



# National Atmospheric Deposition Program

## NADP Scientific Symposium and Fall Meeting

San Diego, CA - Bahia Hotel  
October 30-November 3, 2017

2017 Theme: "NADP data: making the world a better place; one monitor, one network, one study at a time"



## Evaluation of wet atmospheric deposition along the coast of the Gulf of Mexico - an international collaboration opportunity

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National Atmospheric Deposition Program



The evaluation of atmospheric deposition at regional scales requires international collaboration to adequately characterize the occurrence of potential impacts and establish measures to mitigate them. The central theme for the 2017 NADP Meeting, “NADP data: making the world a better place, one monitor, one network, one study at time,” gives us the direction to evaluate atmospheric deposition in the Gulf of Mexico Region.



The Gulf of Mexico Region has important sources of acid rain precursors, both on land and at sea, located in countries bordering the region, such as the USA, Mexico and Cuba. It is very important to study the chemical composition of atmospheric wet deposition through international cooperation.



# 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.

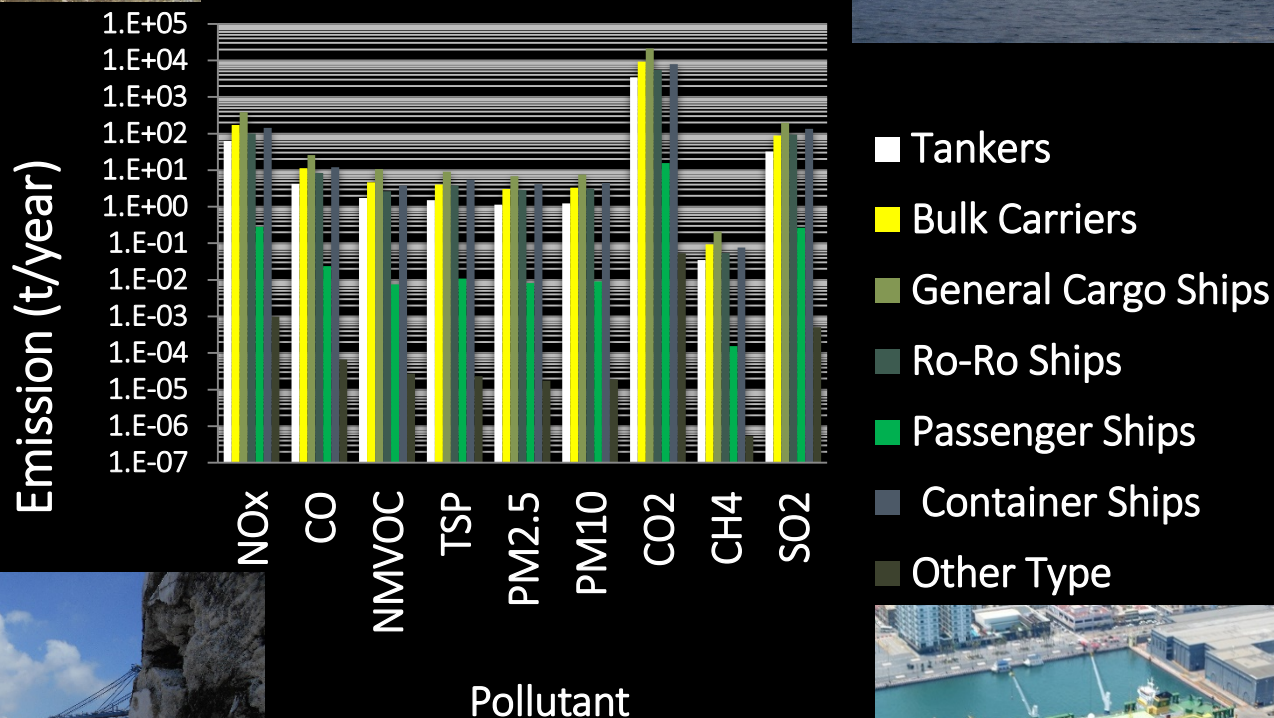


# Non-platform sources in the Gulf of Mexico are:

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



# EMMISSION INVENTORY PORT OF VERACRUZ



# 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.

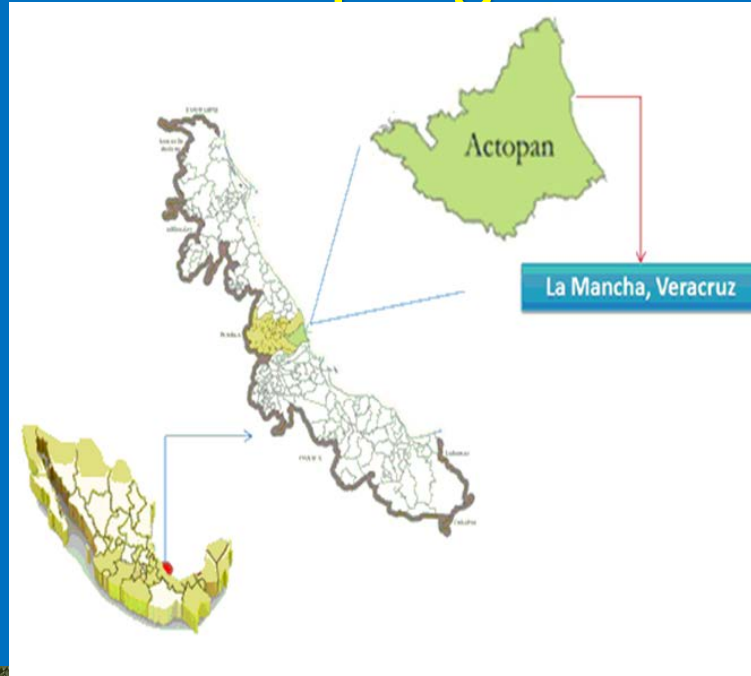


Studies on the Mexican coast have recorded the presence of acid rain since 2003. The aim of this study was to evaluate the major ions ( $\text{Na}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{SO}_4^{2-}$ ,  $\text{NO}_3^-$  and  $\text{Cl}^-$ ), pH and conductivity in atmospheric wet deposition, collected daily from 2003 to 2015 at a sampling site located along the coast of Mexico (La Mancha, Veracruz) and compare the values with the NADP sampling sites located along the Gulf of Mexico coast from Texas to Florida.





# Sampling site

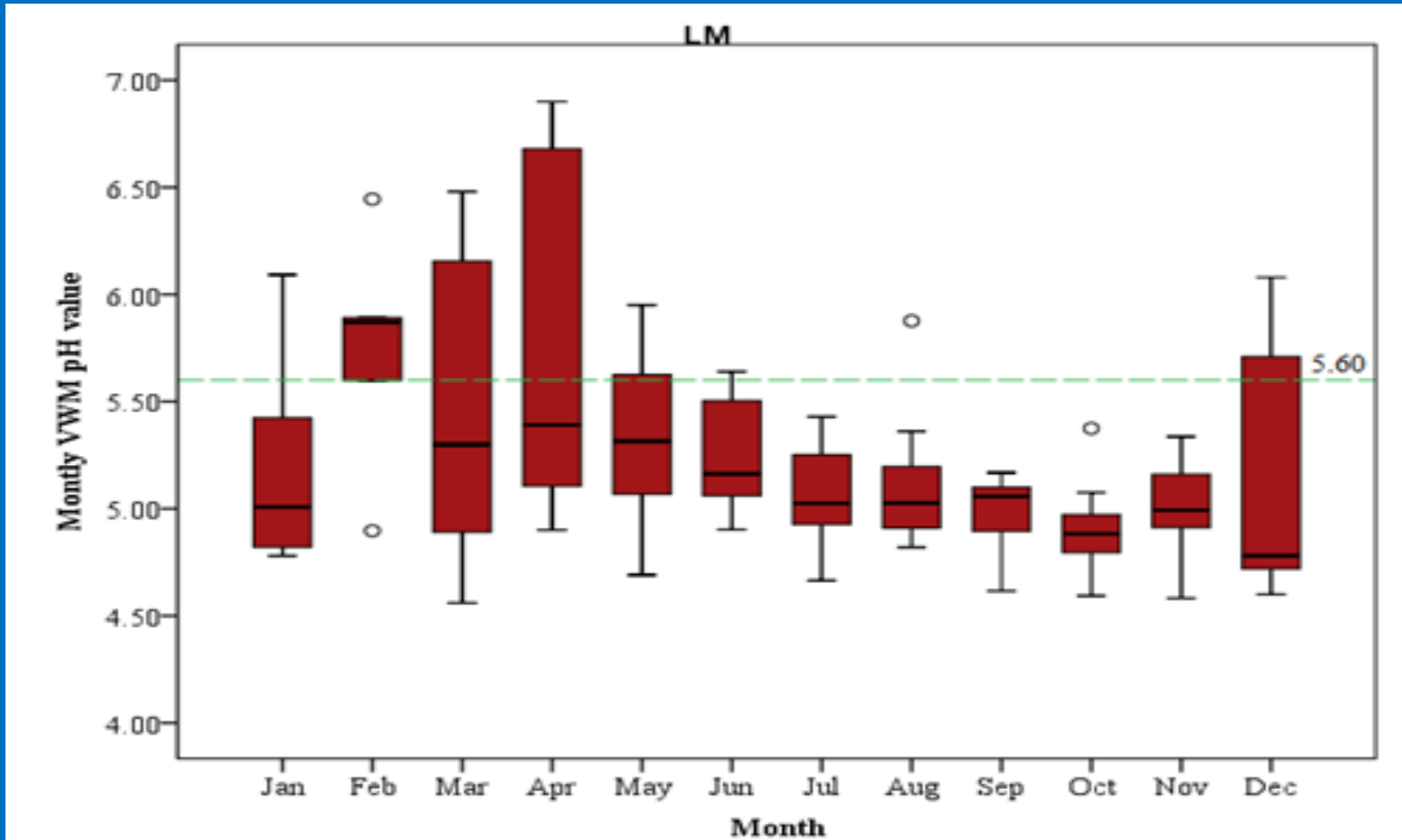


**Among the major findings: all ions were present in greater levels in “La Mancha” in comparison with each one of the sampling sites in the USA, with exception of nitrogen compounds ( $\text{NO}_3^-$  and  $\text{NH}_4^+$ ), which were comparable to the USA sites. The levels of sulfates in Mexico were comparable to the highest US NADP sites.**

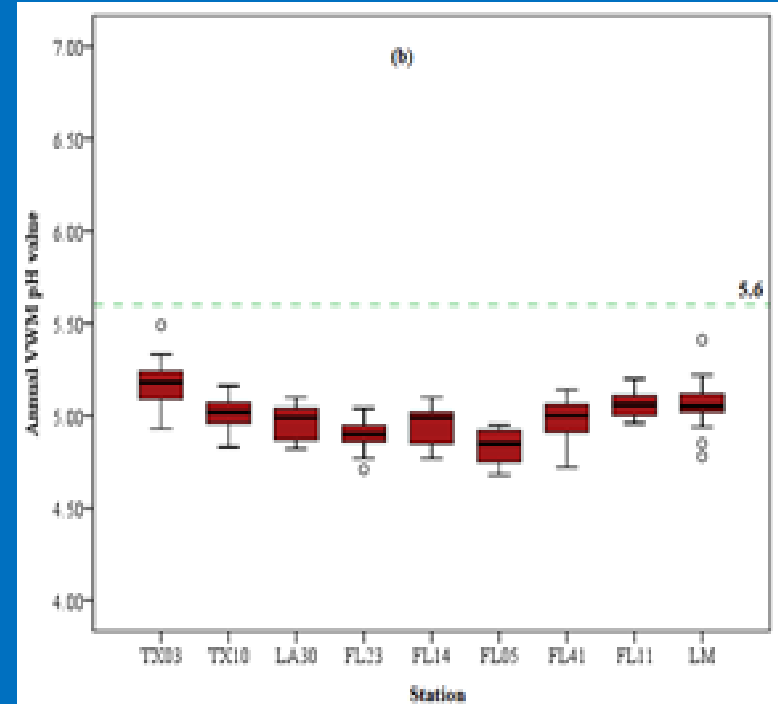
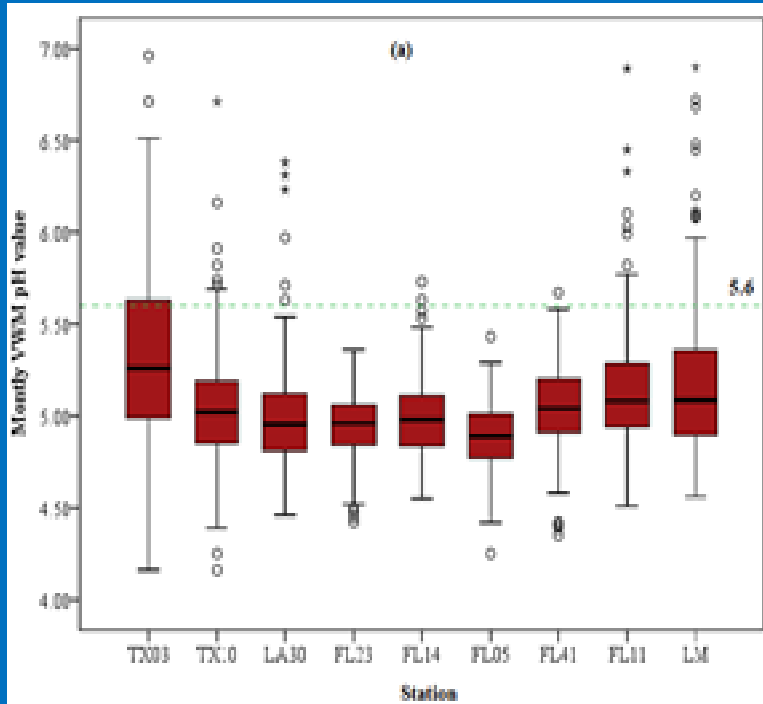


# RESULTS pH

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

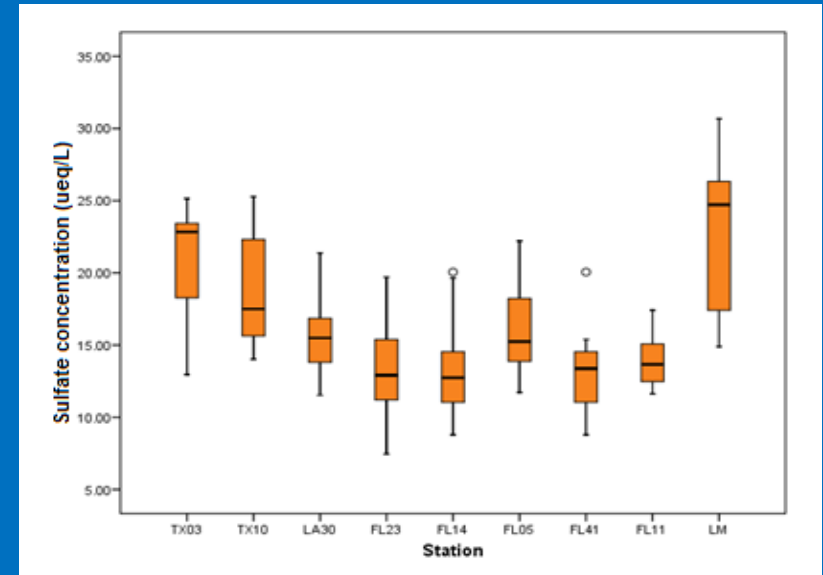


# Monthly (a) and Annual (b) VWM pH values for the sampling sites along the coast of the Gulf of Mexico.

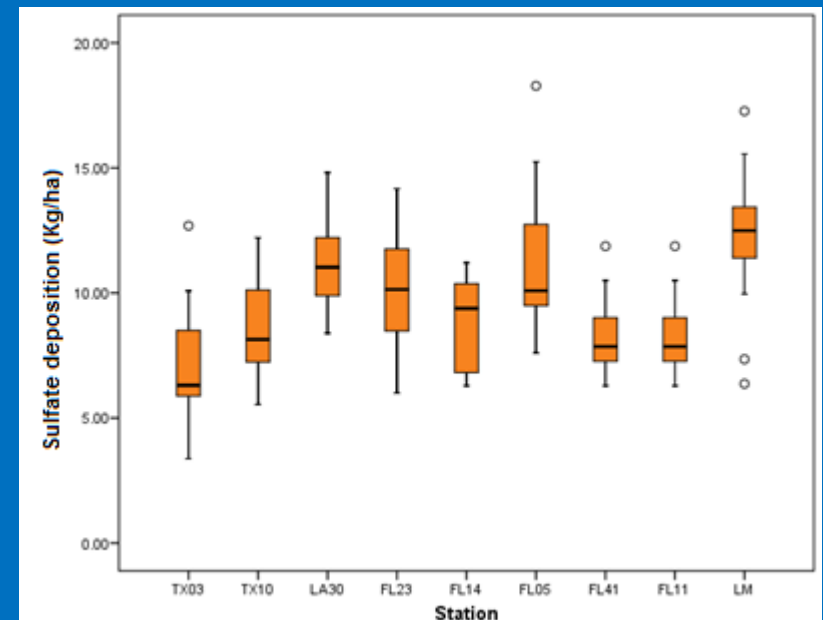


# Sulfate

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

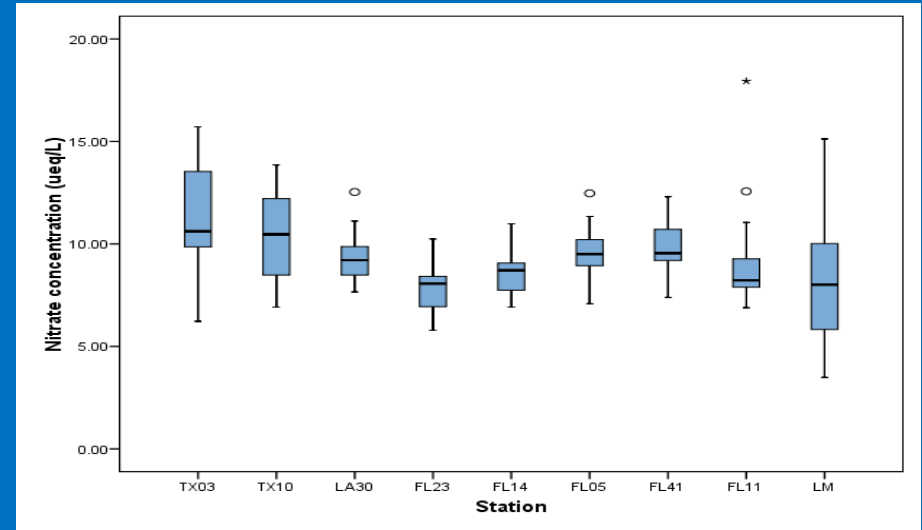


Sulfate			
Station	Min (Kg/Ha)	Max (Kg/Ha)	Median (Kg/Ha)
LM	6.37	17.27	12.49
TX 03	3.37	12.69	6.31
TX 10	5.54	12.21	8.14
LA 30	8.39	14.81	11.03
FL 23	6.00	14.17	10.14
FL 05	7.60	18.28	10.09
FL 14	6.29	11.21	9.38
FL 41	6.29	11.87	7.86
FL 11	7.64	13.66	9.54

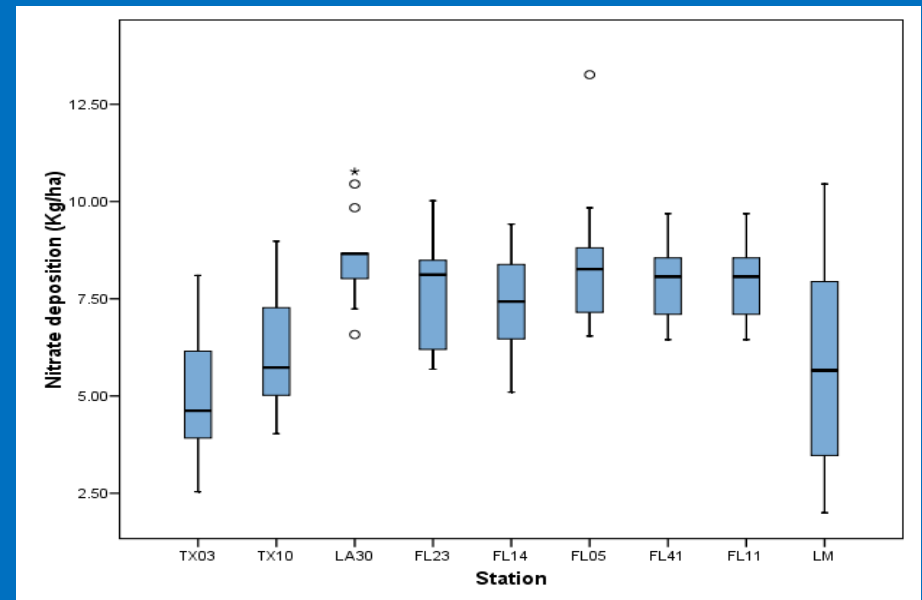


# Nitrate

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

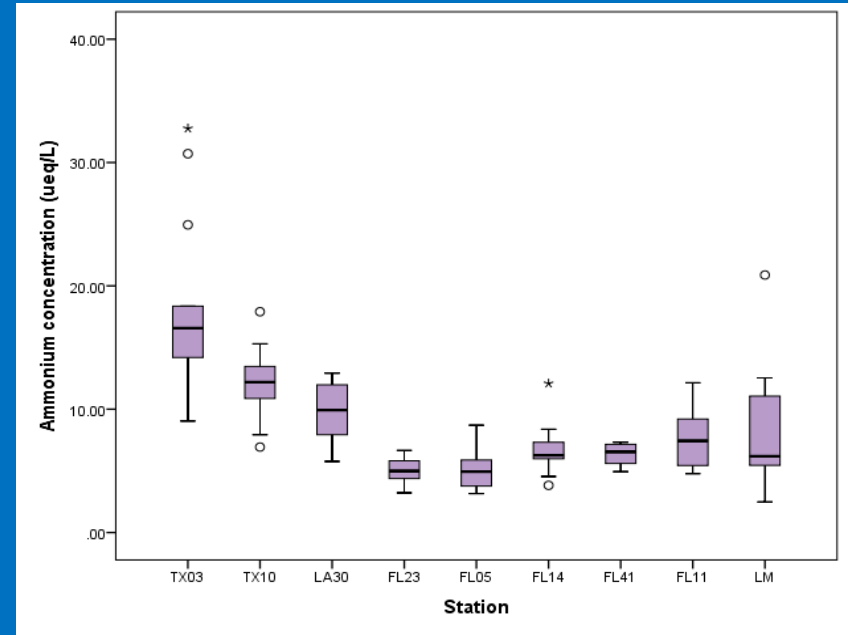


Nitrate			
Station	Min (Kg/Ha)	Max (Kg/Ha)	Median (Kg/Ha)
LM	2.00	10.45	5.66
TX 03	2.54	8.1	4.62
TX 10	4.03	8.98	5.73
LA 30	6.58	10.77	8.66
FL 23	5.69	10.02	8.12
FL 05	6.54	13.26	8.26
FL 14	5.10	9.42	7.43
FL 41	6.45	9.69	8.07
FL 11	6.15	10.73	7.94

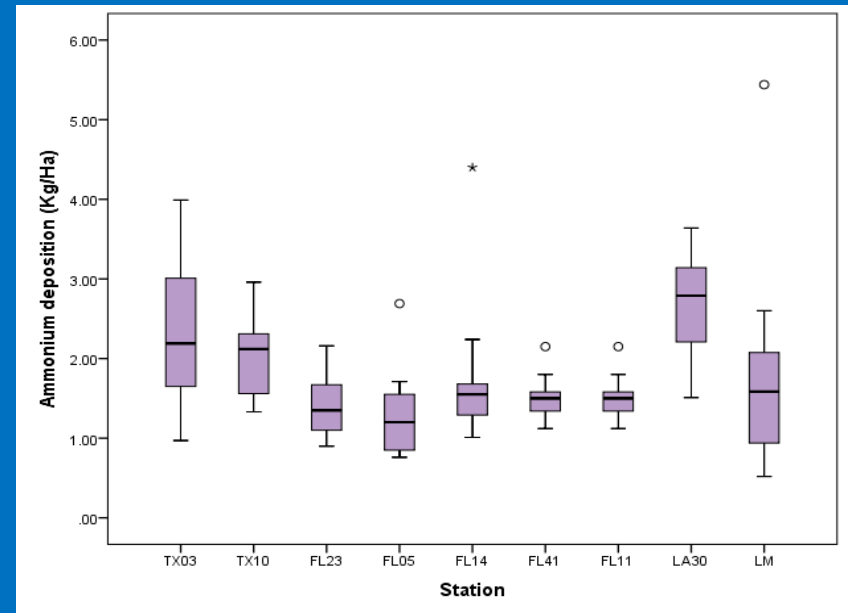


# Ammonium

Annual ammonium concentration ( $\mu\text{eq/L}$ )			
Station	Min	Max	Median
TX03	9.04	32.77	16.57
TX10	6.93	17.91	12.19
LA30	5.77	12.92	9.92
FL23	3.22	6.65	4.99
FL05	3.16	8.70	4.93
FL14	3.83	12.09	6.26
FL41	4.93	7.32	6.54
FL11	4.77	12.14	7.42
LM	2.48	20.88	6.18



Ammonium deposition (Kg/Ha)			
Station	Min	Max	Median
TX03	0.97	3.99	1.78
TX10	1.33	2.96	1.76
LA30	1.51	3.64	2.79
FL23	0.90	2.16	1.35
FL05	0.76	2.69	1.20
FL14	1.01	4.40	1.50
FL41	1.12	2.15	1.50
FL11	1.12	2.15	1.50
LM	0.52	5.44	1.58

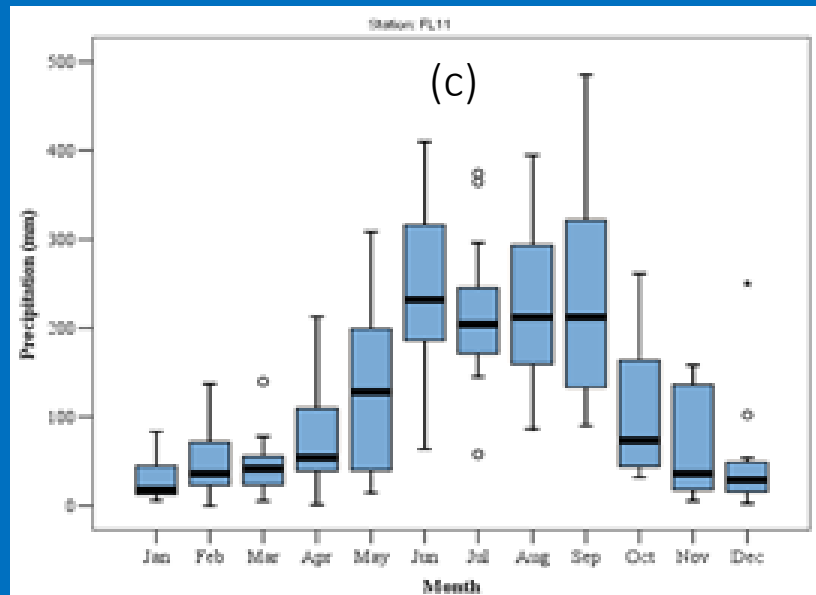
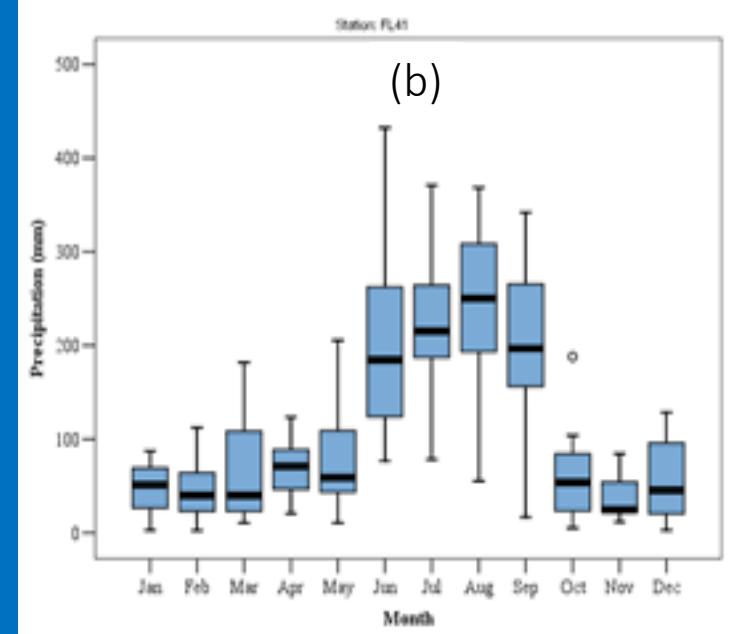
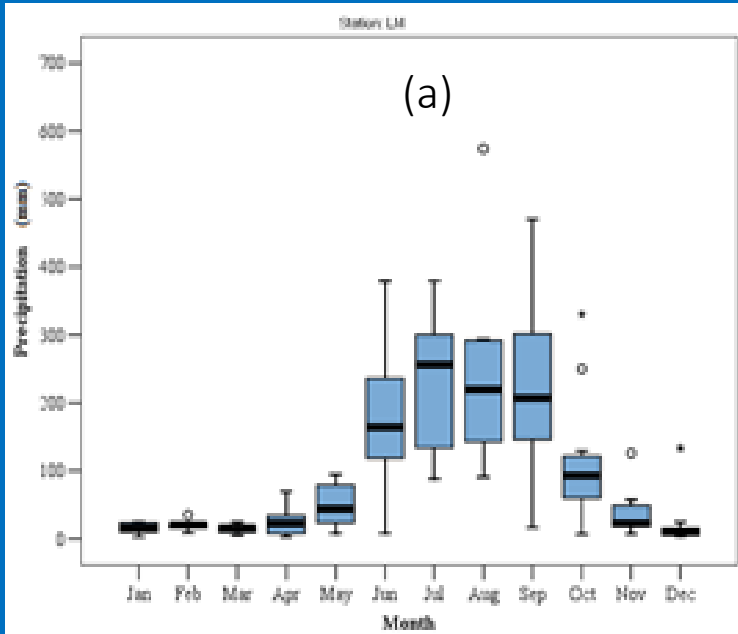


# NADP /LM ratio median value

	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



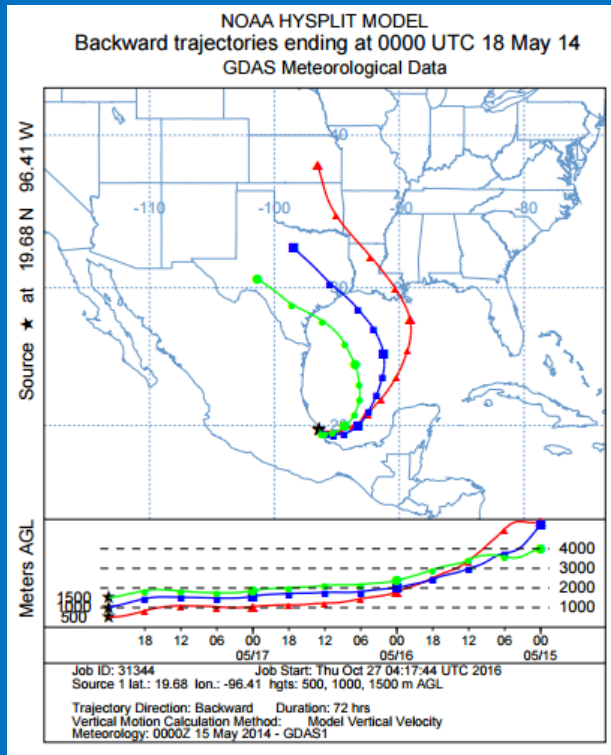
# Monthly variation of the precipitation at La Mancha (a), FL 41 (b) and FL 11 (c) sampling site.



# Back trajectories

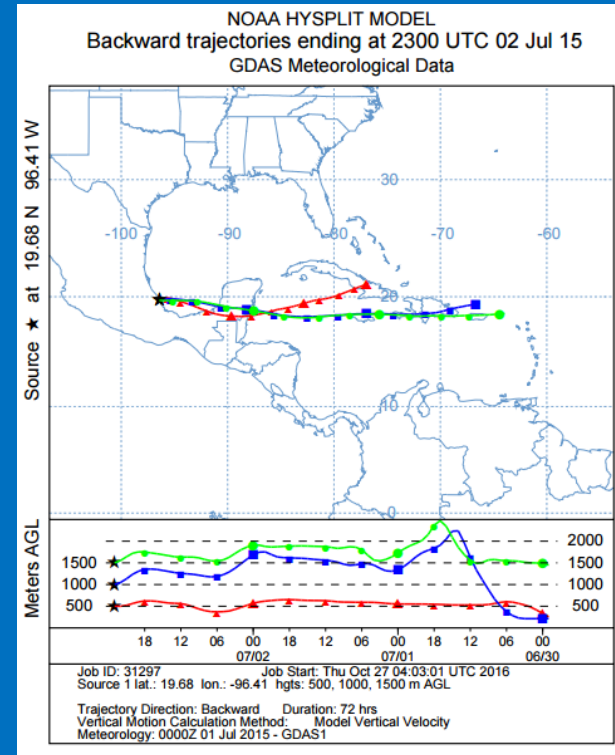
Trajectories showed an important transport to the sampling site from the East during rainy season (June-October). The region located east to “La Mancha” is the Gulf of Mexico presenting offshore operations for the exploration and production of petroleum.

20 % from the North-East



Dry season

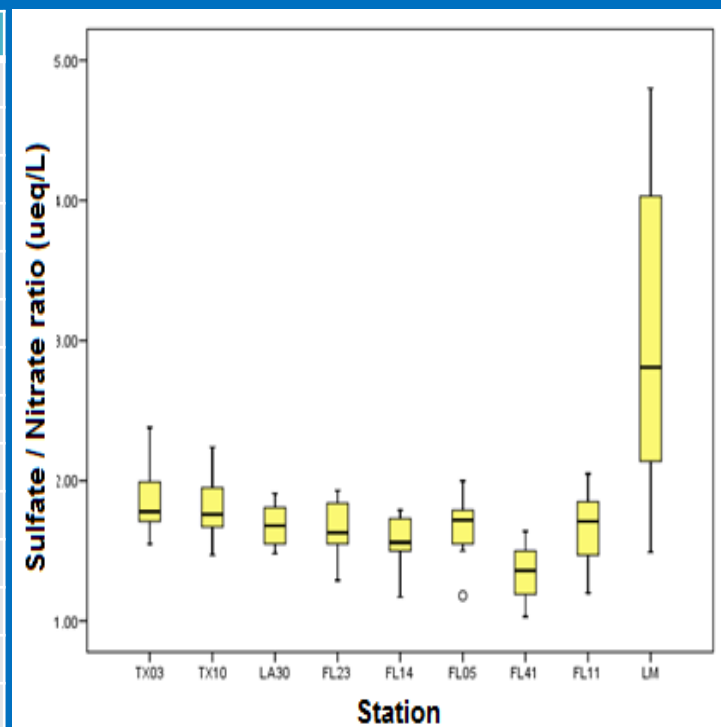
80 % from the East



Rainy season

# Ratio $\text{SO}_4^{2-}/\text{NO}_3^-$ at all the sampling sites along the coast the Gulf of Mexico.

Year	Station								
	TX03	TX10	LA31	FL23	FL14	FL05	FL41	FL11	LM
2003	1.71	1.67	1.83	1.79	2.00	1.56	1.58	1.92	1.52
2004	2.02	1.76	1.68	1.84	1.79	1.54	1.50	2.05	2.86
2005	1.78	1.76	1.90	1.83	1.78	1.73	1.64	1.85	2.24
2006	1.82	2.06	1.71	1.92	1.90	1.79	1.42	1.20	2.19
2007	1.78	1.67	1.68	1.87	1.79	1.59	1.63	1.72	1.67
2008	1.99	2.08	1.91	1.93	1.66	1.74	1.36	1.94	2.13
2009	2.38	1.83	1.81	1.60	1.50	1.75	1.25	1.40	3.55
2010	2.08	1.68	1.50	1.63	1.72	1.50	1.45	1.62	2.29
2011	1.71	1.77	1.63	1.53	1.56	1.59	1.19	1.47	4.12
2012	1.75	1.47	1.48	1.36	1.75	1.36	1.24	1.69	4.70
2013	1.55	2.24	1.64	1.55	1.51	1.51	1.12	1.71	3.45
2014	1.60	1.63	1.55	1.61	1.55	1.30	1.14	1.31	4.46
2015	1.87	1.95	1.50	1.29	1.18	1.17	1.03	1.48	4.90



- The ratio of  $\text{SO}_4^{2-}$  to  $\text{NO}_3^-$  has been used as indicator of the effectiveness of  $\text{SO}_2$  and  $\text{NO}_x$  emissions reductions in the USA. The  $\text{SO}_4^{2-}/\text{NO}_3^-$  ratio found for “La Mancha” in 2015 was 4.9, the highest value when compared to other sites in the Gulf of Mexico, which had ratios between 1.03 and 1.87. Due to the high levels of  $\text{SO}_4^{2-}$  and the ratio  $\text{SO}_4^{2-}/\text{NO}_3^-$  found at “La Mancha,” it is important to monitor the sulfur dioxide emission sources in Mexico.



**Sulfate / Nitrate  
ratio by 2015**

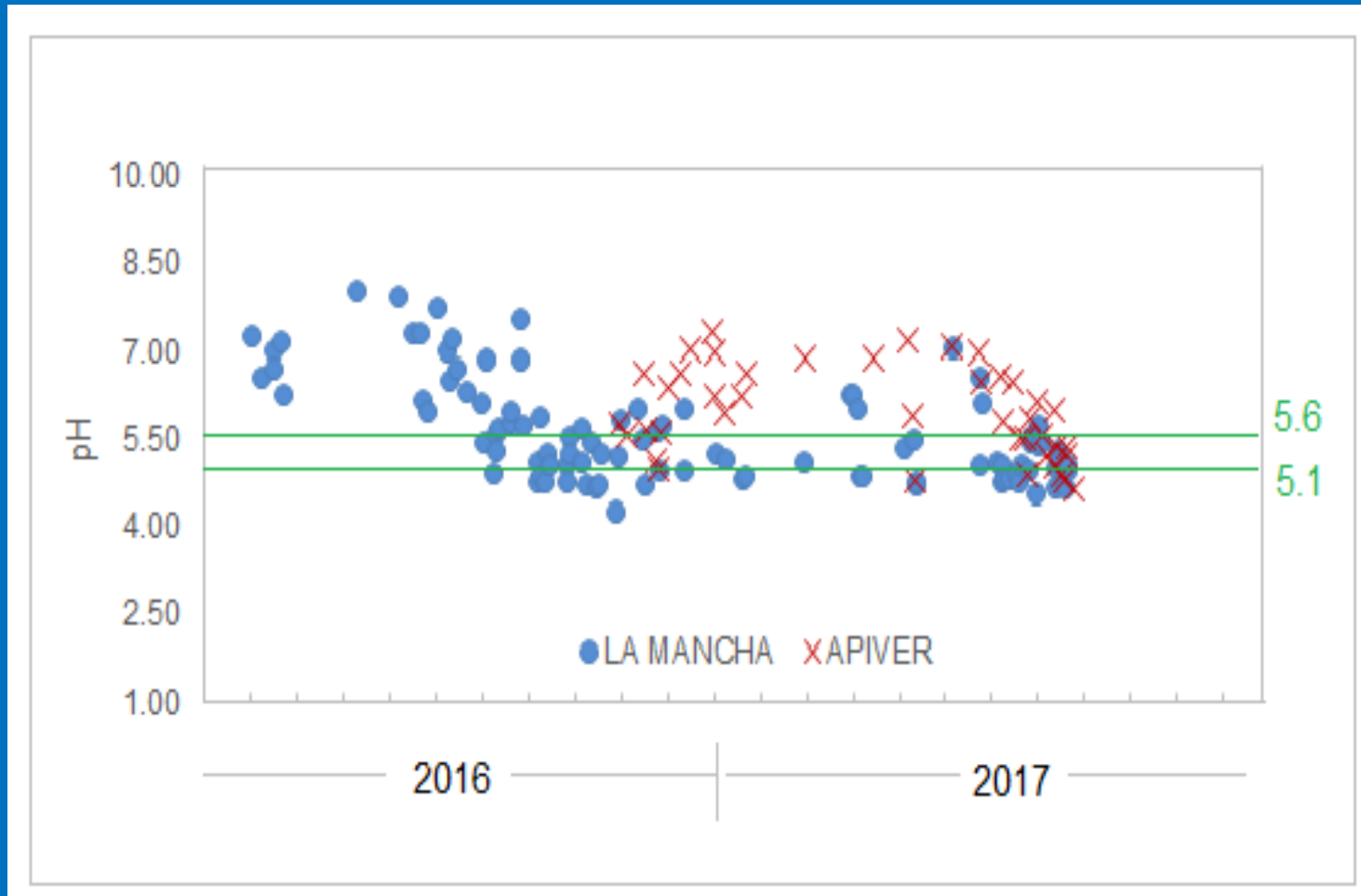
**In addition to “La Mancha” sampling site, two additional sampling sites, in Mexico, have recently been incorporated to the atmospheric deposition study: one in the City of Campeche and another in the Port of Veracruz.**



# Atmospheric Deposition, Air Quality and Meteorology Sampling Site in Veracruz Port

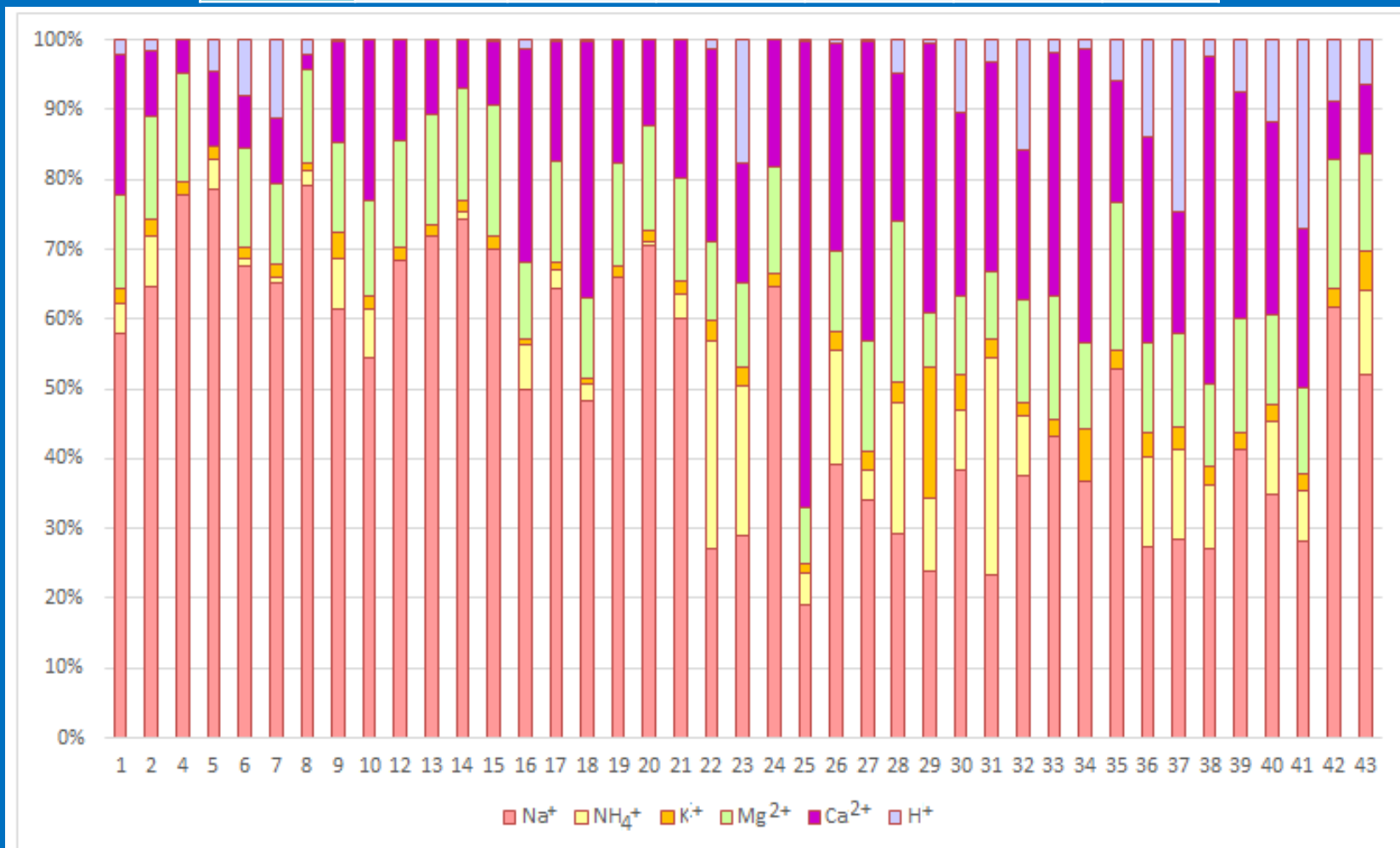


# Wet atmospheric deposition at “La Mancha” Station and the Port of Veracruz (APIVER), México.



# Cation concentrations in wet deposition samples.

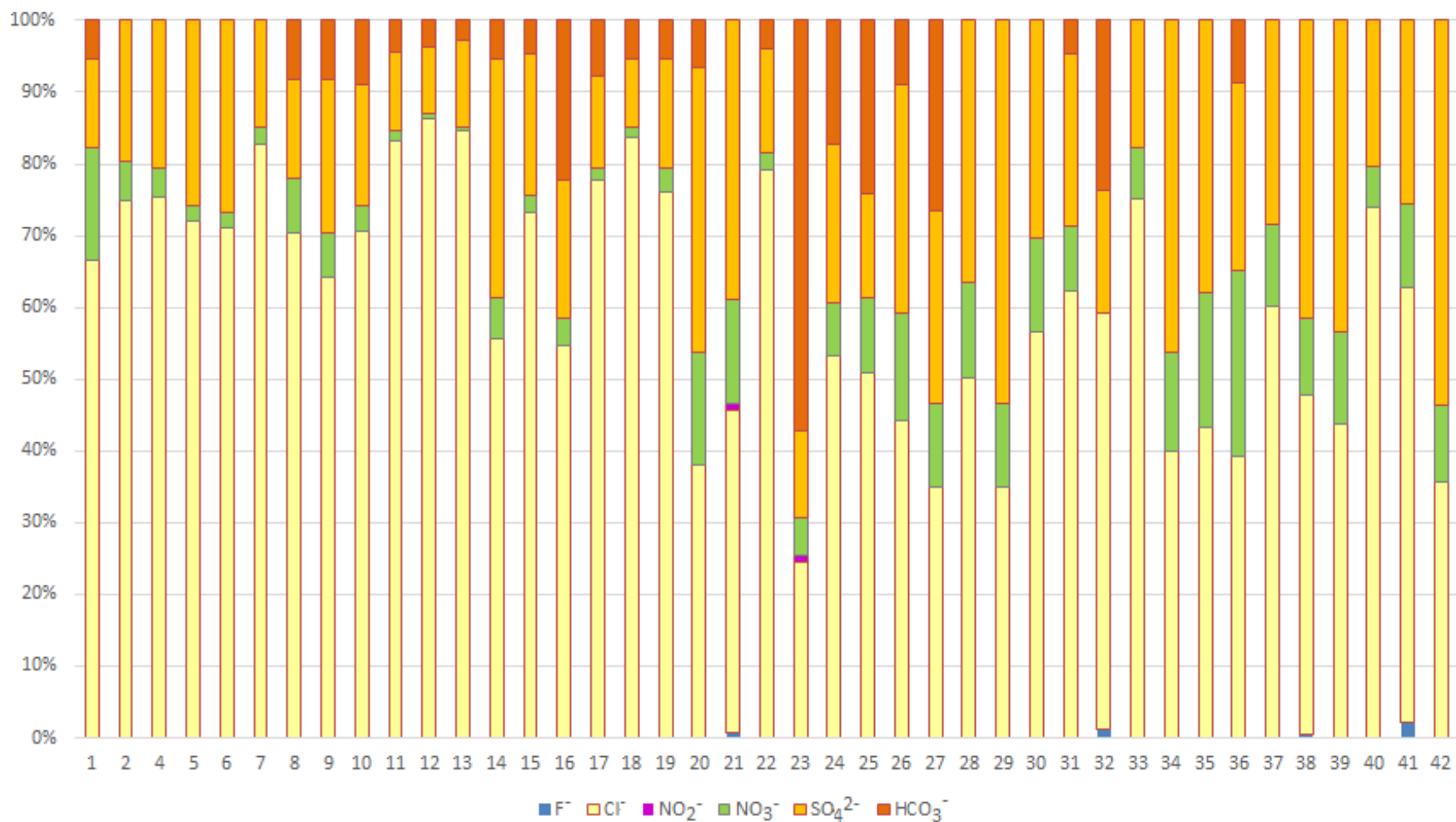
SAMPLE	Na <sup>+</sup> (μEq/L)	NH <sub>4</sub> <sup>+</sup> (μEq/L)	K <sup>+</sup> (μEq/L)	Mg <sup>2+</sup> (μEq/L)	Ca <sup>2+</sup> (μEq/L)	H <sup>+</sup> (μEq/L)
Mín	11.39	<LD	<LD	4.28	3.05	0.06
Máx	3692.39	53.89	83.17	804.53	550.00	27.54
Median	45.83	7.11	2.40	14.16	27.60	1.66





# Concentration of anions in samples of wet atmospheric deposition.

Parámetro	Cl <sup>-</sup> (μEq/L)	NO <sub>3</sub> <sup>-</sup> (μEq/L)	SO <sub>4</sub> <sup>2-</sup> (μEq/L)	*HCO <sub>3</sub> <sup>-</sup> (μEq/L)
Mínimum	15.82	2.04	8.98	3.19
Máximum	4176.55	70.52	547.50	222.11
Medium	56.46	8.87	25.33	20.56

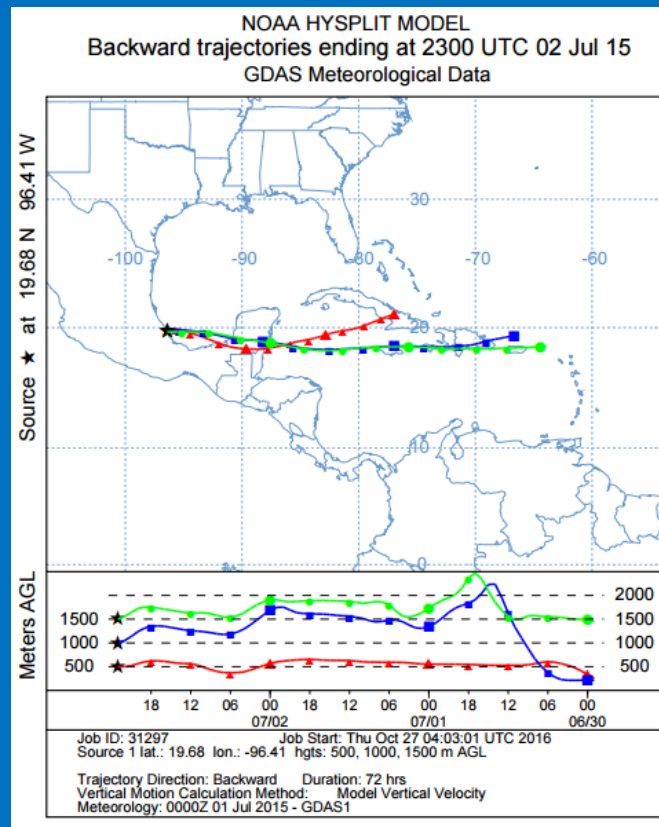


# Conclusions and recommendations

- In the Mexican sampling site “La Mancha”, located 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 greater than nitrate concentration.
- Over the duration of the study to date, 2003 to 2015, the VWM pH annual average values at “La Mancha” has been increasing along of the years but all the pH values are below 5.4; the lowest value of 4.81 was measured in 2007; whereas the highest value of 5.22 was for the year 2015.

# Conclusions and recommendations

The establishment of the international network for the evaluation of atmospheric deposition in the Gulf of Mexico represents a great opportunity for international collaboration. NADP protocols for sampling and analysis will be adopted, including quality-assurance and quality-control protocols, to ensure that information generated is comparable between current participating countries, USA and México and possibly Cuba.



# What will we do?



# Aknowledgements

- **INECOL A.C:** Dr. Jorge Lopez Portillo, Enrique López B., Enrique López M
- **UNAM staff in APIVER:** Jose Hernandez T., Humberto Bravo W.
- **WMO:** Van Bowersox, Richard Artz
- **PAPIIT UNAM:** Project IN116215





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# THANK YOU



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