ACID-RAIN DAMAGE TO CARBONATE STONE: A PRELIMINARY QUANTITATIVE ASSESSMENT BASED ON THE AQUEOUS GEOCHEMISTRY OF RAINFALL RUNOFF

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 87-4016

Prepared in cooperation with the
NATIONAL PARK SERVICE

DEPARTMENT OF THE INTERIOR

DONALD PAUL HODEL, Secretary

U.S. GEOLOGICAL SURVEY

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METRIC CONVERSION FACTORS

For use of readers who prefer to use International System (SI) units, rather than inch-pound terms used in this report, the following conversion factors may be used:

Multiply	By	To obtain
foot (ft)	0.3048	meter (m)
foot squared per day (ft²/d)	0.0929	meter squared per day (m²/d)
cubic foot per second (ft³/s)	0.02832	cubic meter per second (m³/s)
gallon per minute (gal/min)	0.0630	liter per second (L/s)
million gallon per day (Mgal/d)	0.0438	cubic meter per second (m³/s)
inch (in.)	25.40	millimeter (mm)
inch per year (in./yr)	25.40	millimeter per year (mm/yr)
mile (mi)	1.609	kilometer (km)
square mile (mi²)	2.590	square kilometer (km²)

Temperature in degree Celsius (°C) can be converted to degree Fahrenheit (°F) by using the following formula:

$$°F = 1.8 \times °C + 32.$$

ACID-RAIN DAMAGE TO CARBONATE STONE: A PRELIMINARY QUANTITATIVE
ASSESSMENT BASED ON THE AQUEOUS GEOCHEMISTRY OF RAINFALL RUNOFF

By Michael M. Reddy

ABSTRACT

An onsite experimental procedure was used to identify and quantify acid-rain damage to carbonate stone, based on the change in rain-runoff chemical composition. Observed changes in stone runoff are attributed to the interaction of acidic species present in the rain with the stone surface. Onsite data obtained during the summer and fall of 1984 at three locations in the northeastern United States indicates that carbonate-stone surface recession is related to acid deposition. Although the study is continuing, current data are not adequate to distinguish differences in the acid-stone reaction between limestone and marble nor among the three study sites. A single linear relation between carbonate-stone surface recession (the dependent variable) and hydrogen ion loading to the stone surface (the independent variable) appears to describe the data set.

INTRODUCTION

Environmental damage to commercial materials and historical structures has been recognized during the past century, and has been the focus of recent research. Damage to both metals and building stone has been documented in several areas of Europe and North America (Environmental Resources Limited, 1983; Del Monte and others, 1981; Camuffo and others, 1982; Cheng and Castillo, 1984). Research on building-stone damage by air pollution has focused on the net long-term effect (Sharp and others, 1982) and the specific effect of sulfur dioxide (Luckat, 1977). In the United States, damage to carbonate stone by sulfur dioxide has been reported by Haynie (1983).

Previous studies of environmental damage to carbonate stone have dealt with the effect of air pollutants in general and sulfur dioxide in particular. Air-pollution levels in the northeastern United States have decreased during the past decade. Air-pollutant damage to building stone and, in particular, that due to sulfur dioxide, may be less significant currently than in the past because of decreased urban pollution. In contrast to the decrease in sulfur dioxide concentrations, acidic deposition in the northeastern United States appears to remain significant.

Because of the anticipated decrease in sulfur dioxide damage to carbonate stone in the northeastern United States, it is appropriate to identify and quantify the effect of acid deposition on carbonate building stone. Separation of the effect of air pollutants and dry deposition from that of acid precipitation may be necessary to determine the mechanism of damage to building stone in the environment.

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Previous Work

The study of damage to carbonate-building stone by air pollutants has focused on the reaction of gaseous sulfur dioxide forming calcium sulfate minerals on the stone surface. This surface-sulfate formation process has been a particularly effective damage mechanism where dioxide concentrations in air are large. Sulfate-formation damage is affected by those factors that control transfer of sulfur dioxide to the liquid film (when present) on the stone surface.

Procedures used to characterize carbonate-stone erosion have involved characterization of surface crusts on carbonate stone (DelMonte and others 1981; Camuffo and others 1982; Cheng and Castillo 1984; and Camuffo and others 1984), weight-loss measurements (Haynie 1983), microerosion measurements (High and Hanna 1970; Sharp and others 1982), and comparison of current stone dimensions with historic records (Husar and others 1985; Sharp and others 1982). Results obtained by previous investigations of carbonate-stone damage have emphasized the importance of atmoshperic pollutants, that is, contaminants on the stone surface that facilitate pollutant transformation and the effect of rain.

High and Hanna (1970), in an early streambed geomorphology application of microerosion techniques, stress that numerous microerosion measurements must be made over a large area before an average erosion rate can be considered significant. Sharp and others (1982) using both a microerosion technique and a historical-based retrospective approach at St. Paul's Cathedral, London, England, reported that weathering rates differed depending on the stone-surface microhydrology. Weathering was more rapid in drip zones than in exposed flow zones. Husar and others (1985) in a retrospective tombstone study in the northeastern United States, reported a linear relation between weathering rates and estimated sulfur dioxide concentrations. A value of 0.1 micrometer per year per part per billion sulfur dioxide was derived as the best estimate for weathering of fine-grained marble from New York City.

Haynie (1983) related marble erosion in St. Louis, Missouri, to stone surface time-of-wetness, wind speed, temperature, and air-pollutant concentrations. Stone surface time-of-wetness was the only statistically significant factor in stone damage. The effect of sulfur oxides was found to be not significant. Cheng and Castillo (1984) reported carbonate-stone damage in Schenectady, New York, attributable to sulfur dioxide uptake facilitated by soot particles on the stone surface. Luckat (1977) reported that onsite damage to carbonate stone at the Cologne Cathedral, West Germany, correlated with the rate of sulfur dioxide uptake.

Del Monte and others (1981) examining marble deterioration in northern Italian urban areas, reported that carbonaceous particles, serving as catalysts, are important agents of deterioration. Camuffo and others (1982) stressed the importance of rainfall in carbonate-stone deterioration: moisture condensation was believed to play only a minor role. Studies in Venice, Italy, by Camuffo and others (1984) where rain acidity is uncommon, have demonstrated only rare instances of acid-rain damage to carbonate stone.

Acid-deposition damage to carbonate stone may be an important stone-damage mechanism, but few quantitative data are available that relate acid loading to stone deterioration (Sherwood and Doe, 1984). In addition to onsite studies, laboratory investigations (Reddy and others, 1981) and chemical modeling (see for example Nordstrom and others, 1979) can be used to estimate the extent of acid dissolution of carbonates. Laboratory studies and chemical modeling may have direct application in understanding acid-rain damage to carbonates. However, the fact remains that little fundamental understanding of the processes involved in environmental damage to stone is available. The most relevant demonstration of acid-deposition damage to carbonate stone appears to be onsite measurements of representative carbonate stone under carefully monitored conditions.

Purpose and Scope

Research in the fields of geochemistry (Reddy and others, 1981 and references therein) and geomorphology (High and Hanna, 1970) demonstrates that reaction of calcium carbonate with aqueous solutions in the laboratory and onsite follows behavior anticipated from chemical equilibrium and kinetics. However, little fundamental understanding of the processes involved in environmental damage to stone is available. In particular, quantitative estimates of carbonate-stone acid-precipitation reactions are not reliable. This situation leads to large uncertainties in projecting acid-precipitation effects on limestone and marble.

The objective of this research program is to characterize and quantify environmental damage on carbonate stone. The program focus will be to address the effect of acidic precipitation on stone. Where possible, the separate contributions of wet and dry deposition on the observed stone deterioration will be evaluated.

This report presents initial data obtained with an onsite, acid-rain stone-damage technique at three locations in the northeastern United States during the last half of 1984. Work was done in cooperation with the National Park Service in conjunction with the National Atmospheric Precipitation Assessment Program (NAPAP) to characterize acid-rain damage to carbonate building stone (Sherwood and Doe, 1984). Onsite measurements of physical and chemical characteristics of rainfall and stone runoff, and laboratory analysis of rainfall and stone runoff samples have been used to estimate stone dissolution and acid loading to limestone and marble reference stones. Exposure conditions have been patterned after the American Society for Testing Materials (ASTM) protocols developed for metal-damage studies (David Flinn, U.S. Bureau of Mines, Avondale Research Center, Avondale, Md., oral commun., 1986).

A multivariate statistical analysis, using linear-regression models, has been conducted to identify environmental conditions related to carbonate-stone damage. This preliminary analysis has been restricted to those experimental and environmental variables available at the time of sample collection. Detailed climatological, meteorological, and air-pollution data will be available eventually, and can be incorporated into a more general analysis of the onsite data.

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The onsite experimental procedure consisted of exposing carbonate stones and monitoring changes in rain composition due to rain reaction with the stone surface. Stones, representative of those used in commerce (Ross and Knabe, 1984; Ross, 1985), were boldly exposed at 30 degrees from the horizontal facing south, and were uncovered at all times. The experiment employing a fixed-sample orientation was not planned to reflect all the actual orientations and exposures of materials in place but did enable direct comparison between sites.

During environmental exposures, processes other than acid attack can occur and lead to carbonate-stone damage. The experimental procedure adopted in this study minimized extraneous experimental variability. Runoff experiments have several advantages in the assessment of acid-rain damage to stone. Equipment, analytical procedures, and quality-control techniques are readily available. Moreover, runoff experiments can yield carbonate-stone-damage rates in a short time. In contrast, weight-loss experiments, for example, may require several years to yield valid carbonate-stone damage. These experimental attributes can be contrasted with disadvantages which deal mainly with separation of the effects of wet and dry acidic deposition on stone damage. These disadvantages involve the interaction of several environmental processes including: (1) Wet and dry deposition; (2) gaseous pollutants and wet deposition; (3) biological effects and wet deposition; and (4) aging of the stone surface and wet deposition. Several descriptions of the installation and operation of materials damage field sites have been recently published (Sherwood and Doe, 1984; Reddy and others, 1985a and b; Reddy and Werner, 1985).

PROCEDURES

At the present time, four NAPAP research stone-exposure sites have been established. These sites are operated in the eastern United States at Newcomb, N.Y.; Chester, N.J.; Washington, D.C.; and Research Triangle Park, N.C. (fig. 1).

Study-Site Design

Four stone-exposure racks, fabricated of polypropylene and capable of holding two stones each, are located at each research site. Stone-exposure racks have been designed to facilitate collection of rain runoff from the stone surface (fig. 2) for comparison with the composition of incident rainfall. Stones are 1 foot by 2 feet by 2 inches in size, are sloped (30 degrees to the horizontal), and face south.

The design of the stone-runoff racks incorporated features to minimize the effect of processes other than rain interaction with the stone surface. Specific experimental complications that were avoided include: (1) Development of standing water on the stone surface; (2) presence of accumulated moisture on the back side of the stones; (3) accumulation of particulate material in the runoff sample; and (4) exposure of an ill-defined stone-surface rainfall interception area. Reference stones are held slightly off the collector base by rails. Slotted and circular openings (shown in fig. 2 in an unoccupied rack) are intended to decrease the accumulation of moisture
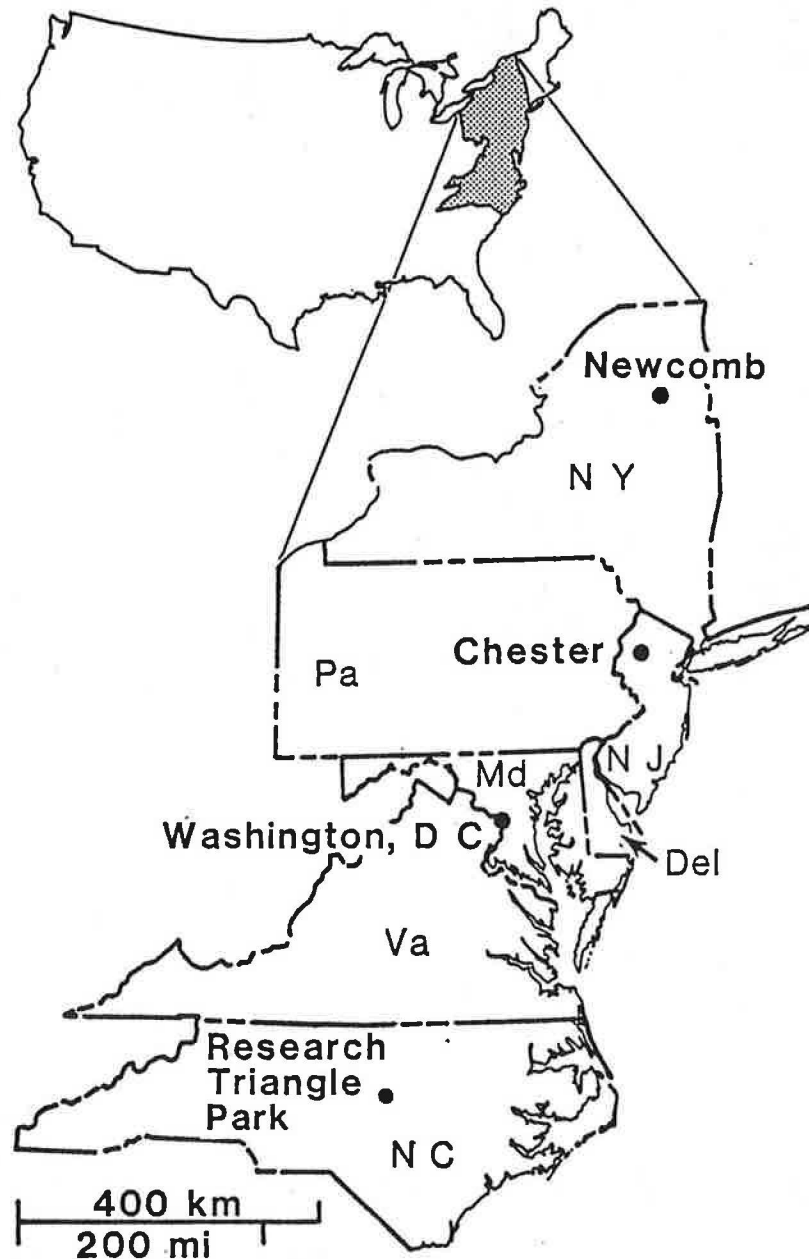
Figure 1.--Stone-exposure site locations in the
eastern United States.

on the lower stone surface. Incident rainfall strikes the inclined (30 degrees) stone surface and runs over the stone. At the base of the rack, this runoff is directed through a plastic tube to a covered plastic collection bottle. A glasswool filter was placed in the tube to prevent particulate material from entering the sample-collection bottle.
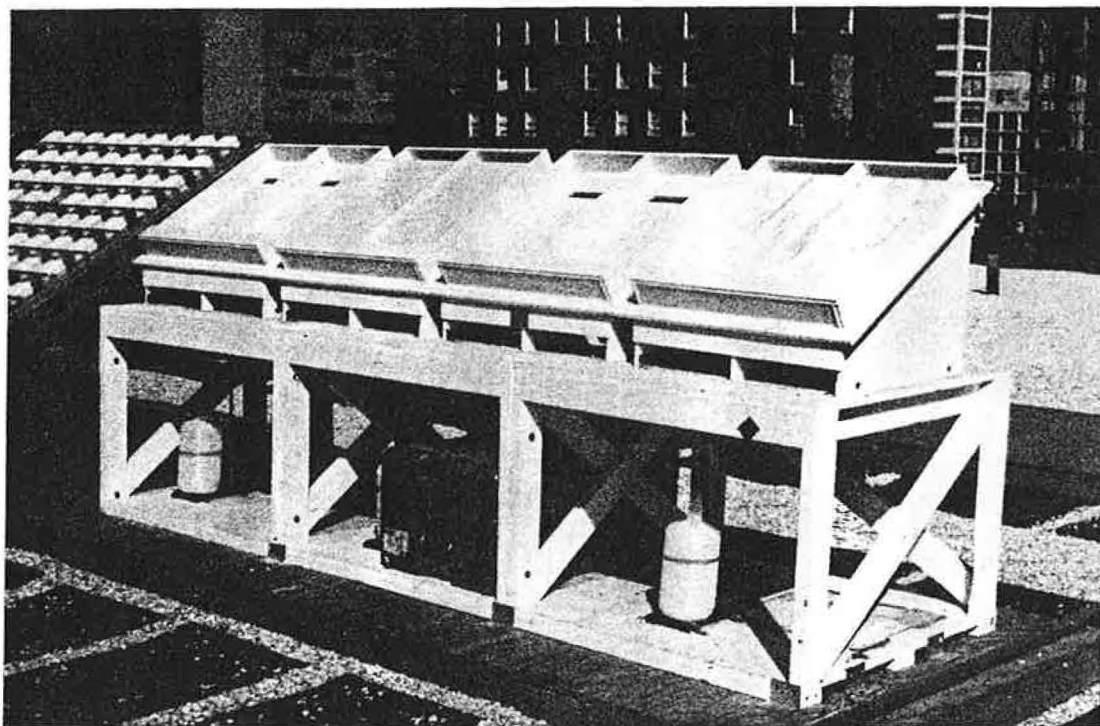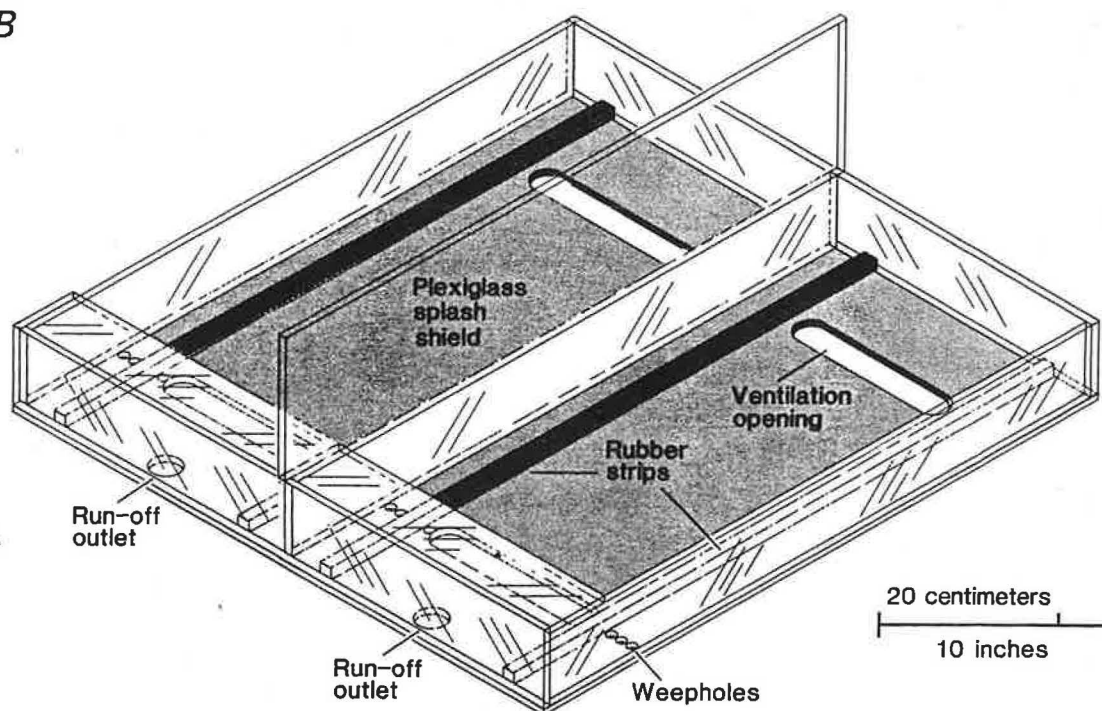
Figure 2.--*A*, typical completed research stone-exposure site with research stones in place; *B*, Isometric projection of a single research stone-exposure rack.

Details of runoff-experiment operation were developed based on actual onsite operation of the equipment. These details then were incorporated into a Site Operators Manual that is supplied to each site and members of NAPAP Task Group G.

Limestone and marble stones are located in two of the racks; a third empty rack (without a stone) is used as a control (hereafter referred to as a blank sample). At the end of each rainstorm, after measurement of the total runoff volume, a 1-liter subsample, or the total runoff if less than 1 liter, was taken for subsequent analysis. Runoff volume, specific conductance, and pH measurements were determined at the research-stone exposure sites as soon as possible after collection, typically within a few hours. Samples then were filtered through a 0.45-micrometer pore-size Schleicher and Schuell filter (grade OE67)[1], placed in a clean polyethlyene bottle, and sent to the U.S. Geological Survey National Water Quality Laboratory in Denver, Colo., for chemical analysis. Samples from Chester, N.J., were not processed onsite. Unprocessed samples were mailed directly to Denver. Details of the onsite and laboratory procedures, as well as a brief summary of results, are given by Reddy and Werner (1985). Sample preparation, analytical procedures, and laboratory quality-control procedures for the water sample are described by Fishman and Friedman (1985).

Ancillary Study-Site Measurements

Each research-stone exposure site has other materials-damage experiments in addition to those discussed in this report. These supplemental data include an array of meteorological, climatological, air-pollution, and rainfall-chemistry measurements. The character of the general environment in which the rock samples were exposed has been given by Flinn and others (1986).

Analytical Techniques and Quality-Control Procedures

Rain and runoff samples were chemically analyzed by the U.S. Geological Survey National Water Quality Laboratory. The chemical analysis of the runoff sample has been recently described by Reddy and Werner (1985). Blank and stone runoff, pH, and specific conductance were measured in the field. Upon receipt of samples in the laboratory, pH and specific conductance were re-measured, and sample alkalinity was determined. Each sample was analyzed for calcium and sulfate ion concentrations. On selected samples more extensive chemical analyses were performed as a quality-control procedure. In addition, blank, duplicate, and Standard Reference Water Samples (SRWS) were processed onsite and submitted for analysis at the same time as field samples. In general, results for the blank samples were less than the detection limit of the methods used. Analytical method detection limits and precision values are given by Fishman and Friedman (1985).

Analytical precision for SRWS and duplicate samples was typically better than 10 percent (expressed as percent relative standard deviation). Recovery values for the SRWS were always within two standard deviations of the most probable value.

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[1]Use of trade names used in this report are for identification purposes only and does not constitute any endorsement by the U.S. Geological Survey.

As an additional check on analytical accuracy, ionic balances were calculated for the major components determined in each sample. A summary of the ionic-balance data is given in table 1. These ionic balances show a slight anion excess, that may result from the absence of ammonium ion determinations. Ammonium ion was not determined, because the samples were not appropriately preserved for this determination.

Table 1.--*Summary of ionic-balance calculations for rainfall-runoff solutions from three stone-research sites: Newcomb, N.Y.; Chester, N.J.; and Research Triangle Park, N.C.*

Type of data	Number of cases	Mean absolute value of the difference in ion balance[1] (percent)	Standard deviation of the mean difference (percent)
Stone------------	74	7.7	4.5
Stone[2]------------	81	9.9	9.6
Blank------------	37	25	15

[1]Calculated by dividing the absolute value of difference between the cation concentration and anion concentration by the sum of the anion and cation concentrations. This ratio is expressed as a percentage by multiplying by 100.
[2]Includes ion-balance outliers.

RESULTS AND DISCUSSION

Onsite results obtained during the summer and fall of 1984 are summarized in table 2; rainfall amount data were not available for the Washington, D.C., site during the period covered here. Tabulated values include the number of rainfall events for each stone type at each site, the range of rainfall amounts; the ranges of incident rainfall and runoff pH, the calculated hydrogen-ion loading, the calculated stone recession per rainfall event, and a parameter (sulfur dioxide) related to sulfate formation on the stone surface. The data set used for this summary is listed in tables 7 through 12 at the back of this report.

Rainfall-Runoff Measurement

Carbonate-stone-surface loss is calculated from the amount of calcium ion added to rainfall as it reacts and flows from the surface of the stone. The concept of surface recession due to marble dissolution by acid rain is shown in figure 3. With rainfall runoff from a marble surface, minimal porosity restricts acid reaction with the carbonate mineral of the surface zone.

Table 2.--*Summary of ranges for stone rainfall-runoff experiments for a selected data set for for three stone-research sites: Newcomb, N.Y.; Chester, N.J.; and Research Triangle Park, N.C., during the summer and fall of 1984*

[mm, millimeter; meq/m^2 milliequivalent per square meter; μm, micrometer; ppb SO$_2$*days, parts per billion of sulfur dioxide gas in air times the number of days between rain events]

Type of data	Research Triangle Park, N.C.	Chester, N.J.	Newcomb, N.Y.
LIMESTONE EXPERIMENT			
Rain events-----------	13	10	16
Rain (mm)-------------	5-55	6-57	4-28
Incident rainfall pH---	4-4.5	3.9-4.7	4.0-4.7
Runoff pH-------------	7.4-9.1	5.9-8.1	7.7-8.6
H$^+$load (meq/m^2)--------	0.2-2.3	0.3-3.6	0.1-1.7
CaCO$_3$ lost (μm)--------	0.02-0.6	0.04-0.3	0.04-0.17
Antecedent SO$_2$ (ppb SO$_2$*days).	4-40	20-50	2-16
MARBLE EXPERIMENT			
Rain events-----------	18	9	15
Rain (mm)-------------	2-50	6-41	4-28
Incident rainfall pH---	3.8-5.5	3.9-4.9	4.0-4.6
Runoff pH-------------	7.0-8.8	6.5-7.8	7.1-8.3
H$^+$load (meq/m^2)--------	0.03-2.3	0.2-3.7	0.2-1.7
CaCO$_3$ lost (μm)--------	0.02-0.35	0.05-0.28	0.01-0.16
Antecedent SO$_2$ (ppb SO$_2$*days).	4-40	20-50	2-16

Acid-deposition interaction with a porous carbonate stone differs from rainfall interaction with a marble surface. Additional factors that may affect acid reaction with a porous carbonate surface (fig. 4) include: rain infiltration, dissolution and precipitation reactions within the stone, and leaching and subsequent movement of solutes from the interior to the stone surface.
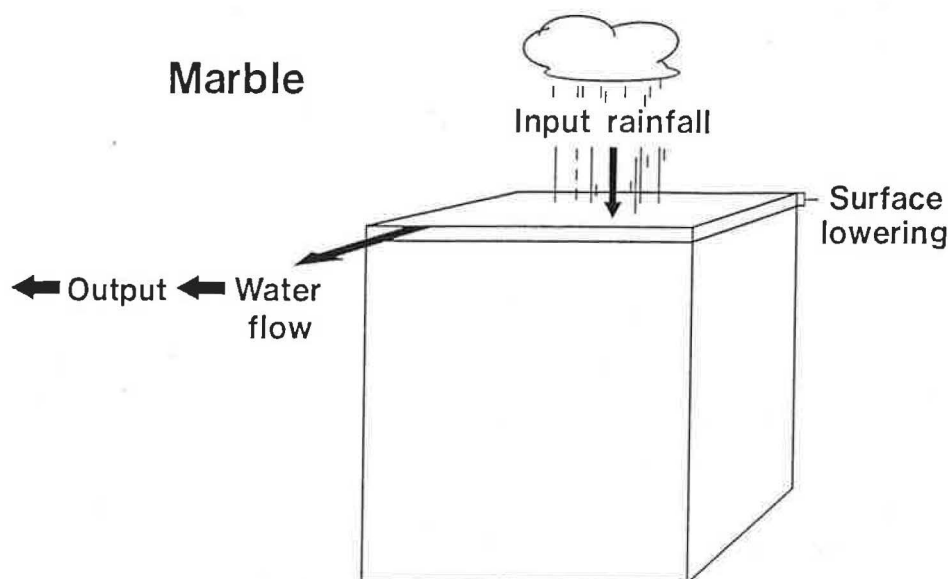
Marble

Figure 3.--Schematic diagram of surface recession from rain flowing over a low porosity marble stone.

In addition to stone characteristics, the amount and intensity of rainfall will affect the runoff characteristics from a porous limestone. Small amounts of light rain falling on a dry, porous stone will cause little or no rainfall runoff. If none of the incident rain runs from the surface of the stone, no calcium ion is removed from the stone surface; thus, no observable net dissolution of the stone surface has occurred. With a porous limestone, in addition to loss of surface material through surface runoff, rain may infiltrate the interior of the stone. This infiltrating solution subsequently may reprecipitate calcium carbonate within the pore spaces, perhaps decreasing the limestone porosity. Surface loss by other processes, such as granular dissaggregation, may lead to additional stone-surface damage.

Incident rainfall amount (expressed as depth, in millimeters) and the stone rainfall-runoff volume (expressed in liters) are variables used to calculate acid-rain loading and damage to stone (Reddy and Werner, 1985). The relation between rain amount and runoff volume (that is, the microhydrology of the test stones) can be determined by direct measurement. In addition, the geometric projection of the stone surfaces can be used to calculate an intercepted volume of rain.

Samples collected at Research Triangle Park during 1984 (fig. 5) illustrate several features of the sample microhydrology. Runoff volumes from each of the three sample types (that is, limestone, marble, and a blank) have been analyzed using a statistical linear regression. In figure 5 the calculated interception volume for stone is referred to as ideal stone runoff. The blank collector (fig. 2B) has a smaller interception area because of the weep holes and vent openings. The calculated blank interception volume is referred to as ideal blank runoff in figure 5.
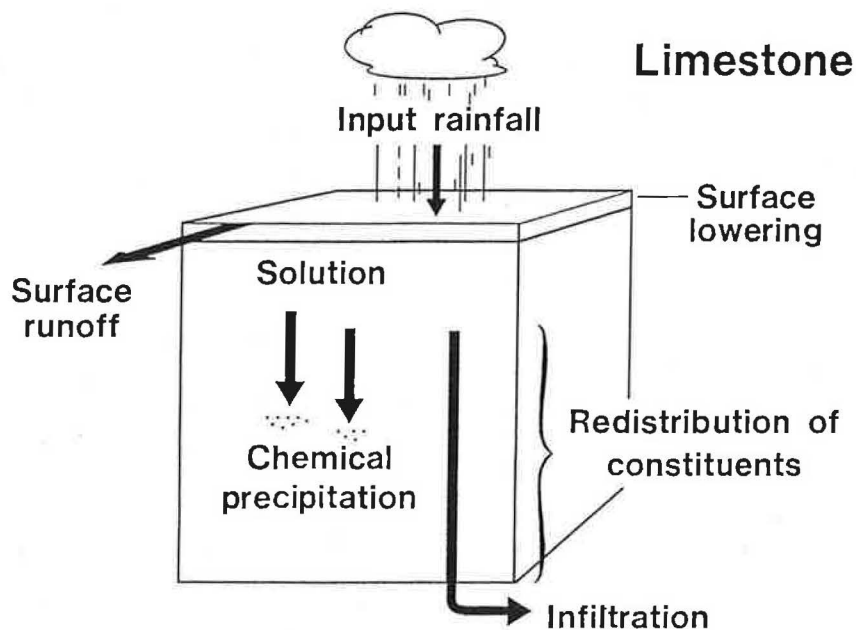
Figure 4.--Surface recession from rain flowing over a porous-
limestone surface.
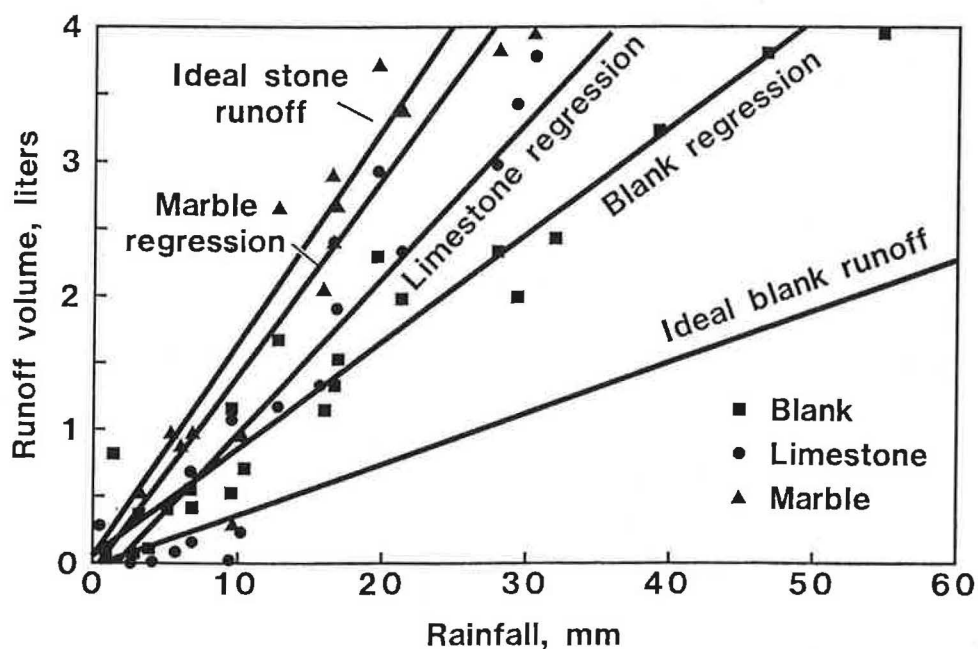
Figure 5.--Runoff volume versus rainfall amount for samples collected at
Research Triangle Park, N.C., during the summer and fall of 1984.

Regression analysis for each of the three test surfaces shows significant correlation. The slope and intercept values among the test surfaces are consistent with the properties of each surface. The intercept obtained from the regression analysis is the rainfall volume collected by the test surface allowing measurable runoff. Regression analysis slope values of each data set in figure 5 correspond to the runoff produced per rainfall amount when the surface is fully wet. For the marble and the blank surface the volume of rain needed to wet the surface is about 25 milliliters. Limestone, because of its greater porosity, requires approximatly 200 milliliters of rain to wet the surface.

The slopes of the regression lines are consistent with the runoff surfaces. Marble has a slope similar to that for ideal stone runoff, indicating that little rain infiltrates the marble surface. Limestone regression lies well below that for marble, indicating that the porous stone apparently adsorbs additional water after that needed for surface wetting. The blank-sample regression lies well above the ideal value, which implies that rain may be more efficiently collected than that anticipated based on the apparent interception area. Incident rain may flow or splash over the weep holes, giving a greater collection efficiency than that calculated from the geometric interception area.

For rainfall greater than 20 millimeters the rain amount needed to wet the limestone is only a fraction of the total incident rainfall. Under these circumstances the runoff amount for limestone increases. Rainfall-runoff data for the other sites studied are similar to rainfall-runoff data for Research Triangle Park.

Several approaches have been examined for comparing rainfall-runoff amount to rainfall. Linear least-squares regressions of log-transformed rainfall amount to log-transformed runoff volume appear to give a useful representation of the statistical relation between rainfall and runoff.

As a test of the goodness-of-fit of the rain-runoff rain-amount regressions, runoff amounts were calculated and compared with observed values. For limestone and for marble the values of actual-minus calculated volume are scattered. Reasons for this scatter are not known but may arise because rain-collection efficiency is extremely dependent on local meteorological conditions. During some onsite runoff measurements, rainfall-runoff volume from one or both stones was unavailable and was calculated from the linear-regression equation.

Factors Affecting Stone-Surface Recession

Rainfall Amount

Loss of carbonate stone under a fixed set of conditions, if there is not a kinetic limitation, is regulated by mineral solubility, expressed in units of mass per volume of solution. If, at equilibrium, the volume of aqueous solution reacting with a carbonate-stone surface doubles, then the carbonate-stone loss would also double. If the dissolution reaction approaches equilibrium then the stone loss would be directly proportional to the amount of

rain. Surface recession of carbonate stone is thus expected to be related to the amount of rain falling on the stone surface. (A detailed discussion of the calculation of surface recession from measured rain-runoff composition has been presented by Reddy and Werner (1985).) Surface recession, for both carbonate building stones (expressed as calciumcarbonate recession in micrometers per rain event) is plotted as a function of rainfall (in millimeters) in figure 6. The data points show a trend of increasing surface recession with increasing rain amount. These data indicate that calcium carbonate loss from both stone types is directly proportional to rainfall amount.
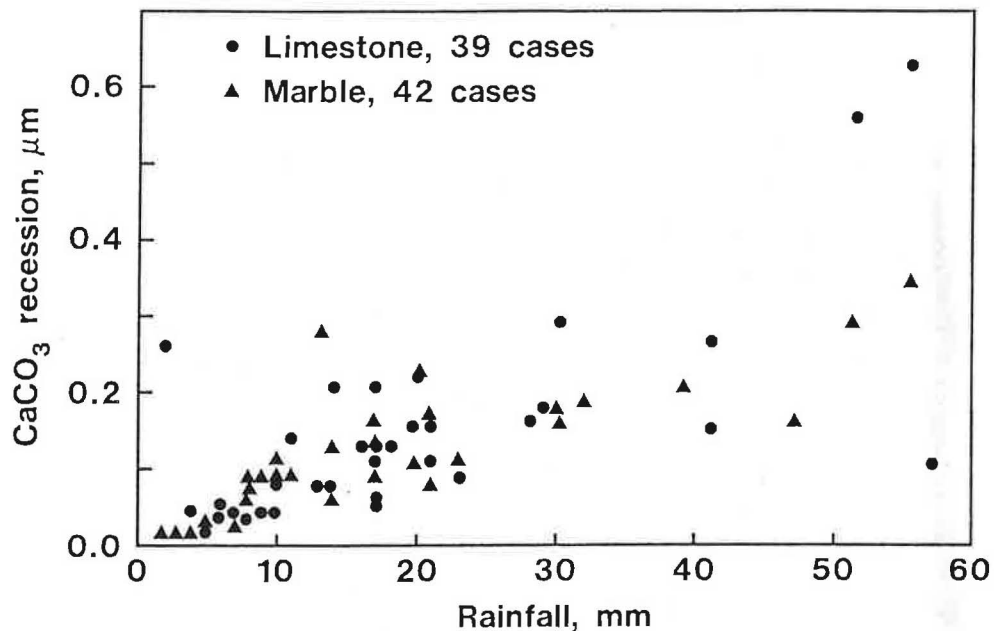
Figure 6.--Stone-surface recession for limestone and marble plotted as a
function of rain amount at Newcomb, N.Y.; Chester, N.J.; and Research
Triangle Park, N.C., during the summer and fall of 1984.

Data shown in figure 6 illustrate that there are no pronounced systematic differences between recession data for limestone and marble. Smallest recession values are associated with small rainfall amounts on the limestone samples. These very small limestone recession values may be due to the low runoff volume because of water uptake by limestone. :

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Incident Rain pH

Since carbonate-stone surface recession appears to be directly proportional to rainfall amount (fig. 6), the recession values can be normalized to the rainfall amount (that is, expressing the surface recession in micrometers of recession per millimeter of rain depth). This normalized surface recession has been found to correlate with incident rain pH (Reddy and Werner, 1985). Thus, rainfall amount and rain pH both appear to contribute in a significant way to loss of carbonate stone.

Air Pollutants

The effect of air pollutants on carbonate-building-stone damage has been described by Luckat (1977) and others. Typically such research has been conducted at locations with large pollutant concentrations and identifiable stone damage. In contrast to the large increased sulfur dioxide concentrations at European research sites, sulfur dioxide concentrations at the NAPAP Task Group G stone research sites shown in figure 1 (table 3) are small.

Table 3.--*Average sulfur dioxide concentrations at each stone-research site*

Site	Average sulfur dioxide concentration, in parts per billion	
	[1]1983	[2]1984
Research Triangle Park, N.C.--------	2	4.0
Chester, N.J.-----------------------	7	7.0
Newcomb, N.Y.-----------------------	3	1.8

[1]David Flinn, U.S. Bureau of Mines, Avondale, Md. (written commun., 1985).
[2]S.I. Sherwood, National Park Service, Washington, D.C., (oral commun., 1985).

Atmospheric concentrations of sulfur dioxide and the presence of moisture on the stone surface between rain events are important characteristics affecting the transfer of sulfur dioxide to the stone surface. In the stone-damage study being conducted at the four Task Group G research sites, air-pollution information is obtained simultaneously with damage measurements. Onsite meteorological, climatological, and air-pollution data are being quality assured and verified. Thus, a detailed evaluation of the air-pollution contribution to stone damage has not yet been completed.

Because atmospheric sulfur dioxide is a recognized source of carbonate-stone damage, an attempt was made to estimate sulfur dioxide effect on the carbonate stones exposed at the Task Group G sites. An index of carbonate-stone sulfur dioxide exposure was incorporated into the analysis of surface recession. This index is termed the antecedent sulfur dioxide exposure. It is calculated by multiplying the estimated site average sulfur dioxide concentration (table 3) by the number of days between precipitation events.

The rationale for use of a surrogate sulfur dioxide exposure variable is that sulfur dioxide transport to the stone surface will be related to atmospheric sulfur dioxide concentration and the length of exposure. Sulfur dioxide uptake by stone is a complex process mediated in large measure by stone-surface moisture. Spedding (1969), for example, has found that sulfur dioxide uptake by limestone was dependent on the humidity. A better estimate of sulfur dioxide effect on carbonate-stone damage would include accurate 6-hour or 1-hour concentrations as well as peak values and durations. This information coupled with stone-surface time-of-wetness information might allow future accurate calculation of sulfur dioxide movement to the stone surface.

Hydrogen Ion Loading

Because carbonate-stone surface-recession depends on both rainfall amount and rain-hydrogen ion concentration, surface recession will be correlated strongly to the product of these two terms. This product, hydrogen ion loading, is conveniently expressed in units of milliequivalents of hydrogen ion deposited per square meter of stone surface.

In assessing acid-rain effects, acid-loading values commonly are used as independent variables in part because many environmental data bases have been developed using hydrogen ion loading as an estimate of acid deposition. Carbonate-stone-surface recession values, plotted as a function of hydrogen ion loading (fig. 7) exhibit a direct relation that is similar to that for loss due to rain amount. This similarity arises because, in part, rain amount is used in the calculation of hydrogen ion loading. Runoff amount, which is correlated to rainfall, is used in the calculation of recession. Data points lie along a line having a positive slope, indicating that surface recession is directly proportional to hydrogen ion loading.

The hypothesis of a linear relation between carbonate-stone surface recession and hydrogen ion loading was evaluated using onsite data obtained during the summer and fall of 1984. Linear least-squares regressions were done relating the surface recession to hydrogen ion loading (table 4), and to hydrogen ion loading with antecedent sulfur dioxide (table 5).
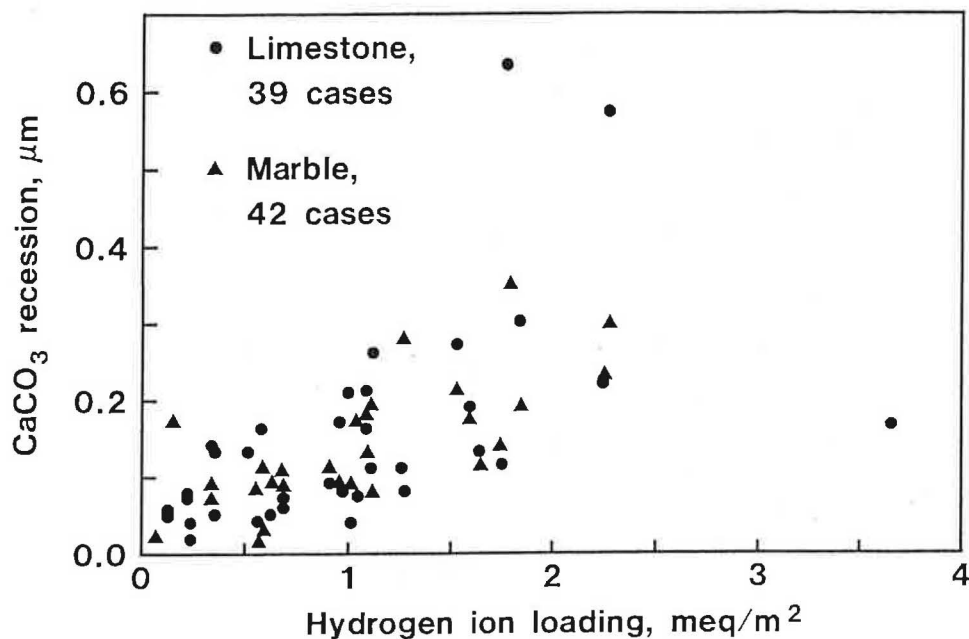
Figure 7.--Stone-surface recession for limestone and marble versus hydrogen ion loading at Newcomb, N.Y., Chester, N.J., and Research Triangle Park, N.C., during the summer and fall of 1984.

Table 4.--*Linear least-squares regression relation for limestone- and marble-surface recession, in micrometers per event, at three stone research sites in the eastern United States, using hydrogen ion loading as the independent variable*

[Surface recession, in micrometers (μm), is the dependent variable calculated from the equation: surface recession = mx+b; m, slope of regression line, in micrometers per milliequivalent of hydrogen ion per square meter (μm/meq of hydrogen ion/m^2); b, intercept of regression line with y axis, in micrometers (μm); n, number of data pairs for each stone type at each stone-research site; r, coefficient of correlation; p, probability that r will be equaled or exceeded in n pairs of randomly selected data pairs; <, less than; >, greater than]

	Newcomb, N.Y.	Chester, N.J.	Research Triangle Park, N.C.
		LIMESTONE	
m (μm/meq of hydrogen ion/m^2).	0.038	0.046	0.23
b (μm)--------------	0.060	0.068	-0.033
n-------------------	16	11	13
r-------------------	0.36	0.54	0.81
p-------------------	>0.1	<0.1	<0.001
		MARBLE	
m (μm/meq of hydrogen ion/m^2).	0.051	0.042	0.12
b (μm)--------------	0.062	0.091	0.03
n-------------------	15	9	18
r-------------------	0.52	0.56	0.83
p-------------------	<0.05	>0.1	<0.001

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Table 5.--*Multiple linear least-squares-regression relation for limestone- and marble-surface recession, in micrometers per event, at three stone-research sites in the eastern United States, using hydrogen ion loading and antecedent sulfur dioxide as independent variables*

[Surface recession, in micrometers (μm), is the dependent variable calculated from the equation: surface recession=mx+lz+b; m, hydrogen ion loading, in micrometers per milliequivalent of hydrogen ion per square meter (μm/meq of hydrogen ion/m^2); l, regression coefficient for antecedent sulfur dioxide in micrometers per part billion sulfur dioxide times days between events (μm/ppb SO_2*days); b, intercept of regression line with y axis, in micrometers, (μm); n, number of data triplets for each stone type at each stone-research site; r, multiple correlation coefficient; p, probability that r will be equaled or exceeded in n triplets of randomly selected data triplets for unrelated variables; >, greater than]

	Newcomb, N.Y.	Chester, N.J.	Research Triangle Park, N.C.
LIMESTONE			
m (μm/meq of hydrogen ion/m^2).	0.046	0.045	0.23
l (μm/ppb SO_2*days)---	-0.003	0.001	-0.01
b (μm)---------------	0.076	0.025	-0.03
n----------------------	16	11	13
r----------------------	0.45	0.56	0.81
p----------------------	>0.1	>0.1	>0.001
MARBLE			
m (μm/meq of hydrogen ion/m^2).	0.048	0.039	0.12
l (μm/ppb SO_2*days)---	0.002	0.003	0.0
b (um)---------------	0.051	-0.019	0.027
n----------------------	15	9	18
r----------------------	0.55	0.71	0.83
p----------------------	>0.05	>0.05	>0.001

In this statistical analysis, the known chemical solubility of calcium carbonate in the presence of acids allows the assignment of stone-surface recession as a dependent variable and hydrogen-ion load as an independent variable. Both variables are subject to random error.

Coefficients of correlation for the regression on hydrogen ion loading (table 4) exhibit a range of significance. Regression equations for both stone types at Research Triangle Park, N.C., are significant at the 99.9-percent confidence level. The regression equations are less significant for the New York and New Jersey sites. Coefficients of regression for the two stone types at each of the three research sites are similar. A detailed statistical analysis of the differences between these coefficients is limited by the small number of cases; however, the regression coefficient for hydrogen ion load appears to be larger at Research Triangle Park than at the other two sites for reasons that remain unclear.

Statistical analysis included antecedent sulfur dioxide loading, as an independent variable, in addition to hydrogen ion loading. The results of the statistical analyses are summarized in table 5.

Surface-recession measurements for each stone type and site yielded data sets containing relatively small numbers of cases; these data sets were combined to examine the complete data set more fully. The statistical analysis of the combined data set, incorporating surface-recession values for limestone, marble, and combined limestone and marble for all three sites, gave results similar to results for the smaller data sets. The most statistically significant, partial-correlation coefficient reflects the effect of hydrogen ion loading, as was true in the analysis by research site and stone type. Other potential stone-damage factors associated with sulfur dioxide, site, and stone type are small and not significant. The hydrogen ion-load coefficient is affected only slightly by incorporation of other terms in the regression. Statistical analysis of the combined site and stone data supports to a large degree the relation between surface recession and hydrogen ion load (table 6). Multiple correlation-coefficient values and the significance level for the linear relation improve when the larger data set is used. Each of the combined site regressions is significant at greater than the 90-percent confidence level. Regression coefficients change slightly for the two independent variables, going from marble, to limestone, to the marble-plus-limestone data set. Intercept values are uniform for the individual stones and the combined data; moreover, intercept values are similar to the values obtained by regression of the individual site data. Occasional negative values are probably within the experimental error.

Although the regression coefficients relating hydrogen ion loading to surface recession are significant, the regression coefficients for antecedent sulfur dioxide are not. This result indicates that sulfur dioxide levels may be too small at the stone-research sites to yield a useful regression relation between surface recession and sulfur dioxide exposure. Additional studies are being conducted to incorporate actual sulfur dioxide concentrations and time-of-wetness information into the data analyses.

Table 6.--*Multiple linear least-squares-regression relation for limestone-and marble-surface recession, in micrometers per event, using hydrogen ion loading and antecedent sulfur dioxide as independent variables*

[Surface recession, in micrometers (μm), is the dependent variable calculated from the equation: surface recession=mx+ly+b; m, slope of regression coefficient for hydrogen ion load, in micrometers per milliequivalent of hydrogen ion per square meter (μm/meq of hydrogen ion/m^2); 1, partial regression coefficient for antecedent sulfur dioxide, in micrometers per part per billion sulfur dioxide times days between events (μm/ppb SO$_2$*days); b, intercept of regression line with y axis in micrometers, (μm); n, number of data triplets for each stone type or for both stone types combined; r, multiple correlation coefficient; p, probability that r will be equaled or exceeded in n triplets of randomly selected data triplets for unrelated variables; >, greater than]

	Limestone	Marble	Combined
m (um/meq of hydrogen ion/m^2).	0.11	0.071	0.091
1 (μm/ppb SO$_2$*days)-------	-0.001	0.0004	-0.0005
b (μm)--------------------	0.052	0.051	0.053
n------------------------------	39	42	81
r------------------------------	0.60	0.70	0.61
p------------------------------	>0.001	>0.001	>0.001

The surrogate variable used to identify stone type also was not significant in the regression equation, which implies that, with the current data, the two stone types respond in a similar fashion to hydrogen ion loading in spite of large differences in permeability.

Differences in hydrogen ion loading between sites may be significant. Elaboration of the reason for these site differences must await additional experimental data for each site. At present, the combined data set and the associated regression parameters appear to be the most useful quantitative expression that is available, which relates environmental hydrogen ion loading (that is, acid rain) to carbonate-stone damage, but more data are needed.

Application of Surface-Recession Relation to Composite Materials

The chemical reaction between aqueous hydrogen ion and solid calcium carbonate surfaces, quantified from the onsite-exposure data, also may apply to composite construction or geological materials that have calcium carbonate as the bonding agent. Common examples of such materials are lime mortar and carbonate-cemented sandstone. These materials commonly consist of unreactive

mineral grains (for example, quartz grains in the case of calcite-cemented sandstone) held in place by a crystalline calciumcarbonate matrix. In mortar, carbonation proceeds from the surface as a slowly moving front. Thus, although mortar contains hydroxides, the portion exposed to acid and sulfur dioxide attack can be regarded as being predominantly crystalline or microcrystalline calcium carbonate.

In view of the unique structural role of calcium carbonate in these materials the experimental results for limestone and marble dissolution also may describe the loss of the calcium carbonate matrix. Quartz grains in a lime mortar or sandstone may function as an inert material that will be removed from the surface by granular dissaggregation as the carbonate-bonding matrix is lost. If this hypothesis is correct, the mortar linear-recession rate would increase as the amount of quartz increases in the composite material.

SUMMARY AND CONCLUSIONS

A goal of this research program is to develop reliable methods to identify and quantify environmental damage to carbonate stone. The onsite experimental program used in the investigation reported here satisfies this goal. Rainfall runoff from the research stones exhibits microhydrological characteristics which are compatible with measuring stone damage due to acid rain reacting with the carbonate-stone surface. Dissolution of the stone surface increases calcium concentration in the rainfall runoff. This increase can be converted into a surface loss of calcium carbonate or a uniform carbonate surface recession. Stone-surface recession was found to be directly proportional to rainfall amount. No pronounced differences in surface recession were observed between limestone and marble.

Identification and quantification of the effect of acid precipitation on carbonate-stone damage are additional goals of this program. Results presented here have indicated that surface recession is directly proportional to rainfall hydrogen ion loading to the stone surface. A preliminary estimation of the effect of sulfur dioxide deposition on stone damage implies that damage to the stone by sulfur dioxide is not significant. Multivariant statistical analysis, using linear-regression models, demonstrates that neither stone type nor location is statistically related to stone-surface recession.

The multivariant statistical linear-regression model relating carbonate-stone-surface recession to hydrogen ion loading may also have application to composite materials which have calcium carbonate as a binding matrix.

Table 7.--*Rainfall quantity and pH, antecedent sulfur dioxide, hydrogen ion loading, and surface recession for a marble reference stone at Research Triangle Park, N.C., June to October 1984*

U.S. Geological Survey sample no.	Rainfall (milli-meters)	Rainfall event pH	Antecedent sulfur dioxide (parts per billion times days)	Hydrogen ion loading (milli-equivalents per square meter)	$CaCO_3$ lost (micrometers per event)
1-M (NC)------	17	4.53	0	0.50	0.13
2-M (NC)------	16	3.98	12	1.63	.12
4-M (NC)[1]----	41	4.43	16	1.51	.21
5-M (NC)------	17	4.19	12	1.07	.13
6-M (NC)------	5	4.38	16	.21	.04
7-M (NC)------	3	4.04	12	.23	.02
8-M (NC)[1]----	32	4.46	12	1.10	.19
10-M (NC)[1]----	29	4.27	4	1.57	.17
11-M (NC)[1]----	46	5.55	4	.13	.17
12-M (NC)------	7	4.06	4	.58	.03
13-M (NC)------	4	4.91	16	.05	.02
14-M (NC)------	6	4.71	8	.11	.05
16-M (NC)[1]----	55	4.49	16	1.77	.35
21-M (NC)------	21	4.30	40	1.07	.18
26-M (NC)------	2	4.67	20	.03	.02
28-M (NC)------	10	4.51	4	.31	.07
30-M (NC)[1]----	51	4.35	4	2.27	.30
31-M (NC)------	2	3.83	4	.23	.02

[1]Sample overflowed collection bottle.

Table 8.--*Rainfall quantity and pH, antecedent sulfur dioxide, hydrogen ion loading, and surface recession for a limestone reference stone at Research Triangle Park, N.C., June to October 1984*

U.S. Geological Survey sample no.	Rainfall (milli-meters)	Rainfall event pH	Antecedent sulfur dioxide (parts per billion times days)	Hydrogen ion loading (milli-equivalents per square meter)	Surface recession (micrometers per rainstorm)
1-L (NC)---	17	4.53	0	0.50	0.13
2-L (NC)---	16	3.98	12	1.63	.13
4-L (NC)[1]--	39	4.43	16	1.51	.27
5-L (NC)---	17	4.19	12	1.07	.21
6-L (NC)---	5	4.38	16	.22	.02
8-L (NC)[1]--	32	4.46	12	1.10	.26
10-L (NC)---	29	4.27	4	1.57	.19
12-L (NC)---	7	4.06	4	.58	.05
14-L (NC)---	6	4.71	8	.11	.06
16-L (NC)[1]--	55	4.49	16	1.77	.63
21-L (NC)---	21	4.30	40	1.07	.16
28-L (NC)---	10	4.51	4	.31	.04
30-L (NC)[1]--	51	4.35	4	2.27	.57

[1]Sample overflowed collection bottle.

Table 9.--*Rainfall quantity and pH, antecedent sulfur dioxide and hydrogen ion loading, and surface recession for a marble reference stone at Chester, N.J., June to October 1984*

U.S. Geological Survey sample no.	Rainfall (milli-meters)	Rainfall event pH	Antecedent sulfur dioxide (parts per billion times days)	Hydrogen ion loading (milli-equivalents per square meter)	Surface recession (micrometers per rainstorm)
5-M (NJ)[1]-----	41	4.05	28	3.65	0.16
6-M (NJ)[1]-----	23	4.42	49	.88	.10
9-M (NJ)------	13	4.00	49	1.26	.28
10-M (NJ)------	20	3.96	49	2.24	.23
11-M (NJ)------	14	4.85	28	.20	.07
12-M (NJ)------	6	4.36	21	.28	.05
13-M (NJ)------	10	4.17	28	.67	.11
14-M (NJ)------	8	3.89	49	.99	.09
15-M (NJ)------	29	4.20	35	1.84	.19

[1]Site rainfall values were unavailable. Rainfall amount was calculated from the volume of the blank sample.

Table 10.--*Rainfall quantity and pH, antecedent sulfur dioxide and hydrogen ion loading, and surface recession for a limestone reference stone at Chester,N.J., June to October 1984*

U.S. Geological Survey sample no.	Rainfall (milli-meters)	Rainfall event pH	Antecedent sulfur dioxide (parts per billion times days)	Hydrogen ion loading (milli-equivalents per square meter)	Surface recession (micrometers per rainstorm)
5-L (NJ)[1]-----	41	4.05	28	3.63	0.16
6-L (NJ)[1]-----	23	4.42	49	.88	.09
7-L (NJ)------	57	4.66	35	1.24	.11
8-L (NJ)------	14	4.16	49	.98	.21
9-L (NJ)------.	13	4.00	49	1.26	.08
10-L (NJ)------	20	3.96	49	2.24	.22
12-L (NJ)------	6	4.36	21	.28	.04
13-L (NJ)------	10	4.18	28	.67	.07
14-L (NJ)------	8	3.89	49	.99	.04
15-L (NJ)------	29	4.2	35	1.84	.30

[1]Site rainfall values were unavailable. Rainfall amount was calculated from the volume of the blank sample.

Table 11.--*Rainfall quantity and pH, antecedent sulfur dioxide and hydrogen ion loading, and surface recession for a marble reference stone at Newcomb, N.Y., June to October 1984*

U.S. Geological Survey sample no.	Rainfall (milli-meters)	Rainfall event pH	Antecedent sulfur dioxide (parts per billion times days)	Hydrogen ion loading (milli-equivalents per square meter)	Surface recession (micrometers per rainstorm)
3-M (NY)---	28	4.47	5	0.94	0.16
5-M (NY)---	10	4.24	5	.54	.08
6-M (NY)---	17	3.98	11	1.73	.14
7-M (NY)---	9	4.16	9	.62	.09
8-M (NY)---	8	4.57	13	.21	.08
9-M (NY)---	8	4.61	4	.19	.06
12-M (NY)---	9	4.47	5	.32	.06
13-M (NY)---	20	4.54	4	.57	.11
15-M (NY)---	21	4.28	5	1.09	.08
17-M (NY)---	4	4.10	11	.54	.01
18-M (NY)---	10	4.62	2	.95	.09
19-M (NY)---	17	4.39	7	.67	.09
20-M (NY)---	17	4.22	16	1.03	.17
24-M (NY)---	18	4.74	11	.32	.14
25-M (NY)---	11	4.54	4	.31	.09

Table 12.--*Rainfall quantity and pH, antecedent sulfur dioxide and hydrogen ion loading, and surface recession for a limestone reference stone at Newcomb, N.Y., June to October 1984*

U.S. Geological Survey sample no.	Rainfall (millimeters)	Rainfall event pH	Antecedent sulfur dioxide (parts per billion times days)	Hydrogen ion loading (milliequivalents per square meter)	Surface recession (micrometers per rainstorm)
1-L (NY)-----	28	4.47	5	0.94	0.17
3-L (NY)-----	9	4.24	5	.54	.05
4-L (NY)-----	17	3.98	11	1.73	.11
7-L (NY)-----	9	4.16	9	.62	.05
8-L (NY)-----	8	4.57	13	.21	.04
9-L (NY)-----	8	4.61	4	.19	.04
12-L (NY)-----	10	4.47	5	.32	.05
13-L (NY)-----	20	4.54	4	.57	.16
15-L (NY)-----	21	4.28	5	1.09	.11
16-L (NY)-----	4	4.62	2	.10	.04
17-L (NY)-----	7	4.10	11	.54	.04
18-L (NY)-----	10	4.02	2	.95	.08
19-L (NY)-----	17	4.39	7	.67	.06
20-L (NY)-----	17	4.22	16	1.03	.07
24-L (NY)-----	18	4.74	11	.32	.13
25-L (NY)-----	11	4.54	4	.31	.14

DISCLAIMER

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