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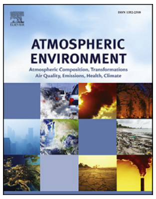

Acid rain attack on outdoor sculpture in perspective

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HIGHLIGHTS

- Most significant sculptural materials are carbonate stone and bronze.
- Weathering processes due to rain can be measured by the mass balance method.
- Geochemical modeling can be applied to analyze mass balance data.
- Rain acidity effects are negligible compared to dry deposition.
- Organic acids may also have a significant effect.

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ABSTRACT

A major concern motivating research in acid rain materials effects has been the potential for damage to cultural heritage, particularly outdoor marble and bronze sculpture. However, a combination of field and laboratory studies has failed to show a correlation between rain pH and loss of materials. In order to understand this counterintuitive lack of acid rain effect, an aqueous geochemical modeling approach was used to analyze rain runoff chemistry for the relative importance of acid rain neutralization, dry deposition, and in the case of marble, natural carbonate dissolution. This approach involved the development of pH − SO_4^{2-} phase diagrams for marble (calcium carbonate) and bronze (copper) under ambient environmental conditions. This then enabled reaction path modeling of the acid neutralization process using the pH range typically found in wet deposition (3.5–6). The results were for marble that the theoretical maximum amount of Ca^{2+} ion that could be lost due acid rain neutralization would be 0.158 mmol/l compared to 10.5 mmol/l by dry deposition, and for bronze, the Cu^{2+} ion losses would be 0.21 mmol/l and 47.3 mmol/l respectively. Consequently dry deposition effects on these materials have the potential to dominate over wet deposition effects. To test these predictions the geochemical models were applied to examples of data sets from mass balance (runoff vs rainfall) studies on a marble statue in New York City and some bronze memorial plaques at Gettysburg PA. Although these data sets were collected in the early 1980s they remain valid for demonstrating the mass balance method. For the marble statue, the mean Ca^{2+} losses by dry deposition was about 69% of the total compared 0.3% for acid rain neutralization, which was less than the natural carbonate dissolution losses of 0.8%. For the bronze, the mean Cu^{2+} losses were 70.6% by SO_4^{2-} dry deposition and 23% by NO_3^- dry deposition compared to 6.4% by acid rain neutralization. Thus for both cases the wet deposition component was less than the variability of the dry deposition components, which explains the observed lack of correlation between the rain pH and the material losses. In addition, for the marble case, there was evidence for HCl acid vapor attack resulting from nitric acid/sea salt interactions and for bronze, ammonium ion may be important. In both cases, significant imbalances suggested that unmeasured organic acids may have a significant effect.

1. Introduction

During the 1970s and 1980s, public concern about acid rain effects often focused on its potential damage to outdoor works of art, which includes both sculptural details on buildings and free standing statues. In fact one eminent scientist in the field of stone conservation predicted in 1973 that the loss of cultural heritage would increase exponentially by the end of the millennium (Winkler, 1973). However, after over a decade of research, it was

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concluded that for marble and bronze, the two materials most often used for outdoor sculpture, the effect of acid rain was negligible (Meakin et al., 1992; Mossotti et al., 2001). In order to understand this counterintuitive result, geochemical reaction path models have been developed that make it possible to investigate the contributions of the individual processes that are involved in the weathering of these materials.

Outdoor sculpture has traditionally been made from two major groups of inorganic materials: stone and metals. A rough idea of the relative frequency of occurrence of these materials in outdoor sculpture in the United States is given by Table 1, which has been compiled from a data base that is maintained by the American Art Museum of the Smithsonian Institution (Smithsonian American Art Museum, 2015).

Although many different types of stone have been used for sculpture, the most vulnerable to potential acid rain damage are marble and limestone (Steiger, 2015). The former is essentially a recrystallized form of the latter; both are composed of calcite ($CaCO_3$). Other types of stone which are composed of silicate minerals such as granite or sandstone are intrinsically more resistant to acid attack.

A variety of metals have been used in sculpture including cast iron, steel, zinc and lead and bronze. Tidblad (2015) has made a recent review of the literature on air pollution effects on metals. Bronze has been preferred for sculpture since antiquity because of its resistance to corrosion and favorable casting properties. As indicated in Table 1, it is by far the most widely used metal in sculpture in the United States.

The term “bronze” actually covers a wide range of compositions in the quaternary system Cu-Zn-Sn-Pb. Pure copper is too soft for practical applications. Consequently, other elements have usually been added to harden it and possibly also to change its color. These has varied over time as shown in Table 2. In antiquity, tin was the major alloying element, despite its high cost. Small amounts of lead improve the flowability of the molten bronze and enhance its ability to reproduce fine details. Since the Renaissance the trend has been to replace tin with lower cost zinc. Since the 19th century sculptural bronze has contained 85–95% copper (Selwyn, 1996). The term “architectural bronze” is currently in wide use for a 57% Cu 40% Zn 3% Pb composition, although technically a copper alloy with this level of zinc should be called brass (CDA, 2015).

The total erosion rate of a material exposed to the outdoor environment consists of two components: chemical dissolution and granular disintegration. The latter consists of the loss of solid grains of the material due to mechanical forces of gravity, wind, thermal cycling etc. Chemical dissolution often facilitates granular disintegration by attacking the intergranular binding phases that hold the grains together.

Table 1
Occurrence of outdoor sculptural materials in the United States (number of entries).

Stone		Metal	
Marble	4483	Bronze	13,151
Limestone	2048	Steel	7270
Sandstone	597	Aluminum	1400
Granite	8668	Cast iron	462
		Zinc	188
		Lead	131

The three metrics of erosion rates are: surface recession, weight loss or solution mass balance. Their features are compared in Table 2. Surface recession is measured in terms of the displacement of a point on the current surface from a reference point representing the original position of the surface. This usually done using a micrometer depth gauge mounted in a frame attached to some bolts or studs that are permanently installed in the surface (Stephenson and Finlayson, 2009). Mass loss is the method typically used for measuring atmospheric corrosion of metals. It consists of measuring the weight change of tablets or coupons of material after exposure to the atmosphere (ASTM, 2011). Finally, the mass balance method consists of collecting rain water falling on the surface and simultaneously collecting the runoff. The difference in solution chemistry is the result of reactions taking place with the material (Livingston, 1986). The magnitude of the attack is estimated by the increase in the concentration of a characteristic cation that is representative of the material, Ca^{2+} in the case of carbonate stone and Cu^{2+} for bronze.

The three metrics are incommensurate, strictly speaking, since each concerns a different type of dimension: distance for surface recession, mass for mass loss and concentration for mass balance. It is possible to make some approximate conversions from one metric to another using various assumptions. For example, with knowledge of the sample's surface area and material density, a mass loss measurement can be converted into a penetration depth which approximates an average surface recession. However, the uncertainties in the calculated penetration depth can be significant in the case of a granular and porous material such as limestone.

As shown in Table 2, both surface recession and mass loss measure the total erosion rate, but cannot distinguish between granular disintegration and chemical dissolution. Moreover, they cannot resolve acid deposition attack into its wet and dry deposition components. On the other hand, the mass balance measurement can discriminate explicitly between acid rain damage and other types of damage using geochemical modeling as described in Section 2. However, since it measures only chemical dissolution, it can't give an estimate of total erosion rate.

Finally, micro-erosion meter measurements are difficult to apply to outdoor sculpture because a horizontal planar surface is required. Moreover, it involves installing a set of studs into the surface, which could be objectionable on esthetics grounds. Similarly, mass loss measurements are not practical for outdoor sculpture which typically consists relatively massive objects permanently fixed in place. Only the solution mass balance approach, which is nondestructive and can be applied to irregularly shaped objects, is feasible.

The mass balance method provides data consisting of concentrations of ions. To order to extract useful information from these data, it is necessary to apply geochemical modeling techniques. In the following sections, geochemical models for the attack of acidic

Table 2
Comparison of damage quantification metrics.

	Surface recession	Mass loss	Solution mass balance
Measurement method	Micro-erosion meter	Gravimetry	Rainfall/runoff difference
Erosion processes	Chemical dissolution + granular disintegration	Chemical dissolution + granular disintegration	Chemical dissolution
Acid deposition components	No	No	Yes
Precision	5 μm	10 μg	1 μg/l
Dimensionality	Point	Volume	Area
Applicable to sculpture	No	No	Yes

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