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**THE CATION DENUDATION RATE
MODEL - ITS CONTINUED VALIDITY**

by

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ABSTRACT

The rationale of the cation denudation rate (CDR) model is reviewed, and the history of the application of the model is described. Analytical problems encountered in strongly coloured coastal rivers in the determinations of sulfate and chloride ions, and their effects upon the application of the model are discussed.

In rivers that carry a significant concentration of organic anions, the methyl thymol blue (MTB) method for sulfate, which incorporates part of the organic anion, here called soluble reactive organic anion, or SRA^- , gives better results when used in the model, because the model assumes charge balance, and charge balance is better obtained between conventional ionic species and MTB sulfate.

As the model predicts, the mean pHs of these rivers were generally higher in the early 1980s than in the early 1970s, in accordance with the observation that the sulfate yields were lower in the latter period. The model is also used to predict the change in pH to be expected in the absence of SRA^- , LC sulfate, or both.

RÉSUMÉ

On revoit la justification du modèle d'établissement du taux d'appauvrissement en cations (TAC) et on décrit ses applications antérieures. On examine les problèmes analytiques qu'a posés la détermination des ions sulfate et chlorure dans les rivières côtières grandement colorées et leur incidence sur l'application du modèle.

Dans les rivières qui contiennent une forte concentration d'anions organiques, la méthode du bleu de thymol et de méthyle servant à colorer les sulfates, et qui intègre une partie des anions appelés ici anions organiques réactifs solubles ou ARS, donne de meilleurs résultats lorsqu'elle est utilisée dans le modèle, car ce dernier suppose qu'il y a équilibre des charges. L'équilibre des charges est plus facilement obtenu entre les espèces d'ions classiques et des sulfates traités au bleu de thymol et de méthyle.

Comme le prévoit le modèle, le p^H moyen de ces rivières était généralement plus élevé au début des années 80 qu'au début des années 70, ce qui correspond à la plus faible production de sulfates observée au cours de cette dernière période. Le modèle sert également à prévoir la variation du p^H à laquelle on peut s'attendre en l'absence de ARS^- , de sulfate - Cl ou des deux.

INTRODUCTION

The cation denudation rate (CDR) model (Thompson, 1982) is here once again applied to data for rivers in Nova Scotia (Figure 1). The model was developed using data for these rivers, some of which were sampled, at monthly intervals, from 1965 through 1973. The CDR model depends upon charge balance being obtained between conventional major cations ($\text{Ca}^{++} + \text{Mg}^{++} + \text{Na}^{+} + \text{K}^{+}$) and anions ($\text{Cl}^{-} + \text{SO}_4^{--} + \text{HCO}_3^{-}$). Because these are coastal rivers, which receive considerable amounts of seasalt, in some rivers amounting to 75% or more of the major cations, it was necessary to correct the data for seasalt. Cl^{-} was used as the seasalt-indicator species, and the same ratios of cations and marine sulfate to Cl^{-} as in open seawater were assumed, based upon data on precipitation chemistry for nearby coastal sampling stations (Thompson 1982B).

CDRs are calculated as mean discharge-weighted seasalt-corrected sums of cations (DWSU+) times mean annual runoff. Excess sulfate yields (ESYs) are calculated similarly. The difference between CDR and ESY is assumed to be a measure of the bicarbonate ion yield, and model pH is calculated from the estimated bicarbonate ion concentration.

If the ESY is greater than the CDR, charge balance is assumed to be made up by hydrogen ion, and pH is taken as the negative log of the hydrogen ion concentration. ESYs are used as proxies for atmospheric deposition rates of excess sulfate.

Comparisons of ESYs with atmospheric deposition data show good agreement. See, for example, Thompson and Hutton, 1985.

The CDR model plot can be used to predict the change in pH to be expected in the event of a change in ESY - either a decrease or an increase. For such a prediction, CDR is assumed to be constant, and questions have been raised as to whether this is a valid assumption (Henriksen, 1982; Baker et al., 1985; Galloway et al., 1983).

The CDR model has been labeled empirical (Baker et al., 1985; Galloway et al., 1983), but it is actually a phenomenological model, being based upon the principal that charge balance must obtain in aqueous solutions, and that pH is related to bicarbonate ion concentration via the dissolved carbon dioxide pressure.

The data for the rivers in Nova Scotia and Newfoundland fit the model well, and the statement was made that the pHs of the rivers could be explained on the basis of simple inorganic chemistry (Thompson 1982A). In the interim, however, it has been learned that the colorimetric method for Cl^- , used until mid 1978, was affected by colour, and resulted in the reporting of too high Cl^- concentrations, especially in the more strongly coloured rivers. Seasalt corrections made using these Cl^- data were too great, resulting in underestimations of mean DWSU+.

It has also been learned that the methyl thymol blue (MTB) method for sulfate analysis incorporates some organic anions,

especially in the more strongly coloured rivers, resulting in the reporting of falsely high sulfate concentrations.

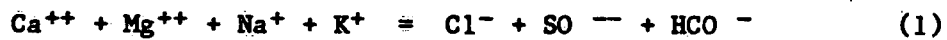
Recognition of these analytical problems for two key species, Cl^- and SO^{--} , made it doubtful that the CDR model could readily applied to such waters, but, as will be shown, analytical problems have been resolved, and the model works well when applied to more recent data for the same rivers. It is necessary only to be sure that the appropriate anion yields are plotted on the X-axis for the model to predict a pH that agrees well with observed mean pH values.

DESCRIPTION OF THE MODEL

The CDR model plot is shown (Figure 2) for data averaged over the period November 1981 to December 1983, and the data used for the model plot are listed in Table 1.

The cation denudation rate (CDR) model is based upon two simple principles:

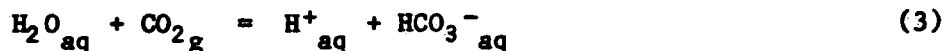
At pHs between 7.0 and 5.2, a charge balance should exist among these major ion species



where all species are in $\mu\text{eq L}^{-1}$, and

$$\text{pH} = \text{pK} + \text{pPCO}_2 - \text{pHCO}_3^- \quad (2)$$

where pPCO_2 is the negative logarithm of the carbon dioxide pressure, pHCO_3^- is the negative logarithm of the bicarbonate ion concentration, and pK is the negative logarithm of the equilibrium constant for the reaction:



where aq stands for aqueous, i.e., species dissolved in water, and g stands for gaseous.

This reaction is used because it is written in terms of all but one of the variables measured or to be calculated; the equilibrium constant for this reaction has the advantage of being relatively insensitive to temperature over the temperature range of interest, pK being 7.8 at 25° and 7.7 at 0° (Garrels and Christ, 1965). As temperature data are not generally available for application of the model, a temperature-insensitive constant is desirable.

A special case of (1) above occurs in acid waters, where the charge balance includes hydrogen ion but not bicarbonate ion

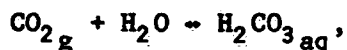


and $\text{pH} = -\log [\text{H}^+]$.

This simple model does not deal with aluminum species, and only now deals explicitly with organic anions, although the proviso has always been made that if significant concentrations of other acid-forming anions, e.g., nitrate, are present, then such species should be considered in the charge balance equations (1) and (4). MTB sulfate, as it turns out, fulfils that proviso, by incorporating both SO_4^{--} and soluble reactive organic anion, SRA^- .

Model pHs are calculated using equation (3), and, in most cases, an assumed CO_2 pressure of $10^{-2.5}$, or ten time atmospheric. This is the value for P_{CO_2} that most generally relates the measured pH to the measured alkalinity, in soft water samples.

The hydration and dehydration of carbon dioxide,



have the slowest reaction rates in the system $\text{CO}_2 + \text{H}_2\text{O}$ 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, Algoma District, Ontario, 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).

- HISTORY OF THE CDR MODEL

The CDR model was developed during 1979 and 1980, being first applied to data for rivers in Nova Scotia and Newfoundland (Thompson, 1982a). Samples from these rivers are analyzed at the laboratory of the Water Quality Branch, Atlantic Region of Environment Canada at Moncton, New Brunswick. The data are stored in NAQUADAT, Canada's national water quality data storage system (Demayo, 1970). Most of the rivers are gauged by Water Survey of Canada, and discharge data are available by application to the Regional Chief of the Water Resources Branch, Dartmouth, N.S., or to the Director, Water Resources Branch, Department of the Environment, Ottawa.

Discharge data are important, because in its more predictive form, the CDR model compares the rate of atmospheric deposition of acid-forming species, especially sulfate, with the rate of chemical weathering of base cations, or more specifically, the rate at which rivers carry off the four major cations, Ca^{++} , Mg^{++} , Na^+ and K^+ .

The CDR model plot has been used to predict the change in mean annual pH to be expected if the ESYs are reduced and if CDRs are constant (United States - Canada Memorandum of Intent 1983). CDRs, calculated as mean DWSU+ times runoff, actually vary from year to year because runoff varies. There is little evidence that mean DWSU+ varies significantly in most of these rivers, if a sufficiently large number of samples are used to calculate the mean. This sufficiently large number is commonly about 35; therefore, the data are averaged

over three years or more, because the rivers are sampled only about 12 times a year.

Sulfate and Organic Anions

After the laboratory acquired an ion chromatograph, during 1981, it was found that sulfate measured in strongly coloured waters by the colorimetric methyl thymol blue (MTB) method was reported as falsely high (Kerekes et al., 1984; Cheam et al., 1985).

Thus, for the strongly coloured rivers of southern Nova Scotia, not only were the CDRs underestimated, but the excess sulfate yields were overestimated. It is now known that a large part of the acid state of those rivers is due to the presence of acid organic anions (Oliver et al., 1983). It is impressive, in retrospect, that the data fit the CDR model so well.

One reason that the data fit the model well is that charge balance between $\text{Ca}^{++} + \text{Mg}^{++} + \text{Na}^{+} + \text{K}^{+}$ and $\text{SO}_4^{--} + \text{Cl}^{-} + \text{HCO}_3^{-}$ was, and still is, more closely obtained using MTB sulfate than using ion chromatographic (IC) sulfate. That is because the MTB sulfate method incorporates some of the organic anions, perhaps the more reactive anions, referred to here as soluble reactive organic anion, or SRA^{-} .

The concentration of organic anion, A^{-} , may be calculated from pH and dissolved organic carbon (DOC), using the equations of Oliver et al. (1983). A^{-} calculated in this way is always higher in concentration than A^{-} calculated as the difference between MTB and IC

sulfates. It is now generally agreed that IC sulfate is sulfate ion and that MTB sulfate is sulfate plus some organic anion (Cheam et al., 1985). The MTB method apparently incorporates SRA^- because during the procedure, in the presence of excess Ba^{++} , the pH is taken up to 11 or 12, at which pH part of the organic matter reacts with Ba^{++} . Schnitzer and Hahn (1972) describes the use of $\text{Ba}(\text{OH})_2$ to measure the acid content of humic material. The MTB method for sulfate, therefore, probably incorporates the acid part of the soluble organic anion; the remainder (the difference between A^- calculated by the method of Oliver et al. (1983) and SRA^- , or soluble unreactive A^- (SUA^-), is very likely complexed by Fe^{+++} and Al^{+++} and possibly other metals.

Nomenclature:

<u>Species</u>	<u>Method of Calculation</u>	<u>Shorthand Name</u>
Organic Anion	DOC, pH	A^-
Soluble Reactive A^-	MTB - IC sulfate	SRA^-
Unreactive A^-	$\text{A}^- - \text{SRA}^-$	SUA^-

Thus, when MTB sulfate is plotted on the CDR Model plot, actually sulfate ion plus SRA^- are plotted, and the data, as shown in Table 1 and on Figure 2, fit the model well.

Over the period 1971 to mid 1973, sulfate analyses were done by the Thorin method, a titration carried out at low pH, and, if carefully done, this method yields results similar to those of the ion chromatograph (Cheam et al. 1985). Figure 3 shows ESYs (Thorin method) 1971 - 1973 compared with ESYs 1981 - 1983 (IC method). The yields are consistently lower in the latter period, and the mean pHs, as would be expected, are somewhat higher for most of the rivers. ^(Figure 4) The pH rise is not as pronounced as the decrease in ESYs, because of the influence of organic anions, especially in the more strongly coloured rivers.

Table 2 shows data for 1983, the number of samples, the mean pH, the mean dissolved organic carbon (DOC) in mg L^{-1} , the mean A^- calculated by the method of Oliver et al. (1983) from pH and DOC, mean SRA^- calculated as the difference between MTB and IC sulfates, mean SUA^- calculated as the difference between A^- and SRA^- , the mean $\text{Al}^{+++} + \text{Fe}^{+++}$ concentrations, and the mean IC sulfate concentrations for the eleven rivers in Nova Scotia. The last five species are all in ueq L^{-1} . The data show that DOC, SRA^- and $\text{Al}^{+3} + \text{Fe}^{+3}$ are consistently lower in concentration in rivers with higher mean pH values. SUA^- , on the other hand, is more or less constant in concentration in all of the rivers. In the lower pH rivers, there is more than enough $\text{Al}^{+3} + \text{Fe}^{+3}$ to account for all the SUA^- (assuming complexation), but, in the higher pH rivers, there is insufficient $\text{Al}^{+3} + \text{Fe}^{+3}$ to complex with SUA^- on a one to one basis. Further

explanation of the data shown in this table awaits a better evaluation of the accuracy in the calculation of A^- and in the measurement of the association constants between Al^{+3} and Fe^{+3} with A^- .

As has been mentioned, the CDR model can be used to predict changes in pH if there is a change in ESYs or of yields of SRA^- . The relative impact of SRA^- and of IC sulfate can be seen on Figure 5. Figure 5 shows the 1983 mean pH, the rivers being arranged in order of increasing mean pH, the model-predicted pH in the absence of SRA^- (1), the model-predicted pH in the absence of IC SO_4^{--} , and the model-predicted pH in the absence of both SRA^- and IC SO_4^{--} , that is, for simple cation bicarbonate waters. For all but two of the rivers, the removal of SO_4^{--} has a more beneficial effect on pH than the removal of SRA^- . For these soft water rivers, mean pH cannot be expected ever to rise above 6.5; for the three hardest water rivers, the St. Marys, the Clam Harbour, and the Wallace, the removal of the acid anions would not significantly affect the pH.

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FIGURES

- Figure 1 Map showing the locations of 11 rivers in Nova Scotia.
- Figure 2 The CDR model plot showing data (November 1981 - December 1983) on CDRs, mean pHs and MTB excess sulfate yields.
- Figure 3 Comparison of excess sulfate yields 1971 - 1973 (Thorin method) and 1981 - 1983 (IC method).
- Figure 4 Comparison of mean pH values 1971 - 1973 and 1981 - 1983.
- Figure 5 For 1983, the mean pH, the model-predicted pH in the absence of SRA^- (1), the model-predicted pH in the absence of IC sulfate (2), and the model-predicted pH in the absence of both, that is, for simple cation bicarbonate waters (3).

TABLE 1. Runoff, discharge-weighted sum of cations, CDR, MTB SO_4^{--} , yield, mean measured pH and CDR model-predicted pH are shown for the period November 1981 to December 1983

	Runoff m yr^{-1}	DWSU+ $\mu\text{eq L}^{-1}$	CDR $\mu\text{eq m}^{-2}\text{yr}^{-1}$	MTB SO_4^{--} Yield $\mu\text{eq m}^{-2}\text{yr}^{-1}$	Mean pH	Model pH
Meteghan	0.724	137.0	99.0	58.2	5.7	5.9
Kelley	1.17	79.4	93.0	91.4	5.2	5.2
Wallace	1.23	150.0	186.0	78.0	6.3	6.3
Tusket	0.783	87.2	68.3	78.4	4.6	5.0
Roseway	1.00	61.2	61.5	92.6	4.5	4.5
Mersey GL	1.00	69.2	69.3	60.9	5.0	5.2
Medway	0.860	80.7	69.4	49.8	5.5	5.6
La Have	0.874	125.0	109.0	68.4	5.9	5.9
Liscomb	1.32	77.5	103.0	112.2	4.9	5.0
St. Marys	0.824	105.0	86.6	41.6	6.1	6.0
Clam Harbour	0.877	133.0	116.0	44.9	6.3	6.2

TABLE 2. For 1983, the number of samples, n, the mean pH, the mean dissolved organic carbon (DOC) in mg L^{-1} , the mean organic anion, A^- , calculated from pH and DOC by the method of Oliver et al. (1983), the mean SRA^- calculated as the difference between MTB and IC sulfates, the mean SUA^- calculated as the difference between A^- and SRA^- , the mean $\text{Al}^{+3} + \text{Fe}^{+3}$, and the mean IC sulfate. The last five species are in $\mu\text{eq L}^{-1}$.

	n	pH	DOC mg L^{-1}	A^- $\mu\text{eq L}^{-1}$	SRA^- $\mu\text{eq L}^{-1}$	SUA^- $\mu\text{eq L}^{-1}$	$\text{Al} + \text{Fe}$ $\mu\text{eq L}^{-1}$	IC SO_4^{--} $\mu\text{eq L}^{-1}$
Roseway	10	4.4	13.4	86	53	33	39	39.5
Tusket	10	4.6	11.0	75	39	36	44	56.7
Liscomb	11	4.8	9.2	69	39	30	40	34.5
Mersey	27	5.0	8.4	63	24	39	31	38.8
Medway	12	5.4	6.7	57	21	36	27	36.4
Kelley	11	5.6	6.4	57	19	38	27	54.2
Meteghan	17	5.7	9.1	81	26	55	39	55.7
La Have	11	5.9	6.4	58	16	42	27	58.8
St. Marys	10	6.0	4.6	42	14	28	20	36.4
Clam H.	9	6.1	6.0	55	11	44	15	45.5
Wallace	9	6.5	3.8	37	6	31	15	57.3

