The distribution of dissolved aluminum in Atlantic salmon (*Salmo salar*) rivers of Atlantic Canada and its potential effect on aquatic populations

Ian F. Dennis and Thomas A. Clair

Abstract: Studies from the 1980s concluded that aluminum (Al) was not a significant contributor to Atlantic salmon (*Salmo salar*) toxicity in Nova Scotia, located on Canada's Atlantic coast, because of the presence of dissolved organic matter that rendered ionic Al (Al_i) biologically inaccessible. Since this earlier work, new interpretations of Al_i effects, as well as improved techniques for its measurement, have been developed. However, no new data interpretation has been done to see if the conclusions reached in earlier work for Atlantic Canada were still valid. We sampled 97 salmon rivers from the provinces of New Brunswick (NB), Nova Scotia (NS), and the island of Newfoundland (NF) to determine total and Al_i concentrations to see if results exceeded newer toxicity standards established by the European Inland Fisheries Advisory Commission. We found that southwestern NS, the region with the greatest loss of salmon populations, has seven rivers where autumn Al_i values exceed values identified as toxic to aquatic life. A further three rivers exceed guidelines in NF. Our work shows that the sources of toxicity for salmon and other aquatic species in acidified environments are more complex than previously thought.

Résumé : Des études réalisées dans les années 1980 concluaient que l'aluminium (Al) ne participe pas de manière significative à la toxicité pour le saumon atlantique (*Salmo salar*) en Nouvelle-Écosse, sur la côte atlantique du Canada, en raison de la présence de matière organique dissoute rendant l'aluminium ionique (Al_i) non bioaccessible. Depuis, de nouvelles interprétations des effets de l'Al_i ainsi que des techniques améliorées pour mesurer ce paramètre ont été établies. Aucune nouvelle interprétation des données n'a toutefois été réalisée dans le but de vérifier la validité pour le Canada atlantique des conclusions des travaux antérieurs. Nous avons échantillonné 97 rivières à saumons dans les provinces du Nouveau-Brunswick (NB) et de la Nouvelle-Écosse (NÉ) et dans l'île de Terre-Neuve (TE) afin de déterminer les concentrations d'Al total et d'Al_i pour vérifier si les résultats dépassaient les seuils de toxicité plus récents établis par la Commission européenne consultative pour la pêche dans les eaux intérieures. Nous avons ainsi découvert que le sud-ouest de la NÉ, la région présentant les plus fortes pertes de populations de saumons, compte sept rivières dans lesquelles les valeurs automnales d'Al_i dépassent les seuils de toxicité pour la vie aquatique. Trois rivières à TN dépassent également ces seuils. Nos travaux démontrent que les sources de toxicité pour le saumon et d'autres espèces aquatiques dans les milieux acidifiés sont plus complexes que ce que les interprétations antérieures suggéraient.

[Traduit par la Rédaction]

Introduction

Atlantic salmon (*Salmo salar*) populations in Nova Scotia (NS), Canada, have been seriously affected by acid precipitation (Watt 1987; Clair et al. 2004). Over 30 rivers in that province have populations that have either been eradicated or seriously depleted over the last 40 years because of increased habitat acidification. Another potential cause of salmon pop-

I.F. Dennis. Environment Canada, Water Science and Technology Directorate, P.O. Box 6227, Sackville, NB E4L 1G6, Canada.
T.A. Clair. Environment Canada, Water Science and Technology Directorate, 45 Alderney Drive, Dartmouth, NS B2Y 2N6, Canada.

Corresponding author: Thomas A. Clair (e-mail: tom.clair@ec. gc.ca).

ulation reductions identified in the literature is the complexation of ionic aluminum (Al_i) on fish gills under low pH conditions, which leads to respiratory impairment (Gensemer and Playle 1999; Sparling and Lowe 1996). Work done in Norway (Kroglund et al. 2008), the Adirondack region of New York State (Schofield and Trojnar 1980), eastern Quebec (Roy and Campbell 1995), and elsewhere found that Al_i weathered from bedrock and exchanged from soils under acidic conditions could be linked to salmon mortality or reduced fitness in those areas. Moreover, reduced smolt fitness in fresh waters has also been shown to lead to increased mortality at sea (Kroglund and Finstad 2003; Kroglund et al. 2007; Monette et al. 2008), which is not easily measured using freshwater-based toxicology assessments.

Quantifying the potential impacts of Al_i on ecosystem components is complex. The severity of its effects on aquatic biota will vary depending on the tolerance of the fish or invertebrate species in question and the element's ionic state, which is determined by pH and the concentrations of other dissolved components of the solution. Al_i affects fish when positively charged Al_i species bind with the negatively

charged fish gill epithelium, causing irritation that results in excessive mucous production, which then clogs gill membranes. The excess mucous can eventually lead to severe respiratory reduction in the fish (Rosseland and Staurnes 1994; Sparling and Lowe 1996; Klöppel et al. 1997).

The role of Al_i on the health of salmon and other biota in the acidified fresh waters of the east coast region of Canada (referred to as Atlantic Canada) was not as clear compared with other places such as Norway, because of the presence of high levels of organic carbon (OC) in many of its surface waters. Clair et al. (2007) showed that because of flat topography and the relative impermeability of subsurface geology, large portions of Atlantic Canada contain wetlands generating OC that can complex metals, including Al in natural waters.

OC in fresh waters contains negatively charged carboxylic acid functional groups, which complex metals, including Al, depending in large part on ambient pH. At pH values < 5.5, these sites provide binding opportunities for metal ions (Tipping et al. 1991), thus removing metallic ions from solution into an inert, organically bound complex, making them unavailable for interaction with biota, especially the gills of fish. Because Al ionic state and toxicity also vary depending on ambient pH (Baker and Schofield 1982; Driscoll et al. 2001; Howells et al. 1990), assigning total Al concentration levels to indicate potential harm to aquatic life cannot be done without taking both pH and OC complexation into account.

Assessing the chemical impact and interactions of organic matter in fresh waters is difficult, as OC is operationally defined. In waters containing high levels of suspended matter, samples are prefiltered with a 0.45 µm glass fiber filter before analysis, and the resulting sample is defined as dissolved organic carbon (DOC). OC from unfiltered samples is defined as total organic carbon (TOC). The waters we sampled were all from undisturbed watersheds with little suspended matter (Clair et al. 2007), and no filtering was done on them before OC analysis. Extensive laboratory comparisons in this region have shown that the difference between DOC and TOC in waters draining non-agricultural waters is usually <5%, so filtering is not routinely done for natural samples. OC in this study is therefore defined as TOC.

Based on an extensive review of existing toxicological and geochemical literature, the European Inland Fisheries Advisory Commission (EIFAC) recommended that for protection of aquatic life, Al_i should not exceed 15 µg·L^{-1} at pH levels between 5.0 and 6.0 (Howells et al. 1990). In this pH range, the predominating Al forms were $Al(OH)^{2+}$, $Al(OH)_2^+$, or various other positively charged configurations that were shown to be most irritating to gill epithelia and thus could cause harmful effects. They also show that a number of other aquatic species groups such as macroinvertebrates are affected at these levels. Baker and Schofield (1982) also identified the pH range of 5.2 to 5.4 as leading to the greatest Al_i toxicity effects in fish.

Al_i has also been shown to cause deleterious effects at pH values below 5.0 when it is in the Al^{3+} form, but to a lesser extent than between pH 5 and 5.4 (Howells et al. 1990). Howells et al. (1990) therefore recommended that 30 µg·L^{-1} be used as a harmful Al_i criterion in waters with pH < 5.0. The Al_i toxic effect is generally reduced with increasing pH and is thought to be negligible above pH 6, partly because its solubility is reduced at that acidity level.

In the 1980s a few studies assessed the importance of TOC and pH in determining the potential toxicity of Al in the rivers of Atlantic Canada. However, these were done prior to improvements in speciation and assessment approaches. In particular, Lacroix and Townsend (1987) and Peterson et al. (1989) used an Al_i value of 50 µg·L^{-1} as a critical value where toxic effects would be significant, a value later found to be higher than the EIFAC guideline (Howells et al. 1990).

Earlier analytical approaches for estimating Al_i concentrations, as opposed total Al (Al_t), were also not always successful because of complications caused by complexation with OC. With the advent in the mid to late 1990s of newer, simpler, and field-oriented processing methods, it has become easier to extract and stabilize total and complexed forms of Al in situ, which allows more flexibility in handling samples between field collection and laboratory analysis. With this improved capability, the sampling and analyzing of a large number of samples collected over a wide region has now become much easier, allowing this study to be done.

As no assessment of potential effects of Al_i had been done in Atlantic Canada since the 1980s, and as newer analytical techniques were now available for determining the ionic composition of Al, we thought it useful to reassess its potential contribution to the demise of Atlantic salmon populations as well as its potential effects on aquatic communities in the region. We therefore measured concentrations of total (Al_t) and Al complexed on organic matter (Al_o), and then by difference, estimated Al_i in 97 rivers in Atlantic Canada that had or were known to have had Atlantic salmon populations. Though Al toxicity effects are most severe in the springtime, we sampled the rivers during the autumn base flow period to try to better identify the geological regions most susceptible to producing dissolved Al_i.

Our main goal was therefore to produce an overview of Al_i concentrations in rivers of Atlantic Canada that were known to have had Atlantic salmon populations in the past. We used the survey information to identify where potentially ecologically important Al_i concentrations could be found. We then developed statistical regressions using Al_t, pH, and TOC, as well as other parameters to predict Al_i concentrations in the region's other fresh waters to produce a tool useful for aquatic ecologists to assess its potential toxicological importance. We also tested for the null hypothesis that complexation of Al by TOC is widespread in Atlantic Canadian fresh waters and that concentrations of Al considered deleterious to fish using the EIFAC standard will not be found in the Atlantic salmon streams that we sampled, because of the high ambient TOC concentrations.

Materials and methods

Study area

Atlantic Canada is located at the extreme northeastern portion of North America (Fig. 1). The region contains a wide variety of geological terranes, as well as a wide range of soil types, ranging from thin podsols to well-developed agricultural soils. Over 100 rivers located in the provinces of New Brunswick (NB), Nova Scotia (NS), and the island of Newfoundland (NF, part of the Province of Newfoundland and Labrador) have been identified as having or had Atlantic salmon historically (Watt 1987).

1176

Can. J. Fish. Aquat. Sci. Vol. 69, 2012

Fig. 1. Location of 97 sampling sites in Atlantic Canada. Light bars denote total aluminum (Al$_t$), and dark bars are for ionic aluminum (Al$_i$). Inset shows area location within North America.
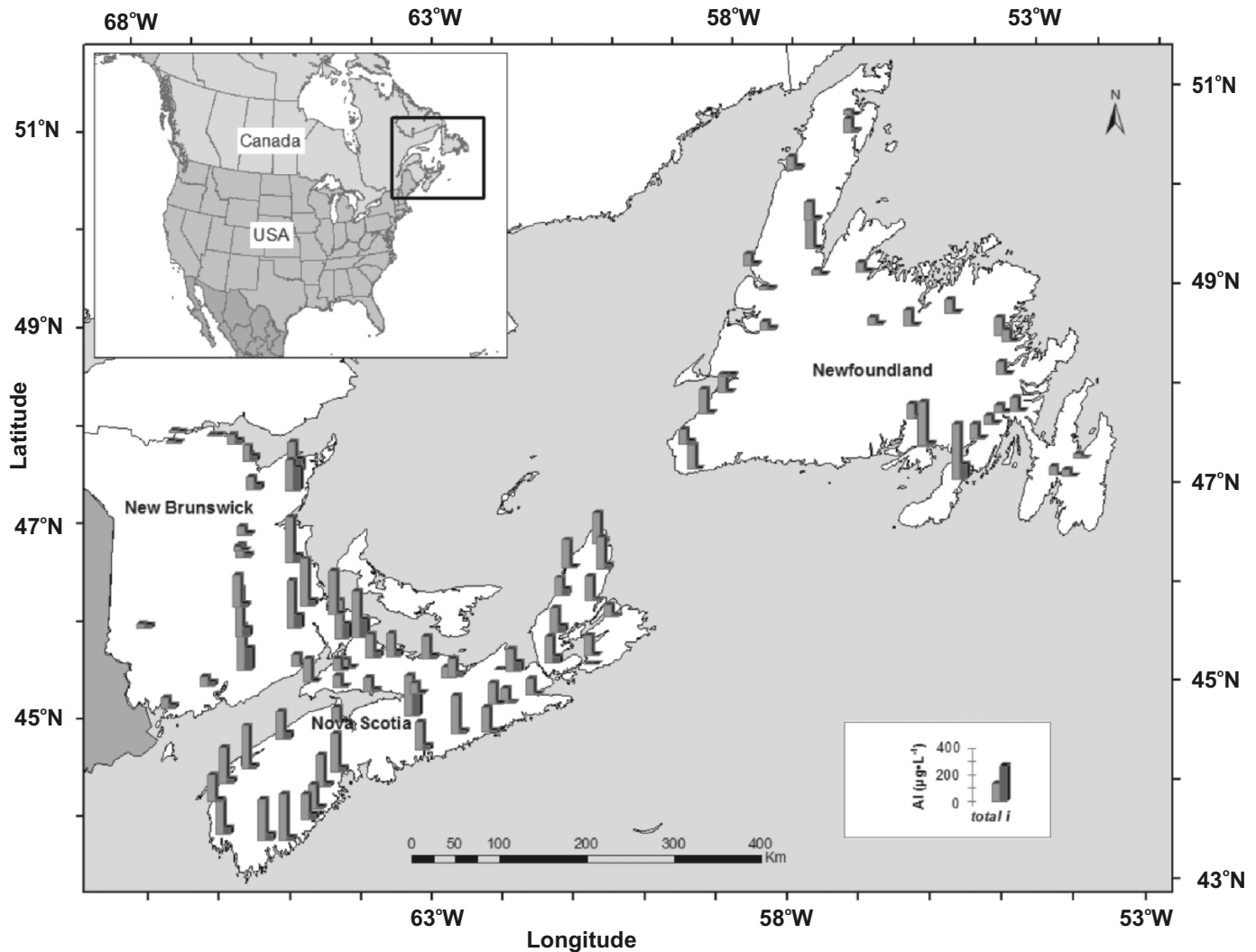
In the fall of 2006, we sampled 97 of these rivers that were undisturbed by industrial or urban development. All of the catchments sampled were forested, though some had small-scale forestry activities. There were occasional small villages or farms in some of the catchments, but as far as could be determined, none had activities that could cause siltation or other major disturbances to the studied river. All were sampled at locations free of estuarine effects.

Forty-two of the rivers were located in NS, most of which were located in catchments overlain by thin, glaciated soils and located over poorly acid-buffering slates and granites, though a number of sites in the northern part of the province were located over sandstone formations and had deeper, better acid-buffered soils (Keppie 2000; Shilts 1981). Twenty-three sites were located in NB, in a region mostly underlain by siliceous sandstones (Fyffe and Richard 2007), while the remaining 32 rivers were located in NF, in catchments underlain mainly by siliceous sedimentary bedrock or granites (Williams and Hayes 2004). Major ion water chemistry was reflective of the soil and bedrock types. Acidity ranged widely in these rivers, with pH values from 8.2 in some NF and NB rivers to 4.5 at some sites in southwest NS, which

receive relative high acid deposition levels from the eastern USA and central Canada (Table 1; Clair et al. 2007).

Clair et al. (2011) have shown that though sulphur deposition from acid rain has decreased by approximately 50% in the last 30 years, there has been no concurrent improvement in lake acidity or acid neutralization capacity over that period in NS and NF, unlike anywhere else in North America and Europe where water chemistry is widely improving (Skjelkvåle et al. 2005; Garmo et al. 2011). This lack of improvement is due to the depletion of base cations from the shallow, podsolic soils found in much of these provinces and is also the potential cause of further stress to biological populations as dissolved calcium has been reduced (Jeziorski et al. 2008). The lack of base cations in soils therefore requires their substitution by H$^+$ and ionic forms of Al to maintain electroneutrality, causing low pH and higher Al$_i$ concentrations (Driscoll 1985). Water chemistry is further complicated in NS and parts of NF by a preponderance of rivers with high levels of dissolved organic matter, which is generated by decaying plant organic matter in wet soils, especially wetlands, that is transported to lakes and rivers (Clair et al. 2007). This material is negatively charged and has the ability

Table 1. Range of values for key parameters in this study for each region studied.

	TOC (mg·L^{-1})	pH	ANC$_G$ (mg·L^{-1})	Al$_t$ (µg·L^{-1})	Al$_o$ (µg·L^{-1})	Al$_i$ (µg·L^{-1})	%AL$_i$
New Brunswick, 22 rivers							
Max.	28.3	8.2	77.7	415.7	364.4	199.8	75.1
Min.	2.4	6.5	5.8	12.5	5.5	5.5	2.4
Med.	6.9	7.6	18.1	106.7	79.5	31.0	33.4
Newfoundland, 32 rivers							
Max.	14.5	8.3	82.2	464.0	352.4	126.1	75.9
Min.	4.6	5.3	0.5	21.0	6.1	0.6	0.4
Med.	8.2	7.0	7.0	110.3	97.6	10.8	11.0
Nova Scotia, 43 rivers							
Max.	29.1	7.6	21.8	394.6	364.7	230.0	70.1
Min.	4.8	4.1	0.0	73.1	60.0	6.9	4.0
Med.	9.8	6.4	3.1	206.0	173.7	25.3	12.4

Note: TOC, total organic carbon; ANC$_G$, Gran acid neutralization capacity; AL$_t$, total aluminum; AL$_o$, Al complexed on organic matter; AL$_i$, ionic aluminum.

to complex positively charged metals in solution (Tipping et al. 1991).

Field sampling and laboratory analyses

At each site, a water sample was collected for major ion analysis, and three unfiltered 500 mL water samples were collected for total metal analysis. Processing and analysis of Al samples was based on the work of Tangen et al. (2002). Three 250 mL samples were drawn directly from the stream or river into a cartridge containing 500 mg of a preconditioned benzene sulphonic acid bound to a silica base cation exchange resin. The cartridges were prerinsed with 28 mL 0.4 mol·L^{-1} NH$_4^+$ acetate buffer at pH 5, followed by 28 mL of river sample water. Thirty millilitres of the sample were then passed through the column and the eluate collected. At each site we therefore had (*i*) three unfiltered samples for Al$_t$, (*ii*) three samples where Al$_i$ had been removed by the exchange resins, so that what remained in the eluate was Al$_o$, and (*iii*) one sample for pH, conductivity, TOC, and major ion analysis. All aluminum values reported are averages of the replicates.

Al$_i$ was not measured directly, but estimated as the difference between Al$_t$ and Al$_o$ (i.e., Al$_i$ = Al$_t$ – Al$_o$). In the presence of suspended or colloidal Al in the water sample, this method could inadvertently cause an overestimation of Al$_i$, as the Al in suspended matter, which would be bound and thus biologically inert, could get trapped by the exchange resins. This issue probably caused complications in data interpretation, which we discuss below.

Both the ion-exchanged and unprocessed water samples were stored in cool conditions until delivered to Environment Canada's Atlantic Laboratory for Environmental Testing in Moncton, NB, a laboratory certified through the Canadian Association for Laboratory Accreditation. The metal samples were acidified to pH < 2 using concentrated HNO$_3$. Total Al was analyzed in both the ion exchanged (Al$_o$) and unfiltered Al (Al$_t$) sample using inductively coupled plasma mass spectrometry (ICP-MS).

All major ion and organic carbon samples were analyzed according to Atlantic Laboratory for Environmental Testing
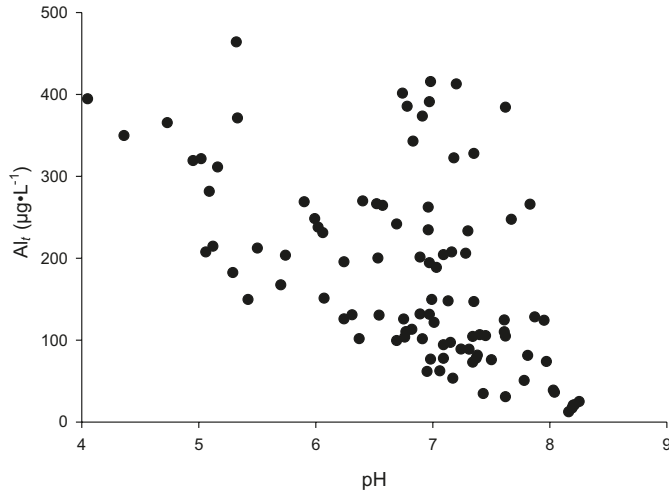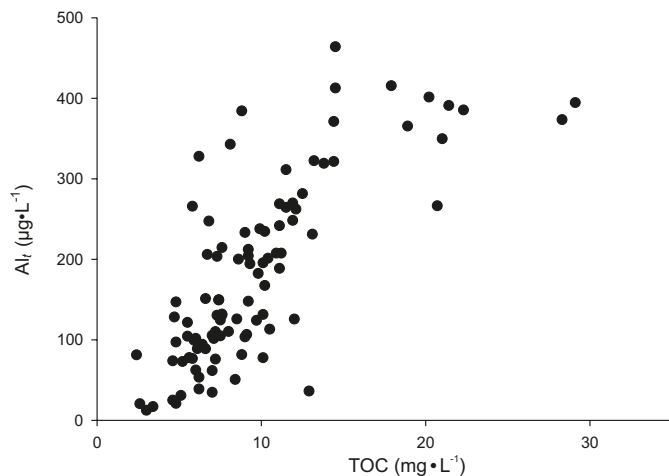
standard protocols. pH was measured potentiometrically, Cl$^-$ and NO$_3^-$ were done by ion chromatography, while Ca^{2+}, Mg^{2+}, K$^+$, and Na$^+$ were done by inductively coupled plasma emission spectrometry. Gran acid neutralization capacity (ANC$_G$) was estimated from the measured titration curve and reported as µequiv.·L^{-1} of HCO$_3^-$. Calculated ANC (ANC$_c$) was estimated by subtracting the sum of base cations (in equivalent units) from the sum of acid anions. TOC was measured using a high temperature combustion method.

Results and discussion

Regional geochemistry

Results revealed distinctive geographical patterns in the distribution of Al$_t$ and Al$_i$ (Fig. 1). Al$_t$ ranged widely, from a low of 12.5 µg·L^{-1} in northern NB's Charlo River to 464 µg·L^{-1} in the Red Harbour River of NF (Table 1). The highest Al$_t$ values, which exceeded 300 µg·L^{-1}, were mostly located in catchments underlain by granitic and slate bedrock in southwest NS and over siliceous sandstones in eastern NB and northern NS (Fig. 1). Soils were very different between these two regions, with southwest NS soils being very thin (~0.5 m), poorly drained, and podzolic (Keys 2007), while eastern NB's were mostly composed of deeper, well-drained sandy–loam tills (Colpitts et al. 1995). One high Al$_t$ value (464 µg·L^{-1}) from Red Harbour in NF did not fit into this regional pattern. That catchment had very shallow soils overlying volcanic bedrock, but received relatively low acid deposition because of its location far from long range emission sources in central Canada and the eastern USA. Though the catchment is located approximately 100 km southwest of the Come By Chance oil refinery, none of the other chemical variables (SO$_4^{2-}$ or other metals) suggested that refinery emissions might be the cause of the high value. A closer look at the local geology may provide answers to this dilemma.

We expected that Al$_t$ values would be greater at lower pH because of enhanced ion exchange in soils and weathering of bedrock. The relationship between Al$_t$ and pH did show a lower limit in the pH–Al$_t$ interaction and that higher Al$_t$ val-

Fig. 2. Total Al (Al$_t$) versus pH for all samples.

Fig. 4. Relationship between % ionic Al (Al$_i$) and TOC.

Fig. 3. TOC versus Al$_t$ relationship for the study samples.
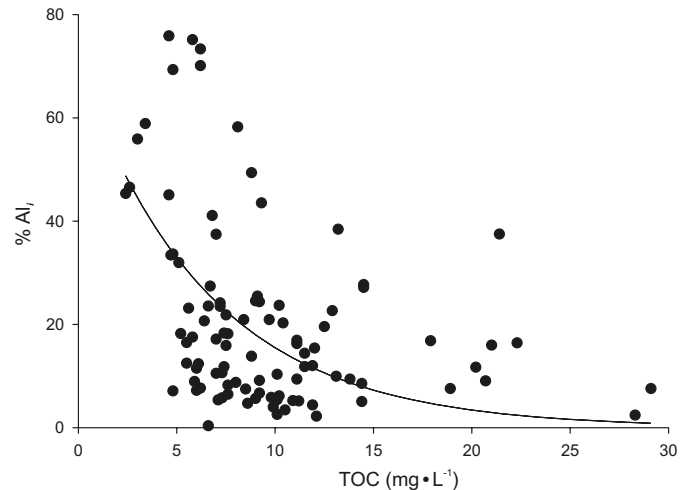
Fig. 5. Ionic Al (Al$_i$) versus pH.
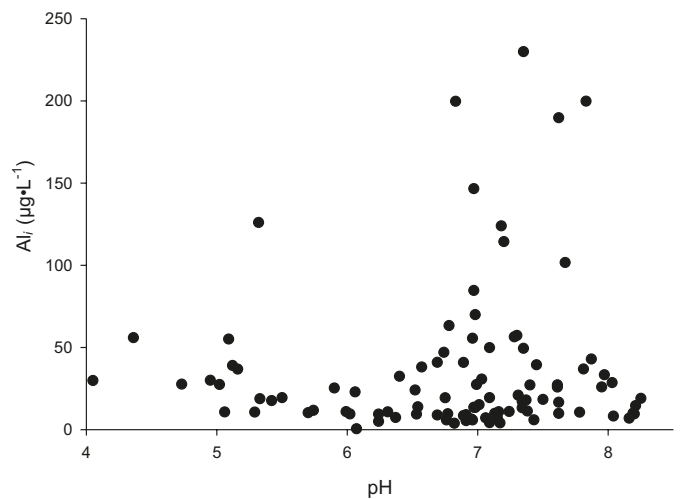
ues roughly correlated with lower pH (Fig. 2). However, a cluster of high Al$_t$ values originating in samples from eastern NB and northern NS was located in the pH range 6.8–8.0, which did not allow a reasonable regression to be calculated. This phenomenon of high Al$_t$ must be due to the influence of the sandstone geological bedrock that underlies most of eastern NB and southeast NS, though this type of relationship also has not been reported elsewhere, as the usual accepted relationship follows the low pH – high Al$_t$ pattern (e.g., Driscoll 1985).

The correlation between Al$_t$ and TOC showed an increasing linear relationship until TOC values reached ~15 mg·L^{-1}, whence Al$_t$ values leveled off at roughly 450 µg·L^{-1} (Fig. 3), a value ~150 µg·L^{-1} lower than the maximum value reported from the Adirondack Mountains of New York State (cited by Howells et al. 1990). These data suggest that there seems to be a limit to how much Al can be weathered from soil solution or bedrock in the geological–soil conditions existing in Atlantic Canada,. It was expected that Al$_i$ values would be greater at low TOC values than at higher ones, which was generally the case (Fig. 4). However, the best statistical relationship we could develop (exponentially decreasing equation between TOC and %Al$_i$) could only explain 20% of the variability in the data.

Al$_i$ values were consistently lower than Al$_o$ (with two exceptions in high pH waters) (Fig. 1) and ranged from a low of 0.06 µg·L^{-1} in Northwest Brook (NF) to a high of 230 µg·L^{-1} in the West River, Antigonish, NS. Based on the work of Driscoll (1985) and Henriksen et al. (1988), we expected that higher Al$_i$ concentrations would be found at lower pH values. This was not always the case in our data, as 8 of the 97 Al$_i$ values were at pH levels > 6.5 (Fig. 5).

We suspected that these high pH, high Al$_i$ values might be an artifact of the ion exchange method used. Teien et al. (2007) showed that in high TOC waters collected during high river flows in Norway, organic colloids could form, which then precipitated onto the ion exchange column, thus giving the false impression of higher Al$_i$ concentrations. Our sampling, quality control, and laboratory assessments, however, did not suggest any problems of this nature, though all of these high pH and "Al$_i$" samples also had high TOC levels. Nevertheless, as not all high TOC, high pH samples showed high Al$_i$ concentrations, we therefore decided that selectively removing data from the analysis without an objective method of identifying obviously incorrect data was not acceptable, so that we kept all the data in our statistical analysis. It is important to note that even if these high Al$_i$ values

are incorrect, that at the measured pH values, the concentrations reported would have no effect on aquatic toxicity (see below).

As we were able to directly measure the complexed portion of Al (Al_o), we developed an equation to predict Al_o concentration with what we assumed to be its major chemistry controls. A multilinear relationship predicting Al_o from Al_t and TOC was calculated that accounted for 90% of the variability (eq. 1):

$$(1) \quad Al_o = -16.4 + 0.57 \cdot Al_t \; (\mu g \cdot L^{-1})$$
$$+ 6.15 \cdot TOC \; (mg \cdot L^{-1}), \quad r^2 = 0.90$$

The addition of pH to the regression only improved its predictability by another 3%:

$$(2) \quad Al_o = 166.4 + 0.50 \cdot Al_t + 5.06 \cdot TOC$$
$$- 23.5 \cdot pH, \quad r^2 = 0.93$$

Converting pH to H^+ activity or adding other cations or anions did not significantly improve the regression, so that most of the Al_o variation in our survey could be accounted for by Al_t, TOC, and pH.

The correlation equation predicting Al_i concentration from Al_t and TOC (eq. 3) was similar to eq. 1, except for sign changes, but only explained 52% of the variability:

$$(3) \quad Al_i = 16.4 + 0.43 \cdot Al_t \; (\mu g \cdot L^{-1})$$
$$- 6.16 \cdot TOC \; (mg \cdot L^{-1}), \quad r^2 = 0.52$$

The addition of pH in the regression equation improved the predictive power for Al_i even though the equation was also similar to that for Al_o, except for the signs on the pH and TOC coefficients.

$$(4) \quad Al_i = -166.5 + 0.5 \cdot Al_t - 5.06 \cdot TOC$$
$$+ 23.5 \cdot pH, \quad r^2 = 0.68$$

The use of these equations can then allow ecologists and water quality specialists to predict biologically reactive Al_i concentrations in Atlantic Canada waters where specialized measurements using ion exchange approaches have not been made.

Other relatively recent studies analyzed fresh waters in other parts of the world, with which we compared our data. Warby et al. (2008) sampled 113 lakes in the northeastern USA in the summer of 2001 and estimated a median Al_t value of 39 $\mu g \cdot L^{-1}$ for a region stretching from Maine to Pennsylvania, compared with our median value of 147.9 $\mu g \cdot L^{-1}$. Their median Al_i value was 12.5 $\mu g \cdot L^{-1}$, while ours was slightly higher at 18.6 $\mu g \cdot L^{-1}$. The USA data shows regionally lower Al_t than ours, even though our study region is further away from anthropogenic acidification sources, a difference we can only ascribe to the influence of geological substrates. Titration of soils and exposed bedrock by acid deposition can be an important contributor to the dissolution of Al in waters (Cronan and Schofield 1990). However, considering that northeastern USA receives two to three times more acid deposition than our study area (Vet et al. 2005), we can see that geology and soil composition also have an important role to play, along with acid deposition in determining Al_t levels.

Table 2. Rivers where Al_i exceeds EIFAC criterion of 15 $\mu g \cdot L^{-1}$ (5 > pH > 6) or are near 30 $\mu g \cdot L^{-1}$ at pH < 5.

Map No.	Site	TOC ($mg \cdot L^{-1}$)	pH	Al_i ($\mu g \cdot L^{-1}$)
pH > 5.0				
82	W Sheet Harbor	14.40	5.0	27.50
97	Tusket	12.50	5.1	55.10
94	Mersey	7.60	5.1	39.03
99	Sissiboo	11.50	5.2	36.83
45	Red Harbour	14.50	5.3	126.06
49	Salmon River 2	14.40	5.3	18.80
33	Cat Arm	7.40	5.4	17.67
93	Medway	9.20	5.5	19.44
92	La Have	11.10	5.9	25.30
98	Meteghan	13.10	6.1	23.00
pH < 5.0				
95	Sable	29.10	4.05	29.90
96	Roseway	21.00	4.36	55.93
100	Bear River	18.90	4.73	27.70
91	Gold	13.80	4.95	30.04

Other studies in Europe have also measured Al_i in lakes and have produced data with which we can compare ours. Rask et al. (1995) sampled water chemistry and fish populations from 80 lakes in Finland to develop a model that could predict fish population tolerances to pH and Al_i. Their Al_i values were relatively similar to those we found in our study and ranged from very low to approximately 150 $\mu g \cdot L^{-1}$, with one outlying value near 230 $\mu g \cdot L^{-1}$. Hesthagen et al. (2008) compared water chemistry with brown trout (*Salmo trutta*) population health in 790 lakes in Norway. Their Al_i values ranged from very low to approximately 300 $\mu g \cdot L^{-1}$, though there was a large group of sites with values near 0 $\mu g \cdot L^{-1}$ and another large grouping in the range 20–100 $\mu g \cdot L^{-1}$, again similar to the range of values we measured. The data from other regions therefore shows that our Al_i values are typical for cool, temperate ecosystems underlain by a range of geological types.

Much of the earlier freshwater Al literature (e.g., Driscoll 1985; Campbell et al. 1992) was developed from samples collected in regions with relatively homogeneous soil and geological and acid deposition conditions. This has allowed an understanding of dissolved Al geochemistry within specific soil and geological types, but has not provided information applicable to regions with wide ranges of characteristics. Our results are therefore less informative concerning geochemical processing, but are more useful in terms of providing an idea of the variability of Al in fresh waters of a glaciated region with a wide range of geological substrates.

One of the limits of this study is that sampling and isolation of Al_i were done in the fall during base flow period, as opposed to the spring when TOC concentrations and Al complexation is at its annual minimum and pH is lowest because of the dilution effects of snowmelt. Campbell et al. (1992) developed a linear–logarithmic equation similar to ours that described the relationship between Al_o with Al_i, H^+ activity, and DOC in rivers from the north shore of the St. Lawrence River in eastern Canada. They found that their statistical relationship broke down during snowmelt periods when they sus-

Fig. 6. Location and relative Al$_i$ concentrations of sites that exceed the $5 < pH < 6$ at 15 µg·L^{-1} criterion (light bars) and those that either exceed or are close to the pH < 5 at 30 µg·L^{-1} criterion (dark bars). The numbers by the bar relate to Table 2, where site name, TOC, and pH are listed.
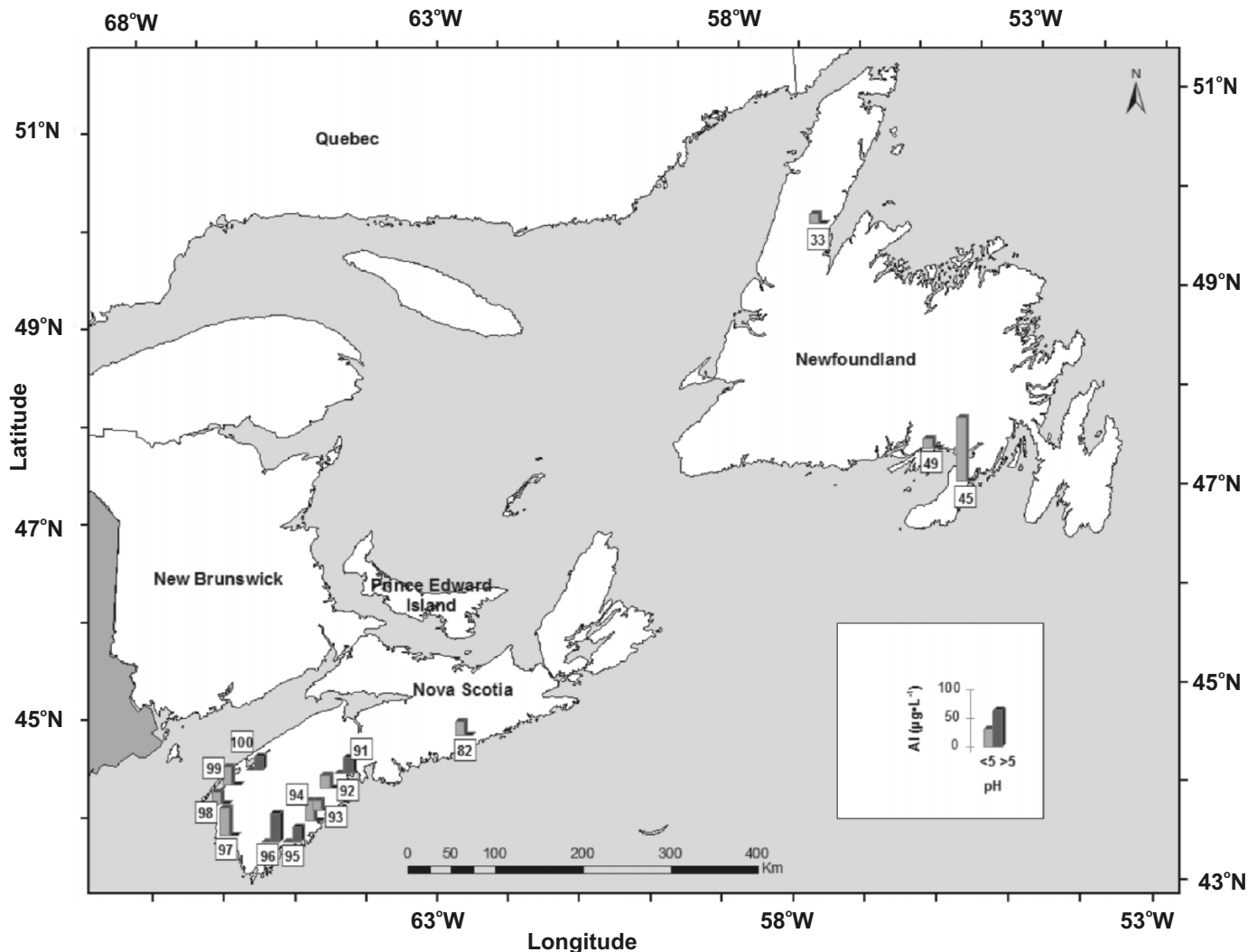
pected that a reduction in the metal complexation capacity of DOC due to its dilution in spring runoff increased relative Al$_i$ activity. In our case, we expect that TOC–Al complexation would be at its maximum during autumn when we sampled and that Al$_i$ might be found at a higher concentration in the spring when pH is lowest and TOC is more dilute and has less complexation capacity.

Ecosystem implications

When we apply the EIFAC effects criterion of 15 µg·L^{-1} Al$_i$ for waters of pH between 5.0 and 6.0 (Howells et al. 1990), 10 of our rivers (7 in NS, 3 in NF) had values that were in exceedance (Table 2; Fig. 6). Further, four other rivers with pH < 5.0 had Al$_i$ values near or greater than 30 µg·L^{-1}, which also exceed or are close to the criterion for that pH category. The conclusion that 14 rivers in Atlantic Canada had Al$_i$ values that exceeded the EIFAC criterion during autumn was somewhat unexpected, as we initially hypothesized that because of generally high TOC concentrations in our study rivers, all Al was complexed and thus not a factor in reducing the ability of aquatic ecosystems to survive or thrive.

There is some subjectivity in assigning Al$_i$ concentrations to lethal and sublethal effects on biota, as other criteria have been used elsewhere. Baker and Schofield (1982) studied a number of fish species from the Adirondack region of New York State and showed differential effects of Al$_i$, which varied between species and pH levels, concluding that Al$_i$ concentrations >100 µg·L^{-1} were important in causing harm to fish. Similarly to Howells et al. (1990), they also showed that Al effects were most important in the pH range of 5.2–5.4, emphasizing the interplay between Al speciation and pH in determining fish survival. The work from the Adirondacks was recently updated by Baldigo et al. (2007), who used 50 and 100 µg·L^{-1} as levels where "low" and "high" mortality effects on caged brook trout (*Salvelinus fontinalis*) could be assigned. Should we use the USA criteria with our data, then Al$_i$ concentrations found in our region would not be considered toxic or harmful to aquatic life.

To complicate matters further, Kroglund et al. (2008) suggest that spring freshwater Al$_i$ levels as low as 5–10 µg·L^{-1} may cause a 25%–50% reduction in salmon smolt survival during migration into the open ocean. Monette et al. (2008)

and McCormick et al. (2009) also confirm the reduced smolt survival rates under low pH, high Al_i conditions based on controlled studies, though their work used higher Al_i values than the Kroglund et al. evaluation. The effect levels shown by these two studies cannot be used to assess our data because we have no spring Al_i values, but provide an indication that dissolved Al_i effects may be more severe and extend to more Atlantic Canadian rivers than shown in this study. Further sampling in the spring is clearly warranted in NS and some NF rivers when this is taken into account.

Another potential wrinkle in assessing Al_i effects is that fluoride (F^-) in water has been shown to have an attenuation effect on toxicity as it outcompetes Al_i for binding sites on fish gills (Wilkinson et al. 1990). It is difficult to assess the importance of this reaction in our study, as F^- was not analyzed because it has rarely been found at analytical detection levels in the region and thus is no longer analyzed in Environment Canada programs. As a first approximation, we will assume, as in USA, Norwegian, and Finish studies, that its effect is negligible.

Regardless of which criteria are used to assess the toxicity of Al_i, it is clear that even at low concentrations, especially in the pH range of 5.0 to 5.6, it will cause an irritation to salmon and other aquatic biota, which, if not necessarily lethal, will cause further degradation in fitness and the ability to adequately deal with other stresses, such as stream acid pulses, moltification, and migration to the ocean. As our study results are also based on autumn data when Al–TOC complexation capacity is at its maximum, we can most likely assume that springtime Al_i conditions will be more deleterious to regional fish survival than in the autumn and therefore need to be further studied.

Because of the landscape, geology, and acid deposition conditions in Atlantic Canada, the regression equations we develop with our data are specific to a geographical area, though the approach we take can be used in other regions, as the types of interactions between the main chemical parameters in our work follow patterns shown elsewhere. The main region that our study identifies as having autumn Al_i values that are high enough to cause mortality or stress to aquatic life is southwestern NS. Our chemistry data correlate almost precisely with the data produced by Watt (1987), who showed that salmon populations in this region's rivers were either extinct or severely depleted. Though it is difficult to separate the exact contribution of Al_i versus pH, it is clear that aluminum is at levels high enough to cause harm to salmon and most likely other fish species.

In this study, we have identified the rivers where Al_i has the potential for causing the most harm for aquatic species in Atlantic Canada. Our data show that predicting ambient Al_i concentrations and their ecological effects is not straightforward. In Atlantic Canadian streams, many of the highest Al_i values were found in high pH (>6.5) waters where Al_i will be in highly hydroxylated form and thus toxicologically unimportant (Howells et al. 1990). Moreover, in the presence of high TOC concentrations such as are found in the region, a major portion of Al_t will be complexed and biologically inert. Nevertheless, in a number of the study area's highly acidic waters containing high TOC concentrations, Al_i can still be measured at levels known to cause harm to aquatic fauna. The need is now to apply this information in more

specific ways and on a seasonal cycle to better quantify the extent of the problem to key indicator aquatic species and ecosystems. Atlantic salmon, as well as many other aquatic biota, are most active and vulnerable to aluminum toxicity in the spring during migration and reproduction when water flows are high and pH is low. Water sampling and Al speciation therefore needs to be done in the spring, especially in southwestern and eastern NS, to get an accurate assessment of the potential biological effects of Al_i in these highly sensitive waters.

Acknowledgements

References

Baker, J., and Schofield, C. 1982. Aluminum toxicity to fish in acidic waters. Water Air Soil Pollut. **18**(1–3): 289–309. doi:10.1007/BF02419419.

Baldigo, B.P., Lawrence, G., and Simonin, H. 2007. Persistent mortality of brook trout in episodically acidified streams of the southwestern Adirondack Mountains, New York. Trans. Am. Fish. Soc. **136**(1): 121–134. doi:10.1577/T06-043.1.

Campbell, P.G.C., Hansen, H.J., Dubreuil, B., and Nelson, W.O. 1992. Geochemistry of Quebec north shore Salmon rivers during snowmelt: organic acid pulse and aluminum mobilization. Can. J. Fish. Aquat. Sci. **49**(9): 1938–1952. doi:10.1139/f92-215.

Clair, T.A., Dennis, I.F., Amiro, P., and Cosby, B.J. 2004. Past and future chemistry changes in acidified Nova Scotian Atlantic salmon (*Salmo salar*) rivers: a dynamic modeling approach. Can. J. Fish. Aquat. Sci. **61**(10): 1965–1975. doi:10.1139/f04-196.

Clair, T.A., Dennis, I.F., Scruton, D.A., and Gilliss, M. 2007. Freshwater acidification research in Atlantic Canada: a review of results and predictions for the future. Environ. Rev. **15**: 153–167. doi:10.1139/A07-004.

Clair, T.A., Dennis, I.F., and Vet, R. 2011. Water chemistry and dissolved organic carbon trends in lakes from Canada's Atlantic provinces: no recovery from acidification measured after 25 years of lake monitoring. Can. J. Fish. Aquat. Sci. **68**(4): 663–674. doi:10.1139/f2011-013.

Colpitts, M.C., Fahmy, S.H., MacDougall, J.E., Ng, T.T.M., McInnis, B., and Zelaszny, V.F. 1995. Forest soils of New Brunswick. Agriculture and Agri-Food Canada, Fredericton, N.B., Canada.

Cronan, C.S., and Schofield, C.L. 1990. Relationships between aqueous aluminum and acidic deposition in forested watersheds of North America and northern Europe. Environ. Sci. Technol. **24**(7): 1100–1105. doi:10.1021/es00077a022.

Driscoll, C.T. 1985. Aluminum in acidic surface waters: chemistry, transport, and effects. Environ. Health Perspect. **63**: 93–104. doi:10.1289/ehp.856393. PMID:3935428.

Driscoll, C.T., Lawrence, G.B., Bulger, A.J., Butler, T.J., Cronan, C.S., Eagar, C., Lambert, K.F., Likens, G.E., Stoddard, J.L., and Weathers, K.C. 2001. Acidic deposition in the northeastern United

1182

Can. J. Fish. Aquat. Sci. Vol. 69, 2012

States: sources and inputs, ecosystem effects, and management strategies. Bioscience, **51**(3): 180–198. doi:10.1641/0006-3568 (2001)051[0180:ADITNU]2.0.CO;2.

Fyffe, L.R., and Richard, D.M. 2007. Lithological map of New Brunswick. New Brunswick Department of Natural Resources, Minerals, Policy and Planning Division, Fredericton, N.B., Canada. Plates 2007–2018.

Garmo, O.A., Skjelkvåle, B.L., Columbo, L., Curtis, C., Dubokova, I., Folster, J., Hoffman, A., Hogasen, T., Jeffries, D., Keller, W., Majer, V., Paterson, A., Rogora, M., Rzychon, D., Srybny, A., Steingruber, S., Stoddard, J.L., Talkop, R., Vuorenmaa, J., de Wit, H., and Worsztynowicz, A. 2011. Trends in surface water chemistry in Europe and North America 1990–2008. *Edited by* B.L. Skjelkvåle and H. de Wit. NIVA, Oslo, Norway. Report SNO 6218–2011.

Gensemer, R.W., and Playle, R.C. 1999. The bioavailability and toxicity of aluminum in aquatic environments. Crit. Rev. Environ. Sci. Technol. **29**(4): 315–450. doi:10.1080/10643389991259245.

Henriksen, A., Lien, L., Traaen, T.S., Sevaldrud, I.S., and Brakke, D. F. 1988. Lake acidification in Norway: present and predicted chemical status. Ambio, **17**: 259–266.

Hesthagen, T., Fiske, P., and Skjelkvåle, B.L. 2008. Critical limits for acid neutralizing capacity of brown trout (*Salmo trutta*) in Norwegian lakes differing in organic carbon concentrations. Aquat. Ecol. **42**(2): 307–316. doi:10.1007/s10452-008-9191-x.

Howells, G., Dalziel, T.R.K., Reader, J.P., and Solbe, J.F. 1990. EIFAC water quality criteria for European freshwater fish: report on aluminium. Chem. Ecol. **4**(3): 117–173. doi:10.1080/ 02757549008035972.

Jeziorski, A., Yan, N.D., Paterson, A.M., DeSellas, A.M., Turner, M.A., Jeffries, D.S., Keller, B., Weeber, R.C., McNicol, D.K., Palmer, M.E., McIver, K., Arseneau, K., Ginn, B.K., Cumming, B.F., and Smol, J.P. 2008. The widespread threat of calcium decline in fresh waters. Science, **322**(5906): 1374–1377. doi:10.1126/science. 1164949. PMID:19039134.

Keppie, J.D. 2000. Geological map of the Province of Nova Scotia, Map ME 2000-1. Nova Scotia Department of Natural Resources, Halifax, N.S., Canada.

Keys, K. 2007. Forest soil types of Nova Scotia: identification, description and interpretation. Manual FOR 2007-2. Nova Scotia Department of Natural Resources, Halifax, N.S., Canada.

Klöppel, H., Fliedner, A., and Kördel, W. 1997. Behaviour and ecotoxicology of aluminium in soil and water — review of the scientific literature. Chemosphere, **35**(1–2): 353–363. doi:10. 1016/S0045-6535(97)00161-6. PMID:9232003.

Kroglund, F., and Finstad, B. 2003. Low concentrations of inorganic monomeric aluminum impair physiological status and marine survival of Atlantic salmon. Aquaculture, **222**(1–4): 119–133. doi:10.1016/S0044-8486(03)00106-6.

Kroglund, F., Finstad, B., Stefansson, S.O., Nilsen, T.O., Kristensen, T., Rosseland, B.O., Teien, H.C., and Salbu, B. 2007. Exposure to moderate acid water and aluminum reduces Atlantic salmon post-smolt survival. Aquaculture, **273**(2–3): 360–373. doi:10.1016/j. aquaculture.2007.10.018.

Kroglund, F., Rosseland, B.O., Teien, H.C., Salbu, B., Kristensen, T., and Finstad, B. 2008. Water quality limits for Atlantic salmon (*Salmo salar*) exposed to short term reductions in pH and increased aluminum simulating episodes. Hydrol. Earth Syst. Sci. **12**(2): 491–507. doi:10.5194/hess-12-491-2008.

Lacroix, G.L., and Townsend, D.R. 1987. Responses of juvenile Atlantic Salmon (*Salmo salar*) to episodic increases in acidity of Nova Scotia rivers. Can. J. Fish. Aquat. Sci. **44**(8): 1475–1484. doi:10.1139/f87-177.

McCormick, S.D., Keyes, A., Nislow, K.H., and Monette, M.Y. 2009.

Impacts of episodic acidification on in-stream survival and physiological impairment of Atlantic salmon (*Salmo salar*) smolts. Can. J. Fish. Aquat. Sci. **66**(3): 394–403. doi:10.1139/F09-002.

Monette, M.Y., Björnsson, B.T., and McCormick, S.D. 2008. Effects of short-term acid and aluminum exposure on the parr–smolt transformation in Atlantic salmon (*Salmo salar*): disruption of seawater tolerance and endocrine status. Gen. Comp. Endocrinol. **158**(1): 122–130. doi:10.1016/j.ygcen.2008.05.014. PMID:18606407.

Peterson, R.H., Bourbonniere, R.A., Lacroix, G.L., Martin-Robichaud, D.J., Takats, P., and Brun, G.L. 1989. Responses of Atlantic Salmon (*Salmo salar*) alevins to dissolved organic carbon and dissolved aluminum at low pH. Water Air Soil Pollut. **46**: 399–413.

Rask, M., Mannio, J., Forsius, M., Posch, M., and Vuorinen, P.J. 1995. How many fish populations in Finland are affected by acid precipitation? Environ. Biol. Fishes, **42**(1): 51–63. doi:10.1007/ BF00002351.

Rosseland, B.O., and Staurnes, M. 1994. Physiological mechanisms for toxic effects and resistance to acidic water: an ecophysiological and ecotoxicological approach. *In* Acidification of freshwater ecosystems: implications for the future. *Edited by* C.E.W. Steinberg and R.F. Wright. John Wiley & Sons Ltd., New York. pp. 227–246.

Roy, R., and Campbell, P.G.C. 1995. Survival time modeling of exposure of juvenile Atlantic salmon (*Salmo salar*) to mixtures of aluminum and zinc in soft water at low pH. Aquat. Toxicol. **33**(2): 155–176. doi:10.1016/0166-445X(95)00019-Z.

Schofield, C.L., and Trojnar, J.R. 1980. Aluminum toxicity to brook trout (*Salvelinus fontinalis*) in acidified waters. *In* Polluted rain. *Edited by* T.Y. Toribara, M.W. Miller, and P.E. Morrow. Plenum Press, New York. pp. 341–366.

Shilts, W.W. 1981. Sensitivity of bedrock to acidification: modification by glacial processes. Paper 81-14. Natural Resources Canada, Ottawa, Ont., Canada.

Skjelkvåle, B.L., Stoddard, J.L., Jeffries, D.S., Torseth, K., Hogasen, T., Bowman, J., Mannio, J., Monteith, D.T., Mosello, R., Rogora, M., Rzychon, D., Vesely, J., Wieting, J., Wilander, A., and Worsztyno-wicz, A. 2005. Regional scale evidence for improvements in surface water chemistry 1990–2001. Environ. Pollut. **137**(1): 165–176. doi:10.1016/j.envpol.2004.12.023. PMID:15944047.

Sparling, D.W., and Lowe, T.P. 1996. Environmental hazards of aluminum to plants, invertebrates, fish, and wildlife. Rev. Environ. Contam. Toxicol. **145**: 1–127. PMID:7494908.

Tangen, G., Wickstrøm, T., Lierhagen, S., Vogt, R., and Lund, W. 2002. Fractionation and determination of aluminum and iron in soil water samples using SPE cartridges and ICP-AES. Environ. Sci. Technol. **36**(24): 5421–5425. doi:10.1021/es020077i. PMID: 12521170.

Teien, H.C., Salbu, B., Kroglund, F., Heier, L.S., and Rosseland, B.O. 2007. The influence of colloidal material on aluminium speciation and estimated acid neutralizing capacity (ANC). Appl. Geochem. **22**(6): 1202–1208. doi:10.1016/j.apgeochem.2007.03.012.

Tipping, E., Woof, C., and Hurley, M.A. 1991. Humic substances in acid surface waters; modelling aluminum binding, contribution to ionic charge-balance, and control of pH. Water Res. **25**(4): 425–435. doi:10.1016/0043-1354(91)90079-6.

Vet, R., Brook, J., Ro, C.-U., Shaw, M., Narayan, J., Zhang, L., Moran, M.A., and Lusis, M. 2005. Atmospheric response to past emission control programs. Chapter 3, Canadian 2004 acid deposition science assessment. Environment Canada, Downsview, Ont., Canada. pp. 15–98.

Warby, R.A.F., Johnson, C.E., and Driscoll, C.T. 2008. Changes in aluminum concentrations and speciation in lakes across the northeastern U.S. following reductions in acidic deposition.

Environ. Sci. Technol. **42**(23): 8668–8674. doi:10.1021/es801125d. PMID:19192779.

Watt, W.D. 1987. A summary of the impact of acid rain on Atlantic salmon (*Salmo salar*) in Canada. Water Air Soil Pollut. **35**(1–2): 27–35. doi:10.1007/BF00183841.

Wilkinson, K.J., Campbell, P.G.C., and Couture, P. 1990. Effect of fluoride complexation of aluminum toxicity towards juvenile Atlantic salmon (*Salmo salar*). Can. J. Fish. Aquat. Sci. **47**(7): 1446–1452. doi:10.1139/f90-163.

Williams, H., and Hayes, J.P. 2004. Generalized interpretive map — Newfoundland Appalachians. Geological Survey, Natural Resources, Newfoundland and Labrador, St. John's, Nfld., Canada.