

Evaluation of Dry Atmospheric Deposition in Two Sites in the Vicinity of Fuel Oil-Fired Power Plants in Mexico

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1. Introduction

Airborne pollutants are involved in a complex cycle in the atmosphere that begins with their release and finishes with their removal and deposition on terrestrial and aquatic ecosystems. Some pollutants as dust or crustal particles remain without changes during this cycle; however, gaseous components undergo physical and chemical changes. This is the case of combustion gases such as SO₂ and NO_x. It is well known that atmospheric particles and gases including those pollutants emitted from natural (biogenic, volcanic activity, marine aerosol, and so on) and anthropogenic sources (vehicular and industrial emissions) are removed by wet and dry deposition processes. The phenomenon of acidic atmospheric deposition has been largely studied in different sites and locations around the world during the last years (Tsitouridou & Anatolaki, 2007), and it has been found that episodes of acid precipitation are directly related to industrial emissions, this is the case of coal and fuel burning power plants (Flues et al., 2002).

In Mexico, 72 % of generated energy comes from burning of fossil fuels ("combustoleo"¹, natural gas and coal). Particularly, in the last decade, "combustoleo" has been the fuel more used in the main productive sectors. Currently, 66.8% of energy is generated from power plants burning "combustoleo", resulting in fly ash emission, and large amounts of gases considered as acid precursors (such as SO₂ and NO_x) that contribute to the acid precipitation in the vicinity of the plants (Zuk et al., 2006). Considering that the residence times in the atmosphere for both acid precursors are different, their deposition rates are different too. Thus,

¹ It is a blend of residua and gas oil cutter stock and meets the viscosity requirements of ASTM D396. It is commonly used in power plants in large steam boilers, drying kilns and ovens.

NO_x are removed in an efficient way by wet deposition, being deposited around the emission source. On the other hand, since SO₂ has a residence time of 13 days, undergoes long-range transport, being deposited in distant places from the emission point. For this reason NO_x are referred as local pollutants whereas SO₂ is considered as a regional pollutant.

Qualitative and quantitative assessment of atmospheric deposition in regions probably impacted by anthropogenic sources is essential for understanding regional variations, to determine if critical loads are exceeded, to assess time-trends in a long-term, and to relate sources contributing to the acidity with local and regional meteorology. Long-term changes in air quality and atmospheric deposition are not obvious, in some cases due to daily and seasonal variations in parameters such as wind, temperature, precipitation and atmospheric circulation patterns which influence on dispersion, transport and deposition of pollutants. For this reason, it is important to measure wet and dry deposition fluxes at various sites all over the country during long-time periods to provide an outline of the main chemical characteristics of the deposition and to assess their trends along time. Concerning monitoring networks, air quality data are useful to determine if the current regulations are effective in the improvement of the air quality, or if it is necessary to promulgate new ones.

In 2009, National Institute of Ecology [INE] sponsored the design and operation (during two years) in a preliminary phase of the Mexican Atmospheric Deposition Network, integrated by four stations (considering both polluted and natural sites). In addition, in 2010, the Mexican Environmental Agency [SEMARNAT] supported a research project focused on the study of atmospheric deposition in five sites located in the surroundings of power plants burning "combustoleo". The aim of this work was to assess the chemical composition of dry deposition in two of these sites: Los Petenes and Tula de Allende, both sites are located in the vicinity of power plants. The first one is a Ramsar site and a Biosphere Reserve located in Yucatan Peninsula at the southeast of the country, and the second one is a polluted site located in an important industrial region of Central Mexico, in whose vicinity there are important historic monuments.

2. Sampling sites description

Dry deposition samples were collected during 2009 and 2010 at two sampling sites: Los Petenes Biosphere Reserve, Campeche and Tula de Allende, Hidalgo.

Sites	Classification area	Altitude (m asl)	Latitude	Longitude
Los Petenes, Campeche	Ramsar Site Biosphere Reserve	4	20° 51' 30" N	90° 45' 15" W
Tula de Allende, Hidalgo	Urban and Industrial, with the presence of historic monuments in the vicinity	2020	20° 05' 08" N	99° 33' 05" W

Table 1. Main features of the sampling sites.

Sampling sites were selected considering proper conditions of accessibility and safety. The specific location and the main characteristics of these sampling sites are shown in Figure 1 and Table 1.



Fig. 1. Location of the sampling sites: Los Petenes Biosphere Reserve and Tula de Allende.

2.1 Los Petenes

Los Petenes site is a natural protected area in a large and narrow coastline. This area covers an extension of 282,857 ha, and it is characterized by the presence of complexes habitats similar to islands with availability of sweet water during all year, called "Petenes" (Figure 2). These are individual areas of tropical forest that reach a diameter ranging from a few meters to kilometers surrounded by wetlands, with a great diversity of flora and fauna. These habitats are only found in Cuba, Florida and Mexico, generally having a "Cenote" in its central part, originating vegetation that flourishes in rings of similar centers (Figure 2). Los Petenes is located within an eco-region that includes Ria Celestún Biosphere Reserve and the Natural Protected Area El Palmar in Yucatan State. Los Petenes is a Ramsar Site and constitutes a representative bio-geographic area of an ecosystem not significantly perturbed, in which representative species of national biodiversity live, including endemic, threatened and in risk of extinction species.

The climate is warm sub-humid (A_w) with summer rains with the presence of the mid-summer drought, and forest fires occurring frequently. Annual rainfall ranges from 729 to 1049 mm and temperature ranges from 26.1 and 28.8 °C. Los Petenes are characterized by four types of soils: a) Sandy soils at the coast (calcareous regosols), b) holomorphic soils in marshes (histosols), c) shallow and rocky soils (rendzina type) and clay soils (gleysols). Specific sampling site was located within the Center for Conservation of Wildfire Life of Autonomous

University of Campeche at 15 km from Campeche City and at 10 km from the fuel oil-fired power plant “Lerma”. Characteristics and capacity of this power plant are shown in Table 2.



Fig. 2. Panoramic view of Los Petenes Biosphere Reserve.

Power Plant, Location	Units	Operation starting date	Installed effective capacity (MW)
Lerma; Campeche, Mexico	4 (combined cycle)	September 9, 1976	150
Francisco Pérez Ríos; Tula, Hidalgo	9 (steam and combined cycle technologies)	June 30, 1991	2000

Source: Zuk et al., 2006.

Table 2. Main characteristics of the power plants located in the vicinity of the sampling sites considered in this study.

2.2 Tula de Allende

The second study site is Tula de Allende, Hidalgo located at the Central Region of Mexico, at 20°03' N and 99° 20' W with an altitude of 2020 m asl, at 70 km from Mexico City and 3 km from the fuel oil-fired power plant “Francisco Pérez Ríos” located along the Tula-Vito-Apaxco industrial complex. Due to large volumes of atmospheric pollutants generated by the Tula-Vito-Apaxco corridor, this region has been classified as a critical zone by the Mexican environmental authorities. Industries located in this area such as an oil refinery, a plant energy (which is one of biggest power plants in Latin America), and two important cement plants, contribute to the development of the region (Figure 3).

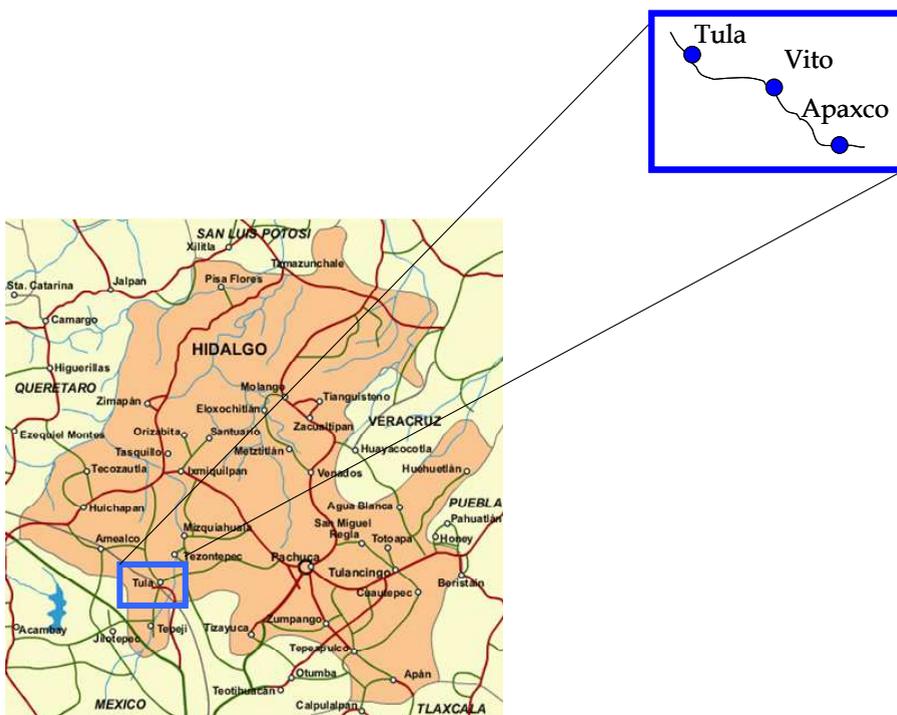


Fig. 3. Location of the Tula-Vito-Apaxco Industrial Complex in the vicinity of Tula de Allende.

According to the latest information from the environmental authorities, 323, 000 tons per year of SO₂ and 44, 000 tons per year of NO_x are released in this region. The main sources are the “Miguel Hidalgo” Oil Refinery and the “Francisco Pérez Ríos” Power Plant. “Miguel Hidalgo” Refinery processes 296,000 barrels per day of crude oil, representing 20% of the total refining capacity in the country. Other industries such as cement plants, open-sky mines and agricultural activities are also responsible of emission of important quantities of particulate matter. Therefore, the coexistence in the area of these industries could produce secondary compounds that can be potentially dangerous and risky for public health, ecosystems, and historic monuments. Nearby to this site, the ruins of the ancient capital city

of Toltecs, also known as “Tula” or as “Tollan”, are located. This site is characterized by a semi-arid climate (BSh) with an annual average rainfall of 600 mm, and an average temperature ranging between 16 and 17°C.

3. Experimental

3.1 Sampling

Dry deposition samples were collected on a weekly basis for a period of two years (from August 2009 to December 2010). Procedures to collect wet deposition are available anywhere since several years (Galloway & Likens, 1976), nevertheless, standard procedures to collect dry deposition are not available. Quantifying dry atmospheric input to natural surfaces is a difficult task due to the complex chemical processes involved (Balestrini et al., 2000). However, investigations using plastic materials, Teflon® and glass surfaces to collect dry deposition have demonstrated the importance of the physical, chemical and geometrical features of the surrogate surface in selecting the depositing material (Dasch, 1985). In this study, dry deposition was assessed using a surrogate surface according to the methodology used by Alonso et al (2005). Sampling was performed using automated wet-dry deposition collectors. Samplers were equipped with two polyethylene buckets and a lid controlled by a humid sensor, which moves depending on the beginning and the end of the rain event. Three nylon filters (Nylasorb, Pall Corporation, Gelman Lab, Michigan, USA; 47 mm diameter, 1 µm pore-size) per site were used as surrogate surfaces. Filters were located on a support within the dry deposition bucket and exposed in horizontal position at about 1 m height above ground. Dry deposition fluxes were calculated based on surface area and time exposure.

3.2 Analysis

After exposition, filters were stored at -18 °C until analysis. Three nylon filters were extracted with 80 ml of deionized-distilled water for 15 min in an ultrasonic bath, the first one was used to determine cations, and the second filter was used to analyze anions. Ammonium, pH and conductivity were determined on extracted solution of the third filter. pH and conductivity measurements were obtained by using precision pH meter (TERMO ORION 290) and a conductivity meter (CL 135). All plastic ware and glassware used to prepare standard solutions, for digestion of samples and for chemical analysis were rigorously washed, brushed and rinsed with distilled water. Plastic ware used for digestion of samples for analysis of cations by atomic absorption spectrophotometer was completely immersed during 24 h in a 20% ultrapure nitric acid bath (J.T. Baker, AA Grade), then rinsed several times with deionized water type I (Hycel) and sealed into double plastic bags. Before using, all material was again rinsed with deionized water. Extract from the first filter was digested in Teflon® closed flasks (Cole-Parmer) of 100 ml, using an autoclave equipment as energy source; subsequently, Na⁺, K⁺, Ca²⁺ and Mg²⁺ were analyzed using an atomic absorption spectrophotometer (Thermoscientific ICE 3300). Extract from the second filter was analyzed for SO₄²⁻, Cl⁻ and NO₃⁻ by ion chromatography (Agilent 1100) with 200 µl sample loop. Finally, extracted solution of the third filter was used to determine NH₄⁺ colorimetrically by means of a spectrophotometer UV (HACH DR 2800). Standard solutions

were prepared by dilution of certified standards (J.T. Baker). The detection limits were calculated as three times the standard deviation of six blank samples.

3.3 Quality assurance

Repeatability was guaranteed by 3 replicate measurements for each sample. Results showed a coefficient of variation < 5% for all elements measured. To verify whether major components had been measured in the analysis, two kinds of quality control were applied. If linear regression analysis between measured anions and cations gives a regression coefficient minor than 0.9, it indicates that anions and organic acids (formate and acetate) were probably present but were not measured.

On the other hand, if linear regression analysis between the measured and the calculated conductivity gives a regression coefficient major than 0.9, it indicates that practically the majority of the ions were analyzed. Balance cation-anion obtained for Tula de Allende showed differences less than 10%, therefore, we considered that all the major ions were analyzed. In addition, measured conductivities in Tula de Allende were in agreement with calculated conductivities. Figure 4 shows the quality of the analytical data in Tula de Allende.

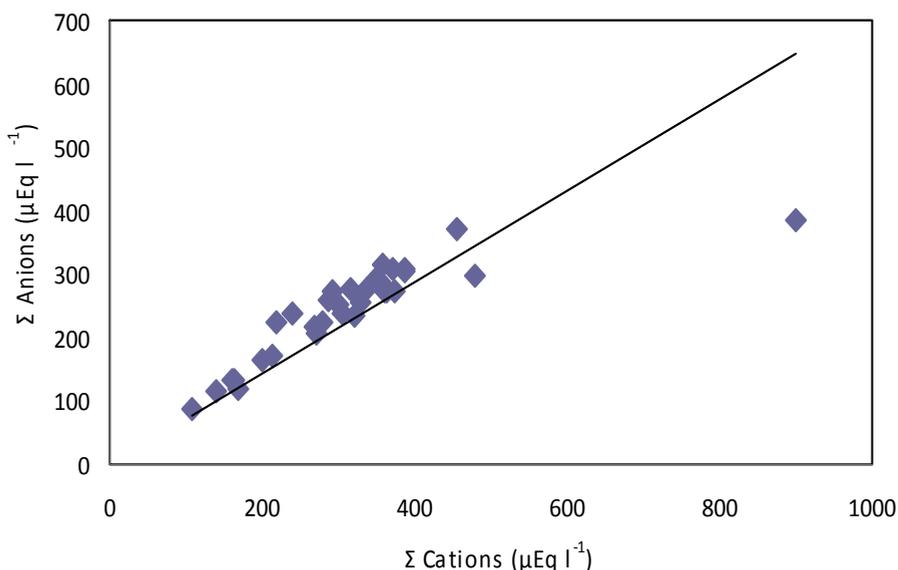


Fig. 4. Quality control (ionic balance) of chemical analysis for dry deposition samples collected at Tula de Allende.

In the case of Los Petenes Biosphere Reserve, conductivity differences were greater than 10%, and ionic balance suggests an ion deficit, probably due to the missing HCO_3^- and the presence of organic acids that are commonly found in natural sites. These short chain compounds were not specifically analyzed in this work.

3.4 Meteorological data

Two portable meteorological stations (Davies Inc, n.d.) that were operating during the whole study period in both sampling sites provided needed meteorological information. From these meteorological data, wind roses were constructed for each site by means of WRPLOT VIEW 6.5.2 (Lakes Environmental Inc, 2011).

To trace the origin of air masses for the whole study period, air-masses backward trajectories were calculated (48 h before) for both sampling sites by means of HYSPLIT-Hybrid Single Particle Lagrangian Integrated Trajectory Model (NOAA, n.d.). From calculated backward trajectories, it was observed that prevailing winds came from N-NE for Tula de Allende (Figures 5, 7) and from E for Los Petenes Biosphere Reserve (Figures 6,8).

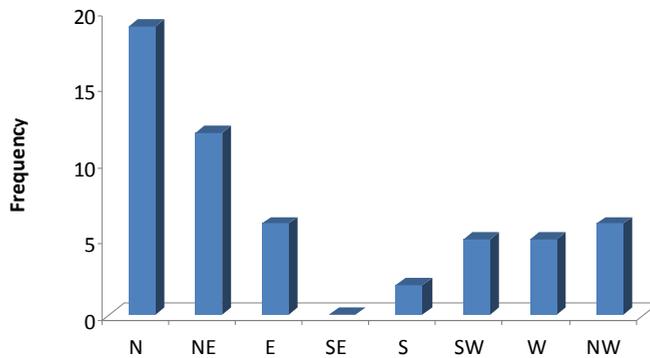


Fig. 5. Wind direction frequency distribution for Tula de Allende during the study period.

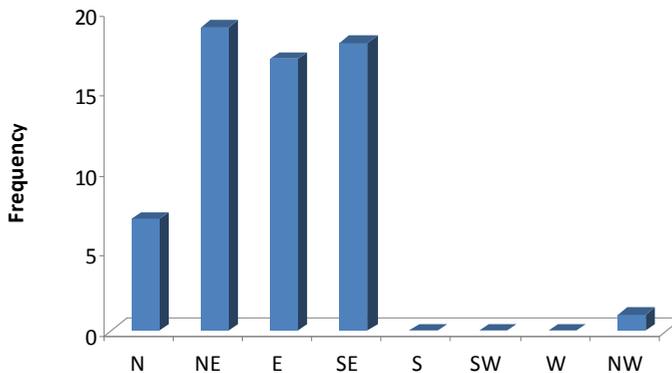


Fig. 6. Wind direction frequency distribution for Los Petenes Biosphere Reserve during the study period.

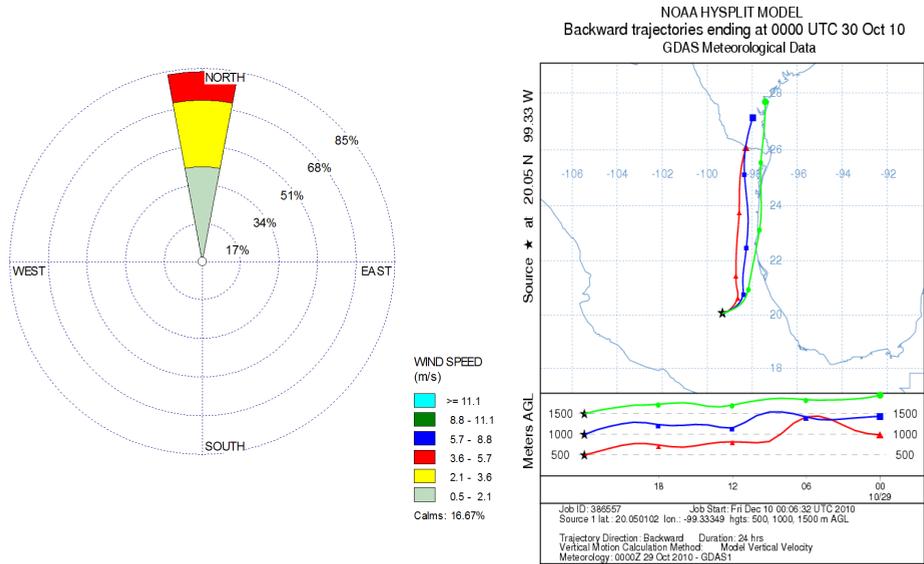


Fig. 7. Typical wind rose and backward air mass trajectory for Tula de Allende during the study period.

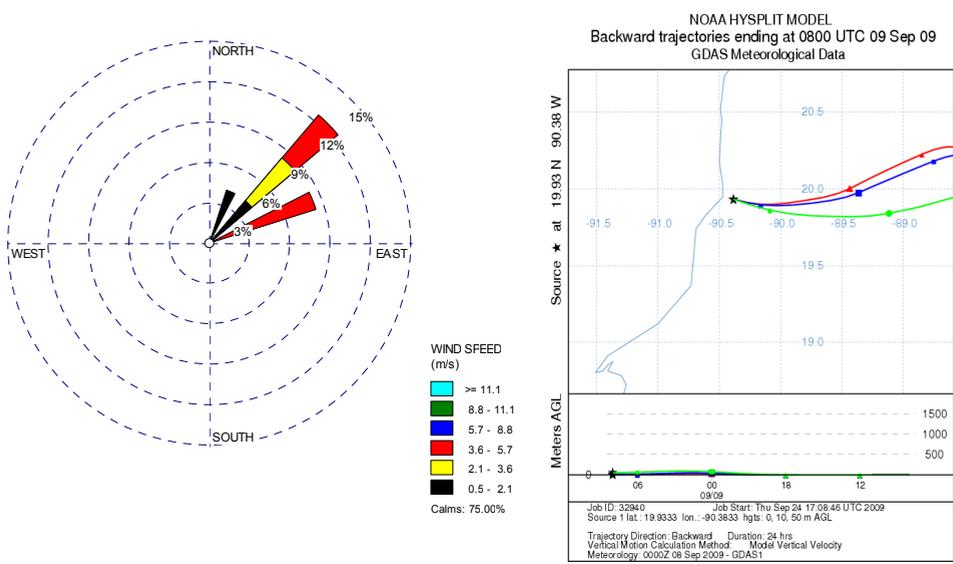


Fig. 8. Typical wind rose and backward air mass trajectory for Los Petenes Biosphere Reserve during the study period.

3.5 Statistical analysis

Pearson's correlation analysis was applied to test the relationship among the total trace element concentrations for each sampling site. ANOVA (GLM) was performed to test the differences between each element.

Means comparison was also performed using the average concentration values for trace elements as well as pH values. The calculations were carried out using SAS 8.0 software (SAS Inc, 1998).

4. Results and discussion

4.1 Chemical composition

Mean concentration values and ionic abundance of principal ions in dry deposition at Los Petenes Biosphere Reserve and Tula de Allende are shown in Table 3.

Site	pH	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
Los Petenes	5.9	2.00	5.79	70.51	16.15	132.75	60.49	14.61	90.63
		Ionic Abundance: NH ₄ ⁺ >NO ₃ ⁻ > Ca ²⁺ > Cl ⁻ > SO ₄ ²⁻ > Mg ²⁺ > K ⁺ >Na ⁺							
Tula de Allende	5.77	153.6	4.30	109.50	26.20	20.50	103.50	83.30	56.40
		Ionic Abundance: Na ⁺ > Ca ²⁺ > Cl ⁻ >SO ₄ ²⁻ > NO ₃ ⁻ > Mg ²⁺ >NH ₄ ⁺ > K ⁺							

Table 3. Mean values of pH and concentration ($\mu\text{Eq l}^{-1}$) of dry deposition samples.

4.1.1 Los Petenes Biosphere Reserve

Ammonium was the most abundant ion in Los Petenes, probably due to agriculture practices and swine husbandry in the zone and biological decay. On the other hand, nitrate was second more abundant ion, probably attributed to biomass burning activities and emissions from a local power plant. The influence of forest fires on nitrate and ammonium levels has been reported in other works (Hegg et al, 1988; Galbally & Gillel, 1988). It is well known that forest fires produce great amounts of nitrogen oxides, which are rapidly converted to nitric acid in the atmosphere. Since marine aerosol does not contribute to the nitrate levels, it can be assumed that total NO₃⁻ content present in samples was in excess, and that it had an anthropogenic origin. In spite of Los Petenes is an important natural protected area, it cannot be considered a remote site, for this reason, nitrate levels ($63.38 \mu\text{Eq l}^{-1}$) exceeded the background hemispheric levels reported for remote sites ($2.8 \mu\text{Eq l}^{-1}$).

On the other hand, since Los Petenes can be considered as a coastal site (8 km from the coastline), it was required to estimate marine aerosol contribution to the sulfate levels, in order to determine the marine and anthropogenic fractions (commonly known as sulfate excess, $[\text{SO}_4^{2-}]_{\text{XS}}$). Sulfate excess levels found ($12.66 \mu\text{Eq l}^{-1}$) were in agreement with the background hemispheric levels reported by Galloway et al (1982) for remote sites ($10 \mu\text{Eq l}^{-1}$), suggesting that there was a minimal influence of local sources that contributed to this ion; this is in agreement to the residence time for SO₂ in the atmosphere. However, $(\text{SO}_4^{2-})_{\text{XS}}/\text{NO}_3^-$ was lower than other coastal sites (0.031), indicating a significant enrichment of nitrates. Clearly, there was a local source influencing on nitrate levels, probably forest fires occurring as a result of the mid-summer drought, and emissions coming from the power

plant located at 10 km from the sampling site. Considering the residence times for SO₂ (13 days) and NO₂ (1 day), it can be assumed that Los Petenes site was not subjected to the input of long-range transported pollutants and probably only had the influence of local and temporal sources.

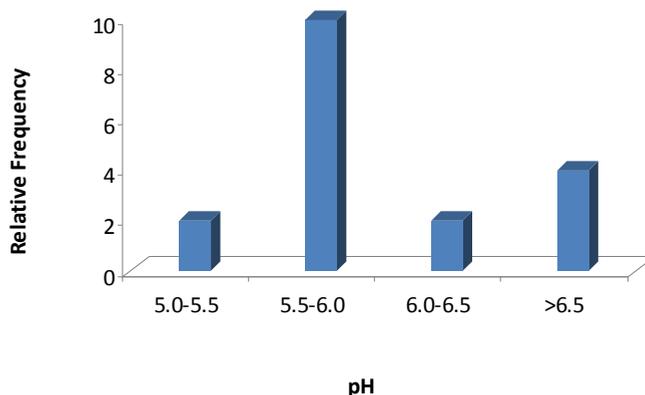


Fig. 9. pH frequency distribution for dry deposition samples collected at Los Petenes Biosphere Reserve.

pH values found in dry deposition samples showed a great variability, 22% of the samples were below of 5.6 (with a mean value of 5.9), and a negligible percentage (5.5%) was in the acid range (pH<5.0) (Table 3, Figure 9). In spite of that nitrate levels exceeded background hemispheric levels, pH values suggest that this site does not have acidity problems, owing to some cations probably played an important role in the neutralization process. This behavior is in agreement with the calcareous soils commonly found in Yucatan Peninsula which is constituted by alkaline particles participating in active way in the neutralization process.

4.1.2 Tula de Allende

Sulfate was the most abundant ion in Tula de Allende, probably attributed to anthropogenic sources. Tula de Allende is not a coastal site; therefore, it can be assumed that the total content of sulfate and nitrate is in excess (anthropogenic origin). Sulfate excess, [SO₄²⁻]_{xs}) levels found (68.78 μEq l⁻¹) exceeded almost seven times the background hemispheric levels reported by Galloway et al (1982) for remote sites (10 μEq l⁻¹). In addition, nitrate levels (56.37 μEq l⁻¹) also exceeded the background hemispheric levels reported for remote sites (2.8 μEq l⁻¹). Both, nitrate and sulfate contributed to the acidity. Considering the residence times for SO₂ (13 days) and NO₂ (1 day), it can be assumed that this site had the influence of local sources (anthropogenic sources such as a local power plant and oil refinery) as well as the input of pollutants subjected to long-range transport process. From Table 3 and Figure 10, it can be observed that pH values found in dry deposition samples ranged from 5.3 to 6.7, with a mean value of 5.77. A great percentage of the samples (59%) was below of 5.6, but any sample was in the acid range (pH<5.0).

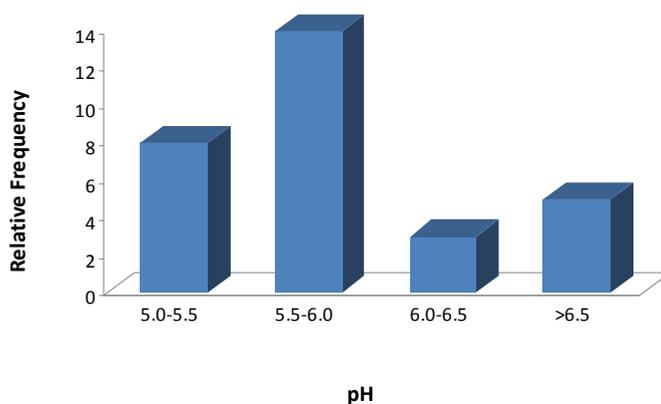


Fig. 10. pH frequency distribution for dry deposition samples collected at Tula de Allende.

In spite of nitrate levels exceeded the background hemispheric levels, it can be concluded that this site has enough buffer capacity to neutralize the acidity, probably due to Ca^{2+} (attributed to Portland cement plants located near this sampling site) playing an important role in the neutralization process.

4.2 Correlation analysis and time trends

The origin of elements in atmospheric deposition samples can be inferred by correlations between elements and let us to identify common sources, similar removal processes or a strong acid-base relationship.

4.2.1 Los Petenes Biosphere Reserve

From Pearson matrix (Table 4), it can be observed that nitrate ion showed a good correlation with Ca^{2+} ($r=0.89$ at $p<0.001$) and Mg^{2+} ($r=0.54$ at $p<0.001$), being evident a strong acid-base relation. In addition, Ca^{2+} was the third more abundant ion, indicating that this alkaline element, derived from crustal, was the main responsible of the neutralization process, resulting in pH values above of 5.6. NO_3^- - SO_4^{2-} correlated significantly ($r=0.63$ at $p<0.001$), suggesting that both ions had a common source.

Figure 11 shows the variations of ionic concentrations in dry deposition with time at Los Petenes Biosphere Reserve. Backward air masses trajectories analysis carried out using the HYSPLIT Model from NOAA demonstrates that winds during the sampling period had an East component. Therefore, it can be inferred that a specific source located in this direction (the power plant near to this site) possibly contributed to the significant levels of nitrate and sulfate.

Some temporal emissions as forest fires occurring as a result of the mid-summer drought could also contribute to these high levels of nitrate and sulfate. In Yucatan Peninsula, the mid-summer drought is associated with warm temperatures and the lack of humidity in soils favoring the conditions for forest fires. It can be observed that NO_3^- and NH_4^+ showed the same behavior, it suggests that both ions had a common source (forest fires). In addition, it can be observed that SO_4^{2-} and NO_3^- showed the same pattern, suggesting that both ions

had a common origin, and being evident an enrichment of nitrates derived from local sources (power plant and biomass burning).

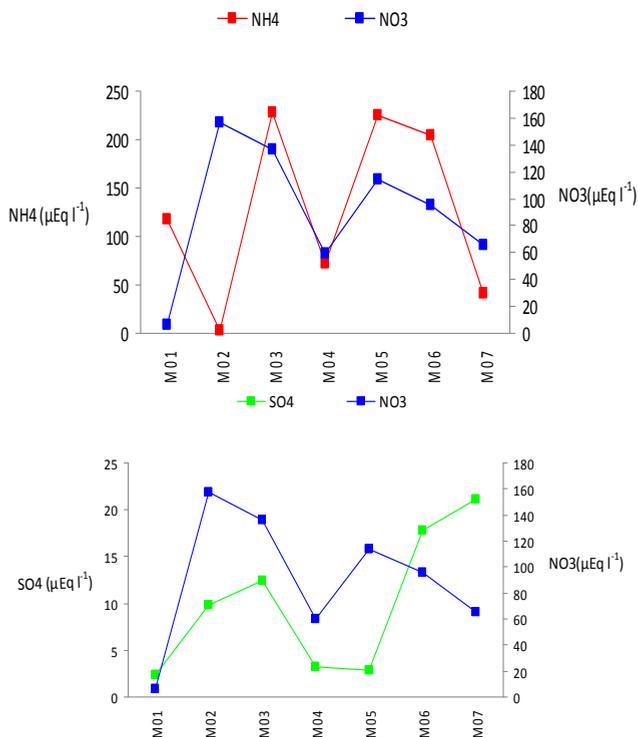


Fig. 11. Time-trends of ionic concentrations in dry deposition in Los Petenes.

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
Na ⁺	1							
K ⁺	0.41	1						
Ca ²⁺	0.52	0.41	1					
Mg ²⁺	0.02	0.09	0.65	1				
NH ₄ ⁺	0.26	0.21	0.26	0.14	1			
NO ₃ ⁻	0.51	0.27	0.89	0.54	0.18	1		
Cl ⁻	0.78	0.67	0.77	0.77	0.33	0.71	1	
SO ₄ ²⁻	0.51	0.37	0.55	0.04	0.26	0.63	0.21	1

Table 4. Pearson's correlation matrix among trace elements for Los Petenes Biosphere Reserve.

4.2.2 Tula de Allende

Pearson matrix (Table 5) indicates that nitrate ion correlated significantly with SO₄²⁻ (r=0.95 at p<0.001) and Ca²⁺ (r=0.74 at p<0.001); whereas SO₄²⁻ correlated with Ca²⁺ (r=0.79 at

p<0.001). It was completely evident a strong relationship acid-base between these ion pairs, suggesting that these ions were deposited as calcium nitrate and sulfate. These results support the fact that the co-existence of cement plant and power plant in the same location resulted in pH values near to neutrality value reported for natural rainwater.

	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	NH ₄ ⁺	NO ₃ ⁻	Cl ⁻	SO ₄ ²⁻
Na ⁺	1							
K ⁺	0.29	1						
Ca ²⁺	0.10	0.74	1					
Mg ²⁺	0.20	0.77	0.91	1				
NH ₄ ⁺	0.38	0.06	0.18	0.11	1			
NO ₃ ⁻	0.14	0.44	0.74	0.51	0.10	1		
Cl ⁻	0.59	0.27	0.10	0.20	0.41	0.13	1	
SO ₄ ²⁻	0.13	0.47	0.79	0.60	0.13	0.95	0.13	1

Table 5. Pearson’s correlation matrix among trace elements for Tula de Allende.

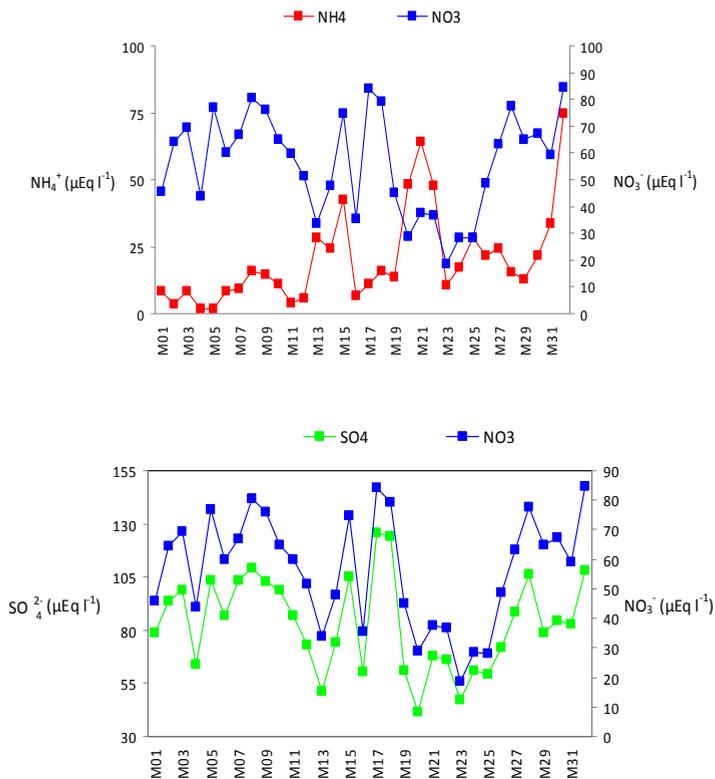


Fig. 12. Time-trends of ionic concentrations in dry deposition in Tula de Allende.

Backward air masses trajectories analysis demonstrated that winds during the sampling period had a N-NE component. These results imply that a specific source located in this direction (the power plant near to this site) contributed to the significant levels of nitrate and sulfate. Figure 12 shows the variations of ionic concentrations in dry deposition with time at Tula de Allende.

Tula de Allende sampling site constitutes a complex mosaic of rural, agricultural and industrialized areas. At the edges of the City, agriculture activities prevail, making evident the influence of ammonium on neutralization process. Furthermore, it can be observed that SO_4^{2-} and NO_3^- showed the same behavior, suggesting that both ions possibly had a common source.

4.3 Annual deposition fluxes

4.3.1 Los Petenes Biosphere Reserve

The average dry deposition fluxes (in $\text{Kg ha}^{-1} \text{ yr}^{-1}$) ranged between 0.39 and 7.19 for Los Petenes.

Figure 13 illustrates that dry deposition fluxes for ammonium and nitrate were the highest. During dry periods, the reduced mixing layer concentrates only ionic species of local origin; it supports the fact of high levels of nitrate and ammonium had a local origin, in this case, forest fires occurring during the mid-summer drought and emissions from "Lerma" Power Plant.

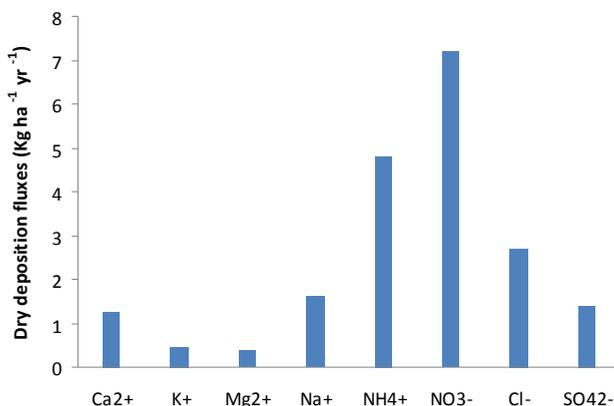


Fig. 13. Dry deposition fluxes for Los Petenes Biosphere Reserve.

4.3.2 Tula de Allende

The average dry deposition fluxes (in $\text{Kg ha}^{-1} \text{ yr}^{-1}$) ranged between 0.34 and 8.04 for Tula de Allende. It can be observed, from Figure 14, that dry deposition fluxes for calcium, sulfate and nitrate were the highest. In this case, anthropogenic emissions from Tula-Vito-Apaxco complex contributed to high levels of calcium, sulfate and nitrate, having in mind that, during dry periods, the reduced mixing layer only concentrates ionic species of local origin.

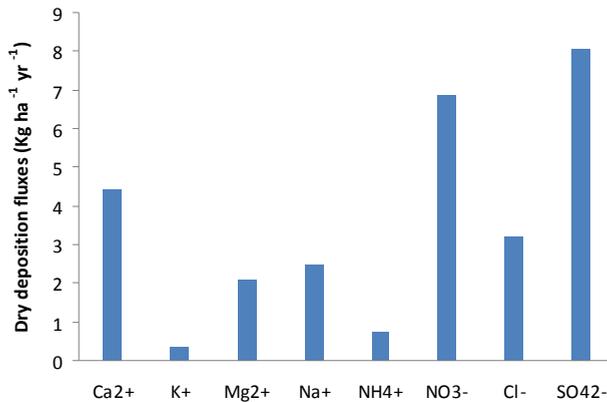


Fig. 14. Dry deposition fluxes for Tula de Allende.

4.4 Deposition fluxes and critical loads

A critical load of 10 Kg N ha⁻¹ yr⁻¹ has been proposed in the United Kingdom (Jones, 2005), however, given that the sensitivity varies from one specie to other, Power et al (2006) proposed a value of 8 Kg N ha⁻¹ yr⁻¹. In addition, it has been proposed a value of 5 Kg N ha⁻¹ yr⁻¹ for sensitive ecosystems. For the impacted ecosystems in U.S, the critical load reported ranges between 3 and 8 Kg N ha⁻¹ yr⁻¹. In the case of S, for natural forests, some authors propose values between 2 and 5 Kg S ha⁻¹ yr⁻¹ (Nilsson & Grennfelt, 1988).

Data on dry deposition inputs of N and S in Mexican sites are scarce, taking in account the critical values reported for Europe and United States of America, we can observe that in Los Petenes Biosphere Reserve, N input (11.99 Kg ha⁻¹ yr⁻¹) is slightly above the critical loads, whereas S input (1.4 Kg ha⁻¹ yr⁻¹) did not exceeded the critical values, this supports the proposal that this site is only subject to local emissions. These results indicate that critical loads of nitrogen can increase in a short time period if strategic measures are not taken. Our results are sub estimated considering that we are not reporting data for wet deposition, since this site is a natural reserve, it can constitute a serious threat to flora and fauna species that live in this ecosystem.

On the other hand, N input (7.6 Kg ha⁻¹ yr⁻¹) for Tula de Allende, exceeds proposed value for sensitive ecosystems, but it is below of critical load reported for American and European sites. However, in the case of S, we can observe that S input (8.04 Kg ha⁻¹ yr⁻¹) exceeded the critical value for various eco-regions in the world. It is clear that emissions released by sources in Tula-Vita-Apaxco industrial complex contributed in a significant way to this input. Alkaline particles emitted from cement plants contributed to neutralize the acidity, therefore, pH values resulting from this neutralization process were not in the acid range. However, pH itself it is not a conservative tracer of ecological effects of acid deposition; for that reason, we propose to improve the current environmental policies and the promulgation of new regulations based on a conservative tracer and focused to decrease sulfate levels in this region.

5. Conclusion

It can be concluded that in Los Petenes site, alkaline particles from the calcareous soil played an important role in the acidity neutralization process derived from high emissions of NO_3^- from the power plant and due to biomass burning in the vicinity of this sampling site. N input in Los Petenes exceeded slightly the critical values reported for other sites of the world. Considering the ecological importance of this site, local strategic policies must be applied focused on protecting the wildfire life in this Biosphere Reserve.

On the other hand, in spite of high sulfate and nitrate levels found in Tula de Allende (attributed to a power plant), acidity neutralization process was improved by the presence of cement plants near to this sampling site. However, S input exceeded critical values reported for several sites around the world. In spite of Tula de Allende is not an eco-region, since is already an industrialized site, S deposition could be a threat to historic wealth located in the vicinity of this place.

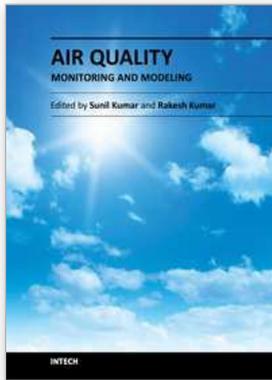
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