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WITHDRAWN

**EFFECTS OF ACID DEPOSITION (RAIN) ON A  
PIEDMONT AQUATIC ECOSYSTEM:  
ACID INPUTS, NEUTRALIZATION and pH CHANGES**

by Alan W. Elzerman

Department of Environmental Systems Engineering

Clemson University *Water resources  
research institute*

Clemson, South Carolina 29631

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B-141-SC

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ACID INPUTS, NEUTRALIZATION and pH CHANGES

by

Alan W. Elzerman and Robert W. Talbot  
Environmental Systems Engineering  
Clemson University  
Clemson, SC 29631

Submitted to:

Bureau of Reclamation  
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Washington, DC 20242

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South Carolina Water Resources Research Institute  
Clemson University  
Clemson, SC 29631  
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## I. INTRODUCTION

This report is a summary of acid rain research conducted during the period March, 1980, through December, 1982. The details of this and related investigations appear in parts of or substantially comprise one or more of seven Master of Science theses (LaManna, Lesan, Norton, Owings, Perry, Pott, Sviatyla) and one Doctor of Philosophy thesis (Heatley) of students in Environmental Systems Engineering, Clemson University. In addition, several literature publications have been or are being prepared which expand on selected aspects of the study, and further research is being developed. Since it would be impractical to reproduce all of the information, the highlights are presented in this report. Readers desiring more information should contact the senior author of this report.

Atmospheric deposition of strong acids (wet and dry fallout of acids from the atmosphere) is a widespread problem that may become more severe with increased use of coal (Likens, 1976; Gorham, 1976). Acid inputs are of immediate concern in areas with watershed systems having low buffering capacities, as found in areas of Scandanavia, the American Northeast, Appalachian Mountain areas, and the South Carolina Piedmont region (Glass, et al., 1979; EPA, 1979). Although the intricacies and relationships in the path from fuel combustion to ultimate ecosystem impact are not fully understood, sufficient evidence of detrimental effects on fish, other biota, and toxic material distribution has been obtained to stimulate multimillion dollar monitoring and research programs in the U.S. and Europe (EPA, 1979a).

However, significant research needs still remain to be addressed. For example, the actual, rather than suspected, importance

of increased acid deposition to Piedmont aquatic ecosystems has received little or no attention. On a broader scale, detailed investigations of selected watershed systems are required to aid in interpretation of results from the large monitoring projects (Galloway, et al., 1978). Investigations of actual interactions of acid deposition with soil and aquatic systems are needed to go beyond currently available predictions based solely on bedrock geologies and water alkalinities.

Ultimate adverse impacts of acid deposition on the biota and water quality of a watershed ecosystem stem from changes in pH, a central biological and chemical variable, induced variations in the chemical composition of soils, sediments, and water, changes in major nutrient fluxes, and mobilization of toxic materials (Galloway, et al., 1978). A prerequisite to the study and prediction of adverse impacts is a knowledge of the composition and amount of acid inputs and post-deposition reactions that occur between the acid inputs and components of the terrestrial and aquatic systems. Both the neutralization mechanisms and the neutralization capacities (over representative time scales) are relevant (Johnson, 1979).

Since fuel combustion products are transported over great distances in the atmosphere, widespread effects of acid deposition, even in rural areas, may be expected. For example, the average pH of rain in the South Carolina Piedmont region decreased from 5.3 in 1955 to 4.4 in 1972 (Galloway, et al., 1978). The current volume-weighted average rain  $H^+$  concentration at Clemson, SC expressed as pH remains approximately pH 4.4 (NADP, 1979-82), but single storm event values as low as pH 3.7 have been observed (NADP, 1979-1982).



Consequently, the intent of this investigation was to provide a first look at the significance of acid deposition in the South Carolina Piedmont and some nearby lakes in the southern Appalachian Mountain region. Specific investigations focused on fundamental questions of the amount and type of acid inputs, neutralization reactions in soil and water phases, storm event changes in streamwater chemistry, and the influence of acid deposition on watershed fluxes of metals and nutrients. Information on these fundamental considerations is requisite for even an initial consideration of the significance of increased acid deposition to South Carolina Piedmont ecosystems and the identification of research and management needs.

## II. STUDY OBJECTIVES

The overall objective of this investigation was to elucidate fundamental information and questions concerning the chemistry of acid deposition and its interactions with watershed and aquatic systems in the South Carolina Piedmont, and to relate this information to an initial assessment of the significance of acid deposition to the region. Specific objectives may be summarized as follows:

1. Survey selected lakes in the South Carolina Piedmont and southern Appalachian Mountain region for evidence of actual or potential susceptibility to acidification.
2. Determine the composition and amount of atmospheric deposition of acidity and related materials to the region.
3. Investigate neutralization reactions, storm induced changes in streamwater chemistry, and acid influences on nutrient and toxic material fluxes in a representative Piedmont watershed (Lake Issaqueena).
4. Identify research and management needs.

### III. EXPERIMENTAL METHODS

#### Study Area

Regional Survey: In the original survey of the western North and South Carolina and northern Georgia area, samples were collected from over twenty lakes (Sviatyla, 1982). As discussed later in RESULTS AND DISCUSSION, ten lakes were included in the final regional survey. The locations and names of these lakes are given in the aforementioned section.

Lake Issaqueena Study: Lake Issaqueena was selected for intense investigation because: 1) it is representative of a Piedmont watershed with rural development, 2) it is a well defined watershed with known, accessible tributaries all draining into a reservoir with one outlet, 3) Clemson University ownership of the reservoir limits access, 4) other past and current investigations of the watershed could provide valuable ancillary information, and 5) it is close enough to Clemson to allow sampling response to storm events.

The Lake Issaqueena watershed is located in Pickens County, in northwestern South Carolina. The watershed drains entirely into Lake Issaqueena, which is about 11.3 km northwest of Clemson. A dam impounds Six Mile Creek 0.54 km above its confluence with Lake Hartwell to make Lake Issaqueena. The watershed is about 12.7 km in length, 2.7 km wide, and has a surface area of  $3.59 \times 10^7 \text{ m}^2$ , excluding the lake area. The lake is relatively shallow with a maximum depth of 10 m, has a surface area of  $4.02 \times 10^5 \text{ m}^2$  and a total volume of  $1.97 \times 10^6 \text{ m}^3$ , according to a survey done by Clemson University students in 1979

(see Heatley, 1982 for more information). The watershed has an average elevation of 305 m.

Sampling sites are presented in Figure 1. Six Mile Creek (C-2) drains most of the upper part of the watershed and generally accounts for approximately 80% of the total tributary input to the reservoir. Wildcat Creek (C-3) flows into (C-2), and together they flow into the head of Lake Issaqueena. Two other streams, Holly Springs Creek (C-1) and Indian Creek (C-4), drain essentially the remainder of the watershed. Sampling sites were located on all four streams, at three free-flowing springs used as groundwater stations (GW-1, GW-2, and GW-3), and at the dam (D-1).

The major soil types of the Lake Issaqueena watershed are Madison, Pacolet and Cecil (see Lesan, 1983 and Owings, 1983 for more information). Soil sampling sites and major distributions are shown in Figure 2.

The Lake Issaqueena watershed is managed by the Forestry Department of Clemson University. Forest practices include constructive logging, prescribed burning, and management of recreational facilities. Most of the forest management activities have occurred in the Indian Creek (C-4) drainage basin (see LaManna, 1983).

#### Water Sampling

Stream sampling was carried out between March, 1980 and September, 1982, with the majority of the sampling after May, 1981. Samples were collected once a month during baseflow conditions by grab sampling. Samples were taken from every station (Figure 1) with the exception of groundwater stations which were dry during periods of the

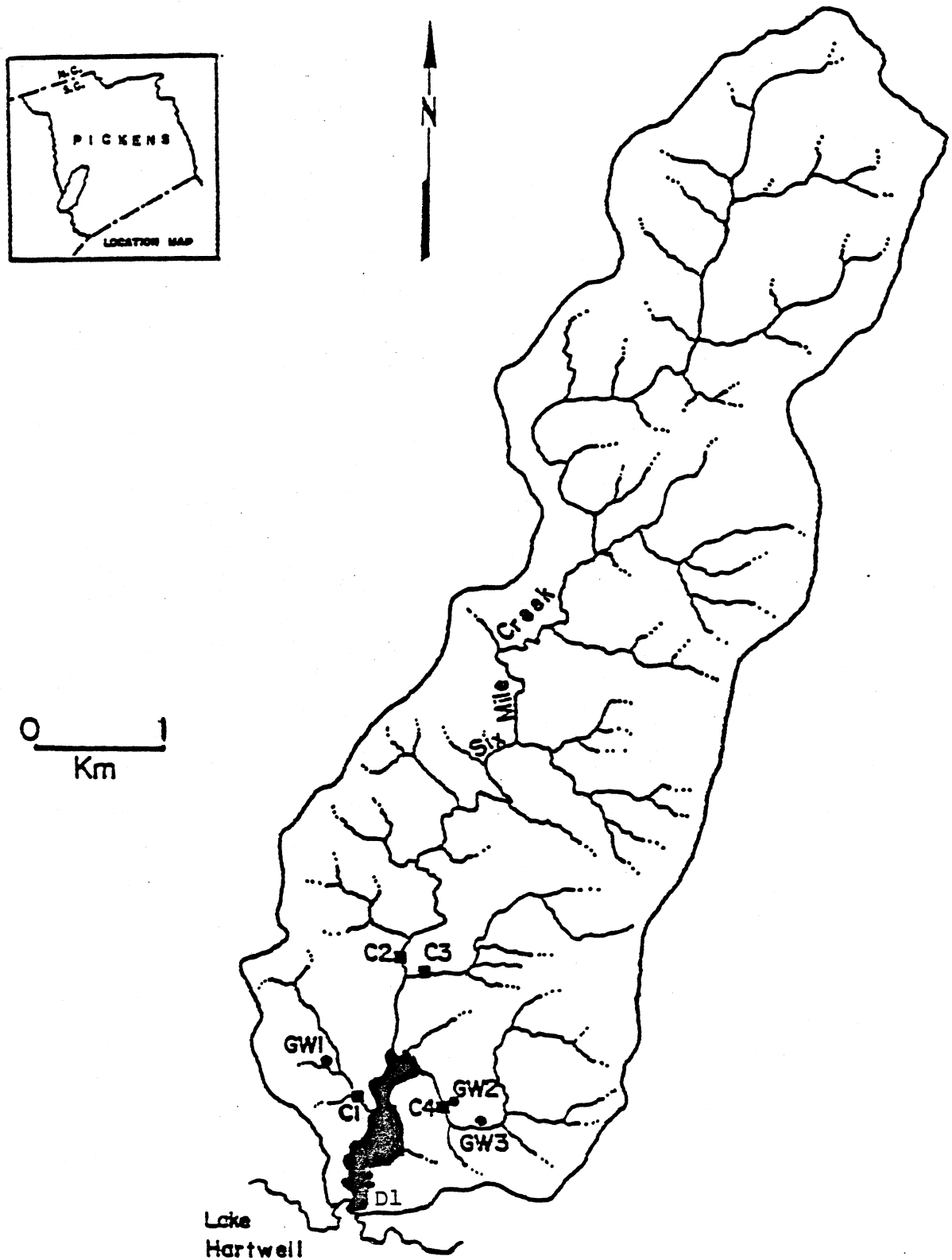


Figure 1. Lake Issaqueena Watershed:

Key: C-1, Holly Springs Creek; C-2, Six Mile Creek;  
C-3, Wildcat Creek; C-4, Indian Springs Creek;  
D-1, Dam.

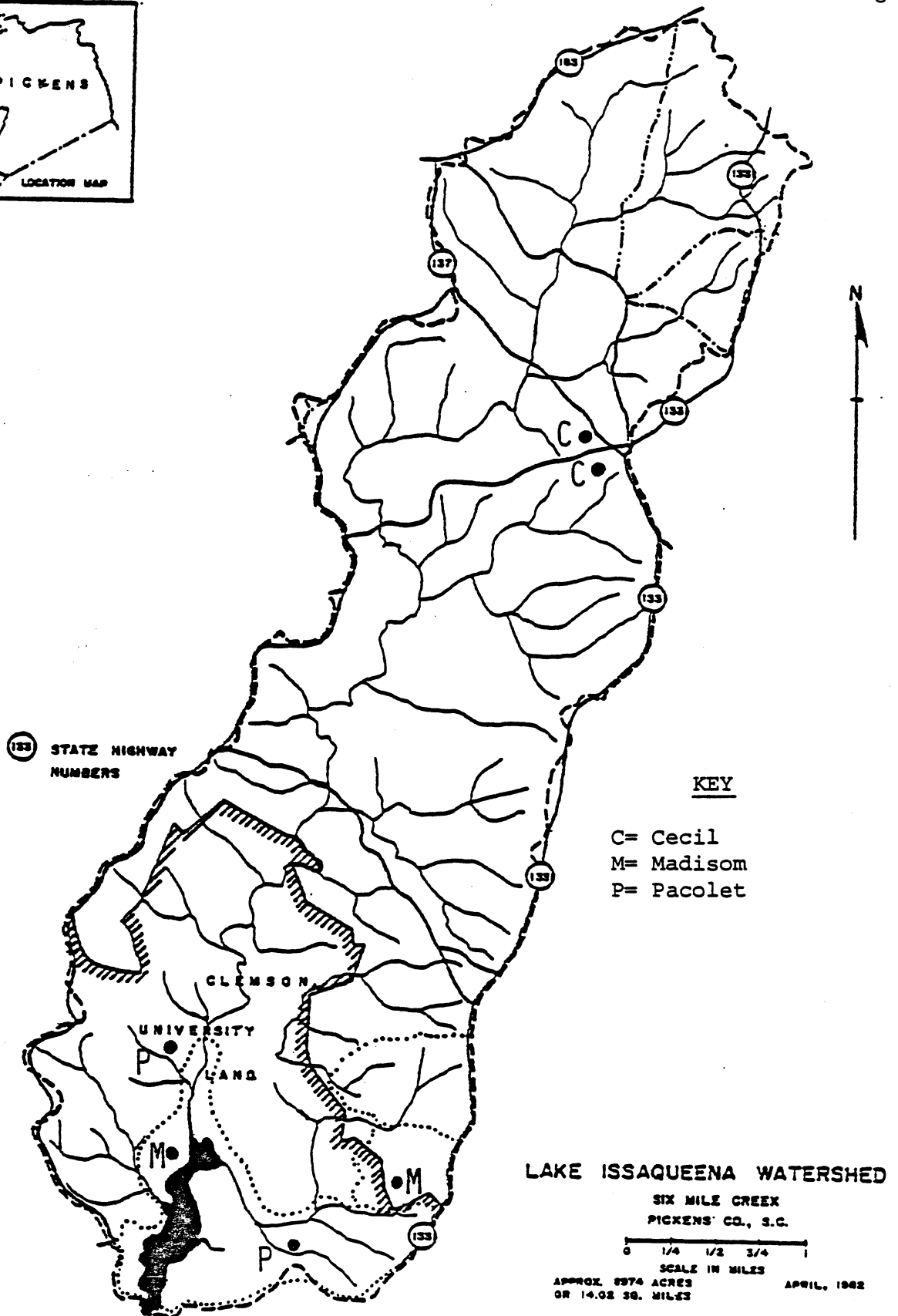
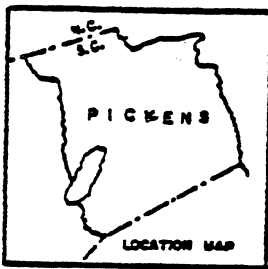


Figure 2. Lake Issaqueena Watershed: Soil Sampling Sites

drought that occurred during the summer of 1981. An approximate depth integrating stream sampling technique was used. Storm events required a series of grab samples to be collected varying in number proportionally to storm intensity and longevity. Due to the nature of sampling conditions during storm events, sampling was often restricted to one or two stations.

Field measurements included temperature, pH, specific conductance, and stream discharge. After May, 1981, specific conductance and pH measurements for Lake Issaqueena were made in the laboratory, since a period of concurrent lab and field measurements indicated little change occurred upon transport of the sample to the laboratory. An asbestos junction, saturated KCl, calomel reference combination pH electrode was found to give satisfactory results. Silver chloride reference and gel-filled electrodes did not give accurate or repeatable results in the low ionic strength samples encountered.

Stream discharge was measured by one of two methods. The first method was accomplished by the measurement of the stream cross-section and flow velocity, which was determined with either a No. 625 pygmy type, a No. 622 Price type AA, or a Marsh-McBirney model flow meter. Current measurements were taken at 60% of the total depth, across the streams at 1.0, 1.5, or 2.0 foot intervals depending on stream width. Flow calculations were then made by the use of a computer program which used the mean-section method (Heatley, 1982). The second method of flow measurement employed weirs. Station C-1 was fitted with a 60° V-shaped weir from which measurements could be obtained and converted into flow data (LaManna, 1983). The dam was also treated as a weir (Heatley, 1982; LaManna, 1983).

Water samples were collected in polyethylene bottles. To minimize contamination, plasticware was used exclusively for collection and storage of water samples, and cleaning procedures were strictly controlled. Bottles were washed and soaked with distilled deionized water, or in the case of metals samples, soaked in 10%  $\text{HNO}_3$  or 1:1  $\text{HCl}$ , and then rinsed with distilled deionized water. Finally, each bottle was rinsed at least three times with streamwater from the collection site immediately before a sample was collected. Once collected, the samples were transported to the laboratory as rapidly as possible and stored at 4°C.

Specific conductance and pH were measured within 6 hours of returning from the field site. Alkalinity samples were stored at 4° until analyzed. Nitrate samples were filtered through Gelman 0.45  $\mu\text{m}$   $\text{HCl}$  washed Metrical filters, stored at 4°C, and analyzed within 48 hours. Sulfate samples were filtered through Gelman Metrical 0.45  $\mu\text{m}$   $\text{HCl}$  washed filters, stored at 4°C, and analyzed within one month of collection. Metal samples were filtered through acid washed Nuclepore 0.4  $\mu\text{m}$  filters, acidified with Ultrex Ultrapure  $\text{HNO}_3$  to a pH of 2, stored at 4°C, and analyzed within 3 months of collection. Samples for Pb and Cd analyses were handled with extra caution to avoid contamination (Heatley, 1982).

#### Soil Sampling and Treatment

Soil sampling sites were selected that were representative of the major soil types found in the watershed. Sampling sites were selected which were located in low slope, undisturbed, non-agricultural areas. Two separate locations for each soil type and two sites per



location were selected. Field tests were performed to verify soil types (Lesan, 1983). After verification, a hole was excavated with an approximate cross section of  $80 \text{ cm}^2$  to a depth reaching the top of the C horizon. The exposed profile was sampled by horizon, following the order of the duff, A, upper B, and lower B horizons.

All samples collected were air dried, ground with a mechanical grinder, and passed through a 2mm mesh brass sieve. Soil pH and cation exchange properties were measured for the soils sampled at each location to assure that no soils collected were effected by recent liming or fertilization. A composite sample was made by combining the soils of the same type collected at separate locations on an equal mass basis.

Soil pH was determined and reported in both distilled water and in 0.01 M  $\text{CaCl}_2$  solution (Lesan, 1983; Owings, 1983). The cation exchange properties measured for each soil type included total cation exchange (CEC), base cation exchange (BEC), and acid cation exchange (AEC). The method utilized was a modified  $\text{BaCl}_2$  compulsive exchange technique in a neutral solution (Lesan, 1983). The procedure was applicable to low cation exchange capacity mineral soils and gave a CEC, BEC, and AEC measurement at field pH.

#### Extraction Studies

A variety of serial, batch, and column extraction studies using soil, sediment, rainwater, and synthetic solutions were conducted. Brief descriptions of the approaches are included with the results in RESULTS AND DISCUSSION. More detail on the methods is available in Heatley (1982), Lesan (1983), and Owings (1983).

### Laboratory Analyses

Calcium, magnesium, sodium, and potassium were determined with a Perkin-Elmer Model 403 atomic absorption spectrophotometer using direct aspiration into an air-acetylene flame (EPA, 1979). Lanthanum oxide was added to all calcium and magnesium samples and standards to eliminate ionization interferences. Calibration of metals was done by comparing the absorption of a sample to a calibration curve for a series of standard solutions. Aluminum was measured by graphite furnace flameless atomic absorption using standard additions calibration. Pb and Cd were determined by anodic stripping voltammetry following an acidification/high intensity UV irradiation digestion (Heatley, 1982).

Alkalinity was determined on 100 mL aliquots by titration, using a Metrohm Model 655 Dosimat titrator, to pH 4.5 and then 0.3 pH units lower, in a sealed Teflon apparatus purged with N<sub>2</sub> gas in a modification of the low-level potentiometric technique in Standard Methods (1980). Bicarbonate was estimated from alkalinity values. Chloride, ammonium, and nitrate were determined by use of Orion specific ion electrodes, by methods described in Standard Methods (1980) and the Orion electrode manuals. Reactive silicate was determined by the method of Strickland and Parsons (1968). Sulfate was determined with the turbidimetric method described in Standard Methods (1980) or, for low levels, the method of Wolfson (1980). Turbidity was determined using a HACH light scattering instrument, and suspended particulate matter concentrations by the weight gain of Nuclepore filters used to filter the sample, after drying at room temperature in a desiccator.

#### IV. RESULTS AND DISCUSSION

##### A. Regional Lake Survey

Little attention has been focused on evaluating the significance and effects of acidic deposition inputs to aquatic ecosystems located in the southeastern United States. The Piedmont and mountain regions of South Carolina and western North Carolina presently receive acidic rainfall that has a mean volume-weighted  $H^+$  concentration corresponding to a pH of 4.4 (NADP, 1979-82). Estimating from the limited data available, this pH corresponds to nearly a 10-fold increase in the hydrogen ion concentration of rain water in this area since 1955, i.e. a 1955 pH of 5.3 (Likens, 1976). Detrimental effects such as lowered pH, reduced fish populations, and increased concentrations of potentially toxic chemical constituents leached from watershed soils (e.g. Al) have been observed in lakes located in areas of southern Scandinavia and the northeastern United States which receive acidic atmospheric deposition (Galloway et al., 1978). Only scattered, incomplete reports of possible effects of acid rain in the Southeastern U.S. are available, however. As part of this investigation, an initial assessment of the status and sensitivity of selected lakes situated in the Carolina Piedmont and southern Appalachian Mountain regions to inputs of acidic atmospheric deposition was conducted. This regional survey provided perspective on the extent of the problem, and data to compare to that obtained in the more intense investigation of Lake Issaqueena (see below).

Initial surveys were conducted on 20 lakes in northwestern South Carolina, western North Carolina, and northern Georgia (see

Figure 3). Data obtained in these surveys is presented in Tables I and II (Sviatyla, 1982). The lakes in general were found to be low alkalinity, low conductivity aquatic systems. Note variations between field and laboratory (measured 1 to 3 days later) pH measurements, indicating that in many cases when sampling far from the laboratory, pH should be measured in the field if a reliable method is available and the extra level of accuracy is desired. Also, note that the "normal alkalinity" direct titration determination of alkalinity (Standard Methods, 1980) leads to higher, probably erroneous values compared to the low level technique described above in Experimental Methods.

Ten lakes were selected for further study which are located in northwestern South Carolina and western North Carolina (Figure 4). Five of the lakes (Mirror, Sapphire, Sequoyah, Thorpe, and Toxaway) are situated in the southern Appalachian Mountains (NC) at an average elevation of 1012 m. These lakes were chosen for investigation since they provided a wide spectrum of watershed/lake area ratios (W/L) and might, therefore, be affected differently by acid inputs. Four of the study lakes (Hartwell, Issaqueena, Jocassee, and Keowee) lie in the Piedmont region of South Carolina and reside at an average elevation of 270 m. Lakes Toxaway, Jocassee, Keowee, and Hartwell are interconnected by rivers and form a chain of lakes extending from the mountain headwater (Toxaway) through Jocassee then Keowee to the lower Piedmont region (Hartwell). Lake Summit is situated at an intermediate elevation (613 m) in the mountain foothills of southwestern North Carolina.

Surface waters most sensitive to damage from acid inputs typically: (1) have low alkalinity, (2) reside in regions dominated by igneous or metamorphic bedrock geology, and (3) have watershed soils

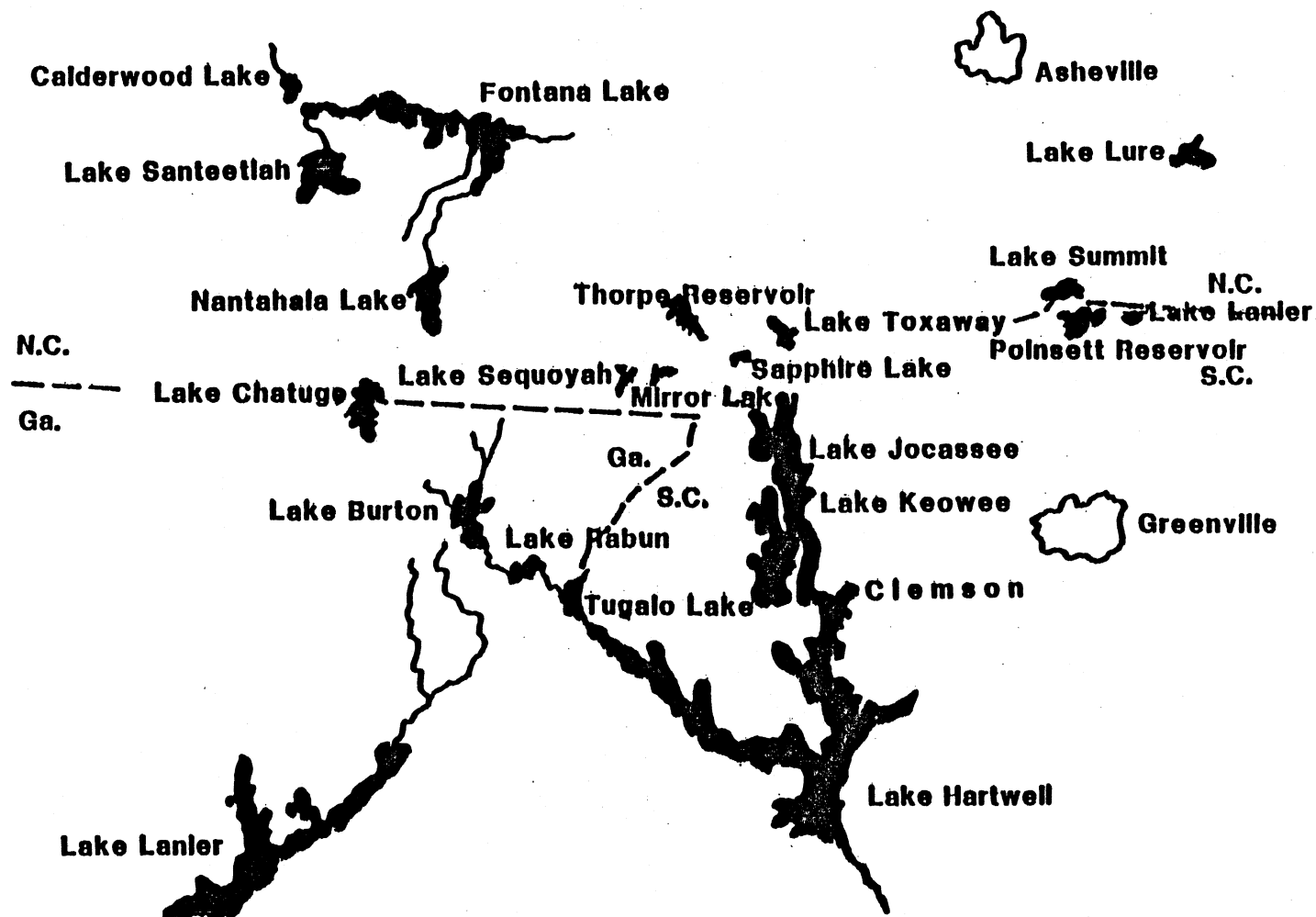


Figure 3. Preliminary Sampling Sites of Mountain Reservoirs in Georgia, North Carolina and South Carolina

Table I. Data For Preliminary Lake Survey (see TEXT for explanation of alkalinity data)

LAKE	STATE	DATE	CONDUCTIVITY (umhos/cm)	TEMPERATURE (°C)	FIELD PH	LAB PH	NORMAL ALKALINITY (ppm CaCO <sub>3</sub> ) (ueq/L)		LOW ALKALINITY (ppm CaCO <sub>3</sub> ) (ueq/L)	
Lure	NC	2/21/81	37.50	8.00	6.10	6.69	12.89	257.8	9.61	192.2
Lanier	NC	"	40.00	7.00	6.20	6.70	17.47	349.4	10.08	201.6
Polinsett	SC	"	25.50	10.00	6.40	6.65	10.17	203.4	6.03	120.6
Summit	SC	"	28.00	8.50	5.80	6.49	7.45	149.0	4.51	90.2
Toxaway	NC	"	13.50	8.00	-	6.02	4.54	90.8	1.19	23.8
Thorpe	NC	"	14.10	7.00	-	5.91	4.82	96.4	0.96	19.2
Sapphire	NC	"	15.90	9.00	-	6.05	5.11	102.2	1.73	34.6
Mirror	NC	2/22/81	26.00	5.00	-	6.00	4.15	83.0	1.36	27.2
Sequoyah	NC	"	15.10	5.00	-	6.05	4.21	84.2	1.24	24.8
Nantahala	NC	"	15.10	8.50	6.10	6.49	7.46	149.2	3.92	78.4
Santeetlah	NC	"	23.50	7.50	6.20	6.65	8.43	168.6	5.06	101.2
Calderwood	NC	"	25.50	7.50	6.00	6.55	9.66	193.2	6.11	122.2
Fontana	NC	"	25.10	9.00	6.10	6.69	9.36	187.2	6.26	125.2
Keowee	SC	3/14/81	22.20	11.00	-	6.80	9.98	199.6	5.92	118.4
Keowee	SC	"	25.50	14.00	-	6.91	9.26	185.2	6.28	125.6
Tugalo	GA	"	18.50	13.00	-	6.70	6.02	120.4	2.58	51.6
Rabun	GA	"	20.00	12.50	-	6.81	7.97	159.4	5.49	109.8
Burton	GA	"	23.00	10.50	-	6.65	7.26	145.2	5.44	108.8
Chatuge	GA	"	23.00	10.50	-	6.60	13.95	279.0	4.76	95.2
Lanier	GA	"	37.00	11.00	-	6.90	11.56	231.2	9.12	182.4
Lanier	GA	"	37.50	9.50	-	7.00	11.08	221.6	8.60	172.0

Table II. Additional Preliminary Lake Survey Data

LAKE	SITE*	DATE	CONDUCTIVITY (umhos/cm)	TEMPERATURE (°C)	FIELD PH	LAB PH	NORMAL ALKALINITY (ppm CaCO <sub>3</sub> )	ALKALINITY (ueq/L)	LOW ALKALINITY (ppm CaCO <sub>3</sub> )	ALKALINITY (ueq/L)
Jocassee	1S	4/4/81	19.00	17.00	-	6.80	6.90	138.0	5.20	104.0
"	1S	6/12/81	29.00	26.00	6.10	6.95	7.25	145.0	3.80	76.0
"	1D	"	22.00	19.50	5.90	-	-	-	-	-
"	2S	"	28.00	26.00	6.10	6.70	5.80	116.0	4.85	97.0
"	2D	"	21.00	20.00	5.70	-	-	-	-	-
"	1S	8/22/81	32.00	24.00	6.85	6.90	17.96	359.2	8.36	167.2
"	1D	"	38.00	21.00	6.70	6.65	11.15	223.0	8.53	170.6
"	2S	"	31.00	24.50	6.75	6.75	11.40	228.0	8.53	170.6
"	2D	"	35.00	22.00	6.80	6.65	11.23	224.6	8.53	170.6
Keowee	1S	3/14/81	22.20	11.00	-	7.30	9.98	199.6	5.92	118.4
"	2S	"	25.50	14.00	-	6.82	9.26	185.2	6.28	125.6
"	1S	6/12/81	35.00	28.50	6.10	6.80	7.25	145.0	5.95	119.0
"	1D	"	31.00	25.00	5.80	-	-	-	-	-
"	2S	"	35.00	28.00	5.80	6.92	6.60	132.0	5.70	114.0
"	2D	"	30.00	24.00	5.70	-	-	-	-	-
"	3S	"	31.00	28.00	6.00	6.92	6.95	139.0	6.35	127.0
"	3D	"	31.00	25.00	5.90	-	-	-	-	-
"	1S	8/22/81	31.00	25.00	6.80	6.70	11.97	239.4	9.68	193.6
"	1D	"	32.00	22.00	6.65	6.55	11.40	228.0	9.59	191.8
"	2S	"	150.00	27.50	6.70	6.50	12.14	242.8	10.41	208.2
"	2D	"	190.50	25.50	6.50	6.30	12.96	259.2	10.00	200.0
"	3S	"	42.00	27.50	6.80	6.40	12.55	251.0	11.41	208.2
Sequoyah	1S	5/30/81	17.00	16.00	-	5.75	1.65	33.0	1.23	24.6
"	1D	"	12.00	14.00	-	5.55	1.81	36.2	1.11	22.2
"	2S	"	20.00	18.00	-	5.45	2.75	55.0	1.85	37.0
"	2D	"	22.00	15.00	-	-	-	-	-	-
"	1S	8/30/81	30.00	19.50	6.80	6.75	11.48	229.6	8.69	173.8
"	1D	"	-	-	6.70	6.50	11.07	221.4	8.36	167.2
"	2S	"	31.00	19.00	6.70	6.55	11.39	227.8	8.35	167.0
"	2D	"	-	-	6.70	6.65	11.73	234.6	9.68	193.6
"	1S	3/27/82	18.00	9.00	-	6.15	-	-	1.03	20.5
"	2S	"	21.00	9.00	-	6.10	-	-	1.54	30.8
"	2D	"	-	-	-	6.00	-	-	1.33	26.7
Thorpe	1S	5/30/81	11.00	19.00	-	5.80	2.81	56.2	2.40	48.0
"	1D	"	11.00	15.00	-	-	-	-	-	-
"	2S	"	12.00	19.50	-	5.85	2.80	56.0	2.30	46.0
"	2D	"	11.00	12.00	-	6.00	-	-	-	-
"	3S	"	12.00	19.00	-	-	2.80	56.0	2.43	48.6
"	3D	"	11.00	14.00	-	6.65	-	-	-	-
"	1S	8/30/81	19.00	23.00	6.40	6.65	7.38	147.6	5.33	106.6
"	1D	"	25.00	18.00	6.20	6.40	7.79	155.8	5.66	113.2
"	2S	"	20.00	21.00	6.90	6.65	7.54	150.8	5.33	106.6
"	2D	"	25.00	19.00	6.70	6.60	7.22	144.4	5.17	103.4
"	3S	"	20.00	22.00	6.95	6.50	7.22	144.4	5.23	104.6
"	3D	"	22.00	21.00	6.60	5.75	7.30	146.0	5.50	110.0
Toxaway	1S	5/30/81	10.00	21.00	-	-	1.48	29.6	1.13	22.6
"	1D	"	10.00	19.00	-	5.65	-	-	-	-
"	2S	"	10.00	20.00	-	-	1.55	31.0	1.10	22.0
"	2D	"	11.00	17.00	-	5.65	-	-	-	-
"	1S	8/30/81	20.00	22.50	6.70	-	5.58	111.6	3.61	72.2
"	1D	"	20.00	21.00	6.40	6.60	5.58	111.6	3.94	78.8
"	2S	"	20.00	23.00	6.90	6.25	5.58	111.6	3.28	65.6
"	2D	"	25.00	22.00	6.20	6.05	5.66	113.2	3.53	70.6
"	1S	3/27/82	17.00	11.00	5.80	5.70	-	-	1.23	24.6
"	1D	"	11.00	10.00	5.60	5.75	-	-	1.33	26.7
"	2S	"	14.00	10.50	5.70	5.90	-	-	1.85	36.9
"	2D	"	12.00	9.50	-	5.95	-	-	1.85	36.9

\* S=surface water sample, D=deep water sample

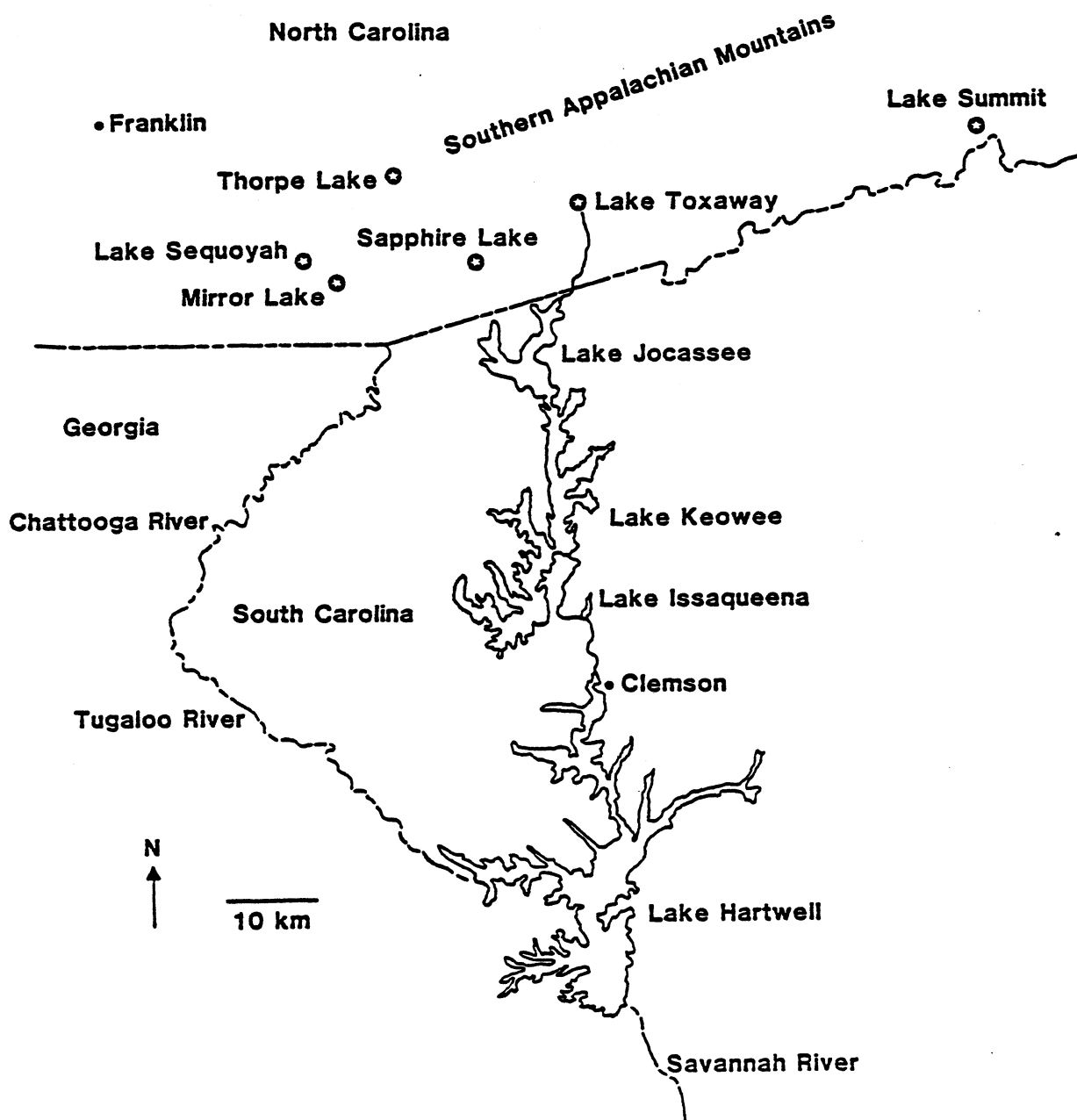


Figure 4. Locations of Lakes in Final Lake Survey



characterized as acidic with low buffer capacity. These conditions predominate within the study area. Since the areal bedrock consists primarily of granites, gneisses, and schists, Galloway and Cowling (1978) classified the region as sensitive to acid inputs. Norton (1980) also evaluated sensitivity of the region to acid inputs, but on a county by county basis using specific geological information. The results of this analysis indicated that the mountain lakes of western North Carolina investigated during this study are located in a particularly vulnerable area.

However, the area is highly weathered, and bedrock generally lies 5-10 m below the surface, suggesting that the soil may profoundly influence watershed/acid precipitation interactions over most of the study area. Soils in both the Piedmont and mountain regions are characterized as well-drained with various sandy and clayey loams predominating. The soils are generally acidic (pH 4.5-5.5), contain little organic matter, are high in  $K^+$ ,  $Cl^-$ , and exchangeable Al, but may contain small amounts of Ca (King *et al.*, 1974). Due to moderately low soil cation exchange capacities (0.6-15 meq/100g), McFee (1980) classified the region as slightly sensitive to acid inputs. Lesan (1983) found, however, that the low Ca and Mg content of the soil leads to a low base saturation index, which indicates potentially more sensitivity to acid inputs than indicated by total cation exchange capacities. In summary, the bedrock and soil in the study area have little neutralizing capabilities, and the potential exists for mobilization of chemical constituents from watershed soils to surface waters due to reaction with acidic atmospheric deposition (see Lake Issaqueena studies below).

Within the study area, annual precipitation averages 132 cm in the Piedmont region to 250 cm at the higher mountain elevations and 170 cm at lower elevations. Snow usually comprises only a few percent of the annual precipitation. Precipitation in the mountains may occur continuously for up to 2 weeks or more at a time during any season of the year. The annual precipitation in the upper mountain regions is greater than anywhere else in the United States except for near the Pacific Ocean. Consequently, the study area, especially the mountain region, is subjected to a potentially large annual atmospheric loading of acid precipitation.

The major element chemistry of the study lakes is presented in Table III. These samples were collected in late winter when the effects of stratification and biological productivity were minimal. For comparison, the mean volume-weighted chemical composition of rain water for the Piedmont (Clemson, SC) and mountain (Franklin, NC) regions has also been included in Table III (also see Lake Issaqueena study below). Only the  $\text{H}^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  concentrations were higher in precipitation than in the lake waters. However, the lake waters were very dilute, with the total ionic constituents averaging about 300 ueq/L in the mountain lakes compared to 450 ueq/L in the Piedmont lakes. In addition, alkalinity values were low, ranging from 26 ueq/L in Lake Toxaway to 217 ueq/L in Lake Issaqueena. The overall average hydrogen ion concentration of the study lakes expressed as pH was 6.8.

Various chemical acidification models have been proposed to distinguish between acidified and unacidified surface waters. The empirical approach of plotting pH versus  $[\text{Ca}^{+2}]$  suggested by Henriksen (1979) has probably been the most widely used. However, Kramer and Tessier (1982) discussed several shortcomings of this method and con-

Table III. Chemical Composition of Areal Rain and Lake Waters in the Carolina Piedmont and Mountain Regions.

Lake	Elev. m	TSS <sup>a</sup> mg/L	Cond. uS/cm (umho/cm)	pH	Alk. <sup>b</sup>	Al	Si	Fe	Mn	Ca uM/L	Mg	Na	K	Cl	SO <sub>4</sub>	NO <sub>3</sub>	Σ Cation/ Anion
Toxaway	914	0.90	10	6.71	25.9	0.93	57.0	1.7	0.29	15.0	8.2	28.3	8.7	33.8	15.6	2.4	0.99
Thorpe	1067	1.9	12	6.99	56.6	1.5	78.3	0.34	0.02	20.7	10.3	47.8	11.0	45.1	10.0	3.5	1.0
Sapphire	946	2.3	11	6.61	66.9	2.9	89.0	7.3	0.87	19.7	9.0	47.8	9.0	39.5	14.6	3.9	1.0
Sequoyah	1097	1.3	15	6.78	74.9	2.3	64.1	5.6	0.51	32.4	13.6	69.6	11.5	59.2	19.8	4.5	0.97
Mirror	1037	4.9	16	6.60	77.9	7.3	64.1	12.0	0.98	34.9	14.8	69.6	13.8	81.8	22.9	15.5	1.0
Jocassee	335	2.3	15	7.14	88.7	1.1	117.5	0.15	0.01	25.0	14.0	56.5	13.8	39.5	12.5	3.1	0.97
Keowee	244	2.2	17	7.12	120.1	1.2	121.1	0.20	0.01	32.4	21.0	65.2	18.9	48.0	14.6	4.0	0.97
Hartwell	201	1.3	33	7.13	138.8	1.6	124.6	0.31	0.02	39.9	26.3	104.4	24.6	56.4	25.0	8.1	1.0
Summit	613	1.8	16	7.26	139.0	2.3	121.1	0.75	0.06	42.4	24.7	65.2	14.1	50.8	17.7	5.3	0.97
Issaqueena	300	8.9	37	6.46	216.8	1.0	NA	NA	NA	54.9	41.1	91.3	28.1	67.7	7.4	3.7	1.0
Rain <sup>c</sup>																	
Clemson, SC <sup>d</sup>	231	-	25	4.40 <sup>e</sup>	-	0.07	0.15	0.03	0.01	3.2	1.6	9.1	0.69	9.3	25.0	17.7	1.1
Franklin, NC	722	-	24	4.56 <sup>e</sup>	-	NA	NA	NA	NA	1.7	0.90	10.4	0.56	7.1	17.0	10.2	0.98

<sup>a</sup> TSS - suspended particulate matter.<sup>b</sup> Expressed as HCO<sub>3</sub><sup>-</sup>.<sup>c</sup> Volume-weighted mean concentrations calculated from NADP (1979-82).<sup>d</sup> Values for Al, Si, Fe, and Mn from Talbot (1983).<sup>e</sup> Calculated from volume-weighted mean H<sup>+</sup> concentration.

Na means not available.

cluded that a more rigorous approach should be employed. They suggested that pH should be plotted against  $\sum z_i [M_i]$ , where M represents the  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Na}^+$ , and  $\text{K}^+$  concentrations and z their respective charge. This approach is especially important when  $\text{Na}^+$ ,  $\text{K}^+$  and  $\text{Mg}^{+2}$  contribute significantly to the total cation concentration. For the lakes investigated in this study, concentrations of  $\text{K}^+$ ,  $\text{Mg}^{+2}$ , and particularly  $\text{Na}^+$  were significant relative to  $\text{Ca}^{+2}$  (Table III), suggesting that the Kramer and Tessier (1982) approach should be used to assess lake acidification.

Briefly, Kramer and Tessier (1982) recommended that the following equation be used to define the theoretical line representing carbonic acid weathering (CAW):

$$\text{pH} = \log \sum z_i [M_i] - \log^* K - \log \text{pCO}_2, \quad (1)$$

where z and M are defined as before. The expression for  $^* K$  is:

$$^* K = K_H K_1 = \frac{[\text{HCO}_3^-][\text{H}^+]}{\text{pCO}_2}, \quad (2)$$

where  $K_H$  is the Henry's law constant for  $\text{CO}_2$  water-air equilibrium and  $K_1$  the first dissociation constant for carbonic acid. A fixed  $\text{pCO}_2$  value of  $10^{-3.52}$  atm was used in theoretical calculations of CAW.

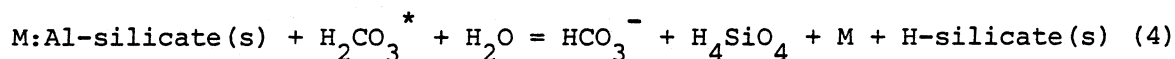
To correct the measured pH values for variations in  $\text{pCO}_2$ , a corrected pH value was calculated using:

$$\text{pH}_{(\text{corrected})} = \text{pH}_{(\text{actual})} - \log \text{pCO}_2 (\text{fixed}) + \log \text{pCO}_2 (\text{actual}), \quad (3)$$

where values for  $\text{pCO}_2 (\text{actual})$  were computed from the measured pH and alkalinity as shown by Kramer and Tessier (1982).

The results of the calculations for the ten study lakes, using the data presented in Table III, are depicted in Figure 5. Several important observations can be made from the information provided in Figure 5. Firstly, all of the data points lie in the region above the theoretical CAW line, suggesting that acidification is occurring and watershed soils are apparently being weathered faster than expected from the action of carbonic acid alone. Secondly, Piedmont lakes had pH values  $>7.0$ , while mountain lakes had pH values  $<7.0$ . The extreme cases are represented by Lake Toxaway, a mountain headwater lake with the lowest pH, and Lake Issaqueena, a Piedmont lake which seems to have been affected the most by cation weathering processes in watershed soils. These two cases will be examined in greater detail.

Since soils in the study area contain readily exchangeable cations (Lesan, 1983; Owings, 1983; Talbot, 1983), we can write a generalized unbalanced weathering reaction as follows:



where M represents various cations such as  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Na}^+$ , or  $\text{K}^+$ . Under natural carbonic acid weathering conditions in this model, equivalent amounts (eq/L) of  $\text{HCO}_3^-$  and cations are produced (Stumm and Morgan, 1981). Thus, alkalinity and cation concentrations should gradually increase in receiving waters draining actively weathered watersheds. A correlation might, therefore, exist between the W/L ratio and the relative amount of  $\text{HCO}_3^-$  (or cations) in the receiving water. By comparing values of the ratio  $\text{HCO}_3^-/\Sigma$  anions for the study lakes (Table IV), it is apparent that the relative proportion of  $\text{HCO}_3^-$  in the lake waters increases regularly from the mountain lakes to the

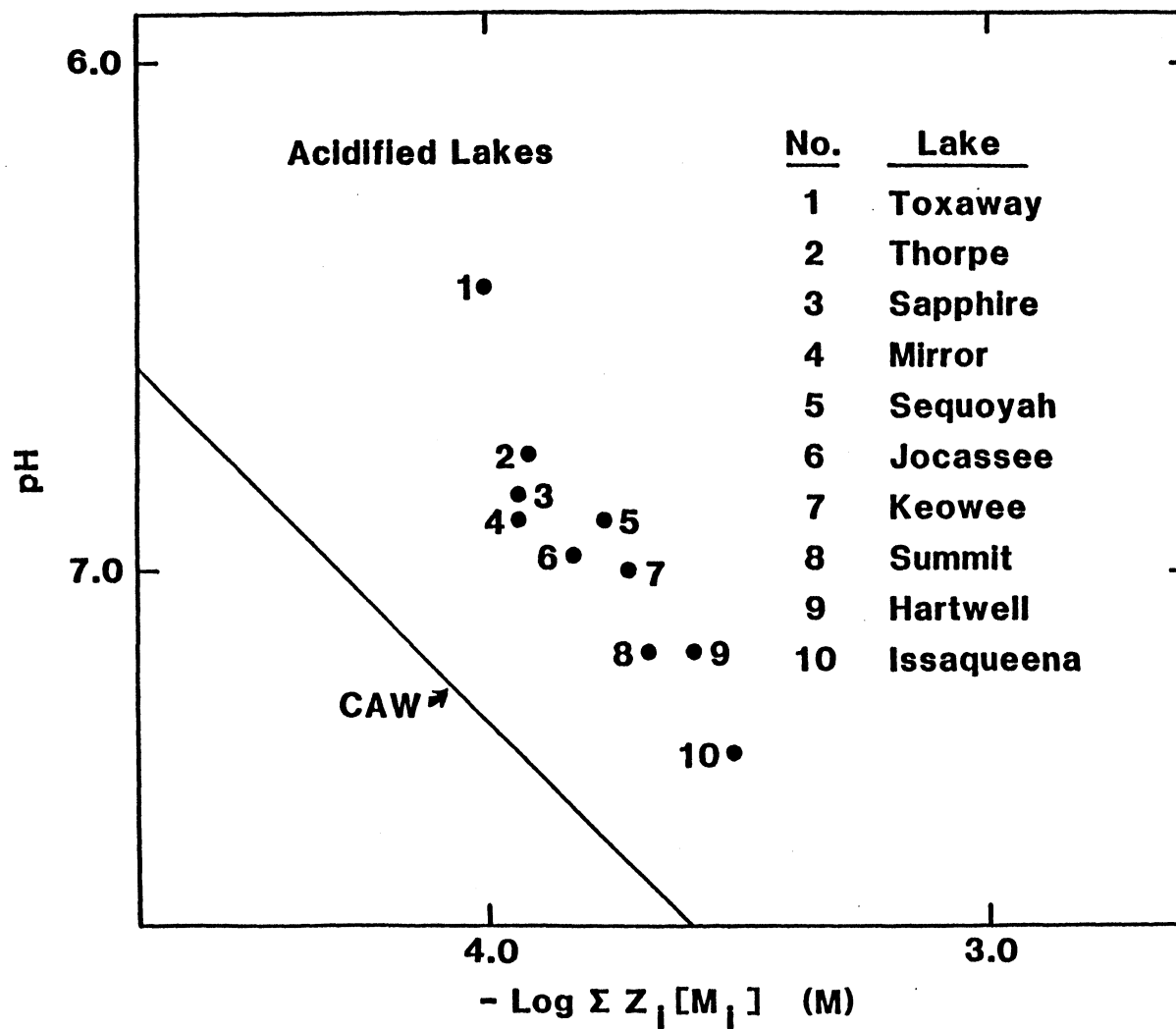


Figure 5. Lake Survey Results Compared to Theoretical Carbonic Acid Weathering

Table IV. Relative Proportion of  $\text{HCO}_3^-$  and  $\text{pCO}_2$  Values in Lake Waters as a Function of Watershed/Lake Area Ratio.

Lake	Watershed/Lake Area Ratio	$\Sigma \text{Base Cations}^a / \text{HCO}_3^-$	$\text{HCO}_3^- / \Sigma \text{Anions}^b$ (ueq/L)	$\text{HCO}_3^- / \text{SO}_4^{-2} + \text{Cl}^-$	$-\text{Log pCO}_2^c$ (atm)
Toxaway	8	3.2	0.28	0.40	3.79
Mirror	157	2.4	0.33	0.56	3.22*
Sequoayah	61	2.3	0.37	0.60	3.40*
Thorpe	16	2.1	0.45	0.87	3.74
Sapphire	256	1.7	0.48	0.96	3.28*
Hartwell	23	1.9	0.55	1.3	3.49
Jocassee	13	1.7	0.57	1.4	3.69
Keowee	15	1.6	0.59	1.5	3.53
Summit	14	1.5	0.61	1.6	3.62
Issaqueena	84	0.99	0.70	2.4	2.62*

<sup>a</sup> $\Sigma \text{Base cations} = \Sigma [\text{Ca}^{+2} + \text{Mg}^{+2} + \text{Na}^+ + \text{K}^+]$ .

<sup>b</sup> $\Sigma \text{Anions} = \Sigma [\text{SO}_4^{-2} + \text{NO}_3^- + \text{Cl}^- + \text{HCO}_3^-]$ .

Sea salt contributions of  $\text{Cl}^-$  and base cations <10% (Talbot, 1983).

<sup>c</sup>Calculated from measured pH and alkalinity (Tessier and Kramer, 1982).

\*Supersaturated with respect to  $\text{CO}_{2(g)}$  equilibrium with atmosphere ( $-\text{Log pCO}_2 = 3.52$  @  $25^\circ\text{C}$ ).

Piedmont lakes. In several of the mountain lakes,  $\text{HCO}_3^-$  was not the most abundant charge balancing anion;  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  comprised a significant fraction of the total anionic constituents. In fact,  $\text{SO}_4^{2-}$  and  $\text{Cl}^-$  combined (eq/L) were 2.5 times greater than  $\text{HCO}_3^-$  in Lake Toxaway (see Table IV). The opposite was true in Lake Issaqueena, where  $\text{HCO}_3^-$  was nearly 2.5 times greater than  $\text{SO}_4^{2-} + \text{Cl}^-$ .

Obviously, there is not a simple correlation evident between the W/L ratio and the relative proportion of  $\text{HCO}_3^-$  in the receiving water. More specific information about each lake system is clearly needed. Watershed development (e.g. percentage of exposed soil) seems to be a key factor. In Lake Issaqueena, for example,  $\text{HCO}_3^-$  comprised a large fraction of the anionic constituents and consequently, the lake had a much higher alkalinity than the other Piedmont lakes. The Lake Issaqueena watershed has been subjected to controlled forest cutting exposing large areas of soil, as well as varied rural development. This is undoubtedly facilitating leaching of soil cationic constituents and contributing alkalinity to the lake water. Drainage basins in the Issaqueena watershed that have seen the most soil disruption also tended to have the highest concentration of  $\text{HCO}_3^-$ .

By comparing  $\text{pCO}_2$  values calculated for construction of Figure 5, it is apparent (Table IV) that the four lakes (Issaqueena, Mirror, Sapphire, and Sequoyah) with largest W/L ratios were supersaturated with respect to  $\text{CO}_{2(g)}$  equilibrium with the atmosphere. Since soil systems typically have  $\text{pCO}_2$  values much greater than that of the atmosphere due to biological activity, runoff waters may be supersaturated with  $\text{CO}_{2(g)}$  (Stumm and Morgan, 1981). The  $\text{HCO}_3^-$  concentration in receiving waters, but not the alkalinity, should



subsequently increase from the added  $\text{CO}_2(\text{g})$ . The apparent  $\text{CO}_2(\text{g})$  supersaturation of the four study mountain lakes mentioned previously is possibly due to this phenomenon.

Although the mountain lakes are situated in an area regarded as sensitive to acid deposition, acidification may not be a widespread problem if  $\text{HCO}_3^-$  contributed via weathering and soil runoff is added at a rate which neutralizes excess  $\text{H}^+$  inputs from precipitation. Of the five mountain lakes investigated, the two with the smallest W/L ratios (Toxaway and Thorpe) had the lowest pH values. These lake systems are probably the most susceptible to pH reduction since they have little capability for neutralizing excess  $\text{H}^+$  inputs. The displacement of Lake Toxaway in Figure 5 from the other mountain lakes indicates that its pH may have already decreased due to acid inputs. Lakes Mirror, Sapphire, and Sequoyah have large watersheds and, therefore, may be more resistant to pH effects.

Watersheds in the Piedmont, despite being smaller than many mountain systems, have been developed more than the mountain watersheds and thus provide ample interaction with acid precipitation to neutralize excess  $\text{H}^+$  inputs. Consequently, pH reductions in Piedmont lakes are probably unlikely in the near future. Piedmont watersheds may, however, be undergoing extensive weathering, which should result in increasing cation (and anion) concentrations in lake waters. Although they may be more susceptible to pH changes, weathering may not be as rapid in the mountain systems since the watersheds are relatively undisturbed compared to the Piedmont region.

The apparently accelerated weathering of watershed soils in the northeastern United States has resulted in elevated dissolved

aluminum concentrations in receiving waters that may be toxic to fish (Cronan and Schofield, 1979). This situation may also be developing in some southern Appalachian aquatic systems. Three lakes (Sapphire, Sequoyah, and Summit) had dissolved Al concentrations averaging 70 ug/L. Lake Mirror had a dissolved Al concentration of 0.2 mg/L, essentially the same level found in the Hubbard Brook system located in the northeastern United States (Johnson et al., 1981). Despite the low total organic carbon (TOC) levels present in these lakes (1-3 mg/L), most of the Al may be organically complexed. Filtrates (0.4 um) of Lakes Mirror, Sapphire, and Sequoyah were noticeably colored, suggesting that most of the TOC may have been in dissolved form (DOC). Johnson et al. (1981) found a strong correlation between DOC and dissolved Al in Hubbard Brook stream waters, and Pott (1982) observed the same relationship in stream waters in the Lake Issaqueena watershed during stormflow events (see below). As in the northeastern United States, Al is apparently being mobilized in watershed soils in Carolina Piedmont and mountain systems and released to surface waters.

Preliminary leaching studies using soil material collected from the Piedmont and mountain regions and rain water with a chemical composition typical of areal rainfall indicate that Al, Si, Fe, Ca, Mg, K, Cl, and Pb are readily leachable from these soils by pH 4.4 rain water (see Lake Issaqueena studies below). Furthermore, field investigations of acid precipitation/soil/stream water interactions in the Lake Issaqueena system indicate that the stream transport of chemical constituents presumably leached from watershed soils is dependent on rainfall amount, rain water pH, and local physical features of the watershed (see below).

The sensitivity of aquatic systems to detrimental effects from acid precipitation inputs should be determined based on specific terrestrial and aquatic chemical and physical parameters. For undisturbed watersheds, historical trends in the ratio  $\text{HCO}_3^-$ /total anions in surface waters may be useful, with certain caveats, for assessing the relative weathering rates of watershed soils.

Some of the lakes in the southern Appalachian mountain system may be highly susceptible to pH reduction. However, leaching of chemical constituents (e.g. - nutrients and toxic materials) from watershed soils and subsequent changes in the chemical composition of stream and lake waters and sediments may be a more widespread and potentially serious problem for, especially, the Piedmont area.

## B. Lake Issaqueena Studies

### Atmospheric Inputs

Atmospheric deposition can be a principal route for input of chemical constituents to terrestrial and aquatic ecosystems (Eisenreich, 1981). Deposition occurs via wet (precipitation) and dry particle fallout. For non-urban locations, input of substances by wet deposition is generally more important than dry particle deposition. Thus, precipitation (rain) was considered a likely important source of chemical constituents, including  $H^+$ , to the Lake Issaqueena ecosystem.

The volume-weighted mean chemical composition of rainfall at Clemson, SC, is presented in Table V. These data were obtained as part of the National Atmospheric Deposition Program (NADP) (NADP, 1979-82), which operates a sampling station at Clemson, SC. Since the Lake Issaqueena system is only about 10 km northwest of Clemson, the annual mean chemical composition of precipitation should be very similar at the two sites. The mean ionic composition of rain water shown in Table V is, therefore, probably representative of areal precipitation at the Lake Issaqueena site.

The rain water was very dilute, with a total ionic concentration of approximately 150 ueq/L. The major chemical components of the rain water were:  $SO_4^{-2}$ ,  $H^+$ ,  $NO_3^-$  and  $NH_4^+$ . Based on the volume-weighted mean  $H^+$  concentration, the average pH of the rain water was 4.40 (range 3.7-5.5). Deviations from the mean pH were associated primarily with storm events where the rainfall amount was either abnormally low or very high.

The mean  $H^+$  concentration of rain water in this area has increased nearly 10-fold since 1955, i.e. from pH 5.3 (Galloway et al.,

Table V. Volume-weighted mean concentrations in rain water at Clemson, SC, for the period 4-30-79 to 9-28-82.<sup>a</sup>

Constituent	mg/L	ueq/L
H <sup>+</sup>	0.040	39.7
NH <sub>4</sub> <sup>+</sup>	0.21	11.6
Ca <sup>2+</sup>	0.13	6.5
Mg <sup>2+</sup>	0.038	3.2
Na <sup>+</sup>	0.22	9.6
K <sup>+</sup>	0.027	0.69
SO <sub>4</sub> <sup>2-</sup>	2.4	50.0
NO <sub>3</sub> <sup>-</sup>	1.1	17.7
Cl <sup>-</sup>	0.33±	9.3
Total: Cations		71.3
Anions		77.0
Cation/Anion = 0.93		
pH = 4.40 (from volume weighted H <sup>+</sup> concentration)		

<sup>a</sup>Calculated from NADP (1979-82).

1978) to pH 4.40. It has been hypothesized that  $\text{SO}_2$  and  $\text{NO}_x$  ( $\text{NO}$  and  $\text{NO}_2$ ) from combustion of fossil fuels are precursors of strong acids in precipitation (e.g.  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$ ) and are subsequently responsible for the increasing acidity of rain water in the United States and Europe (Likens and Borman, 1974). Natural rain water should have a pH near 5.6 due to  $\text{CO}_2(\text{g})$  water-air equilibria (Liljestrand and Morgan, 1978), unless soil or sea derived bases or strong acids have been scavenged by the rain.

Seasonal variation in the chemical composition of rain water may be important to the biogeochemical cycling of substances in terrestrial and aquatic ecosystems. For example, changes in the inputs of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  may greatly influence nutrient cycling and productivity. It is important, therefore, to examine seasonal relationships in the chemical composition of precipitation.

The volume-weighted mean seasonal concentrations in rain water are presented in Table VI. It is apparent that the rainfall pH was lowest during the summer months. Over this same time span, the  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations were also at their highest levels, suggesting that  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  acids may have contributed substantially to the free  $\text{H}^+$  acidity of the rain water. Moreover, there seems to have been a seasonal trend in the  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  rain water concentrations. The  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  concentrations were much higher, 34% and 33% respectively, during the warm season (April-Oct.) than the cold season (Oct.-April). This phenomenon may be related to faster conversion of atmospheric  $\text{SO}_2$  and  $\text{NO}_x$  to strong acids during the warmer months of the year.

Table VI. Volume-weighted mean seasonal concentrations in rain water at Clemson, SC, for the period 4-30-79 to 9-28-82.<sup>a</sup>

Interval	Total Rainfall (cm)	pH <sup>b</sup>	$\text{NH}_4^+$	$\text{Ca}^{+2}$	$\text{Mg}^{+2}$	$\text{Na}^+$ (mg/L)	$\text{K}^+$	$\text{SO}_4^{-2}$	$\text{NO}_3^-$	$\text{Cl}^-$
Jan. - April	104.6	4.45	0.15	0.090	0.032	0.22	0.023	1.90	0.82	0.40
April - July	120.4	4.45	0.30	0.14	0.033	0.22	0.039	2.4	1.1	0.27
July - Oct.	96.7	4.28	0.23	0.18	0.046	0.16	0.023	3.1	1.4	0.23
Oct. - Jan.	68.7	4.57	0.14	0.081	0.038	0.30	0.019	1.8	0.80	0.46

<sup>a</sup>Calculated from NADP(1979-82).

<sup>b</sup>Calculated from average volume-weighted  $\text{H}^+$  concentration.

The concentrations of  $\text{Ca}^{+2}$  and  $\text{NH}_4^+$  were also significantly higher, 50% and 80% respectively, during the summer months. Increased agricultural activity over the April to October time interval compared to the winter months is most likely responsible for the elevated  $\text{Ca}^{+2}$  concentrations, while increased biological activity might explain the higher  $\text{NH}_4^+$  concentrations in the warmer months.

To further evaluate the sources of chemical constituents in rain water, elemental ratios were calculated. Since the Lake Issaqueena system is situated only several hundred kilometers from the Atlantic Ocean, sea salt in addition to continental (crustal) sources were considered. The volume-weighted mean seasonal concentrations of  $\text{Cl}^-$ ,  $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ , and  $\text{K}^+$  in rain water were normalized to  $\text{Na}^+$ , which has a relatively constant concentration in sea salt, and the values are shown as element/Na mass ratios in Table VII. The corresponding ratios for sea salt and average crustal rock are also given in Table VII. It is readily apparent that sea water generated aerosols (sea salt) contributed to the rain water chemical composition, especially in the cases of  $\text{Cl}^-$  and  $\text{Na}^+$ . In fact, the value of the  $\text{Cl}^-/\text{Na}^+$  ratio during the Jan.-April interval (1.82) was essentially identical to that of sea water (1.80). Continental sources appear to have become more important during the rest of the year. These data suggest that Gulf of Mexico storms which commonly sweep through this area in the winter may greatly influence the seasonal chemical composition of precipitation at the Lake Issaqueena site. Because there are no concentrated urban sources within several hundred kilometers of the Lake Issaqueena system, anthropogenic sources probably contributed significantly only  $\text{NO}_3^-$  and  $\text{SO}_4^{-2}$  to the major ions in the rain, although contributions of minor components, such



Table VII. Comparison of seasonal variations of elemental ratios in rain water at Clemson, SC, with average crustal and sea water values.

Elemental Mass Ratio <sup>a</sup>	Crustal Rock <sup>b</sup>	Sea Water <sup>c</sup>	Jan.- April	April- July	July- Oct.	Oct.- Jan.	Annual Mean
$\text{Cl}^-/\text{Na}^+$	0.006	1.80	1.82	1.23	1.44	1.53	1.50
$\text{Mg}^{2+}/\text{Na}^+$	0.99	0.12	0.15	0.15	0.29	0.13	0.17
$\text{Ca}^{2+}/\text{Na}^+$	1.76	0.037	0.41	0.64	1.13	0.27	0.59
$\text{K}^+/\text{Na}^+$	0.89	0.036	0.10	0.18	0.14	0.063	0.12

<sup>a</sup>Calculated from NADP (1979-82).

<sup>b</sup>From Taylor (1964).

<sup>c</sup>From Sverdrup et al. (1942).

as Pb, were probably also significant. In summary, both oceanic and continental sources appear to have influenced the major components of rain water in the Piedmont region of South Carolina. During the winter months, oceanic sources may have become more important for some constituents (e.g.  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{+2}$ ,  $\text{K}^-$ ) than continental sources.

Perhaps the most important aspect of the areal precipitation chemistry is the free  $\text{H}^+$  acidity of the rain water. Anomalously large inputs of  $\text{H}^+$  to aquatic systems can lead to loss of alkalinity and eventually decreased pH. With regard to terrestrial systems, acidity may cause adverse responses and accelerated weathering of rocks and soils due to reaction with rain water  $\text{H}^+$  or may create problems associated with loss of nutrients or mobilization of potentially toxic soil chemical constituents (e.g.-Al). In the American Northeast, reduced pH and elevated Al concentrations in streams and lakes, induced by acid deposition inputs, are believed to be responsible for declining fish populations (Cronan and Schofield, 1979).

To examine the relative contributions of  $\text{HNO}_3$  and  $\text{H}_2\text{SO}_4$  to the free  $\text{H}^+$  acidity of rain water, the mean seasonal equivalent ratios of  $\text{H}^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{-2}$  were calculated and are presented in Table VIII. The constancy in the value of the ratios suggests that  $\text{NO}_3^-$  and  $\text{SO}_4^{-2}$  have relatively constant distant sources and their washout from the atmosphere by rainfall is similar year-round. Since the annual mean  $\text{NO}_3^-/\text{H}^+$  equivalent ratio was equal to 0.45, the maximum that  $\text{NO}_3^-$  ( $\text{HNO}_3$ ) could contribute to the free  $\text{H}^+$  acidity of rain water was 45%. However,  $\text{SO}_4^{-2}$  could more than account for all the free  $\text{H}^+$  acidity (i.e.-equivalents  $\text{SO}_4^{2-}/\text{H}^+=1.3$ ). Some of the

Table VIII. Seasonal variation of equivalent ratios of  $\text{H}^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{-2}$  in rain water at Clemson, SC.<sup>a</sup>

Equivalent Ratio	Jan.- April	April-July	July-Oct.	Oct.-Jan.	Annual Mean
$\text{NO}_3^-/\text{SO}_4^{-2}$	0.33	0.36	0.35	0.34	0.35
$\text{NO}_3^-/\text{H}^+$	0.37	0.50	0.43	0.48	0.45
$\text{SO}_4^{-2}/\text{H}^+$	1.1	1.4	1.2	1.4	1.3
$\text{NO}_3^- + \text{SO}_4^{-2}/\text{H}^+$	1.5	1.9	1.7	12.9	1.7

<sup>a</sup>Calculated from NADP (1979-82).

excess strong acid acidity (equivalents  $\text{NO}_3^- + \text{SO}_4^{2-} / \text{H}^+ = 1.7$ ) was apparently neutralized, or other sources of  $\text{NO}_3^-$  and  $\text{SO}_4^{2-}$  were important, otherwise the free  $\text{H}^+$  concentration of the rain water would have increased by as much as a factor of 1.7, resulting in a pH of 4.17.

Based on stoichiometric considerations, Stevens et al., (1980) concluded that excess  $\text{SO}_4^{2-}$  and  $\text{H}^+$  in aerosols collected in the Great Smoky Mountains was converted to ammonium sulfate,  $(\text{NH}_4)_2\text{SO}_4$ , or ammonium bisulfate,  $\text{NH}_4\text{HSO}_4$ . Perry (1982) and Norton (1982), working with aerosols collected near the Lake Issaqueena system, also provided evidence that  $\text{NH}_4^+$  and  $\text{SO}_4^{2-}$  are closely related (possibly as compounds) in Clemson area aerosols. Due to large uncertainties in estimating the amount of excess  $\text{NO}_3^-$ , analogous arguments are not as easily made for  $\text{NO}_3^-$ . However, it is likely that  $\text{NO}_3^-$  sources other than  $\text{HNO}_3$  are present in aerosols and rain water.

In addition to the chemical composition of rainfall, the annual mean atmospheric flux to the Lake Issaqueena ecosystem is needed to evaluate chemical mass balance relationships (see below). By multiplying the rain water concentrations (Table V) by the annual mean rainfall amount (132 cm/yr), the annual mean wet atmospheric flux was estimated. The results of these calculations are shown in Table IX.

For some constituents, dry deposition can be a significant component of the atmospheric input. Perry (1982) estimated dry deposition fluxes of  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$  to the Lake Issaqueena system and Heatley (1982) estimated wet and dry fluxes of Pb and Cd to the same system. These estimates of dry particle fallout are presented in Table X along with their corresponding estimated wet fluxes. For major components, dry deposition was apparently most important for  $\text{NH}_4^+$

Table IX. Annual mean wet deposition<sup>a</sup> to the Lake Issaqueena ecosystem

Constituent	Wet flux (Kg/ha/yr)
H <sup>+</sup>	0.53
NH <sub>4</sub> <sup>+</sup>	2.8
Ca <sup>2+</sup>	1.7
Mg <sup>2+</sup>	0.50
Na <sup>+</sup>	2.9
K <sup>+</sup>	0.36
SO <sub>4</sub> <sup>2-</sup>	31.7
NO <sub>3</sub> <sup>-</sup>	14.5
Cl <sup>-</sup>	4.4
Pb	0.073
Cd	0.0055

<sup>a</sup>Calculated from NADP (1979-82), except Pb and Cd from Heatley (1982).

Table X. Comparison of wet and dry atmospheric fluxes for selected chemical constituents.

Constituent	Dry Flux <sup>a</sup> _____ (Kg/ha/yr) _____	Wet Flux	Dry/Total <sup>b</sup> %
H <sup>+</sup>	0.01	0.53	1.9
NH <sub>4</sub> <sup>+</sup>	0.27	2.8	8.8
SO <sub>4</sub> <sup>2-</sup>	0.97	31.7	3.0
NO <sub>3</sub> <sup>-</sup>	0.17	14.5	1.2
Pb	0.018	0.073	20
Cd	0.0016	0.0055	23

<sup>a</sup>From Perry (1982), except Pb and Cd from Heatley (1982).

<sup>b</sup>Total = sum of wet plus dry fluxes.

where it represented roughly 10% of the atmospheric input, and for the other major constituents, dry deposition contributed negligibly to the total atmospheric input ( $\leq 3\%$ ). Dry input of Pb and Cd was significant, representing roughly 20% of the total atmospheric input.

The rate of solubilization of aerosol chemical components may also be important to their biogeochemical cycling and fate (Elzerman and Overcamp, 1983). Direct inputs of soluble constituents are immediately available for incorporation into terrestrial and, especially, aquatic chemical cycles. Perry (1982) determined that essentially all the  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{-2}$  in aerosols collected near Lake Issaquena were soluble within minutes in aqueous solutions. Norton (1983) determined Pb and other trace metals can also be quickly solubilized from aerosols, although not generally completely. The soluble fraction of Pb, for example, was released to solution in minutes or less, but only approximately 50% of the total Pb could be solubilized in Lake Issaquena water and 80% in pH 3.6 rainwater. These results strongly suggest that the majority of the  $\text{NH}_4^+$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{-2}$ , as well as significant fractions of other chemical constituents, in precipitation and aerosols are probably readily available (upon deposition) for biogeochemical cycling within the Lake Issaquena ecosystem. For biologically important constituents like  $\text{NH}_4^+$ ,  $\text{NO}_3^-$  and  $\text{SO}_4^{-2}$ , such postdepositional interactions are certainly significant. Furthermore, postdepositional reactions of free (soluble)  $\text{H}^+$  in wet and dry deposition in terrestrial and aquatic environments are critical with regard to pH changes and mobilization of nutrients and toxic chemical constituents. A major component of this study was focused on delineating the results of some of these interactions (see below).

### Storm Event Changes in Streamwater

Changes in the chemical composition of streamwater during precipitation (storm) events are important for at least the following three reasons: 1) significant portions of total annual fluxes of dissolved and particulate materials can occur during storm events, 2) some products of neutralization and other reactions of rainwater with watershed components will appear in stormflows, and, 3) excursions in chemical composition beyond important threshold values may occur, for example transient events in which aluminum reaches toxic concentrations in the streamwater. The importance of transient events may be overlooked in averaging and "spot" sampling approaches. Actual changes in streamwater concentrations, their covariance, and their relationships to rain input parameters, discharge (water flow) and drainage basin characteristics are all relevant and were considered. A comparison of concentrations at various points in a storm event to values typical of the seasonal baseflow and to the incoming rain were also considered useful for this initial investigation.

Storm event research concentrated on Lake Issaquena. Again, this report only summarizes the results of this investigation. Details of storm event and baseflow chemical compositions for most parameters are given by LaManna (1983). Aluminum results are given by Pott (1982), and Pb and Cd by Heatley (1982). Rainfall data was obtained primarily from NADP (1979-82), as discussed above in "Atmospheric Inputs." Some typical compositions of other lakes in the region were also discussed above in Part A: Regional Lake Survey.

Baseflow samples were collected at all stations approximately monthly for the major component parameters from May, 1981 through July,



1982. Pb and Cd investigations were conducted starting in 1980.

Several storms were monitored for initial observations before May, 1981, followed by intense sampling of storms until August, 1982.

Unfortunately, this period was characterized by a drought, which limited the number of useable storm events and may have interjected some bias to the results. Drought-induced bias was obvious in the case of Pb fluxes in the watershed (Heatley, 1982), but was not evident in most other results, however. Longer term investigation would be required to make a valid determination of drought effects.

Site-selective sampling (intensive sampling at single sites through the rise and fall of the hydrograph) and synoptic sampling (sampling all sites as near to the same time as possible) were conducted. Results clearly indicate significant influences of rainfall, season, and drainage basin characteristics (especially development and forest management practices) on individual data points, but many generalization are possible. Seasonal and drainage basin considerations will not be pursued here, leaving the emphasis on changes in streamwater composition during storm events. A particular storm, which occurred on July 29, 1982, only on the drainage basin of C-2, the major tributary, will be emphasized as an instructive example. Storm event sampling at the dam was conducted, but interpretation is more complex due to the added influence of in-lake processes (Heatley, 1982; LaManna, 1983) and will not be discussed here.

Baseflow data for major components are presented in Table XI. Many of the points made above in Part A: Regional Lake Survey could be made again here. Also, some predictable results, such as the lower pH of the groundwaters compared to the surface waters (Stumm and Morgan,

Table XI-A. Baseflow Data for C-1

Date	pH	Specific conductance (umohs/cm)	DISSOLVED							Stream discharge (m <sup>3</sup> /s x10 <sup>-3</sup> )
			Mg	Ca	Na	K	SO <sub>4</sub> =	NO <sub>3</sub>	HCO <sub>3</sub>	
05/81	6.50	21	*	*	*	*	30.6	*	143	*
06/81	5.90	29	10.7	68.8	54.8	26.9	46.8	98.5	158	*
07/81	5.65	28	66.7	64.9	67.4	23.6	13.7	228.5	146	*
08/81	7.00	28	51.8	59.4	56.6	17.9	110.0	8.6	148	*
09/81	6.75	28	64.2	57.9	60.9	21.5	488.6	*	152	*
10/81	6.62	26	66.7	53.9	54.4	*	386.9	12.8	154	4.24
01/82	7.00	24	60.1	60.4	50.5	20.7	62.4	25.7	121	12.46
02/82	6.70	22	60.9	59.9	58.7	21.0	74.9	10.7	131	10.19
03/82	6.80	25	61.7	61.4	59.2	20.7	45.5	0	137	9.06
04/82	6.30	19	65.8	65.9	43.9	20.2	70.5	30.0	*	9.62
06/82	6.40	26	70.8	71.8	67.9	25.1	45.5	10.01	153	6.23
07/82	6.50	27	70.8	76.3	60.0	23.6	*	48.6	165	*

\*Data unavailable.

Table XI-B. Baseflow Data for C-2

Date	pH	Specific conductance (umohs/cm)	DISSOLVED							Stream discharge (m <sup>3</sup> /s)
			Mg	Ca	Na	K	SO <sub>4</sub> =	NO <sub>3</sub>	HCO <sub>3</sub>	
05/81	6.50	39	*	*	*	*	106.1	*	176	0.16
06/81	5.60	38	14.0	154	100	37.6	63.0	167.8	220	*
07/81	6.30	38	83.9	106	100	25.6	84.9	32.1	218	0.08
08/81	6.90	24	81.5	99.8	97.9	23.3	124.8	20.0	206	*
09/81	6.85	42	81.5	96.8	102	29.2	624.0	*	210	*
10/81	6.97	40	88.9	102	104	*	480.5	16.4	230	0.07
01/82	7.00	34	80.6	104	82.2	24.1	95.5	31.4	152	0.45
02/82	6.90	34	77.4	104	94.0	22.8	89.2	22.1	174	0.54
03/82	6.80	37	77.4	97.3	89.6	21.5	76.7	33.6	174	0.37
04/82	6.30	30	91.4	120	60.5	25.6	110.0	20.0	*	0.33
06/82	6.40	36	92.2	123	107	28.7	62.4	55.0	202	0.25
07/82	6.50	41	97.1	125	94.9	27.6	*	0	219	0.25

\*Data unavailable.

Table XI-C. Baseflow Data for C-3

Date	pH	Specific conductance ( $\mu\text{mohs/cm}$ )	DISSOLVED							Stream discharge ( $\text{m}^3/\text{s} \times 10^{-2}$ )
			Mg	Ca	Na	K	$\text{SO}_4=$	$\text{NO}_3$	$\text{HCO}_3$	
05/81	6.70	31	*	*	*	*	40.6	*	201	0.79
06/81	6.20	33	16.5	160	97.9	26.9	60.0	139.9	240	*
07/81	6.80	37	86.4	125	106	22.8	49.9	41.4	260	0.48
08/81	7.25	40	83.9	119	108	20.5	87.4	10.0	251	*
09/81	7.05	37	93.8	131	106	24.8	998.4	*	272	*
10/81	7.09	41	86.4	111	110	*	536.6	24.3	248	0.01
01/82	7.10	31	65.8	91.3	84.0	20.7	114.2	28.6	143	4.50
02/82	6.80	28	65.8	89.3	89.6	20.5	87.4	7.1	161	1.38
03/82	6.80	33	67.5	92.8	97.9	21.0	85.5	15.7	168	2.80
04/82	6.50	27	72.4	96.3	92.6	22.0	78.6	29.3	*	2.26
06/82	6.40	32	77.4	104	97.4	25.1	70.5	45.0	202	1.42
07/82	6.50	37	74.9	112	87.4	24.3	*	0	219	1.36

\*Data unavailable.

Table XI-D. Baseflow Data for C-4

Date	pH	Specific conductance ( $\mu\text{mohs/cm}$ )	DISSOLVED							Stream discharge ( $\text{m}^3/\text{s} \times 10^{-2}$ )
			Mg	Ca	Na	K	$\text{SO}_4=$	$\text{NO}_3$	$\text{HCO}_3$	
05/81	6.70	31	*	*	*	*	34.9	*	236	1.92
06/81	5.40	47	17.3	172	110	31.5	84.9	84.3	270	*
07/81	6.60	36	91.3	117	119	22.8	65.5	19.3	278	0.62
08/81	6.90	29	91.3	126	112	19.2	1,123.2	11.4	272	*
09/81	7.05	36	93.8	124	12.2	19.7	738.2	*	282	*
10/81	7.10	41	101	123	112	*	380.6	2.1	280	0.36
01/82	7.20	34	74.1	104	106	21.5	108.0	27.1	166	6.34
02/82	6.75	32	74.1	101	101	21.0	99.8	10.0	190	2.94
03/82	6.90	35	73.2	97.3	95.6	20.5	79.2	15.7	188	5.01
04/82	5.50	22	79.0	105	105	22.0	97.9	0	*	3.77
06/82	6.40	40	89.7	128	136	24.3	83.0	27.8	228	2.69
07/82	5.60	49	145	137	136	25.1	*	121.4	300	3.68

\*Data unavailable.

Table XI-E. Baseflow Data for D-1

DISSOLVED										Stream discharge (m <sup>3</sup> /s)
Date	pH	Specific conductance (umohs/cm)	Mg	Ca	Na	K	SO <sub>4</sub> =	NO <sub>3</sub>	HCO <sub>3</sub>	
			-----			ueq/L	-----			
05/81	7.00	30	*	*	*	*	83.6	114.2	216	
06/81	6.00	40	17.3	113.8	90.0	31.5	54.9	178.5	252	
07/81	6.30	45	96.3	118.8	95.7	25.1	58.7	32.1	*	
08/81	6.65	45	91.4	116.8	100.0	35.8	624.0	114.2	22	
09/81	7.20	42	91.4	110.3	95.7	24.6	363.8	*	244	
10/81	6.99	41	91.4	119.8	93.5	33.3	293.3	7.1	257	
01/82	7.20	33	59.3	83.3	63.5	28.7	122.9	25.0	109	
02/82	6.60	29	70.0	95.3	75.7	28.4	110.4	15.0	134	
03/82	6.70	35	76.5	103.3	78.7	24.6	93.6	25.7	170	
04/82	6.20	28	76.5	101.8	87.4	24.6	106.1	15.0	*	
06/82	6.20	39	93.0	129.7	116.6	31.2	95.5	212.1	214	
07/82	6.60	37	95.5	136.7	102.7	29.7	*	0	239	

\*Data unavailable.

Table XI-F. Baseflow Data for GW-1

Date	pH	Specific conductance (umohs/cm)	DISSOLVED							Stream discharge (m³/s x10⁻⁴)
			Mg	Ca	Na	K	SO₄=	NO₃	HCO₃	
05/81	5.90	22	*	*	*	*	26.2	80.0	127	*
06/81	5.50	25	14.0	73.3	61.3	29.2	18.7	53.5	168	1.13
07/81	4.90	23	74.1	67.4	58.7	12.3	18.7	15.7	155	0.72
08/81	6.50	29	74.1	65.9	60.9	23.8	33.1	0	156	0.71
09/81	5.70	30	71.6	65.9	58.7	21.0	207.8	*	154	0.73
10/81	5.85	29	71.6	64.4	56.6	21.8	18.7	22.8	162	1.04
01/82	6.80	25	71.6	72.8	61.3	21.0	31.2	14.3	152	*
02/82	6.70	25	71.0	72.8	60.0	21.5	26.8	1.4	156	0.55
03/82	5.80	32	73.2	74.4	55.2	21.0	10.6	10.0	159	0.41
04/82	5.50	22	74.9	75.4	57.0	21.8	33.1	0	*	*
06/82	5.60	26	73.2	75.4	65.2	23.0	33.1	27.8	159	0.85
07/82	5.60	25	73.2	76.3	60.5	23.0	*	0	160	0.37

\*Data unavailable.

1981) could be made. The relative constancy of surface water pH values, and many other constituents, is also evident, as are some apparent "outlier" points. Only dissolved components were considered, except for Pb, Cd, and total suspended solids, as discussed below. During storm events, significant increases in turbidity and total suspended solids (to >10000 mg/L) did occur (also see Figure 8).

Of initial relevance to this discussion is the relationship of baseflow values to the typical composition of rainwater in the area. As shown in Table IX, the primary cations in Clemson area rain are  $H^+$ ,  $NH_4^+$ , and  $Na^+$  (total 85% of cation ueq/L), while the primary anions are  $SO_4^{-2}$  and  $NO_3^-$  (total 88% of anion ueq/L). In contrast,  $Mg^{+2}$ ,  $Ca^{+2}$ , and  $Na^+$  are the most important cations on an ueq/L basis, and  $HCO_3^-$  was generally the major anion in the streams and lake water of the Lake Issaqueena watershed. A notable exception occurred in the streams and lake water in the fall, 1981, when  $SO_4^{-2}$  concentrations and watershed fluxes increased and  $SO_4^{-2}$  became the dominant anion. The increased sulfate may have come from flushing of  $SO_4^{-2}$  accumulated in the watershed by dry fallout and/or soil processes during the drought. In contrast to  $SO_4^{-2}$  and  $NO_3^-$ ,  $HCO_3^-$  was much more significant in the streams and even more so in Lake Issaqueena than in the input rain. Similarly, the surface waters compared to rain were higher in concentrations of  $Cl^-$  and the cations  $Mg^+$ ,  $Ca^{+2}$ ,  $Na^+$  and  $K^+$ , consistent with the watershed flux and neutralization mechanism data presented below. Surface water pH values were significantly higher than in the rain, indicating effective neutralization in the watershed. Synoptic surveys of pH in the lake showed seasonal, depth, and productivity trends and slightly lower values around the inflow at C-2 compared to the rest of the lake.

The hundreds of data points collected during storm events offer significant opportunities and challenges for interpretation. Some example data is presented in Table XII, and some representative summary observations follow. In the example storm event, precipitation occurred for several hours only in the upper part of the watershed and the resulting increased stream flow was observed as a rising and falling hydrograph for approximately 24 hours. As shown in Table XII, the stream flow peaked approximately 5 hours after precipitation and the observations began.

Storm-induced chemical changes are evident in Table XII. During the stormflow, pH decreased slightly (maximum 0.5 pH unit), although not significantly toward the rain value of approximately 4.4. Throughout this investigation, it was evident the watershed was effective in neutralizing incoming free acidity ( $H^+$ ). A small amount of neutralization (approximately 0.2 pH units) was observed in passage of the rain through the tree canopy (Heatley, 1982), but most neutralization occurred in the soil or duff (see Soil Neutralization Mechanisms below). Slight decreases in stream pH during stormflows (0.2 to 1 pH unit) were common but not universal, which might indicate the importance of kinetic factors (e.g. - contact time with the soil) in controlling the effectiveness of neutralization mechanisms. The consistency of pH values indicates the importance of equilibrium controls. Export rates (concentration times flow) for  $H^+$  usually peaked with discharge, so storm events can affect acid fluxes through the watershed.

Specific conductance did not always show a consistent trend during storm events. Slight increases (1 to 3 umhos/cm) were common at

Table XII. 7/29/82 Storm Data for C-2

Storm hours	pH	Specific conductance ( $\mu$ mohs/cm)	DISSOLVED							Stream discharge (m <sup>3</sup> /s)
			Mg	Ca	Na	K	SO <sub>4</sub> =	NO <sub>3</sub>	HCO <sub>3</sub>	
1.2	6.0	36	81.5	110	116	33.8	158	6.4	186	0.27
2.6	5.8	37	91.4	112	109	33.8	119	37.1	193	0.45
3.0	5.9	36	79.0	114	116	32.0	133	47.1	191	0.57
3.7	5.9	35	74.1	107	108	33.8	70.5	44.3	189	0.72
4.0	5.7	36	80.6	109	112	33.5	81.1	39.9	186	1.40
4.7	5.5	36	74.1	107	95.3	47.9	206	9.3	140	1.76
6.2	5.5	35	71.6	84.8	111	42.0	226	12.1	116	1.04
7.2	5.5	33	65.8	107	81.8	58.1	108	4.6	95	0.74
8.2	5.6	31	62.5	87.3	81.3	51.7	122	4.7	88	0.65
14.7	5.7	32	67.5	89.8	80.9	49.7	167	3.0	112	0.30
20.4	5.8	34	73.2	98.8	90.0	47.1	122	41.4	130	0.26
23.0	5.8	37	85.6	110	93.1	58.1	208	7.1	138	0.26

the beginning of storms, perhaps indicating flushing of accumulated ionic materials. A later dilution effect, where specific conductance was inversely related to discharge, was also common, as exemplified in Table XII approximately 8 hours into the observation.

Major cations ( $\text{Mg}^{+2}$ ,  $\text{Ca}^{+2}$ , and  $\text{Na}^{+}$ ) frequently covaried during storm events. As might be expected, concentrations of these major cations often showed a positive correlation with specific conductance, hence showing the dilution effect mentioned above and evident in Table XII. However, export rates of the major cations still increased with discharge (i.e. - the decrease in concentration was not as significant as the increase in flow rate). These results indicate water moving through the watershed picks up the major cations and loses  $\text{H}^{+}$ , as discussed further below in Soil Neutralization Mechanisms. The actual concentration of major cations in streamflow may be a function of contact time of the rain with the soil and equilibrium processes, but the net effect of precipitation is to increase the export of these ions from the watershed.

In contrast to the other base cations ( $\text{Ca}^{+2}$ ,  $\text{Mg}^{+2}$ ,  $\text{Na}^{+}$ ),  $\text{K}^{+}$  usually increased in concentration with stream discharge. As discussed below in Soil Neutralization Mechanisms,  $\text{K}^{+}$  is the most quickly released of the four cations from soil interacting with rainwater and the release is relatively independent of pH. Kinetic factors which might limit the concentration of the other major cations might not, therefore, limit the concentrations of  $\text{K}^{+}$  during storm events.

As expected, alkalinity tended to be inversely related to  $\text{H}^{+}$  export rates and positively correlated with pH. Data for  $\text{NO}_3^{-}$  did



not exhibit clear consistent trends, but  $\text{SO}_4^{-2}$  concentrations, and even more so export rates, increased during storm flows. Incoming  $\text{SO}_4^{-2}$  in the rain and solubilization of  $\text{SO}_4^{-2}$  from the soil and accumulated dry fallout could explain this observation. Note also in Table XII that the ratio of  $\text{SO}_4^{-2}$  to  $\text{HCO}_3^-$  increased and became greater than one during the storm. The sum of  $\text{SO}_4^{-2}$  and  $\text{HCO}_3^-$  was generally positively correlated with specific conductance, consistent with their being the major anions. Both of these anions are probably important to cation mobility based on charge balance considerations. The role sulfate mobility plays in cation mobility is in particular need of further investigation. Occasionally, the pulse of  $\text{SO}_4^{-2}$  brought in by stormflow could be observed, after a lag time, at the dam.

The general effect of the watershed on transition in composition from rainwater to surface water is reviewed in Table XIII. Also, the net direction of the changes during stormflows can be seen by comparing the average values during stormflows to the baseflow data.

Aluminum concentrations and export rates also increased with discharge during storm events (Pott, 1982). Aluminum fluxes may be significant due to potential toxicity to aquatic biota. Baseflow concentrations of dissolved Al were typically 5 to 15 ug/L, whereas concentrations in stormflows reached above 100 ug/L. A positive correlation between Al fluxes and dissolved organic carbon (DOC) (see Figures 6 and 7) may have resulted from Al-organic complexes (see Pott, 1982). Also, calculated cation/anion ratios, not including aluminum, for stormflow data were frequently near one at lower flows but less than one at higher flows, possibly indicating significant concentration

Table XIII. Comparative Ion Concentration Data.

Ion	Rain <sup>a</sup>	Baseflow at C-2 <sup>b</sup>	Stormflow at C-2 <sup>c</sup>
		ueq/L	
H <sup>+</sup>	39.7	0.3	1.9
Na <sup>+</sup>	9.6	94	100
Ca <sup>+2</sup>	6.5	112	103
Mg <sup>+2</sup>	3.2	79	76
K <sup>+</sup>	0.7	27	43
SO <sub>4</sub> <sup>-2</sup>	50.0	174	143
NO <sub>3</sub> <sup>-</sup>	17.7	40	21
HCO <sub>3</sub> <sup>-</sup>	0	198	147

a. From Table V.

b. Average of Data in Table II.

c. Average of Data in Table III.

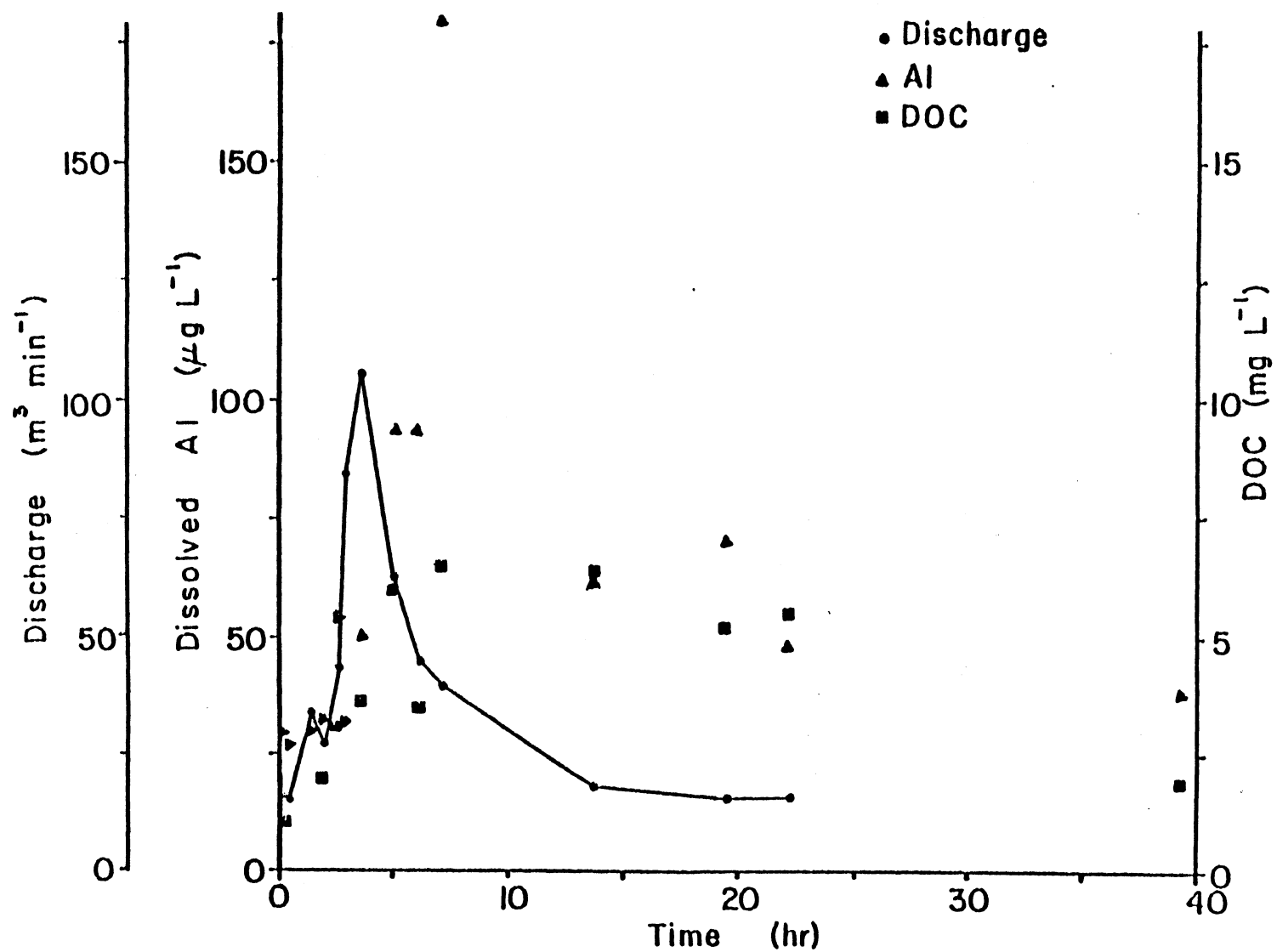


Figure 6. DOC and Dissolved Aluminum During Storm Event in C-2

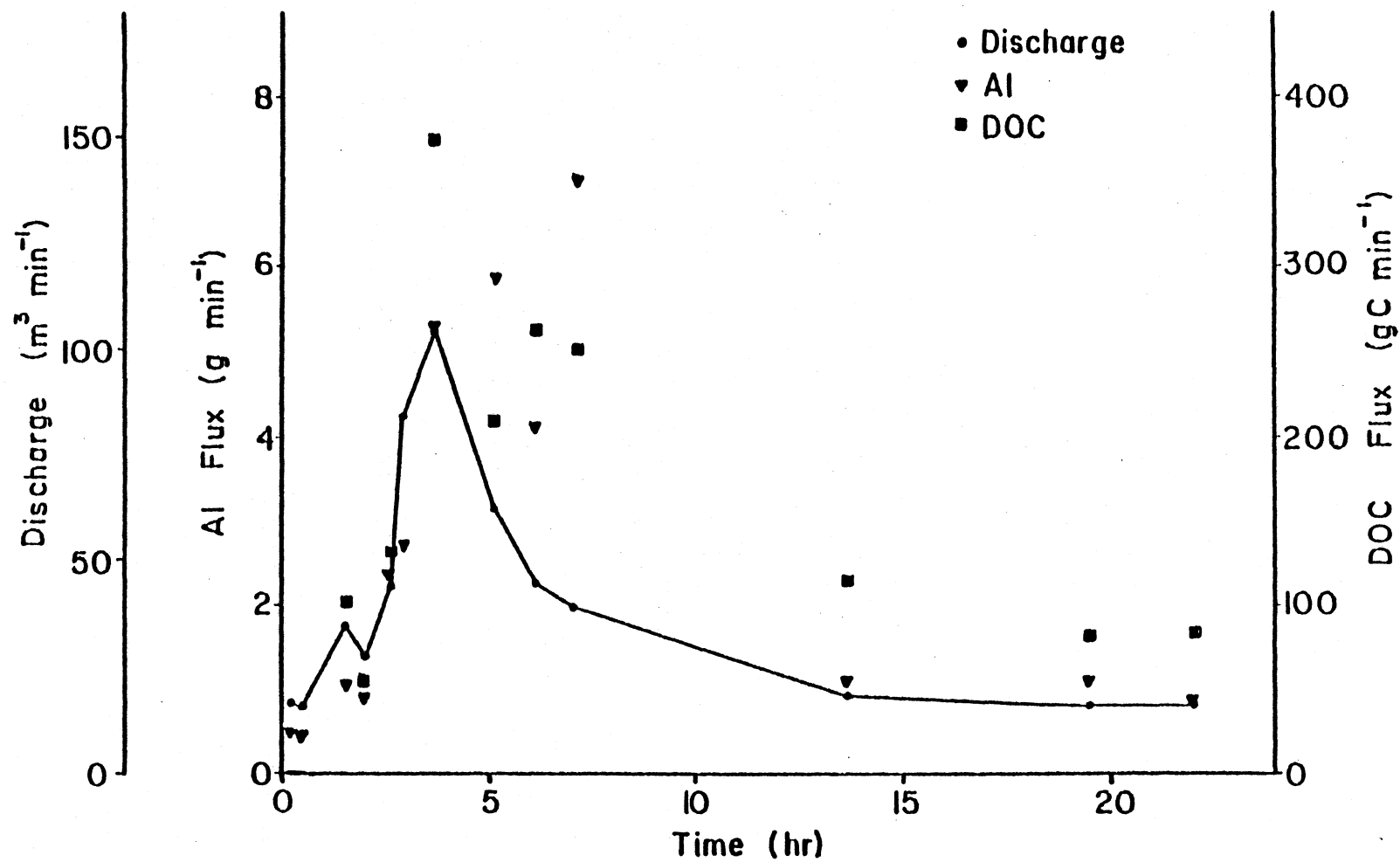


Figure 7. Fluxes of DOC and Aluminum During Storm Event in C-2

increases of some cation such as aluminum at higher flows. Variation of charge of aluminum hydroxide complexes must also be considered, of course, but some positively charged aluminum was probably present in the stormflow samples (Pott, 1982).

Fluxes of Pb and Cd in the Lake Issaqueena watershed provide an interesting case of contrasting geochemical characteristics. An investigation of aspects of the geochemical cycles of Pb, Cd, and TSS (total suspended solids), following their transport from the atmosphere to Lake Issaqueena both directly to the lake's surface and indirectly through the watershed during baseline and storm event conditions and then to the sediments or out the outflow, was conducted (see Heatley, 1982 for details). The importance of considering each form of each metal and each transport mechanism separately was demonstrated. For example, the transport of TSS and Pb through the watershed via streams and runoff was affected significantly by storm events, whereas baseflow and direct atmospheric inputs were relatively more important for Cd (see below). Separate analysis of the sources and sinks allowed the generation of mass balances for Pb, Cd, and TSS.

Most of the baseline fluxes of Pb, Cd, and TSS were transported by C-2, which also had most of the total baseflow (84%) and drained roughly 80% of the watershed. The majority of the added fluxes of Pb and Cd from storm events were also carried by C-2. However, a large percentage of the total annual input of particulate Pb (48%) and TSS (64%) was added via C-4 during storm flows. C-4 is adjacent to a dirt highway that may be high in Pb content from automobile exhaust, and it also drains an area significantly disturbed by forest management practices, which may also contribute to its PPb and TSS inputs. All of

the streams exhibited a general increase in TSS and dissolved and particulate Pb and Cd as flow increased during storm events (see Figures 8-10 for examples). Total and particulate Pb transport was apparently closely related to TSS transport. The added storm inputs were responsible for a majority of the TSS and dissolved (60%) and particulate (73%) Pb inputs to the lake, but baseline stream and atmospheric inputs accounted for most of the dissolved and particulate Cd inputs to the lake (see Table XIV).

#### Soil Neutralization Mechanisms

Initial observations indicated the soils in the Lake Issaquena watershed were the most important point of neutralization of incoming acid deposition. Canopy interactions might be important to nutrient and organic matter cycling, but were found to have very small effects on pH of throughfall. Streamwater pH values generally were at most slightly lower than Lake Issaquena values, indicating most of the neutralization in the overall system occurred in the streams (unlikely due to low alkalinity) or in the soil before the runoff appeared in the streams. Surface water pH values, especially in the lake, which appeared to contain significant phytoplankton communities, were also influenced by biological activity. Of course, acidity can also be produced in soil and aquatic systems. The major point of importance here, however, is that the soils appeared to play the major role in neutralization of incoming acid deposition.

Consequently, further investigation of soil/rainwater interactions in the Lake Issaquena watershed was undertaken. The three major soil types, Cecil, Madison, and Pacolet, all had measured soil pH values in

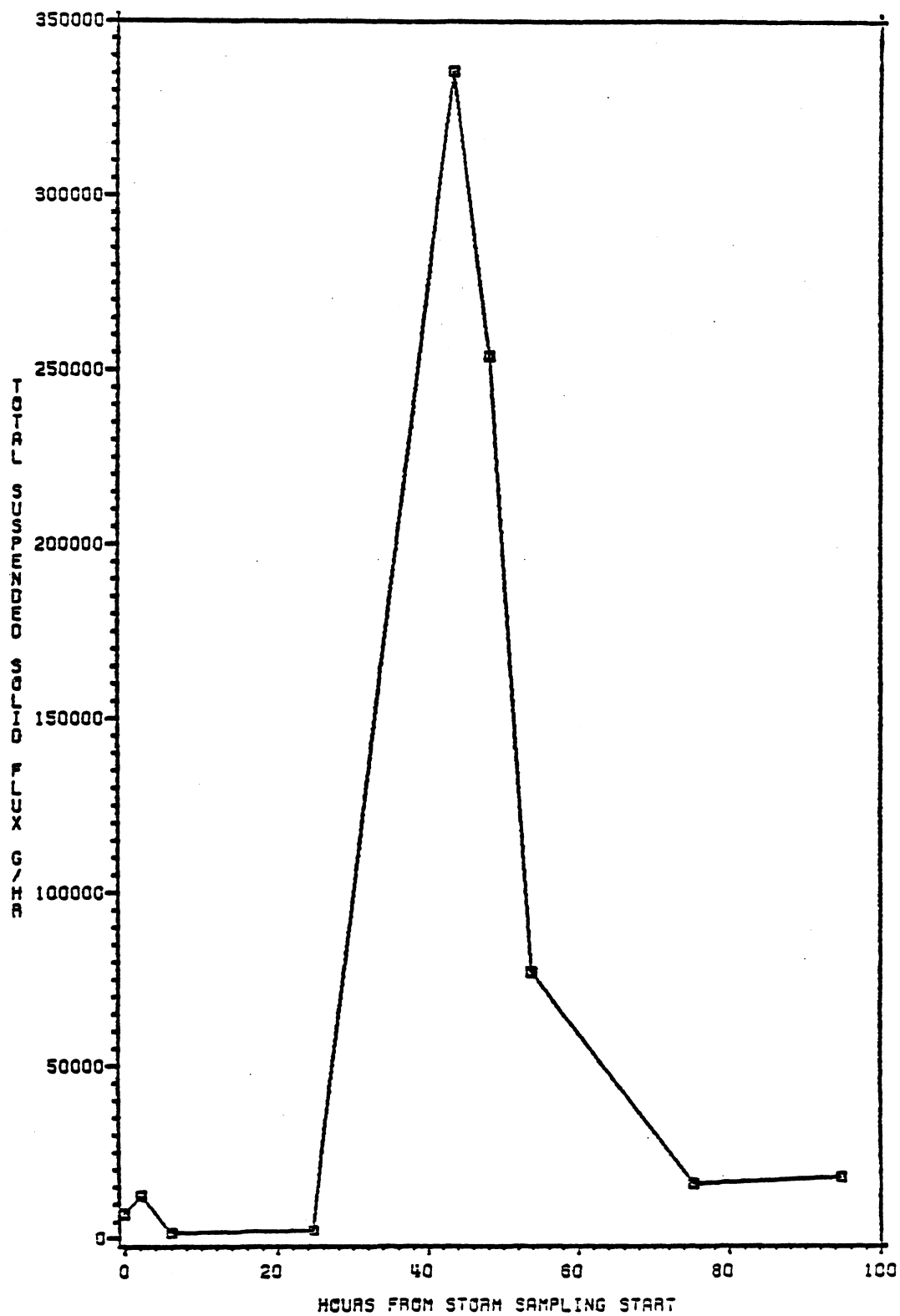


Figure 8. TSS Flux During Storm Event in C-4 (10/23/81)

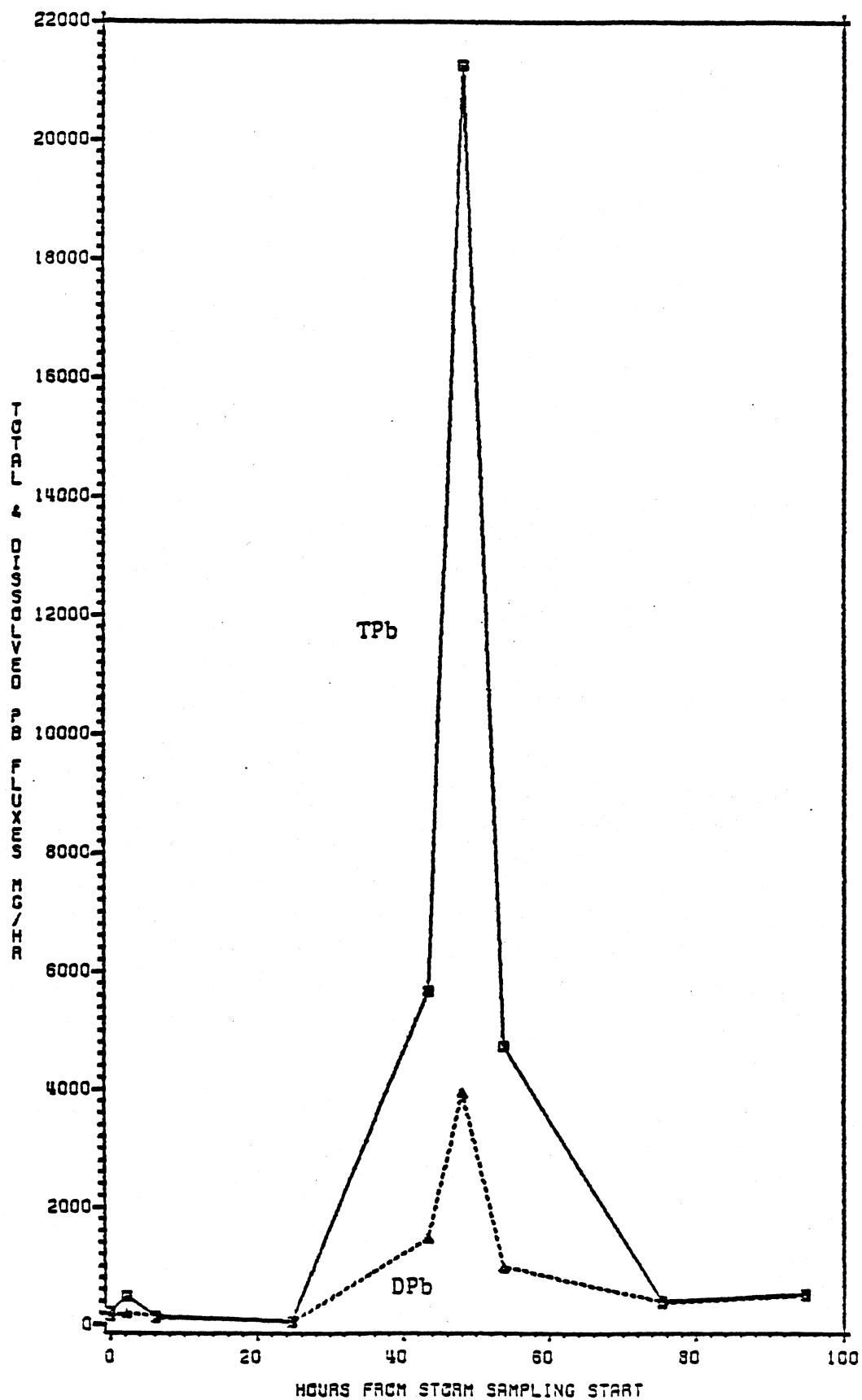


Figure 9. Total and Dissolved Pb Flux During Storm Event in C-4 (10/23/8).



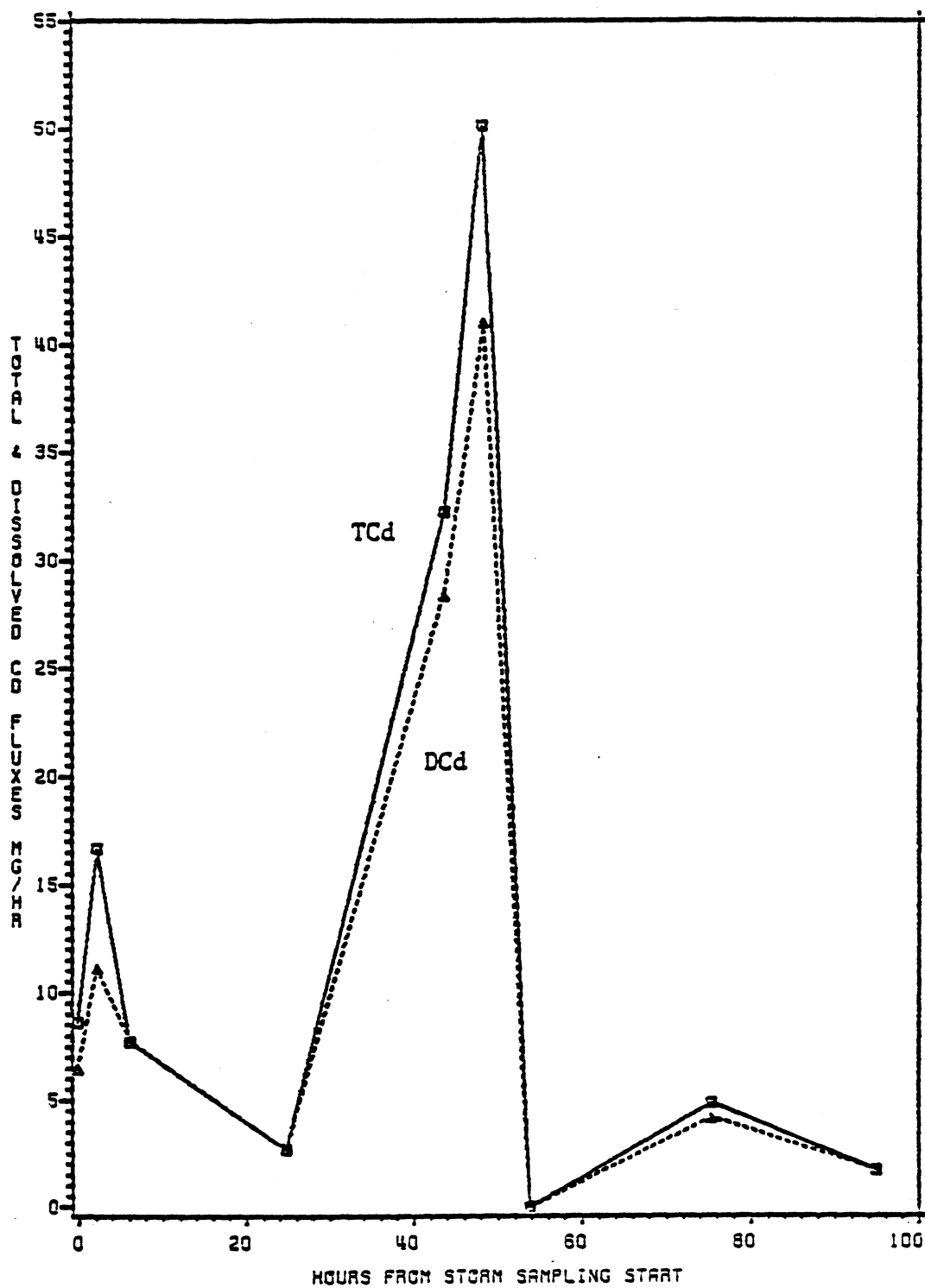


Figure 10. Total and Dissolved Cd Flux During Storm Event in C-4 (10/23/81)

Table XIV. Source of Lake Inputs as Per Cent of Total

Input	Direct Atmospheric	Baseline Stream Flux	Added Storm Stream Flux
		%	
<u>PB</u>			
Total	8.9	32	59
Dissolved	10	36	54
Particulate	5.6	25	69
<u>Cd</u>			
Total	40	53	6.6
Dissolved	46	46	8.3
Particulate	33	63	4.4
<u>TSS</u>	*	24	76
* Negligible			

0.01 N  $\text{CaCl}_2$  of approximately 4.0 to 5.0 and in water of approximately 5.0 to 5.8 (Owings, 1983; Lesan, 1983). Cation exchange capacity, base exchange capacity, and base saturation data (Lesan, 1983) are presented in Table XV. Note that the soils have relatively low cation exchange capacities and, more importantly for consideration of acid inputs, low base saturations. A lower base saturation means a lesser amount of the so called base metals (Ca, Mg, K, and Na) to exchange for  $\text{H}^+$ , hence possibly a lesser capability to neutralize incoming acidity.

Whereas soil pH data showed no consistent trend with depth in the soil other than a consistently lower value in the duff, significant depth trends are evident in Table XV. The duff appears to be significantly different from the remainder of the soil column, as would be expected due to the organic matter and biological activity present there. Since atmospheric deposition generally contacts the duff before the soil, duff characteristics are very important; unfortunately, they also proved to be the most difficult to investigate (Lesan, 1983). Disruption of the duff layer might account for some of the observation that outflows from disturbed drainage basins in the watershed had a chemical composition that varied from the outflows of less disrupted watersheds. The overall importance of the brief contact of rainwater with the duff is still relatively unknown, however. Relatively high base saturations in the duff may result from sequestering of the metals by organic matter, but the characteristics and relatively small total volume (or mass) of duff on soils of the area probably make the duff incapable of protecting the soil below from nutrient leaching by acid deposition. Similarly, duff pH values (approximately 3.5-4.0) indicate little neutralization of incoming acid deposition will occur in the duff.

Table XV. Cation Exchange Capacity (CEC), Base Exchange Capacity\* (BEC), and Base Saturation of Lake Issaqueena Watershed Soils

Soil Type	CEC —— meq/100 g ——	BEC	%Base Saturation (BEC/CEC x 100)
<u>Madison</u> (22% of watershed)			
Duff	13.1	6.41	49
A-horizon	4.31	0.43	10
Upper-B	4.76	0.97	20
Lower-B	4.90	0.67	13
<u>Pacolet</u> (31% of watershed)			
Duff	14.7	12.8	88
A-horizon	4.18	0.70	17
Upper-B	4.31	0.78	18
Lower-B	4.78	0.96	20
<u>Cecil</u> (30% of watershed)			
Duff	-	-	-
A-horizon	3.04	0.49	16
Upper-B	4.20	1.18	28
Lower	4.10	1.20	29

\* A barium chloride compulsive exchange method was used to determine the total CEC and that accounted for by the "base metals" (Ca, Mg, Na, K) as detailed in Lesan (1983).

Within the A and B horizons, there was a common trend of increasing CEC and BEC with depth. Also, the A-horizon was consistently lower in base saturation (the percent of the cation exchange capacity occupied by the base metals Ca, Mg, Na, and K) than the B horizon. Mineral cycling and regeneration processes in soils and watersheds are complex and not well understood, but the two observations above are predictable based on mineral weathering by rain. Relative to acid deposition, the important question is whether the slow leaching of base cations, which are also important nutrients, from the upper levels of the soil is being increased in amount or rate by acid deposition.

Since it appeared significant interaction of the A-horizon with acid deposition was occurring, leaching studies of A-horizon samples of each of the three soils were emphasized (see Lesan, 1983 and Owings, 1983 for more details). Continuous batch, serial batch, and column leaching studies were conducted, each designed to provide different insights. The three soils showed similar characteristics, so will be referred to in this discussion as the "soil".

Continuous batch extractions monitored for up to 9 days indicated that in pH 4.4 rainwater, the soil lost significant amounts of Ca, Mg, and K to solution at about 20°C. Losses of Na proved difficult to monitor and were probably much less than the three metals above. Much of the loss occurred in the first several hours of contact, especially for K. The rate of loss decreased after about 10 hrs. and went to almost zero after 20 hrs. Decreasing the pH to 3.3 had little effect on K release, but increased release of Ca and Mg, and slightly increased Al and Si. Al and Si release increased drastically at pH 2.4, although the release took tens of hours to occur, indicating mineral

dissolution might be responsible. Ion exchange appeared to be the main neutralization mechanism at pH 4.4, with mineral dissolution becoming more important at lower pH values. Release of metals from organic complexes was not specifically investigated, except for Al (Pott, 1982). Data for aluminum indicated significant changes in Al speciation can occur with small changes in pH in the range of 4 to 5.

Plots of amount released vs. time had steep slopes in the first ten hours of contact for K and Mg and less so for Ca, indicating kinetics and contact time may be important in determining the extent and mechanisms of neutralization in the soil. Hence, the composition of watershed outflows are probably a function of the contact time of the rainwater and the soil. Different storm sequences would then result in different stormflow chemical (and flow) patterns, as observed in the section Storm Event Changes in Streamwater above. The actual composition would result from a combination of equilibrium and kinetic control. The storm event data and batch extraction studies above, and other extraction studies below, indicate the exchangeable cations Ca, Mg, and K are significant in these processes primarily through ion exchange mechanisms and that mineral dissolution releasing Ca, Mg, Al and Si can also become significant.

Column extractions (near-saturated gravity flow) indicated a pH 4.7 rain solution compared to a pH 5.8 rain solution lowered soil pH more and released base cations at a faster rate from all horizons of the soil. The duff lost the greatest absolute amount of metal ions, but the A-horizon lost the greatest fraction of its total pool of exchangeable cations. In all cases, the absolute amount of metal released was in the order  $Ca > Mg >> K$ , whereas the fraction of the total pool of the individual

metal released was in the reverse order. At pH 4.7, K was released similarly to pH 5.8, indicating K release was relatively insensitive to pH. However, pH 4.7 and exposure to more solution drastically increased release of Mg and Ca, indicating a long period of precipitation of low pH could greatly increase Ca and Mg mobility and the ratio of their concentrations to K in the streamwater. Hence, K is being depleted at a faster rate but Ca and Mg may be more important to investigation of long term acid neutralization than K in the Lake Issaqueena watershed. Effluent pH for the column studies was similar for both influent solutions. Although this means effective neutralization of even the lower pH rain solution occurred, it also means loss of more exchangeable cations by the soil caused by the lower pH rain solution.

The observed increase in Ca and Mg mobility with decreasing pH is consistent with an ion exchange mechanism of acid neutralization and metal release. Dissolution of solids also appears to occur to a small degree at pH 4.4 and increases at lower pH values, until at pH 2.4 (the lowest pH tested), significant mineral weathering occurs (Owings, 1983). Dissociation of organic complexes may also increase with decreasing pH values, and would probably show a "threshold" level effect relative to pH (see Conclusions). Changes in metal speciation must also be considered. In the case investigated, aluminum binding by humic acid (Pott, 1982), the threshold pH, below which significant fractions of the Al would be expected to be released, was determined to be in the range of pH 4 to 5. Below pH 4, Al release by mineral weathering probably also becomes significant (Owings, 1983). Al speciation also changes significantly in the pH 4 to 5 window (Pott, 1982).

For Pb and Cd, leaching studies with various pH solutions revealed that a higher percentage of metal (Cd and Pb) was leachable from A-horizon soil, duff, and sediment as the pH decreased (see Table XVI). In the range of approximately pH 4 to 6 (final pH), Cd was released more than Pb at any given pH. Solution of solid phases, or probably more importantly, desorption by ion exchange or dissociation of organic complexes, could account for the release of Cd and Pb. This mechanism would not provide significant neutralization of incoming acid, however, increased mobility of Cd and Pb may result. If decreasing the pH results in slight increases in the Cd and Pb leached, the total flux of Cd and Pb out of the watershed with time could increase. This loss could actually be advantageous for the biota of the soil, but overall evaluation must consider the ultimate fate of the Cd and Pb. For example, it could concentrate in the sediments of the reservoir (see next section).

Evidence for a "threshold" effect (see Conclusions) can also be found in Table XVI. The final pH of some of the extraction solutions reached 4 or below. In each case for Cd and almost all for Pb, a step increase in the release of metal occurred between about pH 5 and pH 4 (the release at pH 4 and below was much greater than would have been predicted from an extrapolation of the data above pH 5). Again, changes in surface charges of the solids, metal speciation, organic matter complexation, solid solubility, and surface adsorption (e.g. - ion exchange) could explain the observed "threshold" effect.

#### Watershed Accumulations and Losses

If atmospheric deposition is responsible for inputs to watersheds by wet and dry mechanisms, and for outputs from watersheds by



Table XVI. Leaching Study Results for Pb and Cd\*

Sample	Initial pH	Final pH	Cd (ug/L)	%Cd Leached	Pb (ug/L)	%Pb Leached
Cecil	5.3	6.1	0.93	4.9	1.2	0.016
	4.5	6.0	0.99	5.2	3.5	0.048
	3.3	4.8	1.4	7.3	4.2	0.057
	2.4	3.7	4.6	24	22	0.30
	Total	---	19	----	7350	-----
Madison	5.3	4.9	0.49	5.1	3.5	0.027
	4.5	5.6	0.46	4.8	3.5	0.027
	3.3	4.8	0.90	9.4	8.8	0.068
	2.4	4.0	3.4	35	350	2.7
	Total	---	9.6	----	13000	-----
Pacolet	5.3	6.2	0.56	7.8	0.28	0.0018
	4.5	5.8	0.79	11	0.65	0.0041
	3.3	4.8	1.4	20	3.3	0.021
	2.4	4.6	3.2	44	13	0.081
	Total	---	7.7	----	16000	-----
Madison	5.3	5.5	10	14	81	0.20
Duff	4.5	5.4	11	15	91	0.22
	3.3	5.1	13	17	96	0.23
	2.4	3.8	33	44	110	0.27
	Total	---	74	--	41000	----
Pacolet	5.3	6.2	9.1	12	11	0.031
Duff	4.5	6.1	11	15	28	0.078
	3.3	6.0	13	17	92	0.26
	2.4	5.6	42	55	110	0.31
	Total	---	76	--	36000	-----
Stream	5.3	6.3	0.038	3.9	2.5	0.052
Sediment	4.5	6.2	0.042	4.3	3.2	0.067
	3.3	5.4	0.089	9.1	8.8	0.18
	2.4	3.9	0.29	30	9.8	0.20
	Total	---	0.98	----	4800	-----
Lake	5.3	5.8	2.6	4.8	1.6	0.011
Sediment	4.5	5.7	3.2	5.9	7.2	0.016
	3.3	4.8	6.4	12	11	0.026
	2.4	4.1	43	79	2300	5.1
	Total	---	54	----	45000	-----

\* All tests used 3 g of soil in 30 mL of solution. Soils were leached in synthetic rainwater, stream sediment in streamwater, and lake sediment in lake water. pH was adjusted with 1:1 nitric:sulfuric acids.

physical transport in the aqueous phase, with or without influences of chemical interactions, it is appropriate to consider whether the inputs and outputs are balanced (i.e. - is the watershed in a condition of net accumulation or net loss of a specific material). A specific material in rain may be retained in some component(s) of the watershed, or simply washed through it. Rain may also pick up materials as it moves through the watershed. Unfortunately, these are not easy questions to answer. Total mass balances, or even useful partial mass balances, on watershed systems can be difficult to obtain.

First of all, atmospheric deposition is not the only significant input in most cases, and secondly, base and storm event streamflows may not be the only significant outputs.  $\text{Pb}$  and  $\text{NO}_3^-$  provide contrasting examples. Essentially all of the  $\text{Pb}$  input to the Lake Issaqueena watershed was found to be atmospheric. On time scales of a few years, the  $\text{Pb}$  appeared to be effectively retained in the watershed and that which was exported could be traced to baseflow and, especially, stormflow of the streams followed primarily by accumulation in the lake sediments (see below). In contrast,  $\text{NO}_3^-$  can enter the system by atmospheric deposition but also by biological conversion of other nitrogen forms to  $\text{NO}_3^-$  in the watershed. Similarly,  $\text{NO}_3^-$  may be removed by conversion to other forms. Since interconversion of forms of nitrogen is prevalent and difficult to quantify in watershed systems, simple monitoring of atmospheric inputs and stream outputs of  $\text{NO}_3^-$  is not likely to be as informative as the same approach for  $\text{Pb}$ .

Another important consideration is the availability and quality of data. Watershed export of some materials (e.g. -  $\text{Pb}$  and TSS) is affected more by transient events (e.g. - storms) than export of

other materials (e.g. - Cd, K). In fact, the transient events can actually dominate the export of materials such as Pb, as discussed above (see Table XIV). Consequently, obtaining adequate input and output data to do a mass balance on materials greatly influenced by transient events can be a significant consideration. Actual execution, for example, measuring flow for a wide, shallow plume over a dam at reasonable expense and obtaining properly timed data during storm events, also present challenges.

Detailed mass balances were beyond the scope and data collection ability of this investigation, although they obviously would be valuable. It is possible, however, to make some initial observations. By using long term averages and evaluating the sensitivity of results to the uncertainty in various data, the general observations presented in Table XVII were obtained (see LaManna, 1983 for quantitative calculations and details). Some atmospheric inputs (e.g. -  $H^+$ , Pb, and Cd) are apparently being retained in the watershed, while other materials (e.g. -  $Cl^-$  and  $Ca^{+2}$ ) are being depleted from the watershed.

Note especially the depletion of Ca, Mg, K, and Na, consistent with the storm event and soil neutralization mechanism results discussed above. Based on the storm event and soil leaching data, Al and Si are also probably being depleted from the watershed. Data on nitrogen species ( $NH_4^+$  and  $NO_3^-$ ) were insufficient to make an estimation due to considerations discussed above. Calculations for  $SO_4^{-2}$  indicated sulfate retention was occurring, but the data could not support a conclusive determination. Concentrations of  $SO_4^{-2}$  in stream stormflow frequently exceeded concentrations in incoming rain, so

Table XVII. Estimation of Net Accumulation  
or Net Loss \*

<u>Net Accumulation</u> (output<<input)	<u>Close or</u> <u>Uncertain</u>	<u>Net Loss</u> (output>>input)
H <sup>+</sup>	SO <sub>4</sub> <sup>-2</sup>	Cl <sup>-</sup>
Pb	NH <sub>4</sub> <sup>+</sup>	Ca <sup>+2</sup>
Cd	NO <sub>3</sub> <sup>-</sup>	Mg <sup>+2</sup>
		Na <sup>+</sup>
		K <sup>+</sup>

\* Estimated from ratio of annual mass output at dam to annual total mass of total atmospheric input.

a valid mass balance for  $\text{SO}_4^{-2}$  requires substantial storm monitoring, as well as consideration of all potential sources and sinks of  $\text{SO}_4^{-2}$ .

Mass balances indicated most of the atmospheric input of Pb and Cd (>90%) was accumulating in the watershed. Soil analyses showed a decrease in Pb and Cd concentrations with increasing depth in soil cores collected in the watershed, also indicating Pb and Cd accumulation. The portion of aerosol lead that can be rapidly solubilized (Norton, 1983) is probably sequestered by soil organic matter or adsorbed by soil surfaces. Biological, chemical, and physical in-lake processes interact in a complex manner which subsequently determines the fate of Pb, Cd, and TSS in Lake Issaqueena. The net removal of Pb and TSS from the lake appeared to occur primarily as short-term deposition events possibly related to biological activity. Because Cd appeared to be associated with different in-lake processes and was strongly influenced by direct atmospheric deposition to the lake's surface, its removal involved longer-term deposition events. The biota, fall turnover, and bottom redox conditions in Lake Issaqueena were found to strongly influence transport of Pb and Cd, deposition in the sediments, and removal from the lake over the outfall (Heatley, 1982).

Pb and Cd concentrations in the sediments have increased since the lake was impounded. Mass balances indicate roughly 60% of the Pb, 30% of the Cd, and 90% of the TSS inputs to the lake are accumulating in the sediments. Pb at the head of the reservoir appeared to be increasing at a faster rate than in sediments of the remainder of the lake. This increase was probably due to Pb being transported with the TSS, which settles close to the input streams. The input of anthropogenic Pb and Cd has apparently increased the central basin plain

sediment Pb concentration 1.8-fold and Cd concentration 3.5-fold over the past 43 years. This could be due to either an increase in the anthropogenic source inputs or an increased mobility of watershed accumulated metal due to a pH decrease in rain.

## V. CONCLUSIONS

Since the bulk of this report is already in essence a summary of the technical conclusions of the project, the intent of this section is to provide a more general conclusion related to the overall significance of the results. Acid deposition (rain) is receiving significant attention in political and economic as well as scientific areas, so a general conclusion seems appropriate. In addition, some concepts suggested by the results obtained in this investigation are presented to stimulate analysis of the problems involved.

First, the investigation did not find an "acid rain crisis" in the systems investigated, which is consistent with the fact that it was not (and probably could not be) designed to find one. Results obtained would not, and were not intended to, support a conclusion that acid rain is definitely a significant problem in the Piedmont of South Carolina. On the other hand, this investigation does support the conclusion that acid deposition (rain) could be or become a significant problem in the area. Many potential elements of a problem were uncovered. Only chemical interactions were considered, but the consequences of the chemical interactions to biota could be significant. The overall conclusion, therefore, is to consider acid deposition a very real potential or as yet unrecognized problem in the South Carolina Piedmont and southern Appalachian Mountain regions.

Perhaps an equally important outcome of this investigation is to emphasize the nature of potential acid rain problems. The multidimensional character of the problem must be recognized. For example, in considering chemical interactions, this investigation suggests at least three conceptualizations of potential problems must be

considered: 1) chronic (long-term) changes, 2) critical threshold values, and 3) transient (brief) events with lasting effects.

Chronic exposure of a watershed, for example, to acid deposition may eventually lead to a condition considered unacceptable. Small but persistent processes might, for example, gradually approach damaging losses of nutrients from the soils or accumulations of toxic metals in the lake sediment. Similarly, slow erosion of the surface of a rock sculpture by acid rain will eventually lead to irreversible loss of its important features. In many respects, the influence of acid deposition is to hasten chronic processes, for example, mineral weathering, making the unacceptable result come sooner or making it possible by overloading natural regenerative processes. Materials that tend to accompany acidity in atmospheric deposition (e.g. - Pb) may add new or unique problems, in addition. Once regenerative responses of receptor systems, for example, nutrient regeneration from minerals in soils, are better understood, the effects of chronic inputs will probably be predictable for various scenarios of levels of atmospheric inputs.

Critical threshold values are also very important to the consideration of acid deposition effects. The response of many chemical (and biological) systems to a given perturbation is frequently dependent on whether the magnitude of the stimulus is above or below a particular "threshold" value. For example, the solubilization, adsorption, and complexation of toxic trace metals, hence their speciation and mobility, generally respond to pH displaying a threshold effect. Near the threshold value, small changes in pH correspond to large changes in chemical characteristics. As discussed in previous sections, numerous



instances of important threshold values in the range of pH 4 to 5 were encountered in this investigation. Since the pH of the soils and rain studied were also in this range, a variable and dynamic system would be expected. Responses should be very event-specific (i.e. - effects will depend greatly on the characteristics of the individual event). Small changes in rain pH, intensity, or duration could make significant changes in the chemical interactions that occur.

Threshold effects can also operate on larger scales, for example, the overall ability of a watershed to neutralize incoming acidity. To most observations, the buffering capacity of a watershed will work equally effectively until it is almost depleted. Close to the threshold of total depletion, the watershed will rapidly lose its ability to neutralize acid and a dramatic change in chemical characteristics will occur. Whether the threshold value is reached will depend on as yet poorly known future inputs of acid and the unknown ability of watersheds to regenerate neutralization mechanisms. The important point is that only very close observation and better understanding of watershed processes will elucidate whether the threshold is being approached.

Transient events may also be very important to the effects of acid deposition. In combination with threshold effects, transient events may drastically increase the unpredictability of the consequences of acid deposition. Looking at transient events might be considered the opposite of looking at average values. Just as a mathematical average can hide significant variability or a wide range in a group of numbers, looking at, for example, average rain or stream pH values can be misleading. Consider a process with a threshold value of about pH 4.0

(e.g. - possibly mobilization of Al). With an average pH of 4.4 in rain, little perturbation would be expected (e.g. - little mobilization of Al). However, on some occasions, rain of sufficient duration and intensity and a lower pH may occur to expose soil to conditions below pH 4.0, resulting in dramatic effects for the duration of the event. Over long time scales for this case, therefore, the overall effect will be a function of the frequency and duration of transient events (i.e. - pH<4.0) not of the average condition.

One final perspective regarding threshold effects and transient events results from this investigation. Chronic effects are more likely to be recognized and predicted and, hence, avoided in time to prevent unacceptable results. Threshold effects and the results of transient events are more difficult to recognize and predict since the system will appear unchanged until drastic changes occur. The situation is analagous to driving at 60 mph along a road with a washed-out bridge ahead. Everything goes smoothly until the car reaches the bridge. Avoiding the problem, obviously, requires seeing the washed-out bridge in time to stop.

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