

# On the dry deposition of ionic species at two National Parks located in the vicinity of power plants in Mexico

Julia Cerón., Rosa María Cerón., Beatriz Cárdenas., Abraham Ortinez., Enrique Cruz., Berenice Díaz., Guadalupe Carballo., Tezozomoc Pérez., Javier Reyes., Manuel Muriel., and Jesús Guerra.

**Abstract**—Dry deposition levels of  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{NH}_4^+$ ,  $\text{Cl}^-$ ,  $\text{NO}_3^-$ , and  $\text{SO}_4^{2-}$ , are reported for two sites in Mexico: Biosphere reserve “Los Petenes” in Campeche, and “El Chico” National Park in Hidalgo; during 2009 and 2010. Dry deposition samples were taken using nylon filters as surrogate surfaces for one-week long exposure periods. For both sampling sites, nitrate levels exceeded the background hemispheric value reported for remote sites. In the case of Los Petenes,  $\text{NO}_3^-$  showed good correlation with  $\text{SO}_4^{2-}$ , suggesting that both ions had a common source, probably combustion processes. From backward trajectories analysis, the origin of the air masses for Los Petenes during the study period was traced, identifying local sources (Lerma power plant and biomass burning) as the main sources contributing to the acidity. On the other hand, In El Chico,  $\text{NO}_3^-$  -  $\text{SO}_4^{2-}$  correlation coefficient was negligible, suggesting that this ion pair had an origin in different sources. We conclude that the

high nitrate levels found in El Chico had their origin in forest fires occurring frequently as a part of the natural dynamic of this park. Since only local sources contributed to the N deposition in this site, we conclude that power plant located at Tula, an urban and industrialized site near to El Chico, did not contributed to trace elements dry deposition in El Chico. In spite of nitrate and sulfate levels were elevated, pH values obtained showed that these sites had enough buffer capacity to neutralize the acidity. However, it is necessary to make an accurate diagnosis of both sites, considering that pH value is not a conservative tracer of the potentially ecological effects related to acid deposition. Therefore, we propose that in future works, critical loads for N and S must be estimated in both sites.

**Keywords**—Acid deposition, Dry deposition, El Chico, Ionic species, Los Petenes.

## I. INTRODUCTION

ATMOSPHERIC pollutants can be emitted as gaseous components, particles and/or aerosols, staying in the atmosphere without changes or, being involved in different chemical mechanisms resulting in secondary pollutants even more toxic than their precursors. Atmospheric deposition plays an important role in the transference of chemical compounds from the atmosphere to terrestrial and aquatic ecosystems, where acid compounds deposited can result in eventual significant damage depending on their critical loads [3]. There are two paths to remove pollutants from the atmosphere: dry and wet deposition. When pollutants either in gaseous or particulate form are removed without the occurrence of rain, this process is called dry deposition. During dry periods, particles are removed efficiently only by dry processes such as impaction and diffusion to surfaces of objects [2].

For particle pollutants, removal fates are strongly related to particle size. Large particles are efficiently removed by gravitational settling. On the other hand, for small particles, especially those with diameters below  $0.1 \mu\text{m}$ , Brownian diffusion becomes increasingly important. Inertial impaction is an important removal mechanism when the momentum of a particle is sufficient to maintain a nearly linear trajectory in a moving air mass, this process is important for particles with aerodynamic diameters between  $0.5$  and  $15 \mu\text{m}$ , but is highly dependent on particle size and wind velocity. On the other hand, in wet periods, particles and gases are removed mainly by precipitation. Wet deposition involves chemical

Manuscript received September 28, 2011; Revised version received November 3, 2011. This work was supported by the Mexican Council of Science and Technology Project 107948 (CONACYT-México).

Julia Cerón is with the Chemistry Faculty in the Autonomous University of Carmen City (UNACAR). Carmen City, Campeche, Mexico. (Phone/Fax: +52 938 3826514; e-mail: [jceron@pampano.unacar.mx](mailto:jceron@pampano.unacar.mx)).

Rosa Cerón is with the Chemistry Faculty in the Autonomous University of Carmen City (UNACAR). Carmen City, Campeche, Mexico. (e-mail: [rceron@pampano.unacar.mx](mailto:rceron@pampano.unacar.mx)).

Beatriz Cardenas is with the Mexican Institute of Ecology (CENICA-INE). México, D.F. (e-mail: [bcardenas@ine.gob.mx](mailto:bcardenas@ine.gob.mx)).

Abraham Ortinez is with the Mexican Institute of Ecology (CENICA-INE). México, D.F. (e-mail: [jortinez@ine.gob.mx](mailto:jortinez@ine.gob.mx)).

Enrique Cruz is with the Autonomous University of Hidalgo State (UAEH). Pachuca de Soto, Hidalgo, México. (email: [ecruz@uah.edu.mx](mailto:ecruz@uah.edu.mx)).

Berenice Díaz is with the Chemistry Faculty in the Autonomous University of Carmen City (UNACAR). Carmen City, Campeche, Mexico. (e-mail: [berenice\\_161287@hotmail.com](mailto:berenice_161287@hotmail.com)).

Guadalupe Carballo is with the Chemistry Faculty in the Autonomous University of Carmen City (UNACAR). Carmen City, Campeche, Mexico. (e-mail: [lupis\\_carpat@hotmail.com](mailto:lupis_carpat@hotmail.com)).

Tezozomoc Pérez is with the Researcher Center on Corrosion of he Autonomous University of Campeche. San Francisco de Campeche, Campeche, México. (e-mail: [tezperez@uacam.mx](mailto:tezperez@uacam.mx)).

Javier Reyes is with the Researcher Center on Corrosion of he Autonomous University of Campeche. San Francisco de Campeche, Campeche, México. (e-mail: [javreyes@uacam.mx](mailto:javreyes@uacam.mx)).

Manuel Muriel is with the Mexican Petroleum Institute. Carmen City, Campeche, Mexico. (email: [mmuriel@imp.mx](mailto:mmuriel@imp.mx)).

Jesús Guerra is with the Environmental Sciences Center of the Autonomous University of Carmen City (UNACAR), Carmen City, Campeche, Mexico. (email: [jguerra@pampano.unacar.mx](mailto:jguerra@pampano.unacar.mx)).

constituents sufficiently soluble to dissolve in water associated with in-cloud formation of rain droplets. In both cases, gases and aerosols experience chemical reactions that play an important role in the production of acid species in the atmosphere [3].

Therefore, depending on their residence time, some pollutants can be deposited around the emission source in a short time period, where dominant mechanism can be dry deposition; whereas other atmospheric components (gases undergoing gas-particle conversion processes or particles with a lower sedimentation rate) may be easily transported by the wind action undergoing long-range transport and finally to be deposited in distant places from their emission point as a result of wet deposition processes [4], [5].

Over the previous three decades, understanding of the causes and consequences, temporal trends, and spatial patterns of atmospheric deposition in temperate ecosystems has improved considerably [6]. However, the most of the studies have been carried out in Europe and North America. Only few studies about wet deposition have been carried out in Mexico [7], [8], [9], [10], [11], [12] and studies about dry deposition are null or scarce. It is well known that the main source associated to acidic deposition is energy generation process. Approximately 66.8% of energy produced in Mexico comes from the burning of “combustoleo”, resulting in fly ash emission, and large amounts of gases considered as acid precursors (such as SO<sub>2</sub> and NO<sub>x</sub>) that contribute to the acid deposition in the vicinity of the plants [13]. This fuel is commonly used in Mexico in power plants in large steam boilers, drying kilns and ovens, and it is a blend of residua and gas oil cutter stock meeting the viscosity requirements of ASTM D 396 (Standard Specification for Fuel Oils, Grade Designation No. 6).

In Tropical countries as Mexico, where eco-tourism constitutes an important source of economic resources, and where, natural protected areas with a great bio-diversity are located near industrial sources, there is an increasing concern about the potential ecological effects of acid deposition on the ecosystems. In spite of atmospheric dry deposition can be an important source of nutrients causing changes in natural ecosystems [14 -16], little data on deposition inputs of N and S in Mexican eco-regions have been reported focused mainly to temperate forest of pine, fir and oak.. Nitrogen dry deposition alone may account for as much as 95% of the total terrestrial N load in the Mediterranean ecosystems [14]. To understand regional variations, to determine if critical loads are exceeded and to prove the efficiency of environmental policies, it is necessary to carry out qualitative and quantitative studies of atmospheric deposition in impacted sites [17].

In Mexico, critical loads and the effects of deposition remain uncertain, and there are not a national network operating continuously that provides an outline of the main chemical characteristic of deposition. Notwithstanding the work carried out within the framework of REDDA (Atmospheric Deposition Network of Mexico City), in

Mexico, studies on dry deposition fluxes are scarce and do not provide a firm basis for interpreting long-term trends or regional variations.

In 2008, a national network (RMDA, Mexican Atmospheric Deposition Network) in a preliminary phase began the monitoring of wet and dry deposition at various sites of the country. This network has been coordinated by National Ecology Institute (INE) and Autonomous University of Carmen (UNACAR), and considered both natural and polluted sites.

In addition, in the same year, the Mexican Environmental Agency (SEMARNAT) supported a research project focused to the study of atmospheric deposition in five sites located at the surroundings of power plants burning “combustoleo”. This work reports the dry deposition data obtained for two of these sites of the network: Los Petenes Biosphere Reserve and El Chico National Park, both located in the vicinity of power plants.

## II. MATERIALS AND METHODS

### A. Site Description

Dry deposition samples were collected on a weekly basis during 2009 at two sampling stations in Los Petenes Biosphere Reserve and El Chico National Park, two important natural areas located in the vicinity of power plants. See Fig. 1. In table 1, main features of the sampling stations are shown.

**Table 1.** Main features of the sampling stations.

Sites	Classification area	Altitude (m asl)	Latitude	Longitude
Los Petenes, Campeche State	Biosphere Reserve and Ramsar site	4	20°51'30'' N	90°45'15''W
El Chico, Hidalgo State	National Park and Rural	2570	20°11'09'' N	100°18'57'' W

Los Petenes Biosphere Reserve: A sampling site within the facilities of the Center for the Conservation and Research of the Wild Life of the Autonomous University of Campeche was chosen. This site is located in the Biosphere Reserve named “Los Petenes” and constitutes a large and narrow coastline at the north of the Campeche State at 20°51'30'' N and 90°45'15'' W.

Los Petenes site is characterized by the presence of complexes habitats similar to islands with availability of sweet water all year called Petenes. These ecosystems only are found in Cuba, Florida and Mexico.

The dominant climate is sub-humid warm with rains occurring in summer with the presence of mid-summer drought. Annual precipitation ranges from 729 to 1049 mm and average temperature is 27.5°C. Los Petenes Biosphere Reserve is a Ramsar Site and constitutes a representative biogeographic area of an ecosystem not significantly perturbed.

This sampling site is located at 10 km from the power plant “Lerma” (4 units of combined cycle with an installed effective capacity of 150 MW).

El Chico National Park: El Chico is an important National Park located in a forested region in the State of Hidalgo. See Fig. 1. At the surroundings of this park, much of the original forest cover has been cleared by human activities, and forest fires are frequent mainly during the mid-summer drought. In the middle of this park, an eco-tourism center operates almost all year.

Climate in El Chico is sub-humid, and rains are present during the summer, this site is also influenced by cold fronts named “Nortes” that prevail mainly during winter time. Specific sampling site is located in a sacred fir forest near to Las carboneras Town (20° 11' 09.59"N and 100° 18' 57" W).

This site is located at 50 km from Tula City, where an important oil-fired power plant is located (9 units of vapor and combined cycle technologies with an installed effective capacity of 2000 MW).



Fig. 1. Sampling sites location.

### B. Field Work

Collection methods are the major source of uncertainty in studies of dry deposition [18]. In indirect methods, deposition fluxes are calculated from atmospheric concentrations and estimated deposition velocities. In this case, the main problem is the difficulty to estimating an appropriate deposition velocity. In this study, dry deposition was assessed with a direct method using a surrogate surface according to the methodology used by Alonso *et al* [19].

Automatic dry-wet sampling equipment was used to collect dry deposition. Three surrogate surfaces (Nylon membranes, 47 mm diameter and 45  $\mu\text{m}$  size pore) were located on an aluminum support within the dry deposition bucket (the first one for cation, pH and conductivity analysis, the second one for anion determination, and the last one for ammonium analysis).

Filters were horizontally exposed during one week periods during 15 weeks. At the end of the sampling period, membranes were stored in Petri boxes at  $-18^{\circ}\text{C}$  until analysis.

### C. Analytical Work

Nylon filters were extracted with 80 ml of deionized water for 15 minutes in an ultrasonic bath. pH and conductivity were determined by a pH meter (Thermo Orion 290) and a conductivity meter (CL 135), respectively [20, 21].  $\text{NO}_3^-$ ,  $\text{Cl}^-$ , and  $\text{SO}_4^{2-}$ , were analyzed by ion chromatography (Agilent 1100) with conductivity detection [22]. Extracts used to analyze cations were digested in Teflon closed flasks (Cole-Parmer) of 100 ml using as energy source an autoclave equipment.  $\text{Na}^+$  [23],  $\text{K}^+$  [24],  $\text{Ca}^{2+}$  [25] and  $\text{Mg}^{2+}$  [26] were determined by atomic absorption spectrophotometer (Thermo scientific ice 3000) [27], and ammonium was analyzed by colorimetric with UV detection (HACH DR. 2800) [28]. Standard solutions were prepared from certified standards (J.T. Baker).

Detection limits were calculated as three times the standard deviation of six blank samples, and repeatability was assured from an analysis of 3 replicate measurements for each sample. The quality of the analytical data was checked out by a cation-anion balance and by comparison between measured conductivity and calculated conductivity (from concentrations and specific conductivities for each ionic specie).

## III. RESULTS

### Los Petenes Biosphere Reserve:

It can be observed in Table 2 that except  $\text{K}^+$ , most of the ions showed a great variability. Relative ionic abundance obtained was  $\text{NO}_3^- > \text{NH}_4^+ > \text{Cl}^- > \text{Na}^+ > \text{SO}_4^{2-} > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+}$ .

**Table 2.** Ionic concentrations ( $\text{mg l}^{-1}$ ) for dry deposition in Los Petenes Biosphere Reserve during 2009.

Ionic specie	N	Mean	Minimum	Maximum
$\text{Ca}^{2+}$	18	$0.63 \pm 1.03$	0.40	3.88
$\text{K}^+$	18	$0.23 \pm 0.01$	0.16	0.59
$\text{Mg}^{2+}$	18	$0.20 \pm 0.16$	0.05	0.65
$\text{Na}^+$	18	$0.80 \pm 0.33$	0.25	1.45
$\text{NH}_4^+$	10	$2.39 \pm 1.58$	0.05	4.33
$\text{NO}_3^-$	10	$3.93 \pm 3.76$	0.38	9.75
$\text{Cl}^-$	10	$1.07 \pm 1.68$	0.02	5.00
$\text{SO}_4^{2-}$	10	$0.78 \pm 0.67$	0.11	1.99

N: Number of samples

In coastal and marine sites, it is assumed that relative proportion of elements as  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$ ,  $\text{Cl}^-$  and  $\text{Br}^-$  in deposition samples presents similarity to that reported for sea

water. However, in some coastal and marine sites, the ratios of these elements are different in a significant way from their ratio for sea water, in spite of, it is believed that the sea—salt is the main source of these trace components.

In the most of urban and industrial sites, trace elements atmospheric concentrations are significantly greater than those expected from the dispersion process of marine aerosol.

Human activities are the main responsible of this relative enrichment, and often they are referred as enriched elements or in excess, in this case, local or regional meteorology data are necessary to identify the main responsible sources. Therefore, the excess of a constituent in a deposition sample represents an increase of the element upon the expected levels from sea water.

Los Petenes site can be considered as a coastal site (it is located at 8 km from the coast approximately), for this reason, it was necessary to estimate the contribution of marine aerosol to sulfate levels to determine anthropogenic fraction (commonly known as sulfate excess  $[(S_4^{2-})_{xs}]$ ). Excess sulfate levels found ( $12.66 \mu\text{Eq l}^{-1}$ ) are in agreement with background hemispheric levels reported by Galloway [29] for remote sites ( $10 \mu\text{Eq l}^{-1}$ ); it suggests that there was not a significant enrichment derived from local sources.

Since, marine aerosol does not contribute to nitrate levels; it can be assumed that the total content of nitrate in dry deposition samples was in excess, it means that it had an anthropogenic source. Nitrate levels ( $63.39 \mu\text{Eq l}^{-1}$ ) exceeded background hemispheric values reported for remote sites ( $2.8 \mu\text{Eq l}^{-1}$ ) [29]. It is expected since  $\text{NO}_3^-$  was the most abundant ion. Considering the residence times for  $\text{SO}_2$  (13 days) and  $\text{NO}_2$  (1 day), it can be assumed that there was a local source (Lerma power plant) and a temporal source (biomass burning occurring at the end of October and at the beginning of November, 2009) contributing in a significant way to nitrate levels.

Regarding that pH of natural rainwater is controlled by atmospheric  $\text{CO}_2$  dissociation, it has been established that those sites where deposition has a pH value less than 5.0 have acidity problems [30]. pH values found in dry deposition samples for Los Petenes ranged from 3.99 to 6.97, with an average value of 5.9. 22% of the total samples showed pH values below 5.6 and only 5.5.% showed values below 5.0.

In spite of nitrate levels exceeded background hemispheric values, pH values found suggests that this site does not have acidity problems. From the Pearson correlation matrix, it can be observed that nitrate correlated with  $\text{Ca}^{2+}$  ( $r = 0.56$  at  $p < 0.001$ ) and  $\text{Mg}^{2+}$  ( $r = 0.54$  at  $p < 0.001$ ). It suggests that these ions played an important role in the neutralization processes, it was expected since in Yucatan Peninsula, calcareous soils are abundant and it has been reported that alkaline particles from crustal in this region neutralize the acidity [31]. On the other hand,  $\text{NO}_3^-$  correlated with  $\text{SO}_4^{2-}$  ( $r = 0.63$  at  $p < 0.001$ ), suggesting that both ions had a common source, probably combustion processes.

$(\text{SO}_4^{2-})_{xs}/\text{NO}_3^-$  ratio (0.1996) was lower than other coastal sites, this indicates that there was a significant enrichment of nitrates. To assess the relative contribution of nitrate and sulfate to the acidity, it was necessary to determine  $(\text{SO}_4^{2-})_{xs}/\text{H}^+$  (10.22) and  $\text{NO}_3^-/\text{H}^+$  (51.19) relative ratios. pH had an inverse correlation with  $\text{SO}_4^{2-}$  and  $\text{NO}_3^-$ , indicating that these ions contributed in a significant way to the acidity. See Fig. 2 and Fig. 3.

In spite of, it has been reported that sulfate ion contributes in a greater proportion to the acidity; in this case, nitrate contribution was greater than sulfate did. These results lead to the conclusion that there was an important influence of local sources to the nitrate levels in dry deposition.

#### *El Chico National Park:*

It can be observed in Table 3 that except  $\text{K}^+$ , most of the ions showed a great variability. Relative ionic abundance obtained was  $\text{NO}_3^- > \text{Ca}^{2+} > \text{Cl}^- > \text{Na}^+ > \text{NH}_4^+ > \text{Mg}^{2+} > \text{K}^+ > \text{SO}_4^{2-}$ .

This site is not a coastal site, therefore, it can be assumed that total sulfate content had an origin different from sea-salt, it is to say, total content was in excess (probably with an anthropogenic origin). Excess sulfate levels  $[(\text{SO}_4^{2-})_{xs}]$  found ( $6.42 \mu\text{Eq l}^{-1}$ ) are in agreement with background hemispheric levels reported by Galloway [29] for remote sites ( $10 \mu\text{Eq l}^{-1}$ ); it suggests that this site was not subject to long-range transport processes.

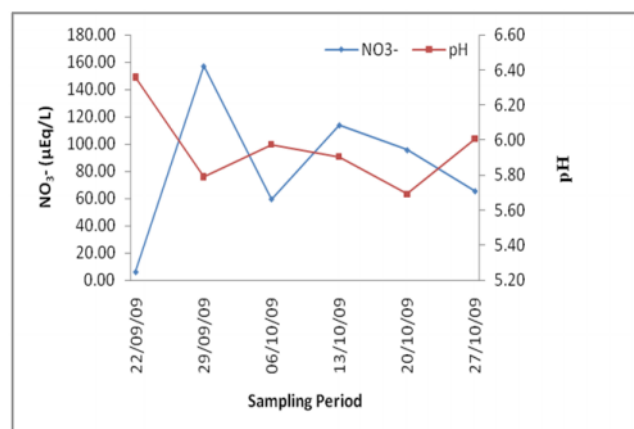


Fig. 2. Time trend of nitrate concentration ( $\text{NO}_3^-$ ) and pH in dry deposition at Los Petenes site.

Since, marine aerosol does not contribute to nitrate levels; it can be assumed that the total content of nitrate in dry deposition samples was in excess, it means that it had an anthropogenic source. Nitrate levels ( $110.11 \mu\text{Eq l}^{-1}$ ) exceeded background hemispheric values reported for remote sites ( $2.8 \mu\text{Eq l}^{-1}$ ) [29].

It was a great discovery, since we had considered El Chico as a control site. Considering the residence times for  $\text{SO}_2$  (13 days) and  $\text{NO}_2$  (1 day), it can be assumed that there was a local and temporal source (biomass burning occurring during all the

sampling period contributing in a significant way to nitrate levels).

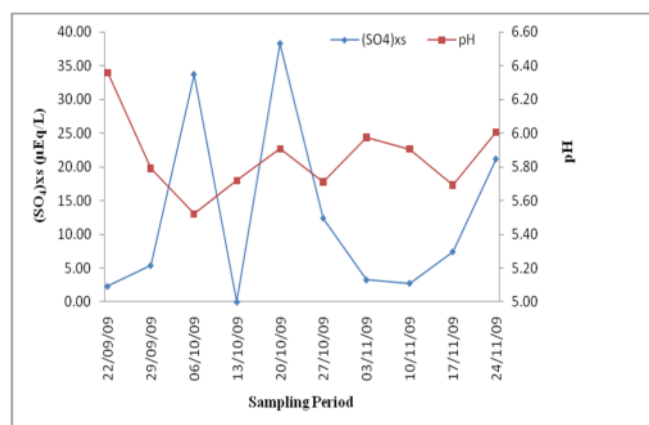


Fig. 3. Time trend of sulfate concentration (SO<sub>4</sub><sup>2-</sup>) and pH in dry deposition at Los Petenes site.

Even in areas considered as free of pollution, pH value for natural rainwater is of 5.6 due to presence of CO<sub>2</sub> that dissolved in water produce carbonic acid, the main responsible of this value. When pH value range from 5 to 5.6, it can be considered that the studied site has enough buffer capacity, but, when pH value is below of 5.0, there is an evident anthropogenic source contributing to the acidity.

**Table 3.** Ionic concentrations (mg l<sup>-1</sup>) for dry deposition in El Chico National Park during 2009.

Ionic specie	N	Mean	Minimum	Maximum
Ca <sup>2+</sup>	16	2.39 ± 1.64	0.61	5.76
K <sup>+</sup>	16	0.19 ± 0.05	0.13	0.31
Mg <sup>2+</sup>	16	0.60 ± 0.64	0.07	1.94
Na <sup>+</sup>	16	1.26 ± 0.94	0.29	3.38
NH <sub>4</sub> <sup>+</sup>	16	0.62 ± 0.28	0.19	1.34
NO <sub>3</sub> <sup>-</sup>	16	6.83 ± 3.1	0.41	9.83
Cl <sup>-</sup>	16	1.69 ± 1.07	0.14	3.68
SO <sub>4</sub> <sup>-</sup>	16	0.32 ± 0.17	0.12	0.85

N: Number of samples

Regarding this fact, we found that in El Chico, dry deposition samples showed pH values ranging from 4.39 to 7.47, with an average value of 6.05. 50% of the total samples showed pH values below 5.0, and nitrate levels were too high, even greater than sulfate levels, suggesting a significant enrichment of nitrates in this site. It demonstrates that, in spite of average pH value is above 5.6, El Chico National Park can

be potentially impacted by the high deposition rate of N. It can be a serious environmental problem, considering that due to their nature, sacred fir forests (dominant vegetation in this site) are considered as fragile ecosystems.

In addition, it has been documented that pH value due to their non conservative character is not a good tracer of potentially ecological effects related to acid deposition, therefore, conservation efforts must be focused to quantify of critical loads of N and S, and promote new regulations on critical loads in natural protected areas.

From the Pearson correlation matrix, it can be observed that K<sup>+</sup> correlated with Ca<sup>2+</sup> (r = 0.62 at p < 0.001). It suggests that this ion pair had a common source, in this case, particles from the crustal.

From correlation analysis, we could not distinguish a main cation that played an important role in the neutralization process.

In addition, correlation between sulfate and nitrate was negligible, suggesting that these anions had their origin in different sources. Since sulfate levels were in according to the hemispheric background levels reported for remote sites, we can conclude that there were not local anthropogenic sources contributing to this ion levels.

On the other hand, nitrate levels were too high. Considering NO<sub>2</sub> residence time in the atmosphere, we can infer that nitrate levels had their origin in a local source, probably forest fires occurring not only as a result of the mid-summer drought, also during all the sampling period.

(SO<sub>4</sub><sup>2-</sup>)<sub>xs</sub>/NO<sub>3</sub><sup>-</sup> ratio (0.05) was lower than other sites, this indicates that there was a significant enrichment of nitrates.

To assess the relative contribution of nitrate and sulfate to the acidity, it was necessary to determine (SO<sub>4</sub><sup>2-</sup>)<sub>xs</sub>/H<sup>+</sup> and NO<sub>3</sub><sup>-</sup>/H<sup>+</sup> relative ratios. In spite of, it has been reported that sulfate ion contributes in a greater proportion to the acidity; in this case, nitrate contribution was greater than sulfate did. pH had an inverse correlation with NO<sub>3</sub><sup>-</sup>, indicating that this ion contributed in a significant way to the acidity. See fig. 4.

These results lead to the conclusion that there was an important influence of local sources to the nitrate levels in dry deposition.

Clearly, there was a local source influenced strongly on nitrate levels, probably forest fires. The influence of forest fires on nitrate levels has been documented in other works [32-33], and low pH values have been reported as a result of biomass burning. Forest researches carried out at El Chico [34-35] report carbonized vegetal fragments and mineral whose formation requires high temperatures, suggesting that forest fires are frequently part of the natural dynamic of this park. In addition, these works conclude that forest fires of canopy type are considered as benefic to the natural reforestation process of sacred fir forest.

Therefore, may be, controlled forest fires be used as a forestry management strategy to improve the natural reforestation process in this site.

It could explain the too high nitrate levels found in dry deposition samples in El Chico National Park.

Potential ecological effects of acid deposition in tropical environments remain uncertain and available data about critical loads area scarce. In addition, deposition patterns and ecosystems responses in tropical countries may be different from those reported for mid-latitudes and temperate regions. In table 4 are shown critical loads values reported for USA and Europe.

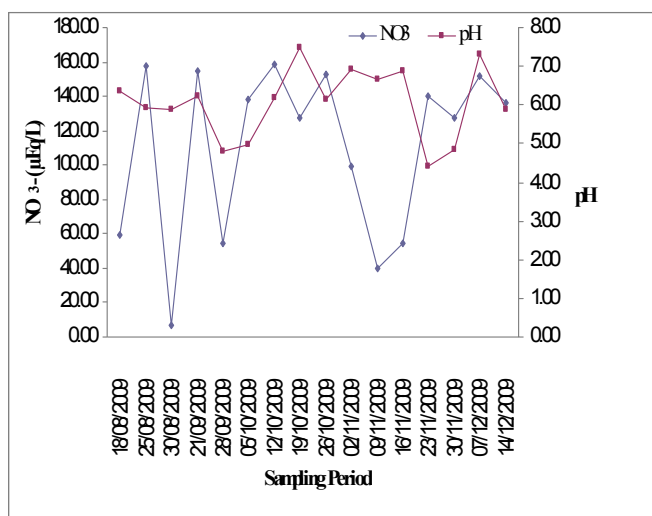


Fig. 4. Time trend of nitrate concentration (NO<sub>3</sub><sup>-</sup>) and pH in dry deposition at El Chico site.

In Mexico, only little data on deposition inputs of N and S in Mexican forests have been published. In table 5 are shown critical loads values for different ecosystems in Mexico.

Comparing the total N deposition fluxes estimated for El Chico National Park (11.22 Kg ha<sup>-1</sup> yr<sup>-1</sup>) with critical loads reported for Pine forests, our results indicate that the critical loads for Nitrogen has been exceeded. On the other hand, comparison of the total Sulphur fluxes for El Chico National Park (2.54 Kg ha<sup>-1</sup> yr<sup>-1</sup>) with the critical loads for forests soils in Europe, USA and other places in Mexico, our results suggest that the critical load for S has not been exceeded and was comparable to the results reported for Central Veracruz and Zoquiapan.

On the other hand, in Los Petenes Biosphere Reserve, N input (11.99 Kg ha<sup>-1</sup> yr<sup>-1</sup>) is slightly above the critical loads, whereas S input (1.4 Kg ha<sup>-1</sup> yr<sup>-1</sup>) did not exceed the critical values.

Our results suggest that these critical loads can increase in a short time period if strategic measures are not taken. In addition, these results are sub estimated considering that we are not reporting data for wet deposition, since these sites are natural reserves, it can constitute a serious threat to flora and fauna species that live in these ecosystems.

Table 4. Critical loads (Kg ha<sup>-1</sup> yr<sup>-1</sup>) for N and S, reported for different ecosystems in USA and Europe.

Critical load for N	Critical load for S	Type of ecosystem	Author
10	-	Upland grasslands in the United Kingdom	Jones [32]
8	-	Budburst <i>Calluna</i>	Power <i>et al.</i> [33]
5	-	Alpine ecosystems	Hiltbrunner [34]
3-6	-	Temperate lands in USA	Fenn <i>et al.</i> [35]
4-7	-	New Mexico and Arizona	Geiser <i>et al.</i> [36]
3-8	-	N-impacted ecosystems in California, USA	Fenn <i>et al.</i> [37]
12-16	17-21	Germany	Dieter and Gouger [38]
	100	Czech Republic	
	20-40	Central Europe	
5-10	2-5	Forest in humid climates	Grennfelt and Nilsson [39]
0.5	1-3	Remote tropical areas	Galloway <i>et al.</i> [40]

Table 5. Critical loads (Kg ha<sup>-1</sup> yr<sup>-1</sup>) for N and S, reported for different ecosystems in Mexico.

Critical load for N	Critical load for S	Type of ecosystem	Author
3.6	17	Mountain forest in Central Veracruz	Ponette <i>et al.</i> [41]
2	12	Coffee agro forests in Central Veracruz	
3	8	Cleared areas in Central Veracruz	
> 15	9-20	Forests in Mexico City Basin	Fenn <i>et al.</i> [42]
5.5	8.8	Pine forests at Zoquiapan, Mexico State	Pérez <i>et al.</i> [43]

#### IV. CONCLUSION

The study of dry deposition at natural sites probably impacted within a region can provide a complete picture of the seasonal evolution of atmospheric pollutants.

Data obtained in this study are the first measurements of dry deposition in these sites, this let us compare in a future with critical loads reported for natural sites in Mexico. The following conclusions can be made from the found results for both studied sites:

##### *Los Petenes Biosphere Reserve:*

For Los Petenes site, alkaline particles from the soil played an important role in the neutralization process of the acidity derived from high levels of nitrate and sulfate.

From the prevailing winds, two local sources were identified: a power plant (Lerma) located near to the sampling site and important episodes of biomass burning in the vicinity of this study site.

Taking in account pH values measured, it can be inferred that probably, there is not a serious environmental impact in this site.

Since pH is not a conservative tracer of the ecological effects of acid deposition, to get a better diagnosis of the buffer capacity of this site, it is necessary to carry out more studies focused on the estimation of dry deposition fluxes and compare with critical loads reported in other eco-regions of Mexico.

##### *El Chico National Park:*

For El Chico site, contrary to nitrate, data obtained revealed that this site is not subject to long-range transport processes that contribute in a significant way to sulfate levels. Therefore, we can conclude that El Chico was only influenced by local sources, in this case, forest fires occurring frequently in this site.

In spite of mean pH value found was above 5.6, the high nitrate levels suggest that this site can be seriously threatened by high deposition rate of N. Therefore, we propose that in future works developed in this site, critical loads for S and in especially for N be estimated.

Since only local sources contributed to the N deposition in this site, we conclude that power plant located at Tula, an urban and industrialized site near to El Chico, did not contributed to trace elements dry deposition in El Chico.

It is necessary to make an accurate diagnosis of these sites, considering that pH value is not a conservative tracer of the potentially ecological effects related to acid deposition.

Therefore, we propose that in future works, critical loads for N and S must be estimated in both sites.

The critical loads found in this study have the potential to be increased in a short time, therefore, considering the ecological

importance of these sites, it must be applied local strategic environmental policies focused to protect the wildfire life in these reserves.

#### ACKNOWLEDGMENT

Authors thank to the Mexican Council of Science and Technology for the financial support to carry out this project (Semarnat-Conacyt Project Number 107948) and for the facilities and support supplied for the Autonomous University of Carmen City (UNACAR) .

#### REFERENCES

- [1] E.A. Kanellopoulou. "Determination of heavy metals in wet deposition of Athens, *Global NEST The Int. J.* Vol. 3, pp. 45-50, 2001.
- [2] M. Zheng, Z. Guo, M. Fang, K.A. Rahn and D.R. Kester. "Dry and wet deposition of elements in Hong Kong", *Marine Chemistry* Vol. 97, pp. 124-139, 2005.
- [3] D. Migliavacca, E.C. Teixeira, M. Pires, and J. Fachel. "Study of chemical elements in atmospheric precipitation in south Brazil", *Atmospheric Environment* Vol. 38, pp. 1641-1656, 2004.
- [4] A. Avila, and A. Rodrigo. "Trace metal fluxes in bulk deposition, throughfall and stemflow at two evergreen oak stands in NE Spain subject to different exposure to the industrial environment", *Atmospheric Environment* Vol. 38, pp. 171-180, in "Atmospheric Chemistry and Physics", Ed- Interscience, United States of America, ISBN 0-471-17815-2, 2004.
- [5] P. Brimblecombe. "Acid rain 2000+1000", *Water air and soil Pollut.* Vol. 130, pp.25-30, 2004.
- [6] A.G. Ponette, K.C. Weathers, and L.M. Curran. "Tropical land-cover change alters biogeochemical inputs to ecosystems in a Mexican montane landscape", *Ecological Applications* Vol. 20, pp. 1820-1837, 2010.
- [7] A.P. Báez, R.D. Belmont, and H.G. Padilla. "Chemical composition of precipitation at two sampling sites in Mexico: a 7-year study", *Atmospheric Environment* Vol. 31, pp. 915-925, 1997.
- [8] H.A. Bravo, M.I.R. Saavedra, P.A. Sánchez, R.J. Torres, and L.M.M. Granada. "Chemical composition of precipitation in a Mexican Maya Region", *Atmospheric Environment* Vol. 34, pp. 1197-1204, 2000.
- [9] H.G. Padilla, R. Belmont, M.B. Torres, and A.P. Báez. "Hurricanes Pauline and Nora rainwater chemical composition", *Canadian Journal of Earth Sciences* Vol. 37, pp. 569-578, 2000.
- [10] R.M.B. Cerón, H.G. Padilla, R.D. Belmont, M.C.B. Torres, R.M. García, and A.P. Báez. "Rainwater chemical composition at the end of the mid-summer drought in the Caribbean shore of the Yucatan Peninsula", *Atmospheric Environment* Vol. 36, pp. 2367-2374, 2002.
- [11] H. Bravo, R. Soto, R. Sosa, P. Sánchez, A.L. Alarcón, J. Kahl, and J. Ruiz. "Effects of acid rain on building material of the El Tajin archaeological zone in Veracruz, Mexico", *Environmental Pollution* Vol. 144, pp. 655-660, 2006.
- [12] R.M. Cerón, J.G. Cerón, J.J. Guerra, E. Núñez, and M. Muriel. "Contribution of anthropogenic and natural sources to the levels of trace elements in two coastal sites in Campeche, Mexico", *Int. J. Sus. Dev. Plann.* Vol. 5, pp. 282-298, 2010.
- [13] M. Zuk, V. Garibay, R. Iniestra, M. López, L. Rojas, and L. Laguna. "Introduction to the impact assessment of power plants in Mexico". National Institute of Ecology. Mexico. ISBN 968-817-804-7, 2006.
- [14] A. Bytnerowicz, and M.E. Fenn. "Nitrogen deposition in California forests: a review", *Environmental Pollution* Vol. 92, pp. 127-146, 1996.
- [15] K.W.T. Goulding, N.J. Bailey, N.J. Bardbury, P. Hargreaves, M. Howe, M., D.V. Murphy, P.R. Poulton, and T.W. Willison. "Nitrogen deposition and its contribution to nitrogen cycling and associated soil processes", *New Phytologist* Vol. 139, pp. 49-58, 1998.
- [16] M.E. Fenn, M.A. Poth, J.D. Aber, J.S. Baron, B.T. Bormann, D.W. Johnson, A.D. Lemly, S.G. McNulty, D.E. Ryan, and R. Stottleyer.

- “Nitrogen excess in North American ecosystems: predisposing factors, ecosystem responses and management strategies”, *Ecological Applications* Vol. 8, pp. 706-733, 1998.
- [17] R. Balestrini, L. Galli, and G. Tartari. “Wet and dry atmospheric deposition at pre-alpine and alpine sites in Northern Italy”, *Atmospheric Environment* Vol. 34, pp. 1455-1470, 2000.
- [18] G.M. Lovett. “Atmospheric deposition of nutrients and pollutants in North America: an ecological perspective”, *Ecological Applications* Vol. 4, pp. 629-650, 1994.
- [19] R. Alonso, A. Bytnerowicz, J.L. Yee, and W.I. Boarman. “Atmospheric dry deposition in the vicinity of the Salton Sea, California-II: Measurement and effects of an enhanced evaporation system”, *Atmospheric Environment* Vol. 39, pp. 4681-4689, 2005.
- [20] EPA 150.1 Method. *Determination of pH in water*. USA Environmental Protection Agency, 1982.
- [21] EPA 120.1 Method. *Determination of specific conductivity for deposition samples*. USA Environmental Protection Agency, 1982.
- [22] EPA 300.0 Method. *Determination of inorganic anions by Ion Chromatography*. USA Environmental Protection Agency, 1993.
- [23] EPA 7770 Method. *Determination of sodium by atomic absorption spectroscopy*. USA Environmental Protection Agency, 1986.
- [24] EPA 7610 Method. *Determination of potassium by atomic absorption spectroscopy*. USA Environmental Protection Agency, 1986.
- [25] EPA 7140 Method. *Determination of calcium by atomic absorption spectroscopy*. USA Environmental Protection Agency, 1986.
- [26] EPA 7450 Method. *Determination of magnesium by atomic absorption spectroscopy*. USA Environmental Protection Agency, 1986.
- [27] EPA 3010A Method. *Acid Digestion of Aqueous Samples and Extracts for Total Metals for Analysis by FLAA or ICP Spectroscopy*. USA Environmental Protection Agency, 1992.
- [28] APHA-AWWA-WPCF. *Standard Methods for the Examination of Water and Wastewater*. 17 th Edition, 1989.
- [29] J.N. Galloway, G.E. Likens, W.C. Keene, and J.M. Miller. “The Composition of Precipitation in Remote areas of the world”, *Journal of Geophysical Research*. Vol. 87, pp. 8771-8776, 1982.
- [30] R.J. Charlson and H. Rodhe H. “Factors controlling the acidity of natural rainwater”, *Nature* Vol. 295, pp. 683-685, 1981.
- [31] R.M. Cerón, J.G. Cerón, J.J. Guerra, E. Núñez, and M. Muriel. “Contribution of anthropogenic and natural sources to the levels of trace elements in two coastal sites en Campeche, Mexico”, *Int. J. Sus. Dev. Plann.* Vol. 5, pp. 282-298, 2010.
- [32] M.L.M. Jones. “Nitrogen deposition in Upland grasslands: Critical loads, management and recovery”. Thesis. University of Sheffield, U.K., 2005.
- [33] S.A. Power, E.R. Green, C.G. Barker, J.N.B. Bell, and M.R. Ashmoore. “Ecosystem recovery: Heath land response to a reduction in Nitrogen deposition”, *Global change Biology* Vol. 12, Issue 7, pp. 1241-1252, 2006.
- [34] E. Hiltbrunner. “How responsive are alpine plants and communities to increased Nitrogen deposition”. C.E.E. Workshop on Modeling and Mapping. 21-23 April, 2008. Berne.
- [35] M.E. Fenn, R. Haeuber, G.S. Tomesen, J.S. Baron, S. Grossman-Clarke, D. Hope, D.A. Jaffe, S. Copeland, L. Geiser, H.M. Rueth, and J.O. Sickman. “Nitrogen emissions, deposition and monitoring in the Western United States”, *Bioscience* Vol 53, pp. 391-403, 2003.
- [36] L.H. Geiser, S.E. Jovan, D.A. Glavich, and M. Porter. “Lichen-based critical loads for atmospheric Nitrogen deposition in Western Oregon and Washington forests, USA”, *Environmental Pollution* Vol. 158, pp. 2412-2421, 2010.
- [37] M.E. Fenn, E.B. Allen, S.B. Weisse, S. Jovan, L.H. Geiser, G.S. Tomesen, R.F. Johnson, L.E. Rao, B.S. Gimeno, F. Yuan, T. Meixner and A. Bytnerowicz. “Review: Nitrogen critical loads and management alternatives for N-impacted ecosystems in California”, *Journal of Environmental Management* Vol. 91, pp- 2404-2423, 2010.
- [38] H. Dieter and T. Gouger. “Critical load, dynamic modeling and impact assessment in Europe”, *C.E.E. Status Report*, 2000.
- [39] P. Grennfelt and J. Nilsson. “Critical loads for Sulphur and Nitrogen”. Report from a Workshop held at Skokloster, Sweden. March 19-24, 1988.
- [40] J.N. Galloway, A.R. Townsed, J.W. Erisman, M. Bekunda, Z.C. Cai, J.R. Freney, L.A. Martinelli, S.P. Seitzinger and M.A. Sutton.
- “Transformation of the Nitrogen cycle: Recent trends, questions and potential solutions”, *Science* Vol. 320, pp. 889-892, 2008.
- [41] A.G. Ponette, K.C. Weathers, and L.M. Currant. “Tropical land-cover changes alters biogeochemical inputs to ecosystems in a Mexican montane landscape”, *Ecological applications* Vol. 20, pp. 1820-1837, 2010.
- [42] M.E. Fenn, L.I. de Bauer, A. Quevedo, and C. Rodriguez. “Nitrogen and sulphur deposition and forest nutrient status in the Valley of Mexico”, *Water, Air and Soil Pollution* Vol. 113, pp. 155-174, 1999.
- [43] M. Perez, M.E. Fenn, V.M. Cetina, and A. Aldrete. “The effects of canopy cover on through fall and soil chemistry in two forest sites in the Mexico City Air Basin”, *Atmósfera* Vol. 21, pp. 83-100, 2008.

**Cerón-Bretón J.G.** Is a professor-researcher in the Chemistry Faculty of the Autonomous University of Carmen City since 2006, has a PhD degree in Earth Sciences from the Autonomous National University of México (UNAM) in 2005. She was carried out several projects on air pollution and its effects on ecosystems and she is author of numerous papers published in refereed journals dealing with the environment, air pollution and earth sciences areas. Dr. Cerón is a membership of the National System of Researchers of México named as Researcher level I since 2007 and she is the leader of the Academic Group in Chemical Engineering of the Chemistry Faculty in UNACAR.

**Cerón-Bretón R.M.** Is a professor-researcher in the Chemistry Faculty of the Autonomous University of Carmen City since 2002, has a PhD degree in Earth Sciences from the Autonomous National University of México (UNAM) in 2004. She was carried out several projects on air pollution and its effects on ecosystems and she is author of numerous papers published in refereed journals dealing with the environment, air pollution and earth sciences areas. Dr. Cerón is a membership of the National System of Researchers of México named as Researcher level I since 2006.

**Cárdenas-González, B.** Is the Director of the Experimental Research on Atmospheric Pollution of the National Center of Research and Environmental Training of the Mexican Institute of Ecology (CENICA-INE). Dr. Cárdenas is a membership of the National System of Researchers of Mexico named as Researcher level I.

**Ortíz-Alvarez, J.A.** Is the Chief of the Department of studies on transport and impact of atmospheric pollutants of the National Center of Research and Environmental Training of the Mexican Institute of Ecology (CENICA-INE). He has participated in several projects on atmospheric pollution.

**Cruz-Chávez, E.** Is a researcher of the Environmental Geology Laboratory of the Research Center on Earth Science and Materials of the Autonomous University of Hidalgo State. Dr. Cruz has carried out several studies of environmental assessment and projects focused on air pollution.

**Díaz-Morales, B.** Is a Master Degree student of the Chemical Engineering Post grade of the Chemistry Faculty of the Autonomous University of Carmen City. Her work is focused in the study of dry and wet deposition in different sites along Mexico.

**Carballo-Pat, C.G.** Is a Master Degree student of the Chemical Engineering Post grade of the Chemistry Faculty of the Autonomous University of Carmen City. Her work is focused in the study of dry and wet deposition in different sites along Mexico.

**Pérez-López, T.** Is a professor-researcher of the Research Center on Corrosion of the Autonomous University of Campeche. Dr. Pérez has carried out many projects focused on the effects of atmospheric pollutants and atmospheric corrosion on materials and cultural heritage.

**Reyes-Trujque, J.** Is a professor-researcher and is the Chief of the Laboratory of Conservation of the Cultural Heritage of the Research Center on Corrosion of the Autonomous University of Campeche. Dr. Reyes has carried out many projects focused on the effects of atmospheric pollutants on materials and cultural heritage.

**Muriel-García, M.** Is a Project Manager of the Environmental Sciences Area in the Mexican Petroleum Institute. Marine Zone, in Campeche, México. Dr. Muriel has an extensive experience on atmospheric pollution studies an environmental impact assessment studies.

**Guerra-Santos, J. J.** Is a researcher-professor of the Research Center on Environmental Sciences of the Autonomous University of Carmen City. Dr. Guerra has carried out several projects focused on the effects of atmospheric pollution on tropical vegetation species.