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Chemical Composition, Fluxes and Seasonal Variation of Acid Deposition in Carmen Island, Campeche, Mexico

R. M. Cerón[1*], J. G. Cerón[1], C. G. Carballo[1], C. A. Aguilar[1], C. Montalvo[1], J. A. Benítez[2], Y. J. Villareal[1], M. M. Gómez[1]

[1]Research Center on Environmental Sciences, Autonomous University of Carmen, Carmen City, Mexico; [2]EPOMEX Institute, Autonomous University of Campeche, San Francisco de Campeche, Mexico.
Email: *rceron@pampano.unacar.mx

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ABSTRACT

Two hundred and seven rain events from April to October 2012 were collected in Carmen Island, Campeche, Mexico, and the concentration of 8 major ions with the pH of the rainwater was analyzed. Chemical composition variations as a result of seasonal patterns, meteorological conditions, and mixed local and regional sources contribution were assessed. In spite of the fact that nitrate and sulfate levels were higher than background hemispheric values, the average pH values were almost neutral. Carmen Island was under the influence of both, local and long-range transported emissions. Chemical composition showed a dilution effect as a result of the monthly rainfall amount. Ca^{2+} and Na^{+} were the most abundant ions, and these ions acted as acid neutralizers and buffered the acidity of the rain, suggesting that marine and crustal aerosols played an important role in the acid-base interactions. Wet deposition fluxes obtained were compared with reference values proposed as critical loads, fluxes obtained in this study did not exceed the critical values reported for sensitive ecosystems in Europe, indicating that this site has yet enough capacity to support acidity, nitrogen and sulfur deposition. However, it is necessary to obtain reference values characteristics for tropical regions.

Keywords: Trace Elements; Acid Deposition; Deposition Fluxes; Critical Loads; Acid Rain; Campeche; Mexico

1. Introduction

Acid rain has been one of the most serious environmental problems in many locations of the world. Atmospheric constituents, and thus pollutant emissions, reach the surface of the Earth by two main processes: 1) atmospheric mechanisms in which precipitation is involved that contribute to wet deposition; 2) processes prevailing during dry periods that involve sedimentation, diffusion, impactation and interception that contribute to dry deposition. In spite of the fact that the chemical composition of wet deposition has been largely studied over the last twenty years in many places around the world, to determine the real effect of acid deposition on ecosystems it is necessary not only to know the ionic levels present in rainwater, it is also required to estimate the deposition fluxes, and the exceedances to the reference values proposed as critical loads for a specific region [1].

Wet deposition is important in coastal zones because of its episodic nature and partial transference in solution to receptors, enhancing biological interactions. Acid components and trace metals present in wet deposition may cause an eventual significant damage to the ecosystems. In Mexico, only a few studies about rainwater chemical composition have been carried out, studies about wet deposition fluxes are scarce and critical loads data are not available [2].

Potential ecological effects of acid deposition in tropical environments remain uncertain, therefore, qualitative and quantitative systematic assessments are required to determine when critical loads are exceeded, to diagnose the state of perturbation of natural sites, to assess annual trends, deposition patterns and ecosystem responses.

This study establish a solid outline of the main chemical characteristics of wet deposition in order to estimate critical loads exceedances and the potential ecological effects related with acid deposition in a Natural Area

*Corresponding author.

Protected in Campeche, Mexico.

2. Material and Methods

2.1. Site Description

This study was conducted in Carmen Island, Campeche, Mexico within the Protected Natural Area named “Laguna de Términos”. Climate in the site is sub-humid warm with rains occurring along the summer. The average annual rainfall is 1300 mm and the mean annual temperature is 27˚C. Prevailing winds blow from NE (from September to March) when the site is under the influence of cold fronts named “Nortes” and from SE during the rest of the year (from April to August) when the site is under the influence of tradewinds. Site is under the influence of maritime air, land and sea-breezes all year.

2.2. Sampling Method

Rain samples were collected from April to October 2012 by using an automated wet-dry deposition collector (Tisch Environmental Inc) located on the roof (at 3 m above the ground) of the Building of the Department of Chemical Engineering at Autonomous University of Carmen in Campeche, Mexico (**Figure 1**).

Sampler has two buckets to collect wet and dry deposition respectively. Collection buckets were washed and rinsed thoroughly with deionized water several times before sampling. Sampler has an automated lid operated by a humid sensor which moves depending on the beginning or the end of the rain event, assuring that only rainwater is collected in the wet bucket during rain events. Samples were collected in a daily basis and a rain gauge registered the precipitation amount daily. Those rain events with volume collected lower than 250 ml were neglected since samples were not enough for the chemical analysis.

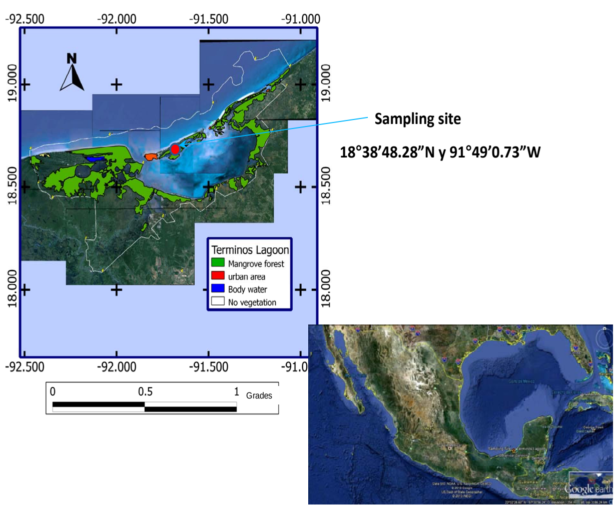

Figure 1. Location of the sampling site.

pH and conductivity were measured in site by using a precision pH meter (TERMO ORION 290) and a conductivity meter (CL 135), respectively. Surface meteorological data were obtained from a portable meteorological station (Davies Inc) operating during the whole study period.

2.3. Analytical Method

The rain samples were filtered through 0.45 µm Millipore membrane filters and stored at 4˚C until analysis.

SO_4^{2-} was analyzed by turbidimetric method [3] NO_3^- was determined by colorimetric method [4], and Cl^- was analyzed according to NMX-AA-073-SCFI-2001 [5]. Cations (Na^+, K^+, Ca^{2+} and Mg^{2+}) were analyzed by Atomic Absorption Spectroscopy (Thermoscientific ice 3000) with the Flame Technique according to EPA methods [6-9]. Ammonium was determined by molecular absorption spectrometry using the indophenol-blue method.

Repeatability was determined by analysis of samples from at least three replicate measurements. The quality assurance was routinely carried out by using ionic balance. The relative standard deviation was less than 5% for reproducibility test

2.4. Meteorological Analysis

Wind roses were constructed for each rain event with WRPLOT VIEW 6.5.2 (Lakes Environmental, 2011) To trace the origin of the air masses during the study period, backward air mass trajectories were calculated for all rain events by using HYSPLIT (Hybrid Single Particle Lagrangian Integrated) from NOAA (US National Oceanic and Atmospheric Administration).

2.5. Statistical Analysis

Pearson’s correlation analysis was applied to test the relationship among the total trace element concentrations. Factor analysis was applied to determine the factors underlying the interactions among the surveyed species. ANOVA was performed to test the differences between each element. Principal components analysis (PCA) was used to visualize the relationship among trace elements focusing on the inter-element correlation coefficients.

3. Results

3.1. Ionic Concentrations

To assure the reliability of these data and to find the possibility of the presence of other ions such as HCO_3^- and CO_3^{2-}, the ionic balance was checked out. Ionic balance obtained was acceptable, the observed ratio of cations to anions in this study was within the acceptable range, indicating that the most of ions present in rainwater samples were analyzed.

Figure 2 shows the concentrations of the major ions in rain samples collected during 2012 in Carmen Island. The concentrations of the major ionic species were in the following order (**Figure 3**):

$$Ca^{2+} > Na^{+} > SO_4^{2-} > NO_3^{-} > Mg^{2+} > K^{+} > NH_4^{+} > Cl^{-}$$

Sulfate levels (86.19 $\mu Eq \cdot l^{-1}$) exceeded almost eight times the background hemispheric values reported by Galloway *et al*. [10] for remote sites.

In addition, nitrate levels (33.94 $\mu Eq \cdot l^{-1}$) exceeded twelve times the reference values for clean atmospheres [10] This fact suggests that there was an evident anthropogenic influence from both, local and regional sources.

Calcium and sodium were the most abundant ions, suggesting a significant contribution from marine aerosol and crustal. Ammonium ion was the least abundant; it is agree with the main economical activities in the island, since agriculture is not developed in this site. Sulfate levels were higher than nitrate, indicating that this site was under the influence of regional sources.

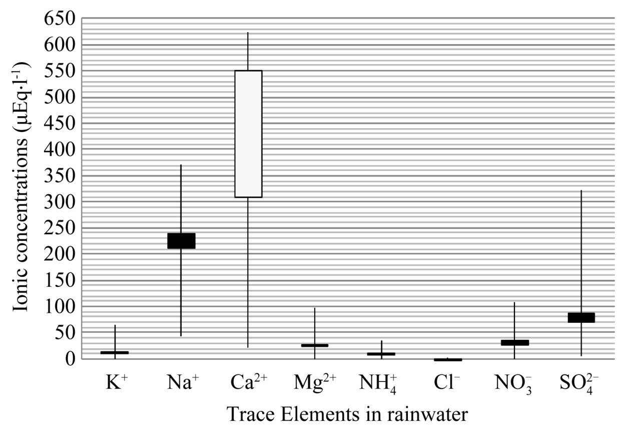

Figure 2. Concentrations of the major ions in rainwater collected in Carmen Island, Campeche, Mexico.

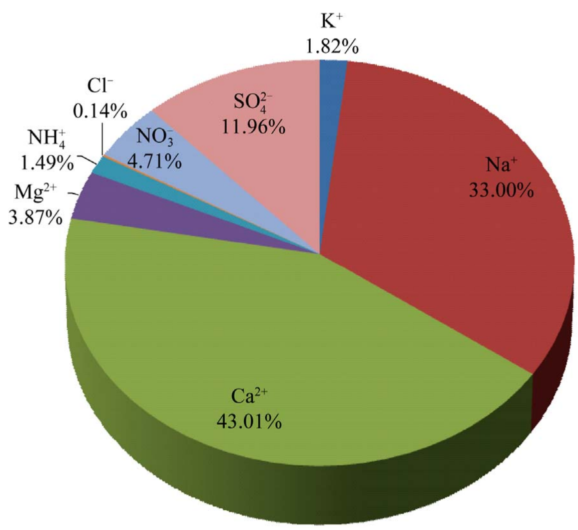

Figure 3. Ionic abundance for rain samples collected in Carmen Island, Campeche, Mexico.

3.2. Acidity of Precipitation

Figure 4 shows the frequency distribution of pH in Carmen Island during 2012. From **Figures 4** and **5**, an evident seasonal pattern was observed in pH, values are higher when rainfall increases, whereas pH decreases during the dry season (April, May). The highest values were observed during August, when hurricane "Ernesto" arrived to the island. It is agree with reported by Padilla *et al.* [11], where a relationship between hurricanes ("Paulina" and "Nora") and high pH levels was reported.

During the occurrence of hurricanes, coastal sites are under the influence of tropical maritime air that brings high amounts of sea salt that contribute to pH and sodium levels.

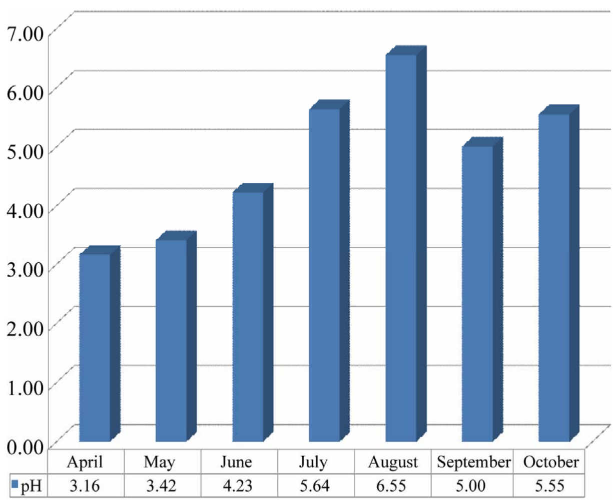

Figure 4. Monthly variation of pH in precipitation.

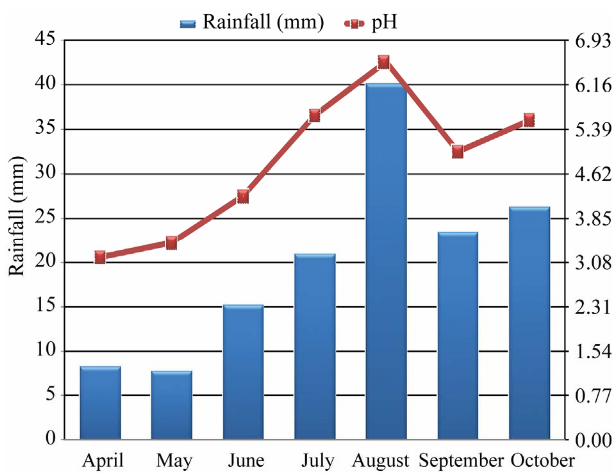

Figure 5. Monthly variation of rainfall and pH in rainwater samples collected in Carmen Island.

pH ranged from 2.02 to 7.18, with an average value of 5.69. 38.98% of the total rain events measured had pH values less than 5, 3.39% of the total samples had pH values between 5 and 5.6, and 57.63% had pH values higher than 5.6.

3.3. Dilution Effect of Rainwater on Chemistry Composition

From **Figures 4** and **5**, it can be observed that pH decreased during September and October, just when prevail wind direction shift from SE to NE, during this period the site is under the influence of cold fronts that promote the long-range transport from sources located at NE from Carmen Island (gas and oil offshore platforms located at Gulf of Mexico, where gases and particles released could produce secondary aerosols which probably were up taken to the rainwater by heterogeneous nucleation, rain-out and wash-out processes, resulting in lower pH values).

In contrast, during August, the site was subjected to tradewinds (from SE) that promoted the uptake of crustal particles from the Yucatan Peninsula, where soils are mainly calcisols, contributing to the neutralization process and resulting in higher pH levels.

The observed ionic concentrations showed a decreasing trend with increasing precipitation amount (**Figures 6** and **7**); it suggests that rainwater had a dilution effect on precipitation chemistry. Precipitation chemistry may also be partially dependent on the residence time of floating particles in the air [12].

During dry season, particles persist in the air for long periods, thereby accumulating to relatively high levels, whereas during the plenitude of the wet season where rain events with high amounts of rainfall are frequent, pollutants and aerosols in the atmosphere are under the influence of scavenging processes, thereby minimizing ion concentrations in rainwater.

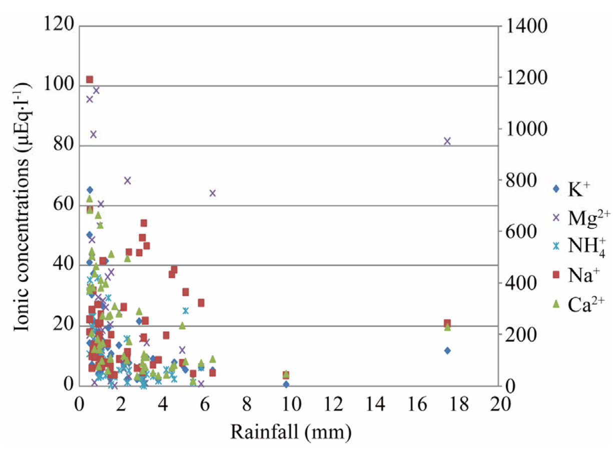

Figure 6. Relationship between rainfall amount and cation concentrations.

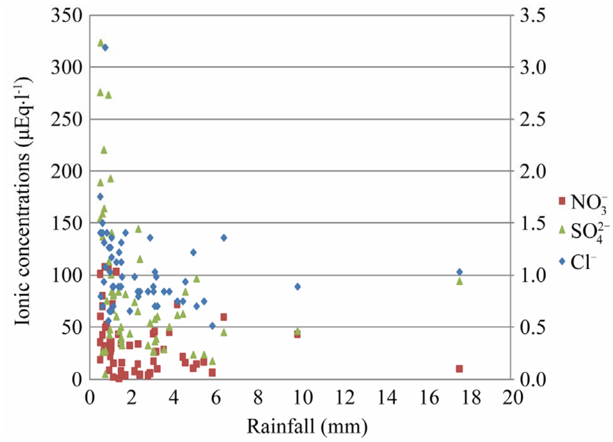

Figure 7. Relationship between rainfall amount and anion concentrations.

3.4. Temporal Trends

From **Figures 8** and **9**, it can be observed that nitrate and sulfate levels were higher during the wet season, suggesting that besides of local sources, regional sources could contribute with significant amounts of precursor gases of acid rain.

A good relationship between nitrate and sulfate was observed (**Figure 8**), being sulfate levels higher than nitrate. It suggests that these ions had a common regional source: sour gas flares from offshore platforms located at NE from this site. In spite of ammonium levels were low; from **Figure 9** it can be observed a similar trend between nitrate and ammonium, suggesting that probably these ions had a common local source: vehicular emissions.

3.5. Inter-Elemental Relationships

To investigate and get a quick overview on the possible source of ions, the correlation analysis was applied and the correlation matrix for the ion pairs is presented in **Table 1**.

The highest correlation appeared for K^+-Ca^{2+}, Ca^{2+}-Mg^{2+}, suggesting that these ionic species had a common origin in marine aerosol and crustal particles. K^+-SO_4^{2-}, NH_4^+-SO_4^{2-} and K^+-NO_3^- were good correlated. These ion pairs probably occurred in precipitation as a result of atmospheric chemical reactions [13].

Some base ions commonly found in precipitation acts as buffers for the acidity of rainwater. To estimate the neutralization capacity of each alkaline compound, the neutralization factors (NF) were calculated.

To verify which cation (Na^+, Mg^{2+}, Ca^{2+}) more frequently neutralized the acidic components in rainwater, a triangular diagram was drawn, showing the relative proportion of these three elements (**Figure 10**).

Calcium and sodium were the most abundant ions in rainwater samples, and the contribution of marine aerosol

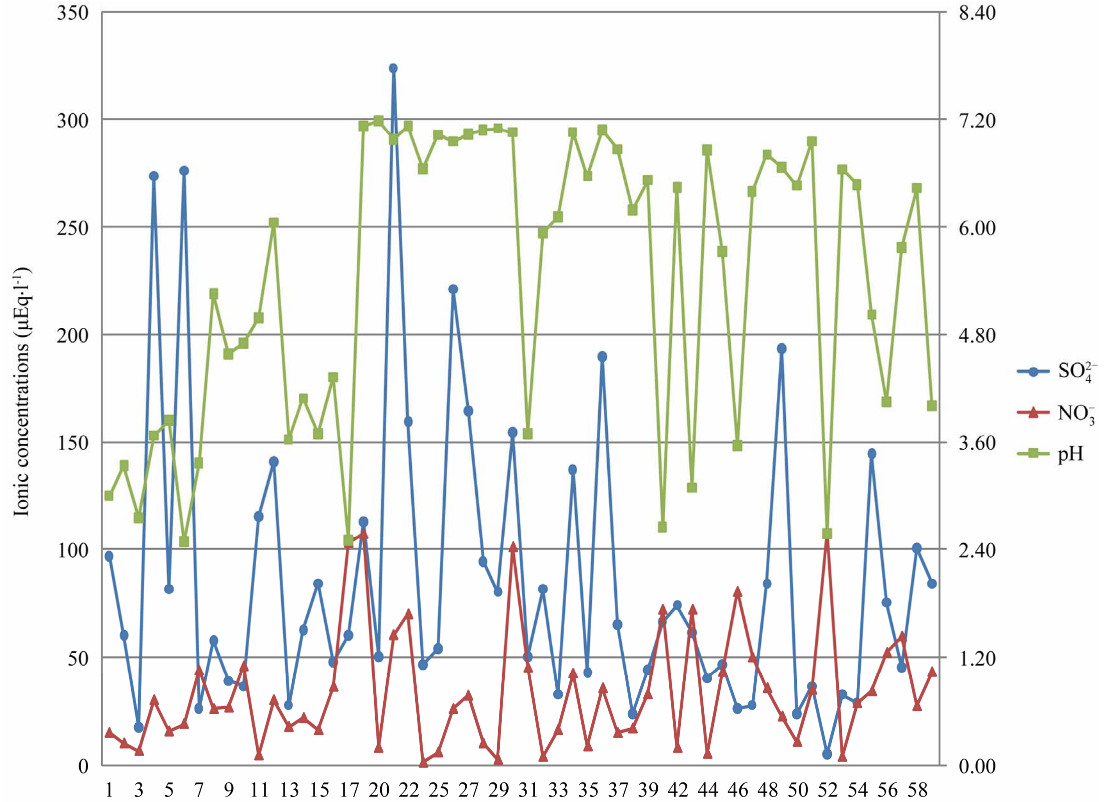

Figure 8. Temporal trends in sulfate, nitrate and pH levels in rainwater.

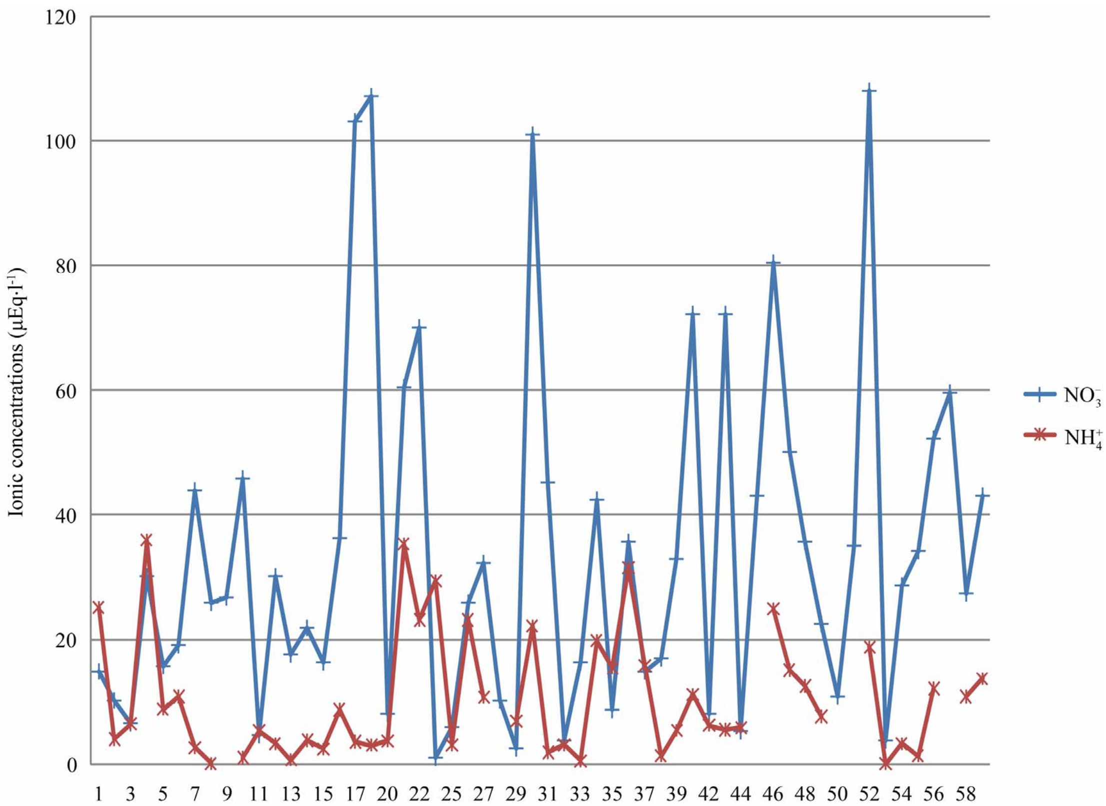

Figure 9. Temporal trends in nitrate and ammonium levels in rainwater.

Table 1. Matrix of Pearson rank correlation coefficients for major ions.

	K	Na	Ca	Mg	NH_4	Cl	NO_3	SO_4
K	1							
Na	0.39	1						
Ca	0.45	0.18	1					
Mg	0.31	0.22	0.46	1				
NH_4	0.37	0.02	0.09	0.04	1			
Cl	0.21	0.03	0.16	0.17	0.16	1		
NO_3	0.41	0.12	0.08	0.08	0.22	0.43	1	
SO_4	0.62	0.48	0.34	0.41	0.54	0.001	0.08	1

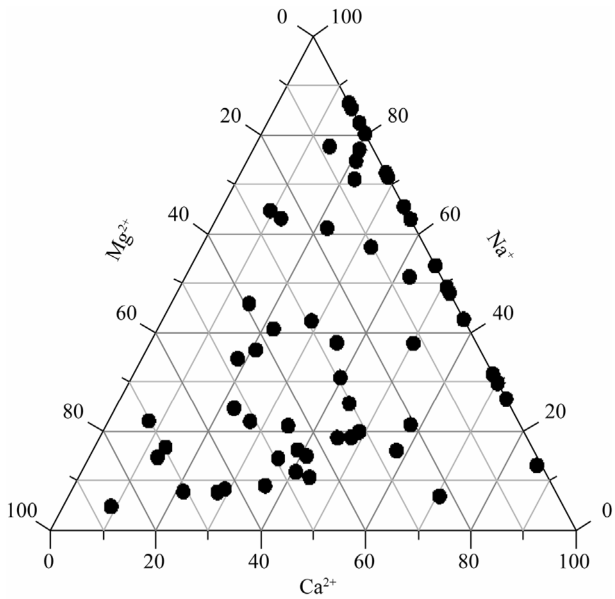

Figure 10. Triangular diagram of NF of predominant alkaline ions.

(as a result of breezes and transported maritime air masses) and crustal dust (since Carmen Island had a sedimentary origin where calcisols are dominant soil type) as a result of the prevailing meteorology was completely evident. It means that crustal and sea salt aerosols played an important role in the neutralization process.

3.6. Wet Deposition Fluxes

In spite of pH levels were almost neutral, nitrate and sulfate levels exceeded the hemispheric values reported for remote and clean atmospheres. Therefore, to estimate the real effect of atmospheric pollution on Carmen Island ecosystems, it was necessary to calculate the wet deposition fluxes.

Critical load is defined as the amount of chemical compound that one ecosystem can tolerate without suffer damages. To obtain a diagnosis of the vulnerability of the ecosystems it is necessary to compare deposition fluxes with reference values proposed as critical load in a specific region, these values are commonly reported for soils, fresh waters or sensitive species of vegetation o fauna. In Mexico, critical load data are not available, therefore, in this work; data obtained were compared with data reported in Europe [14]: 5 $kg \cdot N \cdot ha^{-1} \cdot yr^{-1}$ and 3 $kg \cdot S \cdot ha^{-1} \cdot yr^{-1}$.

Nitrogen and sulfur deposition fluxes in Carmen Island were 0.15 and 0.29 $kg \cdot ha^{-1} \cdot yr^{-1}$. In both cases, fluxes did not exceed the reference values reported for sensitive ecosystems in Europe.

However, it is necessary to estimate critical loads in this specific site, since deposition patterns, prevailing sensitive species, and ecosystem responses may be different in tropical sites than in temperate regions at mid-latitudes.

From **Figure 11**, it can be observed that K^+, Na^+, Ca^{2+}, NO_3^- and SO_4^{2-} showed the highest fluxes, suggesting that mixed local and regional sources contributed in a significant way to deposition process.

4. Conclusions

The analysis of the rain samples collected during 2012 in Carmen Island, Campeche, Mexico showed that:

1) The scavenging of pollutant and geochemical aerosols from the air, and prevailing meteorological conditions affected directly and greatly the pH and chemical composition of the rainwater in this site.

2) The major ions and their concentrations in rainwater followed the order of:

$$Ca^{2+} > Na^+ > SO_4^{2-} > NO_3^- > Mg^{2+} > K^+ > NH_4^+ > Cl^-$$

3) NO_3^- and SO_4^{2-} were the major acidifying ions in rainwater, whereas Ca^{2+} and Na^+ were the predominant basic ions in buffering and neutralizing the acidity in rainwater. Crustal and sea salt aerosols played an important role in buffering rainwater acidity.

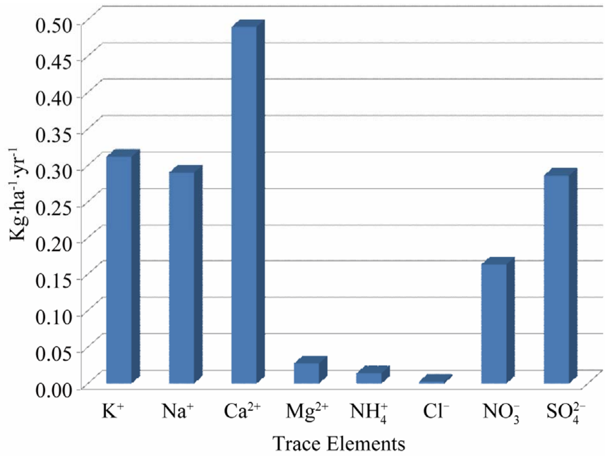

Figure 11. Wet deposition fluxes during 2012 for Carmen Island, Campeche, Mexico.

4) In spite of nitrate and sulfate levels were high and exceeded the hemispheric values reported for clean atmospheres, deposition fluxes did not exceed the critical loads reported for sensitive ecosystems in Europe.

5) It is necessary to estimate reference values of critical loads to obtain an exact diagnostic of the vulnerability of the ecosystems to current deposition fluxes of acidity, nitrogen and sulfur in this region

5. Acknowledgements

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