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Deposition: What Does the Future Hold?

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Sulfur and nitrogen compounds in wet atmospheric deposition and in ambient air as indicators of emissions reduction strategies at Mexico City

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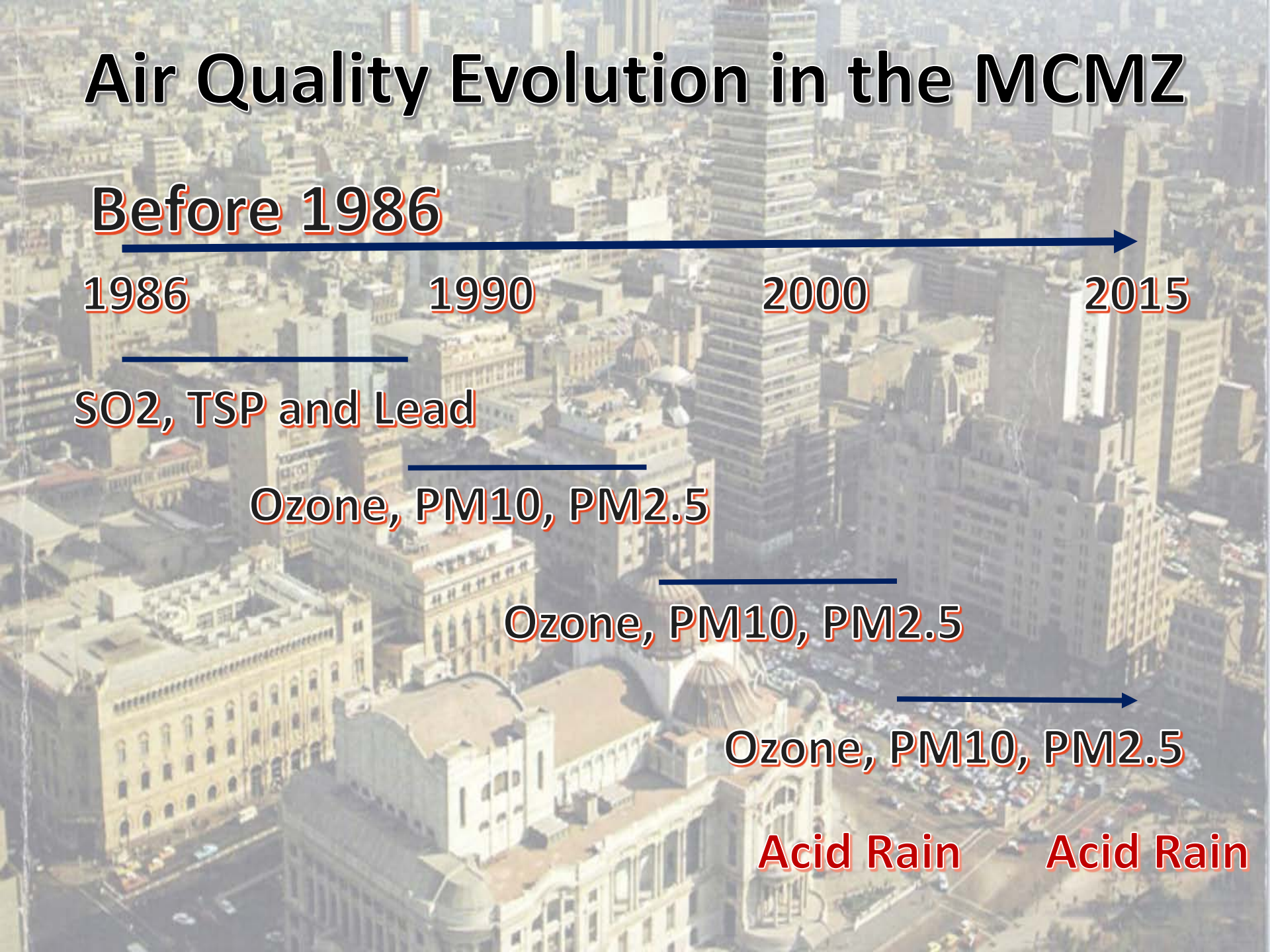
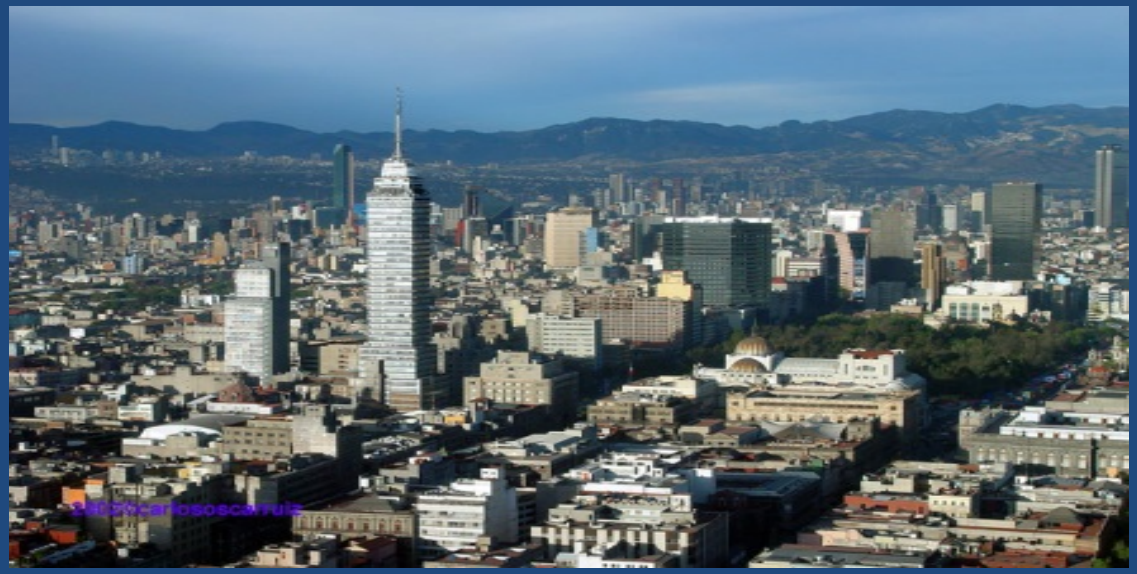
Air Quality Evolution in the MCMZ



Background

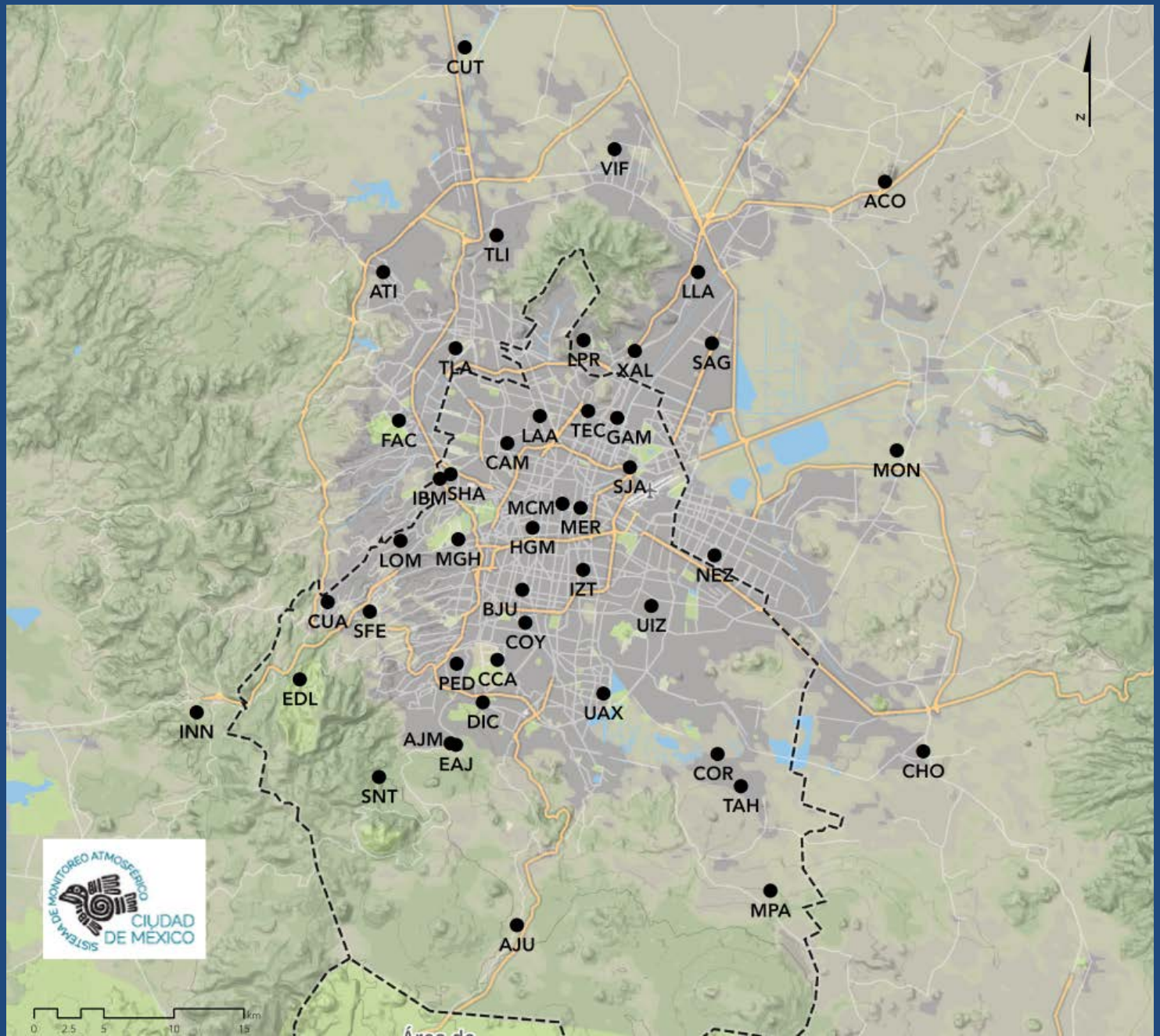
The Mexico City Metropolitan Zone (MCMZ) is accepted as having critical levels of air pollution. In the 1980s, particulates and sulfur dioxide (SO_2) were identified as the main atmospheric pollutants and an effort to reduce emissions in the MCMZ was made by replacing fuel oil with natural gas in power plants located inside. This resulted in the reduction in the levels of both pollutants. Actually SO_2 levels do not exceed its ambient air quality standard; however acid rain is a significant issue.



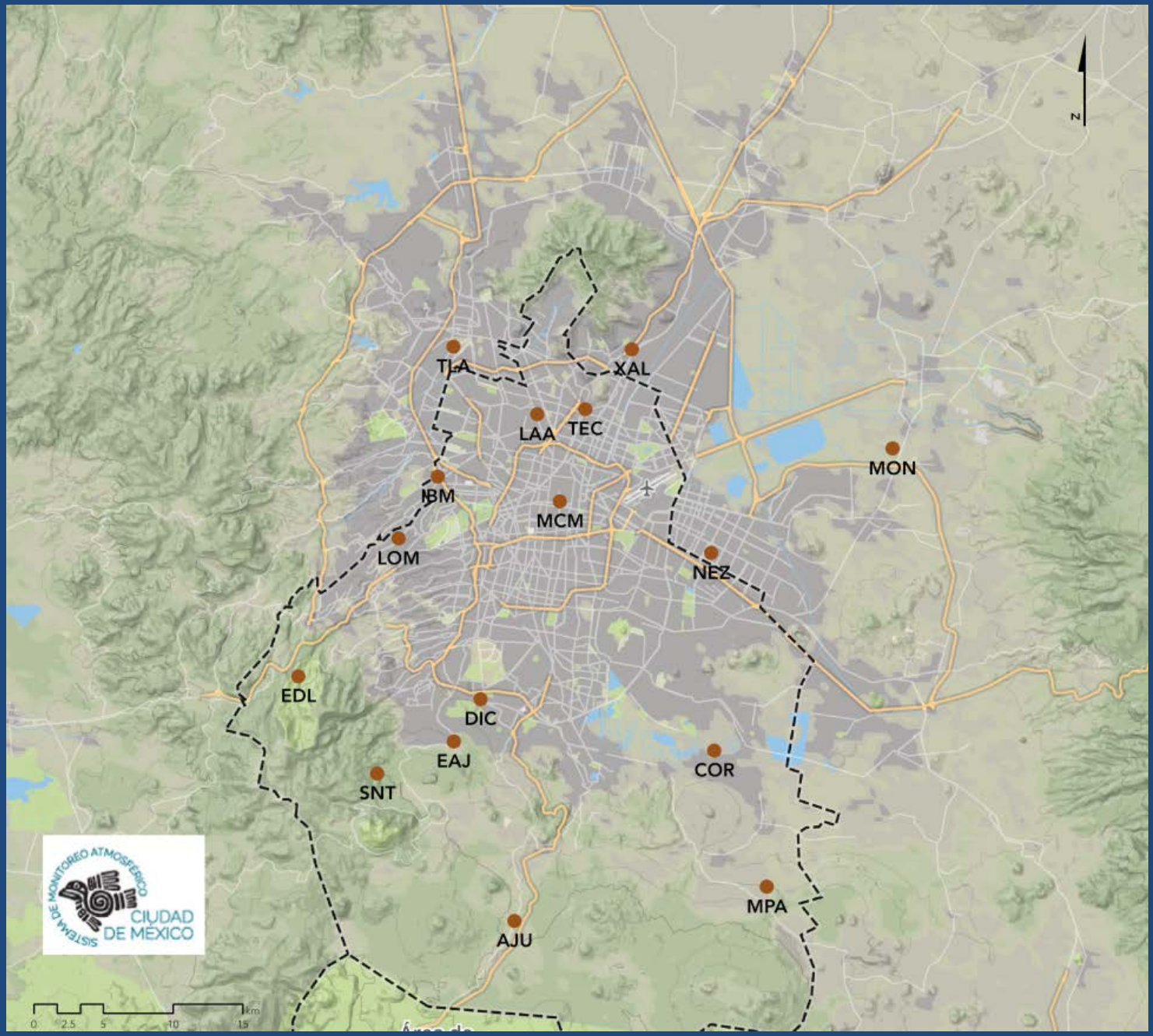
Goal

- In this study, spatial and temporal variations in the chemical composition of rain in Mexico City between 2003 and 2014 were analyzed; sulfate and nitrate ions and pH were obtained weekly at 16 sampling stations located in the MCMZ. Furthermore, sulfur dioxide (SO_2) and nitrogen oxides (NOx) were evaluated from 1990 to 2014 at the MCMZ air quality monitoring network. In order to obtain the magnitude in the emissions reduction of sulfur compounds relative to nitrogen compounds, SO_2/NOx were obtained for ambient air, as well as SO_4^{2-} /NO_3^- in wet atmospheric deposition.

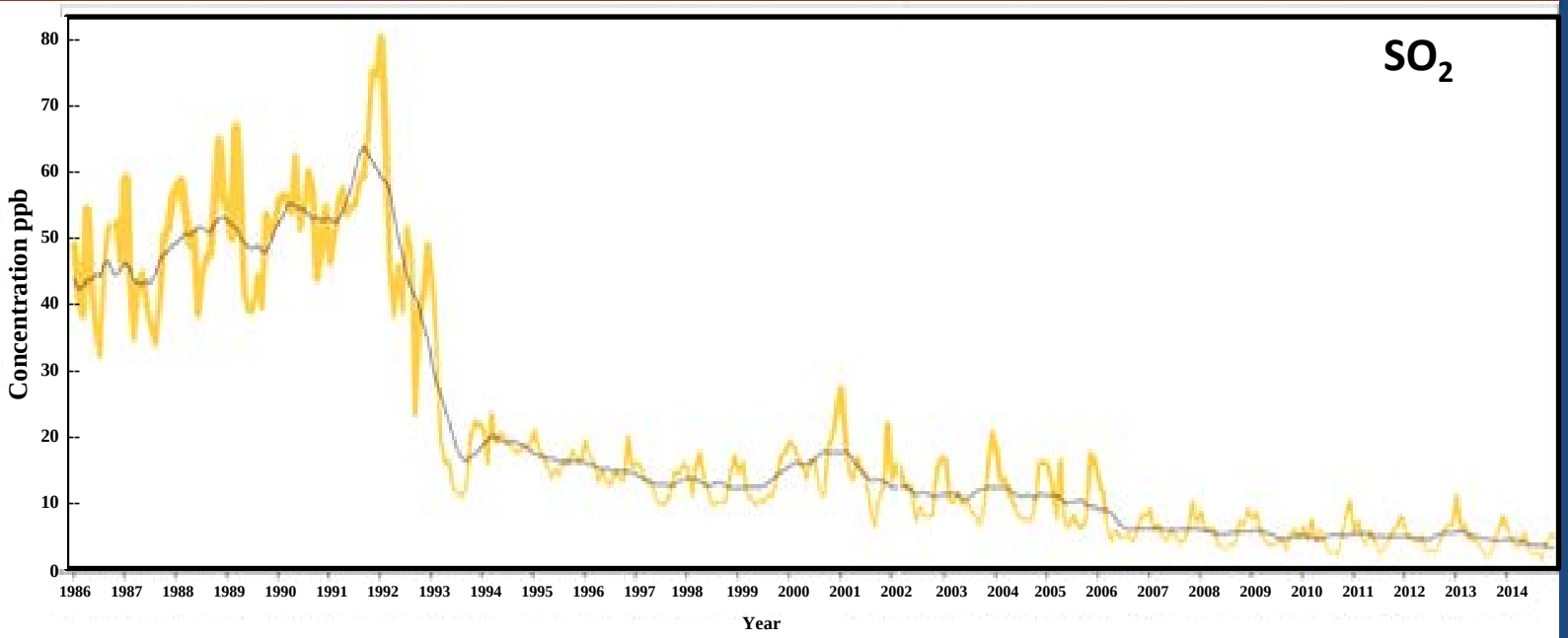
Automatic Monitoring Air Quality Network (SIMAT).

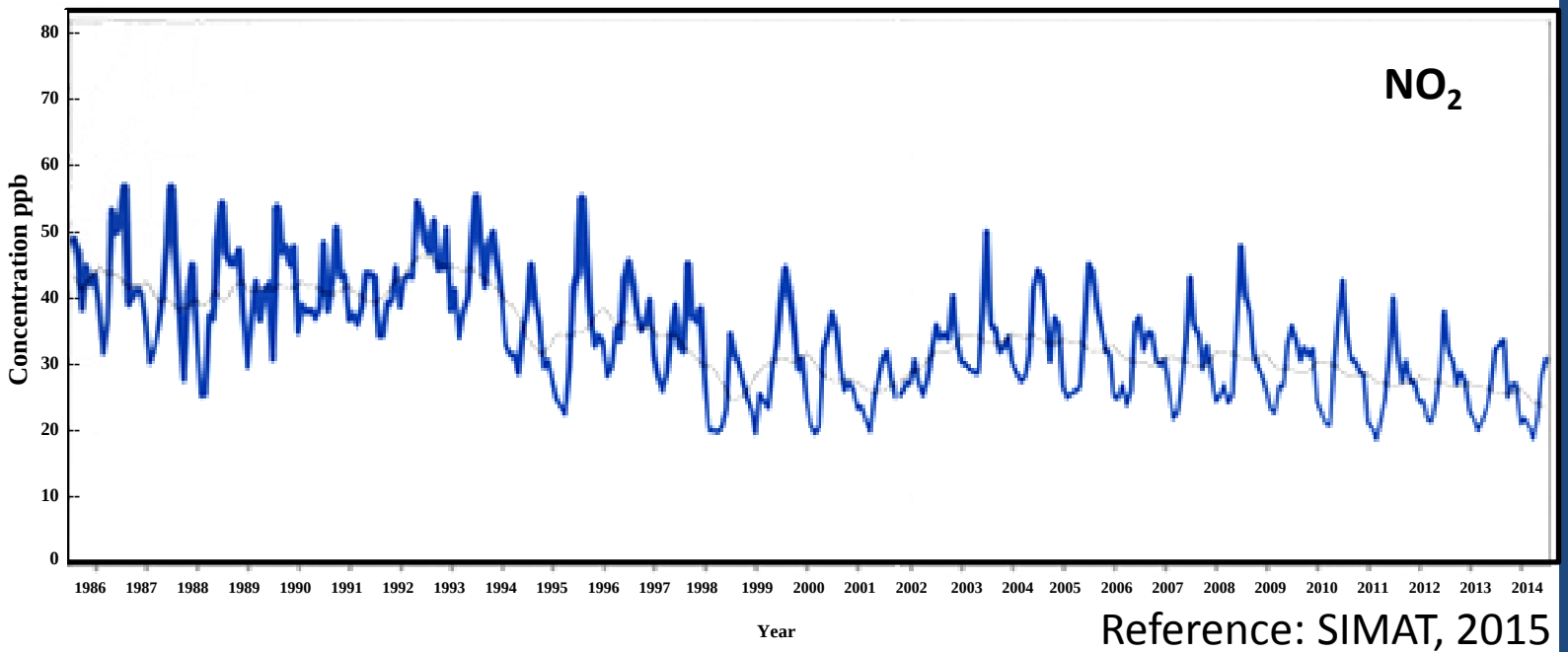


Atmospheric Deposition Network (REDDA).

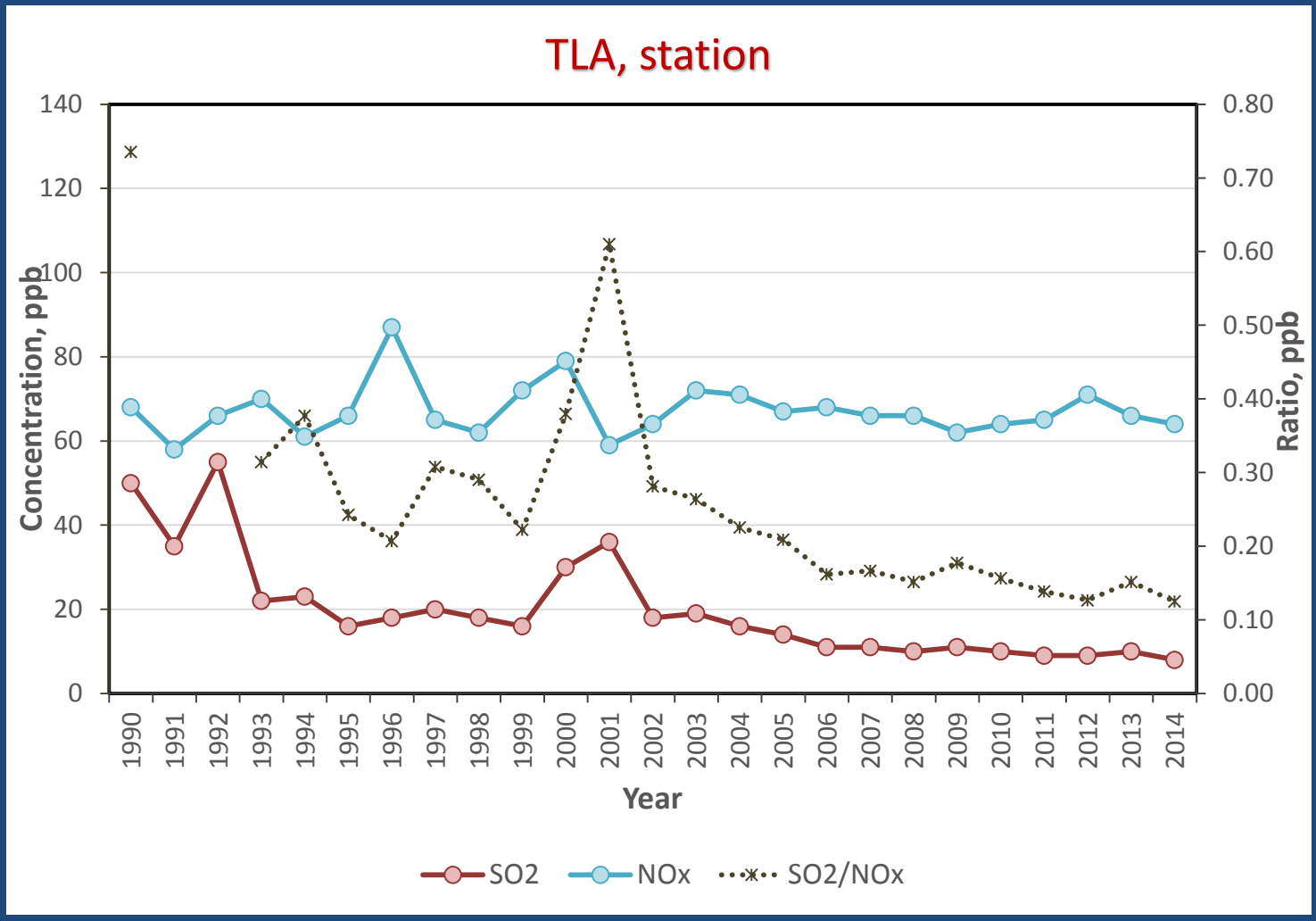


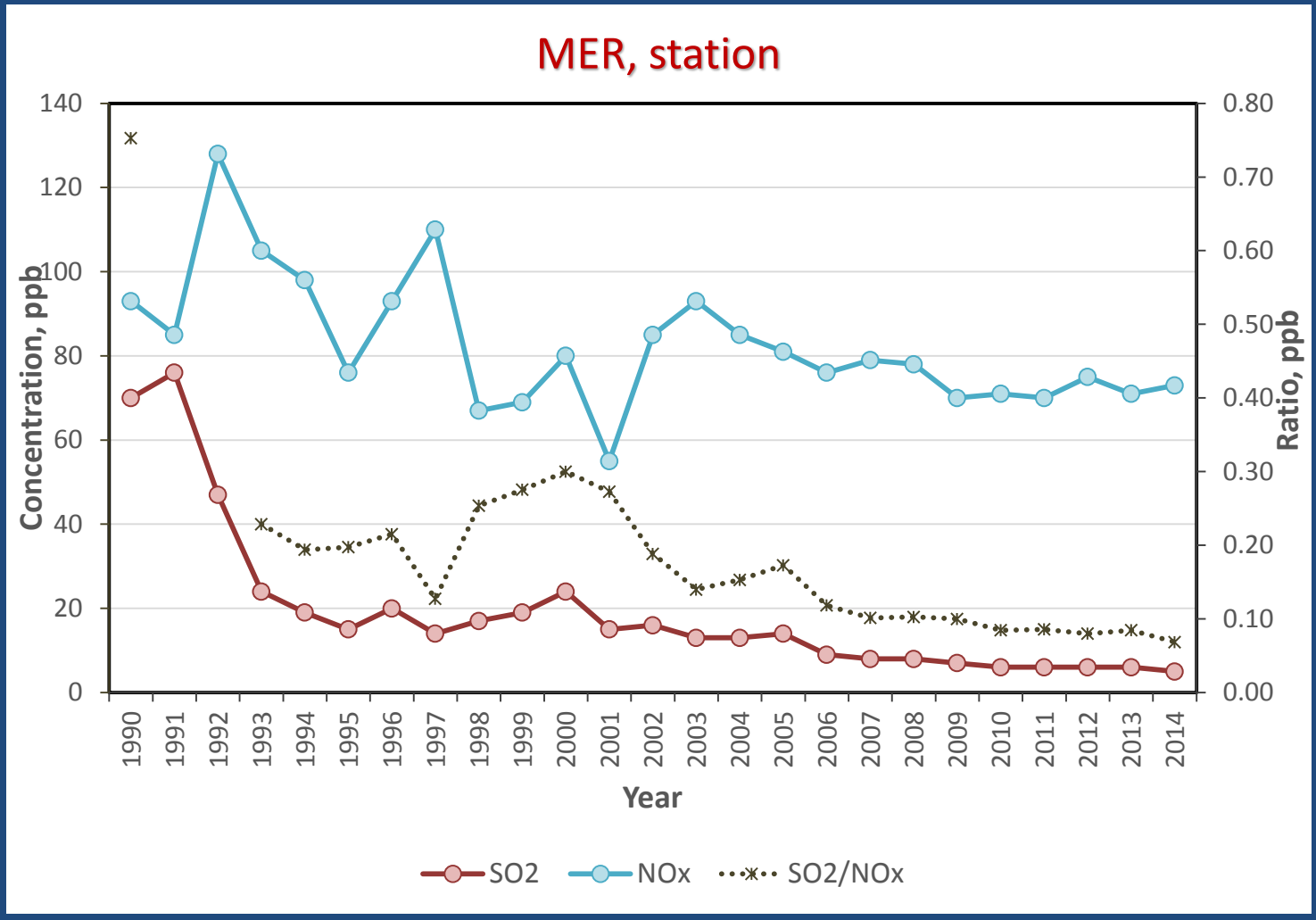
Annual Average Concentrations of SO_2 and NO_2 from 1986 to 2014

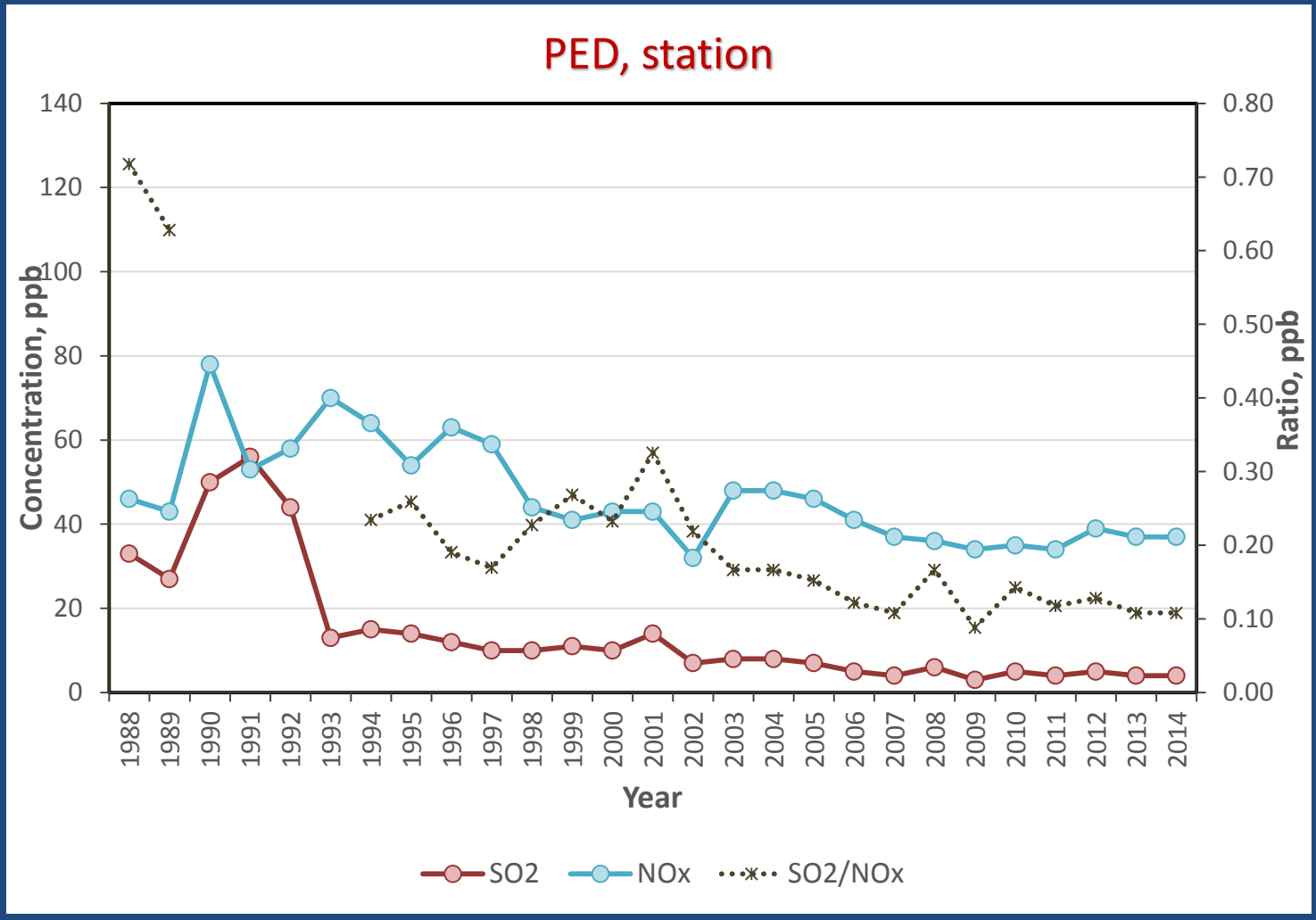




Reference: SIMAT, 2015


TLA, station
Concentration, ppb
Ratio, ppb
Year
0
20
40
60
80
100
120
140
0.00
0.10
0.20
0.30
0.40
0.50
0.60
0.70
0.80
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
SO2
NOx
SO2/NOx


MER, station
140
120
100
80
60
40
20
0
Concentration, ppb
0.80
0.70
0.60
0.50
0.40
0.30
0.20
0.10
0.00
Ratio, ppb
1990
1991
1992
1993
1994
1995
1996
1997
1998
1999
2000
2001
2002
2003
2004
2005
2006
2007
2008
2009
2010
2011
2012
2013
2014
Year
SO2
NOx
SO2/NOx


PED, station
Concentration, ppb
Ratio, ppb
Year
SO2
NOx
SO2/NOx

SAMPLING SITES

The Environmental Pollution Section of the Center for Atmospheric Sciences of the University of Mexico (UNAM: Universidad Nacional Autónoma de México) has maintained a program of sampling and analysis of the atmospheric deposition in several regions of Mexico.

UNAM has conducted studies about acid rain in the MCMZ in collaboration with Atmospheric Monitoring Network of the Mexico City Government at 16 atmospheric deposition sampling sites.

Laboratory Analysis

The collection of rainfall took place weekly at the MCMZ.

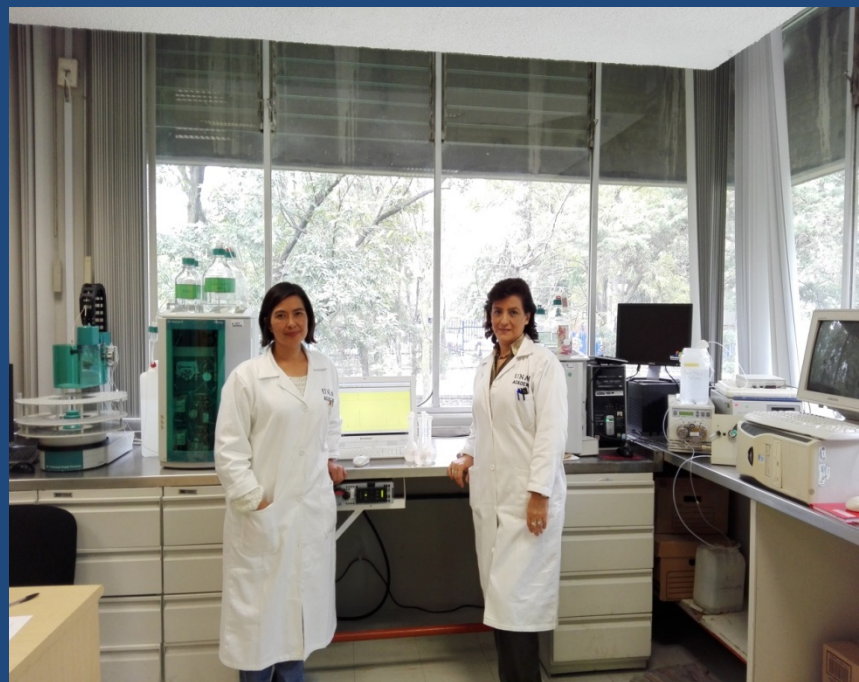
Chemical analysis for each sample to determine the following parameters: pH, conductivity, cations (Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) and anions concentration (Cl^-, NO_3^-, SO_4^{2-}) by means of High Performance Liquid Chromatography (HPLC).

SCA-CCA-UNAM Lab analysis comply with the recommendations from the US-EPA, 1994, the National Atmospheric Deposition Program (NADP, 2015) and the Global Atmosphere Watch (GAW) Precipitation Chemistry Program of the World Meteorological Organization (WMO, 2004).

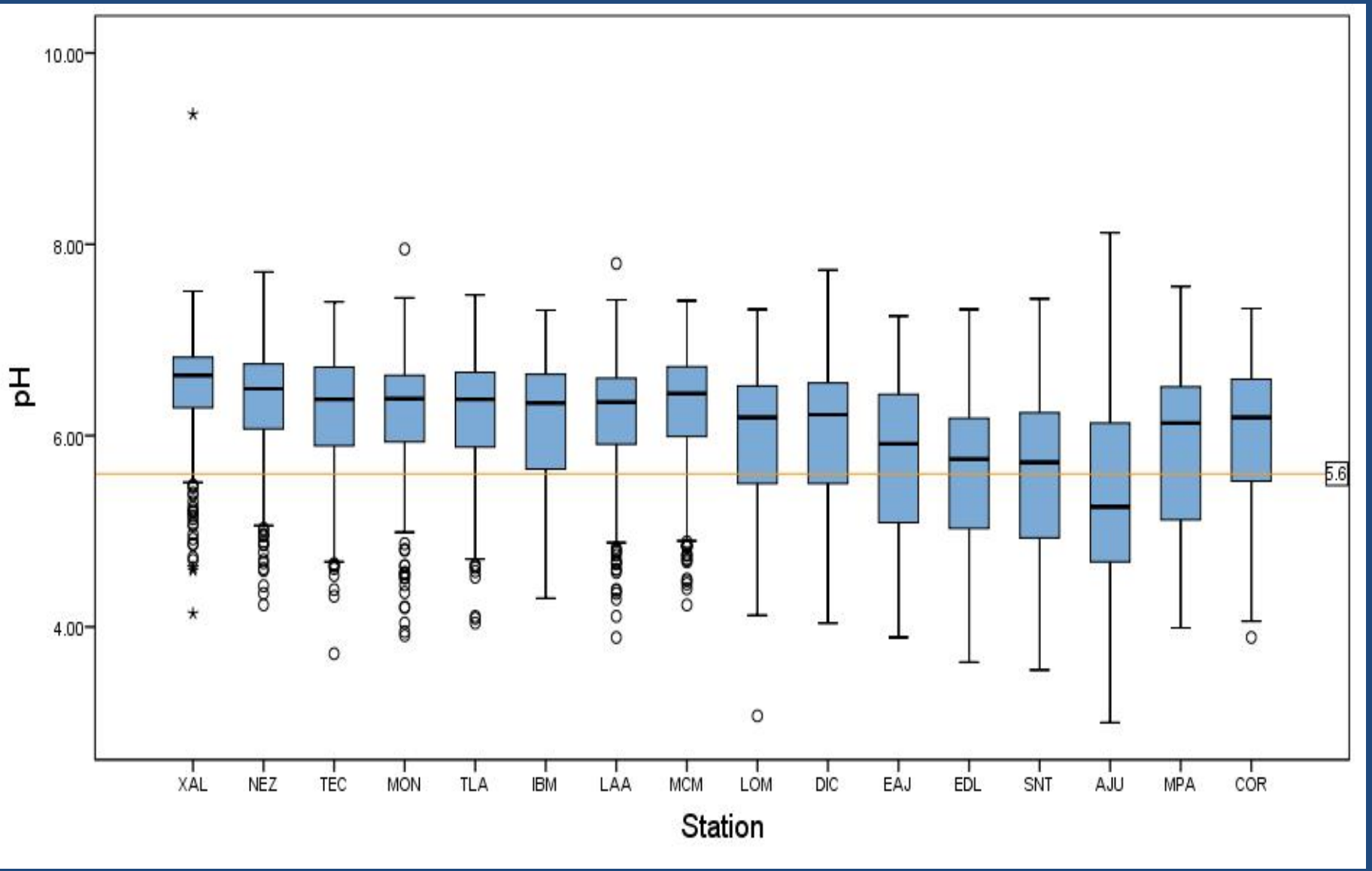
Interlaboratory-comparison Programs.

GAW-WMO, since 2008.

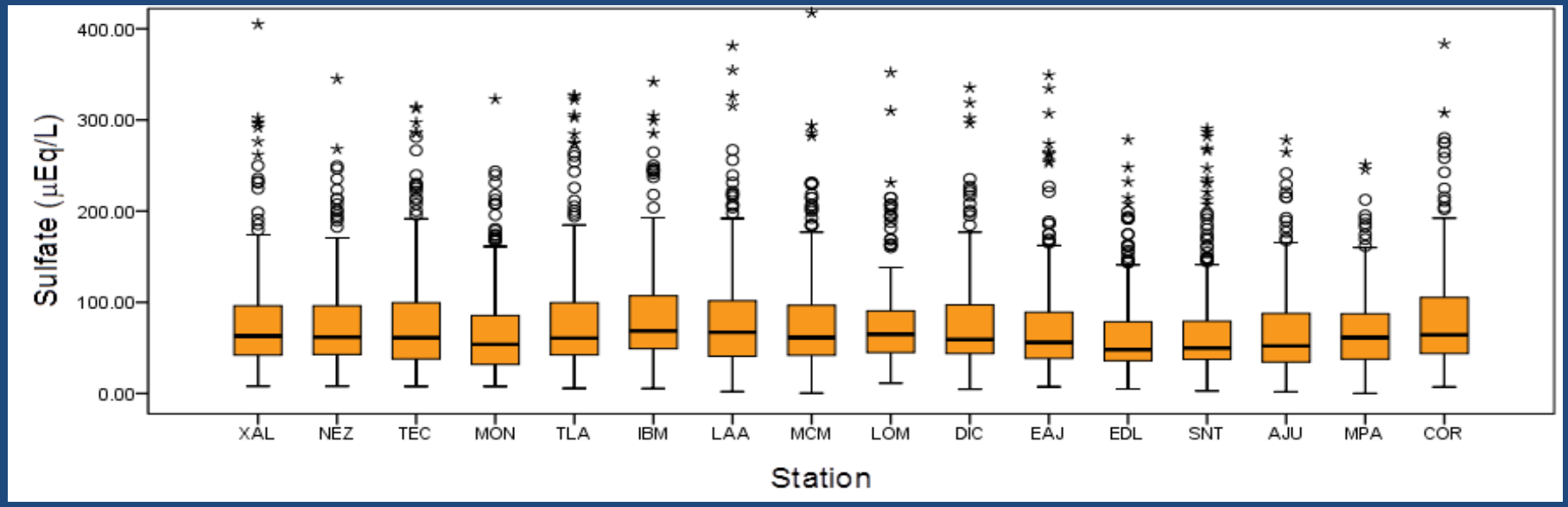
USGS-NADP, since 2016 .

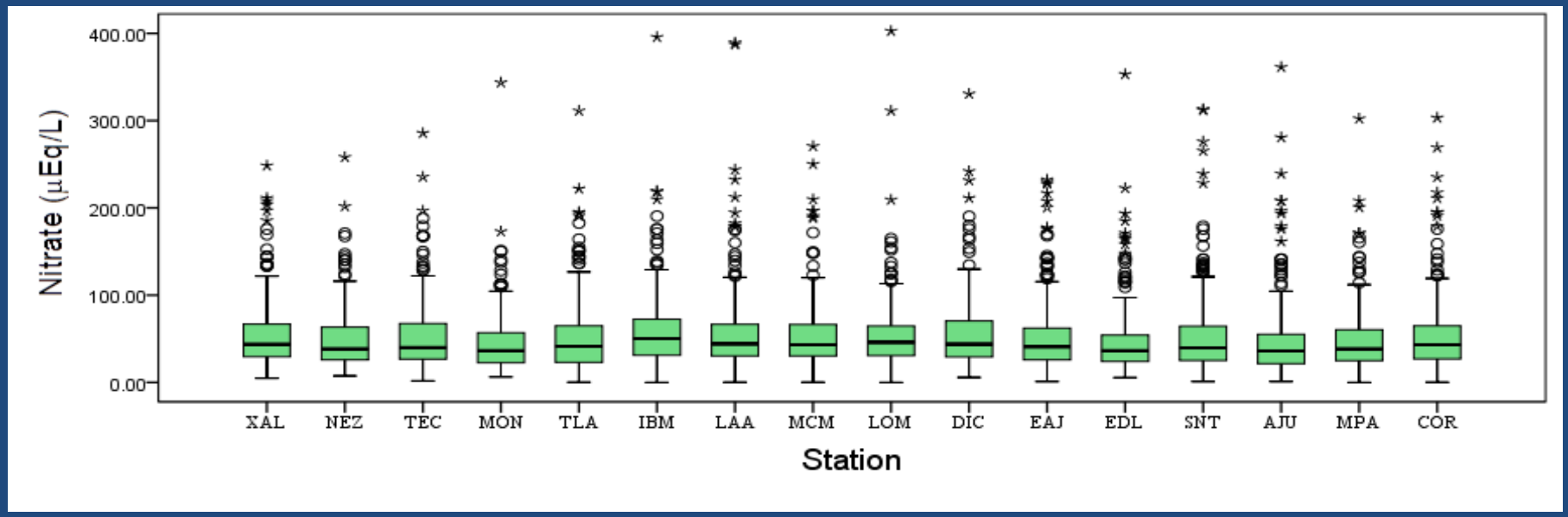


Box plot for pH events at the MCMZ

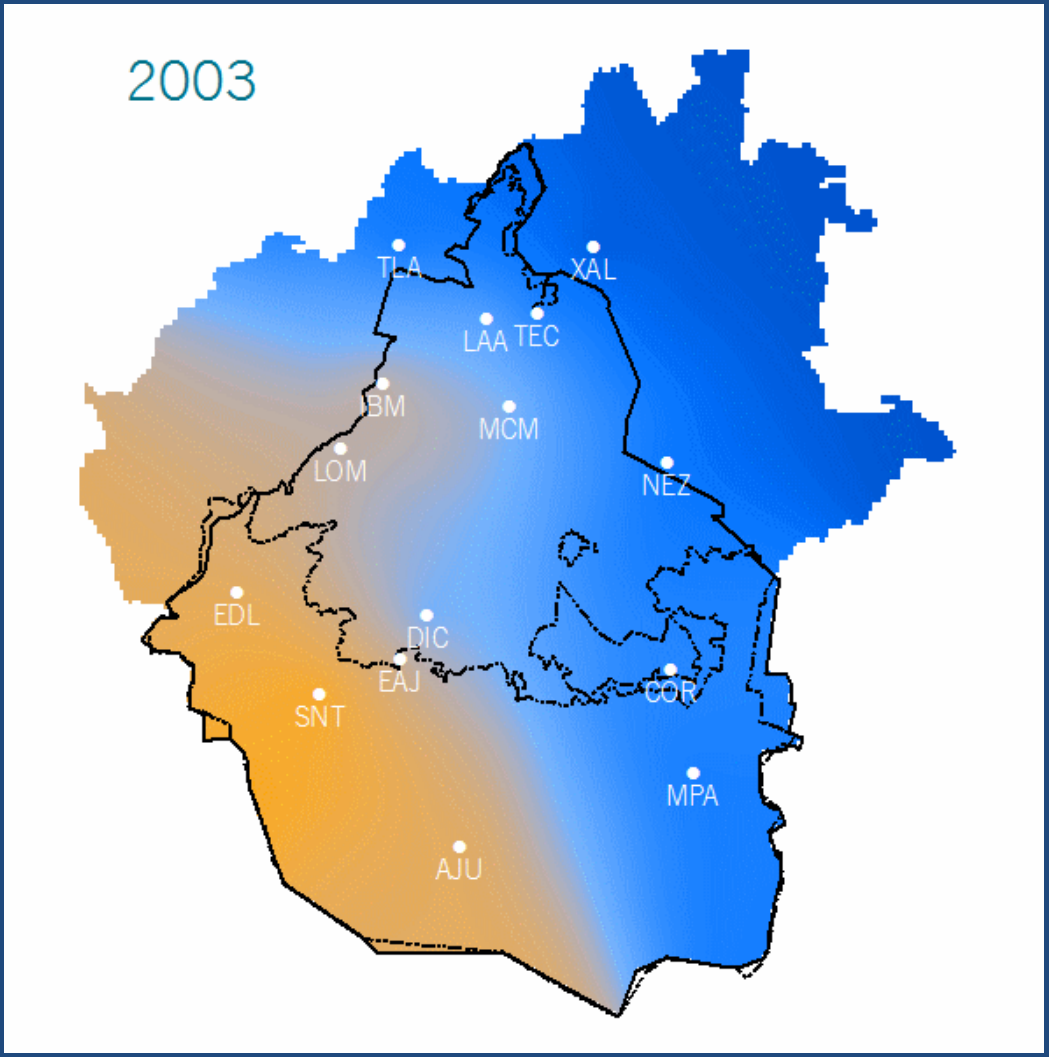


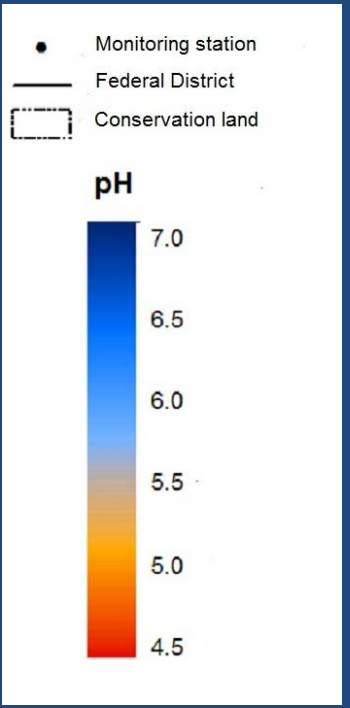
Volume Weighted Mean (VWM) concentrations for SO_4^{2-} and NO_3^-



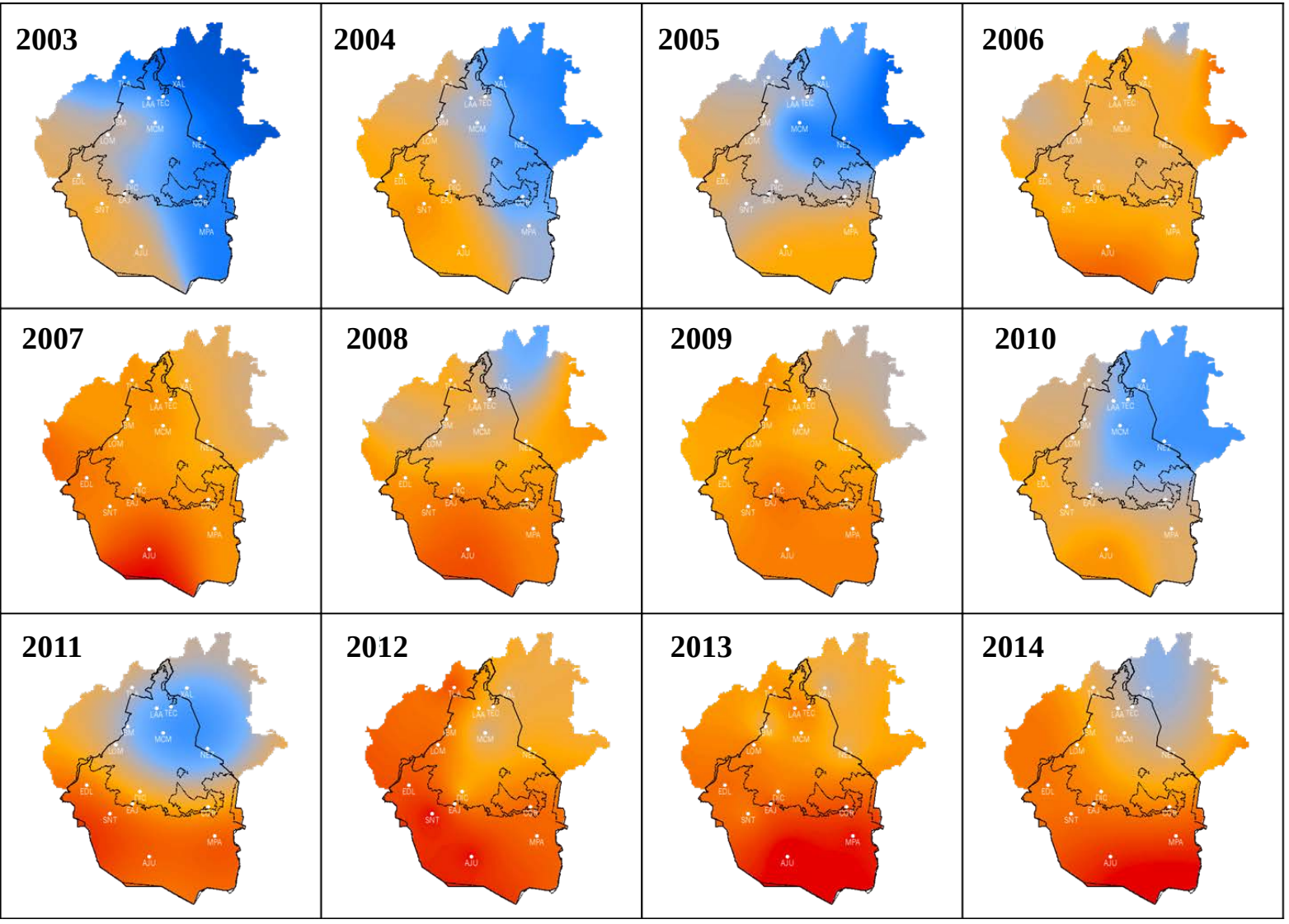


pH

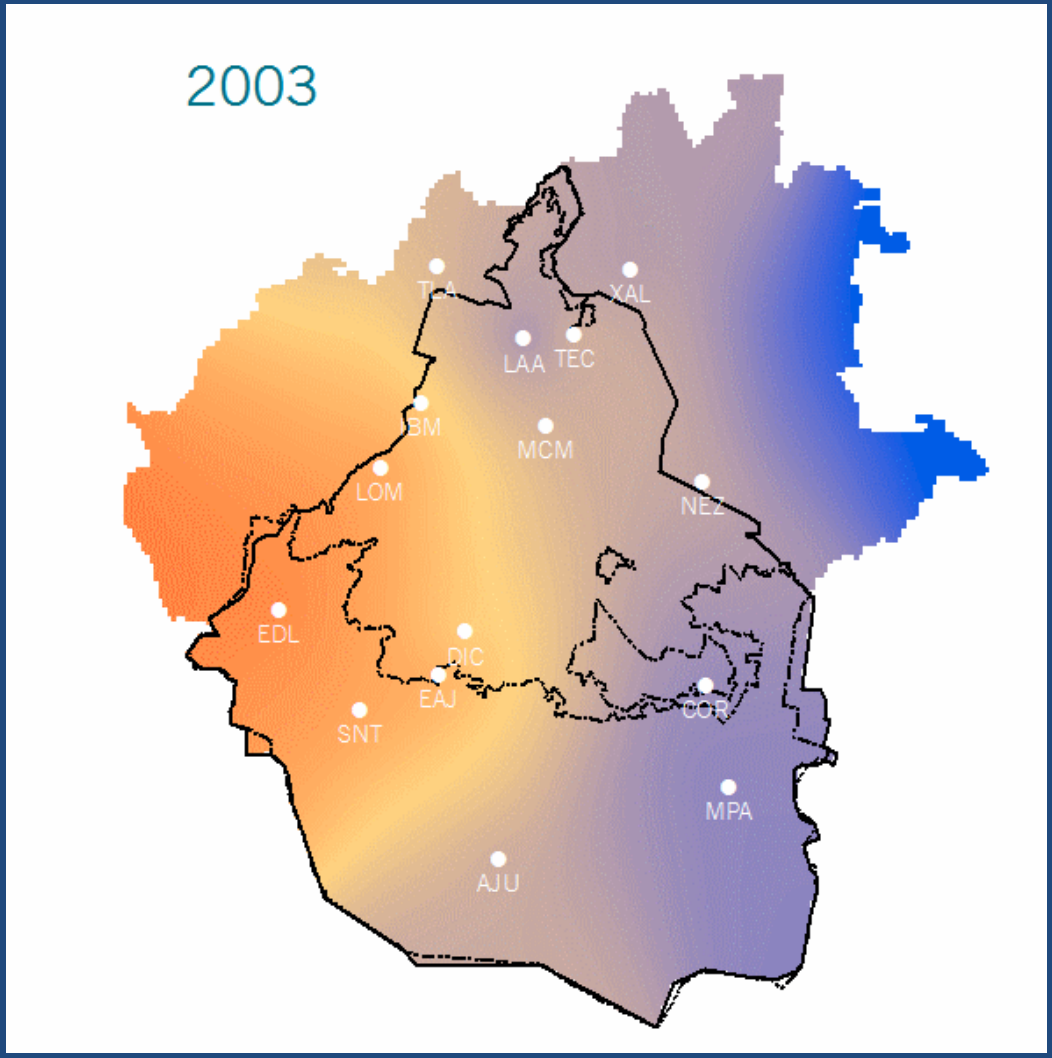

2003
TLA
XAL
LAA
TEC
IBM
MCM
LOM
NEZ
EDL
DIC
EAJ
COR
SNT
MPA
AJU


Monitoring station
Federal District
Conservation land
pH
7.0
6.5
6.0
5.5
5.0
4.5

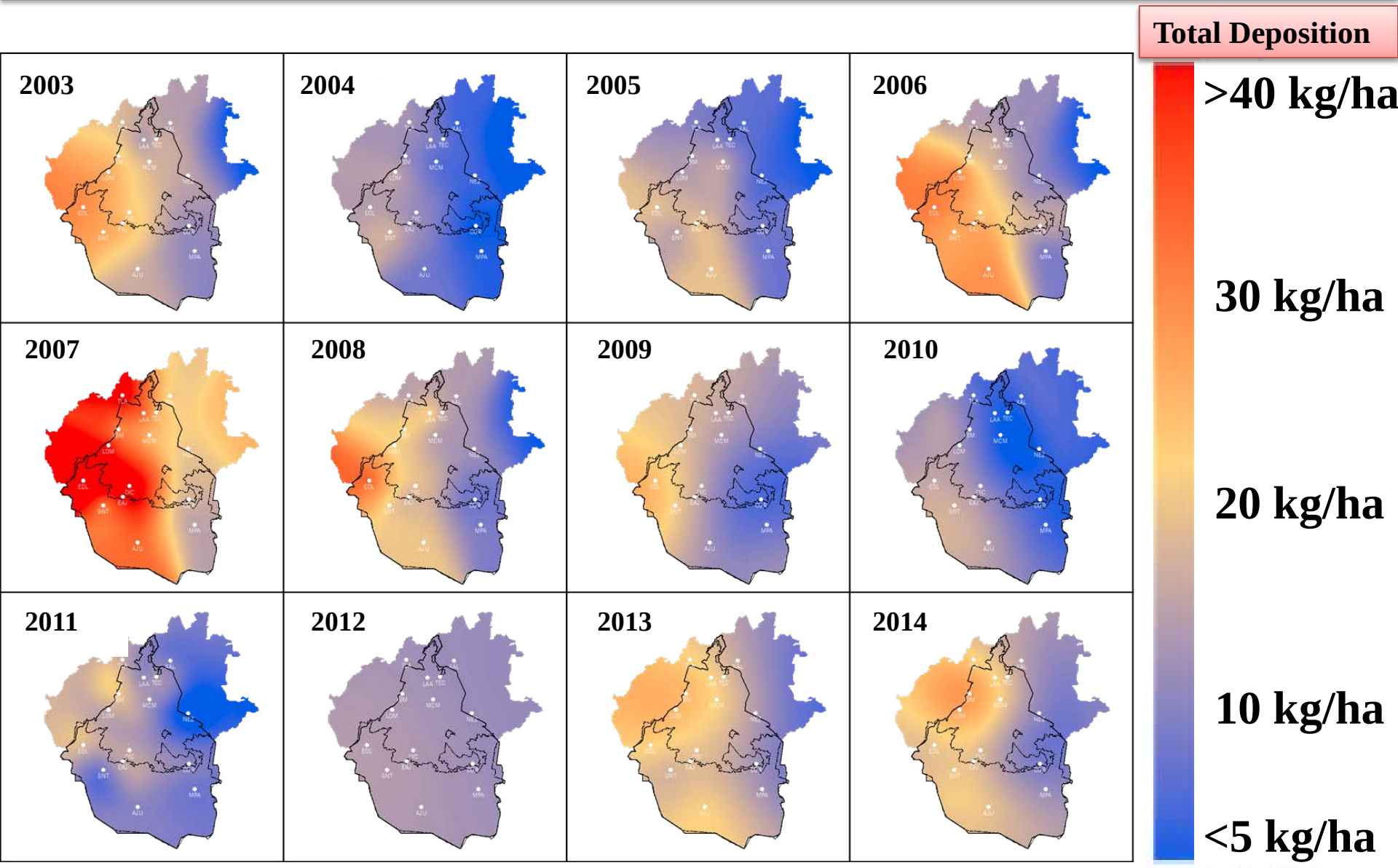
Spatial and temporal variation of pH at the MCMZ



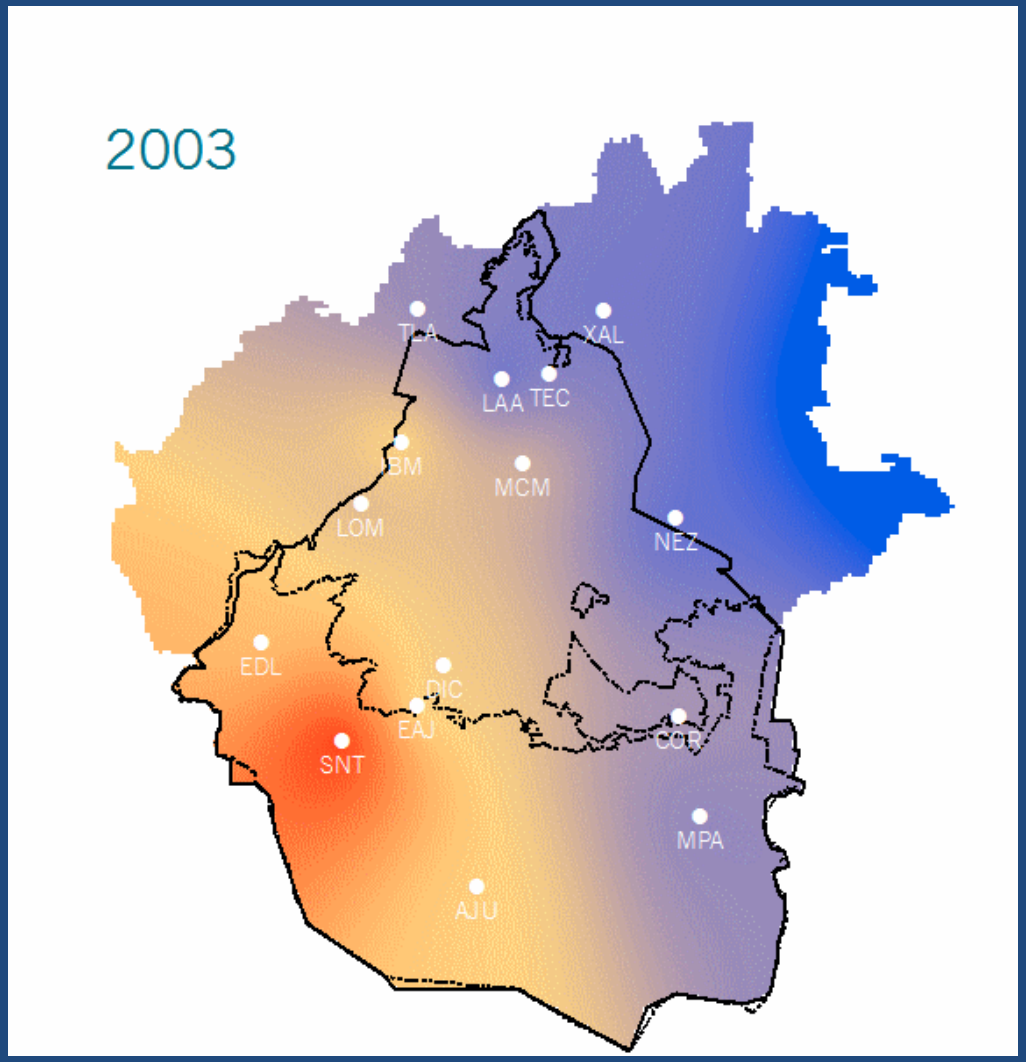
SO_4^{2-}


2003
TLA
XAL
LAA
TEC
BM
MCM
LOM
NEZ
EDL
DIC
EAJ
SNT
COR
MPA
AJU
Monitoring station
Federal District
Conservation land
Sulfate as SO_4^{2-} (kg/ha)
> 40
30
20
10
< 5

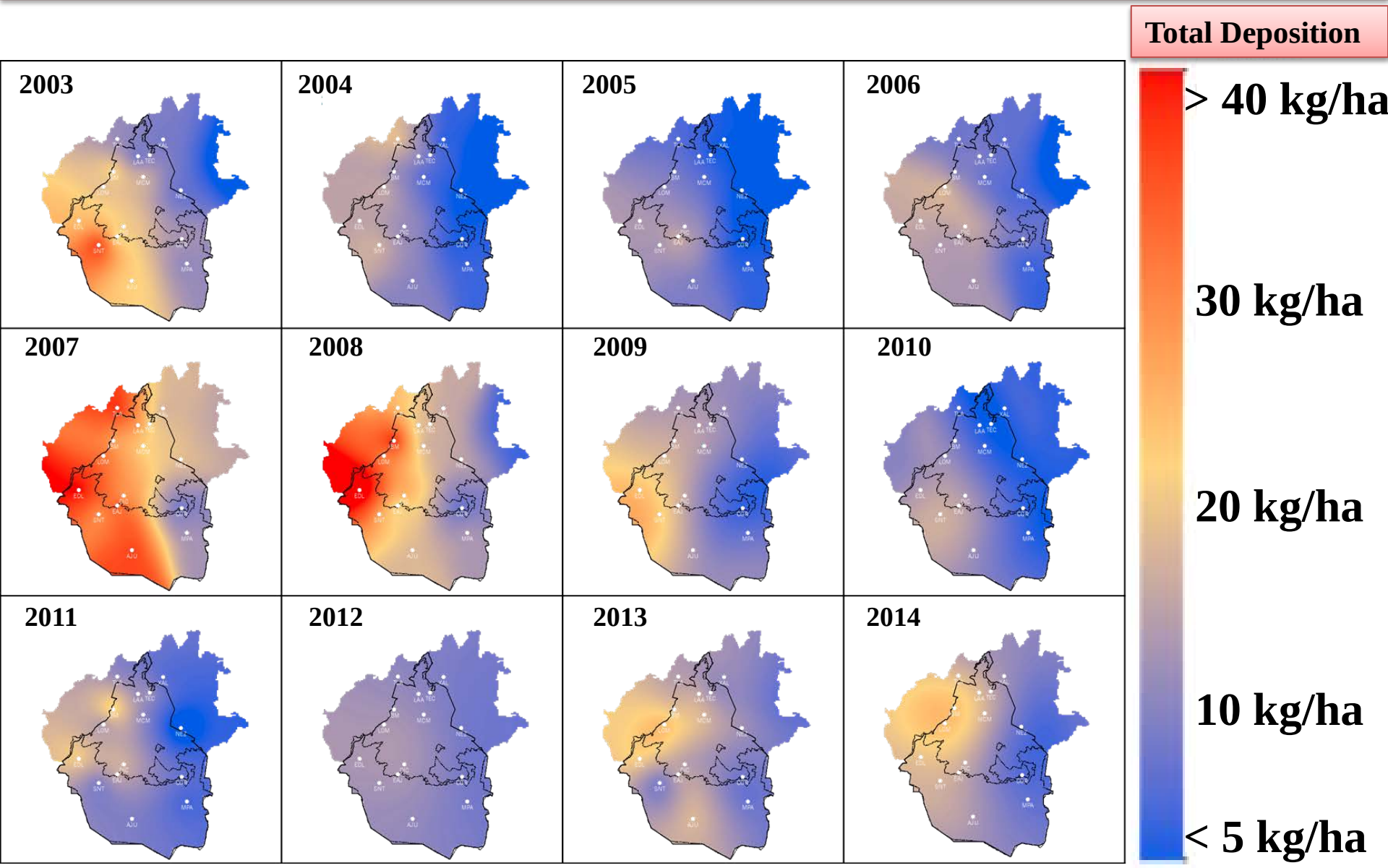
Spatial and temporal variation of SO_4^{2-} wet deposition at the MCMZ



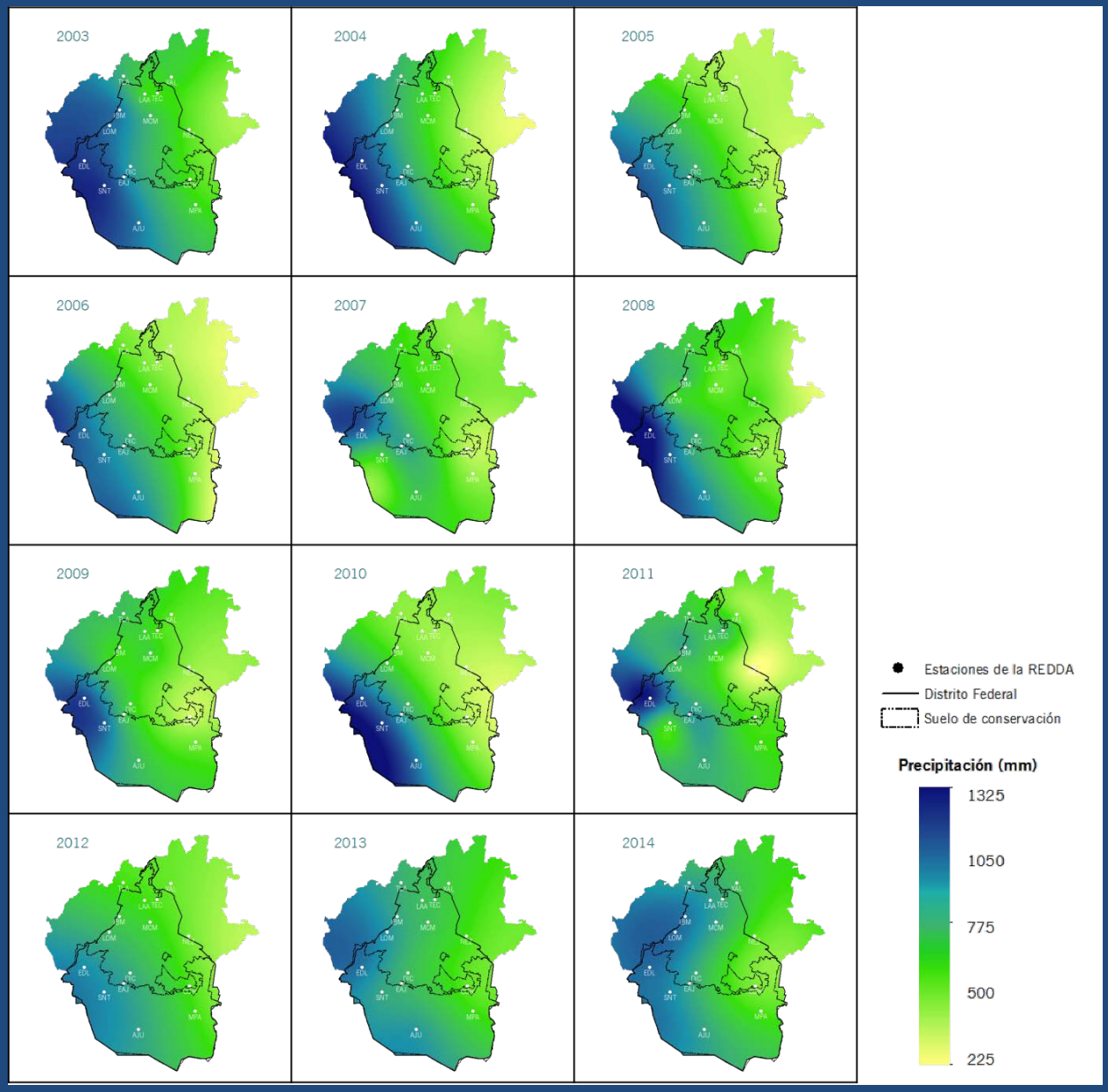
NO_3^-


2003
TEA
XAL
LAA
TEC
SBM
MCM
LOM
NEZ
EDL
DIC
EAJ
SNT
COR
MPA
AJU
Monitoring station
Federal District
Conservation land
Nitrate as NO_3^- (kg/ha)
> 40
30
20
10
< 5

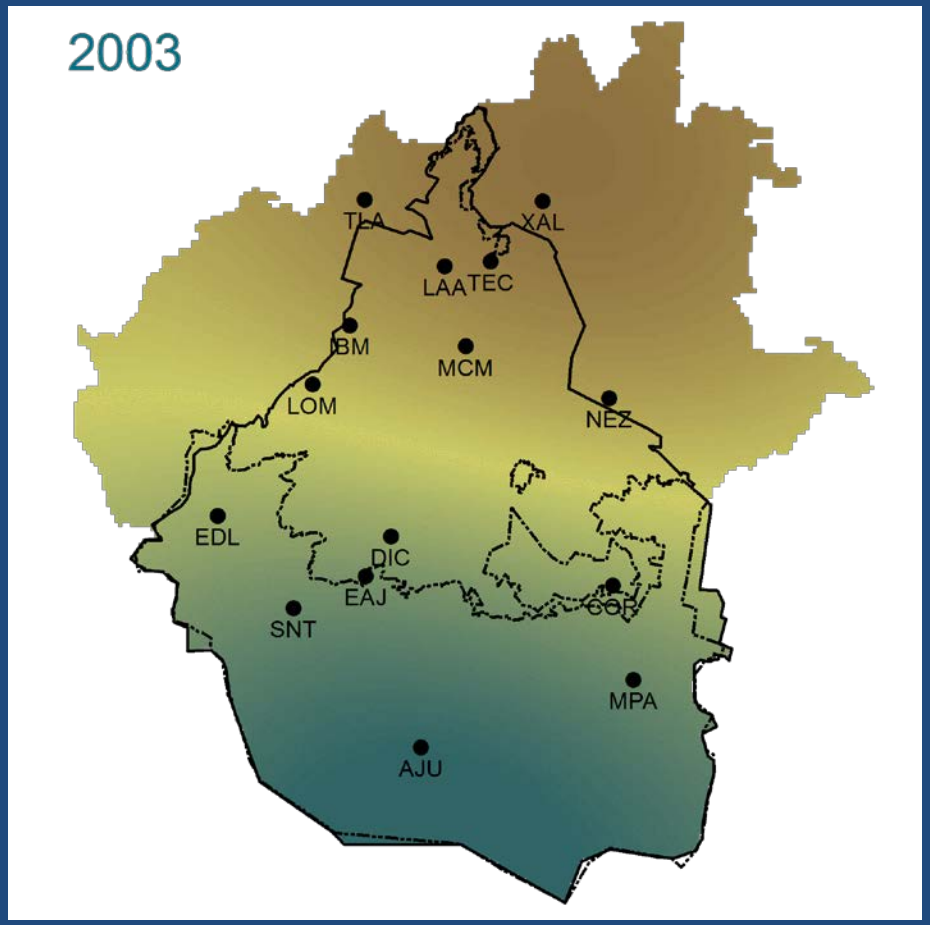
Spatial and temporal variation of NO_3^- wet deposition at the MCMZ



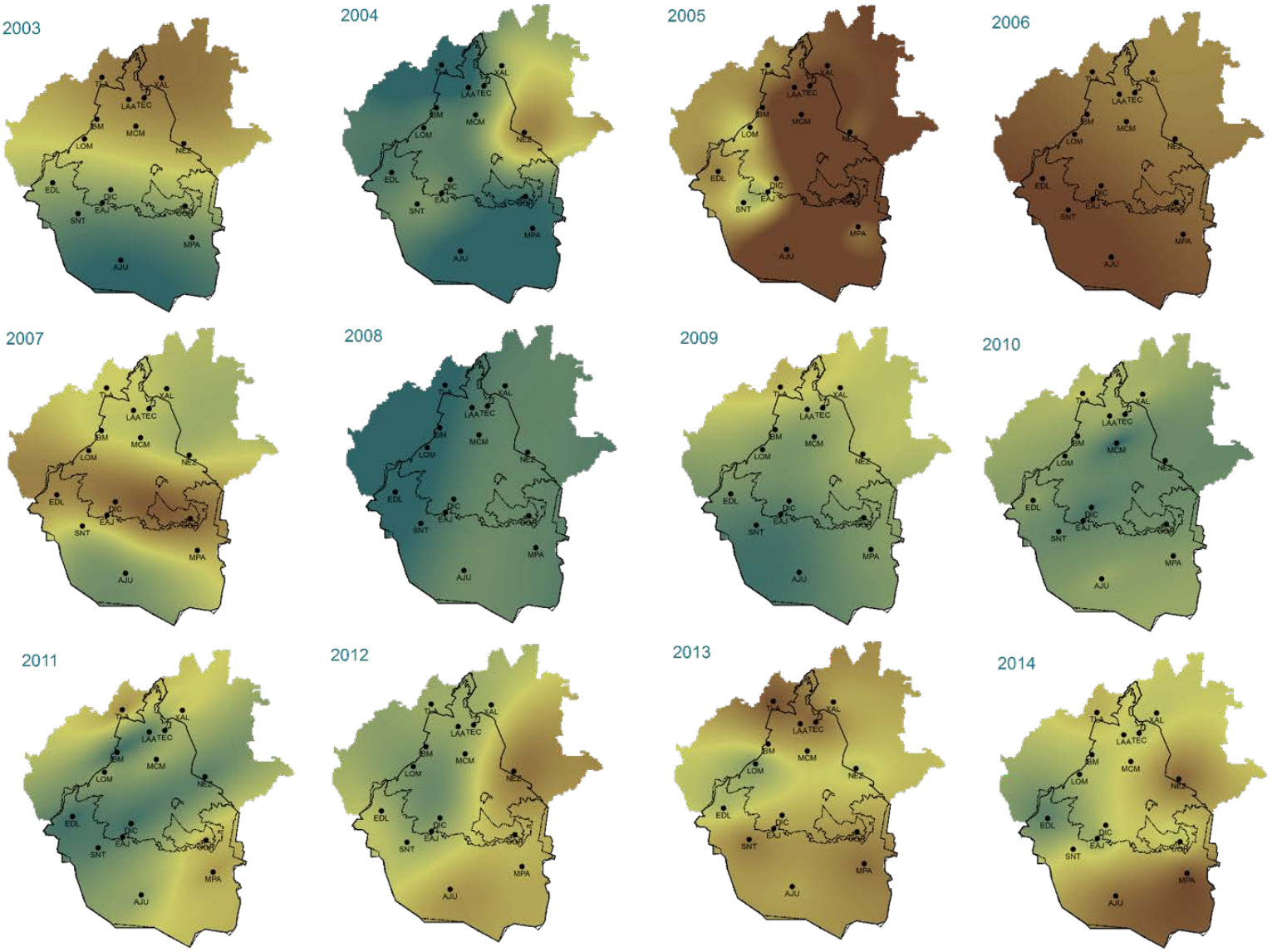
Precipitation at MCMZ



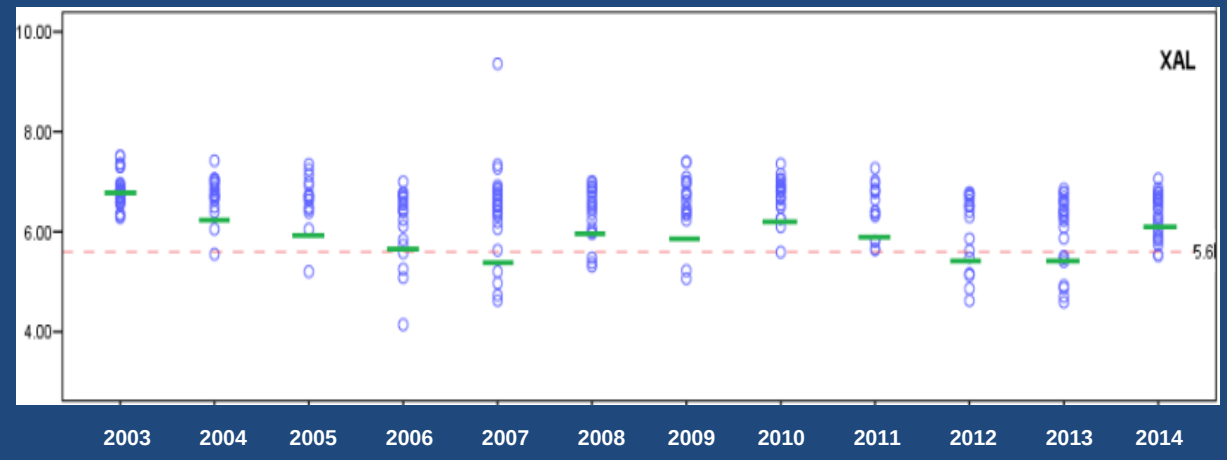
SO_4^{2-}/NO_3^-

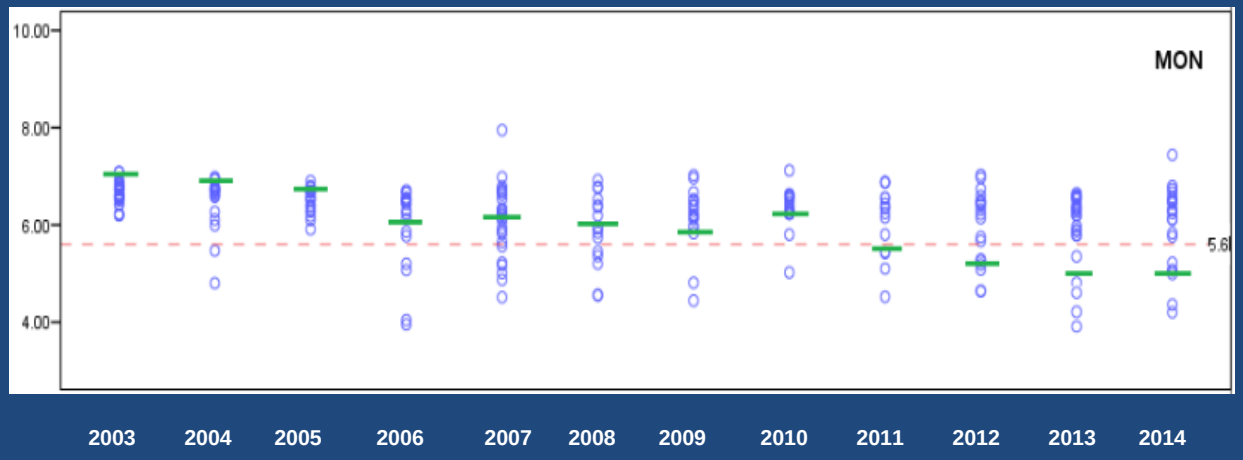

2003
TLA
XAL
LAA
TEC
IBM
MCM
LOM
NEZ
EDL
DIC
EAJ
SNT
MPA
AJU
Estaciones de la REDDA
Distrito Federal
Suelo de conservación
Relación SO4/NO3
(µequivalentes)
1.4
1.3
1.2
1.1
1.0
0.9

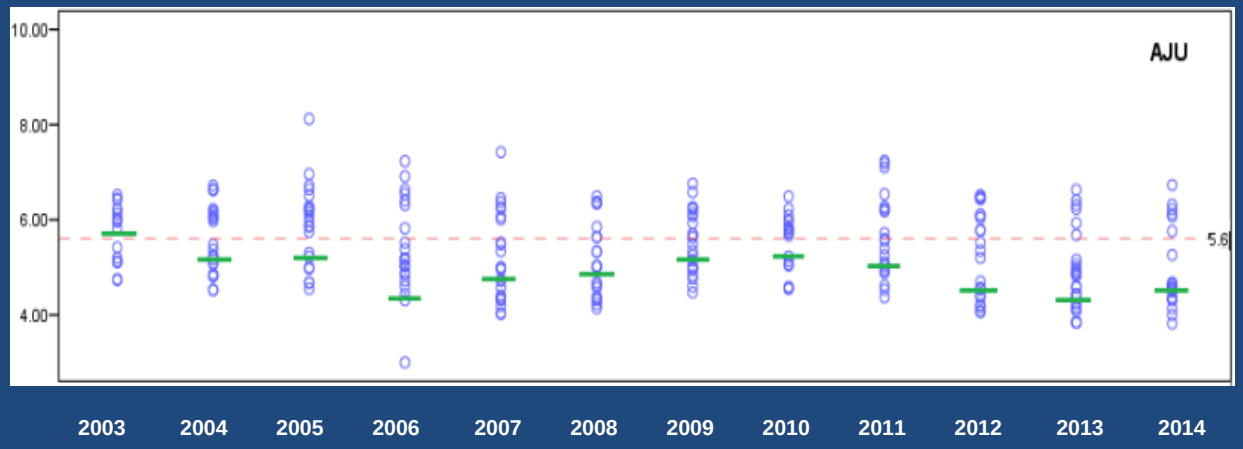
Spatial and temporal variation of SO_4^{2-}/NO_3^- wet deposition at the MCMZ



VWM pH for three stations (XAL, MON, AJU) in the MCMZ



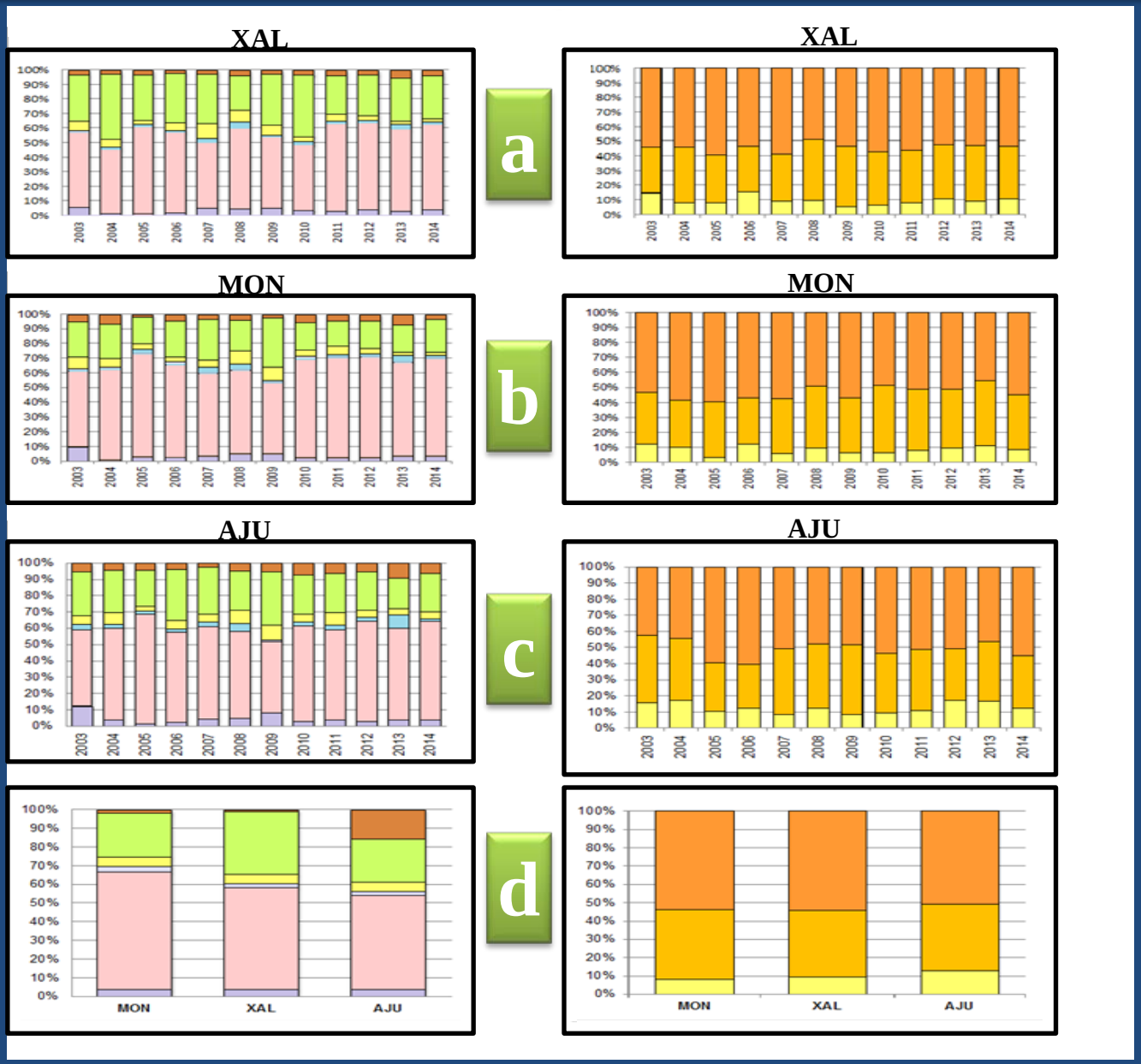




O pH Values

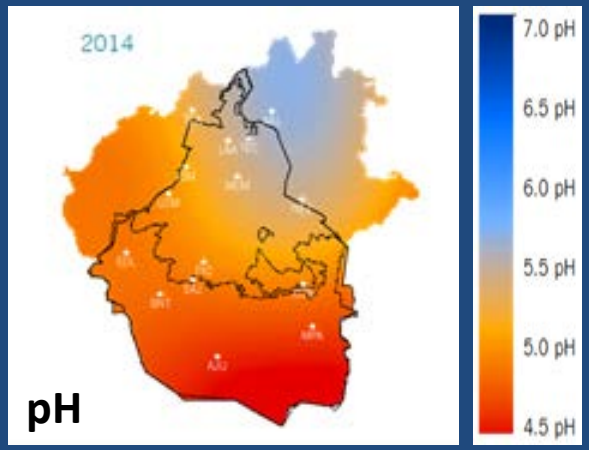
— VWM pH

Ionic composition per year for MON, XAL and AJU stations (a, b and c) and for total of period (d)

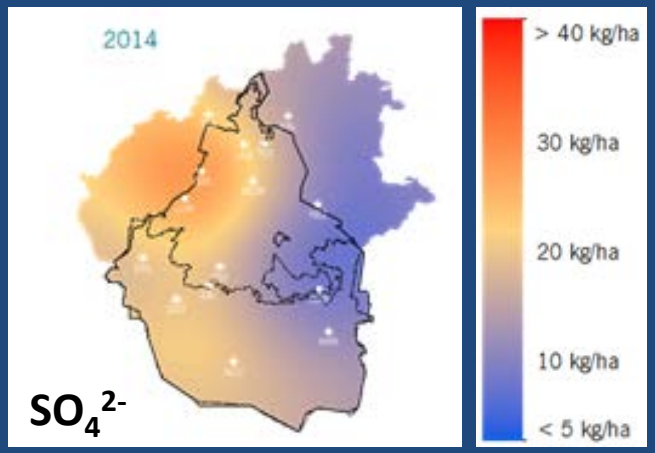


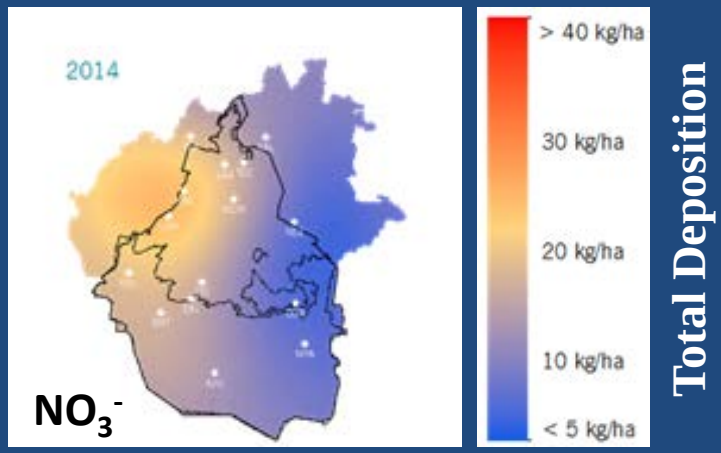
Conclusions

The spatial distribution shows that VWM pH values, decrease from North to South in the MCMZ



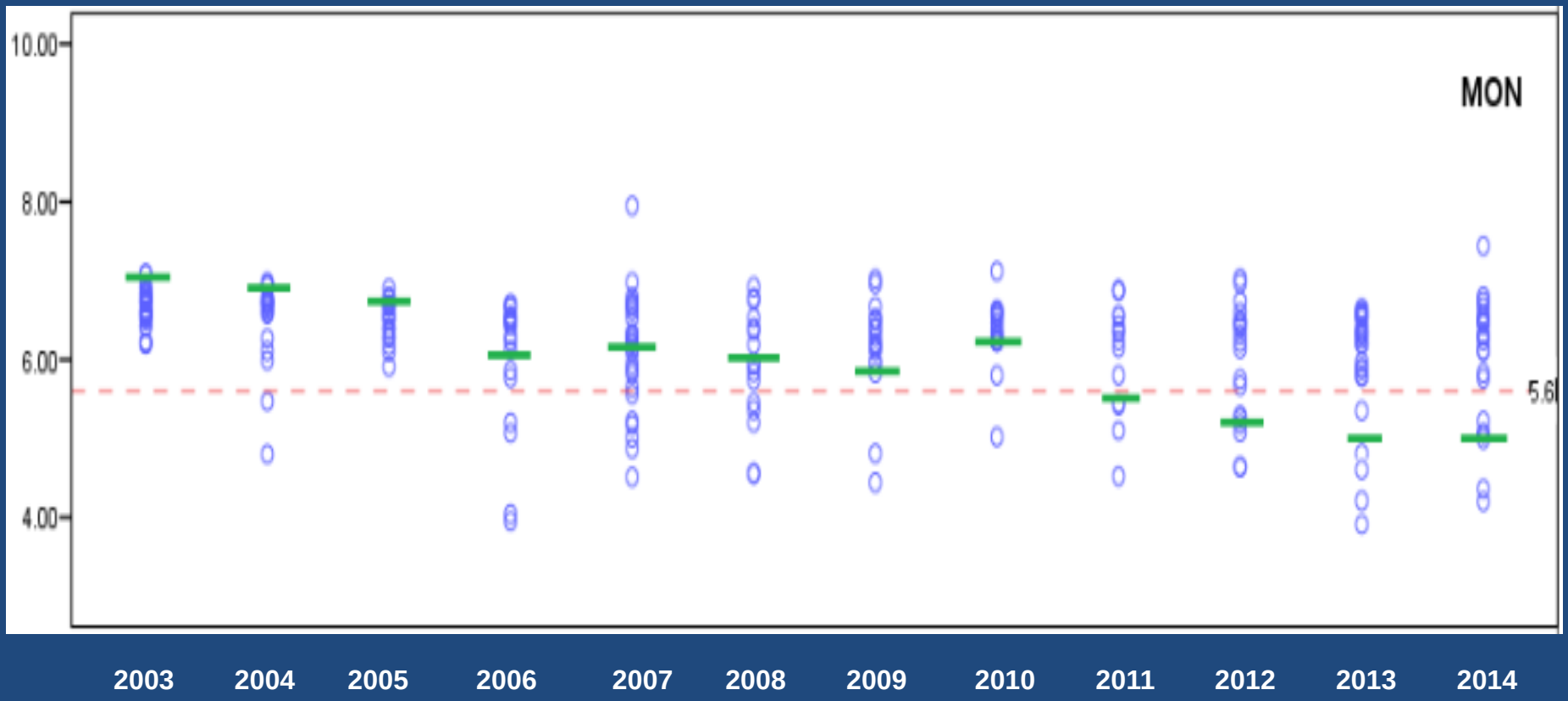
Sulfate and nitrate presented their major deposition in the West area





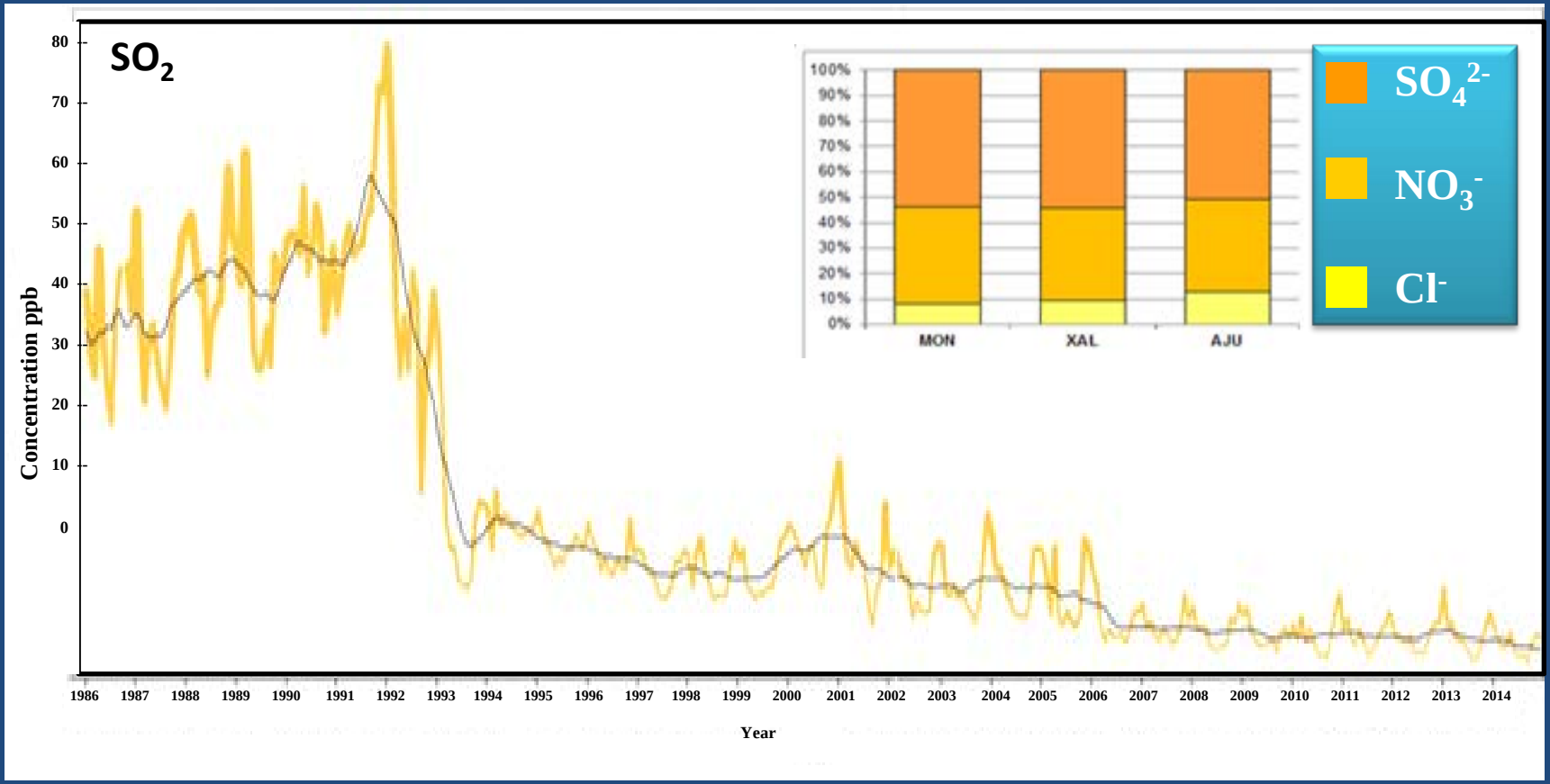
Conclusions

In most of the study sites, a decrease in the VWM pH value was found in the period from 2003 to 2014. For example MON station presented a VWM pH value of 7.48 in 2003 and 5.03 in 2014.



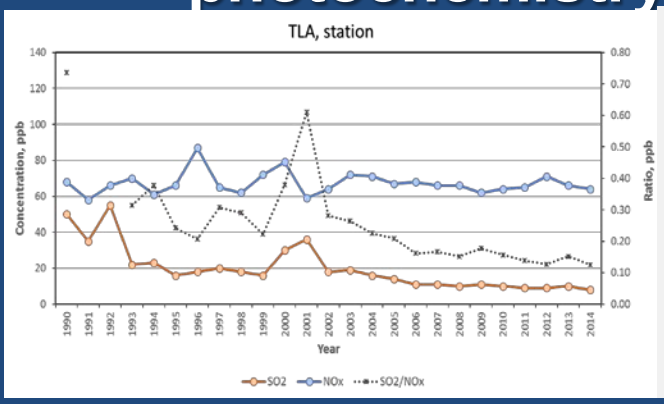
Conclusions

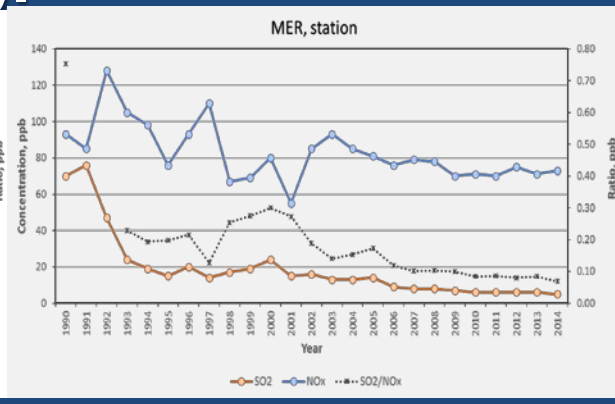
In all wet deposition samples, the SO_4^{2-} presents a higher percentage (60%) with respect to NO_3^- y Cl^-, indicating that the main precursor of acid rain is SO_2, although it levels have been declining at Metropolitan Zone, reinforcing the conclusion that significant emission sources are outside (upwind) of the MCMZ.

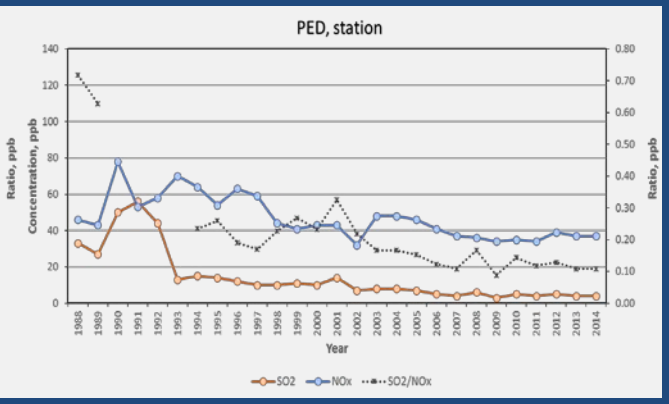


- SO_2 levels have decreased from 1990 to 2014 by about 90%, while those of NOx by 20%.

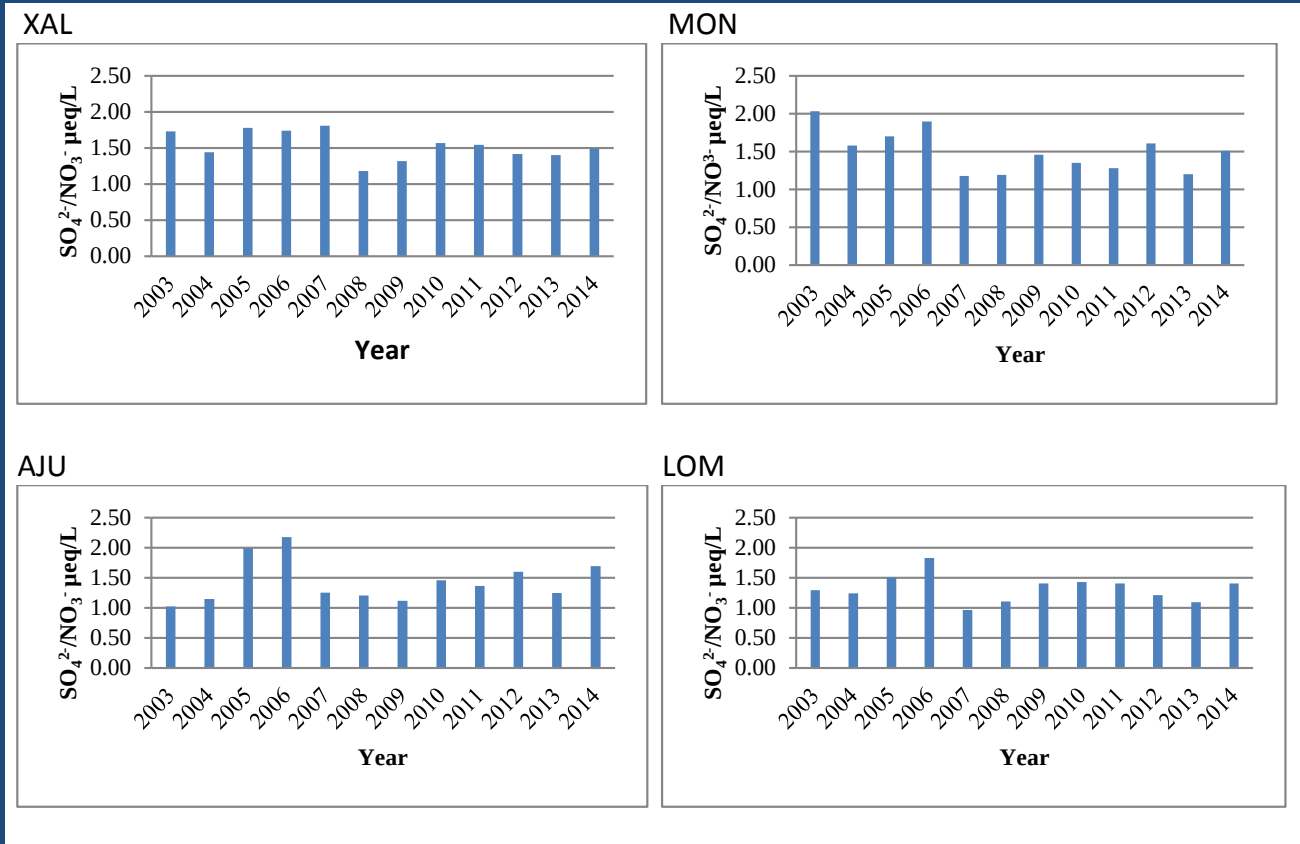
- The SO_2 / NOx ratio has declined about 60% indicating more effective strategies in reducing SO_2 (change of fuel or sulfur reduction) than for NOx emissions. This, because the NOx emission sources are diverse and also NOx are part of complex mechanisms of atmospheric deposition and photochemistry.







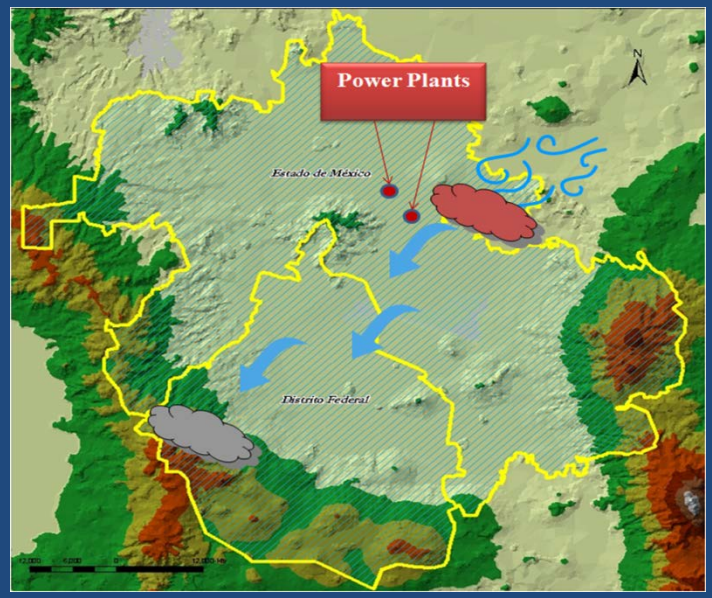
- **In 2003 a difference among the sampling sites was observed in the SO_4^{2-} to NO_3^- equivalents ratio, sites located in the north presented a higher ratio of 2, while the sites located in the south the value was 1. In 2014, a homogeneous distribution was observed, the ratio was the same in all the Mexico City sampling sites: 1.5 (µeq/L SO_4^{2-} to µeq/L NO_3^-).**



Recommendations

To establish strategies for the reduction of precursor's emissions of acid rain in external sources to North of the MCMZ, such as use of fuels with low - sulphur or substitution of fuel oil by natural gas. A reduction of more than 99% of SO_2 is expected by this change.

The change from fuel oil to natural gas should be seen in emission sources, such as the used of the Best Available Control Technology for the NO_x control, consisting of low NO_x burners.



Aknowledgements

- SIMAT: Mexico City Government. Olivia Rivera, Rocío Carmona, Miguel Sánchez, Jorge Rodas, Ernesto González
- NADP: David Gay, Christopher Lehmann
- WMO: Van Wowersox, Richard Artz
- USGS: Gregory Wetherbee
- PAPIIT UNAM: Project IN116215

THANK YOU