

Wet and dry deposition of trace elements in two sites in Carmen Island, Campeche, Mexico

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Abstract: - Wet and dry deposition samples were collected in two sampling sites (urban and mangrove forest) in Carmen Island, Campeche, Mexico from February to November, 2013. Samples were collected with an automatic wet/dry deposition sampler, using a device called DAS (Dry deposition on aqueous surfaces) that uses water as collection surface in the case of dry deposition. Wet deposition samples were collected daily, whereas dry deposition was collected on a weekly basis. In both cases, samples were analyzed for pH, conductivity, Na⁺, K⁺, Ca²⁺, Mg²⁺, NH₄⁺, NO₃⁻, SO₄²⁻ and Cl⁻. Calcium and nitrate were the most abundant ions, contributing in a great proportion to the total ionic mass. In both sampling sites, it was completely evident the influence of local sources, and in the case of the urban site, a local source (building activities) contributed to extremely high values of calcium. N deposition fluxes in both sampling sites exceeded the critical loads and the hemispheric background concentrations proposed for sensitive ecosystems and marine remote sites. Nitrogen total deposition at Carmen Island is already above of the upper extreme of the threshold value reported for sensitive ecosystems. Since only local sources drove the chemistry of the total deposition in both sampling sites, sulfate levels remained below of the background hemispheric values, suggesting that the contribution of regional sources of this ion was not significant. However, it is necessary to take local regulatory measures to avoid that total N deposition be a threat for the ecosystems in Carmen Island.

Key-Words: - Wet deposition, Dry deposition, Trace elements, Mangrove forests, Carmen Island, Campeche.

1 Introduction

Atmospheric deposition of trace elements constitutes the last step in the removal process of pollutants in the atmosphere, changing the natural balance of the cycles of the elements. Atmospheric Deposition has been monitoring in Europe and North America since 15 years ago, and it has been recognized as a potential source of atmospheric inputs to terrestrial and aquatic ecosystems, with subsequent effects on living being and their habitats. In tropical countries as Mexico, the eco-tourism contributes with great economical benefits; however, the sustainable growth has not been applied, resulting in big cities and industrialized areas natural located around areas with a great biodiversity. As a result, regulatory public organisms have a general concern about the effects

of the acid deposition on archaeological zones and the aquatic and terrestrial ecosystems.

In spite of, in many countries around the world, Atmospheric Deposition data are available since several years ago, in Mexico, only a few studies about chemistry of precipitation are published [1,2,3,4,5,6,7], and dry Deposition data are not available.

The qualitative and quantitative assessment of Atmospheric Deposition is required to establish critical loads, to estimate the exceedances to these critical loads, to identify sensitive zones with a great vulnerability to suffer damages, to assess annual trends, and finally to demonstrate the efficiency of environmental regulations applied on Atmospheric emissions [8,9,10].

The systematic and standardized collection at a long-term in the most of the tropical regions has been focused to assess the role of Atmospheric deposition in the biogeochemical cycles, however, these studies have been carried out as a result of specific research projects with international collaboration, and it has been limited only to certain geographical areas. Therefore, critical loads, their exceedances, and the potential ecological effects associated to the acid deposition in tropical countries remain uncertain. In addition, deposition patterns, meteorological conditions and the response of the ecosystems may be different to those reported for temperate regions in mid-latitudes.

In spite of it is well known that Atmospheric pollutants can deteriorate historical monuments and archaeological sites, can cause damages to the human health and harmful effects on vegetation sensitive species, studies about air pollution in the Gulf of Mexico are scarce. Along the coast of the Gulf of Mexico, there are many important cities with a significant urban and industrial development, oil refineries, offshore platforms for the exploring and producing of gas and oil in Campeche, historical monuments, archaeological zones, and aquatic and terrestrial ecosystems of great value.

The annual emissions from urban and industrial sources reported for Campeche State are 205.64 Gg for NO_x and 336.79 Gg for SO_2 ; therefore, it is expected that in the ecosystems located downwind from these sources, N and S Deposition be high. Mangrove forests cover a great extension of territory along the coast of the Gulf of Mexico, being Mexico the fifth country in the world with the highest mangrove cover. In the state of Campeche, mangrove cover accounts with approximately 30% to the total mangrove cover in the country, with an extension of 196, 552 ha. Therefore, Carmen Island in Campeche constitutes a hotspot in Mexico for two main reasons: 1) their proximity to the greatest area of gas and oil offshore production in the country, and 2) for its closeness to the natural protected area "Laguna de Terminos".

Considering that studies about Atmospheric Deposition area scarce along the Coast of the Gulf of Mexico, and critical load data are not available, this work had the following objectives: 1) to establish a solid base line about wet and dry Deposition in Carmen Island, and 2) to compare Deposition data in urban and mangrove forest sites in Carmen Island.

2 Methodology

2.1 Study Area

Climate in Carmen Island is sub-humid warm with rains occurring along the summer, with some transitional periods between seasons. The average annual rainfall is 1300 mm, and the mean annual temperature is 27 °C. Along the summer, this region is under the influence of maritime air masses and tropical storms as a result of the trade winds that prevail during this season.

Prevailing winds come from NE (from September to March) when this site is under the influence of the cold fronts named "Nortes"; and from SE-SW, during the rest of the year (from April to August), when the site is under the influence of tropical maritime air. However, since the site is located at Carmen Island, sea and land breezes prevail the most of the year and contribute in a significant way to the local transport processes. In addition, there are some transitional periods in which meteorology can be complex (during October and November), when the site can be subjected to both, low pressure systems and cold fronts, resulting in stationary phenomena that contribute in a significant way to the annual total rainfall in the site.

The annual cycle of the climate in the South-Southeast region of Mexico shows a rainy season well defined (from May to October), however, the rainy season in this region is characterized by a bimodal distribution, with a maximum value during June and September, and a relative minimum during July-August known as mid-summer drought. Considering the variability in the climatic conditions in this region along the year, it is necessary to estimate the relative contribution of the mechanisms of wet and dry deposition in the removal of atmospheric pollutants and assess their potential ecological implications.

Two sampling sites were selected for this research work taking in account the differences in the land use that prevail along the island. The first site was located in the urban zone within the facilities of the Autonomous University of Carmen, it is necessary to mention that this site was under the influence of building activities during the whole study period since several road repairs and building of two hotels, and one big mall were carried out at 500 m around this site.

In addition, this zone is characterized by a high vehicular traffic, so in peak hours, vehicular transit is intense resulting in high emissions mainly of NO_x . On the other hand, the second site was located within a mangrove forest within the facilities of the Botanical Garden of the Autonomous University of Carmen. This site is very complex because is located in the transition zone between urban area and mangrove forest. This site is characterized by a high vehicular density within a small geographical extension, with few circulation ways. Specific location of these sampling sites is shown in Figure 1.

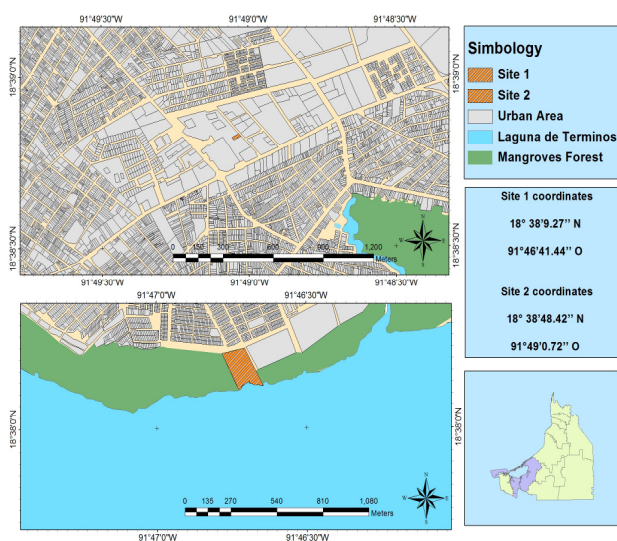


Figure 1. Sampling Site Location.

2.2 Sampling Method

Samples were simultaneously collected in both sites from February 8 to November 1, during 2013. Sampling was carried out by using an automatic two wet/dry deposition sampler (Tisch, Inc). Sampling device is equipped with a sliding cover which moves depending on the beginning or ending of the rain event, it has two buckets for the collection of dry and wet deposition. Wet deposition was collected on a daily basis, whereas dry deposition was collected on a weekly basis.

2.2.1 Wet Deposition

Wet deposition samples were collected by the automatic sampler in the wet mode. Trained technicians checked the samplers daily, typically at 8:00 h, local standard time, to retrieve, preserve

with chloroform and refrigerate any collected precipitation each day.

Samples with a volume lesser than 250 ml or with a visible pollution were discarded. Samples were sent to Environmental Sciences Laboratory at Autonomous university of Carmen, where they were filtered (with a Kontes ® Ultra-ware System, using a vacuum pump and Phenomenex ® membranes) and analyzed for pH, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , NH_4^+ , SO_4^{2-} , NO_3^- and Cl^- .

2.2.2 Dry Deposition

Dry deposition samples were collected by the automatic sampler in the dry mode coupled to a device called DAS (Dry deposition on aqueous surfaces) that uses water as collection surface, according to Tartari [11]. All samples were stored at 4°C and dark until their analysis.

2.3 Analytical Method

All plastic ware and glassware used were rigorously washed and rinsed with deionized water. All material used for cations determination was completely immersed during 24 h in a 20% ultrapure nitric acid bath (J.T Baker ® , AA grade), rinsed at least three times with deionized water type I (Hycel ®) and sealed in plastic bags.

PH and conductivity were measured using a potentiometer (HACH ® model EC10) and a conductivity instrument YSI ® 3200 [12,13]. Field blanks were analyzed to guarantee the cleanness of the sampling material. Standard solutions were prepared by dilution from certified standards (J.T Baker ®).

Anions were analyzed according to standard procedures. Sulfate was determined by turbidimetry [14]. NO_3^- was analyzed by colorimetry [15] and chloride was determined according to [16].

Na^+ , K^+ , Ca^{2+} and Mg^{2+} were determined by Atomic Absorption Spectroscopy (Thermoscientific ® Ice 3000) with the flame technique according to EPA methods [17,18,19,20]. Finally, ammonium was determined by molecular absorption spectroscopy by using the blue indophenol method [21].

2.3.1 Data Quality

The reproducibility of data was assessed by using analysis of at least three replicate. Analytical quality of data was verified from ionic balance. From the comparison between the measured conductivity in the samples and the estimated conductivity (from measured ionic concentrations and their specific conductivities), it is possible to determine if the analysis is full satisfactory. If the difference is minor than 10%, it can be considered that the most of the ions were determined in the analysis, on the other hand, if this difference is major than the unity, it points out the presence of another ions were not measured during the analysis in significant quantities.

2.4 Meteorological Analysis

Portable meteorological stations (Davies ®) were used in both sampling sites to collect meteorological data in situ. Wind roses were obtained from WRPLOT View 6.5.2 (Lakes Environmental, Inc). In addition, the backward air masses trajectories were quoted by using HYSPLIT model (Hybrid Single Particle Lagrangian Integrated) from NOAA [22]. From Figure 2, we can observe that the prevailing winds in Carmen Island during the whole study period came from SE and NE depending on the season of the year.

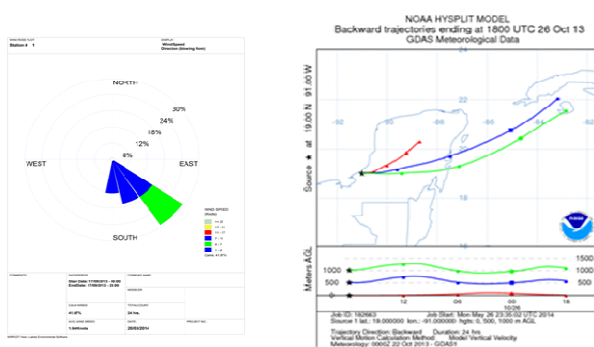


Figure 2. Typical wind rose and backward air mass trajectory for Carmen Island during the study period.

2.5 Statistical Analysis

Pearson's correlation analysis was applied to data set to overview the relationship among trace elements for each sampling site.

In addition, a factor analysis was applied to identify factors underlying the interactions among surveyed species. Calculations were carried out using SAS 8.0 software. Principal Component Analysis (PCA), a linear method for multivariate ordination was used to assess the relationship among trace elements at each sampling site, focused mainly on the inter-elements correlation coefficients.

3 Results

3.1 Trace Elements Concentrations

Figure 3 shows the minimum, maximum and mean concentration values, and standard deviation for trace elements in the urban site for wet and dry deposition respectively.

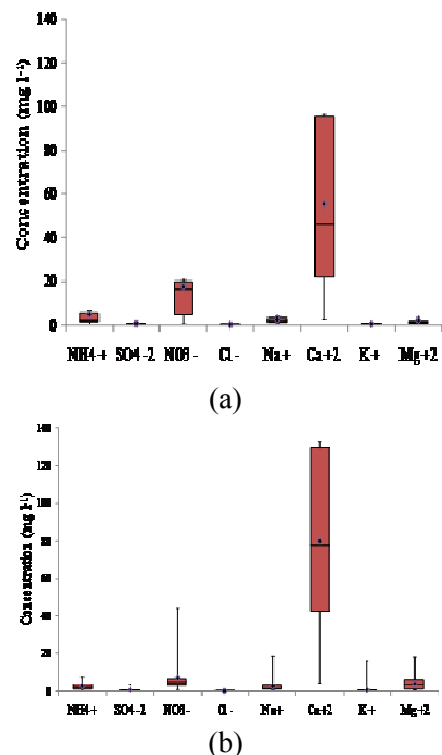


Figure 3. Minimum, mean and Maximum concentrations for major ions in (a) wet deposition and (b) dry deposition for the urban sampling site in Carmen Island.

From Figure 3 (a) and 3 (b), it can be observed that sulfate levels in wet and dry deposition in the urban

site (11.02 and 16.71 $\mu\text{Eq l}^{-1}$, respectively) exceeded slightly the background hemispheric concentrations reported for remote sites (10 $\mu\text{Eq l}^{-1}$), suggesting that there were not regional sources contributing significantly to sulfate levels.

On the other hand, mean nitrate levels in wet and dry deposition in this site (318.4 and 117.47 $\mu\text{Eq l}^{-1}$, respectively) exceeded significantly the reported levels for marine remote sites (2.8 $\mu\text{Eq l}^{-1}$), indicating a clear influence from local sources contributing to nitrate levels. These high nitrate levels can be directly attributed to vehicular sources, since this site constitutes one of the zones with the greatest vehicular traffic, as a result, during peak hours, there is a high density of vehicles in a small geographical area, resulting in high emissions of NO_x .

Figure 4 shows the minimum, maximum and mean concentration values, and standard deviation for trace elements in the mangrove forest site for wet and dry deposition respectively.

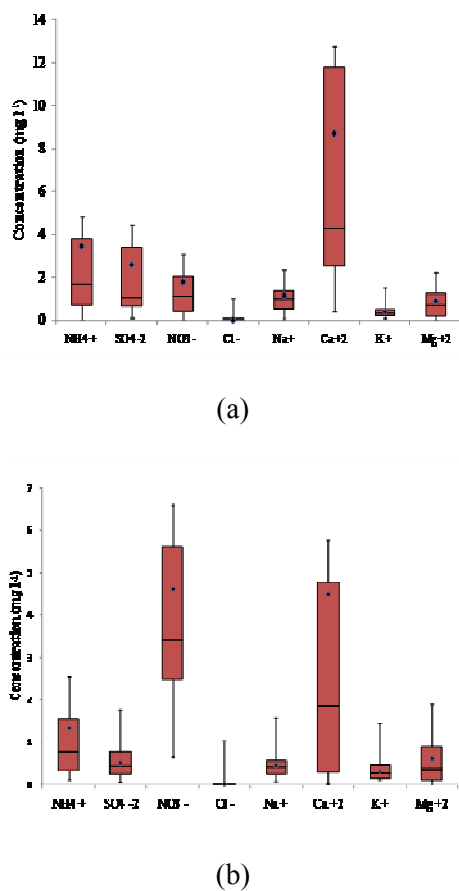


Figure 4. Minimum, mean and Maximum concentrations for major ions in (a) wet deposition and (b) dry deposition for the mangrove forest sampling site in Carmen Island.

Sulfate levels in wet and dry deposition in mangrove forest site were 53.68 and 10.73 $\mu\text{Eq l}^{-1}$, respectively (Figures 4a and 4b). Sulfate levels in dry deposition were in agreement with the background levels for remote sites, however during the rainy season, nitrate levels were higher than those reported for the urban site. It means that during the rainy season, the mangrove forest site was under the influence of emissions transported from regional sources in the offshore oil and gas facilities, where sour gas is burned in elevated flares. In addition, regional sources in Yucatan Peninsula could contribute to these high sulfate levels during the rainy season, when this site is under the influence of the trade winds that promote the long-range transport. On the other hand, mean nitrate levels in wet and dry deposition in this site (28.85 and 74.40 $\mu\text{Eq l}^{-1}$, respectively) were above of the reported levels for marine remote sites (2.8 $\mu\text{Eq l}^{-1}$), indicating a clear influence from local sources contributing to nitrate levels. However, comparing the nitrate levels found in the mangrove forest site with those found in the urban site, nitrate levels were 11 and 1.5 times greater in the wet and dry deposition collected in the urban site. It is expected since the urban site was located in one of the most transited ways of the city.

3.2 Relative Ionic Abundance

Relative ionic abundance in atmospheric deposition for the urban site and the mangrove forest site are presented in Figure 5 and 6, respectively.

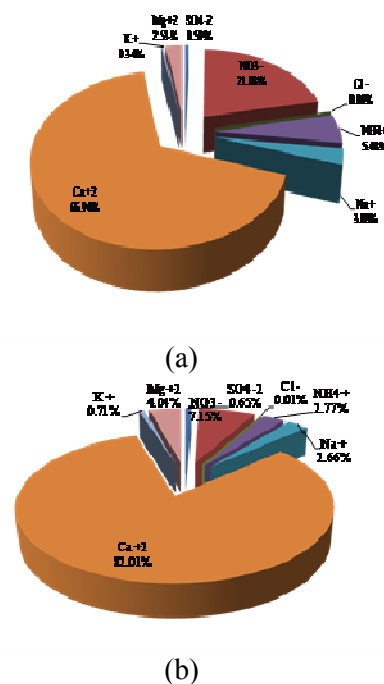


Figure 5. Contribution total of ions to (a) Wet deposition and (b) Dry deposition in the urban sampling site in Carmen Island.

From Figures 5a and 5b, it can be observed that the most abundant ions in wet and dry deposition collected in the urban site were Ca^{2+} and NO_3^- . High calcium levels were expected since the influence of the crustal is significant because of calcareous soils are the dominant type of soil in this site. In spite of the contribution from the crustal was significant in this site, calcium levels were unusually higher than those expected from the soil particles, it means that there was an additional source contributing in a significant way to the calcium levels in the site. The sampling site in the urban zone was located downwind from several building activities (hotels, a big shopping center, parking lots, road paving, and so on) during the whole study period, therefore, the high calcium levels can be directly attributed to the building trade.

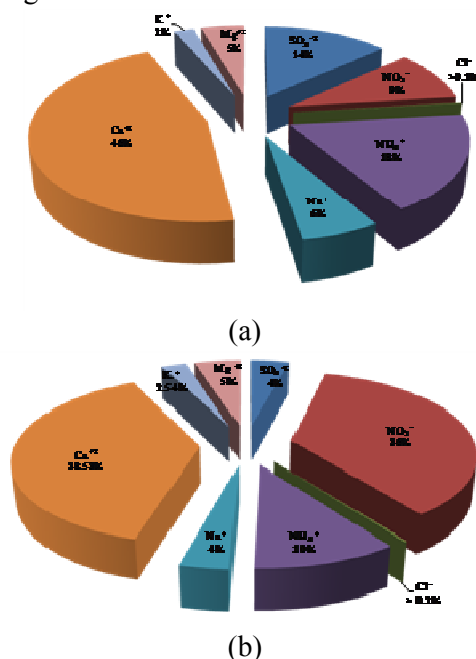


Figure 6. Meteorological influence on carbonyl levels (a) and a wind rose for an air pollution episode in March 8, 2013 (b).

As can be observed from Figures 6a and 6b, calcium levels in wet and dry deposition in the mangrove forest site were almost 5 times minor than those found in the urban site, therefore, it can be established that the high calcium levels in the urban site can be inherently attributed to local and temporal sources of particles during the sampling period (sand and cement used in building activities).

On the other hand, nitrate levels found in both sampling sites suggest that these sites were under the influence of local sources that contributed with significant levels of nitrate, in this case, vehicular sources since the urban site was located in the center of the city where vehicular traffic is high all time.

In addition, emissions transported from regional had a minimal contribution to the sulfate levels. Agricultural practices are not present in Carmen island, for this reason NH_4^+ levels were very low, being relatively higher in the mangrove forest site since this sampling site is subjected to the emissions transported from the oriental edge of the island, where agricultural activities are developed crossing the bridge in the municipalities of Sabancuy and Isla Aguada. Finally, it was clear that marine aerosol had a weak contribution to the levels of Na^+ , Cl^- and Mg^{2+} , whereas K^+ levels from the crustal were minimal.

3.3 pH

Even in areas considered as free of atmospheric pollution, pH value for natural rainwater is 5.6 due to the presence of CO_2 which dissolved in rainwater produce carbonic acid, resulting in pH values minor than 7.

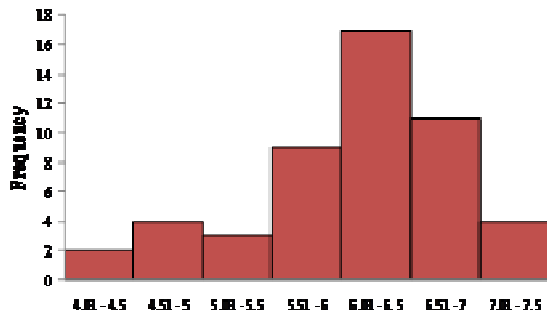
When pH value is between 5 and 5.6, it is considered that the rainwater has enough buffer capacity to neutralize the acidity derived from the contribution of alkaline elements from soil particles or another sources. On the other hand, when the pH value is minor than 5, there is an evident anthropogenic source contributing to the acidity, suggesting that the site can be potentially impacted by acid deposition.

Figure 7 presents the frequency distribution of pH in the urban site for wet and dry deposition, respectively.

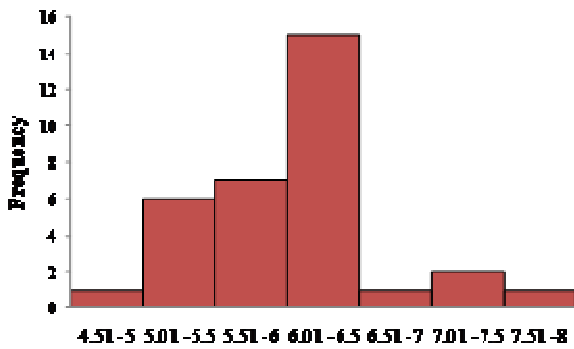
From a total of 56 samples of wet Deposition, only 3 were below 5.6 (9%), and 6 samples were below 5.0 (19%), with a mean pH value of 6.43. It was evident that alkaline pH values were predominant in the urban site (Figure 7a). In the case of dry deposition in the urban site, from the most of the collected were above of 5.6, with a mean pH value of 6.09 (Figure 7b). As a result of the contribution of alkaline particles derived from the building trade, the urban site has enough buffer capacity to neutralize the acidity resulting in high pH values. This is in agreement with the high calcium levels

found, suggesting that crustal and building particles played an important role in the acid-base interactions.

The frequency distribution of pH in the mangrove forest site for wet and dry deposition is given in Figure 8.

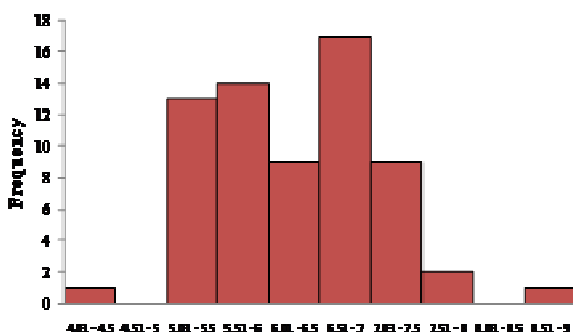


(a)

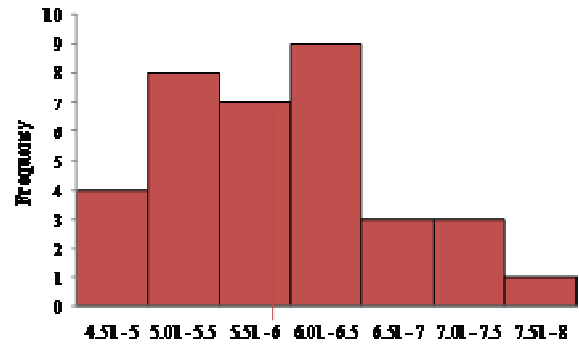


(b)

Figure 7. Frequency distribution of pH for (a) Wet deposition and (b) Dry deposition in the urban sampling site in Carmen Island.



(a)



(b)

Figure 8. Frequency distribution of pH for (a) Wet deposition and (b) Dry deposition in the mangrove forest sampling site in Carmen Island.

On the other hand, in the case of wet deposition collected in the mangrove forest site, from a total of 66 samples, only 1 sample was below 5 (1.5%), and 13 were below 5.6 (19.6%), with a mean pH value of 6.28. In the case of dry deposition, from a total of 35 samples, 4 were below 5 (11.4%), and 8 were below 5.6 (22.6%), with a mean pH value of 5.9. (Figures 8a and 8b). It was evident that the buffer capacity in the mangrove forest site was minor than the capacity found in the urban site, it is expected since the mangrove forest site was not under the influence of particles derived from building activities.

3.4 Temporal Trends

In Figure 9, temporal trends for NO_3^- , SO_4^{2-} , NH_4^+ and pH are shown for (a) Wet deposition and (b) Dry deposition in the urban sampling site in Carmen Island.

It can be observed that whereas sulfate levels remained uniform and presented very low values, in the case of nitrate, significant variations were observed, reaching peak values of up to 45 mg l^{-1} in wet deposition. This nitrate peak values coincided with the most low pH values. It suggests that probably nitrate contributed in a major proportion to the acidity; however this acidity was neutralized in an efficient way by the extremely high calcium values, resulting in alkaline pH values. In addition, sulfate and nitrate had different temporal patterns, indicating that probably had their origin in different sources.

Temporal trends for nitrate, sulfate, ammonium and pH for (a) Wet deposition and (b) Dry deposition

are presented in Figure 10 for mangrove forest sampling site in Carmen Island.

Temporal trends for the mangrove forest site were very different that those obtained in the urban site. Sulfate levels were higher in mangrove forest site than in urban site, and they were not uniformly distributed, suggesting that these levels were strongly influenced by the strength of the sources and the meteorological conditions that improved the long-range scale transport from regional sources. High nitrate levels coincided with the most low pH values, suggesting that contribution of nitrate to the acidity was greater than the sulfate. Temporal trends for nitrate were different from those obtained for sulfate, suggesting that they were originated in different sources.

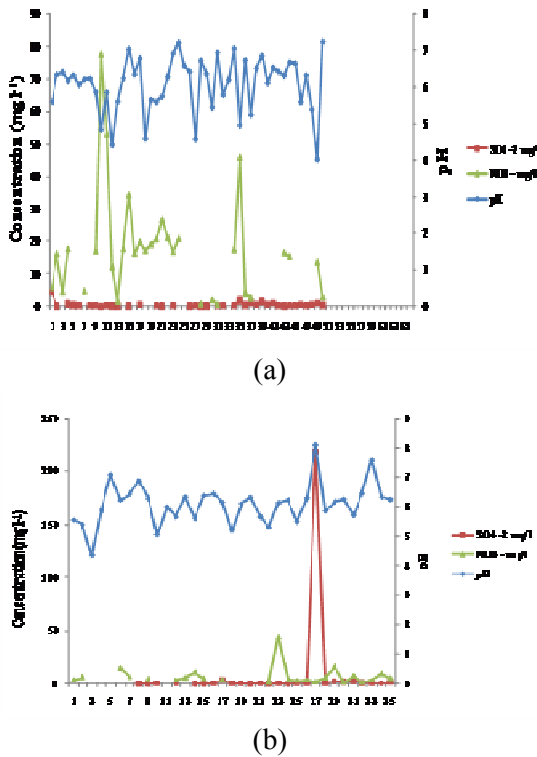


Figure 9. Temporal trends for (a) Wet deposition and (b) Dry deposition in the urban sampling site in Carmen Island.

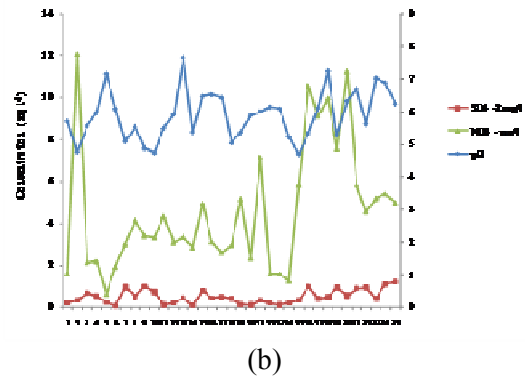
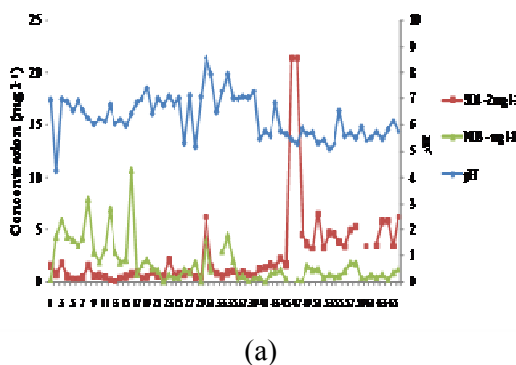


Figure 10. Temporal trends for (a) Wet deposition and (b) Dry deposition in the mangrove forest sampling site in Carmen Island.

3.5 Neutralization factors

To assess the role of the alkaline elements in the interactions acid-base and their neutralization capacity, neutralization factors (NF) were estimated, the following equation was used:

$$NF = [\text{Alkaline ion}] / [\text{NO}_3^- + \text{SO}_4^{2-}]$$

To investigate which cation (Na^+ , K^+ , Ca^{2+} , Mg^{2+} and NH_4^+) more frequently neutralized acidic components in wet and dry deposition in both sampling sites (Figure 11 and 12), triangular diagrams were drawn to show the relative contribution of each alkaline element.

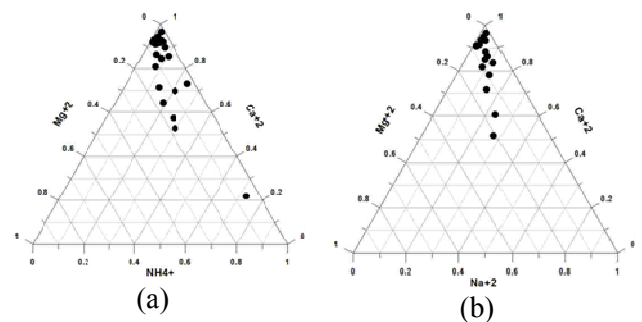
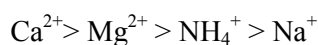


Figure 11. Triangular diagram of NF for predominant alkaline elements in (a) Wet deposition and (b) Dry deposition in the urban sampling site in Carmen Island.

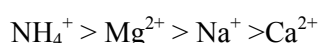
The triangle relating the neutralization factor of Ca^{2+} , Mg^{2+} , Na^+ and NH_4^+ in the urban site (Figure 11a and 11b) revealed that Ca^{2+} was the

predominant neutralizer. The relative importance of alkaline components in the neutralization process in wet and dry deposition collected in the urban site was the following:



It is well known that the high concentrations of Ca^{2+} are related to the surface soil and building activities. Neutralization factors demonstrated that calcium played an important role in the neutralization process suggesting probably the presence of $\text{Ca}(\text{NO}_3)_2$ and CaSO_4 in the atmosphere, originating from alkaline particles derived from the earth crust and the building trade, and from SO_2 and NO_x emitted in combustion processes from local and regional sources.

Neutralization factors (NF) for wet deposition in the mangrove forest site showed the following relative strength in the neutralization process:



It suggests that ammonium derived of agricultural activities developed at the east edge of Carmen Island played an important role in the neutralization process. On the other hand, Ca^{2+} and Mg^{2+} neutralized the acid components in dry deposition collected in the mangrove forest site, it means that crustal particles contributed in major proportion in the acid-base interactions.

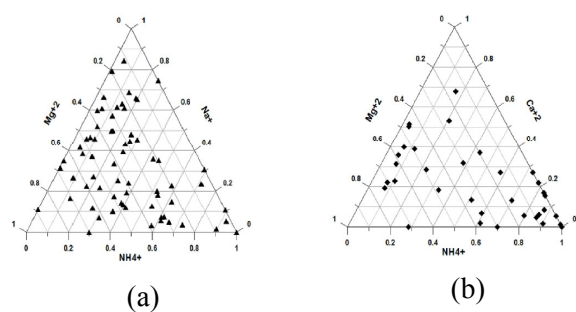


Figure 12. Triangular diagram of NF for predominant alkaline elements in (a) Wet deposition and (b) Dry deposition in the mangrove forest sampling site in Carmen Island.

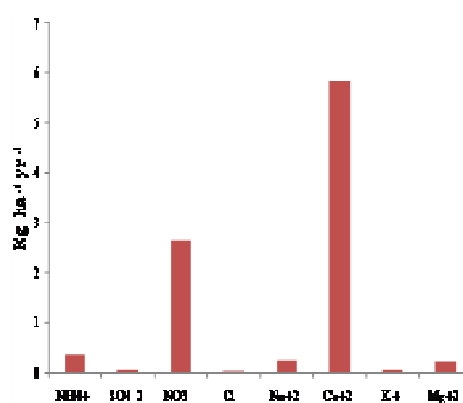
3.6 Atmospheric Deposition Fluxes

As a result of the high calcium levels in both sampling sites, pH values found were slightly alkaline, however, nitrate and sulfate levels

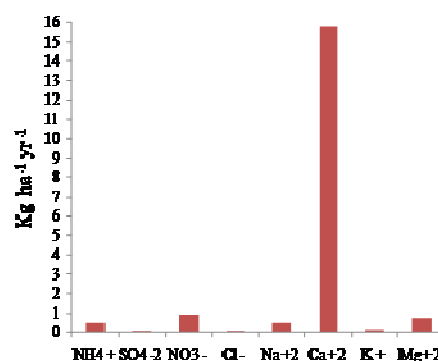
exceeded in a great proportion the hemispheric background levels reported for coastal and marine remote sites. Since, nitrate and sulfate are not criteria pollutants in Mexico, actually, there is not an environmental law which regulate their deposition levels and critical loads for these ecosystems, therefore, to estimate the real effect of atmospheric pollutants in the ecosystems associated to Laguna de Terminos, it is necessary to calculate dry and wet deposition fluxes and compare them with critical load values reported for sensitive ecosystems in other countries. Deposition fluxes for wet and dry deposition in both sampling sites are shown in Figure 13 and 14.

Considering the ionic concentrations in dry and wet deposition, the sampling period and the surface of collection, deposition fluxes were obtained.

In the urban site, wet deposition fluxes ($\text{Kg ha}^{-1} \text{yr}^{-1}$) ranged between 0.030 and 132.19 $\text{Kg ha}^{-1} \text{yr}^{-1}$ (Figure 13a) whereas dry Deposition fluxes ($\text{Kg ha}^{-1} \text{yr}^{-1}$) ranged between 0.002 and 16.42 $\text{Kg ha}^{-1} \text{yr}^{-1}$ (Figure 13b). The highest fluxes were found for calcium and nitrate, being the deposit of the other components not significant.



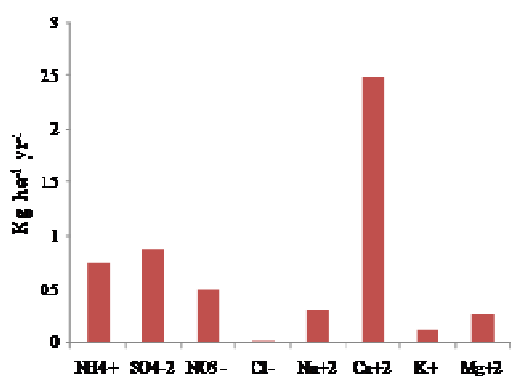
(a)



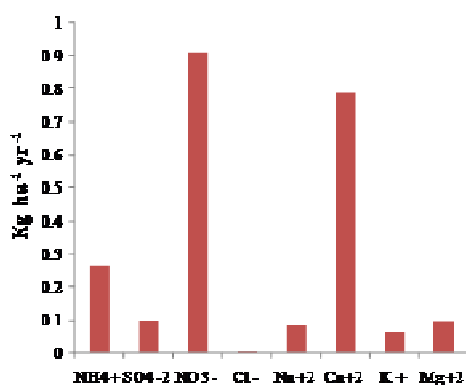
(b)

Figure 13. Deposition fluxes for (a) Wet deposition and (b) Dry deposition for the urban sampling site in Carmen Island.

Deposition pattern in the mangrove forest site was completely different than the urban site. Deposition fluxes presented a great variability, wet deposition ranged between 0.003 and 2.47 ($\text{Kg ha}^{-1} \text{yr}^{-1}$) (Figure 14a), while dry deposition ranged between 0.004 and 0.78 ($\text{Kg ha}^{-1} \text{yr}^{-1}$) (Figure 14b). The highest fluxes were found for calcium and nitrate in dry deposition, and for calcium and sulfate for wet deposition. It is well known that wet deposition is more connected to regional sources; therefore, it was completely evident the long range transport from regional sources that contributed to sulfate and ammonium levels in wet deposition.



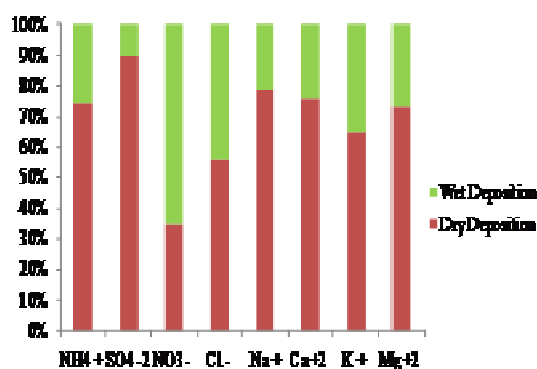
(a)



(b)

significantly the hemispheric background levels reported for remote sites ($1 \text{ to } 3 \text{ Kg ha}^{-1} \text{yr}^{-1}$), therefore, it can be considered that N Deposition is already a problem in the urban site. On the other hand, S total Deposition (wet plus dry Deposition) in the urban site ($0.84 + 0.16 \text{ Kg ha}^{-1} \text{yr}^{-1}$) was below of values reported for sensitive ecosystems ($3 \text{ Kg ha}^{-1} \text{yr}^{-1}$), however, this flux Deposition exceeded slightly the background hemispheric values for remote sites ($0.5 \text{ Kg ha}^{-1} \text{yr}^{-1}$). It suggests that the urban site was only under the influence of local sources.

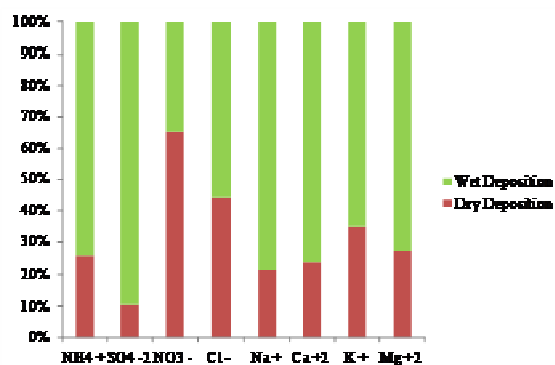
N total Deposition (wet plus dry deposition) in the mangrove forest site ($1.24 + 1.17 \text{ Kg ha}^{-1} \text{yr}^{-1}$) was below of the critical loads reported for sensitive ecosystems in Europe ($5 \text{ Kg ha}^{-1} \text{yr}^{-1}$), and did not exceed the hemispheric background levels reported for remote sites ($1 \text{ to } 3 \text{ Kg ha}^{-1} \text{yr}^{-1}$), therefore, it can be considered that N Deposition is not a problem in the mangrove forest site. On the other hand, S total Deposition (wet plus dry deposition) in the urban site ($0.87 + 0.1 \text{ Kg ha}^{-1} \text{yr}^{-1}$) was in agreement with those found for the urban site, these values were below of values reported for sensitive ecosystems ($3 \text{ Kg ha}^{-1} \text{yr}^{-1}$), however, this flux deposition exceeded slightly the background hemispheric values for remote sites ($0.5 \text{ Kg ha}^{-1} \text{yr}^{-1}$). Figure 15 shows the relative contribution of dry and wet deposition to the total atmospheric deposition in both sampling sites during 2013.



(a)

Figure 14. Deposition fluxes for (a) Wet deposition and (b) Dry deposition for the mangrove forest sampling site in Carmen Island.

N total Deposition (wet plus dry Deposition) in the urban site ($67.36 + 2.06 \text{ Kg ha}^{-1} \text{yr}^{-1}$) was above of the critical loads reported for sensitive ecosystems in Europe ($5 \text{ Kg ha}^{-1} \text{yr}^{-1}$), and exceeded



(b)

Figure 15. Relative contribution of wet and dry deposition to the total atmospheric deposition in (a) the urban sampling site and (b) the mangrove forest sampling site during 2013 in Carmen Island.

From Figure 15a, it can be observed that in the urban site, wet deposition contributed in major proportion to NO₃⁻ and Cl⁻, whereas, dry deposition contributed significantly to the total deposition of Ca²⁺, Na⁺ and SO₄²⁻.

On the other hand, in the mangrove forest, wet deposition contributed to SO₄²⁻, NH₄⁺, Na⁺ and Mg²⁺, while nitrate was deposited in major proportion during dry periods.

4 Conclusion

The study of wet and dry deposition in two sampling sites in Carmen Island (urban and mangrove forest) showed that deposition in the island has a great variability, whereas in the urban site, deposition of Ca²⁺ and NO₃⁻ from local sources was dominant, in the mangrove forest, deposition of Ca²⁺, NO₃⁻, SO₄²⁻ and NH₄⁺ was significant, being evident the influence of both, local and regional sources. Because of nitrate levels were high in both sites, it could be expected that total deposition would be acidic, however the contribution of alkaline components derived from the crustal and local sources as building activities was significant, resulting in deposition with pH values almost alkaline.

In Carmen Island, there is a complex environment of mixed sources with a different geographical distribution along the island driving the atmospheric chemistry (crustal, anthropogenic, marine aerosol, and secondary emissions). It is necessary to appoint

that pH itself; it is not a conservative tracer of the potential ecological effects as a result of the emissions of acid precursors. In spite of, obtained pH values in dry and wet deposition collected in both sampling sites were not in the acid range, the atmospheric deposition fluxes of N could represent a threat to the eco- systems. It was completely evident that local sources are the main contributors to this high N deposition; therefore, local strategic policies focused to protect the ecosystems in this region should be applied. It is necessary to increase the density of the sampling grid along the island by using passive samplers to assess the variability of total N and S deposition along the island, it let to identify critical zones where the vulnerability of the ecosystems to suffer damages may be higher.

References:

- [1] Báez, A.P., Padilla, H.G., Cervantes, J., Pereyra, D. and Belmont, R. Rainwater Chemistry at the Eastern Flanks of the Sierra Madre oriental, Veracruz, Mexico. *Journal of Geophysical Research*, Vol. 102, 1997, pp. 23329-23336.
- [2] Bravo, H., Soto, R., Sosa, R., Sanchez, P., Alarcon, J., Kahl, J. and Ruiz, B. Effects of acid rain on building material of the El Tajin archaeological zone. *Environmental Pollution*, Vol. 144 No.2, 2006, pp. 655-660.
- [3] Padilla, H.G., Belmont, R., Torres, M.B. and Baez, A. Hurricanes Pauline and Nora rainwater Chemical Composition. *Canadian Journal of Earth Sciences*, Vol. 37, No. 4, 2000, pp. 569-578.
- [4] Cerón, R. M., Padilla, G. H., Belmont, R., Torres, M. C., García, R., and Báez, P. A. Rainwater chemical composition at the end of the mid-summer drought in the Caribbean shore of the Yucatan Peninsula. *Atmospheric Environment*. Vol. 36, No. 14. 2002, pp. 2367-2374.
- [5] Bravo, H.A., Saavedra, M.I., Sánchez, P.A., Torres, R.J. and Granada, L.M. Chemical Composition of Precipitation in a Mexican Maya Region, *Atmospheric Environment*, Vol. 34, 2000, pp. 1197 - 1204.
- [6] Cerón, R.M., Cerón, J.G., Guerra, J., Núñez, E., Muriel, M. Contribution of anthropogenic and natural sources to the levels of trace elements in two coastal sites in Campeche, México. *Int. J. Sus. Dev. Plann.* Vol. 5, No. 3, 2010, pp. 282-298.

- [7] Ponette, K. C., Weathers, G., and Curran, L. M. Tropical Land-Cover Change Alters Biogeochemical Inputs to Ecosystems in a Mexican Montane Landscape. *Ecological Applications*, Vol. 20, No. 7, 2010, pp. 1820-1837.
- [8] Cerón, J., Cerón, R., Cárdenas, B., Ortínez, A., Cruz, E., Díaz, B., Carballo, C., Pérez, T., Reyes, J., Muriel, M., Guerra, J. On the dry deposition of ionic species at two National Parks located in the vicinity of power plants in Mexico. *International Journal of Energy and Environment*. Vol. 6, No. 1, 2012, pp. 31-38.
- [9] Cerón, R., Cerón, J., Carballo, C., Aguilar, C., Montalvo, C., Vargas, C., Ortínez, A., Cárdenas, B., Córdova, A., Rodríguez, M.A. Chemical characterization of dry deposition pollutants in one industrial site in Guanajuato, Mexico. *International Journal of Energy and Environment*. Vol. 6, No. 5, 2012, pp. 532-539.
- [10] Quarteri, J., Troisi, A., Guarnaccia, C., Agostino, P.D., D' Ambrosio, S., and Ianonne, G. Development of an environmental quality index related to polluting agents, *Proceedings of the WSEAS International Conference on Environment, Ecosystems and Development*, Puerto de la Cruz, Tenerife (Spain), 2009, pp. 153-161,
- [11] Tartari, G., A. Consuma, R., Balestrini, S., Valsecchi, and M. Camusso. Total atmospheric deposition measurements using an innovative dry deposition sampler. *Life chemistry Reports*, Vol. 13, 1995, pp. 159-175.
- [12] U.S. EPA, 1982. Method 150.1. Methods for chemical analysis of water and wastes. U.S. Environmental Protection Agency. Office of Research and Development, pH in water by electrometric method.
- [13] U.S. EPA, 1982. Método 120.1. Methods for chemical analysis of water and wastes. U.S. Environmental Protection Agency. Office of Research and Development, Specific Conductance in water.
- [14] NMX-AA-074-SCFI-1981, 1981. Análisis de aguas. Determinación del ión sulfato en aguas naturales, residuales y residuales tratadas.
- [15] NMX-AA-079-SCFI-2001, 2001. Análisis de aguas. Determinación de nitratos en aguas naturales, potables, residuales y residuales tratadas.
- [16] NMX -AA-073-SCFI-2001, 2001. Análisis de aguas. Determinación de cloruros totales en aguas naturales, residuales y residuales tratadas.
- [17] U.S. EPA, 1986. Método 7140 Methods for chemical analysis of water and wastes. U.S. Environmental Protection Agency. Office of Research and Development, Calcium-AA, Direct Aspiration SW-846 Chapter 3.3.
- [18] U.S. EPA, 1986. Método 7450 Methods for chemical analysis of water and wastes. U.S. Environmental Protection Agency. Office of Research and Development, MagnesiumAA, Direct Aspiration SW-846 Chapter 3.3.
- [19] U.S. EPA, 1986. Método 7610 Methods for chemical analysis of water and wastes. U.S. Environmental Protection Agency. Office of Research and Development, Potassium-AA, Direct Aspiration SW-846 Chapter 3.3.
- [20] U.S. EPA, 1986. Método 7770 Methods for chemical analysis of water and wastes. U.S. Environmental Protection Agency. Office of Research and Development, Sodium-AA, Direct Aspiration SW-846 Chapter 3.3.
- [21] Fresenius, W., K.E. Quentin, and W. Schneider, (Eds.), *Water Analysis*. Springer Verlag, Berlín, 1988, pp. 804.
- [22] Draxler, R.R., and Hess, G.D. Description of the hysplit_4 modeling system. *Noaa Tech. Memo. erl arl-224, noaa Air Resources Laboratory*, Silver Spring, 1997, pp. 1-24.