THE COMPLEXITY OF THE ACID RAIN - SURFACE WATER

ACIDIFICATION PROBLEM

by

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Abstract

The phenomenon of acid deposition from atmospheric sources has emerged as the most widely-discussed environmental issue of the last five years. Despite the abundance of discussion, the issue is still in the process of being adequately defined <u>scientifically</u>, especially as acid deposition affects the acidity status of surface waters and produces effects in terrestrial systems. The issue to be focussed upon is the anthropogenic contribution to an acidic atmospheric system of approximately 2 billion years. The atmospheric system is dynamic, having both man-made and poorly quantified natural sources, all of which are variable in source strength temporally and spatially. Using the Adirondacks region as an example, it is shown that the atmospheric system is coupled to a terrestrial system of equal complex variables and interrelationships, which are also variable in time and space. The presently slowly emerging scientific picture of a very complex system in which man can significantly control effects upon a limited portion of the system is at odds with political processes building upon an early incomplete scientific understanding of the extent of the complexity of the interrelationship between acidic deposition and surface water acidification.

Geologic Antiquity of the Phenomenon

In order to gain some perspective on the problem of acid rain, it is important to realize the geologic antiquity of the phenomenon of "acid rain," or acidic precipitation, inasmuch as the atmospheric scavenging process involves removal of chemical constituents of the atmosphere by both rainfall

and snowfall. In addition, removal is accomplished by dry deposition, about which even less is known than is known about acid formation and precipitation involving the aqueous phase. The Barberton volcanics of South Africa indicate the presence of volcanic activity at the Earth's surface in excess of four billion years ago, prior to the evolution of the Earth's atmosphere to a composition close to that known today. Rubey (1955) has argued persuasively that the earliest primitive atmosphere was composed primarily of CO_2 and N_2 although others have proposed an initial atmosphere composed predominantly of CH_4 and NH_3 (Urey, 1951). Under such primitive atmospheres, the processes of chemical weathering would have not been significant, depending as they do upon oxygen and acids as the critical chemical components of weathering reactions. Recent work by Hattori et al. (1983) has estimated that the atmosphere became oxidizing on the order of 2.2 billion years ago. The significance of the oxidizing atmosphere is that sulfur compounds from volcanic emissions and nitrogen oxides from lightning would be oxidized to sulfate and nitrate ions, lowering the pH below that of the theoretical atmospheric carbon dioxide - water system having a pH of 5.65. About 400 million years ago, during the Devonian Period, land plants became a major component of terrestrial surface cover. Decay of aquatic and terrestrial organic matter provides additional major natural sources of sulfur and nitrogen compounds to the atmosphere. Thus, the frequently cited "anthropogenic" origin of the "acid rain" phenomenon more properly should be characterized as an anthropogenic addition to precipitation that is inherently acidic as a result of natural sources of sulfur and nigrogen compounds.

Acid Rain pH - A Variable in Time and Space

The natural sources vary in their intensity both spatially and seasonally, as do the anthropogenic sources. There is, therefore, no single value of hydrogen ion concentration that typifies rainfall. It is variable in both time and space as a function of a variety of natural and man-made emissions. Estimates of the most likely midpoint of the range of pH in the absence of anthropogenic contributions have been estimated by Miller and Everett (1981) as 4.5 ± 0.5 pH units, by Charlson and Rodhe (1982) as "well below 5" in some clean, remote areas in a sampling network covering 1800 km^2 for 22 storm events during two years. Semonin (1976) has reported a range of up to 4.8 pH units in a single storm. Stensland and Semonin (1982) have looked at the variability of pH in precipitation in data from Illinois and found a change from 6.5 pH units in 1953 to approximately 4.3 in 1983. However, going further, they examined the meteorology of the 1950's period, finding a drought occurring that artificially elevated the acid rain pH to 6.5 by providing wind-blown soil components composed of calcium and magnesium salts, which buffered the rain upwards. Correcting on an equal ion concentration basis for calcium, they found a change from the 1950's to the present of only about 0.5 pH units.

The frequent citation of pH 5.65 as the baseline that control programs should be expected to achieve and from which estimates of anthropogenic effects have been measured has obscured proper definition of the problem. The magnitude of man-made effects on atmospheric chemistry have been over-estimated but we have an inadequate data base to be able to tell by how much. In the U.S., emission control programs operating during the last decade have had some effect

in reducing atmospheric sulfur loadings but we cannot define how much control
will result in how much of an acid deposition change in what locations on the
basis of existing data.

Natural Sources Are Underestimated

Natural emissions have been significantly underestimated, leading to
overestimation of the effect of anthropogenic sources. A significant example
of the problem of underestimates of natural sources has been the historic
estimates of volcanic emissions and exhalations to atmospheric sulfur loading.
Cadle et al. (1979) noted that Stoiber and Bratton recognized that estimates
of volcanic emissions were about a factor ten too low prior to 1979 as a result
of previous analytical and monitoring techniques. An additional frequent
source of underestimation of volcanic gaseous contributions has been a focus on
emissions only during the spectacular eruptive events but ignoring of non-eruptive
fuming or degassing. The factor of ten change increases world-wide estimates
of atmospheric volcanic contributions of sulfur gases from being about 15 percent
(10 Tg/year of SO_2) of anthropogenic emissions to nearly 150 percent. Such
analytic and methodological problems continue to complicate recent estimates
and perhaps are the basis for Berresheim and Jaeschke (1983) estimating volcanic
emissions prior to 1979 at 15.2 Tg SO_2 but stating that volcanic emissions
subsequent to 1979 may be on the order of a factor of ten greater than those
from 1960 to 1979. Data on volcanic eruptions since 1979 do not support a ten-
fold increase in SO_2 into the atmosphere from volcanic (or any other) sources
(Sedlacek et al, 1983; Simkin et al., 1981; Dr. L. Siebert, Smithsonian
Institution, personal communication, 1983). These considerations suggest the
reasonableness of Stoiber and Bratton's observation on the probable order of

magnitude of error in earlier estimates of volcanic emissions. Supporting

the idea that the atmospheric contribution of volcanoes may be much larger than

previously estimated is the finding by Sedlacek et al. (1983) that "at least

58% of the sulfate aerosol present in the lower stratosphere between 1971 and

1981 was of volcanic origin." Given that only a small portion of volcanic

emissions, and probably little if any non-eruptive degassing, reaches the

stratosphere, the magnitude of tropospheric sulfate from volcanic sources

clearly needs reassessment.

Although there are indications that, in northeastern U.S., both sulfate

emissions and wet deposition has been decreasing over the last decade, the

decline in wet deposition does not appear to be linearly proportional to the

decline in emissions. A larger-than-previously assumed natural background may

be one reason for that conundrum. Not only volcanic contributions are poorly

known, however. The rapidly emerging literature on dimethyl sulfide emissions

from the oceans indicates a source of geographically variable emissions

comparable in volume to estimates of anthropogenic emissions. Such biological

sources are variable temporally as well as spatially. Terrestrial analogues of

this variable oceanic source also exist. EPA (1982) has shown a limited number

of New York and New England samples of soil and water emissions of organic

sulfur compounds with concentrations nearly five times greater than the eastern

U.S. average emissions from such sources. Such a source strength difference

may result in significant differences in regional sulfate deposition.

Complexities in Terrestrial Portions of Affected Watersheds Using the Adirondacks Region as an Example

The acid rain problem has been much over-simplified by a number of

scientists as well as the popular press. Of course it is not the first

environmental issue about which there were "doomsday" predictions at an early

date, based on a slim and inadequate data base. For the most part, the

researchers first to recognize the possible problem and begin to evaluate its

possible ecological consequences were unaware of the substantial amount of

literature on the chemical reactions of water passing through terrestrial

environments. Many of these papers deal with hydrogeochemical processes and

reactions that occur in surface water systems dominated by bicarbonate anions.

The bulk of published water research has dealt with waters having water chemistries

acceptable for potable or irrigation use. There is relatively little information

on the hydrology of waters in glacial terranes (Born et al., 1979), yet the

previously glaciated regions of the northern hemisphere are those now believed

to be most affected by acidic deposition. These terranes are characterized by

boreal forests with acidic podzol soils, bogs, and wet conifer swamps (Larsen,

1982; Foth and Schaefer, 1980; and Duchaufour, 1978). Surface water environments

in these circumboreal regions commonly have higher concentrations of dissolved

organic constituents, including dissolved organic acids, than do other terranes.

The result is low alkalinity waters poorly buffered by bicarbonate but

frequently well buffered by other chemical systems, such as organic acids or

aluminum complexes leached from soils in the watersheds. The waters are of a

mixed inorganic-organic type whose chemical behavior is not well understood.

Traditional inorganic water analyses are not sufficient to characterize

the chemical behavior of such waters. For example, during our Adirondacks water

survey performed in the late autumn of 1981, my colleague, Dr. James Kramer,

found that when samples titrated during Gran analyses were allowed to sit,

hydrogen ion was slowly released for periods of up to 24 hours. These reactions, of apparently organic origin, have slow kinetics in comparison to typical inorganic acid-base reactions that usually characterize such titrations. Stevenson (1982) has concluded that the acidic properties of fulvic and humic acids are not explained entirely by simple ionization reactions but that they also involve formation of carbonions and carbonium ions. Structural reorganizations of the organic anions may be involved as well. Thus, Gran titrations and positive excess ion balances are only qualitative, not quantitative, indications of the presence of organic acids in natural waters. Other qualitative indicators of significant organic constituents in water are: 1) yellow to yellow-brown water color, although we found indications that even clear water streams can be acidified by organic acids, a finding that has recently been observed by Krug in Connecticut waters; 2) substantially increased time of filtration, frequently with the deposition of a clear, waxy material on filter surfaces; 3) high concentrations of aluminum and iron, out of equilibrium with the inorganic chemistry of the sample; 4) depressed dissolved oxygen concentrations under high flow conditions; 5) low positive to negative alkalinity; and 6) very poor correspondence of pH and conductivity.

The waters of the Adirondack region contain a wide spectrum of waters ranging from quite organic to quite bicarbonate rich. Under the heavy rainfall conditions during which we worked, the bulk of the surface waters in streams, lakes and ponds were a mixture of organic and inorganic parameters, in our opinion. They are not adequately characterized solely by inorganic chemical analyses nor will their response to strong inorganic acid addition be predictable from solely inorganic considerations. During dry weather, low-flow conditions,

such waters can be expected to be much more inorganic as a result of the dominance of base flow from the more mineral-rich horizons of the soil profile, glacial strata, and bedrock. Initial results of sampling conducted this past summer by Dr. Carl Schofield and his colleagues at Cornell University appear to verify these differences between high flow and low flow water chemistry.

Not only is the Adirondack region receiving acid precipitation but other factors are operating as well that influence surface water chemistry. Changes in land use practices since the early part of the century have led to a great increase in the area under forest cover, with a concomittant decrease in the number of acres burned annually in forest fires (Figure 1) (Duhaime et al., 1983). The result has been a substantial build-up of organic litter through which precipitation must pass on its way to becoming stream flow. The decrease in forest fires has removed a source of carbonate buffering for the through-flowing waters. Older ash layers become more leached with time and thus are less effective in providing bicarbonate buffering. The long-term effect is that of increased amounts of organic material on the forest floors of the watersheds to provide organic acids upon leaching.

During those eight decades of increased forest cover and litter accumulation, there has been change in the mean precipitation regime. Quinn (1981) has shown a regional trend of increased rainfall since the beginning of the century for the Great Lakes basin, which encompasses most of the area of the northeastern U.S. and northeastern Canada now being studied for acid rain effects. Quinn (personal communication, 1982) provided the regional data for Lake Ontario, which includes the western two-thirds of the Adirondack

region. Figure 2 contains a smoothed plot of that regional data in comparison with data from a set of five stations located in the central part of the Adirondack Park, centered in the area of our 1981 surface water reconnaissance study. The close correspondence of the regional and park data is readily apparent, despite the orographic effect that increases mean Adirondack precipitation above that of the region. It is apparent that increased precipitation, hence increased flushing of naturally organic soils, wetlands, and forest floors, is present in the Adirondack region as well as in the Lake Ontario basin as a whole since about 1940. The difference in mean precipitation during the first four decades of the century in contrast to that of the last four is coupled with the substantial changes in land use and the amount of organic matter in the path of precipitation falling on and moving through watersheds to surface waters. It is to be expected that such concurrent changes would produce increased surface water acidification even in the absence of other contributing factors.

The soils of the Adirondack region are most commonly podzols, acidic soils that produce a low pH in waters passing through them. The characteristics of podzol soils and their effect on through-flowing waters has been reviewed most recently by Krug and Frink (1983). Such soils are enormous reservoirs of hydrogen ion and are quite resistant to further increases in acidity by acid precipitation. The mean hydrogen ion concentration of our twelve soil zone and shallow ground water samples is 73 microequivalents (pH = 4.13); without the two samples in which water was discharging from zones containing carbonate rocks, the hydrogen ion concentration was 88 microequivalents (pH = 4.06). Heimburger (1934) examined 264 soil samples from the Adirondack region and found

that 79 percent had a pH of 5.0 or less. Our examination of soil:water measurements relative to raw organic carbon shows a very strong positive correlation of hydrogen ion to organic carbon. Thus, the water passing through organic-rich podzol soils is strongly buffered to a low pH by organic acids, providing a regionally widespread mechanism for surface water acidification. These acid soils are themselves only minimally susceptible to degradation by acid deposition because of their large reservoir of hydrogen ion (Frink and Voight, 1977; Wiklander, 1973-74; Krug and Frink, 1983). Instead they are a large acidic buffering component in the hydrogeochemical system.

In the surface water reconnaissance study, Everett et al. (1983) found indications that ground water oxidation of sulfide minerals in soils, glacial sediments, and bedrock is contributing to the sulfate loading of Adirondack surface waters. Pyrite and pyrrhotite are sulfides of common occurrence in the Adirondack region and gossans, frequently referred to as "rusty gneisses," are present in a number of localities associated with elevated sulfate levels in water discharging from rock fractures and soil horizons. Twice in the past, the region was considered to have the nation's largest reserves of sulfur in case of national emergency.

In the forty lakes and ponds that we surveyed, sulfate and hydrogen ion are negatively correlated (that is, as sulfate increases, hydrogen ion tends to decrease). That is the opposite relationship to that in the region's rainfall and opposite to what would be expected if surface water acidification were the result of incident rainfall. Our study, made under autumn heavy rainfall conditions, should have encountered maximum rainfall-sulfate relation-ship. In fact, we found a complex situation in which ground water oxidizes

sulfides, producing sulfuric acid which subsequently reacts with other rock-forming minerals and is neutralized. The statistical correlation of sulfate to alkalinity is positive for both the soil-zone and ground water discharge samples and for shallow, internally-drained ponds perched in glacial till. The latter were the waters thought to be most likely to be affected by acid precipitation at the outset of the study. In several cases, it appears that the oxidation reaction was followed by rapid discharge of the acidified waters before neutralization of the sulfide-derived acid, thus the water is acidic in part as a result of the ground water-induced sulfide oxidation process.

Among the various terrestrial environments sampled were some of the Adirondacks' many wetlands. In all of the nine pairs of water samples taken from streams flowing through wetlands, the hydrogen ion concentration was higher in the downstream sample. The increases ranged from 0.2 to 0.8 pH units, showing that water passing through the very extensive wetland areas along streams, lakes, and ponds in the Adirondacks increases in hydrogen ion concentration. In addition to being areas of lush organic growth, these wetlands are also frequently areas of soil zone and ground water discharge.

Fisheries management practices in the Adirondacks have changed substantially during the past twenty-five years with the result that many fewer fish are planted (Figure 3). One major reason given for the reduction in planting was that the planted trout did not successfully reproduce in numerous acidic Adirondack waters. This reduction in fish planting is coincident with the reported reduction in available fish in Adirondack ponds and lakes during a period of heavy recreational fishing pressure, as reflected in part in the data on public campground use (Figure 4).

An additional complicating factor that may have had serious adverse consequences to fisheries, the food-chain, and the development of chronic toxicity in various organisms, was extensive use of DDT to suppress the population of black flies and other biting insects in the Adirondacks. We found that DDT and its metabolites are present in concentration ranging from tenths to several parts per million, concentrated primarily in the surface organic layer of soils. Organic-rich lake sediments also contain DDT metabolite residues in smaller concentrations. Soil pH's are lower than adjacent water pH's for the DDT-containing samples, thus it is quite possible that DDT metabolites are remobilized into the food chain as they are eroded from the soil profile into higher-pH surface waters. Based on the ratio of DDT metabolite isomer, O,P'-DDT to P,P'-DDT, we are of the opinion that the DDT is aged and has undergone extensive metabolic transformation, thus it is not of recent origin, but is the residuum of the extensive 1950's and 1960's period of heavy use.

Conclusion

Using a related set of studies of the history of Adirondacks land use, surface water chemistry, and fisheries management practices (Duhaime et al., 1983; Everett et al., 1983; Retzsch et al., 1982; A. G. Everett, unpublished data), it can be seen that the surface water acidification processes in the Adirondacks are much more complex than simply the deposition of man-made and natural atmospheric acids. The complexly interrelated components of the terrestrial portion of the hydrogeochemical system will take quite a bit of additional study before the relationships, and their variability in time and

space, can be worked out. Only then can the actual amount of surface water effects caused by the atmospheric acidic deposition be determined. Although the picture of a complex interrelated hydrogeochemical system has been sketched here only for the Adirondack region, similar patterns are emerging for parts of New England, Scandanavia, the New Jersey Pine Barrens, and other areas originally believed to be extensively adversely affected by acid precipitation.

It has taken time to develop an understanding of the interrelationships of hydrogeochemical systems, a complexity either not recognized or else ignored in many of the early reports that have influenced widespread political reaction. Now we find that preemptory political dicisions are moving in directions divergent from the accumulating scientific information. Such expedient political decisions, taken in the absence of understanding about what will produce actual ameliorative effects, is doomed to be wasteful and ineffective. Should such action also be accompanied by decreased research emphasis on still unknown relationships, it is probable that the long-term situation will be worsened rather than improved.

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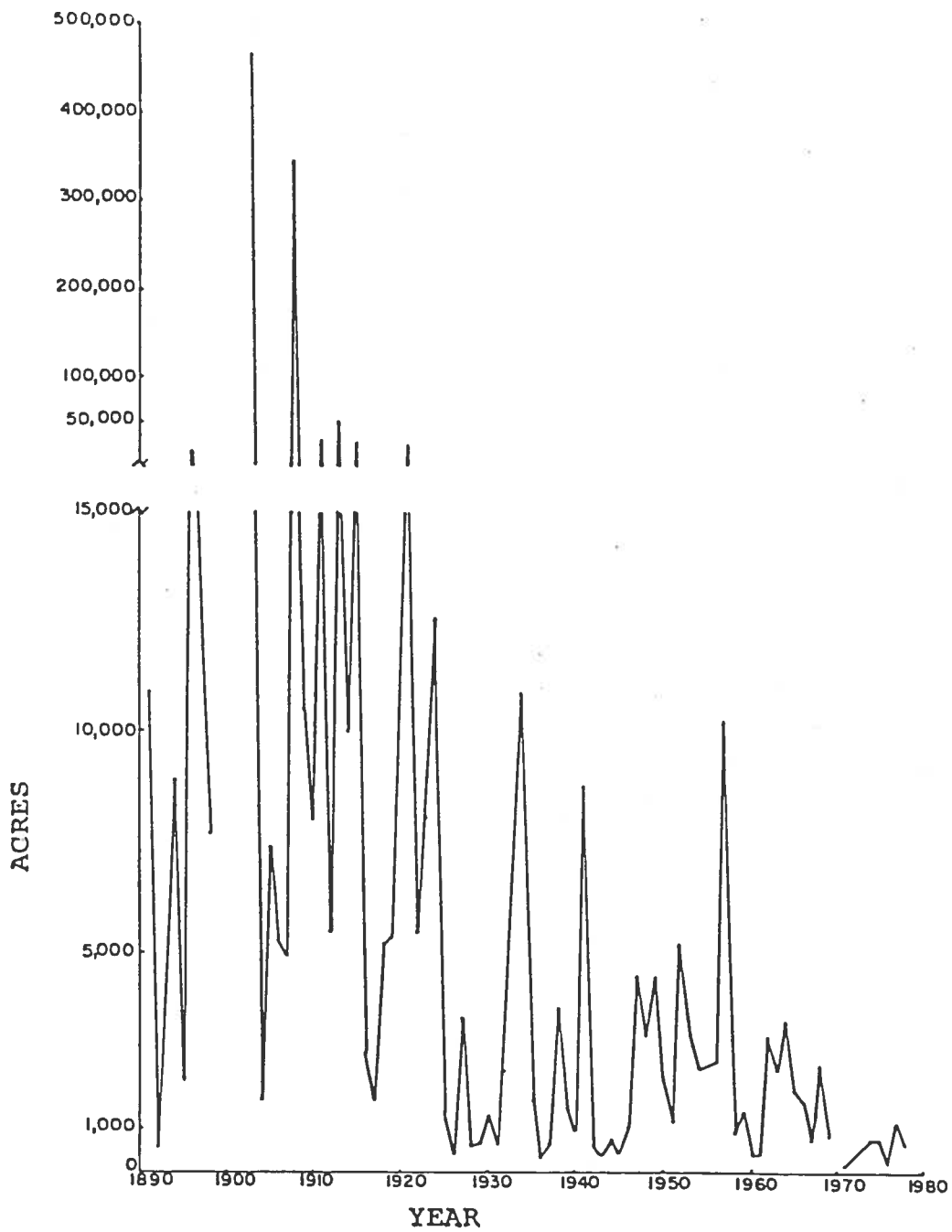
FIGURE 1.   ANNUAL ACREAGE BURNED BY FOREST FIRES IN ADIRONDACK
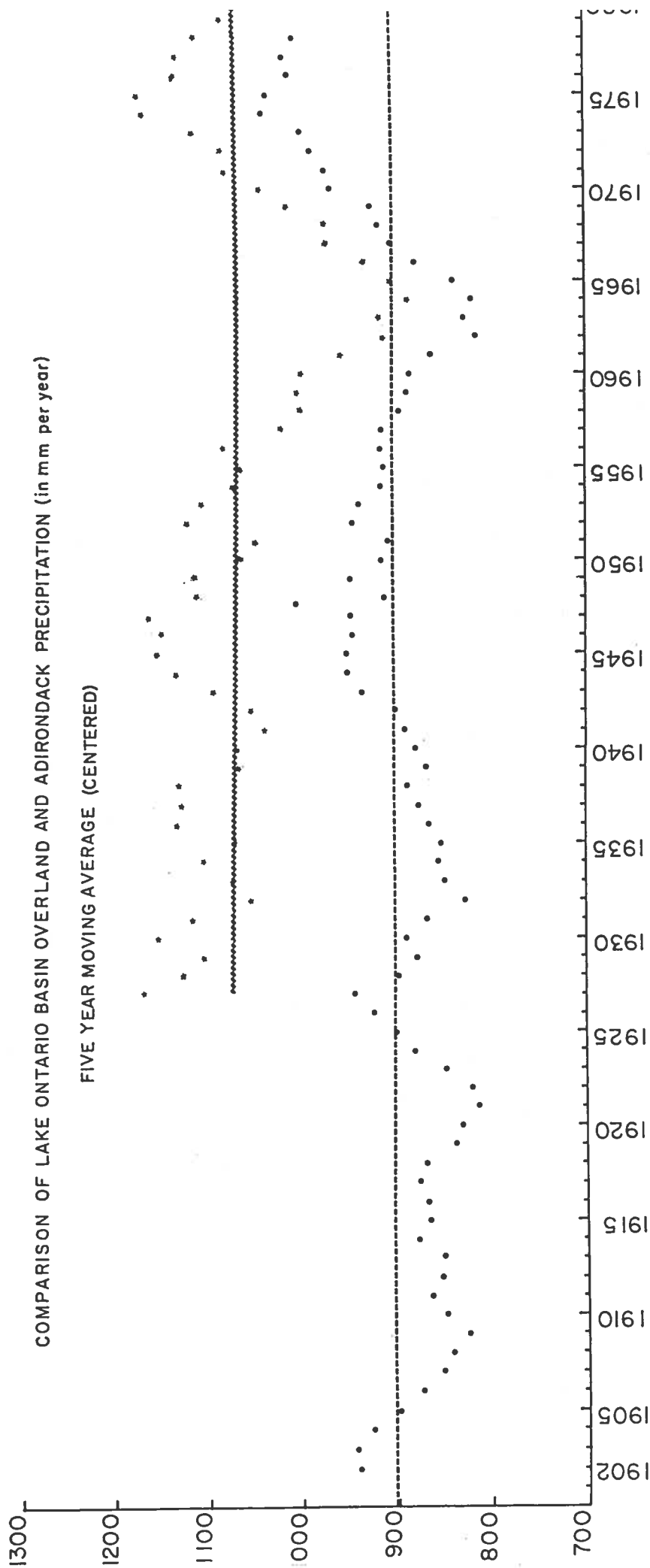   COUNTIES (1891 - 1978).

Source: Duhaime et al., 1983

COMPARISON OF LAKE ONTARIO BASIN OVERLAND AND ADIRONDACK PRECIPITATION (in mm per year)

FIVE YEAR MOVING AVERAGE (CENTERED)

------ REGIONAL ANNUAL MEAN PRECIPITATION 902 mm (1900-1980)
∿∿∿∿ ADIRONDACK ANNUAL MEAN PRECIPITATION 1072 mm (1925-1981)
• REGIONAL FIVE YEAR MOVING AVERAGES (1902-1978) (from Quinn, personal communication 1982)
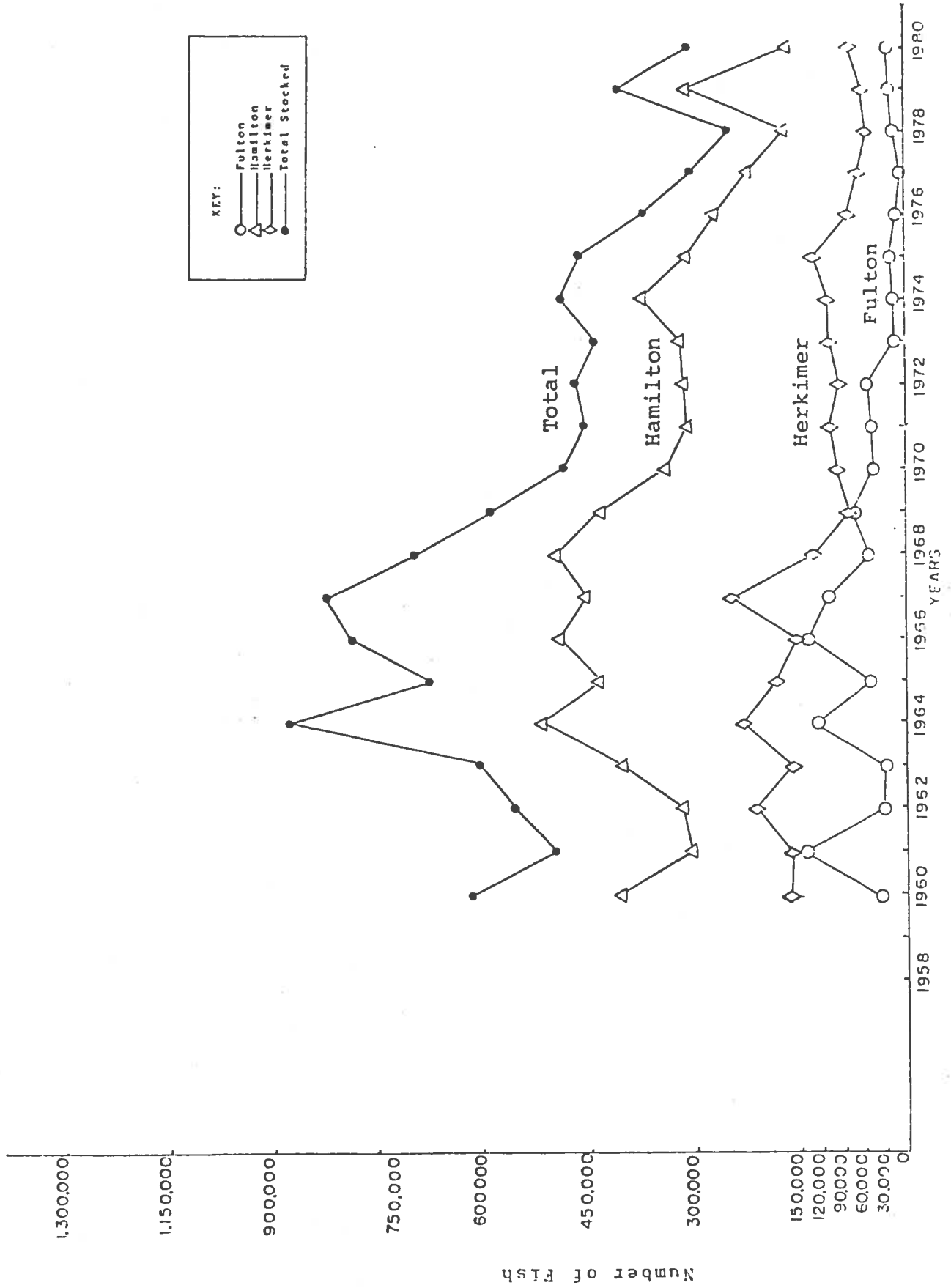★ ADIRONDACK FIVE YEAR MOVING AVERAGES (1927-1979)

FIGURE 2.

FIGURE 3. NUMBERS OF FISH STOCKED ANNUALLY IN
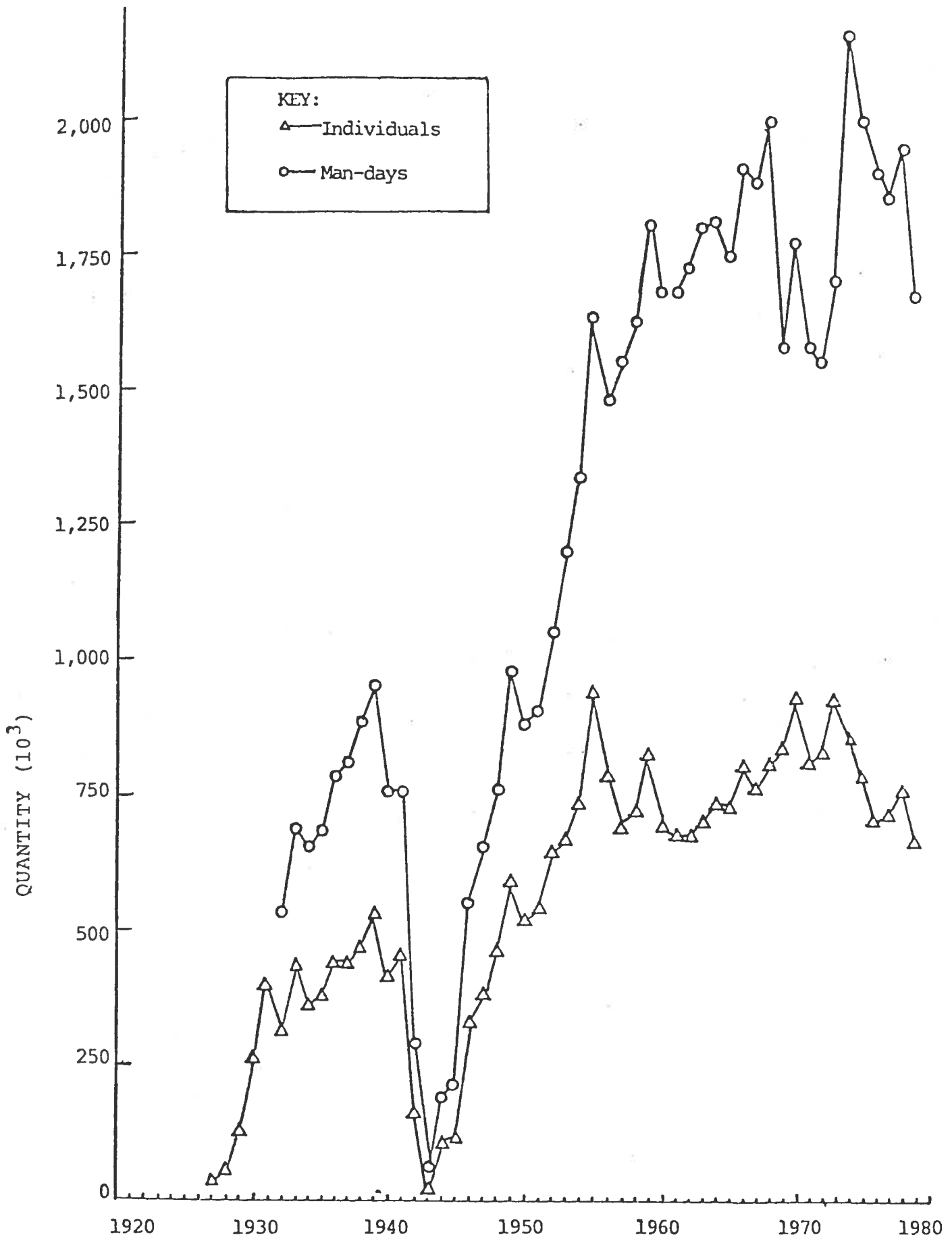LAKES AND PONDS IN THREE ADIRONDACK COUNTIES

Source: Retzsch et al., 1982

FIGURE 4.   ADIRONDACK PUBLIC CAMPGROUND OCCUPANCY (1927 - 1979)

Source: Retzsch et al., 1982