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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The Mexico City Metropolitan Zone (MCMZ) is accepted as having critical levels of air pollution. In the 1980s, particulates and sulfur dioxide ($\text{SO}_2$) 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 $\text{SO}_2$ 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
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.
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).


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 \( \text{SO}_4^{2-} \) and \( \text{NO}_3^- \)
Spatial and temporal variation of pH at the MCMZ
Spatial and temporal variation of SO$_4^{2-}$ wet deposition at the MCMZ
Spatial and temporal variation of NO₃⁻ wet deposition at the MCMZ

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Total Deposition:

- > 40 kg/ha
- 30 kg/ha
- 20 kg/ha
- 10 kg/ha
- < 5 kg/ha
Precipitation at MCMZ
$\text{SO}_4^{2-}/\text{NO}_3^-$
Spatial and temporal variation of $\text{SO}_4^{2-}/\text{NO}_3^-$ wet deposition at the MCMZ
VWM pH for three stations (XAL, MON, AJU) in the MCMZ

- pH Values
- VWM pH
Ionic composition per year for MON, XAL and AJU stations (a, b and c) and for total of period (d)
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.
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.
In all wet deposition samples, the $\text{SO}_4^{2-}$ presents a higher percentage (60%) with respect to $\text{NO}_3^-$ and $\text{Cl}^-$, indicating that the main precursor of acid rain is $\text{SO}_2$, although its levels have been declining at Metropolitan Zone, reinforcing the conclusion that significant emission sources are outside (upwind) of the MCMZ.
• SO₂ levels have decreased from 1990 to 2014 by about 90%, while those of NOx by 20%.

• The SO₂ / NOx ratio has declined about 60% indicating more effective strategies in reducing SO₂ (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 $\text{SO}_4^{2-}$ to $\text{NO}_3^-$ 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 ($\mu$eq/L $\text{SO}_4^{2-}$ to $\mu$eq/L $\text{NO}_3^-$).
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.
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