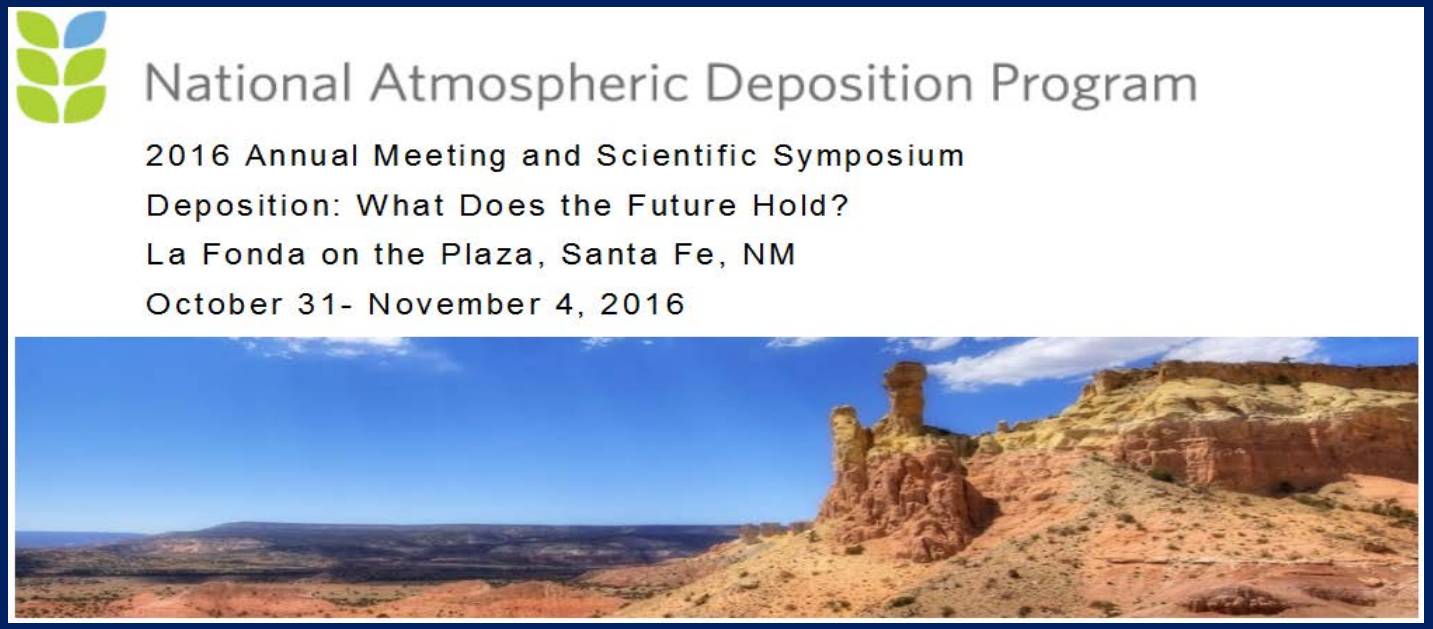


# Sulfate and nitrate in wet atmospheric deposition at the Gulf of Mexico and possible source regions of their precursors.

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# Importance of Gulf of Mexico

The activities (extraction processing and distribution of hydrocarbons, sea port activities, industrial, agricultural, fisheries and tourism) make this area a potential source of acid rain precursors.

# Emission sources in the Gulf of Mexico

The most important sources from the oil and gas production platforms are:
(Wilsson et al, 2004)

- Boilers/heaters/burners
- Diesel engines
- Drilling equipment
- Flares
- Flashing losses
- Fugitive sources
- Vents
- Loading operations
- Cutting and drilling fluids
- Natural gas engines
- Natural gas turbines
- Pneumatic pumps
- Storage tanks
- Etc.

# Non-platform sources in the Gulf of Mexico are:

- Commercial fishing
- Pipe laying operations
- Commercial marine vessels
- Support helicopters
- Drilling rigs ( Exploration )
- Support vessels
- Military vessel operations
- Survey vessels

# Acid rain studies at the Gulf of Mexico

- Studies on the Mexican coast have identified the presence of acid rain since 2003


Acid Deposition Events During the Autumn of 2003 in a research cruise over the Gulf of Mexico.

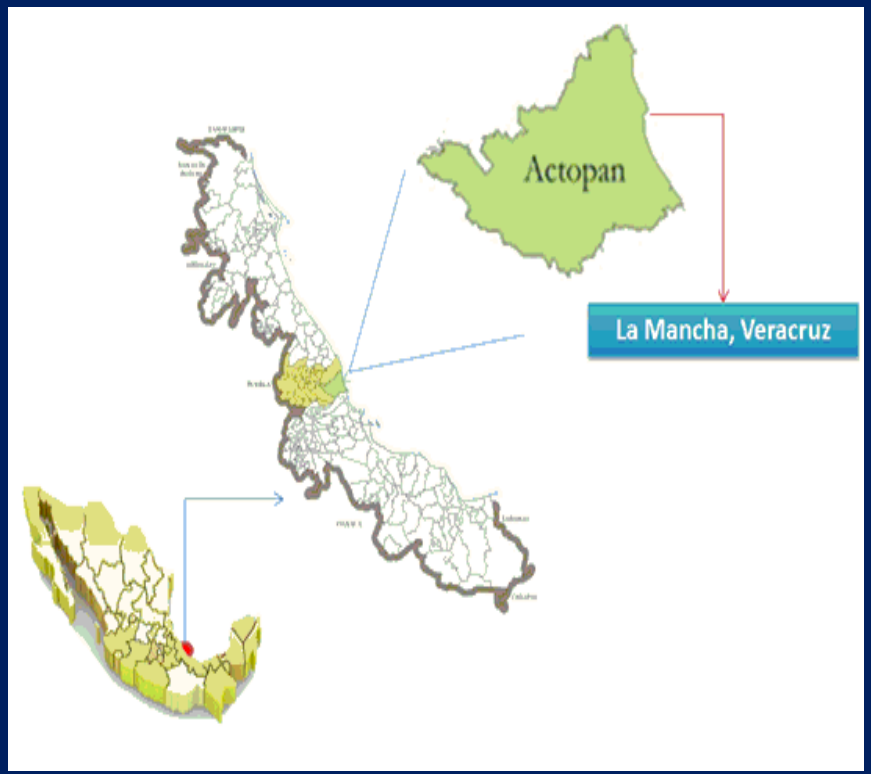
# Acid deposition effects in the coastal area

- Potentially-sensitive receptors in the coastal region of the Gulf of Mexico have become a topic of research:lakes, rivers, forests, soils, and material Monuments of cultural heritage.

- The Mayan Zone, “El Tajín” Archaeological Zone, and The “San Juan de Ulúa” fortress, were built with limestone, which is especially susceptible to deterioration by acid rain.

# Goal

The aim of this study was to evaluate pH, sulfate and nitrate concentrations in wet atmospheric deposition, collected daily from 2003 to 2015 in a sampling site located in the coast of Mexico (“La Mancha”) and compare the registered values, with the NADP sampling sites located in the coast of the Gulf of Mexico from Texas to Florida.



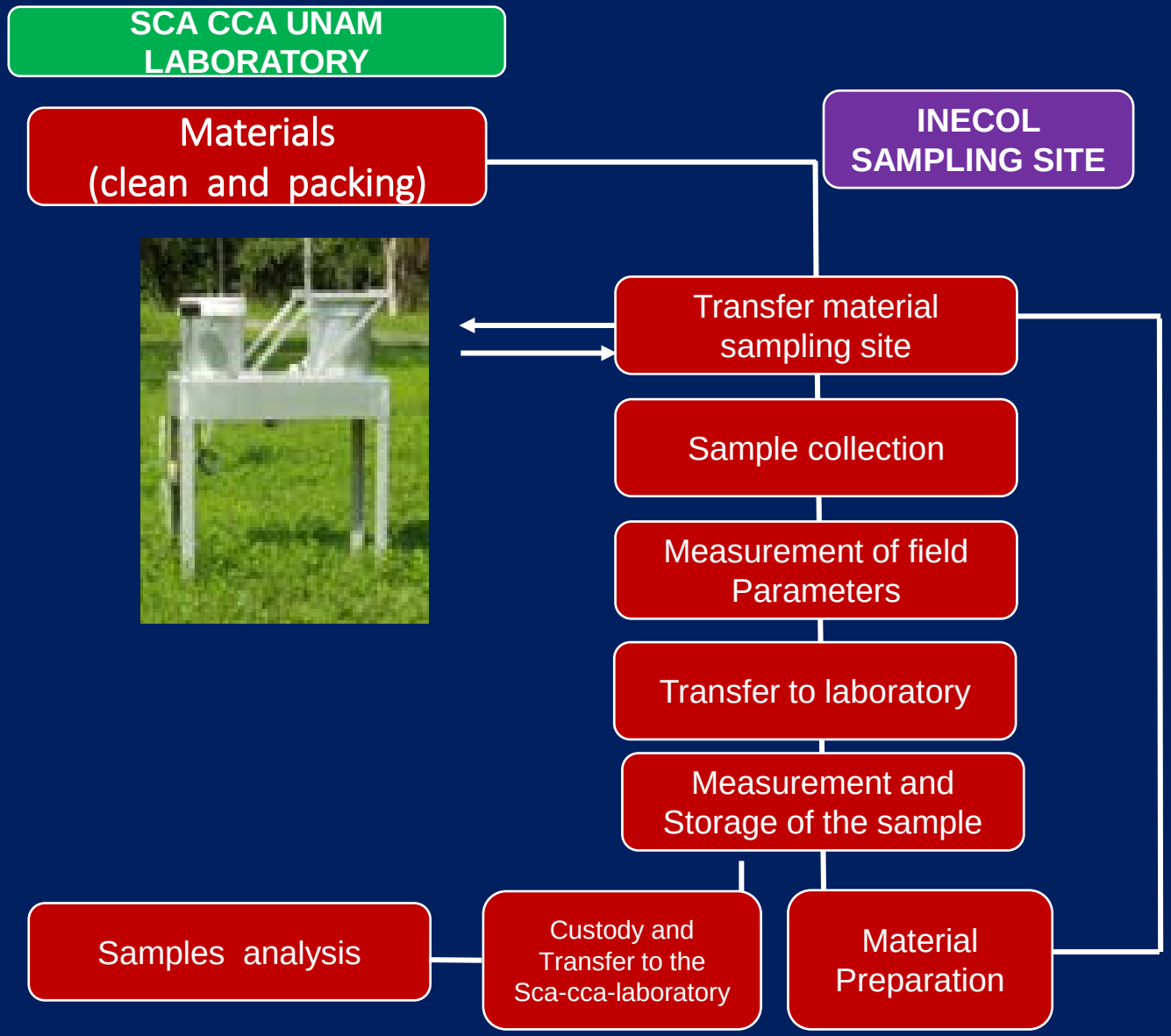

- For several years, at coast of the USA, it has been evaluated the chemical composition of rain, resulting acidic values.

- In relation to acid rain, pH determination it is essential, in addition to the composition of sulfates and nitrates that are formed from its main precursors, sulfur dioxide and nitrogen oxides, respectively.


Available data to compare

http://nadp.sws.uiuc.edu/data/sites/map/?net=NTN

# Wet and dry deposition sampling protocol



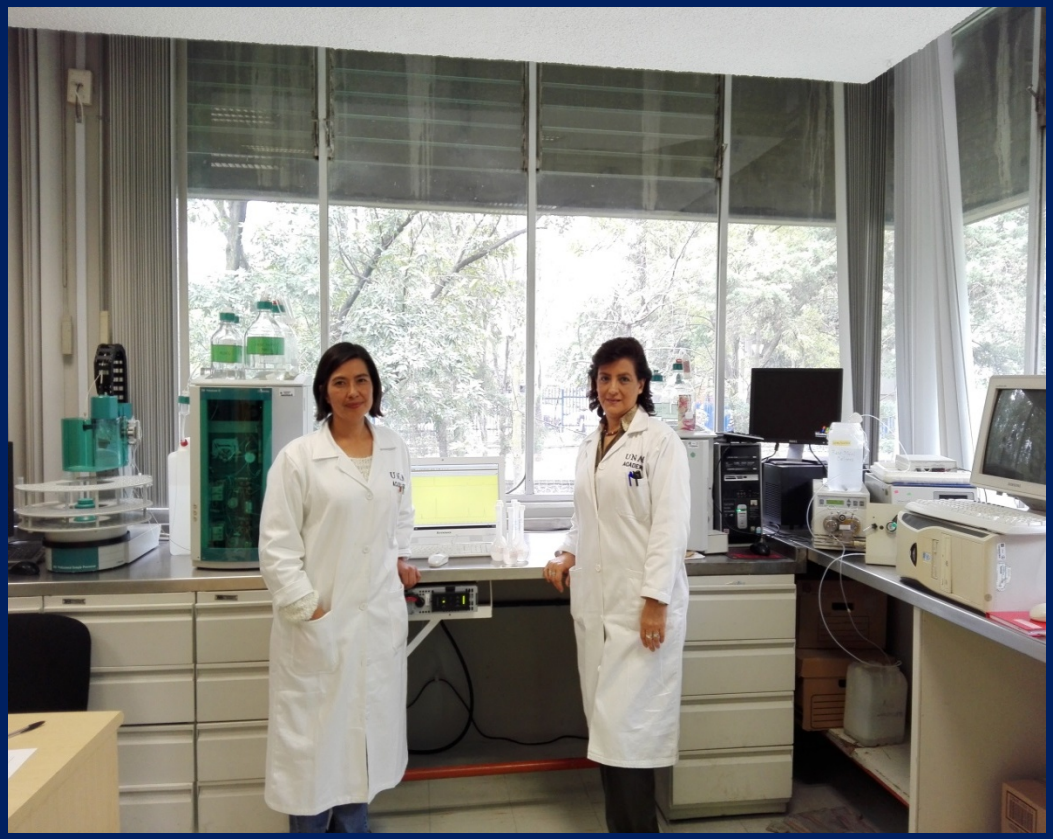
# Atmospheric deposition analysis

The collection of rainfall took place daily, at the Gulf of Mexico, to facilitate a more accurate temporal resolution for wet deposition. Chemical analysis for each sample to determine the following parameters: pH, conductivity, cations ($Na^+$, $NH_4^+$, $K^+$, $Mg^{2+}$, $Ca^{2+}$) and anions concentration ($Cl^-$, $NO_3^-$, $SO_4^{2-}$) by IC

Interlaboratory-comparison Programs.

GAW-WMO, since 2008.

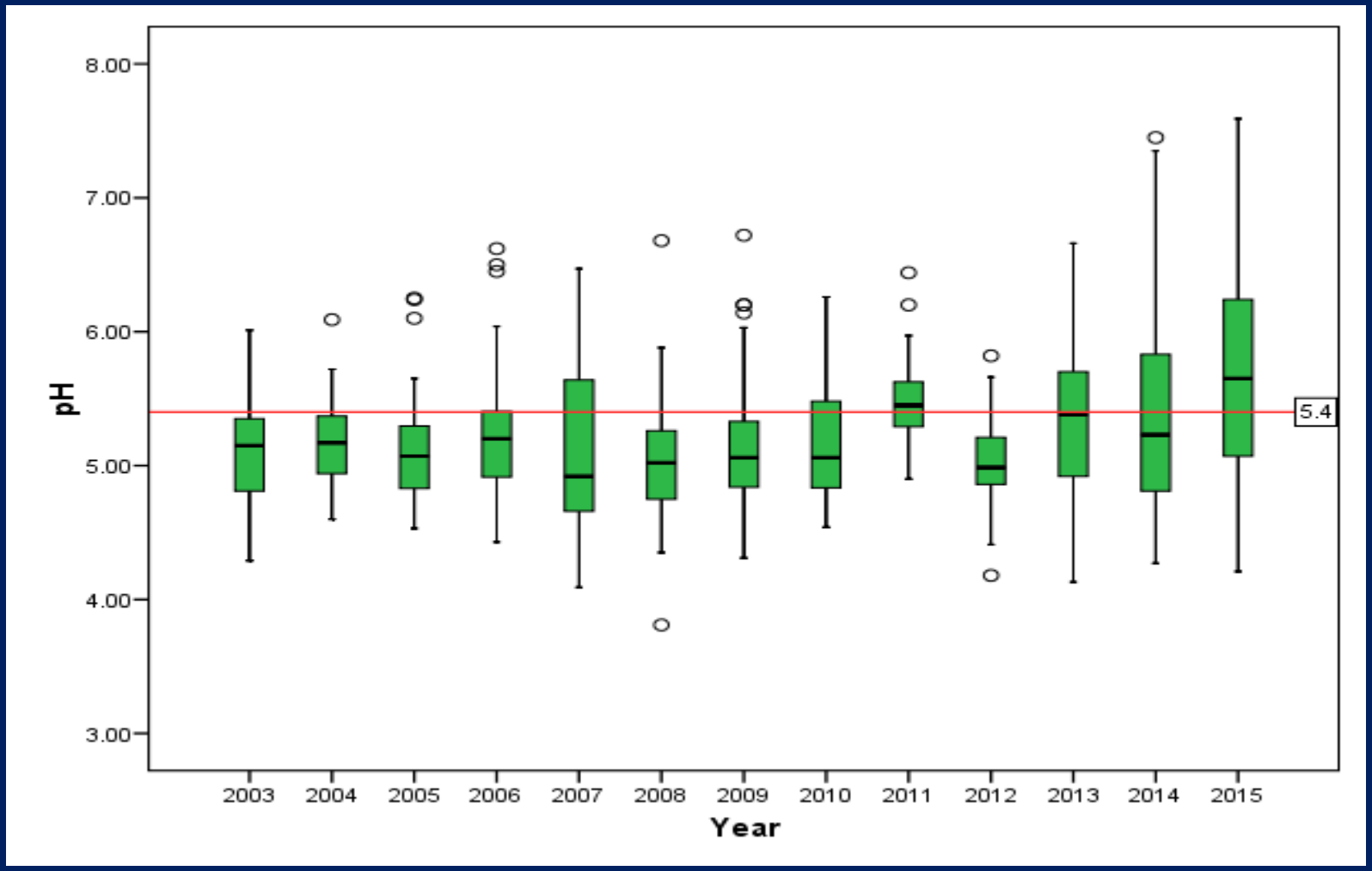
USGS-NADP, since 2016 .



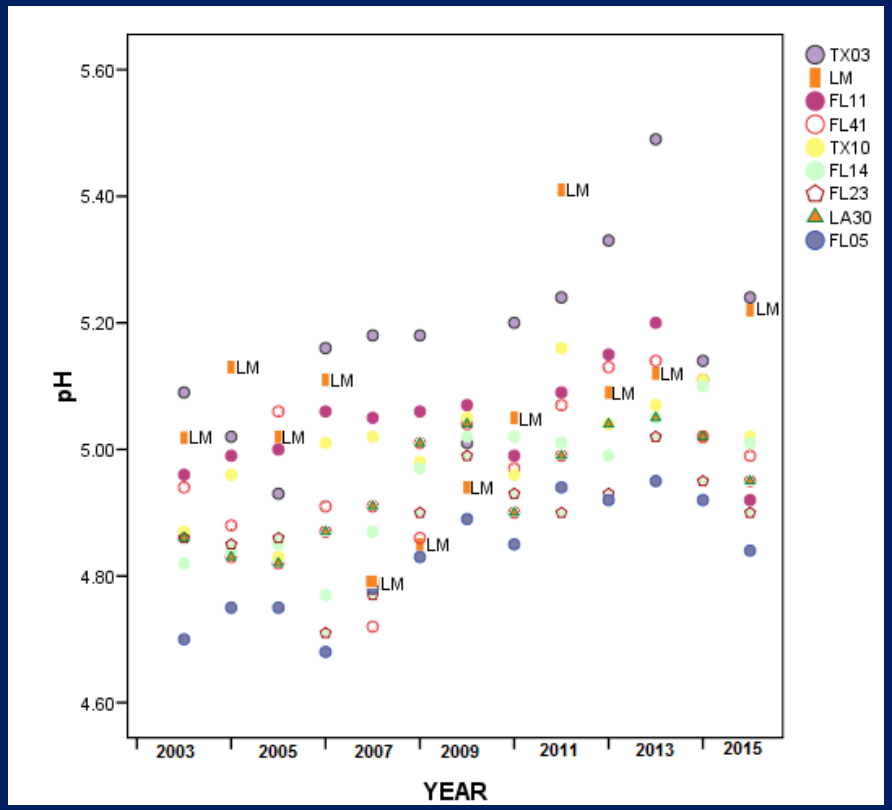
# RESULTS

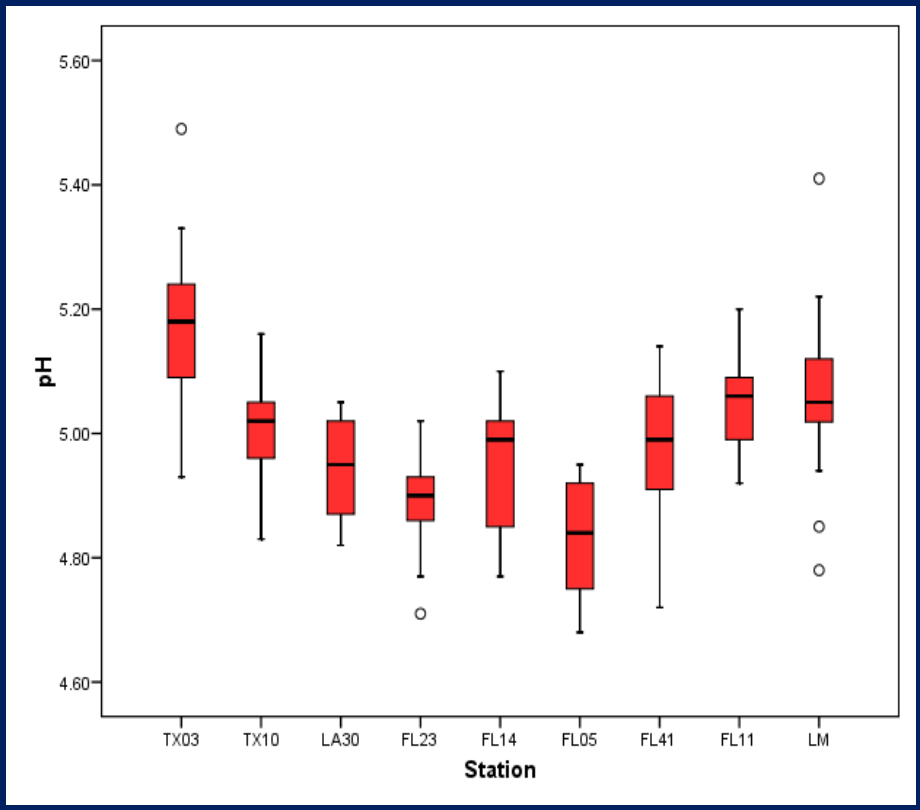
## pH

Box plots for the pH values from 2003 to 2015 at “La Mancha” station



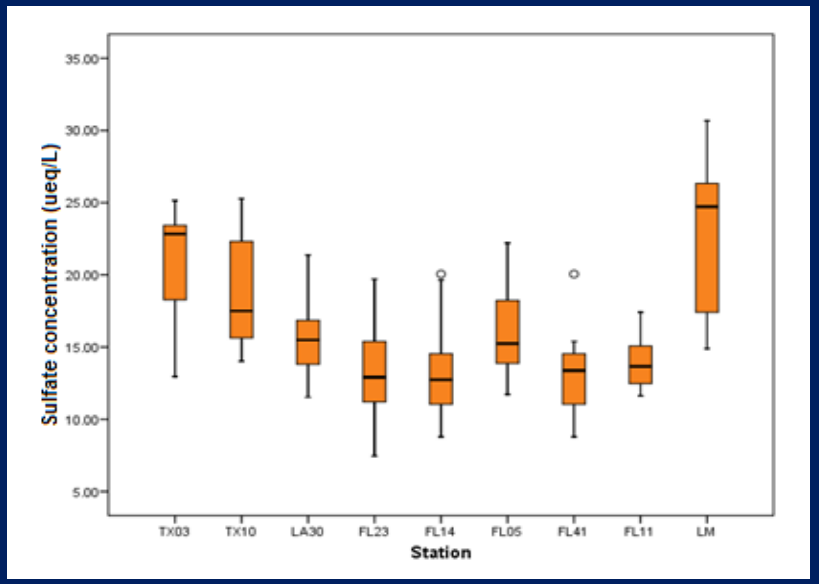
# pH VWM annual at “La Mancha” Station from 2003 to 2015



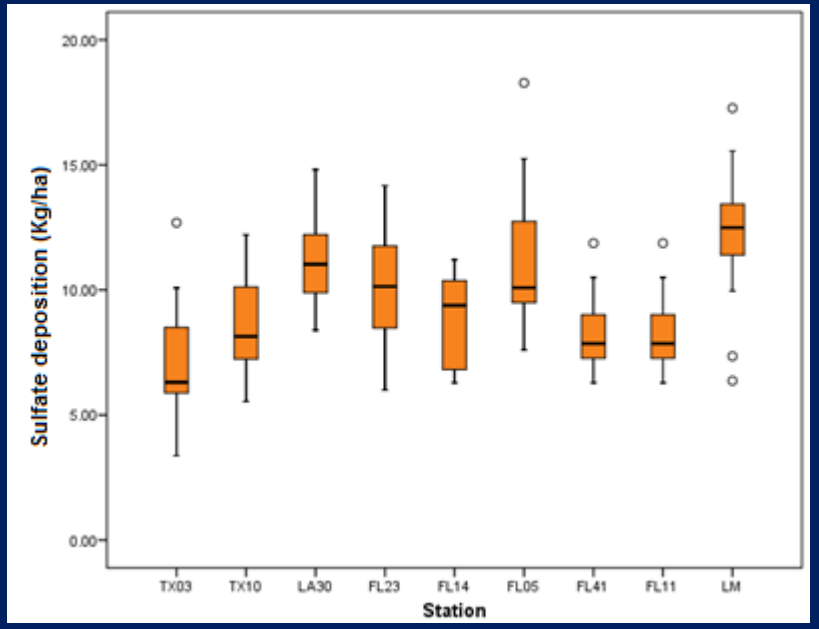



# Sulfate

| Sulfate | | | |
|---|---|---|---|
| Station | Min (µeq/L) | Max (µeq/L) | Median (µeq/L) |
| LM | 14.90 | 30.67 | 24.72 |
| TX 03 | 12.96 | 25.14 | 22.88 |
| TX 10 | 14.02 | 25.27 | 18.20 |
| LA 30 | 11.83 | 21.37 | 15.56 |
| FL 23 | 10.12 | 19.71 | 13.13 |
| FL 05 | 12.17 | 22.21 | 15.53 |
| FL 14 | 9.81 | 19.64 | 12.71 |
| FL 41 | 8.79 | 20.06 | 13.40 |
| FL 11 | 11.62 | 17.41 | 14.06 |

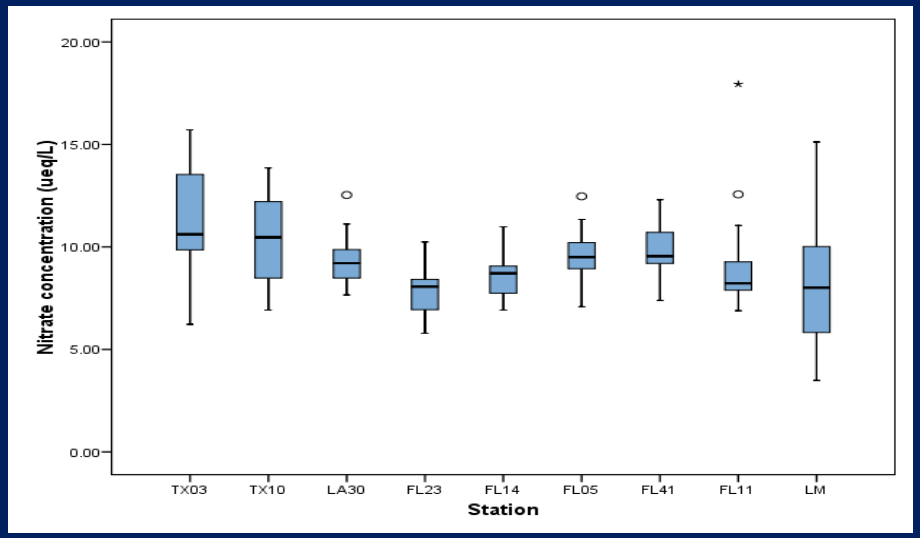



| Sulfate | | | |
|---|---|---|---|
| Station | Min (Kg/Ha) | Max (Kg/Ha) | Median (Kg/Ha) |
| LM | 6.37 | 17.27 | 12.49 |
| TX 03 | 3.37 | 12.69 | 6.31 |
| TX 10 | 5.54 | 12.21 | 8.14 |
| LA 30 | 8.39 | 14.81 | 11.03 |
| FL 23 | 6.00 | 14.17 | 10.14 |
| FL 05 | 7.60 | 18.28 | 10.09 |
| FL 14 | 6.29 | 11.21 | 9.38 |
| FL 41 | 6.29 | 11.87 | 7.86 |
| FL 11 | 7.64 | 13.66 | 9.54 |

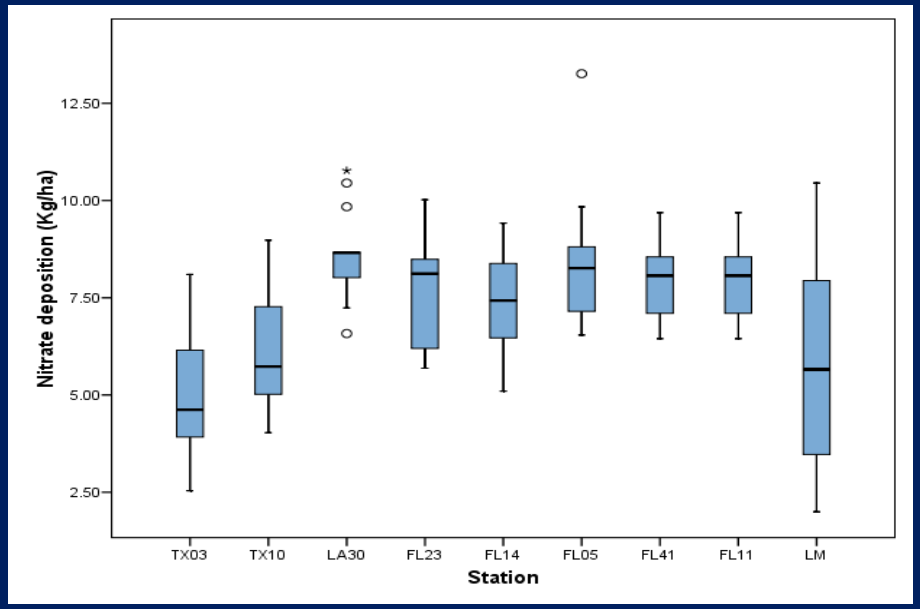


# Nitrate

| Nitrate | | | |
|---|---|---|---|
| Station | Min (µeq/L) | Max (µeq/L) | Median (µeq/L) |
| LM | 3.49 | 15.12 | 8.01 |
| TX 03 | 6.23 | 15.71 | 10.99 |
| TX 10 | 6.92 | 13.86 | 10.61 |
| LA 30 | 8.02 | 12.53 | 9.21 |
| FL 23 | 6.27 | 10.24 | 8.14 |
| FL 05 | 7.08 | 12.47 | 9.37 |
| FL 14 | 6.92 | 10.99 | 8.35 |
| FL 41 | 7.39 | 12.31 | 9.51 |
| FL 11 | 6.89 | 12.56 | 8.11 |




| Nitrate | | | |
|---|---|---|---|
| Station | Min (Kg/Ha) | Max (Kg/Ha) | Median (Kg/Ha) |
| LM | 2.00 | 10.45 | 5.66 |
| TX 03 | 2.54 | 8.1 | 4.62 |
| TX 10 | 4.03 | 8.98 | 5.73 |
| LA 30 | 6.58 | 10.77 | 8.66 |
| FL 23 | 5.69 | 10.02 | 8.12 |
| FL 05 | 6.54 | 13.26 | 8.26 |
| FL 14 | 5.10 | 9.42 | 7.43 |
| FL 41 | 6.45 | 9.69 | 8.07 |
| FL 11 | 6.15 | 10.73 | 7.94 |



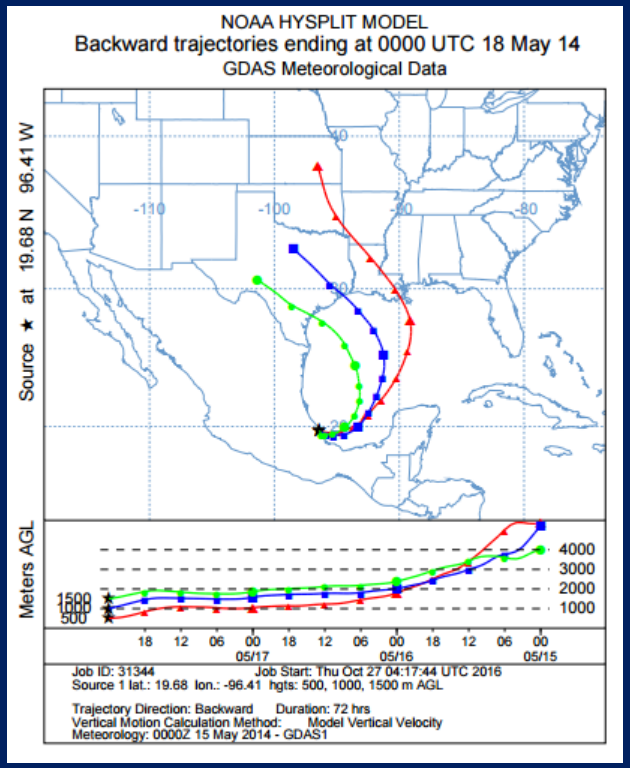
# NADP /LM ratio median value

| | SULFATE µeq/L | RATIO | NITRATE µeq/L | RATIO | HYDRONIUM µeq/L | RATIO |
|---|---|---|---|---|---|---|
| TX03 | 22.83 | 0.92 | 10.61 | 1.32 | 6.58 | 0.73 |
| TX10 | 17.49 | 0.71 | 10.46 | 1.31 | 9.53 | 1.06 |
| LA30 | 15.49 | 0.63 | 9.21 | 1.15 | 10.26 | 1.14 |
| FL23 | 12.91 | 0.52 | 8.06 | 1.01 | 12.59 | 1.40 |
| FL14 | 12.70 | 0.51 | 8.71 | 1.09 | 10.28 | 1.15 |
| FL05 | 15.24 | 0.62 | 9.5 | 1.19 | 14.22 | 1.59 |
| FL41 | 13.37 | 0.54 | 9.54 | 1.19 | 10.06 | 1.12 |
| FL11 | 13.66 | 0.55 | 8.22 | 1.03 | 8.72 | 0.97 |
| LM | 24.72 | 1.00 | 8.01 | 1.00 | 8.97 | 1.00 |

# Back trajectories

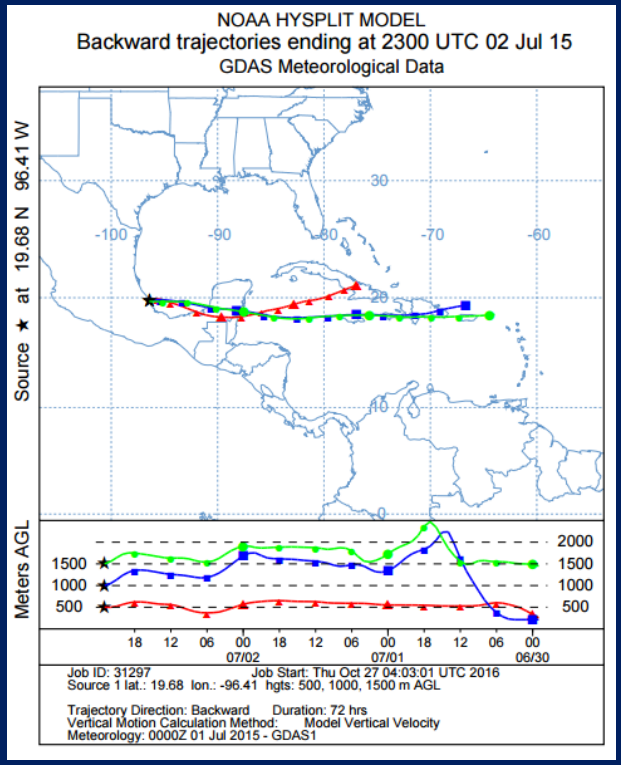
Trajectories showed an important transport to the sampling site from the East during rainy season (June-October). The region located east to “La Mancha” is the Gulf of Mexico presenting offshore operations for the exploration and production of petroleum.

20 % from the North-East



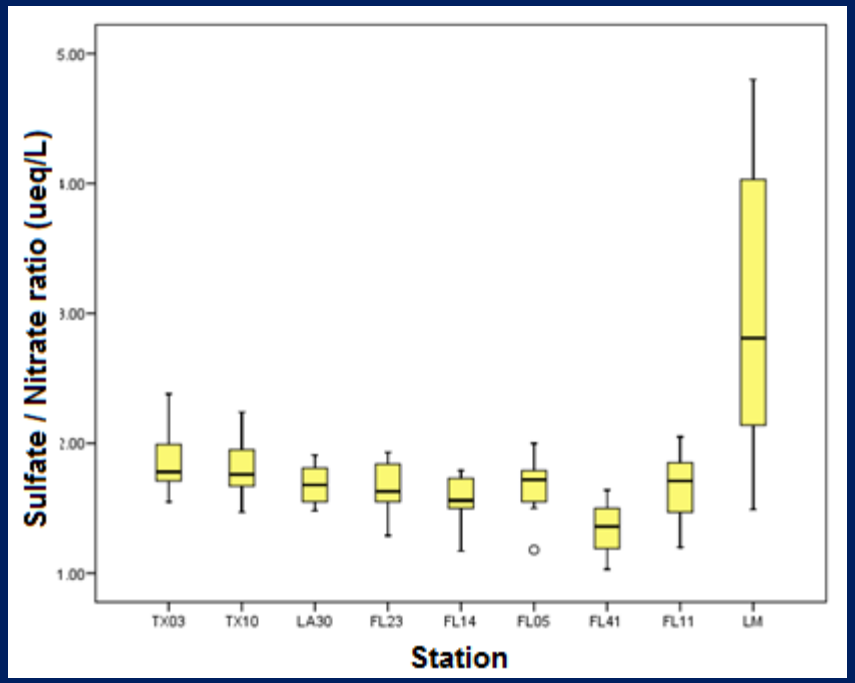

Dry season

80 % from the East




Rainy season

| Sulfate/Nitrate ratio | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Station | FL05 | FL11 | FL14 | FL23 | FL41 | LA30 | TX03 | TX10 | LM |
| 2003 | 2.00 | 1.92 | 1.56 | 1.79 | 1.58 | 1.83 | 1.71 | 1.02 | 1.49 |
| 2004 | 1.79 | 2.05 | 1.54 | 1.84 | 1.50 | 1.68 | 2.02 | 0.91 | 2.81 |
| 2005 | 1.78 | 1.85 | 1.73 | 1.83 | 1.64 | 1.90 | 1.78 | 1.04 | 2.19 |
| 2006 | 1.90 | 1.20 | 1.79 | 1.92 | 1.42 | 1.71 | 1.82 | 0.89 | 2.14 |
| 2007 | 1.79 | 1.72 | 1.59 | 1.87 | 1.63 | 1.68 | 1.78 | 0.90 | 1.63 |
| 2008 | 1.66 | 1.94 | 1.74 | 1.93 | 1.36 | 1.91 | 1.99 | 0.99 | 2.09 |
| 2009 | 1.50 | 1.40 | 1.75 | 1.60 | 1.25 | 1.81 | 2.38 | 1.13 | 3.48 |
| 2010 | 1.72 | 1.62 | 1.50 | 1.63 | 1.45 | 1.50 | 2.08 | 0.92 | 2.24 |
| 2011 | 1.56 | 1.47 | 1.59 | 1.53 | 1.19 | 1.63 | 1.71 | 1.06 | 4.03 |
| 2012 | 1.75 | 1.69 | 1.36 | 1.36 | 1.24 | 1.48 | 1.75 | 1.08 | 4.60 |
| 2013 | 1.51 | 1.71 | 1.51 | 1.55 | 1.12 | 1.64 | 1.55 | 1.06 | 3.38 |
| 2014 | 1.55 | 1.31 | 1.30 | 1.61 | 1.14 | 1.55 | 1.60 | 0.96 | 4.37 |
| 2015 | 1.18 | 1.18 | 1.17 | 1.29 | 1.03 | 1.50 | 1.87 | 1.16 | 4.80 |



# Conclusions and recommendations

- At the Coast of the Gulf of Mexico the phenomenon of acid rain has been present for more than one decade, being the sulfate concentration higher than nitrate.

- From 2003 to 2015, the annual VWM pH values at “La Mancha” have been increasing but all the pH values are below 5.4; the lowest value of 4.81 was measured in 2007 and the highest value of 5.22 was for the year 2015.

# Conclusions and recommendations

- VWM $SO_4^{2-}$ concentration was in the range of 15 to 31 µeq/L, and for the last year was 26 µeq/L, which is similar than the higher level registered in the USA (TX03) site.

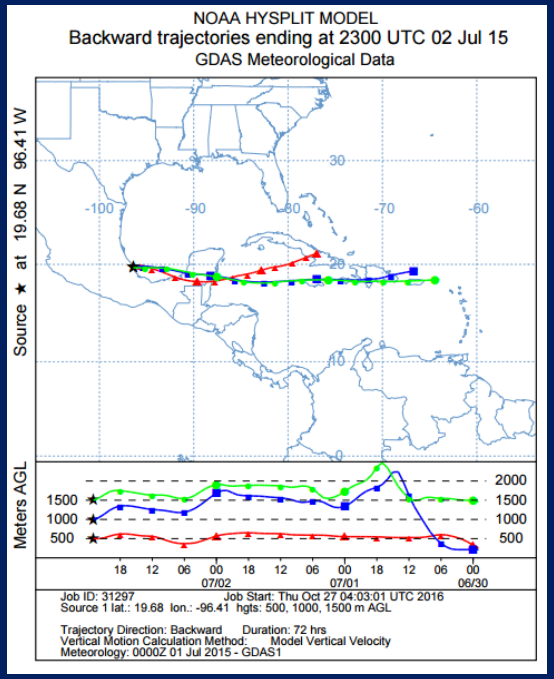
- VWM $NO_3^-$ concentration was in the range of 3.5 to 15 µeq/L and for 2015 was 5.5 µeq/L, which is lower than in the USA sites.

- $SO_4^{2-}/NO_3^-$ ratio found for “La Mancha” in 2015 was 4.8, being the highest value compared to other sites in the Gulf of Mexico whose ratios were between 1.03 and 1.87.

# Conclusions and recommendations

- Therefore it is important to pay attention to the sulfur dioxide emission sources in Mexico.

- According to back trajectories results, It is recommended to extend the atmospheric deposition sampling to other sites in Mexico and Cuba.



# What will we do?


# Aknowledgements


- INECOL A.C: Jorge Lopez Portillo, Enrique López B., Enrique López M
- NADP: David Gay, Christopher Lehmann
- WMO: Van Wowersox, Richard Artz
- USGS: Gregory Wetherbee
- PAPIIT UNAM: Project IN116215


National Atmospheric Deposition Program

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Deposition: What Does the Future Hold?

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# THANK YOU