

Influence of Air Pollution on Degradation of Historic Buildings at the Urban Tropical Atmosphere of San Francisco de Campeche City, México

Javier Reyes¹ et al.,*

¹*Autonomous University of Campeche,*

²*National Center for Scientific Research,*

³*CINVESTAV-Mérida,*

^{1,3}*Mexico*

²*Cuba*

1. Introduction

The role of atmospheric pollution in degradation of historic building has been studied for long time along the world because it increases stone decay and the lost of historic materials (Massey, 1999; Graedel, 2000; Monna, 2008). The preservation of Cultural Heritage is considered a strategic factor in countries integration because of their economical, social and cultural implications (Cassar et al., 2004; Sessa 2004, Moropoulou and Konstanti, 2004).

Latin-american countries have an important building legacy from prehispanic, colonial and modern periods. This is the case of México which currently count with 15 sites included in UNESCO's cultural heritage list. Most of them are located in urban areas like Mexico City, Morelia, Guanajuato, San Miguel de Allende and San Francisco de Campeche, between others. San Francisco de Campeche is a small City located at the south east of Mexican Republic, just in the occidental coast the Peninsula of Yucatan, inside the Gulf of Mexico Basin (Fig. 1). The City was founded in 1527, by Spanish colonizers led by Francisco de Montejo, "el Mozo". During the XVII century, it was the only point for exportation of goodness from Yucatan to Europe. Because of these conditions, French, Netherlanders and British pirates considered the city a legitimate target.

At that time, authorities designed an impressive military defensive system to protect the City and their inhabitants. Forts, batteries and a rampart surrounding San Francisco de Campeche urban core were built by using calcareous materials based on masonry structures made with limestone quarry blocks joined and covered with mortars made with slike lime and sahadab, a typical calcareous clay material used since prehispanic period for building construction. Nowadays, about 1500 buildings are located into the historic and architectonic complex included in 1999 in the UNESCO's Cultural Heritage List.

* Francisco Corvo¹, Yolanda Espinosa-Morales¹, Brisvey Dzul¹, Tezozomoc Perez¹, Cecilia Valdes², Daniel Aguilar³ and Patricia Quintana³

Since their construction, these buildings have been exposed to the action of environmental agents that induce their deterioration. For long time, natural parameters like high relative humidity, extended rainfall periods and the effects of marine aerosols were the principal factors related with buildings degradation (Zendri, 2001, Cardell et al., 2003). Karstification, crust formation, lost of components and biodegradation are typical pathologies of degradation observed in the buildings. Nevertheless, in the last decade, the City has been under a dynamic development. As a consequence, a sensible increase in automobile units has been registered in specific areas of the city, including the historical centre.



Fig. 1. The State of Campeche located at the South East of Mexican Republic. Red dots indicate the location of San Francisco de Campeche City and Iturbide town, current environmental monitoring sites operated by the Corrosion Research Center (CICORR).

Automotive emissions generate atmospheric particles and corrosive gases like sulphur dioxide (SO_2) and nitrogen oxides (NO_x) that, in contact with environmental humidity produce acid precipitation that dissolve calcareous materials, or induce black crust formation (Lipfert, 1989; Gobi, et al., 1998, Kucera, 2007). Systematic studies related to atmospheric pollution and their effects in historic building degradation at San Francisco de Campeche City are scarce.

2. Stone decay

Stone materials have a natural tendency to degradation as a consequence of change in their chemical stability when they are extracted from the quarry and submitted to the building fabric, atmospheric action and change in air quality.

Before industrial revolution, natural agents were the main cause of stone buildings degradation, sometimes through suddenly destructive actions as earthquakes, volcanic eruptions or hurricanes. Most of the times, acting in slow weathering process. Nevertheless, with the appearance of the industrial society, atmospheric pollution got a major role in building deterioration.

In natural conditions atmospheric water is the main agent associated to stone degradation. Its influence is especially important in tropical climates, where high relative humidity and large rain forest period along the year guarantee water availability to lead chemical reaction over stone substrata or to produce secondary pollutant's potentially harmful for stone materials.

In San Francisco de Campeche City, historic buildings were constructed using calcareous stone materials including quarry blocks and mortars. Calcareous stone and traditional mortars used during buildings construction or restitution works usually show a wide interval of porosity (Reyes et al., 2010; Torres, 2009). It is well known that water circulation in porous stones and their exchange with atmosphere or ground, affect their behavior and durability.

The flux of water across porous structure of stones and mortars is consequence of wet- to dry- cycles, that induce chemical reactions and salts crystallization leading materials lost and decreasing their mechanical capabilities. Furthermore, direct impact of rainfall is cause of erosion on stone surface and the appearance of run-off inside of masonry structures. On the other hand, when water table level is high, a capillary effect could appear. Then, a continuous flux of soluble salts inside and outside materials stone structure is established. Water presence also facilitates the development of microorganism colonies and the growth of superior plants. In both cases, their consequences on stone materials are chemical and mechanical damage.

In urban environments, decay of historic buildings is strongly influenced by the presence of atmospheric pollutants like SO_2 , NO_x , atmospheric particles and acid rain.

In the atmosphere water drops incorporates carbon dioxide (CO_2) to produce the weak carbonic acid (HCO_3^-), which is partially dissociated according to the next reaction:



As a consequence, water acquires a pH of 5.65. It means that in unpolluted atmosphere water tends toward acid. Under this condition, dissolution of calcareous materials is possible. Dissolution of carbonates inside walls as their migration and deposition to the evaporation front lead the formation of crusts, as is demonstrated in the next reaction:



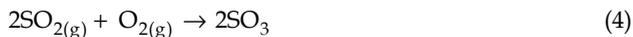
Soluble calcium bicarbonate ($\text{Ca}(\text{HCO}_3)_2$) is transported by water to the surface of stone and mortars across porous system of built and decorative elements. When water evaporates CO_2 drags (equation 3).



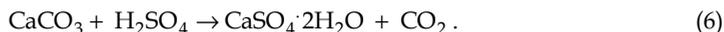
Formation rate of $\text{Ca}(\text{HCO}_3)_2$ depends on CO_2 levels, that is the reason why in urban environments with high levels of this gas, carbonation of calcareous materials is most important than in rural environment. On the other hand, recrystallized calcite is bigger in size and more porous than the microcrystalline original calcite. The increase in size is extreme harmful for stone materials, because it creates conditions for a deep penetration of acidic solutions (like acid rain), insoluble salts and gases like SO_2 and NO_x .

Acid rain is produced when gases like SO_2 or NO_x reacts with water drops, increasing their acidity under pH value of 5.65 to form the so called acid rain. Acid rain is a global phenomena and its effect can be observed at long distances from their precursor sources (Bravo et al., 2000).

The presence of a minimum water amount is enough to oxidize SO_2 to sulphuric acid (H_2SO_4) according to the next reactions:



H_2SO_4 can easily react with calcareous materials to form gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) as is indicated in equation (6)



Gypsum formation is a serious problem because when it crystallizes gradually expands up to 30 % of their original size (Feddemma, et al., 1987). $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$. It is highly soluble at predominant temperatures in tropical regions, so it requires a minimum water amount to dissolve and lead a fast migration to evaporation front by capilar mechanisms. When gypsum lost humidity, it can recrystallize into porous, where induce the formation of microcracks and fatigue of materials. In urban environments, gypsum incorporates into their mineral structure atmospheric particles, dust and biomass to form the so called black crust.

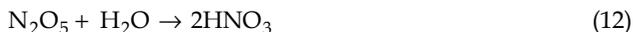
NO_x formation depends on environmental conditions and the kind of pollutant present in the atmosphere. It is expressed in the next reactions:



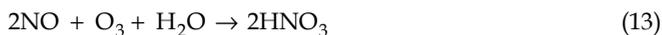
Ozone (O_3), also can also react with nitrogen oxide (NO) and nitrogen dioxide (NO_2):



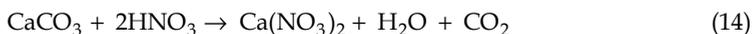
The products of these reactions establishes an equilibrium with dinitrogen pentoxide, which react with water to form nitric acid (HNO_3):



In urban zones, O_3 and NO also react with water to form HNO_3



Nitric acid dissolves calcareous stone to produce calcium nitrate ($\text{Ca}(\text{NO}_3)_2$):



$\text{Ca}(\text{NO}_3)_2$ is more water soluble than CaCO_3 . If it is present, is transported across porous capillars to finally crystallize on monuments surface to be washed during rainy events (Allen et al, 2000). Deposition mechanisms also play an active role in historic building deterioration. Atmospheric particles and aerosols are transported by wind toward monumental structures.

Here, they are incorporated into neo-mineral matrix of degradation products or participate in oxidation reactions induced by carbonaceous particles or metals like iron (Fe), vanadium (V), and nickel (Ni) content in dust.

In coastal zones, marine aerosols also contribute to deterioration of stone. It is primary composed by sea water along with particles naturally generated by the action of the wind on the seawater surface to introduce ionic species into the atmosphere, principally chlorides and sulfates (Stefanis *et al.*, 2009). Chlorides are a destructive agent of porous materials.

Because of its high solubility, it penetrates into porous network, and crystallizes inside the material. Its crystallization produces disruptive pressure forces that lead to microcracks formation (Cardell *et al.*, 2003).

On the other hand, suspended particles are also natural substrata for oxidation reactions (Primerano *et al.*, 2000). New products eventually reach stone surface were they originates physical, chemical and aesthetic changes (Fig. 2).

Once stone materials have been sensitized by physical or chemical factors it is more sensible to the action of biological agent causing biodegradation. Biodegradation is an undesirable change in materials properties caused by the action of microorganisms, animals and plants. The presence of microorganisms causes the formation of biofilms.

Biofilms are sessile communities adhered to substrate enclosed in a polymeric matrix producing metabolites with capabilities to initiate, promote or magnify stone degradation through modification in pH levels, ionic concentrations, and redox conditions at the interfase between substrate and surrounding media to produce chemical and physical alterations (Gorbushina *et al.*, 2002; Ortega- Morales, 2003; Guamet *et al.*, 2005; Little y Ray, 2005).

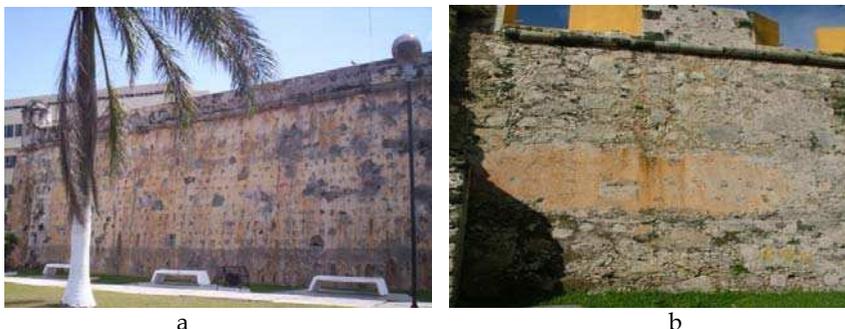


Fig. 2. General aspect of degradation at Forts San Pedro (a) and San Carlos (b), historic buildings of San Francisco de Campeche City.

3. Degradation of historic buildings: the case of San Francisco de Campeche

3.1 Meteorological conditions

San Francisco de Campeche City is located under a gently sloping flood plain. The City is limited at the Norwest by the Gulf of México and at the South, Southeast and Southwest by a group of softened hills. Under these conditions, the natural expansion of the city follows to South and Southeast direction. The City presents a tropical summer rain forest climate (Aw) (Castro Mora, 2002). Table 1 concentrate the annual average value of meteorological parameters registered during 1992 to 2002 period at National Meteorological Service station (SMN), located into the installation of the aeronaval airport of the City.

Year	Meteorological parameter					
	Precipitation (mm)	Temperature (° C)	Relative humidity (%)	Atmospheric pressure (mb)	Predominant Wind direction	Wind velocity (m.s ⁻¹)
1992	1224.30	27.20	73	12198.50	SE	3.40
1993	1294.30	27.60	71	12168.70	E	3.60
1994	1084.80	27.30	73	12166.10	E	2.90
1995	1688.40	26.90	74	12149.10	SE	3.10
1996	938.50	26.40	74	12159.20	ESE	3.10
1997	1115.60	27.30	74	12153.40	SE	2.60
1998	815.40	27.80	71	12143.50	ESE	2.70
1999	1227.70	26.70	73	12164.20	ESE	2.80
2000	927.00	26.70	72	12168.20	E-SE	2.60
2001	1004.70	27.00	73	12159.20	E	3.10
2002	1297.20	27.10	71	12157.50	E	2.80

Table 1. Annual average value of meteorological parameters registered during 1992 to 2002 period at National Meteorological Service station (SMN), at San Francisco de Campeche City.

The existence of high relative humidity values along the year can be observed and the persistent sum of rainfall covering an extended period from June to November. Those conditions guarantee water availability for occurrence of chemical and physic processes able to deteriorate calcareous stone materials through binder dissolution mechanisms, including also the penetration of soluble salts and atmospheric pollutants (Corvo et al., 2010).

Two characteristics regional meteorological phenomena affecting coastal zones are related to inland humidity penetration from the sea: along the autumn season, tropical storms (hurricanes) carry on humidity from Caribbean Sea raising up rainfall precipitation levels. It is especially worthily in September and October. During winter, cool dry fronts come in from North America, drag humidity when they cross the Gulf of Mexico warm water, increasing haze episodes in the coast and eventually the rainfall events. In this period rainfall events tend to minimum, and an extended dry season from November to May begin. In spite of those situations, during this period, San Francisco de Campeche City temperature rise up to its maximum levels, while relative humidity falls to the lowest value.

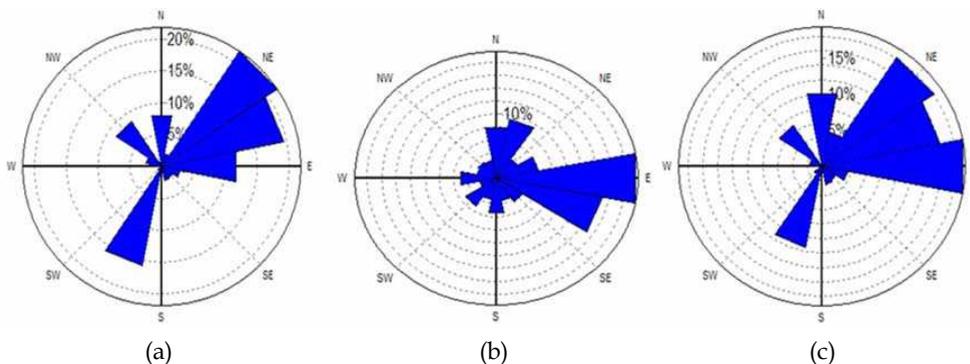


Fig. 3. Characteristics wind pattern observed at San Francisco de Campeche City during 2007. (a). Dry season, (b) rainy season, (c) polar front season. (Miss, 2008).

Along the year, three wind patterns can be observed in dependence of meteorological conditions at San Francisco de Campeche City (Fig. 3). Dry season is characterized by winds from E-ENE and SW directions that increase dust level at the atmosphere. At the rainy season, the wind pattern is dominated by E-ESE and a small contribution from N-ENE, due to, eventually, strong tropical storms hitting the city. In winter, when polar front reaches the coast of Campeche, winds from E-NE, N NW and SW are more frequent.

3.2 Environmental conditions

San Francisco de Campeche City is an emerging place located at the occidental coast of the Peninsula of Yucatan. At the present time, it has about 235,000 inhabitants. Until the last decade of the XX century the City was considered a place of scarce economical and industrial development, since the main productive activities were administration, fishing, and processing of food. There are no installed heavy industries were installed, except by a power plant located at Lerma town, about 6 km SE from downtown.

Nevertheless in 1999, the historic and architectonic complex of the City was included into UNESCO's Cultural Heritage List. It considered the city as a historic and cultural reference in Mexico and other countries. As a consequence, an intense urban and economical development occurs, mainly due to the raising of cultural sector. Also an increasing of infrastructure needs because of the parallel demographic expansion that is occurring in the city. Environmental problematic like water supply, solid residues management, residual water disposition and atmospheric pollution are associated with urban development.

Studies about the number of existing automotive units ordered in 2003 by the Government of Campeche State demonstrated that during 1996 to 2003 period, San Francisco de Campeche City suffered an increasing of 8% the vehicular units, while between 2002 to 2003 the increasing was of 13.13 %, this situation cause serious vial problems. According to this study, projections for 2010 indicates an increase of 69,130 units (Government of the State of Campeche, 2004). Under these conditions, it is expected an increase in atmospheric pollution level.

Atmospheric pollution is mainly related with industrial and vehicle exhaust emissions. Gases like ozone (O_3), carbon oxides (CO , CO_2), nitrogen oxides (NO_2 , NO_3), sulfur dioxide (SO_2), and atmospheric particles (PST, PM_{10} , $PM_{2.5}$), have been used to indicate air quality in urban areas. Those pollutants can be the origin of health diseases, changes in environmental conditions and degradation of materials. In this sense, they are precursors of acid rain and the blackening of stone materials in historic buildings and monuments (Reyes et al., 2009; Corvo et al., 2009).

It is interesting to report that since 1992, atmospheric corrosion under structural materials aluminium (Al), carbon steel (Fe), copper (Cu) and zinc (Zn), was monitored in five sites distributed across urban city area (Fig. 4) (Reyes, 1998; Cook, et al., 2000; Corvo et al., 2008).

These studies were performed according to criteria established by the program ISO CORRAG (Tidblad et al., 2000). During the study, an estimation of corrosion rates was carried out considering deposition rate of corrosive parameters like chloride ions (Cl^-), SO_2 , and their correlation with the temperature-humidity complex represented as time of wetness (TOW) (Tables 2 and 3).

It was established that the corrosion rate at exposures sites depends strongly of their distance to the coast, since Cl^- levels decrease when distance increases (Corvo et al., 2008). Here, SO_2 deposition rate was very low, except for Technological Institute of Campeche (ITC) site located at Lerma town, closer to the Power Station (Table 3).

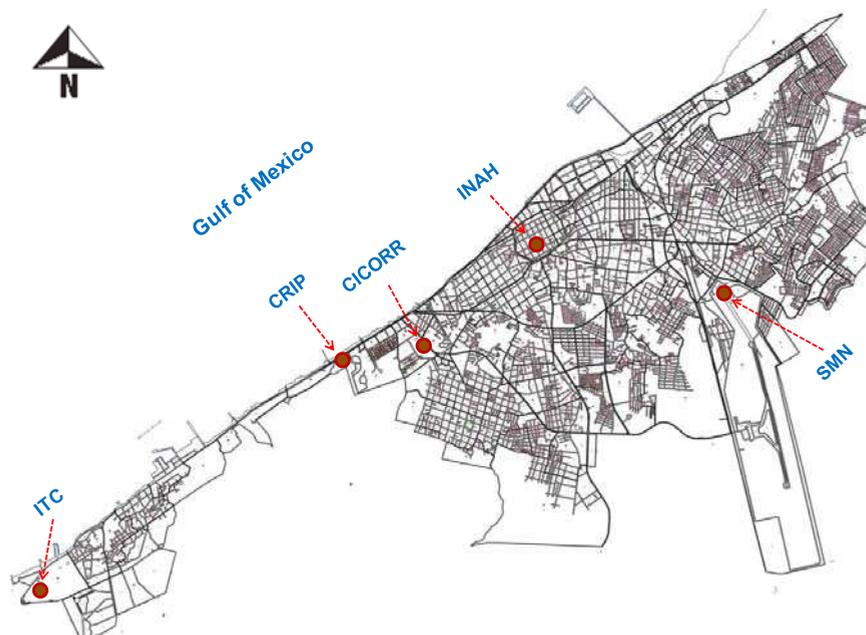


Fig. 4. Map of San Francisco de Campeche City. Red dots indicate the location of selected monitoring sites for atmospheric corrosion research. ITC, Technological Institute of Campeche, CRIP, Regional Center for Fisheries Research; CICORR, Corrosion Research Center; INAH, National Institute for Anthropology and History; SMN, National Meteorological Service.

It has the highest SO_2 content between all exposure sites. Nevertheless, it does not appear as decisive as chloride and TOW in prediction of corrosion rate as usually occurs in Regional Center for Fisheries Research (CRIP) and CICORR stations.

The results of the study also shows that in San Francisco de Campeche atmospheric corrosion rates are lower than those located in Mexican and Cuban coastal stations, where industrial and marine influence was more important.

The only exception to this rule was the station located at the CRIP, located at 4 meters from the coastline. It is an interesting data in order to consider the possible effects of atmospheric condition on stone materials decay.

Station	Atmospheric corrosivity			
	Al	Cu	Fe	Zn
SMN	Medium to high	Medium	Medium	Medium
CICORR	Medium to high	High	High	High
INAH	Medium to high	Medium	Medium	Medium
CRIP	Medium to high	High	High	High
ITC	Medium to high	Medium	Medium	Medium

Table 2. Estimation of atmospheric corrosivity at selected monitoring sites in San Francisco de Campeche City.

Station	Distance to the coast (m)	Corrosive parameters		
		SO ₂ mg.m ⁻² .day ⁻¹	Cl ⁻ mg.m ⁻² .dia ⁻¹	TOW annual hours
SMN	4.000	2.42	19.98	4576
CICORR	0.300	2.61	70.50	4894
INAH	0.615	1.47	18.08	3271
CRIP	0.004	2.64	76.20	4572
ITC	0.300	15.83	29.50	3380

Table 3. Corrosive parameters registered at San Francisco de Campeche City selected monitoring sites.

3.3 Atmospheric pollution

During the dry season of 1998, exceptional natural fires were declared along the south east of Mexican Republic. It was especially worthily at Campeche State, where several health problems like skin, respiratory and ocular diseases were observed in people. For the first time, atmospheric particles considering the fraction of atmospheric particles with diameter below 10 μm (PM₁₀) fraction was measured at San Francisco de Campeche following procedures established by Official Mexican Standards. The study (carried out in May 21th, 1998), yielded average value of 40 $\mu\text{g.m}^{-3}$, that was considered below health risk levels for inhabitants.

This study was the only reference of atmospheric pollution measured at San Francisco de Campeche City until 2005, when an initiative to study the effects of the environment on degradation of Cultural Heritage was driven by Autonomous University of Campeche (Reyes, 2005a, 2005b). Atmospheric parameters like SO₂, atmospheric particles (TSP and PM₁₀ fractions) and acid rain were measured in different periods during 2005 to 2009 following Mexican and International Standards (NOM, US-EPA, ISO and UNE).

Until the beginning of this project, there was no additional information on air pollutants measured using standard methods in the City of San Francisco de Campeche.

3.3.1 Present atmospheric pollution levels at San Francisco de Campeche City

We proceed to determine the levels of air pollutants in the city of San Francisco de Campeche, considering two important aspects: its effect on materials and the possibility of using standardized methods to generate a database that could be used as a reference on air quality in the city (Reyes 2005a, 2005b; Miss 2008, Villaseñor, 2008., Dzul 2010, Góngora 2010, Quirarte, 2010).

Two atmospheric pollution stations were placed at "home of Lieutenant of the King" and San Pablo Buildings, historic buildings belonging to Centro INAH-Campeche (INAH-National Institute of Anthropology and History).

Another station was installed on the Corrosion Research Center (CICORR), main Campus of the Autonomous University of Campeche (Fig.4). Passive (SO₂, NO_x, Cl⁻), active (Total Suspended Particles -TSP and PM₁₀ fraction) and automatic (SO₂) samplers were employed. Also, wet precipitation was sampled by using a wet/dry rain sampler. The results of the sampling are condensed on Table 4.

Table 4, shows medium, maximum and minimum deposition rates and concentrations of the different types of pollutants determined using standardized methods at selected atmospheric monitoring stations.

Pollutant	Method	Standard	Medium value	Maximun value	Minimum value	Station
SO ₂ (mg.m ⁻²) Feb. 2007 to Feb. 2009	Sulphation plate (passive)	ISO 9225:1992	1.31	3.52	0.58	INAH
Cl ⁻¹ (mg.m ⁻²) Feb. 2007 to Feb. 2009	Wet Candle (passive)	ISO 9225:1992	20.28	31.90	3.53	INAH
NO _x (mg.m ⁻²) Feb. 2007 to Feb. 2009	Diffusion tubes (passive)	UNE EN 13528	9.82	13.48	4.71	INAH
TSP (mg.m ⁻²) Nov. 2006 to Dec. 2008	High-volume sampler (Active)	NOM-035- SEMARNAT- 1993	47.23 48.71	101.30 106.67	15.26 23.89	INAH CICORR
PM ₁₀ (mg.m ⁻²) May to August 2007	Low volume sampler (Active)	US-EPA standard	3.54 3.30	8.69 9.72	1.49 1.34	INAH CICORR
SO ₂ (mg.m ⁻³) Jan. 2007 to Jan. 2008	Fluorescence (Automatic)	NOM-038- SEMARNAT- 1993	6.95	74.70	1.30	INAH

Table 4. Average deposition rate and concentration of the different types of pollutants determined by standard methods at monitoring stations in San Francisco de Campeche City during 2006 to 2009.

3.3.1.1 Passive methods

Passive methods consist of an absorbent substrate that reacts with a specific chemical compound in the atmosphere. Afterwards, the samplers are removed and analyzed quantitatively in the laboratory. These devices work by principles of deposition or diffusion, but they are not considered appropriated for air quality studies; however, they provide trends on the spatial-temporal distribution.

Fig. 5 shows the values of SO₂, NO_x and Cl⁻ determined by passive methods in the historic center of the city of San Francisco de Campeche (urban-marine atmosphere). These data can be compared with results obtained in the rural monitoring station installed at Iturbide town (Fig. 6), about 100 km E far away from the City (Fig. 1).

As can be seen, the values of all pollutants are higher in the city of San Francisco de Campeche in comparison with Iturbide, due to the urban nature of the city. Pollutants such as SO₂ and NO_x are usually produced during combustion of fossil fuels and emitted into the atmosphere by motor vehicles.

These gaseous pollutants are considered acid contaminants because they corrode metals and stone materials due to its ability to form acid solutions in contact with environmental humidity on the surface of materials (Tercer 1998; Massey, 1999; Zappia et al., 1998; Allen et al., 2000).

The levels of airborne salinity in a particular site depend upon the geographical position and the existence of orographic accidents. Its marine origin causes a preferential distribution in coastal areas.

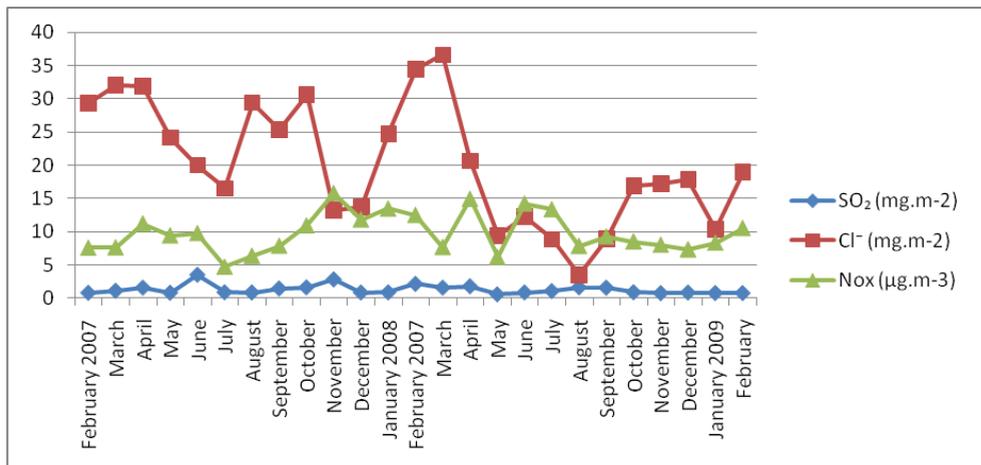


Fig. 5. SO₂, NO_x and Cl⁻ levels determined by passive methods in the urban marine atmosphere of San Francisco de Campeche City (INAH station).

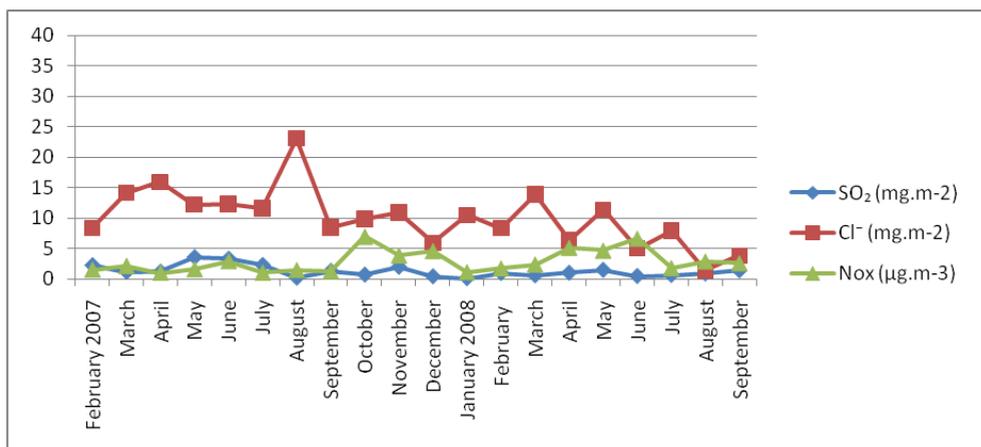


Fig. 6. SO₂, NO_x and Cl⁻ levels determined by passive methods in the rural monitoring station installed at Iturbide Town.

Its concentration decreases when the distance to the coastline increases. This distribution also depends on the speed and wind direction. Higher levels of airborne salinity are expected near the coastline

It is appropriate to mention that despite the proximity to the coast of INAH station (600 m), marine aerosol levels are relatively lower than those observed in Boca del Río coastal stations (600 m from shore line) or Coatzacoalcos petrochemical complex (1000 m from shore line) (Carpio et al., 1996; Reyes 1998; Cook et al., 2000).

It occurs because the prevailing wind patterns in Campeche is most of the year from the E (they are called offshore winds) (Fig. 3), opposing the entry of masses of moisture from the Gulf of Mexico (Reyes, 1998; Cook et al 2000). This wind regime, suffers slight modifications

relatively constant during winter, since the winds from the N increases in intensity and frequency, so that marine aerosol levels tend to rise, increasing the potential corrosivity of the atmosphere.

3.3.1.2 Atmospheric particles

On the other hand, active methods involve a flow of air through an absorbent medium or a physical collecting medium. A suction pump is used. Samples thus obtained are quantitatively analyzed in the laboratory. Two types of samplers are used: high volume and low volume. Two sampling sites were selected: the "Home of Lieutenant King", central building of INAH-Campeche, located in the historic center of the city of San Francisco de Campeche, and the building of the CICORR in the main campus of Autonomous University of Campeche.

The level of total suspended particles (TSP) was determined at both sites during the period August 2006-October 2008. PM_{10} fraction of airborne particles was recorded during the period May to August 2007. Table 4 display the average, maximum and minimum values determined for the corresponding sampling periods.

Table 4 shows statistics for data sets obtained for PST in both sampling stations. In all cases the maximum, minimum and average values were higher for CICORR related to INAH station although a "t" test performed showed no significant differences between the average obtained in both sampling sites ($t = 1.57225$ $p > 0.05$). Moreover, during the sampling period, none of the stations exceeded the maximum permissible limit for Mexican Standard ($210 \mu\text{g}\cdot\text{m}^{-3}$), as shown in Fig. 7.

Higher average values of TSP were monitored during the month of July coinciding with the end of the dry season and beginning of summer rainfall season. Average TSP values were found to be 47.23 and $48.71 \mu\text{g}\cdot\text{m}^{-3}$ for INAH and CICORR monitoring stations respectively. Several authors suggest that in drought periods, atmospheric particles concentration is higher than in rain periods, those because of the lack of washing of the atmosphere caused by rainfall (Muñoz et al. 2001; Miss 2008).

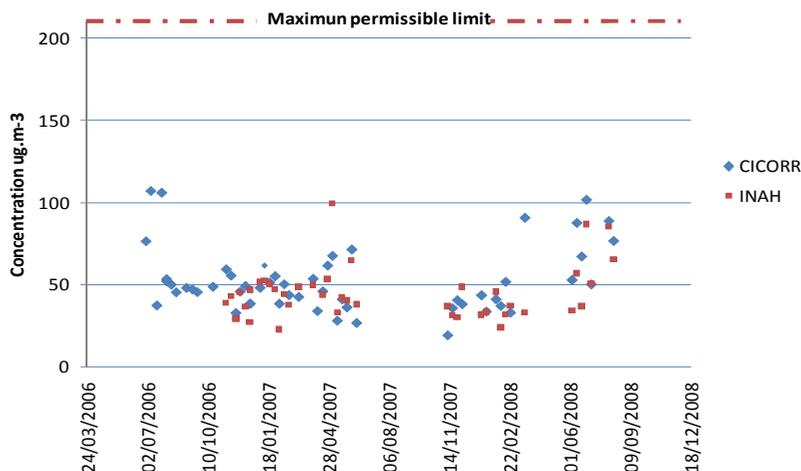


Fig. 7. TSP at San Francisco de Campeche monitoring sites during the period August 2006-September 2008. Red dotted line represents the maximum permissible limit of $240 \mu\text{g}\cdot\text{m}^{-3}$ According to Mexican Legislation.

The city of San Francisco de Campeche is located in the middle of a small valley, surrounded at N, S and E by hills, with elevations not higher than 150 meters. The Bay of Campeche is located in the W. Many of these hills are suffering continuous erosion and clearing of land for the construction of living houses or are employed by construction companies as sources of construction materials. These activities give rise to soil erosion and constant dust storms, which in times of drought contribute to increased levels of local TSP.

In a regional scale, the prevailing winds in the dry season (April to July), converge towards the sea ground by the E-NE quadrant and an important component S-SW (Fig. 3a). It contributes to the transport of atmospheric particles, originated in farming areas, eroded land and cattle ranches in the state, which add to the locally originated TSP.

The role of rainfall in the levels of TSP is evident in urban and industrialized areas, since water acts as a purifier of particles in the atmosphere (Muñoz et al., 200; Sosa et al., 2006; Miss, 2008), also the wind disperse atmospheric particles and reduce their content at the atmosphere.

It is confirmed by the minimum average value of $15.26 \mu\text{g.m}^{-3}$ recorded during the month of March 2007 at INAH, when cool fronts introduce strong wind velocities and eventually rain episodes. During the period from August to November there is a significant decrease in the levels of TSP on both stations as a result of purifying effect of seasonal rains which masses are originated in the Caribbean Sea (Fig. 3b).

The presence of polar fronts in the Gulf of Mexico during the period from December to March becomes a factor of atmospheric instability that contributes to the dispersion of pollutants and the introduction of humidity from the ocean in coastal areas (Reyes 1998).

It coincides with the monthly average minimum of $35.25 \mu\text{g.m}^{-3}$ registered at CICORR during December 2006, precisely at the end of the rainy season and early winter seasonal fronts when the wind increases in strength and components N-NE direction (Fig. 3c).

Atmospheric particulate matter PM_{10} fraction was determined during the end of the dry season and the beginning of the rainy season (May-August 2007). A Student "t" test to compare the arithmetic means of data sets collected at stations CICORR and INAH was used. The test results indicated no significant difference between values observed in the testing sites ($t = 0.612, p > 0.5$).

At both monitoring sites, the concentration of PM_{10} follows the same tendency being the maximum concentration of 9.72 mg.m^{-3} and minimum concentration of 1.34 mg.m^{-3} for CICORR, while for INAH, maximum and minimum concentrations were 8.69 and 1.49 mg.m^{-3} , respectively (Table 4). Regarding the maximum concentrations obtained during evaluation, values of 8.69 and 9.72 mg.m^{-3} for CICORR and INAH were determined, respectively. These values represent no health risk to people and the environment because do not exceed the average value of $120 \mu\text{g.m}^{-3}$ in 24 hours established by the Mexican Standard (Dzul, 2010).

Respecting the average values, a concentration of 3.54 mg.m^{-3} and 3.30 mg.m^{-3} was determined for INAH and CICORR, respectively, indicating a slight difference in concentration between both sites which follow the same behavior. According to the results, a higher concentration of PM_{10} particles in the CICORR station was found with respect to INAH. This behavior coincides with that observed previously for TSP in both seasons, given the prevalence of similar environmental conditions (Miss, 2008).

CICORR station is surrounded by trees and by the athletic field of the Autonomous University of Campeche. In the West side of CICORR is located Juan de la Barrera Street, showing steady traffic during the morning and tends to diminish in the evening during the class activities, a

period which coincided with the sampling. INAH station is located in the center of the city of San Francisco de Campeche in an urban area with heavy traffic flow during most of the day.

3.3.1.3 Sulfur dioxide

SO₂ is considered as an indicator of atmospheric pollution in urban sites. It has been included in air quality indexes in several cities along the world (Valeroso, et al., 1992, Shifer et al., 2000; Raavindra et al., 2003). Industrial emissions and vehicle exhaust are the mains source of this pollutant which is precursor of acid rain and black crust formation (Mala, 1999; Primerano et al., 2000; Reyes 2004; Reyes et al., 2004).

This parameter was monitored during January 2007 to January 2008 in the historic center of San Francisco de Campeche City (INAH station), by using a visible fluorescence automatic equipment (NOM-038-SEMARNAT-1993). Fig. 8 shows the behavior of SO₂ during the sampling. Maximum, minimum and medium values are reported in Table 4. According to the results, both 24 hours maxima and annual arithmetic average were reported below maximum limits established by Mexican Standard. It means that its effects in health are limited. Nevertheless, the behavior of SO₂ during sampling period indicates a continue increase in their atmospheric concentration.

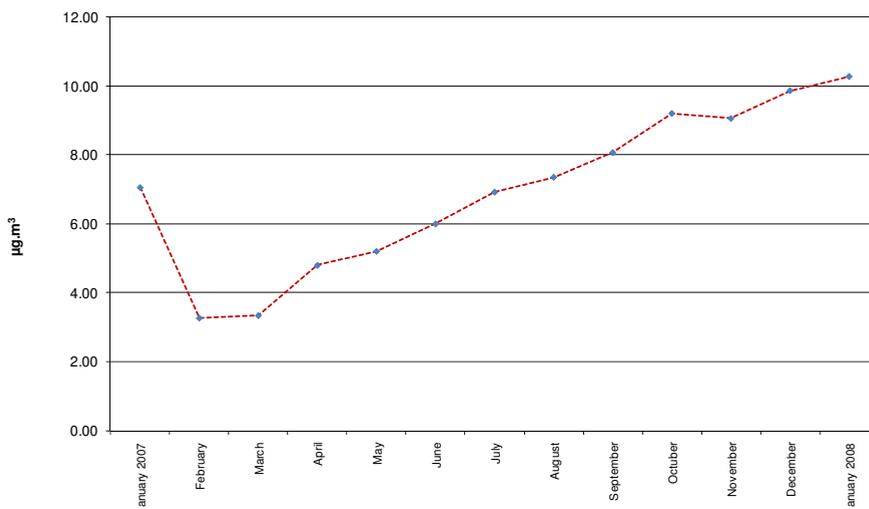


Fig. 8. Monthly average value of SO₂ registered in San Francisco de Campeche City Historic Center (INAH station), during January 2007 to January 2008.

The last one is critical for environmental air quality because this situation may be consequence of an increase in the number of automobiles in the city. That is a critical situation because it could generate traffic jam conditions in the historic center of the city. Vehicle exhausts create adverse conditions that allow the initiation of degradation mechanisms in stone materials, as have been observed in several historic cities along the world (Primerano, et al., 2000).

3.3.1.4 Acid rain

During the years of 2006 and 2007, a wet sample collecting campaign was carried on by using an automatic wet/dry sampler (US-EPA, 1994) installed at the INAH station

(Quirarte, 2010). A total of 147 samples were obtained. Table 5 shows the maximum, minimum and average weighted pH registered during the campaign. Fig. 9, represents the tendency in change of pH value along the rainy period.

It is important to note that in both years, a natural tendency to alkalinity exists in rain water pH. During the months corresponding to dry season (from December to June) rain water pH are usually higher than 6. This general tendency changes from July to November, period in which the atmosphere has been washed of dust particles by the rainy season. Then, the minimum values of pH are reached and eventually, sporadic acid rain events can be observed, probably as a consequence of atmospheric transport (Quirarte, 2010).

Year	Number of samples	PH			% of acid samples
		maximum	minimum	average	
2006	83	7.54	5.19	6.04	12
2007	73	7.80	4.97	6.39	5

Table 5. Maximum, minimum and average ponderated pH registered at San Francisco de Campeche City.

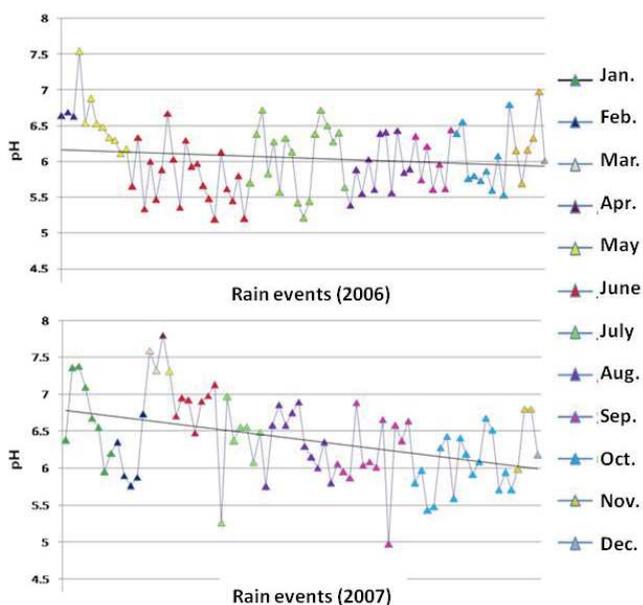


Fig. 9. Tendencies of rain pH during 2006 and 2007 at San Francisco de Campeche City.

Torres (2009), studied the ionic enrichment in rain samples collected at INAH station during 2007. The study indicate an enrichment on sulphates ($SO_4^{=}$), nitrates (NO_3^-), calcium (Ca^{2+}) and Cl^- ions. $SO_4^{=}$ and NO_3^- are acidic compounds present as a consequence of human activity, while Ca^{2+} is dragged from alkaline soils of Peninsula of Yucatan, because it is transported by the wind and incorporated to the rain drops in the atmosphere, contributing to the neutralization of acidic compounds.

Under this condition, rain acidity is not a determinant factor in recession rates of calcareous materials, since volume and intensity of precipitation seems like key factor in deterioration of the historic building at San Francisco de Campeche City.

3.4 Degradation of historic buildings in San Francisco de Campeche City

Two representative building from the old military complex of the City were studied in order to analyze the influence of environmental condition on degradation of their masonry structure: Forts San Carlos and San Pedro (Fig. 10). Both buildings were constructed in masonry base structure made by calcareous stone quarry blocks and mortars, made with slike lime and stone dust named sahabab.

Fort of San Carlos is a pentagonal-shaped structure located at the city's bastions-and-rampart system's northwestern corner, in front of the south of Gulf of Mexico shoreline. Until mid of the XX century, when, state government, public works reclaimed some portion of land from the original previous shoreline, three walls suffered direct wave impact and tidal movements. At present, the State and Municipal Government office buildings as well as the State Congressional offices and Legislature auditorium are located adjacent to Fort San Carlos.

Continuous vehicular movements flow through this immediate area, which houses peripheral urban core lanes and formal entrance into the 8th Street downtown historic district.

Fort San Pedro crowns the city's bastion- and- rampart system's southeaster sector located at the Southeastern sector. While functioning as a bastion against possible inland attacks and "watchtower" for surrounding neighborhoods located to the south, southeast and southwest, this structure does not receive direct marine aerosols and tidal movements as noted in the case Fort San Carlos located in the northern parapet perimeter.

These factors suggest that deterioration followed a slow natural process over a long time period. However, at present this Colonial construction is surrounded by traffic jammed streets, municipal bus terminals and intense anthropogenic activity in the immediate area.

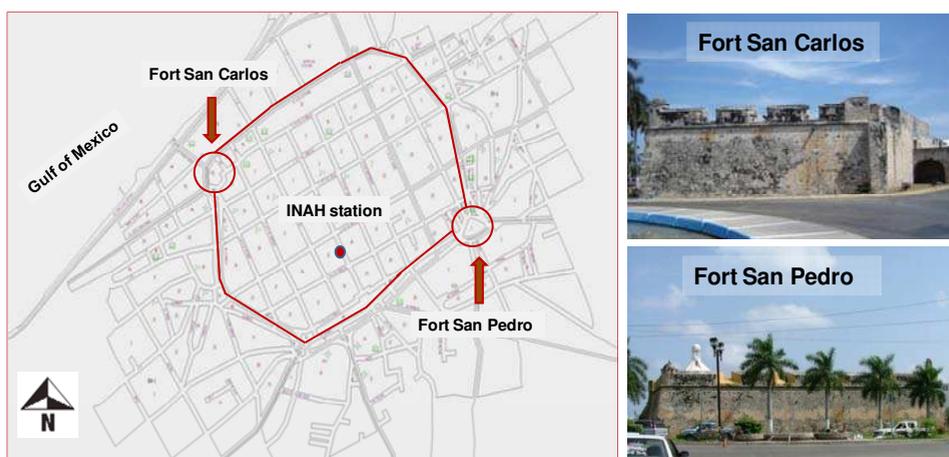


Fig. 10. Location of Forts San Carlos and San Pedro at the historic center of San Francisco de Campeche City. Also location of INAH station is showed.

In spite of consider the effects of environment in degradation of historic buildings, samples were collected from their walls and mineral alteration was investigated by XRD analysis in a Bragg-Brentano geometry X-ray diffractometer (Siemens D5000), and analyzed under the following conditions: Cu K α radiation ($\lambda=1.5416 \text{ \AA}$) and operational conditions of 25 mA and 35 kV at a step size of $2^\circ/2\theta/\text{min}$ in the $2\text{--}60^\circ$ range 2θ .

Table 6, shows the mineral phases identified during the analysis in crusts samples from both Forts. Calcite (CaCO_3), a rhombohedral form of calcium carbonate, seems like the major compounds in all the samples. As have been described before, tropical climate guarantee the water availability to lead dissolution of calcium carbonate content in calcareous materials and their later recrystallization to form crusts. Also minerals like, aragonite (CaCO_3), sodium silicate ($\text{Na}_2\text{Si}_4\text{O}_9$), quartz (SiO_2), dolomite ($\text{CaMg}(\text{CO}_3)_2$) and portlandite (CaOH_2) were present.

There are mineral components of limestone and traditional mortars employed during the construction of the Forts or the utilization of cements to make modern mortars during recent preservation works. Aragonite (CaCO_3), is a polymorphous of calcium carbonate and is present in bioclastic limestones.

The identification of neomineral phases like whewellite ($\text{C}_2\text{CaO}_4\cdot\text{H}_2\text{O}$), and wheddellite ($\text{C}_2\text{CaO}_4\cdot 2\text{H}_2\text{O}$) keep relation with bio-deterioration phenomena. Calcium oxalates are formed during oxalic acid dissolution of calcareous materials (Arocena et al., 2007). Oxalic acid is produced by metabolic activity of microorganisms like cyanobacteria and lichens (Del monte y Sabbioni, 1985; Rampazi et al., 2004). In the walls of Forts San Carlos and San Pedro, was evident the colonization by abundant microbial communities (Fig. 11).



Fig. 11. Aspect of the biodeterioration in the historic buildings of San Francisco de Campeche City. (a) Fort San Carlos. (b). Microbial community at West wall of Fort San Pedro.

On the other hand, it is important to note the presence of gypsum in Fort San Pedro samples while it was absent in Fort San Carlos ones. Gypsum is a neomineral product formed as a consequence of SO_2 reaction with CaCO_3 in urban environments (Graedel et al., 2000; Reyes et al., 2010b). It is an indicator of the certain pollution level in specific areas submitted to the pressure of vehicular and industrial emissions. San Pedro Fort is localized in the east area of the historic centre of the city. All their walls (except the west), are bordered by heavy traffic jams avenues, while south and southwest walls are very close to a bus station from Municipal Urban System.

Mineral phase	Sample code												CNC	PCC		
	1	2	3	4	5	6	7	8	9	10	11	12				
Calcite	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+	+
Aragonite	+	-	+	+	-	+	+	+	-	+	+	+	-	-	-	-
Sodium fedespar	+	-	+	+	+	+	+	+	+	+	+	+	+	-	-	-
Quartz	+	+	+	+	+	-	-	-	-	-	-	-	+	+	+	+
Orthoclase	-	-	-	-	-	-	-	-	-	-	-	+	-	-	-	-
Dolomite	-	-	-	+	+	+	-	-	-	+	+	-	-	-	-	-
¹ Goethite	-	-	-	-	-	-	-	-	-	+	-	-	-	-	-	-
² Iron hydroxide carbonate	-	-	-	-	-	-	-	-	-	+	-	-	-	-	-	-
Clay minerals	-	-	-	-	-	+	-	-	-	+	-	-	-	-	-	-
Whewellite	+	+	+	-	-	+	+	+	-	-	+	-	-	-	-	-
Bassanite	-	-	-	-	+	-	-	-	-	-	-	-	-	-	-	-
Weddellite	-	+	-	-	-	-	-	-	+	-	-	-	-	-	-	-
Portlandite	-	-	-	-	-	-	-	+	-	-	+	+	-	-	-	-
Hidroxiapatite	-	-	-	-	-	-	-	-	+	-	-	-	-	-	-	-
Gypsum	-	-	-	-	-	-	-	-	+	-	+	+	+	+	+	+

Table 6. Mineral phases identified in samples from Forts San Carlos and San Pedro by XRD. Samples CNC and PCC correspond to the Convent of San Francisco de Asís (Havana City). (+) present, (-) not present. ¹ICD card number 29-0713. ² ICD card number 33-650.

3.5 City of Havana: A comparison of air pollution and stone degradation

3.5.1 The City of Havana

The City of Havana was founded on November 16, 1519 by Spanish conquest Diego Velázquez de Cuellar. Its historical center was declared a World Heritage Site by UNESCO in 1982. Havana was strengthened in the XVII century by order of the Spanish kings who signed as "Key to the New World and bulwark of the West Indies".

In 1763 construction began on the fortress of San Carlos de la Cabaña, the largest built by Spain in the New World, which shored up the defensive system of Havana after the British occupation.

The port of Havana was considered one of the most important of the region during the colonial era and one of the strategic points for Spain, which is why the bay was protected with a very important network of fortifications, including the Tower of San Lazarus, El Morro de La Habana, the Fortress of San Carlos de la Cabaña, the Castle of "La Fuerza" and other fortress dedicated to protecting the harbor and the city.

During the colony, Havana was also the major transshipment point between the New World and Europe. As a result Havana was the most fortified City in the Americas. Most examples of early architecture can be seen in military fortifications such as Fortress San Carlos de la Cabaña (1558 - 1577) and the Morro Castle (1589 -1630).

The Convent of San Francisco de Asis, is a religious building of Baroque architecture located in the plaza of the same name in the Old Havana (Figure 12). Construction began in 1548

until 1591, although it opened in 1575, fully completed nearly 200 years later, with a series of structural reforms that occurred from 1731 to 1738. It has a tower of 48 yards high, which in colonial times was the tallest structure in the city for several centuries.

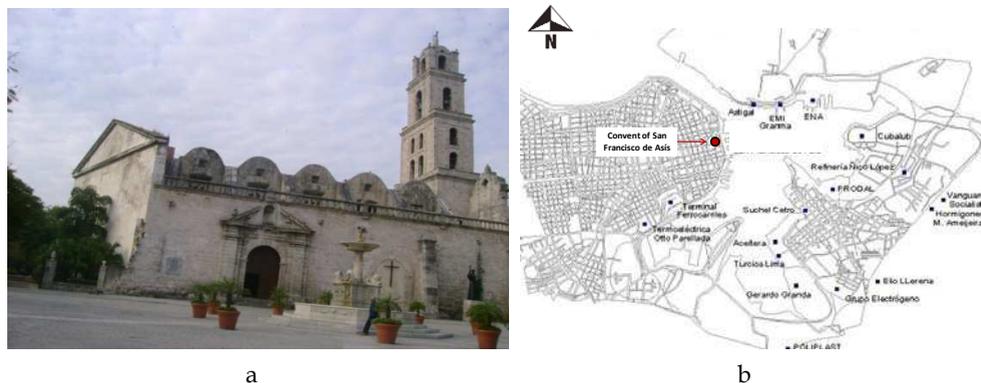


Fig. 12. The Convent of San Francisco de Asis (a). Location of the Convent into the Historic Center of Havana City.

3.5.2 Degradation of historic buildings: a comparative Havana vs San Francisco de Campeche

Nowadays Havana is a City having about 2.2 million inhabitants and different types of industries, particularly around the Bay, a different situation respecting the Mexican City of San Francisco de Campeche. At Havana, air pollution levels are higher than those observed in the Mexican City (Corvo et al., 2010). In this order, a comparison of the influence of air pollution on stone buildings degradation can be made between both cities located in tropical climate.

San Francisco de Campeche City shows a tendency to alkaline rain water with percent of acid rain event of 12% and 5% during 2006 and 2007 respectively (Quirarte, 2010); however, in Havana City, during the period 1981-1994, rain having a pH lower than 5,6 oscillated between 25% and 75% of the samples. It indicates a general tendency to acid rain in Havana. On the other hand, Table 7 shows the results of atmospheric contamination measured in San Francisco Convent and the Basilica. It can be noted that there is an evident difference in the deposition level of sulfur compounds between Havana and San Francisco de Campeche sites (Table 4). Havana sites show a significant higher deposition of sulfur compounds respecting San Francisco de Campeche. The two selected monitoring sites were located inside San Francisco de Asis Convent and Basilica Minor.

This building is located at less than 200 m from Havana Bay shoreline. Under indoor conditions, deposition rate is usually lower than outdoors. One of the monitoring sites was located inside the Basilica building, in the concert hall at about 3 m from the floor. The second monitoring site was located in the Chorus, in the same Basilica Building, at about 10 m from the floor. Evaluation was carried out beginning September 2006 up to March 2007. Chloride deposition rate was negligible because it was determined in indoor conditions, it is very well known that chloride aerosol significantly decreases in indoor conditions; however,

in outdoor conditions, in sites near Havana Bay, an average chloride deposition around 10-20 $\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$ has been measured. It is important to note that even under indoor conditions, values of sulphur and nitrogen compounds inside the Convent are higher than those reported for San Francisco de Campeche outdoors. It confirms that air pollution in Havana City is significantly higher (Corvo et al., 2010; Reyes et al., 2010).

City	Site	Sulphur compounds deposition rate ($\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$)			Chloride deposition rate ($\text{mg}\cdot\text{m}^{-2}\cdot\text{d}^{-1}$)			NO ₂ concentration ($\mu\text{g}\cdot\text{m}^{-3}$)		
		Ave.	Max	Min	Ave.	Max	Min	Ave.	Max.	Min.
Havana										
Indoor	Basilica	10.50	12.50	6.51	Neg.	Neg.	Neg.	16.35	26.08	6.23
Indoor	Chorus	11.60	14.65	7.60	Neg.	Neg.	Neg.	16.29	24.49	11.50

Table 7. Air pollution levels inside San Francisco de Asis Convent and Basilica Minor in Havana, Cuba. Neg: Negligible.



a



b

Fig. 13. Main Façade of San Francisco de Asis Convent and Basilica Minor in Havana, Cuba (a). Black crust deposits (b).

Crust representative samples were taken from the façade of the Convent of San Francisco de Asis and analyzed according the same procedure previously described by Forts San Carlos and San Pedro samples (Fig. 13). Mineral composition of Cuban samples is included in Table 6 (CNC and PCC samples).

Black crusts formed at the Basilica façade (outdoors) in Obispo Street show gypsum as a predominant phase with small amounts of calcite and quartz. It means that black crust

composition is almost completely gypsum due to contamination by atmospheric SO_2 . No presence of nitrogen degradation product was detected.

Crust formed at Forts San Carlos and San Pedro (San Francisco de Campeche) is mainly formed by calcite, the original main content of the stone. Different minor phases are: aragonite, dolomite, and quartz. The presence of whewellite and weddellite in the samples is an index of the influence of biological activity in stone deterioration, although the presence of bassanite in sample 5 from Fort San Carlos, shows the influence of environmental SO_2 . It is important to note that gypsum was identified in samples 9, 11 and 13 corresponding to Fort San Pedro, but not at Fort San Carlos. Gypsum is produced by the action of SO_2 over calcareous materials.

The comparison between crust composition in Campeche and Havana is a demonstration of the role of air pollution in deterioration of stone buildings. According to the present results, the influence of sulphur contamination is higher than nitrogen contamination, because degradation products do not show nitrogen compounds in its composition.

Sulphur dioxide is highly soluble in water; however, nitrogen dioxide is not significantly soluble, it could be a cause for a higher influence of sulphur compounds in stone degradation. In addition, nitrogen degradation compounds are more soluble than sulphur degradation compounds, so the first are easily eliminated by rain.

4. Conclusions

The present contribution, showed a general description of the current air quality conditions at San Francisco de Campeche City. From the health point of view, SO_2 , TSP and PM_{10} fraction are below the limits of risk considered by Mexican Legislation. The creation of a local air monitoring program in order to prevent an increase of atmospheric pollution levels is necessary as a consequence of the recent economical, demographic and urban expansion suffered by the City. In this order, although SO_2 concentration was always below critical risk levels, it suffered a continuous increase during the monitoring period.

From the materials point of view, the tropical climate and the presence of natural and anthropogenic pollutants create conditions for degradation of both, metals and stony materials. In this order, the degradation of historic building in San Francisco de Campeche City shows a closer relationship with the effect of natural environmental factors, led by water actions that induce mechanisms of salt dissolution and recrystallization across wet to-dry cycles.

The majority presence of calcium carbonates in crust formed on walls of Forts of San Carlos and San Pedro seems to confirm this fact. On the other hand, in spite of the low levels of atmospheric pollutants observed in the City, the presence of gypsum (Fort San Pedro) and bassanite (Fort San Carlos), is an indicator of a growing influence that the anthropogenic pollution could have on deterioration mechanisms. The last one result clear in the case of Fort San Pedro, which actually is under high environmental pressure.

In contraposition, samples from San Francisco de Asis Convent (Havana), show gypsum as a majority neomineral phase. Gypsum is produced in urban environments with high content of SO_2 , which agrees with the higher levels of atmospheric pollution detected at Havana City. In case of increase of pollution levels at San Francisco de Campeche City a similar situation will be found.

5. Acknowledgements

The realization of this contribution was possible thanks to the support of FOMIX CAMP2005-C01-025 Project (Urban Environmental Influence on degradation of colonial military and religious buildings at Campeche City) financed by the Government of State of Campeche and the Council of Science and Technology of México. Also thanks to Centro INAH-Campeche for their giving facilities to the development of the project.

6. References

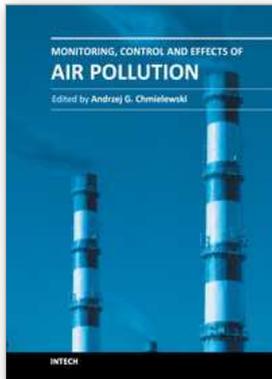
- Allen, G., El-Turki, A., Hallam, K. R., McLaughlin, D., Stacey, M. (2000). The role of NO₂ and SO₂ in degradation of limestone. *British Corrosion Journal*. 35, 35-38.
- Arocena J., Siddique T., Thring R., Kapur S. (2007) Investigation of lichens using molecular techniques and associated mineral accumulations on a basaltic flow in a Mediterranean environment. *Catena* 70, 356-365.
- Castro-Mora, J. (2002). Geological and mineral monography of the State of Campeche. Council for Mineral Resources. Secretary of Economy. Mexico. ISBN 968-6710-95-7.
- Bravo, H., Soto, R., Sanchez, P., Torres, R., Granada, L. (2000) Chemical composition of precipitation in a Mexican Maya región. *Atmospheric Environment*. 34, 1197-1204.
- Cardell, C., Delalieux, F., Roumpopoulos, K., Moropoulou, A., Auger, F., Van Grieken, R. (2003). Salt-induced decay in calcareous stone monuments and buildings in a marine environment in SW France. *Construction and Buildings Materials*. 17, 165-179.
- Carpio, J., Reyes, J., Salazar, J., Parra, A., Martínez, L. (1995) Influence of industrial pollutants on the atmospheric corrosivity of petrochemical installation. Paper LA9635. Proceedings 2nd Latinoamerican Corrosion Congress. Maracaibo, Venezuela.
- Cassar, M., Brimblecombe, P., Nixon, T., Price, C., Sabbioni, C., Saiz-Jimenez, C., Van Balen, K. (2004). Sustainable solutions in the conservation and protection of historic monuments and archeological remains: a critical assessment of European research needs. In: *Air Pollution and Cultural Heritage*. Sáiz-Jiménez Ed. Balkema The Netherlands. ISBN. 905809622.
- Cook, D., Van Orden, A., Reyes, J., Oh, S., Balasubramanian R., Carpio, J., Townsend, H. (2000). Atmospheric corrosion in marine environments along the Gulf of Mexico. In: *Marine corrosion in tropical environments*. Sheldon, W. Dean, Guillermo, Hernandez-Duque Delgado, James B, Bushman Eds. American Society for Testing and Materials. 75-97. STP1399.
- Corvo, F., Pérez, T., Martín, Y., Reyes, J., Dzib, L., Gonzalez, J., Catañeda, A. (2008). Corrosion Research Frontiers. *Atmospheric Corrosion in Tropical Climates*". On the concept of time of wetness and its interaction with contaminants deposition. In *electroanalytical Chemistry: New research*". G. M. Smithe Ed. Nova Science Publishers Inc. 62-9. ISBN 978-1-60456-347-4.
- Corvo, F., Pérez, T., Reyes, J., Dzib, L., Gonzales-Sanchez, J., Catañeda, A. (2009). Atmospheric corrosion in tropical humid climate. In: *Environmental degradation of*

- infrastructure and cultural heritage in coastal tropical climate. J. Gonzalez-Sanchez, F. Corvo, N. Acuña-González. 1-34. ISBN: 978:81-7895-426-4.
- Corvo, F., Reyes, J., Valdes, C., Villaseñor, F., Cuesta, O., Aguilar, D., Quintana, P. (2010). Water, Air and Soil Pollution. 205, 359-375.
- Del Monte, M., Sabbioni, C. (1986). Chemical and biological weathering of an historical building: Reggio Emilia Cathedral. Science of the Total Environment. 50, 65-182.
- Dzul, B. (2010). Elemental analysis of atmospheric particles, PM₁₀ fraction at San Francisco de Campeche City by using PIXE spectroscopy. Undergrade thesis. Autonomous University of Campeche, San Francisco de Campeche, México.
- Gongora, H. (2010). Influence of corrosive environmental parameters on degradation of historical and industrial materials in three microclimates of the State of Campeche. Undergrade thesis. Autonomous University of Campeche, San Francisco de Campeche, México
- Gobbi, G., Zappia, G., Sabbioni, C. (1998). Sulphite quantification on damaged stones and mortars. Atmospheric Environment. 32(4), 783-789.
- Gorbushina, A. (2007). Minireview: Life on the rocks. *Environmental Microbiology* 9(7): 1613-163.
- Government of the State of Campeche (2004). Diagnostic of vial and transport system at San Francisco de Campeche City. Campeche, México
- Graedel, T., (2000). Mechanisms for the atmospheric corrosion of carbonate stone. Journal of the Electrochemical Society, 147 (3), 106-109.
- Guiamet, P., Gómez de Saravia, S., Nuñez G. (2005). *Biodeterioration of buildings stone by cyanobacteria, bacteria and fungi*. In Ortega-Morales, B. O; Gaylarde, C. C.; Narváez-Zapata y Gaylarde P.M. (Eds). LABS 5 Latin América Biodegradation and Biodeterioration Symposium. Autonomous University of Campeche and National Polytechnic Institute. 51-53. ISBN 968-5722-34-X.
- Kuchera, V., Tidblad, J., Kreislova, K., Knotkova, D., Faller, M. Reiss, D. (2007). UN/ECE ICP materials dose-response functions for the multi-pollutant situation. Water Air and Soil Pollution: Focus. 7, 249-258.
- Little, B.J., Ray, R. (2005). *The role of fungi microbiologically influenced corrosion*. En: Ortega-Morales, B. O; Gaylarde, C. C.; Narvaez-Zapata y Gaylarde P.M. (Eds). LABS 5 Fifth Latin América Biodegradation and Biodeterioration Symposium. Autonomous University of Campeche and National Polytechnic Institute. 51-53. ISBN 968-5722-34-X.
- Lpifert, F. (1989). Atmospheric damage to calcareous stones. Atmospheric Environment. 23, 415-429.
- Massey, S. (1999). The effects of ozone and NO_x on the deterioration of calcareous stone. The Science of the Total Environment. 227, 109-121.
- Mala, B. (1999). Global transport of anthropogenic contaminants and the consequences for the Arctic marine ecosystem. Marine Pollution Bulletin. 38 (5), 356-379
- Miss M. (2008). Characterization of aliphatic hydrocarbons and analysis of spacial and temporal variation of atmospheric particles at San Francisco de Campeche City.

- Undergrade thesis. Autonomous University of Campeche, San Francisco de Campeche, México.
- Monna, F., Puertas, A., Leveque, F., Losno, R., Fronteau, G., Marin, B. (2008). Geochemical records of limestone facades exposed to urban atmospheric contamination as monitoring tools?. *Atmospheric Environment*. 227, 109-121.
- Moropoulou, A., Konstanti, A. (2004). European strategies for preservation and managements of Historic Cities: knowledge based decision-making approach. In: *Air Pollution and Cultural Heritage*. Sáiz-Jiménez Ed. Balkema The Netherlands. ISBN. 905809622.
- Muñoz, A., Rodriguez, A., Villalobos, P., MUnive, Z., Martelo, O., Diaz, G., Bravo, C. Gomez, A. (2001). Suspended particles, polycyclic aromatic hydrocarbons and mutagenesis at Southwest of Mexico City. *Revista Internacional de Contaminación Ambiental*. 17, 193-204.
- Ortega-Morales, B.O. 2004. Biofilms fouling ancient limestone Maya monuments in Uxmal, México. *Current Microbiology* 40, 81-85.
- Primerano, P., Marino, G., Dipascale, s., Mavilia, L., Corigliano, F. (2000). Possible alteration of monuments caused by particles emitted onto the atmosphere carrying strong primary acidity. *Atmospheric Environment*. 34, 385-401.
- Quirarte, O. (2010). Variation of rain acidity in San Francisco de Campeche City and Calakmul Biosphere Reserve (archeological zone), during 2006 and 2007. Undergrade thesis. Autonomous University of Campeche, San Francisco de Campeche, México.
- Rampazzi, I., Andreotti, A., Bonaduce, I., Colombini, M, P.; Colombo, C., Toniolo, L. (2004). Analytical investigation of calcium oxalate films on marble monuments. *Talanta*. 63, 967-977.
- Ravindra, K., Mor, S., Kamgotra, J., Kaushin, C. (2003). Variations in spatial patterns of criteria air pollutants before and during initial rain in Monsoon. *Environmental Monitoring Assessment*. 87, 145-153.
- Reyes, J. (1998). Influence of the main atmospheric and air quality factors on metals atmospheric corrosion along the southeast cost of the Gulf of México M. Phil. Thesis. Universidad Veracruzana. Boca del Rio, Veracruz. Mexico.
- Reyes, J. (2004). Diagnostic criteria for the identification of particular matter organic compounds from vehicular exhaust and their application to study the deterioration of the Cathedral of Seville. PhD. Thesis. University of Seville. Spain.
- Reyes, J. Hermosin, B., Sáiz-Jimenez, C. (2004). Organic analysis of aerosols in Seville Atmosphere (2004). In: *Air Pollution and Cultural Heritage*. Sáiz-Jiménez Ed. Balkema The Netherlands (ISBN. 905809622).
- Reyes, J. (2005a). Research Project CONACYT-46434-Y. National Council for Science and Technology. Autonomous University of Campeche. Mexico.
- Reyes, J. (2005b). Research Project FOMIX-CAMP-2005-C01-028. National Council for Science and Technology -Government of the State of Campeche. Autonomous University of Campeche. México.
- Reyes, J., Hermosín, B., Sáiz-Jimenez, C. (2006). Organic Composition of Seville Aerosols. *Organic Geochemistry*, 37, 2019-2025,

- Reyes, J., Torres, F., Ché, I., Corvo¹, F., Pérez, T., Bravo, H., Sánchez, P., Aguilar, D., Quintana, P. (2010a), Dissolution of Traditional Mortars under Artificial Rain Conditions: A Laboratory Test. In: José Luis Ruvalcaba Sil, Javier Reyes Trujeque, Jesús A. Arenas Alatorre, Adrián Velázquez Castro Eds. Proceedings of 2nd Latin-American Symposium on Physical and Chemical Methods in Archaeology, Art and Cultural Heritage Conservation & Archaeological and Arts Issues in Materials Science - IMRC 2009, Mexico. 195-200. ISBN: 978-607-02-2017-3.
- Reyes, J., Corvo, F., Espinosa-Morales, Y. Valdes, C., Bartolo, P., Aguilar, D., Quintana, P., Hermosín, B., Saiz-Jimenez, C. (2010b). Analysis of Black Crust from a Cuban Historic Building . In: José Luis Ruvalcaba Sil, Javier Reyes Trujeque, Jesús A. Arenas Alatorre, Adrián Velázquez Castro Eds. Proceedings of 2nd Latin-American Symposium on Physical and Chemical Methods in Archaeology, Art and Cultural Heritage Conservation & Archaeological and Arts Issues in Materials Science - IMRC 2009, Mexico. 195-200. ISBN: 978-607-02-2017-3.
- Sessa, C. (2004). Cultural Heritage protection with integrated policies. In: Air Pollution and Cultural Heritage, Sáiz-Jiménez Ed. Balkema The Netherlands. ISBN. 905809622.
- Schifter, I., Díaz, L., López-Salinas, E. (2006). "Assessment of new vehicles emissions certification standars in the Metropolitan area of México city. *Environmental Monitoring Assessment*. 114: 419-432.
- Sosa-Echeverria, R., Bravo-Alvarez, H., Sánchez-Alvarez, P., Soto-Ayala R., Alarcón-Jiménez, A., Khal, J. (2006). Determination of total suspended particles during five research cruises at Gulf of Mexico continental platform. *Ingeniería, Investigación y Tecnología*. VII (2), 71,-83.
- Stefanis, N., Theoaulakis, P., Pilinis, C. Dry deposition effect of marin eaerosol to the building stone of the medieval city of Rhodes, Greece. *Building and Environment*. 44, 260- 270.
- Tercer, L. (1998). Laboratory experiments on the investigation of the effects of sulfuric acid on the deterioration of carbonate stone and surface corrosion. *Water, Air and Soil Pollution*. 114, 1-12.
- Tidblad, J., Mikhailov, A., Kuchera, V. (2000) Application of a model for prediction of atmospheric corrosion in tropical environments. In: Marine corrosion in tropical environments. Sheldon, W. Dean, Guillermo, Hernandez-Duque Delgadillo, James B, Bushman Eds. American Society for Testing and Materials. 18-32. STP1399.
- Torres, F. (2009). Effects of rain in stony materials from the Campeche State cultural heritage. M.Phil. thesis. Autonomous University of Campeche, San Francisco de Campeche, México.
- Valeroso, I. I., Monteverde, C. A., Estoque, M. A. (1992). Diurnal variations of air pollution over metropolitan Manila. *Atmosfera*. 5: 241-257.
- Villaseñor, F. (2008). The use of passive techniques for sampling atmospheric pollutants in the State of Campeche. Undergrade thesis. Autonomous University of Campeche, San Francisco de Campeche, México.

- Zappia, G., Sabbioni, C., Riontino, C., Gobbi, G., Favoni, O. (1998). Exposure test of building materials in urban atmosphere. *The Science of the Total Environment*. 224, 235-244.
- Zendri, E., Biscontin, G., Kosmidis, P. (2001). Effects of condensed water on limestone surfaces in a marine environment. *Journal of Cultural Heritage*. 4, 283-289.



Monitoring, Control and Effects of Air Pollution

Edited by Prof. Andrzej G. Chmielewski

ISBN 978-953-307-526-6

Hard cover, 254 pages

Publisher InTech

Published online 23, August, 2011

Published in print edition August, 2011

The book addresses the subjects related to the selected aspects of pollutants emission, monitoring and their effects. The most of recent publications concentrated on the review of the pollutants emissions from industry, especially power sector. In this one emissions from opencast mining and transport are addressed as well. Beside of SO_x and NO_x emissions, small particles and other pollutants (e.g. VOC, ammonia) have adverse effect on environment and human being. The natural emissions (e.g. from volcanoes) has contribution to the pollutants concentration and atmospheric chemistry governs speciation of pollutants, as in the case of secondary acidification. The methods of ambient air pollution monitoring based on modern instrumentation allow the verification of dispersion models and balancing of mass emissions. The comfort of everyday human's activity is influenced by indoor and public transport vehicles interior air contamination, which is effected even by the professional appliances operation. The outdoor pollution leads to cultural heritage objects deterioration, the mechanism are studied and the methods of rehabilitation developed. However to prevent emissions the new technologies are being developed, the new class of these technologies are plasma processes, which are briefly reviewed at the final part of the book.

How to reference

In order to correctly reference this scholarly work, feel free to copy and paste the following:

Javier Reyes, Francisco Corvo, Yolanda Espinosa-Morales, Brisvey Dzul, Tezozomoc Perez, Cecilia Valdes, Daniel Aguilar and Patricia Quintana (2011). Influence of Air Pollution on Degradation of Historic Buildings at the Urban Tropical Atmosphere of San Francisco de Campeche City, México, Monitoring, Control and Effects of Air Pollution, Prof. Andrzej G. Chmielewski (Ed.), ISBN: 978-953-307-526-6, InTech, Available from: <http://www.intechopen.com/books/monitoring-control-and-effects-of-air-pollution/influence-of-air-pollution-on-degradation-of-historic-buildings-at-the-urban-tropical-atmosphere-of->

INTECH
open science | open minds

InTech Europe

University Campus STeP Ri
Slavka Krautzeka 83/A
51000 Rijeka, Croatia
Phone: +385 (51) 770 447
Fax: +385 (51) 686 166

InTech China

Unit 405, Office Block, Hotel Equatorial Shanghai
No.65, Yan An Road (West), Shanghai, 200040, China
中国上海市延安西路65号上海国际贵都大饭店办公楼405单元
Phone: +86-21-62489820
Fax: +86-21-62489821

© 2011 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the [Creative Commons Attribution-NonCommercial-ShareAlike-3.0 License](#), which permits use, distribution and reproduction for non-commercial purposes, provided the original is properly cited and derivative works building on this content are distributed under the same license.