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Study of Trace Ions in Wet Deposition of an Industrial Site in Monterrey's Metropolitan Area, Mexico

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Abstract

The chemistry of rainwater has been subject to numerous investigations during the last two decades due to the increase of environmental problems caused by the acid deposition. The present study focuses on one aspect of air pollution, the chemical composition of wet deposition of an industrial zone. The sampling period was from March to December 2009. The station was located on the roof of the Chemistry School at the University of Nuevo León, an area in the north of Monterrey where the majority of pollution is generated. Twenty-five wet precipitation samples were collected with an automatic sampler and analyzed for pH, ions (SO_4^{2-}, NO_3^-, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, K^+) and conductivity. The results show that the average pH is higher than 5.6; the characteristics of the rainwater studied are of alkaline nature due to the values of pH found; there is an evident anthropogenic source contributing to the alkaline of rain water. In order to find possible association between ions and consequently the possible sources of pollutants correlation study was applied using the program SPSS v.12. Good correlations were found between ions SO_4^{2-} and NO_3^- along with Ca^{2+} and Mg^{2+}. The local extraction industry and surrounding aerosols might be causing of alkaline rain which may be due to the neutralization effect of particulate matter. This study represents a continuation of the studies of rainwater chemistry in the Northeast of Mexico.

Keywords

Wet Deposition, Air Quality, Monterrey, Air Pollution

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1. Introduction

The chemistry of rainwater has been subject to numerous investigations during the last two decades due to the increase of environmental problems caused by acid rain. Due to the rapid worldwide economic development and its associated increase in energy consumption, air pollution has risen important social concern in developing countries [1]-[3]. Wet deposition constitutes an important natural pathway for the removal of atmospheric pollutants. However, contamination of rainwater by atmospheric pollutants is of growing concern on both regional and global scale [3] [4].

The composition of the rainwater plays an important role in the transport of the soluble components of the atmosphere, which helps in understanding the contribution of atmospheric polluting agents from different sources. The chemical composition of the rainwater varies from one site to another and from one region to another, due to the influence of local sources.

The problems caused by acid rain are associated to ecological deterioration, deterioration of forests, acidification of lakes and grounds, sulfation of marble, affectation of antique buildings and monuments [5] [6]. Acid rain and its effects in the monument deterioration and buildings have reached alarming levels nevertheless this phenomenon is as old as the contamination itself, being able to be of natural or anthropogenic origin.

In Mexico, during the last two decades, a number of studies have been carried out on chemical composition of precipitation in different areas. The chemical composition of rainwater varies site to site and is conditioned to influence of local sources.

Baez and Belmont [7] conducted a study to compare water chemistry of heavy rain in 3 different areas of the country, the first was an urban area, the second one was an agricultural area and the third one was a coastal region. The parameters analyzed were: pH, Ca^{2+}, Mg^{2+}, NH_4^+, SO_4^{2-}, NO_3^- the highest concentrations of these inorganic ions founded in the urban and industrial areas.

Fieldwork in coastal sites was done by Bravo *et al.* [8], wet deposit from Puerto Morelos Quintana Roo was analyzed for pH, conductivity and Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} ion concentrations from April 1994 to December 1995. The mean [SO_4^{2-}] was 9.7 $l \cdot \mu Eq \cdot l^{-1}$ and for [NO_3^-] was 11.4 $l \cdot \mu Eq \cdot l^{-1}$, the volume-weighted mean pH for the period was 5.45, a major component causing the slight acidity character of rain in these zone seems to be H_2SO_4.

Cerón *et al.* [9] report a study in samples of rain from a coastal site impacted by gas and oil industry in southeastern Mexico by using air-mass back trajectories. The study was conducted from July to November 2004 San Antonio Cardenas, Campeche. The results showed that the most abundant cations were Na^+, Cl^-, Ca^{2+} were the most abundant ions under the influence of marine aerosols and particles of crustal. The NO_3^- and SO_4^{2-} exceeded the background level for marine sites. The mean pH value was 4.64 suggesting a direct anthropogenic influence over chemical composition of rainwater. From air-mass back trajectories analysis, they concluded that the main source for high levels SO_4^{2-} y NO_3^- was a sour gas recompression plant located to 10 km at NE from the study site.

Considering the importance of acid deposition and the relationship with the population growth of industrial cities, Ramírez *et al.* [10] commenced the rainwater chemistry studies in Monterrey Nuevo León, the third largest industrial city in Northeast of Mexico. The present work proposes a study to the understanding of the chemical composition of rainwater over an industrial zone during different months, and to determine the influence of diverse sources.

2. Experimental Methods

2.1. Sampling Collection and Analysis

Monterrey city, the third largest city in México, is located in the State of Nuevo León (lat 25˚40'N; long 100˚18'W). Its average altitude is 537 m above sea level, and has an area of 580.5 km^2 (**Figure 1**).

Monterrey's Metropolitan Area is the third most populous city in México, it is considered a high profile center of education, tourism and business with a population of 4,000,000 in habitants with 85% in urban areas. The Metropolitan Area involves 12 cities (municipalities): Apodaca, Escobedo, García, Guadalupe, Cadereyta, Juárez, Salinas Victoria, San Nicolás de los Garza, San Pedro Garza García, Santa Catarina, Monterrey and Santiago.

The weather patterns over the area are influenced by frontal systems coming from the north of the continent. The climate is classified as semi-arid. Monterrey has a humid subtropical climate. Its weather, though reasonably

Figure 1. Nuevo leon state map.

pleasant in spring and autumn, is hot in the summer; the average of the highest temperature reaches 35˚C (95˚F) in August, with an average low of 23˚C (74˚F). Winters are cool but not cold.

The average January high is 19˚C (67˚F) and the average low in January is 8˚C (48˚F); however, temperatures below freezing are rare. Rainfall is scarce, but more prominent during May through September. Humidity in winter can be high, although without showers. Snowfall is a very rare event. The annual average precipitation is 615 mm, temperature ranges are between 2˚C in winter and 45˚C in summer.

Industrial activities and vehicular fleet are common potential pollution sources. More than 60% of total emissions of NO_x, CO, HC and Pb are due to vehicular fleet, and 92% of SO_2 emissions are due industrial activities.

2.2. Rain Collection

Precipitation samples were collected at the Campus of the University of Nuevo León located in an urban area. Collection was carried out continually from March to December 2009 on an event basis with wet-only collectors according to ASTM-1989 and ASTM-1995 [11] [12].

The wet-only collector (TISCH ENVIRONMENTAL) had a lid that opened during rainfall and closed after rainfall had stopped. Standard operating procedures included routine checks and maintenance of wet-only precipitation samplers. All sampler surfaces that in contact with the rain were cleaned with deionized water between collections at the analytical laboratory.

2.3. Chemical Analysis

Before sampling for wet deposition, collector components were washed, soaked in distilled water for 24 hours and then rinsed with deionized water. After drying in clean enclosed areas, the components were assembled and packed individually into large plastic bags. Samples were shipped to Laboratory for analysis.

Each wet deposition sample was divided into two aliquots of 250 ml: the first one was used to determine cations, and the other was used to analyze anions, pH and conductivity.

Measurements of pH, conductivity and volume were conducted immediately on rain samples, before filtration through 0.45-μm Teflon membrane filters. pH and conductivity measurements were obtained using a precision pH meter (TERMO ORION 290) and a conductivity meter (Hanna Instrument HI 255 combined meter) according to EPA Methods 150.1 and 120.1, respectively [13] [14].

All plastic ware and glassware used to prepare standard solutions for chemical analysis (buckets, funnels, filtration system, tubing and bottles) were rigorously washed, brushed and rinsed with distilled water. All of the materials used for sample digestion were completely immersed for 24 h in a 20% ultrapure nitric acid bath (J.T. Baker, AA grade), rinsed several times with deionized water type I (Hycel) and sealed into double plastic bags. Before use, all of the material was again rinsed with deionized water. Standard solutions were prepared by dilution from certified standards (J.T. Baker). All solutions were prepared with deionized water supplied by a Milli-Q-Millipore system and the standard solutions by dissolution of the 99% purity analytical grade salts. The standard solution of the anions and cations as well as blank samples were prepared with different concentrations and assigned random numbers among real samples. The quality assurance procedures included the routine running of blanks and control samples as well as replicate samples.

Cl^-, SO_4^{2-} and NO_3^- were analyzed by Ion Chromatography (by ion chromatography Metrohm 882) using a conductivity detector with a 200-µl sample loop according to EPA Method 300.0 modified [15]. For cations analysis, samples were submitted to a digestion process carried out in 100-ml Teflon closed flasks (Cole-Parmer) using autoclave equipment. Na^+, K^+, Ca^{2+} and Mg^{2+} were analyzed by Atomic Absorption Spectroscopy (GBC 932 AA) with the Flame Technique according to EPA Methods 7770, 7610, 7140, and 7450, respectively [16]-[19]. The detection limits were calculated as three times the standard deviation of six blank samples.

2.4. Meteorological Data

Surface meteorological data were collected using portable meteorological stations (Davies Inc., http://www.davisnet.com.au/) operating during the entire study period. Wind roses were constructed for each site using Wind Rose using READY from ARL NOAA [20]. Air-mass backward trajectories were calculated for all days with rain events. These trajectories were used to trace the origin of the air masses for the studied period. Individual trajectories for each day were estimated 24 h before using HYSPLIT (Hybrid Single Particle Lagrangian Integrated) from NOAA (US National Oceanic Atmospheric Administration, http://www.arl.noaa.gov/) [21]. From the calculated backward trajectories, it was observed that the prevailing winds came from the NE.

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. Principal components analysis (PCA), a linear method for multivariate ordination, was used to visualize the relationship among trace elements at the sampling site, focusing on the inter-element correlation coefficients [22]. The sample points and variables together form a bi-plot that displays the approximate inter-variable correlations. An ANOVA test by permutation was performed to test the significance of the factors in explaining these variations. Analysis was carried out using R Statistical Software InfoStat [23].

3. Results and Discussion

A total of 25 rainwater samples were collected in 25 rain events from March to December 2009. The precipitation levels ranged from 6.3 to 79.0 mm and were compared to the data from Integral System of Monitoring System (ISEM) Meteorological Station located 10 km from the sampling site.

The volume weighted mean for pH and conductivity, are presented in **Figure 2**.

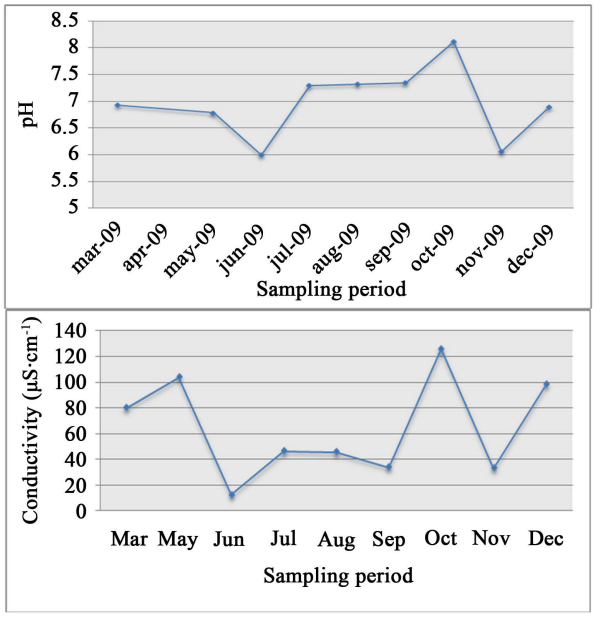


Figure 2. Volume weighted mean pH and conductivity.

For wet rain samples, pH varied from 5.99 to 8.11 with an average of 6.96. The lowest sample pH values were observed in June (summer). The highest pH values were recorded in October (autumn).

On the other hand the conductivity and ionic concentrations decreased throughout the course of the rainy season (September). The cations and anions detected and their concentrations are showing in **Figure 3**.

In **Figure 3** it is observed that ions found in highest concentrations were of Ca^{2+} followed by SO_4^{2-}, Cl^- and Mg^{2+}. The presence of alkaline substances in the atmosphere, influence the natural composition of rainwater.

During the month of October a high concentration of ionic species in the sampling site was observed, this can be a result of the presence of thermal inversion through the season coupled with low wind speed, as a result of the zone being surrounded by mountains and the hills which prevent wind circulation.

The correlation coefficients presented in **Table 1** allowed estimation of the origin of rainwater ionic species. The NO_3^- and SO_4^{2-} ions, precursors of acid rain, show significant correlation with different ions like Ca^{2+}, Mg^{2+} and K^+ ion the other hand the NO_3^- only show significant correlation with SO_4^{2-} (r = 0.990).

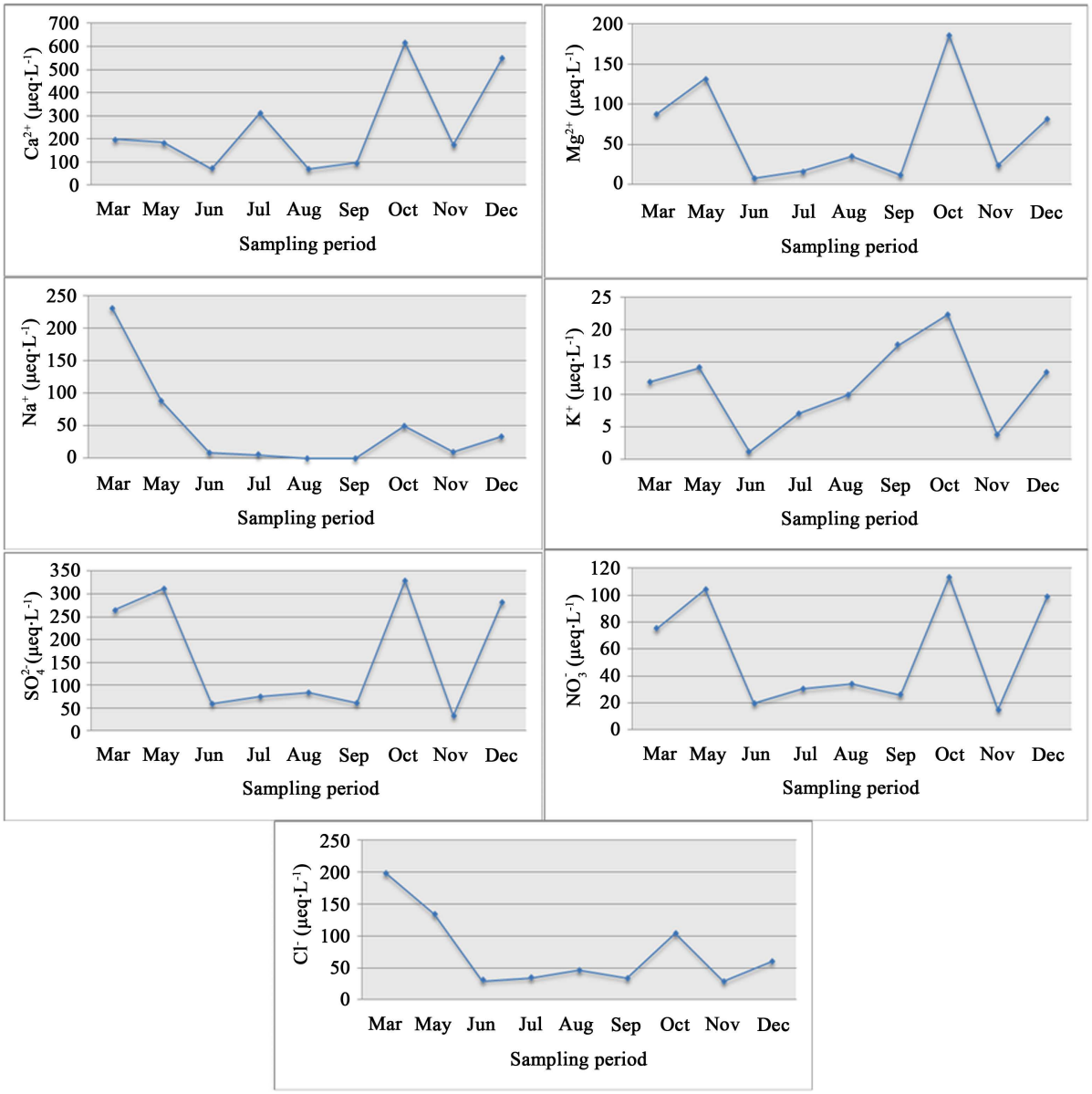


Figure 3. Cations and anions concentrations in wet rain samples.

Table 1. Pearson correlation matrix for each measured trace elements.

	Mg^{2+}	Na^{+}	K^{+}	Ca^{2+}	Cl^{-}	NO_3^{-}	SO_4^{2-}
Mg^{2+}		0.452	0.717**	0.668**	0.663**	0.932**	0.923**
Na^{+}			0.214	0.062	0.955**	0.482	0.598**
K^{+}				0.540**	0.47	0.702**	0.663**
Ca^{2+}					0.167	0.711**	0.659**
Cl^{-}						0.667**	0.757**
NO_3^{-}							0.990**
SO_4^{2-}							

**($p < 0.01$).

A significant correlation between Ca^{2+} and Mg^{2+} (r = 0.668) can be observed thus explains the variation between pH slightly acidy and slightly alkaline that were detected in the samples. SO_4^{2-} - NO_3^{-} had good correlation (r = 0.990) indicating that these ions could have sources in common, probably combustion sources. A good correlation between Cl^{-} and Na^{+} indicates that the study area was probably influenced by inputs of maritime air from marine aerosols. Ca^{2+} and Mg^{2+} showed a moderate correlation, indicating that at least partially these ions could be originated from common sources, such as soil particles and marine aerosol.

High levels of calcium suggest a significant contribution from crustal sources; this was expected because calcisols are the dominant soil type in Monterrey Area [10] [24]. High levels of chloride and sodium were found during spring season (March-May) and during the norths season (October) when winds blew from ENE (from the Gulf of Mexico) bringing maritime air enriched with these ions. This behavior has been reported for other authors, who have found an abrupt increase of sea spray droplets when wind speed increases as hurricanes approach the coast. This was also observed by Padilla *et al.* [25] in Huatulco Bay and Manzanillo, Colima in Mexico. Cerón and collaborators [21] found high levels of sodium and chloride in Monterrey after the passage of the Hurricane "Alex" in 2010. This could explain the unexpected high levels of these ions at this site, as Monterrey is not a coastal site.

The Principal Component Analysis (PCA) has been used for extracting factors controlling the major ion chemistry of atmospheric deposition and to identify the possible source of the major ions in wet atmospheric deposition [26] [27]. The data matrix of 8 variables (pH, SO_4^{2-}, NO_3^{-}, Cl^{-}, NH_4^{+}, Ca^{2+}, K^{+}, Mg^{2+}, Na^{+}) and 25 observations were used in the present factor analysis. Principal components with eigenvalues >0.7 were extracted from the principal factor matrix (**Table 2**).

pH was closely related with Ca^{2+} (**Figure 4**). This analysis shows a very close relationship between Ca^{2+}, Mg^{2+} and K^{+}, which agrees with the neutralisation effect of these cations and suggests the important role of crustal sources in the neutralisation process at this site. Na^{+} and Cl^{-} show a close relation indicating that these ions could be originated from a common source (inputs of maritime air coming from Gulf of Mexico during spring and and norths seasons). NO_3^{-} and SO_4^{2-} showed a very good relation, indicating that these ions could have common sources (combustion sources). **Table 2** shows the factor loading of the two major principal components, which represent together 83.1% of the cumulative variance percentage. High loadings were found for SO_4^{2-}, NO_3^{-}, Cl^{-}, Mg^{2+}, Na^{+} and K^{+} indicating that PC1 was influenced by anthropogenic emissions and maritime air masses coming from ENE.

Meteorological Analysis

Monthly Meteorological conditions are shown in **Table 3**. Prevalent winds blew from East-Northeast, maximum temperatures were registered during July with a mean value of 30.1˚C and minimum values of temperature were registered during December with a mean value of 12˚C. Wind speed ranked from 1.5 to 2.8 m/s as it can be observed in **Table 3**.

According to **Table 3**, in this urban site, low wind speed values were registered due to the Metropolitan Area of Monterrey is surrounded by hills and mountains which act as natural barriers that contributed to slow down

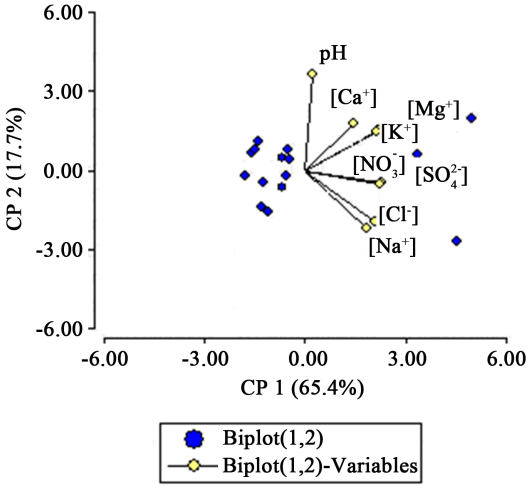


Figure 4. Principal component analysis: Ordination biplot for wet deposition samples collected at the Metropolitan Area of Monterrey.

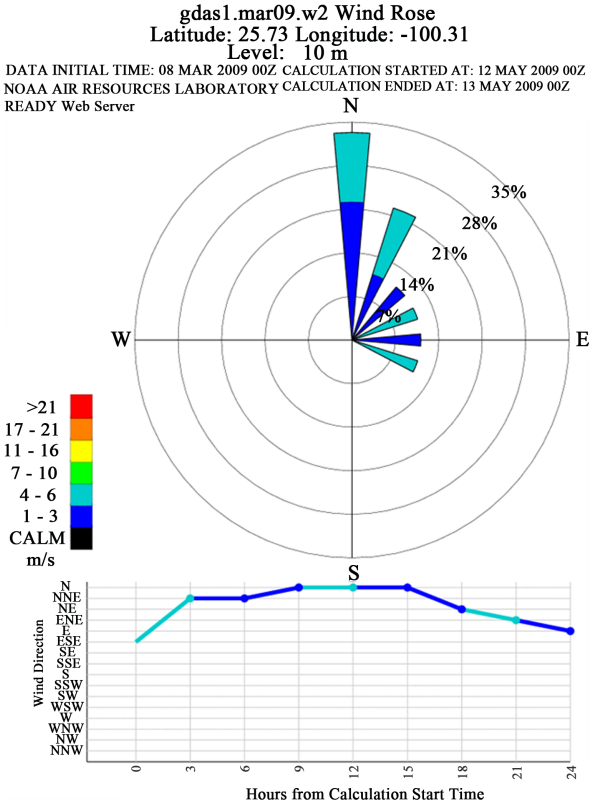
Table 2. Factor loading of the principal components for the data set of wet deposition in the study site using PCA.

Variables	CP 1	CP 2
pH	0.11	**0.79**
$[SO_4^{2-}]$	**0.97**	−0.09
$[NO_3^-]$	**0.94**	−0.11
$[Cl^-]$	**0.88**	−0.42
$[Ca^{2+}]$	0.62	**0.39**
$[Mg^{2+}]$	**0.91**	0.33
$[Na^+]$	**0.77**	−0.47
$[K^+]$	**0.91**	**0.32**

Table 3. Prevalent meteorological conditions in the study site during the sampling period.

Month	Sampling total volume (mm)	Mean Temperature (˚C)	Mean Wind Speed (m/s)	Wind Direction Frequency
March 2009	6.3	19.8	2.2	ENE
April 2009	0.0	24.7	2.5	ENE
May 2009	16.4	26.7	2.5	ENE
June 2009	12.0	28.6	2.8	E
July 2009	56.9	30.1	2.6	E
August 2009	21.0	29.2	2.7	E
September 2009	79.0	24.9	2.0	NE
October 2009	16.2	22.4	1.8	ENE
November 2009	26.2	18.4	1.5	NNE
December 2009	24.5	13.0	1.6	NE

wind flux. During summer (July-September) it can be observed an increase in the wind speed values; these conditions could contribute to high air pollutants dispersion. During the dry season (February-May), the influence of anti-cyclonic systems in this area causes a great atmospheric stability with a minimum dispersion and an increase in the air pollutants concentrations. In order to know the origin of air masses, wind roses and 24 h back trajectories of air masses were constructed for each sampling day. This analysis let us to know the probable origin of the air pollutants present in wet deposition samples and the location of the possible sources. **Figures 5(a)-(i)** shows typical wind roses for each month and it can be observed that most of the time, winds were blowing from E-NE.


gdas1.mar09.w2 Wind Rose
Latitude: 25.73 Longitude: -100.31
Level: 10 m
DATA INITIAL TIME: 08 MAR 2009 00Z CALCULATION STARTED AT: 12 MAY 2009 00Z
NOAA AIR RESOURCES LABORATORY CALCULATION ENDED AT: 13 MAY 2009 00Z
READY Web Server
N
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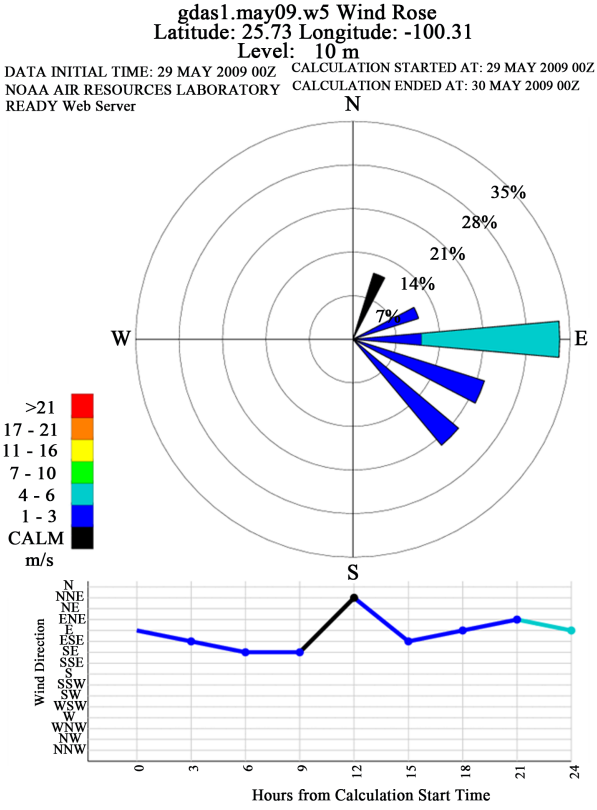
S
W
35%
28%
21%
14%
7%
>21
17 - 21
11 - 16
7 - 10
4 - 6
1 - 3
CALM
m/s
Wind Direction
Hours from Calculation Start Time

(a)


gdas1.may09.w5 Wind Rose
Latitude: 25.73 Longitude: -100.31
Level: 10 m
DATA INITIAL TIME: 29 MAY 2009 00Z CALCULATION STARTED AT: 29 MAY 2009 00Z
NOAA AIR RESOURCES LABORATORY CALCULATION ENDED AT: 30 MAY 2009 00Z
READY Web Server
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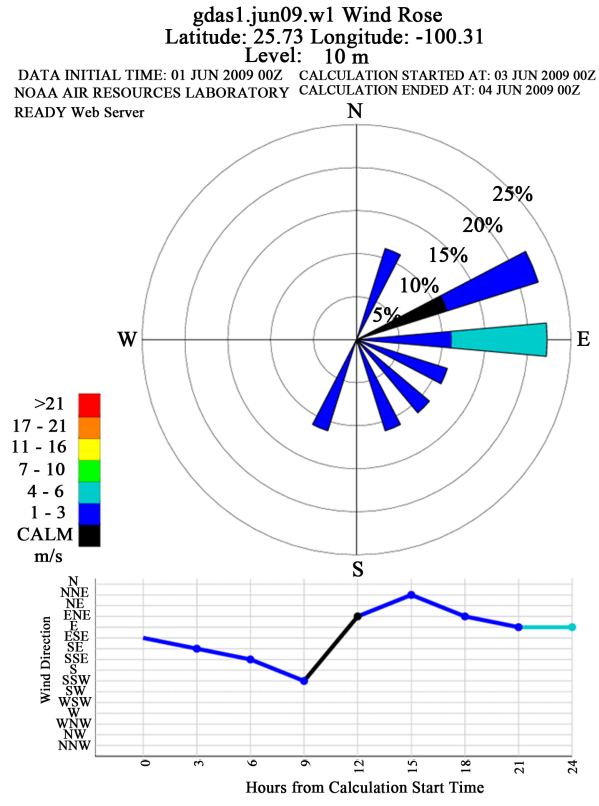
1 - 3
CALM
m/s
Wind Direction
Hours from Calculation Start Time

(b)


gdas1.jun09.w1 Wind Rose
Latitude: 25.73 Longitude: -100.31
Level: 10 m
DATA INITIAL TIME: 01 JUN 2009 00Z CALCULATION STARTED AT: 03 JUN 2009 00Z
NOAA AIR RESOURCES LABORATORY CALCULATION ENDED AT: 04 JUN 2009 00Z
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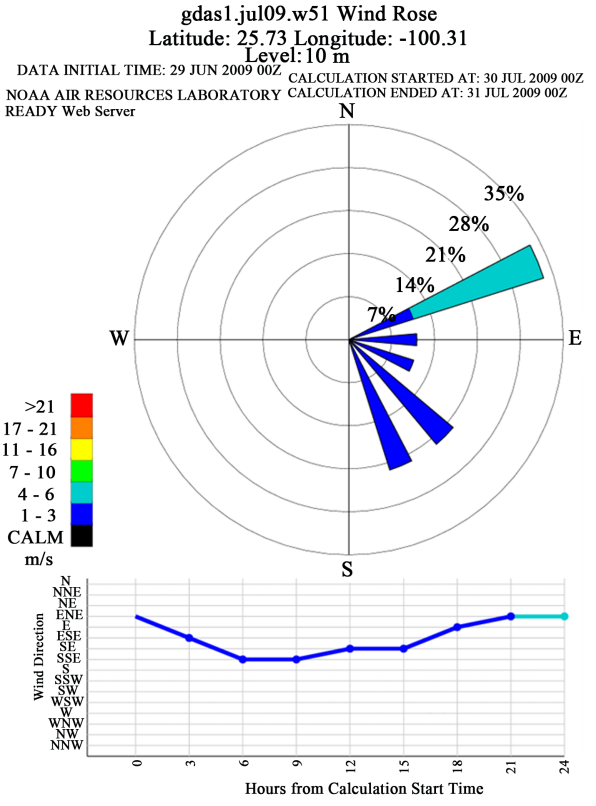
Wind Direction
Hours from Calculation Start Time

(c)


gdas1.jul09.w51 Wind Rose
Latitude: 25.73 Longitude: -100.31
Level: 10 m
DATA INITIAL TIME: 29 JUN 2009 00Z CALCULATION STARTED AT: 30 JUL 2009 00Z
NOAA AIR RESOURCES LABORATORY CALCULATION ENDED AT: 31 JUL 2009 00Z
READY Web Server
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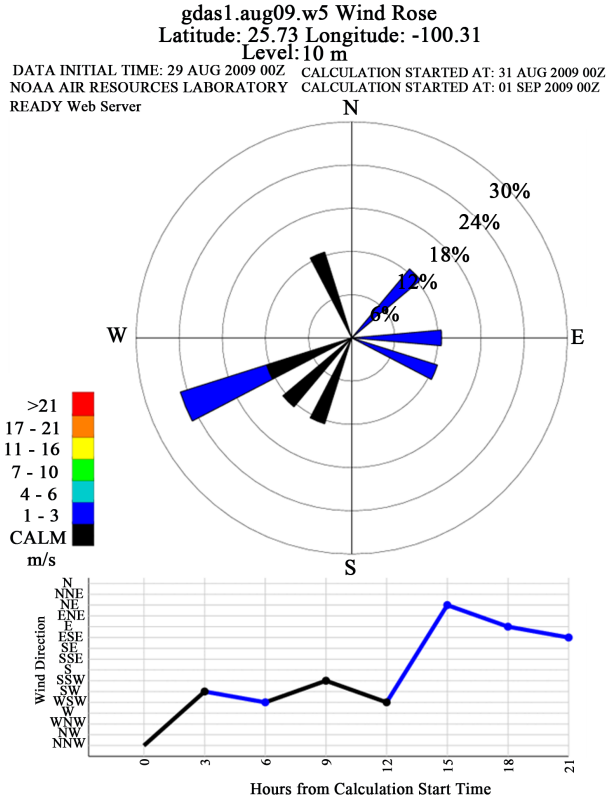
Wind Direction
Hours from Calculation Start Time

(d)


gdas1.aug09.w5 Wind Rose
Latitude: 25.73 Longitude: -100.31
Level: 10 m
DATA INITIAL TIME: 29 AUG 2009 00Z
NOAA AIR RESOURCES LABORATORY
READY Web Server
CALCULATION STARTED AT: 31 AUG 2009 00Z
CALCULATION STARTED AT: 01 SEP 2009 00Z
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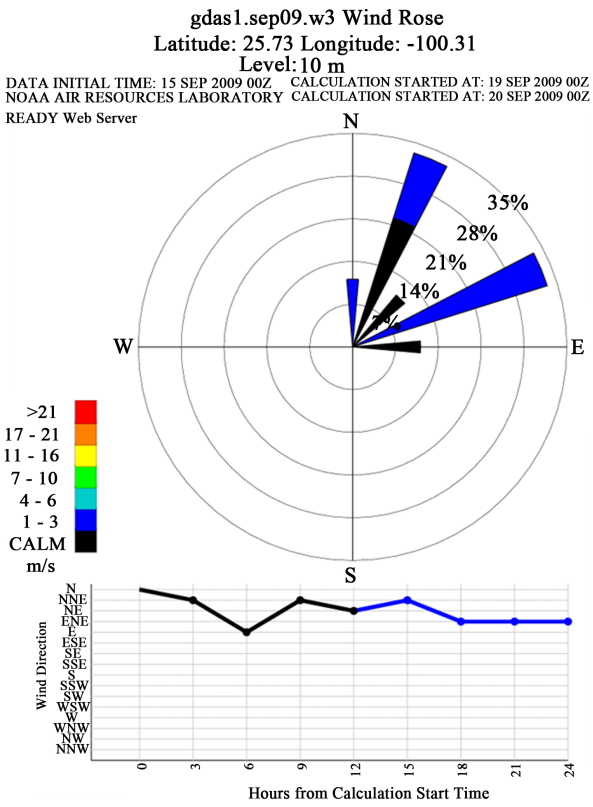
m/s
Wind Direction
Hours from Calculation Start Time

(e)


gdas1.sep09.w3 Wind Rose
Latitude: 25.73 Longitude: -100.31
Level: 10 m
DATA INITIAL TIME: 15 SEP 2009 00Z
NOAA AIR RESOURCES LABORATORY
READY Web Server
CALCULATION STARTED AT: 19 SEP 2009 00Z
CALCULATION STARTED AT: 20 SEP 2009 00Z
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7 - 10
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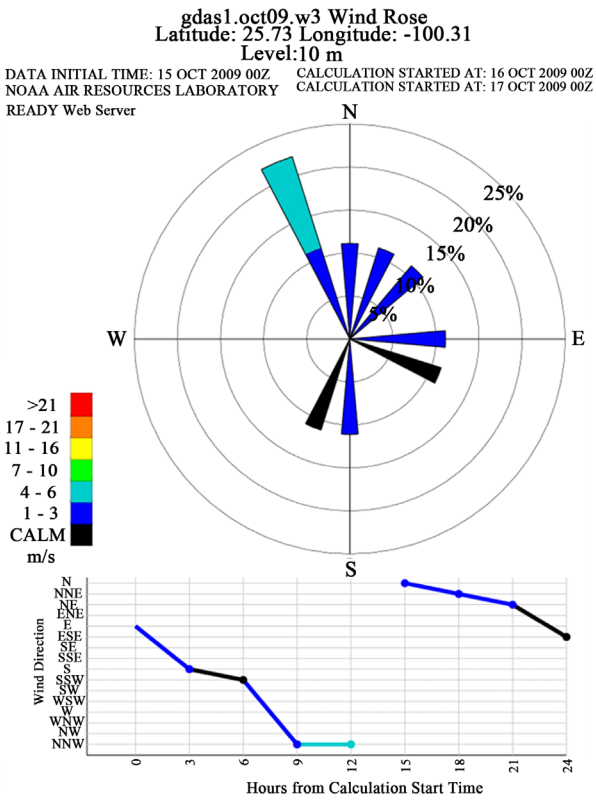
CALM
m/s
Wind Direction
Hours from Calculation Start Time

(f)


gdas1.oct09.w3 Wind Rose
Latitude: 25.73 Longitude: -100.31
Level: 10 m
DATA INITIAL TIME: 15 OCT 2009 00Z
NOAA AIR RESOURCES LABORATORY
READY Web Server
CALCULATION STARTED AT: 16 OCT 2009 00Z
CALCULATION STARTED AT: 17 OCT 2009 00Z
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CALM
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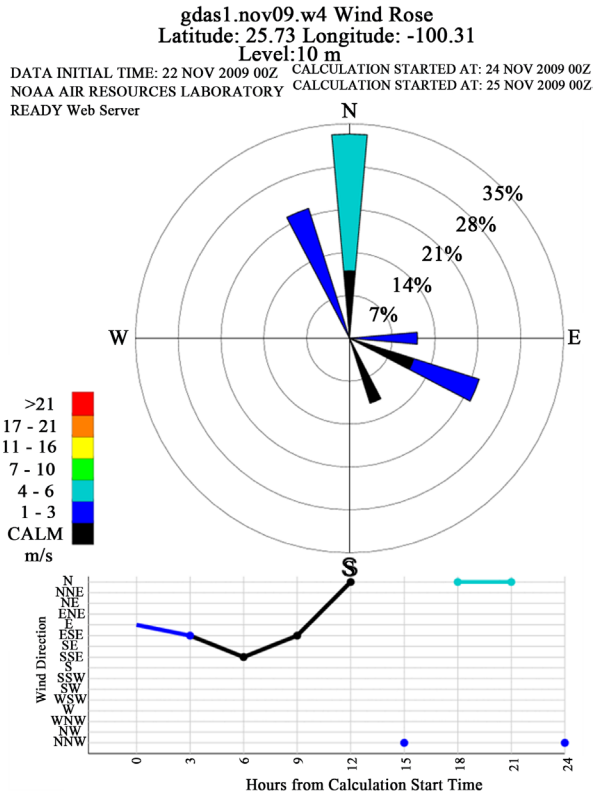
Wind Direction
Hours from Calculation Start Time

(g)


gdas1.nov09.w4 Wind Rose
Latitude: 25.73 Longitude: -100.31
Level: 10 m
DATA INITIAL TIME: 22 NOV 2009 00Z
NOAA AIR RESOURCES LABORATORY
READY Web Server
CALCULATION STARTED AT: 24 NOV 2009 00Z
CALCULATION STARTED AT: 25 NOV 2009 00Z
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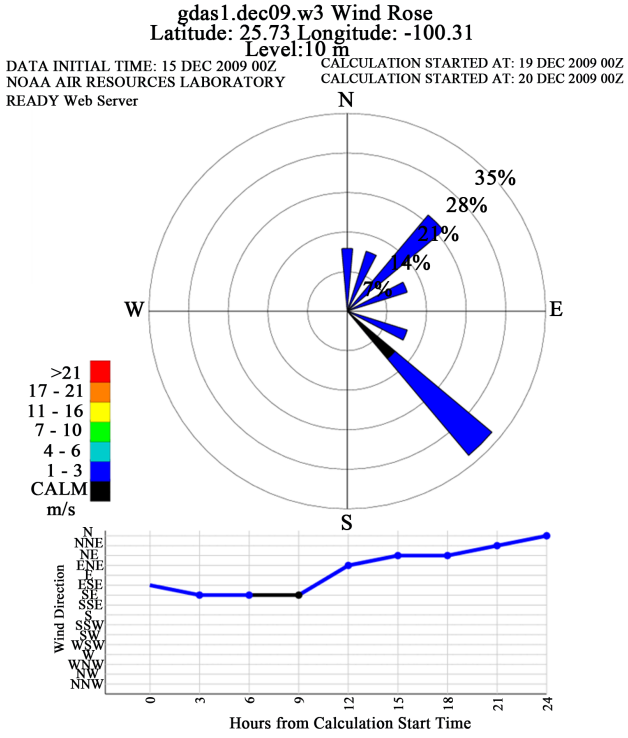
7 - 10
4 - 6
1 - 3
CALM
m/s
Wind Direction
Hours from Calculation Start Time

(h)



(i)

Figure 5. Typical wind roses for each month during the sampling period. (a) March 2009 (12/03/2009); (b) May (29/05/2009); (c) June (3/06/2009); (d) July (30/07/2009); (e) August (31/08/2009); (f) September (19/09/2009); (g) October (16/10/2009); (h) November (24/11/2009); (i) December (19/12/2009).

According to the meteorological analysis, sources located at the East -Northeast of the study site could influence the air pollutants concentrations (Apodaca and Esobedo municipalities) in a local scale and from the Gulf of Mexico in a regional scale). In Apodaca is located the Monterrey International Airport, as well as numerous industries involved in manufacturing of industrial lubrication additives, fertilizers, insecticides, steel products and so on. Also important roads with high vehicular traffic such as Apodaca-Dr Gonzalez highway, Monterrey -Laredo highway and Monterrey-Miguel Aleman road. In the municipality of Escobedo , Nuevo Leon numerous manufacturing and service industries, agricultural and livestock activities, as well as the General Mariano Escobedo Industrial Park (one of the most important in the region) are located. All these sources (vehicular and industrial) could contribute to the air pollutants levels found in this site.

4. Conclusion

A whole study of the chemical composition rainwater over an industrial zone located at the northeast of Mexico was carried out from March to December, 2009. A seasonal variation was found and highest values were found for Ca^{2+} and SO_4^{2-}. During the autumn season (October), the influence of a thermal inversion was evident, this condition caused that all the ionic species concentrate in the atmosphere of the study site due to low wind speed and a poor dispersion. During spring (March to May) and during norths season (October) high values of sodium and chloride were found, probably due to inputs of maritime air coming from the Gulf of Mexico. Mean pH value was within the alkaline range, it could be explained due to the presence of a cement industry, whose emissions could neutralize sulfate and nitrate ions in the study site, mainly during the autumn season. Calcium levels were high suggesting a significant contribution from sources of crustal material (re-suspended soil particles: calcisols are the dominant soil type in the study area; and emissions from a cement industry). Influence of sources located at Apodaca and Mariano Escobedo municipalities (a local scale) and from the Gulf of Mexico (at a regional scale) located at the East-Northeast (ENE) was evident. Mean nitrate and sulfate values are comparable to those obtained in other mega cities around the world, considering that Monterrey city is the third largest city in

Mexico with the corresponding increase in the fuel consumption, industrial development and vehicular fleet, resulting in high emissions of SO_2 and NO_x, forming high concentrations of acids in the study site.

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