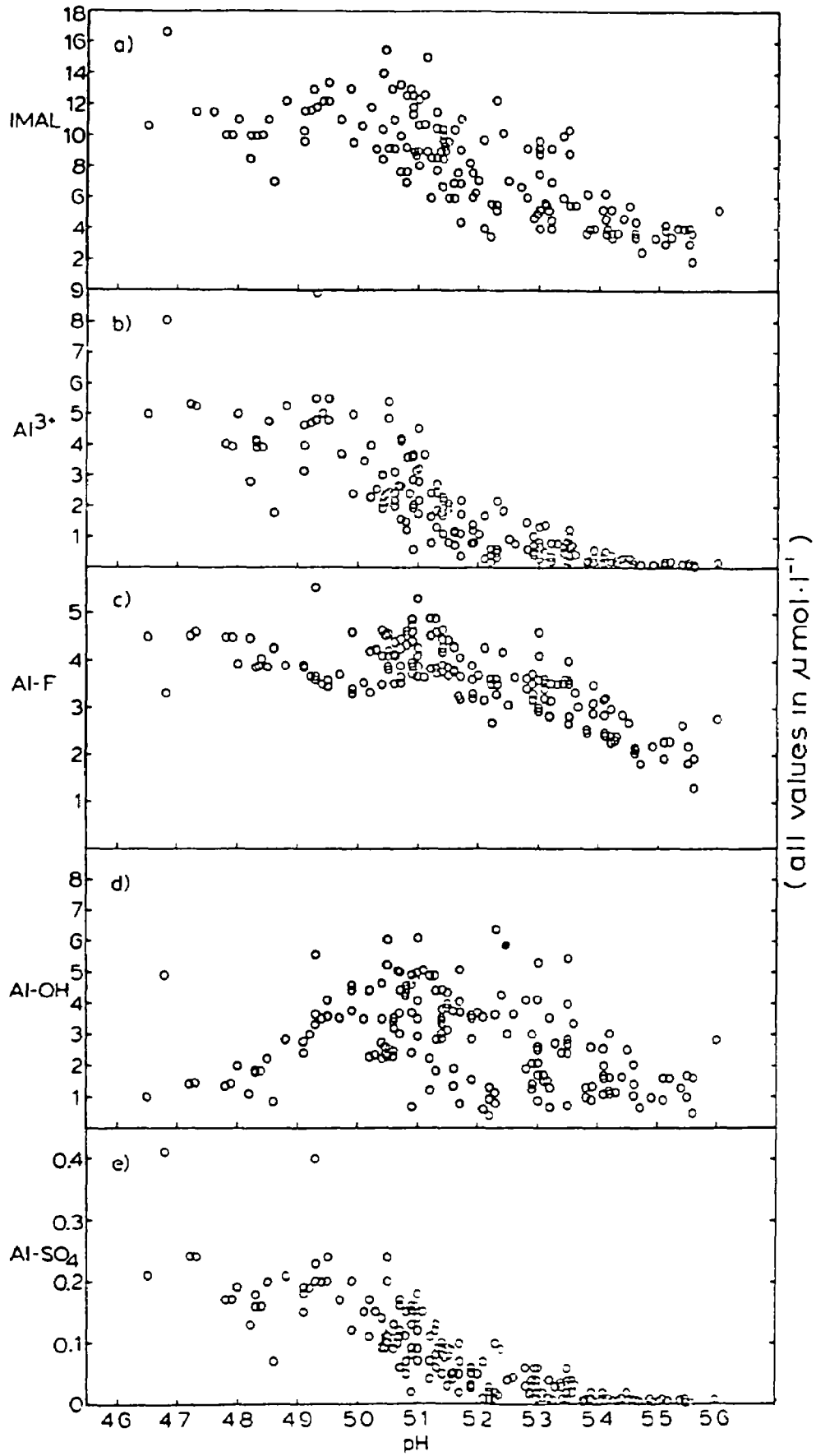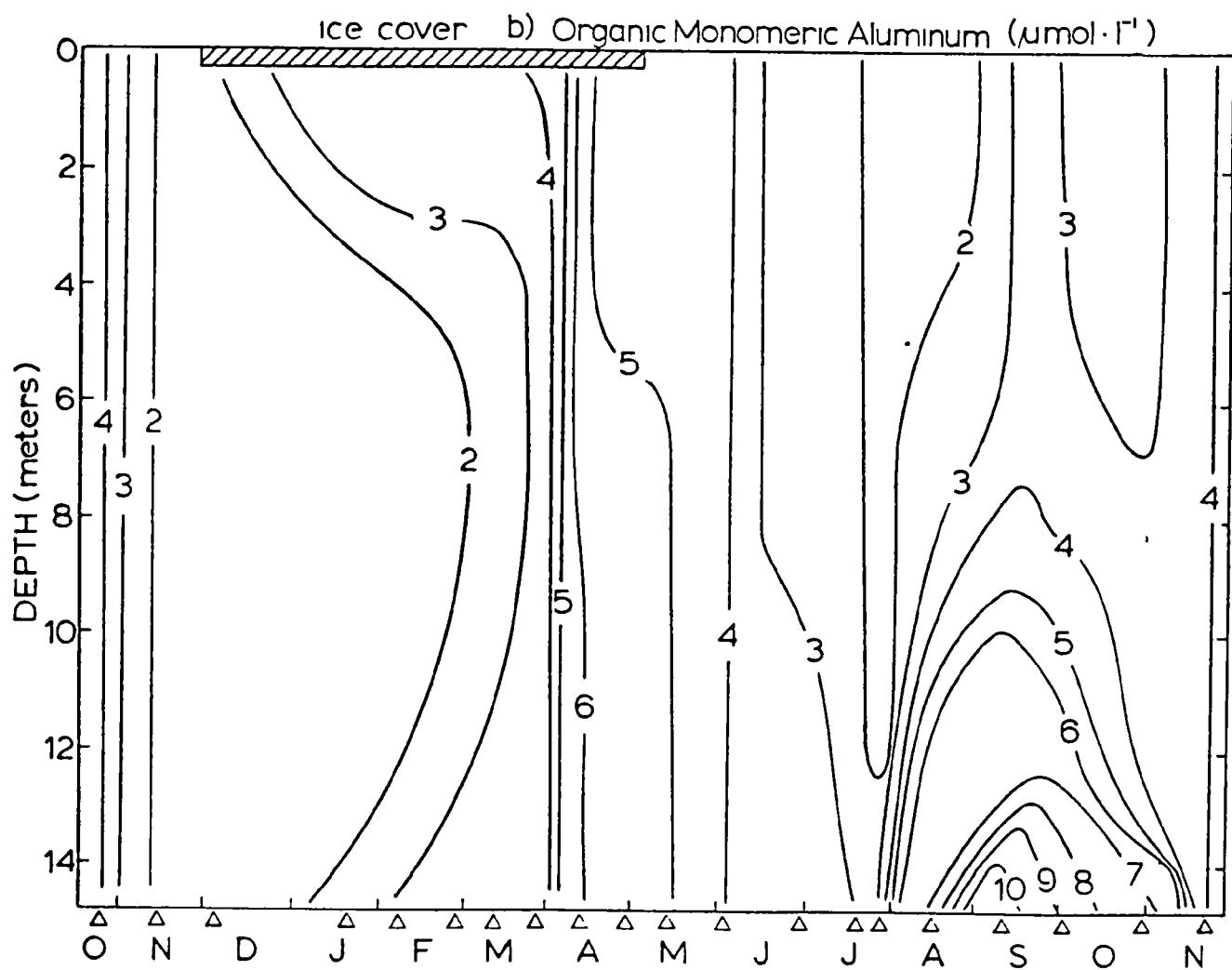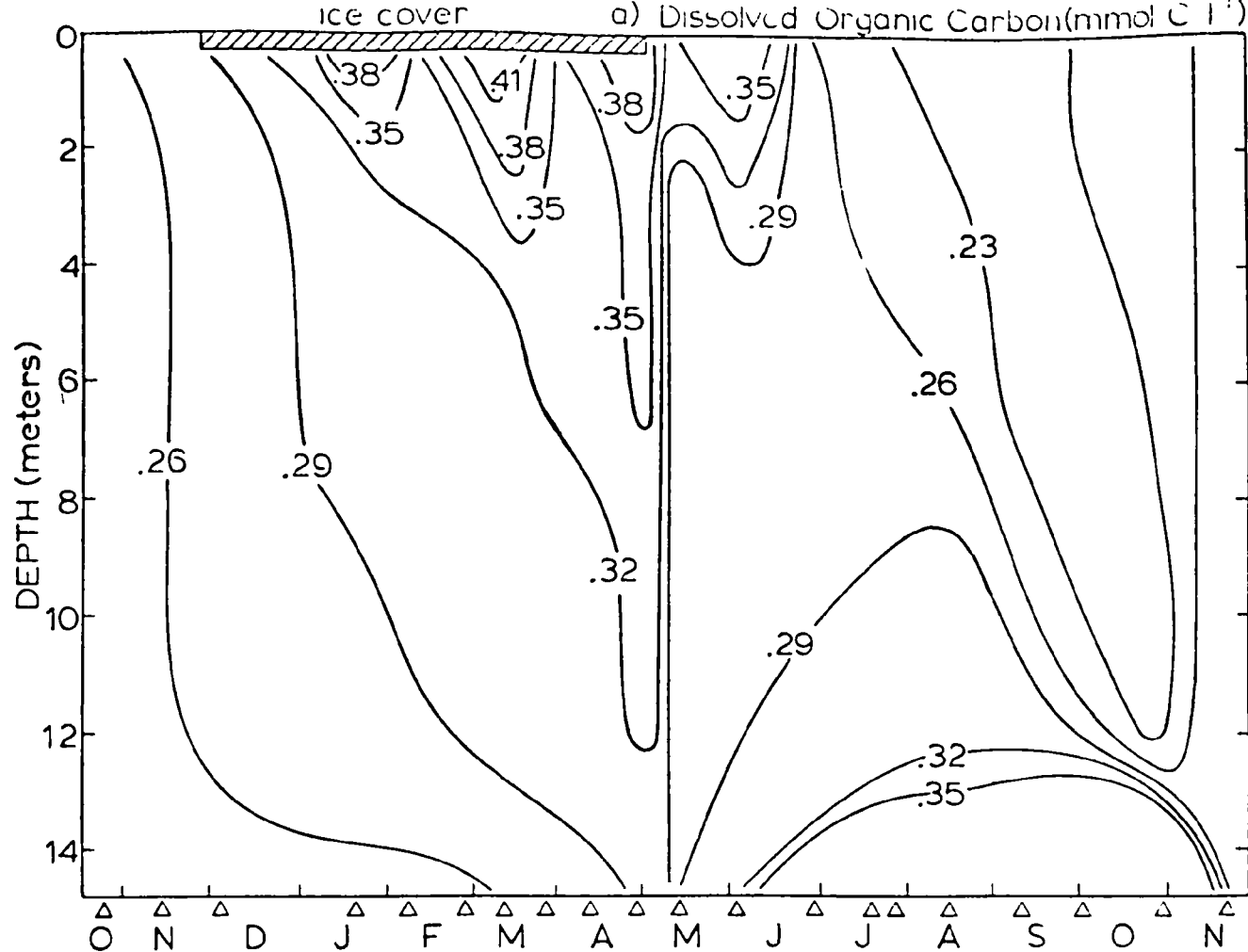
Figure 7

SEDIMENT ALUMINUM FRACTIONS

Figure 8

drainage
inputs of Al

IMAI
OMAI
hydrous
Al oxides

epilimnion

OMAI — (oxidation?) → IMAI ← (precipitation) → hydrous Al oxides

(dissolution)

(sorption on hydrous oxides)

DOC
$H_2PO_4^-$

sedimentation

drainage
exports of

IMAI
OMAI
hydrous
Al oxides

soil
sediment
water seepage inputs

IMAI?
OMAI?

diffusion

hypolimnion

seepage
exports?

IMAI?
OMAI?

(oxidation?)   (precipitation)

OMAI → IMAI → hydrous Al oxides

(sorption on hydrous oxides?)

sedimentation

diffusion   sedimentation

sediments (mineralization?) (dissolution?)
(desorption?) (desorption?)

organic Al ← → hydrous Al oxides

organic monomeric aluminum-OMAI

Inorganic monomeric aluminum-IMAI
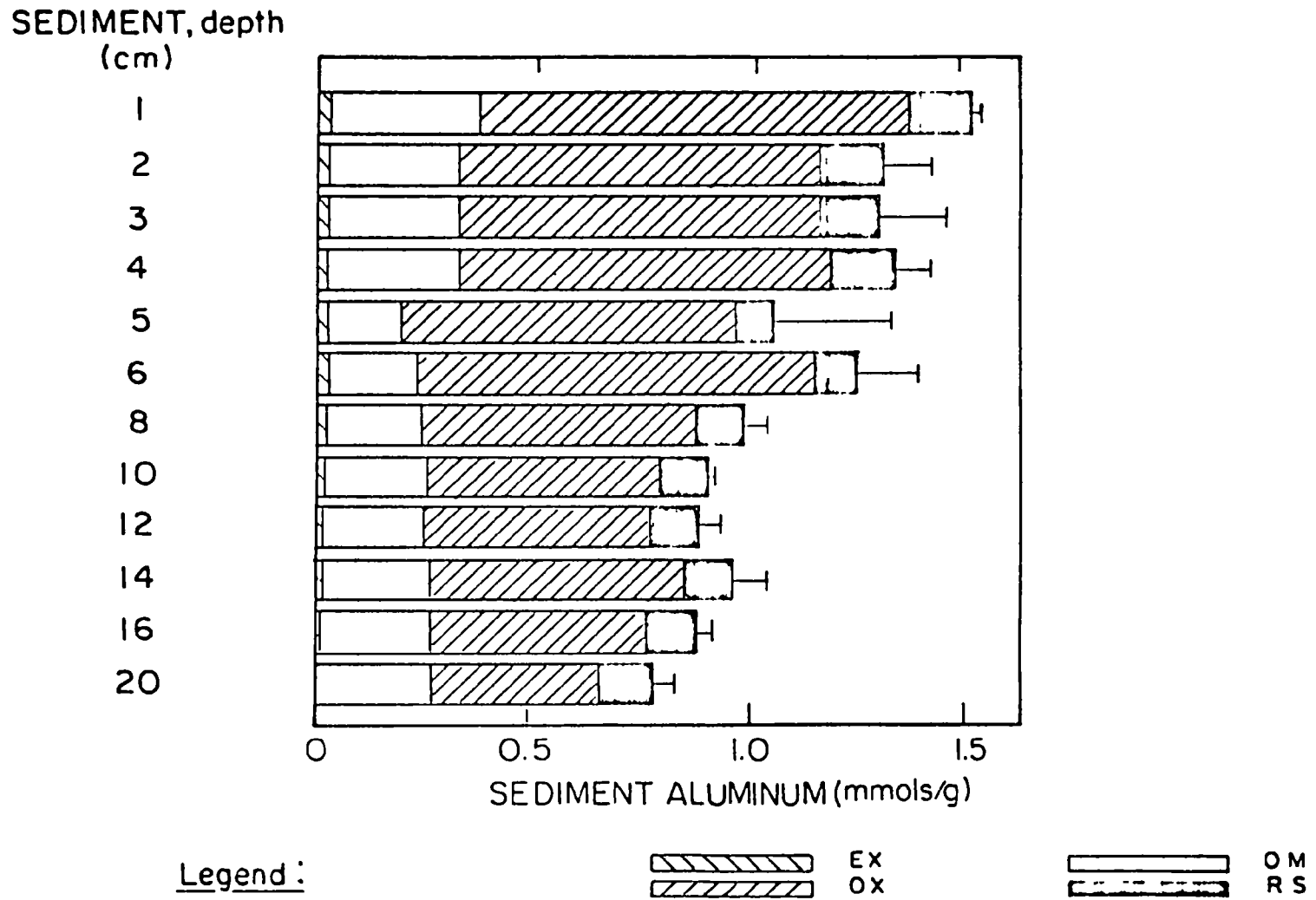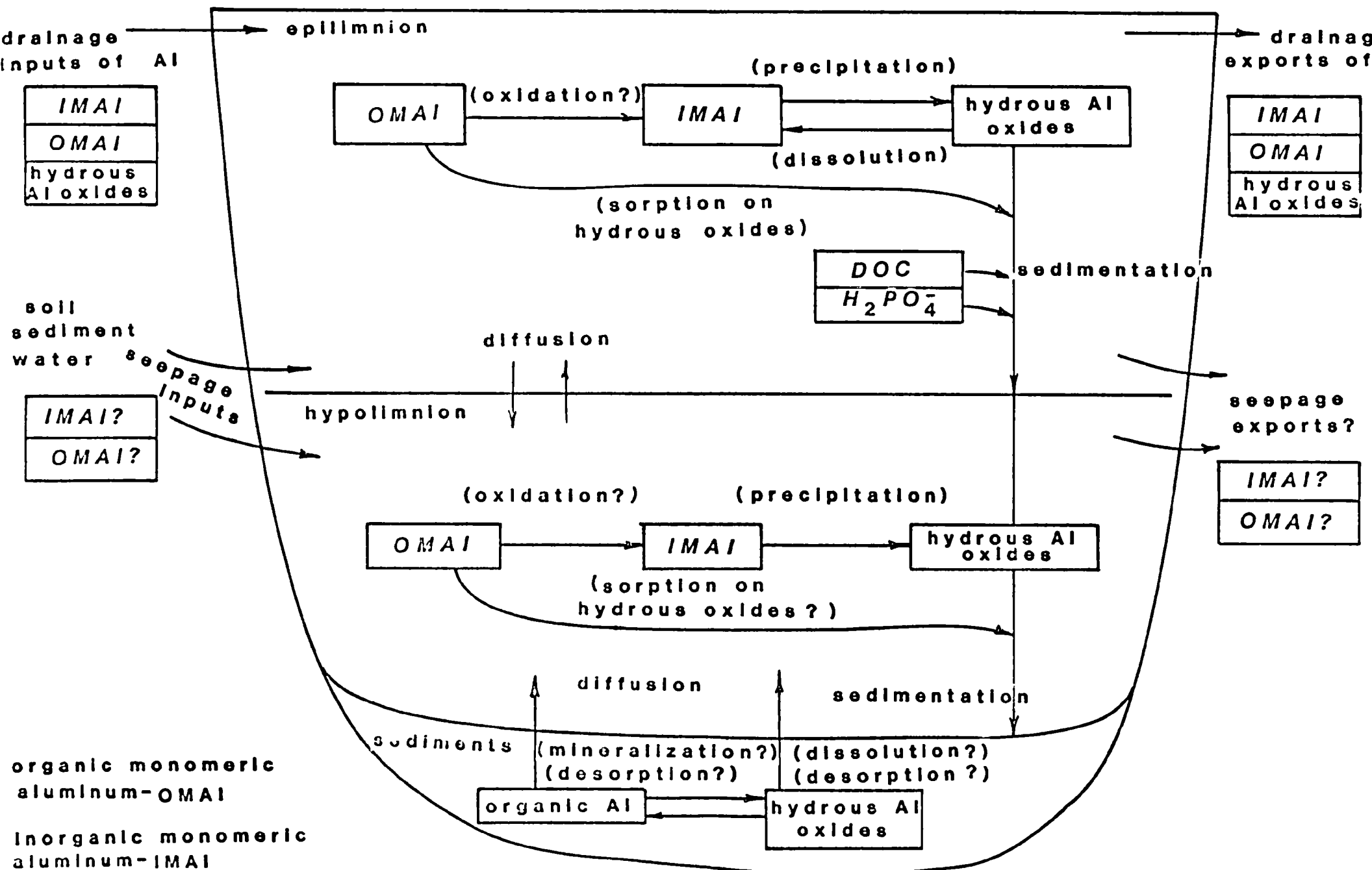
Figure 9

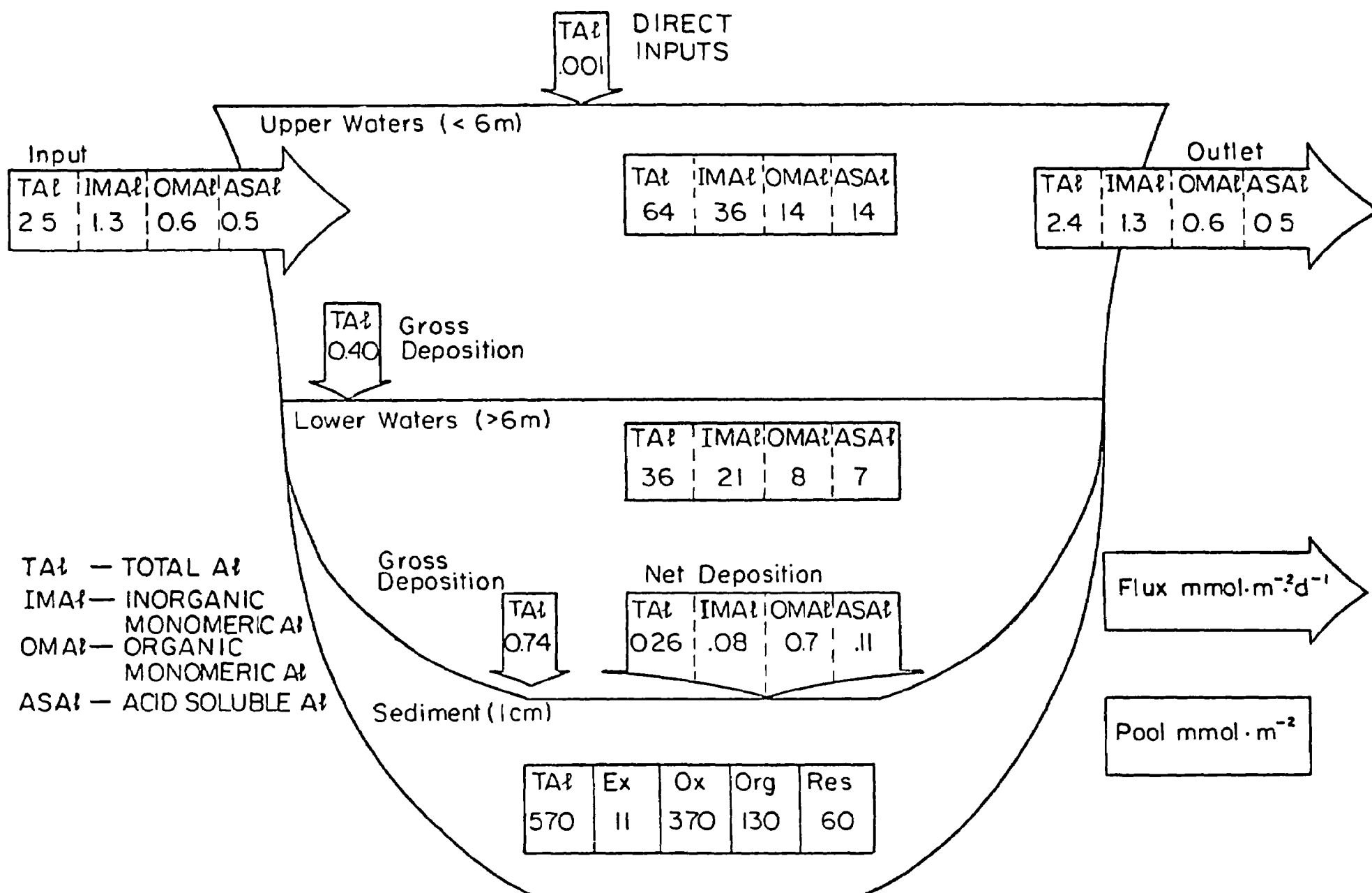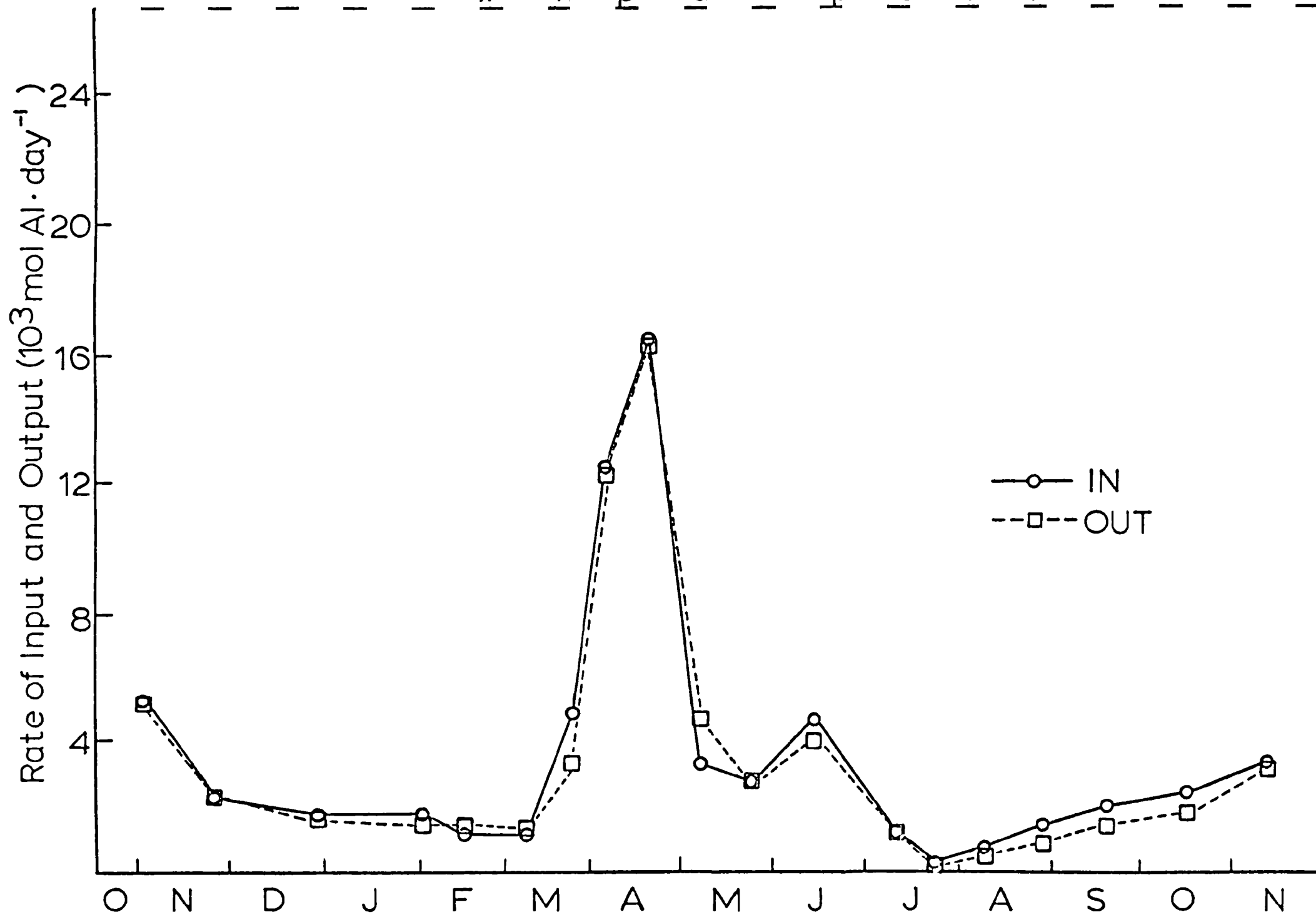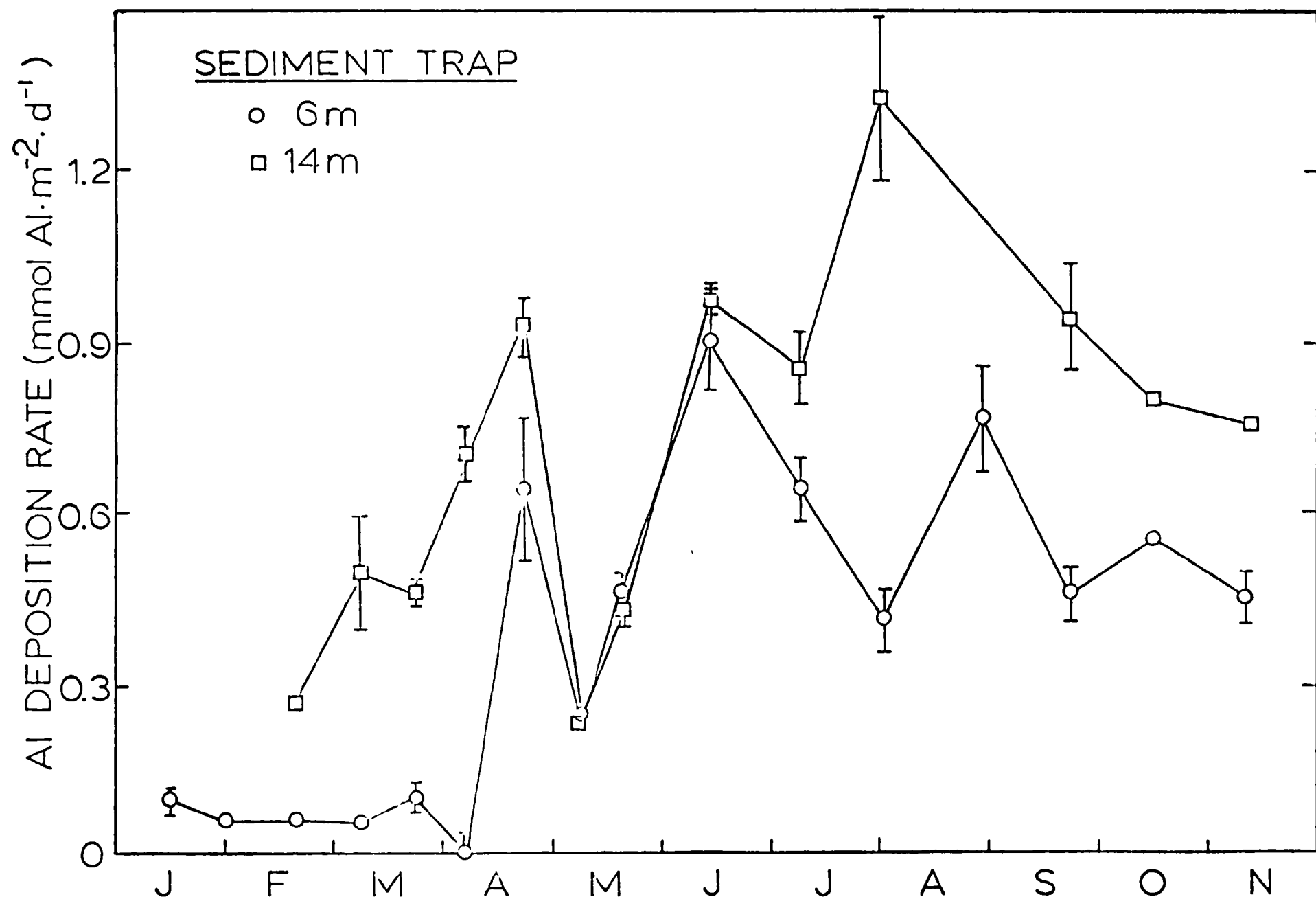ANNUAL FLUXES AND POOLS OF ALUMINUM IN DART LAKE (10/1982-10/1983)

Figure 10

Stream Input and Output of Aluminum
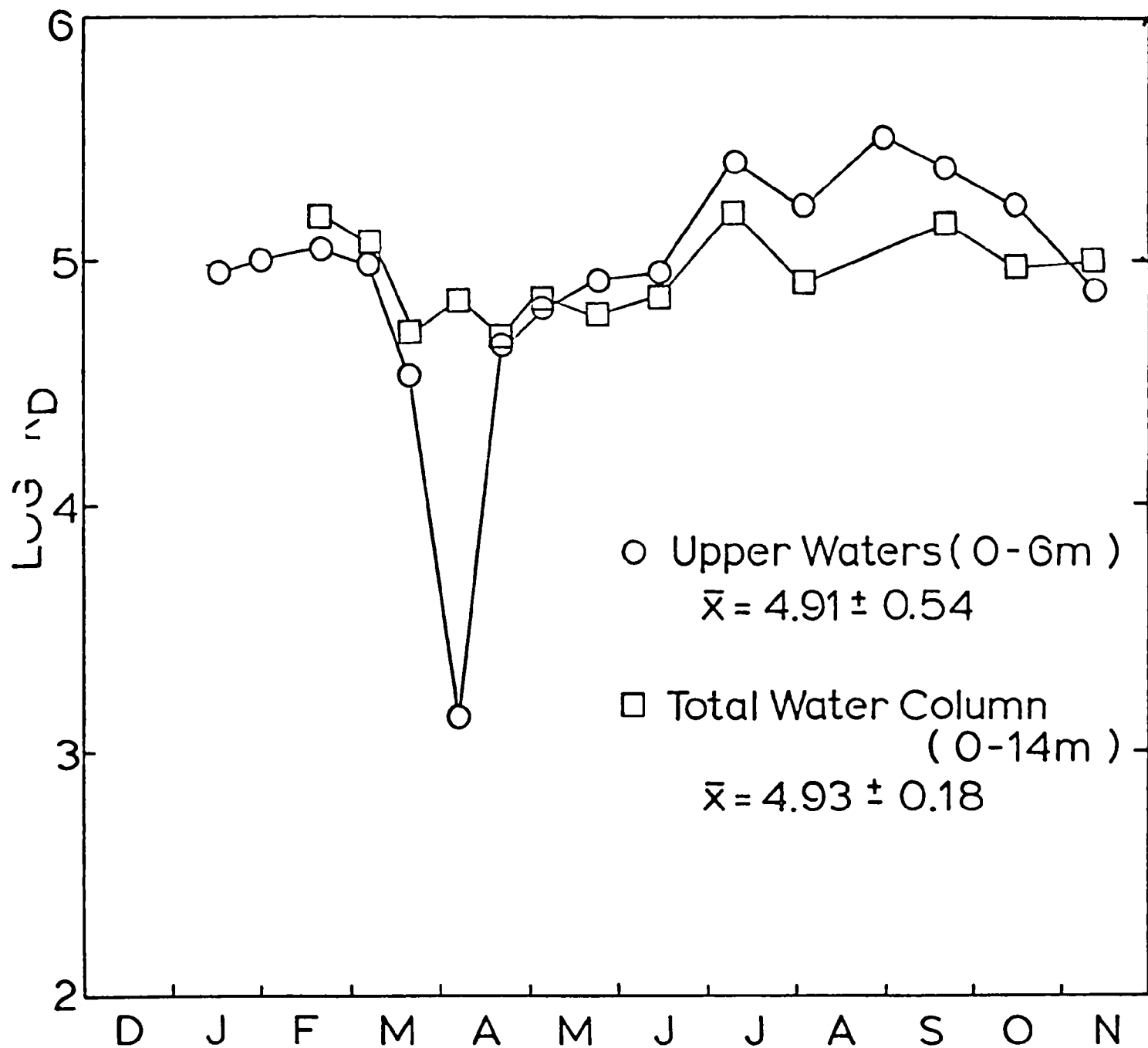
Figure 11

Figure 12

Figure 13

Figure 14

FLUXES AND POOLS OF ALUMINUM DURING LAKE TURNOVER CONDITIONS
(3/28/1982 – 6/29/1982)

	TAℓ	IMAℓ	OMAℓ	ASAℓ
Inlets	5.2	3.0	1.5	0.8

DIRECT INPUTS: ?

Upper Waters (<6m)

	TAℓ	IMAℓ	OMAℓ	ASAℓ
	83	47	20	17

	TAℓ	IM Aℓ	OMAℓ	ASAℓ
Outlets	5.2	2.8	1.4	1.0

Gross Deposition: TAℓ 0.58

Lower Waters (>6m)

	TAℓ	IMAℓ	OMAℓ	ASAℓ
	37	25	11	1

Gross Deposition: TAℓ 0.66

Net Deposition

TAℓ	IMAℓ	OMAℓ	ASAℓ
0.13	0.48	-.43	0.09

Sediments

TAℓ – TOTAL Aℓ
IMAℓ – INORGANIC MONOMERIC Aℓ
OMAℓ – ORGANIC MONOMERIC Aℓ
ASAℓ – ACID SOLUBLE Aℓ

Flux mmol·m^{-2}d^{-1}
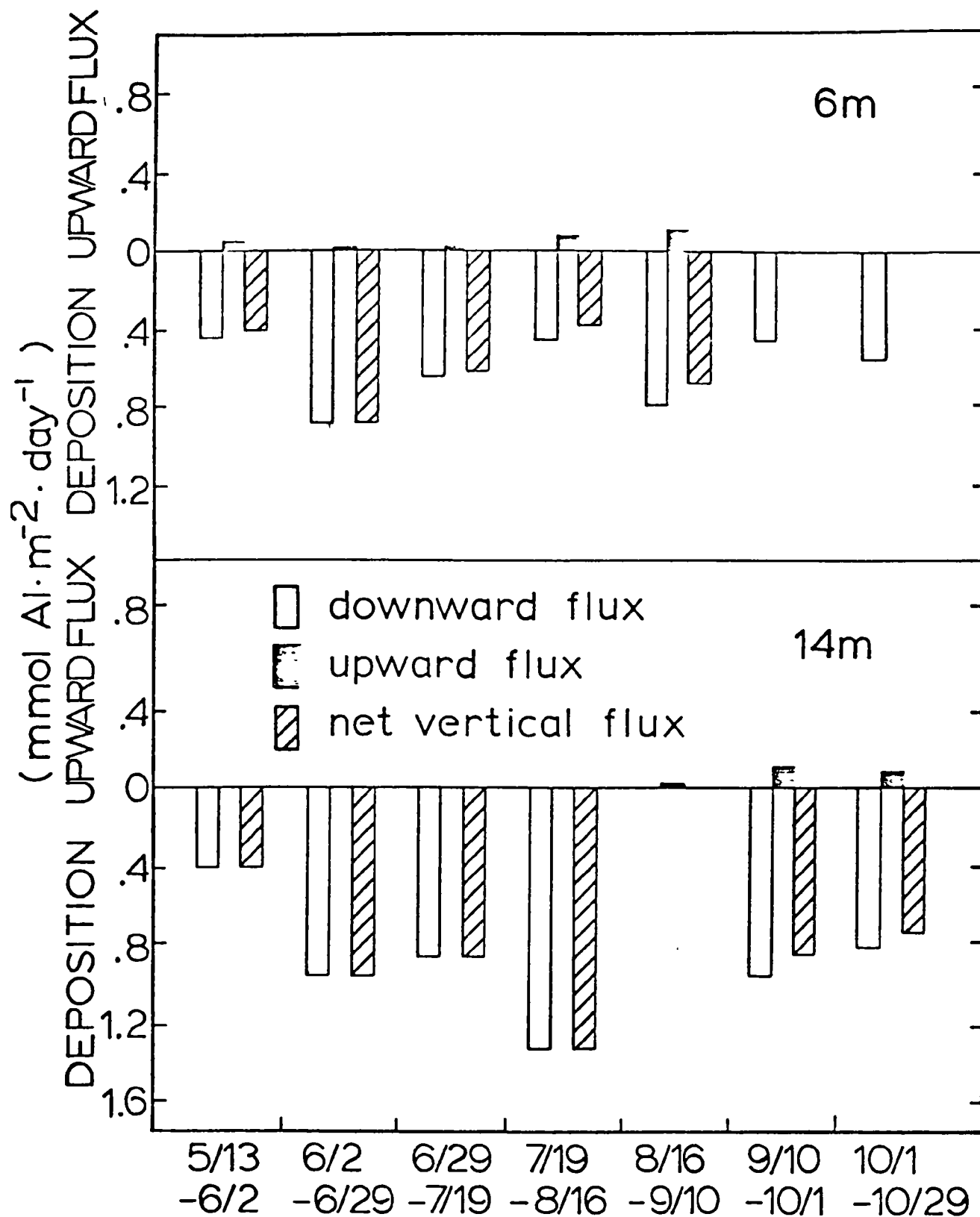
Pool mmol·m^{-2}
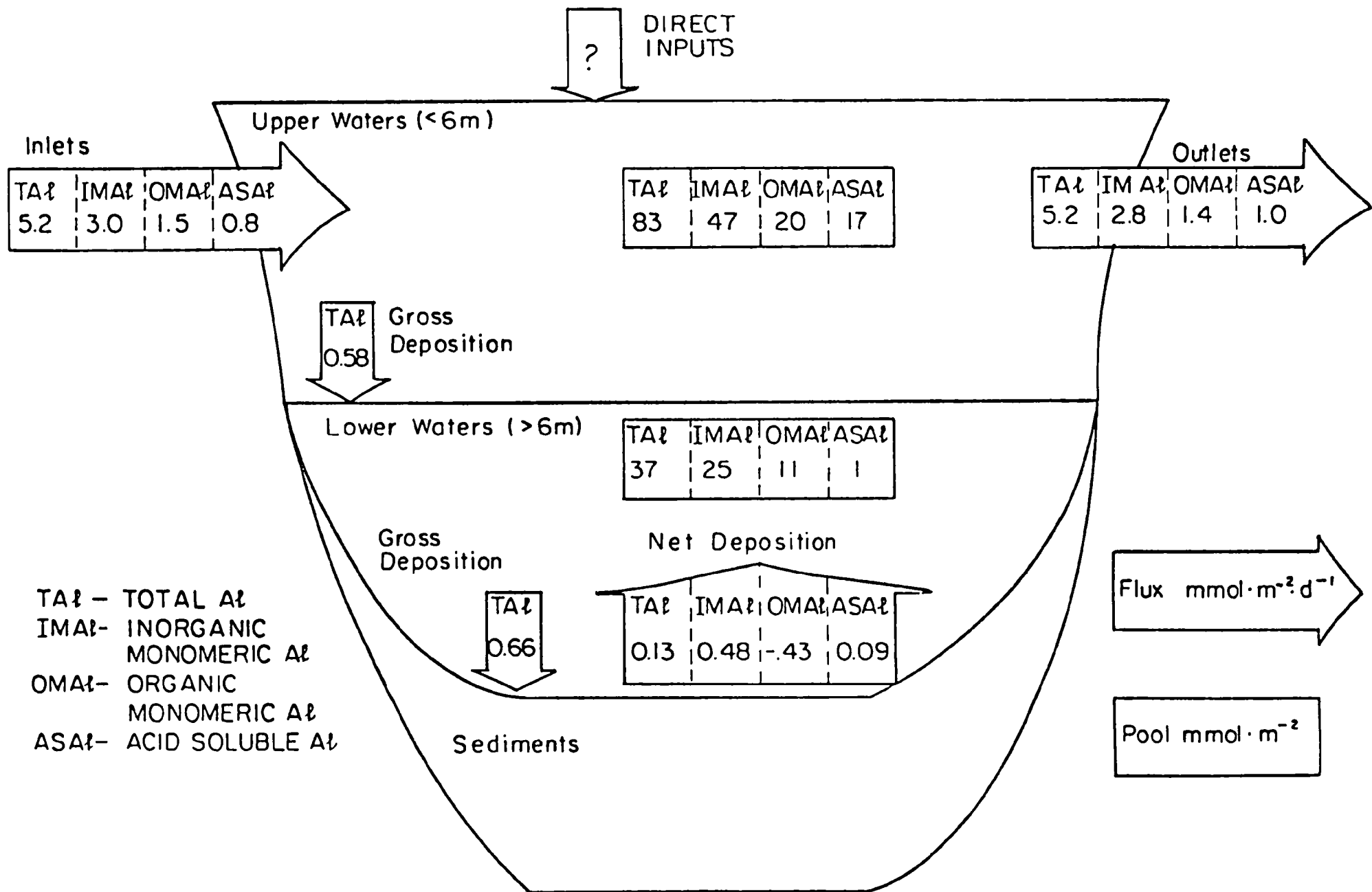
Figure 15

FLUXES AND POOLS OF ALUMINUM IN DART LAKE DURING SUMMER
LOW FLOW CONDITIONS
(7/28/1982-10/29/1982)

DIRECT INPUTS

TAℓ .001

Upper Waters (<6m)

Input

TAℓ	IMAℓ	OMAℓ	ASAℓ
1.2	0.5	0.3	104

TAℓ	IMAℓ	OMAℓ	ASAℓ
38	18	10	9

Output

TAℓ	IMAℓ	OMAℓ	ASAℓ
0.9	0.4	0.2	0.2

TAℓ 0.53 Gross Deposition

Lower Waters (>6m)

TAℓ	IMAℓ	OMAℓ	ASAℓ
32	20	8	4

Upward Flux

.002

TAℓ — TOTAL Aℓ
IMAℓ— INORGANIC MONOMERIC Aℓ
OMAℓ— ORGANIC MONOMERIC Aℓ
ASAℓ—ACID SOLUBLE Aℓ

Gross Deposition

Net Deposition

TAℓ 105

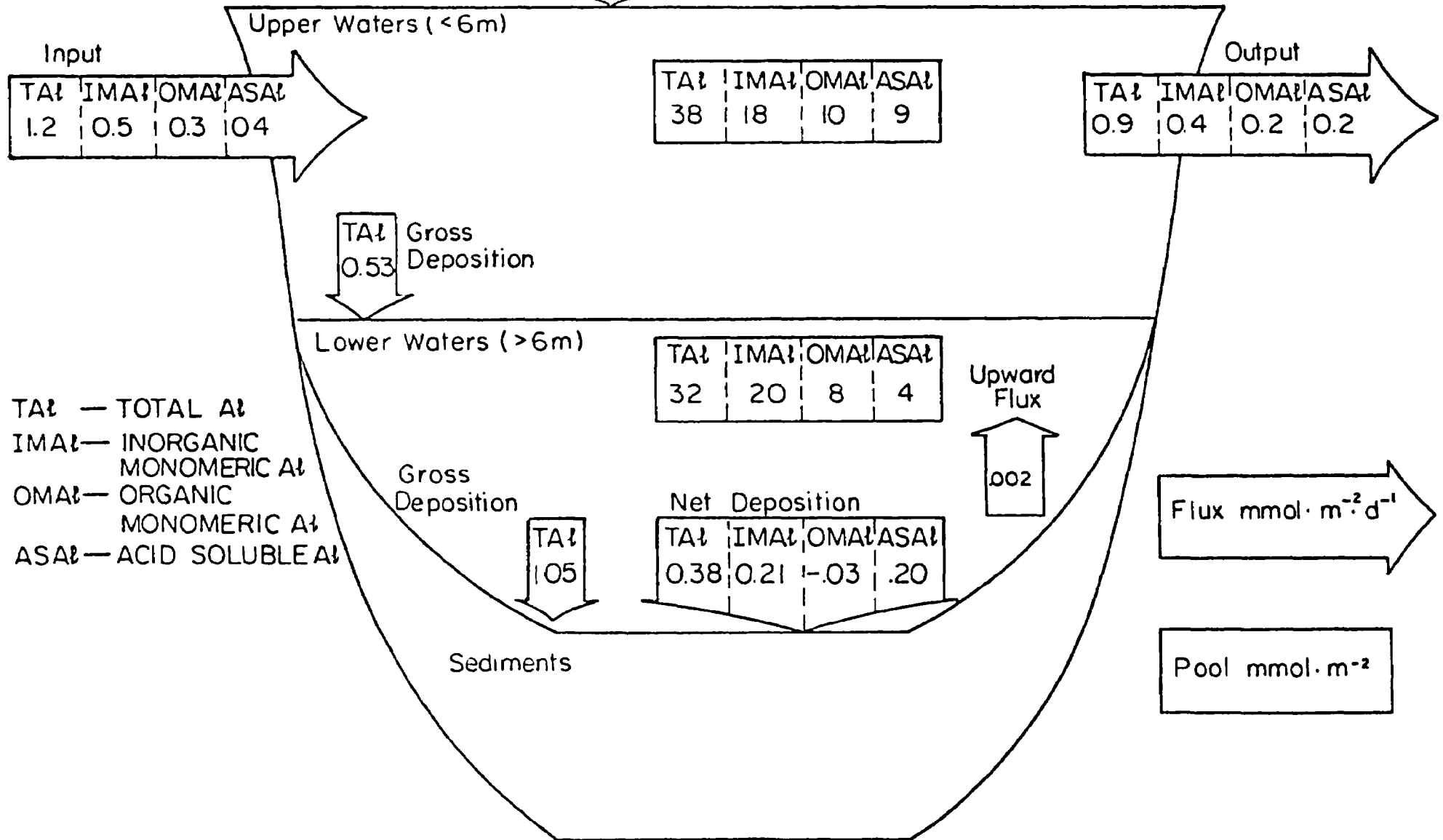| TAℓ	IMAℓ	OMAℓ	ASAℓ
0.38	0.21	-.03	.20

Flux mmol·m⁻²·d⁻¹

Pool mmol·m⁻²

Sediments

Figure 16

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APPENDIX 1

Driscoll, C.T. 1984. A procedure for the fractionation of aqueous aluminum
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A Procedure for the Fractionation of Aqueous Aluminum
in Dilute Acidic Waters

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ABSTRACT

A procedure was developed for the fractionation of aqueous aluminum. This procedure results in the determination of acid soluble aluminum, non-labile monomeric aluminum and labile monomeric aluminum. Acid soluble aluminum is thought to include colloidal aluminum and extremely non-labile organic complexes. Non-labile monomeric aluminum is thought to include monomeric alumino-organic complexes. Labile monomeric is comprised of aquo aluminum as well as inorganic complexes of aluminum. The inorganic speciation of aluminum may be calculated by using labile monomeric aluminum, pH, fluoride and sulfate data with a chemical equilibrium model.

This procedure was evaluated using synthetic and natural water solutions. In natural waters, levels of labile monomeric aluminum increased exponentially with decreases in pH below 6, while non-labile monomeric aluminum was strongly correlated with organic carbon concentration. Non-labile monomeric aluminum was observed to be relatively insensitive to changes in solution pH. Results of the aluminum fractionation procedure were in relative agreement with an independent evaluation using the fluoride ion selective electrode.

INTRODUCTION

Aluminum is the third most abundant element within the earth's crust[1]. It occurs primarily in aluminosilicate minerals, most commonly as feldspars in metamorphic and igneous rocks and as clay minerals in well weathered soils. In high elevation, northern temperate regions, the soils encountered are generally podzolic[2]. The process of podzolization involves the transport of aluminum from upper to lower soil horizons by organic acids leached from foliage as well as from decomposition in the forest floor[3,4,5,6]. Ugolini et al.[7] have observed that during podzolization there is little mobilization of aluminum from the adjacent watershed to surface waters. Concentrations of dissolved aluminum are low in most circumneutral waters due to the relatively low solubility of natural aluminum minerals. Stumm and Morgan[8] report a median aluminum value of 10 μg Al$\cdot$l^{-1} for terrestrial waters, while Bowen[9] gives a higher average concentration of 240 μg Al$\cdot$l^{-1} for freshwaters, however this includes bogs.

It has been hypothesized that mineral acids from acidic depostion have remobilized aluminum previously precipitated within the soil during podzolization or held on soil exchange sites[10]. Elevated levels of aluminum have been reported for acidic waters within regions that are receiving elevated inputs of acidic deposition[10,11,12,13,14,15,16].

Elevated levels of aluminum in dilute (low ionic strength) acidic waters are of interest because: (1) aluminum is an important pH buffer[13,17,18, 19], (2) aluminum may influence the cycling of important elements like phosphorus[13,20] and organic carbon[13,21], and (3) aluminum is potentially toxic to aquatic[22] and terrestrial organisms[23]. An understanding of the speciation of aluminum is essential for the evaluation of these processes.

Dissolved monomeric aluminum occurs as aquo aluminum, as well as hydroxide, fluoride, sulfate and organic complexes[24,25]. Past investigations of aluminum have often ignored non-hydroxide complexes of aluminum[10, 26, 27]. More recent studies of Driscoll et al.[28] and Johnson et al.[29] have demonstrated the significance of organic and fluoride complexes of aluminum in dilute acidic surface waters.

Baker and Schofield[22] observed that aluminum toxicity varies with pH and life history stage of white suckers (Catostomus commersoni) and brook trout (Salvelinus fontinalis). Aluminum solutions (> 100 to 200 μg Al·l^{-1}) resulted in reduction of survival of fish larvae. Aqueous hydroxy-aluminum forms were considered to be the most toxic to fish. pH, natural organic and inorganic (e.g. F$^-$) ligands significantly influence aluminum toxicity[22,28]. Elevated levels of soluble ligands restrict aluminum hydrolysis and mitigate aluminum toxicity to fish.

In terrestrial systems, Ulrich et.al.[23] have hypothesized that acidic deposition has reduced forest productivity. Vegetation mortality is thought to occur from dissolution of aluminum mediated by mineral acids and subsequent uptake by fine roots. While considerably less well understood than aquatic toxicity, the work of Moore[30] suggests that aluminum toxicity to vegetation is also linked to aqueous speciation.

In view of the current interest in the effects of acidic deposition and the biogeochemistry of aluminum, it is desirable for researchers to be able to analytically differentiate between forms of aqueous aluminum. In this paper I will present an analytical procedure that can be used to fractionate aqueous aluminum, and an evaluation of this procedure using synthetic and natural water samples. Potential errors associated with this technique will also be discussed.

ANALYTICAL METHODS

In this methodology three measurements of aluminum were made:

Acid Reactive Aluminum (Alr)

Solutions were acidified to a pH value of 1 for one hour and analyzed using a modification of the method of Barnes[31]. The original procedure was developed to detect levels of aluminum down to 2 µg Al · 1^{-1}. Because this level of sensivity is generally not necessary for acidic natural waters I increased the volume ratio of solvent, methyl isobutyl ketone (MIBK), to sample from 1:27 to 1:4.

Monomeric Aluminum (Ala)

Solutions were rapidly extracted with 8-hydroxyquinoline in MIBK as described by Barnes[31].

Non-labile Monomeric Aluminum (Alo)

Non-labile monomeric and labile monomeric aluminum were separated by passing an aliquot of sample through a column of strongly acidic cation exchange resin (Amberlite 120). The cation exchange column used in this study was 1 cm in diameter and contained 9.5 ml of prepared resin. Batches of resin were prepared by displacing some of the exchangeable hydrogen ion with sodium, resulting in a resin that contained both hydrogen and sodium ions on exchange sites. The amount of sodium on the exchanger was adjusted such that when an eluant of comparable ionic strength to the solutions being analyzed was passed through the exchanger, the effluent pH was similar to the pH of the solutions being analyzed. In this way the pH change that samples experienced when processed through the exchange column was minimized.

This procedure was originally developed to evaluate aluminum chemistry in surface waters and soil solutions from the Adirondack region of New York and the Hubbard Brook Experimental Forest (HBEF), New Hampshire. An eluant ionic strength of 3 x 10^{-4}, which was comparable to the mean ionic strength of these waters was used[29, 32]. In addition, two columns were used with prepared exchanger that resulted in effluent target pH values of 5 and 7. Target pH values of 5 and 7 were chosen because poorly buffered waters in New York[19] and in New Hampshire[29] often have pH values in this range. However, an exchange resin should be prepared so that the pH of processed samples will be comparable to the pH of the solutions being analyzed. If the ionic strength of a sample was less than the ionic strength of the eluant, then the pH of a sample after passage through the exchanger was greater than the target pH. Conversely, if the ionic strength of a sample was greater than the eluant, then the pH of the processed sample was generally less than the target pH of the exchanger.

An aliquot of water sample was placed in a sample reservoir and was passed through the cation exchange column with a peristaltic pump. After an initial volume of sample (50 ml to displace the eluant) was discarded, a volume of exchanger processed sample, sufficient to perform the aluminum determination, was collected. After the sample was processed, eluant (3 x 10^{-4} mol NaCl$\cdot$l^{-1}) was passed through the column to rinse the exchanger bed prior to introduction of the next sample. Samples were extracted for analysis of aluminum immediately after processing through the cation exchange column using the method of Barnes[31].

With these three measurements of aluminum, three aluminum fractions were determined (Figure 1). Non-labile monomeric aluminum (Alo) was measured directly and is an estimate of monomeric aluminum that is organically complexed. Labile monomeric aluminum was determined by the difference between monomeric aluminum

and non-labile monomeric aluminum (Ala-Alo). This fraction of aqueous aluminum would include aquo aluminum as well as hydroxide, sulfate and fluoride complexes of monomeric aluminum. Acid soluble aluminum, which is acid reactive aluminum less total monomeric aluminum (Alr - Ala), represents an estimate of the aluminum that requires acid dissolution for the determination. This fraction would include colloidal aluminum, polymeric aluminum and very strongly bound alumino-organic forms.

The inorganic speciation of aluminum can be calculated by using measured values of labile monomeric aluminum, pH, fluoride and sulfate with one of the chemical equilibrium models that are currently available[33]. Chemical equilibrium relationships for aqueous aluminum species used in this study are listed in Table 1 and these calculations are summarized by Driscoll[16] and Johnson et al.[29]

To independently evaluate the aluminum fractionation procedure I used the fluoride ion selective electrode. Free fluoride was determined by direct potentiometric determination using the fluoride ion selective electrode. Total fluoride was determined by electrode after addition of a total ionic strength adjustor and buffer (TISAB II) solution[34]. TISAB decomplexes fluoride, provides a constant solution ionic strength, and adjusts solution pH so that hydrogen ion and hydroxyl interference are minimized. With values of free and total fluoride, aquo aluminum (Al^{3+}) activity was calculated with thermodynamic relationships (Table II). In turn, inorganic species of aluminum and organic aluminum were calculated (Table II). While it is possible to use the fluoride ion selective electrode as an independent method to fractionate aluminum, this procedure has not been fully evaluated. Therefore, I have chosen to use the fluoride electrode method just as a quality assurance check on the cation exchange separation procedure.

For additional analytical details or description of the study sites from which the Adirondack New York or HBEF surface water samples were collected see Driscoll[16] or Johnson et al.[29] respectively.

DISCUSSION OF THE PROCEDURE

Short-term transformations of aqueous aluminum are generally dependent on the concentration of monomeric aluminum (or more specifically the activity of aquo aluminum), rather than particulate aluminum. Because of the tendency for aluminum hydroxy cations to polymerize through double OH bridging when values of solution pH exceed 4.5[36], a considerable fraction of the "dissolved" aluminum reported in many analyses of natural water having neutral or slightly acidic pH values may consist of suspended microcrystals of aluminum hydroxide. Filtration of samples through 0.4 μm pore size membranes, a common practice in clarifying natural water prior to analysis, may fail to remove such material[39]. Therefore, it is desirable to use an analytical technique that is selective for monomeric aluminum, rather than assuming that filtration or centrifugation will remove all suspended material. While detection of aluminum by other analytical techniques may be used with this fractionation procedure, the technique of complexation by 8-hydroxyquinoline and rapid extraction has the advantage of selecting for monomeric aluminum. This technique has been evaluated and discussed by numerous researchers[31, 38, 40, 41, 42, 43, 44, 45].

The cation exchange resin has a strong affinity for aluminum. When solutions are passed through the cation exchange column, there is a competition between aqueous ligands and the exchanger for aluminum. Addition of synthetic aluminum solution (18 μmol Al l^{-1} as $AlK(SO_4)_2$ and $AlCl_3$ at pH 5) to the cation exchange

column resulted in complete removal (< 0.1 μmol Al·l^{-1}) at all application

rates evaluated (up to 6.3 ml·min^{-1}·ml of exchanger bed volume^{-1}). Application

of synthetic aluminum fluoride solutions (18 μmol Al·l^{-1} with 1-10 μmol F·l^{-1}

at pH 5) to the cation exchange column revealed that the exchanger competes very

effectively with fluoride for aluminum. Aluminum was completely removed from

solution (< 0.1 μmol·l^{-1}) and total fluoride in the effluent equaled influent

levels. Treatment of synthetic and natural solutions by the cation exchange

column resulted in the conversion of fluoride from predominately aluminum bound

fluoride to free fluoride.

It would appear that aquo aluminum was stripped from inorganic ligands by

the polar cation exchange resin and therefore inorganic forms of aluminum

(e.g. Al^{3+}, AlF^{2+}, AlOH^{2+}) were readily removed from solution. Organic ligands,

however, form strong complexes with aluminum and therefore more effectively com-

pete with the cation exchange resin. Synthetic solutions of aluminum in the

presence of a strong ligand, sodium citrate, (18 μmol Al·l^{-1}, 1 mmol sodium

citrate·l^{-1} at pH 5) were applied to the cation exchange column. The level

of sodium citrate used was comparable to levels of dissolved organic carbon

(DOC) observed in Adirondack New York[16] and HBEF[29] surface waters on an organic

carbon basis. In this experiment, detection of aluminum in influent and efflu-

ent solutions was complicated because citrate effectively competes with 8-hydro-

xyquinoline for aluminum and therefore interfered with the analytical determina-

tion. As a result, in sodium citrate solutions aluminum had to be determined

using the less sensitive and less reproducible method of direct determination by

atomic absorption spectrophotometry (AAS) with graphite furnace. Although

aluminum determinations by AAS should be viewed with caution, the results of this

experiment suggested that aluminum was effectively transported through the cation

exchange column in the presence of relatively high levels of citrate.

Analog organic ligands with a strong affinity for aluminum (such as citrate) not only interfere with the 8-hydroxyquinoline determination of aluminum but are not entirely representative of organic ligands occurring in natural waters. Therefore, this fractionation procedure was evaluated in more detail using samples collected from acidic and non-acidic surface waters in the Adirondack region of New York[16, 32] and at the HBEF New Hampshire[29, 46].

The measured concentration of non-labile monomeric aluminum in natural water samples was somewhat dependent on the flow rate of solution through the column (Figure 2). My results indicate at low application rates to the column, the amount of monomeric aluminum (non-labile) passing through the column was sensitive to flow. However, with higher application rates (above 2.7 ml $\cdot$ min^{-1} $\cdot$ ml of exchanger bed volume^{-1}) the concentration of aluminum passing through the column became constant. These results suggest that natural alumino-organic complexes exhibit a range of stability. Similar results have been demonstrated by Means et al.[47], who observed labile metal complexes as well as very stable complexes in natural water samples.

The longer the sample retention time in the column, the greater the disruption of alumino-organic species by the resin. This disruption was minimized by operating the exchange column at a relatively high application rate (3.7 - 4.2 ml $\cdot$ min^{-1} $\cdot$ ml of resin bed volume^{-1}). As mentioned previously, leakage of inorganic aluminum through the column was not observed at these application rates.

In this analysis it was assumed that organic matter and alumino-organic complexes passed through the exchanger while aluminum associated with inorganic forms was retained on the exchanger, resulting in an effective partitioning between inorganic and organic forms of monomeric aluminum. Several

sources of evidence suggest that this assumption was reasonably valid. (1) In samples from several Adirondack lakes and streams containing a wide range of total organic carbon concentration (0.17 - 1.20 mmol $C \cdot l^{-1}$) and pH values (4.0 - 7.2), the amount of TOC leaving the column ranged from 93 - 105% of that entering the column. Unfortunately, a mass balance on organic carbon is unsuitable to assess the extent to which dissolved organic carbon and organic forms of aluminum are retained within the column due to the potential for organic carbon leaching from the organic resin.

(2) Perhaps a better indicator of the limited extent to which organic carbon was retained within the resin was that there was little difference in the ultraviolet spectral (200 - 400 nm) pattern of exchange column influent and effluent (Figure 3). It is evident that absorbance of column effluent exceeded influent absorbance at low wavelengths in some samples. The nature of this discrepancy was not apparent, although organic carbon leaching from the resin cannot be disregarded. UV absorbance patterns observed in this study were similar to those presented by Schnitzer and Khan[48] as being typical of naturally occuring organic carbon.

(3) Additional evidence for the validity of this fractionation technique is available from field observations. Levels of labile monomeric (and aquo) aluminum increased exponentially with decreases in pH in Adirondack[16,32] ($p \{Al^{3+}\} = -6.55 + 2.55$ pH, $n = 321$, $r^2 = 0.93$, $p < 0.0001$) and HBEF[29] ($p \{Al^{3+}\} = -8.42 + 2.95$ pH, $n = 34$, $r^2 = 0.92$, $p < 0.0001$) surface waters. Non-labile monomeric aluminum was not correlated with pH, but was strongly correlated with organic carbon concentration in both Adirondack[16,32] (Alo $= -3.26 \times 10^{-6} + 0.0204$ TOC, where Alo and TOC are in mols $\cdot l^{-1}$, $n = 322$, $r^2 = 0.76$, $p < 0.0001$) and HBEF (G. Lawrence unpublished data, Alo $= -7.3 \times 10^{-7} + 0.0155$ DOC, $n = 69$, $r^2 = 0.85$, $p < 0.0001$) waters.

Driscoll et. al.[32] observed pronounced temporal variations in aluminum
fractions in Adirondack streams. During snowmelt and autumn rainfall events,
pH values were low and levels of labile monomeric aluminum were high. During
low flow, high pH (pH > 5.5) periods in the summer, monomeric aluminum levels
were elevated (>10 μmol Al $\cdot$ l^{-1}) but this aluminum was entirely attributed to
non-labile monomeric aluminum. Driscoll et al.[32] and Johnson et al.[29] have
reported that when aquo aluminum was calculated from the labile monomeric
aluminum determination, values were compatible with aluminum trihydroxide
solubility.

To evaluate the extent to which non-labile monomeric aluminum was sensi-
tive to variations in pH, I spiked aliquots of Adirondack stream water with
1 mmol $\cdot$ l^{-1} Tris (Tris (Hydroxy methyl) aminomethane) buffer and incrementally
adjusted the pH over a range of values with 0.1 N HCl. This was used to buffer
the solution in the pH range 5.5 - 7.0. Because solution pH values are well
below the proton dissociation constant of Tris (pKa = 8.08), complexation
of aluminum was considered to be insignficant. These solutions were incubated
for one week and analyzed for pH and non-labile monomeric aluminum. Variations
in non-labile monomeric aluminum were relatively insensitive to variations in
pH (Figure 4). The concentration of non-labile monomeric aluminum decreased
24% at pH 3.34 and 15% at pH 6.88 from a maximum value at pH 4.96. The reduction
in the magnitude of the alumino-organic complex in the low pH range might be
attributed to the disruption of the complex by hydrogen ion. The subtle reduc-
tion at higher pH values (> 5) may be due to aluminum hydrolysis and competition
of hydroxide ligands with the organic ligands for the aluminum central metal
cation or possibly due to complexation of aluminum by dissociated Tris.

These results, together with the observation that non-labile monomeric aluminum levels in natural water samples were not appreciably different when analyzed with pH 5 and pH 7 columns suggests that the pH change associated with cation exchange treatment effects the determination of non-labile monomeric aluminum only to a limited extent.

There are a number of potential sources of error associated with this fractionation procedure. (1) 8-hydroxyquinoline may desorb aluminum associated with particulate matter and therefore result in an overestimation of levels of monomeric aluminum. (2) The exchanger may disrupt relatively labile organic complexes as suggested by Means et al.[46]. Although this error is minimized by decreasing the sample retention time in the column, it undoubtedly still occurs to some extent. (3) Alumino-organic complexes may exchange/adsorb on resin sites. If the pH within the exchanger bed is low, organic matter may complex hydrogen ion and thereby release aluminum to the resin and/or precipitate within the column. (4) If the pH within the exchanger bed is higher than the sample pH, aluminum associated with organic ligands may hydrolyze and adsorb and/or precipitate within the column. It is noteworthy that all of these sources of error result in an underestimation of the organically complexed fraction of monomeric aluminum.

As previously mentioned, the fluoride ion selective electrode may be used to independently evaluate the cation exchange column procedure for the separation of inorganic and organic forms of monomeric aluminum. However, as with the exchange column procedure there are a number of potential sources of error associated with using the fluoride ion selective electrode to fractionate aluminum. These potential errors include: (1) hydroxide and

non-aluminum cation interference in the determination of free fluoride, (2) the measurement of fluoride associated with particulate matter in the determination of free fluoride, (3) changes in the pH, aluminum and free fluoride levels after sampling and during the period of time the solution is being analyzed, and (4) errors in and lack of thermochemical data used to make the calculations of ion distribution.

A comparison of the two methods was made on selected Adirondack surface water samples. To minimize problems associated with changes during sample storage, pH and free fluoride levels were measured and monomeric aluminum was extracted in the field shortly after sample collection. Organic monomeric aluminum determined by the fluoride ion selective electrode was compared with non-labile monomeric aluminum determined by the column fractionation procedure (Figure 5). At low aluminum levels, agreement was good between the two methods, but at higher concentrations, organic monomeric aluminum calculated from the fluoride ion selective electrode measurements was generally greater than non-labile monomeric aluminum determined by the cation exchange column procedure. Further research is needed to quantify the errors associated with both fractionation techniques.

CONCLUSIONS

This procedure can be used to fractionate aqueous aluminum into acid soluble aluminum, non-labile monomeric aluminum and labile monomeric aluminum. 'Acid soluble aluminum is thought to include colloidal aluminum as well as very non-labile organic complexes. Non-labile monomeric aluminum is considered to approximate levels of organically complexed monomeric aluminum in solution. Labile monomeric aluminum would include aquo aluminum as well as inorganic complexes of aluminum. This procedure was applied with reasonable success to studies of dilute acidic waters from the Adirondack region of New York and the Hubbard Brook Experimental Forest in New Hampshire. This methodology is significant because it enables researchers to gain a better understanding of the biogeochemistry of aluminum.

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TABLE I

EQUILIBRIUM RELATIONSHIPS USED IN THIS STUDY

Equation (Hydroxide Ligands)		Equilibrium Constant	Reference
$Al^{3+} + H_2O = Al(OH)^{2+} + H^+$;	$KOH_1 =$	1.03×10^{-5}	(35)
$Al^{3+} + 2H_2O = Al(OH)_2^+ + 2H^+$;	$KOH_2 =$	7.36×10^{-11}	(35)
$Al^{3+} + 4H_2O = Al(OH)_4^- + 4H^+$;	$KOH_4 =$	6.93×10^{-23}	(35)
(Fluoride Ligands)			
$Al^{3+} + F^- = AlF^{2+}$;	$KF_1 =$	1.05×10^7	(36)
$Al^{3+} + 2F^- = AlF_2^+$;	$KF_2 =$	5.77×10^{12}	(36)
$Al^{3+} + 3F^- = AlF_3$;	$KF_3 =$	1.07×10^{17}	(36)
$Al^{3+} + 4F^- = Al_4^-$;	$KF_4 =$	5.37×10^{19}	(36)
$Al^{3+} + 5F^- = AlF_5^{2-}$;	$KF_5 =$	8.33×10^{20}	(36)
$Al^{3+} + 6F^- = AlF_6^{3-}$;	$KF_6 =$	7.49×10^{20}	(36)
(Sulfate Ligands)			
$Al^{3+} + SO_4^= = AlSO_4^+$;	$KS_1 =$	1.63×10^3	(37)
$Al^{3+} + 2 SO_4^= = Al(SO_4)_2^-$;	$KS_2 =$	1.29×10^5	(37)

TABLE II

CALCULATION OF ALUMINUM SPECIATION USING THE FLUORIDE ION SELECTIVE ELECTRODE

Aluminum Bound Fluoride

$$[F - Al] = [F_T] - [F^-] = [F_T] - \{F^-\}/\gamma_1$$

$$[F-Al] = [AlF^{2+}] + 2[AlF_2^+] + 3[AlF_3] + 4[AlF_4^-] + 5[AlF_5^{2-}] + 6[AlF_6^{3-}]$$

$$[F-Al] = \{Al^{3+}\}\{F^-\} KF_1/\gamma_2 + 2\{Al^{3+}\}\{F^-\}^2 KF_2/\gamma_1 + 3\{Al^{3+}\}\{F^-\}^3 KF_3 +$$
$$4\{Al^{3+}\}\{F^-\}^4 KF_4/\gamma_1 + 5\{Al^{3+}\}\{F^-\}^5 KF_5/\gamma_2 + 6\{Al^{3+}\}\{F^-\}^6 KF_6/\gamma_3$$

Aquo Aluminum

$$\{Al^{3+}\} = [F-Al] \; (\{F^-\} KF_1/\gamma_2 + 2\{F^-\}^2 KF_2/\gamma_1 + 3\{F^-\}^3 KF_3 +$$
$$4\{F^-\}^4 KF_4/\gamma_1 + 5\{F^-\}^5 KF_5/\gamma_2 + 6\{F^-\}^6 KF_6/\gamma_3)^{-1}$$

Hydroxide Complexed Aluminum

$$[Al-OH] = \{Al^{3+}\}KOH_1/\{H^+\}\gamma_2 + \{Al^{3+}\} KOH_2/\{H^+\}^2\gamma_1 +$$
$$\{Al^{3+}\}KOH_4/\{H^+\}^4 \gamma_1$$

Fluoride Complexed Aluminum

$$[Al-F] = \{Al^{3+}\}\{F^-\}KF_1/\gamma_2 + \{Al^{3+}\} \{F^-\}^2 KF_2/\gamma_1 + \{Al^{3+}\} \{F^-\}^3 KF_3 +$$
$$\{Al^{3+}\}\{F^-\}^4 KF_4/\gamma_1 + \{Al^{3+}\}\{F^-\}^5 KF_5/\gamma_2 + \{Al^{3+}\}\{F^-\}^6 KF_6/\gamma_3$$

Sulfate Complexed Aluminum

$$[Al-SO_4] = \{Al^{3+}\} [SO_4^{2-}] \gamma_2 KS_1/\gamma_1 + \{Al^{3+}\}[SO_4]\gamma_2 KS_2/\gamma_1$$

Inorganic Monomeric Aluminum

$$IMAL + \{Al^{3+}\} /\gamma_3 + [Al-OH] + [Al-F] + [Al-SO_4]$$

Organic Monomeric Aluminum

$$OMAL = Al_a - IMAL$$

where: $\{ \; \}$ is species activity $(mol \cdot l^{-1})$

$[\;]$ is species concentration $(mol \cdot l^{-1})$

TABLE II (continued)

[F-Al], aluminum bound fluoride (mol . 1^{-1})

[F_T], total fluoride (mol$\cdot 1^{-1}$)

[Al-OH], hydroxide complexed aluminum (mol . 1^{-1})

[Al-F], fluoride complexed aluminum (mol . 1^{-1})

[Al-SO$_4$], sulfate complexed aluminum (mol . 1^{-1})

IMAl, inorganic monomeric aluminum (mol . 1^{-1})

OMAl, organic monomeric aluminum (mol . 1^{-1})

Ala, monomeric aluminum (mol$\cdot 1^{-1}$)

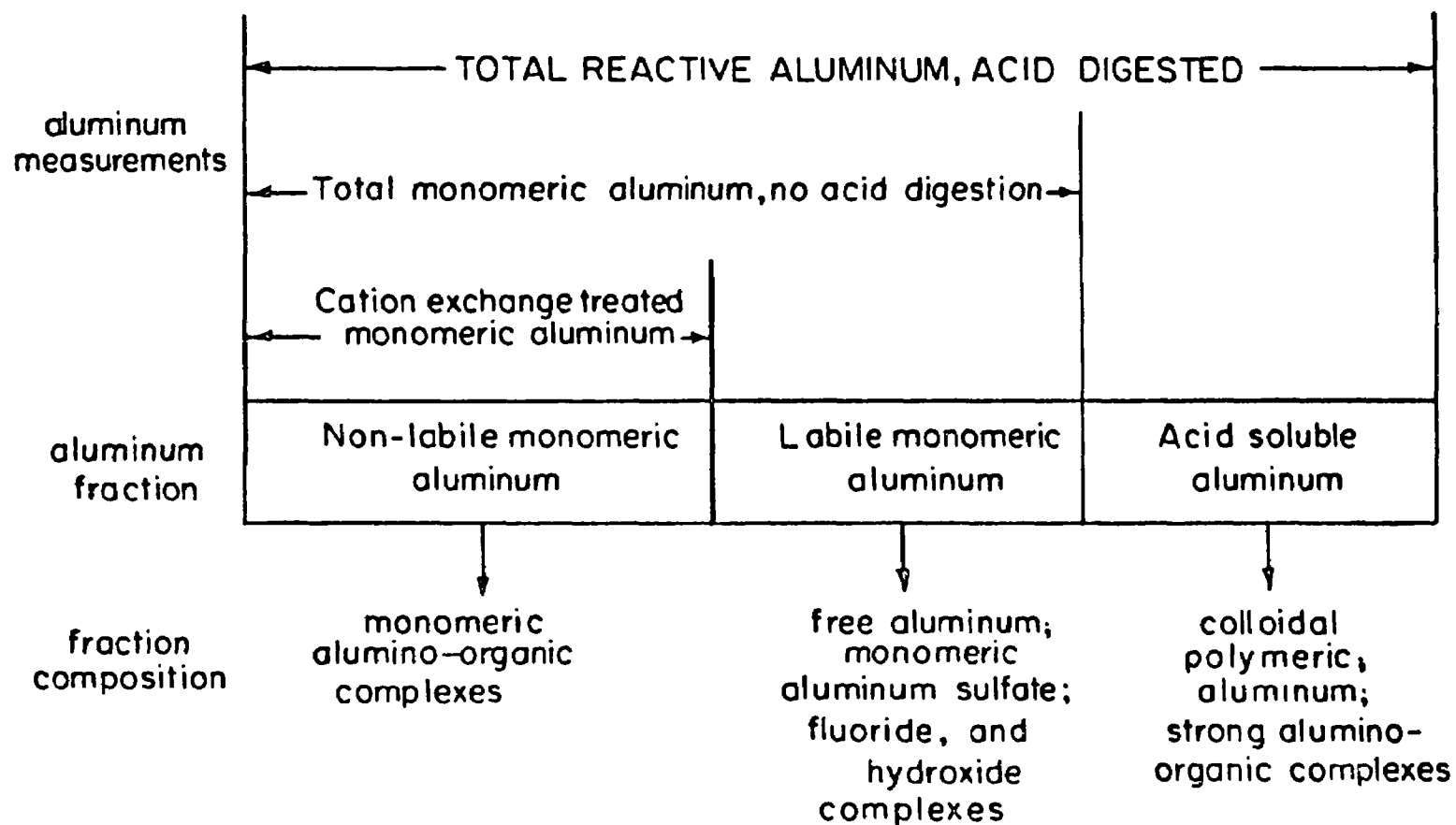γ_1, γ_2, γ_3, mean activity coefficients for monovalent, divalent
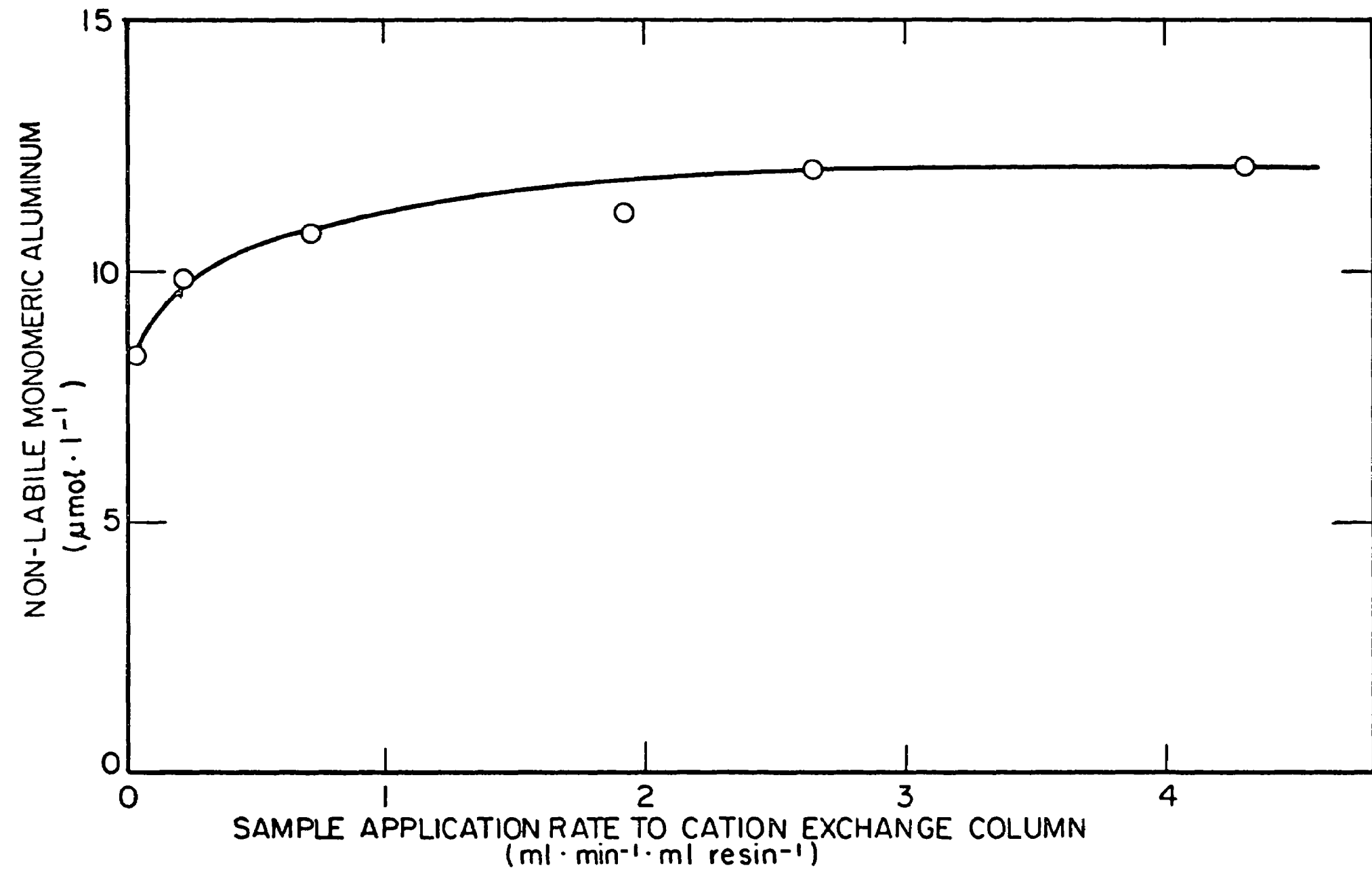   and trivalent species, respectively

KF_n, KOH_n, KS_n, thermodynamic stability constants for fluoride,
       hydroxide and sulfate complexes, respectively; see
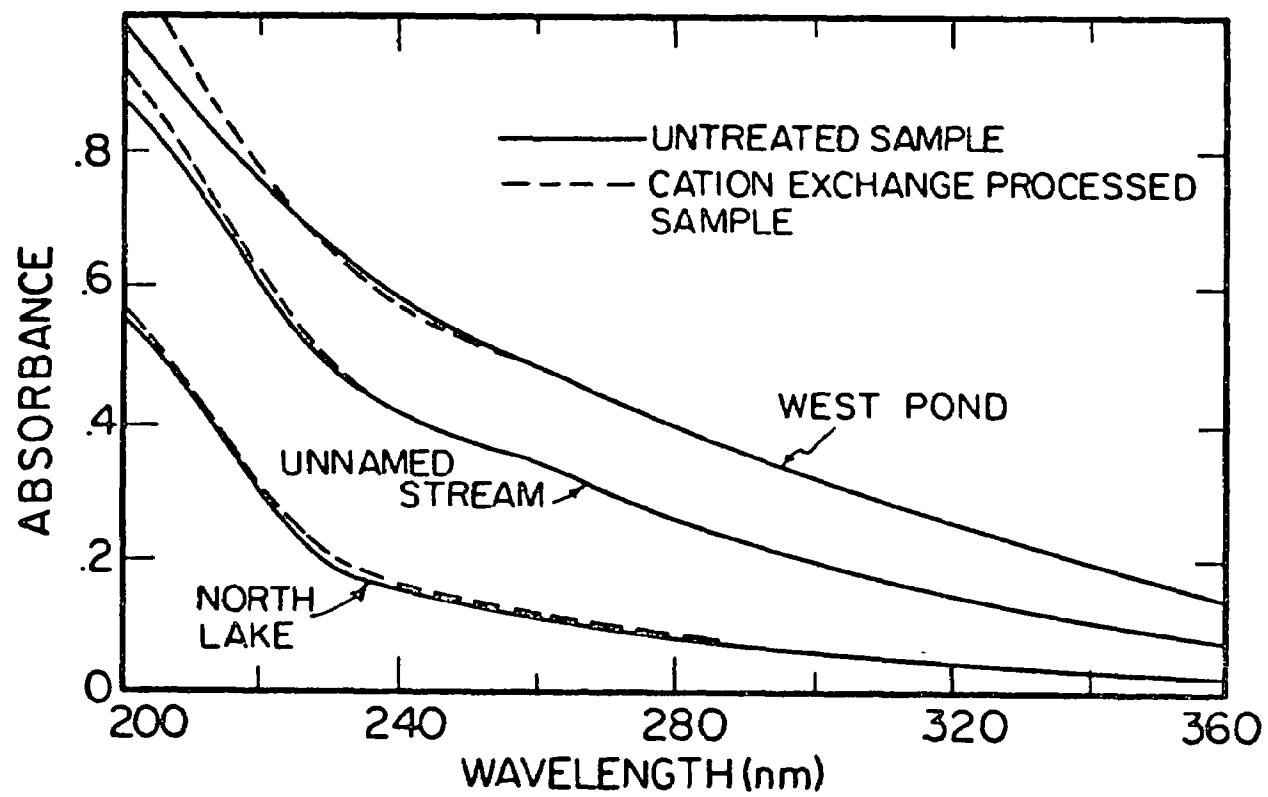   Table I for values

FIGURE TITLES

Figure 1   A schematic representation of the aluminum fractionation
            procedure

Figure 2   Concentration of monomeric aluminum from cation exchange
            column effluent (non-labile monomeric aluminum) as a func-
            tion of the sample application rate to the column. This
            sample was collected from an unnamed stream in the
            Adirondack region of New York on 7/27/77 (pH = 4.32,
            TOC = 1.2 mmol $\cdot$ 1^{-1}).

Figure 3   Ultraviolet wavelength scans of selected Adirondack
            water samples (collected on 7/4/78, West Pond, pH = 6.51,
            TOC = 1.2 mmol $\cdot$ 1^{-1}; unnamed stream, pH = 4.37, TOC =
            0.79 mmol $\cdot$ 1^{-1}; North Lake, pH = 4.96, TOC = 0.41
            mmol $\cdot$ 1^{-1}) for cation exchange column influent and
            effluent.

Figure 4   Non-labile monomeric aluminum concentration of aliquots
            of an unnamed stream sample (collected on 5/18/78
            initially with pH = 4.31, TOC = 0.70 mmol $\cdot$ 1^{-1}, Al_0 =
            15.4 μ mol $\cdot 1^{-1}$) which were buffered (1 mmol Tris $\cdot$ 1^{-1})
            and solution pH adjusted (0.1 N HCl).

Figure 5   A comparison of non-labile monomeric aluminum levels
            determined using the cation exchange column separation
            procedure with organic monomeric aluminum concentrations
            calculated using free and total fluoride determinations
            with thermochemical data (Tables I, II) for selected
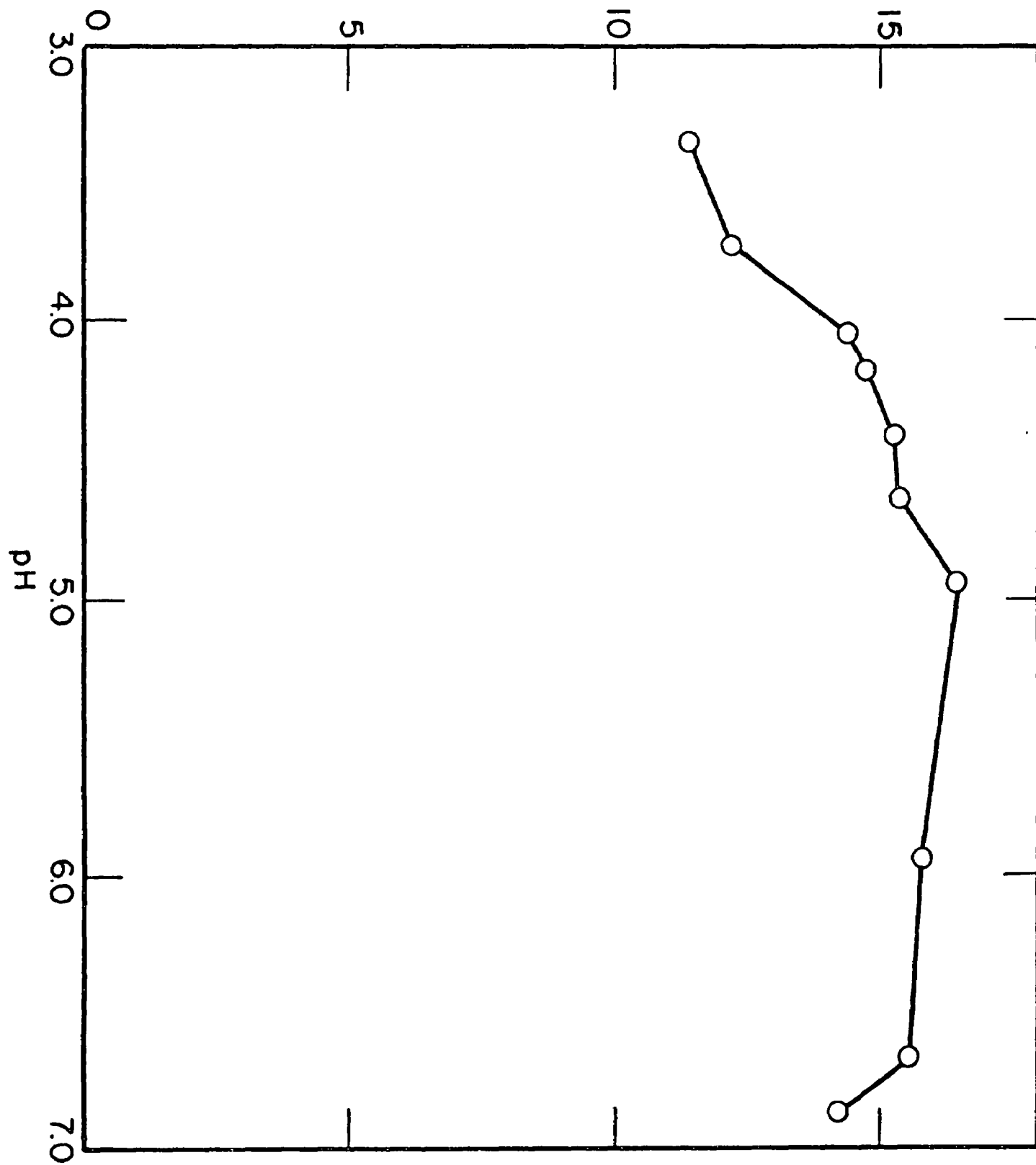   Adirondack surface water samples (collected on 1/20-1/22/83).

SCHEMATIC REPRESENTATION OF THE ALUMINUM FRACTIONATION PROCEDURE

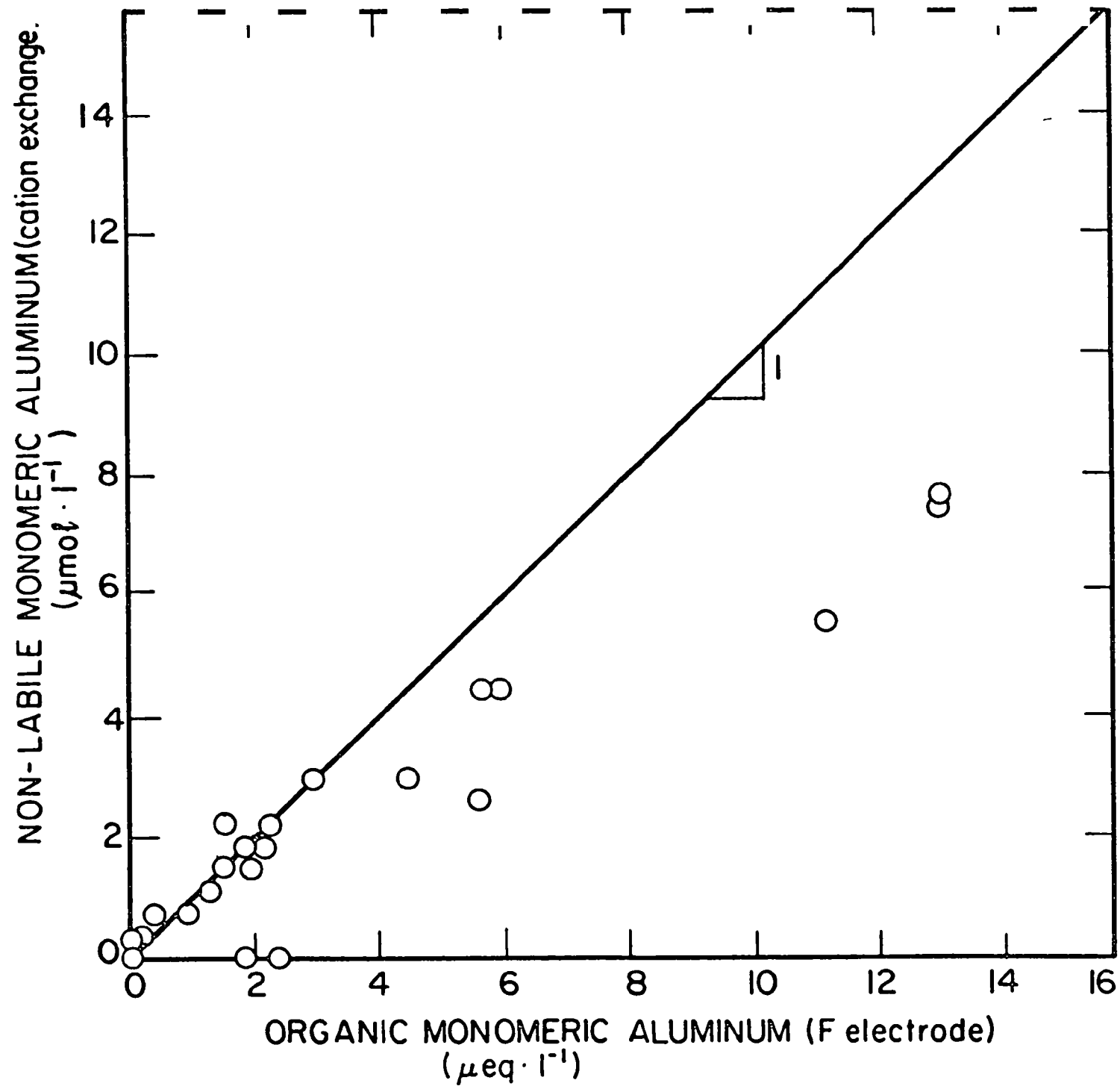| aluminum measurements	TOTAL REACTIVE ALUMINUM, ACID DIGESTED		
	←—— Total monomeric aluminum, no acid digestion —→		
	←— Cation exchange treated monomeric aluminum —→		
aluminum fraction	Non-labile monomeric aluminum	Labile monomeric aluminum	Acid soluble aluminum
fraction composition	monomeric alumino-organic complexes	free aluminum; monomeric aluminum sulfate; fluoride, and hydroxide complexes	colloidal polymeric, aluminum; strong alumino-organic complexes

NON-LABILE MONOMERIC ALUMINUM
(mol · l⁻¹)

APPENDIX 2

Driscoll, C.T. and G.C. Schafran. 1984. Characterization of short term
    changes in the base neutralizing capacity of an acidic Adirondack, NY
    lake. Nature (submitted for publication).

Characterization of Short Term Changes in the

Base Neutralizing Capacity of an Acidic Adirondack, NY Lake

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There is currently much concern and controversy over the effects of acidic deposition on low ionic strength surface waters. As a result, there has been much discussion in the recent literature on the nature and extent of proton transformations within acid sensitive ecosystems[1,2,3,4]. The source of base neutralizing capacity (BNC) within acidic surface waters has been attributed to atmospheric deposition of H_2SO_4 (or SO_2)[5,6] or HNO_3[7] as well as production of soluble organic acids from soils[8]. Unfortunately many of these studies have failed to adequately characterize aluminum, which is often a very significant component of BNC in acidic waters.[9] Because of the current interest in surface water acidification, we have evaluated the nature of short term changes in the BNC of an acidic clearwater lake. Our results suggest that much of the variation in hydrogen ion and aluminum BNC can be attributed to changes in nitrate concentration, rather than variations in sulfate, chloride, or organic anion concentrations.

The study site, Dart Lake, is located in the Adirondack Mountain region of New York State, U.S.A. (74°52'W, 43°48'N). The watershed drainage area is 107 Km^2, and the lake volume is 1.02 x $10^7 m^3$ with a mean depth of 7.1 m. Dart Lake has a single outlet and our water budget indicates that 95% of the outlet flow (7.25 x 10^7 m^3 yr^{-1}) enters the lake at the major inlet. Samples were collected for water quality analysis at the inlet, outlet and at seven depths from a pelagic

sampling station approximately every two weeks over an annual cycle (10/25/81-11/21/82). Shortly after collection samples were measured for pH and dissolved inorganic carbon (DIC), ampulated for dissolved organic carbon (DOC) analysis, and extracted for monomeric aluminum using the procedure of Barnes[10]. Monomeric aluminum was fractionated into labile and non-labile forms using the cation exchange column method of Driscoll[11,12]. Samples were analyzed in the laboratory for all major solutes[13].

Selected samples, collected from drainage waters in the Dart Lake watershed, were processed and titrated[9] to characterize the proton dissociation of naturally occurring organic solutes. These data were fit to a monoprotic proton dissociation model using a modified Gran plot analysis[9]. A statistically significant empirical relationship was observed between DOC concentration and mols of proton dissociation sites per liter (C_T = 0.025 DOC + 8.0; where C_T is the proton dissociation sites on organic solutes in μmols l^{-1} and DOC is in μmols l^{-1}; n = 13, r^2 = 0.69, p < 0.01). A relatively consistent fit to a proton dissociation constant was also obtained (pKa = 4.53 ± 0.25). Our detailed observations of DOC were applied to this model to estimate the BNC due to organic solutes and the organic anion concentration of water samples.

Because of poor precision, slow kinetics associated with heterogeneous phase reactions, and the inability to characterize individual components, BNC was not determined by titration. Rather the individual components of BNC were calculated, using a chemical equilibrium model[14], as the amount of strong base required to increase the pH of a liter of solution to a value of 8.3. The thermochemical data used in our analysis are summarized elsewhere[11,12] and thermodynamic calculations were corrected for the effects of temperature and ionic strength. In these calculations we assumed that labile monomeric aluminum was a good estimate of inorganic forms of aluminum and that non-labile monomeric aluminum did not significantly

accept or donate protons. The close electroneutrality balance supports the assumptions and procedures used in this study for the characterization of aluminum and DOC (Table 1). Further information on the site description, hydrology, sampling and analytical methods, thermal and water quality data, and data analysis are available elsewhere[13].

Although H_2CO_3 was the major component of BNC in Dart Lake (Table 1), levels of hydrogen ion and aluminum BNC in acidic lakes are generally of more interest because of potential toxicity to organisms[15,16]. Variations in hydrogen ion and aluminum BNC (H-Al-BNC) of all samples collected (n = 178) were strongly correlated with variations in nitrate concentration (H-Al-BNC = 0.94 NO_3^- + 2.4; μeq l^{-1}, r^2 = 0.54, p < 0.0001). Note that this empirical correlation is linear with a slope close to one and an intercept near the origin. Although SO_4^{2-} was the dominant anion in Dart Lake (Table 1), no statistically significant relationship with H-Al-BNC was observed. H-Al-BNC was weakly correlated with organic anion concentration (H-Al-BNC = 33.3 ($RCOO^-$) -481; where $RCOO^-$ represents the organic anion content in μeq l^{-1}, r^2 = 0.13, p < 0.0001) and no statistically significant relationship was observed with Cl^-.

Water quality observations in Dart Lake suggest that biogeochemical processes result in temporal and spatial variations in NO_3^-, which influence hydrogen ion and aluminum BNC (Figure 1). In the autumn NO_3^-, H-BNC, and Al-BNC exhibited an orthograde distribution in Dart Lake. During ice cover, NO_3^-, H-BNC, and Al-BNC increased in the upper waters. These trends were presumably due to freeze-concentration at the ice-water interface and/or higher concentrations associated with stream inputs, which flow along the lake surface because of winter thermal stratification[17]. Concentrations of all three constituents decreased with increasing lake depth.

Although the lake was aerobic throughout the study period (a minimum D.O. of 41 μmol l^{-1} was observed at 14 m depth on 1 Oct. 1982), we attribute these lower water depletions of BNC to sediment reduction of NO_3^- and the resulting production of acid neutralizing capacity (ANC).

During the snowmelt period (3/1-5/1), 34% of the annual discharge entered Dart Lake. Inlet concentrations of H-Al-BNC and NO_3^- were significantly greater during snowmelt (3/1 - 5/1, flow = 8.9 ± 6.9 $m^3 s^{-1}$, H-Al-BNC = 52 ± 11, NO_3^- = 51 ± 11) than during either summer - autumn (6/1 - 11/1, flow = 1.7 ± 1.7 $m^3 s^{-1}$, H-Al-BNC = 18 ± 5; p < 0.05 student t test NO_3^- = 24 ± 5, p < 0.05) or winter (11/1 - 3/1, flow = 1.5 ± 1.0 $m^3 s^{-1}$, H-Al-BNC = 23 ± 6; p < 0.05; NO_3^- = 26 ± 6, p < 0.1) base flow periods. These inputs resulted in high levels of NO_3^-, H-BNC and Al-BNC throughout Dart Lake prior to summer stratification (Figure 1).

During summer stratification, NO_3^-, H-BNC and Al-BNC were depleted in the upper and lower waters of Dart Lake, resulting in a positive heterograde distribution. We attribute the upper water depletion to algal assimilation of NO_3^- [18] or littoral sediment denitrification and the lower water depletion to pelagic sediment denitrification. A number of investigators have reported that the net assimilation of nitrate results in the production of ANC and an increase in pH values[19,20]. Groundwater inflow, enriched in ANC, basic cations (Ca^{2+}, Mg^{2+}, Na^+, K^+) and dissolved silica from soil weathering reactions, could also deplete H-Al-BNC during summer low-flow conditions. However, we observed no statistically significant variations in the inlet concentrations of basic cations and dissolved silica over the study period, suggesting that base flow input of ANC was not a significant mechanism of H-Al-BNC neutralization. In the extreme lower waters (below 12m, which is

5% of the lake volume) during stratification, transformations of Fe, Mn, DOC, Ca^{2+}, and NH_4^+ contributed to the depletion of H-BNC and Al-BNC in Dart Lake. However, on a whole-lake basis nitrogen transformations affecting NO_3^- concentration appear to be the predominant mechanism regulating short-term changes in hydrogen ion and aluminum in solution.

The results of synoptic surveys indicate that NO_3^- levels are generally higher in the Adirondack lake district than other lake districts in eastern North America[21] with low ionic strength waters (Table 2). A difficult but critical problem is to identify the source of this nitrate. Johannes et al.[27] indicated that NO_3^- storage in snowpack from the Adirondack region is generally greater than SO_4^{2-}. Galloway et al.[7] have attributed the decrease in the ANC that occurs in the Adirondack lake outlets during snowmelt to a reduction in basic cation release from soils and the addition of nitric acid from snowpack. While snowpack nitrate undoubtedly contributes to the elevated levels observed in Adirondack lake waters, decomposition and oxidation of organic nitrogen within the adjacent soil may also result in the release of nitrate and BNC to solutions[28,29].

Because of these apparently high NO_3^- levels in Adirondack waters we wanted to evaluate the extent to which changes in ambient anion concentrations (SO_4^{2-}, NO_3^-, RCOO$^-$) result in changes in solution pH. To accomplish this, we simulated the response of Dart Lake water (Table 1) to additions and reductions in HNO_3, H_2SO_4, and the protonated form of naturally occurring organic solutes using a chemical equilibrium model[14]. Modest additions and depletions of NO_3^- resulted in significant changes in pH, while Dart

Lake appears to be well buffered with respect to changes in DOC (Figure 2). The latter response may be attributed to the relatively low density of proton dissociation sites per mole of organic carbon and indicates that deprotonation of organic acids probably has not contributed significantly to the acidification of Dart Lake. When NO_3^- levels were reduced to values comparable to other lake districts in Eastern North America ($\sim 2 \mu eq\ l^{-1}$) pH values approached neutrality. Like nitrate, variations in the concentration of H_2SO_4 result in an equivalent change in H-Al-BNC. Because SO_4^{2-} is the dominant anion in Dart Lake solutions (Table 1), neutralization can also be accomplished by a reduction in the concentration of H_2SO_4. Note that in extremely acidic (pH < 4.8) Adirondack lakes H-Al-BNC generally exceeds NO_3^- concentrations[22]. Therefore surface water acidification in the Adirondacks cannot be entirely attributed to HNO_3, but more probably a combination of H_2SO_4 and HNO_3 inputs.

Although SO_4^{2-} is generally the dominant anion in Adirondack surface waters[22] and in atmospheric inputs to the region[29], additions of NO_3^- during snowmelt and depletions of NO_3^- associated with assimilation and reduction processes appear to be very important in regulating short-term changes in hydrogen ion and aluminum concentrations in an acidic Adirondack lake. Moreover, elevated levels of NO_3^- in the Adirondack Lake district, compared to other lake districts in Eastern North America, suggest that nitric acid inputs may have also contributed to the long term acidification of the region. However a more complete understanding of the processes controlling the transport of NO_3^- and H-Al-BNC during snowmelt is essential to assess the mechanisms responsible for surface water acidification.

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Table 1 Mean Chemical Composition (μeq$\cdot$l^{-1}) of
Dart Lake inlet, outlet and water column
solutions, 10/1981 - 11/1982 (n = 172)

	Mean	Standard Deviation
Base Neutralizing Capacity (to reference pH = 8.3)		
hydrogen ion	7.4	3.7
aluminum	19.6	8.2
carbonic acid	62.0	58.9
organic acids	3.0	1.2
total	92.0	59.0
Basic Cations		
calcium	99.5	4.6
magnesium	28.9	2.2
sodium	28.3	4.9
potassium	13.0	1.1
total	169.7	10.0
Anions		
sulfate	137.6	11.0
nitrate	24.4	8.6
chloride	13.5	3.4
organic anions	12.2	0.4
bicarbonate	7.2	11.9
free fluoride	0.9	0.7
total	195.8	25.6
Sum of Cations[1]	196.7	13.9
Sum of Anions	195.8	25.6

[1]Cationic equivalence were computed to be hydrogen ion and aluminum BNC plus basic cations.

Table 2 Average Chemical Composition ($\mu eq \cdot l^{-1}$) of Low Ionic Strength

Waters From Lake Districts in Eastern North America[20]

Region	n	H^+	Ca^{2+}	SO_4^{2-}	NO_3^-	HCO_3^-	Reference
Adirondack NY, USA	206	12	108	135	16	25	22
Experimental Lakes Area Ontario, Canada	102	1	96	78	1	74	23
Sudbury Ontario, Canada	208	4	273	252	2	160	24
Churchill Falls Laborador, Canada	13	1	80	60	2	69	25
Kejimkujik Nova Scotia, Canada	3	18	22	76	3	0	26

Figure Titles

1. Isopleths of nitrate (a), hydrogen ion BNC (b) and aluminum
   BNC (c) in μeq l^{-1} for Dart Lake (10/25/1981 - 11/21/1983).
   Samples were collected at seven depths. Sampling dates are
   indicated (Δ).

2. Simulated changes in the pH of Dart Lake with increases and reductions
   from the ambient nitrate (a) and DOC (b) concentrations. Average Dart
   Lake water (Table 1) was assumed to be in equilibrium with microcrystalline
   gibbsite ($p*K_{so}$ = 9.35; 28) and an organic solute (C_T = 0.025 DOC + 8.0,
   in μmols·l^{-1}; pKa = 4.53). The relatively soluble mineral phase, micro-
   crystalline gibbsite, was selected for our simulations because it is
   considered to represent the solubility of freshly-formed $Al(OH)_3$ (28).
   Moreover, the mean ion activity (Q_{so}) product for $Al(OH)_3$ of Dart Lake
   solutions was very close to the solubility of microcrystalline gibbsite
   (p^*Q_{so} = 9.52 $\pm$ 0.28).

Fig 1

a) NO₃⁻ ISOPLETH (μeq l⁻¹)

b) H-BNC ISOPLETH (μeq l⁻¹)

c) Al-BNC ISOPLETH (μeq l⁻¹)

TIME (months)

Fig 2