

# Effects of Acid Rain and Sulfur Dioxide on Marble Dissolution

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*Acid precipitation and the dry deposition of sulfur dioxide (SO<sub>2</sub>) accelerate damage to carbonate-stone monuments and building materials. This study identified and quantified environmental damage to a sample of Vermont marble during storms and their preceding dry periods. Results from field experiments indicated the deposition of SO<sub>2</sub> gas to the stone surface during dry periods and a twofold increase in marble dissolution during coincident episodes of low rain rate and decreased rainfall pH. The study is widely applicable to the analysis of carbonate-stone damage at locations affected by acid rain and air pollution.*

Acid deposition, which occurs as wet deposition in the form of acid rain, acid snow, or acid fog and as the dry deposition of atmospheric pollutants such as sulfur and nitrogen oxides, has been linked to the acidification of European and North American lakes,<sup>1</sup> and to forest decline.<sup>2</sup> In unpolluted atmospheres, carbonate-stone dissolution is a slow process; however, dissolution is accelerated when the stone is exposed to atmospheric pollutants such as oxides of sulfur and nitrogen that are delivered to the stone surface in the form of wet deposits or that are delivered directly to the stone surface by dry deposition.<sup>3-5</sup>

Acid rain reacts directly with the stone surface. Gaseous and particu-

late pollutants also react with the stone surface in the presence of moisture. Luckat<sup>6</sup> showed sulfur dioxide (SO<sub>2</sub>) caused carbonate-stone damage on the Cologne Cathedral and that stone damage correlated well with SO<sub>2</sub> uptake. Kulshreshtha et al.<sup>7</sup> noted that "in industrial environments, the decay of marble takes place primarily due to atmospheric SO<sub>2</sub>." However, at this writing, no procedure is available to identify and quantify stone damage mechanisms.

Other investigations have shown that rain rate and chemistry fluctuate during individual storms.<sup>8,9</sup> The National Atmospheric Deposition Program/National Trends Network (NADP/NTN), the U.S. National Atmospheric Precipitation Assessment

Program (NAPAP; 1980 to 1990), determines the acidity of rainfall from integrated samples that represent average concentrations over a period. Integrated samples obscure the fluctuations of acidity of rainfall and the chemistry of runoff from carbonate stone during individual storms. Thus, there is little understanding of how within-storm fluctuations affect carbonate-stone dissolution.

Dissolution of carbonate-stone building materials by acid deposition requires knowledge of rainfall and runoff characteristics as a storm progresses. Sequential sampling of runoff from individual storms can provide detailed records of the fluctuations of rainfall and runoff chemistry during those storms. Such records could be critical in determining mechanisms responsible for dissolution of carbonate stone due to acid deposition.

The goal of our research is to characterize and quantify the processes by which carbonate stone may be damaged or degraded by acid deposition. Quantification of these

processes will aid in describing any incremental effects of wet and dry deposition of hydrogen ions,  $\text{SO}_2$ , nitrous oxides, or organic acids on the chemical weathering of carbonate stone. This article describes results from a prototype experimental system designed to monitor marble dissolution; this system may have wide application to the study of carbonate-stone deterioration by atmospheric processes.

### Experimental System

The on-site experimental system was located in Huntington Wildlife Forest in the Central Adirondack Mountains of New York State. It consisted of two microcatchments: a  $0.1858\text{-m}^2$  ( $2\text{-ft}^2$ ) slab of Shelburne marble, a stone commonly used as a building material and in monuments<sup>10</sup>; and a borosilicate (glass) reference plate of the same size (sandblasted to simulate the roughness of the marble surface). Exposure conditions of the glass and marble microcatchments were chosen to be the same as those for other materials-damage studies sponsored by NAPAP. The microcatchments were tilted at 30 degrees from the horizontal facing south, and the exposed section was uncovered at all times. Runoff was collected from the microcatchments using volume-based sequential samplers. In addition, meteorological, climatological, and atmospheric-pollutant data were recorded continuously at the site. Detailed descriptions of the glass and marble microcatchments, ancillary equipment, and on-site and laboratory analytical procedures are given elsewhere.<sup>11,12</sup>

### Results and Discussion

Results from seven selected summer storms are listed in the appendix of Schuster et al.<sup>12</sup> The chemical composition of the rainfall runoff from the marble and glass surfaces helps explain the nature of environmental damage to carbonate stone.

#### Glass Runoff

Figure 1 is a time series of rainfall-runoff pH for one representative

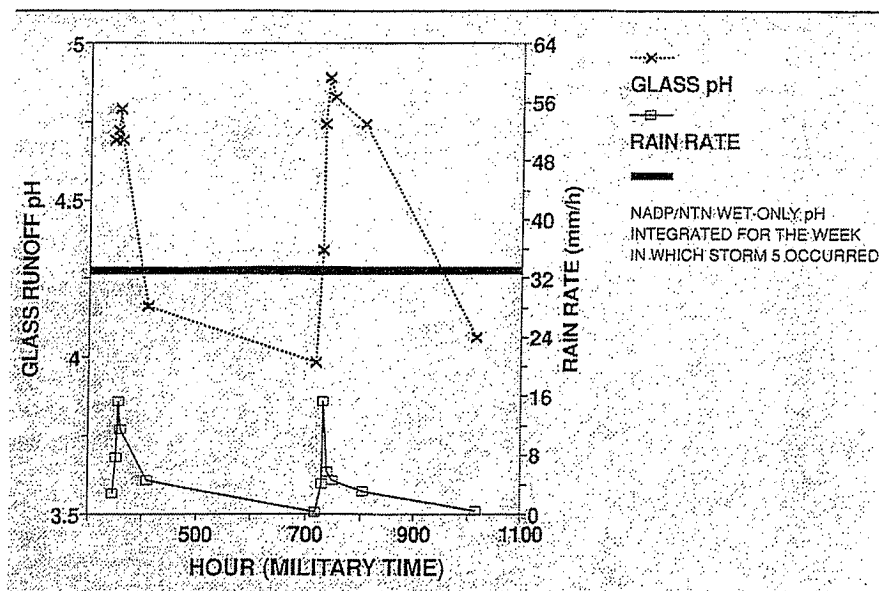


FIGURE 1  
Time series of pH of runoff from a glass surface and concomitant rain rate (storm 5, September 13, 1988).

storm (storm 5, which occurred on September 13, 1988). Results from six other storms were similar. The sequential-sampling strategy revealed episodes, or pulses, of acidic rainfall. The glass-runoff pH fluctuated more than one unit but remained below 5.0 during most storms. Minimum pH occurred at the start of most storms and resulted from acid species washout and washoff of dry-deposited materials from the glass surface. Rainfall pH was related to the rain rate. Minimum pH usually coincided with low rain rate and maximum pH with high rain rate.

Also shown in Figure 1 is the NADP/NTN wet-only precipitation pH for the week in which storm 5 occurred. Although the NADP/NTN-determined rain chemistry is not directly comparable with sequential sample-determined rain chemistry, because it is from wet-only conditions and typically represents more than one storm, it appears that the NADP/NTN sampling technique underestimates rainfall acid peaks during storms at this site and possibly at other acid rain-affected regions.

#### Marble Dissolution

Net calcium concentrations from the marble runoff, a measure of stone dissolution, were calculated by sub-

tracting glass runoff concentrations of calcium from marble runoff concentrations. Net concentrations calculated in this way correspond to the amount of calcium dissolved from a marble surface by incident rainfall. Reactions of gaseous and particulate pollutants with marble during dry periods between storms and the reaction of marble with acid rain are sources of calcium in the runoff. In the present study, the net calcium concentrations were equivalent to fluxes from the marble surface because samples were collected at a fixed rain volume (volume-weighted sampling).

Atmospheric particulates were present in both the marble and glass runoff and thus did not contribute to the net calcium concentration. Marble dissolution fluctuated during storms, with net calcium concentrations varying by a factor of about two. Low-pH rainfall coincided with low rain rate, causing increased marble dissolution (Figure 2). The runoff from episodes of low rain rate contained 21 to 73 percent of the total calcium lost by the marble during a storm.

The effects of rain rate and rainfall pH on marble dissolution were separately quantified by normalizing the marble recession, calculated from stone surface dissolution, to the amount of rain (in mm) (Figure 3).

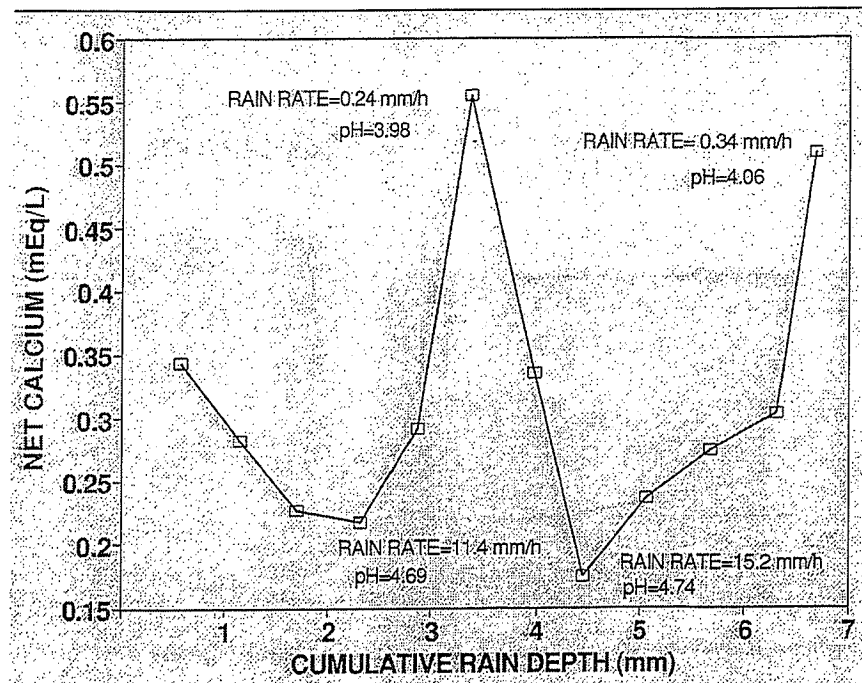


FIGURE 2

Net calcium concentrations in runoff from a marble surface plotted against concomitant cumulative rain depth (storm 5, September 13, 1988). Maximum and minimum net calcium concentrations are labeled with rain rate and rainfall-runoff pH at the time of sample collection.

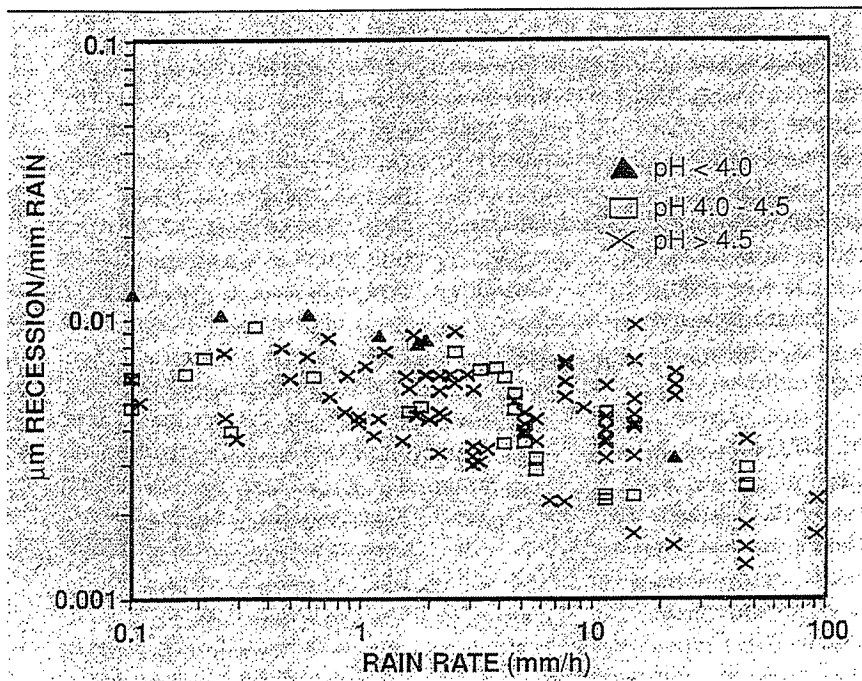


FIGURE 3

Normalized marble surface recession plotted against concomitant rain rate for seven summer storms, 1987 to 1989. The data were stratified by rainfall-runoff pH.

Data from seven storms were grouped according to rainfall pH and plotted against rain rate. At any given rain rate, rainfall pH values greater than 4.0 had little or no effect on marble dissolution. However, at rain-

fall pH values less than 4.0, the quantity of dissolution increased. This increase was greatest at rain rates less than 5 mm/h: stone surface dissolution increased about twofold when the rainfall pH decreased from more

than 4.5 to less than 4.0. This more rapid dissolution was most likely in response to: (1) a decrease in pH during episodes of low rain rate and/or (2) more efficient rainfall reaction with the stone surface. As the rain rate increased, rainfall pH was a less important factor in marble dissolution. Dissolution decreased as the rain rate exceeded about 5 mm/h, most likely in response to (1) a rapid increase in pH during high-rain-rate episodes and/or (2) decreased rainfall contact time with the marble surface.

### The Role of SO<sub>2</sub>

Recently, the dry deposition of SO<sub>2</sub> to carbonate-stone surfaces has been recognized as critical in environmental damage to carbonate stone.<sup>3,13,14</sup> Laboratory investigations have attempted to quantify the role of SO<sub>2</sub> dry deposition in environmental carbonate-stone damage.<sup>14,15</sup> Although laboratory investigations have been useful in characterizing the mechanisms of SO<sub>2</sub> dry deposition to carbonate stone, two questions on the quantification of SO<sub>2</sub> dry deposition in environmental carbonate-stone damage remain unanswered:

- How important is the SO<sub>2</sub>-dry-deposition component of carbonate-stone damage due to environmental conditions?
- What are the relative contributions of damage due to acid rain and dry-deposited SO<sub>2</sub>?

We use results from this field study to address these questions.

Research into the dry deposition of gaseous pollutants such as SO<sub>2</sub> is ongoing. While it is not possible to summarize the field here, a recent publication<sup>3</sup> suggests that computational procedures may allow integration of field measurements with theory to estimate dry deposition of SO<sub>2</sub> to carbonate-stone surfaces.

SO<sub>2</sub> reaction products accumulate on the marble surface during the dry period before a storm. However, atmospheric conditions during this dry period, such as atmospheric SO<sub>2</sub> concentrations, the marble surface's moisture content, the length of the dry period, solar irradiation, and

wind speed, are important factors in the effects of dry-deposited  $\text{SO}_2$  on marble dissolution.  $\text{SO}_2$  reacts with marble in the presence of moisture, such as dew, fog, or high relative humidity,<sup>3</sup> to produce gypsum on the marble surface. The formation of gypsum on the marble surface by dry deposition and its interaction with rainfall runoff are discussed in more detail elsewhere.<sup>3,13</sup>

In this study, the quantity of dry-deposited  $\text{SO}_2$  on the marble surface was estimated using a bulk transfer method. This method used  $\text{SO}_2$ -dry-deposition algorithms<sup>3</sup> modified by the authors to include surface moisture content. The mass of the  $\text{SO}_2$  deposited to the marble surface before a storm was calculated in  $\mu\text{g}/\text{day}$  and multiplied by the number of dry days before that storm. The results were converted to sulfate concentrations, assuming all  $\text{SO}_2$  gas deposited to the marble surface reacted to form gypsum and that this gypsum was washed off the marble surface during the next storm. The calculation is described below:

$$F_s = [\text{SO}_2] / (r_g + r_c)$$

where  $F_s$  = dry deposition rate of  $\text{SO}_2$  to a marble surface, expressed in  $\mu\text{g}/\text{m}^3\text{-s}$ ;  $[\text{SO}_2]$  =  $\text{SO}_2$  concentration expressed in  $\mu\text{g}/\text{m}^3$ , the average value recorded hourly by a low-level- $\text{SO}_2$  analyzer;  $r_g$  = gas phase resistance, expressed in  $\text{s}/\text{m}$ ; and  $r_c$  = surface resistance, expressed in  $\text{s}/\text{m}$ .

$$r_g = 475[(G/200)^2 + U^2]^{-1/2}$$

where  $G$  = solar radiation, expressed in  $\text{W}/\text{m}^2$ , and  $U$  = wind speed, expressed in  $\text{m}/\text{s}$ .

$$r_c = r_{cd}^{-b(\theta/6m)}$$

where  $r_{cd} = 800 \text{ s}/\text{m}$  (from Baedecker et al.,<sup>3</sup> pp. 151-153);  $b = 1$  to 10. (The value of  $b$  is determined empirically. Use of  $b = 10$  is based on studies of evaporation from bare soils. Currently, a value of  $b = 3$  is used to obtain a best fit with net sulfate concentrations in marble runoff); and  $\theta/6m$  = card wetness. (See See et al.<sup>11</sup> for description.)

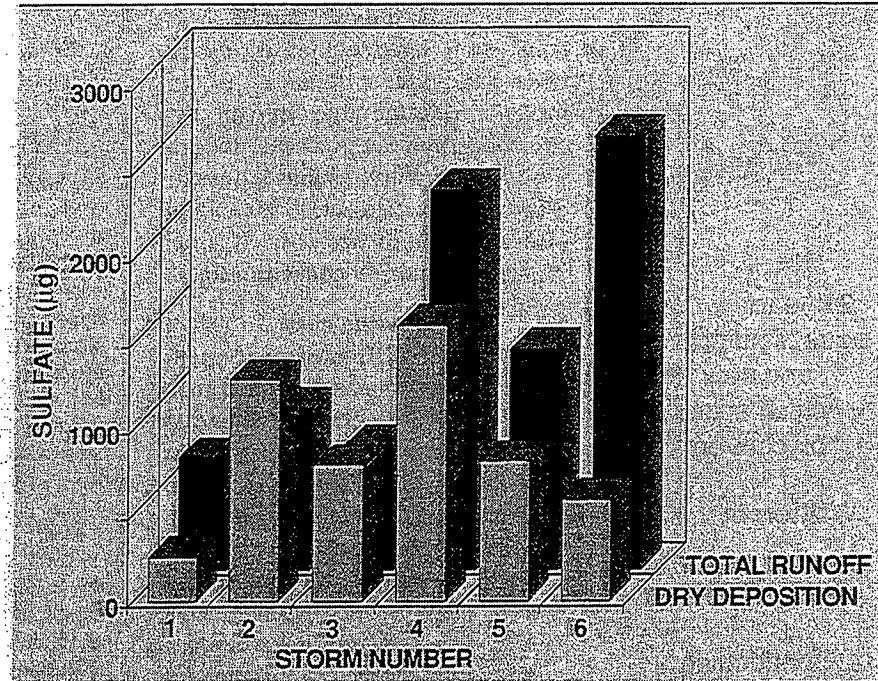


FIGURE 4

Total net sulfate for storms 1 to 6 compared with  $\text{SO}_2$  (as sulfate) dry deposited to the marble surface during the dry period before each storm.

Results from six storms were compared with the net mass of sulfate in the marble runoff from the storm (Figure 4). The algorithms overestimated  $\text{SO}_2$  dry deposition for two of the six storms, by 9 and 38 percent. The algorithms underestimated the levels in four storms, by 23 to 86 percent. Possible explanations for the differences between calculated  $\text{SO}_2$  dry deposition and net sulfate in the marble runoff are discussed elsewhere.<sup>12,13</sup>

Net sulfate and calcium concentrations were elevated in the initial runoff of the storms studied here, suggesting that  $\text{SO}_2$  deposited to the marble during dry periods formed gypsum.<sup>12</sup>  $\text{SO}_2$  accumulates on wet marble surfaces but not on glass surfaces.<sup>3</sup> The net calcium concentration thus reflects sulfate accumulation on marble. The agreement between algorithm-generated values and measured sulfate washoff from the stone surface suggests transformation of  $\text{SO}_2$  to gypsum is rapid at the stone surface. Gypsum accounted for 10 to 50 percent of the calcium washed from the marble surface during storms. These preliminary results suggest that dry-deposited  $\text{SO}_2$  is very

important in environmental carbonate-stone damage.

Development of reliable, reproducible procedures for identifying and quantifying damage to and deterioration of carbonate stone is the area of greatest need in studies of environmental stone damage. Techniques and results reported here are reliable and reproducible and can be employed in other environments, such as urban centers. Because our field site is subjected to very low ambient  $\text{SO}_2$  concentrations, this study may represent a "best case" scenario for the effects of  $\text{SO}_2$  dry deposition on carbonate stone.

Figure 4 shows that the dry deposition algorithm may prove useful in predicting  $\text{SO}_2$  accumulation on carbonate stone, and it may be employed to identify anticipated carbonate-stone damage in areas of much higher ambient  $\text{SO}_2$  concentrations.

Further research is needed to validate the dry-deposition algorithm currently used so that it can be incorporated into a damage function. Results presented here suggest that, with further refinement, environmental damage to carbonate stone can be reliably estimated using this algorithm

and that stone damage can be calculated using SO<sub>2</sub>-dry-deposition data. Once validated, a damage function incorporating the algorithm for SO<sub>2</sub> dry deposition can be developed and used to identify threshold values for acceptable SO<sub>2</sub> concentrations and can also be used in areas with much higher ambient SO<sub>2</sub> concentrations.

### Conclusions

Understanding of carbonate-stone damage and dissolution by acid deposition is hampered by the lack of procedures to measure dissolution rates and identify deterioration mechanisms. Damage to marble in the environment is influenced by physical, chemical, and biological processes. These processes are not yet well understood; only recently have test design and precision become sufficient to detect marble damage caused by humans.

Estimates of environmental damage to carbonate stone require standardized methods and appropriate reference materials. This article details our expansion of carbonate-stone damage studies developed during the NAPAP program by the identification and quantification of marble damage to a Vermont marble reference sample.

The most important factors in marble dissolution were coincident low rain rate and decreased rainfall pH. At pH values less than 4.0, marble dissolution was greatest. Episodes of high rain rate and increased rainfall pH were associated with less marble dissolution than episodes of low rain rate and decreased pH.

The dry deposition of sulfur is also recognized as an important factor in the dissolution of carbonate stone. Preliminary results from modified dry-deposition algorithms showed that 10 to 50 percent of the calcium washed from the marble surface during a storm was from the dissolution of gypsum formed by the reaction of SO<sub>2</sub> with the marble surface during dry periods. Further research is needed to validate and refine these algorithms so that they can be incorporated into a damage function for carbonate stone.

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