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COMPARISON OF CATION DENUDATION RATES, EXCESS SULFATE YIELDS, AND WET DEPOSITION OF EXCESS SULFATE FOR THE MERSEY RIVER BELOW MILL FALLS, KEJIMKUJIK NATIONAL PARK, NOVA SCOTIA, 1980 - 1985

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MANAGEMENT PERSPECTIVE

This is a contribution to the LRTAP Modelling/Monitoring Research Project, and is a further description of the properties of the intensively monitored Mersey River below Mill Falls, Kejimkujik National Park, Nova Scotia. This report contains data relevant to continuing validation of the CDR model. It helps to clarify the relative importance of 'natural' vs 'anthropogenic' sources of acidity to the Mersey River. It contains information relevant to the Departmental policy on reduction of SO_2 emissions.

PERSPECTIVES DE GESTION

Il s'agit là d'une contribution au Projet de recherche modélisation/surveillance TADPA, et d'une autre description des propriétés de la rivière Mersey étroitement surveillée, en aval de Mill Falls, dans le Parc national Kejimkujik, en Nouvelle-Écosse. Ce rapport contient des données relatives à la validation permanente du modèle TAC. Il aide à clarifier l'importance relative des sources d'acidité 'naturelles' par rapport aux sources 'anthropogènes' de la rivière Mersey. Il renferme de l'information sur la politique ministérielle en matière de réduction des émissions de SO_2.

ABSTRACT

Cation denudation rates and excess sulfate yields of the Mersey River below Mill Falls for the years 1980-1985 have been calculated and compared with wet deposition of excess sulfate at Kejimkujik National Park, and show little relation to each other, although the excess sulfate yields and wet deposition of excess sulfate are of the same order of magnitude.

The runoff of the Mersey River in 1981 was higher than the mean runoff for the other five years by 40%, whereas the CDR for 1981 was higher than the mean CDR for the other five years by 69%.

The mean monthly ratio of IC to MTB excess sulfate, 1982-1985, matched to mean colour among months that displayed a wide range of ratios, was used to correct the 1980 and 1981 MTB sulfate data.

RÉSUMÉ

Le taux d'appauvrissement en cations (TAC) et le rendement de sulfate en excès dans la rivière Mersey, en aval de Mills Falls, ont été calculés pour les années 1980-1985 et comparés au dépôt humide de sulfate en excès dans le Parc national Kejimkujik; les résultats ne présentent entre eux qu'une relation très faible, même si le rendement de sulfate en excès et le dépôt humide de sulfate en excès sont du même ordre de grandeur.

En 1981, l'écoulement de la rivière Mersey était supérieur de 40 % à l'écoulement moyen pour les cinq autres années, alors que le TAC pour 1981 était plus élevé de 69 % que le TAC moyen pour les cinq autres années également.

Le rapport mensuel moyen de sulfate en excès par CI (chromatographie ionique) au sulfate en excès par bleu MTB, en 1982-1985, correspondant à la couleur moyenne de mois qui présentaient une gamme étendue de valeurs, a servi à corriger les données relatives au sulfate MTB pour 1980 et 1981.

INTRODUCTION

The Mersey River below Mill Falls in Kejimkujik National Park (KNP), Nova Scotia, has been sampled frequently, although not at regular intervals, since 1980, making it possible to calculate cation denudation rates (CDRs) and excess sulfate yields with a higher degree of accuracy than for rivers that are sampled only monthly. As a CANSAP or a CAPMoN sampler has been operated at KNP over the same period, it is possible to compare annual CDRs, excess sulfate yields, and wet deposition of excess sulfate in order to establish whether there is a direct relationship between river yields and wet deposition of excess sulfate and also whether variations in the amounts of wet deposition of excess sulfate coincide with annual variation in CDRs, i.e. whether changes in sulfate deposition are responsible for changes in chemical weathering rates.

There is a fairly consistent annual pattern of conditions in the upper Mersey River. Flow tends to be at its lowest in the late summer (Figure 1), and at that time, cation, sulfate, and DOC concentrations are also low. As flow increases in the fall, however, cation, sulfate, and DOC concentrations increase. This is contrary to conditions observed in many other rivers, which commonly display a strong inverse correlation between cation concentrations and flow because cation-rich groundwater dominates during periods of base flow. The chemical properties of the upper Mersey River are apparently governed by runoff from bogs and wetlands, and groundwater flow is of lesser importance.

Samples are analyzed at the Moncton, N.B. laboratory of Environment Canada's Water Quality Branch, Atlantic Region. The analytical methods used are state of the art, with some modifications because of the special properties of some of the highly organic waters encountered in Nova Scotia. The methods used are summarized briefly as follows: pH is measured with a glass electrode; Ca^{++} and Mg^{++} are done by atomic absorption spectrophotometry (automated during 1980); Na^{+} and K^{+} are done by automated flame photometry; Cl^{-} was measured by a specific ion electrode until mid 1986, when a shift was made to ion chromatography (IC); beginning near the end of 1980 sulfate has been measured by IC 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. The IC method for sulfate, on the other hand, measures only sulfate (Cheam et al. 1986). During 1980, for samples at pH 6 or lower, measurements of alkalinity using Gran titrations were begun. The older, 2pH end point method, while suitable for waters with low positive alkalinities, does not report negative values. In the Mersey River, alkalinities are negative for about half of the year. DOC was measured by infrared (IR) analysis until mid 1982, when a shift was made to a colorimetric method (NAQUADAT Code 06107). According to P.L. Pollock (personal communication, May 1987), the earlier IR method relative to the later colorimetric gave results that were 10 to 15% higher, and much less precise. Al is measured by atomic absorption after solvent extraction, and Fe is measured by atomic absorption with direct aspiration. Water colour is measured by visual comparison with a series of standard colour solutions. Until late in 1982, high levels of colour were reported as greater than 100; since then such samples are diluted and compared, and the original colour is calculated.

CALCULATIONS

Because more than half of the cations carried by the Mersey River are marine in origin, it is necessary to correct the data for seasalt. Cl^- is used as the seasalt indicator species and the same ratios in weight units of major ionic species as in open seawater are assumed (Thompson, 1982).

The number of samples available for CDR calculations by month and year for the period 1980-1985 is shown in Table 1. To avoid any bias in results because of the variable number of samples per month or per season, CDRs were calculated by summing CDRs per month. The calculation may be represented as:

$$CDR_{ANN} = \sum_{mo} \left[RUNOFF_{mo} \left(\frac{\sum_{D} (Q_D)(SUM+_D)}{\sum_{D} (Q_D)} \right) \right] ,$$

where CDR_{ANN} is the annual CDR in meq m^{-2} yr^{-1}, $RUNOFF_{mo}$ is the mean runoff for the month in m^3 m^{-2} mo^{-1}, Q_D is the mean daily flow in m^3 s^{-1} on the sample date, and $SUM+_D$ is the sum of cations for a given sample date, in meq m^{-3}.

Excess sulfate yields were calculated by a similar procedure, and the mean annual DOC concentration was arrived at similarly, except that a concentration, not a yield was wanted, so the annual DOC yield was divided by the annual runoff to obtain the mean annual concentration. Data for pH were not discharge-weighted; instead each monthly mean pH was weighted by the number of days in that month, and the sum of pH values times days was divided by the number of days in the year. Anomalously low values of pH were eliminated from the calculations. The anomalously low values of pH generally occured together with anomalously high concentrations of SO_4^{--} and/or NO_3^-, and may have been due to inadequately rinsed sample bottles.

Mean monthly excess MTB sulfate data for 1980 and 1981 were corrected for the organic interference by considering the mean monthly ratios of IC to MTB sulfate for the years 1982-1985 (Table 2). There is a fairly consistent annual pattern of changes in this ratio, which is quite closely related to the annual pattern of changes in colour. Mean monthly colour values are shown in Table 3. Until early 1983, high values of colour were reported as greater than 100. As it happens, during 1980 no colour values were reported as greater than 100, but during the last three months of 1981 almost all of the colour values were reported as greater than 100. The actual colour values were estimated from a regression between MTB sulfate and colour, using data from September and October 1981. This regression gave n=26, r^2=0.58, F=33, and P 0.0000.

$$\text{MTB } SO_4^{--} = 2.75 + 0.02\ (\text{COLOUR})$$

This regression is highly significant, but a problem for extrapolating from September and October to October, November and December is that real sulfate concentrations in other years typically increase at the end of the year.

Next a regression was obtained between 30 pairs of mean monthly sulfate ratios and colour, for which r^2=0.38, F=17, and P=0.0001.

$$\text{Ratio} = 0.796 - 0.00266\ (\text{COLOUR})$$

This regression was then used to obtain appropriate mean monthly ratios of sulfate from mean monthly colour values for 1980 and 1981.

By applying these corrections, the annual excess sulfate yield for 1980 was estimated to be 31 meq m^{-2} yr^{-1}, and for 1981 to be 47 meq m^{-2} yr^{-1}. The uncertainties on these estimates are about ±5.

Howell and Pollock (1986) considered the relationships among the two sulfates, colour and DOC for a number of surface waters in Nova Scotia. For the Mersey River below Mill Falls, they obtained:

$$n = 268,\ r^2 = 0.32$$

$$\Delta\text{sulfate} = 0.061 + 0.015\ (\text{COLOUR})$$

where Δsulfate is the difference between MTB and IC sulfates.

If this regression is applied to the mean annual data for colour and excess MTB sulfate for 1980 and 1981, the estimated yield is 36 meq m^{-2} yr^{-1} for 1980 and 58 meq m^{-2} yr^{-1} for 1981. These results are probably less reliable than those obtained above.

DISCUSSION

The annual runoff and the results of calculation of CDRs, excess sulfate yields, and the geometric mean annual pH of the Mersey River below Mill Falls, and the annual wet deposition of excess sulfate at KNP for the years 1980-1985 are shown in Table 4.

The CDRs and the excess sulfate yields (except for 1980 and 1981) are considered to be accurate to ±1 meq m^{-2} yr^{-1} (neglecting the inherent error in the discharge data). The long-term mean runoff of the Mersey River at this station to 1985 (17 years) was 0.942 m yr^{-1}. For most of the years considered here, runoff was rather lower than the long-term mean; 1981 is the exception. Runoff in 1981 was 40% higher than the mean of the other five years whereas the CDR for 1981 was higher than the mean CDR of the other five years by 69%. The reason for the high CDR was carefully investigated. The cation data for 1981 were carefully checked, and the evidence for a high CDR (higher flow and higher sums of cations) was present throughout the year. The high CDR calculated for 1981 was not dependent upon a small number of samples or even upon a small number of months. During this year of high flow chemical weathering rates must have been enhanced throughout the year. Not enough is yet known about rates of chemical weathering to permit us to conclude that the high rate of flow itself was principally responsible for the enhanced weathering rate; certainly, water is the prime agent of chemical weathering.

The excess sulfate yields of the Mersey River are typically higher than the wet deposition rates; the difference has been attributed to dry deposition. It is unfortunate, for the sake of these comparisons, that the exact sulfate concentrations and yields are not known for 1980 and 1981. Wet deposition of excess sulfate in 1981, however, was higher than the mean deposition for the other five years by 33%, so the claim may be made that deposition of excess sulfate was responsible, in part, for the high CDR in 1981. The river yields of excess sulfate do not compare well on an annual basis with the wet deposition rates. It is likely that this river, which has a drainage area of 295 km^2 that contains many lakes and bogs, does not respond rapidly to annual changes in deposition rates. Wet deposition of excess sulfate was unusually low during 1983. The river yields of excess sulfate do not reflect this low deposition rate. Wet deposition rates were higher during 1984 and again during 1985.

The mean annual pH of the river, which, as has been mentioned, is probably buffered by weak organic acids, changed little over this period, although the data show a small decrease with time. A comparison of the mean monthly pH for 1980 and 1985 (Figure 2) shows clearly that there has been a definite decrease in pH. It may be, however, that the pH has not so much decreased as it has failed to increase over the summer, perhaps due to an increased buffering capacity of the weak organic acids.

Another indication of a dampening of the annual pH cycle of the river is the decrease in standard deviation of the simple arithmetic mean of all pH values (paired with excess IC sulfate values) (Figure 3). Figure 3 is a plot of standard deviation by year. The numbers above the lines are mean annual pH, the numbers below the line are the number of samples. Preliminary examination of data for the first ten months of 1986 show that this trend continues with mean pH 4.94, n 144, and standard deviation of the mean of 175 samples being 0.129.

SUMMARY AND CONCLUSIONS

Cation denudation rates of the Mersey River below Mill Falls, calculated with a greater than usual degree of accuracy because of the large number of samples, ranged from 56 to 102 meq m^{-2} yr^{-1}, being much higher on the wettest year, proportionately, than the runoff. There is little apparent relationship between CDRs and excess sulfate yields or wet deposition of excess sulfate. There is also little relationship between excess sulfate yields and wet deposition of excess sulfate, although they are of the same order of magnitude.

There has been a small decrease in mean pH since 1980, and there is some evidence that the change in pH is not so much a reduction as it is a decrease in range, perhaps due to increased buffering capacity of organic acids.

REFERENCES

Cheam, V., Chau, A.S.Y., and Todd, S. 1986. Sulfate in coloured waters: investigation on methodologies, data reliability and approaches for salvaging historical colorimetric data. NWRI Contribution No. 85-95.

Howell, G.D. and Pollock, T.L. 1986. Sulphate, water colour and dissolved organic carbon relationships in organic waters of Atlantic Canada. <u>In</u> Statistical Aspects of Water Quality Monitoring. Developments in Water Science, Vol. 27, A.H. El Shaarawi and R.E. Kwiatkowski, editors, Elsevier Science.

Thompson, M.E. 1982. Exchange of marine sodium for calcium during chemical weathering in the Isle aux Morts River basin, Newfoundland. Geochim. Cosmochim. Acta, Vol. 46, 361-365.

Thompson, M.E. 1987. Comparison of excess sulfate yields and median pH values of rivers in Nova Scotia and Newfoundland, 1971-1973 and 1982-1984. Water, Air, and Soil Pollution, Vol. 35, 19-26.

TABLES

TABLE 1. The number of samples of major ions by month and year for the Mersey River below Mill Falls, for the years 1980-1985

Month	1980	1981	1982	1983	1984	1985
	Year					
January	5	14	8	8	15	19
February	4	18	13	25	11	28
March	5	20	19	30	6	26
April	8	23	19	13	5	8
May	3	17	21	8	4	5
June	21	15	15	1	4	5
July	28	18	4	7	5	6
August	18	18	4	6	6	4
September	16	17	4	7	5	4
October	18	17	14	7	21	5
November	16	18	16	5	29	15
December	18	16	19	8	29	31
Total	160	211	156	125	140	156

TABLE 2. Ratios of mean monthly discharge-weighted excess IC to MTB sulfate, for the Mersey River below Mill Falls, 1982-1985.

Month	1982	1983	1984	1985	MEAN	Std. Dev.
	Year					
January	0.543	0.520	0.533	0.508	0.526	0.015
February	-	0.568	0.546	0.540	0.551	0.015
March	0.685	0.644	0.716	0.611	0.664	0.046
April	0.682	0.561	0.613	0.599	0.614	0.041
May	0.667	0.486	0.818	0.631	0.651	0.136
June	0.655	0.616	0.504	0.601	0.594	0.064
July	0.671	0.584	0.466	0.546	0.567	0.085
August	0.730	0.558	0.548	0.729	0.641	0.102
September	0.588	0.676	0.609	0.537	0.603	0.058
October	0.579	0.562	0.521	0.559	0.555	0.024
November	0.525	0.455	0.515	0.439	0.484	0.043
December	0.522	0.491	0.481	0.504	0.500	0.018

TABLE 3. Mean monthly colour values for the Mersey River below Mill Falls 1980-1985

Month	Year					
	1980	1981	1982	1983	1984	1985
January	83	68	100	105	93	119
February	81	60	88	100	86	93
March	51	55	51	87	78	77
April	46	52	46	79	70	58
May	52	64	63	93	86	61
June	57	87	67	100	97	78
July	50	78	73	89	109	90
August	43	67	82	108	112	85
September	31	62	65	92	116	85
October	52	122	81	89	113	82
November	56	144	100	100	104	98
December	67	100	110	104	123	100

TABLE 4. Mean annual runoff, CDR, excess sulfate yield, and mean annual pH of the Mersey River below Mill Falls, and annual wet deposition of excess sulfate at Kejimkujik National Park, Nova Scotia, for the years 1980-1985.

Year	Runoff $m\ yr^{-1}$	CDR $meq\ m^{-2}\ yr^{-1}$	Excess Sulfate Yield $meq\ m^{-2}\ yr^{-1}$	pH	Wet Deposition of Excess Sulfate $meq\ m^{-2}\ yr^{-1}$
1980	0.671	60.7	31	5.21	34.9
1981	1.07	102	47	5.07	38.9
1982	0.855	65.1	35.2	5.03	29.8
1983	0.755	65.9	30.5	5.02	20.4
1984	0.839	62.1	33.0	5.00	28.3
1985	0.710	54.5	27.6	5.00	32.8

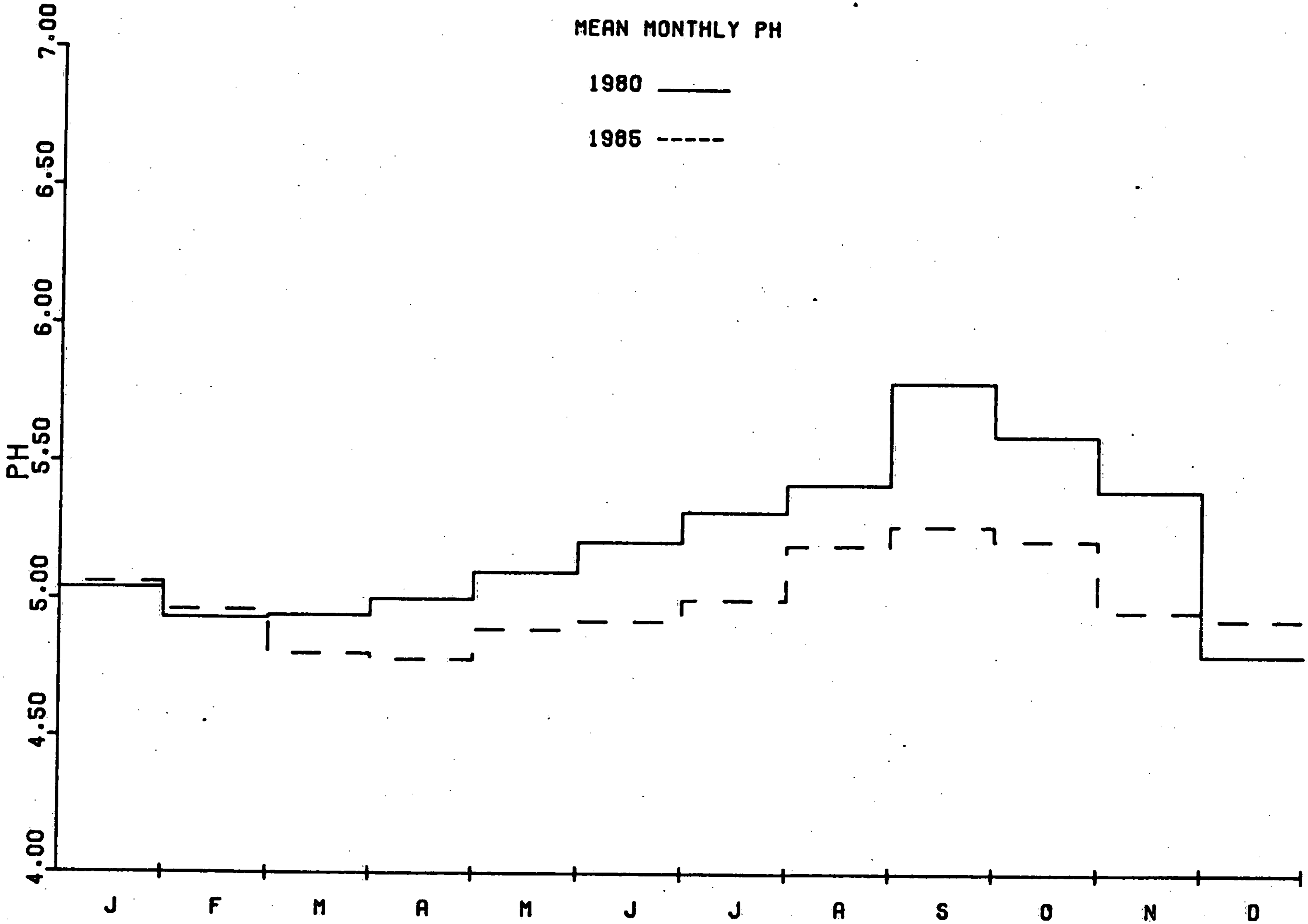

Figure 1. Comparison of the mean monthly pH of the Mersey River below Mill Falls, 1980 and 1985.

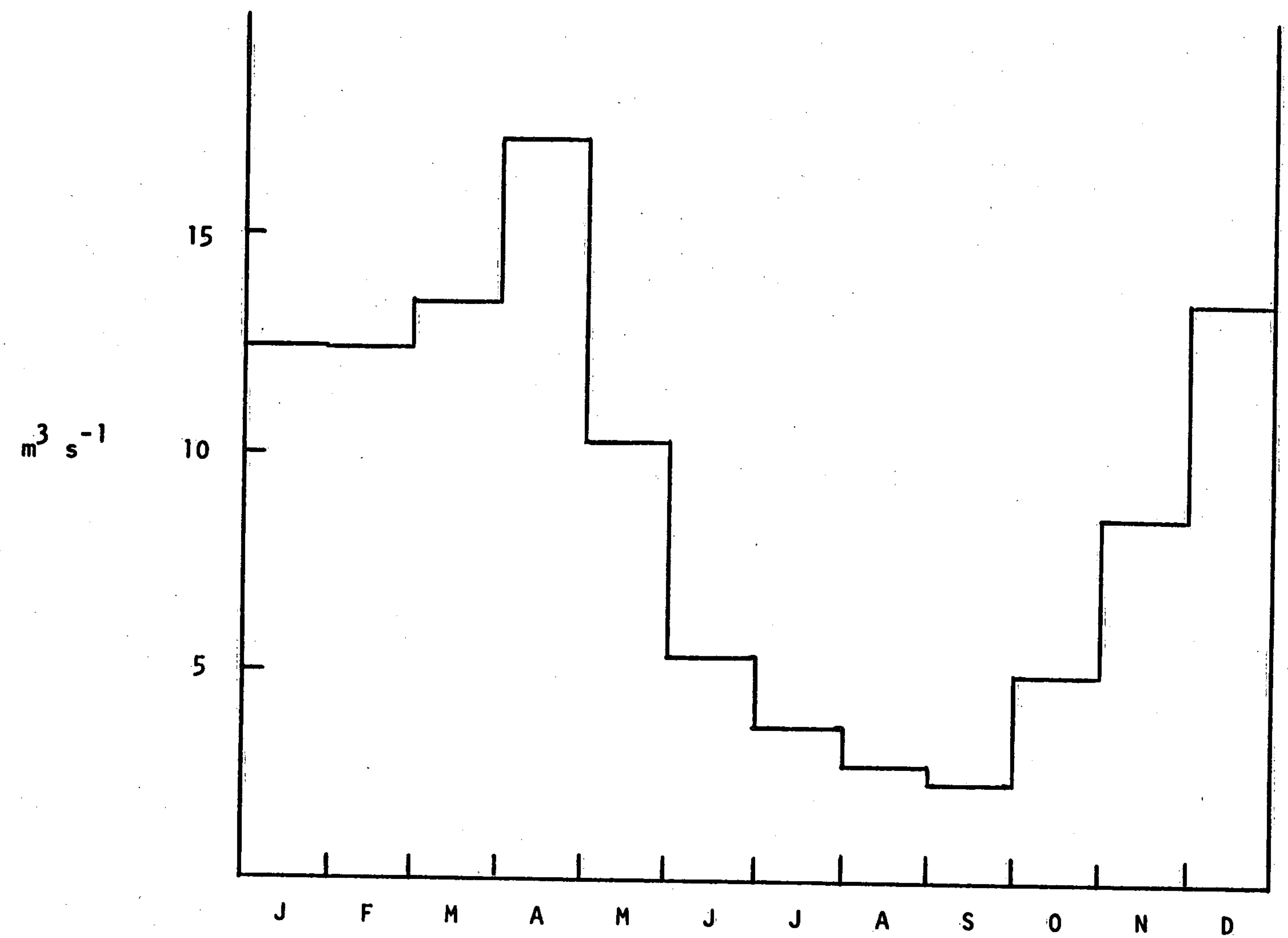

Figure 2. Mean monthly flow of the Mersey River below Mill Falls, 1969 - 1984.

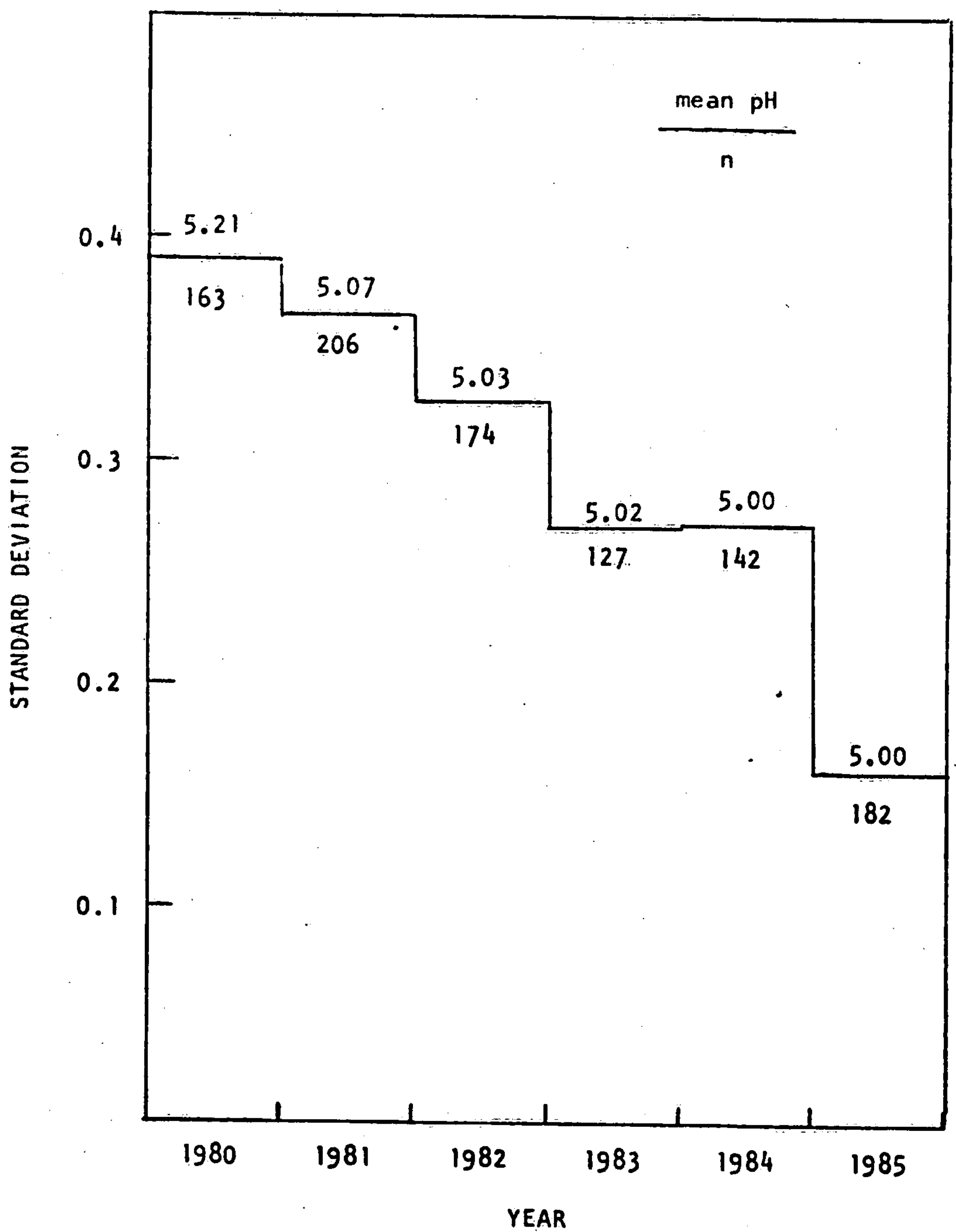

Figure 3. Standard deviation of the mean annual pH of the Mersey River below Mill Falls, 1980-1985. The upper number is the mean annual pH, the lower is the number of samples.