Spatial and Temporal Troughfall Deposition Patterns on two regions at the Center and at the Southeast of Mexico

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Abstract: - In this study, throughfall deposition of N and S was measured in two regions at the center and at the southeast of Mexico. In the region 1, sampling was carried out from June 6, 2014 to January 6, 2015 at Xicalango-Atasta region. In the region 2, throughfall deposition was collected from November 29, 2014 to February 7, 2015 at Córdoba-Orizaba region. Passive throughfall collectors were used to collect samples in 23 sampling points distributed along these two regions in a multiple transects design. Ions retained (NO_3^-, NH_4^+, and SO_4^{2-}) by the resin column were extracted with 2N KCl, and analyzed by colorimetry and turbidimetry. Mean throughfall deposition fluxes for N (NO_3^- + NH_4^+) and S (SO_4^{2-}) were 0.8 and 9.22 Kg ha^{-1} yr^{-1}, respectively in region 1. N deposition flux in Xicalango-Atasta region did not exceed the critical load proposed; however, throughfall deposition flux for S was 3 times higher than those proposed for sensitive areas, suggesting that S deposition could be a threat for the mangrove ecosystems and fisheries in the region 1. On the other hand, mean throughfall deposition fluxes for N (NO_3^- + NH_4^+) and S (SO_4^{2-}) were 0.38 and 46.97 Kg ha^{-1} yr^{-1}, respectively in region 2. Long-range transport of regional pollutants was completely evident during autumn and winter seasons in Córdoba-Orizaba region. N deposition flux in region 2 did not exceed the critical load value proposed for sensitive ecosystems; however, S throughfall deposition flux exceeded almost 15 times the critical load value, suggesting that this region is highly polluted.

Key-Words: - Throughfall Deposition, Nitrogen, Sulphur, Campeche, Veracruz, Mexico.

1 Introduction

Acidification and eutrophication damage aquatic and terrestrial ecosystems, not only in the vicinity of the sources, but also in sensitive background regions. Precipitation is an important source of elements to forested ecosystems. The quality of precipitation on forests is altered as a result of its interaction with the surface of trees; as a consequence, additional matter is deposited to the forest floor by two main mechanisms: throughfall and stemflow [2]. These mechanisms play an important role in the nutrient cycling, in the annual nutrient return to the forest soil, in the plant nutrition, in the soil fertility, and in general, in the biogeochemical cycles of the involved elements. Therefore, the estimation of element flows in throughfall and stemflow is required to study nutrient budgets in forests ecosystems and to diagnose their vulnerability to acid compounds. Studies about nutrient budgets in undisturbed ecosystems provide a conceptual and empirical framework to assess the ecosystem function in other geographical regions in order to assess the man's impact on the natural landscape [1].

Due to agriculture activities, density population, industrial development and traffic intense, the NO_x and SO_2 emissions have been increased. As a consequence of the high inputs of these elements to the forest ecosystems, changes in biogeochemical cycles and severe damages to the trees can be expected. Ecological potential effects related to S deposition are known. In addition, when the input of nitrogen exceeds the sum of biotic and abiotic fixation, the ecosystems become nitrogen-saturated, threatening their biodiversity. Therefore, it is necessary to quantify the fluxes and deposition patterns for N and S in different climates and canopies to identify the factors controlling throughfall and stemflow composition.

As a result of reformulations of fuels and national regulations in Mexico, sulphur emissions were reduced between 1991 and 2011, therefore, the emissions target were almost satisfied in the most of the cities. However, regulations at national scale only are valid for sources considered as "typical" in the entire country, and do not consider some regions in which atypical industrial sources exist, contributing in a great proportion to local and regional deposition process. Therefore, it is required to establish regional standards for air quality, to assure that in these atypical regions, air quality be acceptable. In addition, national law about air pollution does not consider secondary standards. Therefore, environmental policies in Mexico have to define specific target and goals to protect both, public health and ecosystems. To obtain this target and goals, it is necessary to know the effects of air pollution, to establish the cause-effect relationships, and to carry out monitoring for the main air pollutants at a long-term [1]. Integrating all these items, it will be possible to establish public policies focused to protect human health, biodiversity and ecosystems in Mexico.

Regarding this, threshold values for the effects of air pollutants play an important role in the estimation of these environmental goals. Critical loads constitute a good approximation to obtain these threshold values. Critical loads can be defined as the limit to which a receptor system may be exposed to air pollution levels without detectable damages in the long term [1]. To establish these critical loads, the knowledge about current deposition fluxes is required. The critical load value is then compared to the actual load deposition, and the difference describes the exceedance, so, the environmental goal must be established to reduce this value to zero, assuring the protection of the ecological receptor over time. Throughfall data and information on stand structure, seasonal trends and patterns, and spatial distribution are needed to quantify elements deposition to forests exposed to chronic air pollution. Some of stand-level estimates of atmospheric inputs of N and S to forest in Mexico have been limited to studies carried out in pine forests at the surroundings of Mexico Valley [2,3,4]. However, in spite of critical loads, current loads and exceedances have been mapped in Europe and United States since several years ago, measurements of throughfall deposition inputs, specific critical loads values and maps are not available for ecosystems in Mexico. The establishment of critical loads and the estimation of their exceedances will let to identify critical zones, to assess their vulnerability and to develop environmental policies for reduction and control of emissions in a given area. This work constitutes the first step in Mexico to diagnose the sensitivity in some regions of Mexico to the acidity using the mapping of N and S throughfall deposition.

The present paper reports throughfall deposition fluxes for two different regions in Mexico: Region 1 located at the southeast of the country, during the period summer-autumn-winter for Xicalango-Atasta region in Campeche State; and Region 2, located at the center of the country, during the period autumn-winter for Córdoba-Orizaba region in Veracruz State.

1.1 Available methods to measure atmospheric deposition.

A variety of approaches such as the wet-dry deposition collectors method, inferential method, simulation modeling and throughfall collection systems have been used to estimate N and S deposition. Fluxes in wet deposition are frequently measured because this is an easier and more reproducible method. However, there are some areas where fog or dry deposition can be more significant than wet deposition, being precipitation only a small component of the total input to the ecosystems [5]. On the other hand, in spite of bulk deposition is an inexpensive method, it has the disadvantage of possible contamination of samples with insects, leaves and bird droppings due to the collector opening is continuously exposed to the atmosphere[6].

Fenn and Bytnerowicz [7]proposed a method of branch washing to measure dry deposition fluxes to foliar and branches surfaces, however, it is not applicable during fog and rain events, and in the case of arid regions, where dry periods are long, this method can overestimate dry deposition fluxes.

Inferential methods have also used to estimate dry deposition fluxes [8], however, this method requires a great quantity of input data. In addition, it is very expensive to implement it at multiple sites and often, deposition velocity values are uncertain. Another available choice is simulation modeling method, but their results must be validated with field sampling, increasing the associated costs [9].

Empirical deposition modeling method let to estimate deposition over heterogeneous landscapes, but over large scales, it shows big uncertainties [10]. Economical methods like lichen bio-monitoring provide relevant data, but it is an indirect method and nutrient accumulation depends on studied specific species [11].

The use of passive devices to collect gaseous pollutants is recognized as an important method to assess the exposure to air pollutants in forest and remote sites, where measurements with active devices can be prohibitive [12, 13].

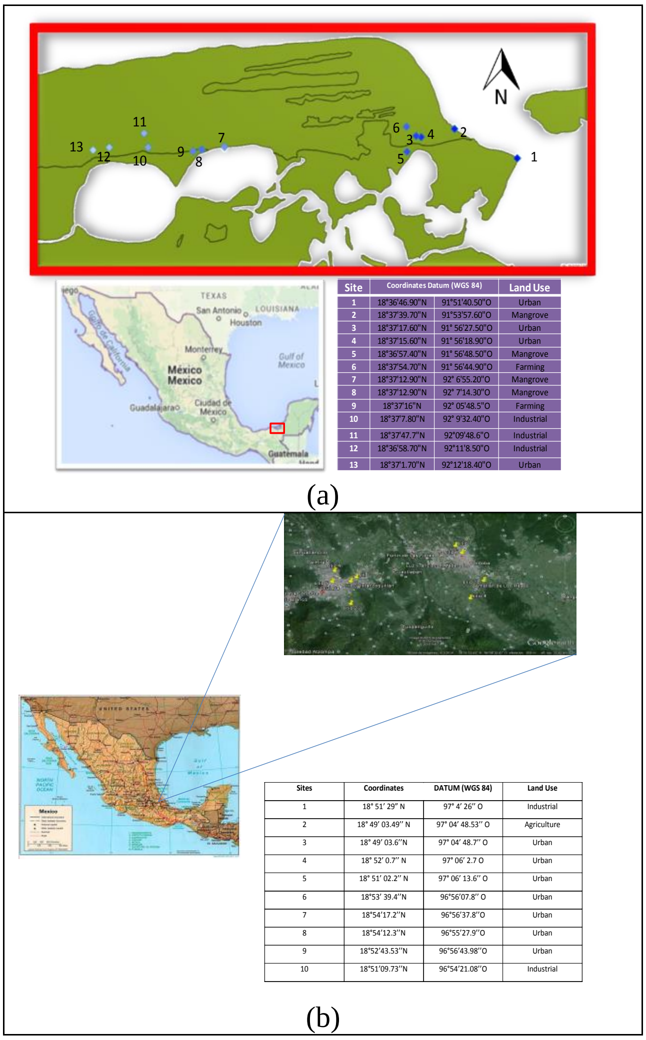
Throughfall collection systems provide data on nutrient solution fluxes to soil. Deposition fluxes include inputs from precipitation, dry deposition and cloud water. Total atmospheric deposition can be calculated from throughfall flux data. This method is an attractive choice to estimate atmospheric deposition to ecosystems [14]. This kind of sampling device seems to have a greater potential in comparison with other available methods for widespread monitoring atmospheric deposition, it can dramatically reduce the number of trips to field sites, sample numbers and analysis cost. Pan European Intensive Monitoring Program of the European Union International Cooperative Programme (ICP forests) has chosen throughfall collectors to monitor at large scale N deposition. Therefore, in this study, atmospheric deposition was studied by collecting throughfall deposition with ion exchange resins columns (IER).

2 Study Area

2.1 Observation Site

Region 1: Research was conducted in the region of Xicalango-Atasta in Campeche State at the Southeast of Mexico (Figure 1 a). A sour gas recompression station is located at 2 km from the sampling sites, this facility re-compress sour gas obtained from offshore platforms and send it to petrochemical complexes. Climate in this region is sub-humid warm with rains occurring along the summer. The annual mean precipitation is 1300 mm, and the annual mean temperature is 27°C. The prevailing winds come from NE from October to March when this region is influenced by cold fronts named “Norths” and from SE from April to September, when this site is under the influence of tropical storms and trade winds. In the region, soils are saline and lightly alkaline, and dominant vegetation is mangrove forest. This area is important due its proximity to the Protected Area named “Laguna de Terminos”.

Region 2: Throughfall measurements were carried out in the region of Córdoba-Orizaba in Veracruz State at the Center of Mexico (Figure 1 b). Climate is humid sub-warm with heavy rains and storms occurring along the summer. Annual mean temperature is 19.12°C, and the annual mean precipitation is 2237.9 mm. This region is located at the edge of Sierra Madre Oriental, the biggest mountainous system in Mexico. This region has an extensive industrial zone that includes a variety of sectors, such as beer, paper, pharmaceutical, metallurgic, cement, vegetal oils and food industry. Agro-industrial activity is extensive and it is based in crops of sugar, coffee, banana, bean and corn. In addition, coffee industry is the biggest in the country. In this region there are three types of forests: deciduous forest, high-deciduous forest and cloud forest, where dominant vegetation is mainly walnut, poplar, oak and ferns.



Site	Coordinates Datum (WGS 84)		Land Use
1	18°36'46.90"N	91°51'40.50"O	Urban
2	18°37'39.70"N	91°53'57.60"O	Mangrove
3	18°37'17.60"N	91° 56'27.50"O	Urban
4	18°37'15.60"N	91° 56'18.90"O	Urban
5	18°36'57.40"N	91° 56'48.50"O	Mangrove
6	18°37'54.70"N	91° 56'44.90"O	Farming
7	18°37'12.90"N	92° 6'55.20"O	Mangrove
8	18°37'12.90"N	92° 7'14.30"O	Mangrove
9	18°37'16"N	92° 05'48.5"O	Farming
10	18°37'7.80"N	92° 9'32.40"O	Industrial
11	18°37'47.7"N	92°09'48.6"O	Industrial
12	18°36'58.70"N	92°11'8.50"O	Industrial
13	18°37'1.70"N	92°12'18.40"O	Urban

(a)

Sites	Coordinates	DATUM (WGS 84)	Land Use
1	18° 51′ 29″ N	97° 4′ 26″ O	Industrial
2	18° 49′ 03.49″ N	97° 04′ 48.53″ O	Agriculture
3	18° 49′ 03.6″N	97° 04′ 48.7″ O	Urban
4	18° 52′ 0.7″ N	97° 06′ 2.7 O	Urban
5	18° 51′ 02.2″ N	97° 06′ 13.6″ O	Urban
6	18°53′ 39.4″N	96°56′07.8″ O	Urban
7	18°54′17.2″N	96°56′37.8″O	Urban
8	18°54′12.3″N	96°55′27.9″O	Urban
9	18°52′43.53″N	96°56′43.98″O	Urban
10	18°51′09.73″N	96°54′21.08″O	Industrial

(b)

Fig. 1 Sampling Site Location. (a) Region 1. (b) Region 2.

3 Methodology

3.1. Sampling Method

Throughfall deposition may be defined as the hydrologic flux to the forest floor of ions and other compounds contained within the throughfall solution. Many studies have been published, providing a large database of throughfall deposition inputs to forests. The main advantages of throughfall collectors are: 1) Infrequent sample collection and analysis (e.g., once, or twice a year); 2) Major cost savings; 3) The method facilitates monitoring a greater number of sites, including remote locations; 4) They can measure deposition of many inorganic ions: NO_3^-, NH_4^+, SO_4^{2-}, and others; and 5) Data generated from the IER collectors represent accumulated atmospheric deposition over the time of exposure.

This method is commonly used to estimate atmospheric inputs to the ecosystems, since; it includes both, wet and dry deposition. Since throughfall is spatially heterogeneous, varying at local scale [15], quantifying fine resolution spatial patterns requires high-density sampling. To study this spatial variability, often it is required a large number of samples collected with a high frequency. In this case, automatic collectors are not a good choice, and it becomes an extensive and difficult procedure in field, therefore, ion-exchange resins (IER) constitute valuables tools that can be useful in this type of studies. The main advantage of passive sampling devices as IER columns is that it is possible to increase the density of the sampling grid at a low cost at different locations in a simultaneous way.

Nitrate, ammonium and sulfate ions in throughfall can be exchanged by anion IER and cation IER, and locked by functional groups with opposite electronic charges [16]. A mixed resin column design was chosen, considering that it is an efficient technique to capture ions from throughfall samples as the flow is direct through the ionic exchange resin column (IER). Mixed bed refers to the fact that the resin contains both anion and cation exchange resin beds.

In this study, the methodology proposed by Fenn et al [3] was used. The IER columns consist of a funnel attached to PVC tubes, the solution was channeled to the mixed resin bed through the column, where ions were retained. The resin used for the IER collectors was a mixed polystyrene bed for anions and cations (Amberlite^{TM} IRN 150). The funnel was covered with a fine mesh screen to avoid the intrusion of material such as leaves and insects. The IER column was inserted into the inner PVC tube (30 g of IER), the inner tube was sealed with glass fiber at the bottom (as a support platform) and at the top (as a filter). The inner PVC tube was contained within an outer PVC tube to protect it from solar radiation. The bottom end of the IER column was closed using standard PVC caps with an

"X" cut into it to allow drainage. Finally, IER columns were assured at ground level in open areas in each of the sampling sites [17].

IER columns were used to evaluate throughfall deposition at two regions in Mexico, with 23 sampling points in total. In this study, nitrate, ammonium and sulfate were collected each two months, from July 6, 2014 to January 6, 2015 in Xicalango-Atasta region, and from November 29, 2014 to February 7, 2015 in Córdoba-Orizaba region; using IER (Amberlite^{TM} IRN 150). Sampling points in each studied region were distributed in an array of multiple transects during summer, autumn and winter in the period 2014-2015. The inner PVC tubes were replaced each two months. Samples were collected and extracted at the end of each sub-period (two months). PVC tubes were sealed and transported to Laboratory of Chemistry Faculty of UNACAR in Ciudad del Carmen, Campeche. Ions were released by extracting with 2 M KCl solution. This procedure was repeated by duplicate. Extracts were frozen until analysis to assure their stability.

3.2 Analytical Method

Potassium chloride (KCl) is commonly used elsewhere as a resin-extractant [3,18]. Ions captured on the resin columns were extracted into solution with 100 ml of extractant solution (2 M KCl). Extraction efficiency was calculated as the percentage of the ions loaded on the columns that was recovered in sequential extractions. Percent ionic recovery was determined by extracting ions from the loaded IER columns with three 100-ml extractions. Each 100-ml aliquot was collected, weighed and analyzed separately. Because of recovery percentage of N and S for the third extraction was not significant, each resin received only two successive extractions, therefore, at the end of extraction period a composite sample with a total volume of 200 ml was obtained. From these two extractions, approximately 98.86% of the ions on the IER were recovered

Three IER columns used as blanks were extracted y analyzed; the average blank IER column values for nitrate, ammonium and sulfate were calculated and subtracted from the total ions recovered from each loaded resin column [19].

Nitrate and ammonium were determined by colorimetry [20, 21], and sulfate was analyzed by turbidimetry [22].The surface area of the funnel opening and the sampling period were used to estimate the deposition fluxes of N (as NO_3^- + NH_4^+) and S (as SO_4^{2-}) in Kg per land area per year (Kg ha^{-1} yr^{-1}).

3.3. Statistical Analysis

The statistical evaluation of the observations on the atmospheric deposition fluxes was made in order to test the hypothesis on equal deposition fluxes in sampling sites with different land-use type and during different sampling period (seasonal variation). Barlett's test was used for the normally distributed deposition parameters (NO_3^-, SO_4^{2-} and NH_4^+ fluxes) for both study regions and Kruskal Wallis test was used to test the hypothesis on equal means of atmospheric deposition fluxes among different use-land categories (urban, farming, mangrove and industrial). Statistical Analysis was carried out using XLSTAT software (Statistics Package for Microsoft Excell)

4 Results

Because of the large worldwide database of throughfall deposition to forests [8, 23, 14, 24, 25, 26], throughfall inputs reported can be used for comparison with N and S inputs in other regions of the world. In Mexico, critical loads for atmospheric deposition are not available, and only few studies have been carried out at the surroundings of Mexico Valley and in the central region of Veracruz [4, 27]. Since there are not available reference values, this comparison can provide an indication of the relative severity of N and S deposition. Estimates of N and S throughfall deposition are useful data in setting the lower bounds of N and S deposition for unstudied regions as Mexico.

Ponette el at [27] measured throughfall deposition of S to forests and coffee soils in central region of Veracruz. They reported 7-17 Kg ha^{-1} yr^{-1} for forests, 7-12 Kg ha^{-1} yr^{-1} for coffee agroforests, and 8 Kg ha^{-}1 yr^{-}1 for cleared areas. On the other hand, several studies reported the effects of canopy cover on throughfall in two forest sites in the Mexico City Air Basin: National Park of Desierto de los Leones and National Park of Zoquiapan [4,28]. Pérez-Suárez et al [4] and Fenn et al [28] reported throughfall deposition fluxes of 5.5-18.5 Kg N ha^{-1} yr^{-1} and 8.8-20.4 Kg S ha^{-1} yr^{-1}. Burbano-Garcés et al [29] evaluated the input flux of nitrogen compounds through an Andean forest canopy adjacent to a semi-natural wetland in Southwestern Colombia in South America. They found 16.08 Kg ha^{-1}yr^{-1} for N-NO_3 and 1.8 Kg ha^{-1} yr^{-1} for N-NH_4, respectively.

In Canada and United States of America, throughfall deposition fluxes have been reported since several years ago. Kochy and Wilson [30] found 5-11 Kg N ha^{-1} yr^{-1} in Canada; whereas Kopacek et al [31] reported 4-8 Kg N ha^{-1} yr^{-1} in the Northeastern of United States. In addition, Fenn and Bytnerowicz [7] reported summer throughfall and winter deposition in the San Bernardino Mountains in Southern California. They measured 4 Kg N ha^{-1} yr^{-1} and 0.4 Kg S ha^{-1} yr^{-1}. In addition, Fenn et al [32] studied throughfall deposition of nitrogen and sulfur at an N-limited and N-saturated site in the San Bernardino Mountains (18.8 Kg N ha^{-1} yr^{-1} and 2.9 Kg S ha^{-1} yr^{-1}). Burns [33] reported 7 Kg N ha^{-1} yr^{-1} in the Rocky Mountains of Colorado.

In other regions of the world, there are several works reported about througfall deposition. Mitchell et al [34] measured throughfall deposition fluxes to Japanese forests; they reported 3.5-10.5 Kg N ha^{-1} yr^{-1}. In China, Sheng et al [16] and Huang et al [35] studied throughfall deposition, reporting fluxes of 1.3-29.5 Kg N ha^{-1} yr^{-1} and >40 Kg N ha^{-1} yr^{-1}. Studies carried out in forest ecosystems in Europe report 12.3-61 Kg N ha^{-1} yr^{-1} [36]. In addition, atmospheric deposition of elements was measured at one open area and two throughfall plots located in Norway spruce stands at different altitudes in the Bohomien forest from 1998 to 2005 [37]. They observed that element deposition was higher at higher altitudes, and reported 25 Kg ha^{-1} yr^{-1}, 9 Kg ha^{-1} yr^{-1} and 6 Kg ha^{-1} yr^{-1} for SO_4^{2-}, NO_3- and NH_4^+, respectively. Boxman et al [38] studied long-term changes in atmospheric N and S throughfall deposition and their effects on soil solution chemistry in a Scots pine forest in the Netherlands. They reported throughfall deposition fluxes from 1982 to 2008 (15-48 Kg S ha^{-1} yr^{-1} and 9-18 Kg N ha^{-1} yr^{-1}).

Studies in the San Bernardino and San Gabriel Mountains in California, suggest that the threshold N deposition level at which N saturation effects are evident in mixed conifer forests is approximately 25 Kg ha^{-1} yr^{-1}[39]. In addition, a survey of 65 forested plots throughout Europe also indicate that above an N deposition threshold of 25 Kg ha^{-1} yr^{-1}, significant N saturation occurs, being it evidenced by N leaching [40]. A reason to quantify N and S deposition in forests is to increase the ability to predict the levels of deposition at which ecological and environmental impacts can be significant. In a broad survey of watersheds in Europe, it was reported that below a throughfall deposition threshold of 10 Kg N ha^{-1} yr^{-1}, no significant NO_3^- leaching from the forest occurred, while at intermediate levels of 10-25 Kg N ha^{-1} yr^{-1},leaching occurred at some sites. Above a throughfall deposition level of 25 Kg N ha^{-1} yr^{-1}, N leaching occurred at all sites [40].

A critical load value of 5 Kg N ha^{-1} yr^{-1} has been proposed for alpine ecosystems [41,42], whereas a value of 3 Kg S ha^{-1} yr^{-1} has been proposed as a reference value for very sensitive areas, and a range of 2-5 Kg ha^{-1} yr^{-1} as critical load for natural forests in European countries [43].

4.1 Region 1

In this study mean fluxes of throughfall deposition for N (NO_3^- + NH_4^+) and S (SO_4^{2-}) at Xicalango-Atasta region were 0.8 and 9.22 Kg ha^{-1} yr^{-1}, respectively. N deposition flux was lower than those reported for other sites in Canada, United States of America, China and Europe. In addition, throughfall deposition fluxes for N did not exceed critical loads proposed for sensitive ecosystems.

On the other hand, S deposition flux was higher than those reported in cleared areas in Veracruz [27], and in San Bernardino Mountains in Southern California[7]. On the other hand, this value was comparable to those found in the forest located at Desierto de Los Leones in Mexico Valley that can be considered as perturbed [4], and in forest and coffee agroforests in Central Veracruz [27], but lower than those reported for European countries. However, throughfall deposition fluxes for S were 3 times higher than those proposed for sensitive areas, and 2 times higher than value reported for natural forests, suggesting that S deposition could be a threat for the mangrove ecosystems in the region.

Escoffie et al [26] measured throughfall deposition fluxes for N and S in Carmen Island, (a city located 40 km at East from region 1 in this research), where N deposition fluxes were almost 3 times higher than the values reported here due to the high density of vehicular traffic in that city. However, in the case of S deposition fluxes, values reported by Escoffie et al [26] (4.7 Kg ha^{-1} yr^{-1}) were lower than values found in this study (9.22 Kg ha^{-1} yr^{-1}). Therefore, this high sulfate contribution to deposition in the region of Xicalango-Atasta could be attributed to air pollutants emitted from a sour gas re-compression station located in the surroundings of this zone [44]. The safety system of this recompression plant has four flare burners that use sour gas as fuel, releasing air pollutants to the atmosphere, mainly SO_2 that is deposited as SO_4^{2-} in this zone. To infer the local or regional influence of N and S, the sulfate: nitrate ratio in throughfall deposition was estimated. A ratio of 13 was obtained, almost three times higher that obtained by Escoffie et al [26] for Carmen Island; suggesting that this region is subjected to the influence of long-range transport. It is agree with the local and regional character of nitrate and sulfate, respectively.

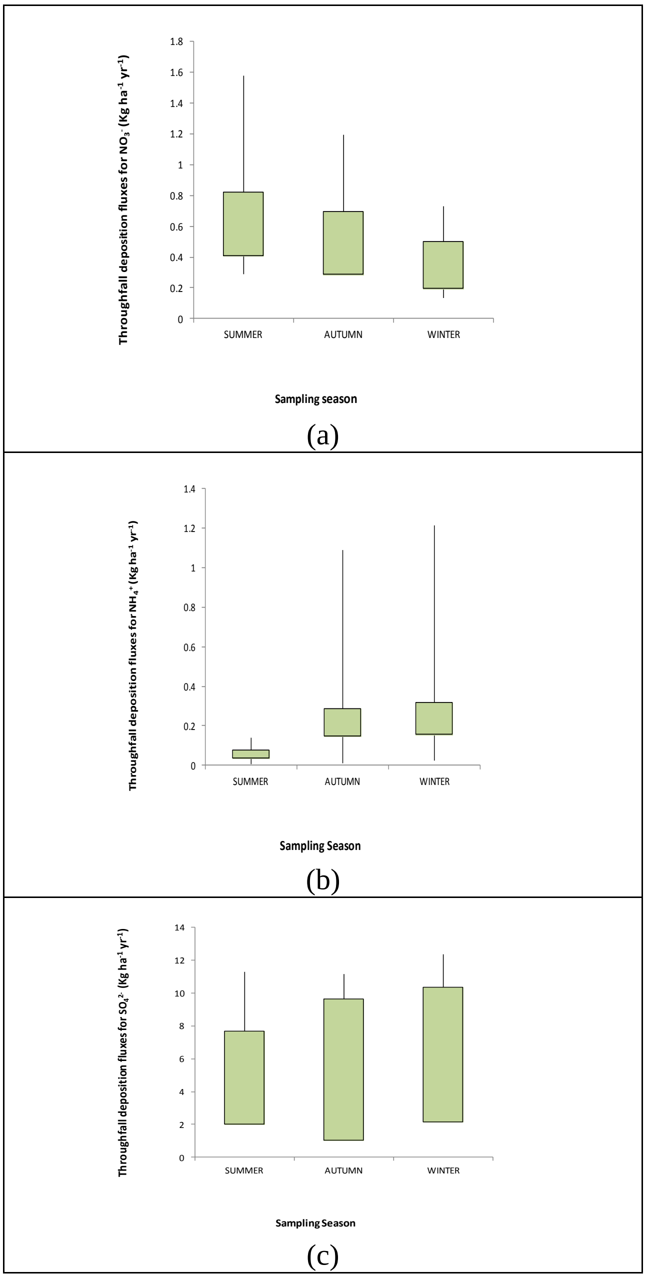


Fig. 2 Atmospheric deposition fluxes for (a) NO_3^-, (b) NH_4^+, and (c) SO_4^{2-} at Xicalango-Atasta region (region 1) for each sampling period.

Nitrate and Ammonium showed an opposite seasonal pattern, suggesting that they were originated from different sources. From Figure 2, it can be observed that NO_3^- deposition fluxes were higher during the summer, whereas NH_4^+ fluxes were higher during winter season. On the other hand, SO_4^{2-} deposition fluxes were higher during winter and autumn seasons, just in the plenitude of the rainy season, and at the beginning of the cold fronts named "Norths". These meteorological phenomena promote the long-range transport of air pollutants from offshore platforms in the Gulf of Campeche, where, flares (that are used as safety systems in platforms to avoid over-pressure in compression equipment) are burning sour gas periodically, as a result of a lack of capacity in the gas management system.

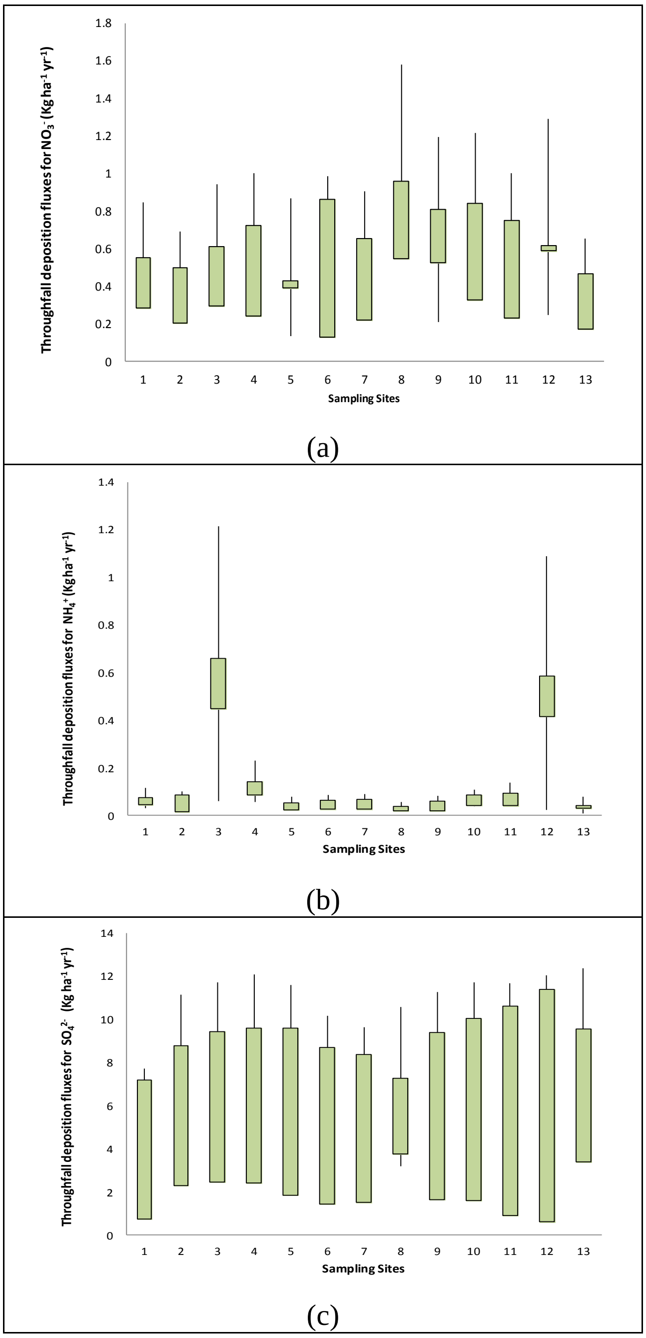
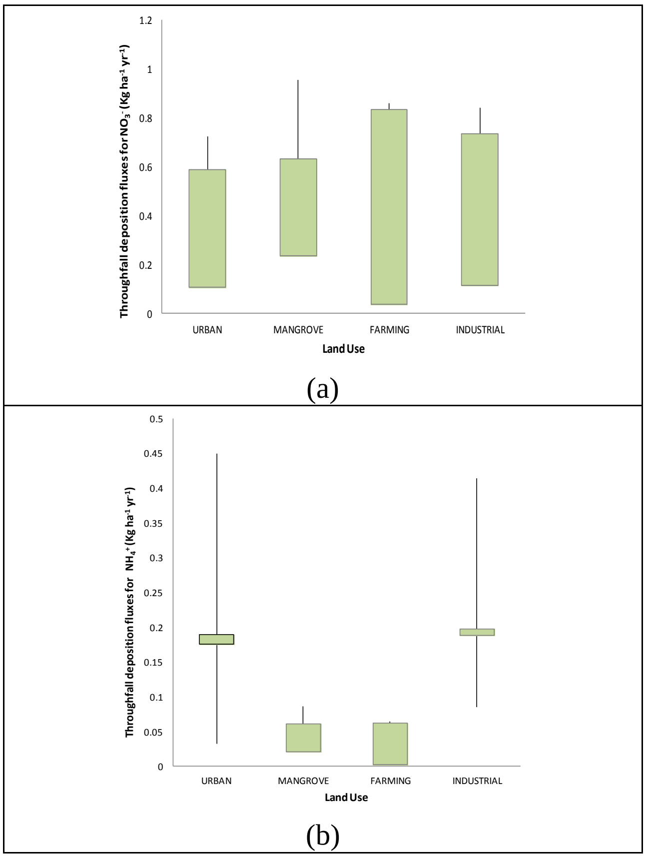


Fig. 3 Atmospheric deposition fluxes for (a) NO_3^-, (b) NH_4^+, and (c) SO_4^{2-} at Xicalango-Atasta region (region 1) for each sampling site.

Sampling points, in which throughfall deposition was collected, were grouped in four zones according the land- use type for each sampling site. Identified zones were the following: mangrove zone, industrial zone, urban zone and farming zone.

From Figures 3 and 4, it can be observed that mean throughfall deposition fluxes for nitrate were higher in the sampling points labeled as 8, 10, 11 and 12, corresponding to a land use of farming and industrial type. However, it is necessary to consider that these points are located just at federal highway 180, therefore, nitrate origin can be attributed to both, industrial and vehicular sources. In addition, sampling points 10-12 are located in the surrounding of gas recompression plant.



(a)

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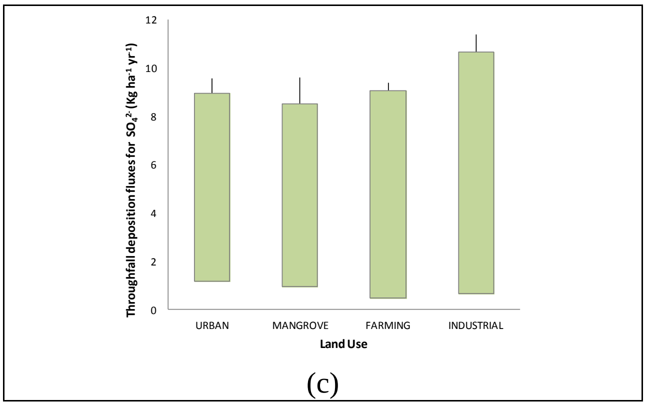


(c)

Fig. 4 Atmospheric deposition fluxes for (a) NO_3^-, (b) NH_4^+, and (c) SO_4^{2-} at Xicalango-Atasta region (region 1) for different land use.

In the case of ammonium, mean throughfall deposition fluxes were higher in the sampling points 3 and 12. NH_3 emissions from gasoline and diesel vehicles have been reported, this NH_3 is finally deposited as NH_4^+ on soils and receptors. Point labeled as “3” is located at federal highway 180, specifically next to a parking lot for heavy vehicles that travel to Yucatan Peninsula by this way, therefore, the high ammonium levels found in this sampling site could be attributed to these sources.

Finally, SO_4^{2-} deposition fluxes were higher in sampling points 10, 11 and 12, that correspond to a land use of industrial type; therefore these high sulfate levels can be attributed to local sources as flares in the recompression plant that are burning periodically sour gas. However, it is necessary to consider the significant contribution of regional sources (offshore platforms) during autumn and winter seasons as a result of the cold fronts that transport pollutants from these sources.

4.2 Region 2

In this study mean fluxes of throughfall deposition for N (NO_3^- + NH_4^+) and S (SO_4^{2-}) at Córdoba-Orizaba region were 0.38 and 46.97 Kg ha^{-1} yr^{-1}, respectively. N deposition flux was lower than those reported for other sites in Canada, United States of America, China and Europe. In addition, throughfall deposition fluxes for N did not exceed critical loads proposed for sensitive ecosystems.

However, throughfall deposition fluxes for S were too high (almost 15 times higher than those proposed for sensitive areas). In addition, throughfall deposition flux for S was higher than reported for forests in Veracruz and Mexico Valley, and was comparable with those reported in Europe [37, 38], with values as high as 40 Kg S ha^{-1} yr^{-1}. It suggests that S deposition can be a threat for the ecosystems in the region. To infer the local or regional influence of N and S, the sulfate: nitrate ratio in throughfall deposition was estimated. A ratio of 173 was obtained, suggesting that this region is subjected to the influence of long-range transport. It is agree with the local and regional character of nitrate and sulfate, respectively.

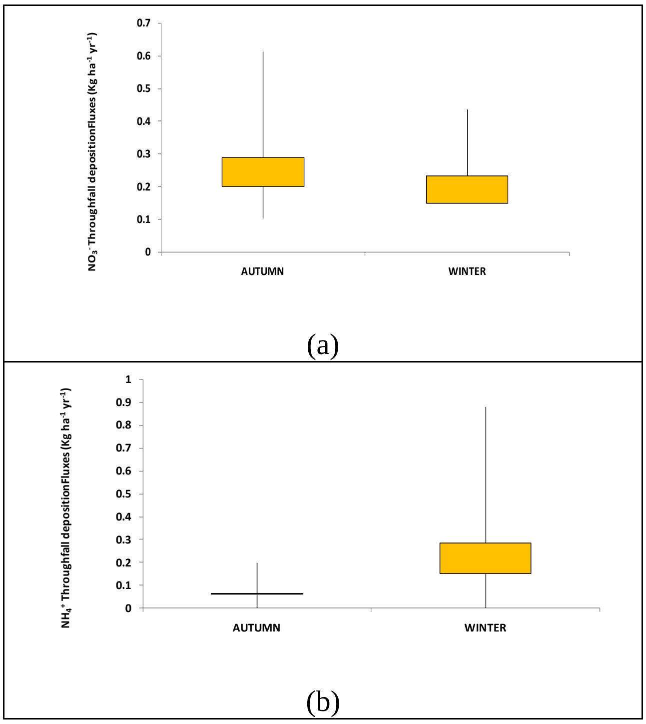
S deposition flux in region 2 was almost 5 times higher than that found in region 1. Region 1 is 1000 km away from the region, so air-masses coming from Yucatan Peninsula travel approximately 1000 km before arrive to the coast in the central zone of Mexico, once air masses arrive to the coast , they find a barrier to flow, because region 2 is located at the edge of Sierra Madre Oriental, the biggest mountainous system in Mexico. Therefore, the effect “Mountain-Valley” was evident, resulting in higher deposition fluxes in region 2 in comparison with region 1. Region 2 is located east-facing (in the direction of prevailing winds) of hill slopes, contrasting to Region 1 which is located at sea level.

In addition, since region 2 is located downwind region 1, air masses arriving to region 1 are relatively clear, in comparison with air masses arriving to region 2. Therefore, the vulnerability to be impacted in a greater proportion as a result of their location could be an important factor influencing on this difference between regions.

Long-term monitoring of air concentrations in the United States has shown that the relative contribution of SO_2 and aerosol SO_4^{2-} deposition to ecosystems is strongly related to distance from local and regional emissions sources, and the age of air masses [45]. Electricity generation, diesel-burning sugar mills, oil and gas extraction and refining, are the largest sources of SO_2 along the coastline of the Gulf of Mexico. These industries emit significant amounts of sulfur-containing compounds that can be incorporated into air masses and deposited to downwind ecosystems hotspots of deposition as a result of spatial heterogeneity. Air masses from region 1 cross this zone (coastline of the Gulf of Mexico), so air masses uptake these air pollutants before arrive to region 2. In addition, deposition fluxes were enhanced due to increased fog and aerosol impactation rates that result from upslope air flow and contrasting vegetation. It suggests that long-transport is a significant mechanism influencing on throughfall deposition in region 2. In addition, S deposition fluxes can be enhanced as a result of unfavorable topographic conditions since the effect “Mountain-Valley” was evident in region 2.

Other inherent characteristic to the sites that could influence on these values, was the altitude, region 1 is located at sea level whereas region 2 is located at 890-1300 m asl. Pérez-Suárez et al [4] found that net SO_4-S fluxes were three to fivefold greater at the high deposition sites than at the low deposition sites.

In addition, population in both regions is different; region 1 has only 2096 inhabitants whereas region 2 has approximately 275,000 inhabitants. Since, the grade of develop is different between these two regions, vehicular fleet and economical activities related to this develop are different too. Whereas in region 1, there is only one identified industrial source (sour gas recompression station), in region 2, many industries operate and result in more emissions to the atmosphere in comparison with region 1.



(a)

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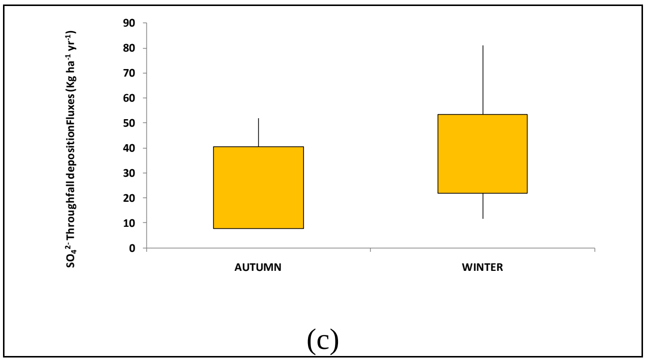
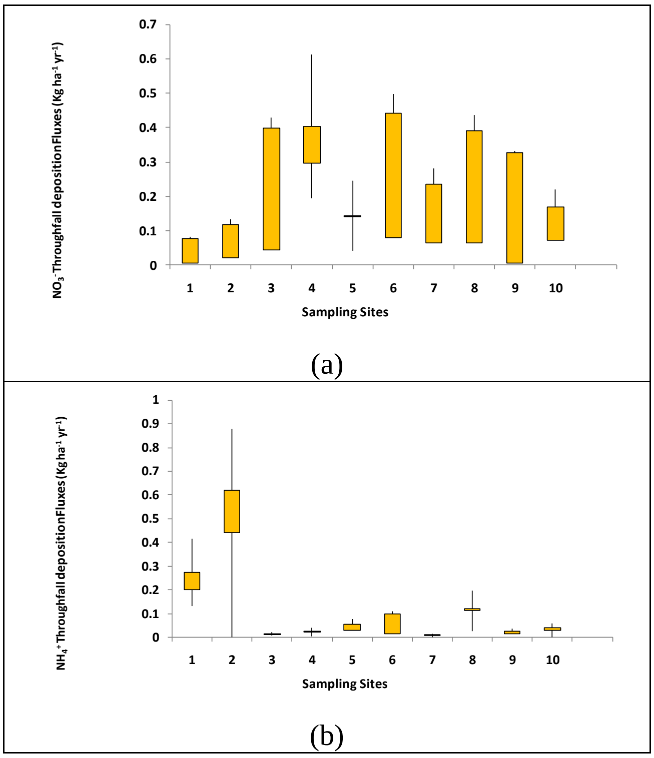


(c)

Fig. 5 Atmospheric deposition fluxes for (a) NO_3^-, (b) NH_4^+, and (c) SO_4^{2-} at Córdoba-Orizaba region (region 2) for each sampling period.

Nitrate and Ammonium showed an opposite seasonal pattern, suggesting that they were originated from different sources. From Figure 5, it can be observed that NO_3^- deposition fluxes were higher during autumn, whereas NH_4^+ fluxes were higher during winter season. These results were consistent with the agriculture patterns in this region, since; field workers begin to sow their crops in February.

On the other hand, SO_4^{2-} deposition fluxes were higher during winter season when cold fronts named “Norths” influenced on Gulf of Mexico. These meteorological phenomena promote the long-range transport of air pollutants from regional sources.



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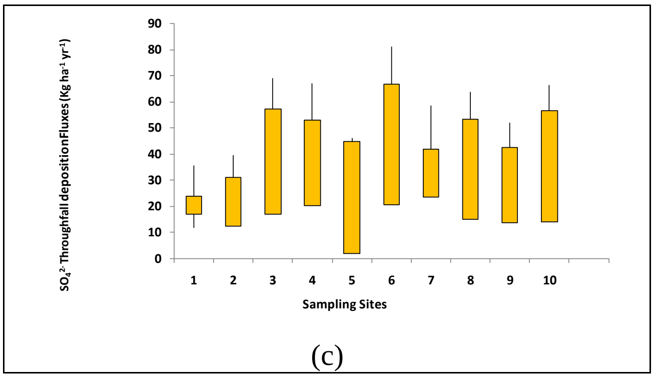
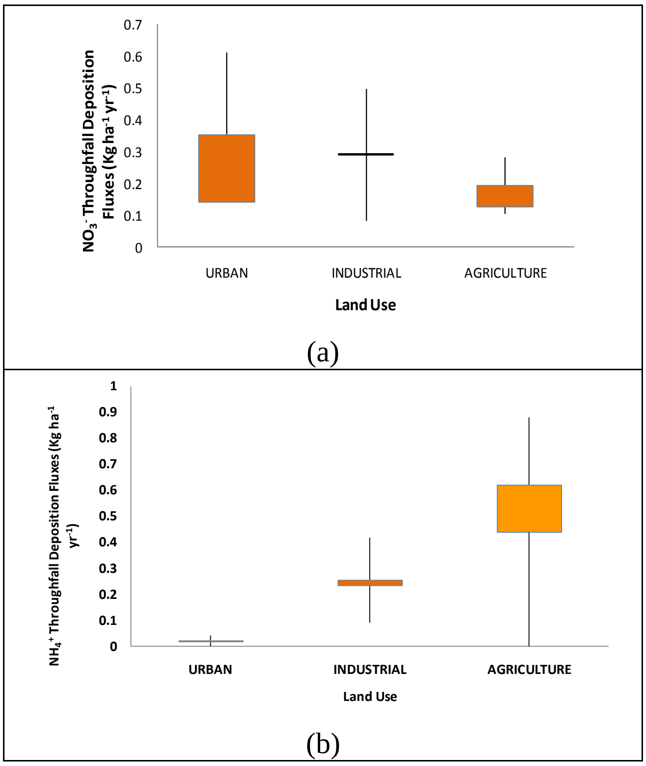


(c)

Fig. 6 Atmospheric deposition fluxes for (a) NO_3^-, (b) NH_4^+, and (c) SO_4^{2-} at Córdoba-Orizaba region (region 2) for each sampling site.

Sampling points in which throughfall deposition was collected, were grouped in three zones according the land use in each of the sampling sites. Identified zones were the following: industrial zone, urban zone and agriculture zone.

From Figures 6 and 7, it can be observed that mean throughfall deposition fluxes for nitrate were higher in the sampling points labeled as 3, 4, 6 and 8, corresponding to a land use of urban and industrial type. Therefore, nitrate origin can be attributed to both, industrial and vehicular sources. In addition, sampling point labeled as 6 is located in the surrounding of a zone with extensive industrial activity.



(a)

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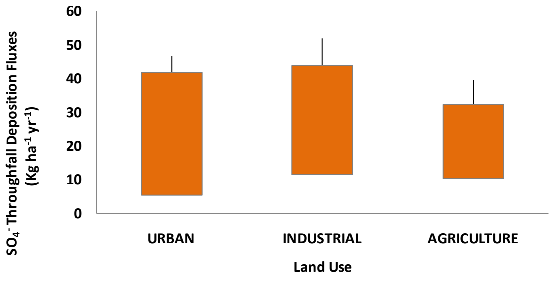

(c)

Fig. 7 Atmospheric deposition fluxes for (a) NO_3^-, (b) NH_4^+, and (c) SO_4^{2-} at Córdoba-Orizaba region (region 2) for different land use.

In the case of ammonium, mean throughfall deposition fluxes were higher in the sampling point 2 which corresponds to a site with agriculture land use. Since the most important economical activities in region 2 are agriculture and agro-industry; the high ammonium levels found in this sampling site can be attributed to extensive agriculture activity developed in this site. Finally, SO_4^{2-} deposition fluxes were higher in sampling point 6, that correspond to a land use of industrial type; therefore these high sulfate levels can be attributed to local combustion sources. However, it is necessary to consider the significant contribution of regional sources not only during winter and autumn seasons as a result of the cold fronts, but also the rest of the year as a result of a greater vulnerability to be exposed to aged air masses of region 2 (as a result of its location) that transported pollutants from sources located along coastline of Gulf of Mexico.

4.3 Statistical Analysis

The Barlett's test statistics for the normally distributed deposition parameters (atmospheric deposition fluxes for NO_3^-, NH_4^+, and SO_4^{2-}) showed that the hypothesis on equal variances has to be rejected at 95% level for all the measured parameters for both studied regions, excepting NO_3^- deposition fluxes in Orizaba-Córdoba region. Table 1 shows the results of the test of hypothesis on equal variances of normally distributed atmospheric deposition fluxes for the studied ions in both studied regions. The hypothesis on atmospheric deposition fluxes for NO_3^-, NH_4^+, and SO_4^{2-} are independent of the land-use type was assed using the Kruskal-Wallis test. All measured ions in both sampling regions during the whole study period showed that the hypothesis on equal deposition fluxes must be rejected at the 95% significance level according to Kruskal-Wallis test statistic (Tables 2-3).

Thus, the differences in the deposition fluxes among the different site categories according to the use-land type is statistically significant for all measured ions due to the specific land cover, source types and anthropogenic activities carried out in each site category.

Table 1. Results of the test of hypothesis on equal atmospheric deposition fluxes. Barlett's test at 95% significance level.

Region 1: Atasta-Xicalango						
	SO_4^{2-}		NO_3^-		NH_4^+	
Barlett's test statistic	X^2_{Ob}	X^2_C	X^2_{Ob}	X^2_C	X^2_{Ob}	X^2_C
	6.057	5.991	6.045	5.991	34.1	5.99
Hypothe-sis on equal variances is rejected	Yes		Yes		Yes	
Region 2: Córdoba-Orizaba						
	SO_4^{2-}		NO_3^-		NH_4^+	
Barlett's test statistic	X^2_{Ob}	X^2_C	X^2_{Ob}	X^2_C	X^2_{Ob}	X^2_C
	7.765	3.84	0.071	3.84	14.3	3.84
Hypothe-sis on equal variances is rejected	Yes		No		Yes	

X^2_{Ob}: Observed Chi square statistic value

$X^2_{C:}$: Critical Chi square statistic value

Table 2. Results for the test of hypothesis on atmospheric deposition fluxes are independent of land-use type for Region 1: Atasta-Xicalango. Kruskal-Wallis test at 95% significance level.

SO_4^{2-}						
	Summer		Autumn		Winter	
Kruskal Wallis test statistic	K_{Ob}	K_C	K_{Ob}	K_C	K_{Ob}	K_C
	17.62	3.84	18.94	3.84	8.94	3.84
Hypothesis on atmospheric deposition fluxes are independent on land-use type is rejected	Yes		Yes		Yes	
NO_3^-						
	Summer		Autumn		Winter	
Kruskal Wallis test statistic	K_{Ob}	K_C	K_{Ob}	K_C	K_{Ob}	K_C
	11.03	3.84	15.53	3.84	18.95	3.84
Hypothe-sis on atmospheric deposition fluxes are independent on land-use type is rejected	Yes		Yes		Yes	
NH_4^+						
	Summer		Autumn		Winter	
Kruskal Wallis test statistic	K_{Ob}	K_C	K_{Ob}	K_C	K_{Ob}	K_C
	18.95	3.84	17.19	3.84	17.1	3.84
Hypothesis on atmospheric deposition fluxes are independent on land-use type is rejected	Yes		Yes		Yes	
K_O: Observed Kruskal Wallis statistic value $K_{C:}$: Critical Kruskal Wallis statistic value						

Table 3. Results for the test of hypothesis on atmospheric deposition fluxes are independent of land-use type for Region 2: Orizaba-Córdoba. Kruskal-Wallis test at 95% significance level.

SO_4^{2-}				
	Autumn		Winter	
Kruskal Wallis test statistic	K_{Ob}	K_C	K_{Ob}	K_C
	14.92	3.84	14.92	3.84
Hypothesis on atmospheric deposition fluxes are independent on land-use type is rejected	Yes		Yes	
NO_3^-				
	Autumn		Winter	
Kruskal Wallis test statistic	K_{Ob}	K_C	K_{Ob}	K_C
	14.925	3.84	14.925	3.84
Hypothe-sis on atmospheric deposition fluxes are independent on land-use type is rejected	Yes		Yes	
NH_4^+				
	Autumn		Winter	
Kruskal Wallis test statistic	K_{Ob}	K_C	K_{Ob}	K_C
	14.925	3.841	14.925	3.841
Hypothesis on atmospheric deposition fluxes are independent on land-use type is rejected	Yes		Yes	
K_O: Observed Kruskal Wallis statistic value $K_{C:}$: Critical Kruskal Wallis statistic value				

5 Conclusion

Results found in this research work suggest that NO_3^- and NH_4^+ levels had a local origin, whereas, sulfate levels can be attributed to both, local and regional sources. Regional contribution is significant mainly during autumn and winter seasons, when long-range transport of air pollutants enhanced the background levels in these regions.

In the case of region 1, it was clear that the sour gas recompression plant had a great influence on these background levels in the region of Xicalango-Atasta. S atmospheric deposition can be considered as a serious threat to the mangrove ecosystem and the fisheries in this region.

In the case of region 2, it was completely evident that this region is highly influenced by long-range transport of air pollutants emitted from regional sources along the coast of the Gulf of Mexico in both seasons (autumn and winter). During autumn season, Center of Mexico is under the influence of trade winds that transport air pollutants from sources located in Tabasco and Campeche states, where oil and gas facilities could contribute in great proportion to background levels in the region. On the other hand, during winter season, wind blows from North as a result of cold fronts named “Norths”, transporting air pollutants from sources located in the Northeast of the country, where significant industrial activities are developed, contributing in a great proportion to background levels in this region.

In addition, it is important to consider that region 2 is located at a Valley; therefore, topography of the sampling sites is not favorable to dispersion of air pollutants resulting in a high deposition of sulfate and nitrate.

There were evident dissimilarities between region 1 and region 2. The possible and potential explanations of this difference include: 1) local differences in air quality, 2) intra- and inter-site differences in canopy structure, topographic characteristics, elevation and exposure patterns as a result of its location and the contribution of local and regional sources, 3) effects of inter-annual precipitation variability on atmospheric deposition.

Regarding to N deposition, atmospheric deposition of N in both studied regions is not expected to cause serious perturbations in nutrient cycling, according to the current understanding of atmospheric deposition effects in forests. However, in the case of S deposition, in spite of region 1 has a high soil buffering capacity, this region is characterized by nutrient-poor and sandy soils, which are vulnerable to acidification and/or euthrophication; whereas in region 2, there are several protected areas, crops and natural sites than can be threatened by this high deposition of S. From this comparison, it can be concluded that current upward trends in population growth and energy may reveal more widespread trends in N and S deposition in the future.

5.1 Future works

It is necessary to establish a range of critical loads for N and S for some ecosystems in Mexico. This information, and current deposition fluxes, will let estimate their exceedances. These exceedances will be related to sensitivity classes, to indicate if current S and N deposition levels are a risk or not for Mexican Ecosystems. Data obtained in this study are preliminary, once the database is completed; interpolation kriging will be applied to obtain continuous patterns and isolines of concentration that will be mapped using geo-statistical methods. Finally, from the maps and sensitivity classes, it will be possible to identify vulnerable zones, and establish a solid base line to develop regional policies focused to regulate and control emission sources to protect the biodiversity in these regions.

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