

**WATER, ENERGY, AND BIOGEOCHEMICAL BUDGETS
INVESTIGATION AT PANOLA MOUNTAIN RESEARCH
WATERSHED, STOCKBRIDGE, GEORGIA--A RESEARCH PLAN**

By Thomas G. Huntington, Richard P. Hooper, Norman E. Peters, Thomas D. Bullen,
and Carol Kendall

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CONVERSION FACTORS, VERTICAL DATUM, ACRONYMS AND CHEMICAL SYMBOLS

<u>Multiply</u>	<u>by</u>	<u>to obtain</u>
<i>Length</i>		
micrometer (μm)	3.93×10^{-5}	inch
centimeter (cm)	0.393	inch
meter (m)	3.281	foot
<i>Area</i>		
kilometer (km)	0.6214	mile
square kilometer (km^2)	2.59	square mile
hectare (ha)	2.471	acre
<i>Volume</i>		
liter (L)	0.2642	gallon
<i>Mass</i>		
kilograms (kg)	2.2046	pound
gram (g)	3.52×10^{-2}	ounce
milligram (mg)	3.52×10^{-5}	ounce
microgram (μg)	3.52×10^{-8}	ounce

Temperature

Temperature in degrees Celsius ($^{\circ}\text{C}$) can be converted to degrees Fahrenheit ($^{\circ}\text{F}$) as follows:

$$\text{F} = 1.8^{\circ}\text{C} + 32$$

VERTICAL DATUM

Sea level--In this report, "sea level" refers to the National Geodetic Vertical Datum of 1929 -a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

ACRONYMS

ANC	Acid neutralizing capacity
DCP	Direct Coupled Plasma
EPA	U.S. Environmental Protection Agency
GDNR	Georgia Department of Natural Resources
GIT	Georgia Institute of Technology
IC	Ion Chromatography
ILWAS	Integrated Lake Watershed Acidification
LTER	Long-Term Ecological Research
NOAA	National Oceanic and Atmospheric Administration
PMRW	Panola Mountain Research Watershed
PVC	Polyvinyl Chloride
REE	Rare Earth Elements
SCS	Soil Conservation Service
SRM	Standard Reference Material
TDR	Time Domain Reflectometry
USGS	U.S. Geological Survey
WEBB	Water, Energy, and Biogeochemical Budgets

CHEMICAL SYMBOLS

Al -- aluminum	NH ₄ -- ammonium	Ba -- barium
Br -- bromine	Ca -- calcium	C -- carbon
CO ₂ -- carbon dioxide	CO -- carbon monoxide	Cs -- cesium
Cl -- chloride	D -- deuterium	Eu -- europium
Fe -- iron	La -- lanthanum	Li -- lithium
Pb -- lead	Mg -- magnesium	Mn -- manganese
CH ₄ -- methane	NO ₃ -- nitrate	N -- nitrogen
HNO ₃ -- nitric acid	NO _x -- nitrogen oxides	O -- oxygen
O ₃ -- ozone	PO ₄ -- phosphate	K -- potassium
KCl -- potassium chloride	SiO ₂ (aq) -- silica (aqueous)	SO ₄ -- sulfate
S -- sulfur	SO ₂ -- sulfur dioxide	Sr -- strontium
Th -- thorium	T -- tritium	U -- uranium
Yb -- ytterbium		

WATER, ENERGY, AND BIOGEOCHEMICAL BUDGETS INVESTIGATION AT PANOLA MOUNTAIN WATERSHED, STOCKBRIDGE, GEORGIA-- A RESEARCH PLAN

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ABSTRACT

The Panola Mountain Research Watershed (PMRW), located in the Panola Mountain State Conservation Park, near Stockbridge, Ga., has been selected as a core research watershed under the Water, Energy, and Biogeochemical Budgets (WEBB) research initiative of the U.S. Geological Survey (USGS), Global Climate Change Program. This research plan describes ongoing and planned research activities at PMRW from 1984 through 1994.

The watershed is 25 kilometers southeast of Atlanta, Ga., in the southern Piedmont physiographic province, and has an area of 41 hectares. The watershed is forested, except for a 3-hectare bedrock outcrop in the headwaters, in a second-growth oak, hickory, tulip poplar, and loblolly pine assemblage. Historical land use has included forestry, cultivation, and pasture. The forest composition and age structure reflects the periods of agricultural abandonment. Deciduous and mixed forest stands are present in areas where agriculture was abandoned in the early 1900's. Coniferous stands occur in areas farmed as recently as the 1960's. The bedrock is dominated by Panola Granite (granodiorite composition) in the uplands; pods and lenses of Clairmont Formation (biotite plagioclase \pm potassium-feldspar) gneiss) are present in the lowlands.

Since 1984, PMRW has been studied as a geochemical process research site under the USGS Acid Precipitation Thrust Program. Research conducted under this Thrust Program focused on the estimation of dry atmospheric deposition, short-term temporal variability of streamwater chemistry, sulfate adsorption characteristics of the soils, ground-water chemistry, throughfall chemistry, and streamwater quality. The Acid Precipitation Thrust Program continues (1993) to support core-data collection and a water-quality laboratory.

Proposed research to be supported by the WEBB program is organized in three interrelated categories: streamflow generation and water-quality evolution, weathering and geochemical evolution, and regulation of soil-water chemistry. Proposed research on streamflow generation and water-quality evolution will focus on subsurface water movement, its influence in streamflow generation, and the associated chemical changes of the water that take place along its flowpath. Proposed research on weathering and geochemical evolution will identify the sources of cations observed in the streamwater at Panola Mountain and quantify the changes in cation source during storms. Proposed research on regulation of soil-water chemistry will focus on the poorly understood processes that regulate soil-water and ground-water chemistry.

The proposed investigations will be strengthened by numerous historical, ongoing, and future collaborative research studies. The USGS PMRW program encourages cooperation with scientists from other Federal agencies and from the academic community. Ongoing investigations highlighting collaborative research efforts include an assessment of hydrologic pathways using stable isotopes (oxygen-18 and deuterium); automated, continuous monitoring of soil-moisture content using a computerized time-domain reflectometry system; an investigation of weathering processes using the evolution of radiogenic and stable isotopic chemical ratios and rare earth element concentrations; and a comparison of alternative methods for the calculation of dry deposition.

INTRODUCTION

Understanding and predicting the influence of global climate change on environmental processes have become major societal and scientific concerns of the late 20th century. Scientists from many disciplines and nations around the world have been mobilized to improve understanding of the linkage between climate and hydrology, geochemistry, and ecosystem function. During the past three decades, atmospheric scientists have made substantial progress in developing computer models that account for most of the important components of the climate system. However, less progress has been made in understanding the processes associated with the exchanges of water, energy, and carbon between the land surface (including vegetation) and the atmosphere. Relatively little is known about how climate affects geochemical and biological processes that control elemental flux within ecosystems. Understanding the climatic effects on geochemical and biological processes requires the knowledge and skills of specialists in fields of hydrology, ecology, geology, geochemistry, and the atmospheric sciences. Knowledge of ecosystem sensitivity and future response to environmental change is crucial to predict the effects of potential climate change on water-quality and terrestrial resources.

To strengthen terrestrial process research, especially that associated with the interactions of water, energy, gases, nutrients, and vegetation, the U.S. Geological Survey (USGS), as part of its Global Climate Change Research Program, initiated intensive investigations of Water, Energy, and Biogeochemical Budgets (WEBB) in selected research watersheds. The purpose of these studies is to improve understanding of processes controlling terrestrial water, energy, and biogeochemical fluxes, their interactions, and their relations to climatic variables; and to improve the capability to predict continental water, energy, and biogeochemical budgets over a range of spatial and temporal scales.

WEBB process studies are being implemented as a systematic program of intensive, long-term field investigations in Colorado, Georgia, Puerto Rico, Vermont, and Wisconsin. Study sites were selected on the basis of geographical and environmental diversity. Sites having existing biogeochemical investigations already underway were given priority, especially such established multidisciplinary research locations as the National Science Foundation-sponsored Long-Term Ecological Research (LTER) sites; the U.S. Forest Service Experimental Forests; and United Nations Educational, Scientific, and Cultural Organization study areas, known as International Biosphere Reserves. A major emphasis of WEBB investigations is the development and maintenance of strong collaborative research relations among scientists in other Federal agencies and with the academic community. This report describes the research plan at one such WEBB site, the Panola Mountain Research Watershed (PMRW) near Stockbridge, Ga.

Purpose and Scope

This report describes research at PMRW under the WEBB program, which is organized in three interrelated categories: streamflow generation and water-quality evolution, weathering and geochemical evolution, and regulation of soil-water chemistry. Proposed research on streamflow generation and water-quality evolution will focus on subsurface water movement, its influence in streamflow generation, and the associated chemical changes of the water that take place along its flowpath. Proposed research on weathering and geochemical evolution will identify the sources of cations observed in the streamwater at PMRW and quantify the changes in cation source during storms. Proposed research on regulation of soil-water chemistry will focus on the poorly understood processes that regulate soil-water and ground-water chemistry. The WEBB program was initiated in October, 1990, and was scheduled to last for three years. These investigations were intended to be long-term, biogeochemical process studies; and therefore, are likely to receive continuing support.

Previous Investigations

Research at Panola Mountain State Conservation Park began prior to the establishment of the hydrologic and meteorologic monitoring network by the USGS in 1985 as part of the Acid Precipitation Thrust Program. Brief descriptions of the historical research investigations at the Park are outlined below:

Matthews (1941) and Bostick (1968, 1971) provided taxonomic descriptions of the flora of Panola Mountain. Rodgers (1971) studied shrub-tree communities in small forested stands on the crest of the outcrop, and Ragsdale and Harwell (1969) mapped the soil-island communities of Panola Mountain. Braun (1969) studied nutrient cycling in granite outcrop soil island ecosystems of Panola Mountain.

Primary succession of plant and micro- and macroarthropod communities on granite outcrop surfaces were studied by Schure and Ragsdale (1977). The accumulation of various fallout radionuclides in lichen communities on granitic bedrock outcrops in the Georgia Piedmont, including Panola Mountain, was studied by Plummer (1969).

Community analysis of above-ground vegetation was conducted in 1977 at 160, 10-m diameter plots distributed throughout the 259-ha Panola Mountain State Conservation Park by Carter (1978). Twenty of these plots are located in a 10-ha subcatchment, where streamwater is being monitored. These plots were resurveyed in 1986 and the biomass increments determined (Cappellato and Carter, 1988). In 1992, 67 plots within the basin were resurveyed and cores were taken from selected trees to determine the age and chemical content of the boles.

The geology of the Panola Mountain area in relation to other southeastern outcrops was described by Holland (1954). Rates and mechanisms of chemical weathering of Panola Granite were investigated by Nixon (1981). Nixon (1981) confirmed that gibbsite is the first mineral produced from chemical weathering of the granite. Chemical weathering consists of alteration of micas and feldspars to halloysite through intermediate gibbsite and allophane, where allophane results from a reaction of gibbsite and dissolved silica. Weathering of biotite produces an aluminous vermiculite.

Dry deposition of acidic substances was studied by several investigators using independent methods. Dry deposition to a granite outcrop was estimated by Peters (1989) using a mass balance approach to be about 33 percent of total atmospheric deposition. Meyers and others (1991) estimated dry deposition with an inferential technique involving the calculation of deposition velocity from meteorological measurements and leaf area, and measurements of ambient gaseous and aerosol sulfur and nitrogen concentrations. With this technique Meyers and others (1991) estimated that dry deposition was about 50 percent of total (wet + dry) deposition at PMRW. Dry deposition was also estimated by measurements of solute fluxes in throughfall under both deciduous and coniferous canopies (Cappellato and others, in press).

Contributions of soil organic matter to stream acidification were investigated by Cantrell (1989). Cantrell (1989) tracked the mobilization of organic carbon during several storms, and assessed the potential contribution of soil organic acids to stream acidification.

Nutrient pathways from canopy to forest floor have been investigated and fluxes and concentrations of all major solutes were compared for deciduous and coniferous vegetation by Cappellato (1991). This study, which began in October 1987, included the continuous sampling of litterfall, major-ion content of living leaves and litterfall, leaf-washing experiments, sampling and chemical determinations of throughfall under the two dominant canopy types, and solute-flux estimates of dry atmospheric deposition to surrogate surfaces.

Temporal and spatial variations of solute concentrations and fluxes at several points along various hydrologic pathways at PMRW have been studied by several investigators. These studies included intra-storm-sequential water-quality sampling from October 1986 to October 1988, and fixed time interval sampling before and after this time (Shanley, 1989; Peters, 1989; Shanley and Peters, 1988; Hooper and others, 1990b).

Continuous monitors for nitrogen oxides (NO_x), sulfur dioxide (SO_2), carbon dioxide (CO_2), and ozone (O_3) are located near PMRW. The Georgia Institute of Technology (GIT), Department of Geophysical Sciences, Atmospheric Sciences Unit maintains (NO_x), (SO_2), (CO_2), and (O_3) monitoring at the campus in downtown Atlanta, 25 kilometers (km) to the northwest, and at a site on Stone Mountain, Ga., 20 km to the north of PMRW (fig. 1). Sites maintained by GIT are also equipped for continuous meteorological monitoring. The Georgia Department of Natural Resources, Environmental Protection Division, Ambient Monitoring Program, maintains continuous O_3 -monitoring equipment and continuous meteorological monitoring at a site 13-km east of PMRW in Conyers, Ga. Additionally, an ozone monitor was installed at PMRW for ambient monitoring during 1992.

Fernandez (1989) studied lichens and mosses growing on the bedrock outcrop within PMRW. He found that both lichens and mosses retained nutrients and some metals. His work also showed that the weathered surface of the bedrock was porous and demonstrated that water was transported within the rock itself.

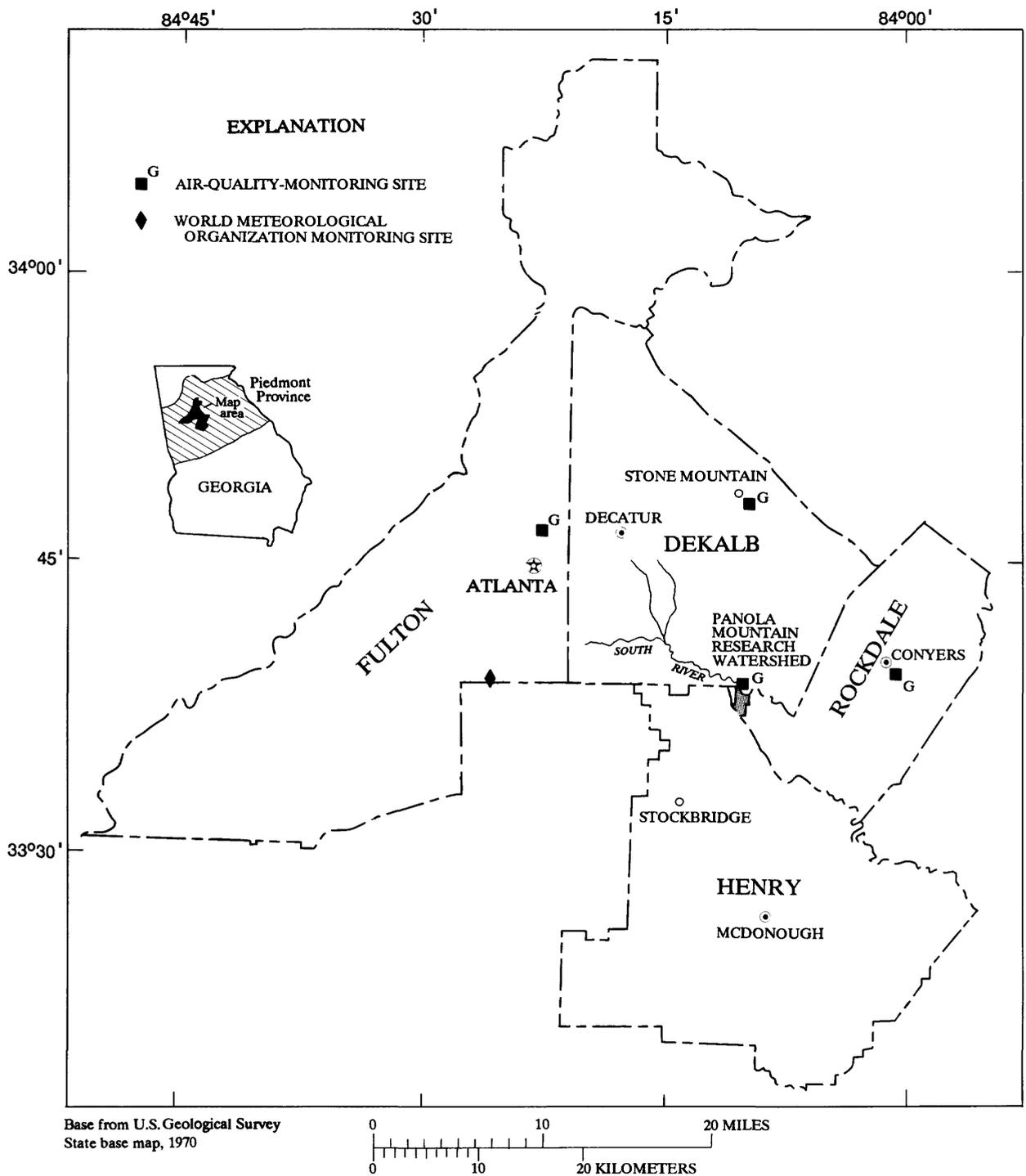


Figure 1.--Location of the Panola Mountain Research Watershed, air-quality monitoring sites, and World Meteorological Organization monitoring site.

SITE DESCRIPTION

The Panola Mountain Research Watershed (PMRW) is approximately 25 km southeast of Atlanta, Ga. (84°10'W, 33°37'N) and is located on the USGS Redan 7 1/2-minute topographic map. A compound, 90°-V-notch weir, sealed to bedrock, is used to monitor drainage from a 41-hectare (ha) area within the basin. Nested subcatchments of approximately 0.1 ha (bedrock outcrop) and 10 ha are hydrologically monitored within the basin (fig. 2). The maximum elevation in the watershed is 279 m above sea level, and the relief is 55 m. PMRW is in the Southern Plains ecoregion, the largest ecoregion in the conterminous United States (Omernik, 1987). Because the watershed is a headwater catchment, the slopes at PMRW are somewhat steeper than average for the southern Piedmont physiographic province. Nonetheless, PMRW contains soil series representative of soil associations that cover 98 percent of the physiographic province. PMRW is forested, like 65 percent of the southern Piedmont, and contains both dominant forest types of the ecoregion, southern hardwood and loblolly pine.

Bedrock Geology

The bedrock is dominated by Panola Granite (granodiorite composition) of Mississippian and Pennsylvanian age described as a “very homogeneous, medium-grained, dark-gray, biotite-oligoclase-quartz-microcline ‘granite,’ having no discernible foliation” (Atkins and Higgins, 1980). Panola Mountain and the outcrop within the study watershed are plutons that intruded older (Late Proterozoic-Early Ordovician) surrounding country rock of the Clairmont Formation (Atkins and Higgins, 1980). Preliminary evidence from bedrock cores indicates that pods and lenses of Clairmont Formation are present at lower elevations within the watershed. Higgins and others (1988) describe the Clairmont Formation as a “spectacular melange in which fragments, chips, blocks, and slabs of amphibolite, amphibolite and light-gray granofels, light to medium-gray, equiangular biotite granitic gneiss, epidosite, light-gray granofels, metagranite, and ‘clean’ quartzite ‘float’ in a polydeformed, locally scaly, light- to dark-gray biotite plagioclase (\pm K-feldspar) gneiss matrix”. Typical proportions are 1 to 10 percent amphibolite, 10 to 15 percent granitic or pigmatic K-feldspar, trace quartzite, and 80 to 85 percent biotite-plagioclase (\pm K-feldspar) gneiss. From a geochemical standpoint, the weathering products of these two lithologies (Clairmont Formation and Panola Granite) might not be substantially different because of the similarity in their composition. However, weathering products could be more variable from the Clairmont Formation than from the Panola Granite because of its more variable composition. The proportion of amphibole found in the Clairmont Formation might be particularly important in regulating water quality, because amphibole weathers more rapidly than the feldspar that dominates the mineralogy of both lithologies.

Surficial Geology

Soils are predominantly Ultisols developed in colluvium and residuum intergrading to Inceptisols developed in colluvium, recent alluvium, or in highly eroded landscape positions. Smaller proportions of Entisols, developed in alluvium, occur along streambanks and in a poorly drained floodplain near the confluence of the three tributaries near the watershed outlet. Soil profiles typically contain from 0.6 to 1.6 m of soil over saprolite of variable thickness. The depth of saprolite typically ranges from 0 to 5 m over granodiorite and 5 to 20 m over the Clairmont Formation. Cores collected as deep as 25 m into the bedrock indicate the presence of weathered fractures within the rock. The dominant clay minerals are kaolinite, hydroxy-interlayered vermiculite, mica, and gibbsite (Nixon, 1981; Shanley, 1989). A substantial part of the watershed has deep gullies (1 to 5 m) like much of the Piedmont that was extensively eroded during cultivation from the mid 1800's until the 1920's.

Climate and Hydrology

For the period 1859 to 1991, mean annual precipitation in Atlanta, Ga. was 124 centimeters (cm), which consisted of greater than 98-percent rain (U.S. Department of Commerce, NOAA, 1931; 1961; 1991). Mean annual temperature was 16.3° C. Frontal storms generally occur in winter (December through March), and thunderstorms occur in spring and summer. Prevailing winds are from the northwest. Streamflow is flashy, and time from maximum rain intensity to peak streamflow is typically 40 minutes (min) or less (Shanley, 1989). Runoff averages about 30 percent of total annual rainfall in the southern Piedmont (Carter and Stiles, 1983). Runoff at PMRW is variable and has been recorded as high as 47 percent of total annual rainfall (Huntington and others, 1992b).

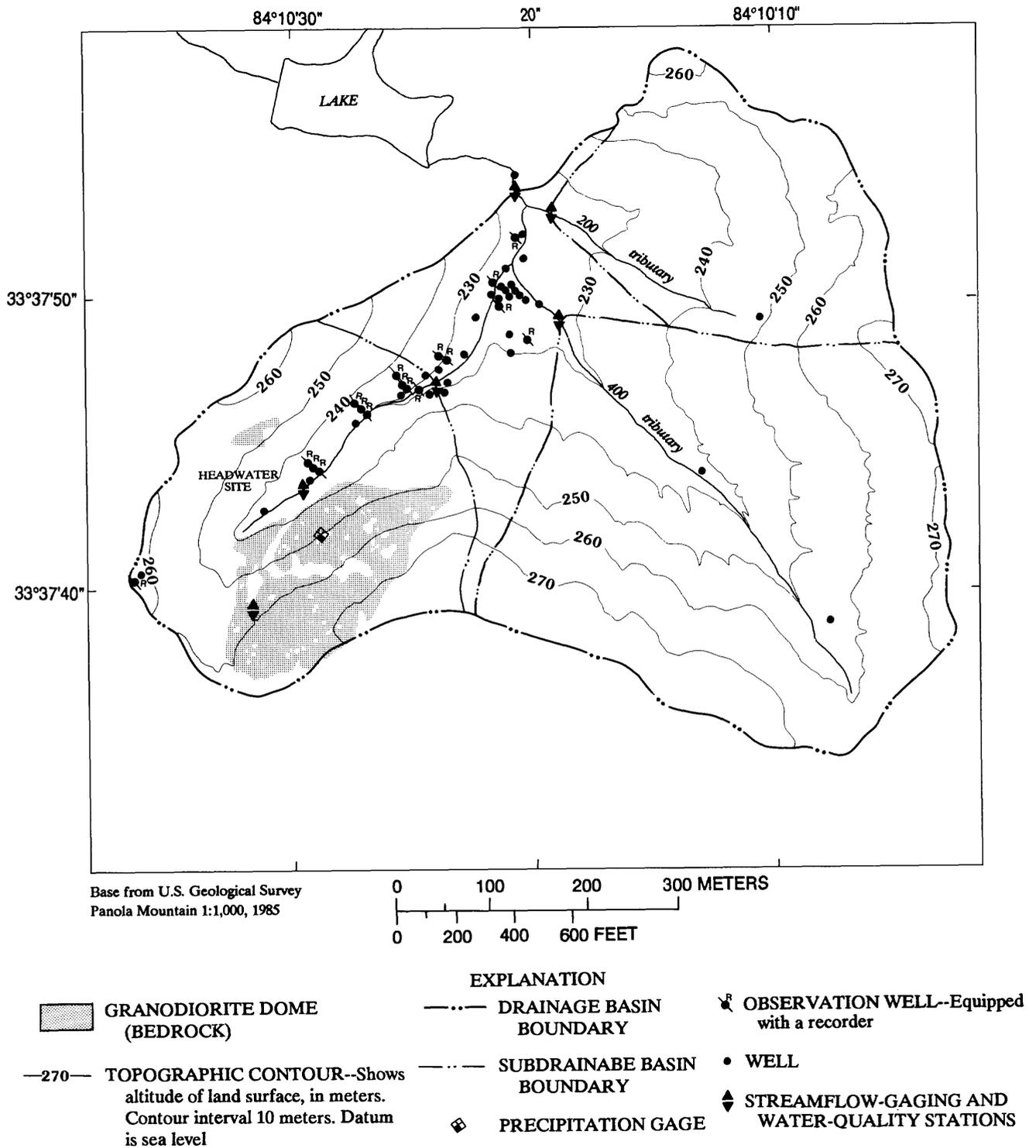


Figure 2.--Location of wells, stream-gaging stations, bedrock outcrops, and precipitation gage.

Land Use

The PMRW is 93-percent forested, consisting primarily of even-aged deciduous or mixed deciduous and coniferous stands and a smaller proportion of coniferous stands. The communities on mesic sites are dominated by *Carya tomentosa* (mockernut hickory), *Carya glabra* (pignut hickory), *Quercus rubra* (northern red oak), *Quercus alba* (white oak), and *Liriodendron tulipifera* (tulip poplar) (Carter, 1978; Skeen and others, 1980). The dominant coniferous species is *Pinus taeda* (loblolly pine). The remaining 7 percent of PMRW consists of a 3-ha bedrock outcrop that includes extensive lichen and moss communities as well as some discrete, small islands of herbaceous and woody vegetation. The watershed is entirely within the Panola Mountain State Conservation Park near Stockbridge, Ga., which was established by the state of Georgia for preservation, education, and research. Historical land use has included forestry, cultivation, and pasture.

The forest composition and age structure reflects past land use and periods of agricultural abandonment (Nelson, 1957; Brender, 1974). Native Americans may have burned the forest prior to settlement by Europeans (Brender, 1974). The forests in this part of the Piedmont were first settled and extensively cleared by about 1800 (Brender, 1974). Subsistence farming was rapidly replaced with cotton. Poor farming practices and steep slopes resulted in extensive erosion, causing substantial loss of topsoil and gullying (Brender, 1974). Currently at PMRW, deciduous and mixed forest stands are present in areas thought to be abandoned in the early 1900's, whereas, coniferous stands are in areas that were farmed as recently as the 1960's.

AVAILABILITY OF DATA

Historical data from PMRW are organized in eight categories:

- (1) hydrologic,
- (2) meteorologic,
- (3) air quality,
- (4) water quality
- (5) mineralogic,
- (6) vegetation,
- (7) seismic, and
- (8) soil.

Data in the first four categories normally have been collected at fixed intervals or on a storm basis. Data in the last four categories generally are collected during a single period as part of academic theses or special, independent projects.

The collection of physical data and most storm-based automatic water-quality samples was controlled by electronic field equipment (fig. 3). Automatic collection of physical data and water-quality samples was programmed by predetermined absolute stage changes, rates of stage change, minimum and maximum peaks and troughs of recorded stage, and fixed-time intervals above preset stage thresholds (fig. 4). Six dataloggers within the basin are linked together within a network connected by modem to a personal computer in the USGS office in Atlanta, Ga. (fig. 5). Two additional dataloggers are located in clearings 1 to 2 km northwest of the basin; one associated with a meteorological data-collection tower and the other with a platform for monitoring precipitation-related information. Dry deposition of sulfate in particulate aerosol form was estimated by capture on surrogate surfaces mounted on a 30 m tower 1 km northwest of the basin (fig. 6).

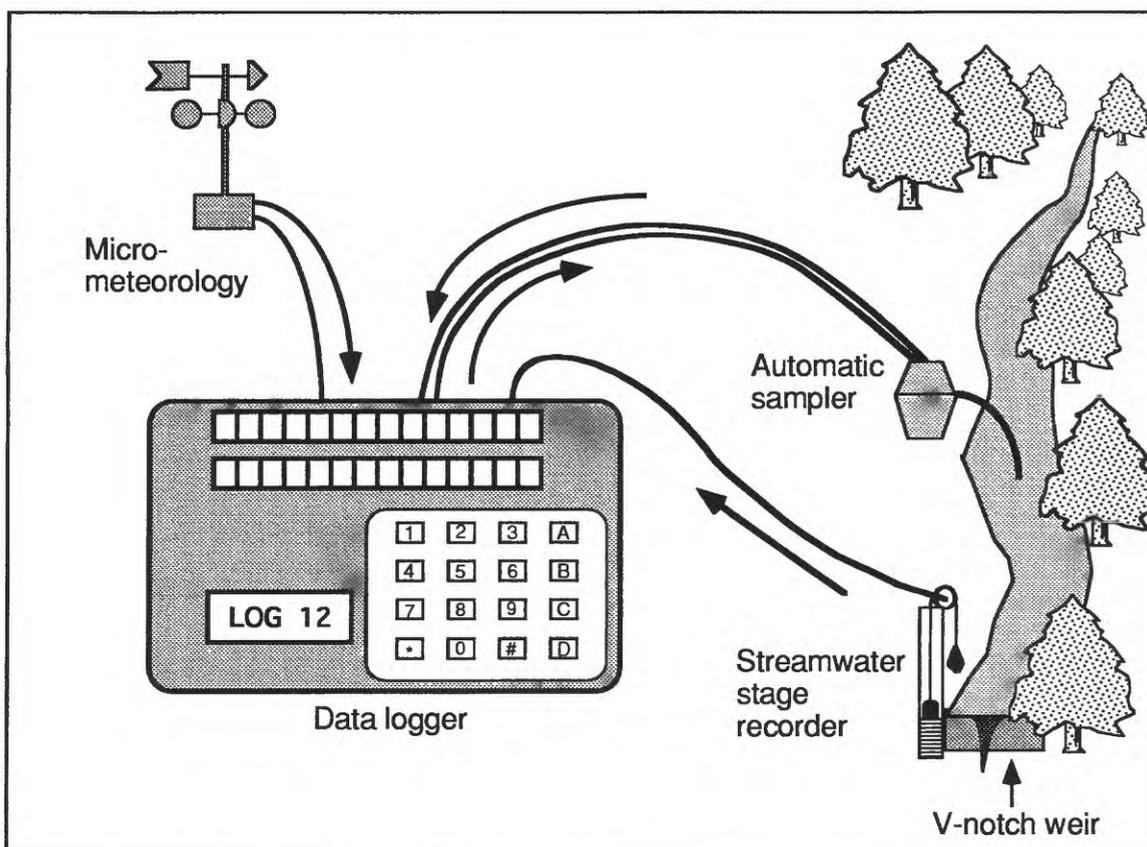


Figure 3.--Automation of physical and water-quality field data collection.

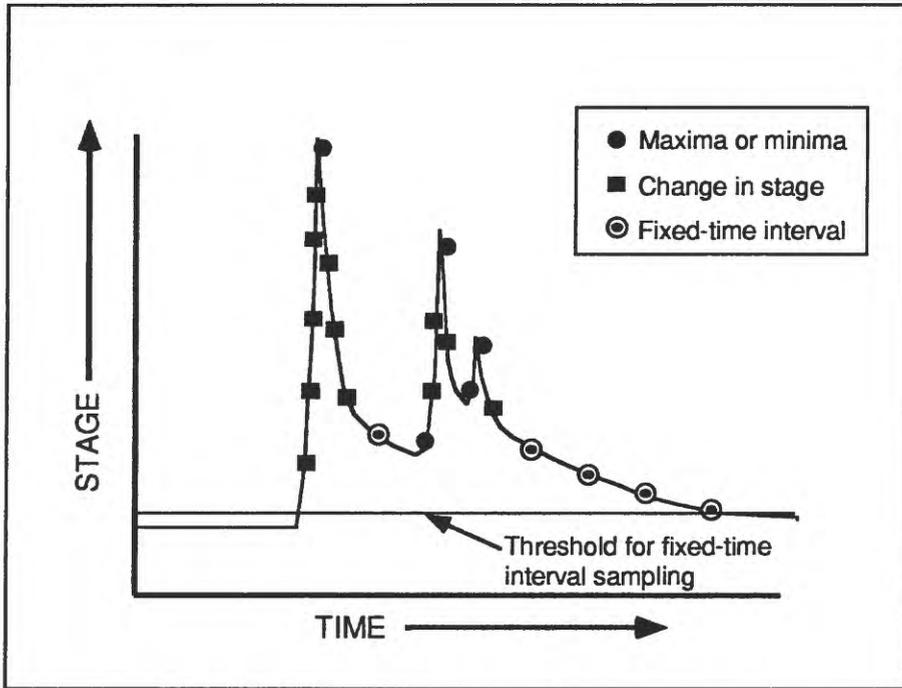


Figure 4.--Simulated stage-actuated automatic-sampling sequence.

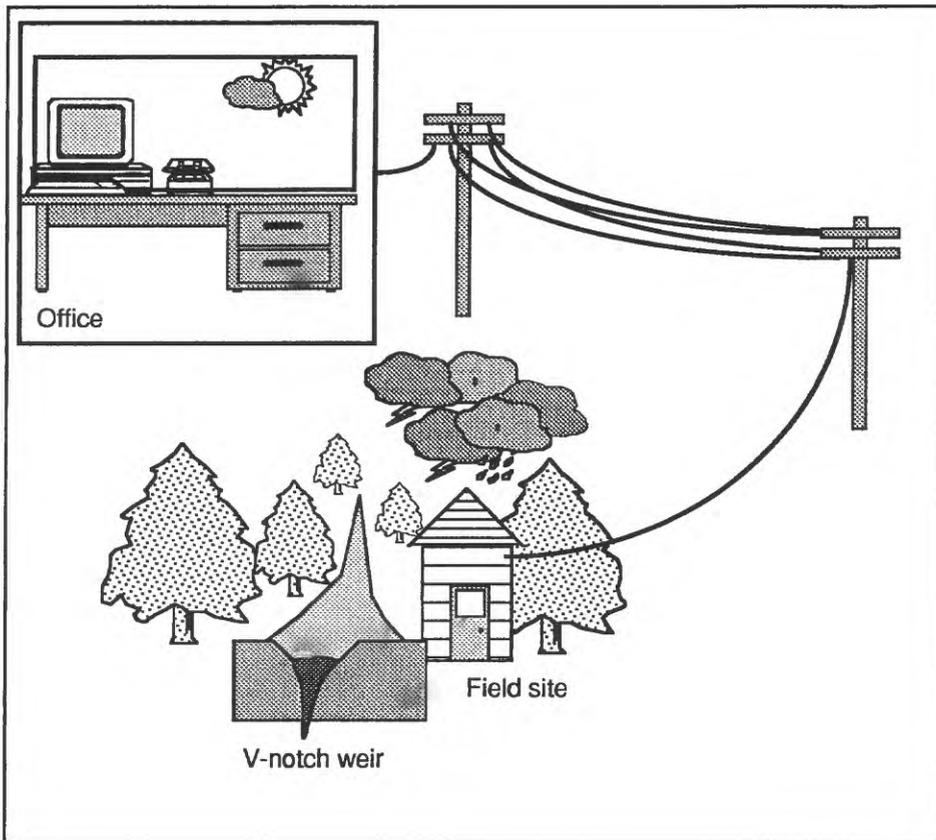
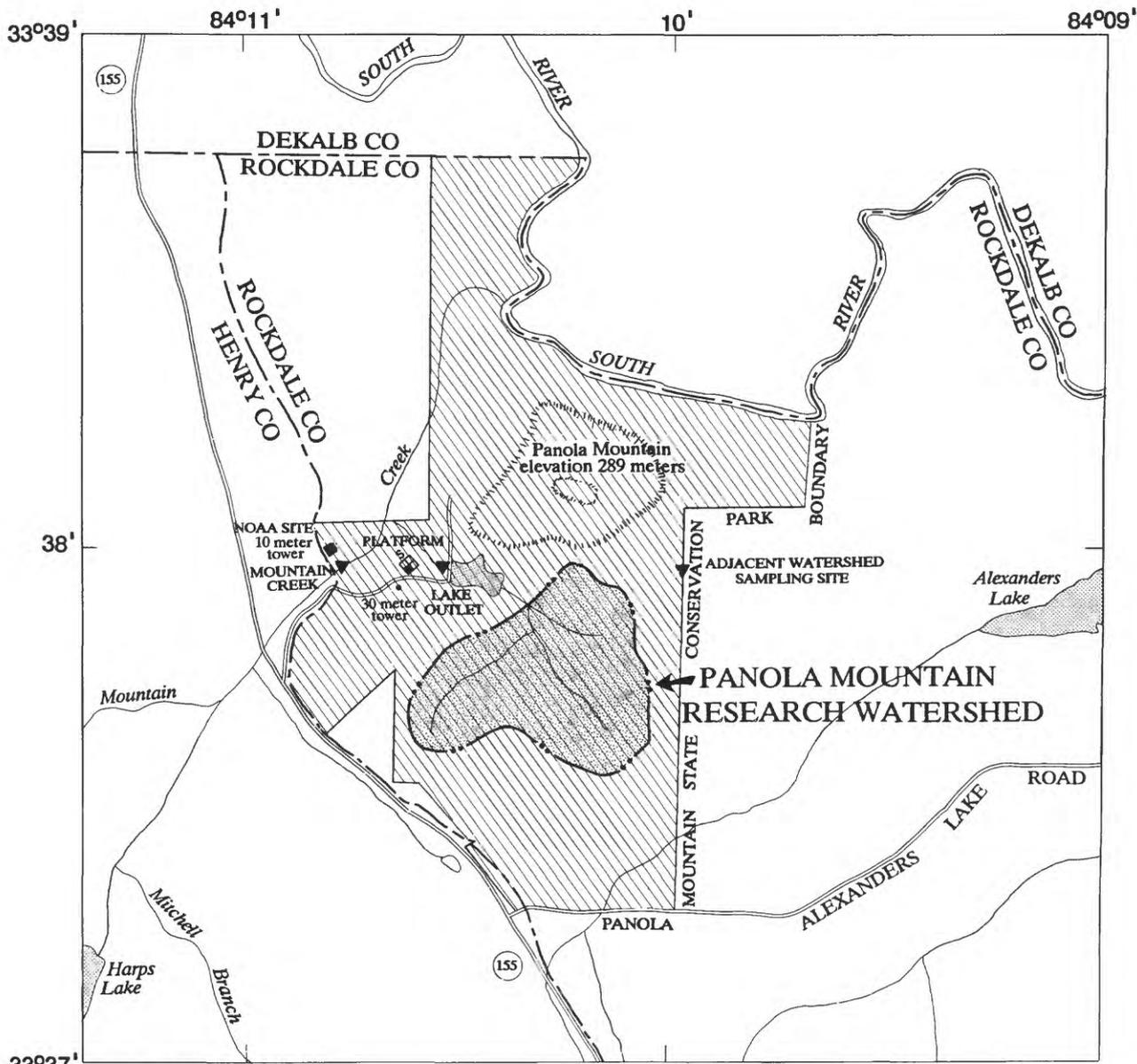
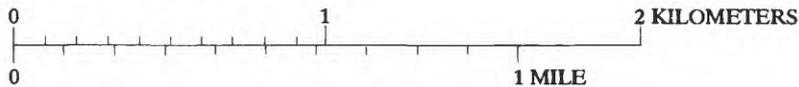


Figure 5.--Automation of data-collection system between U.S. Geological Survey office in Atlanta, Ga., and field site in the Panola Mountain State Conservation Park.



Base from U.S. Geological Survey
 Redan 1:24,000, 1956, Interim revision as of 1983 and
 Stockbridge 1:24,000, 1964



EXPLANATION

- | | |
|-------------------------------------|----------------------|
| ◆ Complete | ▼ WATER-QUALITY SITE |
| ◻ Precipitation and solar radiation | |

Figure 6.-- Location of the Panola Mountain Research Watershed and water-quality, precipitation monitoring, and meteorological monitoring sites in the Panola Mountain State Conservation Park.

Hydrologic, Meteorologic, Air-Quality, and Water-Quality Data

Summaries of hydrologic, meteorologic, air-quality, and water-quality data for PMRW are presented in tables 1 through 4. These tables list measurement frequency, collection method, spatial and temporal coverage, method of storage, and type of quality assurance. Water-quality analytical records, including the analytical method, precision, and quality assurance protocols, are summarized in table 5.

Chemical analyses are available for more than 14,000 water samples for calcium, magnesium, sodium, potassium, ammonium, sulfate, nitrate, chloride, dissolved silica, alkalinity, pH, and specific conductance (tables 4 and 5). Stable isotopes (primarily ^{18}O and some D) have been analyzed for about 3,700 samples. In January 1992, chemical analysis of water samples was expanded to include Al, Fe, Mn, Ba, Sr, and Pb.

Mineralogic Data

Approximately 100 soil samples were collected along traverses perpendicular to Panola Mountain, outside the 41-ha experimental watershed (Nixon, 1981). Samples were collected in 30-cm increments to depth of auger refusal (bedrock), approximately 5 m. X-ray diffraction, thermogravimetric analysis, differential thermal analysis, and scanning electron microscopy were used to identify clay minerals and weathering products (Nixon, 1981).

Whole-rock analyses were performed on 30 samples by microprobe analysis of individual grains within the granite. X-ray diffraction analysis of the greater-than-2 μm (micron)-diameter Fe-free soil indicates that kaolinite is the dominant clay mineral and hydroxy-interlayered vermiculite, mica, and gibbsite also are present in moderate amounts (Shanley, 1992).

Vegetation Data

Community analysis of above-ground vegetation at Panola Mountain State Conservation Park was made in 1977 by Carter (1978); biomass increments for the period 1977 to 1986 were calculated by Cappellato and Carter (1988); and biomass increments for the period 1977 to 1992 were calculated by Cappellato (USGS, written communication). Lichens (*Parmelia conspersa*) and mosses (*Grimmia laevigata*) growing on the bedrock outcrop were studied by Fernandez (1989). Major ion chemical interactions between precipitation and forest canopy were studied, and solute flux estimates were determined by Cappellato and others (in press).

Seismic Data

Depth to bedrock was measured by Nixon (1981) using a portable seismograph at the western and eastern edges of the Panola Mountain pluton, perpendicular and parallel to the traverses sampled for clay mineralogy. Nixon (1981) determined water table when the core tube intersected the piezometric surface.

Fourteen seismic refraction lines were run within the 41-ha watershed using a Nimbus¹ model ES1210 signal-enhancement seismograph and a sledgehammer. The length of the lines ranged from 36 to 56 m and were backshot to determine the actual velocities of the subsurface materials. It was not possible to run longer lines, because high background noise levels were present.

Soil Data

A 1:1,000 topographic map having 1-m contours was constructed by USGS (National Mapping Division) for Panola Mountain State Conservation Park (about 259 ha), which includes the watershed. The topographic map for the watershed within the Park was digitized and is available as an ARC/INFO coverage.

Although the soil survey for Rockdale County, Ga., was not published as of 1992, the U.S. Soil Conservation Service (SCS) has completed soil mapping for the entire County at the standard scale of 1:20,000. Panola Mountain State Conservation Park was mapped by SCS at a scale of 1:8,000.

¹/Any use of trade, product, or firm names is for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey

Table 1.--*Summary of hydrologic data records at the Panola Mountain Research Watershed*
 [Locations of streamflow gaging sites are shown on figure 2; locations of precipitation monitoring sites are shown on figures 2 and 6.
 mm, millimeters; ha, hectare; m, meter; HW, headwater; 200T, 200 tributary; 400T, 400 tributary;
 NOAA, National Oceanographic and Atmospheric Administration; N/A, not applicable]

Type of data	Frequency of collection	Method of collection	Spatial coverage	Temporal record	Method of storage	Quality assurance
Streamflow	5 minutes (1 minute during storms) for streams; 10 seconds on granite	potentiometer to recording data logger	6 sites: lower V-notch weir, upper V-notch weir, granite flume, HW, 200T, 400T	lower and upper V-notches, April 1985 to present; granite, May 1987 to July 1991; HW, October 1991 to present, 200T, April 1992 to present, 400T, April 1992 to present	digital, punch tape	backup at lower V-notch weir using mechanical punch tape recorder (5 minute frequency)
Ground water	5- to 15-minute averages	potentiometer to recording data logger	17 well sites distributed along the major tributary draining the granite	8 wells October 1986 to present	do.	monthly measurement with steel tape
Ground water	annually	steel tape		9 wells November 1988 to present		
Ground water	weekly	steel tape	11 sites distributed adjacent to main tributary draining granite	October 1986 to October 1988	do.	N/A
Ground water	monthly	do.	25 sites distributed adjacent to main tributary draining granite	October 1985 to present	do.	N/A
Ground water	do.	do.	4 sites in headwater areas of the 3 perennial tributaries	February 1992 to present	do.	N/A
Precipitation	0.254 mm per minute	tipping bucket to recording data logger	5 sites, 2 at platform, 2 on granite outcrop, and 1 at NOAA site	1 collector each at platform, granite, and NOAA sites, October 1986 to present for site, second collector each on granite outcrop and at platform sites September 1991 to present	do.	water collected through tipping bucket, etching rain gage, weigh wetfall collections
Throughfall	0.254 mm per minute	tipping bucket to recording data logger	lower gage, upper gage	September 1987 to present	do.	multiple replicates
Streamflow	event composite	collars	12 sites	October 1987 to October 1989	do.	multiple replicates
Soil-moisture content	15-minute instantaneous	time domain reflectometry to recording data logger	4 sites, 12 sensors each	1 site, February 1990 to January 1991	digital	gravimetric measurements of soil moisture content
Soil-moisture tension	intermittent, normally bimonthly	tensiometers	4 sites along a hillslope transect, 5 to 9 depths per site	November 1991 to present	field sheets and digital storage	gravimetric measurements and comparison with time domain reflectometry

Table 2.--Summary of meteorological data records at the Panola Mountain Research Watershed

[Figures 1 and 6 show spatial locations of data-collection sites within the basin; a World Meteorologic Organization station is located 15 kilometers west of site with greater than 30 years of record including upper atmosphere circulation; method of data storage was digital in all cases; NOAA, National Oceanographic and Atmospheric Administration]

Type of data	Frequency of collection	Method of collection	Spatial coverage	Temporal record
Air temperature	5- to 15-minute averages	thermister to data logger	5 sites, platform, NOAA, lower V-notch weir, upper V-notch weir, granite flume	October 1985 to present for NOAA, shorter periods of record at other sites
Water temperature	5-minute average	thermister to data logger	4 sites, 2 at lower V-notch weir, upper V-notch weir, granite flume	October 1985 to June 1990
Soil temperature	5-minute average	thermister to data logger	10 sites, distributed along tributary draining the granite	October 1985 to June 1990
Wind speed and direction	15-minute average	cup anemometer/ wind vane	NOAA site	October 1985- to present
Solar radiation	5- to 15-minute averages	¹ EPLI and PSP radiometer	NOAA and platform sites	October 1985 - to present
Surface wetness	15-minute average	Campbell Scientific model 237	NOAA site	October 1985 - to present
Relative humidity	5- to 15- minute averages	Campbell Scientific model 207 (10-95 percent), in August 1990 lower and upper V-notch weir sites were replaced with Campbell Scientific model N217 Hygrometrix, and in November 1991 with Vaisala HMP 35A probes	4 sites, platform, NOAA, lower V-notch weir, and upper V-notch weir	October 1985 - to present for NOAA and platform, October 1985 to June 1991 for lower and upper gages. In June 1991 lower and upper V-notch weir probes were moved to new locations

Table 3.--Summary of air-quality data-collection records at the Panola Mountain Research Watershed

[Figures 2 and 6 show spatial locations of data-collection sites; NOAA, National Oceanic and Atmospheric Administration; EPA, U.S. Environmental Protection Agency; GDNR, Georgia Department of Natural Resources]

Type of data	Frequency of collection	Method of collection	Spatial coverage	Temporal record	Method of storage	Quality assurance
Sulfur dioxide	weekly	Whatman ^{1/} filter doped with potassium carbonate	NOAA site,	April 1985 to present	digital	standard NOAA protocols
Nitric acid vapor	do.	nylon filter	do.	do.	do.	do.
Fine aerosols complete major ion chemistry	do.	Teflon filter	do.	do.	do.	do.
Coarse aerosols (particulates)	weekly	surrogate surfaces	30-meter tower site	June 1986 to November 1989	do.	do.
Ozone	continuous	Thermoenvironmental ozone analyzer using EPA ultra violet photometric method	platform site	June 1992 to November 1992	do.	periodic tests, and calibrations conducted by GDNR

^{1/} Any use of trade, product, or firm names in tables 2 and 3 are for descriptive purposes only and does not imply endorsement by the U.S. Geological Survey.

Table 4.--Summary of water-quality data at the Panola Mountain Research Watershed

[Figures 2 and 6 show sampling locations; NOAA, National Oceanic and Atmospheric Administration; ha, hectare, m, meter; Aerochem^{1/}, Aerochem Metrics, Inc., Model 301 wetfall/dryfall collector, some were modified for sequential sampling]

Type of data	Frequency of collection	Method of collection	Spatial coverage	Temporal record	Method of storage
Streamwater	weekly at 3 sites, event (40 second, 10-minute intervals);	manual grab for weekly sample, Manning and ISCO automatic samplers for event samples	lower V-notch weir, upper V-notch weir, granite flume	April 1985 to present, October 1985 to October 1988 (granite flume only)	digital
Streamwater	weekly at 3 additional sites	do.	perennial tributaries within 41-ha catchment	July 1990 to present	digital
Streamwater	do.	do.	adjacent watershed, lake outlet, and Mountain Creek	April 1991 to present	digital
Ground water	weekly	wells, manual grab	11 sites distributed adjacent to main tributary draining granite	October 1986 to October 1988	digital
Ground water	monthly	wells, manual grab	11 sites distributed adjacent to main tributary draining granite	October 1985 to present	digital
Ground water	do.	wells, manual grab	14 sites distributed adjacent to main tributary draining granite	October 1985 to present	digital
Ground water	do.	wells, manual grab	4 sites in headwater areas of the 3 perennial tributaries	February 1992 to present	digital
Soil water	weekly	zero tension pan lysimeter	3 sites distributed adjacent to main tributary draining granite	July 1987 to present for 2 sites; July 1987 to July 1991 for 1 site	digital
Soil water	intermittent, following selected storms	suction lysimeter (ceramic cup) (80-centibars suction)	4 sites along a hillslope transect, 5 to 10 depths per site	December 1991 to present	digital
Soil water	do.	zero tension troughs	15 sites distributed along 3 hillslope transects 2 depths per site	November 1991 to present	digital
Precipitation	event sequential	automatic Aerochem wetfall collector	1 site at platform	February 1986 to November 1989	digital
Precipitation	event composite	do.	1 site at platform	February 1986 to present	digital
Precipitation	weekly	do.	1 site at platform	April 1985 to present	digital
Precipitation	do.	do.	1 site on granite outcrop	April 1985 to November 1988	digital
Precipitation	do.	do.	1 site on 30 m tower over canopy	April 1985 - July 1991	digital
Throughfall	event sequential	do.	2 sites (conifer and deciduous)	June 1986 to November 1989	digital
Throughfall	event composite	do.	32 sites (16 conifer and 16 deciduous)	October 1987 to October 1989	digital
Stemflow	do.	collars on trees at breast height	12 sites (4 conifer and 8 deciduous)	October 1987 to October 1989	digital

^{1/}Any use of trade, product, or firm names is for descriptive purposes only, and does not imply endorsement by the U.S. Geological Survey.

Table 5.--Chemical analyses of water-quality samples collected at the Panola Mountain Research Watershed

[$\mu\text{eq L}^{-1}$, microequivalent per liter; $\mu\text{mol L}^{-1}$, micromole per liter; $\mu\text{g g}^{-1}$, microgram per gram; IC, Ion Chromatography; DCP, Direct Coupled Plasma optical emission spectrometry; ANC, acid neutralizing capacity; SRM, standard reference materials; Gran titration, Gran titration method for determination of alkalinity (acid neutralizing capacity) is performed by automated titration; standard reference material from both the National Institute of Standards and Technology and the USGS, Branch of Quality Assurance, Denver Colorado, are routinely analyzed along with duplicates and calibrating standards to quantify precision and accuracy for quality assurance; the laboratory participates in USGS round robin exchange programs and is certified by the USGS, Branch of Quality Assurance, and participates in routine audits; NA, not available]

Analysis	Method	Precision	Mean coefficient of variation for SRMs
H ⁺ (pH)	potentiometric	0.05 (pH units)	NA
Alkalinity (ANC)	Gran titration	1.0	1.1
Specific conductance	potentiometric	NA	NA
Ca ²⁺	IC ¹ /DCP ²	1 $\mu\text{eq L}^{-1}$	5.1
Mg ²⁺	do.	2 $\mu\text{eq L}^{-1}$	4.7
Na ⁺	do.	0.4 $\mu\text{eq L}^{-1}$	7.7
K ⁺	do.	0.3 $\mu\text{eq L}^{-1}$	4.9
NH ₄ ⁺	IC ¹ /colorimetric ³	0.6 $\mu\text{eq L}^{-1}$	5.0
Cl ⁻	IC ⁴	0.3 $\mu\text{eq L}^{-1}$	2.45
SO ₄ ²⁻	do.	0.2 $\mu\text{eq L}^{-1}$	1.5
NO ₃ ⁻	do.	0.7 $\mu\text{eq L}^{-1}$	2.2
Br ⁻	do.	0.1 $\mu\text{eq L}^{-1}$	3.0
PO ₄ ³⁻	do.	1.0 $\mu\text{eq L}^{-1}$	5.0
SiO _{2(aq)}	colorimetric ⁵ /DCP ²	0.8 $\mu\text{mol L}^{-1}$	6.5
Al	DCP ²	0.02 $\mu\text{g g}^{-1}$	8.0
Fe	do.	0.05 $\mu\text{g g}^{-1}$	3.3
Mn	do.	0.02 $\mu\text{g g}^{-1}$	4.1
Pb	do.	0.02 $\mu\text{g g}^{-1}$	NA
Sr	do.	0.03 $\mu\text{g g}^{-1}$	NA
Ba	do.	0.003 $\mu\text{g g}^{-1}$	NA

¹ Ion chromatography, May 1985 to March 1992.

² Direct Coupled Plasma optical emission spectrometry, March 1992 to present.

³ Colorimetric phenate, May 1985 to March 1992.

⁴ Ion chromatography, May 1985 to present.

⁵ Colorimetric, May 1985 to March 1992

A total of 192 soil samples were collected by depth increment in June 1987 at 41 locations along the main tributary draining the bedrock outcrop within PMRW (Shanley, 1989). In general, samples were composited at 10-cm increments to a depth of 40 cm, and by increasing increments from 40 cm to bedrock. Samples were collected by (1) manual coring using an 8-cm diameter bucket auger, (2) removal from the face of seven excavated pits, and (3) gathering of grus from five solution pits on the surface of the granodiorite outcrop. Soils were analyzed for pH, organic matter, and standard extractable S, Al, and Fe fractions.

Radio-carbon dates were determined for the organic matter from samples collected at depths of 30, 61, 91, and 122 cm below land surface, all 12 m from the base of the granite (Nixon, 1981). Carbon dates of these samples were 3,400, 5,700, 5,800, and 5,800 years respectively.

PROPOSED DATA COLLECTION

To implement the WEBB research plan, data collection at PMRW will be expanded. Additional data to be collected are organized in the following categories: hydrologic, water quality, soil chemical, mineralogic, and biologic.

Hydrologic Data

(1) Additional recording wells (12 to 15) will be installed, initially instrumented with crest-stage indicators, and later, with potentiometers connected to floats and counterweights to provide a continuous water-level record.

(2) Soil water will be monitored at intensively instrumented soil plots (fig. 7). Soil-moisture tension will be monitored at selected sites using ceramic cup tensiometers equipped with pressure transducers, and soil-water content measured using time-domain reflectometry (TDR) (fig. 8). Rates and timing of water flow from the lysimeters will be determined by tipping-bucket gages attached to the lysimeter drains (fig. 9).

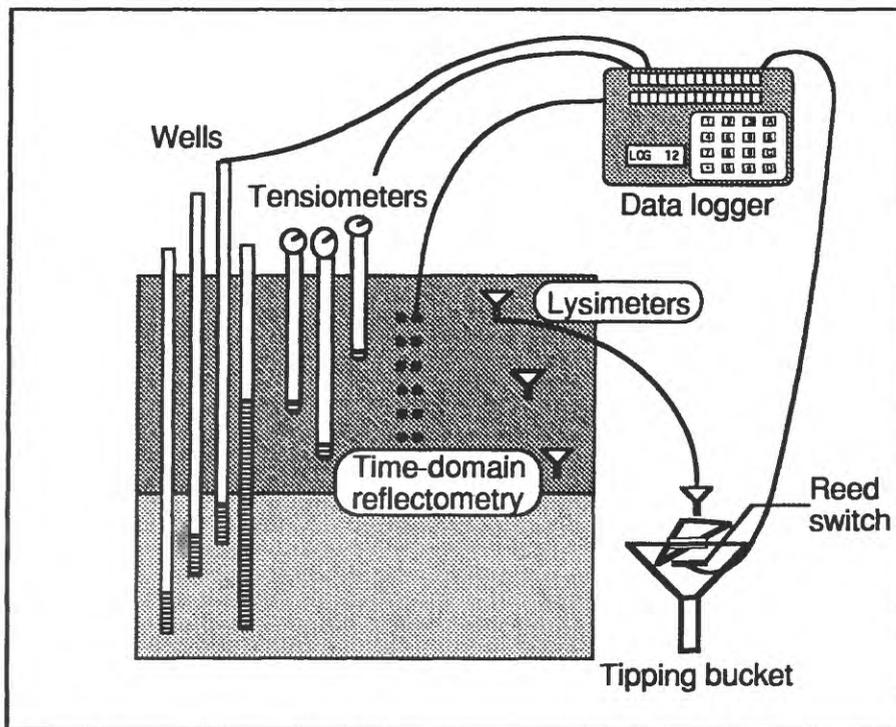


Figure 7.--Automation system for measurement of ground-water levels and soil-water moisture tension, content, and flux.

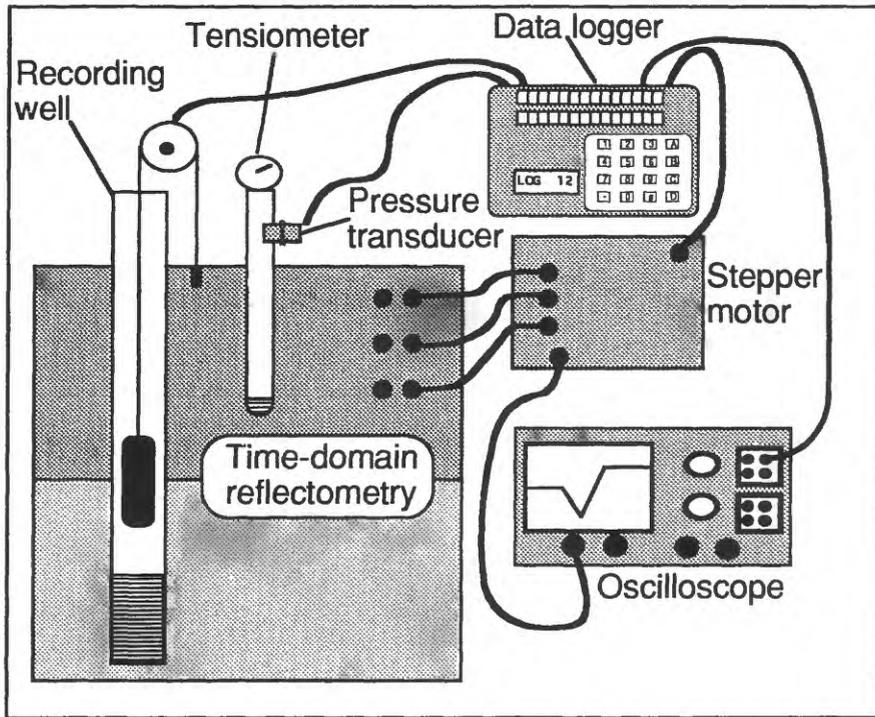


Figure 8.--Automation system for measurement of soil-moisture tension and content.

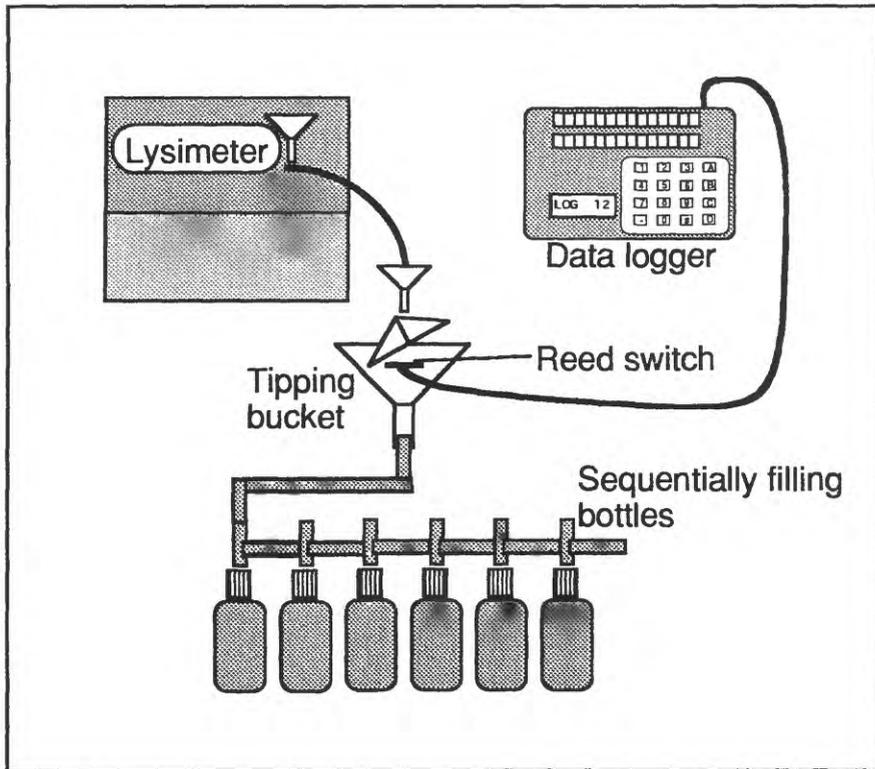


Figure 9.--Automation system for measurement of rate and timing of soil-water flux.

Water-Quality Data

(1) Additional wells (8 to 12), will be installed for monitoring ground water quality. Sampling will be at monthly intervals, except during selected storms.

(2) Chemical analyses of water samples will include pH, specific conductance, alkalinity, silica, major anions and cations, and the trace elements listed in table 5. Quality assurance will include conductivity and charge balance checks, standard reference materials, control charts, duplicates, and participation in National USGS sample exchange programs, audits, and laboratory certification.

(3) At intensively instrumented soil plots, soil water will be collected sequentially during storms using zero-tension lysimeters, and analyzed for constituents listed in table 5.

(4) Zero-tension lysimeters will be installed along transects distributed within the watershed and sampled on a selected-storm basis. Along one hillslope transect, tension and zero-tension lysimeters will be co-located and operated during storms.

Soil-Chemical Data

Six transects will be selected in the watershed that represent suspected gradients in soil chemical or hydrologic properties and representing distinct subsurface flowpaths. At up to five points along each transect, soils will be sampled by horizon or depth increment. Soil bulk density will be estimated independently at each sampling location to permit computation of element pool sizes. Chemical analyses will include exchangeable cations, cation exchange capacity, pH, exchangeable acidity, total C, organic matter, and extractions for fractionating solid phase S, Al, and Fe. Selected samples will be extracted for analysis of isotopic composition of various elements on the exchange complex. Selected soil samples also will be analyzed for particle-size distribution.

Mineralogic Data

Selected soil, sediment, and saprolite samples will be analyzed for identification of minerals present to support studies on weathering and the regulation of soil-water chemistry. Bedrock samples will be analyzed for modal mineralogy, elemental composition, and abundance of selected elemental isotopic ratios.

Biologic Data

Element pool sizes in vegetation will be calculated using: vegetation survey data for tree diameters; biomass regressions, to estimate aboveground biomass from tree diameter; and chemical analysis of tree cores. Tree diameters will be obtained from the vegetation survey data of Carter (1978), Cappellato and Carter (1988), and Cappellato (USGS, written communication, 1992). Tree cores will be collected from representative tree species and analyzed for both dendroclimatological information and chemical content. In addition to the tree surveys, shrub populations will be resurveyed on a subset of the vegetation plots.

PROPOSED WATER, ENERGY, AND BIOGEOCHEMICAL BUDGETS RESEARCH

Proposed research is organized into three categories: streamflow generation and water-quality evolution; weathering and geochemical evolution; and regulation of soil-water chemistry. The objectives of each research activity are complementary, and activities will be integrated; but in this research plan, each category is defined as a separate element having specific hypotheses, research approach, and staffing requirements.

Streamflow Generation and Water-Quality Evolution

Proposed research on streamflow generation and water-quality evolution will focus on subsurface water movement, its influence in streamflow generation, and the associated chemical changes of the water that take place along its flowpath. The emphasis in this element of the research plan will be on the investigation of processes that control the movement and solute composition of water along hydrologic pathways. The research goal will be to determine which soil-water solutions combine to compose streamwater, and in what proportions.

Problem Statement and Theoretical Background

Because watersheds are composed of chemically distinct environments, a mechanistic determination of streamwater chemistry requires an understanding of the hydrologic flowpaths through the watershed, as well as the interactions between soil and water.

Prior to the last few decades, studies of streamflow sources during storms or snowmelt were concerned only with the physics of the processes involved. Hewlett (1961) showed that the water draining from soil contributed to base flow. Betson (1964) suggested that only certain parts of drainage basins contributed runoff during most storms (the partial-area contribution concept). Hewlett and Hibbert (1967) proposed that, during storms, ephemeral streams expanded upstream by collecting overland flow and shallow subsurface runoff along their channels (the variable-source-area concept). In general, the results of physically based models indicated that new rainwater was the dominant source of runoff.

The use of naturally occurring isotopes and solutes to track the movement of water has gained widespread acceptance by the scientific community in recent years. When these tracers were used in a two-component rainfall-runoff mixing model to describe streamwater as a variable combination of rain and existing water, prestorm ("old") water was found to be the dominant component of storm runoff (Sklash and others, 1976; Bottomley and others, 1984; Pearce and others, 1986; Sklash and others, 1986; Hooper and Shoemaker, 1986; Turner and others, 1987). This contradiction between the physical models and chemical- and isotopic-mixing models, which has yet to be resolved, has profound implications for water-quality modeling. If precipitation dominates storm runoff, there is less opportunity for chemical interaction between the precipitation and basin materials, whereas, if ground water dominates, there is a broader range of chemical interactions possible.

Each approach to determine flowpaths has limitations. The physical models have focused on flow through a uniform porous medium, ignoring heterogeneities (such as macropores), which may be important to streamflow because of the differential rates of transport through macropores compared with the matrix (Beven, 1983). Furthermore, the inability to measure vertical and horizontal hydraulic conductivity and effective porosity accurately and unambiguously, limits the usefulness of models that require these critical input parameters. Because water flow is determined by *extremes* of hydraulic conductivity and not by *average* hydraulic conductivity, the problem of characterizing the porous medium is particularly difficult. Generally, models have to be calibrated to match the hydrograph rather than relying on direct measurements. Even simple hydrologic models often have more parameters than can be identified with field data (Hooper and others, 1988), indicating that multiple parameter sets (and, hence, flowpaths) can fit the data equally well.

Mixing models also are oversimplified and have a number of limitations. Foremost, tracers that are assumed to be conservative might not be, especially solutes (Pilgrim and others, 1979). The isotopes (T, D, ^{18}O) of the water molecule are more "conservative" than solutes, but can still be fractionated during evaporation, sublimation, or freezing (Fritz and others, 1976). Secondly, although two-component mixing models are based on the assumption that both the "new" and "old" water are isotopically uniform, their isotopic compositions commonly have large spatial and temporal variability (Kennedy and others, 1986).

Finally, almost all hydrograph separations are made using only two sources of water, ignoring the possibility that soil (vadose) water could be a significant source (Kennedy and others, 1986), and that soil water might have major spatial and temporal chemical and isotopic variations (Kennedy and others, 1986; DeWalle and others, 1987). At PMRW, a three-component mixing model has been developed on the basis of soil-water end members for the six solutes that mix conservatively (Hooper and others, 1990b). Although the three-component model appears to describe accurately the variations in these six solutes, additional work is needed to determine if the model is conceptually valid (Hooper and others, 1990b).

Discussion of streamflow generation and water-quality evolution is now focusing on the role of the unsaturated zone. The mechanistic control of water and solute transport in the unsaturated zone is not well understood. The most comprehensive watershed model, the Integrated Lake Watershed Acidification (ILWAS) model, was developed to understand the effects of acidic deposition on forested watersheds in the Adirondack Mountains, N.Y. (Goldstein and others, 1984), and treats each of several soil layers as stirred-tank reactors (Gherini and others, 1985). In fact, depending on rainfall rate and the soil physics, water will move through soil at different rates, varying from slowly through the soil matrix to rapidly along macropores or preferred pathways (Beven, 1983). Residence time and reactivity of the soil or rock medium through which water moves influence the solution composition. For example, riparian zones could control concentrations of nutrients (Pionke and others, 1988; Triska and others, 1989a; Triska and others, 1989b), but bedrock geology and water-residence time can be the dominant controls for concentrations of most weathering products (Miller and Drever, 1977; Peters and Murdoch, 1985; Newton and others, 1987; Peters and Driscoll, 1987; Bricker and Rice, 1989; Hooper and others, 1990a).

Streamflow during storms (or snowmelt) can be composed of at least four components (Fritz and others, 1976): (1) direct rainfall or throughfall on the stream channel or on contributing wetlands, (2) overland flow, (3) ground-water discharge into the stream or wetlands, and (4) subsurface stormflow (interflow, or mobile unsaturated zone water). The first component is entirely new water, the other three may contain various amounts of new and old (pre-storm) water. For each of the four components, one might expect spatial and temporal variability.

A major uncertainty in hydrologic and chemical modeling of watersheds has been the quantification of the contributions of both water and solutes from various hydrologic pathways. Hydrologic pathways are inaccurately represented in the models, and/or the processes that affect the water chemistry are not well understood. A specific example of the disparity between model results and observations can be seen in the ILWAS model. Calibration results from the hydrologic module of the ILWAS model indicate that hydraulic conductivity of the surficial material is two orders of magnitude greater than those determined from laboratory and field studies (Chen and others, 1982; April and Newton, 1985).

Embedded in the problem of assessing processes related to water-quality evolution and the quantification of hydrologic pathways is the lack of techniques to measure specific properties of the system. Because of technological limitations, it is advantageous to apply multiple and interdisciplinary (isotopic, physical, and chemical) approaches to the same problem, but the limitations of each technique must be addressed, particularly when they are combined with other techniques. For example, isotopic techniques have received considerable attention as useful tools in the investigation of water movement (Bengtsson and others, 1987; Barnes and Allison, 1988), and, specifically, sources of streamflow (Sklash and others, 1976; DeWalle and others, 1987), but the assumptions implicit to their application have yet to be thoroughly addressed.

At PMRW, precipitation, throughfall, soil water, ground water, and streamwater during several storms have been sampled for both major ion chemistry and stable isotope analysis for oxygen and hydrogen. A preliminary analysis of the isotopic data indicates that one assumption for the use of the isotopes for hydrograph separation might be inappropriate (Kendall, 1992). Specifically, the "new" water component, precipitation, is expected to have a constant isotopic composition during a given storm (Kendall, 1992). Not only does the isotopic composition of precipitation usually vary substantially, but as the precipitation passes through the forest canopy, its isotopic signature changes depending on season and vegetative cover (Kendall, 1992). These changes allude to additional processes occurring along the initial part of the hydrologic pathway that were not considered in the conceptual framework of the isotope method. Once these processes become better understood, they could be used in combination with other chemical and physical data to assess how the watershed functions.

Research Objective

The objective of this element of the research study is to investigate processes that control the movement and solute composition of water along hydrologic pathways that produce streamflow in a forested Piedmont watershed. To meet this objective, specific research questions will be addressed. Research questions are followed by numbered research approaches, which are described in the following section.

Research Questions

Specific research questions will be addressed that will assist in meeting the WEBB project objectives. The research questions will be developed as hypotheses to be tested using standard statistical testing procedures. As an example of the hypotheses that will be tested, consider the research question: How does antecedent soil-moisture status affect the flowpath of stormwater draining the unsaturated zone? The working hypothesis is that the wetter the antecedent conditions, the larger the proportion of drainage water that will follow flowpaths involving macropore or preferred flow as opposed to matrix flow. The null hypothesis would be: *The flowpath of stormwater draining the unsaturated zone is not related to antecedent soil-moisture status.* The variables to be measured and used in the test are soil-moisture content using time domain reflectometry (TDR), soil-moisture tension to assess antecedent soil-moisture status and to infer flowpath, and the chemistry of soil solutions sampled from lysimeters to infer flowpath. The null hypothesis would be rejected if a predictable relation is observed between flowpath and antecedent soil-moisture content or tension. For example, if a statistically significant ($\alpha=0.05$) correlation is observed between antecedent soil-moisture content or the timing of the arrival of a wetting front at depth (as determined from TDR, soil-moisture tension, or lysimeter drainage) and soil-solution (sampled during storm drainage) sulfate concentration, the null hypothesis would be rejected.

In the following paragraphs, specific research questions are presented. Following each question, the research approaches that will be used to answer the questions are listed in parentheses; and the research approaches are outlined in the following subheading.

1. How do the streamwater chemistries in the three nested subcatchments compare; and can differences be explained in terms of different flowpaths or different soil-water chemistries among catchments? (*approaches 1 and 2*)
2. How important are riparian zone processes (for example, chemical interactions adjacent to, in, or beneath the stream) in the control of stream chemistry? (*approaches 1 and 2*)
3. How does antecedent soil-moisture status affect the flowpath of storm water draining the unsaturated zone? (*approach 2*)
4. Does the chemistry of throughfall directly influence streamwater quality? (*approaches 1 and 3*)
5. What is the areal extent of the saturated zone within each subcatchment (*approach 4*), and how important is the ground-water component to streamflow generation and water-quality evolution within each subcatchment? (*approach 1*)
6. Does the D and ^{18}O composition of water, originating as precipitation and traveling through the canopy (throughfall) and unsaturated zone (soil water), change within the time span that is important to the use of these isotopes for determining sources of streamflow? (*approaches 2, 3, and 5*)
7. How does the D and ^{18}O composition of canopy throughfall vary over the watershed; and how does this variation affect use of these isotopes for determining sources of streamflow? (*approach 3*)
8. What are the primary processes that control streamwater chemistry in the headwaters of the subcatchment draining the bedrock outcrop? (*approach 1*) What is the relative importance of the interaction of runoff from the outcrop with soils in the vadose zone compared with interactions between water in the seasonally present shallow aquifer in the headwater with soil in the saturated zone? (*approach 2*)
9. Can the isotopic composition of the streamwater be predicted as a mixture of soil waters in proportions determined from end-member-mixing analysis? (*approaches 1 and 2*)

10. Can the isotopic composition of soil water be estimated by using the isotopic composition of the previous storm; and can the conservative nature of D and ^{18}O in the unsaturated zone be demonstrated in laboratory studies? (*approaches 2 and 4*)

11. Is carbon-isotope labeling of shallow soil and ground water a potentially useful technique for quantifying the percentage contribution of water that constitutes stormflow (these waters are often not very usefully labeled by D or ^{18}O). (*approach 2*)

Research Approaches

Approach 1. -- Small catchment streamwater analysis

The streamwater sampling program will be expanded to determine the importance of timing and variability of major dissolved ions and isotopes in streamwater at different locations within the catchment. Extensive physical and chemical information is available for streamwater and runoff obtained at three gaged sites (1) on the bedrock outcrop, (2) on a 10-ha subcatchment that contains the 3-ha outcrop, and (3) at the basin outlet (41-ha drainage). In addition to intensive sampling at the currently gaged sites, streamwater in two additional 10- to 15-ha headwater subcatchments and at the base of the bedrock outcrop (fig. 2) will be gaged and sampled intensively during storm events. Soil characteristics and slopes of the three catchments differ, thereby permitting a comparison of streamflow generation mechanisms and the relative importance of different soil zones and soil-moisture status (for example, well drained as opposed to wetland).

Approach 2. -- Soil physics and chemistry

Extensive and intensive measurements of soil physics and chemistry will be conducted throughout the soil profile in plots positioned along transects perpendicular to stream channels to evaluate chemical changes in the long term and during storms. Soil moisture will be monitored using a combination of time domain reflectometry (TDR) and tensiometers (having pressure transducers). Physical properties of the soil will be measured to enable calibration of the TDR and tensiometer data to actual moisture content (see "Regulation of Soil-Water Chemistry" below). Horizontally oriented TDR rods will provide information on the travel time of water through the soil matrix (generally slow transport). Vertically oriented TDR rods at two to three different depths will provide an integrated measure of soil moisture.

Zero-tension lysimeters will be used to sample water draining through the soil profile. These lysimeters will be fitted with tipping-bucket gages to provide timing of sample collection. These data provide an estimate of minimum travel time through the unsaturated zone. Water-quality and isotopic analyses performed on sequential lysimeter samples will provide detailed information on the transport of solutes and concentration changes associated with reactions and transport from overlying horizons.

Wells will be installed at each of the plots, and the water levels from recording wells (co-located with the sampling wells) will control automatic sampling of ground water at the surface and at several depths below the water table. The computer program and electronic interfaces that control automatic samplers were developed at PMRW. The system was used for streamwater sampling at PMRW and at sites in the Adirondack and Catskill Mountains, N.Y., and in western Pennsylvania. Although a device is not currently available to control the depth of sampling relative to the water table, one has been designed, but needs fabrication and testing.

Approach 3. -- Precipitation and throughfall

Precipitation and throughfall will be sampled intensively during selected storms. Throughfall collection sites will be located adjacent to, and in, the stream channel. All samples will be analyzed for major dissolved solutes, and selected samples will be analyzed for D and ^{18}O . The throughfall fluxes to the open channel reaches will be computed for the major dissolved solutes and compared with fluxes for the stream. Also, precipitation will be collected during storms at six sites throughout the watershed to evaluate variations in quantity and to evaluate the isotopic and chemical composition during selected storms.

Approach 4. -- Extent of saturated zone

To determine extent and timing of saturated conditions, water levels will be monitored continuously at wells installed along transects from stream to top of hillslope. The monitoring wells will be constructed by auguring holes to refusal and installing a 5-cm diameter PVC casing and a 1.5-m screen. Some of these wells will be used in the plots outlined in approach 2.

Approach 5. -- Soil-water isotopic evolution

Field and laboratory experiments will be used to determine whether exchange of soil water with either atmospheric vapor or ground water is a significant process in controlling the isotopic composition of soil water. The purpose of the laboratory experiment is to determine if either process is a dominant factor. For the laboratory experiment, "minimally disturbed" soil cores will be equilibrated by using water of a known isotopic composition. One set of cores (3 to 5) will be placed in a chamber having regulated temperature and humidity, and having a different vapor isotopic composition than that of the soil water in the soil column. Another set of cores will be placed in a chamber having the same vapor conditions as the previous experiment; however, the core will be placed in a reservoir of water that has a different composition than the soil water. In each case, soil cores will be withdrawn from the reservoir at set times, sectioned, and the soil water extracted for isotope analyses. The purpose of the field experiment is to determine the rate at which the isotopic composition of rainfall changes the soil- and ground-water isotopic composition and the rate at which vapor exchange dampens the isotopic signal.

Weathering and Geochemical Evolution

Proposed research on weathering and geochemical evolution will identify the sources of cations observed in the streamwater at PMRW and quantify the changes in cation source during storms. The emphasis in this element of the research plan will be to determine the relative contributions of weathering, ion exchange, and deposition processes as cation sources.

Problem Statement and Theoretical Background

There is an incomplete understanding of the mechanisms, rates, and spatial variability in rates of cation supply from distinct sources within small watersheds that increases the uncertainty of prediction of water quality.

A potentially useful, yet little-used, technique for identifying distinct cation sources within a watershed is the use of solid-source mass spectrometry to determine precisely the diagnostic radiogenic and stable isotopic compositions (isotopic ratios), as well as the relative abundance of a wide variety of solute cations. These compositions can help to determine the relative contribution of primary mineral weathering, cation exchange in the soil, and atmospheric deposition to the cations observed in the stream. Determining the role of each of these mechanisms in supplying base cations is important for future predictions because some sources (such as cation exchange) are limited and could be exhausted, whereas, others (such as primary weathering) are nearly unlimited.

Isotopic studies can be used to identify sources of some constituents in water because the various minerals of the source rocks for the watershed soils are likely to have different isotopic compositions and solute cation abundances. Isotopic variations result from either long-lived radioactive decay processes, or differing preferences of the minerals for the various isotopic species during mineral formation. Variations in aqueous cation abundance distributions develop as functions of source mineral composition, and in response to changing environmental conditions, such as vapor fugacity, pH, and concentration of organic compounds. Incongruent weathering of soil minerals results in a progressively changing suite of cations released by weathering and corresponding changes in cations adsorbed on surficial exchange sites. Thus, as weathering proceeds, the isotopic ratios of certain cations increase or decrease. Furthermore, the distribution of any geochemically coherent group of cations, such as the rare earth elements (REE), may change. An additional important consideration is that under favorable conditions, these diagnostic signatures of lithogenic sources in a watershed will be different than those for solute cations derived from atmospheric sources.

The nature of source-rock lithologies in PMRW makes this site particularly amenable to isotopic studies to define source materials of solute cations, and thus, flowpaths. The mildly peraluminous and alkaline nature of the two-mica Panola Granite (granodiorite composition) should result in large variations in the radiogenic isotopic compositions of a variety of cations in the constituent minerals, and those compositions should be considerably different from those of atmospheric flux components in this region. Furthermore, although little is known about their chemistries, the amphibolite and muscovite schist of the Clairmont Formation should have radiogenic isotopic and element-distribution characteristics that are distinct from the Panola Granite. Assuming solute cations in ground water and streamwater have arisen in part from the variously weathered soils derived from these lithologies, the chemistries of the water should reflect the unique exchangeable element inventories of the particular soils through which they have passed.

The source minerals of the trace-metal cations in ground water and streamwater can be identified by using either the diagnostic isotopic compositions of cations such as Sr, Ca, Pb, and Li, or the relative distribution of a geochemically coherent group of cations such as the REE. These particular elements vary dramatically in their tendency to sorb onto weathered mineral surfaces and to be transported by ground water. Multi-dimensional end-member analysis can be applied to separate the streamwater into $n+1$ solute sources, if n independent isotopic signatures or REE ratios can be identified.

The isotopic compositions of Sr ($^{87}\text{Sr}/^{86}\text{Sr}$), Ca ($^{40}\text{Ca}/^{42}\text{Ca}$), and Pb ($^{206,207,208}\text{Pb}/^{204}\text{Pb}$) reflect the long-lived decay of ^{87}Rb to ^{87}Sr , ^{40}K to ^{40}Ca , ^{238}U to ^{206}Pb , ^{235}U to ^{207}Pb , and ^{232}Th to ^{208}Pb . The distinctiveness of the isotopic composition of these elements in the various mineral phases listed above, reflects different Rb/Sr, K/Ca, U/Pb, and Th/Pb ratios averaged over the life of the minerals. The isotopic composition of Li reflects variations in the abundance of the stable isotopes ^6Li and ^7Li . The variations in the abundance of the stable isotopes mainly are a result of contrasting site-occupancy preference in minerals. The distribution of the primarily trivalent REE in the various minerals reflects the preference of each mineral for the light REE (for example, La) relative to the heavy REE (for example, Yb). In addition, the various minerals have differing preferences for Eu^{2+} relative to Eu^{3+} , of importance in the magmatic evolution of the granite, and for Ce^{4+} relative to Ce^{3+} , of importance in the more oxidized weathering environment.

Considering a situation in which minerals on bedrock surfaces or in soils derived from that bedrock weather at highly variable rates, one can predict that the isotopic composition of Sr, Ca, and Pb, as well as the REE distribution of the exchangeable component, will vary in an orderly manner. The variation in isotopic composition and REE distribution will depend upon the degree of weathering of the soil. The magnitude of the variations for the radiogenic isotopic systems depends on the age of the source rock, and the extent of differences in Rb/Sr, K/Ca, U/Pb, and Th/Pb ratios in the individual minerals. Variations in $^6\text{Li}/^7\text{Li}$ ratios and REE distribution among mineral phases occur, regardless of the source rock age.

Isotopic studies (currently in progress at USGS, Menlo Park, Calif.) of granitic alluvial soils from the Merced River drainage basin in California indicate that the isotopic compositions of exchangeable Sr, Ca, and Pb, and the distribution of REE on mineral surface sites vary consistently with age of the soil, and thus, with the degree of weathering. For example, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is highest on the surface sites of the youngest soils, reflecting the early breakdown of biotite (high Rb/Sr ratio) (Thomas D. Bullen, USGS, written commun.). The $^{87}\text{Sr}/^{86}\text{Sr}$ ratio decreases with increasing age of the soils, reflecting the more retarded breakdown of hornblende and plagioclase, both having low Rb/Sr ratio. However, the rate of decrease of $^{87}\text{Sr}/^{86}\text{Sr}$ ratio slows considerably as K-feldspar (moderate Rb/Sr ratio) weathers and its Sr is added to the surficial sites of minerals in the oldest soils (Thomas P. Bullen, USGS, written commun.). Variations observed for the Ca and Pb isotopes and the REE are consistent with this scheme of progressive mineral breakdown.

Considering the foregoing discussion, substantial and diagnostic variations in both isotopic abundances and REE distributions are likely to occur in PMRW soils. The bedrock lithologies are all Paleozoic in age, and thus, have had sufficient time to undergo considerable radiogenic isotope evolution. Moreover, at least in the case of the Panola Granite, the variations in radiogenic isotope character of constituent minerals may be extreme. Preliminary geochemical analyses of the Panola Granite indicate high whole-rock Rb/Sr and K/Ca ratios, reflecting the mildly alkaline nature of the intrusion, and exceptionally high Th/U ratio. This latter characteristic should result in elevated and diagnostic $^{208}\text{Pb}/^{204,206,207}\text{Pb}$ ratios, particularly when considered relative to typical North American atmospheric Pb, much of which is anthropogenic. Of course, lacking geochemical data for the other bedrock lithologies, the total potential range of isotopic and REE variation for the watershed soils cannot be determined.

Research Objective

The objective of this part of the study is to determine the relative contributions of a variety of sources, including primary mineral weathering, cation exchange, and atmospheric deposition, to the cations observed in streamwater. The data obtained in this section will also be used to estimate weathering rates. To meet this objective, specific research questions will be addressed. Research questions are followed by the research approach, which is described in the following section.

Research Questions

1. Do distinct cation sources, that is, weathering minerals, exchangeable cations, or atmospheric deposition, exhibit different isotopic compositions of Sr, Ca, Pb, Li, and REE concentrations, and what is the spatial variability of these sources?

2. What is the spatial variability, both geographically over the watershed and with depth in a soil and saprolite weathering profile, of distinct cation sources, that is, weathering minerals, exchangeable cations, or atmospheric deposition?

3. Can intra-storm variations in isotopic compositions of Sr, Ca, Pb, Li, and REE concentrations in streamwaters be used to determine distinct cation sources, that is, weathering, cation exchange, or atmospheric deposition?

4. Can intra-storm variations in isotopic compositions of Sr, Ca, Pb, Li, and REE concentrations in streamwaters be used to infer probable flowpaths and systematic changes in the contributions from the various lithogenic and atmospheric components assuming that different flowpaths impart chemically distinct isotopic signatures to drainage water?

Research Approach

The isotopic composition of potential cation sources, such as precipitation, vegetation, bedrock lithologies, soil horizons, and saprolite, need to be characterized. To accomplish this, analysis of the following materials for isotopic composition of Sr, Ca, Pb, Li, and REE concentrations is proposed:

(1) samples of fresh bedrock and weathered bedrock (saprolite) lithologies (whole-rock) and their constituent minerals (mineral separates),

(2) soils collected at various locations and depths within the watershed including analysis of both the exchangeable and non-exchangeable components of the soils,

(3) soil-water (unsaturated zone) collected from known soil horizons adjacent to the locations where soil samples will be collected,

(4) ground water (saturated zone) collected from known soil horizons at locations near the soil-sample collection locations,

(5) precipitation and throughfall, and

(6) streamwater collected before, during, and after selected storms.

In addition, total procedural blanks will be measured several times throughout the collection process to demonstrate that variations observed in the water are, in fact, due to watershed or atmospheric sources and not analytical artifacts. Bedrock samples will be about 2 kilograms (kg) in total mass. Individual soil samples will be about 50 grams (g) in total mass. All water samples will be about 1 liter (L) in volume, filtered to 0.45 micron (μm), and acidified to pH 2 using ultra-pure HNO_3 . Dedicated automatic samplers will be necessary for sample collection.

Regulation of Soil-Water Chemistry

Proposed research on regulation of soil-water chemistry will focus on the poorly understood processes that regulate soil-water and ground-water chemistry. The emphasis in this element of the research plan will be on the investigation of processes of ion exchange and sulfate adsorption along reactive flowpaths. The research goal will be to determine the critical soil properties that determine the chemistry of soil solutions and to predict their evolution through time in response to environmental change.

Problem Statement and Theoretical Background

The regulation of soil-water chemistry is poorly understood because the principles of thermodynamics governing solubility and the theory of ion exchange, adsorption, and kinetics cannot be readily applied to complex natural systems.

One approach to understanding the regulation of soil-water chemistry has been the application of thermodynamics and ion exchange theory. This approach has been used in acidification models such as Model of Acidification of Groundwater In Catchments (Cosby and others, 1985) and Integrated Lake Watershed Acidification Study (Goldstein and others, 1984). Reuss and others (1986a,b) critiqued these models and noted the following assumptions:

- (1) ion exchange processes can be adequately described by activity ratio equations;
- (2) solid-solution contact is sufficient so that reactions proceed to equilibrium; and
- (3) aluminum concentrations are determined either by mineral solubility or by ion exchange.

The first assumption has two major limitations: (1) there is no consensus on the form of the activity ratio equations (Bohn and others 1985), and (2) selectivity coefficients are not constant over broad ranges in element adsorption ratios (Gobran and Ågren, 1989; McBride and Bloom, 1977), pH, or salt concentrations (Bohn, and others 1985). It has been suggested by McBride and Bloom (1977) that adsorption isotherms might be more appropriate conceptual models in the case of Al adsorption.

The second assumption is an oversimplification for natural systems, because contact time and surface-area interaction may be limited if water moves through macropores and mesopores rather than through the soil matrix. Macropore flow may be the dominant transport process under saturated conditions (Beven and Germann, 1982; Wilson and Luxmore, 1988; White, 1985). For reactions that are limited by kinetic considerations or by the reactive capacity of the surface area, macropore flow may not allow equilibrium to be attained. Jardine and others (1989) demonstrated that the attenuation of reactive solutes, such as Mg, NH₄, and natural dissolved organic carbon, was far less than predicted from estimated soil cation exchange capacity and breakthrough curve modeling.

The third assumption was supported by early studies that suggested that crystalline solid phases (such as gibbsite) controlled Al solubility (Johnson and others, 1981, Driscoll and others, 1984). Later studies indicated that solubility was not controlled by simple trihydroxy-aluminum minerals but by the presence of poorly crystalline 1:1 aluminosilicates (including imogolite and allophane) or Al hydroxy-interlayered 2:1 clay minerals and exchangeable Al (Walker and others, 1988; Bertsch 1989). Aluminum solubility may, in fact, be controlled by solubility of amorphous solid phases (Bertsch 1989, David and Driscoll, 1984; Dahlgren and others, 1989) or Al adsorbed to solid-phase organic compounds (Bloom and others, 1979; Driscoll and others, 1984; Cronan and others, 1986), that for practical purposes, defy thermodynamic characterization. As noted by Bertsch (1989), there is a need for studies that relate these various Al-solid phases to an easily mobilizable Al fraction.

The complexity of natural systems makes the direct application of thermodynamics impractical. Two additional approaches to the problem that may be more fruitful are the use of mass balance accounting procedures and the use of operationally defined soil-chemical properties. In the first of these, changes in pool size and fluxes are estimated and these changes, which allude to processes, can be used to predict long-term characteristics of the system (Abrahamsen and others 1989; Bjørnstad, 1991; Johnson and others, 1991; Kuylenstierna and Chadwick, 1991). In the second approach, measurements are performed that are thought to assess specific labile or potentially labile fractions, such as organically bound, exchangeable, specifically adsorbed, amorphous, or interlayer. The proposed research will emphasize the latter approach, which can integrate the properties of an arbitrary, undisturbed pedon. Fresh soils, rather than air-dried and sieved soils, will be used to better capture the true potential of the soil for chemical interactions (including surface properties and biological influences). Undisturbed soil cores and soil plots will be used to assess the influence of soil structure (for example, macropores) on soil-water chemistry.

PMRW offers a unique, natural laboratory because the historical pattern of sulfur deposition has provided a gradient in soil loading. Initial investigations at PMRW indicated that sulfate-retention capacity was high and increased with soil depth (Shanley, 1992). Different mechanisms of sulfur adsorption were suggested at different depths and were apparently complicated by organic matter coatings blocking adsorption to sesquioxides. The pattern of sulfate concentration in streamwater indicates a well buffered system involving reversible adsorption, but the precise mechanism is unknown (Shanley and Peters, in press). The mechanism of sulfur retention may be dependent upon soil type, soil horizon, solution residence time, and sulfate concentration.

Soil-base saturation is a critical soil property regulating soil-water chemistry (Reuss, 1983). Once the sulfur adsorption potential for a soil is exceeded, further inputs of sulfur will result in increased cation leaching (Ulrich and others 1980; Lee, 1985; Cronan and Schofield, 1979; Linthurst, 1984). If the rate of cation supply from mineral weathering is not sufficient to replace base cations lost from the exchange complex, the result will be a reduction in base saturation. Model predictions using Gapon exchange equations indicate that soils possess a critical threshold below which further reductions in base saturation will result in substantial increases in soil-water Al concentrations (Reuss, 1983). Some amelioration may occur as acidification increases pH-dependent anion exchange capacity, providing an increase in sulfur adsorption potential (Gillman and Sumner, 1987).

Soil-sulfate adsorption is a controlling factor in determining ecosystem sensitivity to acidic deposition (Reuss and Johnson, 1986; Johnson and Cole, 1980; Galloway and others, 1983; Church and others, 1989; Gaston and others, 1986). The results of one study comparing sulfate dynamics among several sites confirmed the usefulness of a conceptual model in which sensitivity to acidification is dependent upon the capacity of the soil to retain elevated sulfate inputs (Mitchell and others, 1992). Acid neutralizing capacity in low-order streams of the Southern Blue Ridge physiographic province has declined as a result of atmospheric sulfur deposition (Eshleman and Kaufman, 1988), illustrating the limits on sulfate retention capacity in southeastern soils. Recent studies at PMRW also have demonstrated an important linkage between climate, hydrologic conditions, and sulfate retention (Huntington and others, 1992a; Huntington and others, 1992b).

Vegetation plays a major role in regulating soil-water chemistry. Transpiration continuously concentrates the soil solution. Nutrient uptake and incorporation into live biomass and organic matter pools sequesters significant proportions of some elements and generates substantial soil acidity (Johnson and others, 1991). The PMRW forest is aggrading (Cappellato and Carter, 1988); therefore, there is a net flux of base cations and P from the soil to the vegetation. During the period of extensive cultivation in the Georgia Piedmont, soil-organic matter pools probably were reduced below pre-settlement levels because of both cultivation (Giddens and Garman, 1941; Giddens, 1957; Mann, 1985, 1986) and erosion (Trimble, 1974; Mann, 1985; Voroney and others, 1981; Schlesinger, 1985). The forest ecosystems are now aggrading, and C, N, and S are accumulating in biomass and soil organic matter pools. Upon reaching equilibrium (forest "maturation"), the system will no longer be a sink for solutes which are important to the study goals.

Cultivation and other forms of soil disturbance can result in a redistribution of carbon from surface soil horizons into deeper horizons (Mann, 1985; Huntington and Ryan, 1990; Sollins and McCorison, 1981; Gholz and Fisher, 1982). Transport and accumulation of carbon along principal flowpaths in deeper soils could affect surface chemical reactions. Several studies have shown that organic matter inhibits the adsorption of sulfate in soils (Couto and others, 1979; Johnson and Todd, 1983; Singh, 1984; Gobran and Nilsson, 1988).

Production of soluble organic matter by vegetation through direct means (such as, root exudate or leaf leachate) or indirect means (such as, humus produced from litter decomposition) contributes to the reactivity of the soil solid phase and influences the cycling of most elements (such as, Johnson and Todd, 1983; Vance and others, 1986; Evans and Anderson, 1990). Recent studies show that under different forest types (such as, coniferous and deciduous), properties of soil water, and specifically the nature of organic molecules, are qualitatively different (Evans, 1980; Kovacic and others, 1989; Pohlman and McColl, 1988; Huang and Schnitzer, 1986). Evans (1980) demonstrated that the contents of low molecular weight organic compounds increase in surface mineral horizons of Spodosols as the proportion of coniferous to deciduous tree species increase in the forest canopy. Different organic molecules react differently in soil processes such as chelation (McColl and Pohlman, 1987), transport (Evans, 1986; Pohlman and McColl, 1986; Evans and Anderson, 1990), and facilitation of weathering (Schalascha and others, 1967; Boyle and others, 1974; Pohlman and McColl, 1988). Forest maturation and changes in species composition resulting from environmental stresses associated with climate change or acidification will potentially alter the carbon budget. For

example, lower rainfall and drier soil conditions would favor coniferous tree species over deciduous ones, which in turn would affect litter quality, rates of organic matter decomposition, and the chemical nature and reactivity of organic acids in soil solutions. Forest maturation implies that the ecosystem will no longer be aggrading and carbon will no longer be accumulating in living plant biomass.

Research Objectives

The objective of this element of the study is to investigate the major processes that regulate soil-water chemistry. To meet this objective, specific research questions will be addressed. Research questions are followed by numbered research approaches, which are described in the following section.

Research Questions

1. Can inter- or intra-storm variation in soil-water sulfate concentration be explained by flowpath? For example, under hydrologic conditions that favor macropore flow, does minimizing length of flowpath, residence time, interactions with mesopore and micropore water, and interactions with the solid phase result in less alteration of solute composition? (*approaches 1 and 2*)
2. Is the extent of sulfur saturation in soils along a hydrologic gradient draining the bedrock outcrop related to proximity to the outcrop, as would be expected as a result of high sulfur inputs in bedrock runoff? (*approach 1*)
3. What soil properties best explain the observed variations in soil-water sulfate concentration? (*approaches 1 and 2*)
4. Can soil organic matter effectively block sulfate adsorption on sesquioxides? (*approaches 1 and 3*)
5. Is soil base saturation inversely related to soil sulfur saturation? (*approaches 1 and 3*)
6. What soil properties best explain the observed variations in soil-water Fe and Al concentrations; specifically, are standard extractions for exchangeable, amorphous phase, and organically bound Fe and Al fractions useful predictors of soil-water Fe and Al concentrations? (*approaches 1 and 2*)
7. Assuming that element pools in biomass and soil organic matter are currently aggrading, what will the impact on water quality be after "equilibrium" is attained at forest maturation, that is, are current sequestration rates sufficiently high compared with other fluxes that net increases in solute export following "equilibrium" will be detectable? (*approaches 1 and 4*)
8. Assuming that carbon and nitrogen pools in biomass and soil organic matter are currently aggrading, how long will the ecosystem continue to serve as a net sink for these elements? (*approaches 1 and 4*)

Research Approaches

The first research approach describes the extensive study of soil-water chemistry to accomplish the goal of understanding soil matrix and solution processes in different soil environments. The second approach describes the intensive plot-scale studies where processes can be studied by analyzing variations in chemistry and flow rates along vertical profiles. The third approach describes laboratory investigations that will be used to study specific soil processes. The final approach involves additional data that will be collected on an extensive basis to provide a more complete understanding of biogeochemical budgets.

Approach 1. -- Matrix-solution processes -- extensive measurements

Zero-tension lysimeters will be installed at several locations in the watershed to compare soil-water chemistry in different soil environments, focusing on soil type, drainage class, and vegetation type. One set will be installed along a transect perpendicular to the bedrock outcrop-soil boundary, which is thought to be along a gradient in sulfur loading and soil saturation. During installation, soils representative of those above each lysimeter will be sampled for chemical analysis. Extractions will be performed to quantify adsorbed sulfur, exchangeable cations, and labile or "mobilizable" Fe and Al fractions. Iron and Al fractions to be assessed include: organically bound (pyrophosphate extractable), quasi-crystalline/amorphous (ammonium oxylate extractable), and exchangeable (1 N KCl). Properties of the soil solution and soil matrix will be analyzed in relation to ion exchange, mineral dissolution and precipitation, and microbial processes to identify mechanisms that regulate solute concentrations in each soil environment. Lysimeters will be sampled during selected storms to address specific hypotheses, such as the affects of antecedent dry period, rainfall intensity, and season on solute concentrations.

Alternative extraction procedures will be developed for the analysis of intact, fresh, soil cores. Recent investigations have shown differences between traditional extractions performed on air-dried soils and fresh soils (Bartlett and James, 1980). Extractions of fresh soils in intact cores, that to a first approximation retain soil structure, will be compared with traditional extraction procedures as predictors of soil-water chemistry.

Approach 2. -- Matrix-solution processes -- intensive plot studies

The intensively instrumented plots described for Approach 2 under the section entitled "Streamflow generation and water-quality evolution" also will be used to study soil processes that regulate solution chemistry. During installation of lysimeters, soils representative of those above the lysimeters will be sampled and chemically analyzed using the extractions specified in Approach 1 above (Matrix-solution processes - extensive measurements). Sequential sampling of soil water during storms will provide the opportunity to evaluate the kinetics of matrix/solution interactions. Extensive instrumentation in the vertical dimension will provide direct field measurement of solution quality input to, and output from, specific soil compartments under a variety of antecedent soil-moisture conditions. Results of these studies may indicate key mechanisms of sulfur adsorption or desorption, the relative importance of ion exchange and mineral weathering as proximal cation sources, and mechanisms of Fe and Al mobilization and precipitation.

Approach 3. -- Laboratory studies

To address research questions about the importance of specific solid-phase constituents in the regulation of solution chemistry, soil columns will be constructed and leached with solutions of known chemical composition. Soil columns will consist of natural intact cores, as well as reconstructed soils. Reconstructed soils will permit analysis of specific, homogeneous horizons of known mineral and "mobilizable" solid-phase composition as well as standard clay materials in different proportions. This methodology will study the importance of different surface chemical properties in the regulation of solution chemistry. Treatments will include modification of antecedent dry periods, variable concentration of sulfate and dissolved organic carbon, as well as leachate from coniferous and deciduous litter.

Approach 4. -- Additional data collection:

Major element pools and fluxes will be quantified on a watershed scale to provide further core data for comparative watershed research, long-term trend analysis, and proposed process level studies.

<i>Major pools:</i>	Live biomass	<i>Fluxes:</i>	Atmospheric deposition
	Dead biomass		Rock weathering
	Soil		Streamwater export
	Stream sediments		Sediment transport
	Saprolite		Biomass uptake
	Bedrock		Decomposition/mineralization
			Secondary mineral formation
			Sulfur adsorption

The existing data base on vegetation and biomass increments for the period 1977-1986 will be used to quantify biomass pool sizes. Additional surveys will be conducted at a subset of the vegetation plots in the watershed. Element pool sizes in soils, sediments, and saprolite will be quantified using both the existing data base and additional sampling stratified by soil type, landscape position, and vegetation. Soils will be sampled using a cylindrical core sampler to permit calculation of bulk density. Exchangeable cation pools and total pools on an areal basis will be estimated using bulk density, soil depth, and element concentrations.

The depth of saprolite overlying bedrock will be estimated using the existing seismic refraction data. Saprolite chemistry will be evaluated using samples collected from test drilling. Total rock analyses will be performed on selected bedrock samples.

The existing USGS data base will be used to quantify deposition and streamwater export (see "Streamflow generation and water-quality evolution"), sulfur adsorption, and biomass uptake. Elemental flux associated with decomposition and mineralization will be estimated from appropriate models of litter decomposition. Flux associated with sediment transport will be estimated using standard sampling and filtration techniques. Estimates of weathering flux will depend heavily on mass balance and isotopic ratio studies described in "Weathering and geochemical evolution". Flux due to secondary mineral formation will be based on computation of primary mineral weathering and the equations governing secondary mineral formation in these soils (Nixon, 1981). The flux of sulfur associated with adsorption/desorption will be estimated from previous studies at PMRW (Shanley, 1989), and proposed soil characterizations.

Existing data on mineralogical composition will be augmented with further extensive characterization using a subset of the soil, sediment, and saprolite samples collected throughout the watershed. Methods for this characterization will include X-ray diffraction analysis (mineral identification), electron microscopy (micromorphological analysis for qualitative description of particle arrangement, size, and weathering products), and thermal analysis such as differential thermal analysis and differential scanning calorimetry (mineral identification and characterization of hydroxy-interlayered vermiculite).

Techniques will be evaluated for the measurement of gaseous transfers. Ultimately, gaseous transfers will be explored in various soil and vegetation environments to estimate fluxes for CO, N₂O, CO₂, SO₂, and CH₄. Passive collectors will be evaluated for monitoring SO₂ and various N gases.

COLLABORATIVE RESEARCH

An objective of the WEBB program is to foster cooperative efforts within the USGS, between Federal agencies, and between Federal agencies and academic institutions. The multidisciplinary research approach of the WEBB program is strengthened by these interactions. Existing research collaboration at the Panola Mountain Research Watershed is listed below by researcher or agency. Brief descriptions of the research are also given.

Existing Research Collaboration

Paul Bierman, Department of Geology, University of Washington, Seattle, Wa., is involved in a regional comparison of weathering and isotopic evolution of granite boulders exposed to cosmogenic radiation. Paul has evaluated the ^{36}Cl content of the granodiorite and has a preliminary physical denudation estimate of 10 m per million years. He will evaluate this estimate independently using isotopes of Al and Be, and is in the process of writing his dissertation.

Owen P. Bricker, USGS, Reston, Va., has been using the Panola Mountain data as part of a National assessment of the effects of acidic atmospheric deposition on streamwater quality in "sensitive" watersheds. Trend analysis of precipitation quality and streamwater quality is being conducted for all NTN sites including PMRW by Brent T. Aulenbach, Richard P. Hooper and Owen P. Bricker.

Thomas D. Bullen, USGS, Menlo Park, Calif., has been evaluating the use of heavy isotopes for separating atmospheric deposition, internal release, and mobilization as sources of Sr and Pb.

Rosanna Cappellato, Assistant Professor, Human and Natural Ecology Program, Emory University, has re-surveyed about 70 vegetation plots, which were originally surveyed by Dr. Eloise Carter in 1977, and biomass increments have been determined for the trees. In addition, several cores were collected of the boles for dendrochronology and chemical determinations. Rosanna also completed her Ph.D. dissertation on an evaluation of nutrient pathways from the atmosphere through the deciduous and coniferous canopies at PMRW (Cappellato, 1991; Cappellato *et al.*, in press).

Nils Christophersen, Department of Informatics, University of Oslo, Norway has been involved with the development of hydrochemical models using the Panola data set. Three journal articles that used Panola data on which Nils is a co-author have resulted from the collaboration. Collaboration on model development is on-going.

Christopher E. Johnson, Department of Civil Engineering, Syracuse University, Syracuse, N.Y., is involved with the characterization of soil-chemical properties at Panola Mountain. Chris helped collect soil samples, extracted samples for exchangeable cation content, and analyzed C, H, N, and S in the samples.

Carol Kendall, USGS, Menlo Park, Calif., is assessing the isotopic variation of sequential precipitation and throughfall to test one of the major assumptions of the isotopic hydrograph separation technique. One chapter of Carol's Ph.D. dissertation evaluates the isotopic composition of precipitation and throughfall at PMRW (Kendall, 1993). The results of her investigation suggest that canopy exchange processes are affecting the isotopic composition of the throughfall and that the processes differ by canopy type.

Nathan Melear, Ph.D. candidate, University of Georgia, Department of Geology, and his major professor, Paul Schroeder, have sampled bedrock cores and Nate is determining whole rock chemistry, mineralogy, and iron site occupancy differences between fresh and weathered bedrock.

Tilden P. Meyers, National Oceanic and Atmospheric Administration (NOAA) is working closely with PMRW staff to compare methods for measuring dry deposition. Tilden will continue the assessment of dry deposition at PMRW using an inferential technique (Meyers and others, 1991).

Robert L. Michel, USGS, Reston Va., is investigating ^{35}S weekly variations in precipitation and throughfall under coniferous and deciduous canopies.

Paul Quinn, Department of Environmental Sciences, Lancaster University, Lancaster, United Kingdom, is attempting to model the stream discharge at PMRW using TOPMODEL. Paul has modeled 14 catchments some of which have similar characteristics to PMRW, i.e., a sustained baseflow and flashy response to intense rainfall, and he believes he will be able to modify the model to work at PMRW.

Martyn Tranter, Department of Geography, University of Bristol, Bristol, United Kingdom, has submitted two Ph.D. studentship applications to the National Environmental Research Council of the United Kingdom to assess processes controlling short-term chemical variations in precipitation, throughfall, soil water, and acid-base chemistry of streamwater. One studentship already has been approved for an evaluation of short-term variations in water chemistry.

EPA and U.S. Forest Service are investigating forest response to environmental stress as part of their joint Environmental Monitoring and Assessment/Forest Health Monitoring Program (Forest EMAP/FHM). The objective of this study is to monitor a suite of ecological indicators on a regional scale to detect and assess forest response to future environmental change. The Forest EMAP field crew visited Panola in July 1992 and sampled soils and vegetation. The samples are in process for dendrochronology and chemistry.

EPA and the Georgia Institute of Technology, Department of Geophysical Sciences, Atmospheric Sciences Unit, are using ambient ozone data collected by USGS staff as part of the EPA-sponsored Southern Oxidants Study. The Southern Oxidants Study also involves ambient gaseous hydrocarbon sampling at PMRW during selected elevated ozone episodes.

Lawrence West, Department of Agronomy, University of Georgia, Athens, Ga., has analyzed particle size on soil samples collected at PMRW and may study geomorphological and pedogenic processes and their role in regulation of solute transport.

Arthur F. White and Alex E. Blum, USGS, Menlo Park, Calif., are quantifying mineral weathering processes and distinguishing between mineral weathering and ion exchange as the proximal sources of streamwater cations.

REFERENCES

- Abrahamsen, G., Seip, H.M., and Semb, A., 1989, Long-term acidic precipitation studies in Norway, *in* Adriano, D.C. and Havas M., eds., *Acidic Precipitation, Volume 2: Case Studies*, New York, Springer-Verlag, v. 1, p. 137-139.
- April, R.H., and Newton, R.M., 1985, Influence of geology on lake acidification in the ILWAS watersheds: *Water, Air and Soil Pollution*, v. 26, p. 373-386.
- Atkins, R.L., and Higgins, M.W., 1980, Superimposed folding and its bearing on geologic history of the Atlanta, Georgia, area, *in* Frey, R.W., ed., *Excursions in Southeastern Geology*, v. 1., Atlanta, Ga., American Geological Institute, p. 19-40.
- Barnes, C.J., and Allison, G.B., 1988, Tracing of water movement in the unsaturated zone using stable isotopes of hydrogen and oxygen: *Journal of Hydrology*, v. 100, p. 143-176.
- Bartlett, R.J., and James, B.R. 1980, Studying dried, stored soil samples - some pitfalls: *Soil Science Society of America Journal*, v. 44, p. 721-724.
- Bengtsson, L.R., Saxena, R.K., and Dressie, Z.R., 1987, Soil water movement estimated from isotope tracers: *Hydrologic Science Journal*, v. 32, p. 497-520.
- Bertsch, P.M., 1989, Aluminum speciation: methodology and applications. *in* Adriano, D.C. and Johnson, A.H., eds., *Acidic Precipitation Volume 4 Soils, Aquatic Processes, and Lake Acidification*: New York, Springer-Verlag, p. 63-105.
- Betson, R.P., 1964, What is watershed runoff?: *Journal of Geophysical Research*, v. 69, p. 1541- 1551.
- Beven, Keith, 1983, Surface water hydrology - runoff generation and basin structure: *Reviews of Geophysical Space Physics*, v. 21, p. 721-730.
- Beven, Keith, and Germann, Peter, 1982, Macropores and water flow in soils: *Water Resources Research*, v. 18, p. 1311-1325.
- Bloom, P.R., McBride, M.B., and Weaver, R.M., 1979, Aluminum organic matter in acid soils: buffering and solution aluminum activity: *Soil Science Society of America Journal*, v. 43, p. 488-493.
- Bohn, H.L., McNeal, B.L., and O'Connor, G.A., 1985, *Soil chemistry*: New York, John Wiley and Sons, 341 p.
- Bostick, P.E., 1968, The distribution of some soil fungi on a Georgia granite outcrop: *Bull. Ga. Acad. Sci.*, v. 26, p. 149-154.
- Bostick, P. E., 1971, Vascular plants of Panola Mountain, Georgia: *Castanea*, v. 36, p. 194-209.
- Bottomley, D.J., Craig, D. M., and Johnston, L.M., 1984, Neutralization of acid runoff by groundwater discharge to streams in Canadian Precambrian Shield watersheds: *Journal of Hydrology*, v. 75, p. 1-26.
- Boyle, J.R., Voight, G.K., and Sawhney, B.L., 1974, Chemical weathering of biotite by organic acids: *Soil Science*, v. 117, p. 42 - 45.
- Bjørnstad, O. N., 1991, Changes in forest soils and vegetation in Sogne, southern Norway, during a 20-year period: *Holarctic Ecology*, v. 14, p. 234-244.
- Braun, D.G., 1969, Soil factors and sub-annual nutrient cycling in two types of granite outcrop soil island ecosystems, unpublished M.S. Thesis, Emory University, Atlanta, Ga., 89p.
- Brender, E.V., 1974, Impact of past land use on the lower Piedmont forest: *Journal of Forestry*, v. 72, p. 34-36.
- Bricker, O.P., and Rice, K.C., 1989, Acidic deposition to streams: *Environmental Science and Technology*, v. 23, p. 379-385.
- Cantrell, K.J., 1989, Role of soil organic and carbonic acids in the acidification of forest streams and soils: Atlanta, Ga., unpublished Ph.D. Thesis, Georgia Institute of Technology, 168 p.
- Cappellato, Rosanna, and Carter, M.E.B, 1988, Successional changes in a Piedmont deciduous forest at Panola Mountain State Conservation Park, [abs]: *Association of Southeastern Biologists Bulletin*, v. 35, no. 2, p. 67.
- Cappellato, Rosanna, 1991, Atmospheric deposition, canopy interactions and nutrient cycling in adjacent deciduous and coniferous forests of the Georgia Piedmont. Atlanta, Georgia. Ph.D. Thesis, Emory University, Biology Department
- Cappellato, Rosanna, Peters, N.E., and Ragsdale, H.L., Acidic atmospheric deposition and canopy interactions of adjacent deciduous and coniferous forests in the Georgia Piedmont: *Canadian Journal of Forest Research* [in press].

REFERENCES--Continued

- Carter, M.E.B., 1978, A community analysis of the Piedmont deciduous forest of Panola Mountain State Conservation Park: Atlanta, Georgia, unpublished M.S. Thesis, Emory University, 126 p.
- Carter, R.F., and Stiles, H.R., 1983, Average annual rainfall and runoff in Georgia, 1941-1970: Georgia Geologic Survey, Hydrologic Atlas 9, 1 sheet.
- Chen, C.W., Dean, J.D., Gherini, S.A., and Goldstein, R.A., 1982, Acid rain model - Hydrologic module: Journal of Environmental Engineering, Division of the American Society of Civil Engineering, v. 108, p. 455-472.
- Church, M.R., Thornton, K.W., Shaffer, P.W., Stevens, D.L., Rochelle, B.P., Holdren, G.R., Johnson, M.G., Lee, J.J., Turner, R.S., Cassell, D.L., Lammers, D.A., Campbell, W.G., Liff, C.I., Brandt, C.C., Liegel, L.H., Bishop, G.D., Mortenson, D.C., Pierson, S.M., and Schmoyer, D.D., 1989, Direct/delayed response project: future effects of long-term sulfur deposition on surface water chemistry in the Northeast and Southern Blue Ridge Province (Results of the DDRP): U.S. Environmental Protection Agency EPA/600/3-89/061a-d, Corvallis, OR., 887 p., plus appendices.
- Cosby, B.J., Hornberger, G.M., Galloway, J.N., and Wright, R.F., 1985, Modelling the effects of acid deposition - assessment of a lumped parameter model of soil-water and streamwater chemistry: Water Resources Research, v. 21, p. 51-63.
- Couto, W.W., Lathwell, D.J., and Bouldin, D.R., 1979, Sulphate sorption by two Oxisols and an Alfisol of the tropics: Soil Science, v. 127, p. 108-116.
- Cronan, C.S., and Schofield, C.L., 1979, Aluminum leaching response to acid precipitation: effects on high elevation forests in the Northeast: Science, v. 204, p. 304-306.
- Cronan, S.C., Walker, W.J., and Bloom, P.R., 1986, Predicting aqueous aluminum concentrations in natural waters: Nature, v. 324, p. 14-144.
- Dahlgren, R.A., Driscoll, C.T., and McAvoy, D.C., 1989, Aluminum precipitation and dissolution rates in Spodosol Bs horizons in the Northeastern USA: Soil Science Society of America Journal, v. 53, p. 1045-1052.
- David, M.B., and Driscoll, C.T., 1984, Aluminum speciation and equilibria in soil solutions of a Haplorthod in the Adirondack Mountains (New York, USA): Geoderma, v. 33, p. 297-318.
- DeWalle, D.R., Swistock, B.R., and Sharpe, W.E., 1987, Three-component tracer model for stormflow on a small Appalachian forested catchment: Journal of Hydrology, v. 104, p. 301-310.
- Driscoll, C.T., Baker, J.P., Bisogni, J.J., and Schofield, C.L., 1984, Aluminum speciation and equilibria in dilute acidic surface waters of the Adirondack region of New York State: in Bricker, O.P. ed.: Geologic Aspects of Acid Deposition, Boston, Mass., Butterworth, p. 55-75.
- Eshleman, K.N., and Kaufmann, P.R., 1988, Assessing the regional effects of sulfur deposition on surface water chemistry: the Southern Blue Ridge: Environmental Science and Technology, v. 22, p. 685-690.
- Evans, A.J., 1986, Effects of dissolved organic carbon and sulfate on aluminum mobilization in forest soil columns: Soil Science Society of America Journal, v. 50, p. 1576-1578.
- Evans, A.J., and Anderson, T.J., 1990, Aliphatic acids: influence on sulfate mobility in a forested Cecil soil: Soil Science Society of America Journal, v. 54, p. 1136-1139.
- Evans, L.L., 1980, Podzol development north of Lake Huron in relation to geology and vegetation: Canadian Journal of Soil Science, v. 60, p. 527-539.
- Fernandez, L.R., 1989, The effects of lichens (*Parmelia conspersa*) and mosses (*Grimmia laevigata*) on throughfall rain chemistry within a granite outcrop ecosystem in the Georgia Piedmont: Atlanta, Ga., unpublished Senior Honors Thesis, Emory University.
- Fritz, Peter, Cherry, J.A., Wyer, K.U., and Sklash, M.G., 1976, Storm runoff analyses using environmental isotopes and major ions in Proceedings of IAEA: Interpretation of Environmental Isotopes and Hydrochemical Data in Ground Water Hydrology, Advisory Group Meeting, 1975, Vienna, Austria, p. 111-131.
- Galloway, J.N., Norton, S.A., and Church, M.R., 1983, Freshwater acidification from atmospheric deposition of sulfuric acid: a conceptual model: Environmental Science and Technology, v. 17, p. 541A-545A.
- Gaston, L.A., Mansell, R.A., and Rhue, R.D., 1986, Sulfate mobility in acid soils and implications with respect to cation leaching: a review: Soil and Crop Science Society of Florida Proceedings, v. 45, p. 67-72.

REFERENCES--Continued

- Gherini, S.A., Mok, L.F., Hudson, R.J.M., Davis, G.F., Chen, C.W., and Goldstein, R.A., 1985, The ILWAS model: formulation and application: *Water, Air and Soil Pollution*, v. 26, p. 425-459.
- Gholz, H.L., and Fisher, R.F., 1982, Organic matter production and distribution in slash pine *Pinus elliotii*: *Ecology*, v., 66, p. 647-659.
- Giddens, J.E., 1957, Rate of loss of carbon from Georgia soils: *Soil Science Society of America Proceedings*: v., 21, p. 513-515.
- Giddens, J.E. and Garman, W.H., 1941, Some effects of cultivation on the Piedmont soils of Georgia: *Soil Science Society of America Proceedings*, v., 6, p. 439-446.
- Gillman, G.P., and Sumner, M.E., 1987, Surface charge characterization and soil solution composition of four soils from the southern Piedmont in Georgia: *Soil Science Society of America Journal*, v. 51, p. 589-594.
- Gobran, G.R. and Nilsson, S.I., 1988, Effects of forest floor leachate on sulfate retention in a spodosol soil: *J. Environ. Qual.*, v. 17, p. 235-239.
- Gobran, G.R., and Ågren, G.I., 1989, Significance of changes in Kc values for Ca-Al exchange and its effects on soil and water acidification predictions: *Ecological Modelling*, v. 44, p. 165-175.
- Goldstein, R.A., Gherini, S.A., Chen, C.W., Mok, L.F., and Hudson, R.J.M., 1984, Integrated acidification study (ILWAS): a mechanistic ecosystem analysis: *Philosophical Transactions of the Royal Society of London B*, v. 305, p. 409-425.
- Hewlett, J.D., 1961, Soil moisture as a source of baseflow from steep mountain watersheds: U.S. Department of Agriculture, Southeast Forest Experiment Station, paper 132, 10 p.
- Hewlett, J.D., and Hibbert, A.R., 1967, Factors affecting the response of small watersheds to precipitation in humid areas, Sopper, W.E. and Hull, H.W. eds., in: [Proceedings] *Forest Hydrology: International Symposium on Forest Hydrology*, Proceedings: University Park, Pa., Pennsylvania State University.
- Higgins, M.W., Atkins, R.L., Crawford, T.J., Crawford, R.F. III, Brooks, Rebekah and Cook, R.B., 1988, The structure, stratigraphy, technostratigraphy, and evolution of the southernmost part of the Appalachian Orogen: U.S. Geological Survey Professional Paper 1475, 173 p.
- Holland, W., 1954, The geology of the Panola Shoals area: DeKalb County, Georgia: Atlanta, Ga., unpublished M.S. Thesis, Emory University.
- Hooper, R.P., and Shoemaker, C.A., 1986, A comparison of chemical and isotopic hydrograph separation: *Water Resources Research*, v. 22, p. 1444-1454.
- Hooper, R.P., Stone, Alex, Christophersen, Nils, de Grosbois, Edward, and Seip, H. M., 1988, Assessing the Birkenes model of stream acidification using a multi-signal calibration methodology: *Water Resources Research*, v. 24, p. 1308-1316.
- Hooper, R.P., West, C.T., and Peters, N.E., 1990a, Assessing the response of Emerald Lake, an alpine watershed in Sequoia National Park, California, to acidification during snowmelt by using a simple hydrochemical model: U.S. Geological Survey Water-Resources Investigations Report 90-4000, 68 p.
- Hooper, R.P., Christophersen, Nils, and Peters, N. E., 1990b, Modelling streamwater chemistry as a mixture of soilwater end-members -- an application to the Panola Mountain catchment, Georgia, U.S.A.: *Journal of Hydrology*, v. 116, p. 321-343.
- Huang, P.M., and Schnitzer, M.A., 1986, Interactions of soil minerals with natural organics and microbes: *Soil Science Society of America*, Special Publication 17, 606 p.
- Huntington, T.G., Hooper, R.P., Shanley, J.B., and Peters, N.E., 1992a, Soil sulfate retention in relation to hydrologic conditions: implications for watershed acidification [abs.]: *American Society of Agronomy, Annual Meeting, Agronomy Abstracts*, p. 348.
- Huntington, T.G., and Ryan, D.F., 1990, Whole-tree-harvesting effects on soil nitrogen and carbon: *Forest Ecology and Management*, v. 31, p. 193-204.
- Huntington, T.G., Aulenbach, B.T., and Hooper, R.P., 1992b, Hydrologic processes controlling sulfur adsorption: a small watershed approach [abs.]: *American Geophysical Union Fall Meeting, Abstract Supplement*, v. 73, no. 43, p. 160-161.
- Jardine, P.M., Wilson, G.V., Luxmore, R.J., McCarthy, J.F., 1989, Transport of inorganic and natural organic tracers through an isolated pedon in a forested watershed: *Soil Science Society of America Journal*, v. 53, p. 317-323.

REFERENCES--Continued

- Johnson, D.W., and Cole, D.W., 1980, Anion mobility in soils: relevance to nutrient transport from terrestrial to ecosystems: *Environment International*, v. 3, p. 79-90.
- Johnson, D.W., and Todd, D.E., 1983, Relationships among iron, aluminum, carbon, and sulfate in a variety of forest soils: *Soil Science Society of America Journal*, v. 47, p. 792-800.
- Johnson, D.W., Cresser, M.S., Nilsson, S.I., Turner, John, Ulrich, Bernard., Binkley, Dan. and Cole, D.W., 1991, Soil changes in forest ecosystems: evidence for and probable causes: *Proceedings of the Royal Society of Edinburgh*, v. 97B, p. 81-116.
- Johnson, N.M., Driscoll, C.T., Eaton, J.S., Likens, G.E., and McDowell, W.H., 1981, "Acid rain", dissolved aluminum and chemical weathering at the Hubbard Brook Experimental Forest, New Hampshire: *Geochimica Cosmochimica Acta*, v. 45, p. 1421-1437.
- Kendall, Carol, 1992, Temporal, spatial, and species effects on the oxygen and hydrogen isotopic composition of throughfall [abs.]: *American Geophysical Union Fall Meeting Abstract Supplement*, v. 73, no. 43, p. 160-161.
- Kendall, Carol, 1993, Impact of isotopic heterogeneity in shallow systems on stormflow generation: College Park, Md., unpublished Ph.D. Thesis, University of Maryland.
- Kennedy, V.C., Kendall, Carol, Zellweger, G.W., Wynman, T.A., and Avanzino, R.J., 1986, Determination of the components of stormflow using water chemistry and environmental isotopes, Mattole River basin, California: *Journal of Hydrology*, v. 84, p. 107-140.
- Kovacic, D.A., Leff, A.A., Civavolo, T.G., and McLeod, K.W., 1989, Potential cation leaching losses following disturbance across southeastern coastal plain landscape gradients: *In Proceedings, Sharitz, R.R. and Gibbons, J.W., eds.: Oak Ridge, Tennessee, Freshwater, Wetlands and Wildlife Symposium, 1989*, p. 113-126.
- Kuylenstierna, J.C.I. and Chadwick, M.J., 1991, Increases in soil acidity in North-West Wales between 1957 and 1990: *Ambio*, v. 20, p. 118-119.
- Lee, J.J., 1985, Effect of simulated sulfuric acid rain on the chemistry of a sulfate-adsorbing forest soil: *Water, Air and Soil Pollution*, v. 25, p. 185-193.
- Linthurst, R.A., 1984, The acidic deposition phenomenon and its effects: Critical assessment review papers. U.S. Environmental Protection Agency, Effects Sciences, v. 2, USEPA-600/83-016BF, Washington, D.C.
- Mann, L.K., 1985, A regional comparison of carbon in cultivated and uncultivated Alfisols and Mollisols in the Central United States: *Geoderma*, v. 36, p. 241-253.
- Mann, L.K., 1986, Changes in soil carbon storage after cultivation: *Soil Science*, v. 142, p. 279-288.
- Mathews, J., 1941, A survey of the flora of Mount Panola: Atlanta, Ga., unpublished M.S. Thesis, Emory University, 94 p.
- McBride, M.B., and Bloom, P.R., 1977, Adsorption of aluminum by a smectite, II, an Al^{3+} - Ca^{2+} exchange model: *Soil Science Society of America Journal*, v. 41, p. 1073-1077.
- McCull, J.G., and Pohlman, A.A., 1987, Soluble organics and their chelating influence on Al and other metal dissolution from forest soils by soluble organics: *Water, Air, and Soil Pollution*, v. 31, p. 917-927.
- Meyers, T.P., Hicks, B.B., Hosker, R.P. Jr., Womack, J.D. and Satterfield, L.C., 1991, Dry deposition inferential measurement techniques-II. Seasonal and annual deposition rates of sulfur and nitrogen: *Atmospheric Environment*, v. 25A, p. 2361-2370.
- Miller, W.R., and Drever, J.I., 1977, Chemical weathering and related controls on surface water chemistry in the Absaroka Mountains, Wyoming: *Geochimica Cosmochimica Acta*, v. 41, p. 1693-1702.
- Mitchell, M.J., R.B. Harrison, R.B., Fitzgerald, J.W., Johnson, D.W. Lindberg, S.E. Zhang, Yi, and Autry, A.A., 1992, Sulfur distribution, and cycling in forest ecosystems, *in Johnson, D.W. and Lindberg, S.E., eds., Atmospheric deposition and forest nutrient cycling, a synthesis of the Integrated Forest Study: New York, Springer-Verlag*, v. 91, p. 72-149.
- Nelson, T.C., 1957, The original forests of the Georgia Piedmont: *Ecology*, v. 38, p. 390-397.
- Newton, R.M., Weintraub, Jill, and April, R.H., 1987, The relationship between surface water chemistry and geology in the North Branch of the Moose River: *Biogeochemistry*, v. 3, p. 21-35.
- Nixon, R.A., 1981, Rates and mechanisms of chemical weathering in an organic environment at Panola Mountain, Georgia: Atlanta, Ga., unpublished Ph.D. Thesis, Emory University, 172 p.

REFERENCES--Continued

- Omernik, J.M., 1987, Ecoregions of the conterminous United States: *Annals of the Association of American Geographers*, v. 77, p. 118-125.
- Pearce, A.J., Stewart, M.K., and Sklash, M.G., 1986, Storm runoff generation in humid catchments - 1. where does the water come from?: *Water Resources Research*, v. 22, p. 1263-1272.
- Peters, N.E., and Driscoll, C.T., 1987, Hydrogeologic controls of surface-water chemistry in the Adirondack Region of New York State: *Biogeochemistry*, v. 3, p. 163-180.
- Peters, N.E., and Murdoch, P.S., 1985, Hydrogeologic comparison of an acidic-lake basin with a neutral-lake basin in the west-central Adirondack Mountains, New York: *Water, Air, and Soil Pollution*, v. 26, p. 387-402.
- Peters, N.E., 1989, Atmospheric deposition of sulfur to a granite outcrop in the Piedmont of Georgia, U.S.A.: *International Association of Hydrologic Science Publication*, v. 179, p. 173-181.
- Pilgrim, D.H., Huff, D.D., and Steele, T.D., 1979, Use of specific conductance and contact time relations for separating flow components in storm runoff: *Water Resources Research*, v. 15, p. 329-339.
- Pionke, H.B., Hoover, J.R., Schnabel, R.R., Gburek, W.J., Urban, J.B., and Rogowski, A.S., 1988, Chemical-hydrologic interactions in the near-stream zone: *Water Resources Research* v. 24, p. 1101-1110.
- Plummer, G.L., 1969, Fallout radioisotopes in Georgia lichens, *in* [Proceedings] Nelson, D.J. and Evans, F.C. eds. *Symposium on Radioecology, Proceedings of the Second National Symposium, Ann Arbor Michigan, May 15-17, 1967*, p. 571-577.
- Pohlman, A.A., and McColl, J.G., 1986, Kinetics of metal dissolution from forest soils by organic acids: *Journal of Environmental Quality*, v. 14, p. 86-91.
- 1988, Soluble organics from forest litter and their role in metal dissolution: *Soil Science Society of America Journal*, v. 52, p. 265-271.
- Ragsdale, H. L. and Harwell, M. A., 1969, A map of the island ecosystems of Panola Mountain: *Bull. Ga. Acad. Sci.*, v. 27, p. 83.
- Reuss, J.O., 1983, Implications of the calcium-aluminum exchange system for the effect of acid precipitation on soils: *Journal of Environmental Quality*, v. 12, p. 591-595.
- Reuss, J.O., and Johnson, D.W., 1986, *Acid Deposition and Acidification of Soils and Waters*: New York, Springer-Verlag, 119 p.
- Reuss, J.O., Christophersen, Nils, and Seip, H.M., 1986a, A critique of models for freshwater and soil acidification: Oslo, Norway, Center for Industrial Research Report SI-850137-1, 43 p.
- Reuss, J.O., Johnson, D.W., and Seip, H.M., 1986b, A critique of models for freshwater and soil acidification: *Water, Air and Soil Pollution*, v. 30, p. 909-930.
- Rogers, 1971, Vegetational and environmental analysis of shrub-tree communities on a granite outcrop: Atlanta, Ga., unpublished M.S. Thesis, Emory University.
- Schallascha, E.B., Appelt, H.H., and Schatz, A.A., 1967, Chelation as a weathering mechanism: I, Effects of complexing agents in the solubilization of iron from minerals and granodiorite: *Geochimica et Cosmochimica Acta*, v. 31, p. 587-596.
- Schlesinger, W.H., 1985, Changes in soil carbon storage and associated properties with disturbance and recovery, Sixth ORNL Life Sciences Symposium: *The Global Carbon Cycle*, Knoxville, Tenn., October 31 - November 2.
- Shanley, J.B., 1989, Factors controlling sulfate retention and transport at Panola Mountain, Georgia: Laramie, Wyo., unpublished Ph. D. Thesis, University of Wyoming, 79 p.
- 1992, A comparison of sulfate retention characteristics in soils receiving differential sulfate loadings at Panola Mountain, Georgia: *Soil Science*, v. 153, p. 499-508.
- Shanley, J.B. and Peters, N.E. Variations in aqueous sulfate concentrations at Panola Mountain, Georgia: *Journal of Hydrology*, in press.
- 1988, Preliminary observations of streamflow generation during storms in a forested Piedmont watershed using temperature as a tracer: *Journal of Contaminant Hydrology*, v. 3, p. 349-365.
- Shure, D. J. and Ragsdale, H. L., 1977, Patterns of primary succession on granite outcrop surfaces: *Ecology*, v. 58, p. 993-1006.

REFERENCES--Continued

- Singh, B.R., 1984, Sulfate sorption by acid forest soils, 2 Sulfate adsorption isotherms with and without organic matter and oxides of aluminum and iron: *Soil Science*, v. 138, p. 294-297.
- Skeen, J.N., Carter, M.E., and Ragsdale, H.L., 1980, Yellow poplar: The Piedmont case: *Bulletin of the Torrey Botanical Club*, v. 107, p. 1-6.
- Sklash, M.G., Farvolden, R.N., and Fritz, Peter, 1976, A conceptual model of watershed response to rainfall, developed through the use of oxygen-18 as a natural tracer: *Canadian Journal of Earth Science*, v. 13, p. 271-283.
- Sklash, M.G., Stewart, M.K., and Pearce, A.J., 1986, Storm runoff generation in humid catchments - 1. A case study of hillslope and low-order stream response: *Water Resources Research*, v. 22, p. 1273-1282.
- Sollins, Phillip, and McCorison, F. M., 1981, Nitrogen and carbon solution chemistry of an old growth coniferous forest watershed before and after cutting: *Water Resources Research*, v. 17, p. 1409 - 1418.
- Trimble, S.W., 1974, Man-induced Soil Erosion in the Southern Piedmont, Ankeny, Iowa, *Soil Conservation Society of America*.
- Triska, F.J., Kennedy, V.C., Avanzino, R.J., Zellweger, G.W., and Bencala, K.E., 1989a, Retention and transport of nutrients in third-order stream: channel processes: *Ecology*, v. 70, p. 1877-1892.
- 1989b, Retention and transport of nutrients in third-order stream in northwestern California: hyporheic processes: *Ecology*, v. 70, p. 1893-1905.
- Turner, J.V., MacPherson, D.K., and Stokes, R.A., 1987, The mechanisms of catchment flow processes using natural variations in deuterium and oxygen-18: *Journal of Hydrology*, v. 94, p. 143-162.
- Ulrich, Bernard, Mayer, R.J., and Khanna, P.K., 1980, Chemical changes due to acid precipitation in a loess-derived soil in Central Europe: *Soil Science*, v. 130, p. 193-199.
- U.S. Department of Commerce, National Oceanic and Atmospheric Administration, 1931, Climatic summary of United states through 1930, Atlanta, Fulton County, Georgia: U.S. Department of Commerce, Asheville, N.C.
- 1961, Local climatological data with comparative data, 1960, Atlanta, Georgia: U.S. Department of Commerce, Weather Bureau, Asheville, North Carolina, no. 850, 3 p.
- 1991, Local climatological data, annual summary with comparative data, 1990, Atlanta, Georgia: U.S. Department of Commerce, Weather Bureau, Asheville, North Carolina, ISSN 0198-1560, 6 p.
- Vance, G.F., Mokma, D.L., and Boyd, S.A., 1986, Phenolic compounds in soils of hydrosequences and developmental sequences in Spodosols: *Soil Science Society of America Journal*, v. 50, p. 992-996.
- Voroney, R.P., VanVeen, J.A., and Paul, E.A., 1981, Organic carbon dynamics in grassland soils: 2. Model validation and simulation of the long-term effects of cultivation and rainfall erosion.: *Canadian Journal of Soil Science*, v. 61, p. 211-224
- Walker, W.J., Cronan, C.S., and Patterson, H.H., 1988, A kinetic study of aluminum adsorption by aluminosilicate clay minerals: *Geochimica Cosmochimica Acta*, v. 52, p. 55-62.
- White, R.E., 1985, The influence of macropores on the transport of dissolved and suspended matter through soil: *Advances in Soil Science*, v. 3, p. 95-120.
- Wilson, G.V., and Luxmore, R.J., 1988, Infiltration, macroporosity, and mesoporosity distributions on two forested watersheds: *Soil Science Society of America Journal*, v. 52, p. 329-335.