

A Summary of the International Workshop on the Influences of Air Quality on the Mayan Heritage Sites in Mesoamerica

Summary prepared and edited by

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Thousands of Mayan sites exist in

Mesoamerica, from southeastern Mexico through Guatemala, Belize, Honduras, and El Salvador. From the playing field of Chichén Itzá (see Figure 1), to the ornate temple at Uxmal (see Figure 2), the splendor of Tikal, Guatemala (see Figure 3), and the quiet serenity and archeological importance of Copán, Honduras (see Figure 4), these sites inspire the international community. Their presence remains the cultural patrimony of the proud people who inhabit the region today. The ancient monuments of the Mayan civilization are now endangered. Painted murals on stucco surfaces flake. Inscriptions on stones disappear as salts leach from the rock. Limestone deteriorates. Mold forms. Acid rain appears to be the principal cause. Noted art historian Dr. Merle Greene Robertson has described acid rain as “the number one man-made problem” affecting Mayan monuments.¹

Professionals from Guatemala, Mexico, Honduras,

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and the United States met in Cancun, Quintana Roo, Mexico, October 16–20, 2005, to discuss the problem at a bilingual conference funded through a U.S. National Science Foundation grant and through funding from the Consejo Nacional de Ciencia y Tecnología (CONACyT) in Mexico. The workshop was organized by researchers from the Department of Civil and Environmental Engineering at the University of Cincinnati and the Sección de Contaminación Ambiental del Centro de Ciencias de la Atmósfera

de la Universidad Nacional Autónoma de México (UNAM). The goal of the workshop was to explore the potential impact of acid rain on the Mayan monuments, taking into account that the main construction materials used were composed of calcium carbonate (limestone). While the primary goal was to review the effects of acid rain on the monuments, a key objective was to review the effects on mural paintings of the Mayan monuments due to air pollutant effects on the pigments and colorants. Archaeologists, artists, preservationists, scientists, and engineers are working together to preserve the cultural patrimony of Mesoamerica.



Figure 1. Playing field at Chichén Itzá, México.



Figure 2. Temple at Uxmal, México.

The purpose of this article is to recognize the accomplishments of the research teams and organizations and to summarize the findings of the conference. Discussions on the first day of the workshop, concerning the archeological and cultural importance of the Mayan sites, were intended to educate the scientists and engineers about the national importance of these sites. On Tuesday, experts from the environmental sciences shared their research on acid rain. Researchers delineated the types and levels of degradation that were being seen at many of the sites and described the methods of restoration. The workshop attendees toured Tulum on Wednesday, before Hurricane Wilma forced an evacuation of the area. The workshop continued in Mérida on Thursday. Topics included the effect of meteorology on the dispersion of pollutants in the Yucatán region, the level of acid precursor emissions from point sources, the use of denuders to capture acidic particles, and possible funding for future research. The names of the presenters, their affiliations, and their presentation titles are included in Table 1. Copies of the presentations are available at www.eng.uc.edu/mayan.

BACKGROUND

Some of the first studies on acid rain in Mexico started in the 1960s in Puerto Vallarta, Mexico.² In the 1980s, studies of acid rain precipitation were conducted in Mexico City with the backing of Captain Silvino Aguilar Anguiano, then-Director of the National Meteorological Services (SMN). This early research looked at wet deposition in the Metropolitan Zone

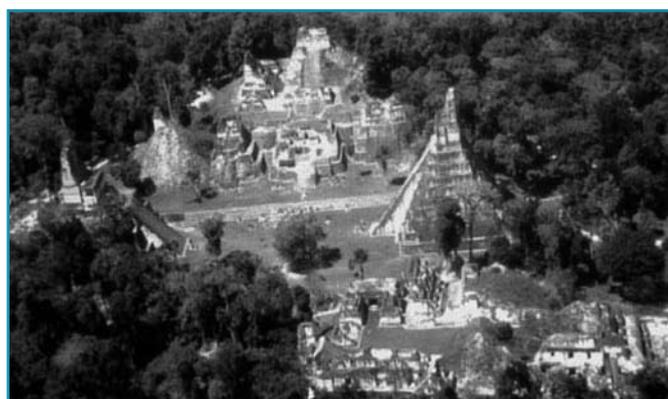


Figure 3. Tikal, Guatemala.



Figure 4. Copán, Honduras.

of Mexico City (MCMZ) and was carried out in 12 observatories of the SMN (the Airport, Chapingo, Cincel, Cuajimalpa, Cuatepec, Iztapalapa, Molinito, San Gregorio, San Juan Ixhuatpec, Tacuba, Tacubaya, and Tizayuca).^{3,4} The pH values found at that time were between 6.2 and 6.8. These studies indicated the need to modify the sampling system of the total deposition samples (dry and wet together in open-container “bulk deposition”) for the collection of rain (wet) as well as dry deposition using an automatic sampling system. In 1984, the first automatic collector of acid rain was installed at UNAM, which would then permit the separation of wet and dry depositions. This sampler is still in operation (see Figure 5). During the 1990s, measurements of wet and dry deposition were recorded by the Post Graduates College of the University in Chapingo in the Northeast area of the MCMZ. Samplers are now located in different areas of the country, since the interest in this kind of study has grown (see Figure 6).⁵

Studies on atmospheric chemistry and acid rain have also been conducted in the coastal region of the Gulf of Mexico by the Environmental Pollution Section of the Atmospheric Science Center (SCA-CCA-UNAM) and the U.S. National Oceanic and Atmospheric Administration (NOAA), dating back to 1986 when the first research studies on the ocean-atmosphere in the Gulf region were conducted.^{6,9}



Figure 5. Automatic wet/dry deposition sampler at UNAM.

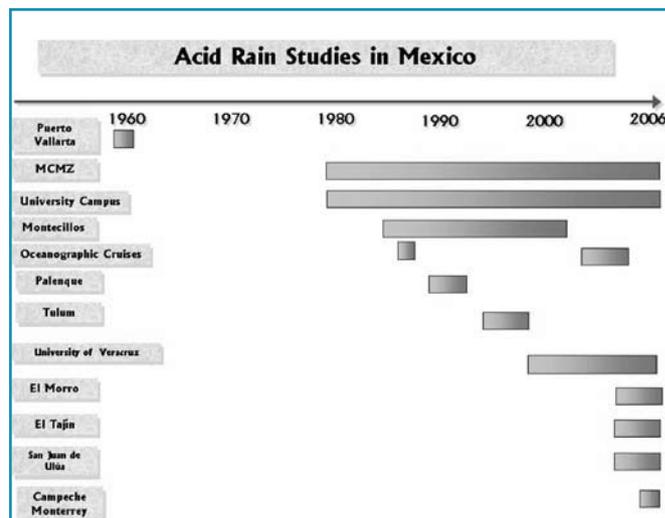


Figure 6. Acid rain studies in Mexico.

This research was done in collaboration with the Mexican Navy (aboard the Oceanographic Ship H-02) and with the participation of the Oceanographic Laboratory of Veracruz, Mexico. The research activities consisted of identifying the transport, transformation, and occurrences of atmospheric pollutants, as well as the pH determination of the depositions in the Gulf of Mexico. This bilateral effort between Mexican and U.S. scientists developed an important understanding of the atmosphere-ocean relationship on the Gulf region.⁹

In 2002, studies of air quality were completed in the continental platform of the Gulf of Mexico with the participation of the Institute of Limnology and Ocean Sciences from the UNAM. Since then, four research cruises have been carried out and completed, one in the east and three in the southern part of the continental platform in the Gulf region.^{10,11} More recently, in 2003 work began, in collaboration with the Atmospheric Monitoring System of Mexico City, to determine the wet deposition at 16 stations in the MCMZ.

In the 1980s, studies of acid precipitation were conducted in Tulúm, Quintana Roo, and Palenque, Chiapas.¹²⁻¹⁶ Additional studies of acid deposition have taken place at the archaeological zone of El Tajin, Veracruz (Central Institute of Anthropology and History) and the Coastal Ecological

in the New World. Many kingdoms flourished with their own ruling dynasties. Rulers engaged in long distance trade of exotic and rare objects such as jade and marine shells.

During the Post Classic period (900–1521 A.D.), these great kingdoms declined and were finally abandoned. The supporting populations never returned. Various theories and hypotheses have been proposed.²² A combination of factors contributed to their collapse, including external conflicts or wars among the Classic Mayan societies (wars), revolts against the kings,²³ climatic changes,²⁴ and overpopulation. When the Spaniards came to the Mayan area in the 16th century, the Mayan civilization was history.

The rediscovered sites of the great Mayan society are fueling an economic renaissance in Mesoamerica. Individual nations have identified thousands of sites, often as a result of clearing land to accommodate a growing local population. Government officials in these areas must choose one of several competing land use options: agriculture, petroleum extraction, mining, housing, transportation, or restoration and tourism. Powerful business interests may trump all other considerations. Archaeologists joke that the best preserved sites are the ones still buried.

Laura Pescador works to preserve the cultural patrimony of the Mayan people. In her workshop presentation, she detailed the problems associated with urban sprawl. The most common method used to clear the land (jungle) for farming is “slash and burn.” Hundreds of archeologically significant structures

The ultimate goal is to establish a Mayan Air Sampling Network to determine air emissions and meteorological conditions that contribute to the overall deterioration of these cultural heritage sites.

Station of El Morro de la Mancha in Veracruz (Institute of Ecology);^{17,18} in the Fortress of San Juan de Ulua in Veracruz;¹⁹ and the Engineering Institute of the University of Veracruz.¹⁹ Recently, studies have taken place in Monterrey, Nuevo Leon, an important urban and industrial area in the North of Mexico, and in the historic fortified town of Campeche, according to the United Nations Educational Scientific and Cultural Organization (UNESCO). The sampling and analysis method used in all the studied sites are those recommended by the U.S. Environmental Protection Agency²⁰ and the U.S. National Acid Deposition Program.²¹

The workshop planning took place in Cancun, Quintana Roo, Mexico, with the support of the National Council of Science and Technology in Mexico, and the U.S. National Science Foundation.

ARCHEOLOGICAL/CULTURAL IMPORTANCE

The height of Mayan civilization is called the Classic period, which lasted from 250 to 900 A.D. During that time, the ancient Maya reached intellectual and artistic heights incomparable

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have been uncovered—and destroyed—in this way. Fire, ash particulates, carbon dioxide (CO₂), and other pollutants have damaged the limestone rock and obliterated petroglyphs at Mayan sites. Residents have taken stones from the sites to rebuild their homes. Thieves have stolen artifacts to sell on the black market.

Restoration of archaeological sites requires money and, often, international cooperation. Dr. Seiichi Nakamura, for example, accompanied a team of Japanese archeologists who worked with the Programa de Investigación y Conservación del Parque Arqueológico Copán in Copan, Honduras, in uncovering a royal tomb during a road construction project. The tomb contained a skeleton covered with jade ornaments, including depictions of the Corn God, the Wind God, large earrings, and a woven mat. This site contains significant stone inscriptions, which indicate that the dynasty in Copán may have originated from Tikal, Guatemala.

According to Sofia Paredes Maury of the Fundación para la Conservación de los Recursos Naturales y Ambiente en Guatemala (FCG), “Every cubic meter of Guatemala contains an item of historic interest.” FCG uses a multi-disciplinary team to determine which sites to develop. It administrates projects and provides assistance through loans, monitoring and evaluation of projects, and implementing conservation initiatives in public and private lands. She invited the workshop participants to join the millions of people who have visited Tikal in the past decade. Rosa

Maria Chan, an archaeologist with ProPeten in Guatemala, presented photos from Tikal and Piedras Negras that illustrate the effects of oil and gas exploration, forest fires, and urban development.

More than five centuries ago, San Juan de Ulúa in Veracruz, Mexico, was a sand reef bank called Tecpantlayácac, used as a ceremonial port associated with a temple in honor of Tezcatlipoca. The Spaniards built a fortress on this site (between 1544 and 1779), using mainly petrified coral remains. The fortress was first used as a jail, then, after the independence of Mexico, it became an asylum, which was finally taken during the invasions by France (1838) and the United States (1847 and 1914). Later, it became the official residence for the President of the República Mexicana (1860–1915) and a military arsenal for the navy (1915–1962). Today, it is a Colonial monument and an international tourist destination.

José Hernández Téllez, a physicist, explained how the Spaniards, using the labor of African slaves, excavated the foundations and sacked part of the coral reef. They used coral to build the fortified constructions of Ulúa and the city of Veracruz. For lime, the Spaniards incinerated coral to obtain calcium. Since the 20th century, the fortress has suffered a lot of damage, including cracks in its walls, while the foundations have been weakened by the action of the waves and are gradually washing away. The warm and humid climate during summer, the urban development, and the

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expansion of the port of Veracruz have all accelerated the deterioration processes (e.g., the dilution of the coral by carbonic acid). Stalactites have formed under the vaults, and lichen and ferns grow on the walls. To mitigate the fortress' deterioration there is a need to continue with the environmental, chemical, and weather change studies.

ENVIRONMENTAL DEGRADATION

Calcium carbonate was used to build many of the Mayan structures, noted Elda Anrubio Vega. White, yellow, gray, and black limestone and iron oxide were used for ornamentation. The hot and humid environment facilitated the dissolution of calcium carbonate, the formation of carbonic acid, and the deposition of salts on the surface of the stones.

Historic stone structures in Europe, notably the Cathedral of Seville, Spain, have been damaged by air pollution. In his presentation, Dr. Javier Reyes Trujeque explained the connection between the black crust formations on the cathedral's exterior, fossil-fuel combustion, and the meteorological conditions. He studied the organic composition of black crusts and identified aliphatic, aromatic, and organic compounds, including molecular markers emitted to the atmosphere during the fossil-fuel combustion process. While microorganisms are protective agents under certain conditions, microbial biofilms on stone buildings reduce their aesthetic appeal by trapping dirt and blackening the surface. Microorganisms

also contribute to decay through chemical and physical deterioration induced by microbial activity. Figure 1 shows some of this damage being inflicted on the ball court at Chichén Itzá, Mexico. Dr. Benjamin Otto Ortega Morales observed that most black surfaces are covered by cyanobacterial films and often these organisms are the first colonizers in limestone monuments in unpolluted tropical environments. Negatively charged exopolymers synthesized by biofilms may promote weathering by chelation of solubilized cations (both as a consequence of microbial or abiotic processes), which weakens the mineral matrix.²⁵ Some exopolymers also contribute to the transportation of salts. On Mayan monuments, more abundant biofilms formed mainly by phototropic organisms were found on the inner walls where humidity and protection against direct sunlight promoted microbial growth.

Exposure to sunlight causes murals to fade, according to Dr. Daniel Grosjean. Color changes result from the interaction of air pollutants, such as ozone (O₃), sulfur dioxide (SO₂), and nitrous oxides (NO_x), with the colorants and pigments widely used in murals, frescoes, paintings, textiles, and other works of art. The Central Institute of Anthropology and History has restored several significant Mayan murals in Quintana Roo, Mexico, under the direction of Mónica López Portillo Guzmán. In the Yucatán Peninsula, Mayas painted iconography on the walls of a diverse collection of rocks, including calcite, aragonite, and dolomite covered with a plaster compound of limestone and sands.

UNAM has been involved with acid rain deposition research since 1964, according to Dr. Rodolfo Sosa Echeverría. Since then, approximately 25 sites have been evaluated for acid deposition in Mexico. The Oceanographic Laboratory in Veracruz, the Mexican Navy, and NOAA jointly conducted surveys of the air quality in the Gulf of Mexico in 1986 and then from 2002 to 2005 to determine the acid deposition in the Gulf region. In 1994, a study of the chemical composition of precipitation in Quintana Roo, Mexico, revealed that the pH in rainwater was less than 5.6 approximately 57% of the time.²⁶ This was recently confirmed in a study of rainwater along the Caribbean shore of the Yucatán Peninsula.²⁷

Pablo Sánchez maintained the UNAM sampling equipment at remote sampling stations sites in Veracruz. These stations used portable power systems and special refrigerated boxes to store the rain samples. The rate of surface degradation was studied in the laboratory at UNAM. Dr. Rogelio Soto Ayala used an acid deposition chamber to expose samples of coral from the fortress at San Juan de Ulúa and limestone from Tulum to artificially created acid rain in the laboratory.

When the shellfish industry was threatened by pollution, Dr. Alfonso Vasquez Botello examined marine sediments, organisms, and water samples in the Gulf of

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Table 1. Mayan workshop speakers, affiliations, and topics.

Name and Affiliation	Title of Presentation
Elda J. Anrubio Vega Central Institute of Anthropology and History, Mexico	Deterioration of Stone Due to Environmental Pollution in Quintana Roo, Mexico
Dr. Patrick L. Brezonik BES/Environmental National Science Foundation	Research Activities/Opportunities at the U.S. National Science Foundation
Rosa Maria Chan ProPeten Foundation, Guatemala	Conservation of Prehispanic Monuments in Peten, Guatemala. Cases: Tikal and Piedras Negras
Dennis Fitz College of Engineering, Center for Environmental Research and Technology, University of California, Riverside	Measurement of Nitric Acid and Particulate Acidity Using Inexpensive Fabric Diffusion Denuders
Dr. Daniel Grosjean DGA, Ventura, CA	Impact of Air Pollutants in Color and Pigments: Change of Color and Chemical Reactions Mechanics
José Hernández Téllez Central Institute of Anthropology and History, Mexico	Construction, Deterioration, and Reconstruction of Fort San Juan de Ulúa, Veracruz, Mexico
Dr. Jonathan Kahl Department of Mathematical Sciences, University of Wisconsin-Milwaukee	1. Meteorology of Southeastern México 2. Meteorological Aspects of Acid Rain 3. Trajectory Modeling Applications to the Mayan Zone
Dr. Tim C. Keener Environmental Engineering, University of Cincinnati	Source Inventory of Acid Rain Precursors for the Mayan Ruins
Monica López Portillo Guzmán Central Institute of Anthropology and History, Mexico	Conservation of the Mayan Mural Paints in the North of Quintana Roo, Mexico
Dr. Mingming Lu Environmental Engineering, University of Cincinnati	The Impacts of Hydrocarbons on Historic Structures
Dr. Seiichi Nakamura Japan Foundation in Guatemala	Conservation Actions in the Maya's Archeological Zones in Copán, Honduras
Dr. Benjamin Otto Ortega Morales National University of Campeche, Mexico	Bio-Deterioration on the Cultural Heritage and the Environmental Quality
Sofia Paredes Maury Foundation for the Preservation of Natural Resources and Culture of Guatemala (FCG), Guatemala	Integrated Conservation of the Natural and Cultural Resources: FCG an Opportunity in Guatemala.
Laura Pescador National Institute of Anthropology and History, Mexico	The Importance of Preserving Our Cultural Heritage
Dr. Javier Reyes Trujeque Corrosion Research Center Autonomous University of Campeche, Mexico	Deterioration of Stone Due to Environmental Pollution Case Study: Sevilla, Spain
Pablo Sánchez Alvarez Environmental Pollution Section at the Center of the Atmospheric Sciences, National University of México (UNAM)	Measurement and Analysis of Acid Rain Deposition for the Mesoamerican Network
Dr. Peter Scheff Environmental and Occupational Health Sciences, University of Illinois	Measurement of Acid Particles and Gases
Dr. Rodolfo Sosa Echeverría Environmental Pollution Section at the Center of the Atmospheric Sciences, National University of México (UNAM)	Research Concerning Acid Rain in Mexico
Dr. Rogelio Soto Ayala Environmental Pollution Section at the Center of the Atmospheric Sciences, National University of México (UNAM)	1. Characterization of Acid Deposition in Southeastern México 2. Deterioration of Limestone Building Materials due to Acid Rain Deposition
Dr. Alfonso Vazquez Botello Laboratory of Marine Contamination, National University of México (UNAM)	Laboratory Analysis of Water Pollution in the Gulf of Mexico

Mexico to identify contributing sources. The environmental impact study of biological specimens, air samples, and soils combined the research capabilities of Secretariat of Environment, Natural Resources and Fisheries (SEMARNAP), Petroleos Mexicanos (PEMEX), UNAM, Battelle, and the Instituto Mexicano del Petroleo.

Methods to measure both organic and inorganic gases must be considered when planning for receptor modeling at Mayan sites. Dr. Peter Scheff recommended the use annular of denuders in coastal areas, such as Tulum, to measure ambient concentrations of nitric acid.

Costs associated with an air sampling program may be reduced by using an inexpensive cotton cloth fiber diffusion denuder to capture nitric acid and ammonia. Dennis Fitz demonstrated 96% collection efficiency using his experimental denuder.

SOURCES OF AIR POLLUTION AND THE EFFECTS OF METEOROLOGY

The dispersion of pollutants over Mexico is influenced by large-scale climate features, as well as local influences. Meteorologist Dr. Jonathan Kahl explained how the complex meteorological conditions within this region add to the difficulty of pinpointing the sources of pollution. Enforcement of environmental policy requires the ability to identify point sources and to apportion responsibility for emissions. The necessary data do not exist to locate sources using trajectory modeling south of the Rio Grande.

Oil and coal combustion, industrial boilers, and petroleum refinery plants contribute to the acid rain problem. The location of point sources, their emissions profiles, and the fate of acidic emissions within Mesoamerica remain unknown. Without such data, enforcement of existing regulations is impossible. Dr. Tim Keener suggested that a comprehensive emissions' inventory is needed to understand the impact of point sources, perhaps one modeled after the economically successful acid rain cap-and-trade program in the United States.

Studies are also needed to characterize hydrocarbon emissions from the different sources and their impact on Mayan sites. Typical sources of hydrocarbons include petroleum-based hydrocarbons from the oil platforms in the Gulf of Mexico, as well as from automobiles and buses in the parking lot of tourist sites; biogenic emissions from tropical vegetation; emissions from forest fires and agricultural burning; and the secondary hydrocarbons formed from photochemical reactions. Dr. Mingming Lu discussed the possible mechanisms by which hydrocarbons may contribute to the stone decay process. The metals released during combustion can serve as

catalysts for SO₂ oxidation to SO₃. The formation of gypsum through this process is the primary mechanism of limestone damage. Soft and porous, gypsum provides large surface areas to absorb carbonaceous particles, which nourish certain microorganisms known to cause stone deterioration.

CONCLUSIONS AND FUTURE RESEARCH NEEDS

The workshop participants agreed that air pollutants are causing significant deterioration at the Mayan sites. The pollutants of concern include acid precursors, such as SO₂ and NO_x, and hydrocarbons from petroleum and biogenic sources. The potential sources include large petroleum point sources in the Gulf region, the long-range transport of pollutants, and local sources. The immediate need is to conduct monitoring at selected sites for wet/dry deposition to evaluate the contributions of these pollutants. Due to the omnipresence of microbial biofilms on Mayan monuments it is also important to conduct studies to determine the effects on building stone of microorganisms in association with the selected pollutants.

It was agreed that a follow-up workshop should be held in Guatemala in 2007 at Tikal National Park to discuss the progress made in resolving the problems highlighted at this first workshop. Committees were formed to determine the location of point sources, investigate systematic monitoring methods, document sites and damage, and identify potential funding sources. Maury Parades of FCG is to chair the organizing committee for the next workshop, depending on the availability of resources.

The ultimate goal is to establish a Mayan Air Sampling Network to determine air emissions and meteorological conditions that contribute to the overall deterioration of these cultural heritage sites. There is a need for a comprehensive database, containing the location and emissions profiles of local point sources and regional meteorological information. The effects of long-range transport must also be studied. Methods are required to characterize the various contributing sources, such as a tracer study or receptor source apportionment. A number of air monitoring stations, coupled with adequate meteorological monitoring, are needed at the key Mayan sites, such as Tikal, Copán, and Chichén Itzá, or sites with unusual pollutant profiles. These stations must be able to monitor and sample gases and particles, as well as acid deposition levels to determine in situ concentrations and air quality trends. The importance of an emissions inventory program cannot be overstated.

Laboratory facilities are needed for analysis. The future preservation of the Mayan region requires the financial and technical support of developed nations and private organizations.

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