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MODELLING ACIDIFICATION PROCESSES IN REMOTE LAKES

by

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MANAGEMENT PERSPECTIVE

The acid rain problem is among the top priority environmental issues in many countries. It affects all kinds of lakes, particularly where the natural buffering is weak. To some countries, of considerable concern are remote mountain lakes. The Commission of the European Community (CEC) has recently organized a special workshop on acidification processes in remote lakes. In recognition of the expertise in watershed acidification modelling at NWRI, the workshop organizers invited the authors of this report to review several mathematical models for potential application to remote lakes. This report is one such contribution.

PERSPECTIVES-GESTION

Les pluies acides constituent l'un des problèmes écologiques prioritaires dans maints pays. Elles affectent tous les types de lacs, y compris ceux où la capacité tampon naturelle est faible. Dans certains pays, les lacs alpins éloignés présentent des problèmes énormes. La Commission des Communautés européennes (CCE) a récemment organisé un atelier spécial sur l'acidification des lacs dans les régions éloignées. Reconnaissant le savoir-faire de l'INRE en matière de modélisation de l'acidification des bassins hydrographiques, les organisateurs de l'atelier ont invité les auteurs du présent rapports à examiner plusieurs modèles mathématiques en vue de leur application aux lacs éloignés. Le présent rapport est le résultat de l'un de ces examens.

SOMMAIRE

Plusieurs modèles ont été mis au point pour décrire et prévoir l'acidification des bassins d'alimentation terrestres et de leurs eaux de drainage. Certains des principaux modèles de simulation des processus hydrogéochimiques sont brièvement décrits, et l'un d'eux (le modèle Turkey-Mersey) est étudié de façon plus détaillée. Les propriétés physiques et les données utilisées pour décrire les bassins d'alimentation alpins laissent supposer que les modèles Birkenes ou Turkey-Mersey sont les plus appropriés pour simuler l'hydrochimie épisodique de ces bassins. Les modèles MAGIC et ETD permettent de prévoir la chimie annuelle ou saisonnière moyenne. Il faut ajouter des sous-modèles pour simuler les principaux processus intralacustres durant les longues périodes d'étiage.

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Summary

Several models have been developed to describe and predict acidification of terrestrial catchments and their drainage waters. Some of the prominent models that emphasize simulation of hydrogeochemical processes are briefly reviewed, and one of them (the Turkey-Mersey Model) is presented in greater detail. The physical characteristics and data available to describe alpine catchments suggest that the Birkenes or Turkey-Mersey models would be most useful as a starting point for simulating the episodic hydrochemistry of such basins. The MAGIC or ETD models would provide useful predictions for average seasonal or annual chemistry. Consideration should be given to adding sub-models to simulate the within-lake processes that may be important during extended periods of low flow.

1. INTRODUCTION

Acidification modelling may serve many purposes. Simulation of processes and prediction of specific chemical responses to changes in deposition are the most common. This may permit evaluation of the likely effect of various management options, e.g. SO_2 emission control scenarios. Models also present a convenient mechanism for information synthesis and suggest research directions through identification of knowledge gaps and/or weaknesses.

The purpose of this paper is to summarize the properties and usage of existing acidification models, and to describe one of them in greater detail to illustrate their application. Both time-dependent and steady-state models exist; however, since this workshop emphasizes "acidification processes", only time-dependent versions will be discussed. Reviews of acidification models already exist (1,2); consult these papers for a more substantive evaluation than is possible here. None of the models were specifically developed for alpine settings, and a short discussion of modelling considerations for this type of terrain is included.

2. MODELS SIMULATING ACIDIFICATION PROCESSES

2.1 Birkenes and Turkey-Mersey Models

These models are of intermediate complexity. The Birkenes model was developed to simulate stream chemistry for a forested catchment in southern Norway (3). It is a soil-oriented, charge balance model, incorporating the mobile anion concept (4), and requiring SO_4 deposition as input. Geochemical processes considered are S-oxidation/reduction, SO_4 adsorption/deposition, cation exchange, primary weathering, the

H_2CO_3-HCO_3 system, and Al solubility. Some but not all processes are operable in each of the 2 hydrological compartments used to simulate flow generation. A later version (5) applied to a Harp Lake catchment in south-central Ontario, Canada also included organic anions (A^-). As well as the catchments noted above, the Birkenes model has been applied to Storgama (Norway), and Lake Gardsjon catchments in Sweden (6).

The Turkey-Mersey model (7,8) was orginally developed for the forested Turkey Lakes Watershed (TLW) in central Ontario, Canada and uses a 3-compartment hydrological submodel in place of the Birkenes' 2-compartment version permitting simulation of detailed hydrological processes and relating geochemical processes to the computed hydrological results. The Birkenes geochemical submodel (without the Al component) is used although assignment of specific processes within each of the 3 compartments obviously differs. A separate module to account for A^- has been developed (9). Since long-term data are not available for model calibration, model performance is assessed on the ability to simulate episodic and seasonal changes in flow and chemistry. The model has been applied to the Harp Lake catchment, Lac Laflamme in southern Quebec, and Kejimkujik in Nova Scotia, Canada (10). Further detail for the Turkey-Mersey model is given below.

2.2 ILWAS Model

The ILWAS model (Integrated Lake-Watershed Acidification Study) is the most complex of all acid precipitation models being composed of many detailed submodels, each simulating specific hydrological or geochemical processes (11,12). It uses both equilibrium and rate limited expressions to describe mass balances for 18 chemical constituents (major ions, monomeric Al, A^-, DIC and DOC). Processes considered include those occurring in the canopy, snowpack, soils, and lakewater. Much emphasis has been placed on hydrological processes in determining neutralization of acidic inputs. Even plant respiration, nutrient uptake, nitrification, litter decomposition, and within-lake SO_4 reduction are included.

The ILWAS model was developed for 3 watersheds in the Adirondack Mountains of New York State. Application to other sites is limited due to the need for a large amount of input data describing catchment characteristics and a very large computer to run it. Like the Birkenes and Turkey-Mersey models, performance of the ILWAS model is evaluated by its ability to reproduce episodic and seasonal variations in water chemistry. Application of the ILWAS model to different catchments has proven difficult even for experienced acidification modellers with previous ILWAS model experience. For example, application to the TLW required several months of effort. Calibration of the model could not be carried out to adequately simulate measured data for key processes such as terrestrial hydrologic flow routing, lakewater chemistry, and temperature profiles. While explicit consideration of many hydrogeochemical processes is appealing, the model complexity this engenders may make it difficult to determine what is actually controlling catchment responses.

2.3. MAGIC Model

MAGIC (Model of Acidification of Groundwater in Catchments) is a relatively simple, process-oriented model designed to simulate average annual catchment response to acidic deposition. Hence one of its primary purposes is to predict long-term changes in water chemistry. It emphasizes processes occurring in the soil environment (e.g. ion exchange,

Al solubility, SO_4 adsorption, and primary weathering) and treats the entire soil column as one unit. Because of the long time step and single soil layer structure, only a very simple water mass balance is required to describe catchment hydrology. Input data requirements (including weathering rates) are quite modest for MAGIC; hence, it is readily applied to new catchments. It runs efficiently on a simple personal computer.

The model was originally developed for White Oak Run, Virginia, USA (13,14). This basin has well developed soils, does not experience snowpack/snowmelt effects, and rarely exhibits overland flow, thereby justifying the simple hydrological and soil-layer components of MAGIC. While it may be questionable to apply it to basins having dissimilar characteristics, it has simulated successfully water chemistry for the experimental RAIN catchments in Norway (15). Its capability for long term simulation has been assessed by comparing model results to the pH history (paleoecological reconstructions) of 4 lakes in Europe and North America (16).

2.4 ETD Model

The ETD model (Extended Trickle Down) is a simple to intermediate complexity model meant to simulate seasonal to long-term changes in water chemistry. It is a lumped-parameter model based on the ANC mass balance for the watershed and lake (17). Processes considered include weathering, cation exchange, SO_4 reduction (all three described by rate expressions), carbonic acid chemistry, and SO_4 adsorption/desorption (both described by equilibrium expressions). Aluminum chemistry, NO_3 and A^- are not considered. The current version presents mass balances for SO_4, Cl, as well as ANC. The unique feature of ETD is the assumption of a kinetically controlled supply of ANC; the rate is a function (fractional exponent) of the deposition input.

The ETD was developed for seepage lakes in the midwestern US (18) and has been applied to 3 Adirondack Mountain lakes (19). It is probably most applicable to "sensitive" terrain in which the assumption of a SO_4 input-output balance is valid.

2.5 Considerations Relevant to Alpine Lakes

As noted above, none of the acidification models have been developed for alpine lake catchments. Such catchments are generally characterized by high relief, orographically influenced precipitation, poorly developed soils, significant snowpack development and major snowmelt event(s) each year, small lakes having extended periods of ice-cover, episodic hydrology and spatial gradients in surface water chemistry. Evidence exists (20,21) showing that both terrestrial and aquatic processes are important in regulating surface water chemistry in these catchments.

Selection of a suitable model for such systems is dependent on the questions being asked. If the intent is to study or simulate processes on a time scale permitting detection of episodic events, then the alternatives are the Birkenes, Turkey-Mersey, or ILWAS models. The large data and computational requirements of ILWAS and the potential problems of its transportability probably eliminates its usage, at least in the early stages of investigation. The Birkenes and Turkey-Mersey models are likely most suitable although an additional submodel may be needed to account for within-lake alkalinity generating processes (22) that may be significant during extended periods of low-flow. Models simulating within-lake processes exist (23). Definition of mechanisms

controlling water chemistry on a seasonal or annual time step may be achieved using the MAGIC or ETD models.

3. THE TURKEY-MERSEY MODEL

The Turkey-Mersey model was developed for the Turkey Lakes Watershed (24), a catchment, while certainly not "alpine" in character, does have several features typical of mountainous terrain, e.g. 300 m relief, orographic effects, gradients in surface water quality, and significant snowmelt and other episodic events.

3.1 Hydrological Component

The model expresses the watershed as a set of reservoirs of determinable capacities that temporarily hold water and gradually recede as their contents are diminished by infiltration, recharge, evapotranspiration and lateral drainage (25).

The structure of the hydrological model is comprised of three distinct soil regimes (see Figure 1): upper soil zone (A), lower soil zone (B) and groundwater zone (C), yielding surface runoff, interflow and groundwater flow, respectively. The sum of these three flows then constitutes the total basin runoff. The model uses mass balance calculations for snow accumulations and melting, soil moisture budgeting, runoff generation and hydrological routing in these regimes.

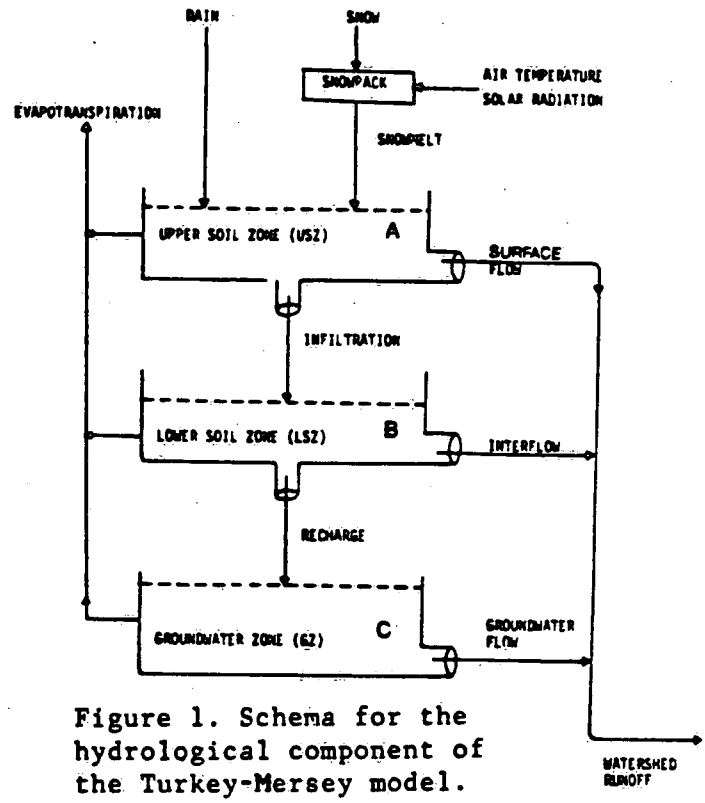

Figure 1. Schema for the hydrological component of the Turkey-Mersey model.

3.2 The Hydrogeochemical Component

Figure 2 shows the hydrogeochemical component for the variables, SO_4, H^+, Ca+Mg, and HCO_3. For the upper soil layer (A), the mass balance of SO_4 is computed from wet and dry deposition, snowmelt and oxidation of S as sources, and reduction and adsorption of SO_4 as sinks. The computed water flow and moisture content in the soil are considered to allow this mobile anion to enter, be retained, or leave the soil layer. SO_4 concentrations are computed for each of the soil layers B and C first, although the sources and sinks of SO_4 in these layers involve only adsorption (desorption) and reduction.

The concentrations of H^+, Ca+Mg, and HCO_3 for soil layer A are then computed from the charge balance equation and the following two equations governing the equilibrium of these concentrations (in mole units):

$$(1)\quad [H^+]/[2Ca + 2Mg]^{1/2} = K_G$$

$$(2)\quad [HCO_3][H^+] = K \cdot PCO_2(soil).$$

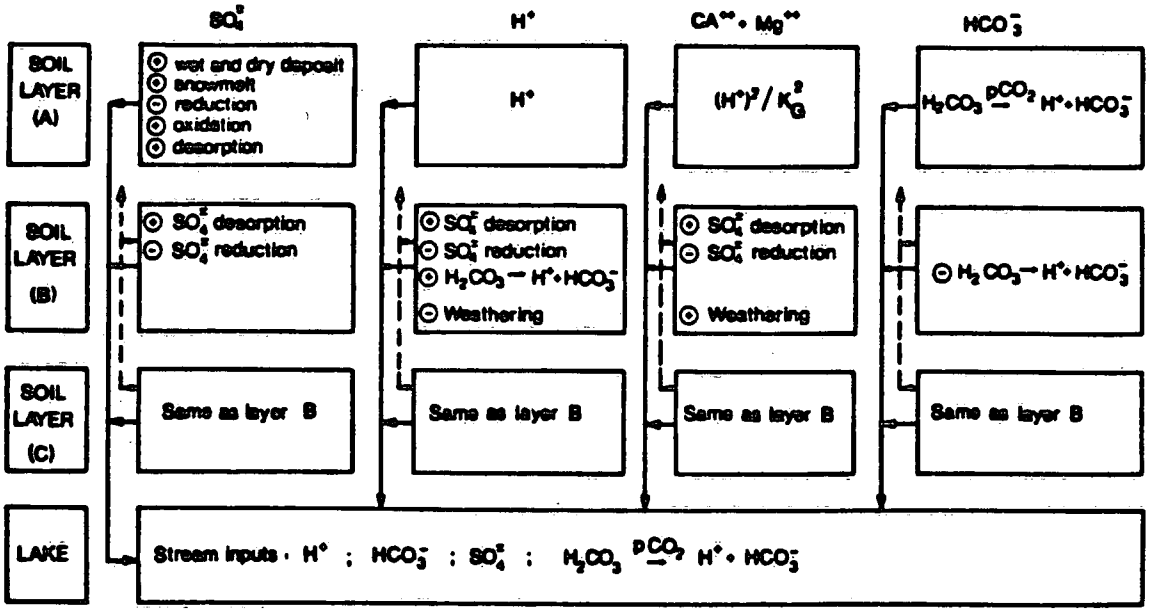

Figure 2. Schema showing the interface between hydrological and hydrogeochemical components of the Turkey-Mersey model.

In Eq. (1), K_G is the Gapon equilibrium constant for cation exchange. For thin, acidic headwater soils, $K_G = 10^{-2.2}$ while at lower elevations $K_G = 10^{-2.3}$. Definition of the CO_2 partial pressure in the soil environment (PCO_2(soil)) is critical. In Eq. (2), K is a constant (e.g. $K = 10^{-7.71}$ for a temperature of 5°C and $K = 10^{-7.80}$ for 25°C). However, PCO_2(soil) can vary from 10-100 times atmospheric PCO_2 in different soil layers. Rustad et al. (5) proposed that this variation be simulated by assuming PCO_2(soil) to be a function of the soil temperature. While such a temperature dependence can produce the desired seasonal variation in PCO_2(soil), the dynamic effect of the hydrology is not considered. Therefore, we propose the following empirical approximation:

$$(3)\quad -\log\,(PCO_2(\text{soil})) = 3.0r + k_1(1 - r)$$

where k_1 is a model constant and r is the ratio of the soil moisture content to the soil moisture capacity, as computed by the hydrological model (7). From model calibration, we found that $k_1 = 2.0$ for the top soil reservoir (A), and $k_1 = 1.5$ for the lower soil reservoirs (B, C). Since the ratio r varies between 0 and 1, -log (PCO_2(soil)) can vary between 2.0 and 3.0 for reservoir A and between 1.5 and 3.0 for reservoirs B and C. Thus for B and C, extremes in PCO_2(soil) would be about 100 PCO_2(air) in dry summer conditions (r = 0), and about 3 PCO_2(air) in wet winter conditions (r = 1). In practice, the normal range is about 10-60 times the atmospheric PCO_2.

The model also includes an A^- submodel (9) that has permitted successful simulation of a wide range of inorganic and organic acidity in Nova Scotia, Canada. Since A^- is of less concern for alpine settings, it will not be discussed further here. At present, the model does not include a nitrogen component, although for episodic events, the nitrogen variables could become important.

3.3 Application: Headwater vs Downstream Lakes, TLW

The TLW is located approximately 50 km north of Sault Ste. Marie, Ontario, Canada. It has an area of 10.5 km^2 and contains four lakes joined by a stream. Relief is 290 m. Total SO_4 deposition (4 year average) is 35.3 $mmol/m^2/yr$ (34.8 kg $SO_4/ha/yr$); precipitation pH is 4.3-4.5. Hydrological and chemical monitoring occurs at the 4 lake outflows and overall exit of the basin. These 5 sites are designated S1-S5 with S1 located at the highest elevation.

Table I. Depths (m) and computed water half-lives (d) for the 3 soil layers used by the hydrological sub model (see Figs.1 & 2).

Station	S1	S2	S3	S4
Soil depth (m)				
A	0.1	0.20	0.25	0.35
B	0.5	2.5	1.5	2.00
C	1.0	2.0	3.5	3.75
Computed Half-life (d)				
A	1.3	1.3	1.3	1.21
B	2.0	2.2	2.3	1.85
C	2.8	3.1	3.5	4.42

The cascading lake system illustrates the effect of acidic deposition on a catchment with varying elevation, soil depth and buffering capacity. For example, the hydrological model computes the half-life residence times of water in each of the soil layers (Table I). The longest residence time and therefore greatest potential mineral-water interaction occurs in the deep "groundwater" layers C in the downstream stations, S3 and S4. The net effect of the size and flow characteristics of the 3 layers is that stream waters at high elevation

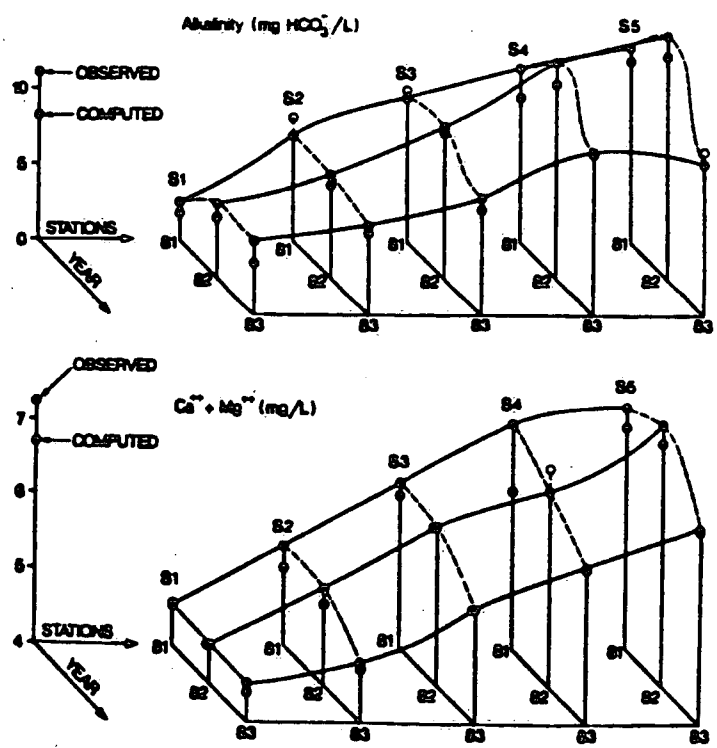

Figure 3. Computed and observed alkalinity and Ca+Mg for 1981-83 for the 5 major stream stations in the TLW.

locations are composed of a higher proportion of output from the near surface layers (A,B) than is the case at lower elevations where a greater proportion originates within lower soil layers.

In the TLW, there is different soil geochemistry in each of the 3 layers. In particular, the small amount (0-2%) of $CaCO_3$ present in the glacial till of the region increases with depth in the soil column and is generally higher at lower elevation. Combined hydrological and geochemical influences cause gradients in surface water chemistry. For example, Figure 3 shows the pre-snowmelt computed and observed alkalinity and Ca+Mg concentrations for 1981-1983 for S1-S5 presented in a timespace perspective. That is, the results for S1 through S5 are aligned along the "stations"-axis as well as displayed in time along the "year"-axis in Figure 3. In the case of Ca+Mg, not only is there a progressive increase in concentration downstream, but also a decline in 1983. In the case of alkalinity, concentrations in 1982 appear to be higher than the other two years due to a relatively dry year (10), i.e. drier years yield a higher proportion of groundwater and therefore alkalinity in the stream.

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