Transactions on Ecology and the Environment vol 21, © 1998 WIT Press, www.witpress.com, ISSN 1743-3541

Acid rain in Mexico case: Maya monuments

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Abstract

The Maya monuments in South East Mexico and Central America are being considered as a whole, "Monuments to Mankind" by UNESCO. However, there is great concern over the unwanted threat potential of acid rain on these buildings of historical importance. Effects of acid deposition on monuments are well known and demonstrated either by natural weathering or by man made pollutants. The occurrence of acid deposition on the Mexican Maya area has been registered by our group at National University of Mexico, suggesting that due to the physical and chemical characteristics of the construction material used by the Mayan civilisation, a potential for deterioration could exist in such monuments. The purpose of this paper is to present the advances and preliminary results of an ongoing research performed in our laboratory on the effects of the acid rain deposition on the construction materials of these monuments.

1 Introduction

Characterization of the chemical nature of precipitation is currently under considerable investigation due to the increasing concern about man's atmospheric inputs of substances and their effects on land, surface waters and materials. Previous work suggested that acidity and concentrations of sulfate, nitrate and some other components of precipitation have been increasing in recent years in certain geographic locations as a result of man's activities.[10] The effect of acidic deposition has particular relevance for cultural materials such as sculpture, monuments, and ornamental elements of buildings.

The occurrence of acid deposition on Mexican Maya area sites has been registered by the Environmental Pollution Section at the Center for Atmospheric Sciences, National University of Mexico, suggesting that the construction material used by Mayas (carbonate stone), has a potential for deterioration by acid rain.[3] Because of the heritage value of Maya monuments, it is very important to know if such potential of degradation does exist.

This paper presents the initial results of an ongoing research study on the potential of limestone dissolution by acid rain on samples of carbonate stones from Tulum at the Mexican Maya area. An experimental rainfall simulator chamber was developed for laboratory experimentation to examine the effects of simulated rain solutions, with ionic concentration similar to average rainfall composition measured previously in this Maya region.

2 Materials and Methods

2.1 Carbonate Stone Samples

The carbonate stone samples used in the experiment were obtained from the vicinity of Tulum, a very important Maya archeological site located in northwestern Quintana Roo State, Mexico (20° 12'N; 87°27'W). The stones were analyzed with regards to their petrographic characteristics by Dr. Ferrusquia at the Institute of Geology, National University of Mexico, following specific procedures mentioned elsewhere.[7,8] According this analysis[6], the stones samples belong to a geologic territory identified as Late Tertiary limestone referred to an undescribed formation. The petrography of the samples shows a megascopic aspect. Though the samples are too small to assess the beding of the unit, given their uniformity, it appears that the rock was thickly bedded, i.e., the strata were at least 80 cm. thick. Fresh surfaces of the stones are very pale orange 10 YR 8/2 in color, that weather to pinkish gray 5 YR 8/1 to light olive gray 5Y 6/1, following Goddard's et. al.,[8] chromatic chart.

Five thin sections sawed at different orientations to insure properly inspection of the rock volume, were studied by microscopy. The inspection shows that limestone consists of a mixture of allochemical grains and microcristalline calcite. The allochemical components form about 65% to 80% of the rock volume, as estimated from the thin sections; chiefly consist of oolites and pseudoolites, spherical to ovoid in shape, about 150 to 200 microns in diameter (the former), and 150-160 microns the lesser diameter to 350 microns the greater diameter of the ovoid forms. The oolites show their characteristic concentric-layer structure, some what obliterated though by micritization, i.e., micritic material forming a solic inner stroma; at least over half of the allochemical grains belong to these category, in most, two or-three layers (from the outside to the inside) are discernible. The pseudoolites do not show any layering, and originally might have been oolites or other kind of allochemical grains, their size and overall resemblance with the true oolites, indicating that probably they are heavily altered ("micriticized") oolites. Besides the oolites, scarce microfossils are present.

The matrix of the stone samples consists of microcrystals of calcite, 2-4 microns long ard/or wide, that make up 20 to 35% of the rock. The micrite does not show any alteration or fracturing. This indicates, that after deposition, there were no important structural deformational episodes that affected the limestone, nor diagenetic other than normal ones conducting to form limestone from the lime ooze deposited in the bottom of a shallow tropical sea.

Following Folk[7], the samples belong to an Oomicrite, i.e., a limestone formed by oolitic grains set in a micritic matrix. This kind of rocks are commonly originated as shallow marine, tropical lime ooze deposits sedimented under low energy-quiet water-conditions.

Other physical characteristics of stones were previously determined in our laboratory. Density and porosity of carbonate stones were determined according procedures by ISRM[9] and RILEM.[24] The percentage of water adsorption by stones was determined according the standard number C97-47 of ASTM.[1] Table 1 shows the resulting data obtained for 4 carbonate stone samples from the Maya region of Quintana Roo State, Mexico.

Table 1. Density, porosity and percentage of water adsorption by carbonate stones samples from the Maya region of Mexico.

No.	Sample origin	Density (g/cm^3)	Porosity (%)	Water Adsorption (%)
1	Carbonate stone from the Monumento del Rey, Cancún.	2.27	13.9	12.5
2	Carbonate stone from the Monumento del Rey, Cancún.	2.05	22.2	11.6
3	Carbonate stone from the Templo del Sol, Tulúm.	2.24	15.5	6.1
4	Carbonate stone from the Templo del Sol, Tulúm.	2.34	10.7	9.2
Average		2.225	15.575	9.850

2.2 Rain Sampling

The sampling station was located at the Institute of Marine Sciences, National University of Mexico at Puerto Morelos, Mexico (20°5'N; 86°54'W) (Figure 1). The site complies with the EPA site selection criteria of precipitation sampling sites of a regional station type.[5] Puerto Morelos is a small town located around 95 km northwestern from Tulum Maya archeological site and 50 km. north of Cozumel Island, where a power plant is located. The wet/dry collector used was an authomatic Aerochem Metrics Collector. The collector was located on a grass yard in order to avoid the resuspension of soil dust of local origin. The yard is located more than 50 m. away from of the beach.

2.3 Methods of Rain and Run-off Analysis

Wet and dry precipitation were sampled on an event basis for two years 1994-1995. pH was determined after collection with a Corning pH Meter Model 3D. Wet precipitation was collected in polypropylene bottles (Nalgene), sealed, and stored in the dark at about 4°C, according EPA recommendations for collection and handling of samples.[5] The Nalgene bottles were periodically sent to Mexico City for Chemical Analysis in the laboratory. Conductivity, and pH were determined with a Corning pH

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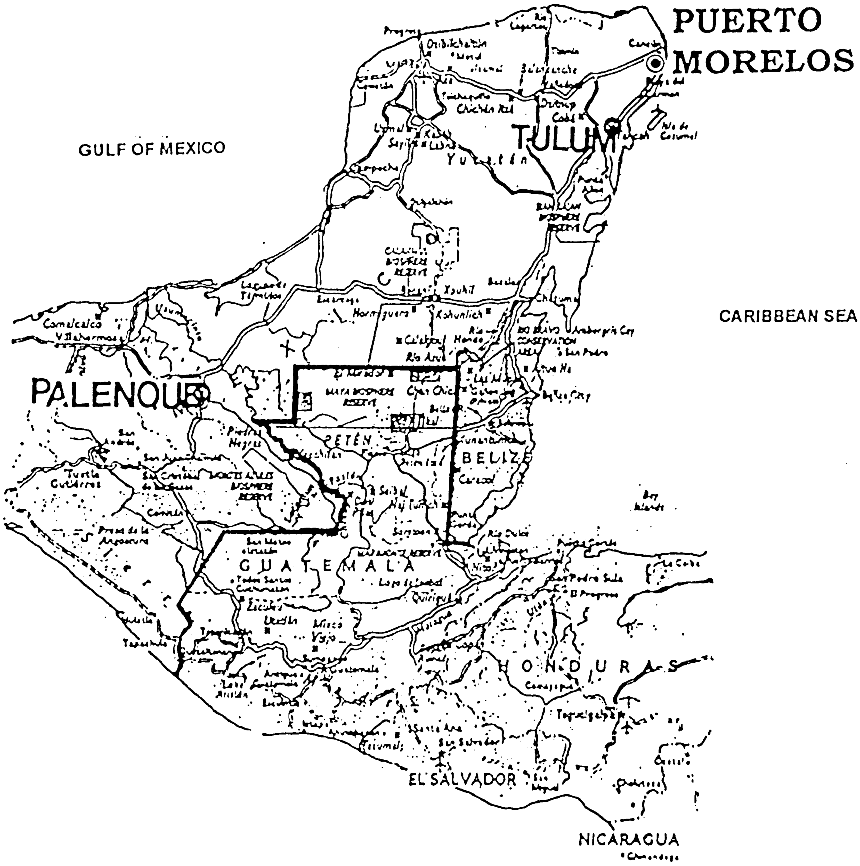

Fig 1: Maya region showing the sites of the study.

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Meter 240 and a YSI Model 32 Conductance Meter, respectively. Ionic concentrations of Ca^{++}, K^{+}, Mg^{++}, Na^{++}, NH_4^{+}, Cl^{-}, NO_3^{-} and $SO_4^{=}$ were analyzed by ion chromatography (Waters Model 510 HPLC). Resulting data were audited according procedures recommended by EPA.[5]

2.4 Experimental Rainfall Simulator Chamber

An experimental rainfall simulator chamber was developed in order to reproduce the expected effect of typical acid rain of the area on slabs of limestone. A schematic diagram of the rainfall simulation chamber is presented in Figure 2.

An acrilate structure (3/8" thick) supports a centrally positioned Pyrex glass distribution manifold which delivers the simulated rain through a series of tygon tubing. The drops fall directly on 2.5 cm. x 2.5 cm. x 0.5 cm. carbonate stone (slabs) samples, positioned in the center of five plastic bowl containers. The slabs are supported on acrylic frame holders with an average inclination of 40° to horizontal to avoid splashing of the drops and to enable the run-off mechanism. The run-off solution is collected within the bowl and delivered to polypropylene bottles through tygon tubing.We use these materials because they are considered as nearly inert to solutions with moderate to low acidity (> pH 3.0). The simulated rain solution is delivered to the chamber by gravity through tygon tubing. Among other flow and electronic controls inside the chamber we included an infrared light lamp to ensure constant ambient temperature and instrumentation for measure ambiental temperature, humidity and pressure. The environmental conditions inside the chamber were maintained the closest as possible to the annual average of ambient temperature (25°C) and relative humidy (75-85%) of the region.

Simulated rain solutions, with ionic concentrations similar to average rainfall composition measured in Puerto Morelos during 1995, were prepared using analytical grade chemicals. Table 2 shows the final composition of rainfall used. The pH of the solution was adjusted to 4.6 by addition of 0.1M HNO_3. The dropping of the simulated solution was adjusted to the average rainfall intensity of the region (1,200 mm/year). The collected run-off solutions were analyzed according the same procedures and instrumentation as previously mentioned for rain analysis. The maximum diameter of the drops is estimated in 0.5 cm. with a

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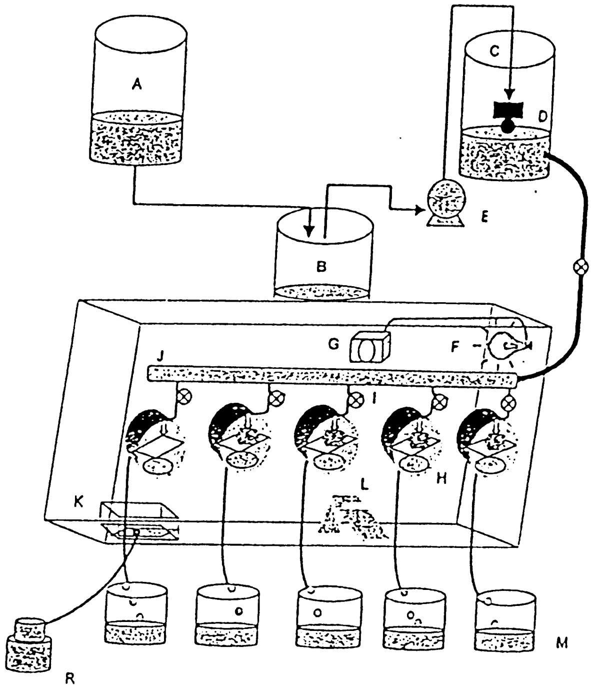

A Simulated rain container
B Equalizer container
C Simulated rain container
D Level controler to assure the same hydrostatic pressure in the manifold "J"
E Water pump
F Infrared light lamp controlled by dimmer "G"
G Dimmer
H Sampler container, slabs holds at 15° of inclination inside a plastic bowl to avoid splashing of the drops and to collect the runoff
Y Valves to control flow of simulated rain and blank from each dispenser
J Manifold distributor of simulated rain
K Container with dionazed water where an inmerse couple variable resistor is located to control the mass of evaporated water (Joule effect)
L Humidity, pressure and temperature meter
M Polypropylene bottles to collect the runoff solution
R Variable resistor (rheostat)

Figure 2: Experimental rainfall simulator chamber scheme.

variation of ±3.56%. The separation distance between the tip dropper and the stone is around 6 cm. The rate of simulated rain impacted on each slab (25 cm^2) was adjusted to 1.25 ml/min. At this dropping rate, the volume of solution and time required to simulate one year of rainfall (1,200 mm/year) was 3 liters and 40 hours of dropping, respectively. The experiment was schedulled to simulate 5 "rain" events of 8 hours each one, with a drying period of 16 hours between them. The run-off for each event was composited to have a solution volume equivalent to 34 rain events. For each event a volume average of 532 ml. of run-off solution was collected.

Table 2. Mean concentrations of major anions and cations in rain samples collected at Puerto Morelos, México during 1995.

Ion	Concentration (mol/lit)
Na^+	3.120×10^{-4}
NH_4^+	2.287×10^{-5}
K^+	1.438×10^{-5}
Mg^{2+}	4.625×10^{-5}
Ca^{2+}	4.387×10^{-5}
Cl^-	4.453×10^{-4}
NO_3^-	3.796×10^{-5}
SO_4^{2-}	3.411×10^{-5}

3 Results and Discussion

Previous reports of analysis results from run-off experiments can be found in Reddy and Youngdahl,[11] Reddy and Baedecker,[12] Baedecker et.al.,[2] Webb et.al.,[15] and Butlin et.al.,[4] In the analysis of the chemical data from the run-off experiments, the quantity of calcium ions in the run-off solutions was taken as a measure of the recession of the carbonate stone surface due to chemical erosion by dissolution. Since the simulated rain itself may contribute to the total calcium measured in the run-off solutions, the calcium concentrations collected from an inert acrylic reference slab was used as a baseline measurement. Thus the reference (or "blank") concentrations were substracted from the stone slabs to obtain a measure of stone dissolution.

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The total annual recession due to dissolution was calculated as the product of volume simulated rainfall amount and calcium concentration, divided by the product of slab area and stone density, according Baedecker et.al.,:[2]

$$R = \left[Ca^{2+}\right] \cdot V_{r-o} \cdot 10^3 / A\rho \qquad (1)$$

where: R is the recession of the stone surface (μm/year); $[Ca^{2+}]$ is the calcium molar concentration in the run-off solution; V_{r-o}, is the total volume of rain-off solution (lit); A is the area of slab (cm^2), and ρ is the stone density (g/cm^3). In equation (1), it is considered that limestone has a retention of incident rain equal to 0.36.

Figure 3 shows the resulting plots of cumulative recession (μm) against simulated cumulative exposure (years) on 4 carbonate stone slab samples and their average. The average data points fall along a curve line which is well represented by the power equation:

$$R = 1.067(T)^{2.489} \qquad (r^2 = 0.99) \qquad (2)$$

where, T is the simulated exposure time (years) and R is the cumulated recession (μm). Taking the average slope of the curve calculated from eq. 2, we found a recession rate of 3.65 μm/year for a 10 year simulated exposure time.

Reinmann and Youngdahl[13] performed an outdoor study in 4 sites of the United States for 4 years, reporting recession rates for limestone slabs which are shown in Table 3. This table also shows the resulting equivalent rate for our experiment for the same period. There is an average difference of 2.7 times between recession rates for U.S. sites and Tulum.

Table 3. Comparison of Estimated Recession Run-off Rates.

Site	Recession Rate (μm/year)
North Carolina[13]	6.8
District of Columbia[13]	7.5
New Jersey[13]	7.6
Tulúm	2.71

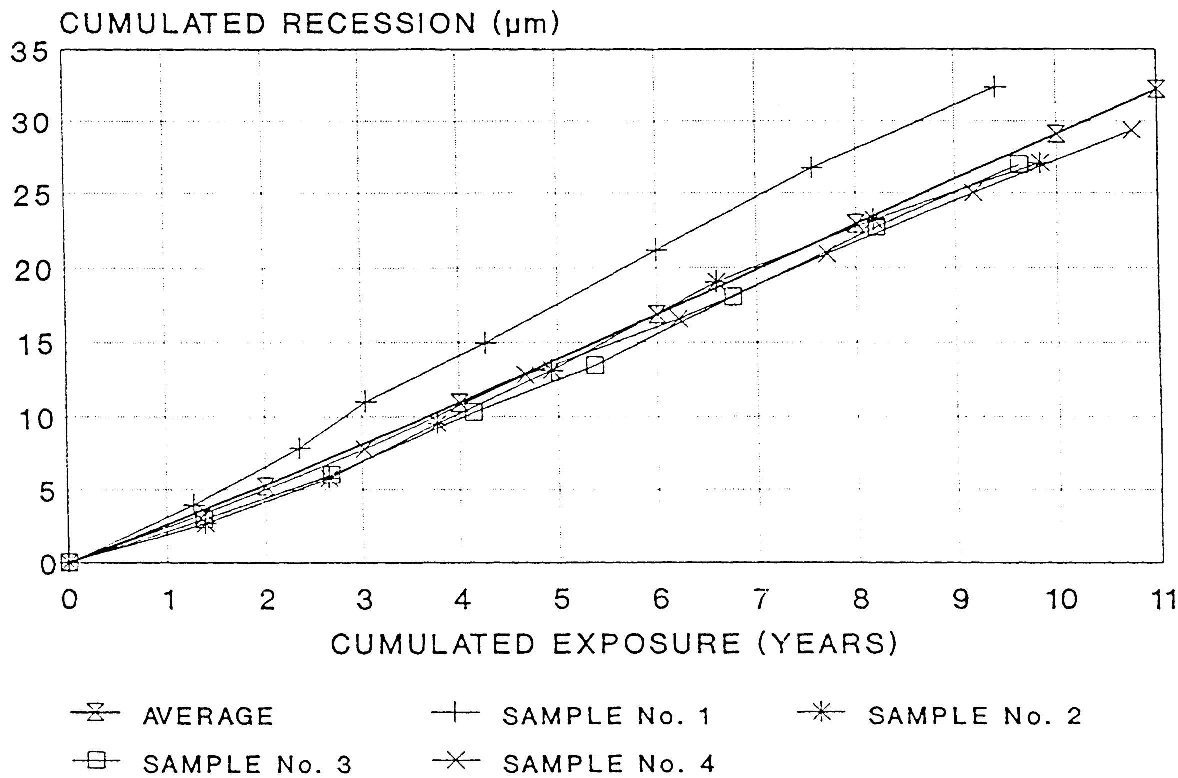

Figure 3: Cumulative recession plotted against cumulative exposure for limestone slabs from Tulum.

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4 Conclusions

Carbonate stones used in construction of Maya monuments and buildings, are potentially subject to a number of physical, chemical and biological weathering processes that may be accelerated by acidic depositon. Of various degradation processes, accelerated dissolution by rain water containing elevated levels of hydrogen ion, is the focus of this ongoing research. The preliminary results described here are based on the data generated from the first stages of the study.

Rates of carbonate stone recession for slab samples from the archeological Maya site of Tulúm, Mexico, were estimated using a rainfall simulator chamber constructed in our laboratory. Simulated rain solutions, with ionic concentrations similar to average rainfall composition measured in the region, were artificially prepared. The pH of the simulated rain solution was adjusted to 4.6 by the addition of diluted HNO_3. This pH was previously measured in rain samples of the region. Dropping of simulated rain on a set of slab stones, was set to represent the typical rainfall amount of the Tulúm region (1,200 mm/year). Cumulative recession estimates were determined following a procedure reported by Baedecker et.al., (1992) which is based on the calcium content of run-off solutions.

The cumulative recession (μm) for a set of four carbonate stone slabs (25 cm^2) mounted at 40° to horizontal, is well represented by a power equation ($R = 1.067\ (years)^{2.489}$). Estimated average recession rates for exposure simulated periods of 4 and 10 years are 2.71 μm/year and 3.65 μm/year respectively. Comparison with published recession rates (4 year period) for several outdoor experiments performed in northern United States, indicates that recession rate for the Tulúm region limestone is around 2.7 times smaller. This difference in observed recession rates, could be explained by the differences in the area and inclination angle of slabs used in both experiments exists. Therefore, as far as we know, a standard slab size and inclination angle for run-off experiments does not exist, so its necessary to issue such standard.

The presence of mechanisms of dissolution on stones were well evidenced in our experiment because of the strong change in pH units observed in the run-off solutions. The pH increases from 4.6 (incident simulated rain) to a range between 7.2 to 7.8 in the run-off solutions. However, since the run-off experiments are based on dissolution of a chemical species measure only the chemical disolution rates, the resulting recession estimates are expected to represent only a portion of the actual stone loss.

This preliminary approach to evaluate the potential deterioration effect by acid rain on Maya monuments in Mexico, should alert the social, political and academic communities about a possible destruction of monuments to mankind heritage.

Acknowledgements

The work described in this paper is a part of the ongoing study "Impact of the Acid Precipitation in the Decay of Mexican Maya Monuments", funded by the National Council of Science and Technology (CONACyT-UNAM project no. 0128-T9106). Special apreciation is extended to Dra. Georgina Fernandez V., Dra. Liliana Saldivar O. from National Univeristy Autonomous of Mexico, Ma. Teresa Franco y González from the National Institute of Anthropology and History (INAH) and the people at Puerto Morelos Experimental Station, Institute of Marine Sciences, University of Mexico (ICM-UNAM). Acknowledgements are also extended to Miss Leticia Valdez Barrón from the Center for Atmospheric Sciences.

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