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UNITED STATES ENVIRONMENTAL PROTECTION AGENCY
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GEOLOGICAL AND HYDROCHEMICAL SENSITIVITY OF THE EASTERN UNITED STATES TO ACID PRECIPITATION

by

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ABSTRACT

A new analysis of bedrock geology maps of the eastern U.S. constitutes a simple model for predicting areas which might be impacted by acid precipitation and it allows much greater resolution for detecting sensitivity than has previously been available for the region. Map accuracy has been verified by examining current alkalinities and pH's of waters in several test states, including Maine, New Hampshire, New York, Virginia and North Carolina. In regions predicted to be highly sensitive, alkalinities in upstream sites were generally low, $<200\ \mu eq/\ell$. Many areas of the eastern U.S. are pinpointed in which some of the surface waters, especially upstream reaches, may be sensitive to acidification. Pre-1970 data were compared to post-1975 data, revealing marked declines in both alkalinity and pH of sensitive waters of two states tested, North Carolina, where pH and alkalinity have decreased in 80% of 38 streams ($\rho < .001$) and New Hampshire, where pH in 90% of 49 streams and lakes has decreased ($\rho < .001$) since 1949. These sites are predicted to be sensitive by the geological map on the basis of their earlier alkalinity values. Thus this mapping of sensitive areas is validated by the observed temporal trends. The map is to be improved by the addition of a soils component.

ACKNOWLEDGMENTS

The authors wish to thank Avis Newell for technical work in the field and laboratory; Fred Liotta, Susan Hall, Lisa Thurlow, Roland Dupuis and Marilyn Morrison for assistance in map preparation; and Ronnie Evans and Charlie Bores for data base management, data reduction, and computer graphics. We appreciate the generous cooperation and assistance by personnel of the Shenandoah National Park, the North Carolina Department of Inland Fisheries, and the New Hampshire Department of Fish and Game.

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I. INTRODUCTION

In recent decades, man's activities have led to significant changes in atmospheric and precipitation chemistry. Among these activities, metal smelting and combustion of fossil fuels have resulted in atmospheric emissions of sulfur and nitrogen oxides. The effect of these emissions has been a dramatic increase in the acidity of rainfall, particularly in areas downwind of major industrial areas. Although the phenomenon of acidic precipitation has been developing on a hemispheric scale, only recently have workers tried to identify those areas in the United States receiving acidic precipitation[16,71] and associated heavy metals.[67] While a reasonably good understanding of the sources and distribution of acid precipitation has been developed,[16,18,19,27,71,72,77] our understanding of the effects of acidic precipitation on terrestrial and aquatic systems is still fragmentary. Reductions of pH and alkalinity of lakes affected by acidic precipitation have been well documented, particularly in the northeastern United States, southeastern Canada, and Scandanavia. In these same areas, declines in fish populations and adverse effects on other aquatic fauna have been widely observed.[1,23,37,38,41,42,49,57,68,86,91,92,103,104]

Studies of the hydrobiological problems caused by acidic precipitation have been primarily qualitative. Biological aspects of the synoptic lake surveys in Sweden,[1] Norway,[49] Canada,[18] and the United States[90] have concentrated on changes in presence or absence of fish and in the kinds and numbers of species. Very little quantitative information is available concerning the effects of acidification on biomass. This is especially true for the bacteria, and other microorganisms. There is strong evidence indicating that processes such as phytoplankton production and microbial decomposition are inhibited, but quantitative data are scarce. Changes in the availability of inorganic nutrients and in nutrient recycling are hypothesized but have not been demonstrated; effects on food chains or webs are not well known, and no quantitative data are available concerning the effects on energy processing in natural aquatic ecosystems.

The overall objective of the sensitive areas project has been to evaluate the eastern United States and determine and map which areas are vulnerable to adverse impacts from acid precipitation. In addition, a review of the biological consequences of freshwater acidification is presented and a regional assessment of effects on fish, which provides a basis for predicting such impacts, is described.

A. Geologic Controls

Impact to aquatic ecosystems is largely based on the chemical characteristics of the bedrock. Limestone terrains yield "infinite" acid-neutralizing (buffering) capacity to acidic precipitation whereas granites (and related igneous rocks), their metamorphic equivalent, and noncalcareous sandstones yield minimal buffering. Several hundred common minerals comprise the huge variety of rocks which comprise the crust of the earth, the surficial overburden, and soils. Of interest in terms of susceptibility of a landscape to acidification from precipitation is the total capacity of the minerals, no matter what their configuration, to assimilate protons (H^+_{aq}). Specific considerations are solubility of the phases and the kinetics of solution.

Certain minerals are soluble and rapidly dissolved but yield no buffering capacity, e.g.:

$$NaCl_{xl} = Na^+_{aq} + Cl^-_{aq} \qquad K_{sp} = 10^{+1.58} = [Na^+]\,[Cl^-] \qquad (1)$$

Others are relatively insoluble and yield no buffering capacity, e.g.

$$SiO_{2_{xl_{quartz}}} + 2H_2O_{aq} = H_4\,SiO_{4_{aq}} \quad K_{sp} = 10^{-4.0} = [H_4SiO_4] \qquad (2)$$

Common rock forming minerals, when placed in water, yield pH's in excess of 7 (commonly in excess of 8) but the kinetics are sufficiently slow so that the total potential H^+ consuming capacity of these minerals is not realized, e.g.:

$$2NaAlSi_3O_{8_{xl_{albite}}} + 2H^+_{aq} + 9H_2O_{aq} = \qquad (3)$$

$$= 2Na^+_{aq} + Al_2Si_2O_5(OH)_{4xl_{kaolinite}} + 4H_4SiO_{4_{aq}}.$$

$$K_{sp} \simeq 10 \simeq \left[[Na^+]^2/[H^+]^2\right]\left[H_4SiO_4\right]$$

Assuming an initial pH of 4.0 and buffering from the $CO_2 - H_2O$ system ($HCO_3^- \simeq 10^{-5.7}$), the expected pH after complete reaction would be approximately 12. This is never achieved.

Additional H^+ sinks available in soils include Al and Fe hydroxides and silicates, e.g.:

$$Al_2Si_2O_5(OH)_{4xl_{kaolinite}} + 6H^+_{aq} = 2Al_{aq}^{+3} + 2H_4SiO_{4_{aq}} + H_2O_{aq} \qquad (4)$$

$$Al(OH)_{3xl_{gibbsite}} + 3H^+_{aq} = Al^{+3}_{aq} + 3H_2O_{aq} \qquad (5)$$

$$FeO(OH)_{xl_{geothite}} + 3H^+_{aq} + e^- = Fe^{+3}_{aq} + 2H_2O_{aq} \qquad (6)$$

These minerals are either developed in sub-soils (B-horizon) in young soils (and thus not necessarily available to overland flow) or dominate in mature/old soils where they may provide extensive acid neutralizing capacity.

The most important mineral for neutralizing acidic waters is calcite (or nearly any other carbonate mineral). The solution at low and at intermediate pH of this mineral is given by:

$$CaCO_3 + 2H^+_{aq} = Ca^{++}_{aq} + H_2CO_{3aq} \qquad \text{at low pH and} \qquad (7a)$$

$$2CaCO_3 + 2H^+_{aq} = 2\ Ca^{++}_{aq} + 2HCO^-_{3aq} \qquad \text{at intermediate pH} \qquad (7b)$$

Further addition of acid to the resulting (7b) solution ($2Ca^{++} + 2HCO_3^-$) will result in the protenation of the HCO_3^-:

$$HCO^-_{3aq} + H^+_{aq} \qquad H_2CO_{3aq} \qquad (8)$$

These reactions (7 and 8) are rapid and for each mole of $CaCO_3$ consumed, 2 moles of H^+ are consumed before the pH is reduced significantly below 5. Reactions, 4, 5, and 6 or similar reactions consume large amounts of H^+ ions at pH's below 5 and may be the primary acid-consuming mechanism for very acidic solutions. They do not contribute HCO_3^- for buffering except by virtue of the dissociation of H_2CO_3 as the pH is raised by the reactions:

$$H_2CO_{3aq} \rightarrow H^+_{aq} + HCO^-_{3aq}.$$

The amount of HCO_3^- produced will be a function of the total CO_2 in the system. It should be noted that the gain or loss of molecular CO_2 to the water, by itself with no addition of cations to balance HCO_3^- production, will not change alkalinity although pH does change.

Thus we have a spectrum of response of minerals (and rocks) to the changing acidity of atmospheric precipitation. Accordingly, rocks may be classified by the buffering capacity or acid-neutralizing capacity which they render to surface waters.

Additional controls on acidification of aquatic ecosystems include: hydrologic characteristics of the terrain (i.e. overland flow versus groundwater flow, soil porosity/permeability, residence time of water in the soil, distribution of precipitation through time, type of precipitation, thickness of soil), types of soils (residual, glacial [till, ice-contact stratified, etc.], aeolian, lacustrine, alluvial, etc.), minerology and age of soil.

Any prediction about the vulnerability of a terrain to acidification from precipitation based solely on bedrock geology must be tempered with consideration of these other factors. For example, Florida is underlain by highly calcareous and phosphatic rocks suggesting that acidification of lakes and streams is highly unlikely. However, many of the soils (particularly in northern Florida) are very mature, highly leached of $CaCO_3$ and as a result, acidification of some lakes with minimal deep groundwater influx has occurred (P. Brezonik, pers. comm. 1979). Conversely, there are areas in Maine underlain by granite and receiving precipitation with an average pH of about 4.3[78] where lakes have not been acidified because of lime-bearing till and marine clay in the drainage basins of the lakes.

B. Mapping of Areas Sensitive to Acid Precipitation.

Other investigations[33,64,71] have defined areas of the United States and Canada as susceptible to impacts from acidic precipitation, from interpretations of large-scale geologic maps. These areas were largely concentrated in Precambrian terrains (the Canadian shield, the Adirondack Massif), the Precambrian core of the Appalachian Mountains, and in younger igneous rocks of the Northwest and Rocky Mountains.

In the United States surface waters acidified from atmospheric deposition have now been identified from New England and New York to Florida, and in the Boundary Waters Canoe Area, Minnesota. Acidic precipitation exists (with pH < 5.6) in all states contiguous to the Mississippi River and east to the Atlantic Ocean[78] as well as in California[72] and in Washington.[6] Because of this widespread aspect of acidic precipitation, it is important to understand the natural characteristics of the landscape which render an area's aquatic ecosystems susceptible to impact. Three major factors can be identified as important. They are: meteorology, pedology, and geology. This report stresses the geological control of sensitivity.

C. Water Quality Data Collection.

The utility of the geologically-based maps of sensitive areas is limited by the accuracy with which they identify areas in which surface waters are actually sensitive. We define sensitive waters as those with alkalinity values less than 500 μeq (micro equivalents) of alkalinity per liter. The accuracy of the maps was checked against actual measurements of lake and stream water chemistry.

Data from existing records in many states of the eastern U.S., from the STORET system, and from field measurements conducted in New Hampshire and North Carolina in 1979 are combined in the Acidification Chemistry Information Database (ACID) at Brookhaven National Laboratory. Data is registered by state, county, station code, station name, data source code, latitude, longitude, and sample date. Data sets include pH, alkalinity (μeq/l), Ca (μeq/l), conductivity (microSiemens), color (mgPt) and fish status. Information on methods used for chemical determinations is also stored in ACID.

II. PREPARATION OF SENSITIVE AREAS MAP

An analysis of the vulnerability of aquatic ecosystems to acidification from precipitation must start with the bedrock geology. The scale of variability of rock types is such that one must literally look at the geology on a drainage basin basis to make predictions about individual lakes and streams. Igneous rocks normally have maximum dimensions less than 10 km. Folded/ faulted metasedimentary/sedimentary rocks may have essentially 1-dimensional distribution. Flat lying sedimentary rocks may be widely distributed but topographic relief commonly intersects many rock types over short distances.

Small amounts of limestone in a drainage basin exert an overwhelming influence on water quality in terrains which otherwise would be very vulnerable to acidification. Consequently, in the regional analysis of vulnerability, areas with intimate mixtures of rocks of varying acid neutralizing capacity have been classified according to the more influential rock types. Analysis of geologic terrain has been undertaken on the scale of the most recent state geologic maps (Table II-1). Rock formations have been classified according to their potential buffering capacity. This judgment was based on map explanations, various stratigraphic lexicons[61,62] and S. Norton's personal knowledge of the geology of areas.

Rock classification was as follows:

Type I - Low to no buffering capacity (labelled 1 on maps)
(Widespread impact from acidic precipitation expected.)
Granite/Syenite or metamorphic equivalent
Granitic gneisses
Quartz sandstones or metamorphic equivalent

Type II - Medium/Low buffering capacity (labelled 2 on maps)
(Impact from acidic precipitation restricted to first and second order streams and small lakes. Complete loss of alkalinity unlikely in large lakes.)
Sandstones, shales, conglomerates or their metamorphic equivalent (no free carbonate phases present).
High grade metamorphic felsic to intermediate volcanic rocks.
Intermediate igneous rocks.
Calc-silicate gneisses with no free carbonate phases.

Type III- Medium/High buffering capacity (labelled 3 on maps)
(Impact from acidic precipitation improbable except for overland run-off effects in areas of frozen ground.)
Slightly calcareous rocks.
Low grade intermediate to mafic volcanic rocks.
Ultramafic rocks.
Glassy volcanic rocks.

Type IV - "Infinite" buffering capacity (labelled 4 on maps)
(No impact to aquatic ecosystems.)
Highly fossiliferous sediments or metamorphic equivalents.
Limestones or dolostones.

Table II - 1 - States and scales of geologic maps used for preparing the maps of sensitive areas.

Alabama	1:500,000	Mississippi	1:500,000
Arkansas	1:500,000	Missouri	1:500,000
California	1:750,000	New Hampshire	1:250,000
Connecticut	1:500,000	New Jersey	1:250,000
Delaware	1:300,000	New York	1:250,000
Florida	1:3,125,000	North Carolina	1:500,000
Georgia	1:500,000	Ohio	1:500,000
Illinois	1:500,000	Oregon	1:500,000
Indiana	1:1,000,000	Pennsylvania	1:250,000
Iowa	1:500,000	Rhode Island	1:250,000
Kentucky	1:500,000	South Carolina	1:250,000
Louisiana	1:1,250,000	Tennessee	1:250,000
Maine	1:500,000	Vermont	1:250,000
Maryland	1:250,000	Virginia	1:500,000
Massachusetts	1:250,000	Washington	1:500,000
Michigan	1:2,500,000	West Virginia	1:250,000
Minnesota	1:1,000,000	Wisconsin	1:1,000,000

The development of vulnerability maps for 3 types of terrains are illustrated in several steps. Figure II-1a represents, unmodified, a tracing of all boundaries of geologic formations shown on part of the North Carolina state geologic map. This area is underlain by precambrian and possibly lower palezoic rocks which are highly folded, faulted and metamorphosed in the core of the Appalachian Mountains. Figure II-1b differs from II-1a in that boundaries between contiguous formations with comparable acid-neutralizing capacities are not shown. Figure II-1c is modified from II-1b by the smoothing of contacts, favoring rocks with higher buffering capacity, and the deletion of small areas or linear outcroppings of low buffer capacity rocks.

Figure II-2a represents, unmodified, a tracing of all boundaries of geologic formations shown on part of the New York state geologic map. This Precambrian terrain is characterized by high grade metamorphic rocks intruded by many igneous rocks, largely granitic. Figures II-2b and II-2c are developed by the same techniques as Figures II-1b and II-1c.

Figures II-3a, b and c represent similar development for a portion of the state of Tennessee in an area of dendritic drainage in flat-lying sedimentary rocks (western half) and valley and ridge topography in the highly folded paleozoic section (eastern half).

The state geologic maps already represent a smoothing and generalization of geologic boundaries. Most state maps utilized in this synthesis have been drawn at a scale of 1:250,000 or 1:500,000 from maps at a scale of 1:24,000 or 1:62,500 with the loss of much small detail. At a scale of 1:250,000 the largest geologic unit that is commonly deleted is approximately 0.2 miles in diameter or width.

"Zero"-dimensional rocks of this size (generally intrusions or erosional remnants of flat lying strata) will not normally affect the chemistry of a large number of streams or lakes. However, one-dimensional rock map units (generally the intersection of moderately to steeply dipping strata or dikes or metamorphic equivalents) commonly affect large numbers of primary and secondary streams and lakes which lie in topographic lows occupied by certain strata. Thus, thin limestones in the Valley and Ridge topographic province (Figure II-3a) may not be shown on a scale of 1:500,000 (and thus not on these maps) but may dominate the area's water chemistry and vulnerability to acidic precipitation.

The geologically based sensitivity maps have also been organized on a county basis to make these data compatible with existing data bases for soils, agriculture, forestry, and other land uses. (A new soils map, being prepared by a separate project[74] will also be organized on a county basis so analyses of county susceptibility to acidification of surface waters may be undertaken.) Each county in the study area states (Table II-1) was analyzed by planimetry for percentage of area underlain by rock types I and II. These data are shown for the Eastern United States in Figure II-4. Although individual drainage systems or lakes cannot be analyzed in this fashion, regions of high vulnerability can be identified. The first digit of the binary number for each county represents the percentage (0-9% = 0, 10-19% = 1 etc.) of rock type I in the county. The second digit represents a similar decade value for rock type II. For example the number 23 indicates that 20-29% and 30-39% of the county is underlain by rock types I and II, respectively. Rock types III and IV are not represented in these maps.

The predictiveness of the maps can be established by comparing the geology-based maps against surface water chemical data in areas receiving acidic precipitation as discussed in section III of this report or by looking at the biological response of aquatic ecosystem to acidic precipitation. A number of lakes in the Adirondack Mountains have been examined in terms of lake pH and fish populations,[92] as discussed in Section VI of this report, and a close correlation between the two was found. Figure II-5 depicts those lakes which have lost their fish populations and the rock type underlying the area. A geographic correlation exists between fish absence and the existence of rock types I and II in this region. Topography and orographic precipitation are factors contributing to the distribution of lakes in which fish are present or absent.

Correlations also exist between acidification of surface waters and bedrock geology (Section III) in a number of states and areas which have thin soils, including New England.[22] This suggests that bedrock geology exerts a very strong influence on the regional extent of acidification of aquatic ecosystems in response to atmospheric loading of acid. Regionally, soils and vegetative types are of secondary importance. However, locally, soils may overwhelm bedrock influences.

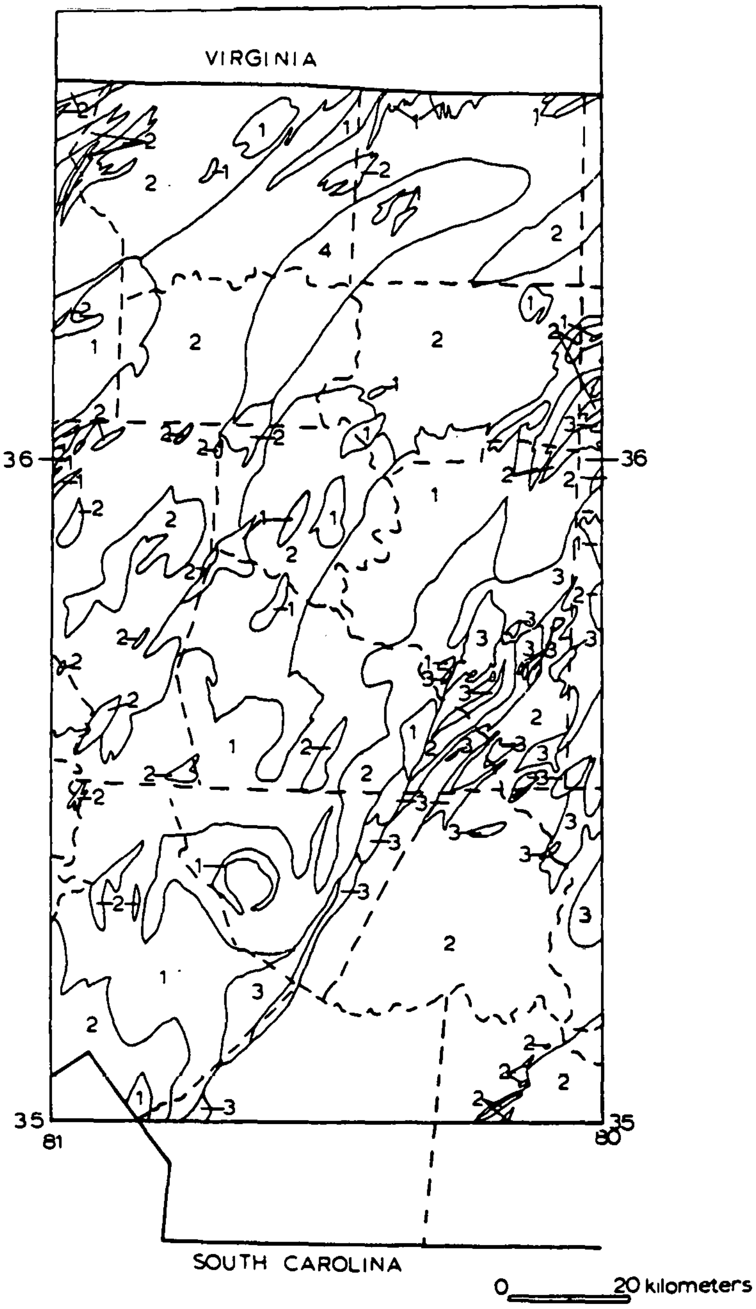


Figure II-1a. Unmodified Tracing of All Boundaries of Geologic Formations Shown on a Portion of the North Carolina State Geological Map. Numbers Refer to Buffering Classification

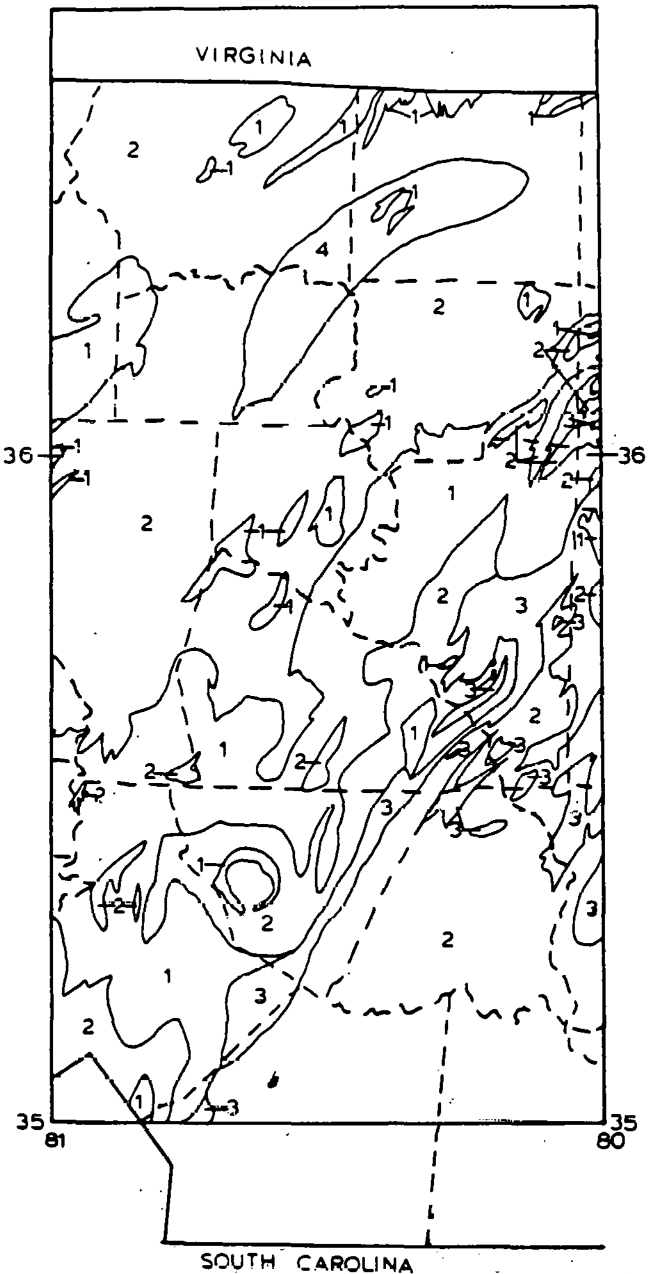


Figure II-1b. Boundaries of Rock Formations in North Carolina Having Comparable Acid-Neutralizing Capacities. Numbers Refer to Buffering Classification

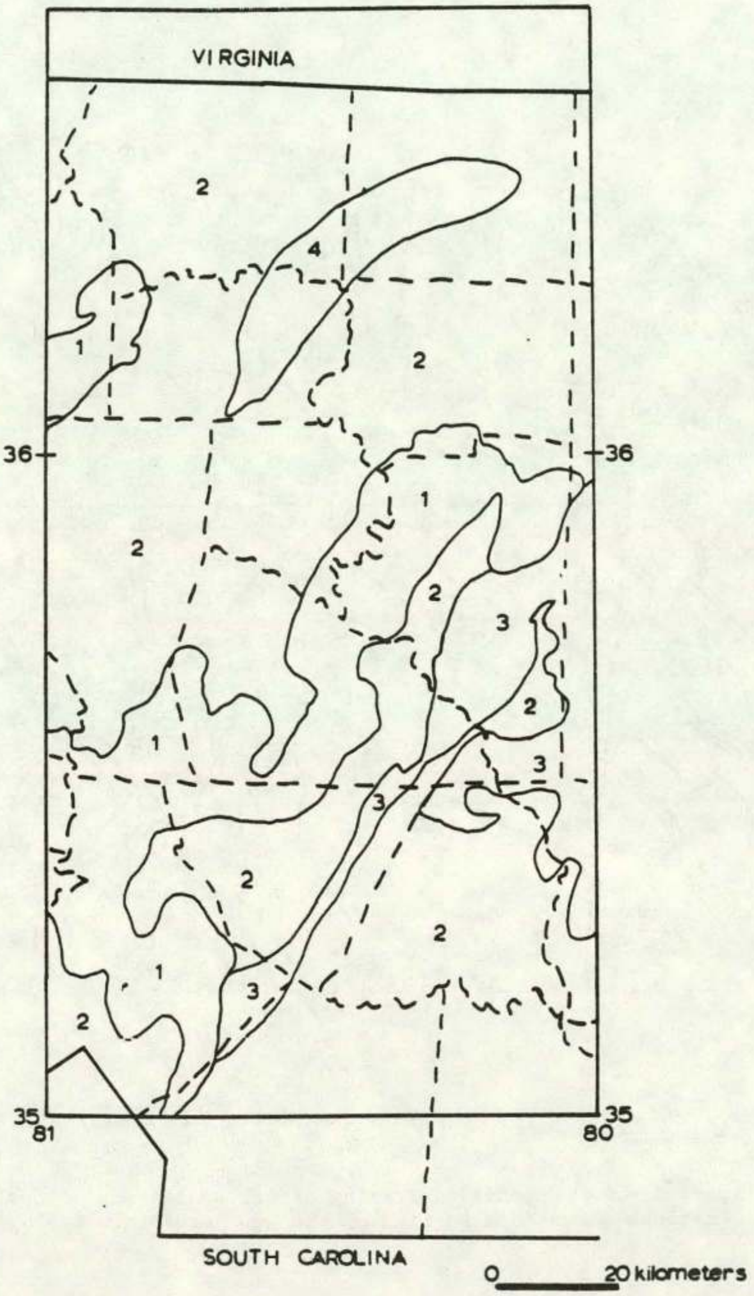


Figure II-1c. Smoothing of Geological Contacts Among Areas of Differing Acid-Neutralizing Capacities Shown in Figure II-1b. Numbers Refer to Buffering Classification

Figure II-2a. Unmodified Tracing of All Boundaries of Geologic Formations Shown on a Portion of the New York State Geological Map

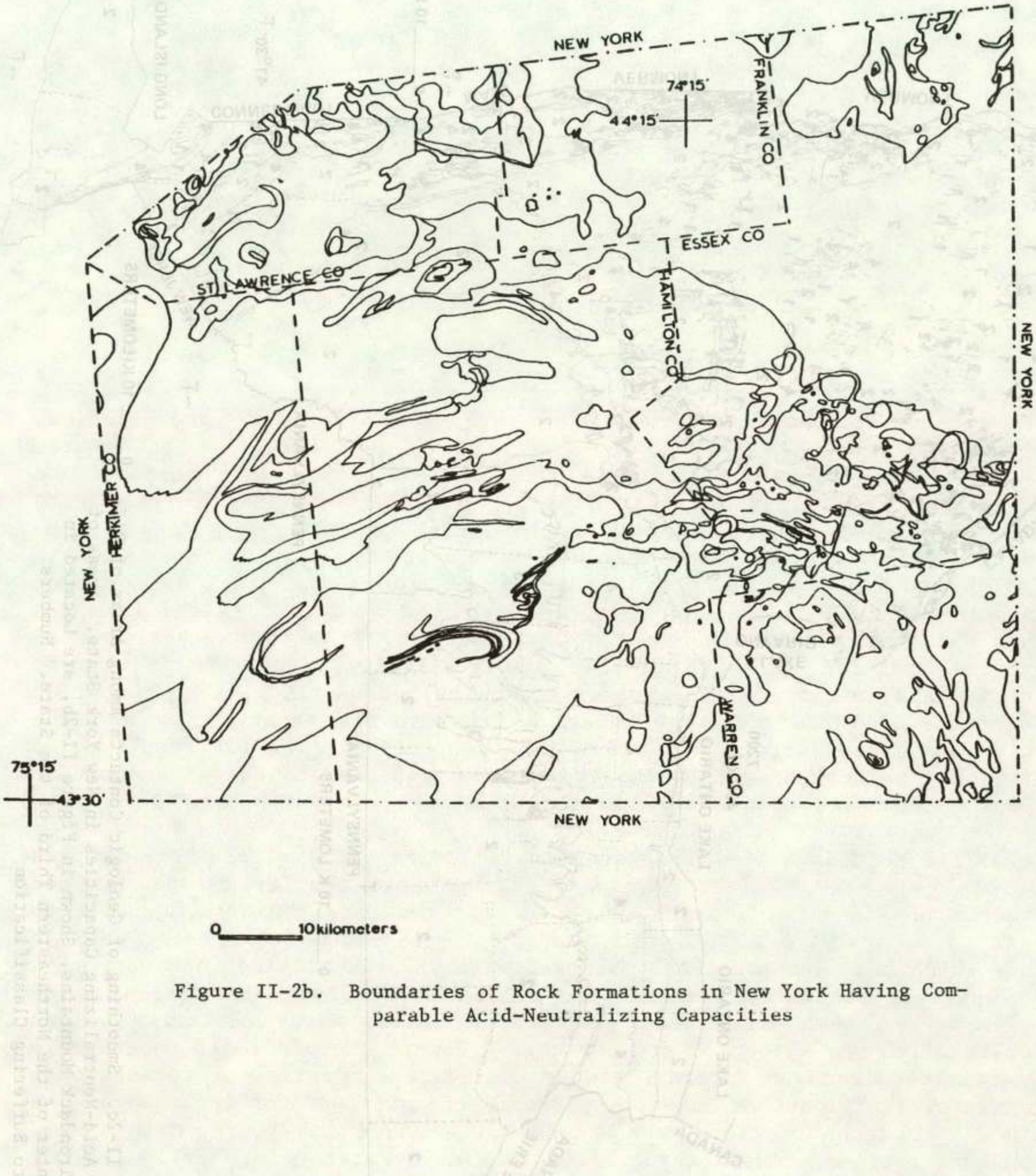


Figure II-2b. Boundaries of Rock Formations in New York Having Comparable Acid-Neutralizing Capacities

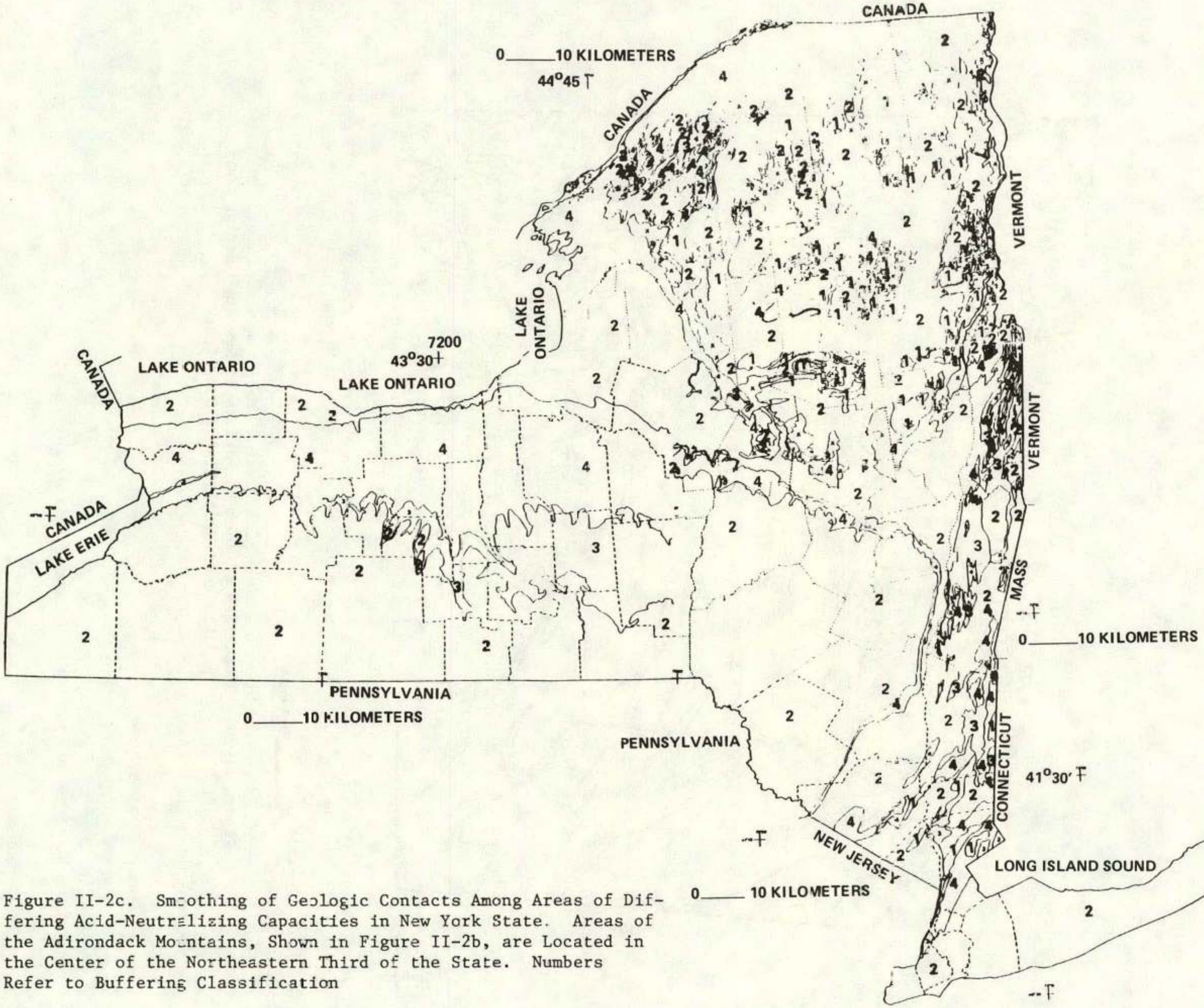


Figure II-2c. Smoothing of Geologic Contacts Among Areas of Differing Acid-Neutralizing Capacities in New York State. Areas of the Adirondack Mountains, Shown in Figure II-2b, are Located in the Center of the Northeastern Third of the State. Numbers Refer to Buffering Classification

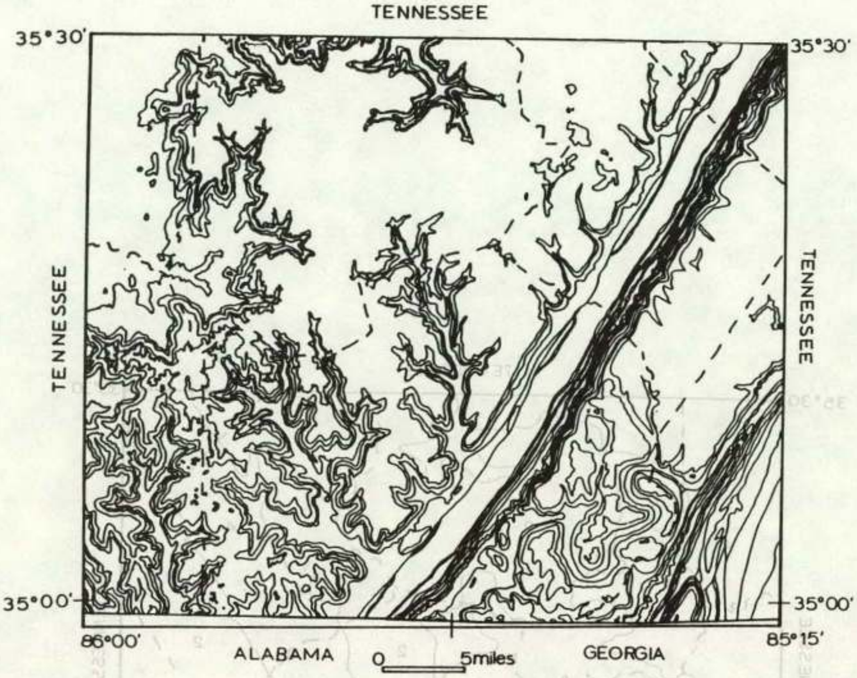


Figure II-3a. Unmodified Tracing of All Boundaries of Geologic Formations Shown on a Portion of the Tennessee State Geologic Map in a Region of Dendritic Drainage in Flat-Lying Rocks and Trellis Drainage in the Valley and Ridge Province.

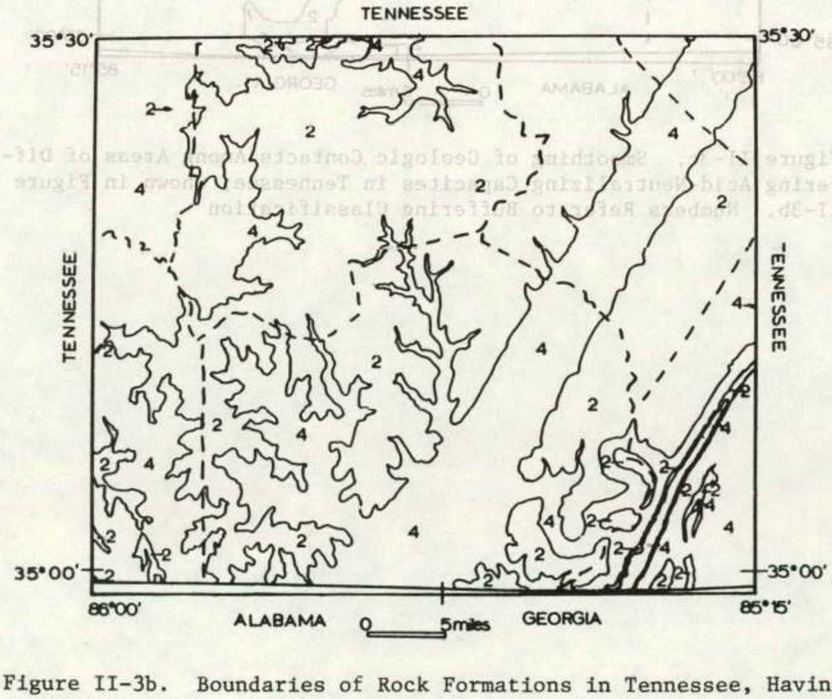


Figure II-3b. Boundaries of Rock Formations in Tennessee, Having Comparable Acid-Neutralizing Capacities, in the Same Region as Figure II-3a. Numbers Refer to Buffering Classification

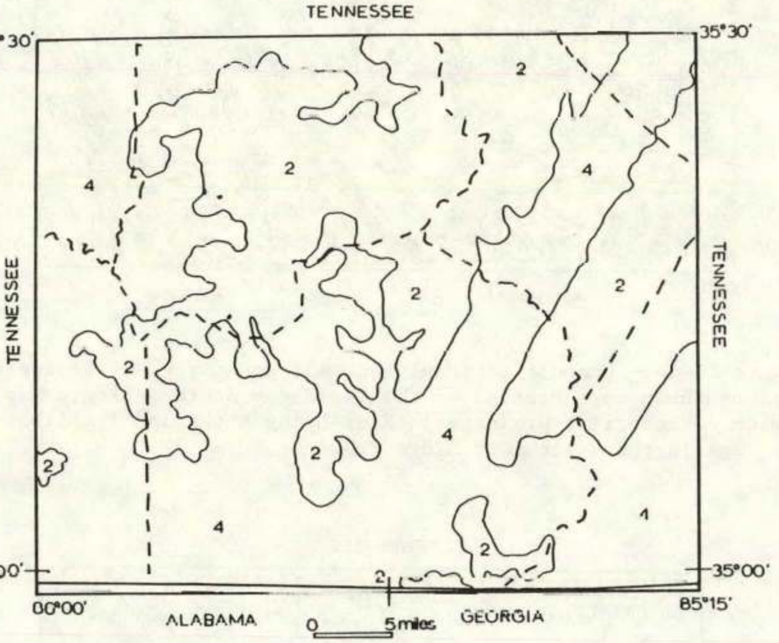
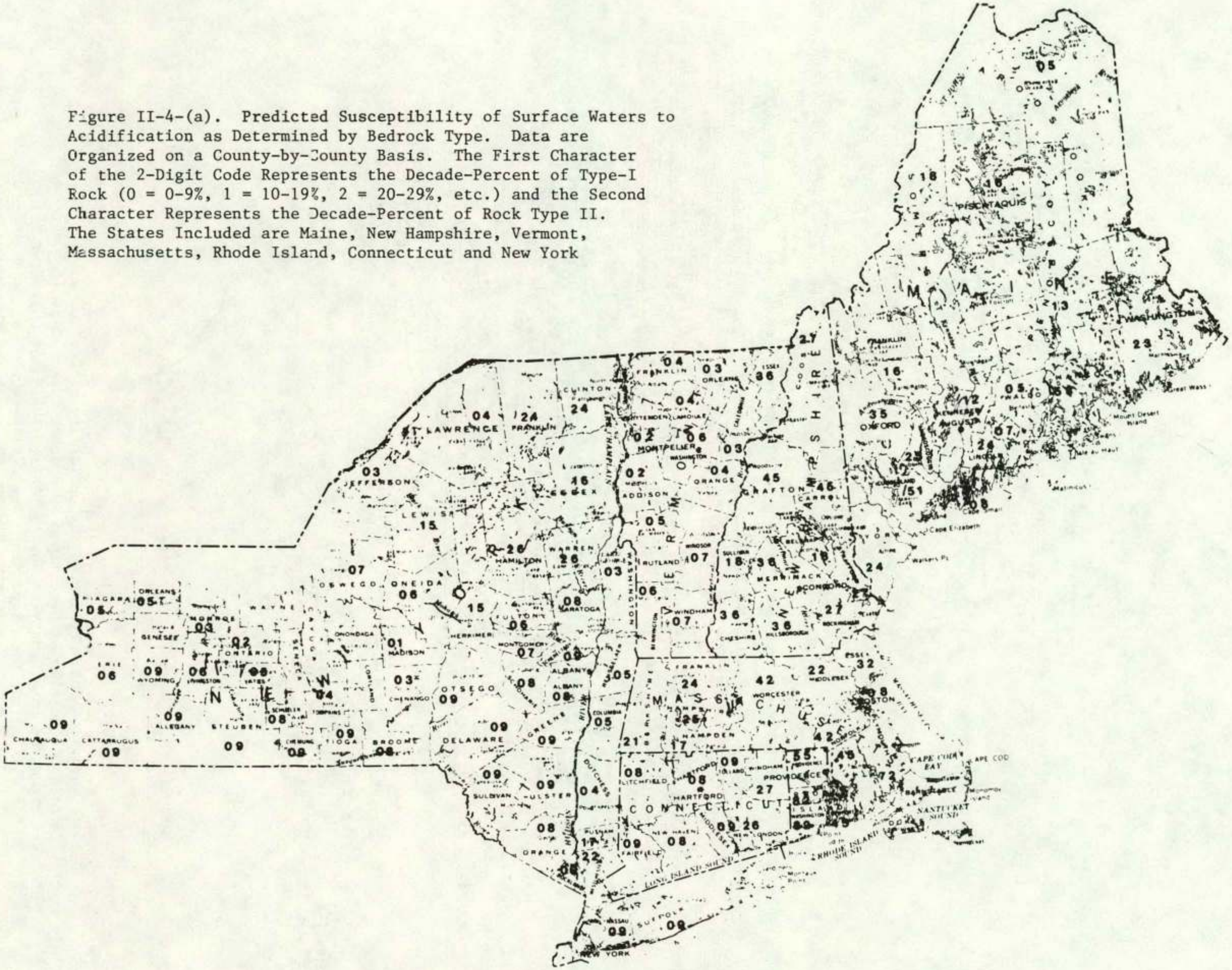


Figure II-3c. Smoothing of Geologic Contacts Among Areas of Differing Acid-Neutralizing Capacites in Tennessee, Shown in Figure II-3b. Numbers Refer to Buffering Classification

Figure II-4-(a). Predicted Susceptibility of Surface Waters to Acidification as Determined by Bedrock Type. Data are Organized on a County-by-County Basis. The First Character of the 2-Digit Code Represents the Decade-Percent of Type-I Rock (0 = 0-9%, 1 = 10-19%, 2 = 20-29%, etc.) and the Second Character Represents the Decade-Percent of Rock Type II. The States Included are Maine, New Hampshire, Vermont, Massachusetts, Rhode Island, Connecticut and New York



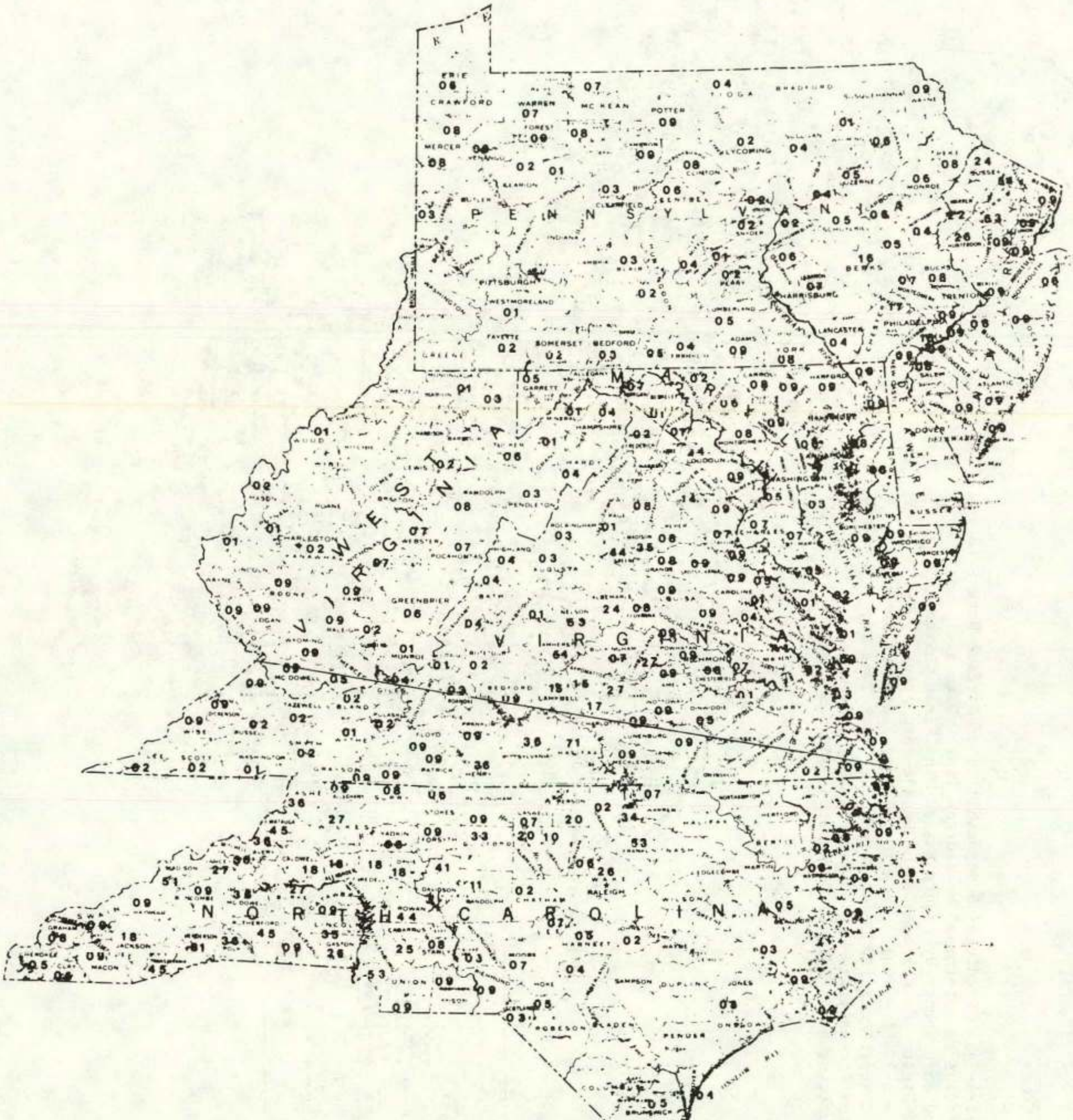


Figure II-4-(b). Predicted Susceptibility of Surface Waters to Acidification as Determined by Bedrock Type. Data are Organized on a County-by-County Basis. The First Character of the 2-Digit Code Represents the Decade-Percent of Type-I Rock (0 = 0-9%, 1 = 10-19%, 2 = 20-29%, etc.) and the Second Character Represents the Decade Percent of Rock Type II. The States Included are Pennsylvania, New Jersey, Delaware, Maryland, West Virginia, Virginia, and North Carolina

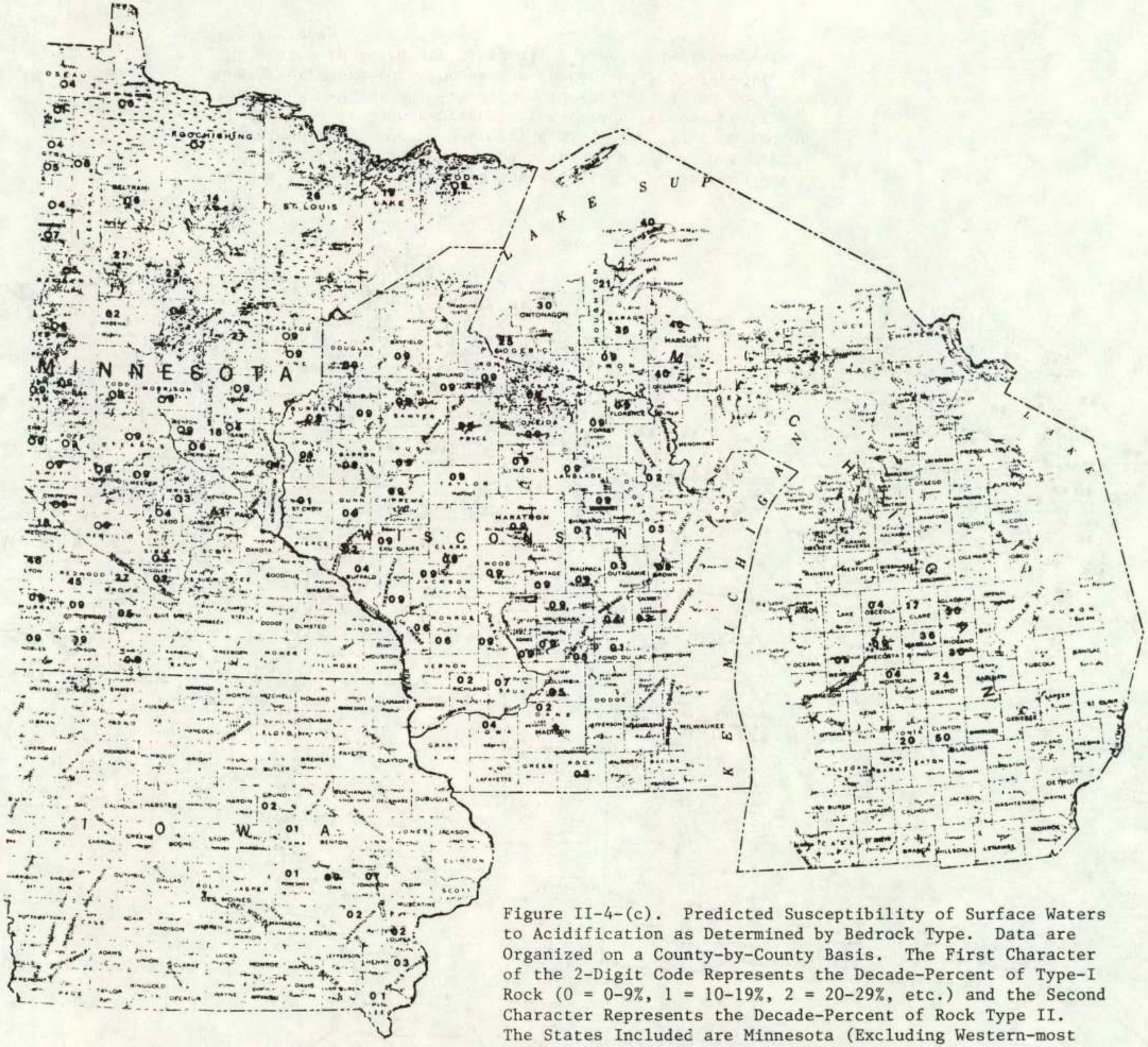


Figure II-4-(c). Predicted Susceptibility of Surface Waters to Acidification as Determined by Bedrock Type. Data are Organized on a County-by-County Basis. The First Character of the 2-Digit Code Represents the Decade-Percent of Type-I Rock (0 = 0-9%, 1 = 10-19%, 2 = 20-29%, etc.) and the Second Character Represents the Decade-Percent of Rock Type II. The States Included are Minnesota (Excluding Western-most Counties), Wisconsin, Michigan, and Iowa

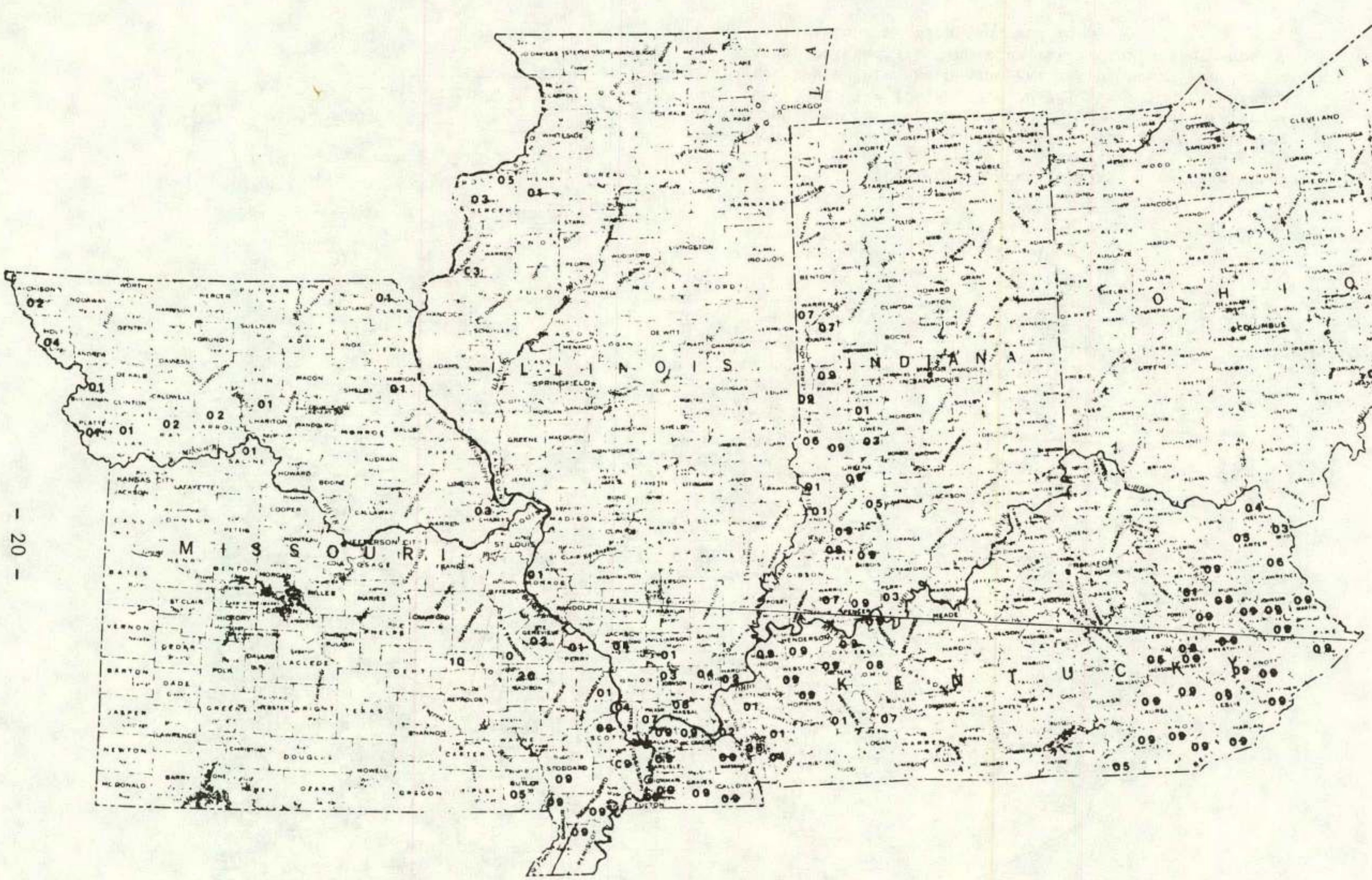


Figure II-4-(d). Predicted Susceptibility of Surface Waters to Acidification as Determined by Bedrock Type. Data are Organized on a County-by-County Basis. The First Character of the 2-Digit Code Represents the Decade-Percent of Type-I Rock (0 = 0-9%, 1 = 10-19 %, 2 = 20-29%, etc.) and the Second Character Represents the Decade-Percent of Rock Type II. The States Included are Missouri, Illinois, Indiana, Ohio, and Kentucky.

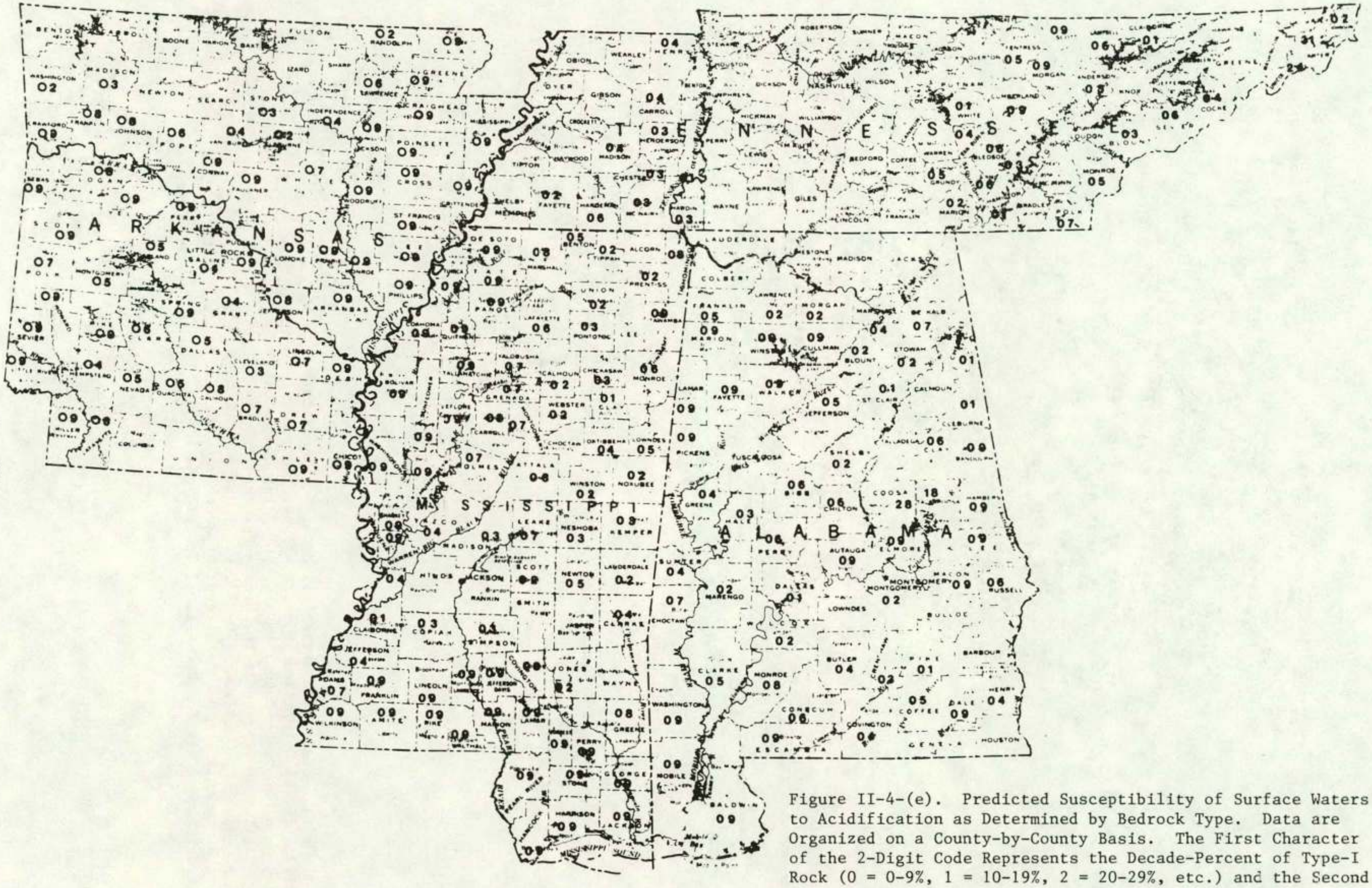


Figure II-4-(e). Predicted Susceptibility of Surface Waters to Acidification as Determined by Bedrock Type. Data are Organized on a County-by-County Basis. The First Character of the 2-Digit Code Represents the Decade-Percent of Type-I Rock (0 = 0-9%, 1 = 10-19%, 2 = 20-29%, etc.) and the Second Character Represents the Decade-Percent of Rock Type II. The States Included are Arkansas, Mississippi, Alabama, and Tennessee

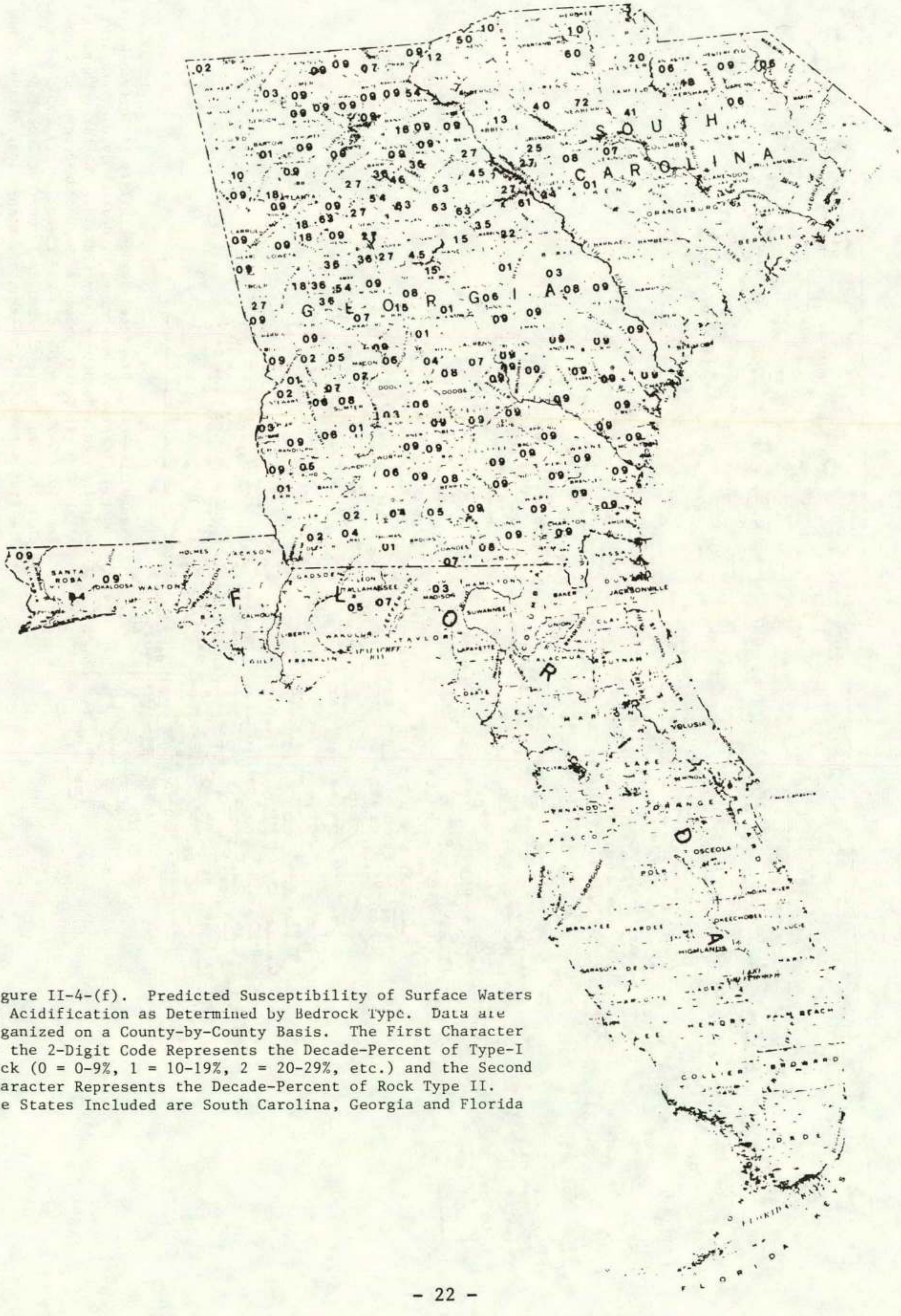


Figure II-4-(f). Predicted Susceptibility of Surface Waters to Acidification as Determined by Bedrock Type. Data are Organized on a County-by-County Basis. The First Character of the 2-Digit Code Represents the Decade-Percent of Type-I Rock (0 = 0-9%, 1 = 10-19%, 2 = 20-29%, etc.) and the Second Character Represents the Decade-Percent of Rock Type II. The States Included are South Carolina, Georgia and Florida

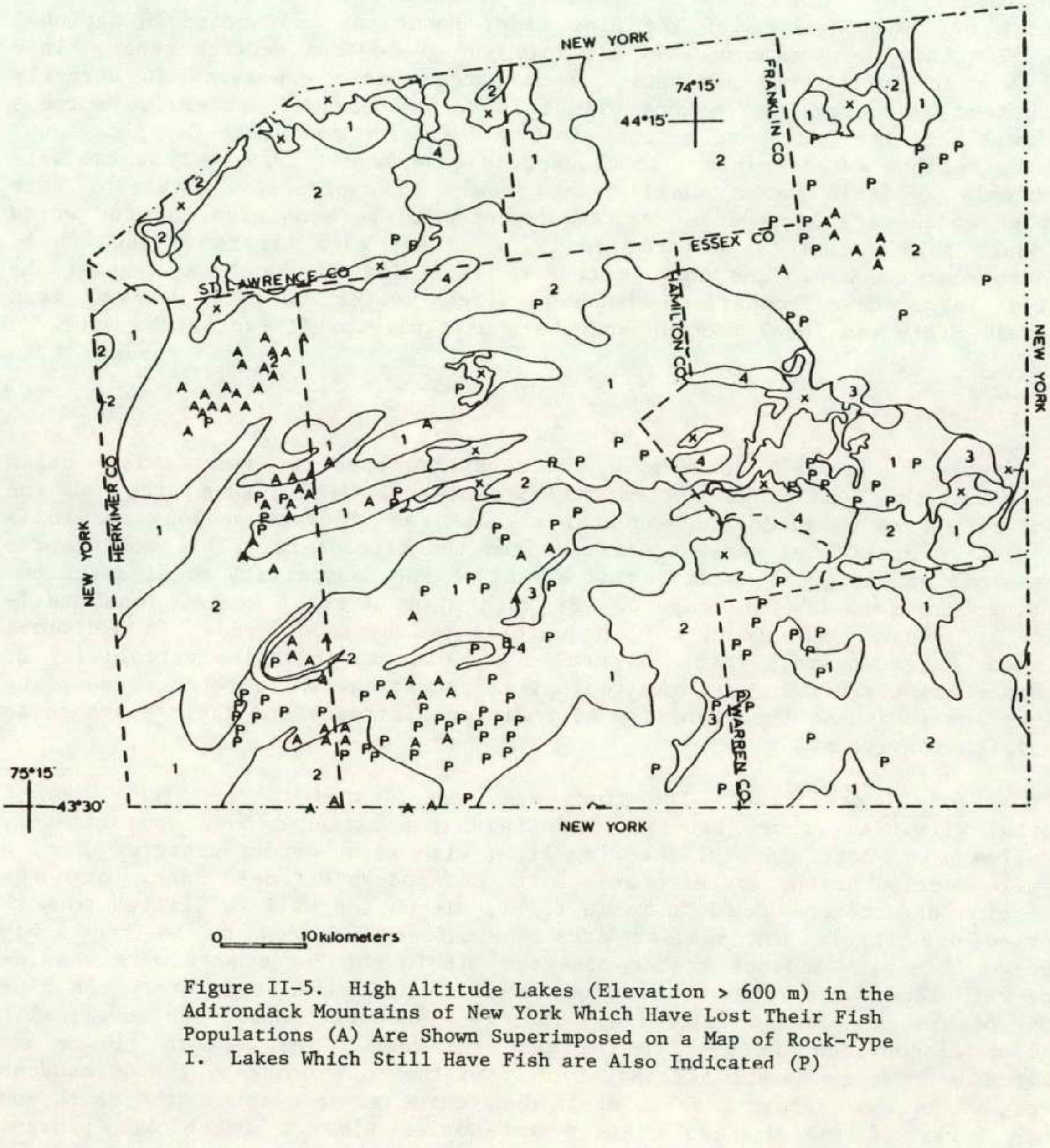


Figure II-5. High Altitude Lakes (Elevation > 600 m) in the Adirondack Mountains of New York Which Have Lost Their Fish Populations (A) Are Shown Superimposed on a Map of Rock-Type I. Lakes Which Still Have Fish are Also Indicated (P)

III. VERIFICATION OF THE SENSITIVE AREAS MAP

The usefulness of the geological delineation of sensitive areas is wholly dependent upon the accuracy with which the geological mapping identifies those areas correctly. To verify the accuracy of the maps, three types of studies were conducted covering geographic regions on three scales. First, an intensive investigation of small headwater streams along a seventy-five mile stretch of the ridgeline of the Blue Ridge Mountains in Shenandoah National Park, Virginia, were sampled over a variety of geological bedrock types. This work was to verify the assumption that stream water chemistry is strongly influenced by bedrock in regions with thin soils. Second, extensive surveys of low alkalinity lakes and streams in New Hampshire and North Carolina mountainous regions were conducted in the period June-August 1979 so that two sets of highly reliable water quality data would be available. Stations were sampled which were located in regions expected to be sensitive and for which we could obtain data taken prior to 1970. These data sets were then to be used to test the map. The third method of verifying the maps was a geographically large-scale comparison between stream water quality derived from Federal, State and local records and the sensitivity predicted by the maps.

A. Intensive Study

Within the overall context of the sensitive areas project, this section focuses on the Blue Ridge of central Virginia.[93] Within this area, pH and alkalinity were measured on headwater streams, and bedrock geology and soils data (where available) were determined from the literature. This work represents both an integrated example and a test of the sensitivity model described in other portions of this report. By working on a small scale, local variation in bedrock geology or soil properties can be considered. In addition, by sampling extensively within a small area, one can determine variability of stream chemistry within a single geological formation, while repeated sampling allows one to assess the stability of individual streams and their response to precipitation events.

1. Site Description. The study area was located in the Blue Ridge of central Virginia (Figure III-1). Sampling sites extended over approximately 75 miles along both sides of the ridgeline, with major effort centered along a 20 mile section at the southern end of the Shenandoah National Park. With the exception of data presented in Table III-1, discussion will be limited to work carried out within the smaller area (hereafter referred to as the study area). Chemistry/bedrock trends observed within the large area were consistent with those occurring in the study area. Within the study area, the Blue Ridge occurs as a single major ridge line 2500-4000 feet above sea level, with smaller discontinuous ridges to the east and west. The western slopes are drained by numerous small streams which feed the south fork of the Shenandoah River, while the eastern side is drained by three river systems, the north and south forks of the Moorman's River and Doyles River. Oak-hickory forest covers most of the study area, with pine and hemlock occurring in many of the deeper stream valleys. Nearly all of the sampling stations are in or adjacent to the Shenandoah National Park, and much of the area is designated as wilderness; thus human impact on stream chemistry is negligible.

Table III-1 pH and alkalinity of streams in major bedrock formations of the Blue Ridge in Central Virginia

Formation	Major Rock Type[a]	Age[b]	Number of Samples[c]	pH		Alkalinity (μeq/ℓ)[d]	
				mean	range	mean	range
Pedlar	granodiorite	pC	22	6.9	5.8 - 7.7	188	40 - 380
Catoctin	meta-basalt	pC	18	7.0	6.5 - 7.65	265	115 - 655
Lovingston	biotite quartz monzonite gneiss	pC	6	6.8	6.25 - 7.15	227	198 - 270
Marshall	biotite quartz monzonite gneiss	pC	3	7.0	6.8 - 7.0	254	205 - 305
Old Rag	granite	pC	9	6.5	5.7 - 6.8	96	39 - 195
Antietam	quartzite	C	10	5.7	5.25 - 6.1	7	-10 - 17.5
Hampton + Antietam	quartzite, shale	C	19	5.7	5.1 - 6.3	11	-5 - 35
various	limestone, dolomite	O	5	8.1	7.65 - 8.3	3600	3360 - 3950

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a) for a better description, refer to text

b) pC = Precambrian, C = Cambrian, O = Ordivician

c) number refers to number of sampling locations. Where samples were taken at one location on more than one date, an average pH and alkalinity for that location are used. Streams passing through more than one bedrock formation are not included in these calculations, except for streams passing through both the Hampton and Antietam formations.

d) 1 eq/ = .05 ppm $CaCO_3$

Soils within the study area fall into two groups; western slopes have coarse thin soils formed from weathering of sedimentary bedrock, while kaolinitic clays are present in large quantities in soils of the eastern slopes. In both cases, soil pH is low (4.5-5.5), and cation exchange capacity, percent base saturation, and organic content are low in all cases.[5,75,87]

Bedrock geology in the study area (Figure III-2a, 2b) and other areas of the Shenandoah National Park is based on the work of Gathright,[36] while bedrock in other parts of the survey area are based on Werner[97] and Bartholomew.[7] Within the study area, five major bedrock formations occur, these are listed below starting with the oldest and easternmost formation:

1. Pedlar Fm - Massive or layered granodiorite or quartz monzonite. Usually fine to medium-grained, composed largely of plagioclase and plagioclase-feldspars and quartz.

2. Catoctin Fm - Thick (2000 ft) beds or flows of metamorphosed basalt, composed primarily of feldspar in a matrix of chlorite, actinolite, epidote and pyroxene. Commonly includes cavities containing quartz and calcite.

3. Weverton Fm - Thin formation (100-500 ft). Pebbly quartzite beds cemented locally by iron oxides. Interlayered with phyllites.

4. Hampton Fm (Harpers) - Thick beds (1800-2200 ft) of metamorphosed sandstones and shale regularly interbedded, locally iron-cemented.

5. Antietam Fm - (Erwin) Thick (700-1000 ft) bedded, very resistant quartzite.

In general, the Pedlar and Catoctin formations occur in the eastern slopes of the Blue Ridge, while the three clastic rock formations are found on the western slopes. Exceptions occur at Madison Run and at the southern end of the study area; the significance of these will be discussed later.

In addition to these five formations, several others are found in the initial survey area:

1. Lovingston Formation - augen gneiss, in gradational contact with the Marshall Formation. Composed primarily of potassic feldspar, quartz, oligoclase-andesine, and biotite.

2. Marshall Formation - gray to green, medium grained gneissic granite, in gradational contact with the Pedlar Formation. Major constituents are potassic feldspar, quartz, oligoclase-andesine, and biotite.

3. Old Rag Granite - massive plutonic granite, in gradational or fault contact with the Pedlar Formation. Light gray in color, composed mainly of blue quartz and perthitic microcline.

4. Various Limestone and Dolomite Formations - light gray, mostly fine grained limestone and dolomite. Beds are a few inches to ten feet thick. Occurrence is at the base of the Blue Ridge in the Shenandoah Valley.

2. Methods and materials. Field samples were collected in 250ml polyethylene bottles and stored on ice until returned to the laboratory, then refrigerated until analysis. pH was measured potentiometrically in the field, temperature and conductivity were also measured in the field for each sample. For sequential sampling, samples were collected using an automatic sampler (model S-4040, Manning Environmental Corp.). These samples were stored on ice for return to the laboratory, and pH and conductivity were measured in the laboratory.

Alkalinity and acidity were determined using a double endpoint titration for alkalinity (to pH = 4.5 and 4.2) and single endpoint (pH = 8.3) for acidity.[3] Titrants were .005N HCl and .005 N NaOH for the respective procedures. Major cations were analyzed by atomic absorption spectrophotometry using an Instrumentation Laboratories 751 spectrophotometer. Major anions and silica were analyzed using standard procedures adopted for Technicon II Autoanalyzer.[32]

3. Results and Discussion. Alkalinity and pH data for the large survey area are summarized in Table III-1, while data for the smaller study area around Shenandoah National Park are presented in Figures III-3 and III-4. Soil chemistry and vegetation are generally similar throughout the survey area, and precipitation chemistry does not vary significantly in the survey area; mean annual pH is approximately 4.2.[34] Consequently, bedrock geology is interpreted to be the primary factor determining stream chemistry in Virginia Blue Ridge; this conclusion is carried through the remainder of this discussion.

Data presented in Table III-1 indicate a wide range of pH and alkalinity regimes for the Virginia Blue Ridge. As should be expected, pH and buffer capacity are highest in those streams originating in limestone and dolomite bedrock. These carbonate rocks react readily with both weak and strong acids, resulting in high bicarbonate concentrations in solution and thus the high pH and alkalinity observed. Only a few such streams were included in this survey, their purpose being to put the relatively low buffer capacity of other systems into perspective.

Streams from the four Precambrian, metamorphic formations (Pedlar, Catoctin, Lovingston, and Marshall) have similar pH and alkalinity ranges, with near neutral pH and alkalinities of about 200 μeq/ℓ (10 PPM as $CaCO_3$). While these levels are far below those of the carbonate streams, buffer capacities in this range are sufficient to maintain a stream in good condition except during extreme episodes of acid input. Even in such cases, the changes should be short-lived and relatively minor. Old Rag granite, while quite similar to the Pedlar and Lovingston formations, imparts a significantly lower buffer capacity to streams flowing from it. Long term acidification appears unlikely, but buffer capacity is sufficiently low that these streams probably undergo moderate to substantial pH shifts during acid precipitation events such as those observed in Madison Run (discussed below).

Streams in the clastic bedrock formations (Antietam and Hampton and to a lesser extent, Weverton) are clearly the most vulnerable to both short and long term acidification. The pH of these streams is well above that of incident precipitation, indicating that some neutralization occurs in the watershed, but the buffer capacity of streamwater is minuscule, at best.

Figures III-3 and III-4 show trends similar to those discussed above, and clearly show the effects of different bedrock formations on the eastern and western slopes of the Blue Ridge in the study area. These figures also show the consequence of a stream passing through several bedrock formations; the pH and alkalinity of such streams reflect the most reactive bedrock in their watersheds. Madison Run (upper left corner) and several streams at the bottom left side of the figures have much higher pH and alkalinity than other streams on the western slopes, these differences are presumably attributable to the presence of Catoctin bedrock in their watersheds.

Many of the streams in the survey area were sampled several times during the summer to determine whether there were substantial changes in pH and alkalinity as a result of seasonal variability or changes in stream discharge. With the exception of Madison Run (see below) there seemed to be relatively little change in chemistry of the streams involved.

It should be noted that in all streams studied the carbonic acid-bicarbonate system was the dominant buffer system. Alkalinity titrations showed pH behavior indicative of bicarbonate as the principal buffer, and there were no data to suggest the presence of any other buffer.

Following the initial survey work in the Blue Ridge, Madison Run was chosen for more intensive study during the remainder of the study period. This stream has major tributaries flowing out of the Catoctin formation and from clastic bedrock (Weverton and Hampton formations). During initial sampling these tributaries had pH and alkalinity values typical of the respective bedrock formations. Two kinds of sampling were done; regular (at least biweekly) sampling at several stations on the main stream and tributaries, and also sequential samples (usually 2 hour intervals) taken at various stations during both dry periods and during and following individual rainstorms. Sequential sampling during storms has allowed us to observe the response of these streams to acid precipitation episodes.

Madison Run is a typical watershed on the western slope of the Blue Ridge, covering about six square miles. Vegetation cover is virtually complete, consisting mostly of oak forest and extensive blueberry coverings. Soils are coarse, thin, and characterized by low pH, cation exchange capacity, and organic matter. The stream system is not gauged, so no budgets can be determined for individual ions.

Total dissolved solids are low in all of the streams of the watershed, typically around 20-30 mg/ℓ. Silica is the major substance in solution, ranging from 7 to 15 mg/ℓ as SiO_2. Bicarbonate is the dominant anion under most conditions, with chloride and sulfate present in lower concentrations on an equivalent basis. Magnesium is the major cation in solution with lower concentrations (equivalents per liter) of calcium, sodium, and potassium. Magnesium is a major constituent of the bedrock formations in the watershed, particularly in the Catoctin formation; so its abundance in comparison to other cations is not unexpected.

Unlike other streams in the survey area, pronounced changes occurred in both Madison Run (Catoctin bedrock), and its major tributary, White Oak Run (clastic bedrock) during the study period. From early June until mid-August, pH increased in both streams, from 6.05 to 6.5 in Madison Run, and from 5.7 to 6.45 in White Oak Run. Alkalinity showed corresponding increases, from 70 to 150 μeq/ℓ and 18 to 80 μeq/ℓ for Madison and White Oak Run's respectively. We are uncertain of the cause of these changes, but changes in stream discharge/ groundwater flow and primary production by mosses and algae growing on bedrock probably both play a role.

In the absence of precipitation, no significant diurnal changes occur in any of the measured parameters on either Madison or White Oak Run. Alkalinity and pH may undergo very small diurnal cycles on White Oak Run in response to photosynthesis. During major precipitation events, however, substantial changes occur, particularly on White Oak Run. On July 16, slightly less than one inch of rain fell during a thunderstorm over the watershed, resulting in major, but brief changes in water chemistry on White Oak Run (Figure III-5) Both pH and alkalinity fell substantially, with a corresponding increase in acidity. Nitrate and sulfate levels showed a sharp increase, presumably caused by precipitation input and washoff from leaf surfaces during the storm, while silicon levels declined, probably from dilution of stream water by precipitation. The concentrations returned to previous levels over about an eight hour period.

A second storm, on August 11 and 12, was observed on Madison Run. About 2.5 inches of rain fell over a 24 hour period during this storm, resulting from passage of a frontal system. Major ion analysis for this storm indicate that its effects were minimal, despite the much larger amount of precipitation (rainwater was not collected for chemical analysis during either storm). Slight increases were observed in nitrate and sulfate concentration, and silicon levels declined slightly during the storm, but no change was observed in pH, alkalinity or acidity. Apparently the higher buffer capacity of the stream, combined with more gradual input of acid (inferred from sulfate and nitrate values) allowed the stream chemistry to remain relatively constant throughout the storm.

A third storm, the remnant of Hurricane David, passed through the watershed on September 3, resulting in about 6 inches of rain over a twelve to sixteen hour period. Although the pH of rain from this storm was rather high (4.9), stream chemistry changed tremendously. Sequential samples on White Oak Run showed a severe depression of pH to 5.1, alkalinity decreased to zero, and acidity showed a major increase as bicarbonate was converted to carbonic acid. Thirty-six hours after the storm, pH was still well below normal (5.6), and alkalinity was only 12 μeq/ℓ, about 20 percent of the pre-storm buffer capacity. Madison Run was also sampled following the storm and it too showed much lower pH and alkalinity (5.85 and 60 μeq/ℓ) than normal.

Data on precipitation events is presented here only to indicate the type of response one might observe in stream chemistry. Clearly, the specific response will depend upon both the pre-storm chemistry of the stream and groundwater in the watershed, and on the composition and magnitude of the precipitation events. In retrospect, Madison Run was probably not an ideal watershed to choose for concentrated study; the pH and alkalinity of Madison and White Oak Run seem to show more seasonal variability than occur on other streams. White Oak Run is clearly not typical of streams flowing from clastic bedrock; by late summer its pH and alkalinity were well above those of other streams originating in clastic rocks.

4. Summary of Intensive Study. Within the Blue Ridge of central Virginia, the pH and buffer capacity of streams varies greatly, with bedrock geology the major factor controlling stream chemistry. With the exception of streams in areas with carbonate-bearing bedrock, buffer capacity is generally low, and virtually nonexistent in streams originating in clastic bedrock. Sensitivity to acidification is presumably greatest in those streams with the lowest buffer capacity, but we have no historical data available to determine whether significant changes in the chemistry of these streams has occurred during recent years. Thus, these data are valuable as baseline data to determine ongoing long-term changes in stream chemistry.

Storm data from the Madison Run watershed clearly demonstrate short-term effects of acid rain on stream chemistry, particularly on White Oak Run. Many streams in the survey area have pH and buffer capacities significantly lower than occur on White Oak Run; episodic changes in the chemistry of such streams are probably more pronounced. The effects of such changes on stream fauna may be substantial,[43] but are beyond the scope of this study.

B. Extensive Surveys Of Mountainous Areas of New Hampshire and North Carolina

The states of New Hampshire and North Carolina, separated by over 800 km, receive acid precipitation with volume weighted mean annual H^+ concentrations of approximately 114 μeq/ℓ (pH 3.94) and 50 μeq/ℓ (pH 4.2).[71] Both states have variable topography with the White Mountains of central New Hampshire and the Blue Ridge mountains of western North Carolina providing terrain with exposed bedrock, grading to regions of thin soil, then to deep soils. The bedrock also is variable with respect to sensitivity, as can be seen in Fig. III-6 and III-7 with abundant outcrops of slow-weathering, igneous and metamorphic rock. Thus these states were selected as ideal regions in which to test the accuracy of the sensitive areas map. The test consisted of identifying specific sites which have low alkalinity (<200 μeq ℓ^{-1}) from historical data, verifying these observations by new sampling, then comparing the locations of these sensitive waters to the map of sensitive areas. The sensitive areas maps were not consulted when selecting sites for sampling, so that the site selection, within the two regions expected to contain sensitive areas was not coupled to the map-making process.

1. Field Methods. The first step in selecting field sites where samples were to be collected, was to examine existing water quality records of the departments of fisheries in each state so that new data could be compared to old data in an analysis of temporal trends, as described below (section IV). Stations which had been previously sampled were then identified on county road maps. Wherever possible, samples were collected at about the same time of year and at the same sites used previously. Sites with alkalinity values greater than 200 μeq ℓ^{-1} or pH greater than 7.0 were excluded. If recent cultural activities such as farming, timber harvest, residential or recreational housing were significant on site or upstream, the site was not included in the sampling. At each location, two samples were taken in 250 m acid washed polyethylene bottles, rinsed three times in sample water before filling. One sample was acidified for metal analysis to a pH of 2 by the addition of 1mℓ of 6N HCl. These samples were not acidified, but because suspended solids were low, and because most Ca occurs in dissolved rather than particulate form (70), the amount of Ca added in particulate form is believed to be negligible.

The other sample was placed in a cooler filled with ice and kept at or below 4°C until pH and alkalinity measurements could be made (usually every two days). Conductivity in microSiemens was measured with either a Beckman or Presto-tek conductivity bridge. For pH and alkalinity determinations, a Beckman pH meter with combination electrode was used. The samples were brought to room temperature before pH was measured. Alkalinity was determined using Gran's plots. Calcium analyses were performed on acidified samples by atomic absorption spectrophotometry.

2. Results of Field Measurements. The observed alkalinity values (Tables III-1 and III-2) in the ranges < 0 μeq ℓ^{-1}, 0-50 μeq ℓ^{-1}, 50-100 μeq ℓ^{-1} and 100-200 μeq ℓ^{-1} are shown for each of the stations sampled in Figures III-8 and III-9. These can be compared to Figure III-6 and Figure III-7, the respective state sensitive areas maps. In New Hamshire all of these low alkalinity waters in the regions sampled fall within regions predicted to have Types I and II sensitivity, and in North Carolina all stations fall in Types I or II sensitive areas. Since stations were selected for sampling only if historical data showed them to have low alkalinities, they were expected to lie in regions underlain by sensitive bedrock. The fact that the geologically based sensitive areas map confirms this expectation constitutes a partial verification of this method of determining sensitive areas.

C. Large-Scale Comparison

1. Acidification Chemistry Information Database. Data on Water Chemistry was collated from many Federal, state and local agency sources (Appendix II). Information stored in computerized data bases (e.g. STORET) as well as raw data from field reports gathered from these sources were used to establish the Acidification Chemistry Information Database (ACID) at Brookhaven National Laboratory. Two factors governed the selection of data. Since alkalinity is the dominant factor of water chemistry which determines sensitivity to acidification, all waters with alkalinity values in excess of 500 μeq/ℓ were excluded. This exclusion selected for moderately to highly sensitive waters and greatly reduced the amount of data to be included in ACID. Second, the time scale for this project limited us to including about half of the available and relevant data which we were able to locate.

A generalized data base management system, SYSTEM 2000 (proprietary system of MRI systems Corp., Austin, Texas) was used for ACID. Analyses were done using a combination of the CDC 6600 and CDC 7600 computers at Brookhaven National Laboratory. Plotting of large scale maps was accomplished with a 36-inch Versatec electrostatic plotter. Some maps and tables were prepared using a FR 80 COM device and many data tables were put onto micro-fiche from the FR 80. Plotting software was developed at BNL and is based on DISSPLA (a plotting software proprietary package of Integrated Software Systems Corp., San Diego).

2. County-by-County Maps. As data is transferred from maps with a scale as fine as 1:62,500 to maps at 1:2,500,000, fine resolution is completely lost. A problem arises in trying to preserve the identity of the isolated sensitive areas. Preserving this information can be accomplished by over-representing the size of the sensitive area. Data in ACID is used to map the current alkalinity and pH on a county by county basis. Alkalinity values

Table III-2. Changes in the chemistry of White Oak Run, 7/16-7/17/79

			(μeq/l)		mg/l		
Time		pH	Alkalinity	Acidity	Si		
7/16	1100	6.2	56	40	2.63	.040	4.02
	1300	6.2	51	39	2.60	.036	4.02
	1500	6.1	55	39	2.60	.035	4.03
	1700	6.1	54	42	2.60	.031	4.02
	1900	6.05	36	65	1.77	.334	5.6
	2100	5.9	29	70	2.24	.203	5.33
	2300	5.95	37	58	2.45	.141	4.45
7/17	0100	5.95	36	53	2.57	.147	4.40
	0300	5.9	43	53	2.52	.112	4.26
	0500	5.9	41	55	2.53	.082	4.24
	0700	5.9	36	55	2.53	.071	4.18
	0900	5.9	34	50	2.53	.052	4.23
	1100	6.15	38	48	2.54	.044	4.14
	1300	6.2	-	43	2.54	.036	4.15

were divided into 3 categories: a) < 100 µeq/ℓ; b) 100 - 200 µeq/ℓ; and c) > 200 µeq/ℓ and values at each station for the period (1976-1979) were used for this analysis. The stations included are shown in Figures III-10 and III-11.

Two types of maps are presented:

1. An entire county is assigned the alkalinity category determined by the lowest alkalinity value for the county and shaded according to that value (Figures III-12 and III-13). These maps ensure that areas known to be sensitive on the basis of current water chemistry are identified.

2. A county was assigned the average value of alkalinity, observed at all stations in the county (Figures III-14 and III-15). The existence of low alkalinity waters is frequently lost in these maps, but, when compared to the minimum value maps, the true sensitivity of a whole county is more realistically interpreted.

Maps for all states included in the ACID system are shown in Appendix I.

Some reservations about these maps must be noted. First, it is most unlikely that ACID contains information on all streams of any county; the sample density must be judged by the site maps for each state (Appendix I), recalling that only waters with alkalinities < 500 µeq/ℓ were included in ACID. Second, for the average pH or alkalinity maps, a single low value may be all that was available for a given county. Again, the site maps (Appendix I) must be consulted. On the other hand, most state water quality data, and especially data in STORET, is biased in favor of downstream locations of water withdrawal for irrigation or municipal use. The water chemistry data from state fisheries agencies is of great value since we suspect it to give a better representation of upstream waters. Inclusion of additional data which we have located from state and local sources into ACID will improve subsequent versions of these maps.

3. Comparing Geologically-Based Maps to Chemistry-Based Maps. The accuracy of the geologically-based sensitive areas maps of North Carolina and New Hampshire (Figures III-6 and III-7) was evaluated by comparing them to the county-by-county maps of current minimum or average alkalinity (Figures III-12 through III-15), which were assumed to be the "correct" maps. (At this stage, the county-by-county maps which show geology as a binary number, Figure II-4, were not tested. One cannot distinguish 0% from 9% on those maps. They are less precise than the parent maps, such as Figure III-6.) The comparison consisted of first making a prediction of "sensitive" or "non-sensitive" for a particular county based on the bedrock geology alone. A county was predicted to be sensitive if either Type I or Type II bedrock was present, and non-sensitive if neither Type I nor Type II was present. The prediction was then compared to the corresponding surface water alkalinity. A correct prediction of sensitivity was scored if a county contained Type-I or Type-II geological areas and the county alkalinity value was ≤ 200 µeq/ℓ. A correct prediction of non-sensitivity was scored if the county contained no Type-I or Type-II geological areas and the county alkalinity value was > 200 µeq/ℓ. A false prediction of sensitivity was scored if the county had only Type-I or Type-II geological areas but the alkalinity value was > 200 µeq/ℓ. A false prediction

of non-sensitivity was scored if the county had no Type-I or Type-II geological areas and the alkalinity value was ≤ 200 μeq/ℓ. Finally, an indeterminate prediction occurred when a county had Type-I and/or Type-II plus Type-III and/or Type-IV geological areas and alkalinity values > 200 μeq/ℓ were in ACID.

Percentages of these predictions were determined by adding the number of each score class (i.e. in North Carolina correct predictions of sensitivity = 38) and dividing by the number of counties with the appropriate alkalinity score (i.e. in North Carolina ≤ 200 μeq/ℓ = 42), since the alkalinity score is presumed to be "correct." Thus, in North Carolina,

$$\text{correct prediction of sensitivity} = \frac{38}{42} = 90\%$$

Several factors confound the reliability of the geologically based map of sensitivity. The false prediction of sensitivity may be due to insufficient data in ACID; there may be streams of < 200 μeq/ℓ for which no data have been located in counties where a false prediction of sensitivity was scored. The false prediction of non-sensitivity may be due to lost resolution of the geological map as contact surfaces were merged and small areas deleted in the mapping process (see Section II of this report). Counties with both sensitive (Types I and II) and non-sensitive (Types III and IV) bedrock may be expected to have waters with alkalinities higher or lower than 200 μeq/ℓ, so absence of low alkalinity data in this evaluation of the geologically based map of sensitivity results in the indeterminate score.

The degree of agreement is rather good between the maps based on water chemistry and the geologically based map. The results, shown in Table III-3 and III-4, indicate that the geologically based map predicted the possible sensitivity in 90% of 42 counties which did indeed have sensitive waters in North Carolina and all of such counties in New Hampshire. The "correct" prediction of non-sensitivity was 17%, one of six counties in North Carolina. These counties are located in the eastern portion of the state where soil factors are more important than in the central and western parts of the state. The other five of these six counties, where the lowest alkalinity in ACID was > 200 μeq/ℓ, were identified by the geologically based map as having Type III or IV bedrock (in some cases, in addition to Type-I and Type-II). The false prediction of non-sensitivity occurred in only 10% of 42 counties.

In New Hampshire, the geologically based map "correctly" predicted the sensitivity of all 8 counties with minimum alkalinities of ≤ 200 μeq/ℓ, and all 5 counties with average alkalinity values ≤ 200 μeq/ℓ. All 10 counties of New Hampshire had Type I and Type II geological areas and 6 had Type III or Type IV. Both counties with minimum alkalinity greater than 200 μeq/ℓ, included Type III or IV geology. Thus two indeterminate predictions and no false sensitivity predictions were scored.

Following this evaluation of the predictive capability of bedrock geology, the utility of the less precise binary number geological map was assessed by using it to also predict the sensitivity or non-sensitivity of the same counties. Here it was necessary to score a correct prediction of sensitivity if the binary number map indicated the presence of at least 10 percent of Type I or Type II rock in a county and the county alkalinity value was ≤ 200 μeq/ℓ. This was the case because zero on the binary number map may actually include up to 9 percent of the particular rock type.

Table III-3. Comparison of the geologically based map of sensitive areas (Fig. III-7) to county-by-county maps of alkalinity (Figs. III-13 and III-15), for 48 of 100 North Carolina counties. See text for definitions of predictions.

	Minimum Alkalinity Basis	Average Alkalinity Basis
Correct prediction of sensitivity	90% of 42 counties	100% of 14 counties
Correct prediction of non-sensitivity	17% of 6 counties	15% of 34 counties
False prediction of sensitivity	17% of 6 counties	38% of 34 counties
False prediction of non-sensitivity	10% of 42 counties	0% of 14 counties
Indeterminate	8% of 48 counties	33% of 48 counties

Table III-4. Comparison of the geologically-based sensitive areas map (Fig. III-6) to county-by-county maps of alkalinity (Figs. III-12 and III-14) for all 10 counties in New Hampshire. See text for definitions of predictions.

	Minimum Alkalinity Basis	Average Alkalinity Basis
Correct prediction of sensitivity	100% of 8 counties	100% of 5 counties
Correct prediction of non-sensitivity	0% of 2 counties	0% of 5 counties
False prediction of sensitivity	0% of 2 counties	60% of 5 counties
False prediction of non-sensitivity	0% of 8 counties	0% of 5 counties
Indeterminate	20% of 10 counties	20% of 10 counties

Predictions based on the binary number map (Table III-5) agreed quite well with the contour maps. The principal difference was a tendency for an increase in the indeterminate category and a decrease in false-sensitive.

D. Map Verification Summary

The ability of the geologically based map to accurately define areas which may be sensitive to acidification has been verified in three ways. An intensive study within the Shenandoah National Park found stream water pH and alkalinity along the Blue Ridge to be controlled primarily by bedrock geology. Data obtained during storm events demonstrate that pH and alkalinity in streams lying on sensitive bedrock fall sharply, presumably in response to inputs of acid precipitation.

Extensive surveys of surface waters with alkalinities $<$ 200 µeq/ℓ, in North Carolina and New Hampshire conducted in 1979, found 83-100% of these sites were located in Type-I and Type-II sensitive areas, as defined by the sensitive areas map.

Information obtained from numerous sources of raw data and from computerized data bases, was used to establish the Acidification Chemistry Information Database (ACID). This was used to plot surface water alkalinity on a county-by-county basis. This map, which for testing purposes was considered to be the "correct" map, was compared to the geologically-based map definitions of sensitive areas for each county in North Carolina and New Hampshire. The geologically based sensitive areas map was "correct" for 90% of the 42 counties in North Carolina, and for 100% of the 8 counties of New Hampshire, which had alkalinities $\leq$ 200 µeq/ℓ.

Table III-5. Comparison of the geologically based binary number map of sensitive areas (Fig. II-4f) to county-by-county maps of alkalinity (Figs. III-13 and III-15), for 49 of 100 North Carolina counties.

	Minimum Alkalinity Basis	Average Alkalinity Basis
Correct prediction of sensitivity	86% of 42 counties	100% of 15 counties
Correct prediction of non-sensitivity	17% of 6 counties	21% of 33 counties
False prediction of sensitivity	83% of 6 counties	0% of 33 counties
False prediction of non-sensitivity	0% of 42 counties	0% of 15 counties
Indeterminate	13% of 48 counties	56% of 48 counties

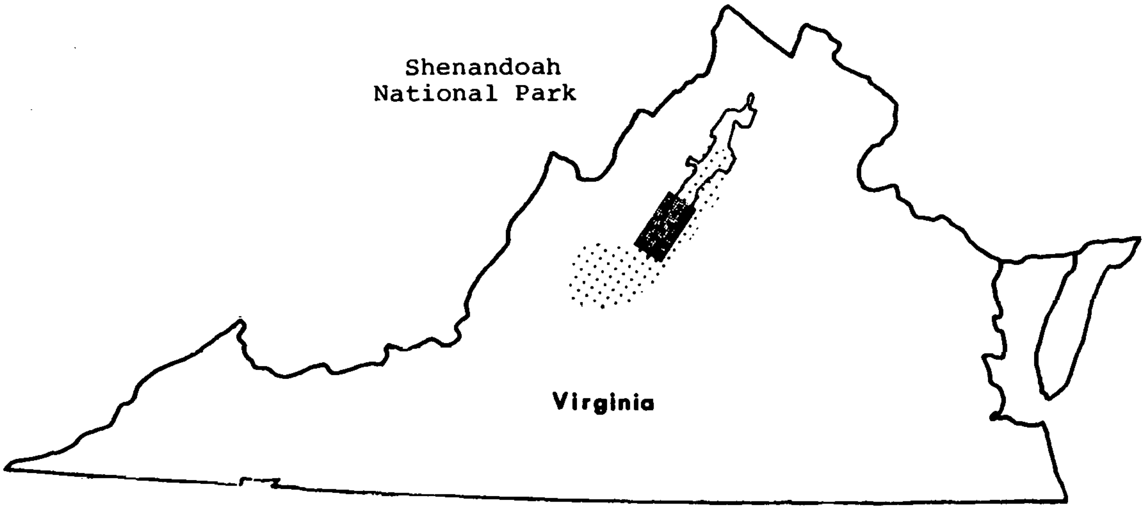

Figure III-1. Location Map of Virginia Showing the Shenandoah National Park, the Original Survey Area (Large, Lightly Stippled Area), and the Smaller Study Area (Darkly Shaded) The Small Study Area is the Same Area as Shown in Figure III-2 to III-4.

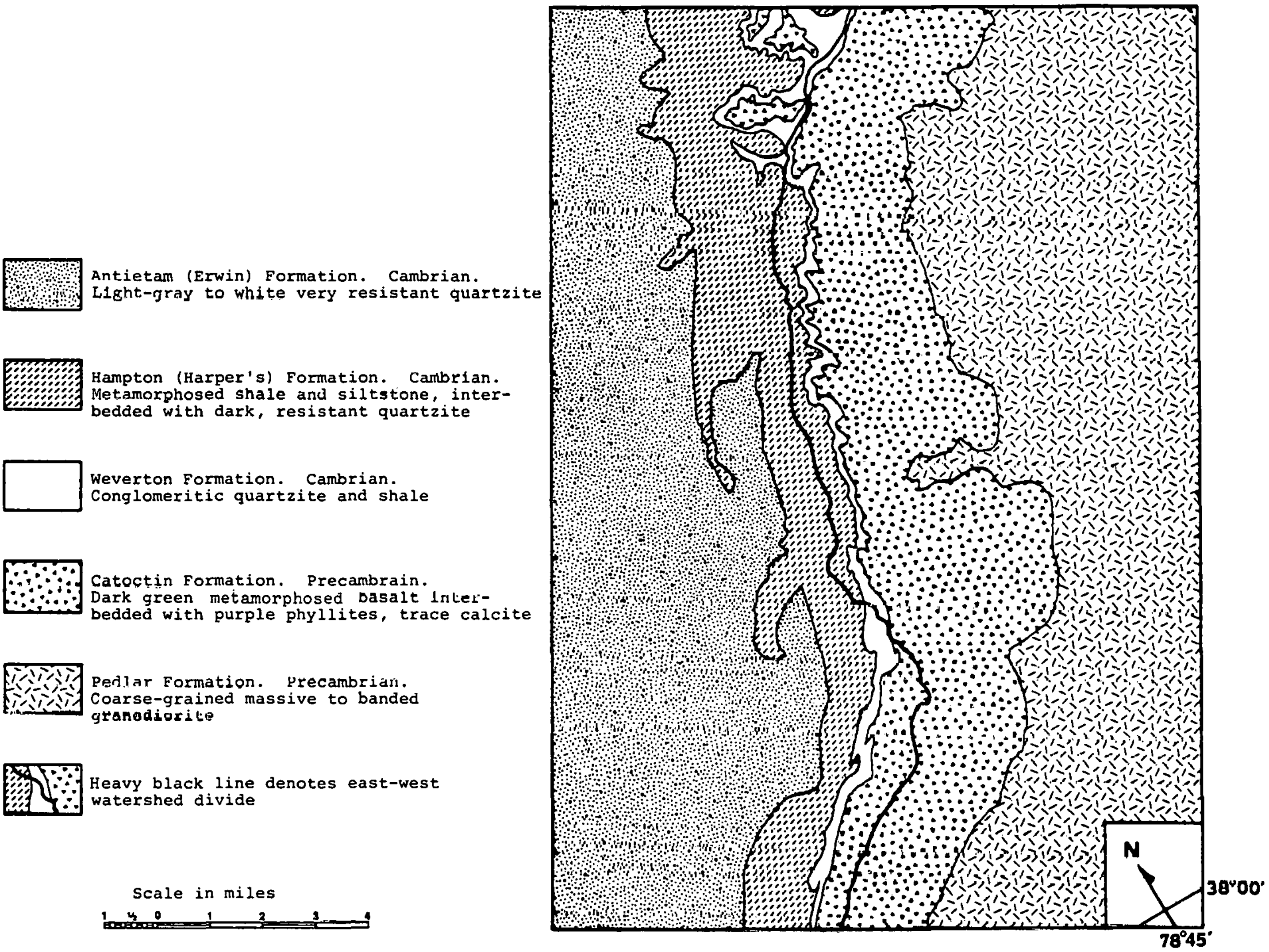

Figure III-2 (a,b). Bedrock Geology in the Study Area in and Adjacent to the Shenandoah National Park

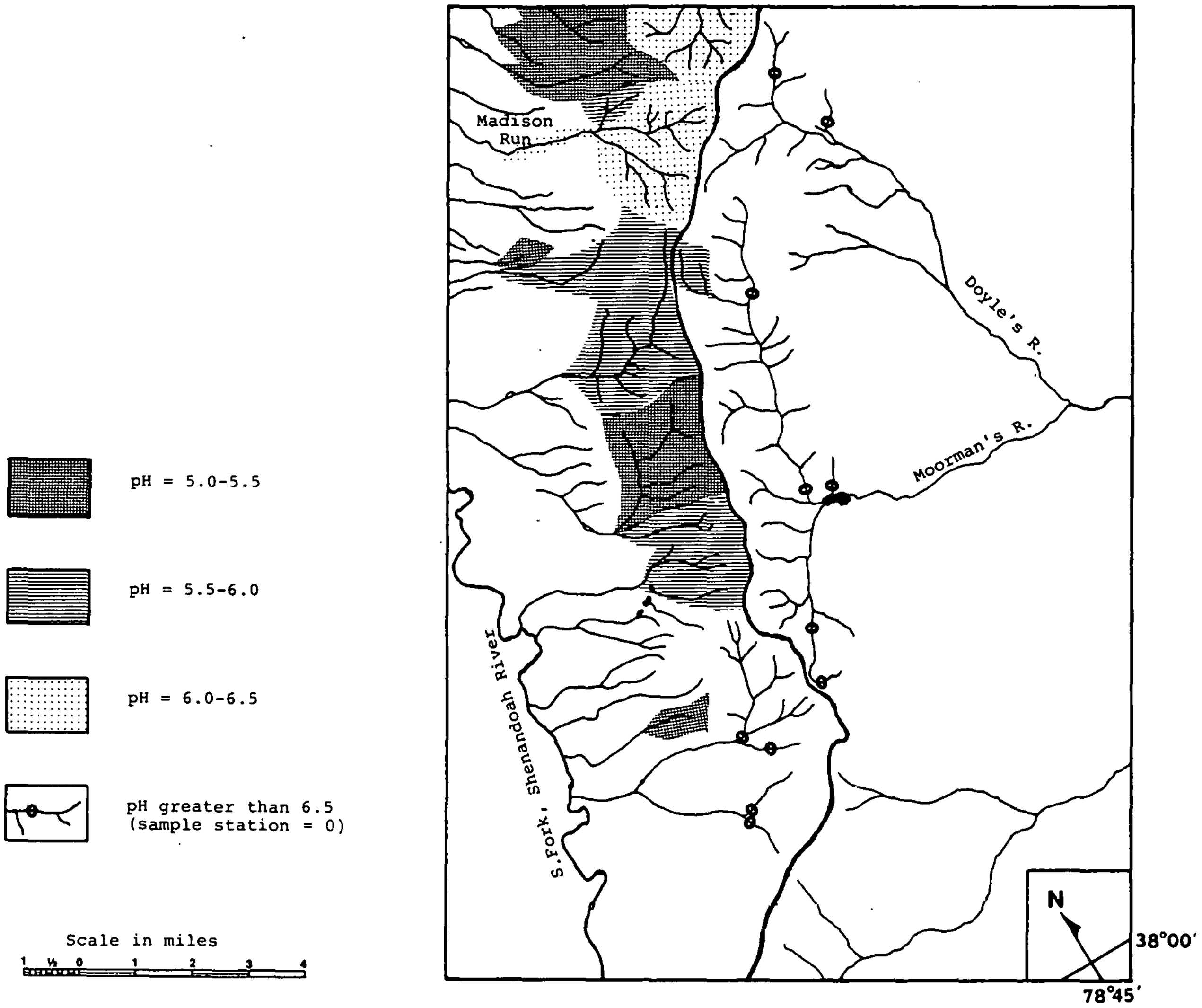

Figure III-3 (a,b). pH of Streams in the Survey Area. Shaded Areas Represent Watershed Areas Upstream From Sampling Locations

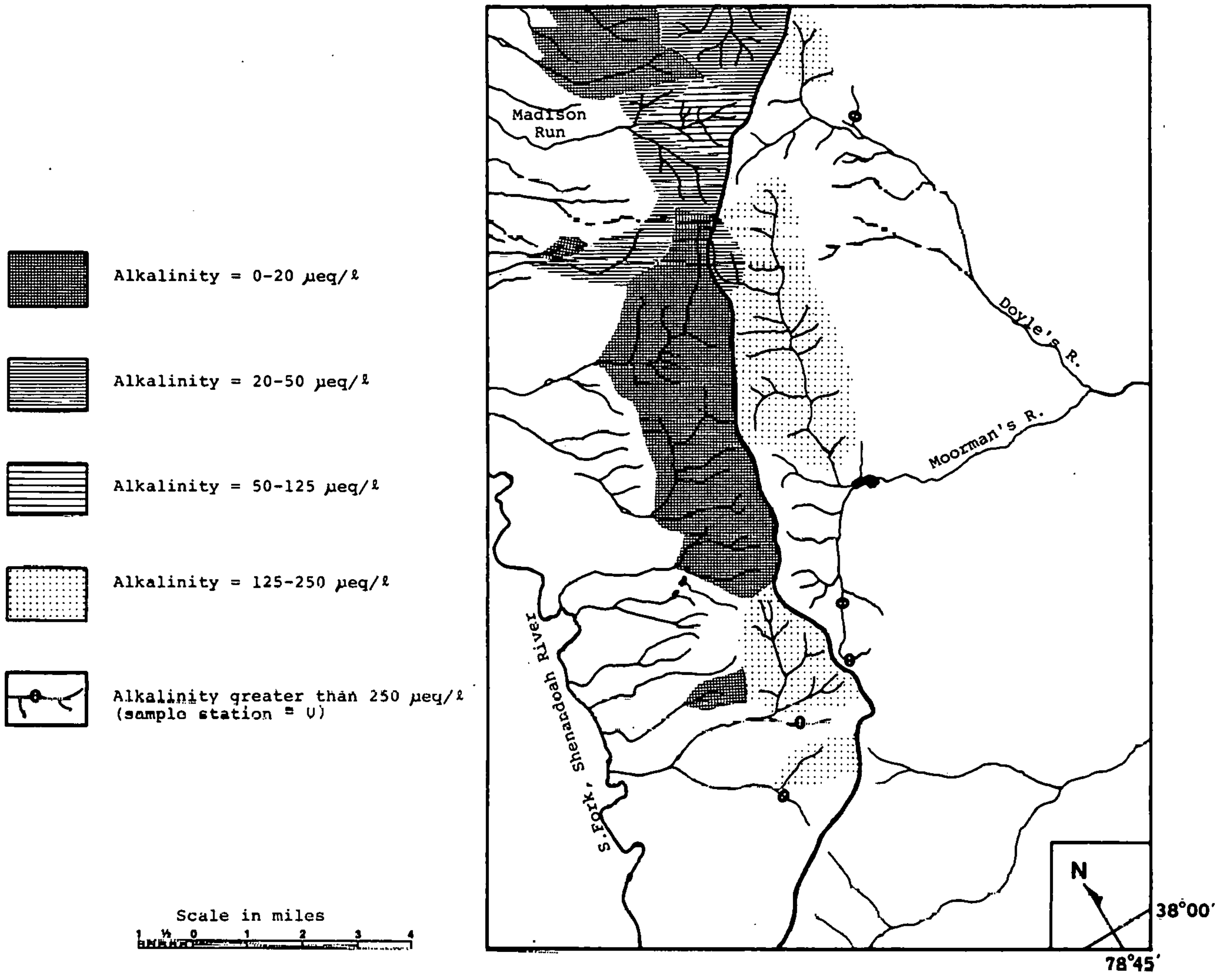

Figure III-4 (a,b). Alkalinity of Streams in the Survey Area. Shaded Areas Represent Watershed Areas Upstream From Sampling Locations

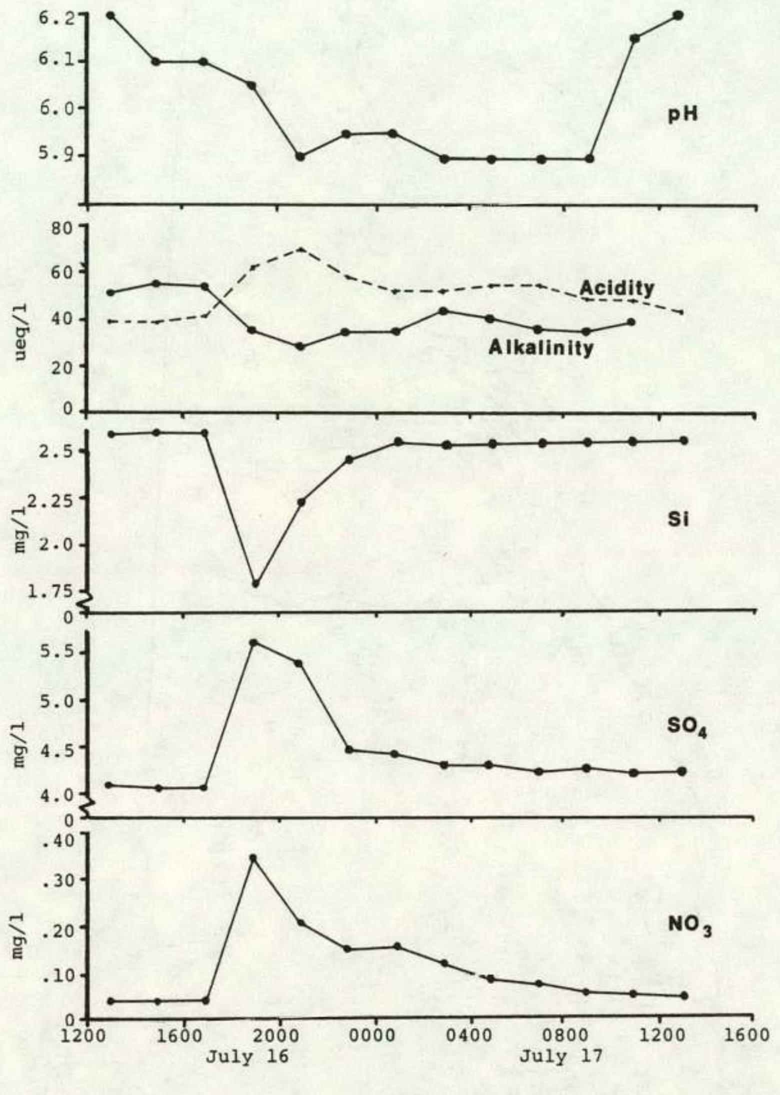

Figure III-5. Changes in Water Chemistry in White Oak Run During the Storm of July 16, 1979. Rainfall Occurred Between 1300 and 1900 Hours

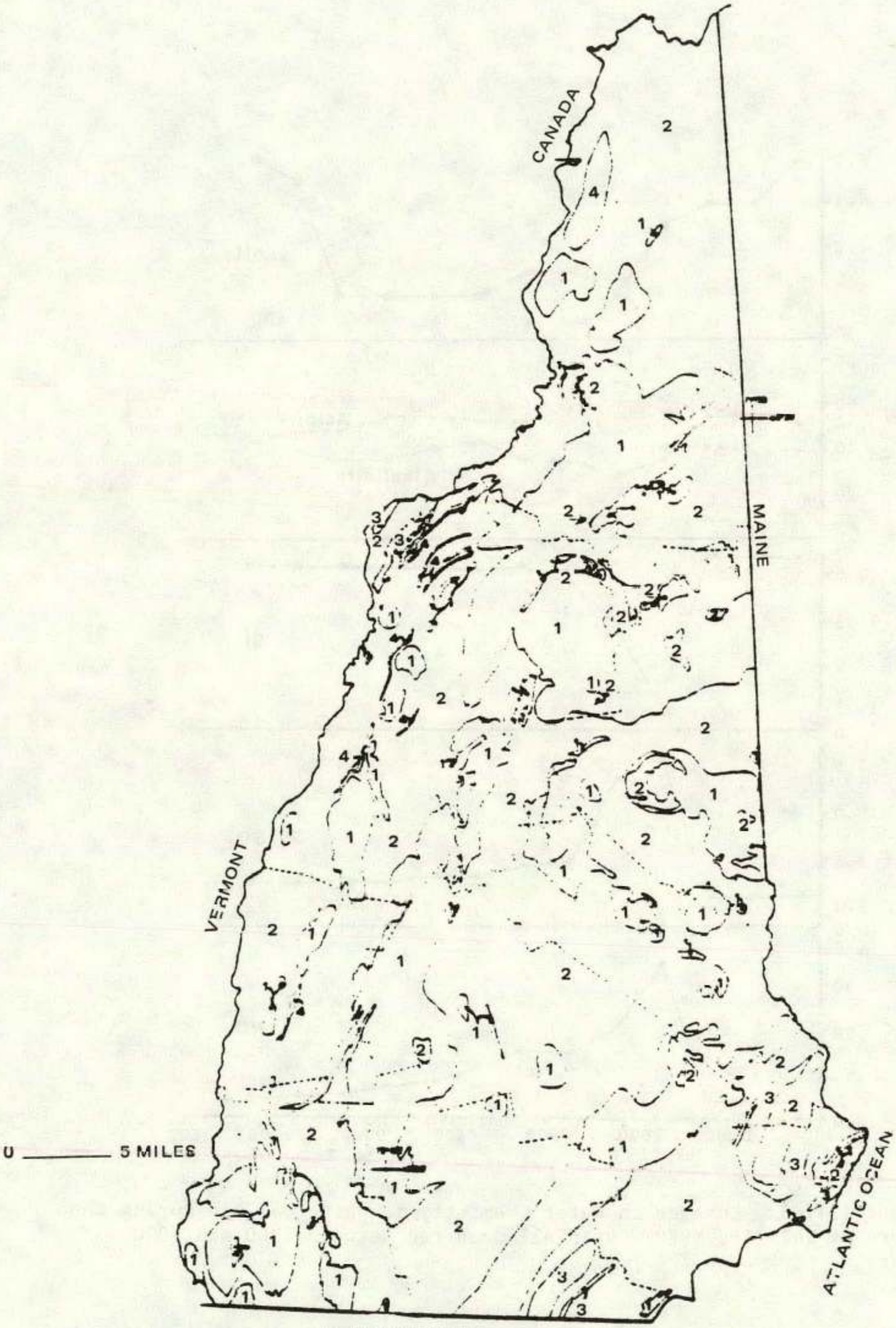

Figure III-6. Geologically Based Sensitive Areas Map of New Hampshire. Highest Sensitivity (Type-I) is Indicated by 1 on the Map With 2, 3, and 4 Indicating Progressively Less Sensitive Areas. Dashed Lines are County Boundaries

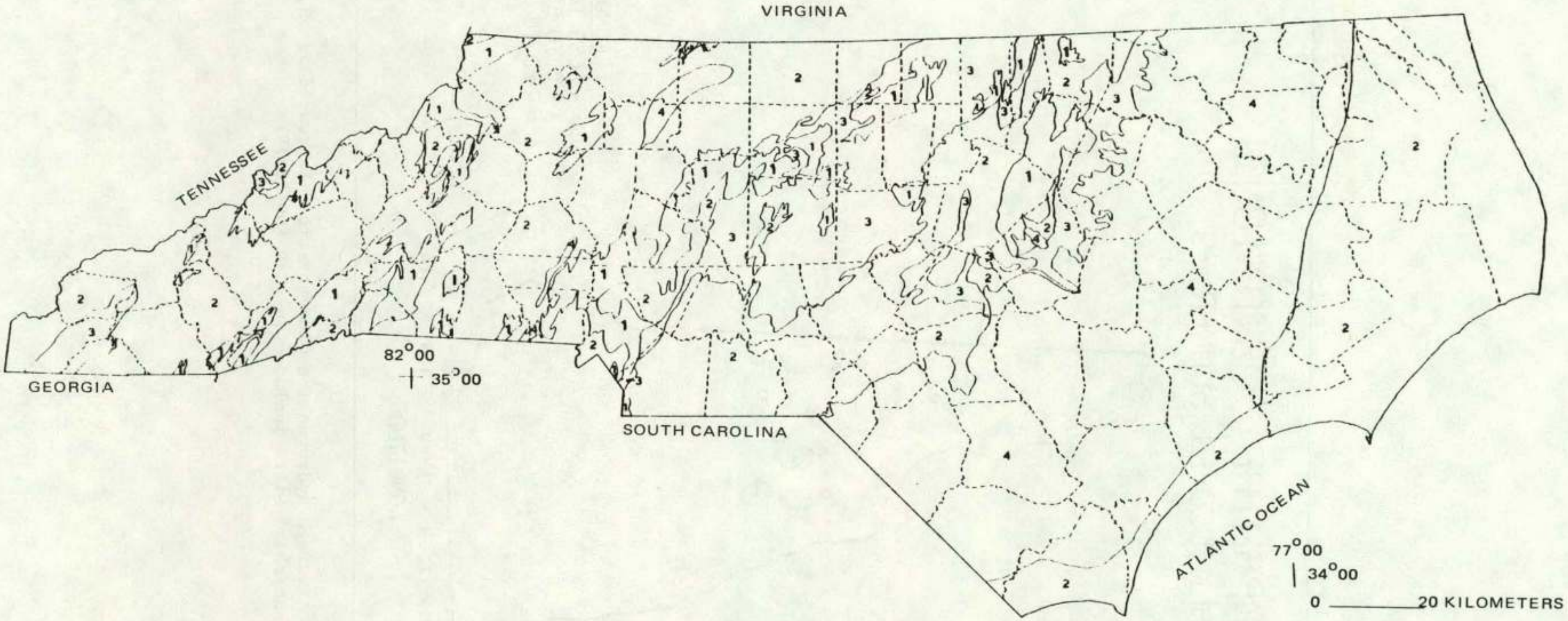

Figure III-7. Geologically Based Sensitive Areas Map of North Carolina. Highest Sensitivity (Type-I) is Indicated by 1 on the Map With 2, 3, and 4 Indicating Progressively Less Sensitive Areas. Dashed Lines are County Boundaries

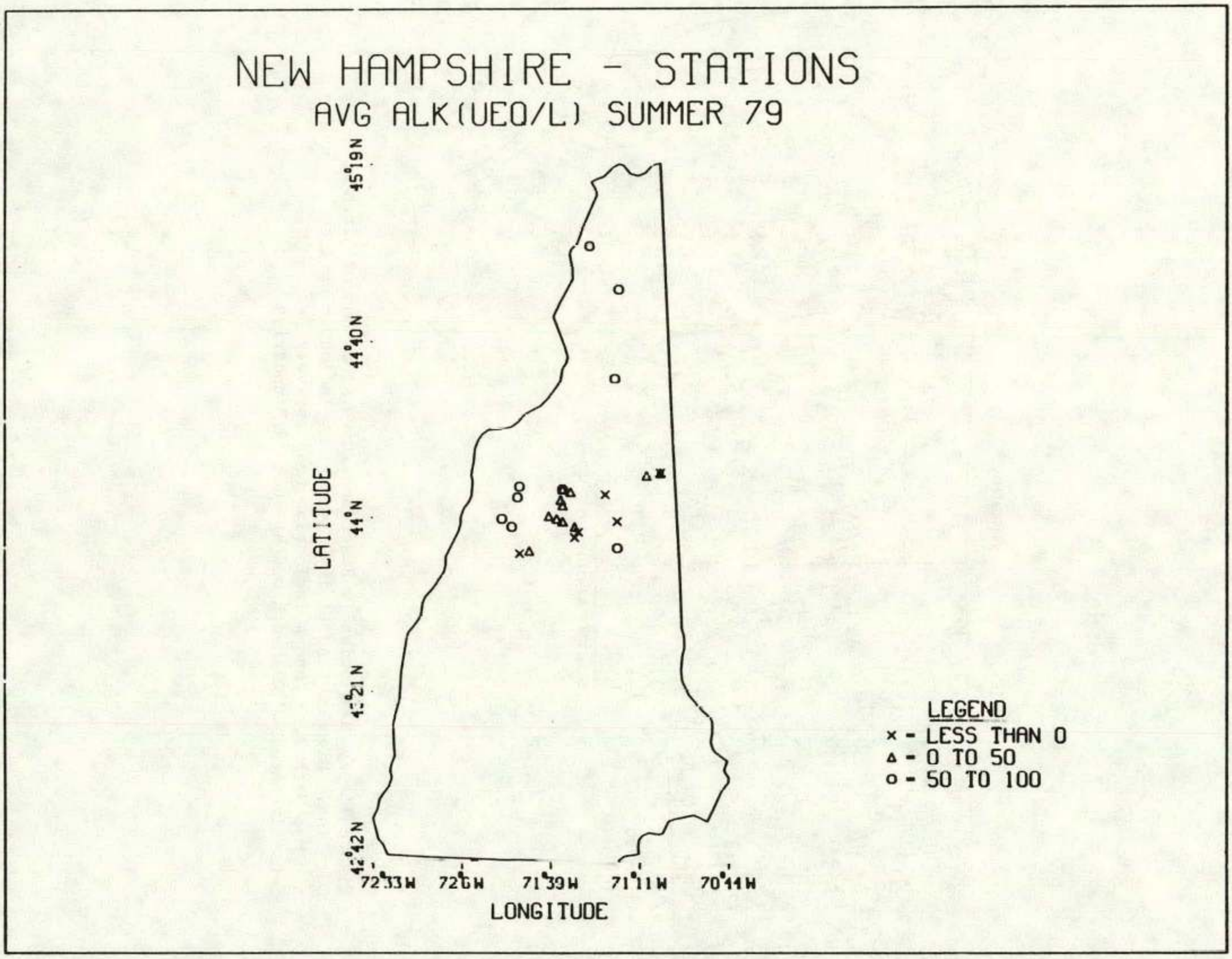

Figure III-8. Average Hydrogen Ion Concentrations Expressed as pH, of New Hampshire Sites Included in ACID (09/28/79)

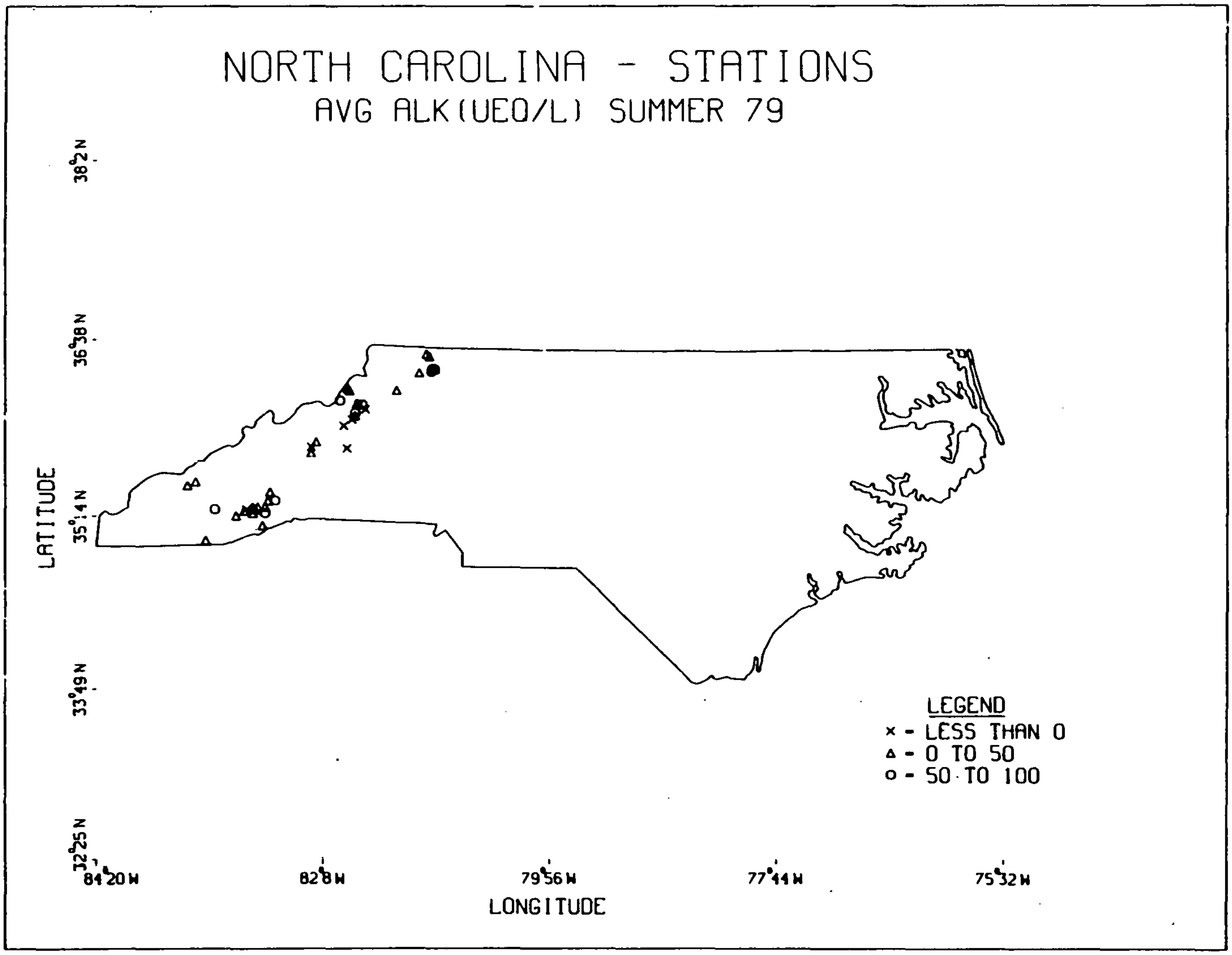

Figure III-9. Average Hydrogen Ion Concentrations Expressed as pH, of the North Carolina Sites Included in ACID

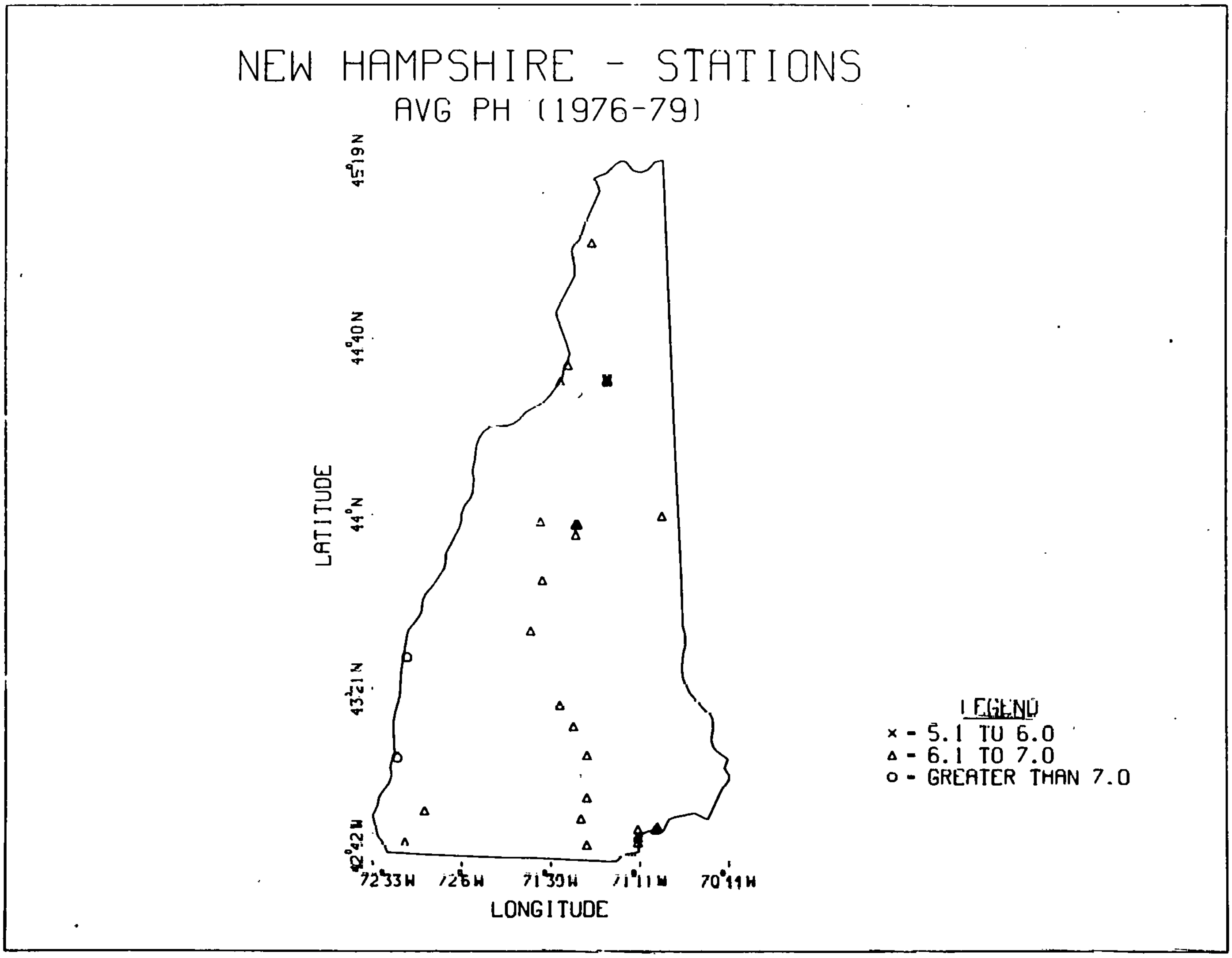

Figure III-10. New Hampshire Counties Shaded According to the Minimum Time-Averaged Alkalinity Observed in Each County.

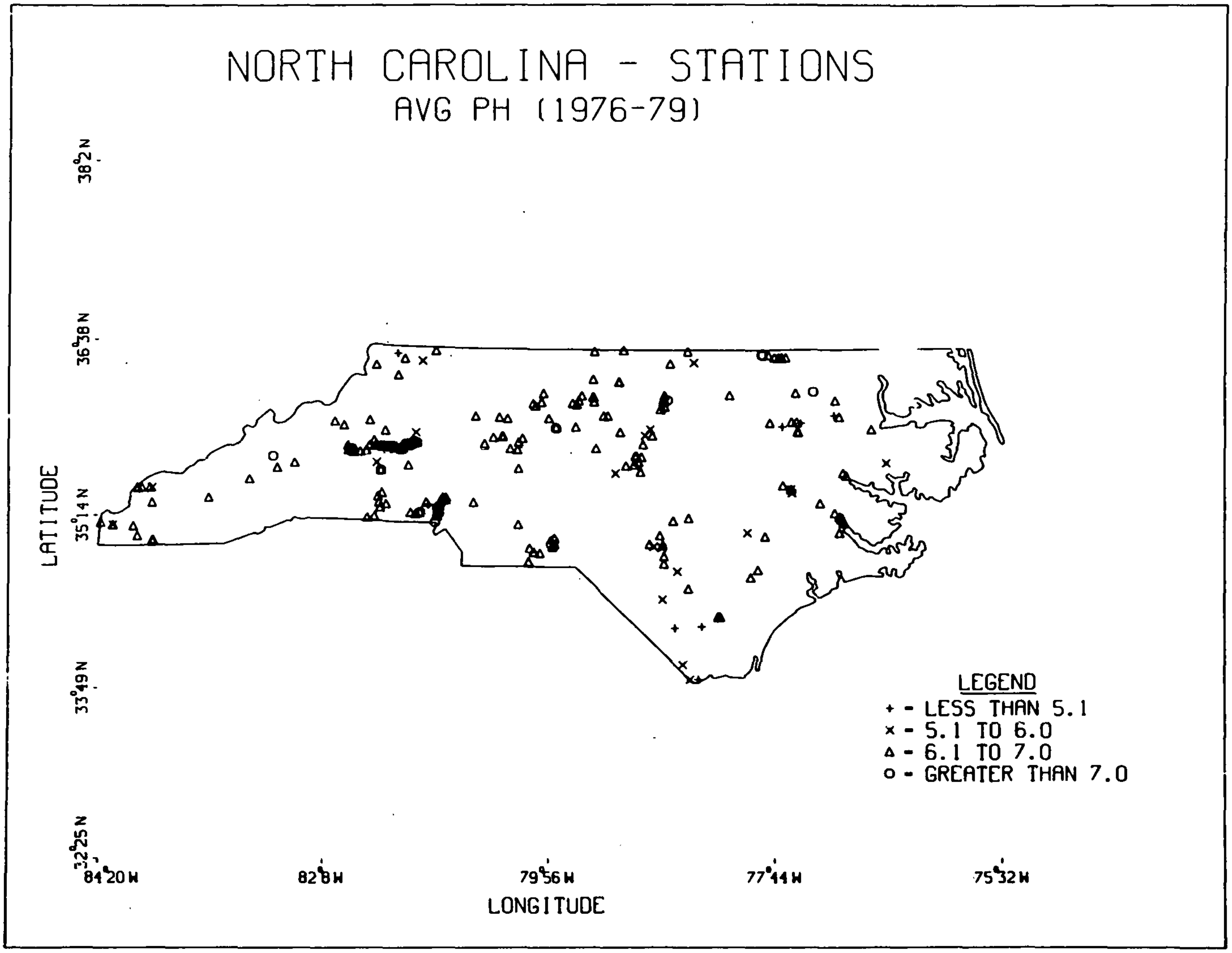

Figure III-11. North Carolina Counties Shaded According to the Minimum Time-Averaged Alkalinity Observed in Each County

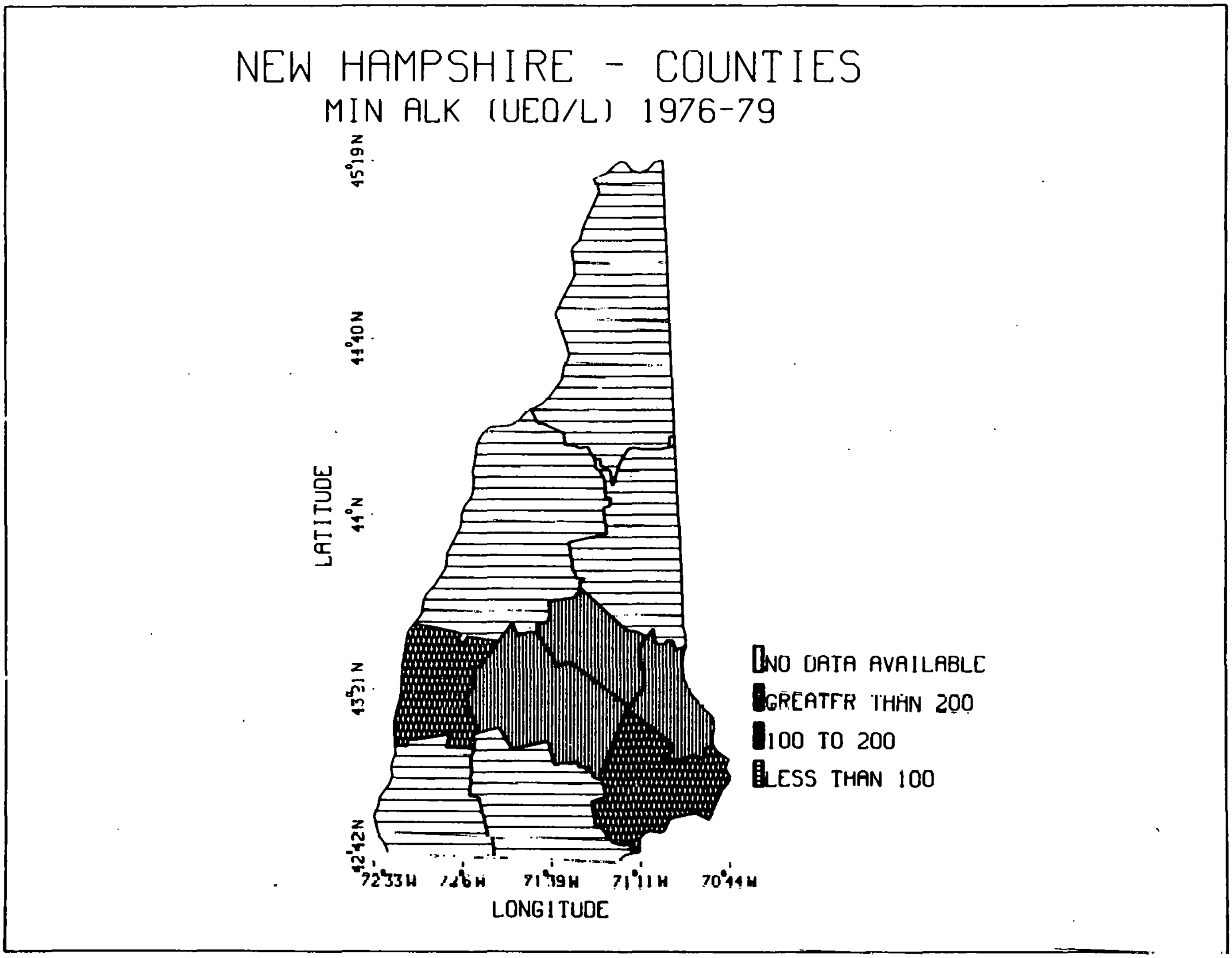

Figure III-12. New Hampshire Counties Shaded According to the Average of All Alkalinity Observations in Each County

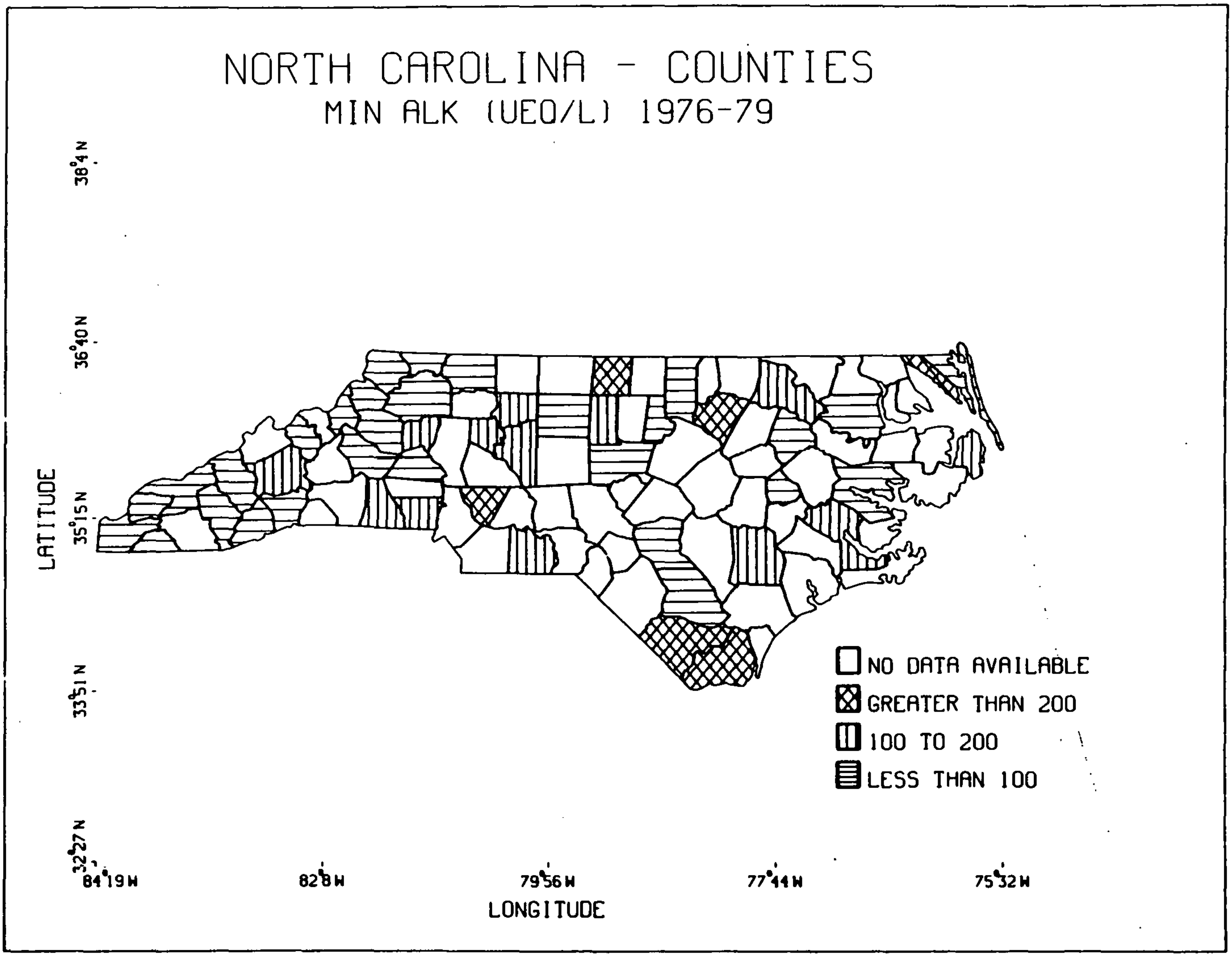

Figure III-13. North Carolina Counties Shaded According to the Average of All Alkalinity Observations in Each County

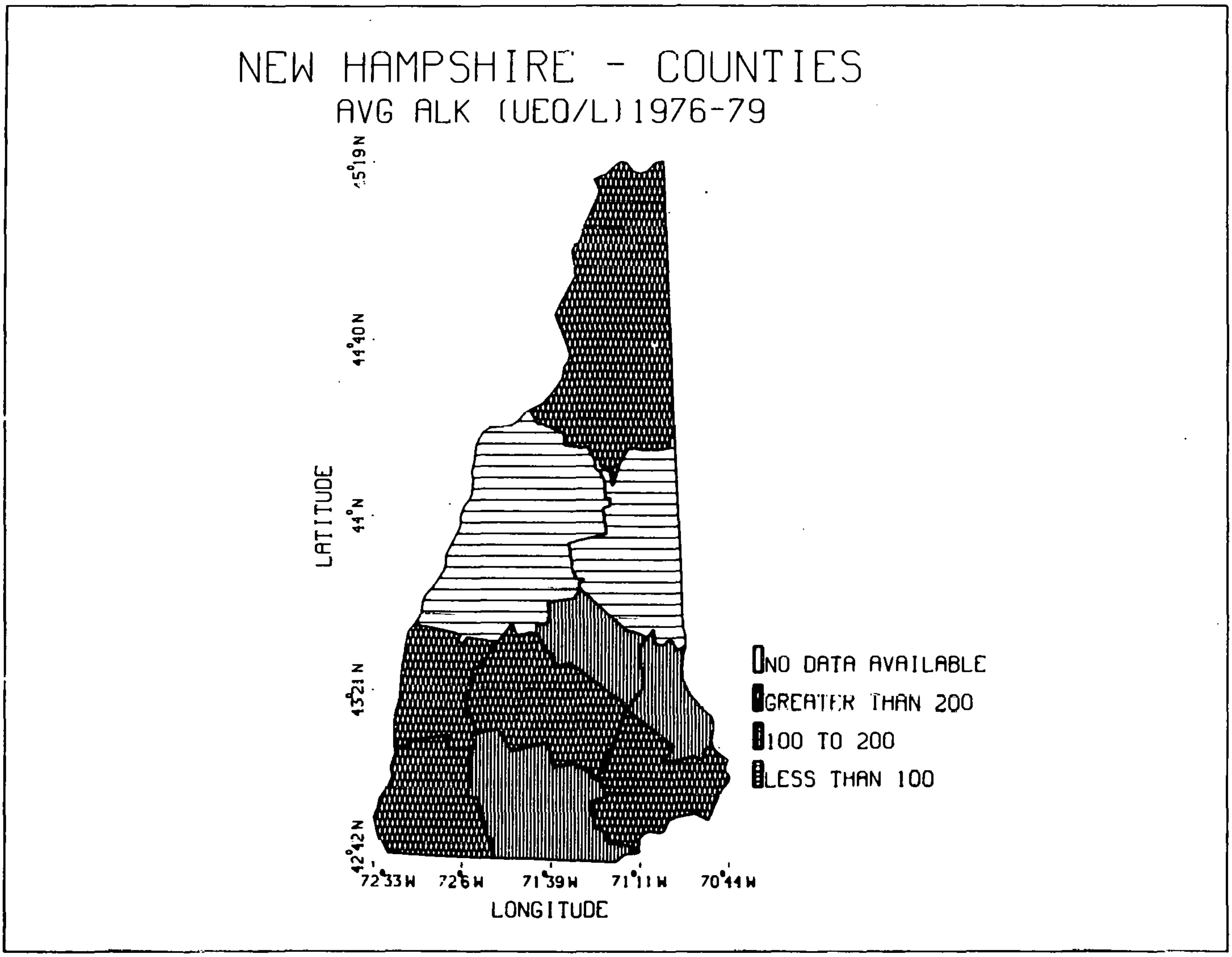

Figure III-14.

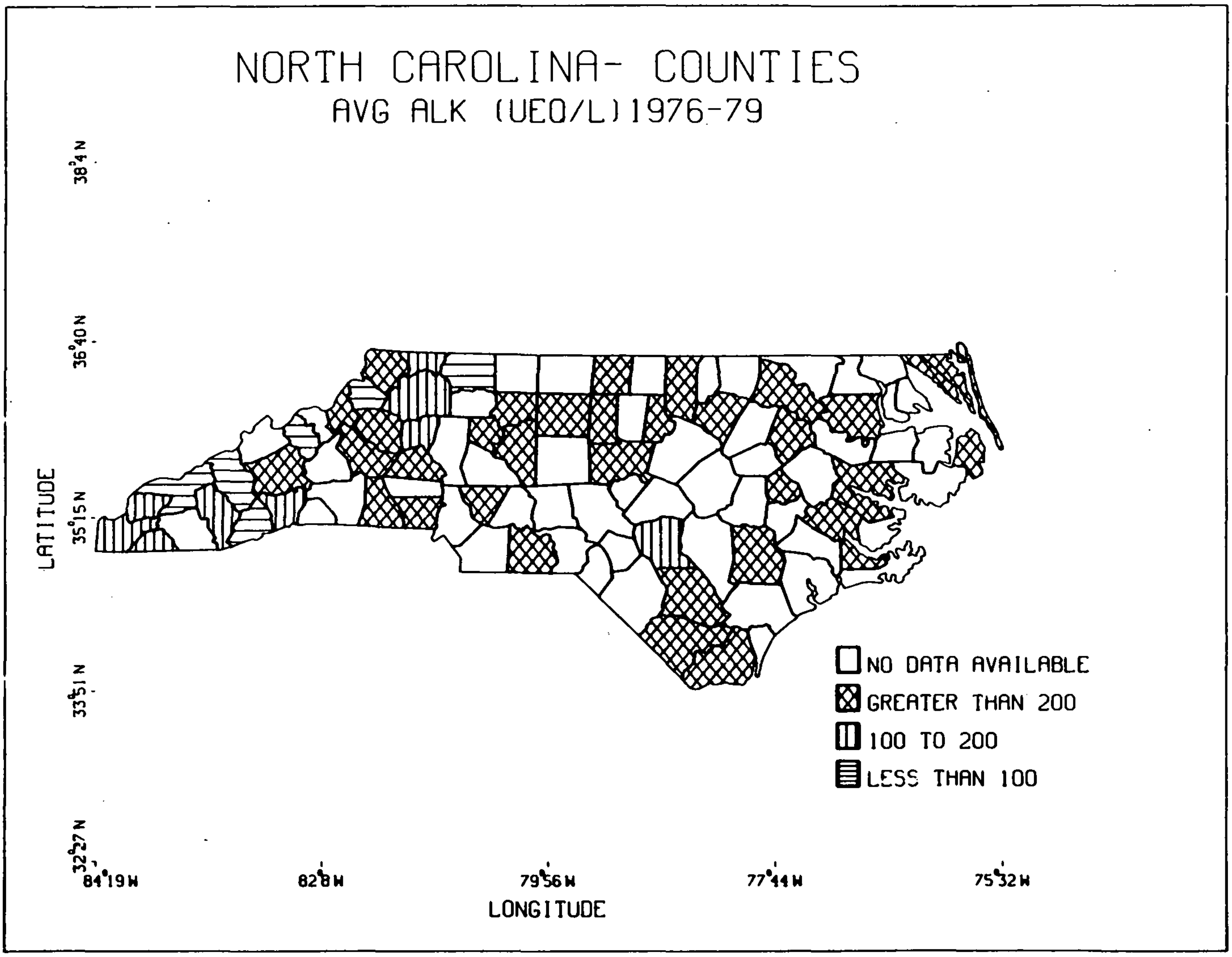

Figure III-15.

IV. TEMPORAL TRENDS IN pH AND ALKALINITY: VALIDATION OF THE SENSITIVE AREAS MAP

Historical records have been used to document temporal changes in the chemistry of lakes brought about by acid precipitation.[1,23,91,96,104] The sensitive areas map, when combined with projections of trends into future air pollution and rain chemistry, may become useful in predicting which regions will be acidified as the deposition of anthropogenic atmospheric acids increases. The fact that acidification has taken place in regions which are both heavily loaded with anthropogenic acids and are predicted to be susceptible to acidification by the sensitive areas map, is in itself a validation of the predictive value of the map.

Temporal trends in water chemistry were determined for low alkalinity (<200 μeq ℓ^{-1}) sites in New Hampshire and North Carolina by comparing historical records to data obtained in the 1979 extensive surveys described in Section III of this report. Historical data from a variety of Federal, state and local sources for most of the other states were also collated and pre-1970 data was compared to post-1975 data.

A. North Carolina and New Hampshire: Data

All of the old data obtained for sites resampled in the 1979 field trip to North Carolina came from the North Carolina Department of Inland Fisheries river basin surveys of the early 1960's. Table IV-1 lists all of the sampling sites from 1979 with the corresponding earlier data. For the old surveys alkalinity determinations were made using the methyl orange technique, and pH was determined colorimetrically.

These methods are less precise and less accurate than methods currently used which are potentiometric pH measurement for pH and multiple end-point potentiometric alkalinity titration. The problems associated with comparing data sets obtained by these different methods are discussed by Zimmerman and Harvey.[105] Determination of alkalinity using a fixed end-point titration to pH 4.5 will require 30 to 40 μeq/ℓ of titrant to remove the free H^+ in solution at this pH, so alkalinity values are overestimated by this amount, compared to the multiple end-point method (Gran's plot). The old alkalinity values were corrected, therefore, by subtracting 40 μeq/ℓ. In some cases this has resulted in obviously erroneous alkalinity values for the old (corrected) data, e.g. Boylston Creek, with pH 6.9 and a corrected alkalinity value of -18 μeq/ℓ (Table IV-1). Use of color-indicator solutions for pH in low-conductivity, poorly buffered waters, will alter the water's pH and cause a spurious reading. There is no way to systematically correct these pH errors mathematically.[105]

One might also question how accurately a single sample represents the water quality of a lake or stream since pH and alkalinity of natural waters fluctuate daily and seasonally. It is assumed that daily and seasonal fluctuation, when sampled during the day and at the same time of year as the previous sampling, are random and normally distributed. Thus, when reasonably large populations of sample pairs obtained in synoptic surveys are compared, the positive and negative errors should cancel each other out and regional, temporal trends may be analyzed.

Distributions of apparent pH and alkalinity changed in the fifteen to nineteen years between samples (Figures IV-1 to IV-6, uncorrected data). Mean hydrogen ion concentration changed from pH 6.77 in the early 1960's to pH 6.51 in 1979, an 82% increase in hydrogen ion concentration. The pH decreased at 79% of the sampling sites. The difference between the two sets of values was found to be significant at the 0.02 probability level. Mean alkalinity values have also experienced a significant decline since the early 60's from 116 μeq/ℓ (corrected) to 80 μeq/ℓ in 1979, with 71% of the 1979 values being lower than the old (corrected) values.

For New Hampshire, extensive sets of old data, collected in the late 1930's, were found. No other data for small streams and lakes were located except for some scattered records from the 1970's done by the New Hampshire Water Pollution Control Commission. Unfortunately, this older survey contained only pH data for small streams, alkalinity titrations were performed only on lakes. It is not known exactly what methods were used to determine pH and alkalinity for these old surveys, but it was almost certainly some form of colorimetric method for both. The old and new data for New Hampshire is listed in Table IV-2.

A comparison of Figures IV-7 to IV-9 reveals that in New Hampshire there has been an apparent decrease in stream pH values since the 1930's. The mean hydrogen ion concentration for the old data is pH 6.66 and in 1979 it is 6.12, a 247% increase in free hydrogen ion. The pH values at 90% of the sampling sites decreased between the 1930's and 1979. Again, the differences between the two sets of data are significant at the 0.02 probability level. Of the five sites where old alkalinity data were available, four of the new samples had lower alkalinity.

B. North Carolina and New Hampshire: Discussion

A method for estimating the expected akalinity value from the observed Ca concentration has been derived by Henriksen[51], based on water chemistry observations obtained in acidified and non-acidified regions underlain by chemically similar bedrock (described further in section VI of this report). These calculated values, Alkalinity (μeq/ℓ) = 1.42 Ca(μeq/ℓ) - 32 for the New Hampshire data are presented in table IV-2. Acidification, defined as loss of alkalinity[51] was estimated by subtracting the expected alkalinity from current measured alkalinity. In this data set, 59 stations had alkalinity values in 1979 which were lower, by an average of 57 μeq/ℓ, than expected. Regional acidification was thus calculated as 57 μeq/ℓ for New Hampshire.

This method of calculating acidification depends on an approximately constant relationship between Ca and Mg. We found that it could not be applied to the North Carolina data.

In 1955-56 the Blue Ridge area of North Carolina was receiving precipitation with a weighted annual average hydrogen ion concentration of pH 4.7-5.2.[69] By 1972-73, the same area was receiving precipitation with a weighted annual average of about pH 4.2.[69] This decline in pH appears to have caused a significant decline in the pH and alkalinity of sensitive streams in the Blue Ridge area of North Carolina. If the pH of rainfall continues to decline in the southeast these streams may experience a continued decline in pH and alkalinity.

The 1979 data for New Hampshire and North Carolina are plotted with Henriksen's[52] empirically derived curve (Fig. IV-10) of pH versus [Ca], which separates acidified and non acidified lakes (for a more detailed discussion, see section VI). Those points lying above the empirically drawn curve are presumed to have been significantly acidified by precipation and those below presumably have not. None of the samples from North Carolina lie above the curve, while there has been a significant decrease in pH and alkalinity. Henriksen's curve assumes a constant Ca/Mg ratio, which may not be valid for the North Carolina waters, which are underlain by sedimentary and metamorphic rocks. Approximately 54% of the data points for New Hampshire lie on or above the curve, indicating that many of the sensitive streams and lakes have become significantly acidified. The average pH of samples in New Hampshire is lower, and their calcium values are higher, than in North Carolina.

Table IV-1 A comparison of Old and New Data for Headwater Streams in North Carolina. Old alkalinity values were corrected by subtracting 40 µeq/ℓ.

	Old				New			(Siemens)	
Stream	Date	pH	(µeq/ℓ.) Alkalinity (as reported)	Alkalinity (corrected)	Date	pH	(µeq/ℓ.) Alk.	Specific Cond.	(µeq/ℓ.) Ca
Roaring Fork	8-3-61	7.4	200	160	6-29-79	6.7	96	21	41
Little Elkin Creek	8-24-61	6.9	180	140	6-29-79	7.1	206	35	103
Pike Creek	8-24-60	7.4	180	140	6-29-79	6.8	96	18	33
Gardner Creek	7-25-61	6.7	200	160	6-29-79	6.9	110	19	35
Rich Mountain Creek	8-25-61	6.9	180	140	6-29-79	6.92	128	22	57
Bullhead Creek	7-2-61	7.0	160	120	6-29-79	6.89	89	15	26
Fall Creek	8-14-61	7.2	200	140	6-30-79	6.8	80	15	35
North Harper Creek	7-19-63	6.9	42	2	6-30-79	6.5	46	10	32
Webb Prong	7-31-63	6.9	176	136	6-30-79	6.78	90	14	44
Wilson Creek	7-31-63	6.9	200	160	7-1-79	6.5	23	18	88
Boone Fork	6-6-63	6.9	200	160	7-1-79	6.52	73	16	77
Laurel Fork	6-6-63	6.7	180	140	7-1-79	6.62	116	32	106
Cold Prong	6-10-63	6.9	140	100	7-1-79	6.3	49	14	41
Moody's Mill Creek	6-12-63	6.7	180	140	7-1-79	6.7	86	19	71
Beech Creek	6-1-63	6.9	200	160	7-1-79	6.8	73	41	108
Buckeye Creek	6-20-63	6.9	160	120	7-1-79	6.59	63	26	76
Blevins Creek	6-25-63	6.7	200	160	7-1-79	6.7	107	50	147
Beetree Creek	6-14-62	6.0	36	-4	7-2-79	6.33	68	12	23
Kiessee Creek	6-14-62		40	0	7-2-79		43	10	24
Cathey's Creek	6-12-62	6.8	100	60	7-2-79	6.4	60	10	22
Cove Creek	6-12-62	6.8	180	140	7-2-79	6.5	77	15	44
Davidson River	6-19-62	6.9	120	80	7-2-79	6.4	61	14	38
Looking Glass Creek	6-12-62	7.0	140	100	7-2-79	6.34	61	14	40
Cooper Creek	7-23-61	6.6	40	0	7-3-79	6.2	60	12	26
Deep Creek	6-28-61	6.7	22	-18	7-3-79	6.4	70	16	48
Dick's Creek	6-27-61	6.8	120	80	7-3-79	6.41	77	19	48
Culowhee Creek	7-19-61	7.2	160	120	7-3-79	6.8	192	29	111
Tanessee Creek	7-24-61	6.6	80	40	7-3-79	6.4	64	13	34
Carson Creek	6-19-62	7.6	140	100	7-4-79	6.4	65	15	38
Williamson Creek	6-19-62	6.9	160	120	7-4-79	6.9	109	18	43
Turkey Creek	6-29-62	6.9	140	100	7-4-79	6.7	67	12	29
South Fork Mill River	7-17-62	6.8	140	100	7-4-79	6.5	57	12	27
Boylston Creek	7-9-62	6.9	22	-18	7-4-79	6.63	145	23	74
North Mill River	7-17-62	6.9	180	140	7-4-79	6.6	67	13	31
South Fork Toe River	6-2-64	6.8	180	140	7-4-79	6.2	23	10	24
Middle Creek	6-8-64	6.8	200	160	7-4-79	5.99	16	10	21
Locust Creek	6-9-64	6.8	180	140	7-4-79	6.4	56	13	38
South Fork Toe River	6-2-64	6.8	200	160	7-4-79	6.7	84	17	48

Table IV-2 - A comparison of Old and New Data for New Hampshire Streams and Lakes
Old alkalinity values were corrected by subtracting 40µ eq/ℓ. Old alkalinity values were also estimated from new Ca concentration using Henricksen's model[51] and the estimated change in alkalinity calculated by subtracting new alkalinity from estimated old alkalinity.

	Old		(µeq/ℓ)		New			Specific		Estimated	
			Alkalinity	Alkalinity			(µeq/ℓ)	(Siemens)	(µ eq/ℓ)	old Alk.	Estimated
Stream or Lake	Date	pH	(as reported)	(corrected)	Date	pH	Alkalinity	Conductance	Calcium	from Ca	Alkalinity
Kimball Cr., Coos Co.	8-1-38	6.6			7-26-79	6.6	196	37	84	87	+109
Millsfield Pond Bk., Coos Co.	7-13-37	7.0			7-26-79	6.9	124	28	155	188	- 64
Horne Brook, Coos Co.	7-8-37	7.0			7-27-79	6.5	151	25	154	187	- 36
Upper Ammonoosuc, Coos Co.	8-3-37	7.0			7-27-79	7.0	189	37	173	214	- 25
Jericho Bk., Coos Co.	8-8-37	7.0			7-27-79	6.4	139	23			
Wild River, Coos Co.	7-7-37	6.8			7-27-79	6.4	39	9	55	46	- 8
Imp Brook, Coos Co.	7-6-37	6.8			7-27-79	6.5	63	16	20	- 4	+ 67
Peabody River, Coos Co.	7-6-37	6.8			7-27-79	6.0	8	44	68	65	- 57
Nineteen Mile Brook, Coos Co.	7-6-37	7.0			7-27-79	6.4	63	19	76	76	- 13
Ellis River, Carroll Co.	6-28-37	7.2			7-27-79	6.1	85	14	52	42	+ 43
Wildcat Brook, Carroll Co.	6-24-37	7.0			7-27-79	6.2	77	20	70	67	+ 10
Great Brook, Carroll Co.	6-24-37	7.2			7-27-79	6.1	85	14	73	72	+ 13
Slippery Brook, Carroll Co.	6-24-37	7.0			7-27-79	6.4	78	13	81	83	- 5
Mountain Pond Outlet, Carroll Co.	7-15-37	6.1			7-27-79	5.6	25	14	61	55	- 30
Paugus Brook, Carroll Co.	6-15-37	7.0			7-29-79	6.2	53	16	100	110	- 57
Swift River, Carroll Co.	6-15-37	7.0			7-29-79	6.8	155	32	157	191	- 36
Wonalancet Brook, Carroll Co.	6-15-79	6.8			7-29-79	6.4	94	29	147	177	- 83
Whiteface River, Carroll Co.	6-11-37	6.4			7-29-79	6.3	91	25	118	136	- 45
Cold River, Carroll Co.	6-20-37	7.0			7-29-79	6.4	66	21	107	120	- 54
Atwood Brook, Carroll Co.	6-17-37	6.8			7-29-79	6.3	127	26	195	245	-118
Bearcamp Brook, Carroll Co.	6-19-37	5.6			7-29-79	6.3	127	26	197	248	-121

Table IV-2 continued

Stream or Lake	Old Date	pH	(μeq/ℓ) Alkalinity (as reported)	Alkalinity (corrected)	New Date	pH	(μeq/ℓ) Alkalinity	Specific (Siemens) Conductance	(μeq/ℓ) Calcium	Estimated old Alk. from Ca	Estimated Alkalinity
White Lake, Carroll Co.	6/21/37	6.5	100	60	7/30/79	5.8	4	12	58	50	- 46
Slater Brook, Carroll Co.	6/12/37	6.2			7/30/79	6.3	119	21	129	151	- 32
Chocorua River, Carroll Co.	6/15/37	7.0			7/30/79	6.3	89	20	129	151	- 62
Cream Brook, Carroll Co.	6/29/37	7.2			7/30/79	6.3	189	52	188	235	- 46
Moat Brook, Carroll Co.	6/23/37	6.7			7/30/79	6.3	138	26	162	198	- 60
Mason Brook, Carroll Co.	6/21/37	6.4			7/30/79	6.4	138	21	162	194	- 60
Weeks Brook, Carroll Co.	6/26/37	7.0			7/30/79	6.6	79	23	118	136	- 57
Upper Kimbal Lake, Carroll Co.	7/23/37	6.0	140	100	7/30/79	6.2	42	16	91	97	- 55
Allard Brook, Carroll Co.	6/29/37	7.2			7/30/79	6.5	105	21	95	106	- 1
Hobbs Brook, Carroll Co.	6/29/37	6.8			7/30/79	6.2	27	20	98	107	- 80
Steam Mill Brook, Carroll Co.	6/30/37	6.4			7/30/79	6.0	50	18	79	80	- 30
Oliverian Brook, Carroll Co.	6/29/37	6.4			7/30/79	6.1	40	23	95	103	- 63
White Brook, Carroll Co.	6/29/37	6.2			7/30/79	6.0	69	23	109	123	- 54
Downes Brook, Carroll Co.	6/29/37	6.8			7/30/79	5.6	-10	16	57	49	- 59
Douglass Brook, Carroll Co.	6/29/37	7.0			7/30/79	6.6	134	18	135	160	- 26
Razor Brook, Carroll Co.	6/28/37	7.0			7/31/79	6.1	103	30	143	171	- 68
Albany Brook, Carroll Co.	6/29/37	7.0			7/31/79	6.1	127	29	157	191	- 64
Sawyer River, Carroll Co.	6/25/37	6.8			7/31/79	5.8	32	24	101	111	- 79
Nancy Brook, Carroll Co.	6/25/37	6.4			7/31/79	5.8	18	18	79	80	- 62
Gibbs Brook, Coos Co.	7/26/38	6.8			7/31/79	5.1	-15	17	52	42	- 57

Table IV-2 continued

Stream or Lake	Old Date	pH	(μeq/ℓ) Alkalinity (as reported)	Alkalinity (corrected)	New Date	pH	(μ eq/ℓ) Alkalinity	Specific (Siemens) Conductance	(μeq/ℓ) Calcium	Estimated old Alk. from Ca	Estimated Alkalinity
Mt. Pleasant Brook, Carroll Co.	7/25/38	6.9			7/31/79	6.0	6	15	79	80	- 74
Clay Brook, Coos Co.	7/25/38	6.9			7/31/79	6.2	29	12	40	25	+ 4
Jefferson Brook, Coos Co.	7/25/38	6.9			7/31/79	6.4	18	12	42	28	- 10
South Br. Israel R. Coos Co.	7/13/38	7.0			7/31/79	6.3	63	19	103	114	- 51
Deception Brook, Coos Co.	7/26/38	6.8			7/31/79	6.3	150	32	155	188	- 38
Zeland Brook, Grafton Co.	7/26/38	6.8			7/31/79	6.4	64	25	119	137	- 73
Little River, Coos Co.	7/26/38	6.4			7/31/79	6.4	52	16	94	101	- 49
Tucker Brook, Grafton Co.	7/14/38	6.8			7/31/79	6.4	123	222	449	607	- 484
Reel Brook, Grafton Co.	7/14/38	6.8			8/1/79	5.9	52	6	98	107	- 55
Ham Branch, Grafton Co.	7/14/38	6.8			8/1/79	6.2	150	37	164	201	- 51
Black Brook, Grafton Co.	7/12/38	6.8			8/1/79	6.3	111	29	107	120	- 9
Lost River, Grafton Co.	8/27/39	6.5			8/1/79	6.1	43	124	105	117	- 74
Walker Brook, Grafton Co.	8/27/39	6.7			8/1/79	6.4	76	21	75	75	+ 1
Cascade Brook, Grafton Co.	8/27/39	5.1			8/1/79	6.5	116	64	150	181	- 65
Hancock Branch, Grafton Co.	8/29/39	6.9			8/1/79	6.0	65	36	116	133	- 68
Cedar Brook, Grafton Co.	8/29/39	6.2			8/1/79	5.9	63	28	97	106	- 43
E. Branch Pemigewasset, Grafton Co.	8/28/39	6.9			8/1/79	6.4	51	24	107	120	- 69
Baker River, Grafton Co.	8/25/39	6.9			8/2/79	6.4	33	18	57	49	- 16
Merrill Brook, Grafton Co.	8/26/39	6.3			8/2/79	6.7	173	38	148	178	- 5

Table IV-2 continued

	Old		(µeq/ ℓ)		New			Specific		Estimated	
Stream or Lake	Date	pH	Alkalinity (as reported)	Alkalinity (corrected)	Date	pH	(µeq/ℓ) Alkalinity	(Siemens) Conductance	(µ eq/ℓ) Calcium	old Alk. from Ca	Estimated Alkalinity
Still Brook	7/19/38	7.0			8/2/79	6.5	111	25	101	111	0
Stinson Lake, Grafton Co.	8/6/38	6.8	70	30	8/2/79	6.2	33	20	88	93	- 60
Ellsworth Outlet, Grafton Co.	8/10/38	6.8	100	60	8/2/38	6.1	57	19	106	119	- 62
Drakes Brook, Grafton Co.	7/21/39	6.8			8/2/79	6.2	46	24	103	114	- 68
Osceola Brook, Grafton Co.	7/24/39	6.8			8/2/79	6.3	74	38	117	134	- 60
Eastman Brook, Grafton Co.	7/24/38	7.0			8/2/79	6.6	90	25	103	114	- 24
Little East Pond Brook, Grafton Co.	7/24/38	7.0			8/2/79	6.6	90	25	89	94	- 4
Russell Pond, Grafton Co.	7/24/38	6.6	90	50	8/2/79	6.1	49	20	101	111	- 62

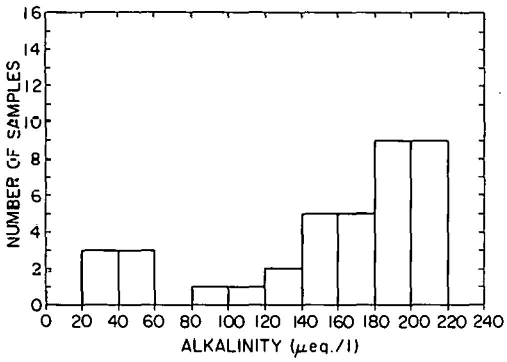

Figure IV-1. North Carolina Fisheries Data (June, July or August 1960-1963)

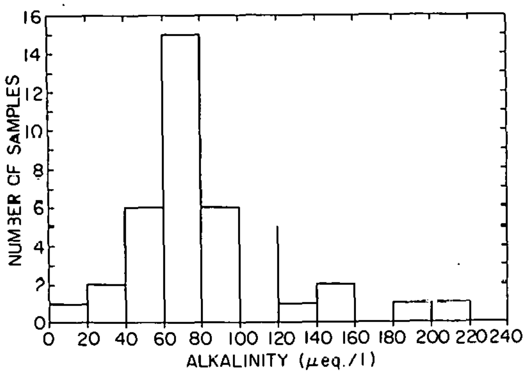

Figure IV-2. North Carolina Field Trip (6-29-79-7-4-79)

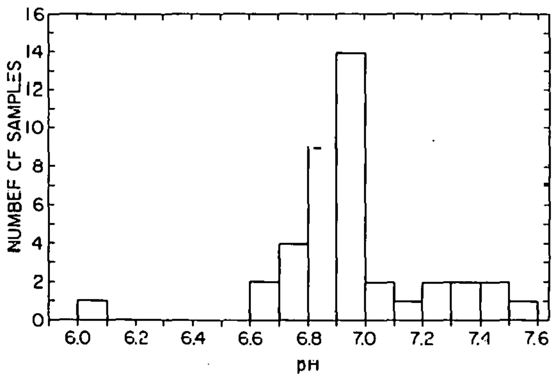

Figure IV-3. North Carolina Fisheries Data (June, July or August 1960-1963)

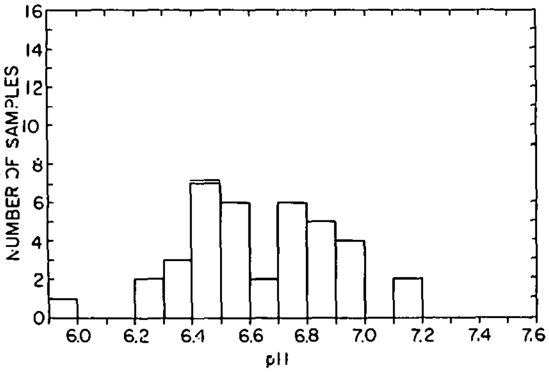

Figure IV-4. North Carolina Field Trip (6-29-79-7-4-79)

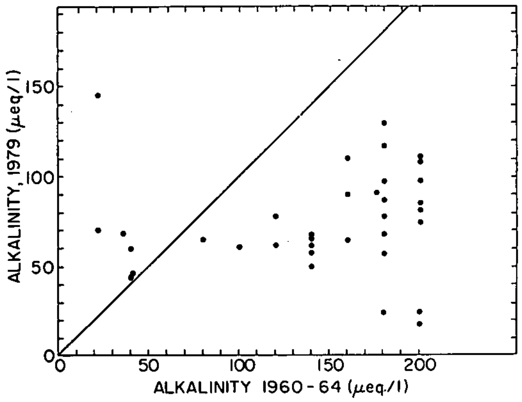

Figure IV-5. Alkalinity vs. Alkalinity for North Carolina Streams

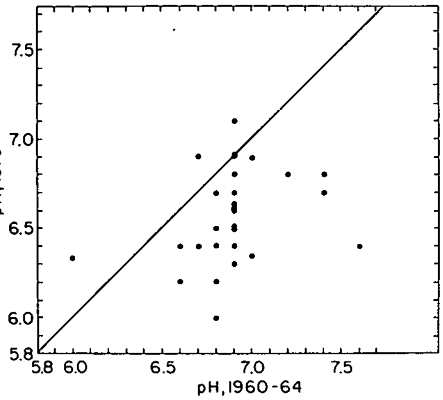

Figure IV-6. pH vs. pH for North Carolina Streams

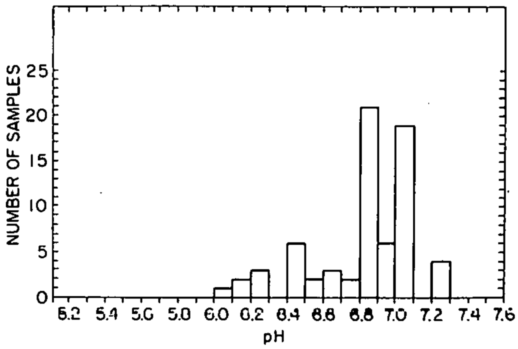

Figure IV-7. New Hampshire Fisheries Data (Summers of 1937, 1938, 1939)

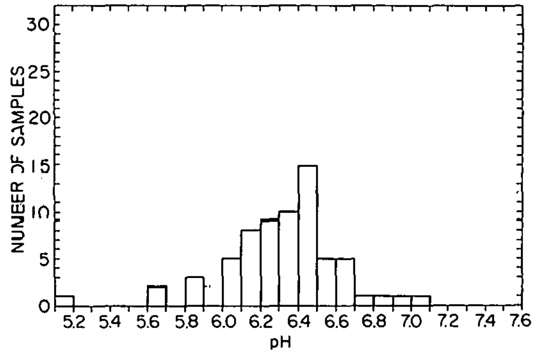

Figure IV-8. New Hampshire Field Trip (7-26-79-8-2-79)

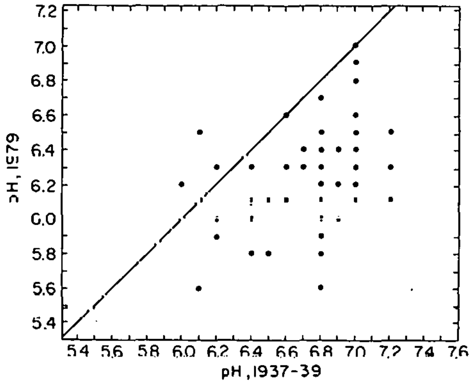

Figure IV-9. pH vs. pH for New Hampshire Streams & Lakes

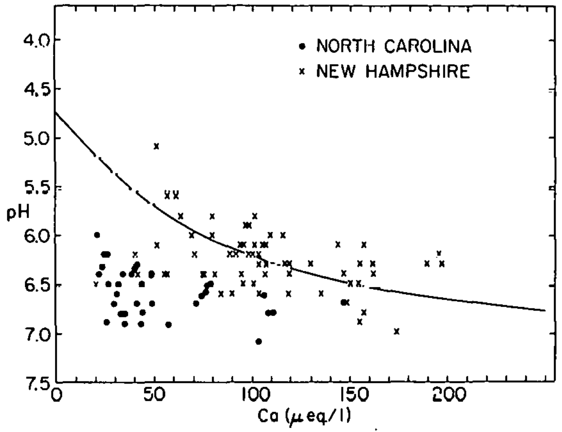

Figure IV-10. Calcium vs. pH for Headwater Streams in N.C. & N.H.

V. IMPACTS OF ACIDIFICATION ON AQUATIC BIOTA

Acidification of surface waters in sensitive areas causes a variety of changes in the aquatic flora and fauna. The extent of this impact ranges from changing population strengths to complete elimination of many species. The purpose of this section is to provide a review and description of the kinds of biological impacts which have been observed and which may be anticipated in sensitive waters which are altered by acid precipitation. Impacts on organisms other than fish are stressed here. Impacts on fish are discussed in section VI. This section is a collation of materials previously presented, and includes references to affects of acid mine drainage on biota.

Although the literature concerning effects of acid mine drainage (AMD) on freshwater ecosystems is extensive, it is not directly applicable to the acid precipitation problem. Often the uncontaminated waters of coal mining areas have higher alkalinity and hardness than the very soft waters acidified by acid precipitation. AMD water usually has a heavy load of iron and other heavy metals, and frequently depresses the oxygen concentration of receiving waters. High turbidity and the presence of chemical floc are also common and greatly alter aquatic habitats. These factors make it very difficult to extrapolate observations from AMD situations to those in the Laurentian Shield, for example.

The variety of species of both plants and invertebrate animals occurring in fresh waters is enormous and speciation differs markedly from one locale to another even though water chemistry may be similar. It is at best difficult and probably futile to try to interpret ecosystem damages at lower trophic levels by comparing lists of species. On the other hand, changes in major processes such as primary and secondary production, and decomposition can be broadly described and compared. Effects of stress on the major functional guilds may be compared from place to place. Finally a few groups of organisms seem to be remarkably insensitive to strong mineral acidity and are common to many acid environments, while some other groups are clearly intolerant of pH levels below 6.0 to 5.5.

A. Effects on Microbiota

The production of fish and other animal life in a lake is ultimately dependent upon the availability of organic food resources, primarily plant materials. The sources of organic materials may be divided into two major categories: autochthonous, originating by primary production in the lake, and allochthonous, transported into the lake by inflowing water, airborne litter, or dissolved in rain. The relative importance of each of these sources varies greatly from lake to lake. One principal route for both authochthonous and allochthonous organic matter into the trophic system of a lake is via the detritus.

Bacterial consumption and mineralization of detrital organic matter, both particulate (POM) and dissolved (DOM), allows a cycling of carbon which dominates the structure and the functioning of the system and provides what Wetzel[98] has called a fundamental stability to the system. In the deep, open water of the pelagic zone, where phytoplankton production normally provides a substantial portion of the nonrefractory organic matter, bacteria rapidly assimilate dissolved labile organic substances (PDOM) derived from photosynthesis[29,46] and convert it into bacterial biomass. Particulate organic matter (POM) from phytoplankton is assimilated at a somewhat slower rate. Only a small portion of the PDOM is refractory material likely to survive longer than 24 hr.[88] The bacterial mineralization rate appears to be rather slow, a few percent per day[17,99], so that this new biomass is actually available to other trophic levels. Not only do the bacteria conserve the energy stored in labile PDOM, which otherwise would be lost from the system, but they also convert (at a slower rate) some of the refractory DOM into a usable form. Fungal and bacterial communities render other POC into forms which are useful for detritovores.[13] The significance of these activities to ecosystem energetics can be better appreciated when one considers that on the order of 90% of the organic carbon in the water column is DOM and that detrital POM is many times larger than the total living carbon biomass.

There are other sources of detritus in the pelagic zone. In some lakes, particularly smaller and/or shallow lakes, macrophytes and benthic algae are important sources of autochthonous organic carbon. Material from these plants may contribute significantly to detritus in the pelagic zone. In deciduous forest lakes, leaf litter falling or blown onto the surface annually has been found to be 200 to 500 g dry leaves per meter of wooded shore line.[35,60] This forest litter, plus that which is added by stream imputs, contributes to both DOM (after leaching) and POM.

Water column detritus generated from all of these sources has three possible fates. It can be transformed biologically, it can sink to the sediments where it accumulates and/or is transformed biologically, or it is lost from the system by outflow. In the first two cases, microbial activity plays a key role in removing detritus.

The inhibition of microbial decomposition can have profound effects throughout an aquatic ecosystem. Detritus removal, conservation of energy, nutrient recycling, primary production, detritivore production and thus production at higher trophic levels, can all be affected by changes in microbial activity. Several investigations have indicated that microbial decomposition is greatly inhibited in waters affected by acid precipitation.

An abnormal accumulation of coarse organic detritus has been observed on the bottoms of six Swedish lakes where the pH decreased by 1.4 to 1.7 units in the past three to four decades.[37] Bacterial activity apparently decreased, while in some of the lakes the sediment surfaces over large areas were made up of dense felts of fungal hyphae. In one of the lakes, Gårdsjön, 85% of the bottom in the 0 to 2 m depth zone was covered with a thick felt of algae and organic debris, plus fungal hyphae. Lime treatment caused a rapid decomposition of the organic litter as well as great reductions of the felt[4], indicating that an inhibition of bacterial activities had taken place at low pH. Similar neutralizations of acidified lakes in Canada resulted in a significant increase in aerobic heterotrophic bacteria in the water column.[89] Results from field and laboratory experiments with litterbags in Norway[49] also indicate reduced weight loss of leaves in acidic waters. Dissolved organic carbon (DOC) in the inflowing water was found to contribute ca. 50% of allochthonous inputs and 8% of all organic carbon in Mirror Lake, while fine particulate organic carbon (FPOC) was negligible.[60] The extent to which this DOC input is converted to bacterial biomass or otherwise enters into the energetics of a lake is not known. Observations of abnormal accumulations of organic debris have also been made in AMD waters in South Africa[44] and West Virginia (J. DeCosta pers. comm.).

In laboratory experiments the decomposition rate of peptone by microbiota decreased with pH and the oxidation of ammonia ceased below pH 5. Bacterial cell counts and the species number of ciliates also decreased.[12] Numerous other studies indicate that the microbial decomposition of organic materials is markedly reduced at pH levels commonly encountered in lakes affected by acid precipitation.[49]

Accumulations of organic debris and extensive mats of fungal hyphae, as observed in the Swedish Lakes[37], both seal off the mineral sediments from interactions with the overlying water and retain organically bound nutrients which would otherwise have become available if normal decomposition had occurred. The reduction in nutrient availability can be expected to have a negative feedback effect on both plants and bacteria, further inhibiting their activities. The reduction of nutrient supplies to the water column from the sediments, because of the physical covering and from reduced mineralization of organic materials in the water itself, will lead to reduced phytoplankton productivity. These ideas have been formulated into the hypothesis of "self-accelerating oligotrophication" by Grahn et al.[37] Qualitative observations support this hypothesis but a quantitative evaluation is lacking.

Reduction of microdecomposer activities may have a direct effect upon the invertebrates. Although certain benthic invertebrates appear to feed directly on the allochthonous detritus material, it seems that "conditioned" (colonized by microorganisms) material is preferred, and that the nutritional value of the detritus is highly increased by conditioning.[13] Bacteria may also be a food source to be removed by the filtering apparatus of organisms such as Calanoida. An inhibition of the microbiota or a reduction in microbial decomposition processes would therefore have a direct impact on the lakes' animal communities.

B. Effects on Benthic Plants

In waters affected by acid precipitation major changes occur within plant communities. Most of the available data are qualitative and descriptive although some experimentation has been done. Intact lake sediment cores which included the rooted macrophyte <u>Lobelia dortmana</u> were incubated at three pH levels (4.0, 4.3 to 5.5, 6.0) at Tovdal in southern Norway. The growth and productivity of the plant (O_2 production) were reduced by 75% at pH 4 compared to the control (pH 4.3 to 5.5) and the period of flowering was delayed ten days at the low pH.[66]

In five lakes of the Swedish west coast, a region severely affected by acid precipitation, in the past three to five decades the macrophyte communities dominated by <u>Sphagnum</u> have expanded. In the sheltered and shaded locality of Lake Örvattnet, in the 0 to 2 m depth zone, the bottom area covered by <u>Sphagnum</u> increased from 8 to 63% between 1967 and 1974. In the 4 to 6 m depth zone, the increase was from 4 to 30%. At the same time, pH in Örvattnet decreased 0.8 units to ca. 4.8.[38] Similar growths of *Sphagnum* occur in other Swedish lakes, in Norwegian lakes, and in AMD water as well.[42,44,45,49] At the pH of these acid waters, essentially all of the available inorganic carbon is in the form of CO_2 or H_2CO_3. Conditions are more favorable for *Sphagnum*, an acidophile which appears to simply outgrow the flowering plants under acid conditions.

In developing their hypothesis on oligothrophication, Grahn et al.[37] have stressed two biologically important consequences of this *Sphagnum* expansion. First, *Sphagnum* has an ion-exchange capacity which results in the withdrawal of base ions such as Ca from solution, thus reducing their availability to other organisms. Secondly, dense growths of *Sphagnum* form a distinct biotope which is unsuitable for many members of the bottom fauna.

Under some acid conditions, unusual accumulations of both epiphytic and epilythic algae may occur. In the Swedish lakes *Mougeotia* and *Batrachospermum* become important components of the benthos.[37] In Lake Oggevatn (pH 4.6), a clear-water lake in southern Norway, not only is *Sphagnum* beginning to choke out *Lobelia dortmana* and *Isoetes lacustris*, but these macrophytes have been observed to be festooned with filamentous algae.[49]

A floristic survey, conducted in Lake Colden (elevation 842m) in 1932, does not mention *Sphagnum*, but describes a macrophyte community typical of clear oligotrophic lakes of the Adirondack Mountains (*Eriocaulon*, *Lobelia*, *Myriophyllum*, *Isoetes*, *Utricularia*, etc.). On 6/11/58 Colden's surface pH was 5.8 In mid-July 1979, pH was 4.9 and the flora from the shore to 0.5 m depth (ca. 2-5m from shore) around most of the lake perimeter was dominated by extremely dense, uniform stands of Sphagnum *pylaesii* Brid. (390 g m^{-2}). In some areas *Utricularia* alone or with *Sphagnum* also formed dense stands which were covered over by flocculent growths of algae in which *Fragilaria viresence*, *Tabellaria fenestrata*, *Eunotia triodon* and *Mougeotia* sp. were abundant. Prominent mats composed primarily of blue-green algae, fungal hyphae and plant detritus were spreading over the dense *Utricularia* stands (G. H. Hendrey and F. Vertucci, unpublished data). Colden, once famous for its trout fishing, is now too acidic to support fishlife. These observations, the first of their kind in North America, parallel findings in some acidified Swedish and Norwegian lakes. The question of why some acidified lakes show these extreme floristic changes, while many others do not, remains a mystery.

Heavy growths of filamentous algae and mosses occur not only in acidified lakes but have also been reported in streams in Norway affected by acidification. In experiments in artificial stream channels using water and the naturally seeded algae from an acidified brook (ph 4.3 to 5.5), an increase in the acidity to pH 4 by addition of sulfuric acid led to an increased accumulation of algae compared to an unmodified control.[48] The flora was dominated by *Binuclearia tatrana*, *Mougeotia* spp., *Eunotia lunaris*, *Tabellaria flocculosa*, and *Dinobyron* spp., each accounting for at least 20% of the flora at one time or another. The rate of radioactive carbon uptake per unit of chlorophyll in the channels, measured on just two occasions, was found to be lower in the acid channel by ca. 30%, suggesting greater algal accumulation at low pH despite lower productivity.

Several factors may contribute to these unusual accumulations of certain algae. The intolerance of various species to low pH or to consequent chemical changes[76] will allow just a few algal species to utilize the nutrients available in these predominantly oligotrophic waters. Many species of invertebrates are absent at low pH, and removal of algae by grazing is probably diminished. Microbial decomposition is inhibited, as was previously noted, also reducing the removal of algal mass.

C. Effects on Phytoplankton

There is no consistency among various investigations as to which taxa are likely to be dominant under conditions of acidification. The Pyrrophyta may be more common (e.g., species of Peridinium and Gymnodinium) than others in lakes near 4.0. With decreasing pH in the range 6.0 to 4.0, many species of the Chlorophyta are eliminated although a few tolerant forms are found in the acid range. In the survey of 155 Swedish west coast lakes, blue green algae became less important with decreasing pH,[1] but Kwiatkowski and Roff[65] found the opposite to be true in lakes of the Sudbury, Ontario, region.

There are, however, conspicuous decreases in phytoplankton species number, species diversity, biomass, and production per unit volume (mg/m^3) with decreasing pH. Lake clarity and the compensation depth increase with lake acidification, so that areal primary production (mg/m^2), although lower in acid than nonacid lakes, is not as severely depressed as is production per unit volume.[1,58,65] The low phytoplankton biomass (< 1 mg/ℓ) has been correlated to the concentration of available phosphorus, which generally decreases with lower lake pH.[1] Low availability of inorganic carbon has also been suggested as a factor limiting primary production in acidic lakes.[58,63]

Kwiatkowski and Roff[65] have carried out a highly quantitative study of phytoplankton in six lakes of the Sudbury region, which are impacted by atmospheric effluents from a huge nickel-copper smelter complex. Curvilinear equations are presented for phytoplankton diversity, secchi transparency depth, Chl. a, and productivity.

D. Effects on Invertebrates

Zooplankton analyzed from net samples collected from 84 lakes in Sweden showed that acidification caused the elimination of many species and led to simplification of zooplankton communities.[1] Crustacean zooplankton were sampled in 57 lakes during a Norwegian lake survey in 1974,[47] and the number of species observed was found to decrease with pH. The distributions and associations of crustacean zooplankton in 47 lakes of a region of Ontario affected by acid precipitation were strongly related to pH and to the number of fish species present in the lakes. However, fish and zooplankton were each correlated with the same limnological variables, especially pH.[94] Zooplankton communities become less complex with fewer species present as acidity increases. Food supply, feeding habits, and grazing of zooplankton will probably be altered following acidification, as a consequence of decreased biomass and species composition of planktonic algae and bacteria. In streams continuously polluted by AMD, the number of zooplankton species was low compared to the number of individuals, was lower than in less polluted conditions downstream.[84]

Surveys at many sites receiving acid precipitation in Norway, Sweden, and North American[4,14,18,47] have shown that waters affected by acid precipitation have fewer species of benthic invertebrates than localities which are less acid. In 832 Norwegian lakes, J. Økland[81] found no snails at pH values below 5.2; snails were rare in the pH range 5.2 to 5.8 and occurred less frequently in the pH range 5.8 to 6.6 than in more neutral or alkaline waters. The amphipod *Gammarus lacustris*, an important element in the diet of trout in Norwegian lakes where it occurs, is not found in lakes with pH less than 6.0.[82] Experimental investigations have shown that the adults of this species cannot tolerate 24 to 48 hours of exposure to pH 5.0.[15]

In the River Duddon in England, pH is the overriding factor which prevents permanent colonization by a number of species of benthic invertebrates, primarily herbivores, of the upper acidified reaches of the river.[95] In the more acid tributaries (pH < 5.7), the fauna consisted of an impoverished Plecopteran community. Ephemeroptera, Trichoptera, *Ancylus* (Gastropoda), and *Gammarus* (Amphipoda) were absent. The epiphytic algal flora was reduced (in contrast to increases noted in Norway), and leaf litter decomposition was retarded. The food supply of the herbivores was apparently decreased, and this may have played a role in the simplification of the benthic fauna. Quantitative data concerning the effects of low pH on the benthic fauna are also available for some acid Norwegian lakes,[49] where notably low standing crops have been observed.

Many studies of invertebrate communities in streams receiving AMD have been conducted. Comparisons are usually made between affected and unaffected zones or tributaries, and experimental acidification has been performed.[54] The numbers of species, species diversity, and biomass are usually greatly reduced. Generally, in AMD waters Chironomidae (midges) and *Sialis* (alderfly) are the most tolerant macroinvertebrates. The order Trichoptera has more tolerant species than does Plectoptera (stone flies), and Plecoptera has more tolerant species than does Ephemeroptera (mayflies).[25,26,44,45,84,102]

This order of tolerance is essentially the same as seen in waters acidified by acid precipitation. However, the Hemiptera, Notonectidae (backswimmer), Corixidae (water boatman), and Gerridae (waterstrider) are often abundant in acidified soft waters at pH as low as 4.0. This may, in part, be due to lack of fish predation.

Benthic plant communities in lakes may be greatly altered as a consequence of lake or stream acidification (as discussed above). Under these conditions, benthic invertebrate populations may be affected by starvation, evacuation, or extinction due to the loss of preferred habitat. Chironomids[83] and other benthic invertebrates,[20] present in many of the poorly buffered northeastern lakes, have diverse feeding habits and habitats. These invertebrates, in many situations, will be affected by altered decomposition cycles and variations in available foods caused by increased acidification.

The tolerance of aquatic invertebrates to low pH varies over their life cycles, and the emergence of adult insects seems to be a period particularly sensitive to low pH levels. Bell[11] and Moss,[76] in similar studies with Trichoptera and Ephemeroptera, found emergence patterns to be affected at pH levels which were higher than the 30-day survival limits. Many species of aquatic insects emerge early in the spring, even through cracks in the ice and snow cover. Because of the contamination of spring meltwaters by atmospheric pollutants, including heavy metals,[41,50,55,56] the early emergers must, in many cases, be exposed to the least desirable water conditions.

Damage to invertebrate communities will influence other components of the food chains. Benthic invertebrates assist with the essential function of removing dead organic material. In litterbag experiments, the effects of invertebrates on leaf decomposition were much more evident at higher pH than at low pH.[49] A reduction of grazing by benthic invertebrates may also contribute to the accumulation of attached algae in acidified lakes and streams.

A short reach of Norris Brook, a tributary to Hubbard Brook in New Hampshire, was acidified to pH 4 in the Spring-Summer of 1977, to evaluate the effects of acidification on a stream ecosystem. Excessive accumulations of algae occurred, bacterial biomass and heterotrophic activity per unit of organic matter were reduced, and both invertebrate diversity and biomass decreased.[43]

In unstressed lake ecosystems there tends to be a continuous emergence of different insect species available to predators from spring to autumn. In acid-stressed ecosystems the variety of prey is reduced and periods may be expected to occur in which the amount of prey available to fish (and waterfowl) is diminished.

E. Effects on Vertebrates

Pough[86] has described effects of acid precipitation on spotted salamanders (<u>Ambystoma jeffersonianum</u> and <u>A. maculatum</u>), which breed in temporary rain pools. Below pH 5 and 7, respectively, these species suffered high mortality during hatching in laboratory tests. This mortality was associated with distinctive embryonic malformations. The development of salamander eggs in five ponds near Ithaca, NY, ranging from pH 4.5 to 7.0, were observed. An abrupt transition from low to high mortality occurred below pH 6. Although a synergistic effect of several stresses may have been possible, the studies suggested that pH was the critical variable. Pough cites studies which indicate a decline in British frog populations.[86]

In Tranevatten, a lake acidified by acid precipitation, near Gothenburg, Sweden, the lake pH has declined to 4.0 to 4.5, and all fish have been eliminated. The frog species <u>Rana temporaria</u> is being eliminated as well. Currently, only adults 8 to 10 years old are found. While many egg masses were observed in 1974, few were found in 1977. The few larvae observed in 1977 subsequently died. Another species, <u>Bufo bufo</u>, is also being eliminated from this lake.[42]

Frogs and salamanders are important predators on invertebrates, including mosquitoes and other pests, in lakes and puddles or pools. In turn, they are themselves important prey for higher trophic levels in an ecosystem.

F. Biological Effects Summary

Acid precipitation, by causing increased acidity in lakes, streams, pools, and puddles, can cause slight-to-severe alteration in communities of aquatic organisms. The effects are similar to those observed in waters receiving acid mine drainage (AMD), but the toxicology and chemistry are not as complicated by the presence of high concentrations of heavy metals, chemical flocs, turbidity, etc., such as are found in AMD.

The kinds of effects that are likely to result from increasing acidification are shown in Table V-1. In order to provide step-functions for damages, which may be of use in modelling ecosystem acidification, a summary of damages to aquatic organisms as functions of pH is presented in Table V-2.

Table V-1

Damages to Aquatic Biota Likely to Occur with Increasing Acidity

1. Bacterial decomposition is reduced and fungi dominate saprotrophic communities. Organic debris accumulates rapidly.
2. The ciliate fauna is greatly inhibited.
3. Nutrient salts are taken up by plants tolerant of low pH (mosses, filamentous algae) and by fungi. Thick mats of these materials may develop which inhibit sediment-to-water nutrient exchange and choke out other aquatic plants.
4. Phytoplankton species diversity, biomass, and production are reduced.
5. Zooplankton and benthic invertebrate species diversity and biomass are reduced. Remaining benthic fauna consists of tubificids and *Chironomus* (midge) larvae in the sediments. Some tolerant species of stone flies and mayflies persist as does the alderfly. Air-breathing bugs (waterboatman, backswimmer, water strider) may become abundant.
6. Fish populations are reduced or eliminated (see Section VI).

Table V-2

Summary of Damages to Aquatic Organisms with Decreasing pH

pH range	Effects
8.0-6.0	Long-term changes of less than 0.5 pH units likely to alter the biotic composition of freshwaters to some degree. The significance of these slight changes is however, not great. A decrease of 0.5 to 1.0 pH units in the range 8.0 to 6.0 may cause detectable alterations in community compositon. Productivity of competing organisms will vary. Some species will be eliminated.
6.0-5.5	Decreasing pH will cause a reduction in species numbers and, among remaining species, significant alterations in ability to withstand stress.
5.5-5.0	Many species will be eliminated, and species numbers and diversity indices will be reduced. Crustacian zooplankton, phytoplankton, molluscs, amphipods, most mayfly species, and some stone fly species will begin to drop out. In contrast, several pH-tolerant invertebrates will become abundant, especially the air-breathing forms (e.g., Gyrinidae, Notonectidae, Corixidae), those with tough cuticles which prevent ion losses (i.e. *Sialis lutaria*), and some forms which live within the sediments (Oligochaeta, Chiromomidae, and Tubificidae). Overall, invertebrate biomass will be greatly reduced.
5.0-4.5	Decomposition of organic detritus will be severely impaired. Autochthonous and allochthonous debris will accumulate rapidly. Most fish species are eliminated.
< 4.5	All of the above changes will be greatly exacerbated, and all fish will be eliminated.

VI. REGIONAL ASSESSMENT OF ACIDIFICATION IMPACTS OF FISH POPULATION

A. Introduction

Acidification of surface waters in geologically sensitive regions by acid precipitation may be viewed as a continuous process of water quality change, analogous to the acidimetric titration of a bicarbonate solution. The "titration curve" can be segmented into three stages, which define both the extent and nature of water quality change and the biological impacts. The initial stage of acidification is characterized by decreased alkalinity, but pH levels remain greater than 6.0 and bicarbonate buffering is maintained. No significant impacts on fish population have been observed at this level of acidification. Loss of HCO_3 buffering, and resulting severe temporal pH fluctuations occur in the second stage of acidification. Stress, reproductive inhibition, and episodic mortalities may initiate recruitment failure and eventual extinction of fish populations during this stage of acidification. The final stage of acidification is characterized by chronically depressed pH and elevated toxic metal levels. Fish are generally absent from waters at this level of acidification. This general view of acidification impact levels on fish populations is supported by extensive, carefully documented data from sensitive regions in Norway[103] and eastern North America.[9,91]

More recently, Henriksen[52,53] has developed models of the acidification process which quantitatively relate the stages of acidification described above to precipitation acidity levels in sensitive regions. These models provide a basis for predicting the regional extent and levels of acidification which have occurred in sensitive areas where historical data are lacking. The models also permit evaluation of expected fish population status on a regional level. Considering the paucity of carefully documented fish population data for waters in sensitive areas of the eastern United States and the time constraints for obtaining and interpreting new data, it was decided to utilize the predictive models to obtain a regional perspective of acidification impacts on fish populations. The approach taken was to first calibrate the Norwegian models using North American data and verify the predictions obtained by comparison with known water quality and fish population data from the Adirondack region (New York) and Experimental Lakes Area (Ontario, Canada). The next step will be to apply the models to water quality data from other sensitive regions in the United States to evaluate acidification and fish population status.

B. Procedure

Data Sources. Water quality and fish population data obtained from the following sources were utilized in model calculation and testing.

1 Water chemistry and fish survey data for Adirondack Mountain lakes (New York): Schofield (1976 and file data); New York State Biological Surveys of the Upper Hudson, Raquette, Mohawk-Hudson, and Black River Watersheds (1931-1934, NYS Dept. Conservation).

2. Stream water quality and fish population status in selected areas of West Virginia: Personal Communication and file data from Donald Gasper, W. Virginia Dept. of Natural Resources.

3. Water quality data for lakes in the BWCA, N.E. Minnesota: G.E. Glass, EPA Research Lab (Duluth), Draft report on Impacts of air pollutants on Wilderness areas of N. Minnesota.

4. Water chemistry and fish population data for Connecticut lakes.[24,79]

5. Water chemistry and fish population data for Rhode Island lakes.[39,40]

6. Water chemistry for Massachusetts lakes.[21]

7. Water chemistry and fish population data for ELA lakes.[9]

8. Water chemistry and fish population data for the North Carolina bay lakes.[30,31]

9. Water chemistry for coastal plain streams in S. Carolina and Georgia.[10]

C. Model Calibration and Verification

1. Acidification. Acidification is defined as the decrease in alkalinity, which results from an equivalent increase in strong acid input. Three independent approaches to estimating regional acidification were applied to the Adirondack lake data base. The first approach developed by Henriksen[51] utilized the empirical relationships between precipitation pH (volume weighted annual mean) and estimated regional acidification of lakes in southern Norway. Regional acidification, a decrease in alkalinity associated with excess sulfate (corrected for seasalt) in precipitation (Ac-S, $\mu eq/\ell$), was calculated by regression as:

$$\text{Ac-S} = \frac{(10^{-\text{pH}} \times 10^{6})-17}{0.38} \qquad (1)$$

The volume weighted, mean annual hydrogen ion concentration for precipitation collected in the western Adirondack region (Hinckley, New York; USGS network) in 1975 was pH 4.26. Substituting this value in equation (1) yields an estimated acidification level of 99.9 eq/ as the average regional acidification of the western Adirondacks.

The second approach to estimating acidification was also as given by Henriksen[51]: Acidification = pre-acidification alkalinity - present day alkalinity. In this case, pre-acidification alkalinities (ALKp) for the Adirondack lakes were estimated from 1975 measurements of calcium concentrations and the empirical relationship between calcium concentration and alkalinity observed in the Experimental Lakes Area (Ontario) waters:

$$ALKp(\mu eg/1) = 1.42\ (Ca\ \mu eq/1)-32 \qquad (2)$$

The assumptions made in employing this method of estimating pre-acidification alkalinities are as follows:

a) Alkalinity in pristine (unacidified) lakes (e.g. the ELA region) is due primarily to HCO_3^-, which is accompanied by approximately equivalent amounts of calcium and magnesium, and the Ca/Mg ratio is relatively constant. This relationship (equation 2) is of a general nature and can be applied to other regions with similar geological settings. This assumption is supported by the similarity of the calcium-alkalinity relationship for pristine lakes in northern Norway and the ELA.[52]

b) Calcium levels do not increase or decrease in response to acidification. Historical calcium data are not available for the Adirondacks region, but estimates of calcium from 1930's alkalinity data and equation (2) were not significantly different ($P=.05$) from calcium levels measured in 1975 for 36 Adirondack lakes. Additional support for this assumption comes from studies in Sweden[73] which demonstrated that no significant changes in calcium concentration were detected in acidified lakes of south-central Sweden, where significant increases in H^+ and SO_4^{-2} did occur. Also, Wiklander[100] reported that base exchange efficiency is very low in acidic podzols, where the exchange complex is typically dominated by H^+ and Al^{+3} ions, rather than Ca^{+2}. Watt (1979) compared the pH and ionic composition of lakes in Nova Scotia sampled in 1955 and 1977. Significant decreased in pH levels were observed but no significant change in Ca^{++} was found.[96]

Acidification (Ac-Ca) was then calculated as the difference between pre-acidification alkalinity (equation 2) and current alkalinity measurements (ALK^*):

$$Ac\text{-}Ca\ \mu eq/\ell = ALKp - ALK^* \qquad (3)$$

The estimated mean acidification for 215 Adirondack lakes sampled in 1975 was Ac-Ca = 99.6 μeq/ℓ (S.D.= 30.6), which compares well with the first estimate of acidification (Ac-S = 99.9 μeq/ℓ). These estimates of lake acidification are not correlated with current pH levels (Figure VI-1), which is indicative of the regional uniformity of acidification. Estimated acidification levels are significantly correlated with sulfate levels (Figure VI-2), indicating that atmospheric strong acid (H_2SO_4) inputs are the primary source of acidification.

The third approach to estimating acidification was to directly compare historical (1930's data) and current (1975) alkalinity measurements. Alkalinity measurements obtained in the 1930's for Adirondack lakes employed methyl orange indicator for end point determination in the titration of water samples for total alkalinity measurment. This method yields an apparent end point pH of approximately 4.4, which over-estimates the true alkalinity (as measured by Gran plot location of the titration curve inflection for the 1975 data) by the amount of free H^+ ions present in solution at this pH level (40 μeq/ℓ H^+).

The 1930's alkalinity measurements were corrected to correspond to true alkalinity levels by subtracting 40 $\mu eq/\ell$ from each value. Acidification was then estimated as the difference between corrected 1930's alkalinity levels and 1975 alkalinity measurements. The mean acidification for 36 Adirondack lakes, where data were available from both periods, was 104.7 $\mu eq/l$ (SD 50.9). Estimated acidification for the same lakes, using the calcium-alkalinity model (equation 2), was 105.7 $\mu eq/l$ (SD 31.8) which is not significantly different from the previous estimate (p .01).

2. Lake Classification. Lakes were classified into three categories, which define acidification and fish population status as discussed previously, utilizing regional acidification estimates and lake calcium concentrations. Henriksen[53] constructed a nomogram by grouping data from 719 lakes in southern Norway into discrete pH classes and then determined the least-squares regressions of calcium on acidification for each class. The resulting nomograph (Figure VI-3) can then be used to predict lake pH (and fish population status) from lake calcium levels and either regional acidification or precipitation pH. The two regression lines derived from the Norwegian lake data define the boundaries for the three classifications:

$$HCO_3 \text{ lake boundary} \quad Ca(\mu eq/\ell) = 49.9(.28 + .0192\ Ac\text{-}S) \qquad (4)$$

$$\text{Acid lake boundary} \quad Ca(\mu eq/\ell) = 49.9\ (.07 + .0139\ Ac\text{-}S) \qquad (5)$$

The characteristics, expected pH levels, and boundary calcium levels for this classification, as applied to the Adirondack data are given in Table VI-1.

The observed pH levels for lakes classified as described below are illustrated in Figure VI-3. For the Adirondack data, 70% of the lakes were correctly classified and 98% of the ELA lakes were correctly designated as HCO^3 lakes. These results are similar to those obtained by Henriksen[53] for classification of lakes in southern Norway. An additional test of the validity of this model for predicting lake pH changes resulting from acidification is illustrated in Figure VI-4. Increase in H^+ concentration between the 1930's and 1975, as determined from differences in pH, were compared to calcium concentrations measured in 1975 for 36 Adirondack lakes. The break in the plot of H^+ against calcium occurs precisely at the calcium level predicted from equation (4). The results of these model predictions for Adirondack and ELA lake data appear to be quite adequate for determining acidification status.

Fish population status in the Adirondack lakes is presented in Table VI-2. The frequencies of lakes not supporting fish life in each of the three lake classifications are comparable to those reported by Henriksen[53] for lakes in southern Norway. The lakes of the ELA are still predominantly pristine, HCO_3 type waters and the fish populations are unaffected.[9]

Table VI-1

Lake Classification for Adirondack Mountain lakes, based on the nomograph of Henriksen.[53]

Lake Class	Expected pH	Fish Population	Boundary Ca µeq/ℓ (Adirondack)
HCO_3	>5.3	Good	>110
Transitional	4.7-5.3	Sparse	73-110
Acid	<4.7	Barren	<73

Table VI-2

Fish population status in 214 Adirondack Mountain lakes, classified according to the nonograph of Figure VI-3.

Lake Type	HCO_3	Trans	Acid
Expected pH	>5.3	4.7-5.3	<4.7
Number of lakes	69	97	48
Number in pH range	61	65	27
% correctly classified	88.4	67.0	56.3
% without fish	2.9	54.6	91.7

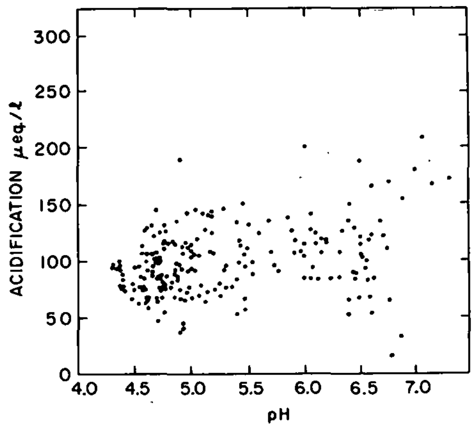

Figure VI-1. Acidification of Adirondack Lakes in Relation to pH measured in 1975 (215 Lakes). Mean Acidification = 99.6 μeqℓ, SD = 30.6, Where Acidification μeq/ℓ = 1.42 (Ca μeq/ℓ)-32 (ALK μeq/ℓ)

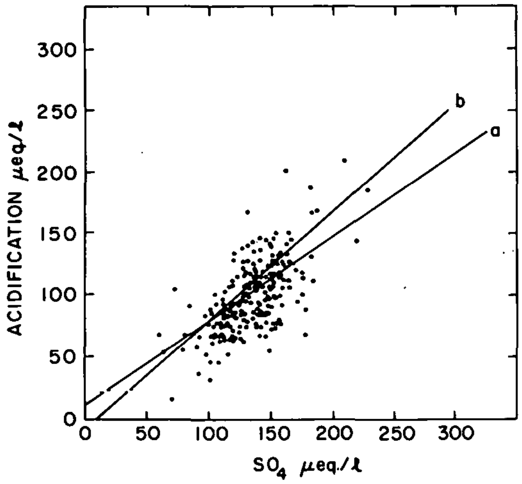

Figure VI-2. Acidification of Adirondack Lakes in Relation to SO_4 measured in 1975 (215 Lakes). Regression:

(a) Acidification = 0.676 (SO_4 μeq/ℓ) +10(data)(r=0.62, $p < .01$);

(b) Acidification = 0.89 (exs. SO_4 μeq/ℓ)-12. Henriksen 1979.[51]

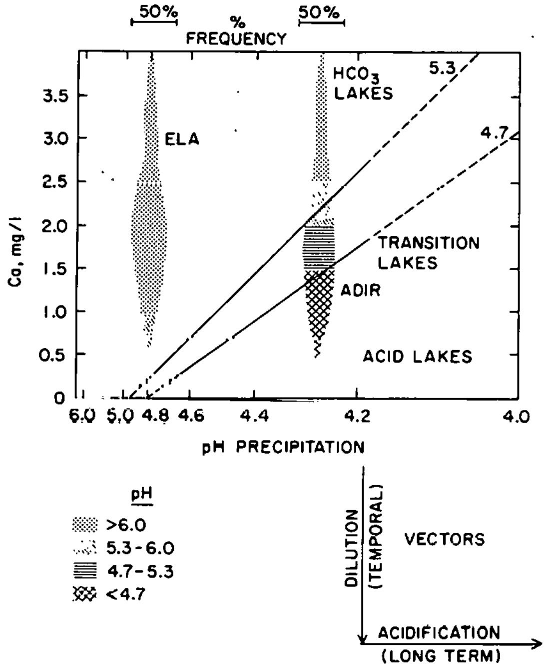

Figure VI-3. Nomograph for Predicting Lake pH and Fish Population Status From Lake Ca Levels and Either Regional Acidification or Precipitation pH. Regression Lines for the Boundary Between HCO_3^- and Transition Lakes, are Given in the Text as Equations (4) and (5) Respectively

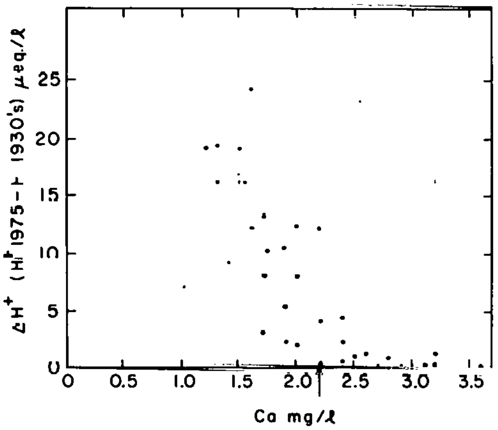

Figure VI-4. Changes in H^+ Concentration in 36 Adirondack Lakes From the 1930's to 1975, in Relation to Ca Levels Measured in 1975. The Arrow Designates the Critical Ca Level for Loss of HCO_3^- Buffering, as Predicted From Henriksen's[53] model for a Region Exposed to Precipitation With a Weighted Mean pH of 4.26

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APPENDIX-I

Water Quality Maps for States of the Eastern U.S.

The maps presented here are based on data in the Acidification Chemistry Information Database (ACID). About half of the currently available data which the authors have located is in ACID.

Station locations are shown in the maps of average pH and/or alkalinity. Data has also been organized on a county-by-county basis, which reflects (a) the minimum alkalinity value observed in each county and (b) the average of all station values, in the period 1976-1979. The minimum value map constitutes a gross-scale sensitive areas map.

The following states are included as of January 1980: Connecticut, Delaware, Georgia, Kentucky, Maryland, Massachusetts, Minnesota, New Hampshire, New Jersey, New York, North Carolina, Rhode Island, South Carolina, Tennessee, Vermont, Virginia, West Virginia and Wisconsin.

APPENDIX-II
Sources of Water Chemistry Data
9/28/79

Reference Code ACID	Source Description
001	USGS Water Supply Paper #1132, Quality of Surface Waters of the United States, 1948, parts 1-6.
002	USGS Water Supply Paper #108, Quality of Water in the Susquehanna River Drainage Basin, 1904.
003	USGS Water Supply Paper #193, Quality of Surface Water in Minnesota, 1907.
004	USGS Water Supply Paper #1290, Quality of Surface Waters of the United States, 1953, parts 1-4.
005	USGS Water Supply Paper #1571, Quality of Surface Waters of the United States, 1953, parts 1-4.
006	USGS Water Supply Paper #1572, Quality of Surface Waters of the United States, 1958, parts 5 and 6.
088	United States Forest Service Research Station, Gatlinburg, TN, unpublished data.
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Reference Code ACID	APPENDIX-II (Continued) Source Description
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Reference Code ACID	APPENDIX-II (Continued) Source Description
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