We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists

6,300

Open access books available

172,000

International authors and editors

190M

Downloads

Our authors are among the

154

Countries delivered to

TOP 1%

most cited scientists

12.2%

Contributors from top 500 universities

WEB OF SCIENCE™

Selection of our books indexed in the Book Citation Index
in Web of Science™ Core Collection (BKCI)

Interested in publishing with us?
Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected.
For more information visit www.intechopen.com

Spatial and Temporal Distribution of Throughfall Deposition of Nitrogen and Sulfur in the Mangrove Forests Associated to Terminos Lagoon

R.M. Cerón, J.G. Cerón, M. Muriel, F. Anguebes,
M. Ramirez, J. Zavala, C. Carballo and R.C. Escoffie

Additional information is available at the end of the chapter

<http://dx.doi.org/10.5772/59726>

1. Introduction

Air pollution is a major environmental concern in most urban areas. Atmospheric emissions of gaseous and particulate pollutants have caused profound environmental and health implications in last years. Sulphur dioxide (SO₂), nitrogen oxides (NO_x) and ammonia (NH₃) are gaseous pollutants commonly present in both, man- made and natural emissions in the lower atmosphere. Industrial processes, vehicular traffic, open biomass burning (including forest fires), dairy farming, intensive animal husbandry, and other anthropogenic activities are the main sources for these gaseous pollutants in the troposphere.

These pollutants may be removed from the atmosphere by two ways: wet deposition, which includes all pollutant material reaching the earth's surface by precipitation; and dry deposition, comprising the processes of adsorption of particulate and gaseous material by land or water surfaces [1]. In a general way, both processes govern the transfer of beneficial and toxic chemicals from the atmosphere on to surfaces.

Sulfur and nitrogen deposition (N and S) occurs as a result of these removal processes and is associated with acidification of soils and surface waters. Some environmental indicators have demonstrated that acidification related to air pollution may have already occurred in developing countries [2- 3]. The deposition of sulphur compounds cause changes in the chemistry and biology of the soils. These changes include decreasing pH and alkalinity, elevated concentrations of soluble aluminium and an imbalance in nutrient cycling leading to a change of ecosystem diversity [4]. There are evidences that nitrogen compounds deposition causes changes in ecosystems through eutrophication and acidification of soils and waters, decline in

trees growth and losses of vitality in forest [5- 6]. In addition, N and S deposition can cause deterioration to historical monuments and diverse materials and can cause damages to human health.

In Mexico, N and S deposition monitoring, its spatial and temporal distribution, and its effects on historical and cultural heritage and sensitive vegetation species have not been sufficiently studied. Comparing current conditions with ten years ago, S emissions' scenarios have decreased as a result of reformulation of fuels and the application of rigorous regulations focused to reduce them; however, it has been reported that the relative importance of N deposition has increased [7].

The coast of the Gulf of Mexico is characterized to be a complex region where the co- existence of oil refineries, offshore platforms and other facilities for oil and gas exploration and production, historical monuments, archaeological zones, and many valuable aquatic and terrestrial ecosystems (this region has the widest mangrove forests cover in the country) occurs. Campeche State is located at the southeast of the Gulf of Mexico and it constitutes the most important oil and gas producer in the country. A total annual emission of 205.64 Gg of NO_x and 336.79 Gg of SO_2 has been reported for this state, mainly produced by urban and industrial sources. Consequently, it is expected that N and S deposition, in ecosystems located downwind from these sources, would be high. This region has important natural reserves, national parks, protected natural areas, historical monuments and archaeological sites that constitute the main support of the eco- tourism industry which generates significant economical resources for Campeche State. Only in Campeche State, mangrove cover accounts for 29.98% of the total country cover, which is, approximately 196,552 ha. Therefore, the potential ecological effects derived from atmospheric deposition on these sites constitute a key concern for this region.

Critical loads estimation method allows to quantify the grade of damage derived from atmospheric pollutants deposition on ecosystems. A critical load can be defined as the input of one pollutant at levels below of which harmful ecological effects do not occur in the long term. To establish these critical load values and estimate their exceedances in a given site, atmospheric deposition measurements in field are required. N and S levels, their spatial and temporal distribution and their deposition fluxes are used in order to determine the actual inputs of these pollutants to ecosystems. This information is commonly represented in deposition maps, most of them are based on three- dimensional chemical transport model results which need to be validated by comparison with field measurements [8- 10]. Such studies represent an opportunity for policy- makers to identify the potential impacts associated with different emission sources and their spatial and geographical distribution. Sensitivity mapping and the critical load approach are methods that may allow analysis of these risks.

Particularly, in Mexico, measurement- based maps are required to assess the current deposition fluxes and the vulnerability of the ecosystems. Considering that studies about critical loads and their exceedances are scarce in tropical humid forests, this research work had the following aims: 1) To establish a solid base line about throughfall deposition of N and S in mangrove ecosystems, and 2) To assess the temporal and geographical distribution of N and S deposition along Carmen Island in order to identify critical zones and seasons in which N and S deposition can be high as a result of the prevailing meteorological conditions.

2. Study area

This study was carried out in Carmen Island, Campeche, Mexico. This site constitutes a complex area due to its closeness to the most important offshore zone for gas and oil exploration and production. In addition, the urban area is located within the buffer zone and in the surroundings of the Natural Protected Area of "Terminos Lagoon". Climate in this site is sub-humid warm with rains occurring along the summer. Annual mean precipitation is 1300 mm and annual average temperature is 27 °C. Prevailing winds blew from NE from March to October (when the island is under the influence of cold fronts called "Norths"); and from SE during the rest of the year (from April to September) when this site is influenced by tropical maritime air as a result of the trade winds. In Figure 1. is presented a typical wind rose and backward trajectory for Carmen Island during the study period. Additionally, Carmen Island is all time under the influence of sea and land breezes as a consequence of differential heating. In this research, a multiple transect sampling schema was designed (13 sampling points were considered along the island) in order to assess N and S deposition temporal and spatial distribution along Carmen Island. Specific sampling points are presented in Figure 2.

Figure 1. Typical wind rose and backward trajectory for Carmen Island during the study period.

Figure 2. Sampling sites location along Carmen Island, Campeche, Mexico.

3. Methodology

3.1. Sampling

Throughfall deposition consists of collected solutes in wet deposition under the forest canopies. This method is widely used to estimate atmospheric deposition inputs to the forest ecosystems, since it includes both, wet and dry deposition. Because of the high cost and difficulty of the measurements of dry deposition fluxes in forest stands, throughfall collectors constitute a good choice to obtain a reliable estimation of N and S atmospheric inputs in a given ecosystem [11]. However, in regions where N deposition is chronic, throughfall collectors underestimate the total N fluxes (wet plus dry) [12]. This underestimation is attributed to the uptake and retention of atmospheric N compounds in tree canopies, especially during dry deposition [13]. In spite of this restriction, throughfall estimations of N and S deposition are useful to establish a base line in sites where atmospheric deposition data are not available as is the case of the tropical forests in Mexico. Since, a worldwide database of atmospheric N and S inputs is available; inputs quantified in a given region can be compared with these reference values to obtain a diagnosis about the severity of N and S deposition and the possible vulnerability of the ecosystems.

Automatic wet/dry collectors are expensive and need to satisfy certain requirements for their installation; therefore, passive sampling devices as throughfall collectors constitute a good sampling alternative in a given region; in addition, it is possible to increase the density of the sampling grid at a low cost. Throughfall deposition can be defined as the hydrologic flux of ions to floor contained within a solution. This work used passive throughfall collectors developed and tested by [14], constituted by an ionic exchange resin mixed bed within a column.

Throughfall deposition in Carmen Island was collected on one- year basis, from July 2013 to June 2014; passive sampling devices were exposed during two months for six periods throughout the year in each of the thirteen sampling points. Samples were collected at the end of each period.

Samples were collected with a funnel; the solution was channeled to the mixed resin bed through the column (particularly, in this work, a mixed Amberlite™ IRN150 ion exchange resin bed was used)., where ions were retained (Figure 3). At the end of the sampling period (two months), retained ions within the same column were extracted by using extraction solutions to recover the sampled elements. Sulfate and nitrate retained within the resin column were selectively extracted with a 2 N KCl solution and analyzed by turbidimetry and colorimetry, respectively.

Figure 3. Throughfall sampling devices used in this study.

Extraction efficiency was calculated as the percentage of the loaded ions on the columns to the recovered in sequential extractions. It was found that recovered N and S percentage from the third extraction was insignificant, therefore; only two extractions were considered for the recovery process, reaching an efficiency of approximately 96.8%. Similar extraction efficiencies have been reported by other authors [15].

Extraction efficiency was calculated as the percentage of the loaded ions on the columns to the recovered in sequential extractions. It was found that recovered N and S percentage from the third extraction was insignificant, therefore; only two extractions were considered for the recovery process, reaching an efficiency of approximately 96.8%. Similar extraction efficiencies have been reported by other authors [15].

3.2. Chemical analysis

NH_4^+ was analyzed by molecular absorption spectrometry using the blue indophenol method [16]. Sulfate was determined by turbidimetric method [17], whereas NO_3^- was analyzed colorimetrically by using the brucine method [18]. The weight of the extractant was converted to volume by using the specific density of the extractant solution ($2\text{N KCl} = 1.05 \text{ g ml}^{-1}$). The amount of each collected ion in a given column was determined as the factor of extractant volume multiplied by ionic concentration in the extractant. The surface area of the funnel opening and the sampling period were used to estimate the deposition fluxes of N and S per land area per year ($\text{Kg ha}^{-1} \text{ yr}^{-1}$).

3.3. Data interpolation and mapping

All methods based on point measurements (e.g., wet deposition, micrometeorological and dry deposition measurements, throughfall deposition), cannot be directly connected to emission inventories. Maps can only be produced directly from these measurements if the network is enough dense to account for spatial and temporal variations. This may be the case for networks measuring compounds with little spatial variation or for measurements of deposition in areas of simple terrain as the case of Carmen Island. A point measurements network should be interpolated using statistical methods as the kriging technique, which allows including monitoring data from neighboring stations for interpolation in a national scale [19]. Considering the characteristics of measured data and the expected interpolation results, diversified methods have been employed with atmospheric deposition network data [10, 20–22].

To obtain N and S deposition maps in Carmen Island, a geostatistical procedure was used to interpolate field measurements into a continuous spatially pattern, where data were interpolated using the kriging interpolation technique. Kriging is a statistical method that provides unbiased estimates of variables in regions where the available data exhibit spatial autocorrelation and these estimates are obtained in such a way that they have minimum variance. The first step was to obtain the statistics summary of primary data. From this, a descriptive report of data was carried out, including mean, maximum, minimum values and their frequency distribution. This analysis was carried out in order to determine if it was necessary to make a data transformation since the results of the kriging interpolation are more reliable when data are normally distributed [20]. Data interpolation was used in this work to obtain a continuous variable by isolines to increase the number of points in the sampling grid. Threshold values definition helps to obtain isolines or imaginary lines in which studied variables become continuous, this method is useful since it takes into account the spatial behavior of the variable from distance and the variability between points.

Values were obtained from a linear combination of the original points with known data. As a result, greater compact areas around the variable maximum values were estimated. Once additional points and isolines were obtained, deposition data were mapped to assess their spatial and temporal distribution along the Island.

4. Results and discussion

Critical loads have been estimated in several regions around the world. A critical load value of 5 Kg N ha⁻¹ yr⁻¹ has been reported for alpine ecosystems [23], whereas for New Mexico and California, values of 3- 8 Kg N ha⁻¹ yr⁻¹ and 4- 7 Kg N ha⁻¹ yr⁻¹, respectively, have been found [24]. On the other hand, a critical load value of 3 Kg S ha⁻¹ yr⁻¹ for very sensitive areas and a range of 2 - 5 Kg S ha⁻¹ yr⁻¹ for natural forests have been proposed [25].

In Mexico, critical loads data are not available and only few studies have been carried out in Mexico Valley, mainly in pine forests. It has been reported an input of 15 Kg N ha⁻¹ yr⁻¹ for pine stands in Desierto de Los Leones in the surrounding of Mexico City [26], whereas in Zoquiapan (a site located at the east and upwind of Mexico City), the reported inputs were 5.5 and 8.8 Kg ha⁻¹ yr⁻¹ for N and S, respectively [27]. A research work carried out in Central Veracruz for several land- cover types reported inputs of 8- 17 Kg ha⁻¹ yr⁻¹ and 2- 4 Kg ha⁻¹ yr⁻¹ for S and N, respectively [28]. Additionally, some authors have studied the acidification in developing countries and have proposed a critical load approach on a global scale [3]. They assigned a relative sensitivity class of 3 to acidic deposition for terrestrial ecosystems in Carmen island region, and the preliminary critical load assigned to this site ranges from 50 to 100 meq m⁻² yr⁻¹.

In this study, mean fluxes of throughfall deposition for N (as N- NH₄⁺ + N- NO₃⁻) and S (as SO₄²⁻) at Carmen Island were 2.15 and 4.7 Kg ha⁻¹ yr⁻¹, respectively. N mean deposition flux did not exceed critical loads proposed for very sensitive ecosystems, however, S mean deposition flux is already in the threshold limit value proposed for natural forests and it is greater than those reported for very sensitive areas.

Sulfur dioxide is oxidized to sulfate, and the oxidation rate determines its lifetime in the atmosphere. Sulfuric acid is produced from the oxidation of sulfur oxides, which in turn form sulfate particles. However, even in the atmosphere of rural or non- industrialized sites, significant levels of sulfate particles have been found, concluding that sulfate in these sites is related to atmospheric reactions from anthropogenic SO₂ [29]. SO₂ has an atmospheric residence time of 13 days, and may be transported great distances from anthropogenic sources [30]. On the other hand, the oxidation of NO₂ at atmospheric conditions is almost 10 times faster than the oxidation of SO₂ to SO₄, resulting in a residence time of approximately 1 day [31]. These chemical properties make nitrate or its parental gaseous precursors NO_x, be commonly known as local pollutants. Since the dry oxidation of SO₂ to SO₄, or wet oxidation via the bisulfate (HSO₃) intermediate at the ambient atmospheric conditions is much slower than that NO_x, SO₂ and its intermediate oxidative products have much longer residence time in the atmosphere. This makes them more susceptible to be transported by the movement of

the air masses in comparison with NO_x . For this reason SO_4 or its parental gaseous precursors are known as regional pollutants.

Additionally, during the rainy season, when the mixing layer is very high, most of pollutants in precipitation derive from the rain- out process of condensation nuclei that have been transported long distances into the region. In contrast, during the dry season, the reduced mixing layer only concentrates ionic species of local origin. Dry deposition is, in general, greater than wet deposition near emission source.

To infer this local or regional influence, the sulfate: nitrate ratio in throughfall deposition was estimated. A ratio of 4.7 was obtained, suggesting that this site was under the influence of long-range transport. NH_4^+ and NO_3^- had a similar pattern in their deposition fluxes, with the highest fluxes occurring during the dry season (Figures 4a and 4b). It is agree with the local character of the emissions of NO_x .

Figure 4. Atmospheric deposition fluxes for NH_4^+ , NO_3^- and SO_4^{2-} for Carmen Island for sampling season.

On the other hand, SO_4^{2-} had a completely different behavior, with the highest levels occurring during the plenitude of the rainy season and at the beginning of the cold fronts season (Figure 4c). This is in agreement with the regional character of SO_2 emissions which are more connected to wet deposition.

Before applying Krigging interpolation, the thirteen sampling points in which throughfall deposition was collected, were grouped in three zones, considering the land- use along the Island. Identified zones were the following: *Industrial zone* (sampling points 1,2,3 and 4) located at the east edge of the island, *Zone with the greatest mangrove cover* (sampling points 5, 6, 7 and 8) located at the middle part of Carmen Island, and *Urban zone* (sampling points 9, 10, 11, 12 and 13) located at the west side of the island.

Figure 5. Atmospheric deposition fluxes for NH_4^+ , NO_3^- and SO_4^{2-} for Carmen Island for sampling site.

Mean throughfall deposition fluxes for NH_4^+ , NO_3^- and SO_4^{2-} were the highest in sampling points labeled as 3, 7 and 2, respectively (Figures 5a, 5b and 5c). Sampling points 7 and 8 are located at the limit of the urban zone; both points are within a complex area at the transition zone between urban area and mangrove forest. Sampling point labeled as “7” is located within an area characterized by a high vehicular density, small geographical extent and few circulation ways, so in peak hours, traffic vehicular is intense, resulting in high NO_x emissions of that are deposited as NO_3^- in the surroundings of the emission points.

Figure 6b illustrates that NO_3^- deposition was higher in the area adjacent to mangrove ecosystem, whereas the highest deposition of NH_4^+ and SO_4^{2-} occurred in the island industrial

Figure 6. Atmospheric deposition fluxes for NH_4^+ , NO_3^- and SO_4^{2-} for Carmen Island for different land use: Urban, Mangrove ecosystem and industrial.

zone (Figures 6a and 6c). On the other hand, mean throughfall deposition fluxes for NH_4^+ and SO_4^{2-} were higher in sampling points 3 and 2, respectively. It is important to mention that the points 1, 2 and 3 are located in the mangrove forests boundaries. These points are placed at the east edge of the island, where some industrial facilities could contribute to deposition of local NH_4^+ and SO_4^{2-} . Since sampling points 2 and 3 were located along the Federal Highway 180, so that NH_3 could be also emitted from light-duty vehicles. Many authors have reported on NH_3 and amine emissions from gasoline-powered automobiles or engines with and without exhaust catalysts in dynamometer experiments [32, 33]. The production of NH_3 emissions depends on the vehicle's ability to produce NO in the presence of a catalytic convertor that has enough stored hydrogen to reduce the NO to NH_3 . However, considering prevailing winds, a great proportion of NH_4^+ could also come from rural areas at the east of Carmen Island, specifically located crossing the bridge "La Unidad" in Isla Aguada and Sabancuy municipalities, where agriculture activities are developed. In addition, sulfate levels in throughfall deposition collected in Carmen Island could be enhanced by the long-range transport of SO_2 emissions from offshore platforms in the Gulf of Campeche where sour gas is burned in elevated flares. These SO_2 emissions could be washed-out during the rainy and cold fronts seasons since the wind roses and backward air mass trajectories pointed out that air masses followed this direction during this climatic period.

4.1. Mapping deposition fluxes of acidic compounds over the study region

Since successive monitoring of precipitation chemistry at the same station is scarce in Carmen Island and the data collected from various sources are highly discrete at the temporal scale, then all the concentration data obtained in this work were employed to produce continuous contours for spatial analysis. One- year mean results for all sites were interpolated to produce N and S deposition loads isopleths (Figures 7, 8 and 9).

Figure 7. Spatial and temporal patterns of NH_4^+ throughfall deposition fluxes ($\text{Kg ha}^{-1} \text{yr}^{-1}$) in Carmen Island: (a) July, (b) September, (c) November, (d) January, (e) March, (f) May.

Figure 8. Spatial and temporal patterns of NO_3^- throughfall deposition fluxes ($\text{Kg ha}^{-1} \text{yr}^{-1}$) in Carmen Island: (a) July, (b) September, (c) November, (d) January, (e) March, (f) May.

NH_4^+ deposition maps indicate a clear seasonal pattern, positioning the highest values during the period September- January, just when the Island is under the influence of cold fronts (Norths). Highest fluxes associated to the spatial distribution, were in the surroundings of point 7 and in the east edge of the Island. This fact demonstrates that NH_4^+ probably could

have two main sources: light- duty vehicles circulating on the road with the highest traffic (point 7) and along the Federal highway 180 (points 1, 2 and 3) at the east edge of the Island. However, NH_4^+ deposition fluxes could be also enhanced by transport of emissions related to agricultural activities in Isla Aguada and Sabancuy municipalities.

Figure 9. Spatial and temporal patterns of SO_4^{2-} throughfall deposition fluxes($\text{Kg ha}^{-1} \text{yr}^{-1}$) in Carmen Island: (a) July, (b) September, (c) November, (d) January, (e) March, (f) May.

Nitrate did not show a clear seasonal trend and presented a similar pattern along the year representing its local character. However, it was observed a clear spatial pattern with peak values in the surroundings of points 6, 7 and 8. This zone is located at the mangrove forest boundaries and it is characterized by high vehicular traffic since there are not enough roads. Moreover, NO_3^- deposition fluxes showed a slight dilution effect, with relatively higher values during dry months, decreasing as rainy season progressed.

In the case of SO_4^{2-} , deposition fluxes were higher in the east edge of the island with a clear spatial trend which decreased progressively westward. Peak values were centered on the points 1, 2, 3 and 4. An evident seasonal pattern was identified since deposition fluxes were higher during Norths season; it suggests that sulfate levels could be enhanced by large-scale transported emissions from offshore platforms in the Gulf of Campeche demonstrating its regional character.

5. Conclusions

Results found in this research work suggest that NO_3^- atmospheric deposition in the study site has a local origin, and is mainly distributed along the urban zone, being its deposition higher during the dry season. On the other hand, NH_4^+ highest deposition fluxes were distributed at the east edge of the island just during the dry season, suggesting a local origin, probably from light-duty vehicles emissions and agricultural activities developed in nearby rural areas. Regarding SO_4^{2-} , its deposition has its origin in both, local and regional sources, being this contribution higher when the Island was subjected to the influence of "Norths". It was quite evident that in addition to local industrial sources in Carmen Island, background levels were enhanced by the long-range transport of SO_2 emissions from offshore platforms in the Gulf of Campeche during the "Norths" season when prevailing winds came from NE.

Exceedance of critical loads represents a potential risk indicator of acidification as well as its impacts on ecosystems; therefore, in order to assess the vulnerability of the mangrove ecosystems in Carmen Island, it is necessary to establish the critical loads and to estimate their exceedances. Only then, it will be possible to develop emissions control programs and propose prevention policies and local regulations focused to protect these ecosystems.

Interpolation of field measurements is one of the most convincing methods to explore N and S budget, even though the accuracy is limited by the characteristics of measured data and uncertainties associated with the interpolation technique.

This research work constitutes the first step to quantify the current status of N and S deposition in the study site. A long-range monitoring network over Mexico will be established in a short-time for estimating nitrogen and sulfur deposition fluxes and their distribution along the country. A series of monitoring stations should be set down in order to keep the uniformity in the measured data, allowing comparability and considering not only urban and industrialized sites but also rural and remote sites. Maps based on measurements are also required in Mexico to validate and calibrate three-dimensional transport models.

Acknowledgements

The authors acknowledge the financial support given to this research work by Autonomous University of Carmen through its Postgraduate Department. Thanks to the people, organizations, institutions and companies that provided a secure location for the sampling devices used in this study.

Author details

R.M. Cerón^{1*}, J.G. Cerón¹, M. Muriel², F. Anguebes¹, M. Ramirez¹, J. Zavala¹, C. Carballo¹ and R.C. Escoffie³

*Address all correspondence to: rceron@pampano.unacar.mx

1 Chemistry Faculty. Autonomous University of Carmen. Ciudad del Carmen, Campeche, Mexico

2 Marine Zone. Mexican Petroleum Institute. Ciudad del Carmen, Campeche, Mexico

3 Research Center of Environmental Sciences. Autonomous University of Carmen. Ciudad del Carmen, Campeche, Mexico

References

- [1] Fowler, D. 1980. Wet and dry deposition of sulphur and nitrogen compounds from the atmosphere. In: "Effects of acid precipitation on terrestrial ecosystems", NATO Conference Series, T.C. Hutchinson and M. Haras Eds., 4: 9- 27.
- [2] Zhao D, Zhang X, Yang J, Mao J and Xiong J. 1995. Critical load of sulphur deposition for ecosystem and its application in China. *J. Environ. Sci*, 7: 325–337.
- [3] Kuylenstierna, J.C.I; Rodhe, H; Cinderby, S; Hicks, K. 2001. Acidification in Developing Countries: Ecosystem Sensitivity and the Critical Load Approach on a Global Scale. *Ambio*, 30: 20- 28. doi: 10.1579/0044- 7447- 30.1.20
- [4] Nilsson, J. 1988. Critical loads for Sulphur and Nitrogen. In: "Air Pollution and Ecosystems", P. Mathy Ed., Proceedings of an International Symposium held in Grenoble, France, 18- 22 May, 1988: 85- 91.
- [5] Goulding, K.W.T; Balley, N.J; Bradbury, N.J; Hargreaves, P; Howe, M; Murphy, D.V; Poulton, P.R; and Willison, T.W. 1998. Nitrogen deposition and its contribution to nitrogen cycling and associated soil processes. *New Phytologist* 139: 49- 58.

- [6] Bishop, K.A. and Hultberg, H. 1995. Reversing acidification in a forest ecosystem: the Gårdsjön covered catchment. *Ambio*, 24: 85–91. doi:10.1021/es903722p.
- [7] Fenn, M.E; de Bauer, L.I; Zeller, K; Quevedo, A; Rodríguez, C; Hernández- Tejeda, T. (2001). Nitrogen and sulfur deposition in the Mexico City Air basin: Impacts on forest nutrient status and nitrate levels in drainage waters. In: M.E. Fenn et al (eds. *Urban Air Pollution and Forests*. Springer- Verlag, New York. Pp. 319.
- [8] Li, C.S.; Mosier, A; Wassmann, R.; Cai, Z; Zheng, X; Huang, Y; Tsuruta, H; Boonjawat, J; Lantin, R. 2004, Modeling greenhouse gas emissions from rice- based production systems: sensitivity and upscaling, *Global Biogeochem. Cycles*, 18. GB1043, doi: 10.1029/2003GB002045.
- [9] Luo, C., John, J.C; Zhou, X; Lam, K.S; Wang, T; Chameides, W.L. 2000. A nonurban ozone air pollution episode over eastern China: Observations and model simulations, *J. Geophys. Res.*, 105:1889–1908.
- [10] Levy, H., Moxim, W. J. 1989. Simulated global distribution and deposition of reactive nitrogen emitted by fossil fuel combustion. *Tellus*, 41: 256–271. doi: 10.1111/j.1600-0889.1989.tb00305.x
- [11] Butler, T.J; and Likens, G.E. 1995. A direct comparison of throughfall plus stemflow to estimates of dry and total deposition for sulfur and nitrogen. *Atmos. Environ*, 29: 1253- 1265. doi: 10.1016/1352- 2310(94)00339- M
- [12] Fenn, M.E; and Bytnerowicz, A. 1997. Summer throughfall and winter deposition in the San Bernardino Mountains in Southern California. *Atmos Environ*, 31: 673- 683. doi:10.1016/S1352- 2310(96)00238- 5
- [13] Garten, C.T; Schwab, A.B; and Shirshac, T.L. 1998. Foliar retention of ¹⁵ N tracers: Implications for net canopy exchange in low- and high- elevation forest ecosystems. *For. Ecol. Manage*, 103: 211- 216.
- [14] Fenn, M.E; and Poth, M.A. 2004. Monitoring nitrogen deposition in throughfall using ion exchange resin columns: A field test in the San Bernardino Mountains. *J. Environ. Qual*, 30: 2007- 2014.
- [15] Fenn, M.E; and Poth, M.A. 1999. Temporal and spatial trends in streamwater nitrate concentrations in the San Bernardino Mountains in Southern California. *J. Environ. Qual*, 28: 822- 836. doi: 10.2134/jeq1999.00472425002800030013x
- [16] Fresenius, W., K.E. Quentin, & W. Schneider, (Eds.), 1988. *Water Analysis*. Springer Verlag, Berlín: 804 p.
- [17] NMX- AA- 074- SCFI- 1981, 1981. Análisis de aguas. Determinación del ión sulfato en aguas naturales, residuales y residuales tratadas.
- [18] NMX- AA- 079- SCFI- 2001, 2001. Análisis de aguas. Determinación de nitratos en aguas naturales, potables, residuales y residuales tratadas.

- [19] Fowler, D; Smith, R.I; Weston, K.J. 1995. Quantifying the spatial distribution of surface ozone exposure at the 1kmx1km scale. In: Fuhrer, Achermann (eds.) (1995): 196-205.
- [20] Van Leeuwen, E. P., Draaijers, G. P. J; Erisman, J. W. 1996. Mapping wet deposition of acidifying components and base cations over Europe using measurements. *Atmospheric Environment*, 30:2495–2511.
- [21] Park, S. U., Lee, Y.H. 2002. Spatial distribution of wet deposition of nitrogen in South Korea, *Atmos. Environ*, 36: 619–628. doi:10.1016/S1352- 2310(01)00489- 7
- [22] Holland, E.A; Braswell, B.H; Sulzman, J; Lamarque, J. F. 2005. Nitrogen Deposition onto the United States and Western Europe: Synthesis of Observations and Models. *Ecological Applications*, 15: 38- 57. doi: 10.1890/03- 5162
- [23] Hiltbrunner, E; Schwikowski, M; Korner, C. 2005. Inorganic nitrogen storage in alpine snow pack in the Central Alps (Switzerland). *Atmos. Env*, 39: 2249- 2259. doi: 10.1016/j.atmosenv.2004.12.037
- [24] Fenn ME, Geiser LH (2011) Temperate sierras. Chapter 15: 175- 180. In: Pardo LH, Robin- Abbott MJ, Driscoll CT, eds. Assessment of nitrogen deposition effects and empirical critical loads of nitrogen for ecoregions of the United States. Gen. Tech. Rep. NRS- 80. Newton Square, PA: U.S. Department of Agriculture, Forest Service, Northern Research Station.
- [25] Grennfelt P, Nilsson J, Critical loads for sulphur and nitrogen. Report from a workshop held at Skokloster, Sweden. March 19- 24, 1988. The Nordic Council of Ministers Report 1988: 15, Copenhagen, Denmark. ISBN: 87- 7303- 248- 4.
- [26] Fenn ME, De Bauer LI, Hernandez- Tejeda T (2002) Summary of air pollution impacts on forest in the Mexico City Air Basin. In: Fenn ME, Bauer LI, Hernandez- Tejeda T eds., *Urban Air Pollution and Forests: Resources at Risk in the Mexico City Air Basin*. Ecological Studies Series, Volume 156. Springer- Verlag, New York, NY.
- [27] Pérez- Suárez M, Fenn ME, Cetina- Alcalá VM, Alderete A (2008) The effects of canopy cover on throughfall and soil chemistry in two forest sites in the Mexico City Air Basin. *Atmósfera* 21: 83- 100.
- [28] Ponette- Gonzalez AG, Weathers KC, Curran LM (2010) Tropical land- cover change alters biogeochemical inputs to ecosystems in a Mexican montane landscape. *Ecol. Applic.* 20: 1820- 1837. doi:10.1890/09- 1125.1. 96
- [29] Khoder, M.I. 2002. Atmospheric conversion of sulfur dioxide to particulate sulfate and nitrogendioxide to particulate nitrate and gaseous nitric acid in an urban area. *Chemosphere*, 49: 675- 684. doi: S0045- 6535(02)00391- 0
- [30] Hitchcock, D.R; Spiller, L.L; Wilson, W.E. 1980. Sulfuric acid aerosols and HCl release in coastal atmospheres: Evidence of rapid formation of sulfuric acid particulates. *Atmospheric Environment*, 14: 165- 182. doi: 0004- 6981/80/0201- 0165

- [31] Howells, G. 1995. Acid rain and Acid water. 2nd Ed. Ellis Horwood Ltd.
- [32] Pierson W.R, Brachaczek, W.W (1983) Emissions of ammonia and amines from vehicles on the road. Environ. Sci. Technol. 17: 757- 760. doi: 0013- 936X/83/0917- 0757
- [33] Bishop, G.A; Peddle, A.M; Stedman, D.H. 2010. On- road emission measurements of reactive nitrogen compounds from three California cities. Environ, Sci. Technol, 44: 3616- 3620. doi: 10.1021/es903722p