# COMPOSITION OF RAINFALL RUNOFF FROM LIMESTONE AND MARBLE AT RESEARCH TRIANGLE PARK, NORTH CAROLINA

By Michael M. Reddy and Marilyn Werner

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# CONTENTS



## TABLES



## CONVERSION FACTORS

The metric units used in this report may be converted to inch-pound units by use of the following conversion factors:

| *Multiply metric units* | *By* | *To obtain inch-pound units* |
|---|---|---|
| gram | 0.03527 | ounce |
| meter | 3.281 | foot |
| millimeter | 0.03937 | inch |
| square centimeter | 0.155 | square inch |
| square meter | 10.76 | square foot |

# COMPOSITION OF RAINFALL RUNOFF FROM LIMESTONE AND MARBLE AT RESEARCH TRIANGLE PARK, NORTH CAROLINA

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## ABSTRACT

As a part of the U.S. National Acid Precipitation Assessment Program, Task Group G--Effects on Materials and Cultural Resourses--has begun a 10-year program to measure and document acid-rain effects on two types of stone, Salem Limestone (from Indiana), and Shelburne Marble (from Vermont), which commonly are used in buildings and historical monuments. Reference specimens of limestone and marble were exposed to measure acid-deposition effects and to separate these effects from air-pollution damage. Rainfall-runoff solution was collected from each reference stone and from an unused stone holder. Runoff volume, specific conductance, and pH were determined on site as soon as possible after collection. Filtered samples were sent to the U.S. Geological Survey laboratory in Denver, Colorado, for chemical analysis. Preliminary data indicate that calcium-carbonate surface recession is correlated with rainfall characteristics. Marble surface recession was significantly correlated with rainfall amount. At the same site, sulfate concentration in stone runoff is significantly greater than that observed in rainfall.

## INTRODUCTION

Rainfall-runoff from Salem Limestone (from Indiana) and Shelburne Marble (from Vermont) was analyzed chemically as part of a study of the effects of acid rain on calcium-carbonate building stone. About 1 liter of runoff solution was collected from each of three experimental racks at the end of each rainstorm. Limestone and marble specimens were in two of the racks; the third rack without a stone specimen was used as a control (hereafter referred to as a blank sample). Runoff volume, specific conductance, and pH were determined onsite as soon as possible after collection, typically within a few hours. Samples then were filtered through a 0.45-micrometer pore size nitrocelluluse filter (Schleicher and Schuell[1]), placed in a clean polyethlyene bottle, and sent to the U.S. Geological Survey laboratory in Denver, Colorado, for analysis. Details of the onsite and laboratory procedures are given elsewhere (Reddy and others, 1985). Sample preparation, analytical procedures and laboratory quality-control protocols are described by Skougstad and others (1979).

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[1]Use of the brand name in this report is for descriptive purposes only and does not constitute endorsement by the U.S. Geological Survey.

## COMPOSITION OF RAINFALL RUNOFF FROM LIMESTONE AND MARBLE

The analytical results presented in this report are intended to assist interested researchers in the Task Group G Program in assessing the effects of acid rain on building stones. Analytical results for calcium and sulfate ions are for the net change in rainfall composition after the rainfall flows over the surface of the exposed stone (tables 1 and 2). The net concentration, assumed to result from the interaction of rain with the stone surface, is calculated by subtracting the blank-sample concentration from the concentration measured for the stone runoff. Granular disintegration of the test stones, a process which may be important in determining the total erosion rate, is not evaluated in these measurements. Sulfate-ion net concentration has been calculated to identify the presence of soluble minerals containing sulfate on the stone surface.

The column-by-column explanation of the entries in tables 1 and 2 is: Column 1 is the U.S. Geological Survey laboratory number for each runoff sample; column 2 is the rainfall, in inches, measured at the site for each rainstorm; column 3 is the rainstorm pH measured for the blank sample at the exposure site; columns 4 and 5 are the net concentrations of calcium and sulfate ions in the stone runoff, in milligrams per liter; and column 6 is loss of calcium carbonate from the stone surface per rainstorm, in micrometers of stone surface lost (surface recession) per rainstorm. Surface recession is obtained by multiplication by the appropriate conversion factors. A sample calculation is given in table 3.

The data in tables 1 and 2 may need to be used with caution because rainfall data reported by the site operator is considered to be preliminary because it has not been verified as correct by the supervising agency. In addition, detailed meteorological and air-pollution data, which may have a substantial effect on the runoff-chemistry data, are not yet available. An additional complicating factor is that the blank-sample surface may have different pollutant-retention properties than the stone surfaces. Dust has been observed to adhere to the polypropylene surface of the blank collector; this dust might contribute extra material to the blank relative to the stone slabs. Constituent concentrations in runoff from the blank, therefore, may be greater than constituent concentrations in the rain. In this case the loss of calcium from the stone surfaces would be somewhat larger.

Calcium-carbonate surface recession per rainstorm is correlated with rainfall characteristics. The relationship may be written as:

$$\text{Surface recession} = A + B\ (\text{Independent variable});$$

where A and B are constants determined from a least-squares regression analysis, and the independent variable may be rainfall quantity, rainfall pH, rainfall hydrogen-ion concentration, or rainfall hydrogen ion loading.

Table 1.--*Rainfall-runoff concentrations for calcium and sulfate ions, and surface recession for a limestone reference stone, June to October 1984*

| U.S. Geological Survey sample no.[1] | Rainfall (inches) | Rainfall pH (units) | Net calcium in runoff (milligrams per liter) | Net sulfate in runoff (milligrams per liter) | Calcium carbonate lost (micrometers per rainstorm) |
|---|---|---|---|---|---|
| 1-L (NC) | 0.66 | 4.53 | 11.55 | 0.35 | 0.11 |
| 2-L (NC) | .62 | 3.98 | 17.50 | -.52 | .11 |
| 4-L (NC) | 1.60 | 4.43 | 7.17 | .95 | .27 |
| 5-L (NC) | .65 | 4.19 | 14.65 | 3.60 | .18 |
| 6-L (NC) | .20 | 4.38 | 11.42 | 1.83 | .02 |
| 8-L (NC) | 1.25 | 4.46 | 8.69 | .00 | .22 |
| 10-L (NC) | 1.15 | 4.27 | 9.44 | 2.30 | .16 |
| 12-L (NC) | .26 | 4.06 | 12.40 | 1.15 | .04 |
| 14-L (NC) | .23 | 4.71 | 18.02 | .70 | .05 |
| 16-L (NC) | 2.15 | 4.49 | 12.30 | 6.40 | .54 |
| 21-L (NC) | .84 | 4.30 | 12.48 | 1.40 | .14 |
| 28-L (NC) | .40 | 4.51 | 24.07 | 7.30 | .03 |
| 30-L (NC) | 2.00 | 4.35 | 11.91 | 5.20 | .48 |

[1]Missing sample numbers correspond to those samples having insufficient data for calculation of surface recession.

Table 2.--*Rainfall-runoff concentrations for calcium and sulfate ions, and surface recession for a marble reference stone, June to October 1984*

| U.S. Geological Survey sample no.[1] | Rainfall (inches) | Rainfall pH (units) | Net calcium in runoff (milligrams per liter) | Net sulfate in runoff (milligrams per liter) | Calcium carbonate lost (micrometers per rainstorm) |
|---|---|---|---|---|---|
| 1-M (NC) | 0.66 | 4.53 | 9.87 | 1.00 | 0.13 |
| 2-M (NC) | .62 | 3.98 | 12.12 | .74 | .12 |
| 4-M (NC) | 1.60 | 4.43 | 6.47 | .667 | .21 |
| 5-M (NC) | .65 | 4.19 | 9.42 | .90 | .13 |
| 6-M (NC) | .20 | 4.38 | 7.75 | 2.63 | .04 |
| 7-M (NC) | .10 | 4.04 | 17.97 | 7.60 | .02 |
| 8-M (NC) | 1.25 | 4.46 | 7.48 | .00 | .19 |
| 10-M (NC) | 1.15 | 4.27 | 7.28 | 1.00 | .17 |
| 11-M (NC) | 1.83 | 5.55 | 4.66 | -.15 | .17 |
| 12-M (NC) | .26 | 4.06 | 8.61 | 2.35 | .03 |
| 13-M (NC) | .15 | 4.91 | 13.00 | 5.50 | .02 |
| 14-M (NC) | .23 | 4.71 | 10.42 | 1.60 | .05 |
| 16-M (NC) | 2.15 | 4.49 | 8.00 | 1.10 | .35 |
| 21-M (NC) | .84 | 4.30 | 10.51 | .30 | .18 |
| 26-M (NC) | .06 | 4.67 | 18.85 | 14.00 | .02 |
| 28-M (NC) | .40 | 4.51 | 14.38 | 2.30 | .07 |
| 30-M (NC) | 2.00 | 4.35 | 7.41 | -.80 | .30 |
| 31-M (NC) | .06 | 3.83 | 17.10 | 11.00 | .02 |

[1]Missing sample numbers correspond to those samples having insufficient data for calculation of surface recession.

Table 3.--*Sample calculation for determining reference-stone surface recession from measured runoff data*

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Net calcium-ion concentration in stone runoff:

Measured calcium-ion concentration in runoff = 12.08 milligrams per liter.

Measured calcium-ion concentration of blank = 0.53 milligrams per liter.

Calcium-ion concentration from reference-stone dissolution (12.08 - 0.53) = 11.55 milligrams per liter.

Total weight of calcium lost from stone surface:

(Net calcium concentration in runoff) × (runoff volume) = milligrams calcium.

11.55 milligrams per liter × 1.91 liters = 22.11 milligrams calcium.

22.1 milligrams calcium × 2.50 $\frac{C_aCO_3}{Ca}$ = 55.2 milligrams calcium carbonate.

55.2 milligrams calcium carbonate × (0.001) = 0.055 gram calcium carbonate.

Volume of calcium carbonate lost from stone surface:

0.055 gram calcium carbonate ÷ 2.7 grams per cubic centimeter = 0.02 cubic centimeter calcium carbonate.

Surface recession of reference stone:

0.02 cubic centimeter calcium carbonate ÷ 1858 square centimeters = 1.1 × $10^{-5}$ centimeter.

0.11 × $10^{-6}$ meter = 0.11 micrometer of calcium carbonate lost.

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Marble surface recession at the North Carolina site was significantly correlated with rainfall amount. The correlation coefficent was significant at greater than the 99-percent confidence level. Thus, in examining the effect of rainfall pH on material loss, surface-recession values were divided by the amount of rain from each storm. In the case of marble, this ratio--loss of calcium carbonate in micrometers per rainstorm per inch of rain--was determined to be significantly correlated to the rainfall pH. The linear relationship was:

Micrometers per rainstorm per inch of rain = 0.52 - 0.078 (pH).

The correlation coefficient for this relationship (-0.43, for 18 degrees of freedom) was significant at the 90-percent confidence level.

Marble surface recession also was significantly correlated with hydrogen-ion deposition on the stone. The linear relationship between surface recession and hydrogen-ion deposition, expressed in units of hydrogen-ion deposition per square meter, was determined to be:

Micrometers per rainstorm = 0.03 + 0.12 × hydrogen-ion deposition.

The units of the regression coefficient (0.12) are micrometers per rainstorm per millimole of hydrogen ion deposited on a square meter of stone surface by rain. This relationship is significant at greater than the 99-percent confidence level.

Net sulfate concentration in stone runoff is significantly greater than zero for marble (significant at the 90-percent confidence level) as well as for limestone (significant at the 99-percent confidence level). That is, rainfall runoff from both reference stones has sulfate concentrations significantly greater than sulfate concentrations in rainfall.

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