Proton-transfer reaction mass spectrometry applications in isoprene photochemistry

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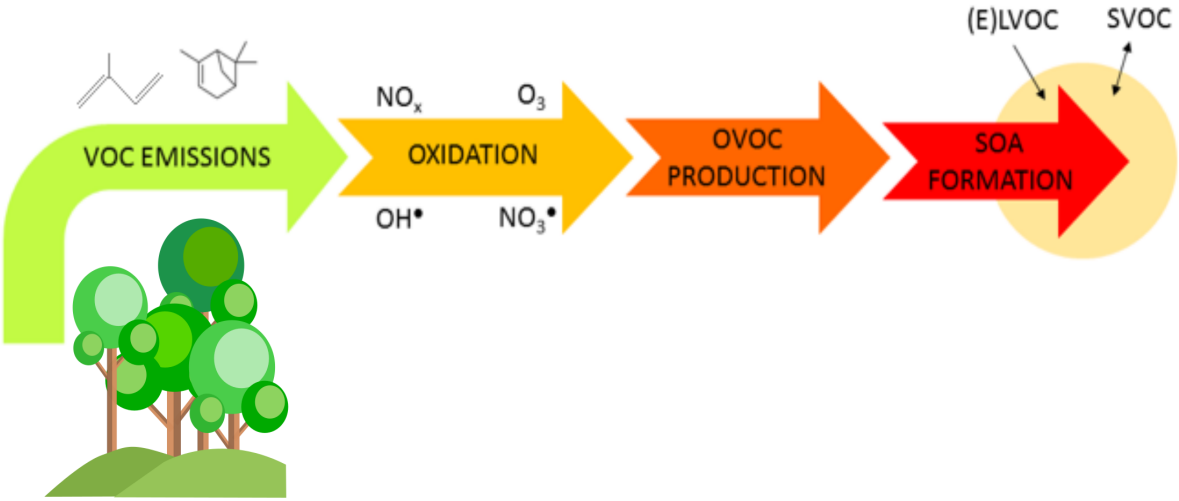
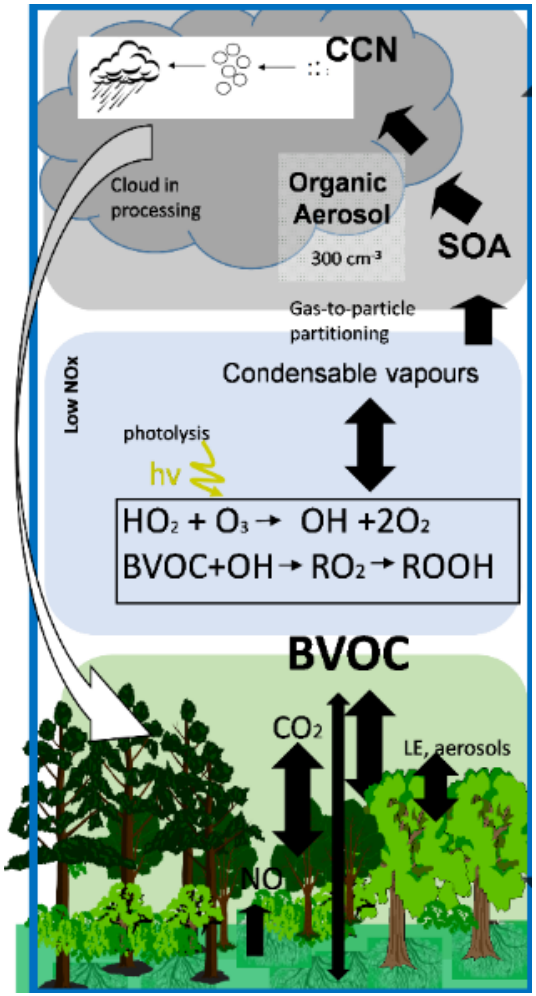
VOCs are precursors for SOA.

- Organic material contributes ~ 90% to total fine aerosol mass in tropical forested areas (Kanakidou, 2005).
- Understanding the processes involving OC depends on how well these compounds are identified.

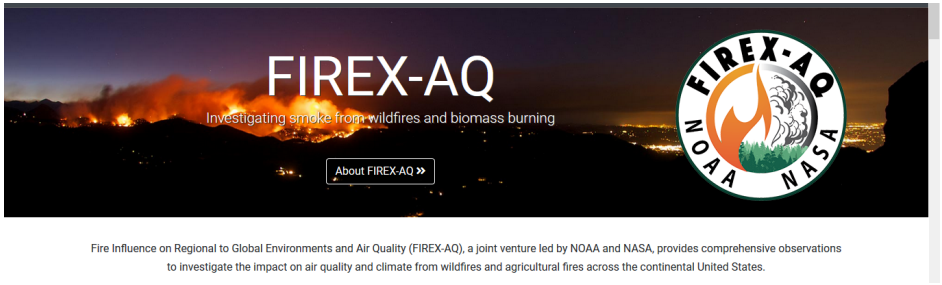


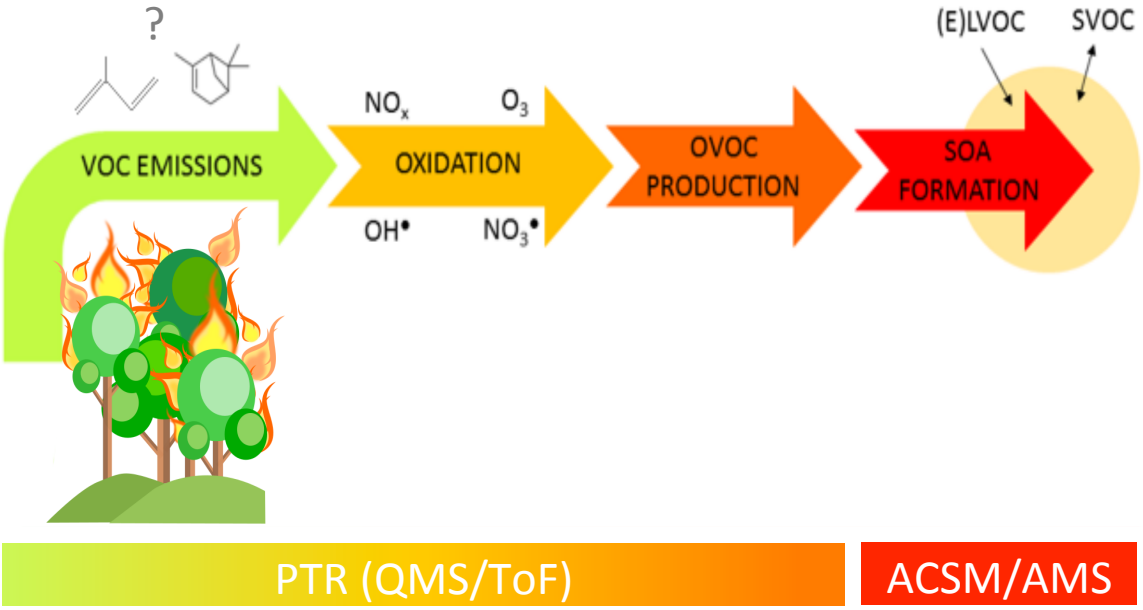
PTR (QMS/ToF) | ACSM/AMS



Biomass burning plume evolution

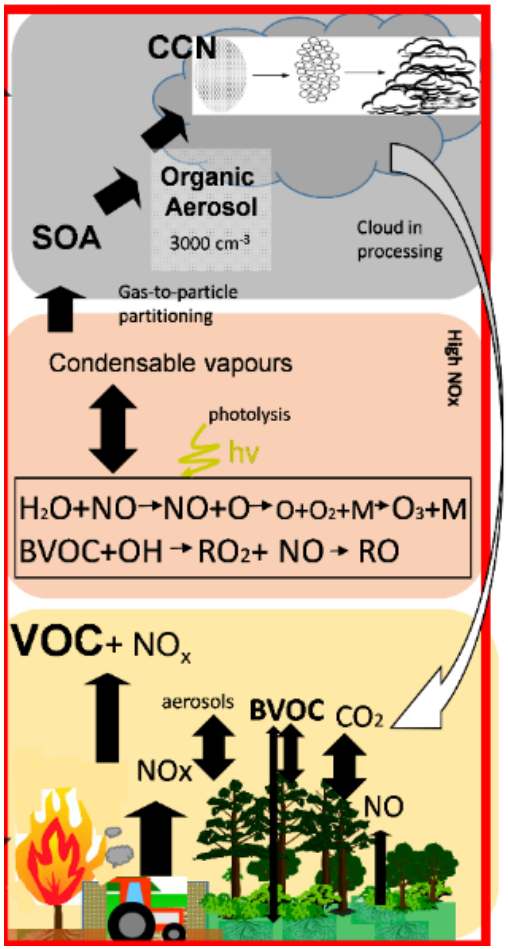
- Understand the differences between undisturbed (or pristine) conditions and biomass burning conditions.





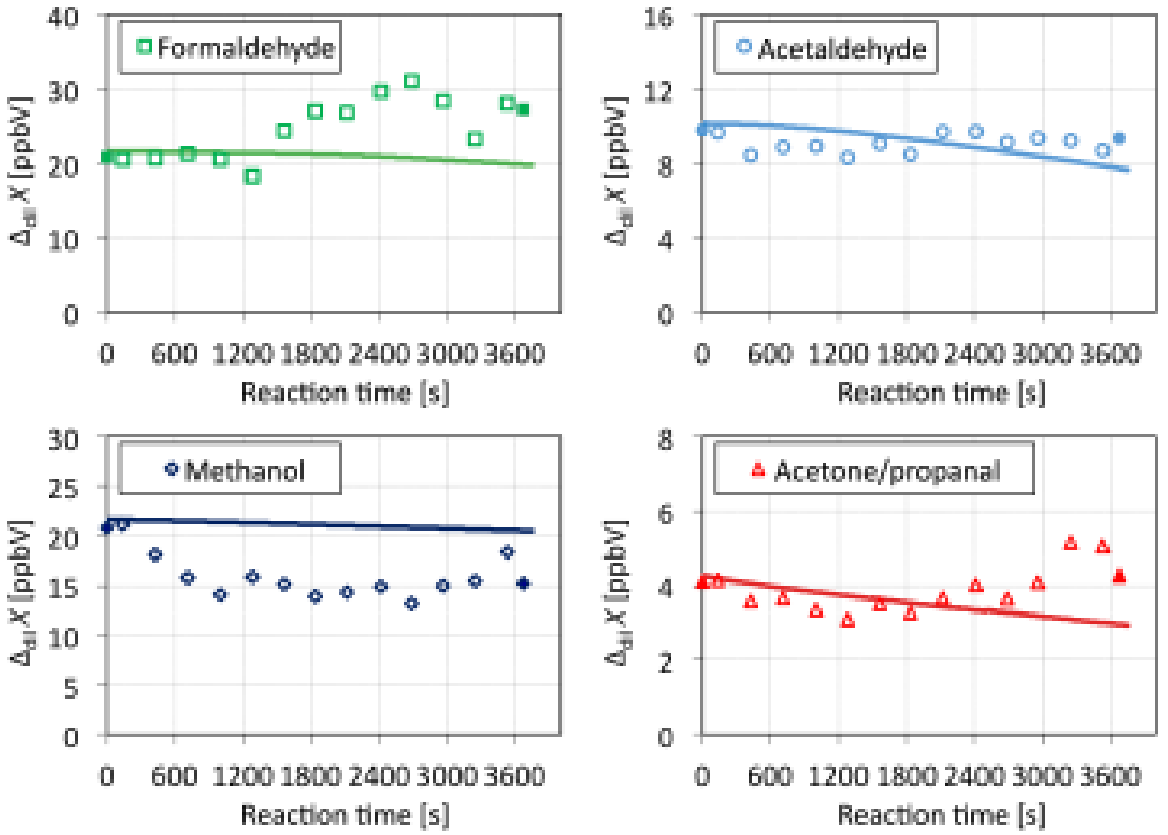
PTR (QMS/ToF)

ACSM/AMS

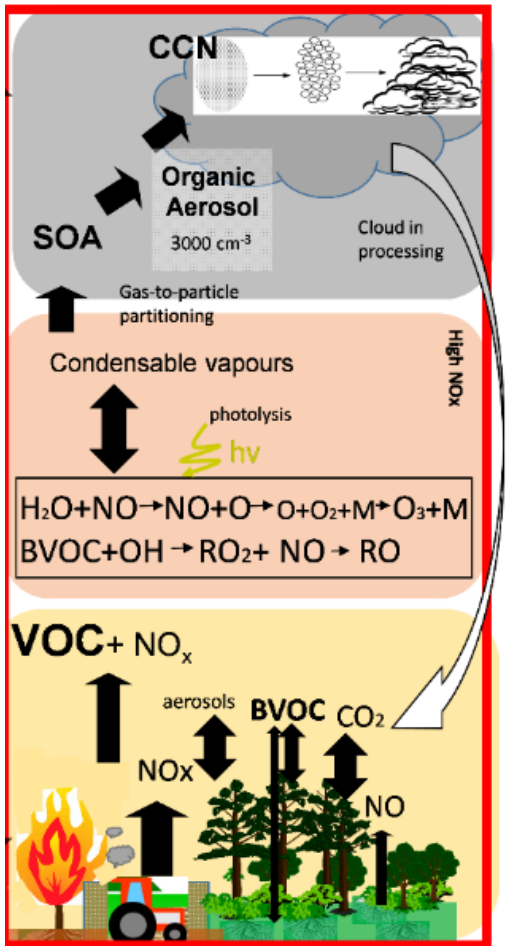


Biomass burning plume evolution

- Müller et al, 2016.: Reactive trace gases in a biomass burning plume.



Dilution-corrected molar excess mixing ratios of formaldehyde **(a)**, acetaldehyde **(b)**, methanol **(c)**, and acetone/propanal **(d)** during 1 h of plume evolution. Point symbols refer to the measured data (1 km bins); solid lines represent the output of the UWCM fed with MCM v3.3 chemistry



PTR Mass Spectrometer

- Ionization Mode: H_3O^+
- Most of atmospheric VOCs have proton affinities higher than water (P.A. = 166.5 kcal/mol).

Compound	Proton Affinity (kcal/mol)
Carbon monoxide (CO)	141,7
Oxygen (O_2)	100,6
Carbon dioxide (CO_2)	129,2
Acetaldehyde (C_2H_4O)	183,8

$$3\ O\uparrow + + M \rightarrow (MH)\uparrow + + H\downarrow 2\ O$$

Soft ionization: non dissociative proton transfer

- The protonated VOC $(MH)^+$ is usually detected at mass to charge ratio (mz) Mw + 1.
- Acetaldehyde (Mw=44): $C_2H_4O + H^+ \longrightarrow C_2H_5O^+$ (mz 45)
- Acetone (Mw=58): $C_3H_6O + H^+ \longrightarrow C_3H_7O^+$ (mz 59)

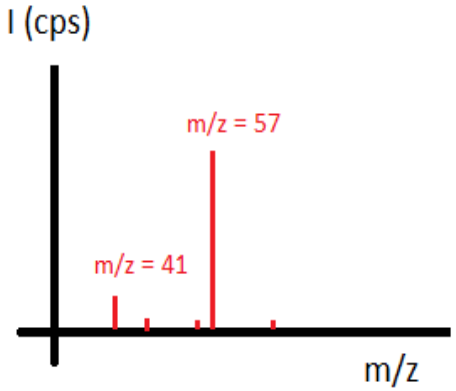
PTR Mass Spectrometer

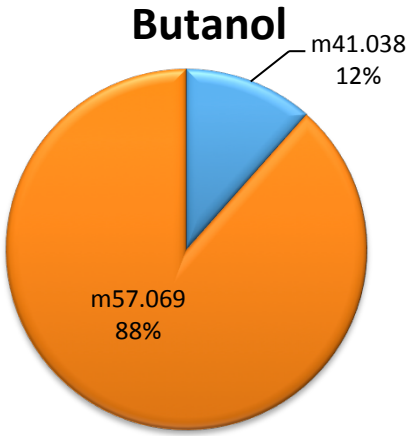
- Soft ionization: non dissociative proton transfer (H_3O^+)

$$H\downarrow 3\ O\uparrow + + M \rightarrow (MH)\uparrow + + H\downarrow 2\ O$$

- For butanol ($C_4H_{10}O$)
- $C_4H_{10}O + H^+ \longrightarrow C_4H_{11}O^+$
- We observe:

Butanol	
Formula	m/z
C_4H_9 +	57.069
C_3H_5 +	41.039



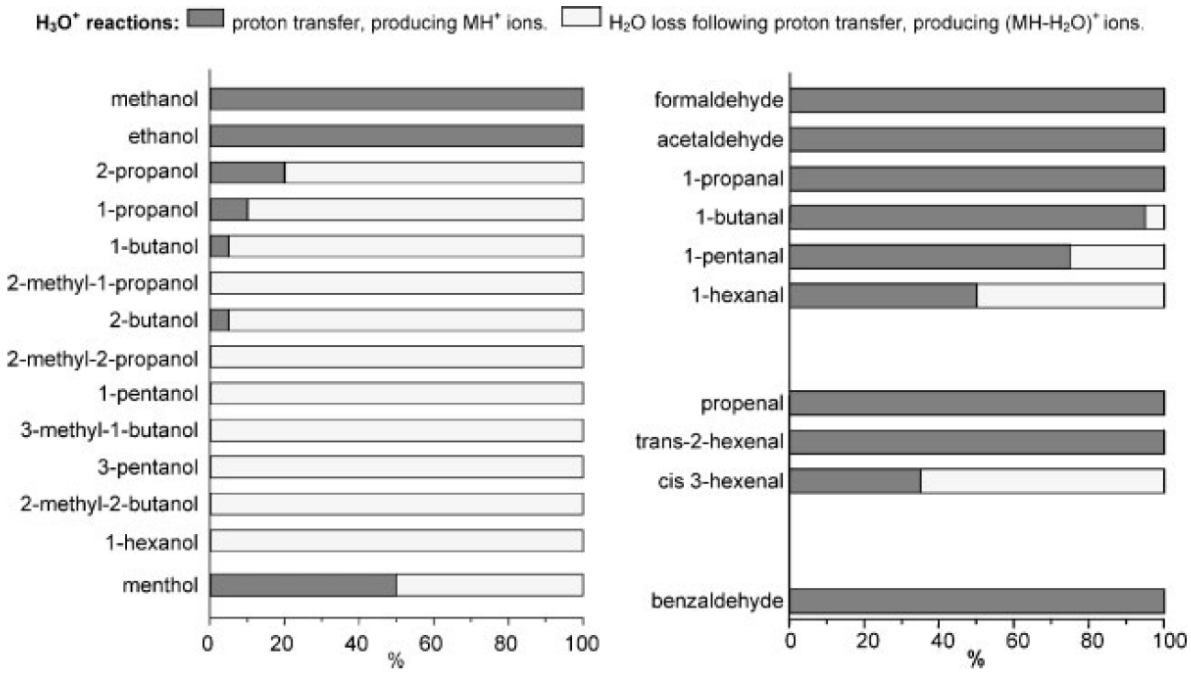


PTR Mass Spectrometer

- Soft ionization: non dissociative proton transfer (H_3O^+)

$$H\downarrow 3\ O\uparrow + + M \rightarrow (MH)\uparrow + + H\downarrow 2\ O$$

- Ionization other than proton transfer can occur:



Smith, D. and Spanel. Mass Spec. Rev., **2005**, 24, 661– 700

PTR Mass Spectrometer

- Soft ionization: non dissociative proton transfer (H_3O^+)

$$H\downarrow 3\ O\uparrow + + M \rightarrow (MH)\uparrow + + H\downarrow 2\ O$$

- Ionization other than proton transfer can occur:

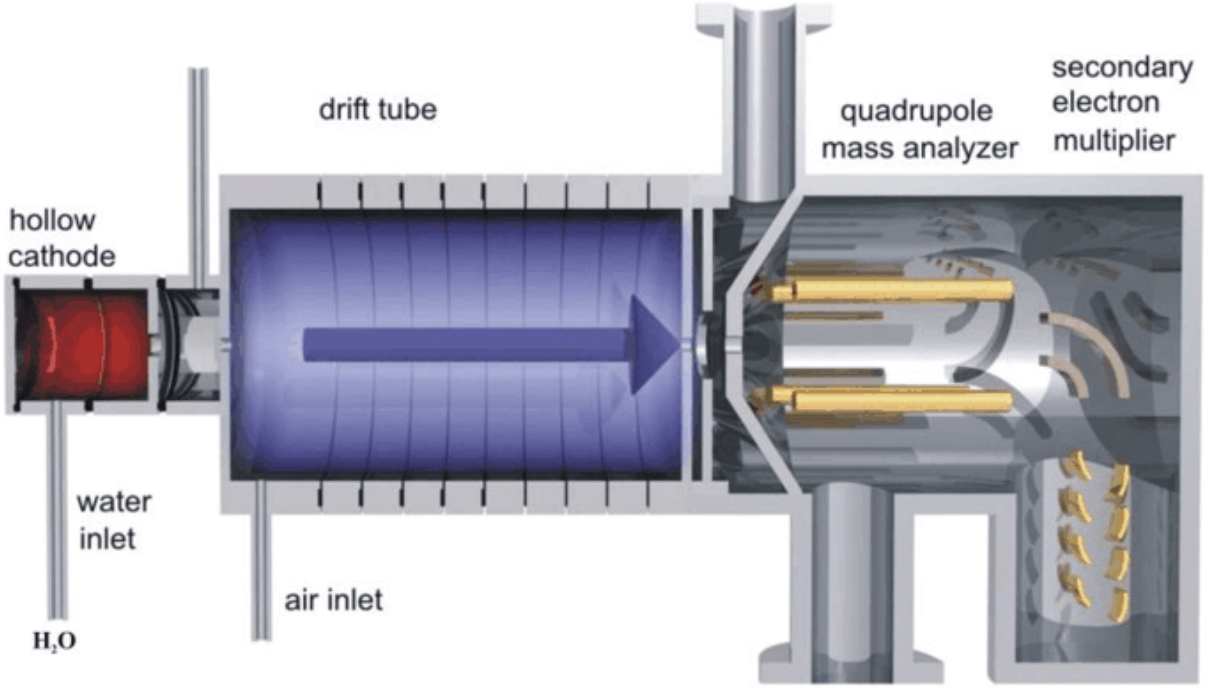
–For alcohols[1]: Main channels $[MH]^+$ $[MH - H_2O]^+$

–For aldehydes[2,3]: Main channels $[MH]^+$ $[MH - H_2O]^+$ $[MH]^+(H_2O)$

–For Ketones[2]: no fragmentation $[MH]^+$

[1] Spanel,P. and Smith, D. *Int. J. Mass Spectrom. Ion Process.* 167/168, 375-388, **1997**
[2] Spanel, P. et al. *Int. J. Mass Spectrom. Ion Process.* 165/166, 25-37, **1997**
[3] Smith, D. et al. *Rapid Commun. Mass Spectrom*, 28, 1917–1928, **2014**

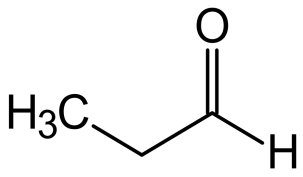
PTR Mass Spectrometer

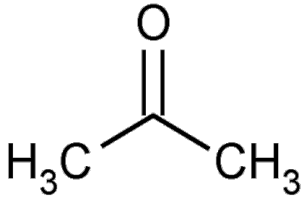


Isomers and isobars

Isomers

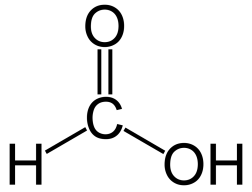
- Same molecular formula and (normally) same functionality.
- C_3H_6O
- Mw = 58.08 g/mol
- Propanal and acetone

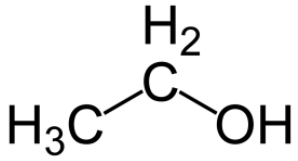




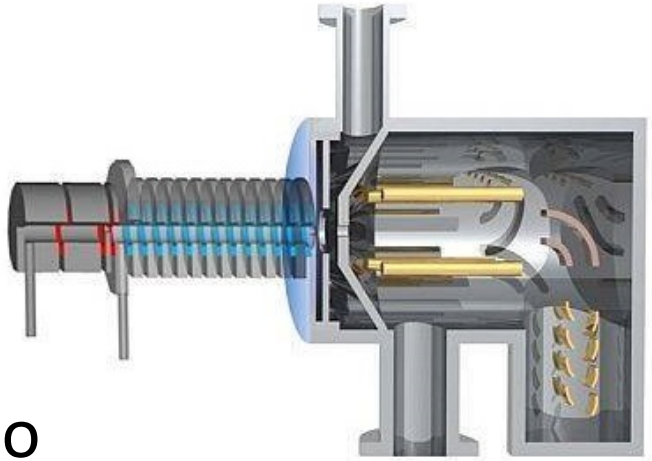
Isobars

- Same nominal molecular weight but different molecular formula.
- CH_2O_2 and C_2H_6O
- Mw = 46.03 g/mol
- Formic acid and ethanol



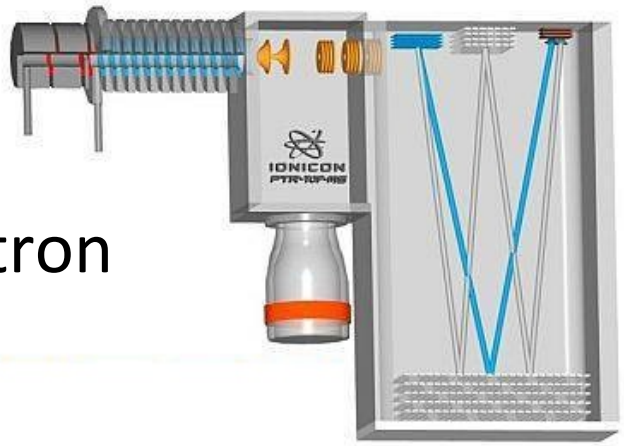


PTR: QMS x ToF



QMS

- Quadrupole
- Is a mass filter that lets one mass to charge ratio pass at a time.

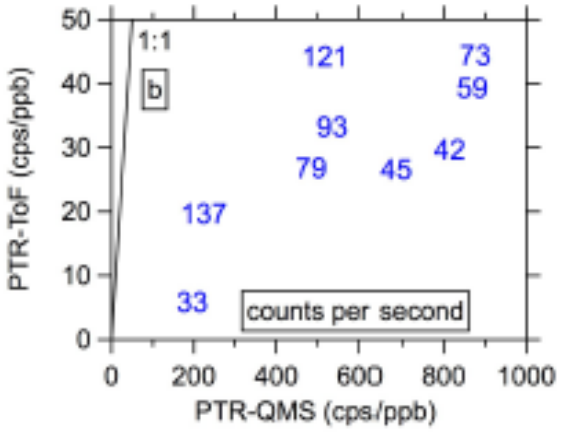


ToF

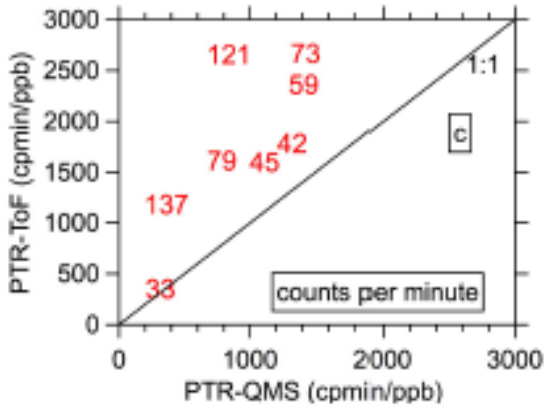
- Ions are accelerated trough a reflectron
- Ions reach the detector at different times, proportional to their mz.

PTR: QMS x ToF

- PTR-QMS measures only pre-selected mass while the PTR-ToF takes full mass spectra.
- QMS sensitivity is inversely proportional to the number of ions measured.



Compared sensitivity in cps ppbv-1, when the PTR-QMS measures only one mass per second.



Compared sensitivity in cps ppbv-1, when the PTR-QMS measured 34 masses in 37 s duty cycles.

Warneke et al. Atmos. Meas. Tech., 8, 411–420, 2015

PTR-MS Highlights

- Online technique
- High time resolution (1 or 2 min) - almost simultaneous response!
- Very sensible, low detection limits (ppt – ppb).
- Notable for a targeted-screening.

- Humidity dependent – care must be taken!
- Complicated interpretation of spectra for a non targeted-screening.

QMS:

- unitary mass resolution
- Pre-selection of ions we want to track
- Sensitivity decreases as we measure many ions

VOCs Biogenic Emissions

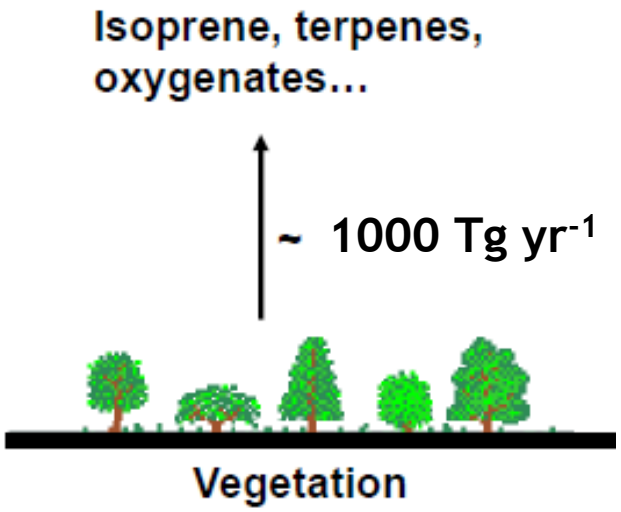


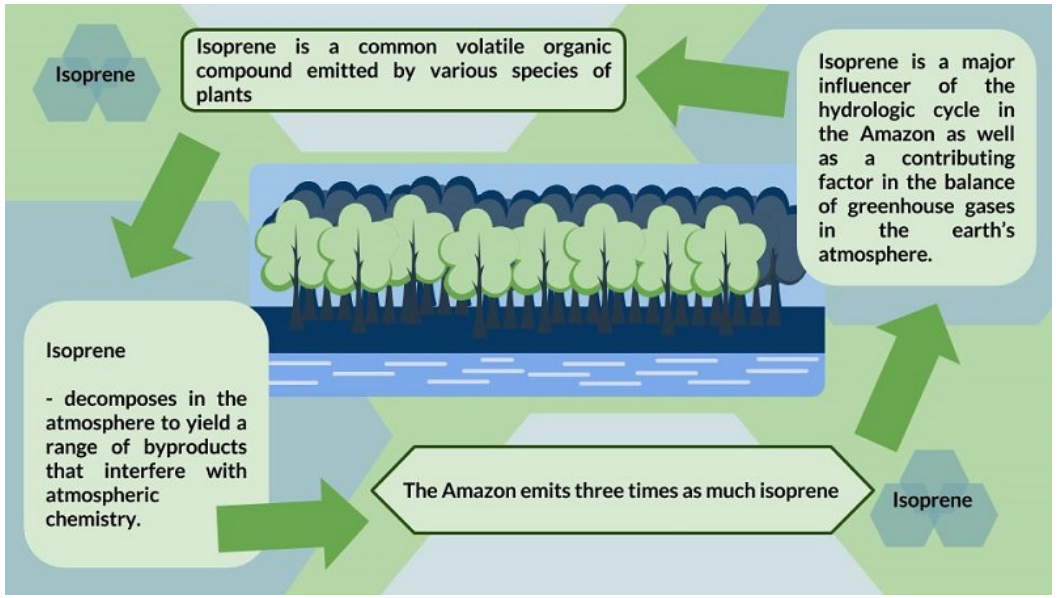
Table 2. Global Biogenic Emissions Estimated for the Year 2000[12]

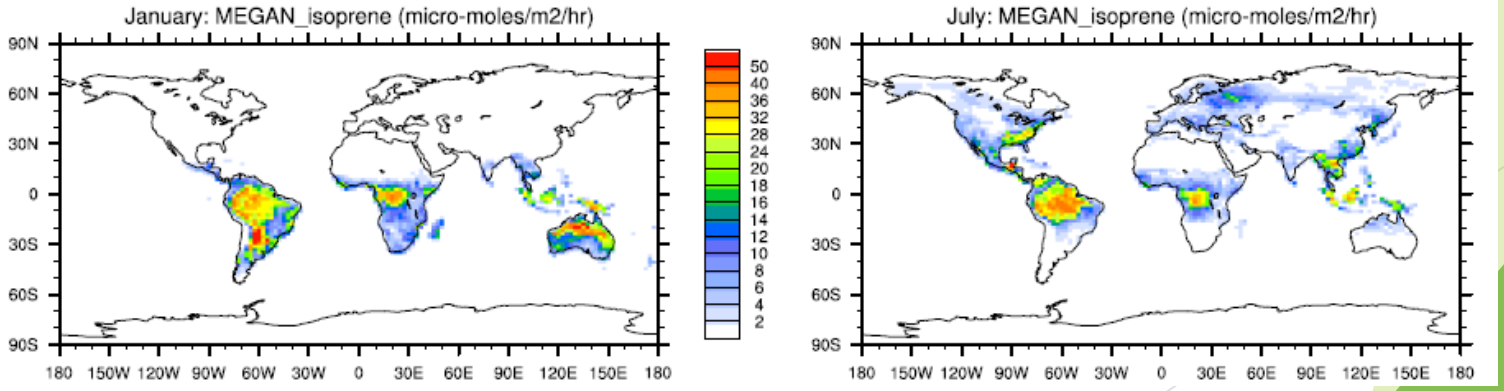
compound	emission (Tg yr^{-1})	compound	emission (Tg yr^{-1})
isoprene	535	β-pinene	18.9
methanol	99.6	propene	15.8
α-pinene	66.1	limonene	11.4
acetone	43.7	sabinene	9.0
ethene	26.9	myrcene	8.7
ethanol	20.7	butene	8.0
acetaldehyde	20.7	β-caryophyllene	7.4
trans-β-ocimene	19.4	total VOC + OVOC	1007

From Melouki et al, Chem. Rev. 2015, 115, 3984−4014

Isoprene (ISOP; C_5H_8) is the most abundant nonmethane biogenic volatile organic compound (VOC) in the atmosphere.

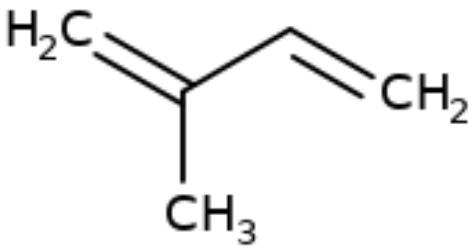
Isoprene in the Amazon



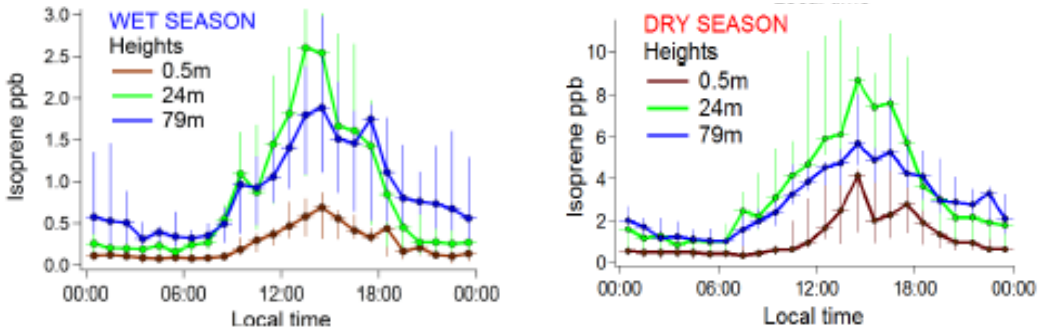


January and July 2000 global emissions of isoprene, simulated with MEGAN 2.1 algorithms.
Guenter et al, 2012

Isoprene



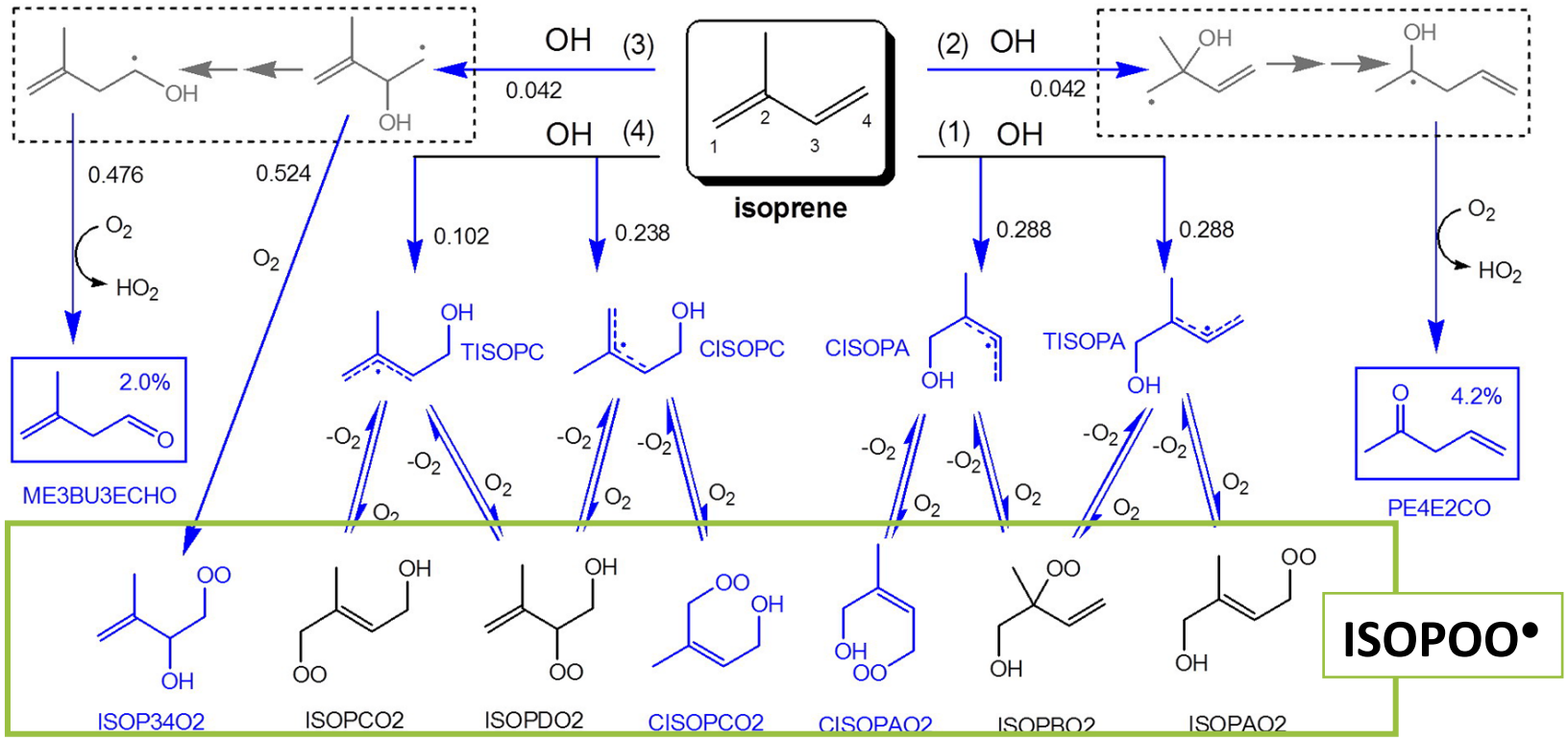
- Contains two double C-C double bonds → readily oxidized in the atm.
- The lifetime of isoprene with respective to the reaction with:
  - OH (2×10^6 molec. cm^{-3}) → 1.4 hr,
  - O_3 (30 ppb) → 1.3 day,
  - NO_3 rad (5×10^8 molec. cm^{-3}) → 48 min
- Oxidation by **OH is the dominant fate** of isoprene in the atmosphere since isoprene is emitted during daytime.



Diurnal hourly medians of isoprene during the wet season and the dry season at ATTO site, Yáñez-Serrano et al. 2015

Isoprene OH oxidation mechanism

- Isoprene oxidation is typically initiated by the addition of a hydroxyl radical (OH) across a double bond.
- Very complex chemistry!!



hydroxyl-substituted alkyl peroxyl radicals

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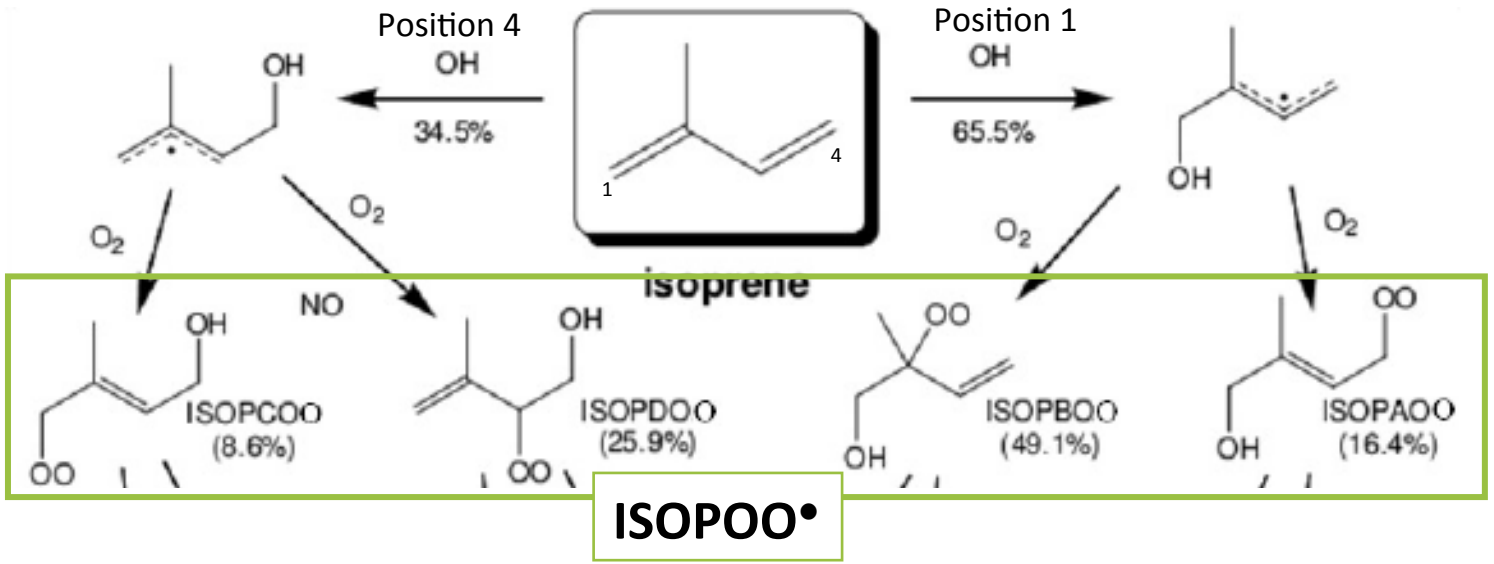
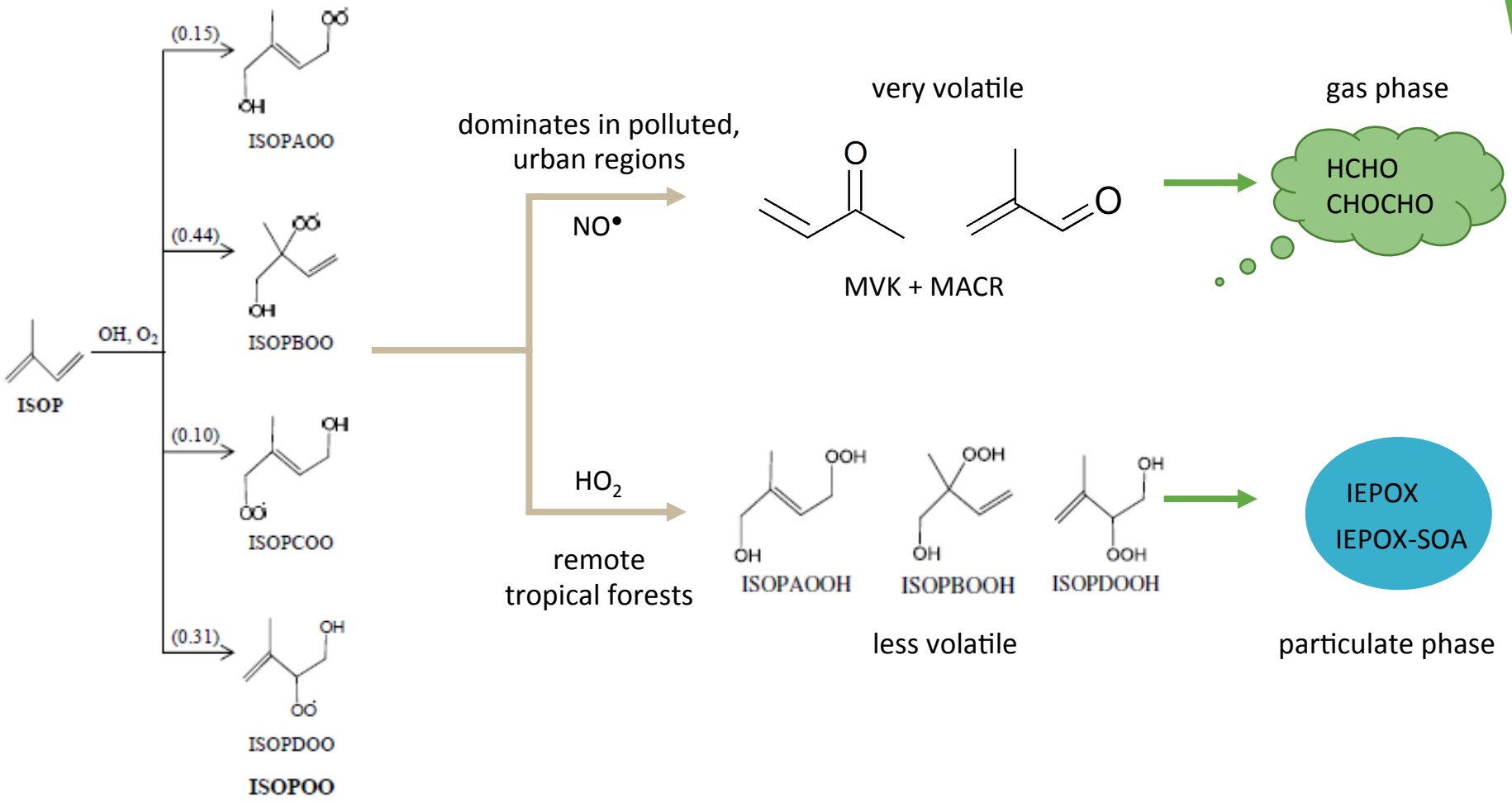


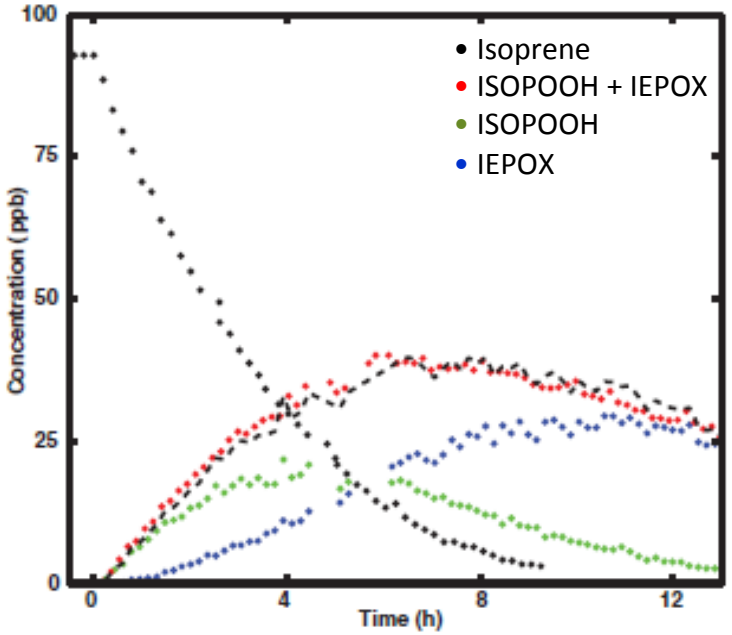
hydroxyl-substituted alkyl peroxyl radicals

Isoprene and ISOPOO oxidation



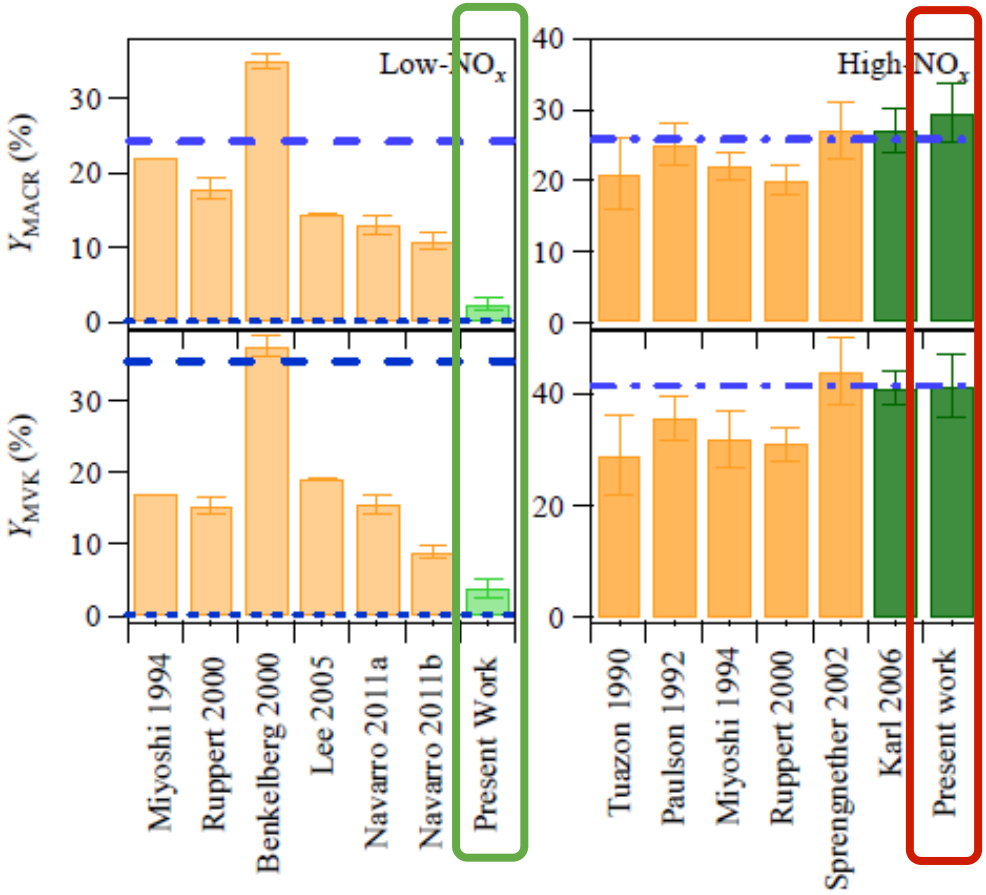
Chamber studies

- Several chamber studies have been done to elucidate isoprene oxidation mechanisms and fates.



Consecutive formation of ISOPOOH and IEPOX in the photooxidation of isoprene. Paulot, 2009

Liu et al, 2013: Y_{MVK}, Y_{MACR} was 60-90% lower than previously reported.

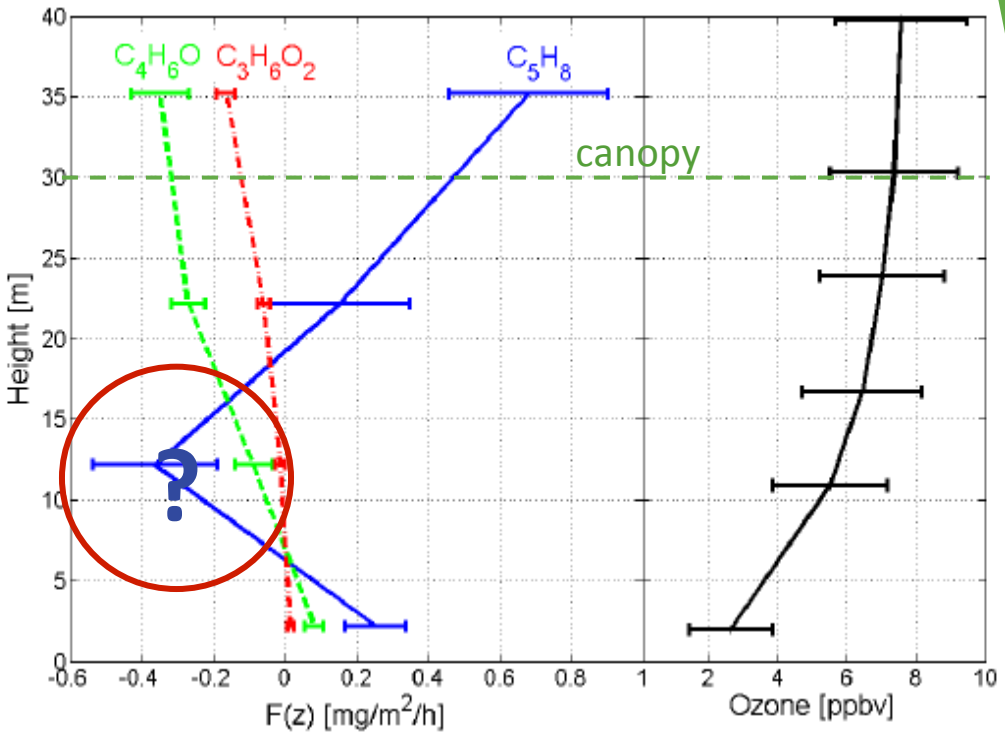


Liu et al. 2013

- Accurate ambient measurements of the molecular identities and concentrations of isoprene oxidation products are essential for testing concepts of the reaction pathways of isoprene and the associated predictions of chemical transport models (CTMs).

Field studies – MVK and MACR as products

- Karl et al, 2009:
  - → Considers NO dominant pathway!
  - → Present MVK+MACR as main isoprene oxidation products.
  - → Hidroxyacetone as secondary (from MACR).



Mean integrated vertical source/sink distribution of isoprene, MVK, MAC and hydroxyacetone measured by PTR-MS at daytime.

- Do not consider influence of ISOPOOHs.
- Epoxides (IEPOX) were newly discovered.

Determine the partition MVK+MACR and ISOPOOHs.

- Instrumental limitation!

ISOPOOH isomers decompose to MVK and MACR on the hot metal surfaces inside PTR (and GC) instruments.

ISOPOOH and MVK+MACR are all detected as the same ion ($C_4H_7O^+$, mz 71)

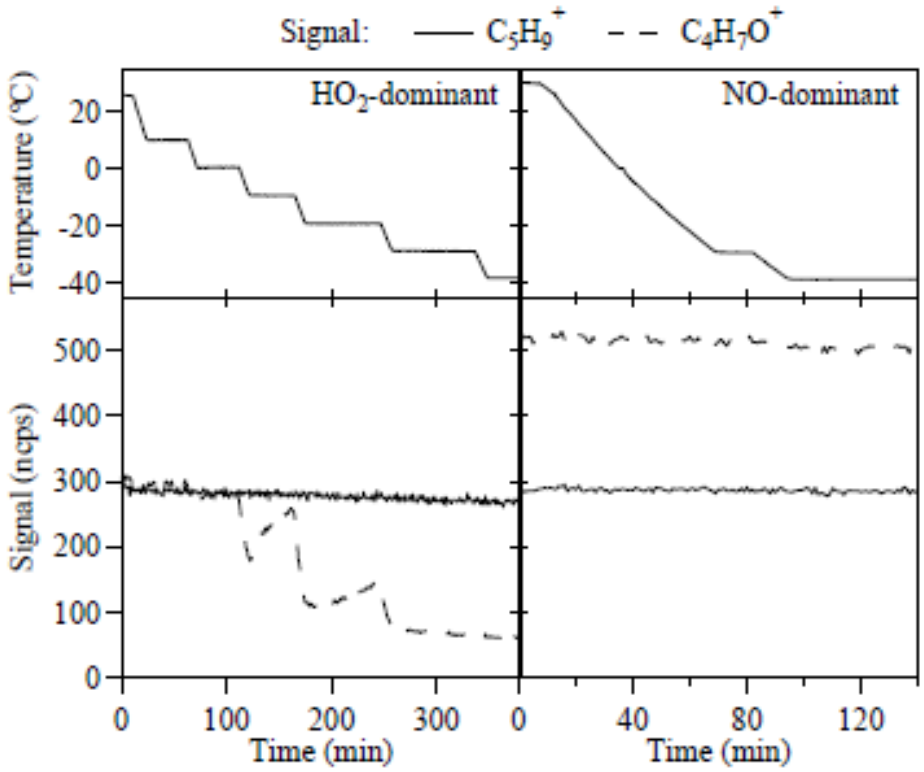
MVK and MACR concentrations reported in the literature can be overestimated for regions where the HO_2 pathway is important.

Need to determine the partition MVK+MACR and ISOPOOHs.

Determine the partition MVK+MACR and ISOPOOHs

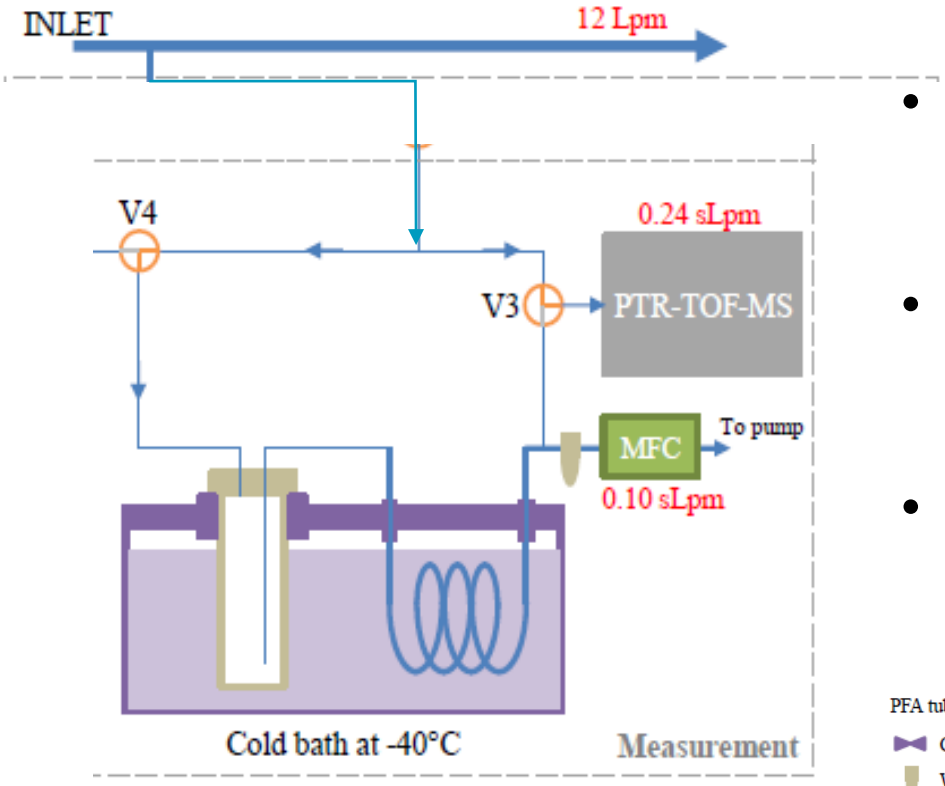
To overcome the instrumental limitation:

- A cold trap was deployed upstream of the PTR-ToF-MS to selectively remove ISOPOOH isomers.



Liu et al. 2013

Sampling setup



Schematic diagram of the gas inlet system for the PTR-TOF-MS.

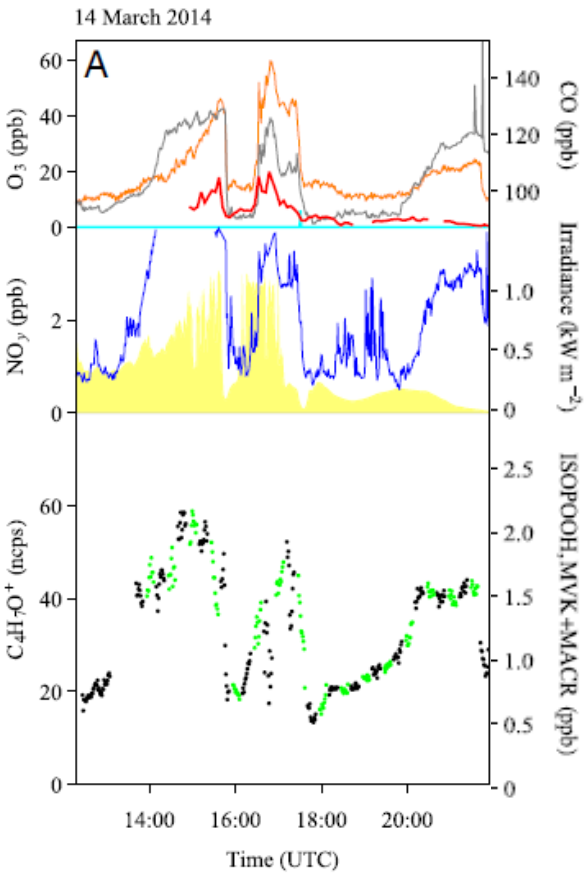
- Collect data for a period of time with the trap in line followed by period of time in bypass.
- A difference signal $\Delta C_4H_7O^+$ measured with and without the trap can be defined.
- The ISOPOOH concentration can be determined.

PFA tubing: 1/2" (12.7 mm) 1/4" (6.35 mm) 1/8" (3.18 mm)
Critical Orifice
Three-way valve (middle port is common and grey port is normally closed)
Water Trap

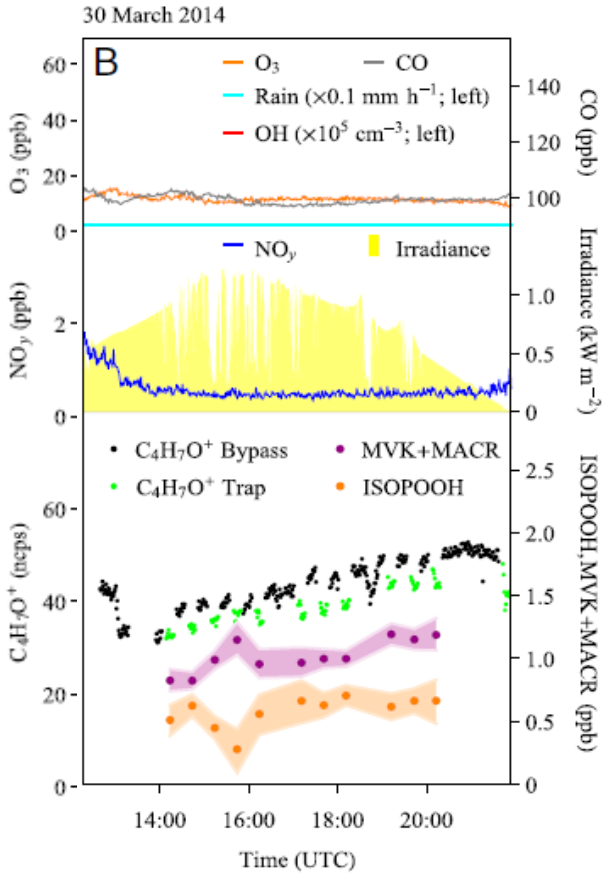
MVK+MACR and ISOPOOHs

- Compares low-NOx e High-NOx events at T3 site in Manaus.

Polluted – High NOx

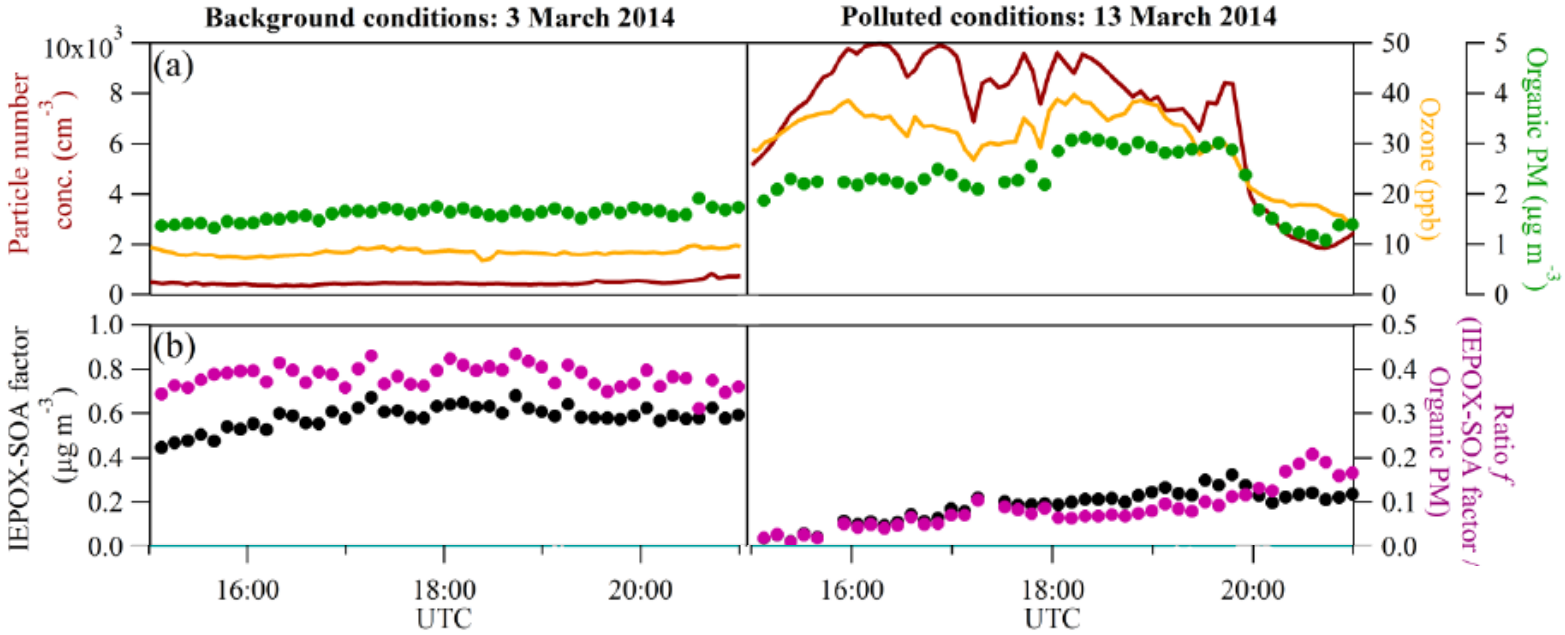


Background – Low NOx



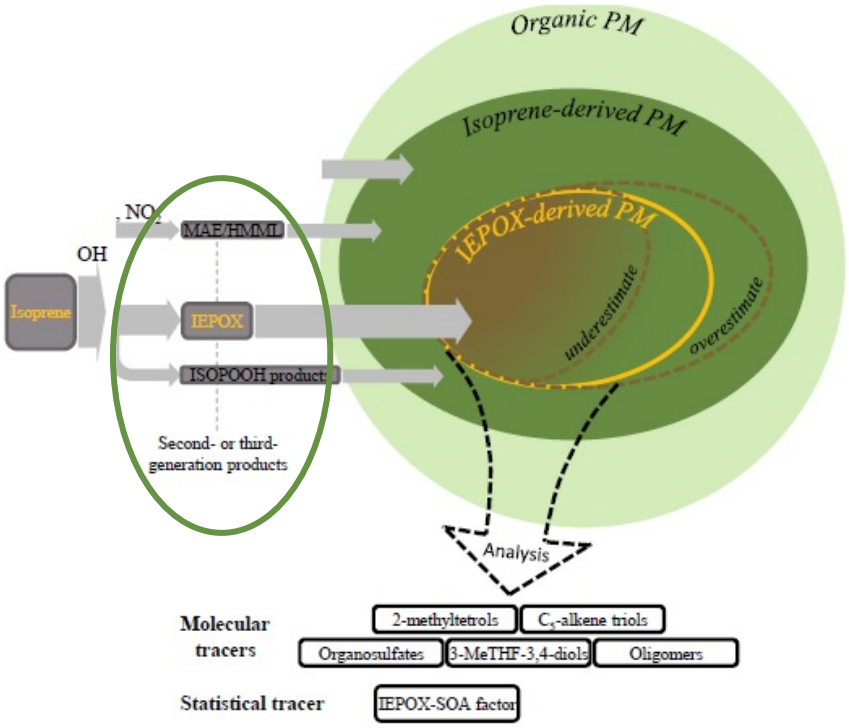
At the same time for particulate phase

- For the same site, same IOP (de Sá et al, 2017).
- Results for the organic particulate matter:



Air masses passing over T3 on afternoons of 3 and 13 March 2014. (a) Ozone, particle number, and organic mass concentration. (b) IEPOX-SOA factor loading and the ratio f of the factor loading to the organic PM concentration. de Sá et al, 2017

- Recently: Papers from GoAmazon characterizing the particulate phase:
- de Sá 2017, de Sá 2018
- Schulz et al. 2018: Observations of IEPOX-SOA in the tropical upper troposphere

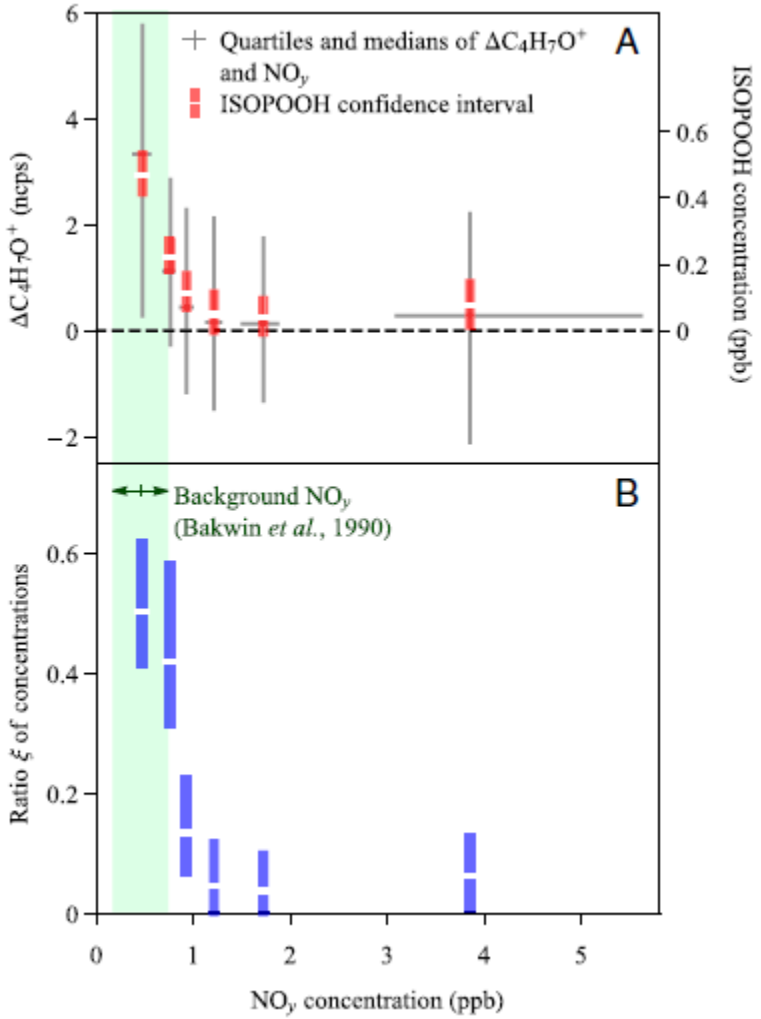


De Sá et al 2017:

- Investigated the particulate matter from isoprene epoxydiols.
- Identified PMF factors associated with IEPOX-derived PM at downwind Manaus
- How the pollution perturbed IEPOX-derived PM production relative to background conditions.

Partition MVK+MACR and ISOPOOHs

- 23 days of measurements alternating by-pass/trap.
- $\Delta C_4H_7O^+$ values were grouped by NOy concentration.



✓ **ISOPOOH concentrations increased with lower NO_y concentrations.**

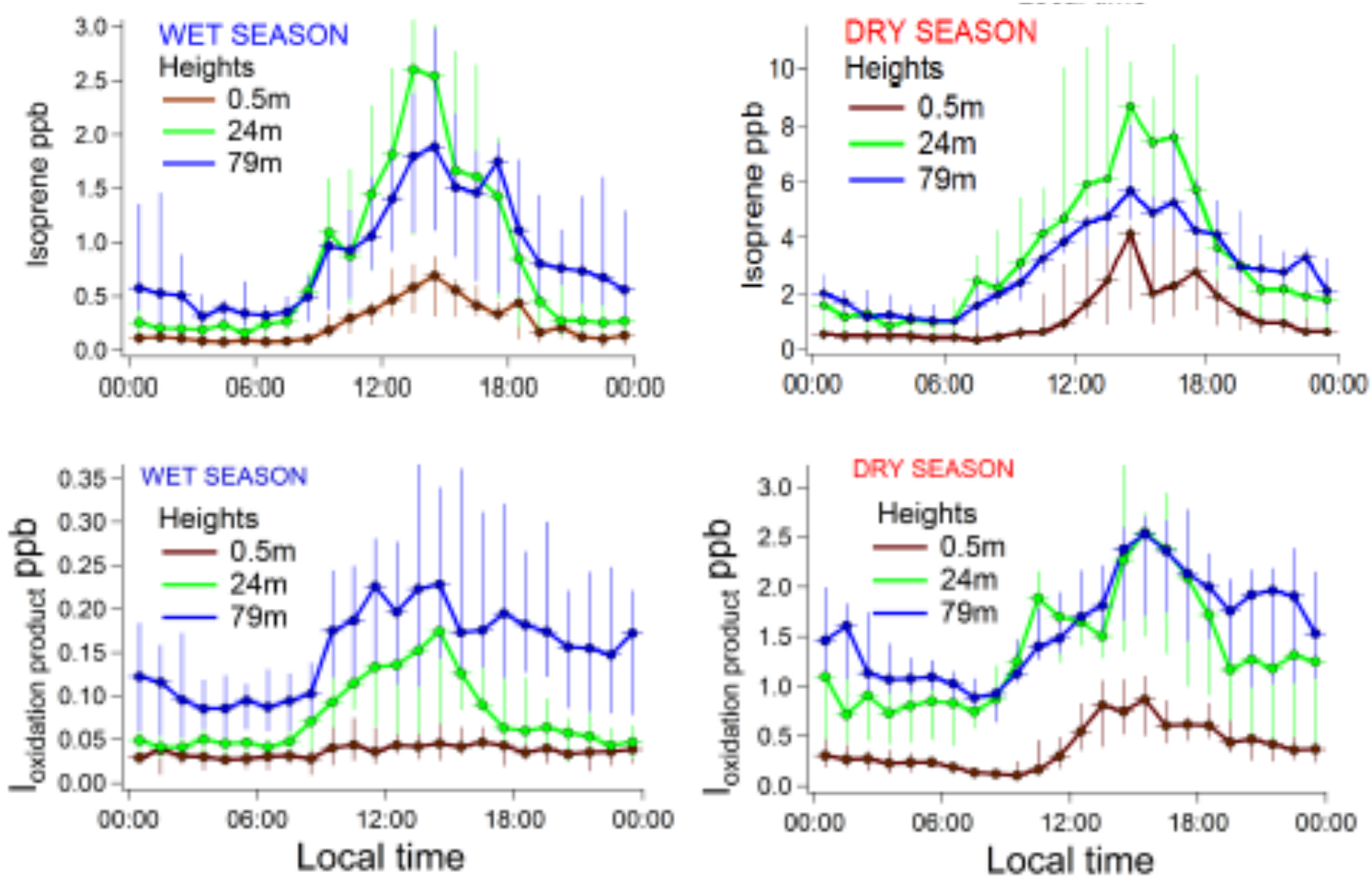
$$\xi = C{\downarrow}ISOPOOH \,/\, C{\downarrow}MKV + MACR$$

✓ **For NOy < 1 ppb → ξ = 0.5 ± 0.1**

✓ **ξ could be regarded as the quantitative error in the historical assumption that $C_4H_7O^+$ ion correspond do MVK+MACR!**

Isoprene "general" oxidation products

Isoprene and its oxidation products at To site. From Yáñez-Serrano et al., 2015



Diurnal hourly medians of isoprene and its oxidation products during the wet season and the dry season.

Isoprene "general" oxidation products

Isoprene and its oxidation products at To site. From Yáñez-Serrano et al., 2015

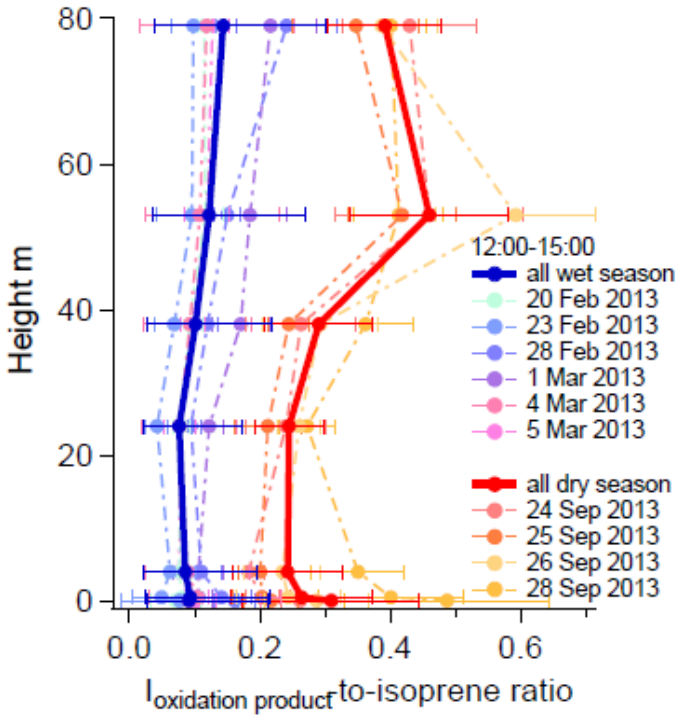
During the dry season, higher ozone and NOx concentrations at the ATTO site were observed.

Whereas isoprene had a 4-fold increase from the wet to the dry season, isoprene oxidation products had a 10-fold increase.

From Liu, 2013:

	Chamber	Mixing ratio at steady state (ppb) [4]					Yield (%) [4]	
		NO^+ mode			H_3O^+ mode			
	Condition [1]	ISOP	MVK	MACR	ISOP	MVK+MACR	MVK	MACR
#1	Main experiment [2]	16.0±0.6	1.3±0.1	0.8±0.1	15.8±1.4	2.1±0.2	4.6±0.7	3.2±0.6
#7	NO-dominant [3]	18.3±0.7	10.3±0.8	7.9±0.4	18.4±1.7	18.1±1.8	41.4±5.5	29.6±4.2

The change in regime from low-NO to high-NO could explain this variability in $I_{oxidation}$???



Average profiles of the isoprene oxidation product (Ioxidation products)-to-isoprene ratio for the dry and wet season for the period of 12:00–15:00 LT

Comments about Liu 2016.

- Ela só mostra os dados horários para um dia de cada caso.
- Senti falta de ver mais time series, que exemplifique a diferença C_4H_7O+ com trap e em by-pass!
- Ela tendo um SRI-PTR-ToF poderia ter reportado resultados com NO+, no qual é possível diferenciar MVK e MACR.

Conclusions

- Switching between low-NO and high-NO regimes has implications in the yield of ISOPOOHs and consequently on the observed differences between wet x dry season for both gas and particulate phases.

- The same is valid for scenarios of Amazonian economic development, where increased emissions of nitrogen oxides are expected -> could alter theses pathways of PM production implying changes to air quality and regional climate.

Obrigada pela atenção!

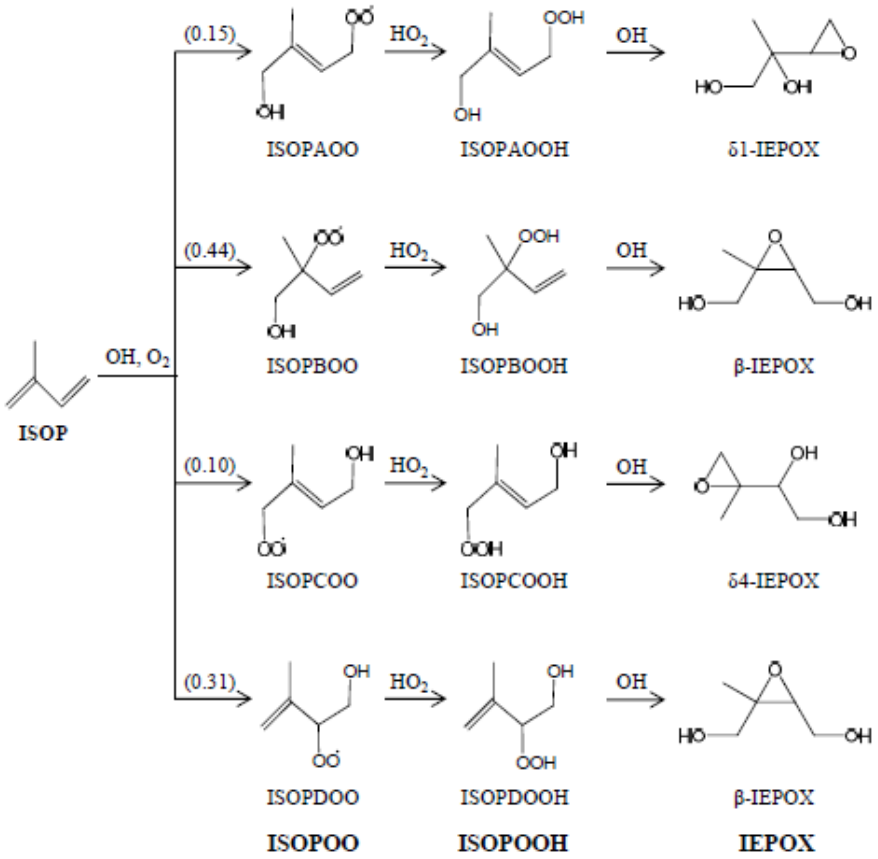
Yingjun Liu et al. PNAS, 2016

Production of methyl vinyl ketone and methacrolein via the hydroperoxyl pathway of isoprene oxidation

Yingjun Liu et al. 2013

Rapid formation of isoprene photo-oxidation products observed in Amazonia

Karl et al. 2009



Mechanism of isoprene oxidation to produce ISOPOOH and IEPOX as represented in MCM v3.2. Branching ratios to specific products are shown in parentheses

Traditional MS technique: Electron Impact (EI)

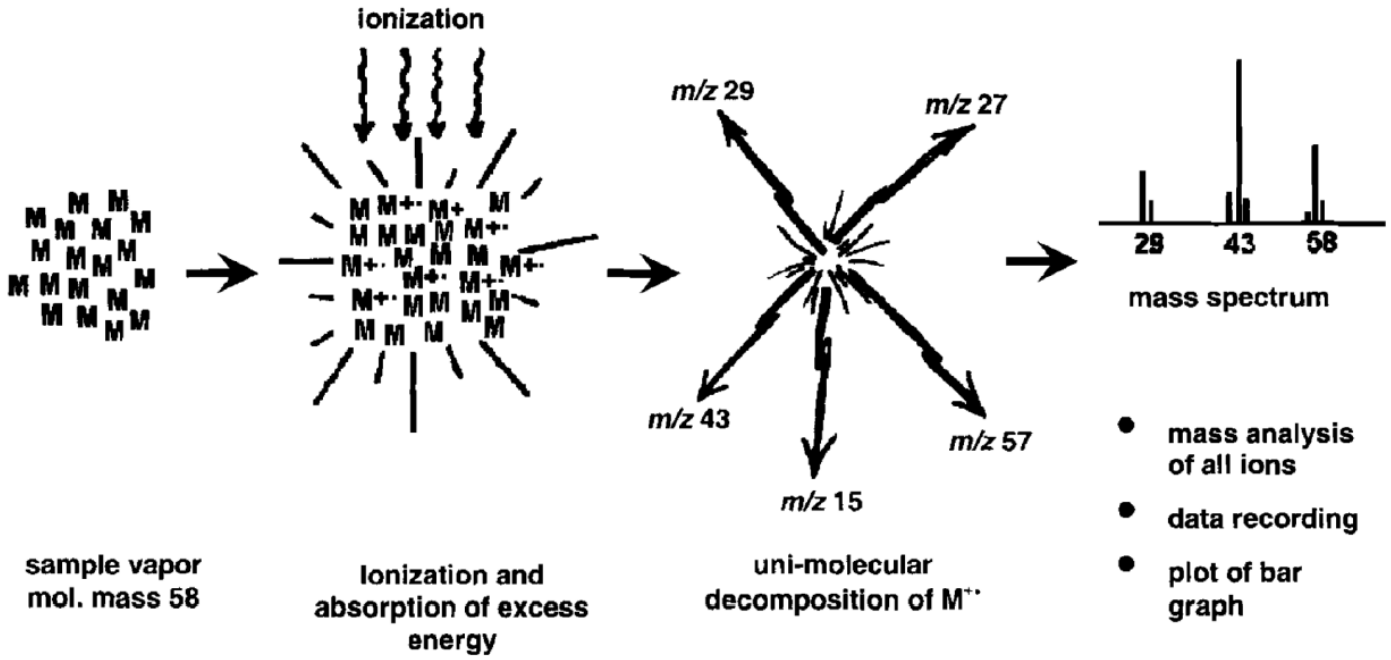
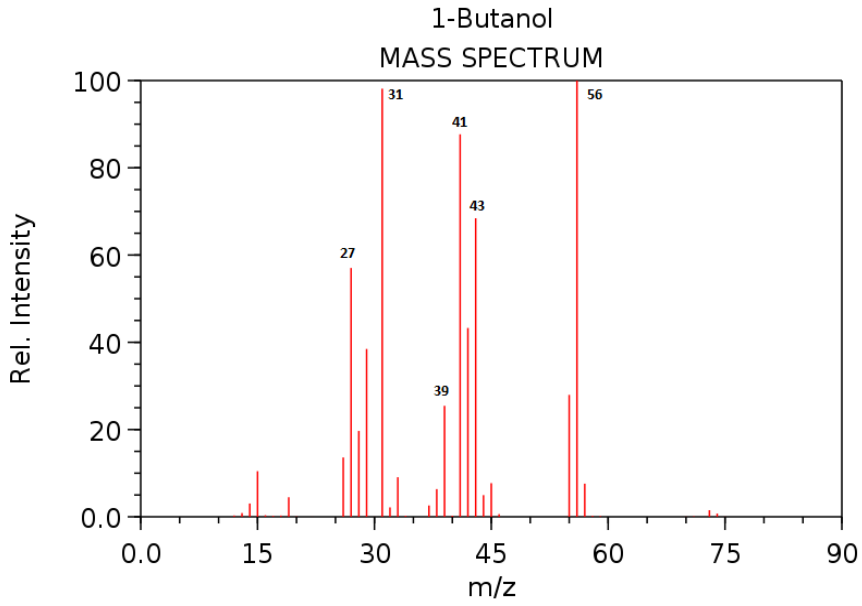
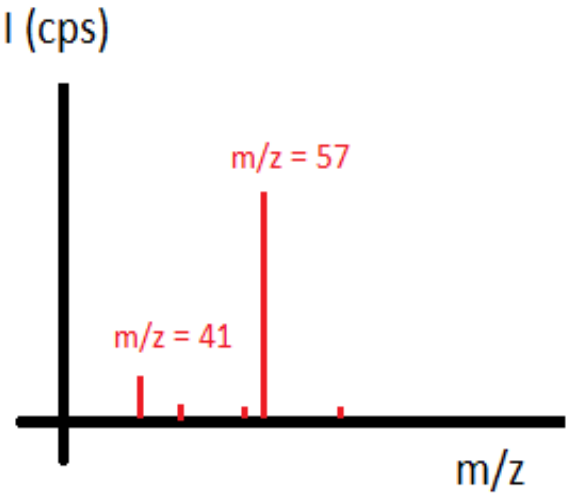


Figure 1-3. Conceptual illustration of gas-phase ionization of analytes followed by ion separation according to the m/z value.

Comparing to EI to PTR

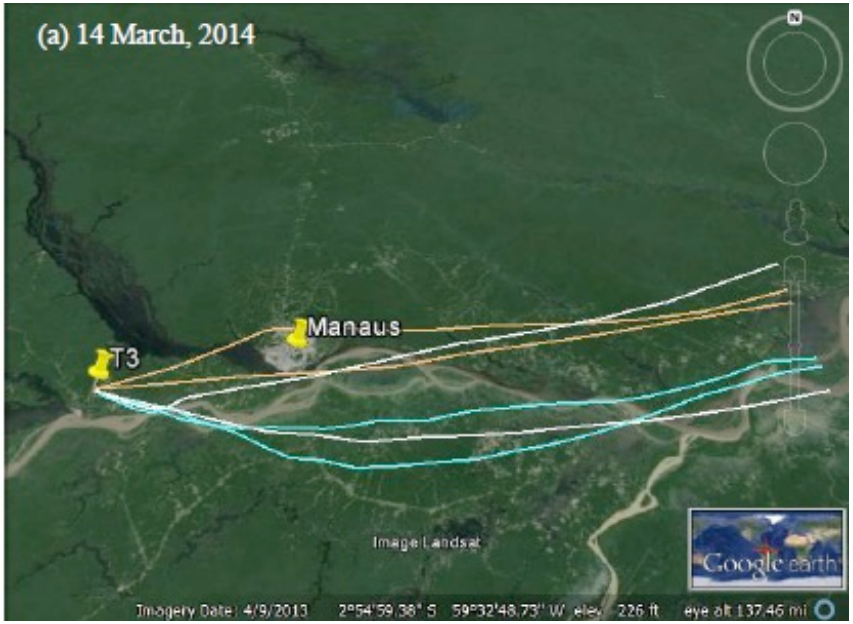


NIST Chemistry WebBook (http://webbook.nist.gov/chemistry)

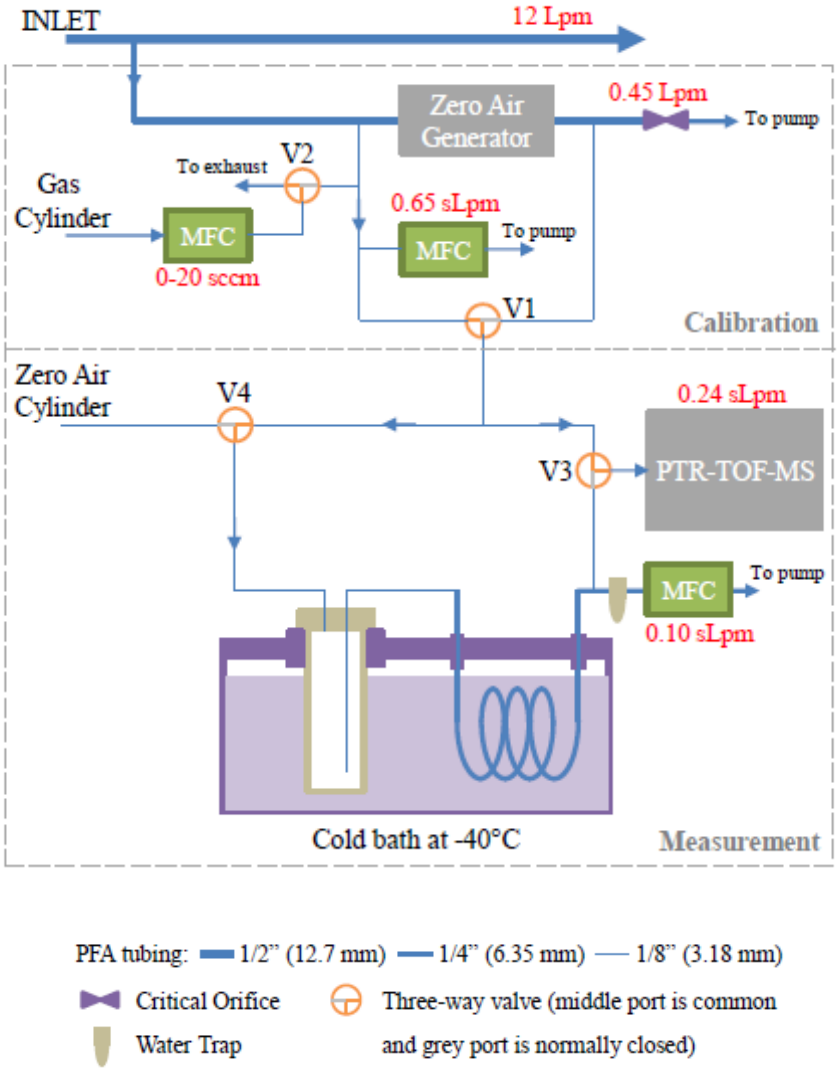


Back-trajectories launched at T3

(a) 14 March 2014 and (b) 30 March 2014.



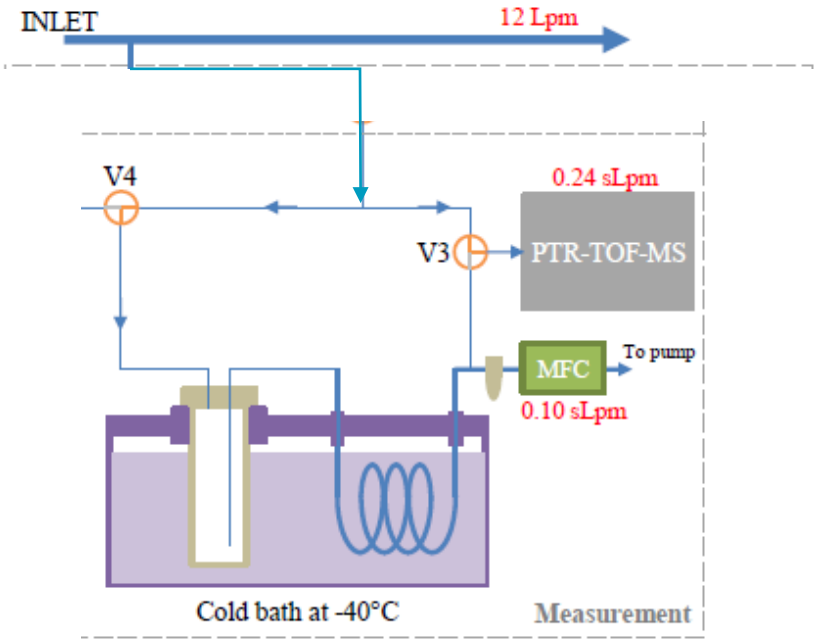
Complete sampling setup



Schematic diagram of the gas inlet system for the PTR-TOF-MS. The top and bottom sections represent calibration and measurement set-ups, respectively.

What we need

- Ozone and NOx monitoring,
- Cold trap,
- PTR calibrations with ISOPOOHs standards,
- Sensibility tests (for MVK and MACR),


INLET
12 Lpm
V4
0.24 sLpm
V3
PTR-TOF-MS
MFC
To pump
0.10 sLpm
Cold bath at -40°C
Measurement