ALUMINUM GEOCHEMISTRY AT THE CATCHMENT
SCALE IN WATERSHEDS INFLUENCED
BY ACIDIC PRECIPITATION
by
Dean S. Jeffries[1] and
William H. Hendershot[2]

[1]National Water Research Institute   [2]Department of Renewable Resources
Canada Centre for Inland Waters   Macdonald College of McGill Univ.
Burlington, Ontario,   Ste-Anne-de-Bellevue, Quebec,
Canada   L7R 4A6   Canada   H9X 1C0

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Dean S. Jeffries,
National Water Research Institute,
P. O. Box 5050,
Burlington, Ontario, Canada L7R 4A6.

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William H. Hendershot,
Department of Renewable Resources,
Macdonald College of McGill University,
Ste-Anne-de-Bellevue, Quebec, Canada H9X 1C0.

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MANAGEMENT PERSPECTIVE

This paper will appear as a chapter in a CRC special volume entitled The Environmental Chemistry of Aluminum (G. Sposito, U. of California, Riverside, editor). The invitation to write the chapter that was extended by G. Sposito permitted the senior author (D. S. Jeffries, NWRI) to seek scientific collaboration with W. H. Hendershot (McGill U., Montreal). The chapter reports and interprets research results that were collected by the NWRI supported LRTAP Project. In particular, results from the Turkey Lakes Watershed Study are described and compared to those from many other locations in the world. The aluminum geochemistry of waters is important since high levels of this metal that sometimes occur in response to acidic deposition may be toxic to aquatic biota. The chapter serves to summarize and provide convincing new evidence as to the geochemical and physical factors that control the concentration of aluminum (and its chemical sub-species) in surface waters. This paper is principally a scientific document and will not effect any changes in departmental LRTAP policy.

PERSPECTIVES - GESTION

Cet article paraître sous forme d'un chapitre dans un volume spécial du CRC intitulé The Environmental Chemistry of Aluminum (Editeur G. Sposito, U. de la Californie, Riverside). L'invitation à écrire ce chapitre de G. Sposito a poussé l'auteur principal (D.S. Jeffries, INRE (Institut national de recherche sur les eaux) à rechercher la collaboration scientifique de W.H. Hendershot) (U. McGill, Montréal)). Le présent chapitre expose et interprète les résultats des recherches obtenus par le Projet de transport à distance des polluants atmosphériques avec l'appui de l'Institut national de recherche sur les eaux. Plus particulièrement, les résultats de l'Étude du bassin des lacs Turkey sont décrits et comparés à ceux d'autres endroits dans le monde. La géochimie de l'aluminium dans l'eau est importante étant donné que les fortes teneurs de ce métal qui sont parfois observées suite aux dépôts acides peuvent être toxiques pour le biote aquatique. Ce chapitre constitue un résumé et fournit de nouveaux indices très éclairants concernant les facteurs géochimiques et physiques qui contrôlent la concentration de l'aluminium (et ses sous-espèces chimiques) dans les eaux de surface. Cet article est d'abord un document scientifique qui n'aura pas d'effets sur la politique ministérielle du Transport à distance des polluants atmosphériques.

ABSTRACT

The geochemistry of aluminum in surface and sub-surface waters is discussed for catchments affected by acidic deposition using, as examples, the Turkey Lakes Watershed (central Ontario, Canada) and the St. Hippolyte calibrated basins (southern Quebec, Ontario). The roles played by water pathways (i.e. hydrology) and soil chemistry in determining the concentration of aluminum in the waters are first summarized, followed by presentation of results from the 2 studies. Specifically, the spatial and temporal variability observed for total aluminum and its species in the waters is discussed, with particular attention being given to elucidating the biogeochemical factors present in each of the basins that can explain the variability. The springmelt episode is discussed in detail, since this period exhibits dramatic peaks in aluminum concentration that may be toxic to aquatic biota. Results from the 2 Canadian basins are placed in a geographically wider context through comparison with those reported for other basins in the United States, Scandanavia, and central Europe.

RÉSUMÉ

La géochimie de l'aluminium dans les eaux superficielles et sous-jacentes est étudiée pour les bassins touchés par des dépôts acides en utilisant comme exemple le bassin des lacs Turkey (Centre de l'Ontario, Canada) et les bassins étalonnés de St-Hippolyte (sud du Québec, Ontario). Les rôles joués par les mécanismes aqueux (p. ex. hydrologie) et la chimie du sol pour déterminer la concentration de l'aluminium dans les eaux sont d'abord résumés et suivis par une présentation des résultats des deux études. Plus particulièrement, la variabilité spatiale et temporelle observée pour l'aluminium total et ses espèces dans les eaux est examinée, avec un accent particulier sur l'élucidation des facteurs biologiques présents dans chacun des bassins qui pourraient expliquer la variabilité. L'épisode de fonte printannière est examiné en détail, étant donné que cette période correspond à des hausses dramatiques des concentrations d'aluminium qui peuvent être toxiques pour le biote aquatique. Les résultats des deux bassins canadiens sont placés dans un contexte géographique plus large par des comparisons avec ceux signalés pour d'autres bassins aux Etats-Unis, en Scandinavie et en Europe centrale.

I. INTRODUCTION

Aluminum is the most abundant metal in the earth's crust, occurring in a host of primary alumino-silicate minerals. "Normal" chemical weathering of these minerals by carbonic acid or various organic acids (i.e. abundantly occurring weak acids) generally causes only a short-lived mobilization of the Al. The high surface affinity of dissolved Al species and the relative insolubility of both primary alumino-silicate minerals and secondary Al-oxide minerals ensure that the quantity of Al released to natural waters is always very small; most of it is retained within the "B" soil horizon. However, since the pool of Al within the soil complex is so large, even a small perturbation of the normal weathering (i.e. soil acidification) process may cause a large increase in Al mobility and profoundly increase the concentration of this element observed in some natural waters, particularly those waters spatially close to the weathering site. Acidic precipitation is one such perturbation[1,2].

Numerous publications have detailed the occurrence of elevated Al concentrations in natural waters due to the effect of acidic deposition (for example, see reviews[3-5]). Environmental concern for this increased Al mobility rests with its toxic effect on both terrestrial[6] and aquatic biota[7-11].

Our purpose is to present and discuss the occurrence and variability of Al concentrations and species in surface and sub-surface waters at the catchment scale, placing particular emphasis on discerning the biogeochemical factors that control the variability. For illustrative purposes, we will use results from watershed studies located in central Ontario and southern Quebec. Consideration of Al behavior on a watershed scale mainly requires definition of how it moves from the soil weathering site into the surface waters. Thus, the hydrology of the watershed becomes very important in determining both the timing and chemistry of the water reaching the stream. Given that the water encounters different materials on its path through the soils to the groundwater, streams, and lakes, soil chemistry is important also. Therefore, we feel that it is useful to present brief summaries of the hydrological characteristics and soil properties that bear on the development of water quality within an "acid susceptible" catchment. These summaries will also serve to establish the terminology that will be used throughout this chapter.

A. The Relationships of Hydrology to Water Quality

The flowpath by which water reaches a stream channel is important. Most of the water reaching the stream during low flow periods (i.e. baseflow) is moving through deeper soil horizons or a porous bedrock. Under baseflow conditions, the water will normally reach the stream from the saturated zone due to the gradient in the water table. Flow from the vadose (unsaturated) zone may be important also, since water held in soil pores in excess of field capacity will drain vertically through this zone to the water table. Baseflow has a lengthy contact time with the matrix through which it flows, and therefore, its composition closely reflects the chemical properties of the matrix material. It almost invariably has a higher pH than the initial precipitation and a low Al concentration.

"Quickflow" describes the situation in which water from a precipitation or snowmelt event, or water already in the soil is displaced by incoming water and

rapidly transmitted through the soil matrix yielding a sharp rise in the hydrograph. The generation of quickflow requires two conditions: 1) a matrix that permits high hydraulic conductivity, and 2) a hydraulic gradient steep enough to cause high flow rates through (or across) the soil. In order to produce the high flow rates, the soil matrix must be saturated, or close to it; unsaturated hydraulic conductivities are too low to generate quickflow.

For humid regions, 3 major sources of precipitation induced quickflow have been identified: 1) "direct precipitation runoff" from saturated soils, 2) "return flow", and 3) "subsurface stormflow"[12]. In most stream basins all three sources will contribute to the storm hydrograph, but the relative importance of each depends on the characteristics of the drainage basin, the antecedent soil moisture content, the water table position, and finally, the nature of the precipitation or snowmelt event.

Near the stream channel where the water table approaches the soil surface, direct precipitation runoff from this saturated area will begin almost simultaneously with the start of the precipitation (or snowmelt) event. If there is a shallow unsaturated zone, it will become saturated before incoming precipitation can flow overland to the stream, thereby creating a short lag in the flow response. When the soils are dry, the area contributing to this type of flow is quite small; however, the area will increase during the event as the surface occupied by saturated soils increases.

Return flow is caused also by a rise in the water table. It occurs in response to the increased hydrostatic pressure exerted by water penetrating an unsaturated zone that is adjacent to areas which are saturated to the surface. The water flows out of the saturated area and joins water flowing over saturated soil. Since return flow is moving towards the soil surface in the direction of least hydrostatic pressure (either horizontally or vertically), it effectively moves upwards through the soil profile from the C horizon, through the B, and E or A horizons, and finally through the O horizon. The runoff water composition will be altered accordingly.

Subsurface stormflow is less well defined than the 2 preceeding mechanisms but is probably the most important for generating quickflow. Subsurface stormflow refers to water moving through the soil at any depth, which means that it can be moving just under the organic soil horizons or through permeable C horizons. The classical concept of subsurface stormflow[13] considers that water flows downward from the surface through the unsaturated zone, and then rapidly through the saturated zone directly into the stream channel. The increased hydrostatic pressure causes displacement of "old" subsurface water (i.e. water that may have spent a long time in the soil), an action sometimes called piston flow. In order for this mechanism to contribute significantly to quickflow, certain limiting conditions must exist. First, the water retention capacity of the unsaturated zone at the time of infiltration must be low relative to the amount of input, or else the incoming water will remain in the vadose zone. Second, the hydraulic conductivity of the saturated zone must be relatively high. Therefore, this mechanism will be most effective when the saturated zone is close to the surface and has a very high saturated hydraulic conductivity as would be found in a glacio-fluvial gravel, for example.

There is another less "classical" occurrence of subsurface stormflow that should be considered. When shallow soils overlay impermeable bedrock or other unconsolidated layers with restricted permeability, part of the soil profile will become saturated, but not up to the surface. Rapid subsurface flow can then be produced in two ways: 1) if part of the profile contains inter-connecting macropores, such as dead root channels, very rapid "pipe" flow can be expected through them; and 2) more permeable near-surface horizons, such as O or eluviated E horizons, also begin to transmit water to the streams as they become saturated[14-16]. The input water to such a system will initially mix with the capillary water previously trapped in the unsaturated zone so that the output stream water will appear older than the input; as subsurface stormflow continues, the relative ages of the input and output waters will merge.

Horton overland flow[17] occurs when the water input rate exceeds the infiltration capacity. It is generally considered to be an insignificant factor in undisturbed, humid, forested watersheds. However, when snowmelt events are taken into consideration it may be possible to have inputs that exceed the infiltration capacity of the soils. Price and Hendrie (18) found that the form-ation of a compact ice layer in the snowpack or at the soil surface resulted in overland flow during one spring snowmelt period. During the intensive water-shed studies presented below, no occurrence of Horton overland flow has been observed during springmelt.

The flowpath of runoff water generated by each of these mechanisms can profoundly affect the water quality. In the case of direct precipitation on saturated soils and Horton overland flow, the water flows over the surface and will contact mainly the surface organic soil horizons. Return flow will move from lower to upper soil horizons and then along the surface. Subsurface stormflow can move through any soil horizon, depending on the relative permea-bility of the soil layers involved. However, since soil permeability is usually greatest nearer the surface than at depth (see discussion below), the water quality of this type of subsurface runoff generally reflects the soil chemistry of near surface horizons. The most striking occurrence of Al movement in a watershed is related to periods of peak stream flow (snowmelt and/or heavy rainfall) when the quickflow component is maximum. Runoff waters at this time have reduced pH and elevated Al.

B. The Relationship of Soils to Water Quality

Those areas where the effect of acidic deposition has been manifested as either long-term or episodic acidification of surface waters (usually with elevated Al concentrations as well) are most commonly situated on acidic soils with natural forest vegetation. The role of soils in the acidification process is important.

Four soil orders are usually associated with watersheds influenced by acidic deposition in eastern North America; they are the Inceptisols, Spodosols, Alfisols and Ultisols, all of which have certain characteristics in common. First, hydraulic conductivity tends to be greater near the surface and decreases with depth. In the case of the Inceptisols and Spodosols, the high hydraulic conduct-ivity near the surface is related to the presence of amorphous sesquioxide material and organic matter that coat the soil particles and tend to create low bulk density and abundant pore space. Deeper in these same soils there are

occasionally, compact layers of low permeability that may be related to compact glacial till, ortsteins, duripans or fragipans. In Alfisols and Ultisols the near surface horizons have lost clay by eluviation creating a zone of relatively high hydraulic conductivity. Lower in the profile, in the illuvial zone or argillic horizon, clay has accumulated and the hydraulic conductivity is much lower. The underlying horizons may also have low permeability due to cementation or consolidation.

The second characteristic common to all 4 soil orders is a general increase in pH with depth. The surface horizons tend to be more acidic due to the more intense leaching that takes place at the surface and to the decomposition of organic matter. Thus the surface horizons are not only more acidic, they also contain more organic matter that can decompose to produce organic ligands capable of complexing Al.

In summary, the impact of acidic deposition on the surface water system will be greatly influenced by the flowpath by which the water reaches the stream channel. Given that ion exchange and adsorption/desorption reactions are extremely rapid, it is clear that water leaving the terrestrial portion of a catchment will have pH and Al concentrations that generally reflect the soil horizon through which it last flowed. Water emerging from C horizons will be low in organic acids and have both high pH and low Al content. In contrast, water flowing from the surface soil horizons will have high concentrations of organic acids, low pH, and high dissolved Al content.

II. STUDY SITES

A. The Turkey Lakes Watershed

The Turkey Lakes Watershed (TLW) is an undisturbed, remote catchment located approximately 50 km north of Sault Ste Marie, Ontario (see Figure 1). Total drainage area is 10.5 km^2. The basin contains a chain of 4 lakes (Batchawana, Wishart, Little Turkey, and Turkey Lakes) that exhibit a gradient in chemical composition and response to acidic deposition. The terrestrial portion of the TLW is completely forested by an "old-growth" mixed hardwood stand dominated by Sugar maple (*Acer saccharum*) and Yellow birch (*Betula alleghaniensis*). The closest point-source emitter of air pollutants is the steel industry located at Sault Ste Marie. Annual atmospheric deposition of SO_4 and NO_3 is approximately 70 and 37 $meq.m^{-2}$ respectively.

Elevation at the lowermost stream gauging station is 340 m AMSL while the highest point is Batchawana Mountain (630 m) on the northern edge of the basin - giving an overall relief of 290 m. The large variations in elevation and the leeward position relative to L. Superior influence the quantity of precipitation received. Semkin and Jeffries (19) recorded an average annual precipitation of 1212 mm from 1981 - 1984 at low elevations and up to 15% more at higher levels. In comparison, Sault Ste Marie which lies south of the highlands containing the TLW, receives only 935 $mm.yr^{-1}$ (long term average).

The watershed is almost entirely underlain by Precambrian silicate greenstone (ie a metamorphosed basalt) with only small outcrops of more felsic igneous rock occurring north of Batchawana L. and near the main inflow to Little Turkey L.[20]. Regional fault systems tending in approximately NW-SE and SW-NE

directions have exerted some control over water drainage giving the rather angular drainage pattern observed in Figure 1. A 2 component glacial till overlies the bedrock, and is composed of an upper, relatively permeable ablation till and a lower less permeable basal till. Till thickness varies from <1 m at high elevation locations (with frequent surface exposure of bedrock) to 1 - 2 m at lower elevation, and with the occasional occurrence of extremely deep till sequences (up to 70 m) where valleys in the bedrock have been entirely filled. The mineralogy of the till is more felsic than the underlaying bedrock showing that the material was likely primarily derived from the large granitic intrusions that occur just north of the basin[21]. Finally, the tills contain a small but measureable amount of $CaCO_3$ (0 - 2%) that increases with depth, and is higher (on average) at lower elevation locations[22]. Soils developing within the till matrix are classified as Typic Haplorthods. More information on basin characteristics is presented by Jeffries et al. (23).

B. The St-Hippolyte Watersheds
1. Lac Pin Blanc Watershed

The Lac Pin Blanc watershed is located in the Station de Biologie de l'Université de Montréal near St-Hippolyte Québec, about 80 km north of Montréal (see Figure 2). The catchment has a surface area of 0.56 km². The drainage system consists of a first-order stream. A depression in the bedrock formed by glacial action is now occupied by a small pond (Lac Pin Blanc) about 0.01 km². The area receives total precipitation of approximately 1100 $mm.yr^{-1}$, 30% as snow[24]. Annual atmospheric deposition of SO_4 and NO_3 is approximately 66 and 34 $meq.m^{-2}$ respectively.

The vegetation on the well drained sites is a dominantly hardwood forest of Sugar maple (*Acer saccharum*), White birch (*Betula papyrifera*), Balsam fir (*Abies balsamea*), and Trembling aspen (*Populus tremuloides*). The poorly drained, organic soils have a vegetation cover of White cedar (*Thuja occidentalis*) and Speckled alder (*Alnus rugosa*). The pond is edged with a mat of Sphagnum moss.

The bedrock of this area is Precambrian anorthosite. Except for outcrops along many of the divides between watersheds, the bedrock is covered by till with a mineralogical composition similar to that of the anorthosite. In most parts of the watershed the till is thin <2 m; here the soils are Typic Haplorthods. In the depression near the pond organic soils have become established, either Saprists or Hemists depending on the degree of decomposition of the material. A more detailed description of the soils can be found in Hendershot et al. (25) and Dufresne (26). This basin was monitored during 1984.

2. Hermine Watershed

During 1985 and 1986, the smaller Hermine watershed was used (Figure 2). This basin has a surface area of 0.06 km² and vegetation dominated by Sugar maple (*Acer saccharum*: 78%) with lesser amounts of American beech (*Fagus grandifolia*: 9%) and Yellow birch (*Betula alleghaniensis*: 6%). It is located about 3 km from the Lac Pin Blanc watershed and has similar geology. The soils are all Typic Haplorthods although differences in morphology and chemical properties have developed due to slope position and drainage[27].

III. MATERIALS AND METHODS

A. Turkey Lakes Studies

Atmospheric deposition was estimated from weekly bulk deposition samples while precipitation quantity was measured daily using appropriate gauges[19]. Water and chemical flux from headwater streams were measured at several gauging stations operated by the Great Lakes Forest Centre[28] and also at the lake outflows. These stations generally have continuous measurements of stream flow and approximately weekly measurements of chemical composition. The lakes were sampled bi-weekly in profile, at the deepest point.

Total Al (Al_t) samples were acidified with high purity HNO_3 (1 ml.L^{-1}) and quantification achieved by graphite furnace AAS. Aluminum speciation was performed using the method of LaZerte (29) in which the most biologically toxic species (i.e. inorganic monomeric forms = Al_i) are physically separated by a 24 hr dialysis using 1000 MWCO membrane. The Al is complexed with oxine and extracted into MIBK. Our procedure differed slightly from LaZerte in that final Al species quantification was achieved by back-extraction into 1% HNO_3 and measurement with a DC plasma emission spectrograph.

In addition to the above, results pertaining to Al_t in throughfall and soil waters[30] and groundwater[31] will also be presented in order to complete the "whole watershed" picture.

B. St-Hippolyte Watersheds

In the Lac Pin Blanc watershed, shallow groundwater wells were located near the stream and pond. The water table height was measured daily and the water sampled about every 5 days. Bulk rainfall was collected in polyethylene bottles using the system described by Likens et al. (32). Snowfall was collected in 6 plastic buckets (25 cm diameter) on an event basis; these samples were combined prior to chemical analysis. Continuous stream discharge was measured at a natural v-notch wier, while water chemistry was determined from samples collected automatically, several times a day. In the Hermine watershed, discharge measurement and stream sampling were performed automatically in 1985 and manually in 1986 at a v-notch weir.

In 1984, Al speciation was determined using the oxine method as discussed in Lalande and Hendershot (33). Research has shown that the first measurement (Al_1) includes mainly monomeric Al such as Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$ and perhaps the dimer $Al_2(OH)_4^{2+}$. The second (Al_2) measures the same forms as Al_1 plus monomeric Al bound to fluoride or organic ligands. The third (Al_3) is considered to be the total reactive Al that, in addition to the forms measured by Al_2, includes polymeric forms of reactive Al that may be in either organic or inorganic form.

In 1985, Al speciation was performed using the PCV method[34,35] modified to give two forms of Al: 1) acid extractable Al (Al_t) was measured after acidifying the sample to 2% HNO_3, and 2) total monomeric Al (Al_{tm}) was measured on an unacidified sample and is believed to include Al^{3+}, and the simple complexes of Al-OH, Al-F, Al-SO_4, and Al-organic.

In 1986 the Al_{tm} was separated analytically into charged and uncharged fractions by passing the solution through a cation exchange column. The

exchangeable fraction is operationally defined to be inorganic Al (Al_i), while the non-exchangeable fraction is considered to be organically complexed Al (Al_o)[7].

IV. RESULTS AND DISCUSSION

A. Aluminum Variability Within a Watershed

Large variations in aqueous Al concentrations occur both within and between specific watershed compartments. For the purpose of this discussion, we will separate Al variability into its spatial and temporal components, realizing that in reality, they are often intimately related.

1. Spatial Variability

Table 1 presents average Al_t concentrations for various watershed compartments in the TLW. Total Al in bulk deposition is low (31-33 μg.L^{-1}) and only slightly elevated by passage through the deciduous canopy that predominates throughout the basin. The <2-fold increase in throughfall concentrations relative to the incident deposition appears to be little influenced by the growth "status" of the trees; i.e. their is little difference between throughfall concentrations for the summer growing season and the winter dormant season. Stemflow is further enriched in Al_t (2-3 fold greater than bulk deposition), but in terms of the metal flux to the underlaying components of the basin, stemflow is of minor importance[30].

Highest Al_t concentrations appear in soil waters. Samples collected under the surface organic horizons had values of 134-183 μg.L^{-1}, while in the B horizon, concentrations were 357-380 μg.L^{-1}. No consistent pattern between growing and dormant seasons is apparent. Leaf litter, which accounts for most of the material in the organic horizons, must contain a substantial quantity of Al that is readily leached, desorbed or exchanged. The high concentrations found in the B horizon presumably reflect the high bulk soil concentrations of adsorbed Al that are present due to the action of normal soil formation processes. Since the B horizon acts as the primary site of Al demobilization, waters below this level have very much lower concentrations. However, the fact that there is a 2-fold decrease (102 to 45 μg.L^{-1}) between the C horizon and slightly deeper ground-water may indicate that some Al mobilization from the B to the C horizon is occurring in response to the elevated strong acid input from above.

The Al_t concentration is highly variable between headwater streams. In the TLW, streams at high elevation (e.g. streams F47, F49, F50) generally occupy sub-basins with shallow surficial deposits. They also exhibit relatively higher, but variable Al levels ranging from 94 to 197 μg.L^{-1}. As will be developed more fully in later discussion, we ascribe high streamwater Al concentrations to geomorpholgical control over the flow pathways by which drainage waters reach the headwater stream channel. That is, we believe that a significant proportion of the water enters the stream by draining directly from the B horizon, the C horizon being excluded from the pathway by the physical constraint imposed by a shallow overburden. There is an obvious corollary to the situation in which only a small hydrological resevoir is available in the soil system; that is, streamflow generation will be dominated by quickflow mechanisms, yielding rapid variations in runoff, and periods of low or "no" flow. All of the above streams exhibit these characteristics. Clearly, flow pathway control existed long before the advent of acidic deposition; hence elevated contemporary Al_t levels in surface

waters probably reflects a deposition induced increase in the mobility of Al.

Table 2 presents the range and median for both Al_t and Al_i obtained for the high elevation streams (i.e. F47, F49, and F50) during the spring melt episodes of 1985 and 1986. In the TLW, over 50% of the total annual flow occurs during spring melt[28]. Inorganic monomeric Al is the species generally considered to be most important from the standpoint of biological toxicity[7]. The difference between Al_t and Al_i is composed of soluble organic monomeric and polymeric species, as well as particulate materials. Since there was a fairly close correspondence in the magnitudes of the Al_t and the non-dialyzed, oxine-MIBK defined species, the organic monomeric species almost always dominates over the polymeric and particulate species in the TLW. As can be seen by the data in Table 2, there is also distinct differences in the Al species distribution among the headwater streams. While the 2 most acidic streams (F47 and F50; median pH = 5.5 and 5.3 respectively) have the highest Al_t values, the proportion represented by Al_i was 69 and 34% respectively. The DOC levels in F47 are also much lower than in F50, see Table 2. The fact that the organic monomeric component is much more important for F50 than F47 implies that there is a difference in the character of the Al supply between these sub-basins. Of the two, F50 is by far the most steeply sloping, and thus it is more likely that subsurface stormflow proceeds through organic soil horizons there, than in sub-basin F47. Consistent with this hypothesis is the fact that the Al_t for F50 is less than that for F47 (despite a lower pH) and similar to the water draining from Oe horizons as given in Table 1. Stream F49 exhibits higher pH and lower Al_t and Al_i than either F47 or F50; however, under these conditions, even the low DOC concentration (i.e. 2.4 $mg.L^{-1}$) is sufficient to reduce the relative importance of Al_i to a proportion comparable to that of F50.

Streams draining low elevation locations in the TLW (e.g. streams F31 and F34) have deeper overburden and a water percolation pathway that probably includes a C horizon. Moreover, these tills contain a small (1-2%) amount of easily weathered $CaCO_3$, a geochemical factor contributing to generally higher soil pH at low elevation and therefore, decreased Al mobility. Total Al in streamwater at low elevation is very similar to input precipitation concentrations.

Finally, whole-lake Al_t exhibits a gradient in concentration, consistent with the stream levels discussed above. Batchawana L. South has the highest concentration rather than the "true" headwater (i.e. Batchawana L. North); however, it receives comparatively more of its input as terrestrial basin runoff. All of the high elevation, high Al_t streams presented in Table 1 drain into Batchawana L. South. Each of the succeeding downstream lakes has a lower average Al_t value. Figures 3 and 4 present isopleths of Al_t for the first 6 months of 1986 for Batchawana L. South and Little Turkey L. respectively. The isopleths show not only the generally different Al_t levels present in the 2 lakes, but also the elevated concentrations that develop in bottom waters during periods of restricted lake circulation. Precipitation of Al species, or adsorption to lake seston followed by settling from the water column is probably an important removal process for these lakes. This process has been implicated in the co-removal of phosphorus and dissloved organic carbon leading to increased clarity and the low trophic status often associated with lakes affected by acidic deposition[36-38].

2. Temporal Variability

Chemical variation in stream and lake waters of northern temperate watersheds is often intimately related to their hydrological variability. In the TLW and St. Hippolyte, spring snowmelt is almost always the most pronounced hydrological event each year often providing 30 - 50% (or more) of the total annual runoff[28,39]; however, heavy rainfall that often occurs during autumn months can also provide significant runoff volume. In either case, during the preceeding periods of low hydrological flux, the soluble material liberated by weathering of mineral or organic material accumulates in the soils where it can be readily flushed by a sudden, high flow event.

During spring snowmelt, the preferential elution of pollutants from the snowpack during the early melt phase[40,41] and the flush of accumulated-weathering products from the terrestrial to the aquatic ecosystems, can cause a sharp drop in the pH of lake or stream waters and a rise in the amount of Al[29,42-44]. Such chemical changes have been related to sudden fishkills, even where the water chemistry during the rest of the year poses no threat to fish[10,45,46]. While the toxic effect of Al is dependent on the chemical species[7], concentrations as low as 100-200 $\mu g.L^{-1}$ have been associated with specific biological effects (see review[3]). Many streams and the headwater lake in the TLW exhibit episodically high concentrations of both Al_t and Al_i during the springmelt period (Table 2) that are within or above these critical levels.

Figure 5 presents the temporal variation observed in Al_t and discharge at the outflow of Batchawana L. during 1984 and 1985. While there is clearly substantial day-to-day variation even at this station where flow through the lake would be expected to "damp" the influence of variable stream inputs, 2 general concentration maxima and minima can be identified each year. Maximum Al_t levels of about equivalent magnitude occur during the high flow periods of each year, i.e. springmelt and autumn. Minimum Al_t occurs during the winter and summer months with the latter being far more pronounced. The marked summer minima are similar to those observed in Adirondack watersheds[47,48] and have been attributed to precipitation and within-lake retention of insoluble Al species in response to production induced increases in water column pH. The sharp concentration minimum that occurred in March 1984 was not manifested in 1985, and may be attributed to the differing character of the spring melt episodes. In 1984, melting occurred abnormally early at the beginning of March; however, over 2 weeks of extremely cold weather followed which reduced the runoff to pre-melt intensity. The sharp minimum in Al_t in mid-March, 1984 corresponds to this cold period; the small amount of early meltwater appears to have displaced relatively low concentration lakewater. This observation is in contrast to the usual runoff process in which the cold, less dense meltwater flows across the lake immediately under the ice and exits via the outflow. In the TLW, such meltwater tends to mix with only the top 1-2 m of lakewater[49].

The variability in Al_t within the lake water column during winter and spring was presented earlier in Figures 3 and 4. High Al stream water and direct seepage inputs to the lakes during snowmelt were manifested as a layer of higher concentration lakewater extending to a depth of approximately 2 m during April, 1986. After ice disappeared from the lakes (end of April), rapid increase in water temperature causes spring turnover - a water column mixing that is typical of the dimictic lakes in eastern Canada. It should be noted that mixing in

Batchawana L. (Figure 3) was incomplete since the small peak in bottom water concentrations was not disrupted. After spring turnover, the small increase in Al_t with depth is re-established.

The Al_i species present in the lakes during this time period were much lower in concentration, often approximately half of the Al_t values. Such Al_i values are probably not detrimental to biota; however it is possible that higher concentrations associated with direct sub-surface seepage into the lakes may be locally important. Other studies in the TLW have shown that a significant portion of the spring runoff water enters the lakes as direct seepage and has followed a flowpath within the top 1 m of the soil/till matrix[50]. High Al concentrations present in this water could affect fishing spawning habitats in nearshore gravel shoals. Gunn and Keller (51) have already noted this phenomenon in other Ontario lakes.

The variations in Lac Pin Blanc stream discharge and water chemistry observed during snowmelt are presented in Figure 6. The figure covers the period March 21 to May 25, 1984. Streamflow (Figure 6a) which was 7 L.sec^{-1} at the initiation of spring melt rose sharply to form three major peaks on April 6 - 7, April 17, and April 25 with a smaller peak on May 9. Streamflow was influenced by both warm temperatures and rainfall causing average daily peak values to reach 160 - 180 L.sec^{-1}. Figure 7 shows comparable information for a groundwater well in the watershed. The water table position followed a similar pattern to that of stream discharge. The water table rose to a maximum during the first major melt event (April 5 - 7) then dropped to a minimum (April 11). A second maximum was observed on April 16 - 18 corresponding to the second major snowmelt event.

Figure 6b shows the variation of Al concentrations in the stream. Before April 4, the amount of total reactive Al (Al_3) is fairly high, around 125 μg.L^{-1}. Beginning on April 5, there is a sharp rise in Al_3 concentration to 180 μg.L^{-1} that corresponds to the first major peak in discharge. During the same period, the concentration of Al_3 in well #7 rose to about 240 μg.L^{-1}. The peak in Al_3 concentration is caused by flushing of readily soluble or exchangeable material from the soils, aided by a rise in the water table and the generation of quick-flow through surface horizons in low lying areas. Once this first flush has passed, the positive correlation between stream water Al and discharge changes abruptly. Thereafter, streamflow peaks are matched by decreases in stream Al values. We term this behavior of decreased Al with increased flow the "dilution" effect, since it arises when a source of relatively pure water (snowmelt) is added to a solution flowing through the watershed[52]. The dilution effect occurs when the rate of water transport through the watershed is faster than the ability of the basin to supply solutes; although desorption or ion exchange reactions are rapid, the absolute concentrations of most cations are ultimately controlled by primary mineral weathering. In small basins experiencing the high water flux associated with spring melt, water-soil contact time is normally too short for weathering to progress significantly. Clearly the pool of material available for dissolution, exchange, etc. during the later melt stages is different in character than that which supplied the initial concentration peaks. The decrease in the ion loading of the meltwater entering the soil over time also has the effect of decreasing the amount of exchangeable ions displaced from the soil particle surfaces. The dilution of both surface and groundwaters in the Lac Pin Blanc

watershed was also manifested by decreased electrical conductivity in both the stream and well water (Figures 6c and 7c respectively) as discharge peaked for the second and third time during the 1984 snowmelt episode. As the hydrological flux through the basin decreased following snowmelt, increasing water-soil contact time permitted a gradual increase in Al (and EC) in both the stream and well water. Increasing soil temperature and biological activity may also increase the rate of formation of the labile Al pool in the soil.

Aluminum speciation in the stream (Figure 6b) shows that aquo- and hydroxy--monomeric Al (Al_1) and polymeric Al (Al_3-Al_2) contribute about equally to the total reactive Al concentration throughout the melt period. Organically and fluoride complexed monomeric Al (Al_2-Al_1) is more abundant than the other two forms with its contribution increasing slightly after approximately May 4. The relative decrease in Al_1 is due to a decrease in the amount of inorganic ligands capable of binding to Al and the increase in pH as the melt period proceeds. In general, Al_1 and Al_2-Al_1 covary although there are periods of exception. On the other hand, temporal variations in Al_3-Al_2 appear to be independent of the other two.

A major difference exists in the temporal variation in Al speciation between the stream and groundwater (Figures 6b and 7b respectively). In the stream, peaks in total reactive Al (Al_3) were caused by increases in Al_1 and Al_2-Al_1 monomeric Al. In the wells most of the variation is in Al_1 with a relatively smaller contribution from Al_2-Al_1. Considering that the most labile forms of Al are the most toxic to aquatic life, it is beneficial that a transformation of the most labile into less labile species occurs as the water moves from groundwater to stream.

Springmelt studies conducted in the Hermine basin during 1985 yielded results (Figure 8) in general agreement with the above discussion. The magnitude of the initial Al pulse that accompanied the first major stream discharge peak was slightly more pronounced, while the degree of dilution of Al during subsequent periods of high flow was slightly less pronounced.

B. Aluminum Variability Between Watersheds

Table 3 presents Al_t concentrations in various compartments from watersheds in North America and Europe. With the exception of Findley Lake, Washington, all of the watersheds receive moderate to heavy levels of acidic deposition. Bulk deposition of Al_t is low at all sites except Solling, FRG. Throughfall is always higher than the incident precipitation, often by a factor of approximately two.

Soil water concentrations vary greatly among basins. Total Al in water collected from within or directly below the organic soil horizons probably reflects the dominant influence of forest type; hence, the highest concentrations are associated with watersheds having coniferous forest (Findley L., L. Gårdsjön, and Solling) although the low value for McDonalds Branch is an exception. Like the TLW, Hubbard Brook, Laurel Hill, and ILWAS (Adirondacks) are all deciduous forest; however they receive comparatively higher levels of acidic deposition which may account for their higher organic horizon Al values. Findley L., which receives very low acid input, has lower Al_t concentrations in the B horizon than in the overlaying organic horizon. In contrast, the heavily acidified European Gårdsjön and Solling basins exhibit very high B horizon Al_t

levels as does Laurel Hill in Pennsylvania. Both Hubbard Brook and ILWAS show a wide range in B horizon concentrations, a reflection of the variability in soil characteristics found in these areas. The low value for the - TLW probably reflects control over soil pH (and therefore Al solubility) exerted by the $CaCO_3$ in the tills of the area.

Output stream concentrations represent the integrated watershed response to all deposition, vegetation, and geochemical factors. In the absence of an external mobilizing factor, very low Al_t concentrations occur in streamwater at Findley L. while geochemical factors influence the low to moderate levels observed in the TLW. The 4 basins in the northeastern USA exhibit a wide range in stream concentrations that is usually attributed to varying water flowpaths (see references in Table 3). The streamwater Al levels at Gårdsjön, Sweden are uniformly high; in fact, even groundwater acidification has been reported for this area[63].

C. Source of Aluminum in Soil Waters and Stream Waters

During the 1986 snowmelt in the Hermine basin, the stream hydrograph was modelled to assess the flow contribution from the solum (the soil horizons above the C horizon) and from the groundwater (the material in or below the C horizon) using the approach of Pilgrim (64) and Pinder and Jones (65). Silicon was used to calculate the relative contribution of water reaching the stream via the groundwater or via the solum[66]. In the Hermine basin, the water flowing over the soil surface during the maximum flow events was observed to have a similar chemical composition to the water flowing in the solum, implying that there has been chemically effective contact between the overland flow water and the soil. As a result we can assume a relatively simple system where there are only two sources of water reaching the stream[27]. The model takes the form:

$$Q_t C_t = Q_g C_g + Q_s C_s \qquad (1)$$

where Q_t = measured stream discharge,

$\quad Q_g$ = groundwater discharge,

$\quad Q_s$ = solum discharge,

$\quad C_t$ = measured stream Si concentration,

$\quad C_g$ = groundwater Si concentration (assumed equal to stream baseflow concentration), and

$\quad C_s$ = measured solum Si concentration.

The model was used to calculate Q_g and Q_s; the best fit relationship to the 1986 data is shown in Figure 9.

According to this model, all of the discharge comes from the groundwater when stream discharge is less than 0.6 $L.sec^{-1}$; at higher discharge most of the increase is due to flow through the solum. At a stream discharge of 20 $L.sec^{-1}$, only about 2 $L.sec^{-1}$ is being contributed by the groundwater, the rest is coming from the solum. The large contribution from the solum in this watershed is explained by the dense C horizon that impedes infiltration, and causes a perched water table to develop during stormflow events. During melt events, therefore, most of the water reaching the stream passes through the solum thereby accounting for the higher H^+ and Al concentrations measured in the stream during high flow (see Figure 8).

Figure 10 shows the relationship between pH and Al^{3+} activity calculated

according to Lindsay (67). These calculations separate the inorganic monomeric Al into Al^{3+}, $AlOH^{2+}$, $Al(OH)_2^+$, $Al(OH)_3$, $Al(OH)_4^-$, AlF^{2+}, AlF_2^+, AlF_3 and $Al SO_4$. Numerous authors have found that the Al^{3+} activity in soil waters appears to be controlled by the solubility of a gibbsite-like mineral. If gibbsite is the mineral controlling Al^{3+} activity in either soil or stream water, then the following equation describes the reaction:

$$Al(OH)_3 + 3H^+ \Longleftrightarrow Al^{3+} + 3H_2O \qquad (2)$$

For this reaction, when log Al^{3+} activity is plotted against pH, the resulting line has a slope of -3 as shown in Figure 10. In soil water from the Hermine watershed, the Al^{3+} concentration closely follows the theoretical solubility relationship of a gibbsite-like mineral (see Figure 10). However, in the podzolic soils of southern Québec, no gibbsite has ever been identified. In fact none would be expected due to the high concentration of organic matter and Si that would interfere with the crystallization of this mineral. Another possibility is that the solid phase responsible for controlling Al^{3+} activity is Al-interlayered vermiculite; however, this mineral is also absent from the clay mineralogy of soils at St-Hippolyte. We conclude that the source of Al in podzols is mainly amorphous material (organic or inorganic) that has a solubility similar to that of $Al(OH)_3$.

In contrast to the relationship observed for soil solutions, log Al^{3+} activity and pH in stream waters are highly correlated, but the slope of the line is >-3 (see Figure 10) even during those periods when most of the water is passing through the solum before reaching the stream. This lower slope is similar to what was observed at Hubbard Brook by Hooper and Shoemaker (68); they hypothesize that the temporal variations in Al concentration observed during snowmelt are caused by "the depletion of a slowly forming, labile pool of Al in the soil". Furthermore, they note adjacent streams exhibit differing relationships, an observation similar to our findings in the TLW where 2 of the 5 headwater streams presented in Table 1 (F34 and F47, a high and low pH example respectively) show a good correlation between Al_t and pH, while the other 3 streams do not. Nordstrom and Ball (69) have observed a similar deviation from the theoretical slope of -3 at pH below 4.6. However, in our study at St-Hippolyte the deviation occurred at pH 5.4, and is probably not due to the same mechanism. Sullivan et al. (70) investigated Al variation in response to episodic increases in flow in the Norwegian Birkenes catchment. Their observations generally agree with those at St. Hippolyte although the peak Al concentrations associated with an initial discharge peak was primarily due to elevated organic-Al species. Perhaps the difference in forest type (coniferous at Birkenes and deciduous at St. Hippolyte) may explain the differing species responses. In all cases, however, after the initial peak, Al concentrations remain relatively low in streamwaters during subsequent increases in flow that occur befor the soils have had time to increase the pool of readily soluble Al. The rate at which the labile Al pool in the soil forms, and the factors influencing the rate are unknown and warrant further study. Observations from the above studies suggest that the rate is on the order of weeks rather than days.

Clearly the supply of Al to soil and surface waters is a complex, hydrogeochemical process. Better knowlege of the flowpaths of water under differing water loading rates, the chemical character of the labile Al pool in soils, and the

factors influencing its supply rate are necessary before it will be possible to quantitatively predict Al behavior in the receiving surface waters.

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Batchawana
Lake

F50
F49
F47

Wishart
Lake

Little
Turkey
Lake

F34

F31

Turkey
Lake

TURKEY LAKES WATERSHED

Man.

Que.

Ont.

U.S.A.

Watershed
Boundary

meters

0   500   1000

N

Figure 1

LAC PIN BLANC
WATERSHED

HERMINE
WATERS-IED

BASIN BOUNDARIES
STATION DE BIOLOGIE

0   500   1000
meters

Man.   Que.
Ont.
U.S.A.

ST. HIPPOLYTE
WATERSHEDS

N

Figure 2

Batchawana Lake South - Al$_t$ (μg.L^{-1})

1986

Figure 3

Little Turkey Lake – Al$_t$ (μg·L^{-1})

1986

Depth (m)

ice cover

Figure 4

BATCHAWANA LAKE SOUTH OUTFLOW
—— Total Al (μg.L⁻¹)
----- Stream flow (L.sec⁻¹)

Flow

500

250

0

Total Al

200

150

100

50

0

Total Al

1984   1985

j f m a m j j a s o n d j f m a m j j a s o n d

Figure 5

LAC PIN BLANC STREAM

(a) Discharge

L.sec⁻¹ axis: 0, 50, 100, 150, 200

(b) Al species

$\mu g \cdot L^{-1}$ axis: 0, 90, 180, 270

Al₃, Al₂, Al₁

(c) H⁺

$\mu g \cdot L^{-1}$ axis: 0, 5, 10, 15

(d) Conductivity

$\mu S \cdot cm^{-1}$ axis: 0, 10, 20, 30, 40

Mar 20   Apr 9   Apr 29   May 19

1984

Figure 6.

LAC PIN BLANC WELL No.7

(a) Water table height

(b) Al species

Al
Al
Al

(c) H⁺

(d) Conductivity

Mar 20   Apr 9   Apr 29   May 19

1984

Figure 7

HERMINE STREAM

(a) Discharge

(b) Al Species

(c) H⁺

(d) Conductivity

Mar 20   Apr 9   Apr 29

1985

Figure 8

Figure 9

$Al^{3+} = 10^{8.5} + (H^+)^3$

O Soil solution

◆ Stream

pH

Log a$_{Al^{3+}}$
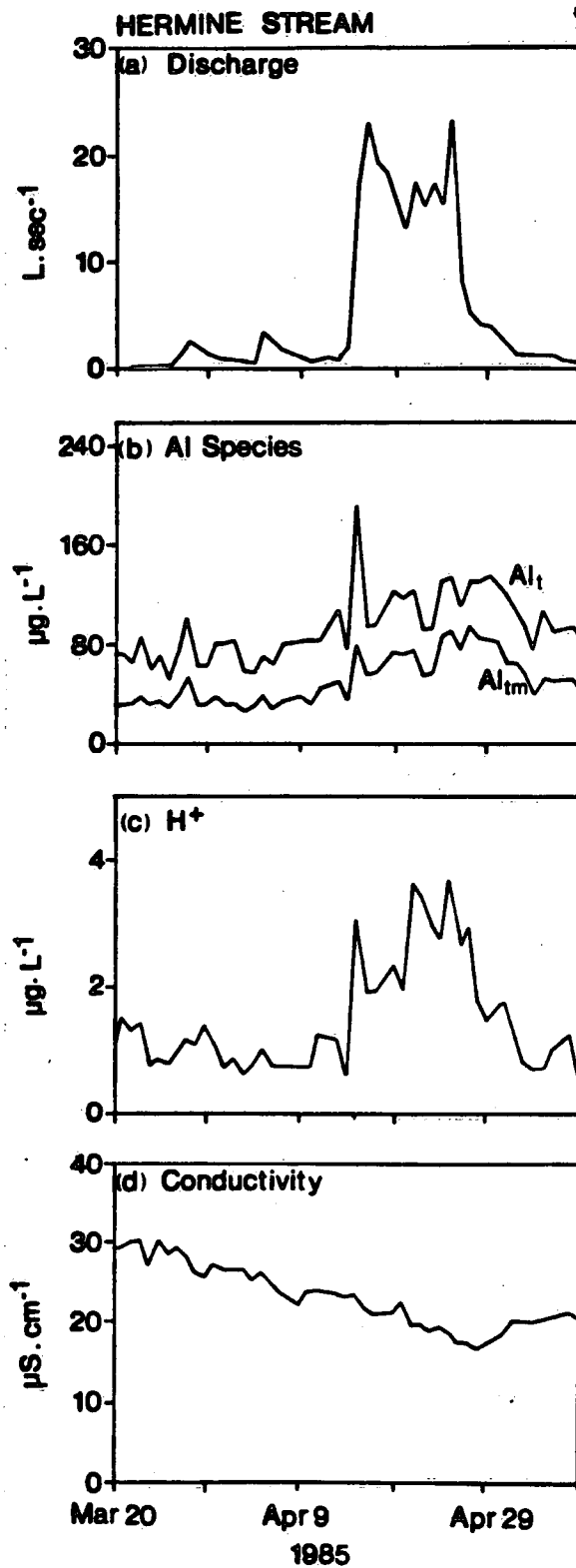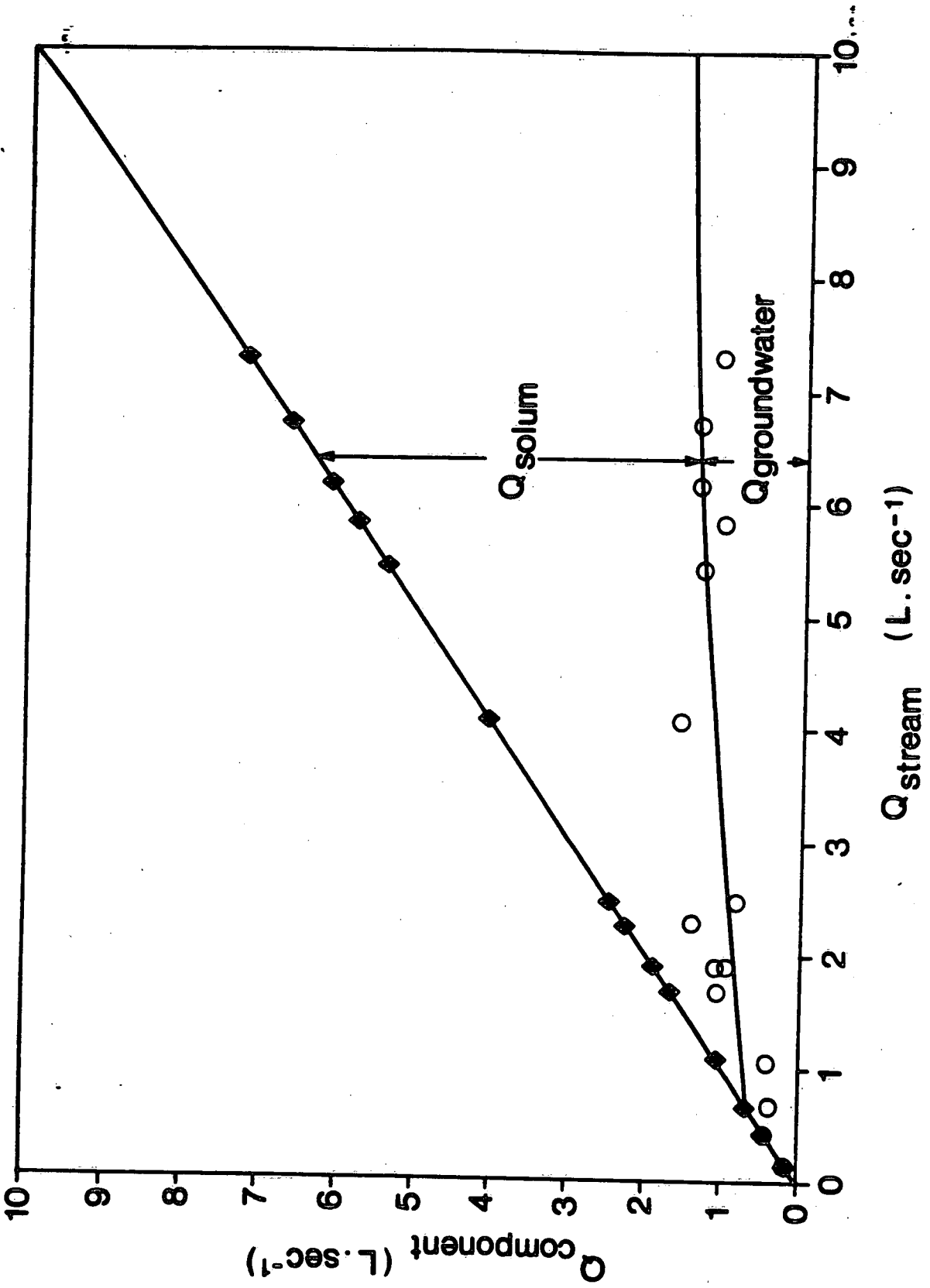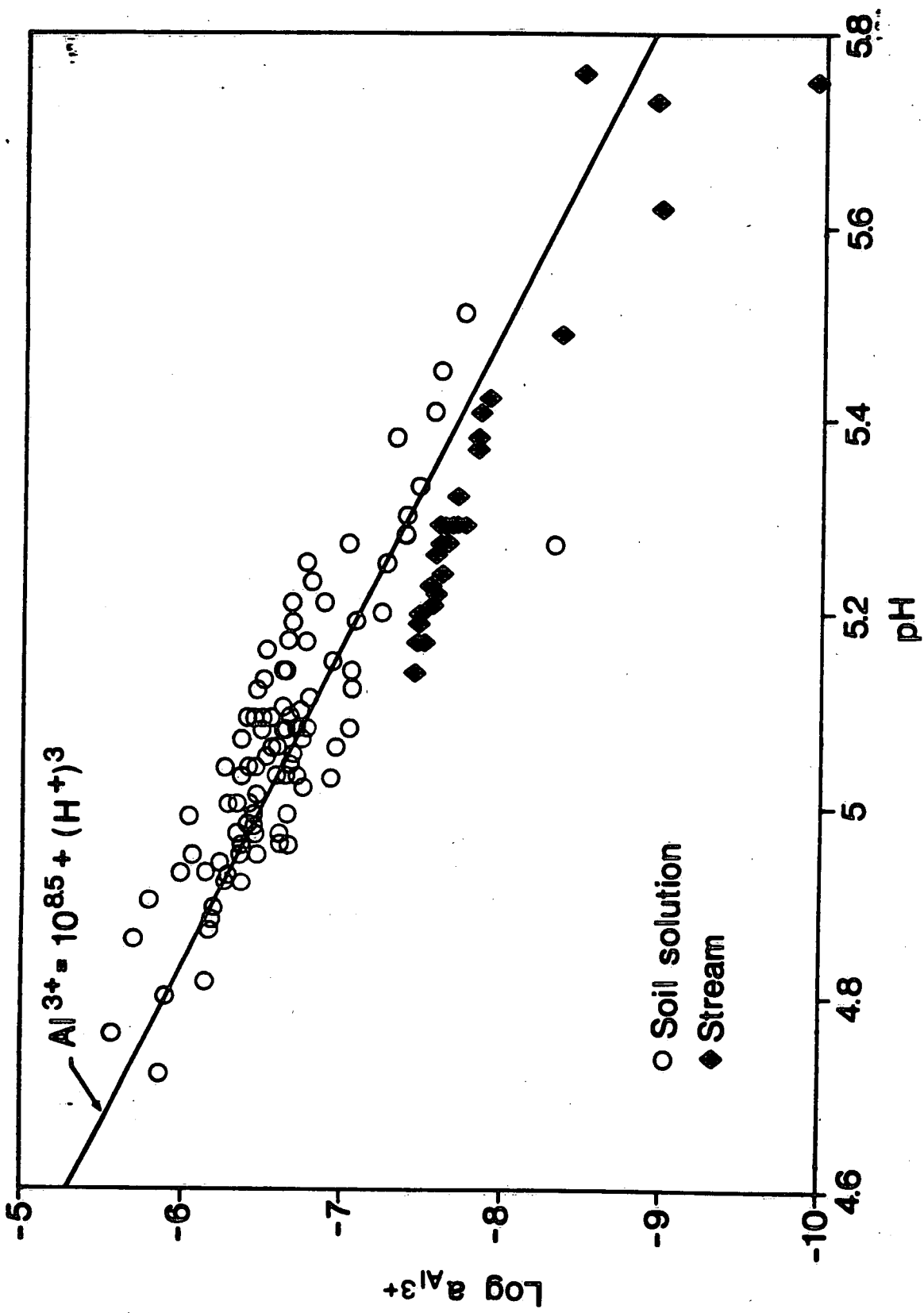
Figure 10

Table 1   Total aluminum concentrations (μg.L^{-1}) for various compartments in the Turkey Lakes Watershed. Data are median values except where noted.

Watershed Location	Sampling Period	Total Al Concentration
Bulk Deposition[a]	1983	31, 33
Throughfall[a]	1983	46, 51
Stemflow[a]	1983	90, 72
Oe Horizon (5-2 cm)[a]	1983	134, 183
B Horizon (60 cm)[a,b]	1983	380, 357
C Horizon (181 cm)[b]	1985	102
Groundwater (280 cm)[b]	1985	45
Stream F47[c]	1984-1985	145
Stream F49[c]	1984-1985	94
Stream F50[c]	1984-1985	197
Stream F31[c]	1984-1985	38
Stream F34[c]	1984-1985	44
Batchawana L. North	1983-1986	87
Batchawana L. South	1983-1986	116
Wishart L.	1983-1986	81
Little Turkey L.	1983-1986	63
Turkey L.	1983-1986	33

[a]   Foster and Nicolson (30); 2 Al$_t$ values correspond to unweighted mean concentrations for the dormant and growing seasons respectively; all samples were collected at a low elevation location within sub-basin F31.

[b]   Chew et al (31); mean values for samples collected from piezometers at a high elevation location near sub-basin F47; piezometer water at 67 cm had 701 μg.L^{-1} total Al$_t$.

[c]   J. A. Nicolson, unpuplished data.

Table 2   Median pH and DOC (mg.L^{-1}), and range and median total Al and inorganic monomeric Al (μg.L^{-1}) observed during the 1985 and 1986 spring melt episodes for selected high elevation streams in the Turkey Lakes Watershed.

Stream	Median pH	Median DOC	Total Al		Inorganic Monomeric Al	
			Range	Median	Range	Median
F47	5.5	2.4	108–420	281	68–371	195
F49	6.1	2.4	50–159	91	5–67	35
F50	5.3	4.1	156–227	193	23–226	66
Batchawana L. Outflow	5.8	4.2	72–159	116	3–244	55

Table 3   Total[a] aluminum ($\mu g.L^{-1}$) in various catchment compartments from selected locations.

Location	Precip-itation	Through-fall	Soil Water[b]			Ground-water	Streams	Reference
			Shallow	Inter-mediate	Deep			
Turkey Lakes Watershed, Ontario	32	49	134-183	357-380	102	45	38-197	30, 31, this study
St. Hippolyte, Quebec	20	-	100-600	47-650	-	-	50-220	52, 53
McDonalds Branch Watershed, NJ	12	46-182	452	604	728	300	14-502	54
Hubbard Brook, New Hampshire	tr	-	189-1010	251-850	-	-	150-710	55, 56
Laurel Hill, Pennsylvania	3	9	850	3590	-	-	81-900	57
Adirondacks, New York	-	-	420-790	220-1200	-	-	0-470	58
Findley Lake, Washington	30	60	720-790	580-740	-	-	20	59
Lake Gårdsjön, Sweden	tr	40	791-1740	2570-3110	-	-	583-828	60, 61
Solling, FRG	190	310-500	560-1100	1700-1900	-	-	-	62

[a] "total" aluminum may be either "acid extractable" or "total monomeric"; see individual references

[b] Shallow = water collected within or below the organic horizons; Intermediate = water collected within the B horizon; Deep = water collected within the C horizon.