

**APPLICATION OF THE CDR MODEL
TO DATA FOR MOOSE PIT BROOK,
MEDWAY RIVER BASIN, NOVA SCOTIA, 1984**
by
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MANAGEMENT PERSPECTIVE

This is a contribution to the LRTAP project. It describes an application of the CDR model to a small, headwater, highly organic stream, and discusses the effect of organic matter on the stream pH.

PERSPECTIVE-GESTION

Cette contribution au programme d'étude du TGDPA décrit l'application du modèle du taux d'apport en cations (TAC) à un petit ruisseau d'amont, à forte teneur organique, et examine l'effet des matières organiques sur le pH du cours d'eau.

ABSTRACT

The attempt to apply the CDR model to data for Moose Pit Brook, a highly organic stream in the watershed of the Medway River, Nova Scotia, is hindered by the lack of charge balance among major ion species and H^+ . Even though the MTB sulfate concentrations exceed the actual sulfate concentrations by as much as $100 \mu\text{g L}^{-1}$ in the presence of high concentrations of DOC, the MTB sulfate apparently does not incorporate all of the organic anion that contributes to charge balance.

RÉSUMÉ

Le manque d'équilibre de charge parmi les principaux ions et H^+ entrave l'application du modèle du taux d'apport en cations (TAC) aux données du Moose Pit Brook, ruisseau à forte teneur organique du bassin versant de la rivière Medway, en Nouvelle-Écosse. Les concentrations de sulfate détecté au bleu de méthylène dépassent les concentrations réelles de sulfate de jusqu'à $100 \mu g L^{-1}$ en présence de fortes concentrations de carbone organique dissous, mais le sulfate détecté au bleu de méthylène ne semble pas comprendre tous les anions organiques qui contribuent à l'équilibre de charge.

INTRODUCTION

Moose Pit Brook is a small, highly organic headwater stream in the watershed of the Medway River, Nova Scotia. The chemical sampling station (NAQUADAT Station Code 00NS01EE0014) at 44°27'42"N and 65°02'54"W, is about 10 km ENE of Kejimkujik National Park.

Daily discharge data for Moose Pit Brook are available from 1982. Moose Pit Brook was sampled about once a week during 1984, for a total of 71 samples.

The watershed of Moose Pit Brook is apparently underlain by highly metamorphosed shales and schists of the Halifax Formation of Cambro-Ordovician age.

Chemical analyses are performed at the Moncton, N.B. laboratory of the Water Quality Branch, Atlantic Region. The analytical methods used are state of the art, and are briefly described as follows: pH is measured with a glass electrode in the laboratory; Ca⁺⁺ and Mg⁺⁺ are done by automated atomic absorption spectrophotometry; Na⁺ and K⁺ are done by automated flame photometry with internal standards; Cl⁻ was measured with a specific ion electrode until mid 1985 when a shift was made to ion chromatography. Sulfate is measured by ion chromatography (IC) and also by the colorimetric methyl thymol blue (MTB) indicator method which is positively biased by organic matter and is considered to incorporate some organic matter at the pH 12 reached during the procedure. The difference between MTB and IC sulfate is considered to be a measure of reactive organic anion and is referred to as SRA⁻

(Thompson 1986); dissolved organic carbon (DOC) is measured colorimetrically (NAQUADAT Code 06107); extractable Fe is done by atomic absorption by direct aspiration; and extractable Al is done by atomic absorption with solvent extraction.

DAILY DISCHARGE AND CHEMICAL CHARACTERISTICS

During 1984, mean monthly runoff (Figure 1) peaked during March and thereafter decreased each month to a minimum in October. Runoff increased slightly in November and more so in December. Mean annual runoff was 0.825 m yr^{-1} .

Moose Pit Brook receives a fair amount of seasalt because of its maritime location. Highest seasalt concentrations, as evidenced by Cl^- , are seen in the winter, lowest during calm weather in the summer. More than half the cations carried by Moose Pit Brook are marine.

Cation concentrations were at a minimum during March, the month with the highest runoff, and thereafter increased each month to a maximum during August. Although runoff continued to decrease into October, cation concentrations decreased after August, and rose again, with higher runoff, in December. Such a pattern is not entirely consistent with a groundwater input of cation-rich water during periods of low flow.

As has been reported by Kerekes et al. (1986), during the summer and early fall, sulfate concentrations decrease from about 3 mg L^{-1} to less than 1 mg L^{-1} reaching minimum concentrations during September.

MTB sulfate concentrations, in contrast, increase from 3 or 4 mg L⁻¹ at the beginning of the year, to maximum values >5 mg L⁻¹ in July, August, and especially in September. DOC concentrations, similarly, are relatively low during the period of maximum runoff in March at about 8 mg L⁻¹, and increase markedly, as runoff decreases, to maximum values greater than 30 mg L⁻¹ during the summer. After August, DOC concentrations decrease each month, but by December 1984 were still twice as high as they were in January.

Fe and Al concentrations follow the same general pattern just described for MTB sulfate and DOC, being lowest during high spring runoff and highest in July, August, and September.

The major ion data for Moose Pit Brook, even when using MTB sulfate data, do not show good charge balance from August to December. There is an excess of cations over anions, even though H⁺ is not considered. This suggests that there may be more organic anion contributing to charge balance than is reported as MTB sulfate. Calculated conductances, however, are close to measured ones, indicating that no unmeasured species can have much effect on conductance.

CALCULATIONS

The data are corrected for seasalt using Cl⁻ as the seasalt indicator species, and assuming, in weight units, the same ratios of major seawater species to Cl⁻ as in open seawater (Thompson 1982).

After seasalt correction, the mean annual discharge-weighted sum of cations ($\text{Ca}^{++} + \text{Mg}^{++} + \text{Na}^+ + \text{K}^+$) (DWSU+) is calculated as the sum of the products of the mean monthly DWSU+ and the mean monthly runoff divided by the mean annual runoff. (The sum of the mean monthly runoffs is not always identical to the mean annual runoff, probably because of the different number of significant digits carried in the calculations).

CDR is the product of the mean annual DWSU+ and the mean annual runoff. The units are $\text{meq m}^{-2} \text{ yr}^{-1}$.

Discharge-weighted annual means and yields of other species are calculated similarly. In the special case of pH, however, it has been found that discharge weighting biases the results toward low values, because of the usual strong inverse correlation of pH with discharge. Better results have been obtained by calculating arithmetic or geometric mean pH. In the case of Moose Pit Brook, however, pH is almost constant and is nearly unrelated to discharge. The annual geometric mean pH is 4.63; the highest monthly mean pH, 4.75, was seen in January, and the lowest monthly mean pH, 4.55, was seen in September.

DISCUSSION

The data used for the application of the CDR model to Moose Pit Brook are summarized in Table 1 and the model drawing is shown in Figure 2. The data show that discharge weighted excess MTB sulfate

(DWExMTB sulfate) exceeds DWSU+ by a small amount, $0.7 \mu\text{eq L}^{-1}$, indicating a pH below 5.15. The annual mean pH of Moose Pit Brook is lower than that however, being 4.63. This pH implies that the difference between DWExMTB sulfate and DWSU+ should be about $23 \mu\text{eq L}^{-1}$. The aforementioned lack of charge balance in the data, especially when H^+ is considered, suggests that MTB sulfate is not incorporating all the organic anion that is present, because charge balance must exist, and there is no other likely anionic species.

The mean annual measured alkalinity is $-21.8 \mu\text{eq L}^{-1}$. If DWExMTB SO_4^{--} were increased by $21.8 \mu\text{eq L}^{-1}$, the model would predict the observed mean pH more accurately, as can be seen in Figure 2, where the parenthetical point represents the yield of DWExMTB SO_4^{--} + $21.8 \mu\text{eq L}^{-1}$.

The hypothesis that the difference between A^- , calculated from DOC and pH by the method of Oliver et al. (1983), and SRA^- , the difference between MTB and IC sulfates, may be due to partial complexing of A^- by Al and Fe, has been tested on data for other streams in the area (Thompson 1987 B,C) with reasonable success. This test for Moose Pit Brook data shows (Figure 3) that for every month but June, A^- is greater than the sum of $\text{SRA}^- + \text{Al} + \text{Fe}$ by 12 to $50 \mu\text{eq L}^{-1}$, for an average of $28 \mu\text{eq L}^{-1}$. This again suggests that MTB sulfate is underreporting the organic anion. This possibility is investigated further in Table 2, in which each monthly mean DWSU+ is compared with the mean MTB sulfate, and a pH is predicted, shown compared with the observed monthly mean pH. As can be seen in

Table 2, the predicted pH is higher than the observed pH for every month. From the observed mean pH, the anion deficit can be calculated and compared with the excess A^- . Although the two are of the same order of magnitude, however, there is not a good relation between the monthly anion deficit and excess A^- .

The IC excess sulfate yield of Moose Pit Brook in 1984, $37.9 \text{ meq m}^{-2} \text{ yr}^{-1}$, is higher than that of the upper Mersey River, $33.0 \text{ meq m}^{-2} \text{ yr}^{-1}$ (Thompson 1987A) but is similar to that of Rogers Brook in 1984, $38.8 \text{ meq m}^{-2} \text{ yr}^{-1}$ (Thompson 1987B).

SUMMARY AND CONCLUSIONS

The CDR model has been applied to data for Moose Pit Brook, Nova Scotia, and predicts a pH that is about 0.5 pH units higher than the observed mean pH. It is likely that an unmeasured organic anion is responsible for the lower than predicted pH. In support of this conclusion is the observation that for every month except June, A^- calculated from DOC and pH by the method of Oliver et al. (1983) is higher than the sum of $SRA^- + Al + Fe$, by an average amount of $28 \mu\text{eq L}^{-1}$. The anion deficit, calculated from the observed pH, is of the same order of magnitude.

The IC sulfate yield of Moose Pit Brook in 1984 was $37.9 \text{ meq m}^{-2} \text{ yr}^{-1}$.

REFERENCES

- 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. 1986. The cation denudation rate model - its continued validity. *Water, Air, and Soil Pollution*, 31: 17-26.
- Thompson, M.E. 1987A. 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 #87- .
- Thompson, M.E. 1987B. The CDR model applied to data for Rogers Brook, a small tributary to the Mersey River, Kejimikujik National Park, Nova Scotia, 1985. NWRI Contribution #87-108.
- Thompson, M.E. 1987C. The CDR model applied to data for Whiteburn Brook below Pollock Lake, Medway River Basin, Nova Scotia, 1985. NWRI Contribution #87-114.

Table 1. Data used for the application of the CDR model, the calculation of the excess sulfate yield, and the comparison of a^- with SRA + Al + Fe for Moose Pit Brook, 1984.

Species	Units	Value
DWSU+	$\mu\text{eq L}^{-1}$	86.9
DWExMTB SO_4^{--}	$\mu\text{eq L}^{-1}$	87.6
ALKALINITY ESTIMATE	$\mu\text{eq L}^{-1}$	-0.7
MODEL pH	-	5.13
ANNUAL MEAN pH	-	4.63
MEAN ALKALINITY	$\mu\text{eq L}^{-1}$	-21.8
DWExIC SO_4^{--}	$\mu\text{eq L}^{-1}$	42.3
SRA ⁻	$\mu\text{eq L}^{-1}$	44.7
DW Al	$\mu\text{eq L}^{-1}$	19.9
DW Fe	$\mu\text{eq L}^{-1}$	10.6
SRA ⁻ + Al + Fe	$\mu\text{eq L}^{-1}$	75.2
A ⁻	$\mu\text{eq L}^{-1}$	95.3
DW DOC	mg L^{-1}	13.9
RUNOFF, ANNUAL	m yr^{-1}	0.897
CDR	$\text{meq m}^{-2} \text{ yr}^{-1}$	77.9
DWExMTB SO_4^{--} YIELD	$\text{meq m}^{-2} \text{ yr}^{-1}$	78.6
DWExIC SO_4^{--} YIELD	$\text{meq m}^{-2} \text{ yr}^{-1}$	37.9

Table 2. Discharge-weighted monthly mean sums of cations and excess MTB sulfate, the predicted alkalinity, and model pH compared with observed pH, Moose Pit Brook, 1984.

Month	DWSU+ $\mu\text{eq L}^{-1}$	DWExMTB SP_4^{--} $\mu\text{eq L}^{-1}$	Alkalinity Predicted $\mu\text{eq L}^{-1}$	Model pH	Observed pH
J	85.2	91.0	-4.8	5.01	4.75
F	76.3	73.8	+2.5	5.23	4.65
M	60.0	66.4	-6.4	4.96	4.63
A	76.9	79.7	-2.8	5.06	4.58
M	77.5	83.1	-5.6	4.98	4.63
J	86.4	103.4	-17.0	4.70	4.60
J	105.4	110.7	-5.3	4.99	4.58
A	151.7	116.5	+35.2	5.85	4.66
S	135.2	121.0	+14.2	5.55	4.55
D	107.8	97.4	+10.4	5.45	4.72
N	107.5	96.8	+10.7	5.46	4.70
D	125.0	114.0	+11.0	5.48	4.53

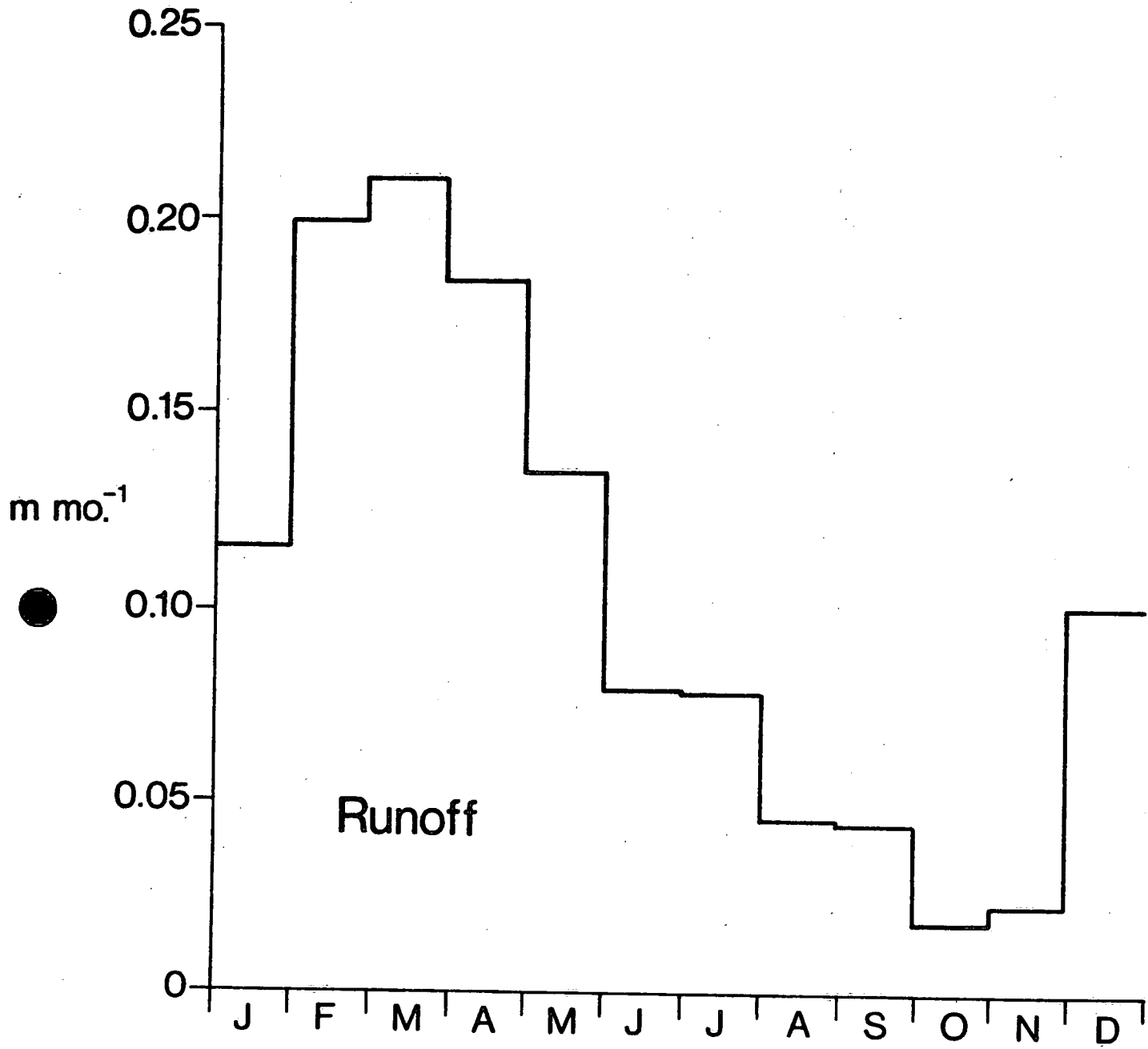


Figure 1. Mean monthly runoff of Moose Pit Brook, 1984.

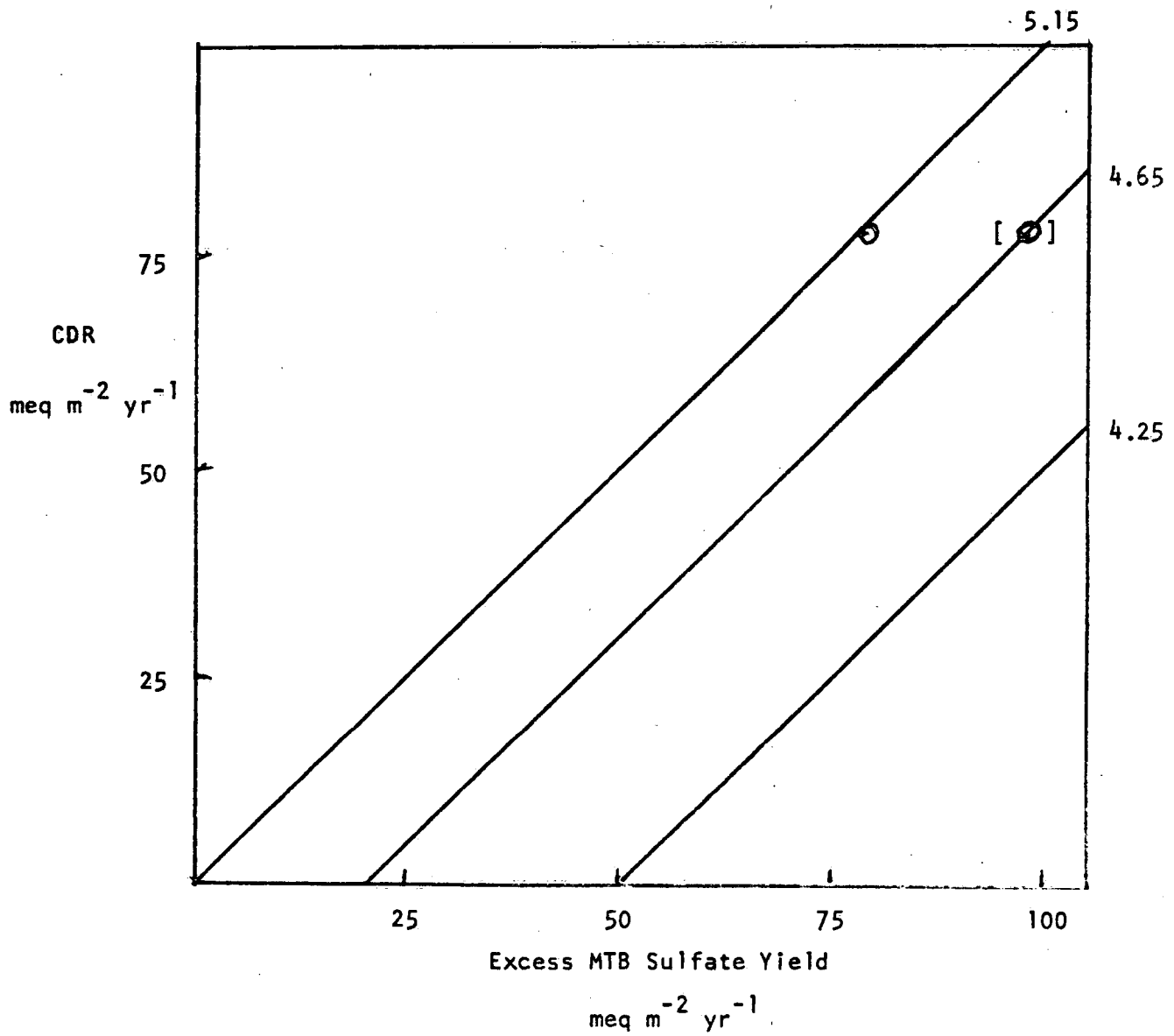


Figure 2. The CDR model plot for Moose Pit Brook, 1984.

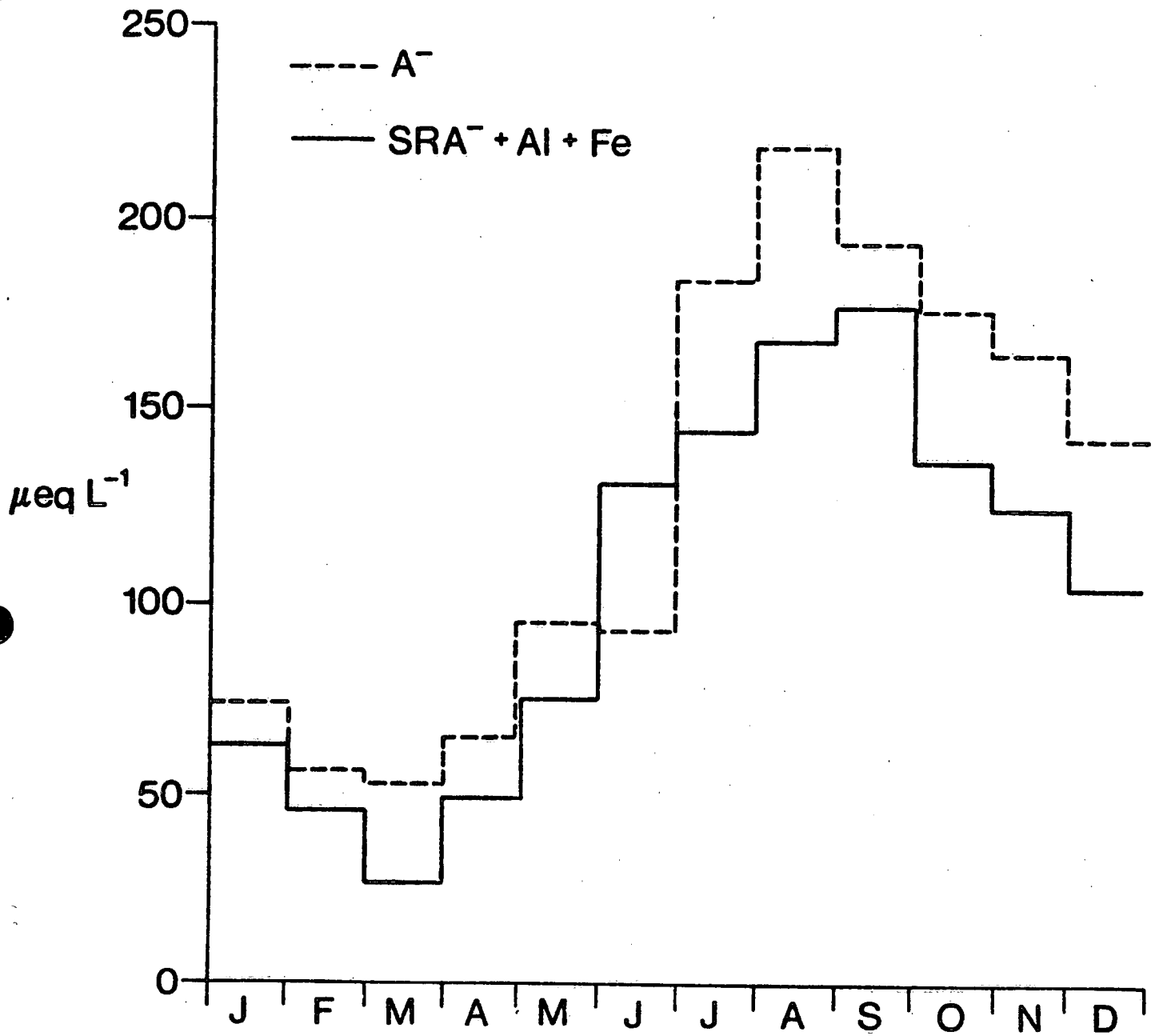


Figure 3. Comparison of mean monthly values of A^- and the sum of $SRA^- + Al + Fe$ for Moose Pit Brook, 1984