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THE EFFECT OF NITRATE ION ON THE CATION DENUDATION RATE MODEL

by

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EXECUTIVE SUMMARY

The cation denudation rate (CDR) model has been applied, for the most part, to waters in which sulfate is the principal acidifying anion. This report shows that the CDR model can be applied to waters containing other acidifying anions, in this case nitrate, and the model predicts the pH correctly in this case too.

RÉSUMÉ EXÉCUTIF

Le modèle du taux de dénudation des cations a été appliqué, la plupart du temps, aux eaux pour lesquelles le sulphate était le principal anion acidifiant. Le présent rapport démontre que le modèle en question peut être appliqué aux eaux qui renferment d'autres anions acidifiants, en l'occurrence le nitrate, et que le modèle prédit aussi correctement le pH.

ABSTRACT

The cation denudation rate model is here applied to waters containing some NO_3^-. Although the data do not display precise charge balance among major ion species, the model predicts the mean pH to about 0.1 pH units.

RÉSUMÉ

Le modèle du taux de dénudation des cations est appliqué ici à des eaux renfermant des NO_3^-. Bien que les données ne démontrent pas l'équilibre précis des charges entre les principaux ions, le modèle prédit le pH moyen jusqu'à environ 0,1 unités pH.

INTRODUCTION

The cation denudation rate (CDR) model compares the rate at which rivers carry off base cations ($Ca^{++} + Mg^{++} + Na^{+} + K^{+}$) with the rate at which the river yields acid anions, especially sulfate ion. The CDR model is versatile, however, and can be applied to waters with various chemical compositions. The model does, however, require charge balance as well as a predictable relationship between alkalinity and pH. Therefore, if several anionic species contribute to charge balance, these must either be corrected for (by an electrically neutral set of correction factors) or be plotted together with sulfate on the x-axis of the CDR model plot, and be considered in the model calculation of pH. Model pH for waters containing positive alkalinities is calculated from the equilibrium constant for the reaction

$$H_2O + CO_2 = H^+ + HCO_3^-$$

for which

$$pK = pH + pHCO_3 - pP_{CO_2}$$

The CO_2 pressure that best relates the measured pH to the measured alkalinity (assuming alkalinity to be equivalent to bicarbonate ion) is used.

The model has been successfully applied to waters with organic anions present (Thompson, 1985). In this report, it is applied to waters having significant concentrations of NO_3^- as well as SO_4^{--}.

Batchawana Lake is the headwater lake in the Turkey Lakes Watershed, an intensively studied watershed north of Sault Ste. Marie, Ontario (Jeffries and Semkin, 1982). The outflow from this lake is gauged, and the water is sampled frequently, especially during spring snowmelt. During winter and spring the water contains significant concentrations of NO_3^- up to 48 µeq L^{-1} (with 105 µeq L^{-1} of SO_4^{--}). During summer, however, NO_3^- concentrations go to zero.

RESULTS

The data used to apply the model are listed in Table 1. CDRs and the anion yields are calculated as mean discharge-weighted species times mean annual runoff. The mean sample date discharge is considerably higher than the mean annual discharge because of the more frequent sampling during periods of high flow in springtime.

The discharge-weighted sums of cations are nearly identical in 1983 and in 1984, but as the runoff is higher in 1984, the CDR is larger. The mean sulfate concentration is lower in 1984 than in 1983, but the sulfate yield is higher in 1984, again because of the higher runoff. NO_3^- and Cl^- concentrations are about the same in both years, but, again, in 1984 the yields are higher.

Note that the mean discharge weighted data do not display charge balance. The model over estimate of alkalinity is a result of lack of charge balance in the data. The model does, however, predict pH to about 0.1 or better. The data are shown on the CDR model plot on Figures 1A for 1983 and 1B for 1984. Because of the different runoff in the two years, the data must be plotted separately, because the runoff affects the pH assignment (Thompson, 1982).

DISCUSSION

The CDR model has been applied to data for waters containing significant amounts of NO_3^- as well as SO_4^{--}, and predicts pH reasonably well, even though the data do not display exact charge balance. In individual samples, the same excess of cations over anions is common. About half of the excess may be due to the lack of consideration of organic anions. For 1984, the organic anion, A^-, calculated from pH and dissolved organic carbon (DOC) by the method of Oliver et al. (1983) for 75 data pairs, had a mean value of 6.4 μeq L^{-1} and a range of 0 to 13 μeq L^{-1}. The remainder of the excess of cations may be due to analytical imprecision.

The model assumes a CO_2 partial pressure of $10^{-2.5}$, ten times atmospheric.

The hydration and dehydration of carbon dioxide,

$$CO_{2g} + H_2O \rightarrow H_2CO_{3aq},$$

have the slowest reaction rates in the system CO_2 + H_2O at ordinary temperatures and pressures (Stumm and Morgan, 1970). Thus it is possible for disequilibrium with respect to carbon dioxide pressure to exist between surface waters and air, if the reactions that produce and consume CO_2 in the water are more rapid.

That excess amounts of carbon dioxide are commonly present in surface waters is indicated by the observation that the pH of such waters tends to rise during aeration or gas washing. Gorham (1957) measured the pHs of lakes near Halifax before and after aeration, and the pHs of his samples having initial pH of 5.5 or higher, increased on the average by 0.59 pH units. Samples from the Turkey Lakes, collected in the winter of 1984-1985, were gas washed, and the pHs increased markedly. When the CO_2 pressure, as calculated from pH and alkalinity, reached atmospheric ($10^{-3.5}$), the pH of 26 samples had increased by an average of 1.07 pH units. This indicates an original average of CO_2 pressure of $10^{-2.43}$ (R. Semkin, 1985; personal communication).

The mean CO_2 pressures calculated from pH and alkalinity for the outflow from Batchawana Lake were $10^{-2.46}$ for 1983, and $10^{-2.56}$ for 1984, both close to the model assumption of $10^{-2.5}$.

In this example of the CDR model, the Cl^- yields were considered as well as the SO_4^{--} and NO_3^- yields. The data could have been corrected for Cl^-, on the assumption that the Cl^- arrived as a neutral salt. However, the location of this lake, a mid-continental headwater lake in the wilderness, makes it unlikely that the Cl^- represents either seasalt or roadsalt. So instead of speculating about its origin, Cl^- was simply included in order to improve the charge balance.

CONCLUSIONS

The CDR model works well, as indeed it must, for data on water chemistry that display charge balance among major ion species and a predictable relationship between alkalinity and pH. It has been applied here to waters containing some NO_3^-, which represents 16 or 17% of $SO_4^{--} + NO_3^-$. The model predicts pH to about 0.1, and would predict pH more closely if the data displayed closer charge balance.

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TABLE 1. CDR Model data for Batchawana Lake outflow

	Units	1983	n	1984	n
Discharge-Weighted Means					
Sum of cations	meq m^{-3}	192	66	195	92
Sulfate	meq m^{-3}	118	72	108	91
Nitrate	meq m^{-3}	23	66	22	92
Chloride	meq m^{-3}	10	71	11	92
Alkalinity	meq m^{-3}	29	74	37	92
Sum of anions	meq m^{-3}	180		178	
Cations - anions	meq m^{-3}	12		17	
Mean annual flow	m^3 s^{-1}	0.020		0.026	
Annual runoff	m yr^{-1}	0.584		0.713	
CDR	meq m^{-2} yr^{-1}	105		139	
Sulfate yield	meq m^{-2} yr^{-1}	64		77	
Nitrate yield	meq m^{-2} yr^{-1}	13		16	
Chloride yield	meq m^{-2} yr^{-1}	5		8	
Alkalinity yield	meq m^{-2} yr^{-1}	16		26	
Mean pH		5.80		5.97	
Model pH		5.91		6.03	

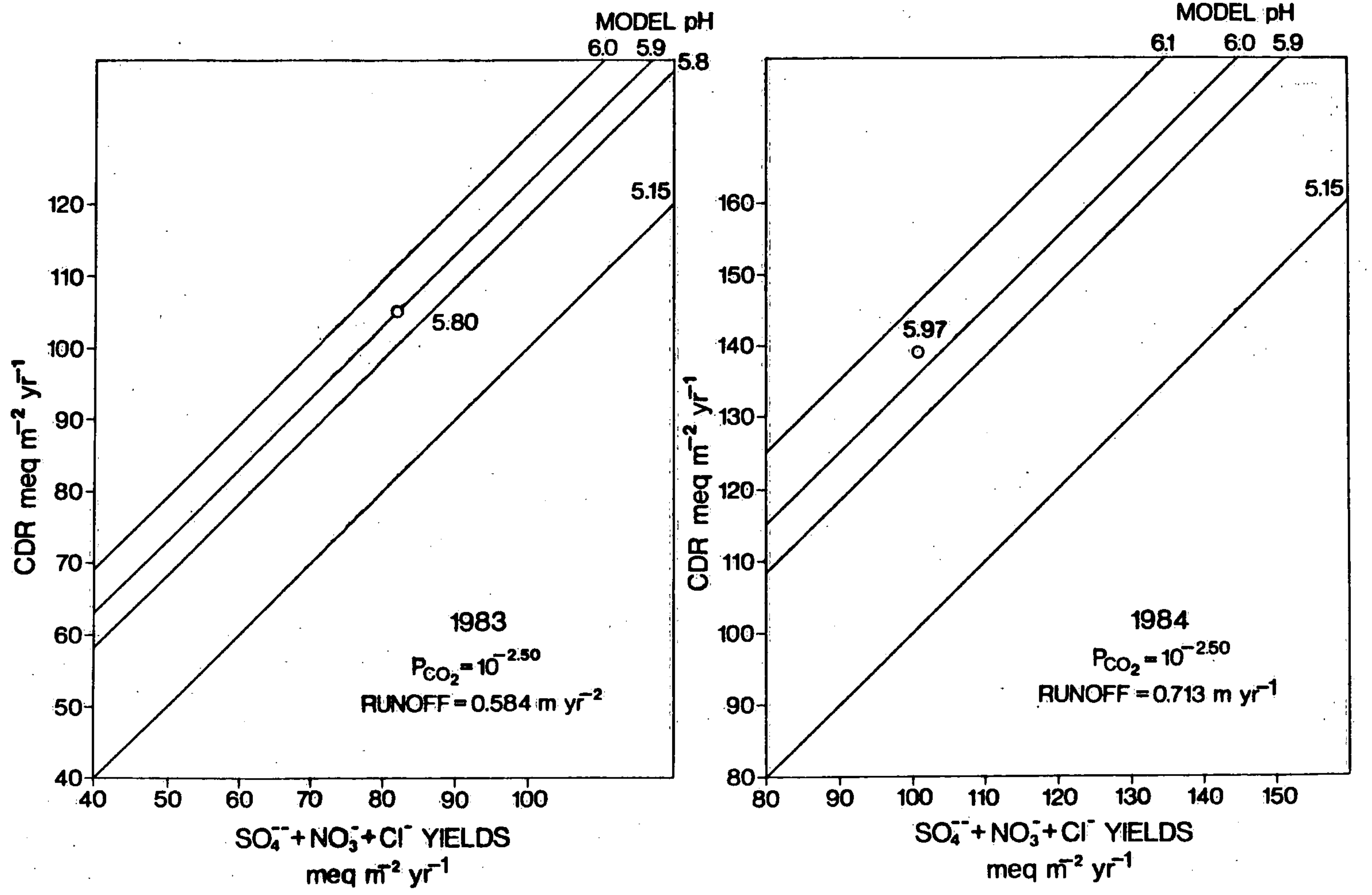

Figure 1. CDR model plot for the outflow from Batchawana Lake, 1983 and 1984.