Chemical composition and source apportionment for particulate matter in São Paulo, Brazil

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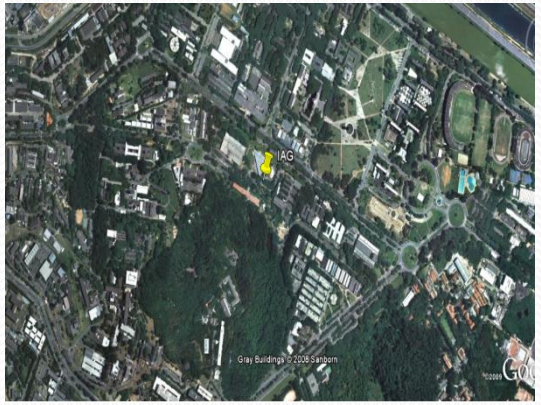
GEQAt - Grupo de Estudos em Química Atmosférica

São Paulo Site

- **São Paulo Metropolitan Area:**
- ~ 20 million inhabitants
- ~ 8 million vehicles in the city
- Atlantic Ocean
- ~ 7000 Industries
- Fuel diversity

- **Campus sampling (IAG/USP):**
- Green area
- Expressway
- Extensive campaigns ($PM_{2.5}$ and PM_{10}) over a a whole year (2014) – $Ext_{2.5}$ and Ext_{10}.
- Intensive campaign ($PM_{2.5}$) in dry season (July) – $Int_{2.5}$.

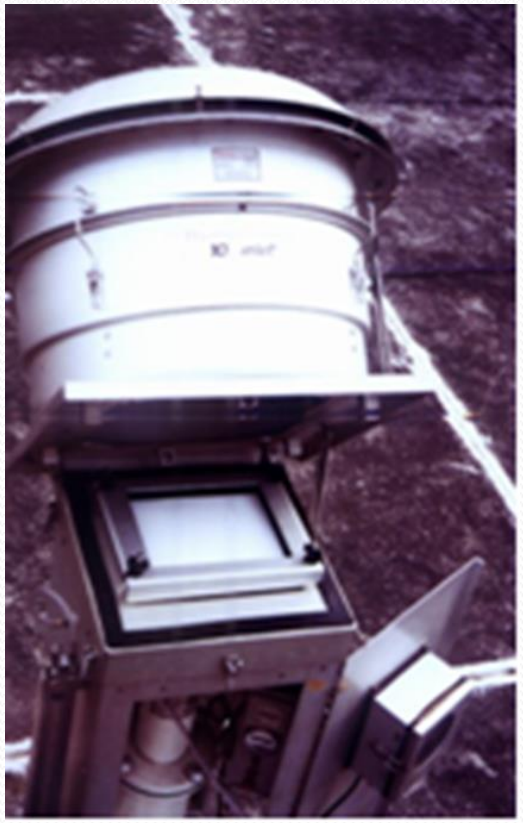
SP - Satellite



IAG – USP

Source : EMBRAPA, DENATRAN

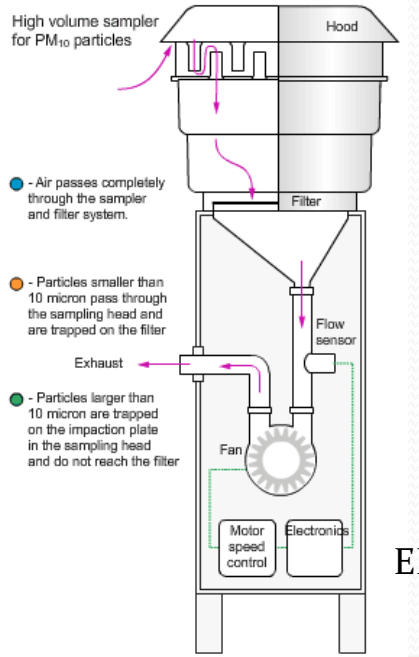
Sampling



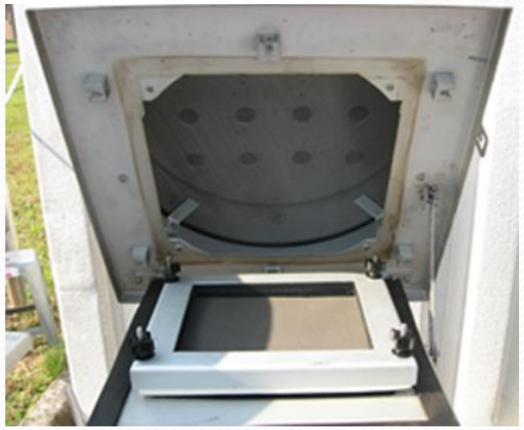
Quartz fiber filters (20 x 25 cm)

Flux of 1.13 m^3 min^{-1}

24 hrs



EPA.gov



Experimental – Carbonaceous species

- **OC and EC**
- University of Aveiro
- Thermal-optical analysis.

Experimental – Monosaccharides

Finnish Meteorological Institute

PUNCH 1 cm x 1 cm

Dissolution in deionized water

10 min

Determination in HPAEC

Levoglucosan, mannosan and galactosan

High Performance Anionic Exchange Chromatography with Mass Spectrometry

Experimental – Water soluble ions

Finnish Meteorological Institute

PUNCH 1x1 cm

Dissolution in deionized water

10 min

Determination in IC

IC – 2000

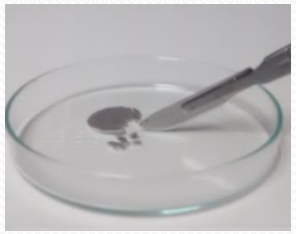
Water soluble ions

Cl^-; NO_3^-; SO_4^{2-}; MSA^-; Ox^-; Na^+; NH_4^+ e K^+

Ion Chromatography.

Experimental – PAH and derivatives

Federal Universty of Bahia



- **Miniaturized ultrasonic extraction for PAH**
- Ultrasonic bath (ACN/DCM),
- PAH, oxy- and nitro-PAH - Analysis in GC/MS.

Gomes et al. 2016.

Statistical treatment

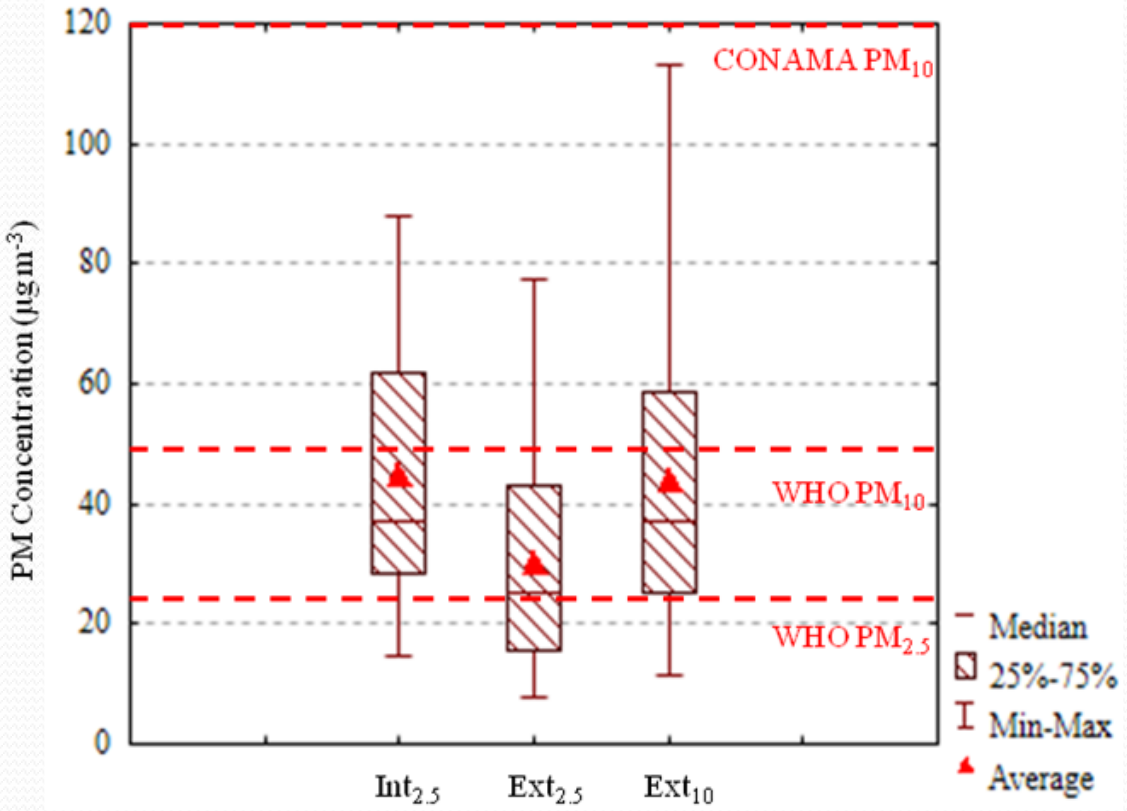
- **Source apportionment with PMF – positive matrix factorization**
- All samples were considered (*n* = 78).

- 11 *strong* species (SO_4^{2-}, nss-K^+, Mg, Cr, Mn, Fe, Ni, Cd, Pb, OC and EC).

- 6 *weak* species (Lev, Man, NO_3^-, NH_4^+, Ca and Cu).

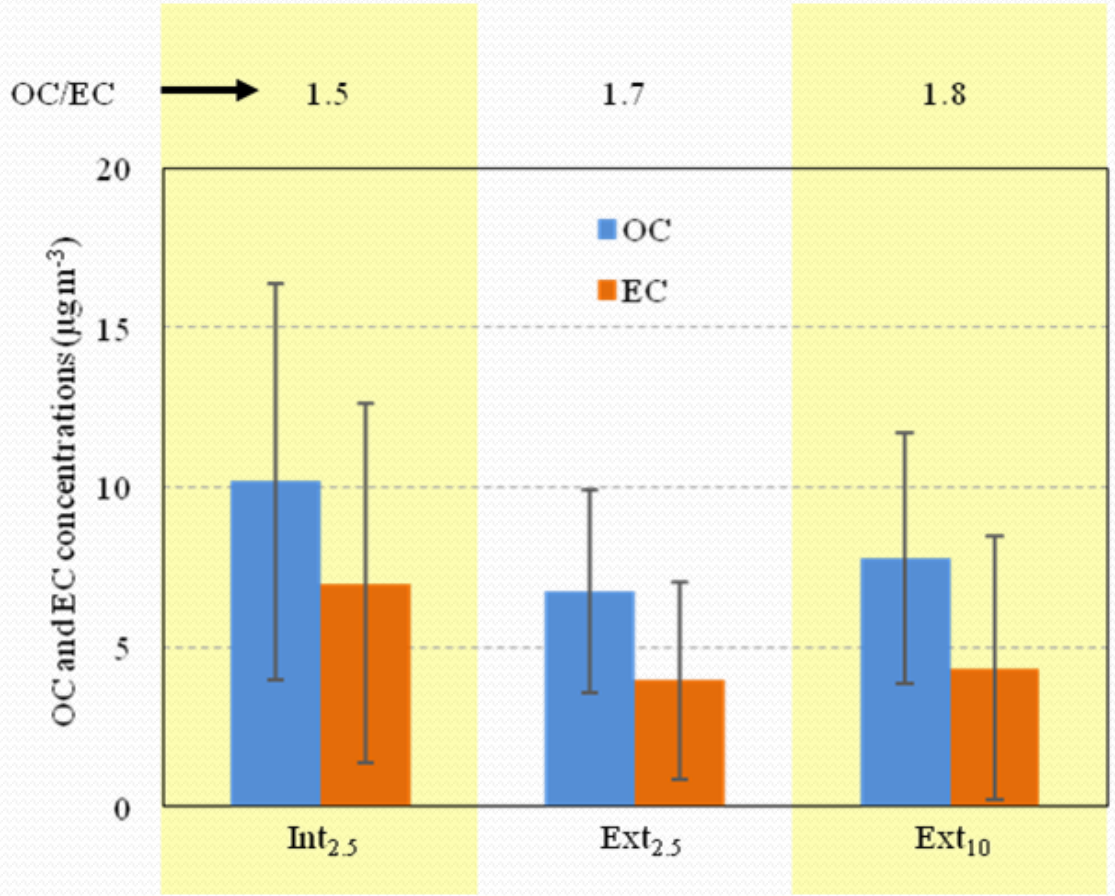
Results and discussion

- **PM concentrations**
- Above WHO guidelines:
- 90 % of the samples in $Int_{2.5}$,
- 50 % in $Ext_{2.5}$ and
- 30 % in Ext_{10}.
- PM concentrations – $Int_{2.5} > Ext_{2.5}$.



Results and discussion

- **OC and EC - $Int_{2.5}$ > $Ext_{2.5}$**
- OC/EC < 1 – *Fresh traffic emissions (Pio et al., 2011).*
- 1.8 < OC/EC < 3.7 – *Urban background sites (Amato et al. 2016).*
- OC/EC in this study – Vehicle emissions with contribution of secondary organic aerosols.



Results and discussion

- **PAHs – $Int_{2.5}$ > $Ext_{2.5}$**
- BaPE -WHO *Values > 1.0 ng m^{-3} cancer risk.*
- BaPE – $Int_{2.5}$ > $Ext_{2.5}$
- BbF – Most abundant PAH – LDV tunnels (Brito et al., 2013).
- Cor – Correlations with Cu and Pb (R > 0.7).
- 2-NFlu - nitro-PAH - highest conc.
- *1-*
- 9,

BaA/Chr and InP/(InP+BPe) – LDV impacted tunnel (Brito et al. 2013).

BPe/BaP ~ 1 –Brazilian LDV exhaust (1.13) (de Abrantes et al., 2004)

	$Int_{2.5}$	$Ext_{2.5}$	Ext_{10}
Total PAHs	23 (6–49)	18.4 (3–62)	24 (5–115)
BaPE	3.4 (0.6–8.0)	2.4 (0.3–10)	3.4 (0.5–18)
ΣLMW/ΣHMW	0.32	0.41	0.43
Flt/(Flt+Pyr)	0.5	0.5	0.5
BaA/Chr	0.5	0.6	0.5
InP/(InP+BPe)	0.5	0.5	0.5
BaP/(BaP+BeP)	0.4	0.4	0.4
BPe/BaP	1	1	1

BaPE = (BaA×0.06) + (BbF×0.07) + BkF×0.07 + BaP×1 +DBA×0.6 + InP×0.08 – Yassa et al., 2001.

Results and discussion

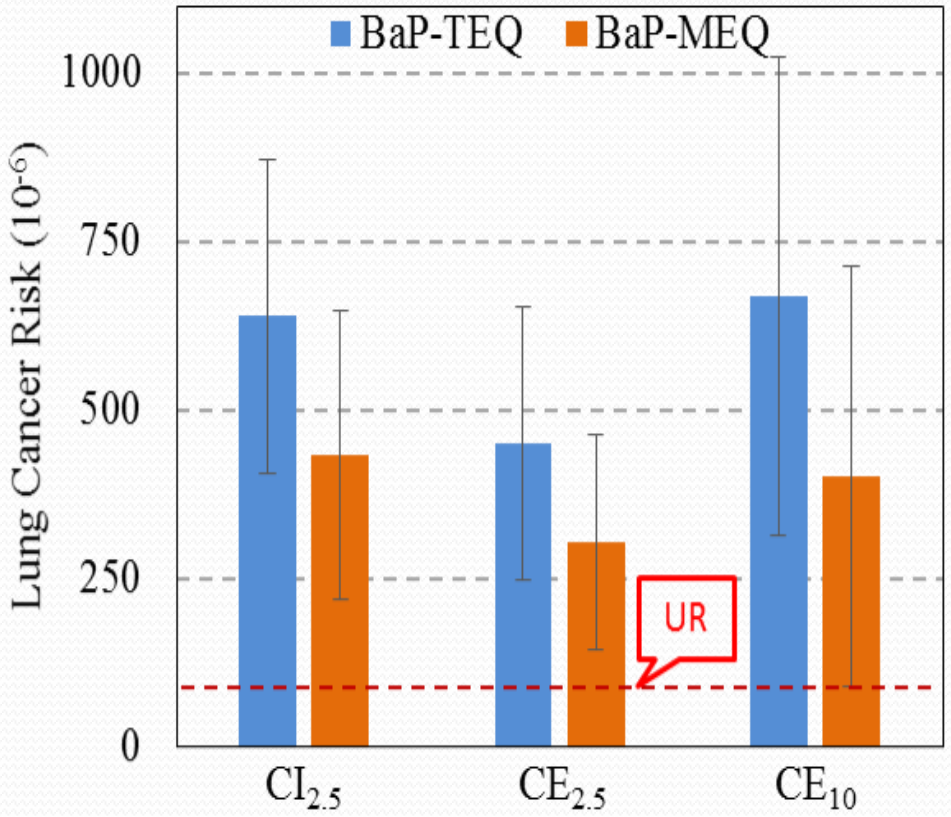
- **Lung Cancer Risk**

- **$Int_{2.5}$ > $Ext_{2.5}$**
- *Higher LCR levels than in Amazon during dry season*

(de Oliveira Alves et al., 2015),

- *in urban areas - New York and Madrid*

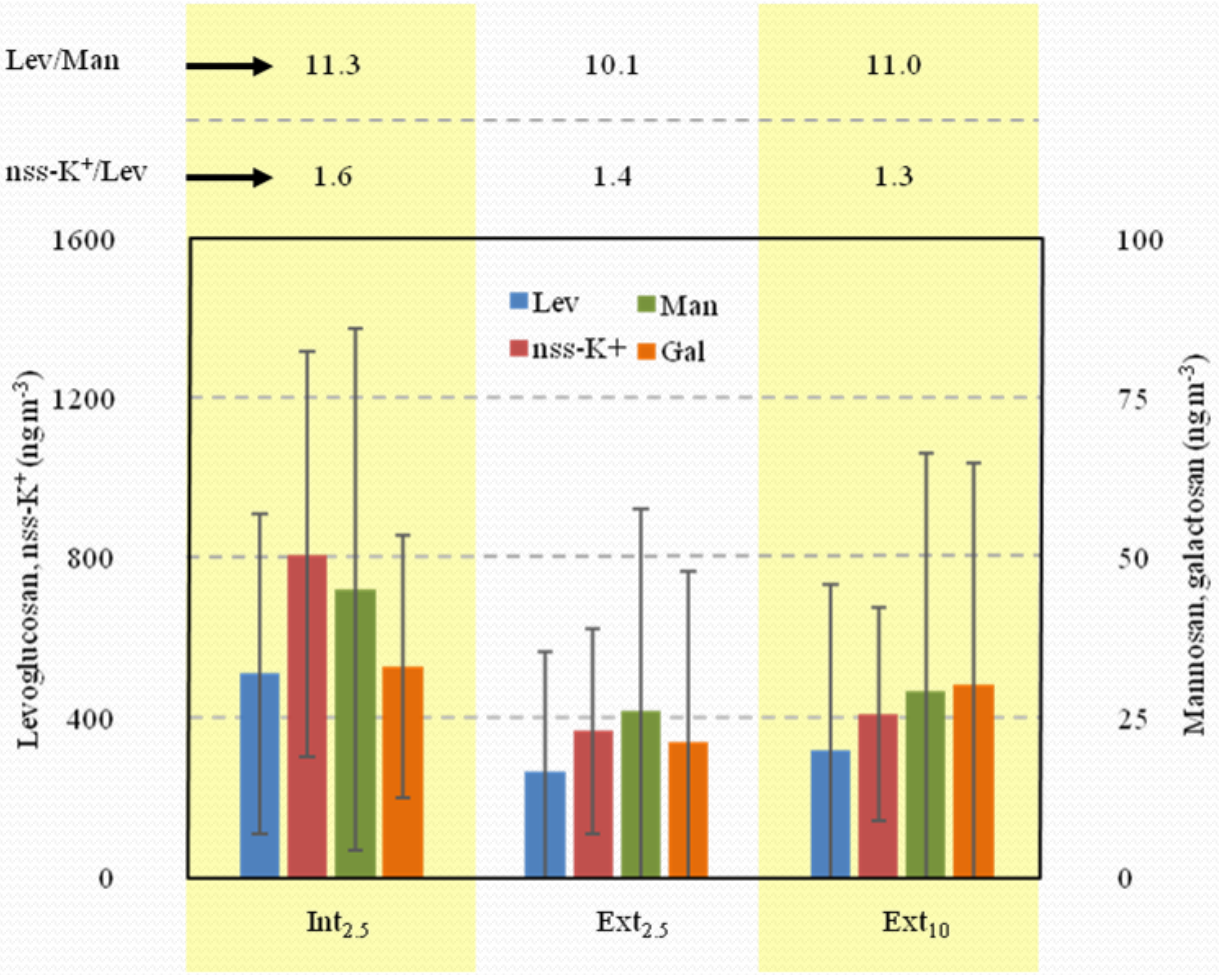
(Jung et al., 2010; Mirante et al., 2013).



The lifetime lung cancer risk (LCR) from exposure to atmospheric PAH was estimated by multiplying BaP-TEQ and BaP-MEQ by the unit risk for exposure to BaP established by WHO (De Oliveira Alves et al., 2015; WHO, 2000) (Figure 7). WHO guideline (87×10^{-6} ng m^{-3}).

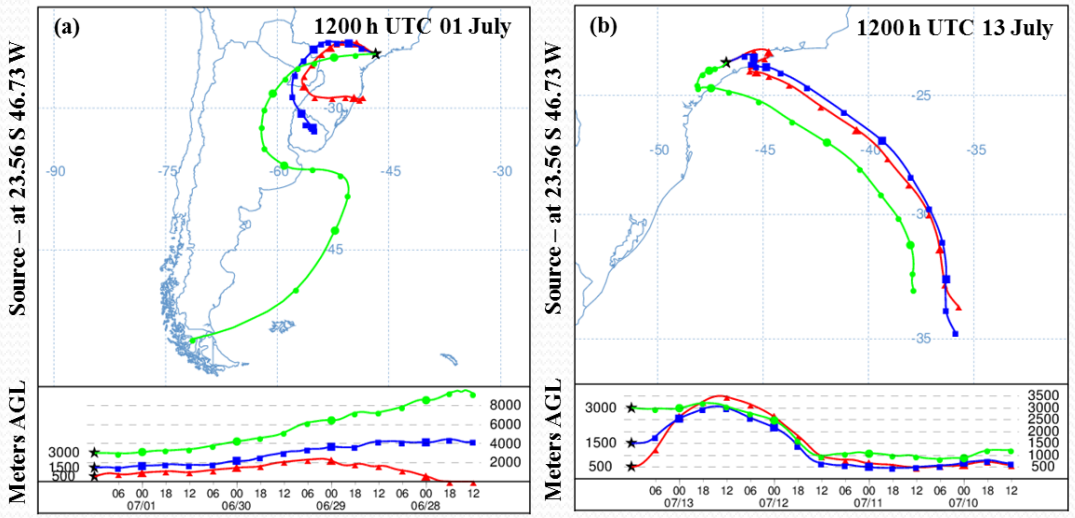
Results and discussion

- **Biomass burning tracers**
- **$Int_{2.5}$ > $Ext_{2.5}$**
- Lev/Man – Sugarcane burning chamber studies in Florida (Lev/Man = 10) (Hall et al., 2012).
- Nss-K^+/Lev – Combination of smouldering and flaming processes (Kundu et al., 2010; Pereira et al., 2017).



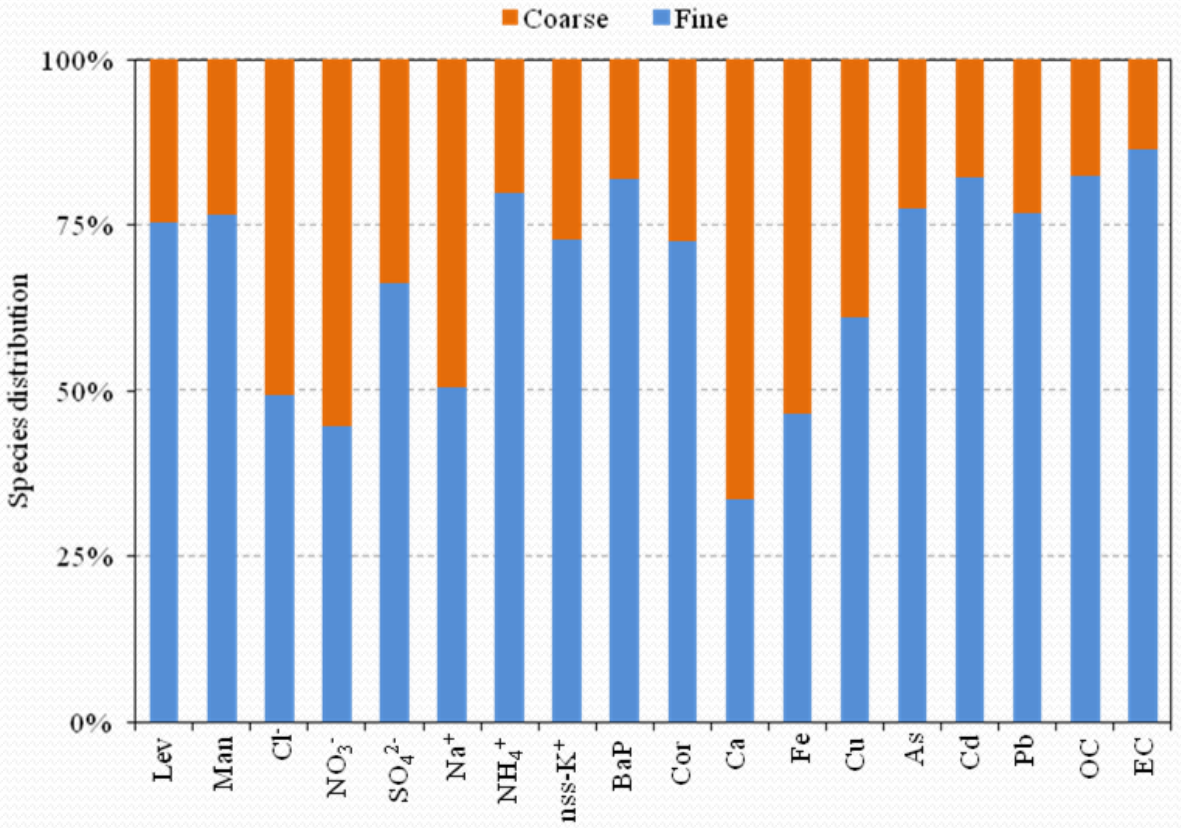
Results and discussion

- **Intensive campaign – Air mass trajectories**
- 65 % of sampling days – biomass burning areas



Results and discussion

- **Species distribution in fine and coarse modes**
- **Fine mode** – biomass burning tracers, vehicular species (BaP, Cor and Cu), secondary species as sulfate and ammonium.
- **Coarse mode** – marine aerosol related species (Na^+ and Cl^-), crustal species (Fe and Ca).

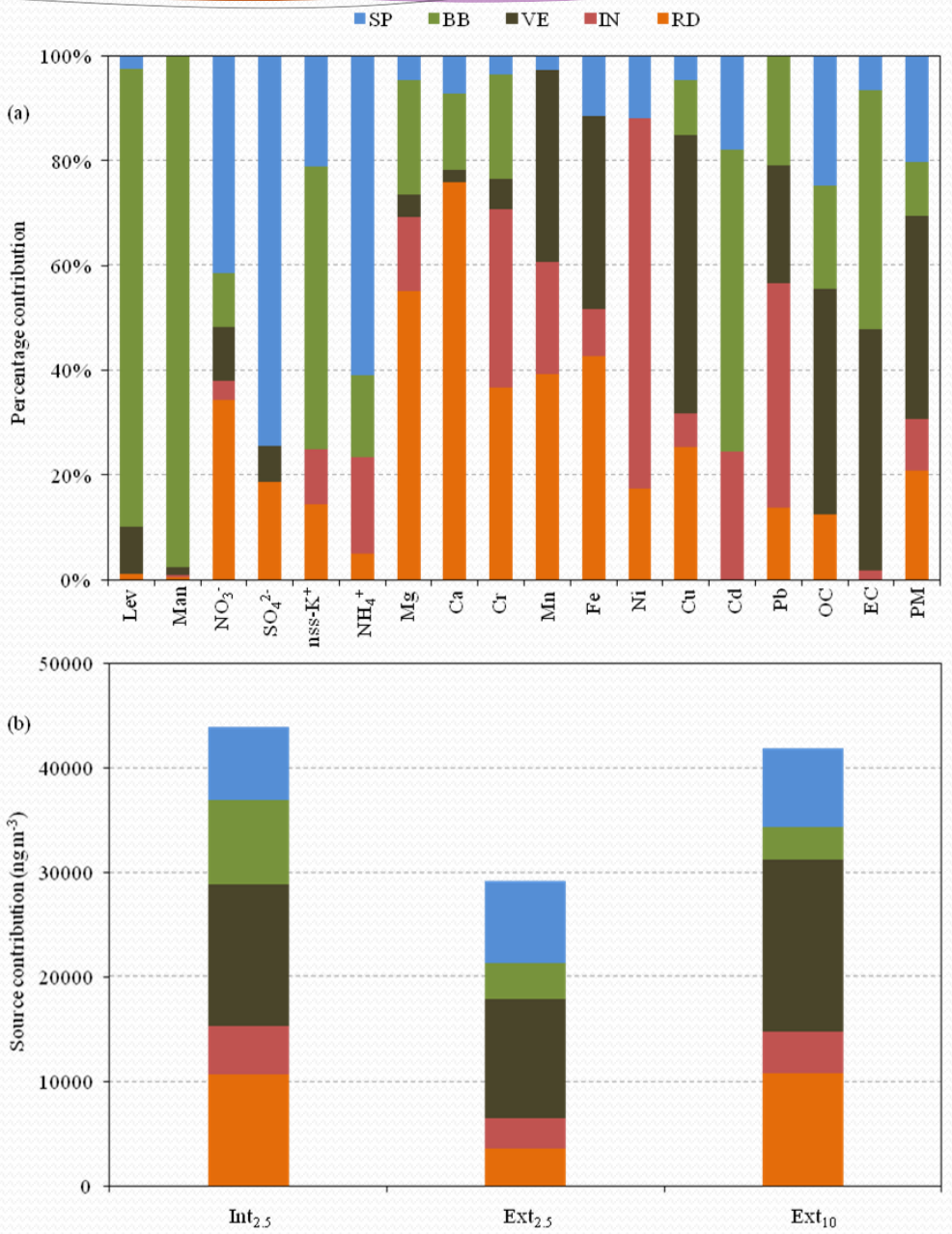


Results and discussion

- **PMF results**
- **Road dust** – Mg, Ca and Fe - *Important source for* $Int_{2.5}$ *and* PM_{10}.
- **Industrial** – Ni, Pb and Cr - *Relatively low contributions.*
- **Vehicular** – Cu, Fe, OC and EC - *Most important sources all campaigns.*
- **Biomass burning** – Levoglucosan, mannosan and non-sea-salt potassium.

Higher in the intensive campaign (sugarcane burning period).

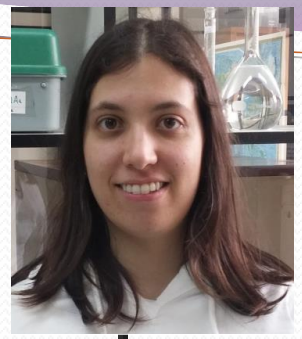
- **Secondary processes** – OC, NO_3^-, SO_4^{2-} and NH_4^+.

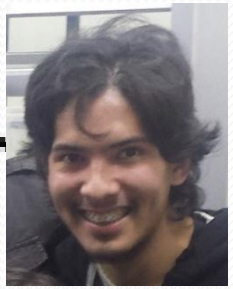


Conclusion

- Risks of PAHs for human – Levels exceeding guidelines.
- Biomass burning tracers – Higher in intensive campaign.
- PMF analysis: road dust, industrial, vehicular, biomass burning and secondary processes.
- Traffic-related sources were the greatest contributors.
- Concentrations Intensive campaign > extensive campaign
- Long-range transport from sugarcane burning areas
- More studies are needed in order to understand local sources of biomass burning.

Acknowledgements


THANK YOU!

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