

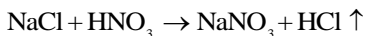
**MASS BALANCE EVIDENCE FOR HYDROCHLORIC ACID VAPOR  
ATTACK ON THE MARBLE OF THE STATUE OF PHOENICIA  
BY SEA SALT DECHLORINIZATION**

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**Abstract**

As part of an investigation the role of acid rain in the deterioration of marble outdoor sculpture in the New York City area, a study was carried out on the pink Holston marble of the statue of *Phoenicia*, which stands on the cornice of the Alexander Hamilton Custom House in downtown Manhattan. During individual rain storms, samples of rain water falling on the statue and runoff from the statue were collected simultaneously, and the solution chemistry was analyzed by ion chromatography and atomic absorption spectroscopy. Eight complete rainfall and runoff samples were collected during the course of the study. The mass balance is the difference between the rainfall and runoff chemistries and represents the amount of material dissolved from the statue. The mass balances for sodium and chloride showed a significant excess of the chloride/sodium molar ratio over the value of 1.174 that would be expected from sea salt particle deposition. The source of the excess chloride may be the sea salt dechlorination reaction between sodium chloride and nitric acid vapor:



The hydrochloric acid vapor can then attack carbonate stone. The source of the nitric acid vapor is NO<sub>x</sub> air pollutant generated by fossil fuel combustion. The sea salt dechlorination reaction has been identified in a number of urban areas located on sea coasts by the presence of coarse sea salt particles with surface layers composed of sodium nitrate. It is estimated to be the dominant source of excess chloride deposition in the New York City region. The HCl deposition mechanism accounted for approximately 2% of the dissolution, which is greater than the sum of wet deposition and carbonate dissolution. The remaining calcium imbalance appears to be due to unknown organic acids.

**Keywords:** New York City, marble, acid deposition, mass balance, organic acids, sea salt

**1. Introduction**

Acid rain has been identified as a potential major cause for damage to carbonate stone used for architectural purposes such as marble or limestone. A major complication is that in most urban areas such stone is also exposed to significant amounts of dry acidic deposition due to reaction of the carbonate with sulfur dioxide gas. Discriminating between the effects of sulfur dioxide and acid rain is important not only scientifically, but also for developing air pollution control policies to protect architectural monuments. Since sulfur dioxide comes from local sources, while acid rain is the result of long-range transport and chemical transformation of sulfur dioxide from distant sources, air pollution control policies may be different for local versus remote sources (Livingston 1997).

In order to investigate the relative importance of wet and dry deposition a mass balance study was conducted on a marble statue in New York City (Livingston 2008). It was found that wet acid deposition contributed very little to the marble dissolution, which was dominated by dry deposition. In the course of the research it was also found that a significant amount of stone dissolution could not be accounted for by either wet or dry deposition. Therefore, the objective of this paper is to extend the geochemical analysis of the data to identify other causes of stone deterioration.

### 1.1 The mass balance approach

Sabbioni (2003) has reviewed the literature concerning research on the effects of air pollution on stone. There are three different and incommensurate approaches to measuring stone damage: weight change, surface recession and mass balance. The mass balance approach consists in exposing stone specimens to rainfall and then collecting the runoff for chemical analysis (Livingston 1986). Any difference in the concentration of a given ion between the precipitation and the runoff can come only from interactions with the stone. For stones like marble or limestone, which are composed largely of calcium carbonate, the increase in  $\text{Ca}^{2+}$  in solution is a direct measure of the amount of stone dissolved during a precipitation event. One advantage of the mass balance approach over the other two methods of measuring stone damage is its high sensitivity. The minimum detectable limit for  $\text{Ca}^{2+}$  can be as low as 20  $\mu\text{g/L}$  (Peden 1983), which implies a surface recession of about 1 unit cell of calcite or 1.7 nm for a single 1 cm rain event. A number of investigators have therefore performed runoff measurements using a variety of experimental designs (Sabbioni 2003).

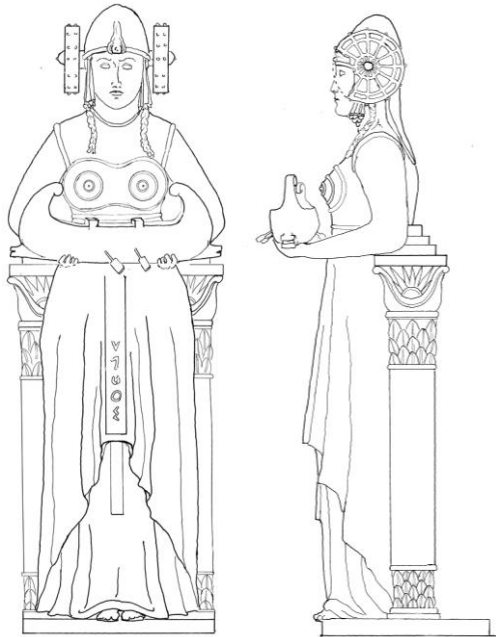
### 1.2 The statue of *Phoenicia*

The mass balance experiments were carried out on the statue of *Phoenicia* (Figure 1a) located on the Alexander Hamilton Bowling Green Custom House, formerly the Bowling Green Custom House, in New York City. This was part of a larger program of studies of air pollution and stone deterioration conducted at the site as part of an international program organized by NATO's Committee on the Challenges of Modern Society (Baer et al. 1982).

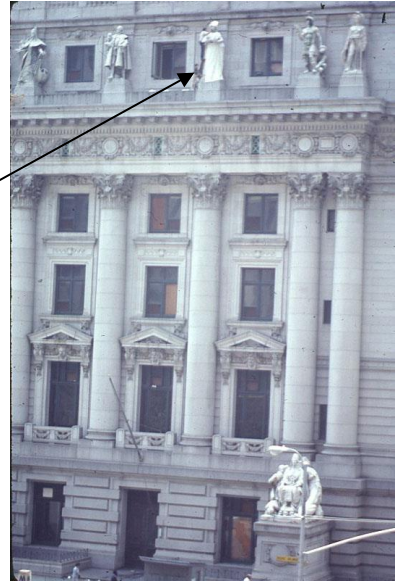
The statue of *Phoenicia* is one of a row of 12 statues representing leading maritime nations that stand on the cornice of the north facade of the Alexander Hamilton Custom House, which is located at the lower end of Manhattan Island (Figure 1b). Frederick W. Ruckstull received the commission for the statue representing the ancient empire of *Phoenicia*. However, the Custom House's architect, Cass Gilbert, made several major suggestions for the statue's design including the pose, the use of columns and, in particular, the elaborate headdress. The latter was modeled after a sculptural artifact, the *Dama de Elche*, which had recently been excavated in 1897 at Elche, Spain, near ancient Cartagena. (Livingston 2008).

The marble used for *Phoenicia* is from the Holston quarries of east Tennessee. This is a major source of sculptural marble in the United States and has been used in a number of other historic monuments including the National Gallery of Art in Washington, DC. The Holston marbles are fine grained in texture and have characteristic colors ranging from pink to a reddish brown. The marble is essentially pure calcite with minor traces of dolomite and clay stylolites (Dale 1924). The pink color is attributed to traces of hematite.

*Phoenicia* was chosen over the 11 other statues at the site because of her relatively simple geometry. She is 274 cm tall and stands on a 101 cm by 101 cm base, which is located on the sixth-floor cornice level of the North facade (Figure 1b). This position,



**Figure 1a.** Statue of Phoenicia



**Figure 1b.** North facade, Alexander Hamilton Custom House, Bowling Green, New York City

30.5 meters above the ground, eliminates the complications from groundwater, road salt and other causes of deterioration found at street level. The statue is mounted in such a way that it is exposed on all sides to the atmosphere and to rainfall. *Phoenicia* was put in place in 1906 and thus had 75 years of exposure to the weather and air pollution at the time the runoff measurements were made. During this period levels of sulfur dioxide in the Manhattan area are estimated to have peaked in the 1950s, but no monitoring data are available. The earliest records, from 1967, show levels as high as  $420 \mu\text{g}/\text{m}^3$  (Ferrand and Blade 1969). Subsequent air pollution control measures reduced the level significantly to the point where the concentration of  $\text{SO}_2$  averaged  $47 \mu\text{g}/\text{m}^3$  at the time of the mass balance measurements (Delaware 1982). Visual inspection showed a characteristic pattern of light-colored stone in the areas washed by rain and darker areas including some biological growth on the rest of the surface.

## 2. Experimental Methods

The procedure called for collecting simultaneous samples of water of incident rain and of the resulting runoff from the statue. The samples were then analyzed using the U.S Environmental Protection Agency's standard protocol precipitation quality analysis for concentrations of several specified ions, which were: sulfate, nitrate, ammonia,

chlorine, sodium, magnesium, potassium, and phosphate (Rockwell International 1982). Also measured in both types of samples were pH and conductivity.

The runoff collection apparatus consisted of plastic guttering fixed around the perimeter of the base of the statue. Plastic tubing led the runoff by gravity from the gutters to 17 liter containers below the base. Leakage was avoided by the use of inert caulking and Teflon paper barriers.

The incident rainfall was collected in 19 liter glass containers fitted with large plastic funnels. It was found necessary to put out several of these collectors in order to acquire enough sample from a given rain event to provide an adequate volume of water (about 2 liters) to carry out all the specified analyses. These containers remained permanently on the roof as passive samplers, collecting all the rainfall that fell over the duration of the sampling cycle. This approach, in which the collector is always open, also collects particulate matter during dry periods, and is known as bulk collection, as opposed to collectors that collect only during precipitation. After each sample was collected for analysis, the containers and funnels were rinsed with distilled water and put back in position. The analyses were performed by Environmental Protection Agency staff at the Edison Laboratory in Edison, NJ. Atomic absorption spectroscopy was used for the metals and ion chromatography for the anions. The precision of these analyses is typically 1-2%.

### 3. Results and Discussion

Although it is preferable to collect the samples immediately after each individual rain event, this was usually not possible. In general the samples were taken during the regularly scheduled weekly visits and thus combined several different rain events. A total of 23 runoff samples were collected. However, due to lack of sufficient volume of rainfall samples for the earlier events, only the eight most recent cases could be fully analyzed. These were taken in the months of March through May of 1981. The sampling program had to be discontinued after that time because of the start of restoration work on the Custom House.

Before calculating the mass balances, the solution chemistry was adjusted for carbonate species and ion pairing. The carbonate species present are the result of the absorption of atmospheric carbon dioxide. It is not directly measured in the acid rain protocol, but rather it is estimated from Henry's Law and the association constants of the carbonate species (Livingston 1992). In the pH range usually found in rainfall or runoff, the dominant carbonate species is the bicarbonate ion,  $\text{HCO}_3^-$ .

Calcium and sulfate ions form a neutral species  $\text{CaSO}_4^0$  by ion pairing, which accounts for 30% of the total gypsum solubility. The atomic absorption analytical method gives total calcium i.e. the sum of  $\text{Ca}^{2+}$  and the calcium ion. On the other hand, ion chromatography gives only  $\text{SO}_4^{2-}$  ion, not total sulfate. The algorithm for finding these missing components is given in Nordstrom and Munoz (1985).

After these adjustments to the individual solutions, the runoff-rainfall differences can be calculated. These are presented in Table 1. Also included are columns for total calcium  $\text{Ca}_T$ , the sum of  $\text{Ca}^{2+}$  ion and the Ca in the  $\text{CaSO}_4^0$ . Similarly  $\text{SO}_{4T}$  is the sum of  $\text{SO}_4^{2-}$  and the  $\text{SO}_4$  in the  $\text{CaSO}_4^0$ . No phosphate ion was detected in any of the solutions. All the ions except  $\text{H}^+$  and  $\text{NH}_4^+$  showed positive differences. The decrease in  $\text{H}^+$ , or increase in pH, is consistent with acid rain neutralization. The  $\text{NH}_4^+$  ion showed no consistent trend, which may be due to its instability relative to  $\text{NH}_3$  gas. The

increases in  $\text{Cl}^-$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$  and  $\text{K}^+$  are possibly the result of sea salt particulate deposition on *Phoenicia*'s surface, given the Custom House's location next to New York Harbor. This is discussed in more detail below.

**Table 1.** Runoff-Rainfall Differences, mmol/L

ID#	H	SO <sub>4T</sub>	SO <sub>4</sub> <sup>2-</sup>	Ca <sub>T</sub>	Ca <sup>2+</sup>	NO <sub>3</sub> <sup>-</sup>	NH <sub>4</sub> <sup>+</sup>	Cl <sup>-</sup>	Na <sup>+</sup>	Mg <sup>2+</sup>	K <sup>+</sup>	HCO <sub>3</sub> <sup>-</sup>
1	-0.0008	0.77	0.68	0.99	0.90	0.029	0.008	0.169	0.100	0.029	0.014	0.0030
2	-0.0004	1.32	1.08	1.83	1.58	0.035	0.068	0.311	0.165	0.016	0.024	0.0060
3	-0.0048	0.38	0.34	0.60	0.56	0.017	-0.028	0.076	0.061	0.012	0.004	0.0121
4	-0.0049	1.08	0.96	1.25	1.13	0.017	-0.061	0.124	0.061	0.012	0.013	0.0246
5	-0.0250	0.80	0.72	0.98	0.89	0.015	—	0.105	0.048	-0.009	0.007	0.0250
6	-0.0392	0.62	0.50	1.23	1.10	0.007	—	0.096	0.039	-0.008	-0.004	0.0039
7	-0.0075	0.48	0.46	0.38	0.36	0.063	—	0.085	0.052	0.007	0.002	0.0060
8	-0.0023	0.42	0.34	0.92	0.84	0.029	—	0.079	0.043	0.008	0.013	0.0116

### 3.1 Acidic deposition mass balance

Livingston (1992) pointed out that the total dissolved calcium in the runoff water is the sum of three different reactions, each of which creates a distinctive signature in the runoff chemistry that can be used to estimate its relative importance. The karst reaction, or natural carbonate stone weathering, increases the  $\text{HCO}_3^-$  concentration. The acid rain neutralization reaction reduces the  $\text{H}^+$  concentration. Finally, the dissolution of gypsum, the reaction product of sulfur dioxide gas or ammonium sulfate particulate dry deposition, increases the concentrations of  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$  ions.

In theory, the mass balance for the acid deposition group can be written as:

$$\Delta\text{Ca}_T = \Delta\text{SO}_{4T} + \frac{1}{2}\Delta\text{NO}_3^- + \frac{1}{2}\Delta\text{Alk} \quad (1)$$

where  $\Delta$  is the runoff-rainfall difference operator and Alk is the carbonate alkalinity, in this case simply as:  $\text{HCO}_3^- - \text{H}^+$ , defined

The differences for this group are plotted in Figure 2. It can be seen that  $\Delta\text{SO}_{4T}$  is much larger than the contribution of the other anions in every sample. This ion can only increase through the dry deposition process. Thus dry deposition dominates over the acid neutralization and karst processes as the major mechanism of marble mass loss in this situation. Not surprisingly, there is no correlation between the acidity of the incident rainfall and the  $\Delta\text{Ca}_T$  ( $r = 0.028$ ). Except for sample pair #7, there is always a significant excess of  $\text{Ca}_T$ .

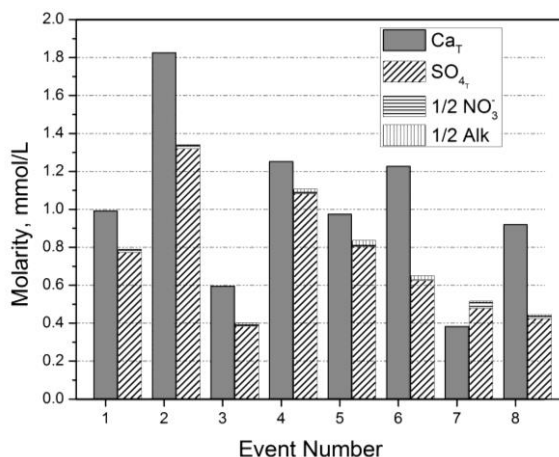
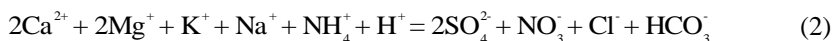


Figure 2. Comparison of Ca<sub>T</sub> vs acid deposition components

### 3.2. Calcium and Chloride Ion Imbalances

The acidic deposition mass balance (Equation 1) does not take into account all the ions in the solution. As shown in Figure 2, there remains an imbalance after taking into account the acid deposition-related anions. The full electroneutrality condition for the measured ions is:

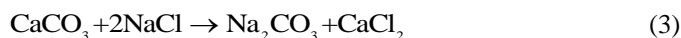


Inspection of Table 1 shows that the only other significant ions are Na<sup>+</sup> and Cl<sup>-</sup>, which are presumably the result of sea salt deposition. From the stoichiometry of pure sodium chloride, these two ions should have a 1:1 ratio, but in sea salt the actual Cl:Na ratio is 1.174 due to the presence of other ions in seawater (Zhuang et al. 1999). However, as shown in Table 2, in the runoff from *Phoenicia* the ratio ranges from 1.6 to 2.5, indicating a significant excess of Cl<sup>-</sup> over Na<sup>+</sup>. This excess is thus available to balance the Ca<sup>2+</sup>.

Table 2. Calcium and chloride imbalances

Event #	1	2	3	4	5	6	7	8
Ca-SO <sub>4</sub> , μmol/L	219 ± 11	506 ± 19	211 ± 7	170 ± 15	171 ± 11	603 ± 12	-95 ± 6	497 ± 9
Cl-Na, μmol/L	69 ± 9	146 ± 16	15 ± 6	63 ± 11	57 ± 9	57 ± 11	33 ± 4	36 ± 8
Cl/Na	1.69	1.88	1.25	2.04	2.19	2.45	1.62	1.82

Apparently a significant amount of the stone is being dissolved as Ca(Cl)<sub>2</sub>. However, the simple exchange reaction between sea salt and calcium carbonate expressed as:



is ruled out based on thermodynamic considerations. Sodium chloride and calcium carbonate form a stable equilibrium mineral assemblage under ambient conditions. The reaction of Equation (3) is in fact the basis for the Solvay process, which is used to

produce sodium carbonate on the industrial scale, but this requires high temperatures and the use of ammonia as an intermediate. As discussed below, another mechanism for chloride attack of the marble is from hydrochloric acid vapor, which is produced by the reaction between nitric acid vapor and sea salt.

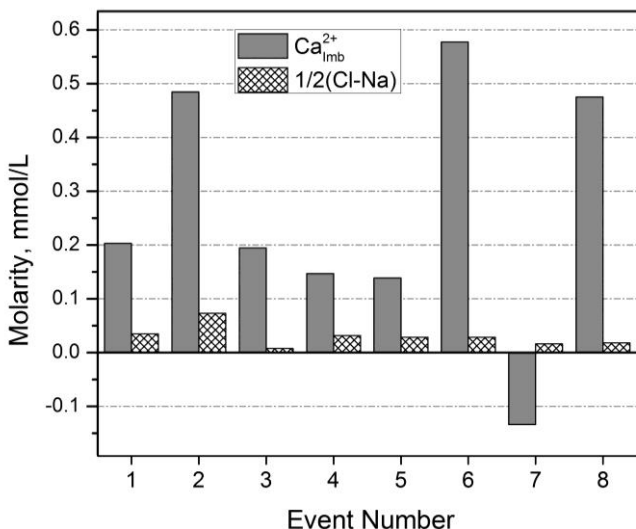


Figure 3: Comparison of Ca<sup>2+</sup> imbalance vs excess Cl

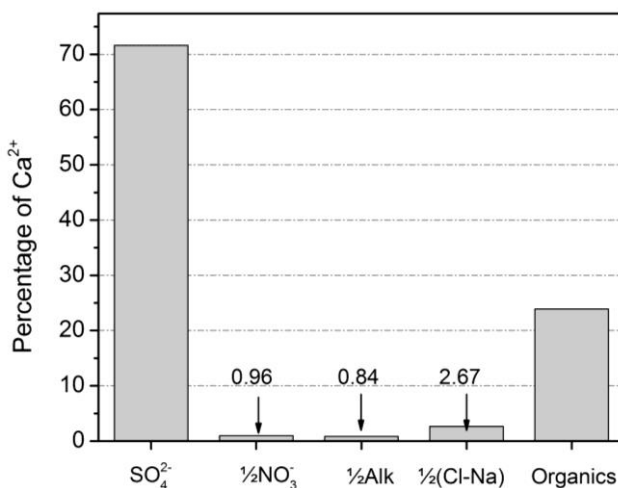
The Ca<sup>2+</sup> imbalances are compared against the excess Cl in Figure 3. Event 7 is an anomaly in which the SO<sub>4</sub><sup>2-</sup> exceeds the Ca<sup>2+</sup>. This indicates some unmeasured cation. For the other events, even taking into account the chloride effect, there still remains a significant positive Ca<sup>2+</sup> imbalance in the runoff associated with some unknown counter ions. The most likely candidates are organic acids, which were not included in the protocol for solution analysis. When the organic content of rain water has been explicitly analyzed, it has been dominated by low-molecular weight carboxylic acids such as acetic, oxalic, formic, pyruvic, etc. (Souza et al. 1999). These are presumably present in the runoff because of biological attack on the Holston marble. There is visual evidence of biological growth on the surface of *Phoenicia*, but the species have not been identified. Moreover, organic acid aerosols and vapors can be produced by a number of other anthropogenic sources such as chemical plants, incinerators and automobiles (Chebbi and Carlier 1996).

Therefore it is possible to write Ca<sup>2+</sup> charge balance in terms of five components:

$$\text{Ca}^{2+} = \text{SO}_4^{2-} + \frac{1}{2}\text{NO}_3^- + \frac{1}{2}(\text{Cl}^- - \text{Na}^+) + \frac{1}{2}\text{Alk} + \text{Organics} \quad (4)$$

Dividing the right-hand side of Equation (4) by Ca<sup>2+</sup> and multiplying by 100 makes it possible to express the relative importance of each of these components as a percentage of the total amount of dissolved calcium. The mean values of these percentages over all the events, except the anomalous Event # 7, are plotted in Figure 4. Since the percentages all have to sum to 100%, the Additive Log Ratio (ALR) method was employed for calculating the means (Aitchison 1986). As noted previously, the sulfate dry deposition process dominated under the environmental conditions prevailing in the New York City region in the early 1980s, accounting for over 70% of the dissolved

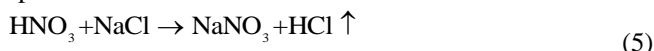
calcium. Next in importance was the inferred organic component, at roughly 24%. The chloride component was third, more than the nitrate and acid neutralization components combined.



**Figure 4.** Mean values of components of calcium dissolution. (Event 7 omitted).

## 5. Sea Salt Dechlorinization

A possible source for the excess Cl component is the sea salt dechlorinization (SSD) reaction in coastal areas between sea salt particles and nitric acid vapor to produce hydrochloric acid vapor:



The nitric acid vapor is a product of a complicated chain of reactions in the atmosphere beginning with nitrogen oxides (NO<sub>x</sub>) emitted from combustion processes (Moussiopoulos et al. 1995). Evidence for SSD is found in the bulk chemistry of the coarse fraction of particulate air pollutants, which shows a depleted chloride content relative to sodium (Bardouki et al. 2003). Complementary evidence is the increase in Cl in rainwater samples due to HCl absorption (Shapiro 2007). In addition, TEM examination of individual coarse particles have shown complete Cl depletion (Roth and Okada 1998). A review of the literature on SSD is given by Evans (2003).

Data relevant to SSD in the New York City area are very scarce. A major campaign of particulates monitoring was carried out at the Queens College site in Manhattan in the early 2000s (Drewnick et al. 2004). However, the analysis did not include Na or Cl. The coarse particulate fraction (>2.5 μm) did show nitrate concentrations that are indicative of SSD. The nearest available acid rain monitoring station is located at West Point, NY, which is approximately 60 miles inland from New York Harbor (Shapiro 2007). Nevertheless, the rainwater samples contained a significant Cl excess, which the authors concluded is due mainly to SSD. The nitric acid vapor is a product of a complicated chain of reactions in the atmosphere.



## 6. Future Pollution Trends and Potential for Stone Damage

Figure 4 indicates the relative impact of various environmental factors on the dissolution of calcium. However, this ranking is specific to a given geographical location, New York City, and time period, the early 1980s. The relative importance could be different at another location due to climate, topography and distribution of pollution sources. Even for a given location, the impacts can change over time as pollution control measures are put into place or urban and industrial development increases. For example, in New York City the concentration of  $\text{SO}_2$  averaged  $47 \mu\text{g}/\text{m}^3$  (17.9 ppb) at the time of the mass balance measurements (Delaware 1982). Since then, because of fuel changes and pollution control technology, the levels have decreased. Current levels are roughly 3.7 ppb (NYDEC 2012). Since  $\text{SO}_2$  deposition is roughly proportional to concentration (Spiker et al. 1995), this implies that the rate of calcium dissolution by this factor has decreased by 80%. Consequently, it would account for only 14% compared to 8% by chlorides, assuming that all other factors stayed the same. On the other hand,  $\text{NO}_x$  related pollution in the region has tended to increase over time. Nitric acid vapor itself is not routinely monitored under EPA regulations. However, monitoring of ozone, which is a precursor to  $\text{HNO}_3$ , is required. Ozone levels in the New York City region have roughly doubled from 1993 to 2011 (NYDEC 2012), implying that the impact of chlorides on stone deterioration could approach that of sulfate dry deposition. The sea salt chloride effect could become even more important in other parts of the world where Mediterranean-type climates favor more intense  $\text{NO}_x$  related pollution such as in the Los Angeles basin (Eldering et al. 1991) or Athens, Greece (Moussiopoulos et al. 1995). Moreover, in the same coastal areas, increased urbanization in the future would increase both  $\text{NO}_x$  and organic acid emissions. To monitor these effects, mass-balance studies of stone rainfall-runoff would be highly desirable.

## 7. Conclusions

The mass balance study of the statue of *Phoenicia* has provided insights into the relative importance of various stone deterioration processes in an urban atmosphere. Concerning the conventional acidic deposition processes, wet deposition i.e. acid rain proved to be insignificant compared to dry deposition. However, in addition to these effects, two other processes were also identified: attack by hydrochloric and organic acid vapors. These may become more significant over time as urbanization continues and sulfur dioxide emissions are controlled. Any future mass balance studies need to include explicit measurement of organic acids.

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