

THE CDR MODEL APPLIED TO DATA FOR
ROGERS BROOK, A SMALL TRIBUTARY TO THE
MERSEY RIVER, KEJIMKUJIK NATIONAL PARK
NOVA SCOTIA, 1985

by
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ABSTRACT

The CDR model is applied to data for Rogers Brook, a small highly organic tributary to the Mersey River above Kejimkujik Lake, Kejimkujik National Park, Nova Scotia.

The organic anion A^- calculated by the method of Oliver et al. 1983, is always higher than SRA^- , the difference between MTB and IC sulfate. Testing whether the higher A^- is due to partial complexing with Fe and Al, using mean monthly data, leads to the conclusion that the organic matter in Rogers Brook is more reactive per gram C during the plant growth period of summer and fall than it is during the winter and spring.

RÉSUMÉ

Le modèle du TAC est appliqué aux données du ruisseau Rogers, un petit cours d'eau à très forte teneur en matières organiques en amont du lac Kejimikujik, dans le Parc national Kejimikujik, Nouvelle-Écosse.

La teneur en anion organique A^- calculée par la méthode d'Oliver et al. 1983 est supérieure à celle de SRA^- , la différence entre le bleu de méthylthymol et le sulfate mesuré par l'ion chromate. Après quelques essais effectués à l'aide des données mensuelles moyennes pour savoir si la valeur supérieure de A^- était due à la complexation partielle avec Fe et Al, nous avons conclu que les matières organiques du ruisseau Rogers sont plus réactives par gramme de C au cours de la période de croissance des plantes en été et à l'automne qu'en hiver et au printemps.

MANAGEMENT PERSPECTIVE

This report is a contribution to the LRTAP Project. It describes another successful application of the CDR model, this time to Rogers Brook, a highly organic stream in Kejimikujik National Park, Nova Scotia.

PERSPECTIVE- GESTION

Voici une contribution au projet TADPA. Il s'agit d'une autre application réussie du modèle du TAC à un petit cours d'eau qui draine les eaux d'un lac d'amont près du Parc national Kejimikujik, Nouvelle-Écosse.

INTRODUCTION

Rogers Brook is a small tributary to the Mersey River above Kejimkujik Lake. The chemical sampling station is at 44°24'50" N and 65°13'18" W. The drainage area is 8.74 km². Discharge data are available for only parts of 1985, but the estimated annual runoff for 1985, 0.751 m yr⁻¹, is only slightly higher than the 1985 annual runoff of the Mersey River below Mill Falls, 0.710 m yr⁻¹. Moreover, discharge was measured on chemical sampling dates, making it possible to calculate discharge-weighted averages.

Its watershed is underlain by strata of the Halifax Formation of Cambro-Ordovician age, consisting of highly metamorphosed slates and schists.

Runoff in 1985 peaked in March and April and was very low during late summer and early fall. Cation concentrations display an inverse relationship to runoff, being lowest in March and April, and thereafter increasing each month to a maximum in October, the month with lowest runoff. High cation concentrations during periods of low flow generally indicate groundwater input.

Rogers Brook, similarly to other highly organic streams in the vicinity (Kerekes et al., 1986), displays low concentrations of IC sulfate during summer months. Other species, however, all tend to increase at lower flow: pH, DOC, MTB sulfate, Fe and Al.

The analytical methods used by the Atlantic Region Water Quality Branch Laboratory in Moncton, N.B., which generated the data discussed

here have been described earlier (Thompson, 1987), but will be briefly recapitulated here.

A glass electrode is used to measure pH; the cations Ca^{++} and Mg^{++} are done by automated atomic absorption and Na^+ and K^+ by automated flame photometry; Cl^- was measured by a specific ion electrode until mid 1986, when a shift was made to ion chromatography; sulfate is also measured by ion chromatography as well as by the older colorimetric methyl thymol blue (MTB) method, which is biased high and is thought to incorporate some organic anion at the pH 12 reached during the analytical procedure. For samples at pH 6 or lower, alkalinity is measured by an automated Gran titration. DOC is measured colorimetrically (NAQUADAT Code 06107). Extractable Al is done by atomic absorption using solvent extraction, and extractable Fe is done by atomic absorption with direct aspiration.

The performance of the Moncton laboratory is generally satisfactory on the LRTAP Interlaboratory Comparison Tests (Aspila, K., personal communication, 1986).

Rogers Brook was sampled frequently during 1985, especially during the winter months of high flow, for a total of 153 samples.

CALCULATIONS

The CDR is the product of the mean annual seasalt-corrected discharge-weighted sum of cations in meq m^{-3} and the mean annual runoff in $\text{m}^3 \text{m}^{-2} \text{yr}^{-1}$. The units of the CDR are $\text{meq m}^{-2} \text{yr}^{-1}$. The

mean annual discharge-weighted sum of cations is calculated by first correcting the data for seasalt, using chloride ion as the seasalt indicator species, and assuming the same ratios of major ions to chloride as in open seawater (Thompson, 1982). Then the mean monthly discharge-weighted sums of cations are multiplied by the runoff per month and summed. The summation for twelve months is divided by the sum of the monthly runoff values (which is not always identical to the mean annual runoff because of differences in the number of significant figures used) to obtain the mean annual seasalt-corrected discharge-weighted sum of cations.

Excess sulfate mean annual concentrations and yield of both MTB and IC sulfate are calculated similarly to the CDR as are the mean discharge-weighted concentrations of DOC, Fe and Al.

Alkalinity is estimated as the difference between the mean annual discharge-weighted sum of cations and excess MTB sulfate. For low concentrations of alkalinity, the definition

$$\text{Alkalinity} = \text{HCO}_3^- - \text{H}^+$$

is used, and the HCO_3^- concentration is estimated and used to calculate the pH assuming $\text{PCO}_2 = 10^{-2.5}$, from

$$\text{pH} = 10.3 - \text{pHCO}_3^-$$

where p is used to indicate the negative log of the molar concentration of a species.

The mean annual pH and alkalinity are calculated differently. Instead each monthly arithmetic mean pH or alkalinity is multiplied by the number of days in that month. The products are summed over twelve months and divided by the number of days in the year. This procedure, although not ideal, is used because it yields a mean pH closest to the model pH. Discharge-weighting pH or $10^{-\text{pH}}$ produces mean pH values that are lower by several tenths of a pH unit.

DISCUSSION

The data used for the application of the CDR model to Rogers Brook, 1985 are shown in Table 1, and the CDR model plot for these data is shown on Figure 1. MTB sulfate is used for the CDR model because it gives charge balance. The model successfully predicts the arithmetic mean pH of the stream.

The IC sulfate yield of Rogers Brook is a little high compared to that of the Mersey River below Mill Falls or to wet deposition at Kejimikujik National Park: $38.8 \text{ meq m}^{-2} \text{ yr}^{-1}$ for Rogers Brook, $27.6 \text{ meq m}^{-2} \text{ yr}^{-1}$ for the Mersey and $32.8 \text{ meq m}^{-2} \text{ yr}^{-1}$ for wet deposition. The difference between Rogers Brook yield of excess sulfate and wet deposition may be due to dry deposition (the larger Mersey River reacting more slowly to annual changes in deposition), or it may be that Rogers Brook has a geological source of sulfur. The unusually high summer Fe concentrations (relative to other streams in the area), more than 2 mg L^{-1} , suggest that pyrite might be weathering in

its watershed, but the isotopic data of Clair (1987) call for a source of heavy (i.e. gypsum) sulfur. More information is needed on bedrock geology and soil mineralogy in this area.

Rogers Brook carries high concentrations of DOC during the summer, and during that season the differences between MTB and IC sulfates (SRA^-) are very large. A^- calculated from DOC and pH by the method of Oliver et al. (198) is even larger. Investigating the hypothesis that A^- is larger than SRA^- because part of it is complexed by Al and Fe, the sums of $SRA^- + Al + Fe$ were calculated from monthly mean data and compared with monthly mean A^- (Figure 2). The results are very interesting; the sum of $SRA^- + Al + Fe$ is less than A^- from January to May, and again in November and December, suggesting that A^- is over-estimated during those months. From June through October, however, the sum of $SRA^- + Al + Fe$ is greater than A^- , suggesting that A^- is underestimated for those months, that is, that the organic matter is more reactive from June to October than from November to May. As the organic matter is produced by biological activity, probably in wetland areas in the watershed, it is reasonable to expect it to be more reactive during the summer period of plant growth.

SUMMARY AND CONCLUSIONS

The CDR model has been successfully applied to Rogers Brook even though it is a highly organic stream. Rogers Brook is unusual for a highly organic stream in that much of the year pH is greater than 5.2

and positive alkalinities are present. Part of the reason for that is the high cation concentrations present during summer low flow.

A^- is greater than SRA^- , and the hypothesis that the difference exists because part of the A^- is complexed by Fe and Al was tested using mean monthly data. The comparison suggests that the organic matter is more reactive during summer and fall and is less reactive during winter and spring.

REFERENCES

- Clair, T.A. 1987. Seminar Presentation, NWRI, May 25 "Sources of stream sulfate in some Nova Scotian Waters; a stable isotope approach".
- Kerekes, J., Beauchamp, S., Tordon, R. and Pollock, T. 1986. Sources of sulphate and acidity in wetlands and lakes in Nova Scotia. *Water, Air and Soil Pollution*, 31: 207-214.
- Oliver, B.G., Thurman, E.M. and Malcolm, R.L. 1983. The contribution of humic substances to the acidity of coloured natural waters. *Geoch. Cosmoch. Acta.* 47: 2031-2035.
- Thompson, M.E. 1982. Exchange of marine sodium for calcium during chemical weathering in the Isle aux Morts River Basin, Newfoundland. *Geoch. Cosmoch. Acta.* 46: 361-365.
- Thompson, M.E. 1987. Comparison of cation denudation rates and excess sulfate yields with wet deposition of excess sulfate for the Mersey River below Mill Falls, Kejimikujik National Park, Nova Scotia, 1980-1985. NWRI Contribution, in preparation.

Table 1. Summary of data used to apply the CDR model to Rogers Brook, 1985.

Discharge-weighted sum of cations	85.3 $\mu\text{eq L}^{-1}$
Discharge-weighted excess MTB sulfate	75.5 $\mu\text{eq L}^{-1}$
Alkalinity estimate	9.8 $\mu\text{eq L}^{-1}$
Model pH	5.29
Day-weighted arithmetic mean pH	5.28
Runoff (estimated)	0.751 m yr^{-1}
CDR	64.0 $\text{meq m}^{-2} \text{yr}^{-1}$
Excess MTB sulfate yield	56.7 $\text{meq m}^{-2} \text{yr}^{-1}$

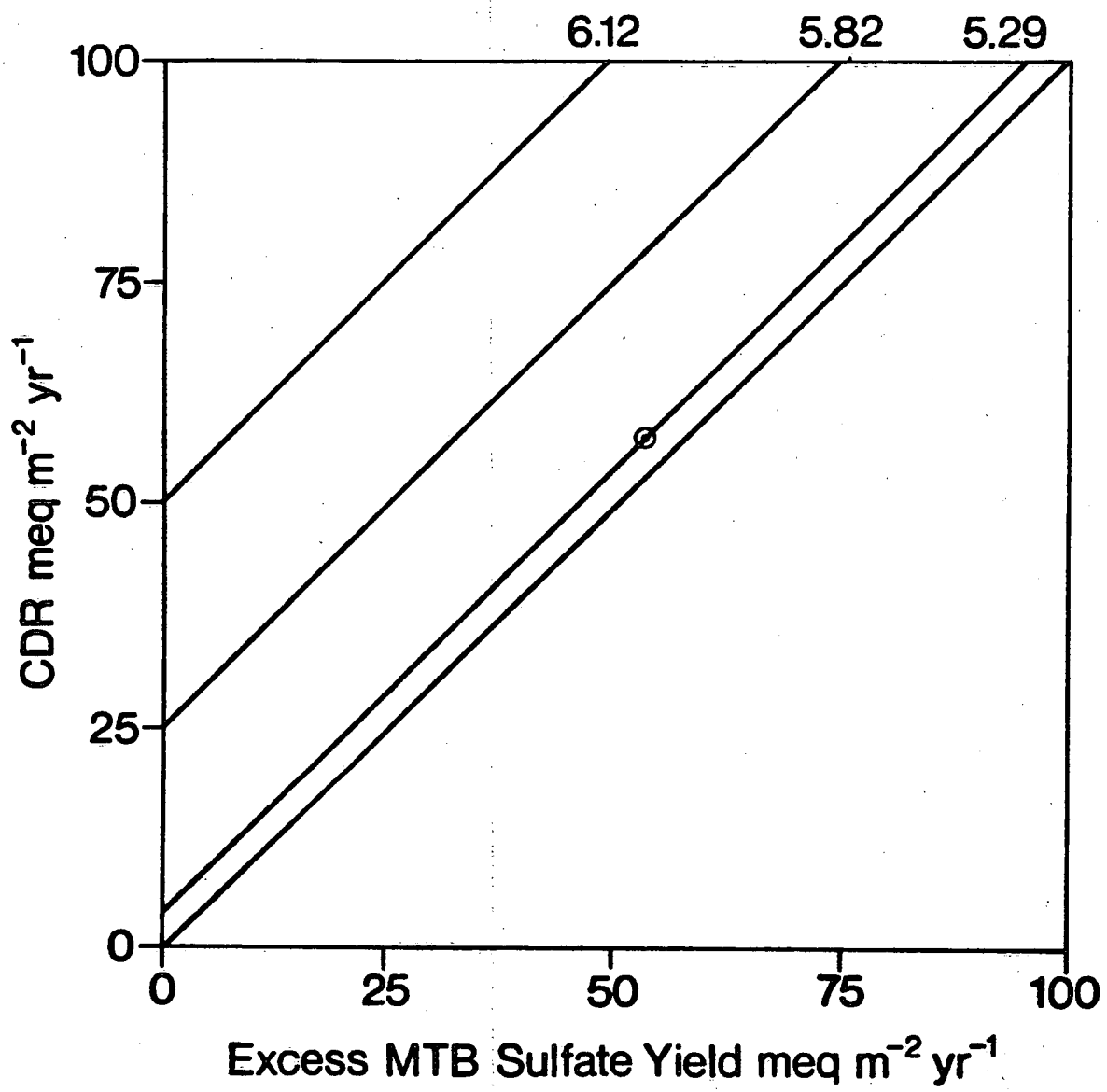


Figure 1. The CDR model drawing for data from Rogers Brook, Kejimikujik National Park, Nova Scotia, 1985.

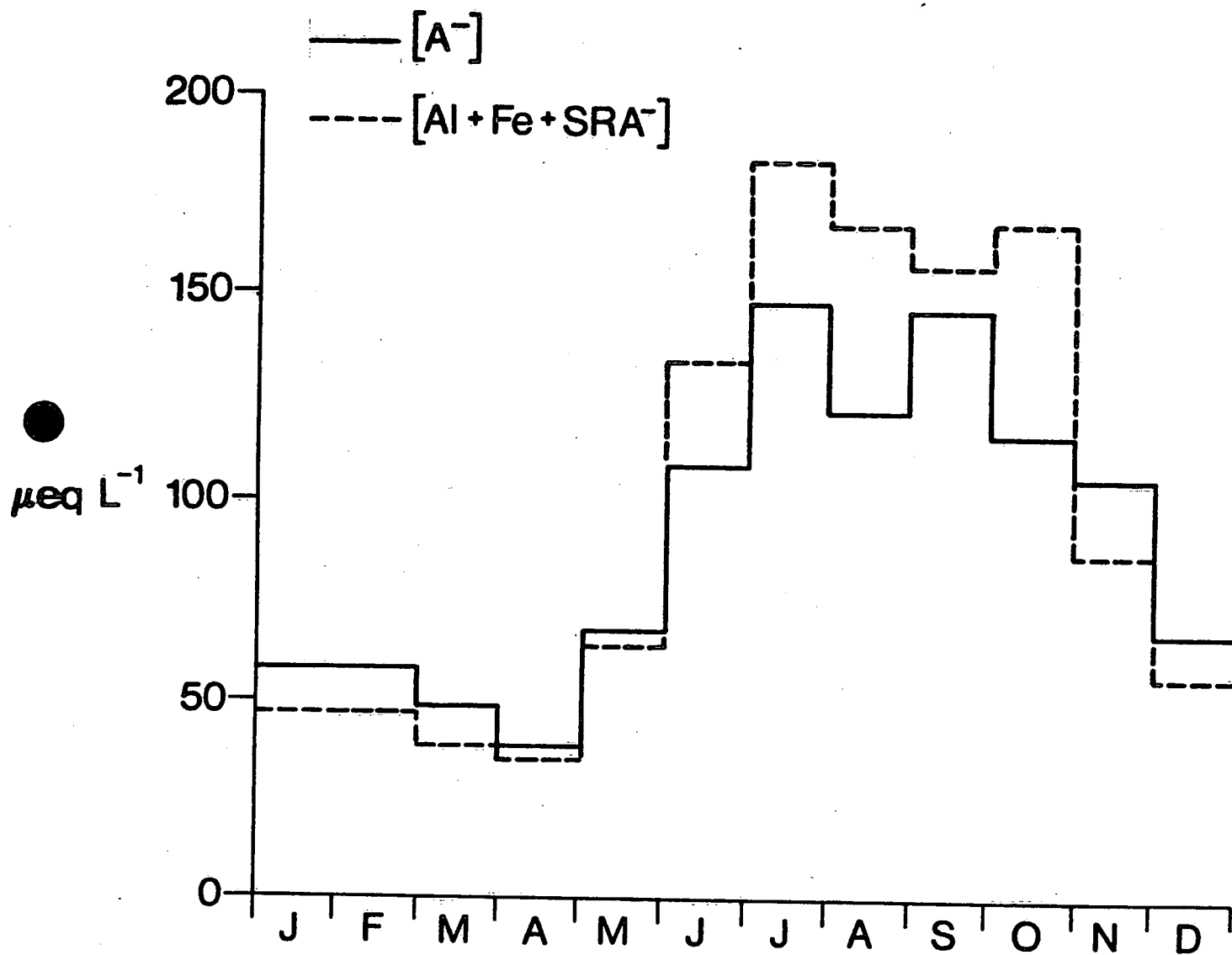


Figure 2. Monthly comparisons of the organic anion A⁻ with the sum of SRA⁻, Al, and Fe for Rogers Brook, Nova Scotia, 1985.