Impact on atmospheric chemistry during Biofuel Ethanol Production: past, current trends and future perspectives

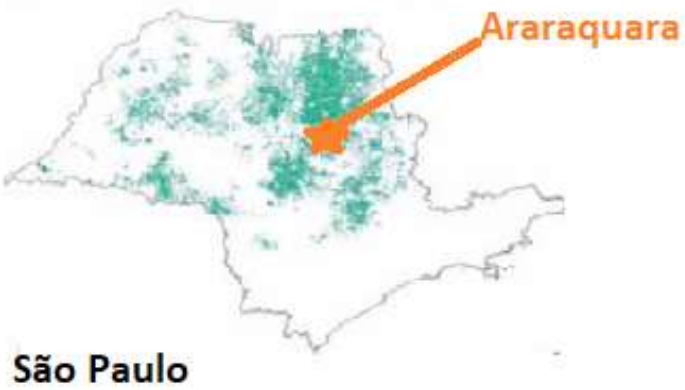
Arnaldo Alves Cardoso

São Paulo State University UNESP, Department of Analytical Chemistry, Araraquara, SP

Brazil

Impact on atmospheric chemistry during Biofuel Ethanol Production

Study area location



2018 population 235,000

Planted area 56,000 Km^2 = 10% territory of France

Predominant economic activity: sugar cane

https://www.iq.unesp.br/

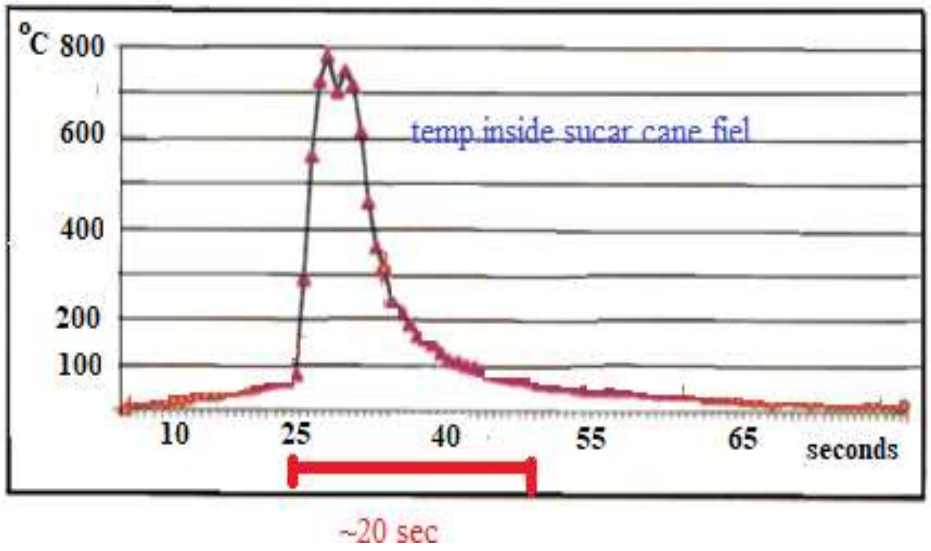
in the past

Sugar cane harvest

- ✓ The sugar cane harvest occurs during the dry season (May to November)
- ✓ The manual harvesting is a common practice with prior burning of the crop.

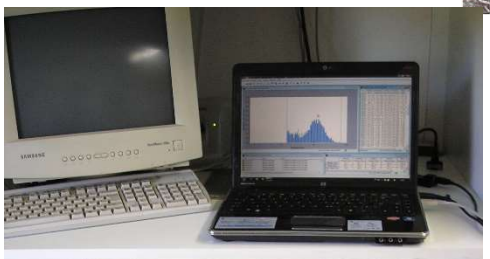
The burning is allowed only after sunset when the winds are less intense.

The burning practice results in emissions to the atmosphere of large quantities of gases and particles



The burning of sugarcane straw is fast

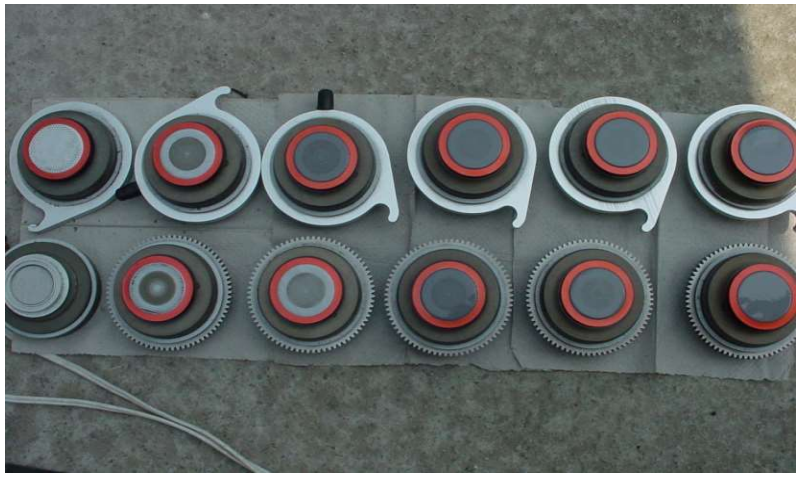
The sampling site on the campus of São Paulo State University situated ~1 km west of the urban limit of Araraquara city



Running towards the fire!

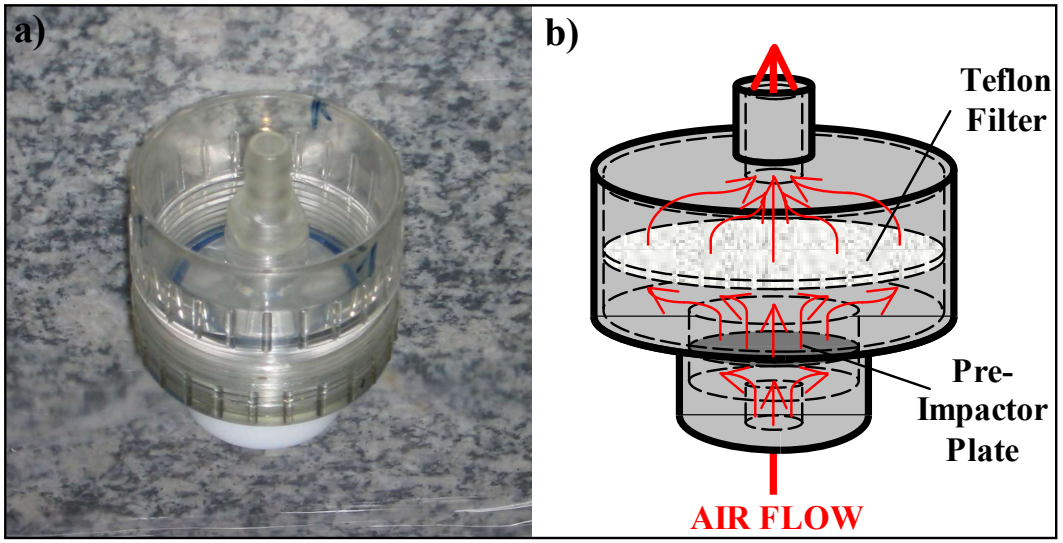
Sugar cane burning plume samples were collected in a rural area 15 km distant from Araraquara

Aerosol Sampling Techniques - Impactor

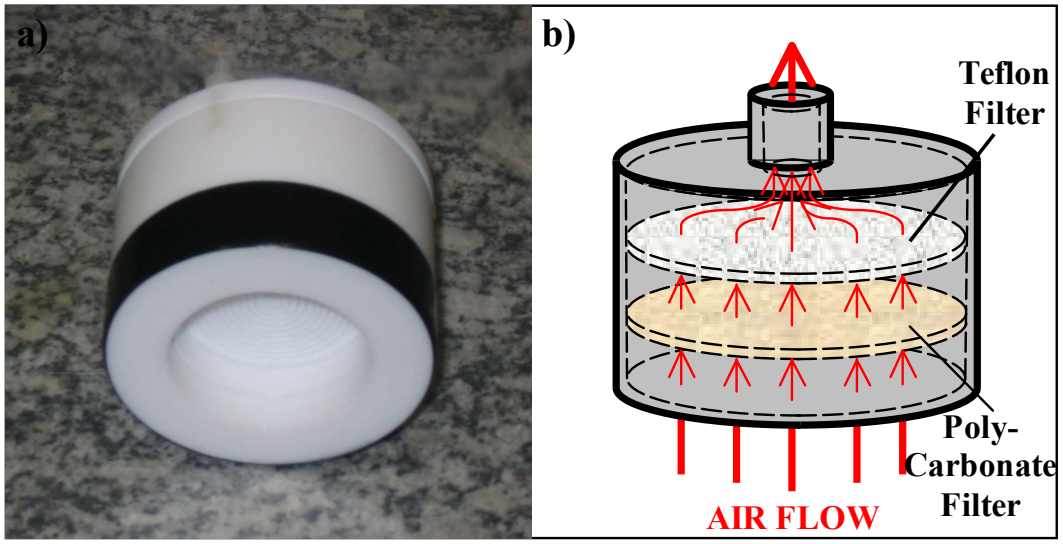


MOUDI Stage Number	*50 % Cut-off Particle Diameter (μm)*
Inlet	18.00
Stage 1	10.00
Stage 2	5.60
Stage 3	3.20
Stage 4	1.80
Stage 5	1.00
Stage 6	0.56
Stage 7	0.32
Stage 8	0.18
Stage 9	0.10
Stage 10	0.06
Backup or Stage 11	0

Aerosol Sampling Techniques - Filters



- PM_{10}
- Steel pre-impactor plate
- 50 % cut-off at flow rate of 8.5 L min^{-1}
- Teflon filter

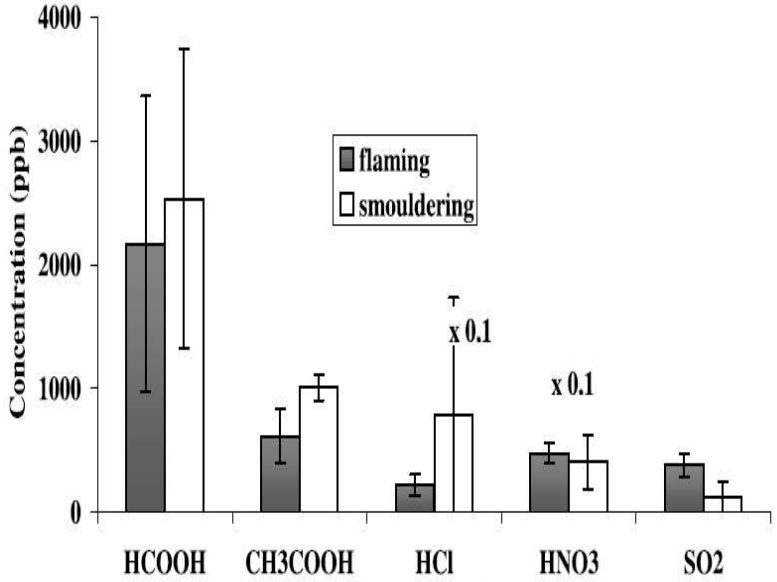


- $PM_{2.5}$ / $PM_{>2.5}$
- Nuclepore pre-filter (12 µm pore size)
- 50 % cut-off at flow rate of 30.0 L min^{-1}
- Teflon filter

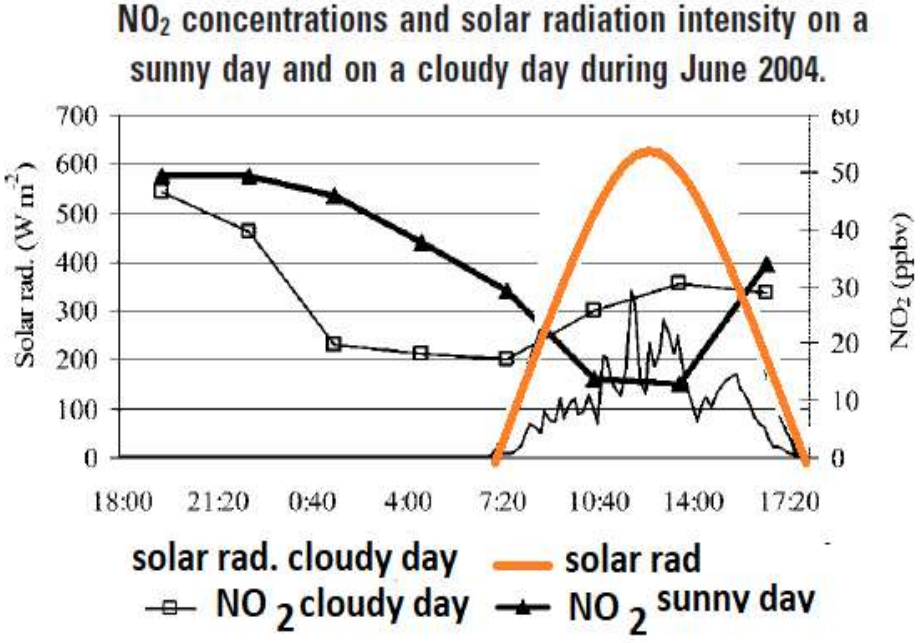
JOURNAL OF GEOPHYSICAL RESEARCH, VOL. 108, NO. D7, 4207, doi:10.1029/2002JD002567, 2003

Sources of atmospheric acidity in an agricultural-industrial region of São Paulo State, Brazil

G. O. da Rocha and A. Franco A. G. Allen A. A. Cardoso



Mean concentrations in primary emissions from sugar cane burning (n = 5 for flaming conditions, n = 4 for smoldering conditions, error bars indicate ± standard error for each datapoint).

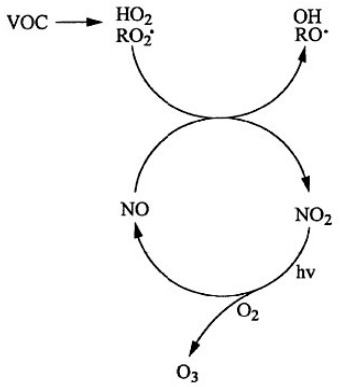


Fine particles: formed in the atmosphere

$NH_{3(gas)} + HNO_{3\ (gas)} \rightarrow NH_4NO_{3\ (solid)}$

NO_x gas is ubiquitous in all types of combustion

Oxidation VOC (photocatalyzed NO_2) → ozone

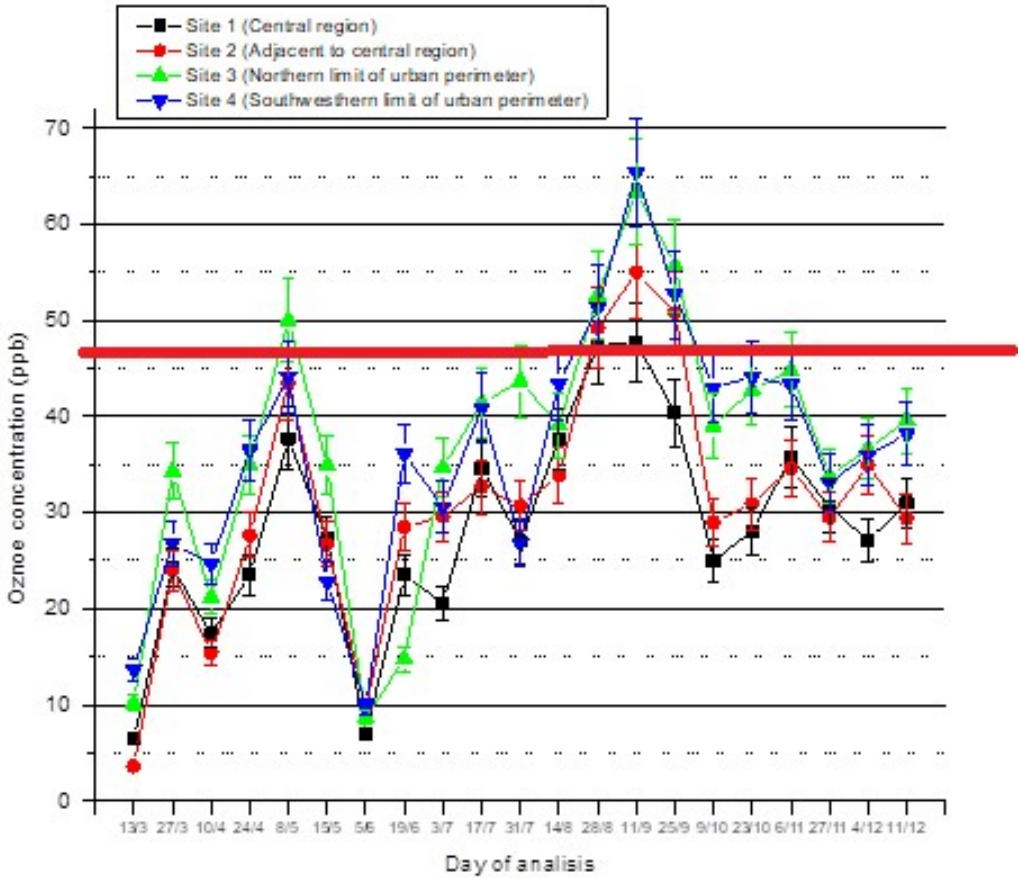


PAPER www.rsc.org/jem J. Environ. Monit., 2010, 12, 1325–1329 | 1325

Development of a sensitive passive sampler using indigotrisulfonate for the determination of tropospheric ozone

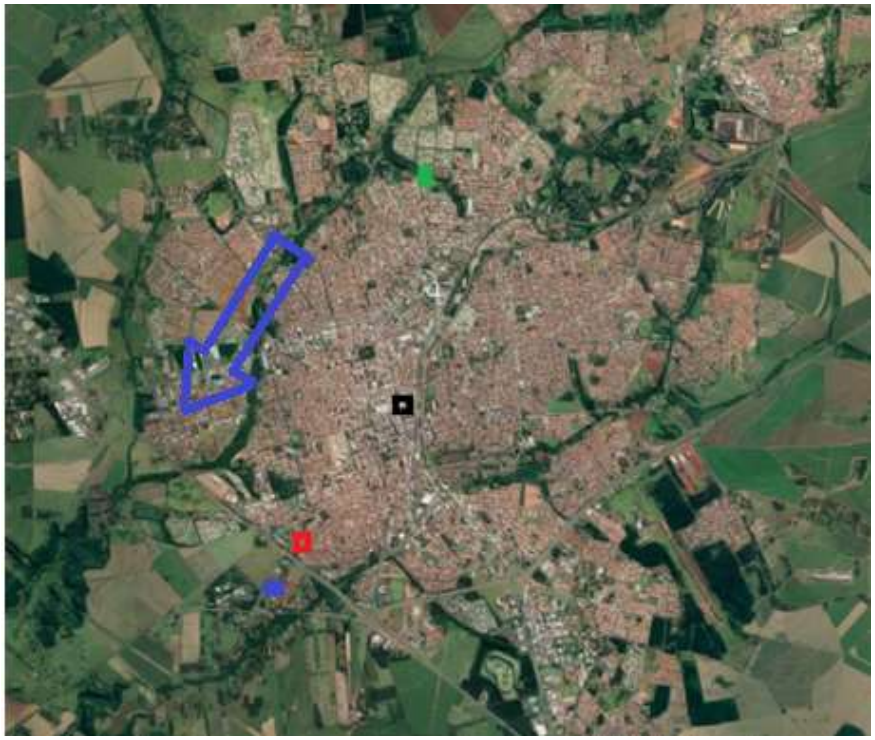
Gabriel Garcia, Andrew George Allen and Arnaldo Alves Cardoso*

DOI: 10.1039/b920254d



Ambient ozone measurements , between March and December 2008

Air Quality Guidelines 2005 (WHO)-- 47 ppb



Four sampling sites Araraquara (Brazil)

wind direction

Mapping and monitoring of ozone concentrations

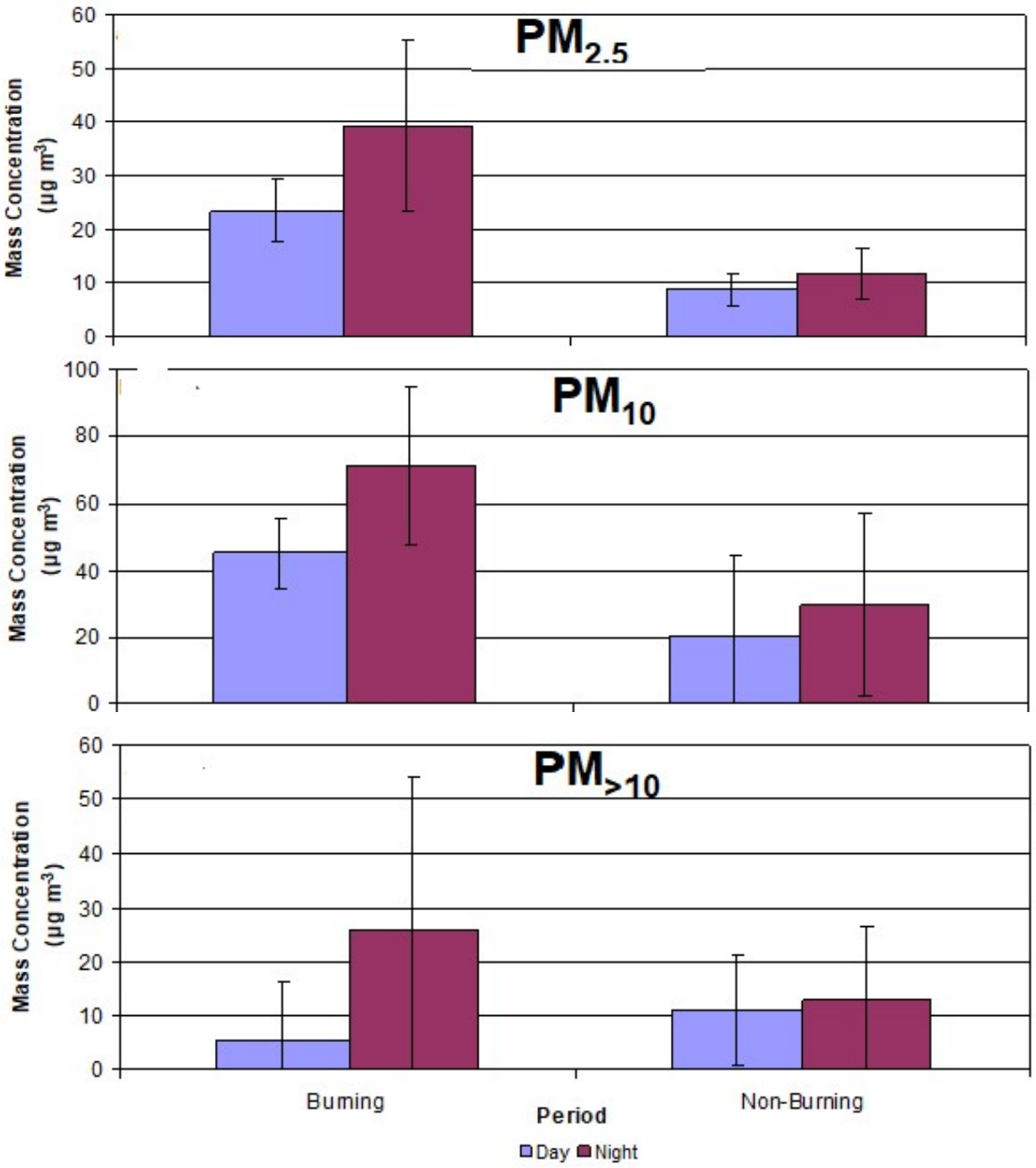
in the past

Influence of Agricultural Biomass Burning on Aerosol Size Distribution and Dry Deposition in Southeastern Brazil

GISELE O. DA ROCHA,† ANDREW G. ALLEN‡ AND ARNALDO A. CARDOSO†

Instituto de Química, Universidade Estadual Paulista (UNESP), CEP 14801-970, Araraquara, SP, Brazil, and School of Geography, Earth and Environmental Sciences, University of Birmingham, Birmingham B15 2TT, U.K.

Environ. Sci. Technol. **2005**, *39*, 5293–5301



Diurnal variation of PM mass concentrations during burning and non-burning periods

ELSEVIER

AE International – Central & South America

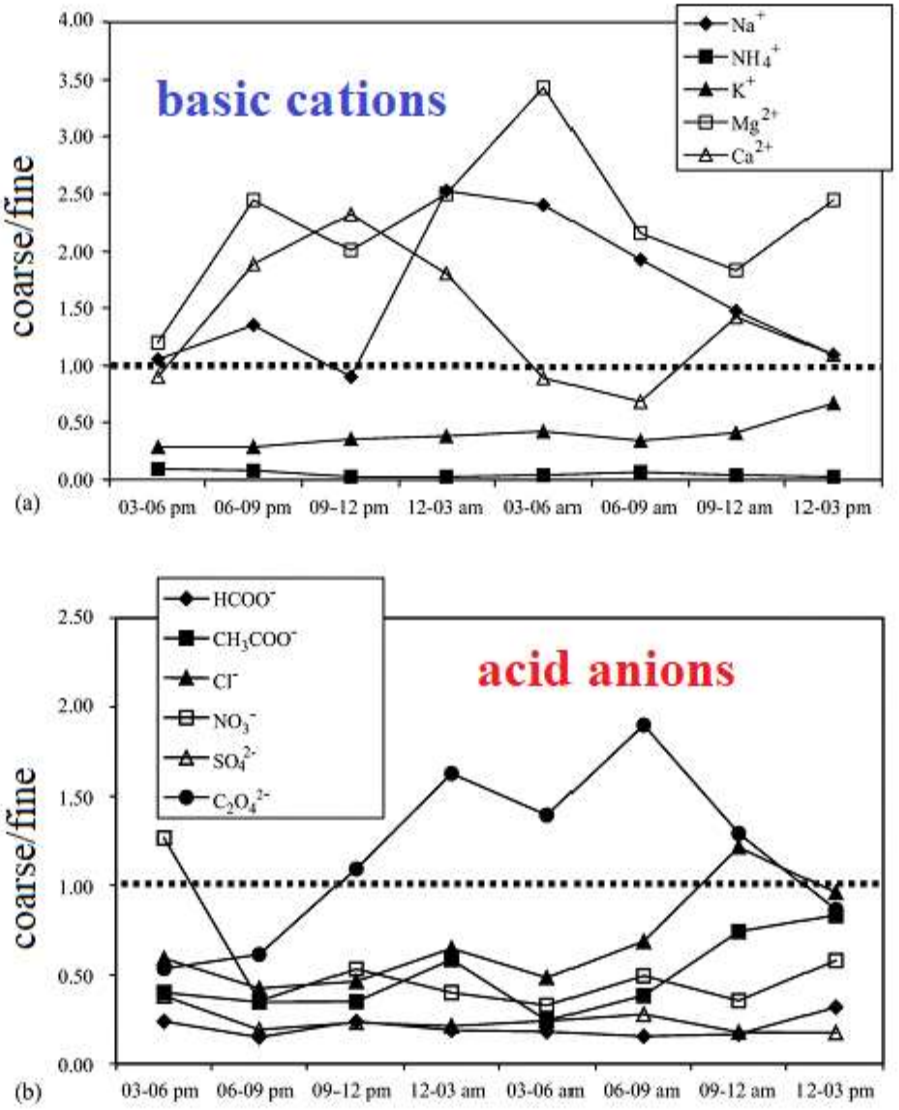
Atmospheric Environment 38 (2004) 5025–5038

ATMOSPHERIC ENVIRONMENT

in the past

Influence of sugar cane burning on aerosol soluble ion composition in Southeastern Brazil

A.G. Allen[a], A.A. Cardoso[b], G.O. da Rocha[b]



Coarse particles: direct emission

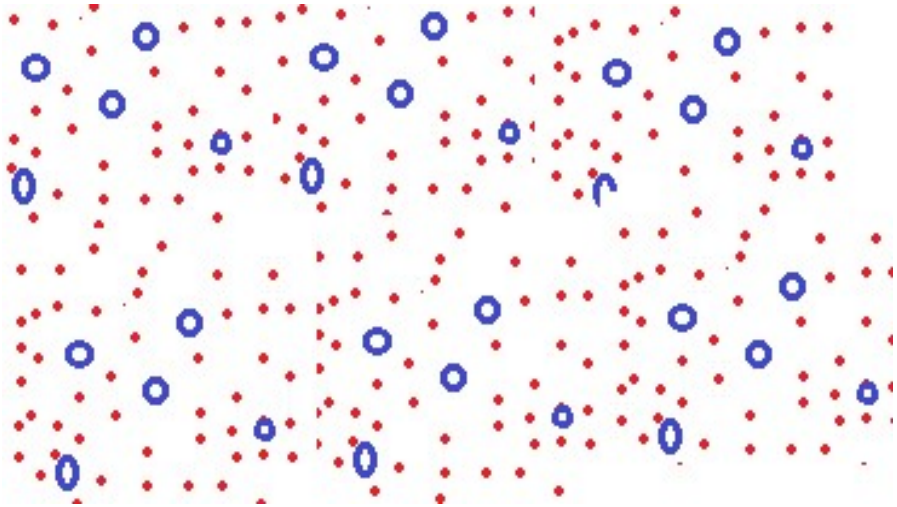
Fine particles: formed in the atmosphere

$NH_{3(gas)} + HNO_{3\ (gas)} \rightarrow NH_4NO_{3\ (solid)}$

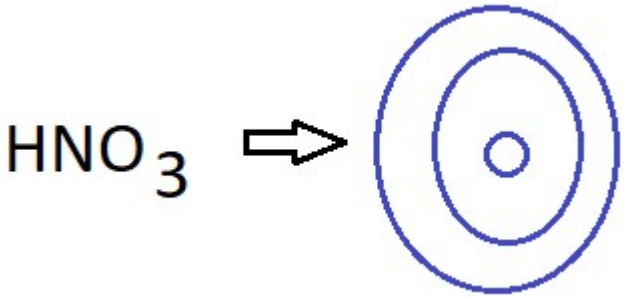
$$SO_2 + H_2O + NH_3 \Rightarrow NH_4HSO_4$$

Distribution of acidic and basic species between coarse and fine particles

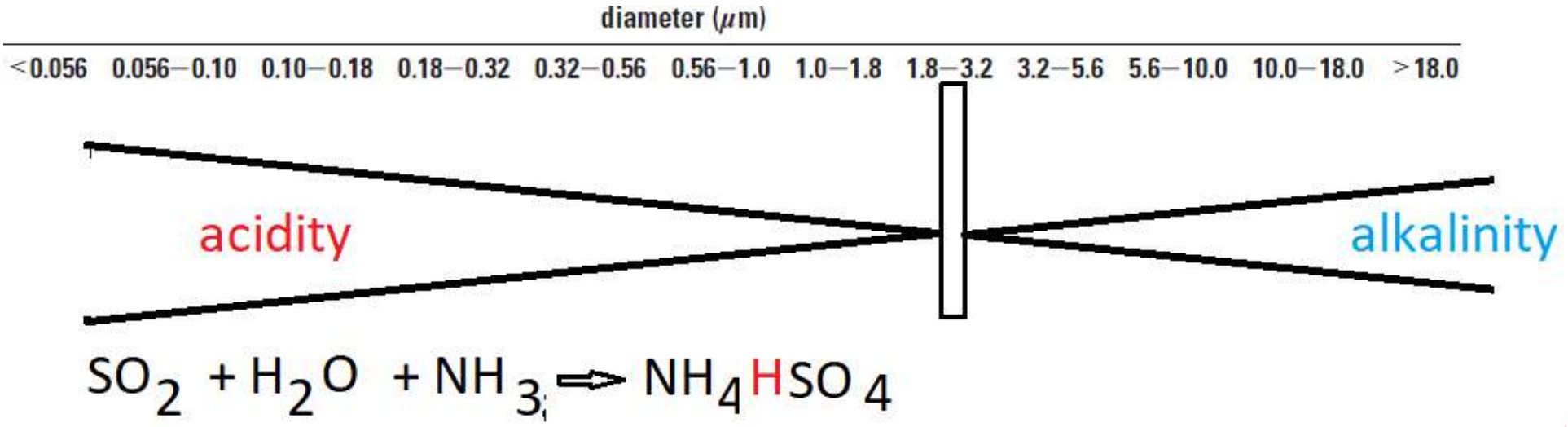
Atmospheric aerosol chemical characteristic



Aerosol



Coarse particles plays an important role in control of atmospheric acidity



Atmospheric Research 183 (2017) 94–103

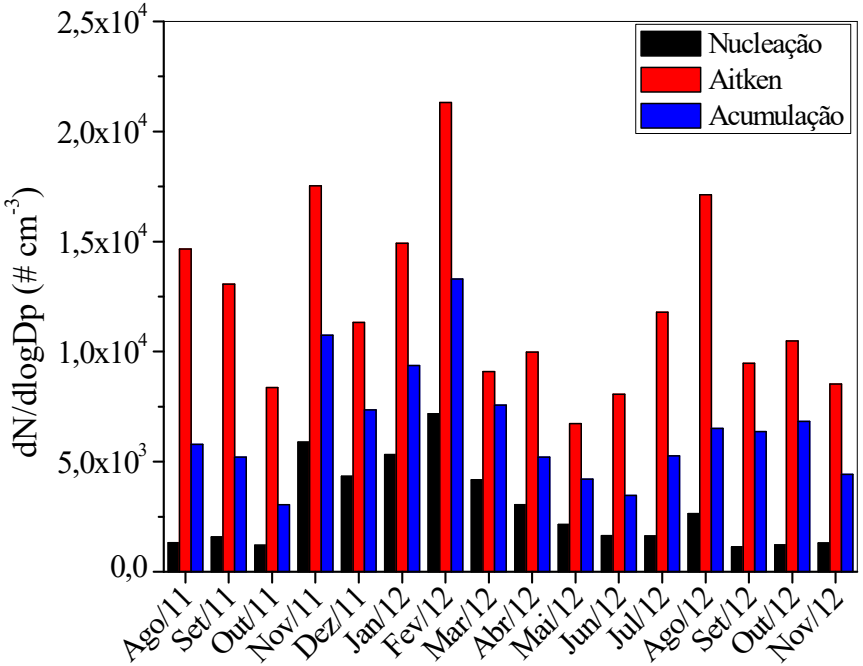
Atmospheric Research

journal homepage: www.elsevier.com/locate/atmosres

Understanding aerosol formation mechanisms in a subtropical atmosphere impacted by biomass burning and agroindustry

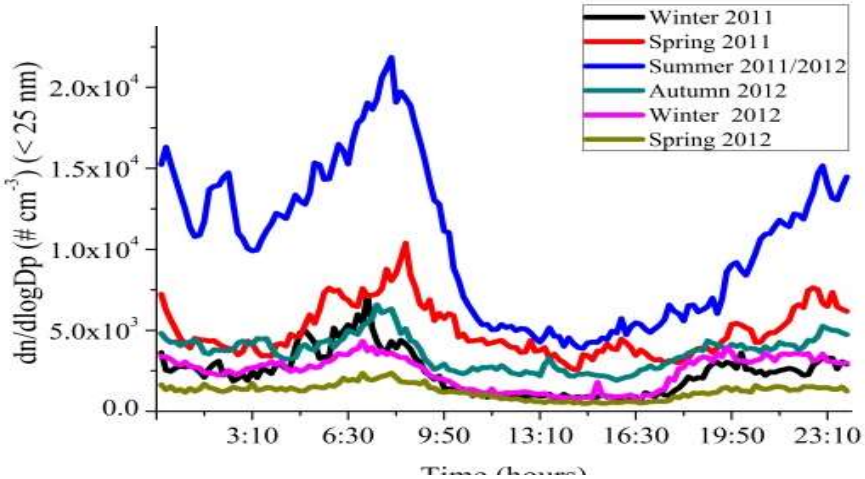
Michele L. Souza, Andrew G. Allen, Arnaldo A. Cardoso *

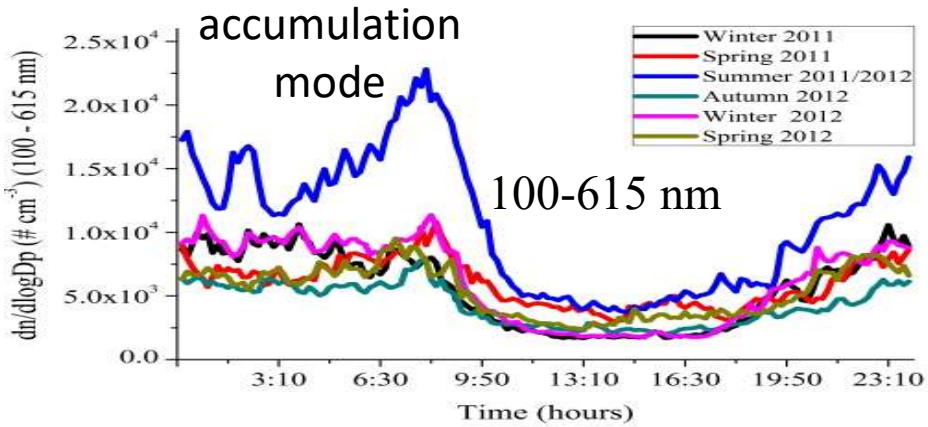
$H_2SO_{4(aq)} + NH_{3(g)} \rightarrow HNH_4SO_{4(aq)}$



Mean aerosol number concentrations in the nucleation, Aitken, and accumulation size ranges period August 2011-November 2012.

<25 nm nucleation mode





Diurnal variation in aerosol number concentrations

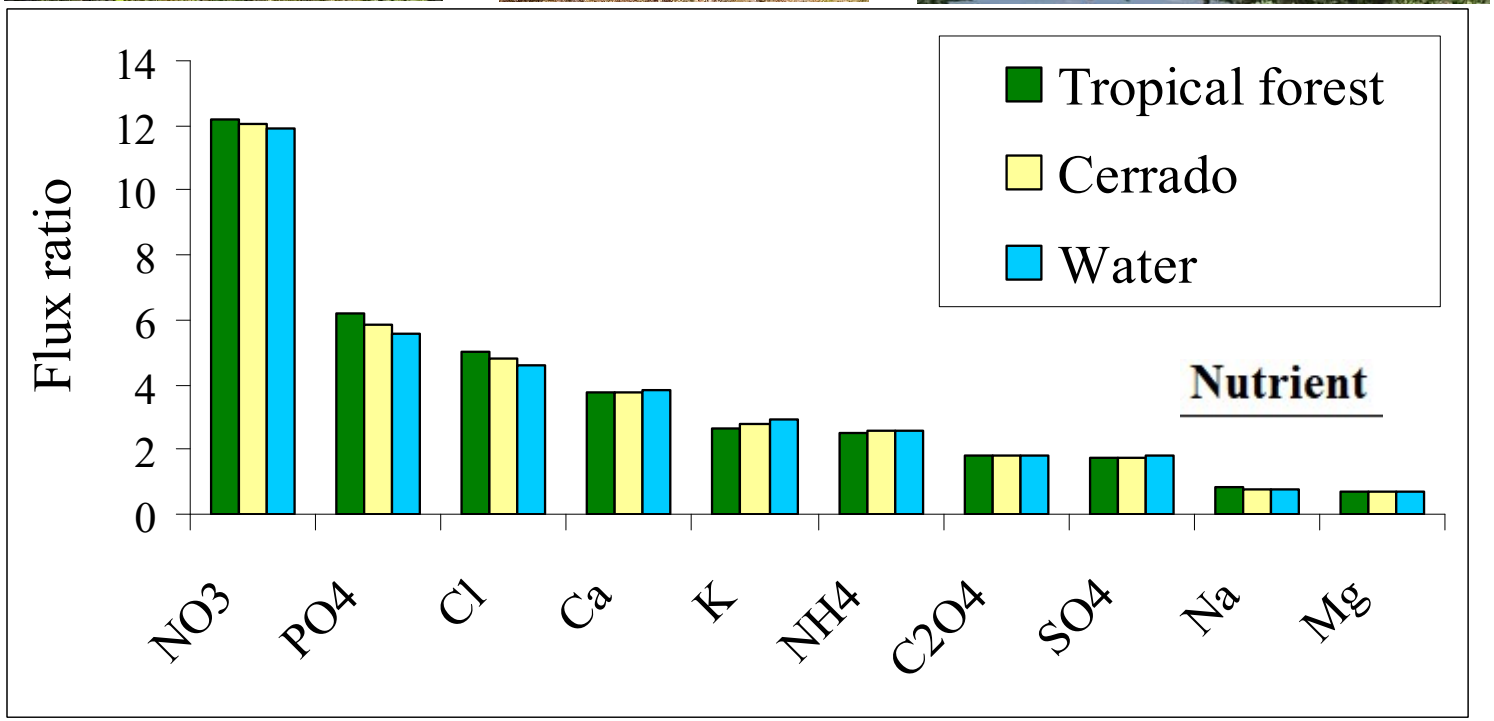
J. Braz. Chem. Soc., Vol. 21, No. 1, 87-97, 2010.
Printed in Brazil - ©2010 Sociedade Brasileira de Química
0103 - 5053 $6.00+0.00

Article

Influence of Intensive Agriculture on Dry Deposition of Aerosol Nutrients

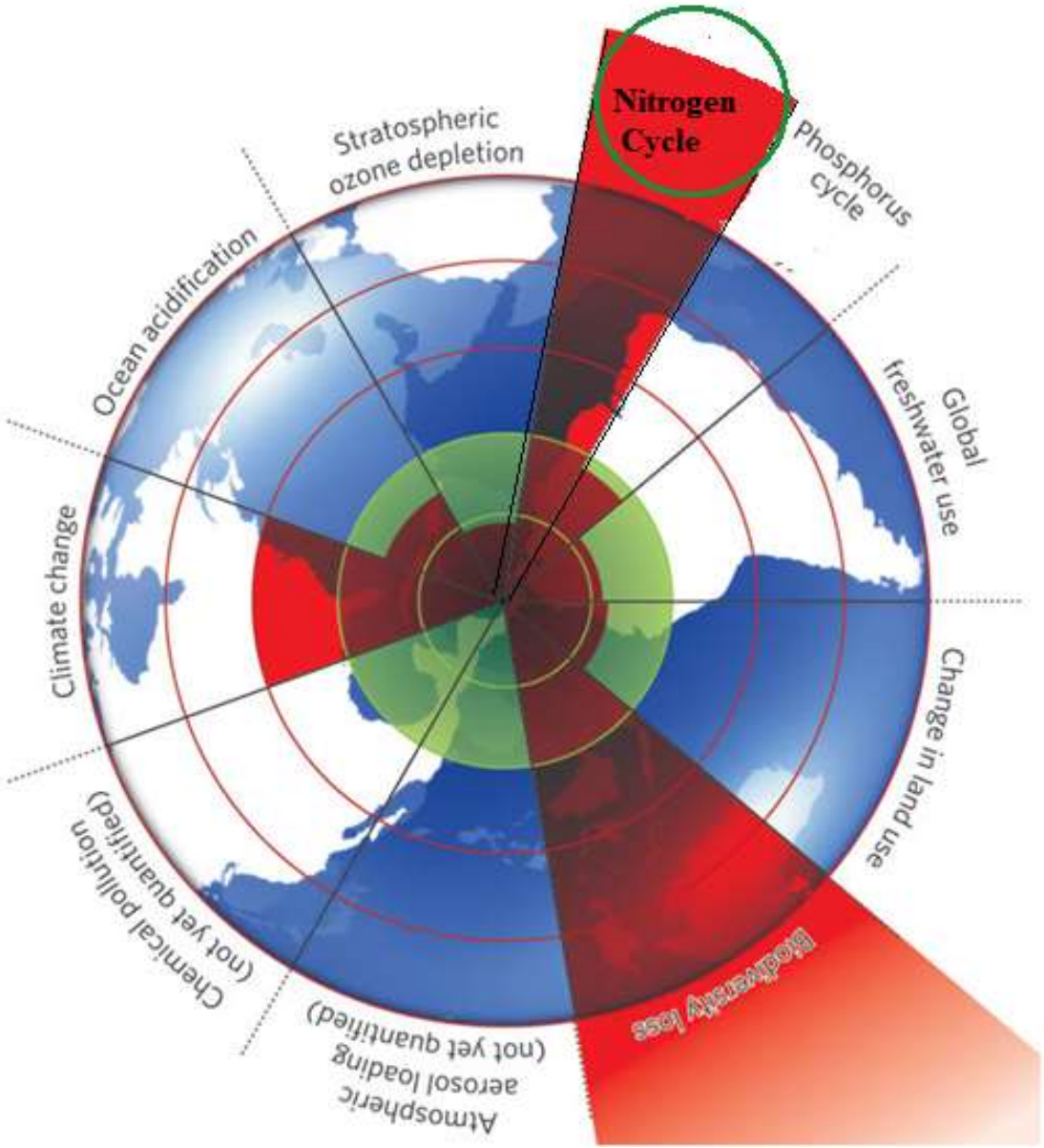
Andrew G. Allen,[,a] Arnaldo A. Cardoso,[a] Antony G. Wiatr,[b] Cristine M. D. Machado,[a] Willian C. Paterlini[a] and Jacob Baker[b]*

in the past



Aerosol Dry Deposition Flux Ratio (Current / Pre-industrial)

A safe operating space for humanity: Planetary boundaries



Nature 461, 472-475, 2009

Environ. Sci. Technol. 2008, 42, 381–385

Atmospheric Emission of Reactive Nitrogen during Biofuel Ethanol Production

CRISTINE M. D. MACHADO, ARNALDO A. CARDOSO,* AND ANDREW G. ALLEN

Environ. Sci. Technol. 2004, 38, 4557–4561

NO_2 Emissions from Agricultural Burning in São Paulo, Brazil

CLIVE OPPENHEIMER,*,† VITCHKO I. TSANEV,† ANDREW G. ALLEN,‡ ANDREW J. S. MCGONIGLE,† ARNALDO A. CARDOSO,§ ANTONY WIATR,‡ WILLIAN PATERLINI,§ AND CRISTINE DE MELLO DIAS§

1. The corresponding emission fluxes are 1.1 Gg NH_3-N yr^{-1}, 0.2 Gg NO_3^--N yr^{-1} and 1.2 Gg NH_4^+-Nyr^{-1}. The total current combined emission of the measured gas phase and particulate species is then ~57 Gg N yr^{-1} (57 x 10^3 ton N yr^{-1})

2. Around 225 x 10^3 ton N yr^{-1} (225 Gg N yr^{-1}) are applied as fertilizer to a total planted area. The quantity of nitrogen released to the atmosphere during burning is equivalent to ~35 % of the annual fertilizer-N application to the plantations.

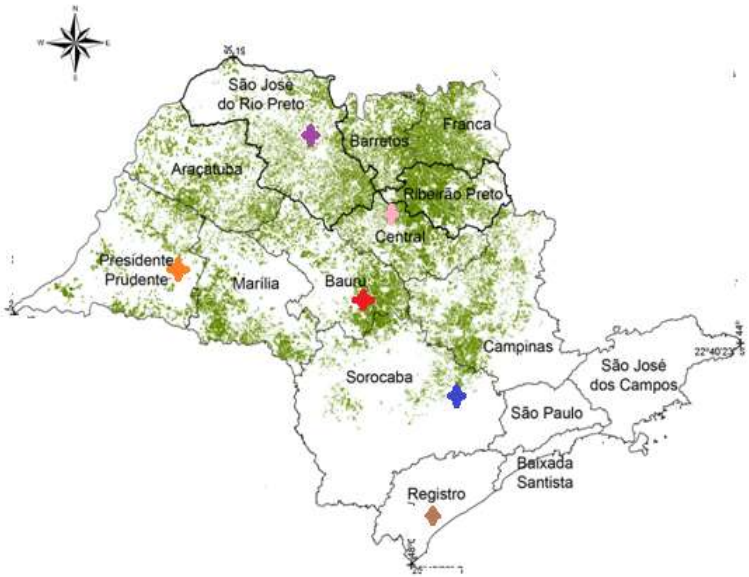
Environmental Pollution 159 (2011) 1190–1197

Environmental Pollution

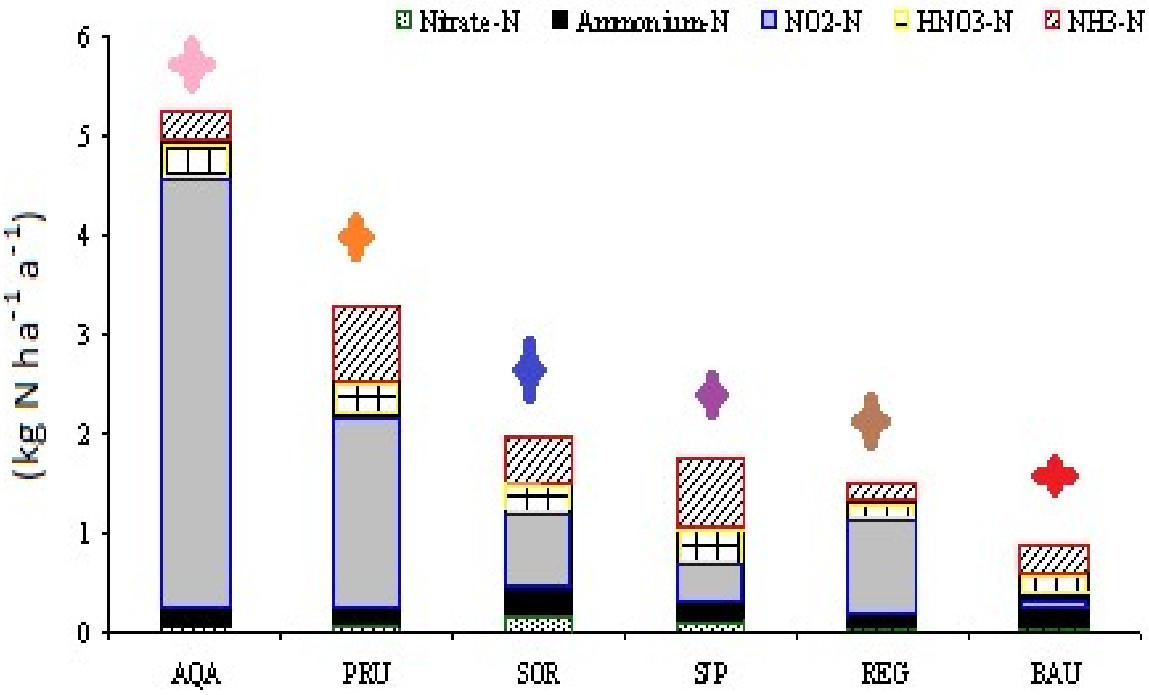
journal homepage: www.elsevier.com/locate/envpol

Measurements and modeling of reactive nitrogen deposition in southeast Brazil

A.G. Allen [a], C.M.D. Machado [b], A.A. Cardoso [a]



Map of São Paulo State showing locations of sampling stations.



Annual deposition fluxes to forest (kg N ha^{-1} a^{-1}) NO_2-N, HNO_3-N, NH_3-N, NO_3^--N and NH_4^+-N at six sites in São Paulo State (2008–2009)

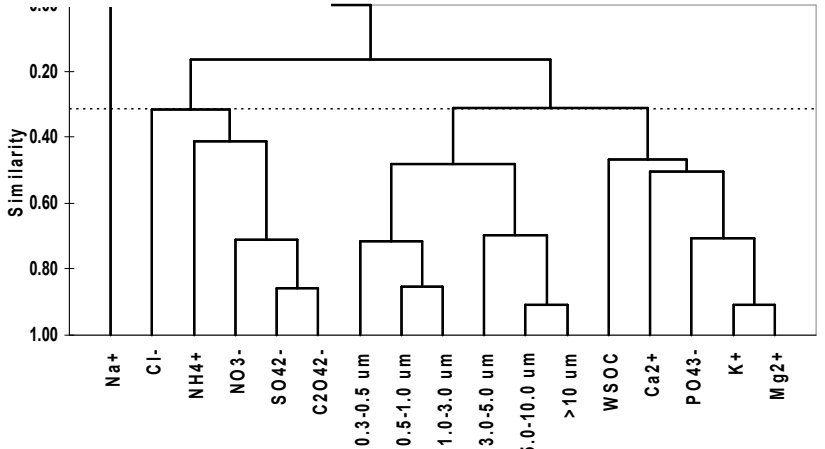
JOURNAL OF GEOPHYSICAL RESEARCH: ATMOSPHERES, VOL. 118, 1–13, doi:10.1002/jgrd.50630, 2013

An analysis of diurnal cycles in the mass of ambient aerosols derived from biomass burning and agro-industry

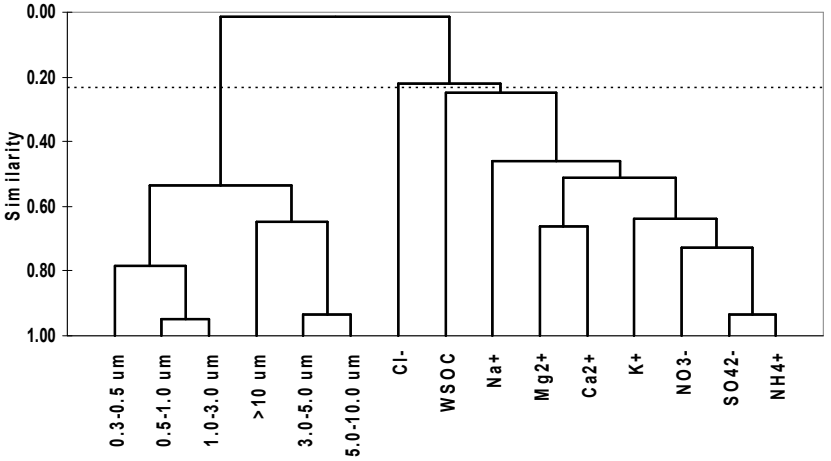
L. Caetano-Silva,[1] A. G. Allen,[1] M. Lima-Souza,[1] A. A. Cardoso,[1]
M. L. A. M. Campos,[2] and R. F. P. Nogueira[1]

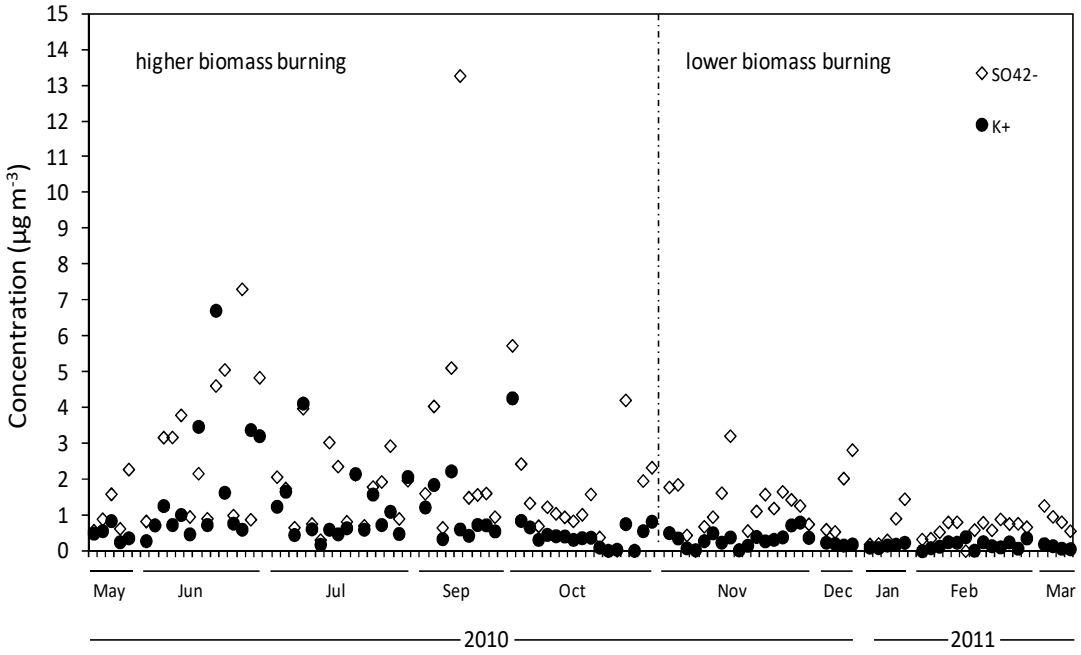
Pearson correlation coefficient

Winter (n=48)



summer (n=56).





Concentrations of sulfate and potassium in total suspended particulates (TSP) between 13 May 2010 and 15 March 2011

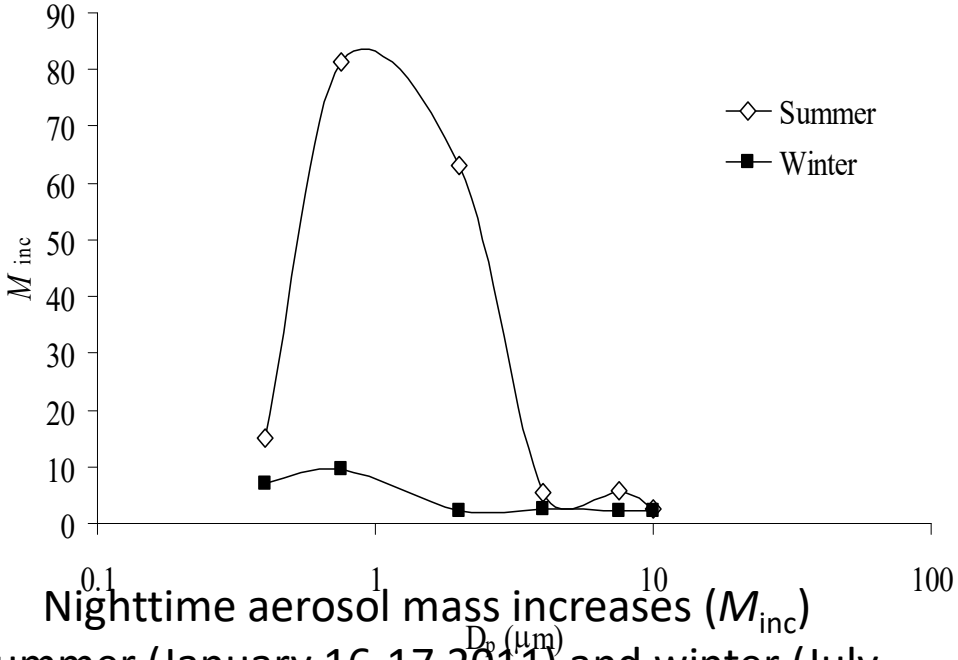
Dendrograms: agglomerative hierarchical clustering (AHC) to aerosol mass concentrations (six size bins) and chemical components

JOURNAL OF GEOPHYSICAL RESEARCH: ATMOSPHERES, VOL. 118, 1–13, doi:10.1002/jgrd.50630, 2013

An analysis of diurnal cycles in the mass of ambient aerosols derived from biomass burning and agro-industry

L. Caetano-Silva,[1] A. G. Allen,[1] M. Lima-Souza,[1] A. A. Cardoso,[1]
M. L. A. M. Campos,[2] and R. F. P. Nogueira[1]

The aerosol composition can affect the hydrological cycle by suppressing precipitation.



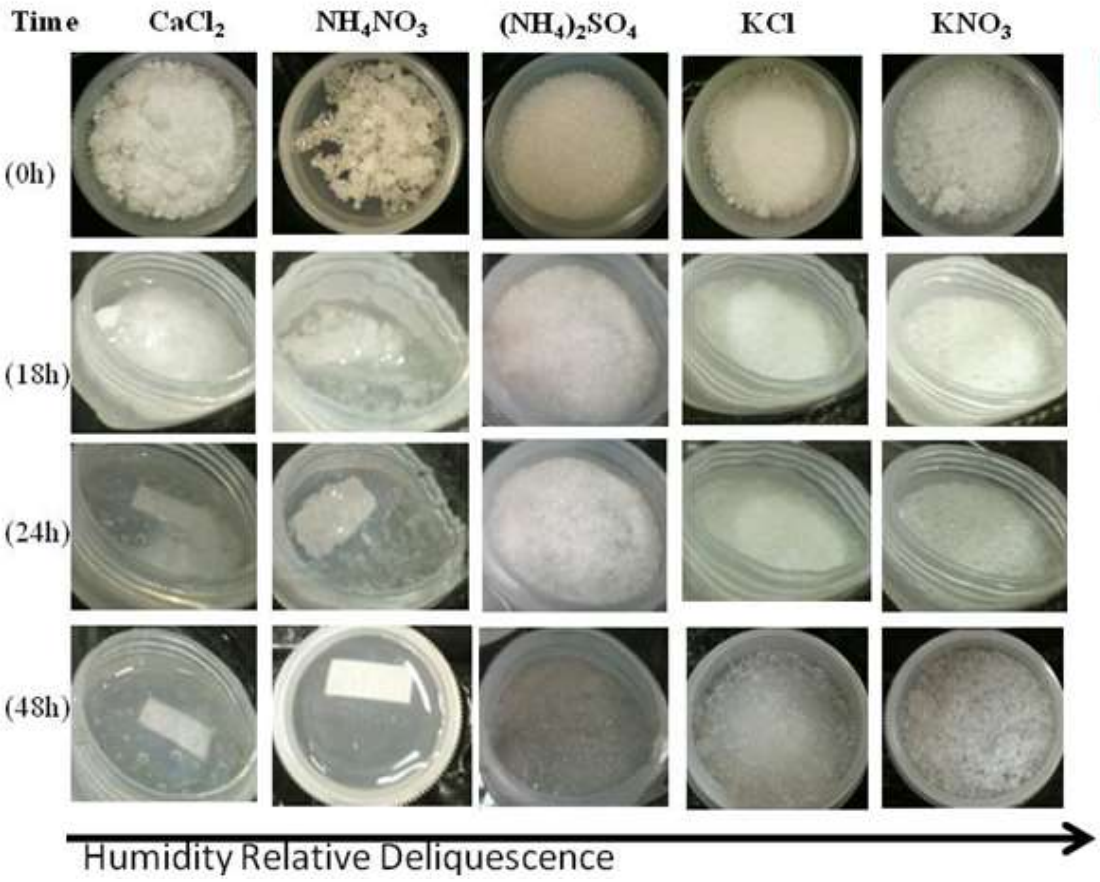
Nighttime aerosol mass increases (M_{inc}) summer (January 16-17 2011) and winter (July 4-5 2010), according to particle diameter (D_p).

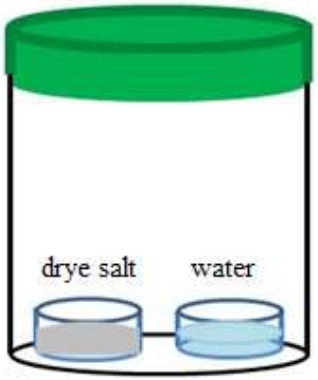
JOURNAL OF CHEMICAL EDUCATION
Activity
pubs.acs.org/jchemeduc

Journal of Chemical Education 92 (4), 672-677 (2014)

"Will It Rain?" Activities Investigating Aerosol Hygroscopicity and Deliquescence

L. Caetano-Silva,*[,†] A. G. Allen,[†] M. L. A. M. Campos,[‡] and A. A. Cardoso[†]





Schematic illustration (left) and photograph (right) of the arrangement used in the experiments employing different salts.

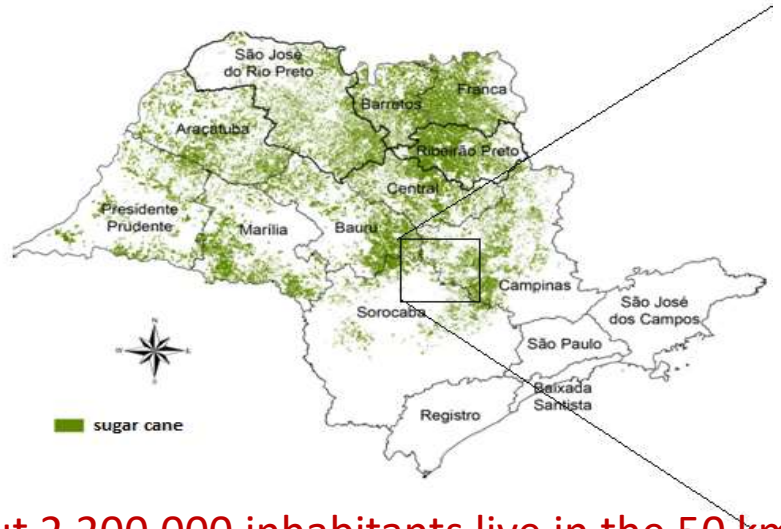
Photographs of the salts studied, immediately prior to insertion in the glass flasks containing water, and then at intervals up to 48 h.

Research Article

Environmental and Molecular Mutagenesis 57:41–50 (2016)

Mutagenicity Profile of Atmospheric Particulate Matter in a Small Urban Center Subjected to Airborne Emission From Vehicle Traffic and Sugar Cane Burning

Debora Kristina M. Alves,[1] Fábio Kummrow,[2] Arnaldo A. Cardoso,[3] Daniel A. Morales,[4] and Gisela A. Umbuzeiro[1,4*]



About 2,200,000 inhabitants live in the 50 km radius of the sampling point

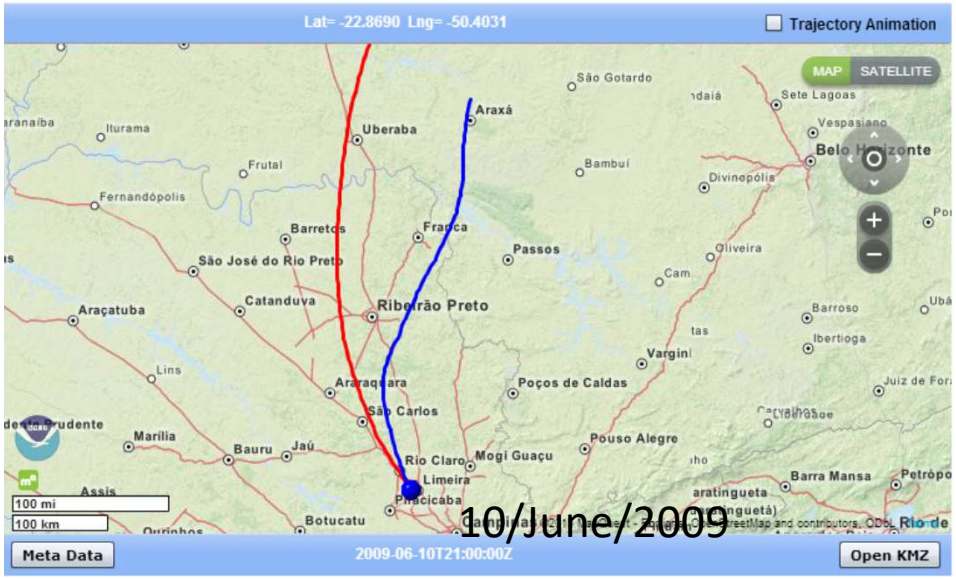
Collection date, number of fire foci in São Paulo State and concentration of each PM sample.

Sample	Number of fire foci**	Date	µg PM*/ m³
1	14	07/May/2009	164.8
2	40	10/May/2009	129.1
3	30	18/May/2009	136.6
4	4	27/May/2009	129.3
5	33	10/June/2009	145.6
6	27	18/June/2009	77.4

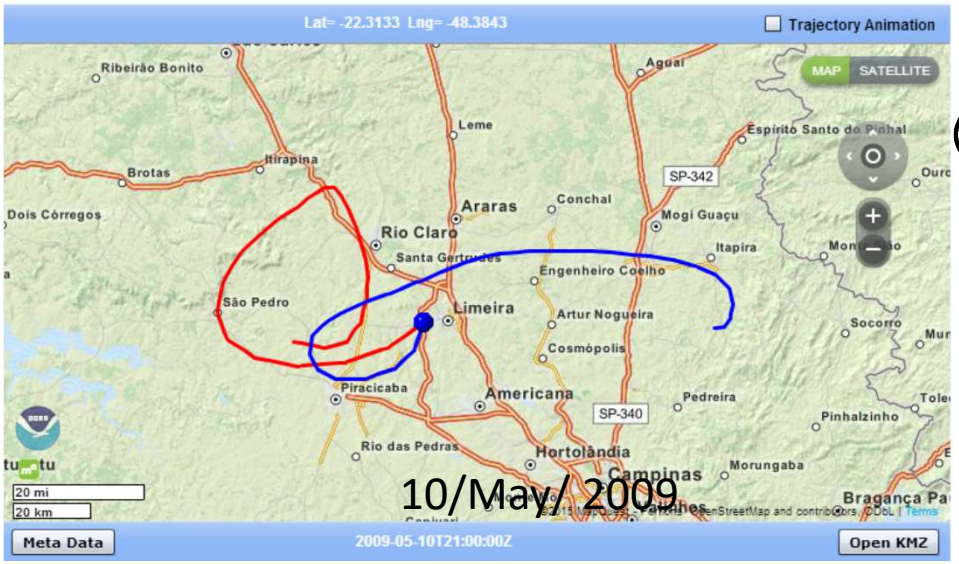
*PM: particulate matter; **Fire focus: number of burning sites per day

Organic extracts were assayed in the *Salmonella*/microsome microsuspension mutagenicity assay using TA98, YG1041, and TA1538, with and without metabolic activation (S9).

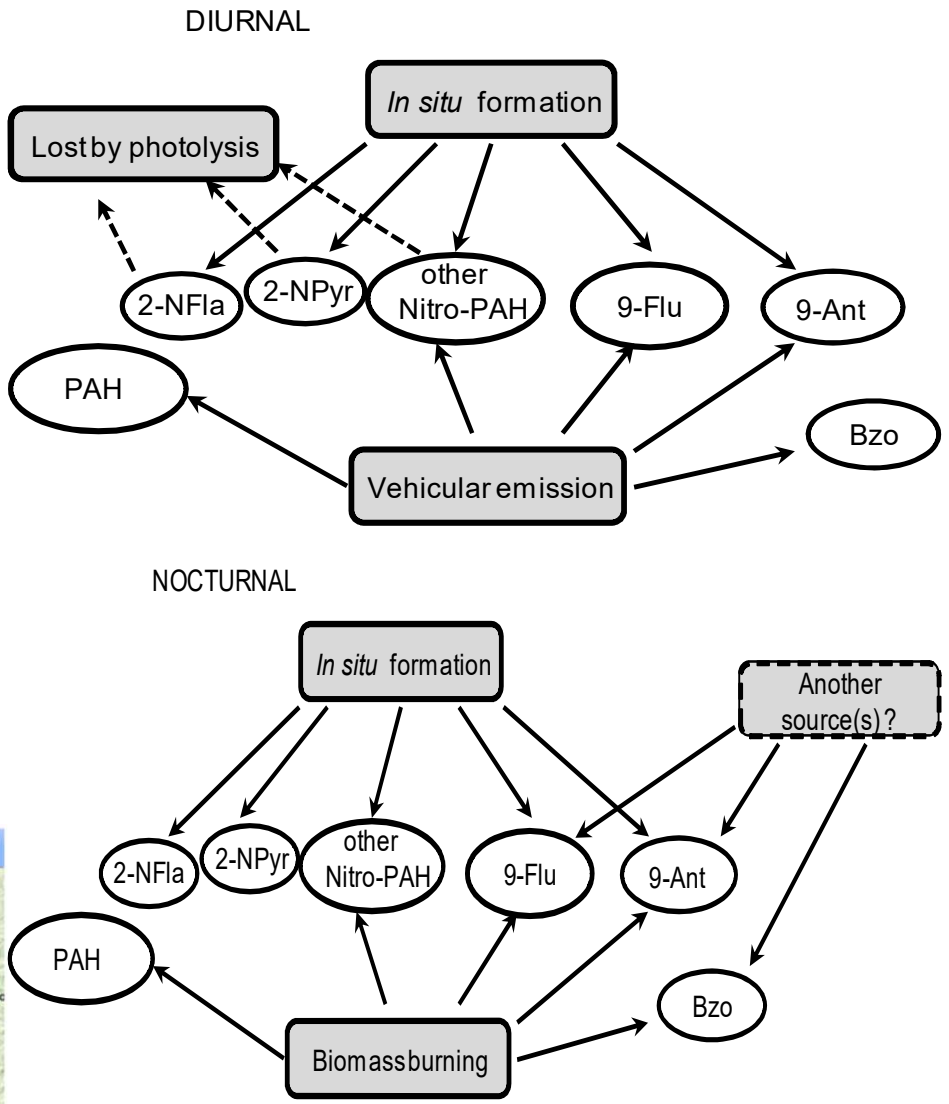
The 24 h back-trajectories arrived at a height of **100 m (blue line) and 500 m above the ground (red line),** over the sampling site.



10/June/2009



10/May/ 2009



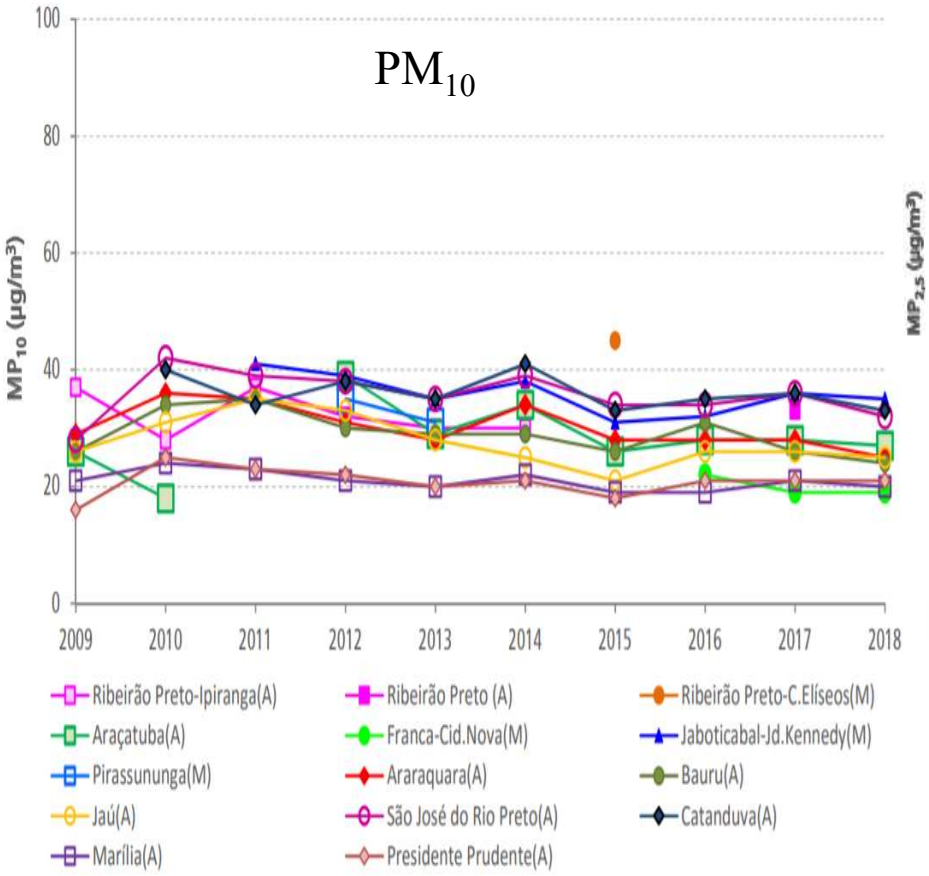
Schematic proposal for the main sources of PAHs; nitro- and oxy- derivatives aerosols during daytime and nighttime.

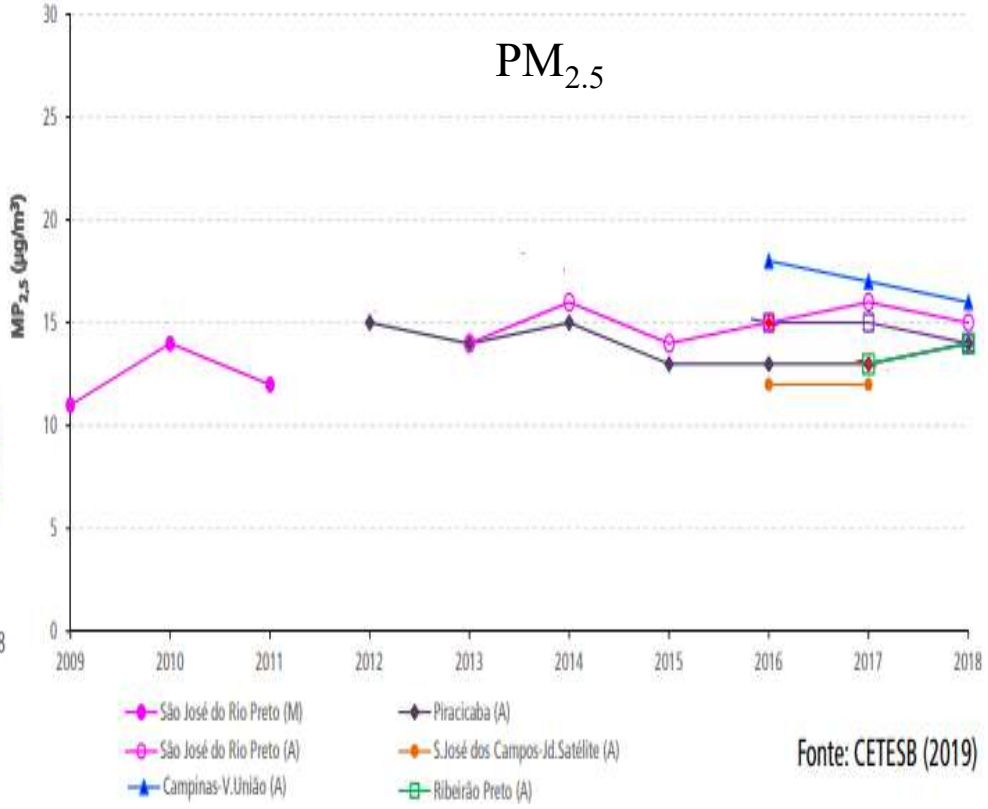
The legislation (State Law no. 11.241/02) requires cessation of sugar cane burning

In 2018: mechanized harvesting was used on 90% of the sugarcane.
This type of harvest does not use previous sugarcane burning.

What changed in air quality in 2019?

What changed in air quality in 2019?
Aerosol concentrations ?



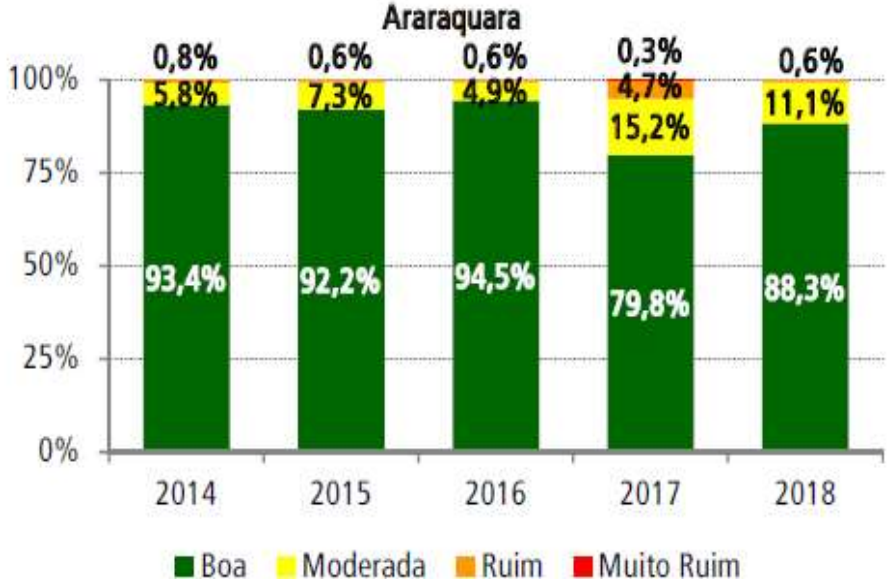


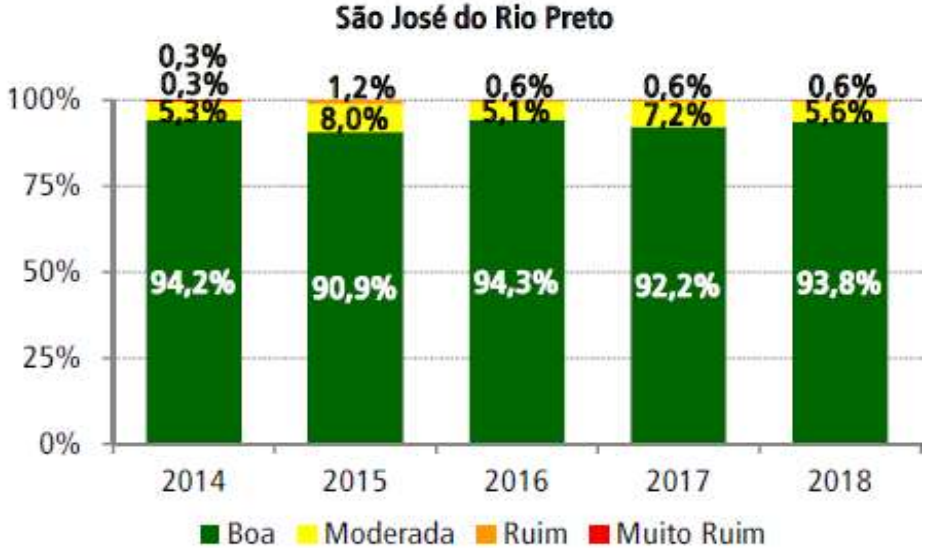
MP_{10} average annual aerosol concentrations (2009 to 2018) in sugarcane production areas

$MP_{2,5}$ average annual aerosol concentration (2009 to 2018) in sugarcane production areas

CETESB : São Paulo State Environmental Protection Agency (report 2019)

What changed in air quality in 2019?
Ozone concentrations ?





O_3 - distribution of air quality (%)

CETESB : São Paulo State Environmental Protection Agency (report 2018)

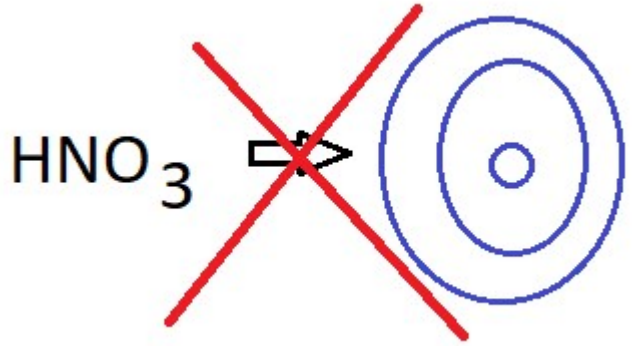
Winter raises risk of respiratory disease

Araraquara

Local Newspaper; 20 September 2019

Other sources of gas and particulate emissions?
Which are? What is the amount of emission of gases and particles to the atmosphere?

Data from the Decennial Energy Expansion Plan (PDE 2024) indicate that the annual energy generation potential for sugarcane biomass can reach two Itaipu-equivalent hydroelectric plants, generating 165 TWh / year by 2024.



Coarse particles plays an important role in control of atmospheric acidity

I hope to answer these questions in the near future!

Acknowledgements

To all the collaborators and students who helped in the development of the all projects.

Merci beaucoup

FAPESP
FUNDAÇÃO DE AMPARO À PESQUISA DO ESTADO DE SÃO PAULO

Grant number: 05/53001-8
Grant number: 08/58073-5
Grant number: 09/16198-9

CNPq
Conselho Nacional de Desenvolvimento Científico e Tecnológico

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