Assessing the impacts of acidification on Atlantic salmon (*Salmo salar*): a simple model of stream chemistry

D.R. Marmorek, G.L. Lacroix, J. Korman, I. Parnell, and W.D. Watt

Abstract: We developed a model that simulates the effects of changes in sulphate (SO_4^{2-}) deposition on the chemistry of naturally organic-rich streams, linked this chemical model to a model of Atlantic salmon (*Salmo salar*) production (Korman et al. 1994. Can. J. Fish. Aquat. Sci. **51**: 662–680), and assessed its performance on three acidified streams in southwest Nova Scotia. The chemical model closely tracked current chemistry by estimating the charge density required for charge balance on each sampling date. Calculated charge densities were generally low (1–3 µequiv./mg dissolved organic carbon (DOC)), inversely related to DOC, and positively related to pH. Predictions of minimum pH and salmon smolt output were relatively insensitive to the assumed *F*-factor (watershed neutralization of deposited acidity) in the parameter range most likely for the three streams. The model permits rapid impact assessment of acid deposition scenarios with a modest amount of input data (acid-neutralizing capacity, pH, SO_4^{2-}, and DOC, ideally sampled weekly) while retaining natural cycles and processes.

Résumé : Nous avons mis au point un modèle qui simule les effets des changements dans les dépôts de sulfate (SO_4^{2-}) sur la chimie des cours d'eau naturellement riches en matière organique, lié ce modèle chimique à un modèle de la production de saumon atlantique, *Salmo salar* (Korman et al. 1994. J. can. sci. hal. aqu. **51**: 662–680), et évalué sa performance dans trois cours d'eau acidifiés du sud-ouest de la Nouvelle-Écosse. Le modèle chimique suivait de près la chimie réelle en estimant la densité de charge nécessaire pour l'équilibre à chaque date d'échantillonnage. Les densités de charge calculées étaient généralement faibles [1–3 µéquiv./mg de carbone organique dissous (COD)], inversement reliées au COD et positivement reliées au pH. Les prédictions du pH minimum et de la production de smolts étaient relativement insensibles au facteur *F* présumé (neutralisation par le bassin versant de l'acidité déposée) dans la fourchette de paramètres la plus vraisemblable pour les trois cours d'eau. Le modèle permet d'évaluer rapidement l'impact de divers scénarios de dépôts acides avec une quantité modeste de données d'entrée (capacité de neutralisation de l'acide, pH, SO_4^{2-} et COD, avec, dans des conditions idéales, un échantillonnage hebdomadaire) en se fondant sur les cycles et processus naturels.

[Traduit par la Rédaction]

Introduction

The acidification of rivers in southwest Nova Scotia has been associated with significant losses of Atlantic salmon (*Salmo salar*) (Lacroix 1987). This acidification is due to the additive effects of anthropogenic deposition of mineral acids and watersheds' natural organic acids, resulting in both chronic and episodic acidic conditions (Kerekes et al. 1986). Watt (1987) suggested that anthropogenic acids may have been responsible for a 50% decrease in salmon production, although his estimates (based on juvenile salmon densities in streams with different pH levels) were very preliminary. Questions remain regarding the actual historical losses of salmon production and the adequacy of recent reductions in S emissions and deposition for initiating recovery. Fishery scientists and managers need to better understand the potential range of responses in acidified, organic streams of Nova Scotia to future deposition changes and their effects on salmon populations.

We have built some tools to explore possible answers to these questions and to assess the uncertainty in these answers. Our strategy was first to build and apply a biological model consistent with field acidification experiments (Atlantic salmon regional acidification model (ASRAM)) and explore its sensitivity to variations in stream chemistry (Korman et al. 1994; Lacroix and Korman 1996). In this paper, we describe a simple model for translating the current chemistry of a stream into the chemistry it would exhibit under a different level of acidic deposition. In building this model, we attempted to satisfy three criteria. First, the chemical model needed to link into ASRAM, so that we could predict the impacts of changes in acidic deposition on Atlantic salmon. Second, limited existing stream chemistry data meant that the model should have modest input data requirements to be able to answer regional-scale questions. Third, to be scientifically credible, the model must also simulate

Received February 18, 1997. Accepted June 17, 1998.
J13876

D.R. Marmorek,[1] J. Korman, and I. Parnell. ESSA Technologies Ltd., Suite 300, 1765 W. 8th Avenue, Vancouver, BC V6J 5C6, Canada.
G.L. Lacroix. Department of Fisheries and Oceans, Biological Station, St. Andrews, NB E0G 2X0, Canada.
W.D. Watt. Department of Fisheries and Oceans, Science Branch, Halifax, NS B3J 2S7, Canada.

[1] Author to whom all correspondence should be addressed. e-mail: dmarmorek@essa.com

Table 1. Summary of stream conditions.

Stream	pH		DOC (mg/L)		ANC (μequiv./L)		SO_4^{2-} (μequiv./L)		C_B (μequiv./L)	FM × 100 (%)	Ion ratio used
	Mean	Range	Mean	Range	Mean	Range	Mean	Range			
Westfield River	5	4.7 to 5.4	9.3	6.4 to 16.1	2.5	−14.0 to 12.0	72.2	56.2 to 85.4	61.5	17.4	Na/Cl
Round Lake Brook	4.7	4.4 to 5.0	12.7	9.9 to 22.6	−6.8	−26.0 to 8.0	77.3	62.5 to 99.9	62.9	18.1	Na/Cl
Moose Pit Brook	4.6	4.4 to 5.0	20.5	7.8 to −43.2	−9.3	−28.0 to 14.0	72.1	43.7 to 131.2	73.2	19.6	Na/Mg

Note: Measured pH and DOC; C_B (total nonmarine base cations) estimated from stream measurements and seasalt correction equations from Thompson (1982*a*) and FM × 100 (% marine SO_4^{2-}) estimated from ion ratios in last column using Vet et al. (1986). Na/Mg used for Moose Pit Brook because it provided more accurate corrections than Na/Cl.

short-term acidic episodes in organically enriched streams, a key driving force in the biological responses of Atlantic salmon (Lacroix and Korman 1996).

Existing models that operate on daily or weekly time scales (e.g., Lam et al. 1989) are calibrated using detailed flow and chemistry measurements over several years (Cosby et al. 1985). Such detailed data sets are rare. For example, there are 63 rivers in the acidified Southern Upland region of Nova Scotia that once supported Atlantic salmon (Watt 1987), and each of these rivers has many tributary streams capable of supporting salmon. However, there are only about 10 streams in that region with measurements of pH, alkalinity (ALK), dissolved organic carbon (DOC), and sulphate (SO_4^{2-}) on a monthly or greater frequency. Our chemical model has fewer input data requirements than most acidification models while maintaining the ability to accurately simulate short-term changes in stream chemistry. While simplification creates some limitations, we consider the model to be a generally applicable tool for organic, acid-sensitive streams, although region-specific calibration and validation should be completed before it is applied outside southwest Nova Scotia.

The model was developed in VisualBasic™ and operates under the Windows™ environment on IBM PC compatible computers, permitting easy adjustment of parameters and Monte Carlo simulations across a range of deposition scenarios and parameter values. (The software and limited documentation are available from Dr. G.L. Lacroix for noncommercial use only (please send a high-density diskette).)

Methods

General modelling approach

Previous work has shown the importance of seasonal changes in wetland retention of mineral and organic acids on the seasonal patterns of chemistry in Nova Scotia streams (e.g., Kerekes and Freedman 1989). We took a modelling approach that would easily *translate* current measured stream ALK, SO_4^{2-}, and pH levels into a new time series, without having to calibrate many equations representing watershed hydrologic and chemical processes. We preserved the seasonal pattern of DOC but changed SO_4^{2-} concentration ($[SO_4^{2-}]$) in response to changes in deposition, and shifted ALK, organic anions, and pH appropriately, based on simple equilibrium calculations. We therefore called this the time series translation model (TSTM). Its output represents the seasonal pattern of pH values once a stream has come to steady state with a new deposition value. The model does not estimate how long it will take for the stream to reach this steady state.

TSTM assesses the current condition of a stream and then projects its future condition (Fig. 1). The assessment of current condition is a calibration to estimate the charge densities that are consistent with the ALK, pH, and DOC measured on each sample date. These charge densities are then used in the projection of future conditions in the stream after the ALK has been adjusted to reflect changes in mineral acids (bottom of Fig. 1). These steps are described below.

Inputs

The data inputs for TSTM are simply (*i*) measurements of stream Gran ALK, pH, $[SO_4^{2-}]$, and DOC measured at a time resolution necessary to capture major seasonal fluctuations and lowest pH values (i.e., ideally weekly during the fall and winter and biweekly to monthly at other periods) and (*ii*) an estimate of the proportion of [SO_4^{2-}] that is from marine sources (requiring at least stream measurements of Cl^- and preferably also Ca^{2+}, Na^+, and Mg^{2+}). We used Vet et al. (1986) to estimate marine [SO_4^{2-}]; their method compares the ratios of Na^+/Mg^{2+}, Na^+/Cl^-, and Mg^{2+}/Cl^- in water samples with the ratios in seawater and chooses the "best" tracer. To simulate a deposition scenario, the user specifies a fractional change in the amount of anthropogenic SO_4^{2-} deposition, relative to the deposition levels associated with the measured time series of stream chemistry. We chose to apply TSTM to three streams of the Medway River, Nova Scotia, for which frequent (i.e., weekly) measurements of water chemistry were available and that spanned a range of pH and DOC levels: Westfield River, Round Lake Brook, and Moose Pit Brook (Table 1). Characteristics and hydrology of the drainage basin for the streams were described by DeGraeve and Peterson (1982). Chemical parameters were measured using standard methods as described in Lacroix and Kan (1986) and Lacroix and Townsend (1987). The dominance of nonexchangeable forms of Al in these organic streams makes pH the main lethal factor directly affecting survival and production of juvenile salmon (Lacroix 1989) and also permits us to ignore Al^{n+} in our charge balance equations.

The biological model (ASRAM) runs from June 1 to May 31 and requires chemical data over this same period. In order to meet this input sequence, we shuffled the order of the annual time series of data (March 1, 1983, to February 28, 1984) for the three streams. The modelled periods were therefore from June 1, 1983, to February 28, 1984, and then from March 1, 1983, to May 31, 1983. This reordering of the time series did not generate any unrealistic discontinuities at the break points.

The parameter assumptions required for the model are (*i*) an estimate of the *F*-factor (Wright and Henriksen 1983) to reflect watershed neutralization of mineral acid deposition, (*ii*) the pCO_2 level, (*iii*) the proportion of SO_4^{2-} that is of marine origin, and (*iv*) functions controlling organic dissociation (either the approach of Oliver et al. (1983) or specified dissociation constants, pK_as). Charge density (CD_t) can be either measured (consistent with the definition below) or estimated by the model from water chemistry data to maintain charge balance for each sampling date. We use the latter approach (dynamic CD_t calculation), as it allows for the best simulation of current seasonal patterns in pH levels. We define CD_t as micoequivalents of total organic anion per milligram of DOC, if all anions are dissociated. We later adjust for the pH-dependent degree of dissociation (eq. 6 below). Total organic anions (A^-) include A^{3-}, HA^{2-}, and H_2A^-.

Model structure

The model is founded upon the following charge balance equation (Stumm and Morgan 1981):

$$(1) \qquad \text{Gran ALK} = HCO_3^{\ -} + CO_3^{\ 2-} + OH^- + A^- - H^+$$

where A^- are dissociated organic anions and all chemical species are expressed in microequivalents per litre. Both CO_3^{2-} and OH^- are close to zero at the pH levels observed in the three streams we modelled. As stated previously, we assume that $Al^{n+} \approx 0$.

In assessing the current condition (Fig. 1), eq. 1 was used to infer CD_t for each day (equations provided below). In projecting future conditions, the model first attempts to estimate how much change in Gran ALK is likely to occur under a given deposition scenario on any given day. It then computes the value of all the variables on the right side of eq. 1, such that the right side equals the projected future Gran ALK. [H^+] influences the concentration of all chemical species on the right side of the equation, so for projecting future conditions the appropriate pH is converged upon by iteration (bottom of Fig. 1). The currently observed time series of DOC, the CD_ts estimated from current chemistry, and the projected pH are used to compute changes in A^-, based on a set of organic acid assumptions described below. We assumed that the seasonal patterns and magnitudes of both DOC and CD_t remain constant as deposition changes.

Hemond (1990) described the relationship between charge balance acid-neutralizing capacity (CB ANC) and the ALK measured by Gran titration:

$$(2) \qquad \text{CB ANC} = \text{Gran ALK} + y \times \text{DOC}$$

where CB ANC is base cations minus strong acid anions and *y* is a constant (Hemond (1990) suggested 4.6 μequiv./mg DOC). We assumed that, as deposition changes:

$$(3) \qquad \Delta\text{Gran ALK} = \Delta\text{CB ANC}$$

and that

$$(4) \qquad \Delta\text{Gran ALK} = \Delta\text{CB ANC} = \Delta SO_4^{\ 2-} \times (1 - F) \times -1.$$

We assume that each date's shift in CB ANC and Gran ALK is proportional to that date's change in [SO_4^{2-}] and that the total amount of organic ions for each day ($y \times$ DOC) remains unchanged from its current value (however, the fraction of organic ion in dissociated form changes with pH, as explained below). The *F*-factor represents the fraction of acid deposition that is neutralized in the watershed or streambed. Alhough this widely used *F*-factor approach greatly oversimplifies the various nonlinear and threshold-driven processes believed to operate in watersheds (reviewed in Thornton et al. 1990), it can be used to approximate the steady-state behaviour of more mechanistic models (e.g., Cosby et al. 1994). Past studies generally assume that the *F*-factor varies with nonmarine base cation concentrations (C_B), although the form of this relationship is uncertain. Brakke et al. (1990) proposed that *F* be a sine wave function of current C_B whereas Marmorek et al. (1990) and Henriksen and Brakke (1988) made *F* a linear function of original or current C_B, respectively. Applying these three approaches to the low C_Bs of our three streams (see Table 1) suggests *F*-factors in the range of 0.23–0.45, so $F = 0.3$ is a reasonable estimate of the most likely value. However, to provide thorough sensitivity analyses of model performance, we explored a range of *F* values from 0.3 to 0.7.

The change in daily [SO_4^{2-}] ($\Delta[SO_4^{2-}]_t$) is simply

$$(5) \qquad \Delta[SO_4^{\ 2-}]_t = [SO_4^{\ 2-}]_t \times \text{FCAD} \times (1 - \text{FM})$$

where $[SO_4^{2-}]_t$ is the current concentration, FCAD is the fractional change in acidic deposition under a given deposition scenario (e.g., –0.5 for a 50% decrease in SO_4^{2-} deposition), and FM is the fraction of [SO_4^{2-}] that is from marine sources. We explored the effects of changes in anthropogenic SO_4^{2-} deposition ranging from 100% decreases (i.e., no deposition) to 100% increases. FM was computed based on the correction equations of Vet et al. (1986) and applied to flow-weighted mean stream concentrations of Cl^-, SO_4^{2-}, Ca^{2+}, Na^+, and Mg^{2+}. We estimated C_B using the method of Thompson (1982*a*). Table 1 lists the estimated percent [SO_4^{2-}] from marine sources and the ion ratio used for correction for each of the three streams.

Concentrations of HCO_3^-, CO_3^{2-}, and OH^- are computed using standard equilibrium equations (Stumm and Morgan 1981). In the absence of accurate field measurements of CO_2, we assumed a constant default pCO_2 value of 3.42 indicative of 20% supersaturation ($10^{-3.42} = 10^{-3.5} \times 1.2$), consistent with measurements of dissolved O_2. The shallow depth and moderate gradient of these streams probably encourage degassing of CO_2 that enters the stream channel in groundwater and soil water. In sensitivity analyses, we varied [CO_2] over a 10-fold range (i.e., pCO_2 from 2.5 to 3.5), consistent with the range observed in lakes (Norton and Henriksen 1983).

In TSTM, the amount of dissociated A^- can be specified using monoprotic, diprotic, or triprotic formulations (i.e., one, two, or three K_a values; Lam et al. 1989) or via the formulae of Oliver et al. (1983). As shown by Lam et al. (1989), in all cases, this can be represented by

$$(6) \qquad [A^-] = CD_t \times DOC \times \left[\frac{[K_{a_1} \times x]}{[K_{a_1} \times x + H^+]} \right]$$

where CD_t is the charge density (μequivalents of A^- per milligram of DOC if all A^- are dissociated), x is a scalar derived from the specified pK_as, and the term in square brackets is the fraction of A^- actually dissociated, given the pH. We varied pK_a as a function of pH, following Oliver et al. (1983), because this method was derived from analyses of Nova Scotia waters similar to those in the streams we examined. The CD_t is calculated for each sampling date from current data to precisely match the daily measured current pH and Gran ALK and the estimated HCO_3^-, CO_3^{2-}, and OH^-. This can be done by rearranging eqs. 1 and 6 so that

$$(7) \qquad CD_t = \frac{[\text{Gran ALK} - HCO_3^- - CO_3^{2-} - OH^- + H^+] \times [K_{a_1} \times x + H^+]}{[DOC \times K_{a_1} \times x]}$$

The CD_t computed for each sampling date are applied to all future deposition scenarios, thereby assuming that the hydrological and microbiological processes that determine the seasonal pattern of DOC and CD_t will remain unchanged with changes in deposition. Because eq. 7 can generate negative estimates for CD_t, we "trapped" estimates less than 0.1 and reset them to 0.1. This method of computing CD_t absorbs the effects of any other incorrect assumptions (e.g., incorrect pCO_2 or pK_a values, changes in equilibrium constants due to temperature fluctuations, changes in the protonization of other ions). We therefore compared CD_t with other studies, examined the relationship between CD_t and DOC over a range of pCO_2 values, and explored the effects of a range of pK_a values (pK_a from 3 to 5).

We examined the biological effects of changes in SO_4^{2-} deposition and uncertainties in chemical parameters to help focus attention on the range of values most strongly affecting juvenile salmon production. We chose two output indicators: minimum annual pH and numbers of smolts per square metre assuming an egg deposition of 2.4 eggs/m^2. The version of ASRAM used to compute smolt output was identical to that described in Korman et al. (1994), except that we maintained the ratio of 1-year-old parr to 2-year-old parr at a constant level (11.7:1 for the Westfield River; Lacroix and Korman 1996). As a result, smolt output is slightly more responsive to changes in pH than if the ratio of 2-year-old smolts to 3-year-old smolts varied with parr density as in Korman et al. (1994).

Results

Charge densities

The dynamic CD approach much more accurately tracked pH fluctuations in the Westfield River than did application of a constant CD (Fig. 2). This constant CD was the best possible single value, set to the mean of dynamic CD values. Using a constant CD caused overestimates of pH during low-DOC periods in July, September, and October and pH underestimates in March–May when ALK was low (Fig. 2; and see Fig. 4).

Both pH and DOC affect CD_t. As expected from eq. 7, CD_t varied inversely with DOC, both within and among streams (Fig. 3). The CD_t values are more sensitive to DOC in Moose Pit Brook than in the Westfield River, due to the greater DOC range in Moose Pit Brook (Fig. 3). The effects of pH on CD_t are not intuitively obvious from eq. 7 (since H^+ affects several terms in the numerator), but the net effect is clear from the results. CD_t was positively correlated with pH both over the complete data set (Pearson product moment $r = 0.62$, $P < 0.01$) and also within each of the three streams. CD_t values were more sensitive to variation in pH in the Westfield River than in Moose Pit Brook (Fig. 3). On a seasonal basis (bottom panel of Fig. 4), the assignment of CD_t by the model apparently minimizes the week-to-week fluctuations in the calculated amount of A^- in order to maintain the charge balance in eq. 1. It is likely that pK_a values also change over time (independent of the pH) and that the computed CD_t values absorb some of the seasonal variation in pK_a.

The CD_t values for the Westfield River were more sensitive to variation in assumed pCO_2 than for the other two streams (Table 2), but changes in pCO_2 still had only a minor effect on smolt production (Fig. 5). Increasing CO_2 changes H^+ and HCO_3^-; the net effect is that less A^- (hence, lower CD_t) is required for charge balance (eq. 1). CD_t estimates are less responsive to variation in pCO_2 in the two lower-pH streams, which have both a smaller fraction of total inorganic C as HCO_3^- and more DOC. When we assumed a pCO_2 level of 2.5, we found that in about 20% of the sampling dates the model ended up computing a CD_t that was negative in order to balance eq. 1 (i.e., too much HCO_3^- for the measured Gran ALK), but a pCO_2 of 3.5 yielded no negative CD_t values.

We explored the effect on Westfield River simulations of estimating CD_t using a constant monoprotic representation of organic acids, rather than the Oliver et al. (1983) approach where pK_a varies with pH. We also did this to understand the effects of K_a on CD_t, pH, and smolt production because K_a appears in both the numerator and denominator of eq. 7. As pK_a increased from 3 to 5, CD_t estimates for the Westfield River also increased (from 0.5–2.3 to 1.0–3.4), A^- concentrations increased, and smolt production declined (Fig. 5). Smolt production estimates were relatively insensitive when pK_a varied from 4 to 5 (Fig. 5).

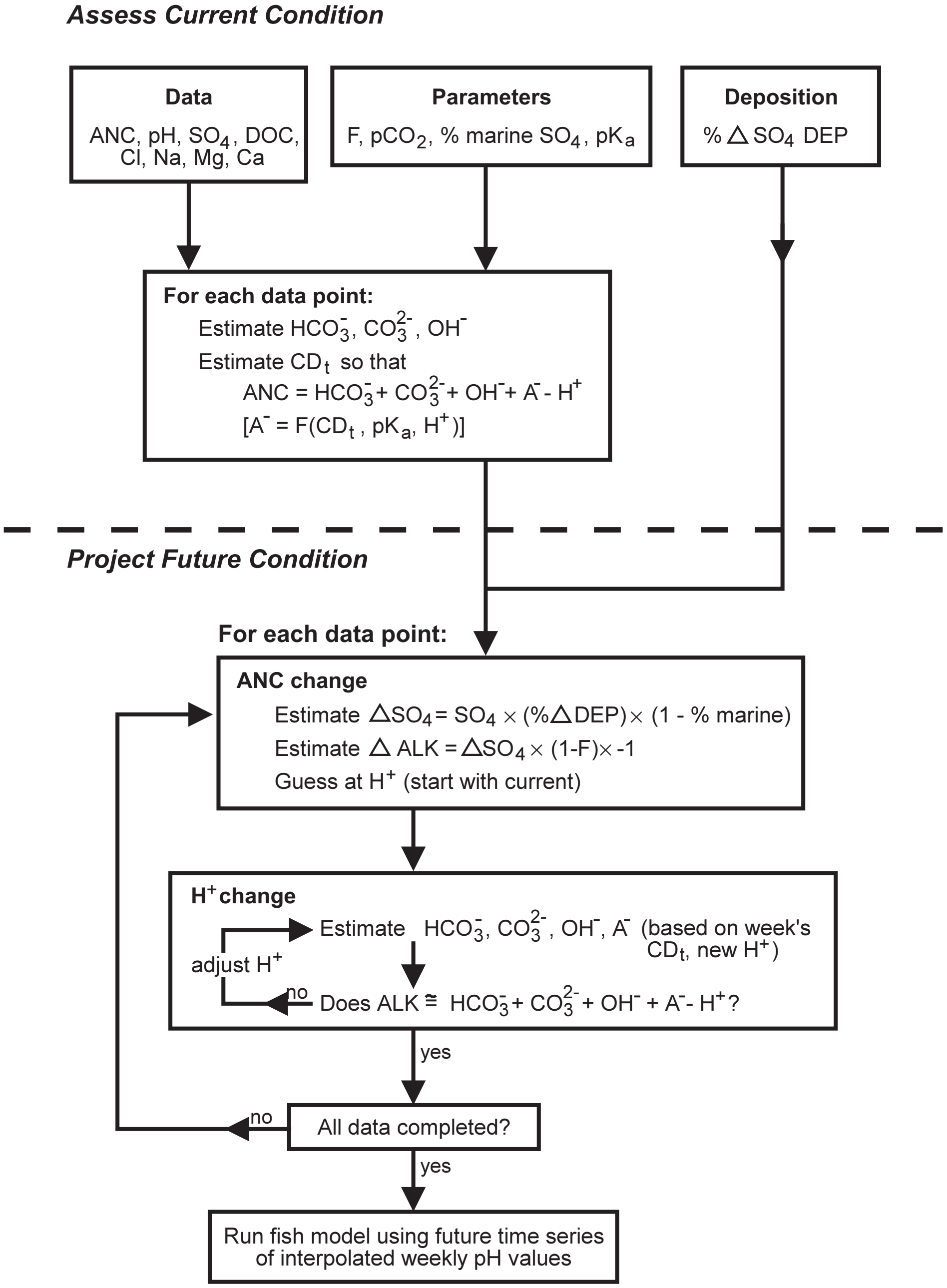
Fraction of marine SO_4^{2-} (FM)

As FM increased, less of the stream SO_4^{2-} (and therefore, ANC) was subject to change through changes in emissions (eq. 5). Consequently, a 30% reduction in deposition at FM = 0.3 caused less of an increase in both pH and smolt production than at FM = 0.1 (Fig. 5). There was very little variation in FM among the three streams simulated here (Table 1), but regional-scale simulations would need to consider this.

Interactive effects of *F*-factor and deposition level

As the *F*-factor is increased, it took a greater reduction in SO_4^{2-} deposition to attain a nontoxic minimum pH (Fig. 6). At $F = 0.3$, a 30% reduction in SO_4^{2-} deposition restored pH levels in the Westfield River to above 5.0 whereas a 70% reduction was required at $F = 0.7$ (Fig. 6). Conversely, higher *F*-factor values conferred a greater resistance to large deposition increases (Fig. 6). We chose a 30% reduction in

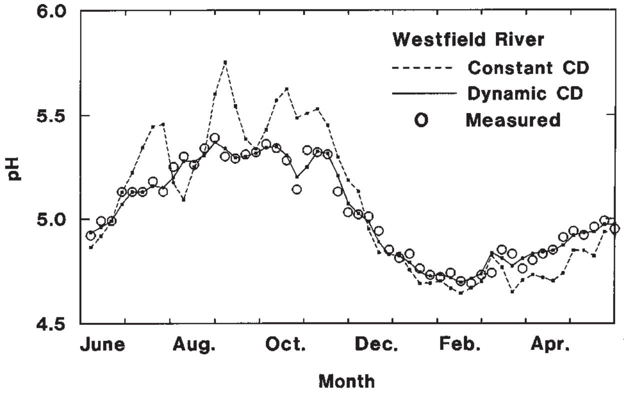
Fig. 1. Flowchart of the time series translation model (TSTM): inputs and structure and procedures for calibration and future projection. FM, fraction of $[SO_4^{2-}]$ from marine sources; FCAD, fractional change in acidic deposition; CD_t, dynamically calculated charge density. Accurate estimates of FM and *F* require stream measurements of Cl^-, SO_4^{2-}, Na^+, Mg^{2+}, and Ca^{2+}.



deposition for Fig. 5 because it maximized the sensitivity of biological predictions in the Westfield River to variations in *F*. Through the most likely range for Westfield's *F* (0.3–0.4), there was not much change in predicted smolt output (about 0.003 smolt/m^2; Fig. 5). By contrast, changing *F* from 0.6 to 0.7 changed smolt output by two and a half times as much (0.008/m^2; Fig. 5). The zone of greatest parameter sensitivity (i.e., *F* and FCAD) will vary from stream to stream. Also, the *F*-factor may vary seasonally (see Discussion).

We used the model to translate the measured SO_4^{2-}, ALK, and pH into future conditions using two *F*-factors (0.3 and 0.7; Figs. 4 and 6). A 50% reduction in anthropogenic SO_4^{2-} deposition (FCAD = 0.5) resulted in a 40% decrease in $[SO_4^{2-}]$ because marine sources constitute about one fifth of stream $[SO_4^{2-}]$ (Fig. 4). The change in ALK was proportional to but smaller in magnitude than changes in $[SO_4^{2-}]$ due to the watershed neutralization effects represented by the *F*-factor. Changes in pH were more variable over time than changes in $[SO_4^{2-}]$ and ANC because of the nonlinearities inherent in the equilibrium calculations. A large jump in pH occurred during periods when the decrease in $[SO_4^{2-}]$ was sufficient to raise the ALK to the steep part of the ALK–pH relationship (July–November in Fig. 4). With an *F*-factor assumption of 0.3 (the most likely *F*-value), the pH rose to as high as 6.5 in Westfield River

Fig. 2. Comparison of constant and dynamic CD calculations of pH with actual pH measured in the Westfield River during 1983–1984. The constant CD line applied a CD = 1.8, the average of the dynamic CD_t values (Table 2).

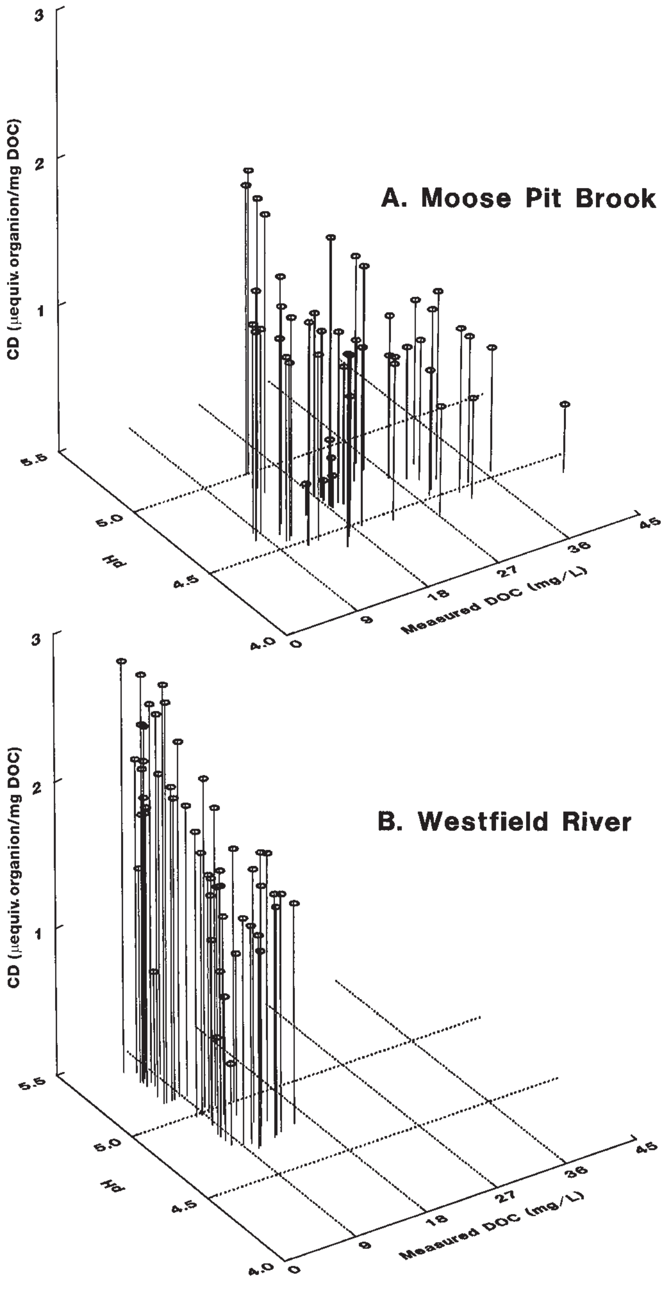


(Fig. 4), but in Moose Pit Brook the pH remained below 6.0 for most of the year due to the effects of organic acids.

The sensitivity of minimum annual pH to *F*-factor assumptions varied with both the deposition scenario and the stream (Fig. 6). The lines represented by different *F*-factors cross at the 0% change in deposition level because low *F*-factor values cause both a greater pH increase with reduced deposition levels and a greater pH decrease with higher deposition levels. The streams with greatest amounts of DOC (Round Lake Brook and Moose Pit Brook) showed a more modest change in the minimum annual pH than did the Westfield River as the result of the buffering effects of organic ions. The results in Fig. 6 imply that even with a complete removal of anthropogenic SO_4^{2-} deposition, Moose Pit Brook would still occasionally experience pH minima below 5 and therefore some Atlantic salmon mortality.

Although the required data inputs to TSTM and ASRAM are modest, the combined models do require frequent chemical measurements to accurately capture the acidic episodes that kill fish. We explored the sensitivity of model predictions to variations in sampling frequency. We first subsampled the weekly data for the three streams to simulate biweekly, triweekly, monthly, or seasonal sampling regimes, then interpolated these coarser data sets to weekly intervals (i.e., the frequency required in ASRAM), and finally ran the "pseudo-weekly" data through TSTM and ASRAM for 0, 25 (for Westfield only), and 50% deposition changes. The results (Fig. 7) illustrate how longer sampling intervals (particularly seasonal) can lead to an overestimate of fish production due to missed acidic episodes or pH minima. Interestingly, this was only a problem for Moose Pit Brook when deposition was reduced by 50% but not under the current highly toxic conditions (Fig. 7). The Westfield River had less variable chemistry than Moose Pit Brook in 1983–1984 and so was less affected by changes in sampling intervals. This analysis suggests that Watt (1987) may have underestimated lost Atlantic salmon production because his classification of streams was based largely on seasonal sampling of stream chemistry. Similarly, the projections in the LaHave River (Korman et al. 1994) were probably biased toward overproduction because the input chemistry data only had a monthly resolution. This overestimation would be greatest in the most acidic tributaries, or those where stream chemistry is temporally more variable, where errors would also have the greatest impact on model projections for the river system.

Fig. 3. Calculated CD versus measured DOC and measured pH for (A) Moose Pit Brook and (B) Westfield River.



Not surprisingly, streams of intermediate toxicity (i.e., pH 4.7–5.3) require the most frequent sampling to accurately assess current smolt production (D.R. Marmorek, unpublished analyses). Whereas frequent sampling of streams with very low or circumneutral pH may be unnecessary to estimate *current* salmon production levels (i.e., mortality is either 100 or 0%), reliable projections of *future* production do require at least biweekly (preferably weekly) sampling during the fall and winter periods of lowest pH, as altered

Fig. 4. Current measured levels of pH, ALK, SO_4^{2-}, and DOC, estimated CD_t, new SO_4^{2-} after a 50% decrease in deposition, and projected range of future ALK and pH (*F* from 0.3 to 0.7) for the Westfield River.

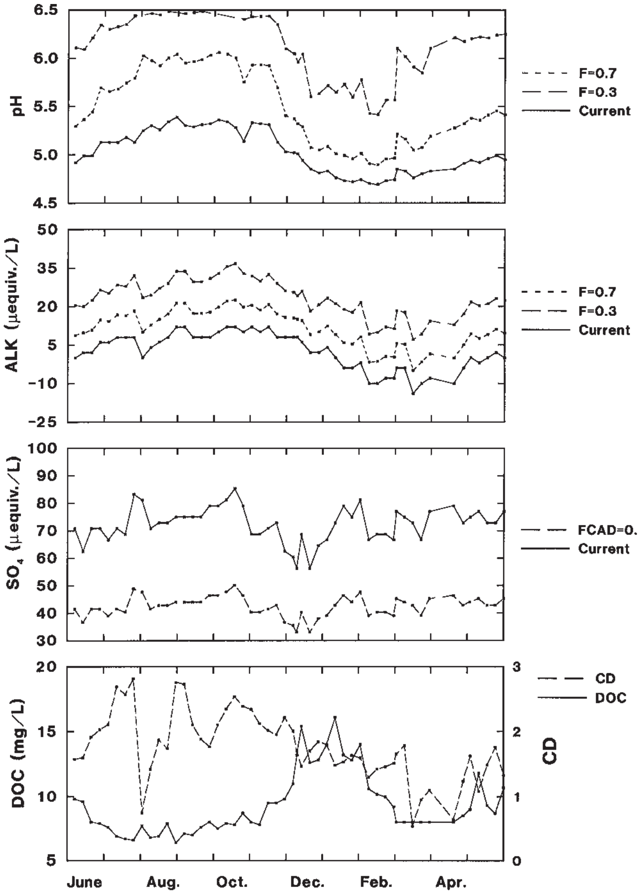


Table 2. Effects of pCO_2 on range and mean value of model-estimated CD_t.

	pCO_2 = 2.5 (lower range)			pCO_2 = 3.5 (upper range)		
Stream	Mean CD_t	Min. CD_t	Max. CD_t	Mean CD_t	Min. CD_t	Max. CD_t
Westfield River	1.1	0.1	1.8	1.8	0.5	2.8
Round Lake Brook	1.2	0.1	1.8	1.5	0.3	2.2
Moose Pit Brook	1	0.1	1	1.1	0.1	2.1

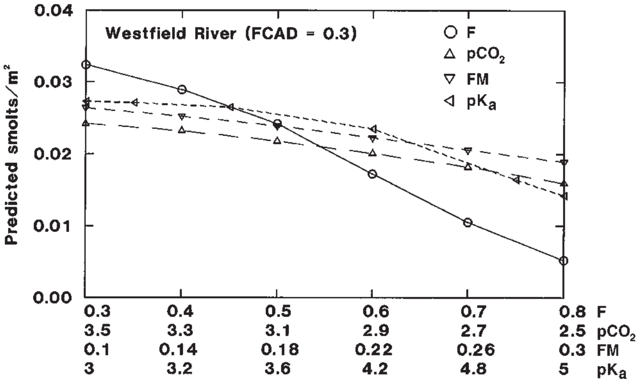
deposition may move the pH of the stream into the zone of intermediate toxicity.

Discussion

Model assumptions and limitations

The key assumptions in TSTM are *F*-factor values, pCO_2 levels, and CD_ts. The simplifications involved in *F*-factor models have been discussed in detail in Thornton et al. (1990, chap. 4). We assumed a reasonable *F*-factor value (0.3) based on the very low C_B values in these streams (61–73 μequiv./L; Table 1). More accurate estimates of *F* require a period with changing SO_4^{2-} deposition, which has not occurred in this region. The greatest risk of the *F*-factor approach is underestimating the damage from acid deposition by not accounting for soil reservoirs of C_B and SO_4^{2-} (Labieniec et al. 1989; Cosby et al. 1994). Seasonal variations in *F* due to changes in hydrology and geochemical processes are not explicitly represented in TSTM, but are implicit in the current patterns of stream chemistry, which in turn affect how TSTM distributes the impacts of deposition changes over the year.

Fig. 5. Effects of independently varying F, pCO_2, FM, and pK_a over a wide range of possible values on predicted Atlantic salmon smolt output in the Westfield River (1983–1984) with a 30% decline in SO_4^{2-} deposition. Default values used: *F* = 0.5, pCO_2 = 3.42, FM = 0.174, pK_a using Oliver et al. (1983). Parameter sensitivity varied with the stream and deposition scenario.



We assumed a constant pCO_2 level (3.42). Several other models vary pCO_2 seasonally with temperature (e.g., Cosby et al. 1985) or assign a lower pCO_2 value, indicating considerable CO_2 supersaturation (e.g., Thompson 1982*b*). However, the small streams we modelled are extremely well mixed, and assuming only a small amount of supersaturation seems reasonable. Only the Westfield River showed significant chemical or biological sensitivity to changes in assumed pCO_2 (Table 2; Fig. 5). This is because its higher pH allows for a greater fraction of carbonic acid to be present as HCO_3^- and because its pH levels straddle the toxic zone.

Previous modelling efforts have generally assumed a constant CD (reviewed by Thornton et al. 1990). There is, however, some empirical justification for assuming that CD varies seasonally with changes in the ratio of humic (lower CD) to fulvic (higher CD) acids (Visser 1984). Our estimates of CD_t decreased from August to March in the Westfield River (Fig. 4), although we do not have empirical evidence that CD_t actually varied in this manner. Obtaining more accurate estimates of CD_t for these streams (e.g., as in Driscoll et al. 1994) would help to test our assumed structure.

Are our estimates of CD_t reasonable? CD_ts calculated by TSTM (1–3 μequiv./mg DOC; Fig. 3) were about 3–4 μequiv./mg lower than those in three other studies (Eshelman and Hemond 1985; Gorham et al. 1985; Wilkinson et al. 1992) but close to the estimates of Driscoll and Schafran (1984) and Driscoll et al. (1994) for the

Fig. 6. Variation in projected minimum annual pH with changes in deposition (± 100%) and assumed *F*-factor (0.3, 0.5, 0.7) for the three modelled streams.

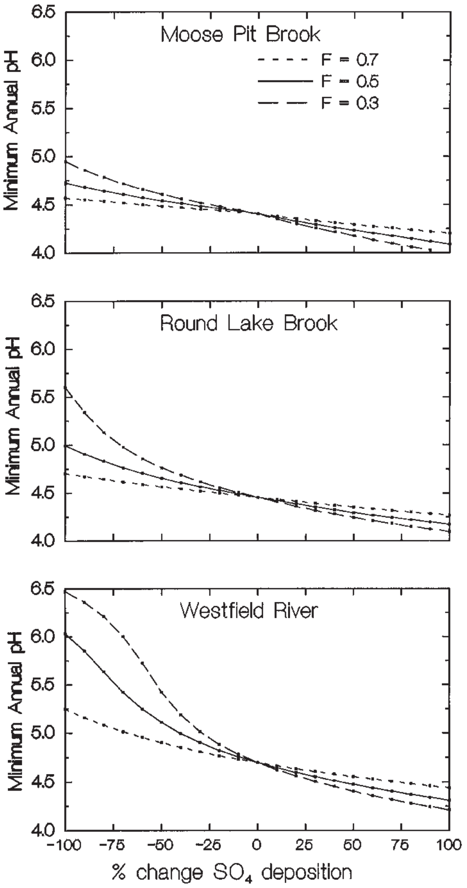
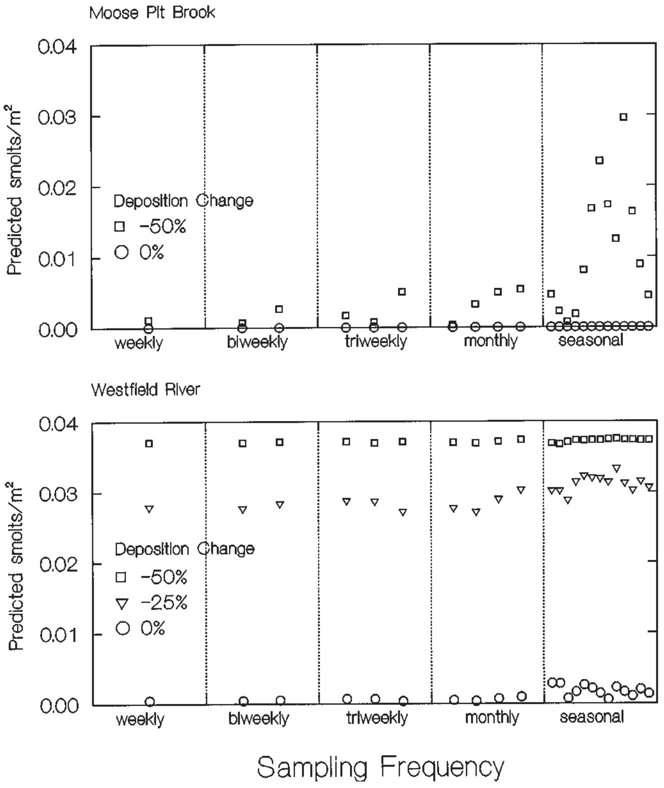


Fig. 7. Simulated effect of sampling frequency on predicted Atlantic salmon smolt output for Moose Pit Brook and Westfield River under 0% (circles), –25% (Westfield only (triangles)), and –50% (squares) changes in SO_4^{2-} deposition.



Adirondacks (2.1 and 2.5–4.2). (Values were calculated from fig. 1*b* of Driscoll et al. (1994) for data with pH <5.3 assuming 1 equiv./mol DOC = 83.33 μequiv./mg DOC.) Adirondack surface waters are similar to Nova Scotia streams in two other respects: both show a positive correlation between CD_t and pH (Driscoll et al. 1994; our Fig. 3) and organic acids play a significant role in later summer and fall acidic episodes in both (Lacroix and Korman 1996; Wigington et al. 1996). Our CD_t values declined with DOC (Fig. 3), a pattern consistent with the results of Wilkinson et al. (1992). We believe that the primary reason that our CD_t estimates are lower than some other studies is that the streams we examined had lower pH values and higher DOC concentrations, both of which act to decrease CD_t.

In TSTM, we assumed that CD_t and DOC remained unchanged for each sampling date as we changed the amount of acidic deposition. There is evidence from a variety of sources that DOC can change with acidic deposition or drought (e.g., Yan et al. 1996), although the magnitude of change is uncertain (Marmorek and Bernard 1990). The critical issue here is whether the total amount of A^- changes. If the generally observed inverse relationship between DOC and CD_t is maintained (Fig. 3), then even if DOC were to change with changes in acidic deposition, the shift in total amounts of A^- (product of DOC and CD) may not be large enough to have a significant effect on stream pH. Clair and Ehrman (1995) detected declining total organic C (TOC) trends in 15 of 18 Nova Scotia streams between 1983 and 1992, which they attributed to reduced runoff and watershed export of TOC and proportionately greater fractions of low-DOC groundwater in stream flow. Although annual mean DOC levels were lower in our streams during this period, the autumn DOC peaks and associated pH minima were more extreme than in years with typical precipitation levels (G.L. Lacroix, unpublished data). Very dry summers followed by typically wet falls may be creating an extra acidification effect in Nova Scotia streams similar to that observed by Yan et al. (1996) after a 2-year drought in northern Ontario.

TSTM provides a picture of the chemical conditions expected under different levels of SO_4^{2-} deposition. It reproduced the seasonal pattern of pH fluctuations currently observed and translated these patterns in a reasonable way. TSTM has several limitations: it does not provide any estimate of how long it might take a watershed to reach a steady-state condition associated with a given level of acid deposition, it does not consider N deposition or long-term changes in climate, and it should not be applied to clear streams with low DOC where Al^{n+} is much more important. The advantage of TSTM, however, is that it does permit an exploration of chemical responses on fine time scales in a realistic way with a minimum amount of data inputs and, when linked to ASRAM, generates projections for Atlantic salmon production as well.

Regional projections of impacts using TSTM–ASRAM will require estimates of a range of potential smolt production values from well-monitored index streams representing different pH–DOC classes. We recommend pH cruises (i.e., detailed snapshots of spatial pH distributions) of other tributaries during the fall and winter to classify the percentage of salmon production areas within these pH–DOC classes and to estimate C_Bs for *F*-factor estimates. Then the smolt production ranges derived from TSTM–ASRAM runs can be applied to generate projections of salmon production within different river basins under different deposition scenarios. The critical assumption in this procedure is that the subset of streams sampled and simulated must be representative of the larger population of streams in southwest Nova Scotia. As improvements are made in the spatial and temporal resolution of chemical data available for acidified salmon rivers in southwest Nova Scotia, we should be able to evaluate the regional impacts of various deposition scenarios and the potential for recovery using the proposed TSTM–ASRAM.

Acknowledgements

We thank John Ritter, Peter Amiro, Dick Cutting, and Joseph Kerekes for their ideas, patience, and continued support, Calvin Peters for technical assistance, and two external reviewers for excellent suggestions. This research was funded by the Canadian Program on Long Range Transport of Air Pollutants (LRTAP) through contracts to ESSA Technologies Ltd. All data used in this paper were provided by G.L. Lacroix.

References

Brakke, D.F., Henriksen, A., and Norton, S.A. 1990. A variable *F*-factor to explain changes in base cation concentrations as a function of strong acid deposition. Verh. Int. Ver. Limnol. **24**.

Clair, T.A., and Ehrman, J.M. 1995. Acid precipitation-related chemical trends in 18 rivers of Atlantic Canada — 1983 to 1992. Environ. Monit. Assess. **35**: 165–179.

Cosby, B.J., Wright, R.F., Hornberger, G.M., and Galloway, J.N. 1985. Modeling the effects of acid deposition: estimates of long-term water quality responses in a small forested catchment. Water Resour. Res. **21**: 1591–1601.

Cosby, B.J., Bulger, A.J., and Wright, R.F. 1994. Predicting recovery of freshwater ecosystems: trout in Norwegian lakes. *In* Acidification of freshwater ecosystems: implications for the future. *Edited by* C.E.W. Steinberg and R.F. Wright. John Wiley & Sons, Chichester, U.K. pp. 355–372.

DeGraeve, G.M., and Peterson, R.H. 1982. Hydrologic and land use surveys of the Westfield River watershed. Can. Tech. Rep. Fish. Aquat. Sci. No. 1095.

Driscoll, C.T., and Schafran, R.C. 1984. Short-term changes in the base neutralizing capacity of an acid Adirondack lake, New York. Nature (London), **310**: 308–310.

Driscoll, C.T., Lehtinen, M.D., and Sullivan, T.J. 1994. Modeling the acid–base chemistry of organic solutes in Adirondack, New York, lakes. Water Resour. Res. **30**: 297–306.

Eshelman, K.N., and Hemond, R.F. 1985. The role of organic acids in the acid–base status of surface waters at Backfired watershed, Massachusetts. Water Resour. Res. **21**: 1503–1510.

Gorham, E., Eisenreich, S.J., Ford, J., and Santelmann, M.V. 1985. The chemistry of bog waters. *In* Chemical processes in lakes. *Edited by* W. Stumm. John Wiley & Sons, New York. pp. 339–363.

Hemond, R.F. 1990. Acid neutralizing capacity, alkalinity, and acid–base status of natural waters containing organic acids. Environ. Sci. Technol. **24**: 1486–1489.

Henriksen, A., and Brakke, D.F. 1988. Increasing contributions of nitrogen to the acidity of surface waters in Norway. Water Air Soil Pollut. **42**: 183–201.

Kerekes, J., and Freedman, B. 1989. Seasonal variations of water chemistry in oligotrophic streams and rivers in Kejimkujik National Park, Nova Scotia. Water Air Soil Pollut. **46**: 131–144.

Kerekes, J., Beauchamp, S., Tordon, R., Tremblay, C., and Pollock, T. 1986. Organic versus anthropogenic acidity in tributaries of the Kejimkujik watersheds in western Nova Scotia. Water Air Soil Pollut. **31**: 165–173.

Korman, J., Marmorek, D.R., Lacroix, G.L., Amiro, P.G., Ritter, J.A., Watt, W.D., Cutting, R.E., and Robinson, D.C.E. 1994. Development and evaluation of a biological model to assess regional-scale effects of acidification on Atlantic salmon (*Salmo salar*). Can. J. Fish. Aquat. Sci. **51**: 662–680.

Labieniec, P.A., Small, M.J., and Cosby, B.J. 1989. Regional distributions of lake chemistry predicted by mechanistic and empirical lake acidification models. *In* Regional acidification models: geographic extent and time development. *Edited by* J Kämäri, D.F. Brakke, A. Jenkins, S.A. Norton, and R.F. Wright. Springer-Verlag, New York. pp. 185–201.

Lacroix, G.L. 1987. Model for loss of Atlantic salmon stocks from acidic brown waters of Canada. *In* Acid rain: scientific and technical advances. *Edited by* R. Perry, R.M. Harrison, J.N.B. Bell, and J.N. Lester. Selper Ltd., London, U.K. pp. 516–521.

Lacroix, G.L. 1989. Ecological and physiological responses of Atlantic salmon in acidic organic rivers of Nova Scotia, Canada. Water Air Soil Pollut. **46**: 375–386.

Lacroix, G.L., and Kan, K.T. 1986. Speciation of aluminum in acidic rivers of Nova Scotia supporting Atlantic salmon: a methodological evaluation. Can. Tech. Rep. Fish. Aquat. Sci. No. 1501.

Lacroix, G.L., and Korman, J. 1996. Timing of episodic acidification in Atlantic salmon rivers influences evaluation of mitigative measures and recovery forecasts. Can. J. Fish Aquat. Sci. **53**: 589–599.

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**: 1475–1484.

Lam, D.C.L., Bobba, A.G., Bourbonniere, R.A., Howell, G.D., and Thompson, M.E. 1989. Modeling organic and inorganic acidity in two Nova Scotia Rivers. Water Air Soil Pollut. **45**: 277–287.

Marmorek, D.R., and Bernard, D.P. 1990. Response to K.C. Krug and W.L. Warnick's comments on: A protocol for determining lake acidification pathways. Water Air Soil Pollut. **50**: 209–213.

Marmorek, D.R., Jones, M.L., Minns, C.K., and Elder, F.C. 1990. Assessing the potential extent of damage to inland lakes in eastern Canada due to acidic deposition. Vol. I. Development and evaluation of a simple "site" model. Can. J. Fish. Aquat. Sci. **47**: 55–66.

Norton, S.A., and Henriksen, A. 1983. The importance of CO_2 in evaluation of effects of acidic deposition. Vatten, **39**: 346–354.

Oliver, B.G., Thurman, E.M., and Malcolm, R.L. 1983. The contribution of humic substances to the acidity of colored natural waters. Geochim. Cosmochim. Acta, **47**: 2031–2035.

Stumm, W., and Morgan, J.J. 1981. Aquatic chemistry. 2nd ed. John Wiley & Sons, New York.

Thompson, M.E. 1982*a*. Exchange of marine sodium for calcium during chemical weathering in the Isle aux Morts River basin, Newfoundland. Geochim. Cosmochim. Acta, **46**: 361–365.

Thompson, M.E. 1982*b*. The cation denudation rate as a quantitative index of sensitivity of eastern Canadian rivers to acidic atmospheric precipitation. Water Air Soil Pollut. **18**: 215–226.

Thornton, K.W., Marmorek, D., Ryan, P.F., Heltcher, K., and Robinson, D. 1990. Acidic deposition: state of science and technology: methods for projecting future changes in surface water acid–base chemistry. NAPAP Rep. 14. National Acid Precipitation Assessment Program, Washington, D.C.

Vet, R.J., Sukloff, W.B., Still, M.E., and Gilbert, R. 1986. Canadian Air and Precipitation Monitoring Network (CAPMoN): precipitation chemistry data summary 1983–1984. Rep. AQRB-86-001-M, Environment Canada, Atmospheric Environment Service, Ottawa, Ont.

Visser, S.A. 1984. Seasonal changes in the concentration and colour of humic substances in some aquatic environments. Freshwater Biol. **14**: 79–87.

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

Wigington, P.J., Jr., DeWalle, D.R., Murdoch, P.S., Kretser, W.A., Simonin, H.A., Van Sickle, J., and Baker, J.P. 1996. Episodic acidification of small streams in the northeastern United States: ionic controls of episodes. Ecol. Appl. **6**: 389–407.

Wilkinson, K.J., Jones, H.G., Campbell, P.G.C., and LaChance, M. 1992. Estimating organic acid contributions to surface water acidity in Quebec (Canada). Water Air Soil Pollut. **61**: 57–74.

Wright, R.F., and Henriksen, A. 1983. Restoration of Norwegian lakes by reduction in sulphur deposition. Nature (London), **305**: 422–424.

Yan, N.D., Keller, W., Scully, N.M., Lean, D.R.S., and Dillon, P.J. 1996. Increased UV-B penetration in a lake owing to drought-induced acidification. Nature (London), **381**: 141–143.