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Mapping of the Atmospheric Deposition of Sulfur and Nitrogen during the dry season 2016 in the Metropolitan Zone of Merida, Yucatan, Mexico

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Abstract. Atmospheric deposition of sulfur and nitrogen was measured in the Metropolitan Area of Merida, Yucatan in Mexico during the dry season of 2016. Passive samplers type "throughfall" based on ion exchange resins were used to measure the hydrological flows in a total of 9 sampling sites distributed throughout the city. The ions retained in the resin were analyzed by turbidimetry and colorimetry to determine Ammonium, Nitrate and Sulfate. Deposition fluxes of S and N obtained were 6.25 and 5.19 Kg ha^{-1} yr^{-1}. Both, sulfur and nitrogen atmospheric deposition fluxes were higher in urban sites, exceeding almost 2 times, the reference values proposed internationally for sensitive ecosystems. From the analysis of wind roses and air masses trajectories, it was possible to establish that during this climatic season, in addition to the local vehicular emissions, regional emissions generated upwind (from E-SE) contributed to atmospheric deposition of these ions. Finally, N and S deposition fluxes and their relationship with criteria pollutants were assessed, and maps for atmospheric deposition fluxes of Ammonium, Sulfate and Nitrate were generated using geo-statistical tools in order to identify critical deposition zones in this Metropolitan zone.

INTRODUCTION

N and S deposition have increased in the last decades as a result of the fossil fuels burning and the use of fertilizers in agriculture (Galloway et al, 2008). For this reason, total atmospheric measurements are required to estimate input-output budgets, to assess the biological response to air pollutants and loads of nutrients, and to relate the emission patterns to actual deposition to ecosystems (Weathers and Lovett, 2000). In addition, observations about chemical and physical characteristics of the atmosphere at local, regional and global scale are required to develop new regulations and environmental policies focused to protect not only public health but also ecosystems. In addition, the key for an effective design of air quality policies requires to establish long-term monitoring programs at global, regional and local scale to understand and quantify the current conditions, and consequently,

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compare them with past conditions and reference values such as critical loads. It will let to diagnose the real effect of current emission patterns and resulting N and S deposition on the ecosystems. Critical loads have been defined as the quantity of an air pollutant to which an ecosystem can be exposed without suffering any damage. This concept is defined for nitrogen and sulphur compounds as a tool to design control strategies based on sensitivity of studied ecosystems (Nilsson and Grennfelt, 1988). However, sensitivity varies between ecosystems due to some factors such as differences in local composition of soil, chemical weathering of basic cations, deposition patterns, type of ecosystem, and so on; resulting in large variations between receptors. Spatial heterogeneity is defined as variability spatially structured of a given property. Most of process, including litterfall (fall of leaf litter), throughfall (passive deposit that consist in solutes collected in wet deposition under canopy) and stemflow (flow through plants stem) act at a local scale to produce this kind of patterns. Differences between atmospheric pollutants inputs and critical load values at a local scale can be identified as exceedances (UNECE, 1996). Atmospheric pollutants concentration maps and Deposition fluxes are used to estimate the exceedances to threshold limit values known as critical loads, used to protect different receptors. Consequently, the range of exceedances can be related with sensitivity categories, to diagnose the vulnerability of an ecosystem to the inputs of N and S.

However, the main problem during this process is to find available deposition data. Dry deposition to ecosystems is usually obtained from theoretical models due to a lack of standardized monitoring methods and the difficulty of measuring dry deposition inputs. On the other hand, wet deposition depends on rain events occurrence, resulting in an insufficient data set to study temporal and spatial variability at a long term. Collection devices for wet deposition involve both, manual and automatic collectors. The first ones are an economic option but difficult to apply in field and remote sites, whereas, automatic collectors are expensive and need to comply with specific criterions of installation and operation. Fenn and Bytnerowicz (1997) proposed passive sampling devices to quantify atmospheric deposition in forests by using ionic exchange resins (IER). The scattered application of throughfall methods in Europe and North America has required to demonstrate a good correlation between measured fluxes and total deposition. About this, it has been reported that atmospheric inputs are similar to throughfall deposition, concluding that throughfall collectors can be used to quantify S total deposition and a good correlation between N throughfall deposition and the presence of nitrates in soils (Warfvinge, 1997).

Biogeochemical cycles are changing as a result of human activities, with serious repercussions not only at ecosystem level, but also at regional and global level. Due to detrimental effects associated to acid deposition, it is necessary to quantify N and S inputs to ecosystems. Biodiversity in the southeast of Mexico is strongly affected by N and S Deposition. Since, a great proportion of economic incomes come from ecotourism industry, there is an increasing concern about possible ecological effects of acid deposition in ecosystems and historical heritage. Particularly, the main terrestrial and offshore facilities for gas and oil exploration and production are located in the southeast of Mexico, coexisting with archaeological monuments and protected natural areas, resulting in a complex environmental framework. Therefore, in this study, N and S throughfall deposition was collected and mapped in the Metropolitan Zone of Merida in Yucatan Peninsula, Mexico during the dry season in 2016 and its relation with criteria air pollutants was also assessed.

METHODOLOGY

Study Area

Merida is the most populated city in Yucatan Peninsula, located at 20°58′04″N and 89°37′18″W with an altitude of 8 m asl. Conurbated area of this Metropolitan zone comprises another municipalities such as Kanasín, Umán, Conkal and Ucú. This zone has a plane orography, classified as barrier plain, with rocky and carbonated soils, where hydrological fluxes are mainly underground streams. Climate is humid warm with rains occurring along the summer and with a monthly mean temperature of 25 °C. Fig. 1, shows the specific location of sampling sites for this study.

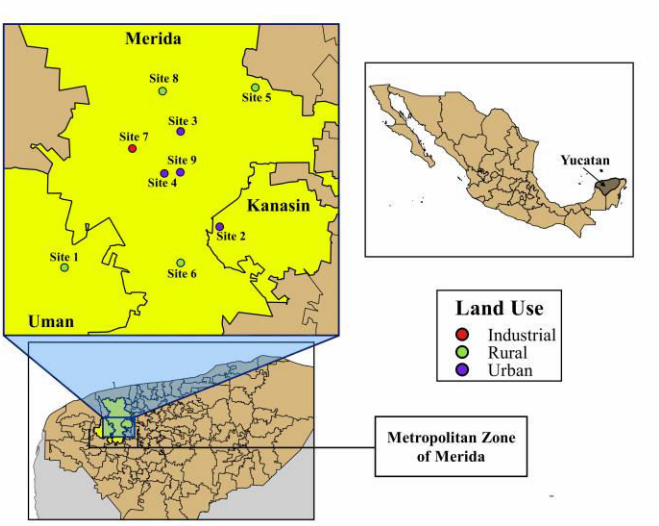


FIGURE 1. Sampling sites location

Sampling

Complex spatial patterns in a given area such as N and S atmospheric deposition must be characterized by using a simple monitoring equipment, not expensive, easy to operate, and which does not require frequent visits to the field. Collectors based on ionic exchange resins (IER) have been used with a high spatial resolution to measure throughfall deposition in forests ecosystems (Fenn and Poth, 2000). IER collectors consist in a funnel connected to an inner column containing 30 g of ionic exchange resin with glass fiber at the top (as filter) and at the bottom (as a support platform). The funnel is covered with a fine mesh to avoid falling solid material. The inner column is inserted within an outer column of PVC to protect it from solar radiation and avoid damages in the properties of the resin. Deposition falls on funnel surface, washing towards the inside column, where hydrological flux is controlled by a PVC valve. The main advantage of this kind of device, is that can be used during time periods relatively long, allowing to increase the sampling grid at a low cost. Nitrate, sulfate and ammonium can be exchanged by IER, by using a mixed resin (AmberliteTM IRN 150). In this study, throughfall deposition was collected in the Metropolitan zone of Merida from April 18 to June 18 during 2016 by using a multiple transects design with 9 sampling sites.

Chemical Analysis

Resin columns were extracted sequentially twice with two aliquots of 100 ml of 2N KCl. Obtained extracts were analyzed for nitrate (NMX- AA- 079- SCFI- 2001), sulfate (NMX- AA- 074- SCFI- 1981) and ammonium (Fresenius et al, 1988). Three IER columns were used as blank, extracted and analyzed, and mean values for nitrate, sulfate and ammonium were estimated and subtracted from total value of recovered ions. Massic solute was divided between surface area of funnel and total exposition period to obtain deposition fluxes of N (as NO_3^- + NH_4^+) and S (as SO_4^{2-}) in Kg ha^{-1} yr^{-1}.

Mapping and meteorological analysis and criteria pollutants

Geo-statistical maps can be defined as analytical production of maps by using field observations and computer programs to estimate new values in a given location. Sites location and concentrations attributed to each site are the input to estimate punctual maps which show spatial distribution, missing data and outliers. In a second stage, concentrations in neighboring points in each cell are averaged to obtain a new value attributed to a specific point. These points are the input to Kriging interpolation to obtain isolines of concentration (UNECE, 1996). In addition,

surface analysis was done by estimating wind roses from Windrose model (NOAA), and back trajectories of air masses were calculated by using HYSPLIT model (NOAA). Frequency histograms were estimated to identify the prevailing wind direction in each sampling site. Finally, data analysis was carried out from April 18 to June 18 during 2016, to correlate N and S throughfall deposition fluxes with meteorological variables (speed and wind direction) and criteria pollutants (SO_2, CO, NO_2, O_3 and $PM_{2.5}$). Air quality data were obtained from National Institute of Ecology and Climatic Change (INECC) through General Coordination of Pollution and Environmental health (SEDUMA station). Concentration roses were calculated for each criteria pollutant for all study period.

RESULTS AND DISCUSSION

A critical load values of 5 Kg N ha^{-1} yr^{-1} has been proposed for alpine ecosystems (Hiltbrunner et al, 2005); whereas a critical load value of 3 Kg S ha^{-1} yr^{-1}, and a range of 2-5 Kg S ha^{-1} yr^{-1} have been proposed for very sensitive areas and natural forests, respectively. Unfortunately, in Mexico, critical loads data are not available, and only few studies have been carried out in pine forests in Mexico Valley and Central Veracruz. Pérez-Suárez et al (2008) reported inputs of 45.5 and 8.8 Kg ha^{-1} yr^{-1} for N and S in Zoquiapan, State of Mexico. In addition, Fenn et al (2002) reported an input of 15 Kg N ha^{-1} yr^{-1} for pine stands in Desierto de los Leones, in Mexico Valley. On the other hand, Ponette-Gonzalez et al (2010) found inputs of 8-17 Kg ha^{-1} yr^{-1} and 2-4 Kg ha^{-1} yr^{-1} for S, and N, respectively. In this study, mean throughfall deposition fluxes for sulfate, ammonium and nitrate were 6.25, 2.32 and 2.87 Kg ha^{-1} yr^{-1}, respectively.

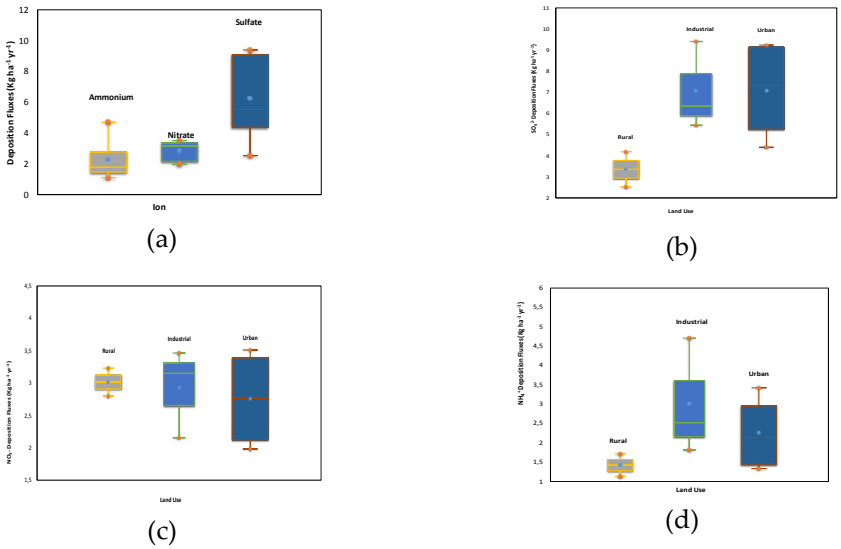
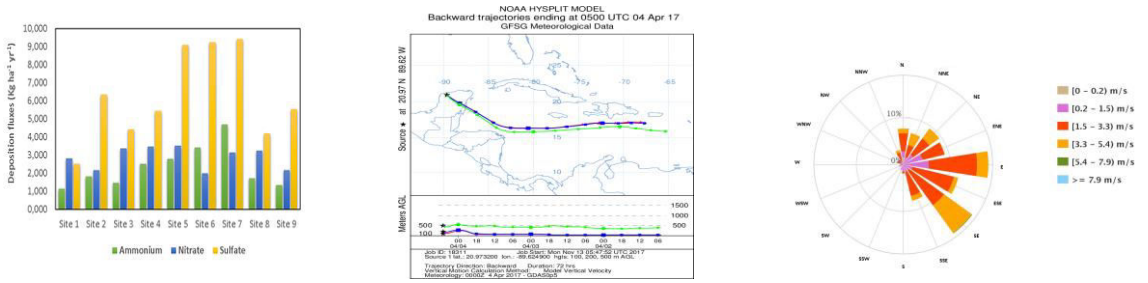


FIGURE 2. Throughfall deposition fluxes. (a) For ammonium, nitrate and sulfate, (b) By land use for sulfate, (c) By land use for nitrate, and (d) By land use for ammonium

From Fig. 2 (a), it can be observed that deposition fluxes were higher for sulfate, whereas nitrate and ammonium presented similar values. It agrees with residence time of their precursors in the atmosphere. S deposition flux (6.25 Kg ha^{-1} yr^{-1}) was almost two times higher than threshold limit value proposed for sensitive areas but lower than values reported by Pérez-Suárez et al (2008) and Ponette-Gonzalez et al (2010), whereas N deposition flux ((NO_3^- + NH_4^+ = 5.19 Kg ha^{-1} yr^{-1}) exceeded slightly the upper limit proposed for alpine ecosystems. Sampling sites were grouped according their land use as rural, industrial and urban. Deposition fluxes were higher in sites with a land use type industrial and urban (Fig. 2 b, c, d).

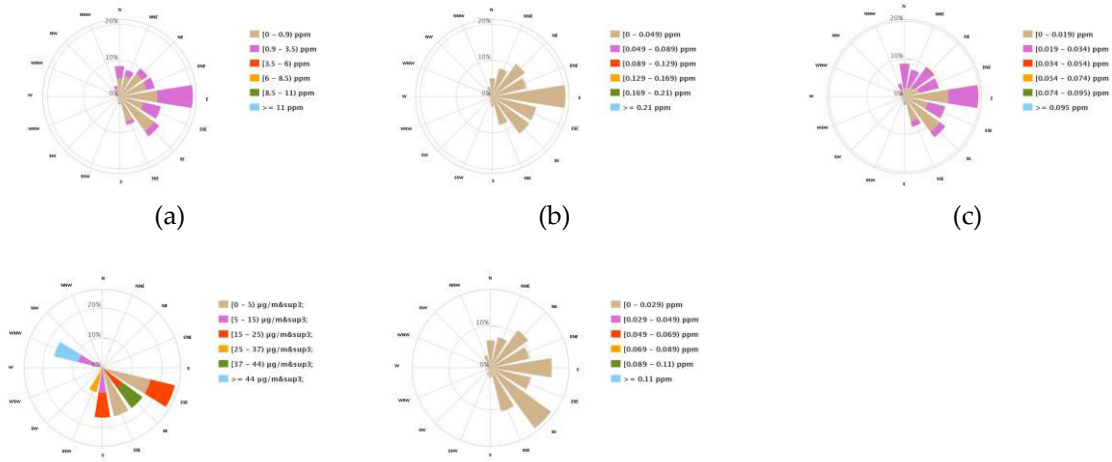
Fig. 3 (a) shows deposition fluxes for nitrate, sulfate and ammonium by sampling site. It can be observed that sites labeled as 5, 6 and 7, showed the highest sulfate deposition fluxes, these sampling sites are located at central and NW part; it agrees with prevailing winds that blowed from SE to NW concentrating air pollutants in this region of the Metropolitan zone. In the case of ammonium, deposition fluxes were also higher in sampling sites labeled as

5, 6 and 7; where prevailing winds resulted in a higher concentration of pollutants. However, besides transport, local sources could contribute to ammonium levels, since sites 5 and 6 have a land use rural, and site 7 is an industrial site. On the other hand, nitrate deposition fluxes were uniformly distributed along the Metropolitan zone, demonstrating their local origin, mainly vehicular sources. From meteorological analysis (Fig. 3 b, c), it could be concluded that the prevailing winds during dry season (spring) came from E-SE, demonstrating that deposition collected in Merida during this season had a local component, however, it is necessary to consider that long-range transport could be important in the case of sulfate, in spite of precipitation was scarce during this period. Regarding to criteria pollutant, it can be also observed (Fig. 4) that excepting $PM_{2.5}$, all pollutants presented higher concentrations when prevailing winds came from E-SE.



(a) (b) (c)

FIGURE 3. (a) Throughfall deposition fluxes by sampling site, (b) Typical air-masses trajectory during the study period, (c) Typical windrose during the study period

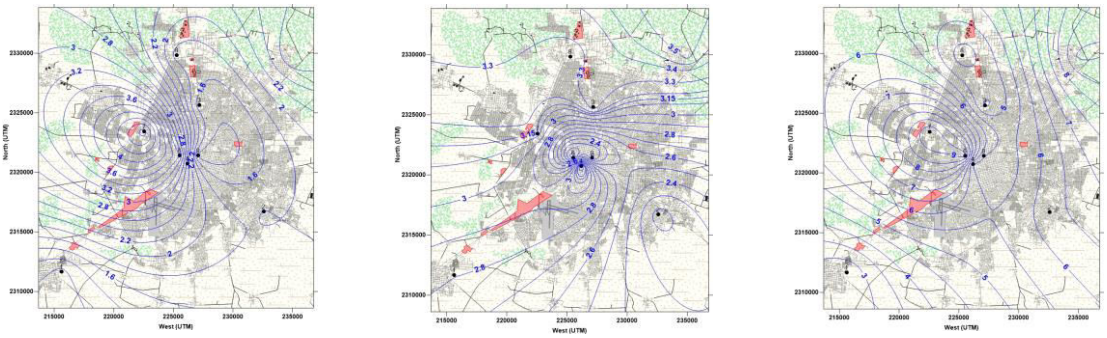


(a) (b) (c)

(d) (e)

FIGURE 4. Windroses for criteria pollutants concentration during the study period. (a) CO, (b) NO_2, (c) O_3, (d) $PM_{2.5}$, (e)SO_2

Data obtained in this work were interpolated to produce N and S deposition fluxes isopleths (Fig. 5). NH_4^+ deposition map indicates that ammonium deposition was higher in the central part and NW region of the Metropolitan zone of Merida. It agrees with prevailing winds which blows from SE to NW, concentrating pollutants in this region (Fig.5 a). In Fig. 5(b), NO_3^- deposition map shows that nitrate deposition was uniformly distributed along Metropolitan zone, demonstrating that this pollutant had a local origin, mainly, vehicular sources. Finally, in Fig. 5 (c), it can be observed that sulfate deposition fluxes were higher in the central part and Northern region, it suggests that both, local sources (central part, where is located the downtown of the city with an intense vehicular traffic); and regional sources (as a result of long-range transport) influenced on sulfate deposition during this season.



(a) (b) (c)

FIGURE 5. Throughfall deposition maps. (a) Ammonium, (b) Nitrate, (c) Sulfate

CONCLUSION

Results found in this work suggest that S atmospheric deposition had urban and industrial sources at a local and regional scale, being higher in the Northern and Northwestern regions of the Metropolitan zone of Merida as a result of prevailing winds. The current value for S deposition flux exceeded twice the reference value and it could be a risk of damage to ecosystems. In the case of ammonium atmospheric deposition, levels found were a result not only of sources at rural and industrial areas, but also in regional sources as a result of prevailing winds transporting air masses from SE to SW. Finally, nitrate showed deposition fluxes uniformly distributed, demonstrating the influence of local sources, mainly vehicular sources. It was not possible to correlate criteria pollutants with atmospheric deposition, however, from analysis of wind rose for concentrations, it was observed that the higher concentrations were also found when winds came from E-SE. Total N deposition flux exceeded slightly the upper limit proposed for alpine ecosystems. It suggests that it is necessary to establish specific critical load values and to estimate their exceedances. From this, it will be possible to develop emissions control strategies and propose policies focused to protect ecosystems in Yucatan Peninsula.

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