

IDENTIFICATION OF ION SOURCES IN RAINWATER OF A COASTAL SITE IMPACTED BY THE GAS AND OIL INDUSTRY IN THE SOUTHEAST OF MEXICO

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ABSTRACT

The purpose of this research was to study the chemical composition of rainwater to assess the impact of marine aerosol and anthropogenic emissions by using back air-mass trajectories. Fieldwork was done from July to November 2004, in a coastal site probably impacted by gas and oil industry in Campeche, Mexico: San Antonio Cardenas.

Na⁺, Cl⁻, and Mg²⁺, were the most abundant ions, being sea-salt aerosol their unique source. A significant portion of K⁺ and Ca²⁺ originated from non-sea-salt sources; and the sulphate excess exceeded the background level reported for remote marine sites, suggesting that besides of marine aerosol, there was a significant contribution of SO₄²⁻ from anthropogenic sources. NO₃⁻ concentrations in San Antonio Cardenas exceeded the background level reported for coastal sites with minimal anthropogenic influence and showed a significant correlation with SO₄²⁻, suggesting a common source. Agricultural practices are null, for this reason NH₄⁺ levels were low.

Mean pH value was 4.64, this acidity showed a good correlation with SO₄²⁻ and NO₃⁻ levels, and with the local meteorology. A sour gas recompression plant located 10 km at NE from San Antonio Cardenas was identified as the main source of this strong acidity.

KEYWORDS: Rainwater chemistry, marine aerosol, coastal rainwater composition, Mexico.

INTRODUCTION

Atmospheric deposition of trace elements derived from natural, geochemical and anthropogenic sources, is the main way for up taking of elements into aquatic systems. Pollutants released to the atmosphere as gases and aerosols from human activities are transported and deposited several kilometres away from their source; being removed by dry or wet deposition, with its consequences over living organisms in the ecosystems (Steinnea, 1990).

The chemistry of trace elements in the atmosphere is influenced by different sources of gases and aerosols, therefore, some elements present in the atmosphere, can be originated in natural (biogenic emissions), geochemical (like marine aerosol and crustal) or anthropogenic sources.

Background levels are useful tools when a diagnosis about the possible environmental impact caused in a specific zone is required, establishing a comparison when reference laws or standards of non-criteria pollutants are not available. Commonly, these values are established for remote areas with a minimal anthropogenic influence, by this way, it is possible to accomplish a diagnosis of impact caused by non criteria pollutants. In fact, research on precipitation chemical composition of probably impacted zones, allow us to identify, first if there is an acidity problem, and second, to identify the main sources contributing to this acidity by means of correlation between elements, local meteorology and back air-mass trajectories. Therefore, to assess the impact from geochemical and anthropogenic sources (marine aerosol, volcanic activity, and crustal) on chemical composition of rainwater in a specific region, knowledge of the background levels of wet deposition is required.

An important feature of the environmental assessment studies is the identification of all possible sources (biogenic, geochemical, natural, and anthropogenic) to determine their relative contribution to the mineralization of rainwater. Human activities have an important effect on global and regional cycles of most of trace elements (Nriagu and Pacina, 1988); however, geochemical sources may also have an important effect (Duce *et al.*, 1991). For this reason, it is essential to discuss the origin of trace elements to identify their main sources using tracers. A method commonly used by geochemists to relate an element in rainwater with its geochemical source, involves the use of a tracer derived from the specific reference source. Therefore, to assess the enrichment of an element relative to its source, it is necessary to define the excess (fraction with an origin different from reference source) in terms of an enrichment factor (EF). The most important geochemical sources contributing to rainwater mineralization in coastal and marine sites, where volcanic activity is not present, are marine aerosol and crustal, where sodium or chloride, and aluminium, are the main tracers, respectively (Chester, 1990).

It has been reported that only nine ions (Cl^- , Na^+ , SO_4^{2-} , Mg^{2+} , Ca^{2+} , K^+ , Ca^{2+} , Br^- and F^-) are present at high enough concentrations to be considered as the main components of seawater. Seawater chemical composition is expressed as the ratio of each element relative to chloride ion concentration (Culkin and Cox, 1966; Morris and Riley, 1966). Sea salt aerosols are produced as bubbles burst at the oceanic surface, and this is the dominant source for elements such as Na^+ , Mg^{2+} , Ca^{2+} , K^+ , Cl^- and Br^- in the marine atmosphere. The physical characteristics and chemical composition of marine aerosol determine the main scavenging processes involved (heterogeneous nucleation and wash-out), which influence in a significant way on rainwater chemical composition (Pruppacher and Klett, 1997). The relative proportions of these elements in atmospheric particles and in rain in marine regions generally are similar to those in bulk seawater. Although the ocean is the major source of atmospheric particulate material in remote coastal and marine sites, the quantity of sea salt aerosols produced and re-deposited in the oceans each year is still quite uncertain (Arimoto *et al.*, 1985).

Arimoto *et al.* (1985) reported that in some coastal and marine sites, the atmospheric concentrations of these elements are substantially higher than those expected from the dispersal of mineral aerosol or the injection of bulk seawater into the atmosphere. To explain this discrepancy, several theories related to an enrichment process have been proposed. According to the chemistry of aerosols, the recycling of components is the most important process occurring at the air-sea interphase (microlayer). This microlayer is a complex marine environment where significant geochemical processes and the air-to sea exchange of components take place, and it has physical, chemical and biological properties different from seawater. Chester (1990) reports an enrichment of the microlayer related to seawater, so the different components in the microlayer are available for an exchange through air-sea interphase. This process may significantly affect the chemistry of marine aerosol and therefore the rainwater chemical composition. Thus, this relative enrichment in non-remote coastal and marine sites can be explained from two sources: enrichment due to surface microlayer on the ocean, or the contribution of sources different from the sea salt aerosol, like anthropogenic sources (Chester, 1990).

To assess the significance of sea surface as a source of aerosols, commonly, enrichment factors (EF) are used as effective tools (Chester, 1990). The enrichment factors (EF) for each ion relative to sea salt are calculated as follows:

$$EF(X) = \frac{(X/Cl^-)_{rain}}{(X/Cl^-)_{sea\ water}} \quad (1)$$

where $(X/Cl^-)_{rain}$ and $(X/Cl^-)_{sea\ water}$ are the mass ratios of substance X relative to Cl^- in rain and in seawater, respectively. An EF approaching to unity suggests that the trace element is originated in sea-salt (no enriched elements), whereas an EF greater than unity, suggests that a significant portion of the trace element has origin in a source different than sea-salt (enriched elements).

The excess of a constituent in a rainwater sample represents an increase of the element upon the levels expected from seawater and crustal particles. In the most of urban and industrial sites, trace constituents atmospheric concentrations such as sulphate, zinc, cadmium and lead are significantly greater than those expected from the dispersion process of marine aerosol and mineral dust (crust) (Steinnea, 1990). Human activities have been implicated as the cause of the enrichment for some of these elements, and often they are referred as enriched elements or excess, in this case, local or regional meteorology data are necessary to identify the main responsible sources (Arimoto *et al.*, 1985).

Bravo *et al.* (2000) found a significant contribution of nitric and sulphuric acids to rain acidity in the Gulf of Mexico, resulting from an air mass movement to the west. Likewise, Parungo *et al.* (1990) reported an enrichment factor value of 10 for SO_4^{2-} , as well as, NO_3^- high levels in the Gulf of Campeche. However, Muriel *et al.* (1998) concluded that according to meteorological conditions prevailing in that zone, air pollutants released from offshore platforms for gas and oil exploration and production might be transported and deposited on Tabasco coastline. On the other hand, Ahmed *et al.* (1990) report that petroleum facilities in the east coast of Arabian affect sulphate and nitrate levels in rainwater, where both contribute in equal proportion to the acidity.

This work had as a main objective to study rainwater chemistry, during the rainy season in 2004, at a coastal site apparently impacted by the gas and oil industry (San Antonio Cardenas, located in Campeche, Mexico).

EXPERIMENTAL METHOD

Sampling site description

The Development of petroleum industry has been accelerated in the last years in the region of Atasta-San Antonio Cardenas located in Campeche, Mexico. In this region, there is a gas recompression plant, where sour gas from offshore platforms is sent to petrochemical facilities to be processed. The safety system of this recompression plant has four flare burners that use sour gas as fuel, releasing pollutants to the atmosphere.

San Antonio Cardenas is into the Natural Reserved Area named "Laguna de Terminos" (Figure 1). This site is located in Atasta Peninsula at $18^\circ 37'$ N latitude and $92^\circ 13'$ W longitude, 40 km away from Carmen Island and 10 km away from recompression plant of sour gas in Atasta.

Mean annual temperature in this region is of $27.2^\circ C$, with rains occurring along the summer. Mean annual pluvial precipitation is of 1500 mm yr^{-1} , and prevailing winds blow from NE and SE almost all the year with average velocities of 1.4 m s^{-1} .

From several years ago, Campeche community, Natural Reserved Area committee and citizens of Atasta and San Antonio Cardenas have shown a constant concern about corrosion effects on their houses' roofs (mainly made of metallic sheets), and also about other possible effects on mangrove and fisheries from Pom-Atasta-Terminos lagoon system.

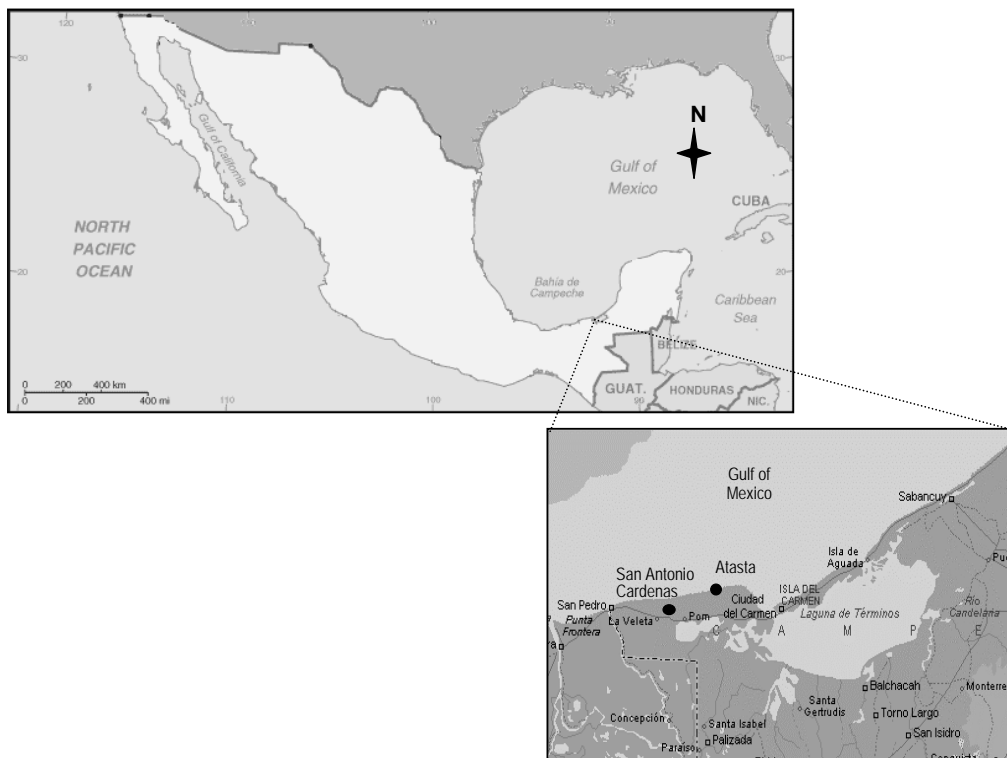


Figure 1. Map of Mexico showing the location of the sampling site (San Antonio Cardenas)

Sampling and analysis methodology

Samples were collected using an automatic wet/ dry deposition collector (Tisch, Inc) from 1 June to 30 October 2004. Two 3.5 gallon HDPE (high density polyethylene) buckets were used as receptacles for wet and dry deposition, only wet deposition samples (precipitation) were considered in this research. The wet/dry deposition collector was installed on the roof of a building in Technological University of Campeche. After recovering rainwater samples, they were preserved with chloroform and kept at 4° C. Samples with a volume smaller than 250 ml or containing some dirty, were discarded.

Samples were filtered using a Kontes Ultra-Ware System, consisting of a vacuum pump and Phenomenex membranes. Chloride, nitrate and sulphate were analysed by non-suppressed ion chromatography with an Alltech chromatograph. For ammonium ion, an UV-Visible spectrophotometer (Perkin Elmer) was used for its determination by a colorimetric method. Na^+ , K^+ , Ca^{2+} and Mg^{2+} were analyzed with a GBC atomic absorption spectrophotometer. The detection limits in mg l^{-1} were: 0.22, 0.04, 0.17, 0.002, 0.006, 0.01, 0.002 and 0.042 for SO_4^{2-} , Cl^- , NO_3^- , Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and NH_4^+ , respectively. pH and conductivity were also measured by using a potentiometer (HACH model EC10) and an YSI 3200 conductivity instrument. Ion balance and conductance percent differences of data were used for quality assurance; field blanks were analyzed to guarantee the cleanness of the sampling material.

Meteorology

Southeast of Mexico shows two climatic periods well defined, a dry season (from November to May) and a rainy season (from June to October). Sampling period occurred during summer and autumn; therefore it was not possible to assess seasonal patterns for each ionic component present in the rainwater of the sampling site. Surface winds data were not available. In this case, back-air mass trajectories were used to identify the possible sources different from marine aerosol or mineral dust (crust) contributing to the excess levels or enrichment of ionic components in rainwater. The specific location of the site, the date and time of each precipitation event were provided to the NOAA Hybrid Single Particle Lagrangian

Integrated Trajectory (HYSPLIT) model to generate 24-hour back trajectories. Example of typical HYSPLIT trajectory is illustrated in Figure 2.

From figure 2, it can be observed that prevailing winds during sampling period had an east component, mainly NE. San Antonio Cardenas was influenced by local anthropogenic sources located at NE from sampling site (Sour gas recompression plant).

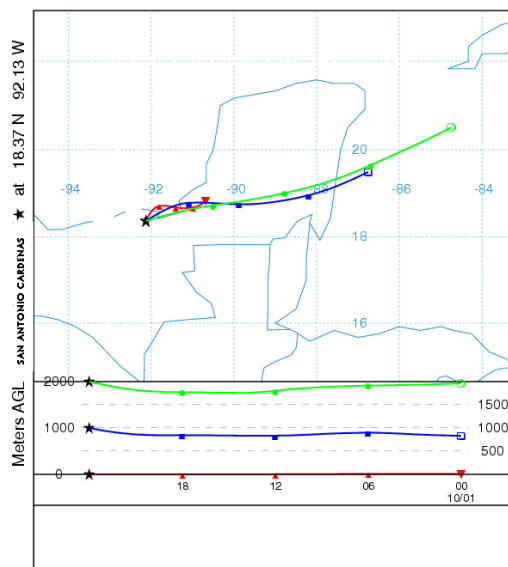


Figure 2. Illustration of a typical 24-hour air mass back trajectory for San Antonio Cardenas at three different heights: 0, 1000 and 2000 m above ground level (AGL)

RESULTS AND DISCUSSION

Ionic abundance obtained in San Antonio Cardenas is presented in Table 1. The most abundant cations were Na^+ and Ca^{2+} , probably due to influence of marine aerosol and crust (because of calcareous soils are abundant in the Southeast of Mexico). NH_4^+ levels were very low because there are not agricultural practices in this region. Most abundant anions were Cl^- (due to influence of sea-salt aerosol) and SO_4^{2-} . High sulphate levels in San Antonio Cardenas suggest an evident influence of sources whose origin is different from marine aerosol.

Table 2 shows the volume-weighted mean concentrations (VWM) for all collected samples in San Antonio Cárdenas and in Table 3 are shown the volume-weighted mean concentrations of precipitation in some marine remote sites of the world (Casimiro *et al.*, 1991; Galloway *et al.*, 1982; Galloway *et al.*, 1983; Junge, 1960; Rhode and Grandell, 1972; Szepesi and Fekete, 1987). In addition, Table 4 shows the volume-weighted mean concentrations for non-remote coastal and marine sites in the Caribbean Sea reported by other researchers (Cerón *et al.*, 2002; Bravo *et al.*, 2000; Clark *et al.*, 1998; Eklund *et al.*, 1997; Hendry *et al.*, 1990; Mc Dowell *et al.*, 1990). According to Table 2, it can be observed that the rainwater chemical composition in San Antonio Cardenas (Na^+ , K^+ , Ca^{2+} , Mg^{2+} , and Cl^-) was similar to that reported in Table 4, except for nitrate and sulphate whose levels were higher than those reported for coastal and marine remote sites (Table 3).

Table 1. Ionic abundance obtained in the rainwater of San Antonio Cardenas

Ions	San Antonio Cardenas
Cations	$\text{Na}^+ > \text{Ca}^{2+} > \text{K}^+ > \text{Mg}^{2+} > \text{NH}_4^+ > \text{H}^+$
Anions	$\text{SO}_4^{2-} > \text{Cl}^- > \text{NO}_3^-$

Table 2. Volume-weighted mean and median concentrations, minimum and maximum values, (mg l^{-1}); enrichment factors and detection limits for wet precipitation collected in San Antonio Cardenas

N= 26									
	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻	NH ₄ ⁺	H ⁺
Mean	2.47 ± 2.74	0.37 ± 0.24	1.06 ± 0.66	0.33 ± 0.16	3.85 ± 1.90	3.84 ± 4.39	2.47 ± 1.26	0.09 ± 0.08	0.09 ± 0.21
Median	1.70	0.36	0.99	0.33	4.44	2.55	2.62	0.07	0.03
Minimum Value	0.33	0.03	0.05	0.08	0.32	0.71	0.37	0.01	0.98
Maximum Value	13.44	0.84	2.41	0.81	6.07	21.50	4.31	0.28	2.41
Enrichment Factor (EF)	1.16	4.7	13.02	1.27	7.17	*	-	-	-
Detection Limits	0.002	0.006	0.01	0.002	0.22	0.04	0.17	0.042	-

*The enrichment factors were calculated from the sea water mean concentration considering chloride ion as the main component of the sea salt aerosol.

High sulphate levels in San Antonio Cárdenas (Table 2) are comparable to that found in sites with anthropogenic influence like Mexico City where Báez *et al.* (1997) found sulphate levels between 3.62 and 6.31 mg l^{-1} . For this study, the average excess sulphate concentration (SO_4^{2-})_{xs} based on chloride ion was 3.32 mg l^{-1} which is almost seven times higher than background hemispheric value for (SO_4^{2-})_{xs} reported by Casimiro *et al.* (1991) for marine remote sites (0.48 mg l^{-1}). These results suggest that anthropogenic influence in San Antonio Cardenas is greater than that observed in other coastal sites in the Caribbean Sea Region.

NO₃⁻ concentrations (2.5 mg l^{-1}) exceeded the background hemispheric concentration proposed by Casimiro *et al.* (1991) for coastal and marine remote sites (0.17 mg l^{-1}), suggesting the direct influence of local anthropogenic sources in this site.

Based on enrichment factors (EF) showed in Table 2, it can be concluded that Na⁺, Mg²⁺ and Cl⁻ had an origin typically marine (EF close to 1), whereas K⁺, Ca²⁺ and SO₄²⁻ were enriched elements and showed a significant excess (EF>1), it means that other sources contributed to their levels present in rainwater. Sea-salt aerosol contributed to 86% of Na⁺ and 79% of Mg²⁺ in the sampling site, suggesting that the influence of marine aerosol was limited in comparison with other coastal sites. Since chloride ion was taken as the basis for excess calculations, sea-salt is assumed to contribute to 100% of Cl⁻. Proportions of sea-salt for K⁺, Ca²⁺ and SO₄²⁻ were lower, contributing to 21% of K⁺, 7% of Ca²⁺ and 14% of SO₄²⁻.

In pollution free areas, pH value for natural rainwater is of 5.6 due to carbonic acid produced from CO₂ – water equilibrium. When pH value ranges from 5 to 5.6, it can be considered that rainwater has enough buffer capacity, so it is not an impacted site; but, when pH value is less than 5, there is an evident anthropogenic source contributing to the acidity of rainwater (Jaeschke, 1986). pH values in this study varied from 3.01 to 6.27 with a mean pH value of 4.64, suggesting a direct anthropogenic influence over chemical composition of rainwater, therefore, San Antonio Cardenas can be considered as an impacted site.

Various proton donors may cause free acidity in precipitation: strong acids (e.g., H₂SO₄, HNO₃), weak organic acids (e.g., acetic, formic), or metal oxides (e.g., Al, Fe) (Galloway *et al.*, 1976). Since all strong acid anions were measured, we determined the possible contribution of (SO_4^{2-})_{xs} and NO₃⁻ to free acidity by using the equivalent ratios (SO_4^{2-})_{xs}/H⁺ and NO₃⁻/H⁺. If the individual ratios are < 1, there is not enough of any one anion to support all the free acidity (Galloway *et al.*, 1982). For this study, these individual ratios were greater than unity, signifying that both acids contributed to pH values observed. Equivalent (SO_4^{2-})_{xs}/H⁺ ratio was greater than NO₃⁻/H⁺ ratio, so it can be assumed that (SO_4^{2-})_{xs} contributed to the acidity in a greater proportion than nitrate in the rainwater in the sampling site.

Correlation coefficients were calculated using a non-parametric Spearman correlation for main ions present in rainwater at San Antonio Cardenas (Table 5). Elements showed a common trend; K^+ and Ca^{2+} had significant correlation, indicating a common source, probably particles of calcareous soils (crustal). On the other hand, a high correlation between $(Na^+)-(Cl^-)$ and $(Na^+)-(Mg^{2+})$ indicates a marine origin since these elements are typically marine. The concentrations of NO_3^- and SO_4^{2-} showed significant correlations, indicating their relationship to common anthropogenic sources and transport processes. H^+ had a significant correlation with SO_4^{2-} and NO_3^- , suggesting that both anions contributed in a great proportion to the acidity of rainwater. NH_4^+ , K^+ and Ca^{2+} showed an inverse significant correlation with SO_4^{2-} and NO_3^- , indicating that they play a significant role in neutralization process of strong acids.

Table 3. Volume weighted mean of precipitation composition, in some marine remote sites of the world ($mg\ l^{-1}$)

Main Ions	Sampling Sites			Background Hemispheric Values proposed by several authors				
	Saint. Georges, Bermuda (Galloway <i>et al.</i> 1982)	Amsterdam, Island (Galloway <i>et al.</i> 1982)	Aveiro, Portugal (Casimiro <i>et al.</i> 1991)	Junge (1960)	Rodhe and Grandell (1972)	Szepesi and Fekete (1987)	Galloway <i>et al.</i> (1983)	Casimiro <i>et al.</i> (1991)
$(SO_4^{2-})_{xs}$	0.88	0.42	1.44	0.48	0.77	0.62	0.91	0.48
SO_4^{2-}	1.74	1.47	2.12	-	-	-	-	-
NO_3^-	0.34	0.11	0.49	-	-	-	-	0.17
Cl^-	6.20	7.37	5.89	-	-	-	-	-
Mg^{2+}	0.42	0.47	-	-	-	-	-	-
Na^+	3.38	4.07	-	-	-	-	-	-
K^+	0.17	0.14	-	-	-	-	-	-
Ca^{2+}	0.19	0.15	-	-	-	-	-	-
NH_4^+	0.07	0.04	0.35	-	-	-	-	-
H^+	0.02	0.01	0.003	-	-	-	-	-

Table 4. Volume weighted mean of precipitation composition, in some coastal and marine sites in the Caribbean Sea Region ($mg\ l^{-1}$)

Main Ions	Sampling Sites					
	Puerto Morelos, Quintana Roo, Mexico, (Bravo <i>et al.</i> 2000)	Yucatan Peninsula, Mexico, (Cerón <i>et al.</i> 2002)	Monteverde, Costa Rica, (Clark <i>et al.</i> 1998)	La Selva, Costa Rica, (Eklund <i>et al.</i> 1997)	Turrialba, Costa Rica, (Hendry <i>et al.</i> 1984)	El Verde, Puerto Rico, (Mc Dowell <i>et al.</i> 1990)
$(SO_4^{2-})_{xs}$	0.47	0.13	-	0.62	0.36	0.41
SO_4^{2-}	1.227	0.98	-	0.85	0.43	0.82
NO_3^-	0.71	0.27	0.47	0.33	0.09	0.27
Cl^-	5.34	4.72	-	1.69	0.53	2.91
Mg^{2+}	0.35	0.31	0.11	0.12	0.05	0.18
Na^+	2.96	2.67	1.73	0.89	0.26	1.52
K^+	0.23	0.06	0.16	0.09	0.15	0.07
Ca^{2+}	0.36	0.05	0.13	0.14	0.06	0.17
NH_4^+	0.12	0.05	0.16	0.16	0.08	0.05
H^+	0.005	0.01	0.01	0.005	0.004	0.008

Table 5. Spearman Rank correlation for some ions concentration, at San Antonio Cardenas

	SO ₄ ²⁻	Cl ⁻	NO ₃ ⁻	Na ⁺	K ⁺	Ca ⁺	Mg ²⁺	NH ₄ ⁺
Cl ⁻	-0.2607*							
NO ₃ ⁻	0.7798*	-0.0952						
Na ⁺	-0.2718*	0.9831*	-0.0810					
K ⁺	-0.6280*	0.0918	-0.8585*	0.0602				
Ca ⁺	-0.6501*	0.1891*	-0.8573*	0.1656*	0.9525*			
Mg ²⁺	-0.3448*	0.9298*	-0.0614	0.9580*	-0.0280	0.0632		
NH ₄ ⁺	-0.7880*	0.0535	-0.9870*	0.0352	0.8632*	0.8655*	0.0243	
H ⁺	0.7884*	-0.0631	0.9938*	-0.0504	-0.8220*	-0.8235*	-0.0331	-0.9498*

* Significant at $p \leq 0.01$.

CONCLUSIONS

A one-year rainwater chemistry study was carried out at a coastal site in Campeche, Mexico. Except for NO₃⁻ and SO₄²⁻, ionic concentrations were in agreement with values reported for the Caribbean Region (Cerón *et al.*, 2002; Bravo *et al.*, 2000; Clark *et al.*, 1998; Eklund *et al.*, 1997; Hendry *et al.*, 1990; Mc Dowell *et al.*, 1990). Marine aerosol contributed in a great proportion to Na⁺, Mg²⁺ and Cl⁻, whereas K⁺ and Ca²⁺ showed enrichment and probably were derived from crust. On the other hand, NO₃⁻ and SO₄²⁻ levels, exceeded background levels reported for coastal and marine remote sites, suggesting that sources different from sea-salt aerosol contributed to the mineralization process of rainwater in San Antonio Cardenas. From the air mass-back trajectories analysis we could conclude that the main source for these high levels of NO₃⁻ and SO₄²⁻ was the sour gas recompression plant located 10 km at NE from San Antonio Cardenas.

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