Influence of urban pollution on the production of organic particulate matter from isoprene epoxydiols in central Amazonia

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Summary

- Measurements of atmospheric particle and gas composition were made at the T3 site, 70 km west of Manaus, in central Amazonia, from 1 Feb 2014 to 31 Mar 2014.
- Positive matrix factorization (PMF) was applied to the organic mass spectra, and six factors were resolved.
- The IEPOX-SOA factor, a surrogate for PM derived from isoprene epoxydiols (IEPOX), had generally lower loadings under polluted conditions when compared to background conditions at the T3 site.
- While sulfate can be a first-order predictor for IEPOX-SOA loadings, an important modulating role of NO on the production of IEPOX-derived PM was revealed.
- An increase in NO_y from 0.5 ppb to 1.5 ppb was associated with a decrease of two- to three-fold in IEPOX-SOA factor loadings, demonstrating the significant dependence of IEPOX chemistry on NO.
- Comparison of probability distributions for NO_y and sulfate between background sites and T3 suggests that Manaus city contributes more significantly to NO_y than to sulfate over background concentrations
- The interpretation of these findings is that the suppressing effect by elevated NO in plume outweighs the enhancing effect by (moderate) additional sulfate with respect to the production of IEPOX-derived PM.
- Further analysis, looking into all PMF factors and including the use of airmass backtrajectories and other pollution indicators, is ongoing.

Source apportionment of organic PM_1 during the wet season

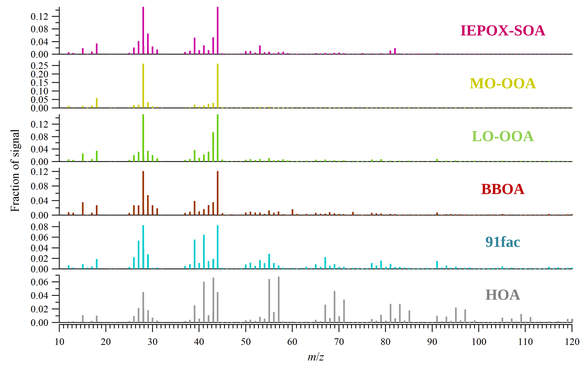

Figure 1. Profiles of the factors resolved by positive matrix factorization (PMF). Legend for factors' labels is displayed at the bottom panel of poster (by Fig. 11).

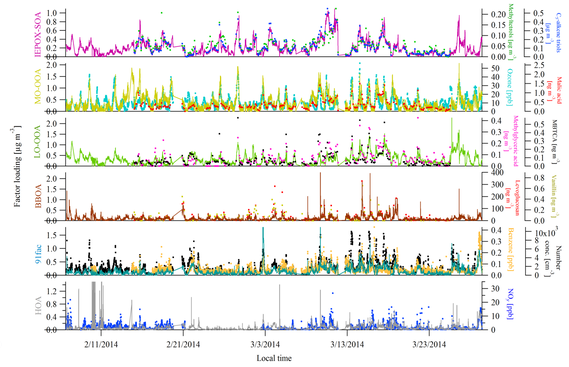

Figure 2. Time series of the six PMF factors resolved (left axis) and correlated externally measured gas and particle-phase species (right axis).

Figure 3. Mean mass fraction of PMF factors.

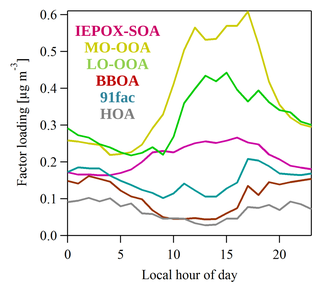

Figure 4. Mean diel patterns of PMF factors.

Influence of urban emissions on the production of IEPOX-derived PM

Chemical mechanism and pollution two-lever effect

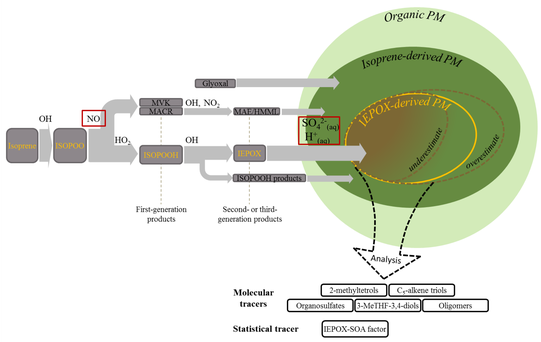

Figure 5. Schematic diagram for the production of IEPOX-derived PM from the photooxidation of isoprene. Thickness of arrows qualitatively illustrates background conditions.

- Competing pollution effects: enhanced sulfate may lead to higher IEPOX-derived PM concentration by means of enhanced particle acidity and volume, whereas higher NO may lead to lower IEPOX-derived PM concentration by means of consumption ISOPOO to produce MVK/MACR at the expense of ISOPOOH and consequently IEPOX.

The Manaus urban plume: a case study

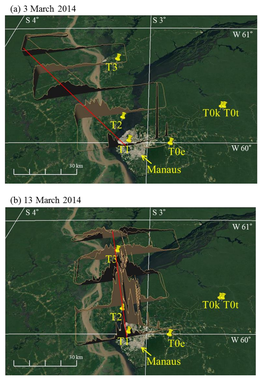

Figure 6. Visualization of the Manaus plume by plotting particle number concentration measured onboard the G1 on the vertical axis.

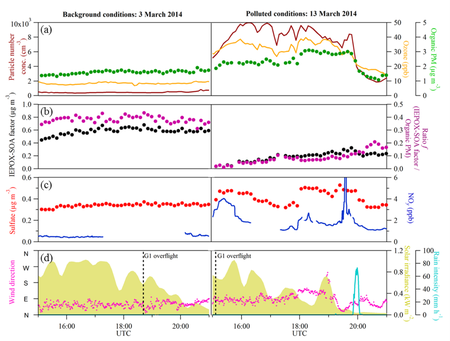

Figure 7. Case comparison of measurements at T3 ground site between background and polluted conditions.

- IEPOX-SOA factor loadings decrease in polluted compared to background conditions.
- NO_y is employed as an indicator of integrated exposure of airmass to NO chemistry.

The important modulating role of nitrogen oxides

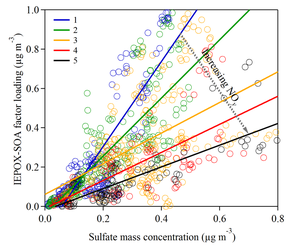

Figure 8. Afternoon data (12-16 local time) is plotted. Linear fits for 5 subsets of data based on NO_y concentration are shown. Fit parameters are in table below. R^2 for the full dataset is 0.37.

Group	NO_y range (ppb)	Fit slope	Fit intercept	Fit R^2
1	< 0.66	2.16	-0.13	0.75
2	0.66 – 0.92	1.48	-0.04	0.64
3	0.92 – 1.55	0.78	0.06	0.24
4	1.55 – 2.45	0.71	-0.01	0.44
5	> 2.45	0.55	-0.02	0.62

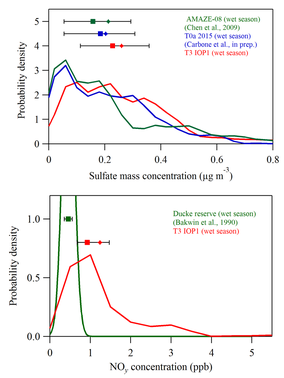

Figure 9. Probability density functions for sulfate (top) and NO_y (bottom) concentrations for background sites (blue/green) and T3 site (red).

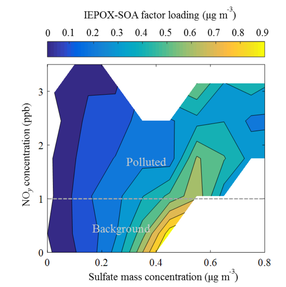

Figure 10. Dependence of IEPOX-SOA factor on both sulfate and NO_y concs.

- Manaus contributes more significantly to NO_y than to sulfate relative to background conditions → suppressing effect > enhancing effect of plume with respect to IEPOX-derived PM production.

Key

IEPOX-SOA: isoprene epoxydiols – derived secondary organic aerosol
MO-OOA: more oxidized - oxygenated organic aerosol
LO-OOA: less oxidized - oxygenated organic aerosol
BBOA: biomass burning organic aerosol
91fac: factor with characteristic m/z 91 peak, anthropogenic correlated
HOA: hydrocarbon-like organic aerosol

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