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Concern has been growing over the acidity of atmospheric precipitation in Canada, and in 1977 the Canadian Network for Sampling Precipitation (CANSAP) was established[1]. Cumulative samples of wet precipitation are shipped each month to Department of Environment Water Quality Branch Laboratories at the Canada Centre for Inland Waters for analysis. Early results (Figure 1) show that the highest levels of acid precipitation loading are concentrated over the St. Lawrence Valley in Ontario and Quebec, and extend as far as Labrador and the Atlantic Provinces.

Concern for the effects of such precipitation on surface waters has led to a compilation of data from various sources to permit identification of the vulnerable areas of eastern Canada. The softest waters are the most vulnerable because of their limited buffering capacities. Where the waters are soft, the soils are generally nutrient poor, and the land is left mainly to forest. This in turn means that the chemistry of rivers draining such areas is little affected by local human activities. The first maps showing vulnerable areas were based mainly upon the systematic surveys of the industrial waters of Canada carried on from the late 1940s until the early 1960s. These reliable data sets have provided useful "base line" data with which to compare more recent observations of surface water chemistry.* To identify areas vulnerable to acidification, rather simple criteria were used, e.g., Ca^{++} 0 to 4 mg/L, alkalinity 0 to 0.2 meq/L, conductance 0 to 70 μS/cm. These criteria resulted in the identification of large areas of eastern Canada as vulnerable (Figure 2): most of the Canadian Shield areas of Ontario and Quebec, the upland areas of Nova Scotia and Newfoundland, and numerous basins in New Brunswick.

* The early surveys of surface water quality were carried out by a Canadian government laboratory that is now known as the Water Quality Branch of Environment Canada. The data used in this comparison are from the report of Thomas[2], in which data for Nova Scotia rivers in 1954-55 and Newfoundland, 1955-56 are given. Sampling sites were carefully selected to be representative of the main flow of a river or tributary; if possible, sampling sites were established where river discharge records were also obtained. Typically, samples were taken once each month for a year. pH and some other properties were measured in the field, and again in the laboratory. The pHs used for comparison were measured in the laboratory, at room temperature, on samples that had been kept tightly stoppered and in the dark. As the only important biological changes that can go on under such circumstances are respiration and decay, these pHs probably represent the values at the lower end of the range to be expected in that water body in nature.

More recent data on the quality of surface waters in Canada are also reported by Environment Canada's Water Quality Branch, and are stored in NAQUADAT, Canada's Nation water quality data archive.

Rather good long term records of water quality exist for several soft water rivers in Nova Scotia and Newfoundland; the locations of the rivers to be discussed are shown in Figures 3 and 4. The older data are from the report of Thomas[2]; the more recent data are in NAQUADAT. Although these data were collected as part of a routine water quality monitoring program, they have proved to be useful (with some limitations) for the purpose of assessing the impact of acid precipitation.

The kinds of changes in pH seen in these rivers - decreasing rather steadily until 1973, and apparently increasing nearly as steadily since then, make it highly desirable to have comparative data on acid loads and on river chemistry, such as are only now becoming available. From Figure 1 it may be seen that in 1977 Nova Scotia received about 40 meq H^+/m^2, and Newfoundland received from 20 to 30 meq H^+/m^2. Herman and Gorham[3] sampled atmospheric precipitation at Kentville, Nova Scotia, from June, 1952, until May, 1954, and reported volume weighted mean pH of 5.7, range 5.3 to 6.7, suggesting a "normal" or relatively insignificant atmospheric load of acid.

Figure 5 shows a plot of pH versus log Ca^{++} (mg/L) for the three rivers in Nova Scotia, in 1954-55 and 1973. The plot is modified from that of Henriksen[4] who used an empirical test for evidence of acidification. It is obvious that all of these rivers were significantly more acid in 1973 than in 1954-55.

In calculating mean annual H^+ as pH, the results may be biased by the time of sampling in relation to the river hydrograph. The presumption is that the pH is apt to be lower at times of high flow, and higher at times of low flow. The data were tested by dividing the mean annual discharge by the mean of the discharges on the days of sampling, and plotting that ratio against mean pH, by year. That simple test showed that, although sampling in various years was commonly biased toward either high or low flow, there was no consistent relationship between mean pH and such bias. All the rivers show the same general time-dependent trend in pH, indicating that the calculated mean pHs are reasonably representative and comparable.

The rate at which cations are leached from a drainage basin by processes of chemical weathering can be called the cation denudation rate or, alternatively, the proton absorptive capacity (PAC) of the basin. The Tusket and Medway Rivers in Nova Scotia have PACs of about 80 meq m^{-2} a^{-1}. It is clear that in 1973, when the pH of the Tusket was little higher, if at all, than the pH of precipitation, that its basin had received an acid load equal to or greater than its PAC. The Medway, a little further up the coast, probably received a somewhat smaller acid load, but its mean pH, 4.88, is hardly to be desired. The basin of the St. Mary's River has a somewhat larger PAC, of about 115 meq m^{-2} a^{-1}, and because of its location even further to the northeast, may well have received an even smaller acid load, yet its mean pH was as low as 5.16.

The three rivers in Newfoundland have somewhat higher PACs than the Nova Scotia rivers - the Isle aux Morts River about 200 meq m^{-2} a^{-1}, the Garnish and the Rocky Rivers about 150 meq m^{-2} a^{-1}. It is, of course, not known how the atmospheric load of acid varied in the past, but the CANSAP data in Figure 1 show that in 1977 it tends to decrease from west to east. The mean pHs, shown in Figure 4, certainly indicate that the Isle aux Morts River, in extreme southwest Newfoundland, receives the highest acid load.

The question is often raised as to whether atmospheric loads of strong acid alter the rates of chemical weathering. The data for the Nova Scotia rivers indicate that such changes are very small, if any, but there might be a slightly reduced rate of cation denudation (or proton absorption capacity) with time (Figure 5). The reasons for such a decrease are only speculative at present, and may be related to such subtle processes as a reduced rate of forest growth and root development. It is hoped that the calibrated watershed studies now being carried out in various parts of eastern Canada will answer such questions.

That the acid loading to the Atlantic Provinces has apparently been somewhat reduced since 1973, presumably because of changed weather patterns, is little grounds for optimism. Few of the biota of such river systems can tolerate the fluctuations of pH to as low as 4.5 that still occur at times.

REFERENCES

[1]D. M. Whelpdale, R. L. Berry, The Canadian Precipitation Chemistry Network, Atmospheric Environment Service, Department of Environment, Downsview, Ontario, Canada, 1978.

[2]J. F. J. Thomas, Water Survey Report No. 11, Industrial Water Resources of Canada, Dept. of Mines and Technical Surveys, No. 864, 1960.

[3]F. A. Herman and E. Gorham, Tellus IX (2) 180-183, 1957.

[4]A. Henriksen, Nature 278, 542-545, 1979.

FIGURES

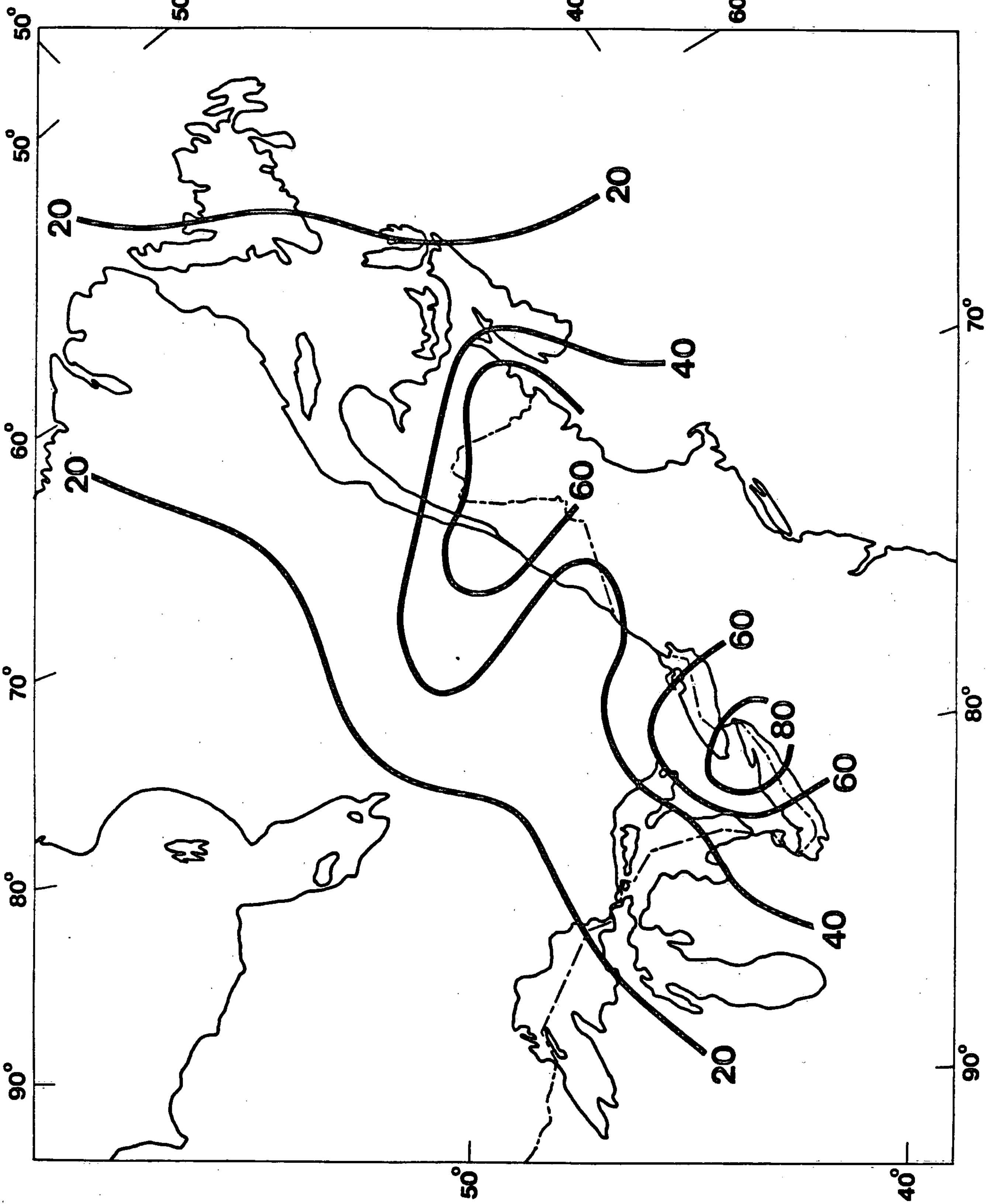


Figure 1. Atmospheric deposition of H^+ in 1977, mg H^+ m^{-2} a^{-1}.

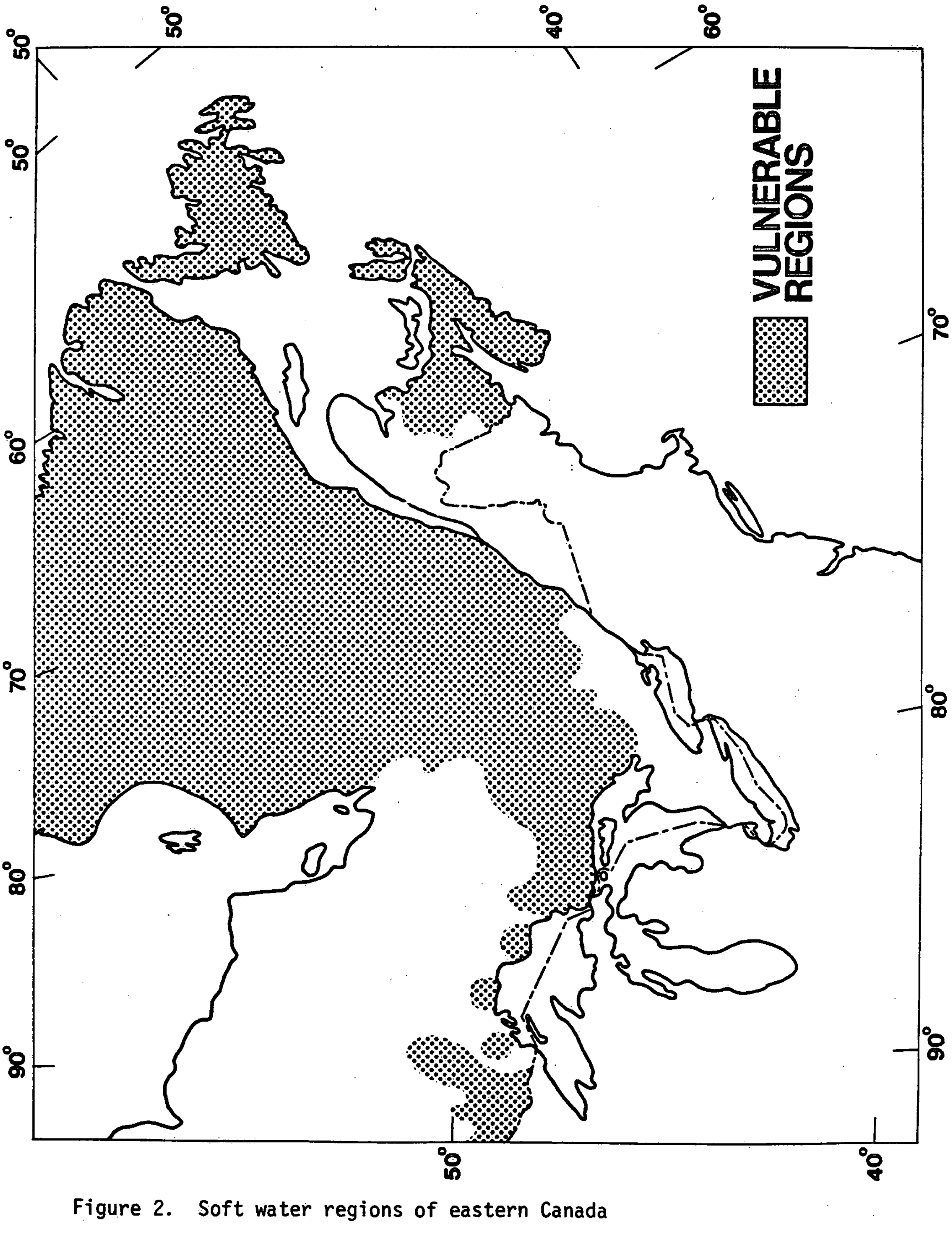


Figure 2. Soft water regions of eastern Canada

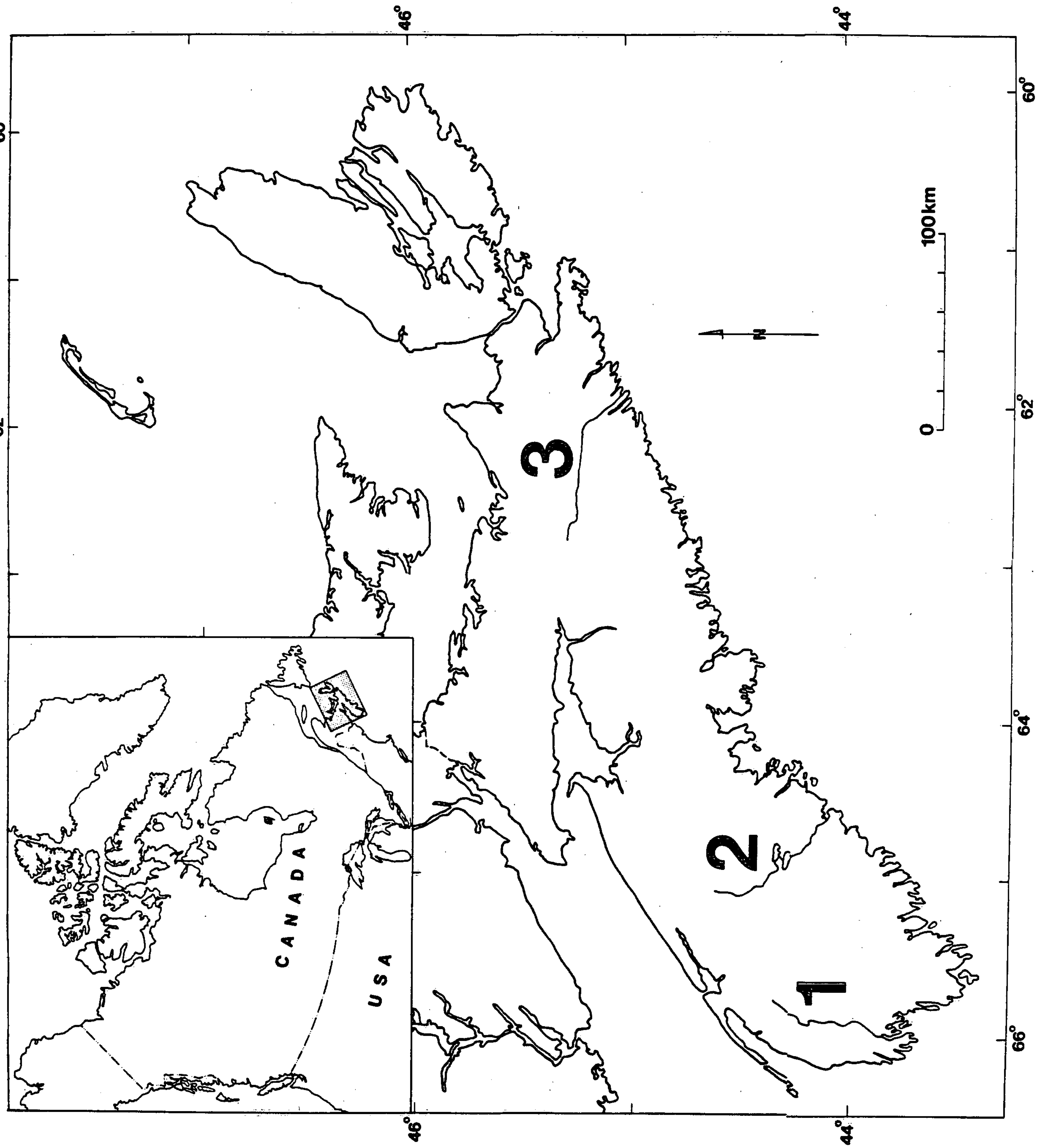
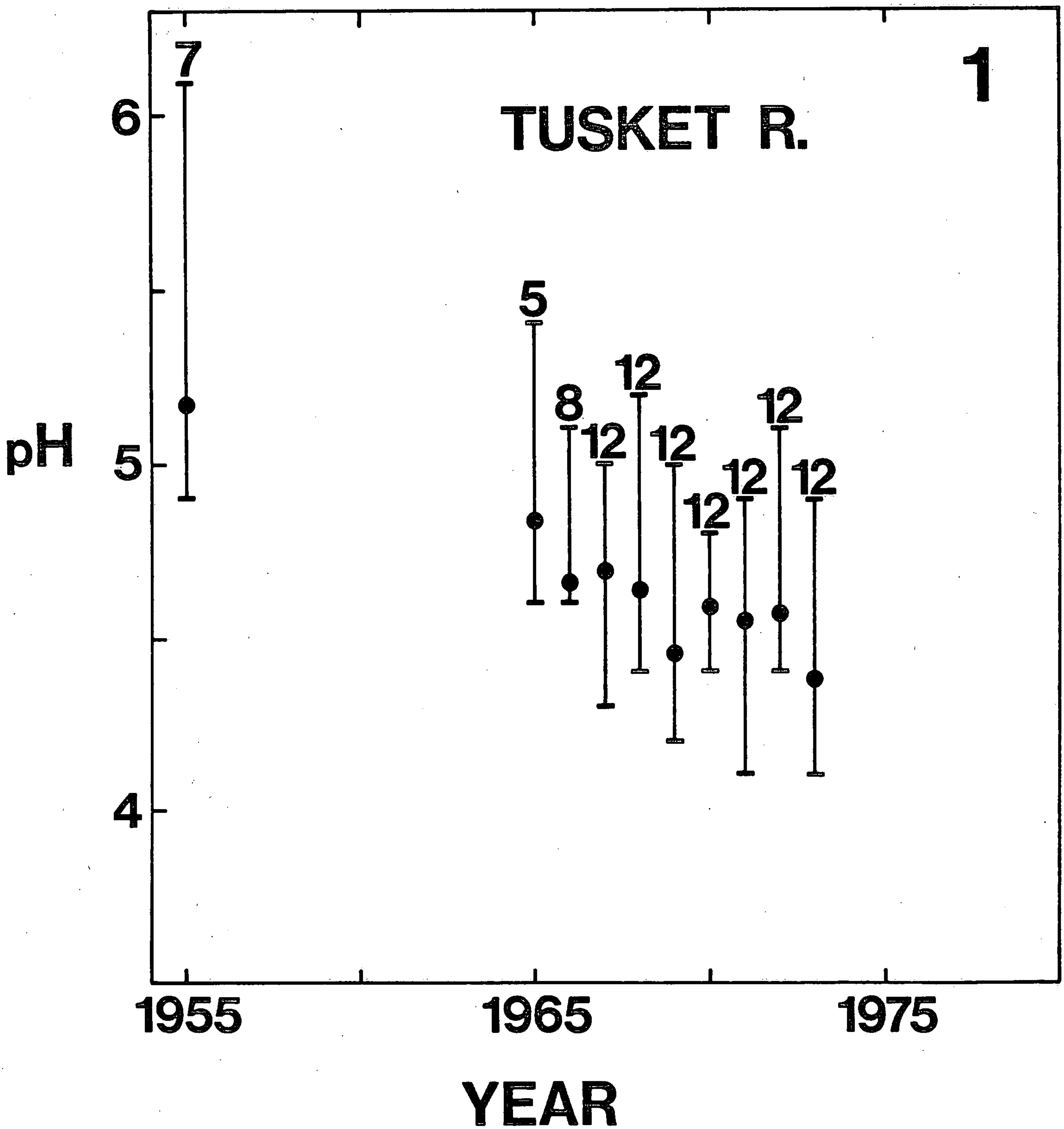


Figure 3. Discharge weighted mean H^+ as pH for three Nova Scotia Rivers



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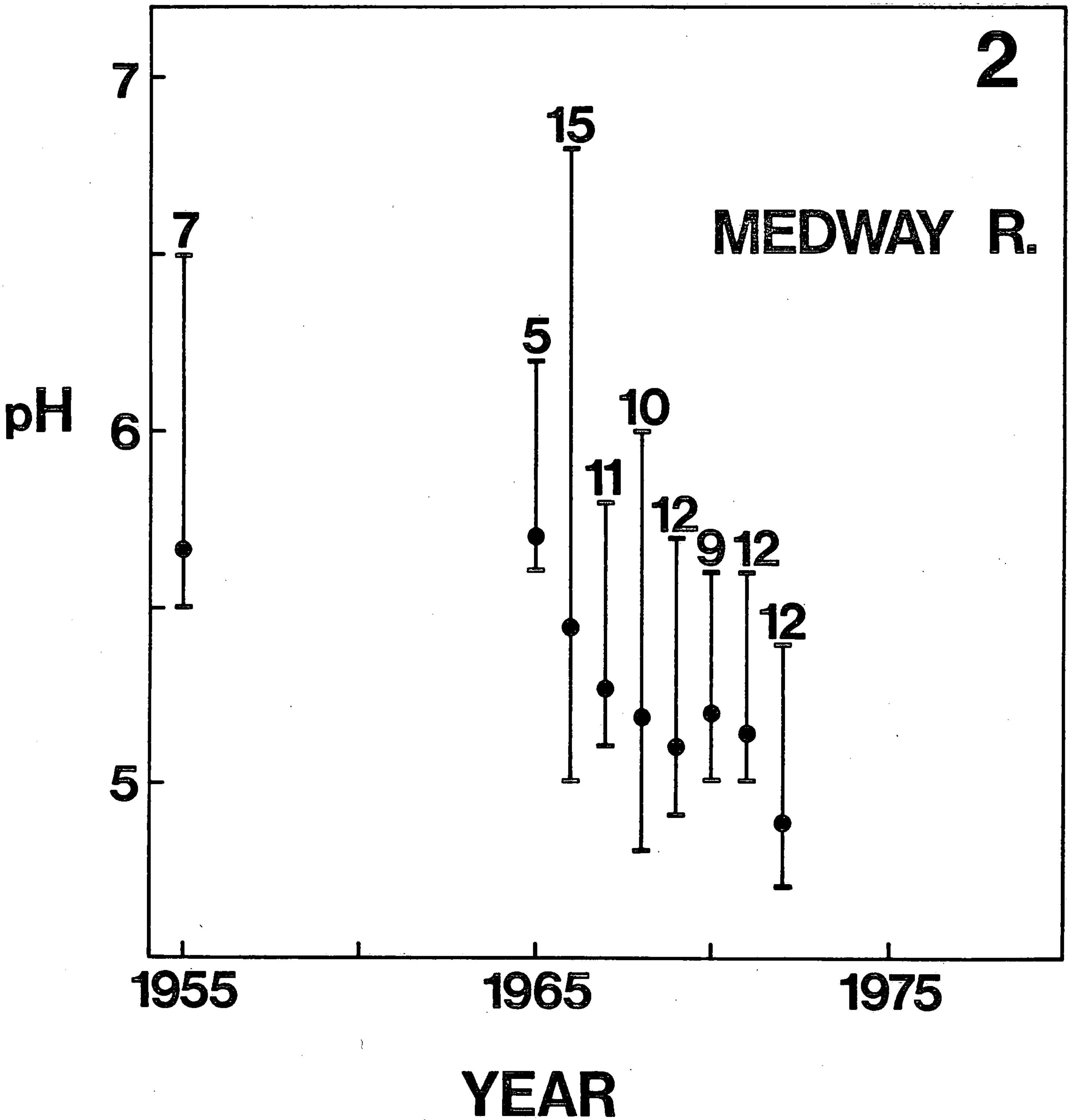

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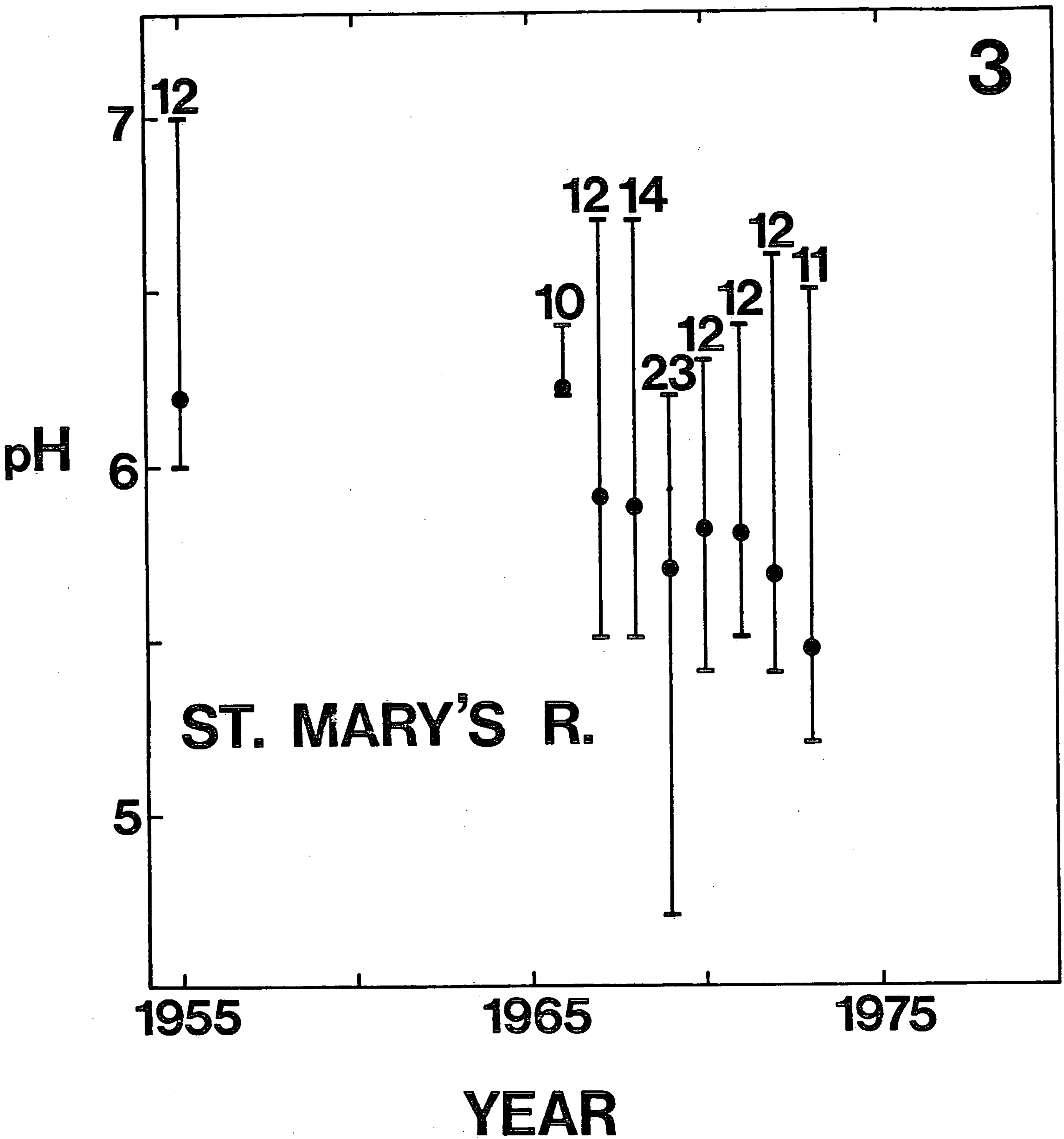

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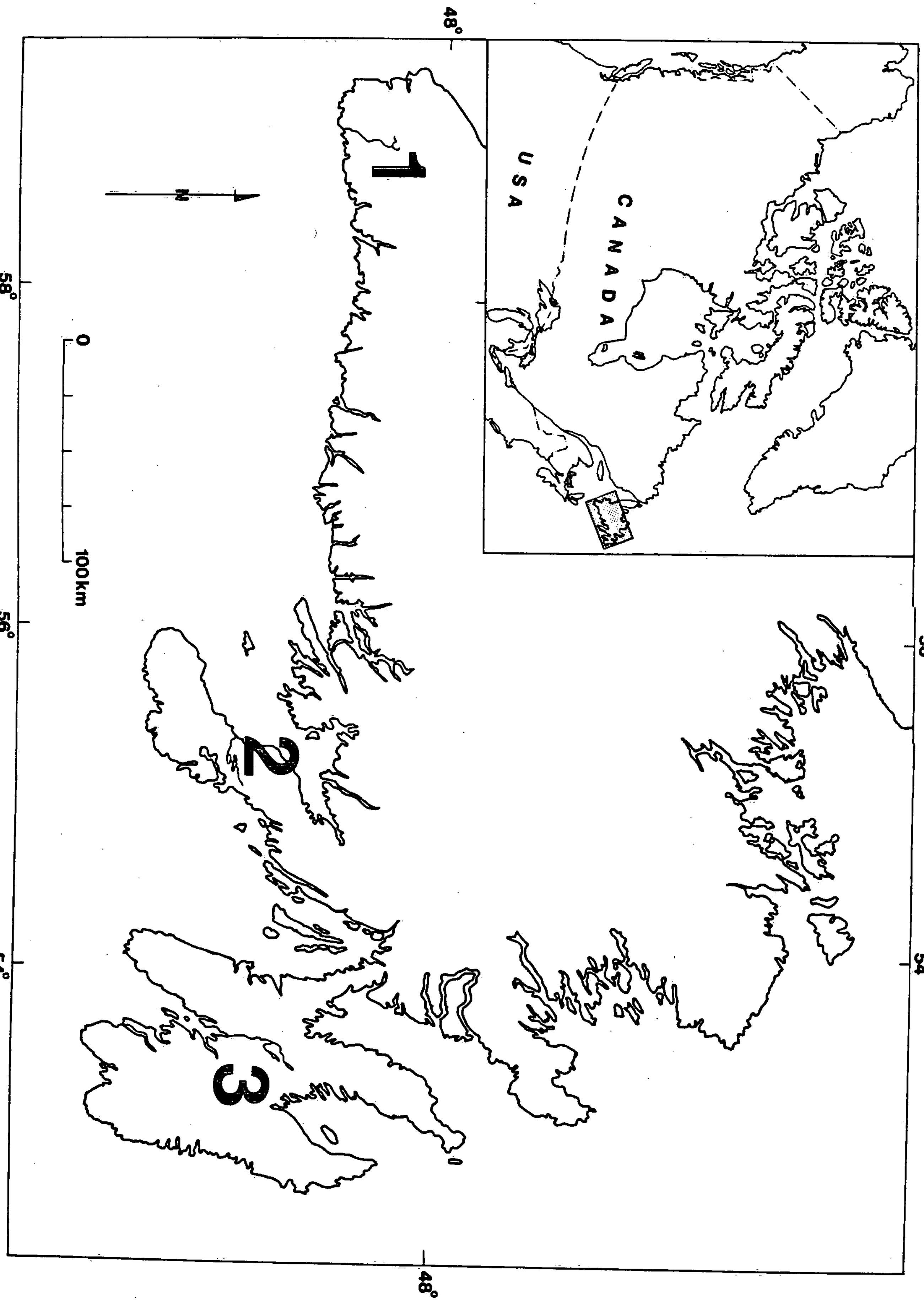

Figure 4. Discharge weighted mean annual H^+ as pH for three Newfoundland rivers.

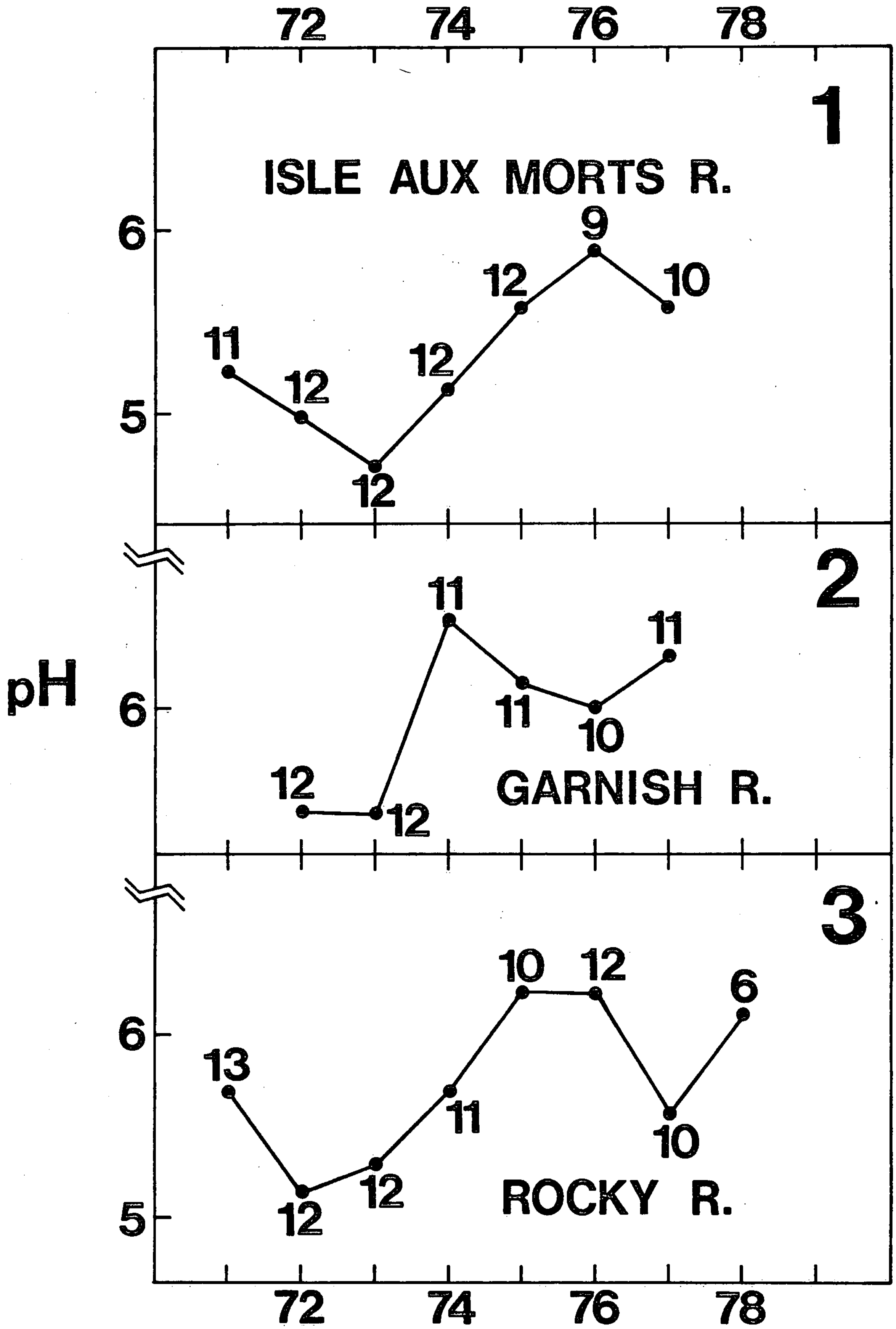
72
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Figure 4.

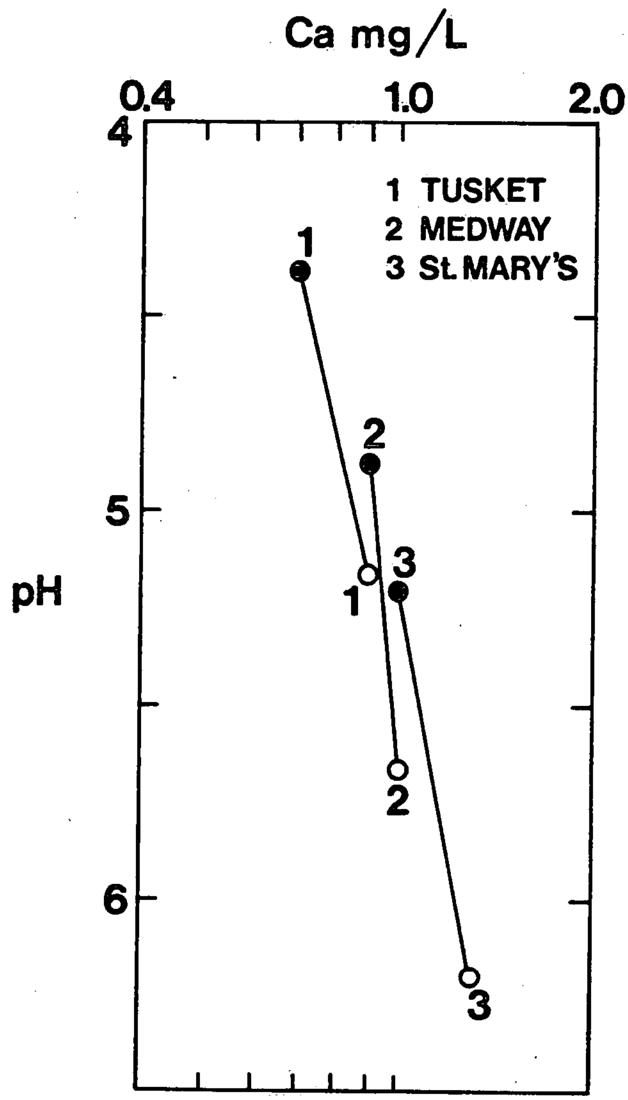

Figure 5. Log Ca^{++} versus pH for the three Nova Scotia Rivers, 1954-55 and 1973.

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