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## **The Atlantic Region Acid Rain Monitoring Program in Acidified Atlantic Salmon Rivers:**

### **Trends and Present Status**

by

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<sup>1</sup> La présente série documente les bases scientifiques des évaluations des ressources halieutiques du Canada. Elle traite des problèmes courants selon les échéanciers dictés. Les documents qu'elle contient ne doivent pas être considérés comme des énoncés définitifs sur les sujets traités, mais plutôt comme des rapports d'étape sur les études en cours.

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## Abstract

The Atlantic salmon resource of the Maritimes is impacted by acid rain in the Southern Upland (Atlantic Coast) area of Nova Scotia. Salmon runs in this area are extinct in 14 rivers, severely impacted in 20 rivers, and lightly impacted in 16 rivers. There are 13 other salmon rivers, with higher ANC generation capacity, that do not have acid toxicity. Over the period 1981-1990, water temperatures rose and dissolved organic carbon levels declined in Nova Scotian rivers. The pH-levels in the rivers were controlled by organic acid levels, and pH rose as the organic acid levels fell. The 1991 Pinatubo eruption produced two years of lower water temperature, and subsequently lower pH levels and higher levels of DOC. This result is evidence of the role of water temperature in controlling DOC/pH levels. Levels of sulphate and hardness (magnesium plus calcium) in river water declined by equivalent amounts over the period 1981-1995. The most likely explanation is that  $\text{SO}_4^-$  levels are declining in response to the declining deposition, but instead of the hoped for decline in  $\text{H}^+$  there have been declines in deposition and leaching of  $\text{Ca}^{++}$  and  $\text{Mg}^{++}$ . More base cation retention in the soils and biota will increase the capacity for ANC generation and will eventually result in rising pH levels in the rivers, but this has not yet become noticeable. The decline in sulphate emission/deposition should become more pronounced over the next 5-10 years, as the Canada/USA Air Quality Accord takes effect, and water temperatures may continue to rise; so we anticipate a return of the trend toward less toxic salmon habitat. At sites which are borderline for acid toxicity, the population densities of Atlantic salmon juveniles rose in response to the lower river toxicities in the eighties and early nineties, and then fell again when the pH levels declined. There were no population trends at sites with higher (non-toxic) pH levels, or for any of the other nine fish species encountered in the acidified rivers.

## Résumé

La ressource en saumon de l'Atlantique des Maritimes subit les effets des pluies acides dans le Southern Upland (côte de l'Atlantique) secteur de la Nouvelle-Écosse. Les remontées de saumon sont disparues dans 14 rivières de cette zone, fortement affectées dans 20 rivières et légèrement affectées dans 16 rivières. On trouve 13 autres rivières à saumon à PNA plus élevé sans toxicité acide. De 1981 à 1990, la température de l'eau a augmenté et les teneurs de carbone organique dissous ont diminué dans les rivières de la Nouvelle-Écosse. Le pH des rivières était régi par les acides organiques et a donc augmenté avec la disparition de ces acides. En 1991, l'éruption du Pinatubo a donné lieu à deux années de température de l'eau inférieure et, par voie de conséquence, à des pH plus bas et des teneurs en COD plus élevées. Cela démontre l'effet de la température de l'eau sur le pH et le COD. Les teneurs de sulfate et la dureté (magnésium et calcium) de l'eau ont diminué de valeurs équivalentes au cours de la période 1981-1995. L'explication la plus probable est sans doute que les teneurs de  $\text{SO}_4^-$  diminuent suite à une baisse des dépôts, mais au contraire de la baisse de  $\text{H}^+$  espérée il y a eu baisse du dépôt et du lessivage de  $\text{Ca}^{++}$  et de  $\text{Mg}^{++}$ . Une plus grande rétention de cations par les bases du sol et du biote accroîtra le PNA ce qui se traduira par une élévation du pH dans les rivières, mais cela n'a pas encore été noté. La baisse de l'émission et du dépôt du sulfate devrait être plus prononcée au cours des cinq ou dix prochaines années, à mesure que l'accord sur la qualité de l'air entre le Canada et les États-Unis entrera en vigueur et la température de l'eau pourra continuer de s'accroître. Nous prévoyons donc le retour d'un habitat du saumon moins toxique. Dans les sites où la toxicité par acidité est sur la limite, la densité de population des saumons juvéniles s'est accrue suite à une baisse de la toxicité des eaux au cours des années 1980 et du début des années 1990 pour ensuite retomber encore une fois avec les valeurs du pH. Les populations des sites à pH plus élevé (non toxique) ne présentaient pas de tendances et il en était de même pour les neuf autres espèces de poisson se trouvant dans les rivières acidifiées.

## Introduction

Acid rain has had a major destructive impact on sport fishing in many of Canada's lakes and rivers. In northern Nova Scotia most of the freshwater habitat is protected from acidification by acid neutralization capacity (ANC) that is produced by natural weathering of the bedrock and soils. In southwestern Nova Scotia, an unfortunate combination of hard-rock geology, poor soils and prevailing weather patterns that cause much of the atmospheric pollution produced by U.S. industry to rain out over the Maritimes has resulted in severe acidification of the rivers and lakes. As a result, Nova Scotia is the most heavily impacted province in Canada in terms of the percentage of fish habitat that has been damaged or destroyed by acid rain. It is the only region in North America where entire river systems have been acidified by atmospheric pollution.

Since acid rain is a trans-boundary problem, Canada has promoted and participated in both national and international air pollution control agreements. The Eastern Canadian SO<sub>2</sub> (Sulphur dioxide) Control Program was established in 1985 whereby the seven eastern provinces agreed to achieve, by 1994, a 50 percent reduction in annual SO<sub>2</sub> emissions from the 1980 base level of 4516 kilotons. In the United States, the Clean Air Act of 1990 requires a 9000 kilotons reduction in SO<sub>2</sub> emissions by the year 2000. This latter reduction, representing about 40% of their 1980 level, will be achieved in two phases; phase I affecting 110 sources took effect on January 1, 1995, and phase II affecting >2000 sources is due to come into effect on January 1, 2000. The Clean Air Act paved the way for the negotiation and signing of the Canada/United States Air Quality Accord in March of 1991. The first annex to the accord sets a permanent cap on SO<sub>2</sub> emissions from Canada of 3200 kilotons and from the United States of 13,300 kilotons. These reductions in emissions will obviously result in less acid deposition, and a substantial degree of recovery is to be expected in Nova Scotia's acidified rivers over the next 5-10 years, especially in rivers with 'borderline' toxicity (mean annual pH 5.0-5.4).

The primary freshwater sport fishes in Nova Scotia are sea-run and landlocked Atlantic salmon, sea-run and freshwater brook trout, lake trout, brown trout, rainbow trout, and striped and smallmouth bass. All seven species are sensitive to acidification, but the Atlantic salmon (sea-run) is the only species for which enough historical data are available to trace the history of the impact of acidification on the resource.

This publication has been prepared to document the trends to date and the present status of river water chemistry and fish in nine acidified rivers of southwestern Nova Scotia where data have been collected for the past 16 years to monitor the impact of acid rain on Atlantic salmon rivers, and the rates of chemical and fishery recovery as emission controls are implemented. This may be the last report of the program. All DFO funding for acidification (LRTAP) monitoring will cease at the end of March, 1997, and the acid rain staff are being disbanded.

## Synoptic Surveys

After a 1978-80 survey and review of water chemistry data from salmon rivers in Nova Scotia, New Brunswick and Prince Edward Island, Watt (1981) concluded that severe (toxic) acidification was restricted to the Southern Upland, an area of granites and metamorphic rocks along the Atlantic coast, comprising about half of mainland Nova Scotia's land area. During 1980-81, monthly water chemistry was done on 23 rivers flowing through the Southern Upland (Watt *et al.*, 1983), and acid levels were compared with fish population (electrofishing) levels. Atlantic salmon juveniles were absent from all rivers with mean pH of 4.7 or less, even though angling records showed salmon present up to about 1960. Also, when historical chemistry data from 1954-55 (Thomas, 1960) on four rivers were compared to those from 1980-81, all four

ivers showed pH and alkalinity (double end point) declines.<sup>1</sup> Angling records from 22 of the rivers indicated that yields had declined (beginning about 1954) on ten rivers where the pH was now less than 5, but there was only one decline in the angling data from twelve rivers with pH greater than 5. Subsequent surveys (Watt, 1986; and more recent unpublished data) show that of the 63 rivers (Table 1) containing salmon habitat and flowing through the Southern Upland: the salmon populations are extinct in 14 rivers where the mean annual pH of the main stem is less than 4.7; reduced 90% (Watt, 1986) in 20 rivers where the main stem pH is 4.7-5.0 (Small remnant populations survive in these rivers, typically in tributaries that are less toxic than the main stem.); reduced about 10% in 16 rivers with pH 5.1-5.4 (most of the impact is in the more acidic tributaries); and apparently unaffected in 13 rivers with pH above 5.4.

### Monitoring

The Atlantic salmon populations of Nova Scotia's Southern Upland rivers are the only Canadian fishery resource for which strong internationally accepted scientific evidence has been published that directly links the decline of the resource to the long range transport of acid pollution (Watt, 1981; Watt *et al.*, 1983; Watt, 1986; Watt, 1987; Lacroix and Townsend, 1987; Lacroix 1989; Watt, 1989 and ICES, 1989). The fate of the remaining Southern Upland salmon populations, and chemical trends in the waters of these rivers are considered to be key indicators of the success or failure of the interprovincial and international acid emission accords.

Since 1981 the Canadian Department of Fisheries and Oceans (DFO) has carried out a monitoring program to follow the fate of fish populations in a selection of Southern Upland rivers. River invertebrate monitoring was also added to the program in 1987. The monitoring program was designed to detect major chemical and biological trends. It was not intended to be representative of the entire acid-sensitive Southern Upland area of Nova Scotia.

The rivers in the monitoring program were chosen to provide a wide range of toxicity (pH) conditions, so as to be able to detect the biological and chemical changes that could result from either increasing or decreasing levels of acid precipitation. Most of the chemical monitoring sites were chosen to be representative of the largest feasible drainage area with year-round access. Consideration was also given to avoiding an excess of road salt and drainage from upstream urban areas and major highways. Generally the sites are just upstream of a highway bridge. At the beginning of the program there were twelve water chemistry monitoring sites, of which nine remain. They are on Canaan, Gold, Ingram, Middle, Nine Mile, Sackville and Salmon rivers, and two on the LaHave River (main LaHave and West River). Sites in the East (Chester), East (St. Margarets Bay) and Sackville rivers were dropped: East River because of a liming program (begun in 1986), Sackville River because of the establishment of a major landfill on the drainage in 1983 (the remaining site on Sackville river is above the landfill), and East (St. Margarets Bay) because of major housing and industrial developments upstream of the site (in 1985). All of the rivers are in Lunenburg and Halifax counties. Three of the rivers (Nine Mile, Sackville and Salmon) were deliberately selected to surround the city of Halifax, N.S., so as to be able to isolate and quantify the local sulphate emission problem reported by Watt *et al.* (1979). Initial runs of the statistical model (see below) showed a high level ( $p < 10^{-6}$ ) of river-year interaction for most variables (i.e., the time trends were different in different rivers). This heterogeneity problem was resolved by separating out the three Halifax rivers from the other six. The Halifax influence is apparent from Fig 1 where the overall (1982-95) mean sulphate levels

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<sup>1</sup> The data also show increases in sulphate levels, but this is less certain because the technique employed for the sulphate analyses in 1980-81 were subsequently shown to be subject to interference from the coloured organic carbon compounds that are also present in Nova Scotia river waters (Cronan, 1979; Kerekes *et al.*, 1984).

for each river are depicted in a west-to-east arrangement. Sackville River also has some gypsum in its drainage, which accounts for about 40 µeq/L of additional sulphate in that river. Nine Mile river is east of Halifax, and Salmon River is west (downwind). Ingram River, the drainage area of which is 30-40 km west (upwind) of Halifax power station (the major local sulfur source), appears to be beyond significant local influence (Fig 1). Watt *et al.* (1979) also concluded that the local effect of Halifax emissions disappeared beyond a 40 km distance.

The water chemistry data are monthly field analyses done by DFO for water temperature, pH, alkalinity<sub>dep</sub>, acidity, hardness, colour and conductivity; and monthly laboratory analyses, done by the Environment Canada (EC) Water Quality Laboratory in Moncton, N.B., after refrigerated storage for 3-8 weeks, for conductivity, pH, ANC (Gran titration), colour, dissolved organic carbon (DOC), Na<sup>+</sup>, K<sup>+</sup>, Mg<sup>+</sup>, Ca<sup>+</sup>, NH<sub>4</sub><sup>+</sup>, SO<sub>4</sub><sup>-</sup>, Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, F<sup>-</sup>, SiO<sub>2</sub>, Al, Fe, and Mn. The DFO and EC Water Quality Lab. pH data are well correlated ( $r^2 = 0.96$ ) in spite of the long storage time between analyses. Only the SO<sub>4</sub><sup>-</sup> data from ion chromatography analyses were used, available from mid 1982 on. The earlier data, from barium-methyl thymol blue technique, are considered unreliable (Cronan, 1979; and Kerekes *et al.*, 1984). DOC analyses commenced in mid-1982. The data, detailed site descriptions and methods are in Watt *et al.*, (1996). The data are also available on the Environment Canada data base ENVIRODAT; the site numbers are:

Canaan	NS01EH0009	Gold	NS01EG0007
Ingram	NS01EH0004	LaHave	NS01EF0002
Middle	NS01EG0009	NineMile	NS01EJ0002
Sackville	NS01EJ0017	Salmon	NS01EK0001
West	NS01EF0004		

The electrofishing data are from a subset of six of the chemically monitored rivers. Nine Mile River no longer has salmon (too acidic), and Gold, Sackville and West are being stocked with hatchery produced Atlantic salmon, so the electrofishing data are less useful for acidification-related trend analysis. Unfortunately, the LaHave River is also stocked, but the LaHave electrofishing data are used for control purposes (no pH toxicity) only. The rivers, with their number of electrofishing sites in each pH class, are listed in Table 2. Details of site location and methodology are the subjects of a data report (Watt *et al.*, 1997). All of the electrofishing sites are riffle areas with habitat physically suited to juvenile salmonids, and all of the sites are in rivers that have wild populations of Atlantic salmon. Canaan River (Table 2) is the name given to the main stem of East River (Chester), above the confluence with the East Branch which has been limed by DFO since 1986 to sustain the local wild salmon stock (Watt and White, 1992). The liming program was stopped in 1997, due to a lack of funding.

### Statistical Models for Monitoring

The water chemistry data collection program was designed to supply input to a series of linear covariance analysis models, as per Neter *et al.*, (1985) and Wilkinson (1980), with environmental and seasonal variables to control the error component while testing for long-term chemical trends. Perturbations other than monotonic (straight line) trends are detected with a Durban and Watson (1951) test of the year-to-year residuals for positive first order serial correlation, and by graphical examination of the residuals.

The principal data analysis for the sampling design was intended to be a test for long-term monotonic time trends while isolating the variance components associated with the categorical variables of river sampling sites (9), which controls for spatial and geological effects; and months, which controls for the seasonal changes. Water temperatures are collected to

provide a covariant to control for the level of biological activity. Levels of pH are positively correlated with water temperature. Higher water temperatures favour anabolic activity which generates alkalinity, and lower temperatures favour catabolic activity which consumes alkalinity. These processes in turn affect pH, which shows a similar positive correlation with water temperature (Psenner and Schmidt, 1992). Part of these relationships is also due to the lower solubility and higher exchange rate (with air) of carbon dioxide at higher temperatures. High temperature and greater anabolic activity also favour retention of sulphate in the biosystem, hence temperature is inversely correlated with  $\text{SO}_4^{2-}$  levels in the rivers. Flow data (from Environment Canada) were used as an index of the degree of dilution of the relatively high ANC and pH ground water component (due to cation exchange with soil minerals) by the relatively acidic surface runoff. This covariant is especially important to pH and ANC, both of which show strong ( $p < 0.001$ ) negative correlations with flow. Of course, water temperature and flow are themselves correlated, but the collinearity between these two covariants is not a source of concern in the model. This model can also be used as a graphic filter for visual examination of time trends after the variance components attributable to other environmental variables have been removed<sup>2</sup>. The experimental design will also allow the use of a high pH control (LaHave River) as a covariant, but the output from this form of the model is only in a preliminary stage of assessment.

An alternative for examining monthly time trends is to use annual means, which is the statistical approach employed in relating trends in annual estimates of fish population levels to water chemistry (Fig 8). This form of the model is also used to estimate the year-to-year component of serial correlation.

### Water Chemistry Trends

Watt (1994) used linear covariance modelling to test 1980-91 data for possible collinearity problems within the primary model. No correlation should exist between flow or temperature and years. A covariance model was calculated using flow as the dependent variable and rivers, months, years and water temperature (with their first order interactions) as independent variables. The model accounted for 76% of the variance and showed no evidence of correlation between flow and year, and no evidence of serial correlation. (The present data set, for 1981-95, shows a similar picture.) When water temperature was tested for possible correlation with years, a different picture emerged. The model was an exceptionally good fit ( $r^2 = 0.955$ ) and showed a significant ( $p < 0.001$ ) upward trend of temperature over the twelve-year period. The Durban-Watson test showed no significant serial correlation, which suggests that the relationship was adequately represented by a simple linear monotonic trend with mean annual water temperature rising about  $0.5^\circ\text{C}$  over the 12 years of record. Several Canadian weather stations have shown a similar warming trend for air temperatures over this period (Gullet and Skinner, 1992), and Schindler *et al.* (1996) have reported a warming trend in Ontario lakes for the period 1971-90. Globally, the 1980's was the warmest decade in this century (Japan Climate Data Centre, 1997).

Watt (1994) decided to proceed with covariance analyses of the water chemistry variables by running the statistical model both with and without water temperature, so as to compare the effect of the temperature trend on the results. The results of an analysis of pH, without water temperature as a covariant showed a significant increase in pH over the twelve-year period. ANC also showed a positive increase, while DOC showed a significant decline.

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<sup>2</sup> The procedure is to run the model without the main effect for years, then plot the residuals which contain both the time trend and the error component.

When the covariance analysis models were run with water temperature included as a covariant, then all significant trends with respect to years disappeared. The upward trends in pH and ANC and decline in DOC (all at  $p < 0.001$ ) appear to have been directly related to the increase in water temperature.

Watt's (1994) data included the year 1980 in the series, but that year only had data for five of the nine rivers in the project. In 1981 all nine rivers were included. Because of the rather high river-to-river heterogeneity for variables other than temperature, it was decided to drop the first year (1980) from the analysis. Mean annual water temperatures from 1981 to 1995 are depicted in Fig 2. The generally upward trend, until about 1990, is apparent. In June of 1991, Mt. Pinatubo erupted in the Philippines, injecting many megatons of dust and aerosol particles into the upper atmosphere, and causing a two-year decline in global air temperatures (McCormick *et al.*, 1995) and also in Nova Scotia river water and air temperatures (1992-93 in Fig 2). The water (and air) temperatures rose again in 1994-95, so the 1981-95 data again show an upward trend ( $p = 0.05$ ). The significance level drops to  $< 0.001$  if either of the post-Pinatubo years is omitted from the analysis. To prevent a collinearity conflict, water temperature was not used as a covariant in the model when testing for time trends of the other variables.

The temperature perturbation has provided a test of the link between water temperature and acidity. The initial concept was: when water temperature went down, the pH should also go down. What actually happened is not quite that straight forward. The pH levels have fallen, but not in such a manner as to be very convincing of a direct causal relationship between pH and temperature (Fig 3). River water DOC levels do show a close inverse fit with pH (Fig 3), and DOC levels did eventually rise after the fall in temperatures. What we are seeing is the same effect that causes peat bogs to grow at high latitudes (and altitudes). Biomass accumulation is limited by the availability of light and nutrients, but is insensitive to temperature. Biomass decomposition is dependent on temperature; biomass tends to accumulate when conditions for preservation are good and temperatures are too low for complete decomposition. So, when water temperatures are low, organic matter accumulates and river DOC levels rise. When water temperatures rise, organic matter decomposes faster and river water DOC levels fall (Fig 3), but this process cannot be instantaneous. Time lags are to be expected and should become more apparent when the temperature perturbation is sudden. The low temperatures in 1992-93 have caused a rise in DOC. The time lag (about two years) for the response of pH/DOC levels to the lower water temperatures would have been exaggerated by the low flows in 1992.

The year-to-year serial correlation for water temperature, and DOC and pH levels is high ( $p < 0.05$ ), indicating that trends other than linear have occurred. These trends were explored using the LOWESS program (Cleveland, 1981). The overall trends for these three variables are: rising water temperature, falling DOC and rising pH until about 1990 (similar temperature and DOC changes were reported for this time period by Schindler *et al.* (1996) in northwestern Ontario lakes), then falling temperature, rising DOC and falling pH. In 1995 the water temperature rose again, but the DOC and pH levels have not yet responded (Fig 2 and 3).

The prevailing theory of the long-range transport of acid pollution is that gaseous sulphur and nitrogen pollutants are converted to acid in the atmosphere and the acid falls to earth primarily in precipitation. These strong acids in turn increase the rate of leaching of base cations and of metals, and reduce the solubility of humic substances. Humic substances are less soluble in acid solution because the effective pK of the acidic components of this material is a positive function of the pH of the water that the humic material is dissolved in (Oliver *et al.*, 1993). We would thus expect to find lower levels of DOC in rivers that have declined in pH, and this appears to be the case in Nova Scotia's Southern Upland rivers, where apparent colour (which is

well correlated with DOC) was much less in the 1980's than it was in the 1950's (Thomas, 1960; Watt *et al.*, 1983).

Sulphate deposition levels in Nova Scotia have declined over the period 1981-94 (Beattie and Keddy, 1996), and sulphate levels in the river water show a similar significant decline over the period 1981-95 (Figs 4 and 5). Fig 4 shows raw data from six rivers (West, LaHave, Gold, Middle, Canaan and Ingram). Three rivers (Nine Mile, Sackville and Salmon) are omitted from the analysis because of the influence of Halifax emissions. The raw data show a declining time trend, but the data are not normally distributed. In the covariance model the declining time trend for sulphate concentrations is significant to the  $P < 10^{-6}$  level. Fig 5 shows the result of using the statistical model as a filter to remove the effects of season (month), flow and river differences. The overall decline in sulphate has been about -19  $\mu\text{eq/L}$  since 1981.

Similar declines have occurred in the river water concentrations of calcium (-11  $\mu\text{eq/L}$ ) and magnesium (-8  $\mu\text{eq/L}$ ). Fig 6 and 7 show the statistically filtered time trends for calcium and magnesium.

The levels of calcium+magnesium (hardness) in river water have declined by an amount similar to the decline in sulphate levels, so it would appear that the reduction in acid sulphate levels is being compensated for by reduced leaching of base cation rather than direct reduction of  $\text{H}^+$  levels. The interprovincial and international air quality agreements are based on the hypothesis that reducing sulphate emission/deposition will result in a reduction of acid toxicity in the impacted rivers and lakes. Indeed, the trend of lower sulphate levels and rising pH levels over the period 1981-91 can be interpreted as supporting this hypothesis, but not the dramatic drop in pH for 1992-95 that was accompanied by low and declining sulphate levels (Fig 5). We would also expect, if sulphate levels are directly controlling pH, that DOC levels would have increased at the higher pH levels of the late eighties; however, the opposite appears to have happened.

Between 1980 and 1994 there was a decline in wet sulphate deposition (rain and snow) at Kejimikujik N.S. of -10  $\mu\text{eq/L}$  (Beattie and Keddy, 1996). There was also a decline in calcium wet deposition of -5  $\mu\text{eq/L}$ , but no similar trend in magnesium. The calcium drop appears to have occurred prior to 1990, and deposition has been stable since then.

Given the addition of dry deposition (about 30% of wet deposition) and the concentrating effect of evapotranspiration (about 33%), the declines in sulphate input (from the atmosphere) and output (in river water) are approximately in balance- *i.e.* the decline in deposition can account for the entire decline in river water sulphate concentrations.

Deposition data can only account for about half of the decline in output of calcium, and none of the magnesium decline. These differences must be a result of reduced leaching of base cations from the drainage basins. Similar declines of base cations in river runoff that are concomitant with sulphate declines have also been reported from the northeastern USA (Likens *et al.*, 1996) and from Scandanavia (Kirchner and Lydersen, 1995), so the phenomenon appears to be general in all acid rain impacted regions. Among other things, this means that chemical models designed to simulate the recovery from acidification under future scenarios of declining sulphate deposition, such as the DFO river chemistry module under development by Marmorek *et al.* (in prep) for the ASRAM model (Korman *et al.*, 1994), will have to be modified to incorporate base cation changes into their design, otherwise they will be much too optimistic in their forecasts. It is not yet clear whether the general decline of base cation concentrations in surface waters is due to reduced deposition, to soil depletion, or to reduced leaching by the lower acid sulphate concentrations. At this point the bulk of the evidence favors the latter explanation for at least part of the decline, which implies that base cations are now accumulating in the biota



and soils (which is another form of recovery from acidification). Higher levels of base cation retention within the drainage basins will eventually lead to higher pH levels in the river water.

Higher temperatures could also partially account for declining sulphate levels. Sulphate levels in the river water are negatively correlated with water temperatures, being retained in the biosystem in warmer weather and seasonally released when temperatures decline in the fall. However, in that case, there would have been an increase in sulphate level when temperatures fell after the Pinatubo eruption, but instead it continued its steady decline (Fig 4 & 5). Another possible explanation for the lower sulphate levels is that higher air temperatures have increased the rate of oxidation of SO<sub>2</sub> to SO<sub>3</sub>, and so the atmospheric transport phase (the plume) may have become shorter, with less sulphate reaching as far as Nova Scotia.

All this is not to say that the acid rain (SO<sub>2</sub>) paradigm is not operational in these rivers, but only that, with the small changes in mean pH ( $\pm$  0.1 unit, Fig 3) we have seen to date, it is difficult to distinguish the effect of declining sulphuric acid deposition from that of the climatically driven variation in organic acid release. Historically, the pH declines associated with acid precipitation (1954-1980) were of the order of 1 pH unit in N.S. rivers that lacked appreciable ANC (Watt *et al.*, 1983). The interprovincial and international agreements only came into effect in 1994 and 1995, and the Canada/USA accord does not compel a major emission reduction until after the year 2000. The next 5-10 years should bring much less acid-sulphate deposition and a much clearer response from the river water chemistry.<sup>3</sup>

### Trends in Juvenile Salmon Density Levels

DFO is monitoring population levels in the fish communities of Southern Upland rivers (Tables 2 and 3). Ten fish species (Table 3) have been encountered, but the Atlantic salmon is the only one to show significant population changes that appear to relate to the acidity changes. Noticeable biological responses are only to be expected where there are substantial changes in toxicity levels. Acid toxicity levels for Atlantic salmon reach acute sensitivity near pH 5. Below a mean pH of 5.0 the species disappears, and above mean pH 5.4 there is no significant toxicity. Five electrofishing sites in the data record have a mean pH within the range 5.0-5.4 (Table 2). All five show rising pH levels over the period 1981-92 and then reduced levels in 1993-96. Mean pH levels for these five sites and the corresponding mean population density levels of juvenile Atlantic salmon are shown in Fig 8. It is apparent that there was an increase in the salmon population levels at these sites ( $p < 0.001$ ) until the early nineties, but that levels have since declined. The species has a life cycle of four/five years, so the pattern of population increase is in agreement with the increase in pH (*i.e.* the progeny of 1987 fry would be in the river as fry in 1991 and 1992). The salmon density decline in 1994 is probably a response to the higher toxicity levels (lower pH's) brought about by the influx of organic acid (Fig 3).

An extremely acidic water chemistry event occurred in all monitored rivers early in 1994 (Fig 3 and Fig 10), and this was the primary cause for lower juvenile salmon numbers in borderline toxicity rivers in the summer of 1994 (Fig 8). The 1994 acid event in Ingram River (borderline toxicity) is examined in detail in Fig 9. The pH levels in this river were below 4.5 for

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<sup>3</sup> Please note that this is a report on work in progress, subsequent results may change the tentative conclusions presented here. The primary concern of this report is with the time trends of the most significant acid toxicity-related variables: pH, DOC, SO<sub>4</sub><sup>-</sup>, Ca<sup>++</sup>, and Mg<sup>++</sup>, and usually only their main effects have been examined. Several small but significant first order interactions (primarily to do with individual river differences) may change the tenor of these tentative conclusions when they have been fully explored. Other work that still has to be done includes: a check for other chemical changes that may have occurred to accommodate the observed pH and SO<sub>4</sub><sup>-</sup> changes; a time trend analysis of NO<sub>3</sub><sup>-</sup>, which requires a different model because of the large number of zero observations; and the preparation of input/output (deposition/discharge) budgets for the major ions.

at least four weeks in February-March of 1994. Electrofishing in the following summer revealed very low fry numbers in Ingram River, but an apparently normal parr density. Parr were not detected in this river (two sites) in the subsequent summer (1995), and it is believed that this year class was extirpated. At the three other monitored sites with mean pH 5.0-5.4 (in Salmon and Middle rivers) both fry and parr were impacted in 1994, so, on average, the densities of both year classes were lower in 1994. This would impact on grilse returns in 1996, both grilse and 2SW salmon in 1997, and 2SW salmon returns in 1998. For rivers with borderline toxicity the acid event of 1994 will impact primarily on the returns in 1997 when both grilse and salmon will be affected. However, rivers at this level of toxicity (Category B in Table 1; which includes East R. Sheet Hbr. and Liscomb R.) are generally low producers of wild stocks and many are hatchery stocked, so the resulting drop in overall salmon production is not likely to be noticed. The acid event also occurred in category C rivers, but in many of these rivers it may not have reached toxic levels. Fig 10 shows a graph of recent acid events in LaHave River. The main stem of Gold River showed a more extreme pH decline ( $5.0 > \text{pH} > 4.5$  for four months) than LaHave during the 1994 event, and Gold River has several acid tributaries in the pH range of category B. In Gold River the 1994 event should impact returns of wild fish to this river in 1997. Other category B and C (Table 1) rivers were probably also impacted by this event. For a better assessment, the event could be simulated with the ASRAM model (Korman *et al.*, 1994). As shown in Fig. 8, 1996 was also a very acidic year, with probable deleterious consequences for future salmon returns.

The LaHave River is the high-pH (non-toxic) control for the study. Fig 11 shows average Atlantic salmon juvenile densities for three sites above Morgan Falls, and potential egg deposition data calculated from the salmon count at Morgan Falls fishway. There are three other LaHave River sites (not shown) with similar juvenile numbers but without egg deposition data. The normal population density for non-toxic (mean pH > 5.4) salmon habitat in this area is about 30 juvenile salmon per 100 square metres, but densities do vary considerably from year to year, and these variations do show some correlation with the population density variations in Fig 8. Such correlation is to be expected, and it is a reassuring indication that juvenile salmon levels in the LaHave River were subject to some of the same environmental controlling factors as in the more severely acidified rivers.

The non-toxic sites (Fig 11) do not show any statistically significant trend in juvenile population densities for the time period 1981-92. The decline in both eggs (adult returns) and juvenile densities in 1993-95 (thought to be the result of low marine survival) may have contributed to the decline for 1994-96 that is shown in Fig 8 for the more acidic rivers. Unfortunately, there are no juvenile data from the LaHave for 1996.

Two of the ten fish species encountered (Table 3) are in the LaHave River only. The data do show a significant positive relationship between species diversity (expressed as species number, or as Shannon's 'H', or as Simpson's 'D') and pH, but the diversity indices do not show any significant time trends. Nor were there significant time trends in population density for any of the other fish species, or for total (summed over species) fish density.

### Summary

Acid rain has had a major destructive impact on sport fishing in many of Canada's lakes and rivers. The Atlantic salmon is particularly vulnerable to acidification, but over most of their range the salmon are protected from acidification by high ANC levels that are produced by natural weathering of the bedrock and soils. In Nova Scotia, an unfortunate combination of hard-

rock geology, poor soils, and prevailing weather patterns that cause much of the atmospheric pollution produced by US industry to rain out over the Maritimes, has resulted in severe acidification of the rivers in the southern portion of the province. As a result, Nova Scotia is the most heavily impacted province in Canada in terms of the percentage of fish habitat that has been damaged or destroyed by acid rain. It is the only region in North America where entire river systems have been acidified by atmospheric pollution. The impacted area is the Atlantic coast from Yarmouth to Guysborough. There are 63 Atlantic salmon rivers flowing through this area. Salmon have been extirpated from 14 rivers, production is heavily impacted in 20 rivers, lightly impacted in 16, and there is no discernible impact in the 13 other rivers. The fate of Nova Scotia's Atlantic salmon played a significant role in the negotiation of international controls on acidic emissions, so a local monitoring program (there is also a national one) was set up to keep track of changes in the water chemistry and fish populations. Water chemistry data from this program show increases in mean annual pH and ANC over the period 1981-1991. Over this same period there was also a significant increase in mean annual river water temperatures and a decline in DOC (dissolved organic carbon). The tentative conclusion was that temperatures were controlling DOC levels and DOC levels (organic acids) were in turn controlling pH.

The eruption of Mt. Pinatubo in June 1991, and the resulting global climatic perturbation has provided a test of the temperature/DOC hypothesis. The years 1992 and 1993 were the two coldest since the river monitoring program began in 1981, and the two lowest pH (and ANC) years were 1993 and 1994. Ion balance indicates that the low pH levels were primarily caused by an increase in organic acids. The low temperatures of 1992-93 would have caused a higher accumulation of organic matter in the soils and bogs, and the subsequent leaching led to higher levels of organic acids in rivers during 1993-95. Water temperatures recovered upward in 1994 and 1995, but pH levels have remained low due to continuing high DOC levels.

Sulphate levels over the 1981-95 period show a statistically significant decline (about 20%). The acid rain paradigm predicts that declines in sulphate should eventually result in increases in pH, but instead of a pH increase ( $H^+$  decline) there has (thus far) been an equivalent decline in calcium and magnesium levels. Deposition data can only account for about half of the decline in output of calcium, and none of the magnesium decline, so the reduced base cations in the river waters must be being made up by reduced leaching of base cations from the drainage basins. Higher levels of base cation retention within the drainage basins is itself a form of recovery from acidification that will eventually lead to higher pH levels in the river waters.

In the monitored rivers, the population densities of Atlantic salmon juveniles rose in response to rising pH levels (1981-91), and then fell as pH levels declined after 1992. These changes occurred only at those sites where toxicity was borderline (near pH 5). There were no corresponding population trends at sites with higher (non-toxic) pH levels, or for any of the other nine fish species in the rivers.

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Table 1. The Nova Scotian rivers listed below contain habitat that is physically suited to the rearing of juvenile Atlantic salmon, but the water quality is impaired by acidification. They have been classified according to the mean annual pH of the main stem of the river near its mouth. There is a seasonal variation in the pH of all rivers: pH falls rapidly in October and remains low (a typical minimum pH is 0.5 units below the mean) from October to March, then there is a slow rise to a peak in September. In Class A rivers the native salmon runs are now extinct. In Class B rivers only remnant populations survive in one or two higher pH tributaries. In Class C rivers salmon stocks have been depleted by acidification of some of the smaller tributaries, but in the main stem and most tributaries salmon production rates appear to be normal. In the Class D rivers the pH's have not yet been depressed to the point of major toxicity, and the Atlantic salmon stocks have not been significantly impacted.

Class	Mean pH	No. in Class	Rivers	Rivers
A	<4.7	14	Argyle	Nine Mile
			Barrington	Patterson
			Broad	Pennant
			Clyde	Roseway
			Indian (Guysborough)	Sable
			Jordan	Tidney
			Larrys	East (Shelburne Co.)
B	4.7-5.0	20	*Bear	Martins
			Cole Harbour	*Mersey
			East (Chester)	Middle
			East (Sheet Harbour)	*Nictaux
			East (St. Margarets)	Salmon (L. Echo)
			*Indian (Halifax)	Salmon (L. Major)
			Ingram	*Sissiboo
			Isaacs Harbour	Tangier
			Liscomb	Tusket
C	5.1-5.4	16	Annis	New Harbour
			Chezzetcook	Round Hill
			Gaspereau Bk. (Liscomb)	Sackville
			Gold	Salmon (Digby)
			Kirby	Salmon (Jeddore)
			LaHave	Salmon (Dufferin)
			Medway	Taylor Bay Brook
			Moser	Necum Teuch
D	>5.4	13	Belliveau	Mushamush
			Boudreau	Musquodoboit
			Gegogan	Petite
			Country Harbour	Quoddy
			Ecum Secum	Ship Harbour
			*Meteghan	St. Marys
Indian Harbour				

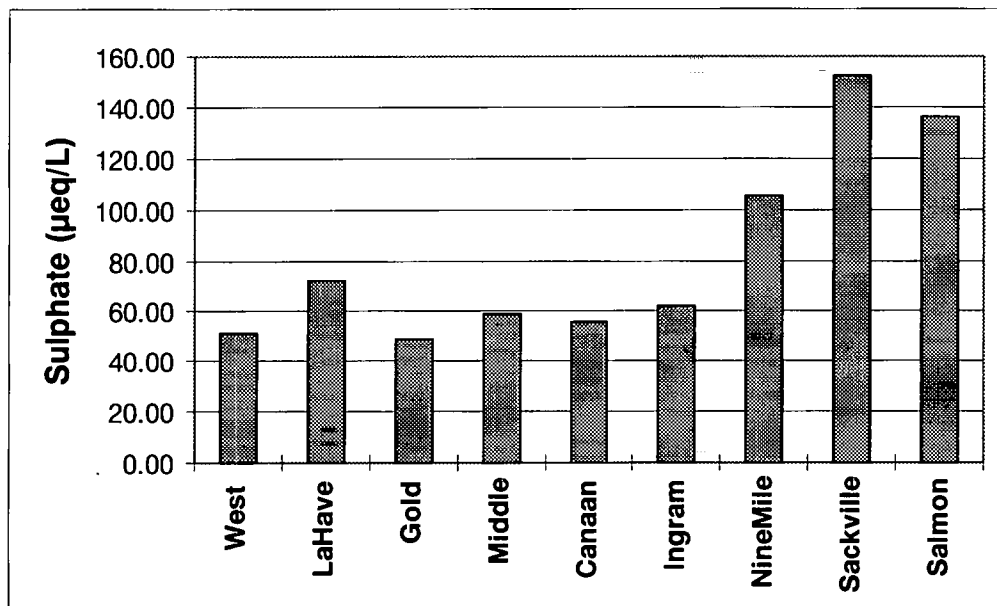
\*In these rivers most of the salmon habitat is unavailable due to impassable dams or falls.

Table 2. Number of electrofishing sites arranged by river and pH class. The LaHave River sites are used here for control purposes (no acid toxicity), the LaHave data were collected for stock assessment purposes (a different program).

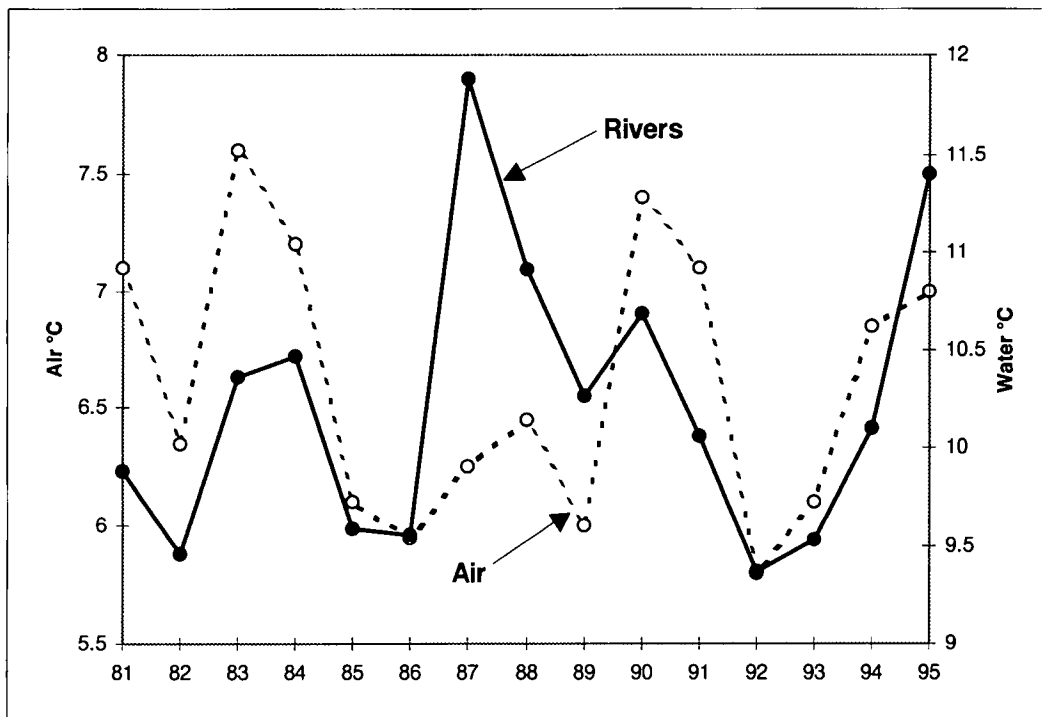
River	pH<4.7	5.0<pH<5.4	pH>5.4
Canaan	4		
Ingram		2	
LaHave			6
Middle		2	
Salmon	2	1	
<b>Total Sites</b>	6	5	6

Table 3. Fish species encountered and enumerated. The numbers are mean fish/100m<sup>2</sup> for all stations (Table 2) in the river (1982-95).

	Canaan	Ingram	LaHave	Middle	Salmon
American eel, <i>Anguilla rostrata</i> (Lesueur)	15	33	1	45	34
Atlantic salmon, <i>Salmo salar</i> (Linnaeus)		7	29	4	6
Banded killifish, <i>Fundulus diaphanus</i> (Lesueur)			0.4	0.8	0.1
Brook trout, <i>Salvelinus fontinalis</i> (Mitchill)	1	1	0.04	0.04	0.2
Common shiner, <i>Notropis cornutus</i> (Mitchill)			Rare		
Lake chub, <i>Couesius plumbeus</i> (Agassiz)	0.8		0.8	2	
Ninespine stickleback, <i>Pungitius pungitius</i> (Linnaeus)			Present		Rare
Sea lamprey, <i>Petromyzon marinus</i> (Linnaeus)			Common		
White sucker, <i>Catostomus commersoni</i> (Lacépède)	0.1	1	0.4	2	0.4
Yellow perch, <i>Perca flavescens</i> (Mitchill)	Present	Present			
<b>Total species</b>	5	5	9	6	6

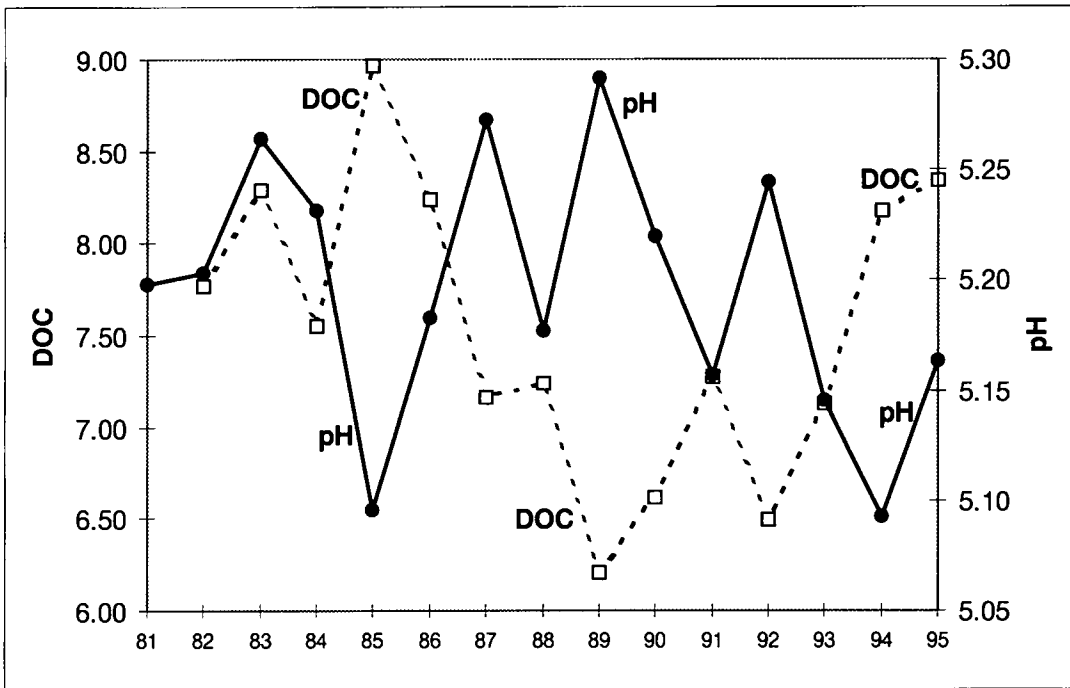


**Fig 1.** Mean (1982-95) sulphate concentration in the monitored rivers. The rivers are arranged from west to east. Nine Mile, Sackville and Salmon rivers are adjacent to the Halifax metropolitan area.

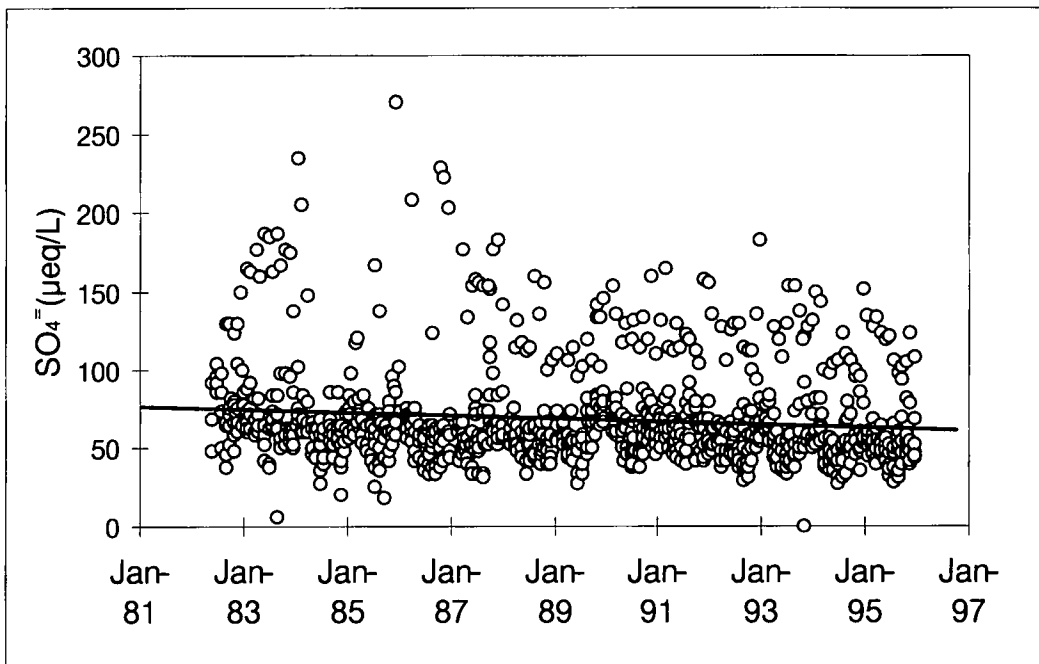


**Fig 2.** Nova Scotia mean annual river water temperatures show an overall increasing trend ( $p=0.05$ ) over the period 1981 - 1995. The global climate perturbation caused by the eruption of Mt. Pinatubo, in June 1991, resulted in the lowest water temperatures of the series in 1992-1993, but higher temperatures have since returned. Nova Scotia air temperatures were also unusually low in the two years following Pinatubo. The unusually high (relative to the air) mean river water temperature for 1987 was due to low rainfall/flows (lowest in the series) and high insolation for that year.

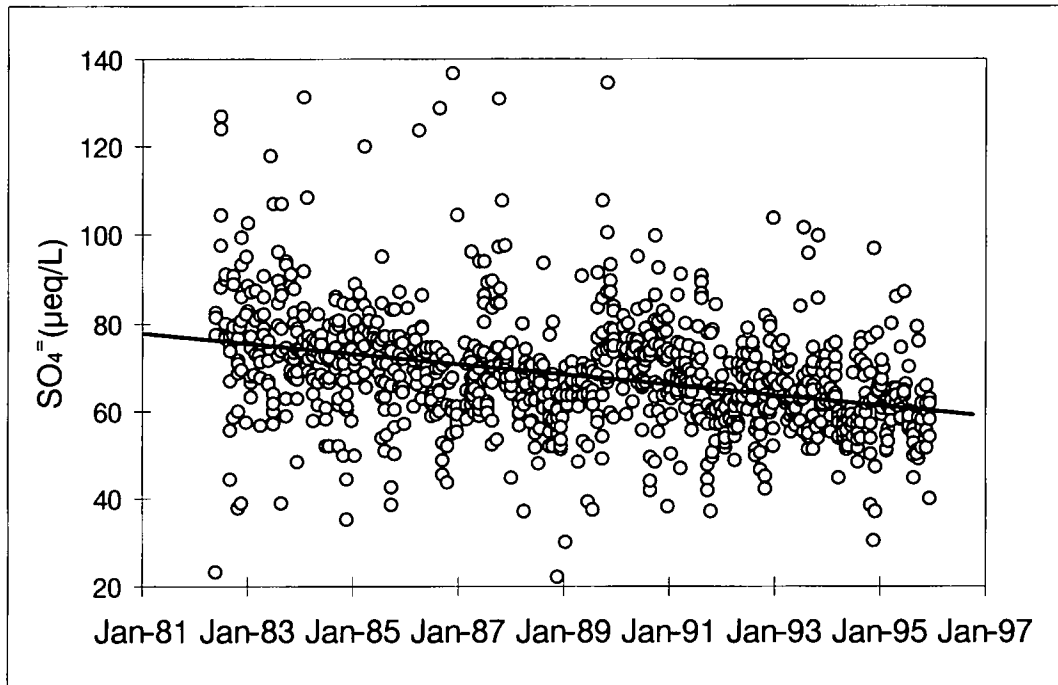




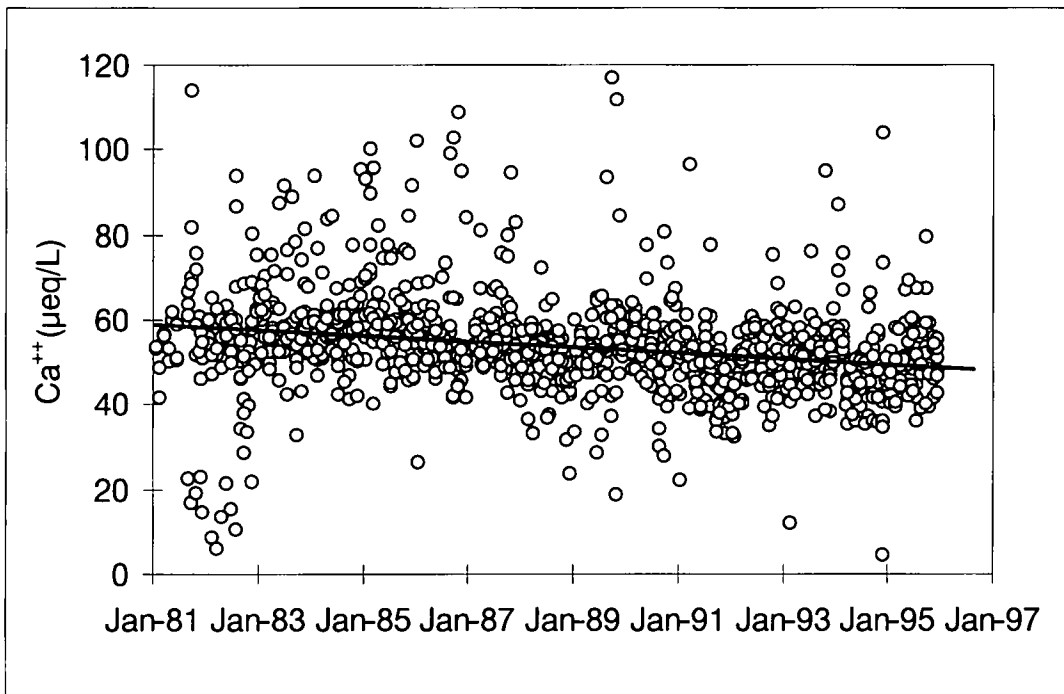
**Fig 3.** The pH is inversely correlated with DOC levels. This is a close correlation, indicative of a direct causal relationship, *i.e.* the year-to-year variation in the production of dissolved organic acids accounts for most of the year-to-year pH variation.



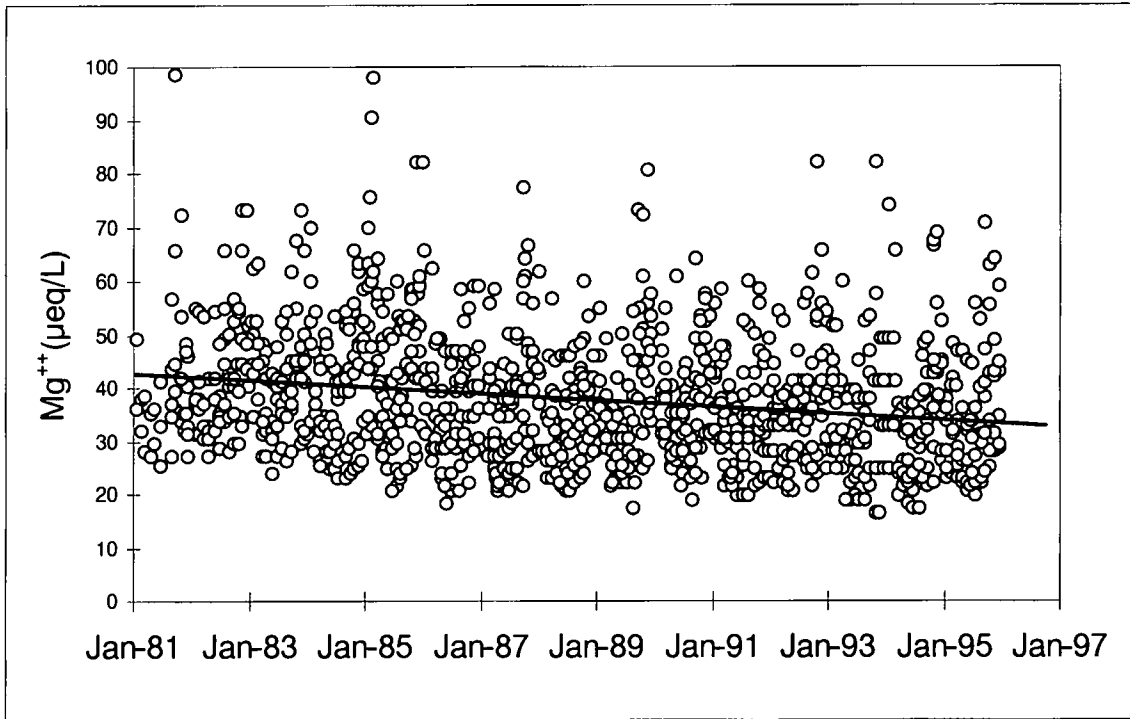
**Fig 4.** Monthly sulphate levels in six monitored rivers. The line is a least squares fit. The declining trend is significant to the  $p < 0.01$  level, but it is obvious that the data are not normally distributed about the regression line.



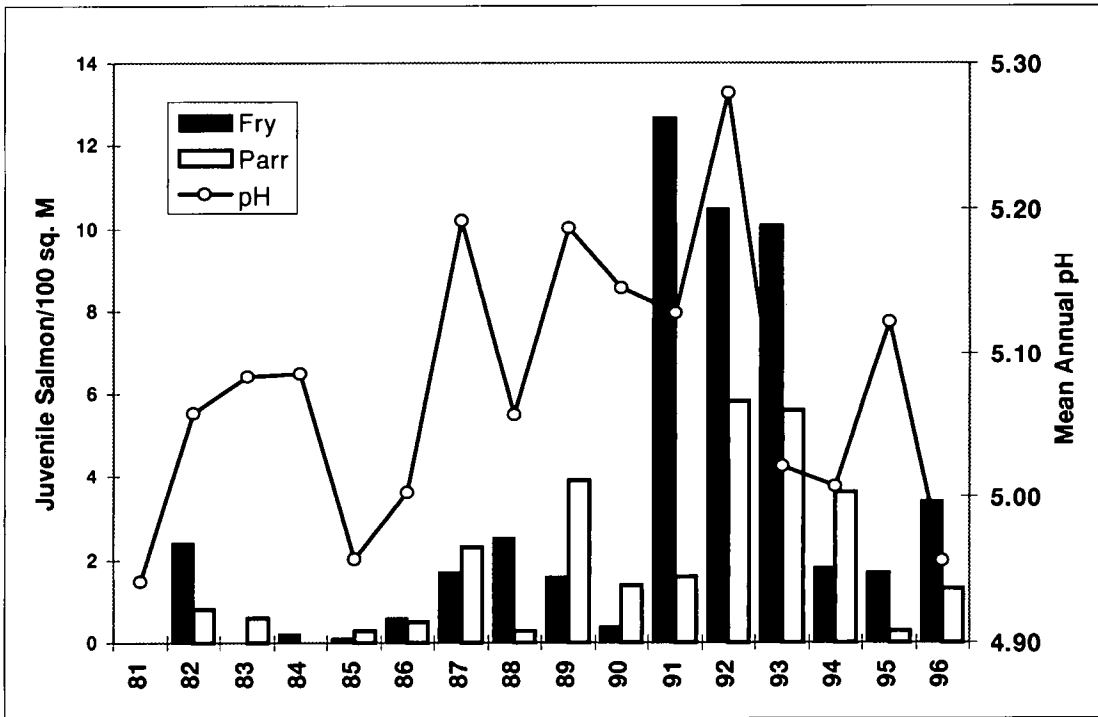
**Fig 5.** Statistically filtered monthly sulphate data from six monitored rivers. The declining trend is significant to the  $p < 10^{-6}$  level, and the data points are much closer to a normal distribution.



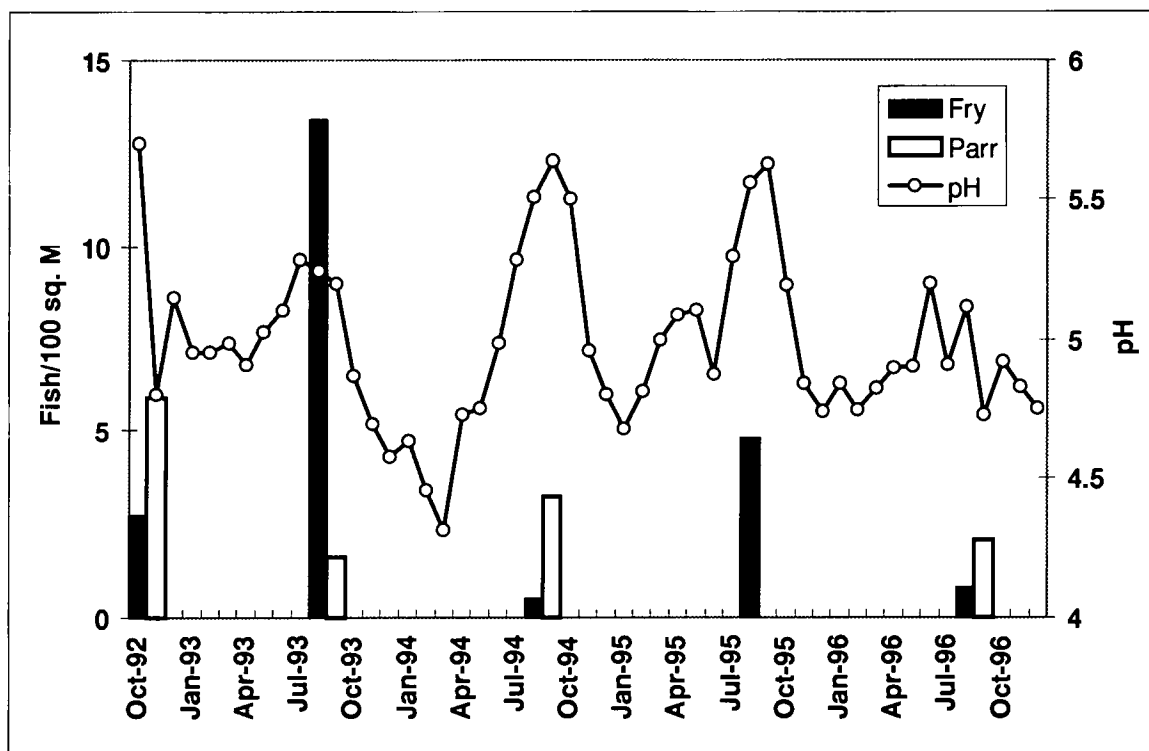
**Fig 6.** Statistically filtered monthly calcium data from six monitored rivers. The declining trend is significant to the  $p < 10^{-6}$  level.



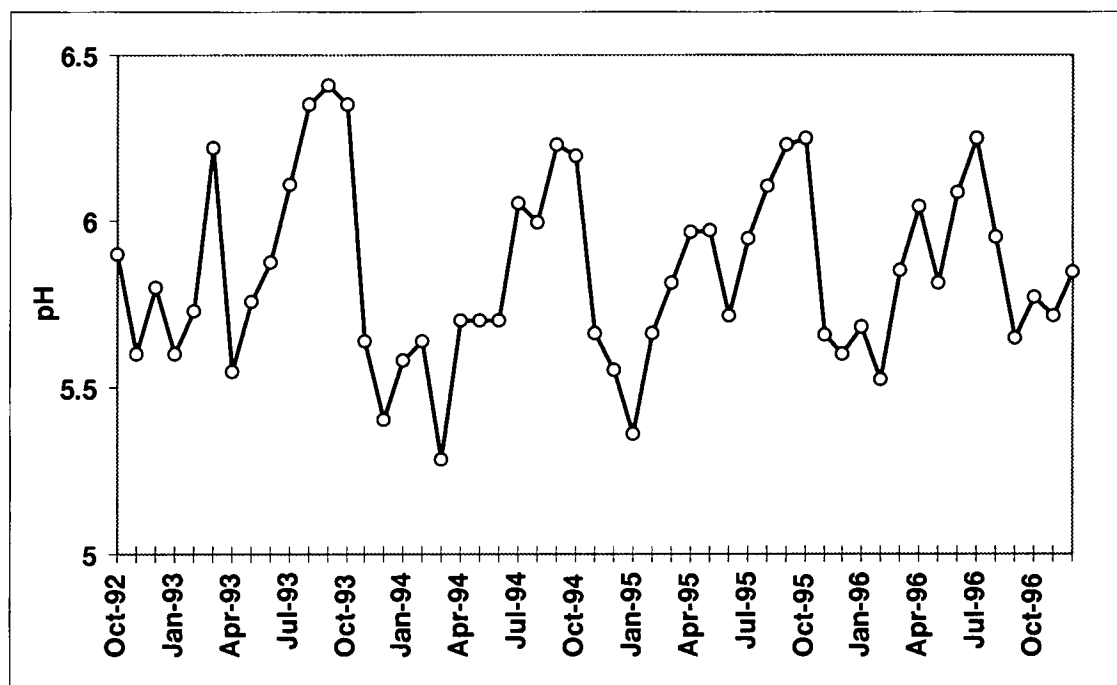
**Fig 7.** Statistically filtered monthly magnesium data from six monitored rivers. The declining trend is significant to the  $p < 10^{-6}$  level.



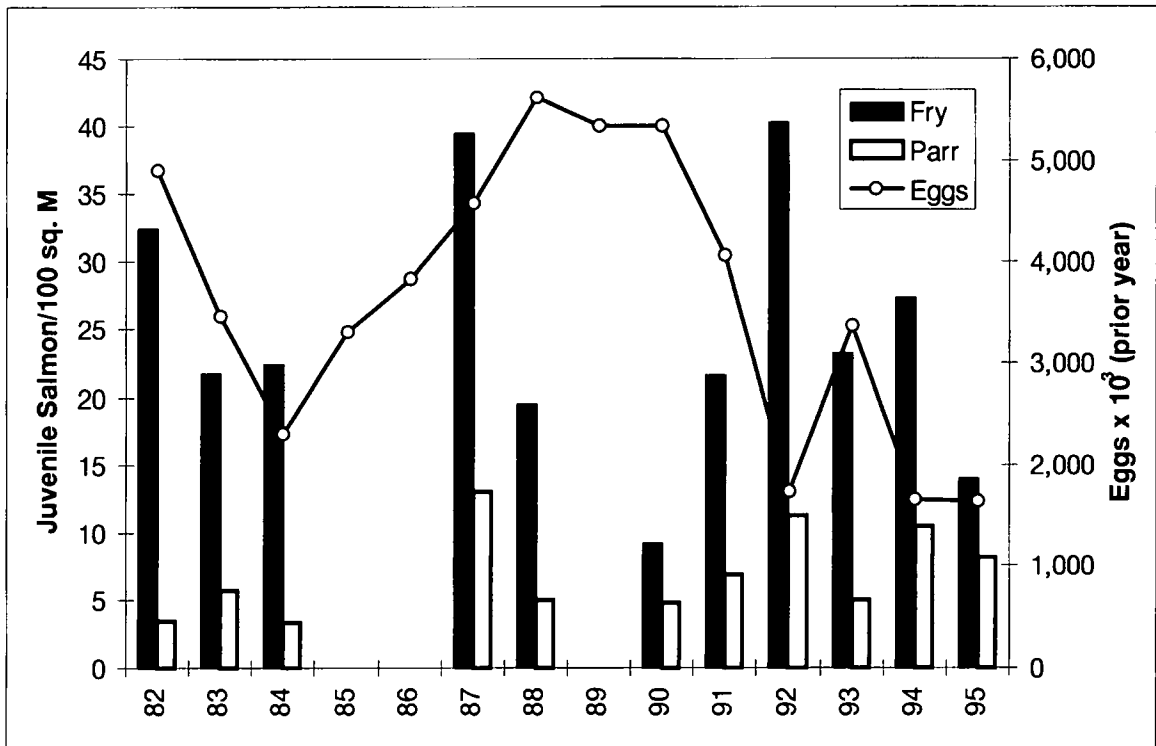
**Fig 8.** The line represents the mean annual pH levels for five electrofishing sites with borderline toxicity levels ( $5.0 < \text{pH} < 5.4$ ). The black and white bars are the corresponding mean population density levels of juvenile Atlantic salmon fry and parr at the five sites.



**Fig 9.** The acid event of 1994 in Ingram River (the water was <math>pH < 4.5</math> for two months), and the impact on juvenile Atlantic salmon.



**Fig 10.** The acid event of 1994 in LaHave River, where the pH dipped to 5.3 for a short period. A short exposure to this pH level will not kill juvenile salmon.



**Fig 11.** The bars are mean population density levels of juvenile Atlantic salmon fry and parr at three sites on the LaHave River above Morgan Falls fishway, and the line is potential salmon eggs (from counts of salmon passing through the fishway) from one year earlier than indicated on the chart. Thus the egg data points are plotted in the same year as their corresponding salmon fry progeny. The water at all three sites has a mean annual pH >5.4, which is generally considered non toxic for juvenile Atlantic salmon. These data are presented as a non-toxic (higher pH) control for comparison with the data of Fig 8.