Interconnection of day- and night time chemistry for VOC degradation and SOA formation

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Motivation

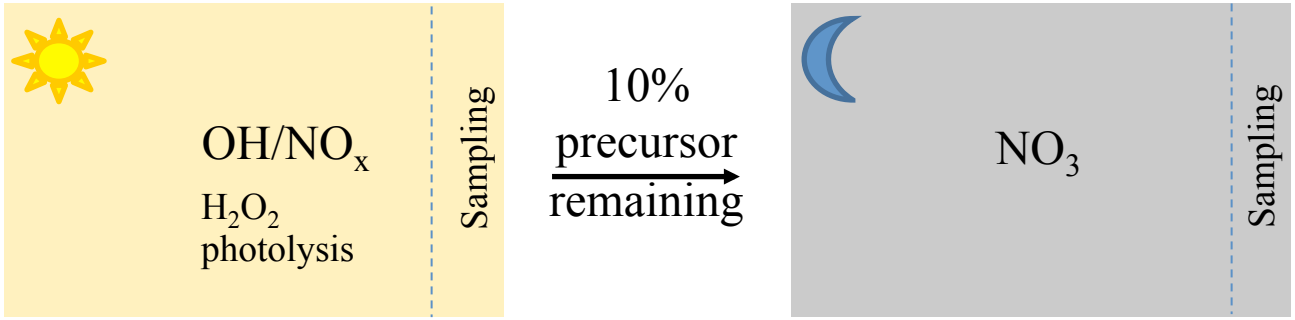
- Day-time chemistry influences subsequent nighttime chemistry and vice versa
  - Compounds emitted during daytime are continuously oxidized by OH or O_3 to form semi-volatile organic compounds
  - In the evening OH radical production drops down -> VOCs/OVOCs that remain in the atmosphere are subjected to the nighttime chemistry
- Day- and nighttime chemistry cannot be considered separately
- Laboratory SOA formation studies have focused on either daytime chemistry (OH, O_3) or nighttime chemistry (O_3, NO_3)
- Project **DARK KNIGHT**: **D**aytime **A**tmosphe**R**ic chemistry of **K**ey compounds provo**K**ed by **NIGHT**time atmospheric chemistry

  -> Simulate **day-night** and **night-day** atmospheric processing in **one single chamber run**

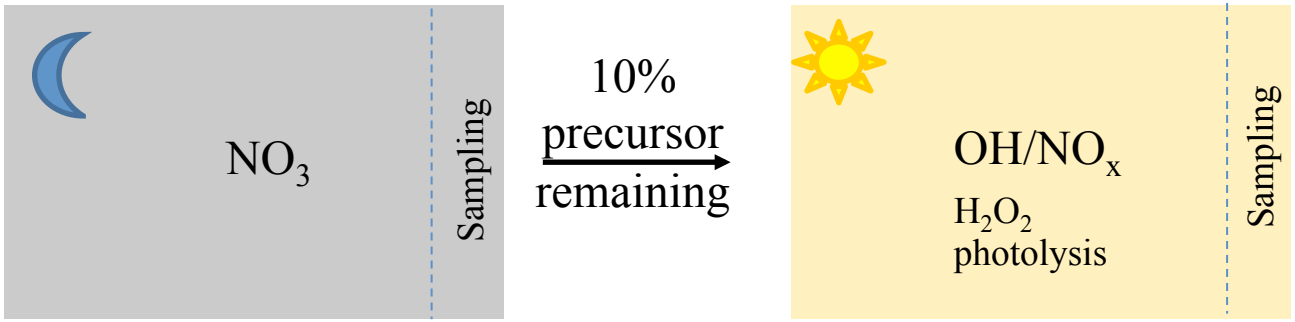
Project idea

Two types of experiments

Typ A



Typ B



Seed: $(NH_4)_2SO_4/H_2SO_4$ pH=4
RH: 0, 50, 75%
Samples: 2 PTFE, 2QF per experiment

Instruments: PTR-TOFMS, C-TOF, SMPS, AMS
Precursors: a-pinene, limonene and **m-cresol** (60 ppb)

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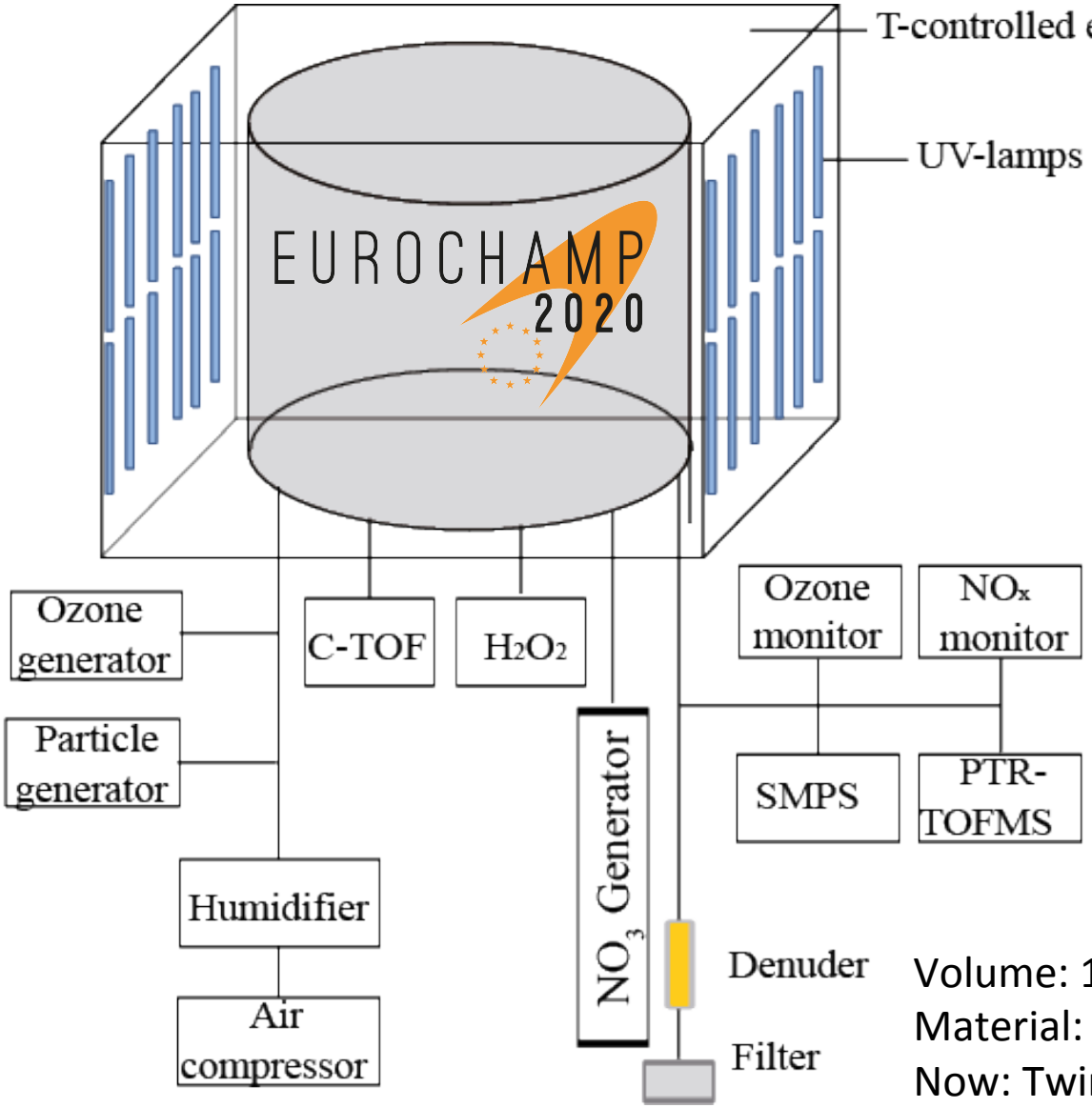
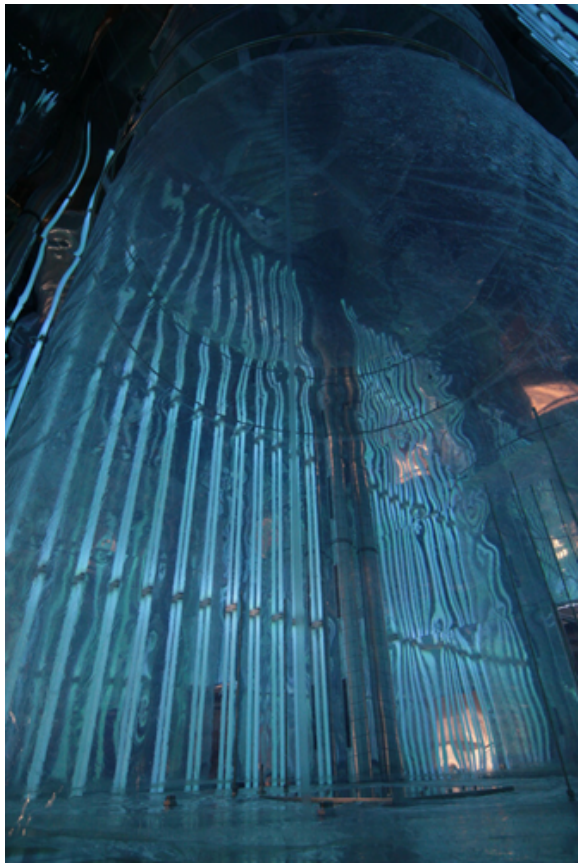
Experimental Set-up





Volume: 19m3
Material: Teflon FEP 500A
Now: Twin chamber

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Cresol Experiments

	Typ	Precursor	RH [%]	pH	Hc_{ini} [ppb]
#1	Day 0%	m-Cresol	0%	4	60
#2	Day 50%	m-Cresol	50%	4	60
#3	Day 75%	m-Cresol	75%	4	60
#4	Night 0%	m-Cresol	0%	4	60
#5	Night 50%	m-Cresol	50%	4	60
#6	Night 75%	m-Cresol	75%	4	60
#7	Day-Night 0%	m-Cresol	0%	4	60
#8	Day-Night 50%	m-Cresol	50%	4	60
#9	Day-Night 75%	m-Cresol	75%	4	60
#10	Night-Day 0%	m-Cresol	0%	4	60
#11	Night-Day50%	m-Cresol	50%	4	60
#12	Night-Day75%	m-Cresol	75%	4	60
#13	Photolysis	m-Cresol	0%	4	60
#14	Wall loss	m-Cresol	0%	No seed	60
#15	Typ A Blank			4	60
#16	Typ B blank			4	60

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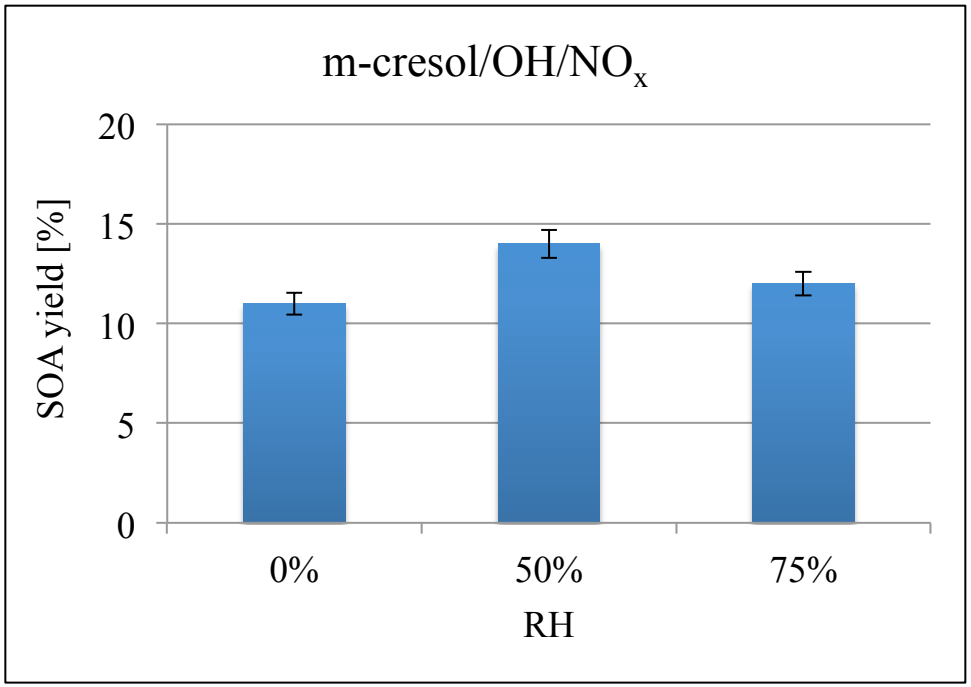
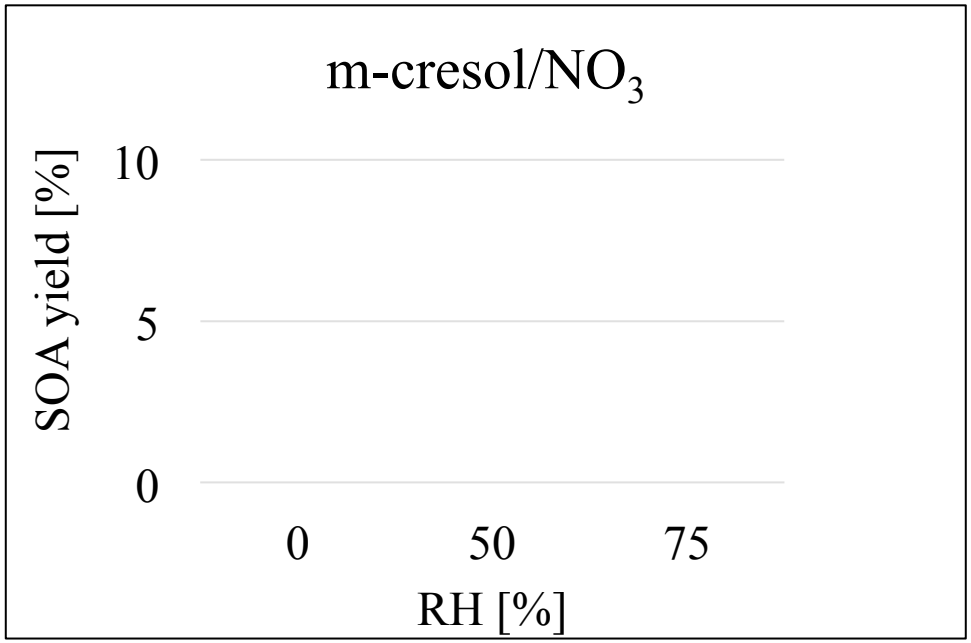
SOA yield



- SOA yields are in the same range
- No effect of RH observed
- Higher SOA yield from Nakao et al., -> absence of NO_x

m-cresol/OH		
SOA yield	Reference	Comment
11 – 14 %	**This work**	**H_2O_2/NO (no RH dependency)**
4.9	Iinuma et al., 2010	CH_3ONO/NOx
27 – 31	Nakao et al., 2011	H_2O_2

SOA yield



- **No Data** are reported from m-cresol+NO_3
- No SOA produced -> oxidation forms mainly gas-phase oxidation products

cresol/NO_3		
SOA yield	Reference	Comment
0	**This work**	

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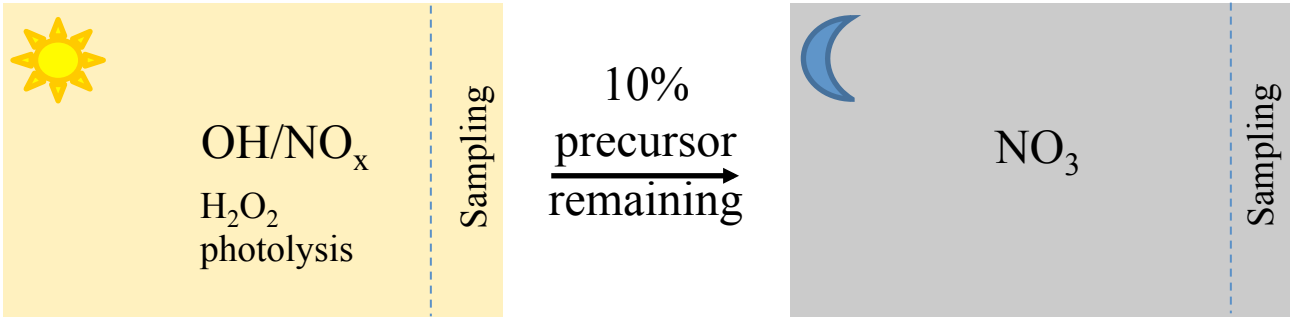
Typ A


OH/NO$_x$
H_2O_2
photolysis
Sampling
10%
precursor
remaining
NO$_3$
Sampling

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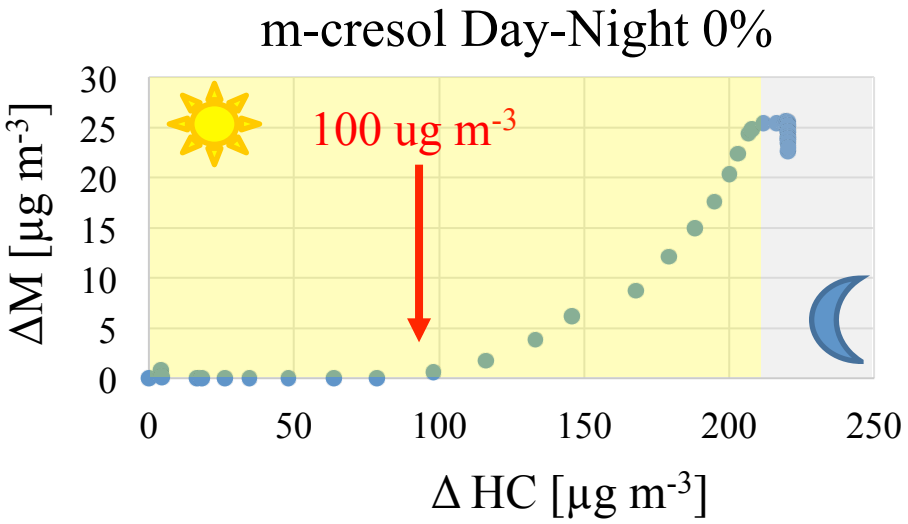
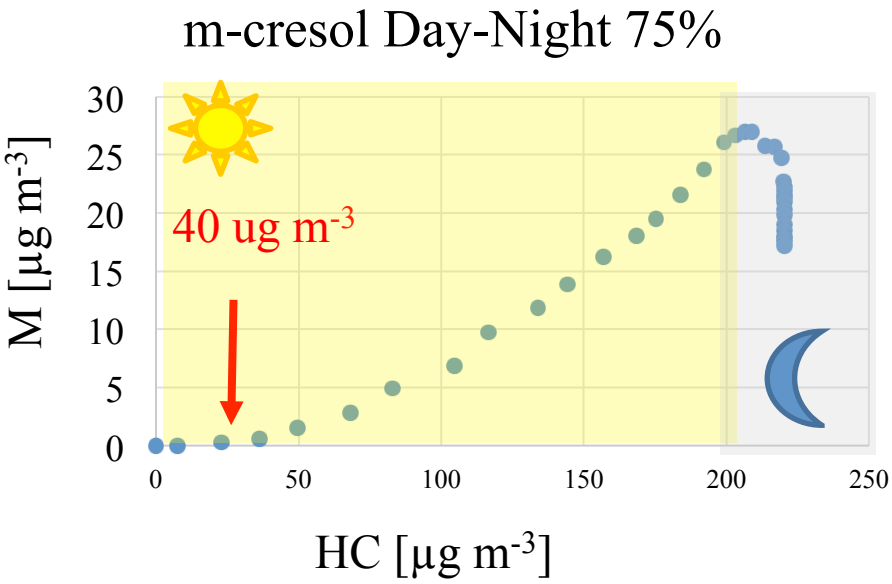
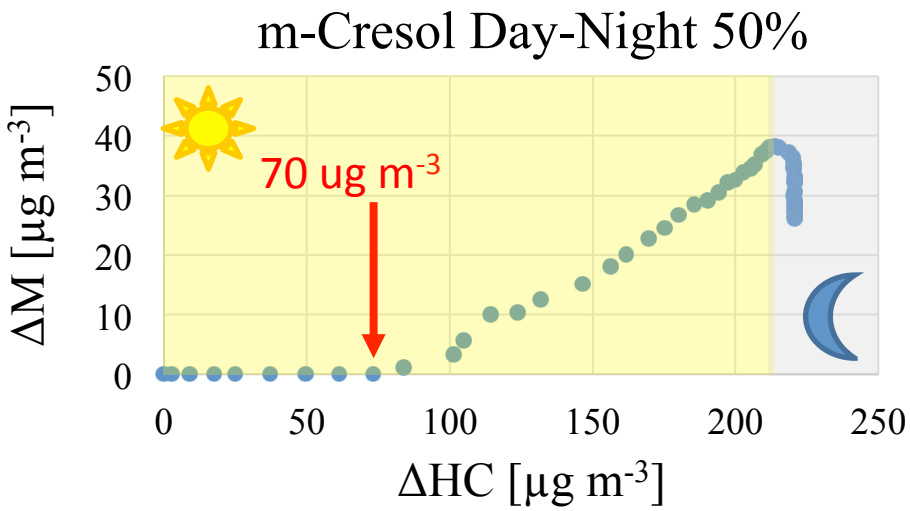
SOA formation DAY-NIGHT







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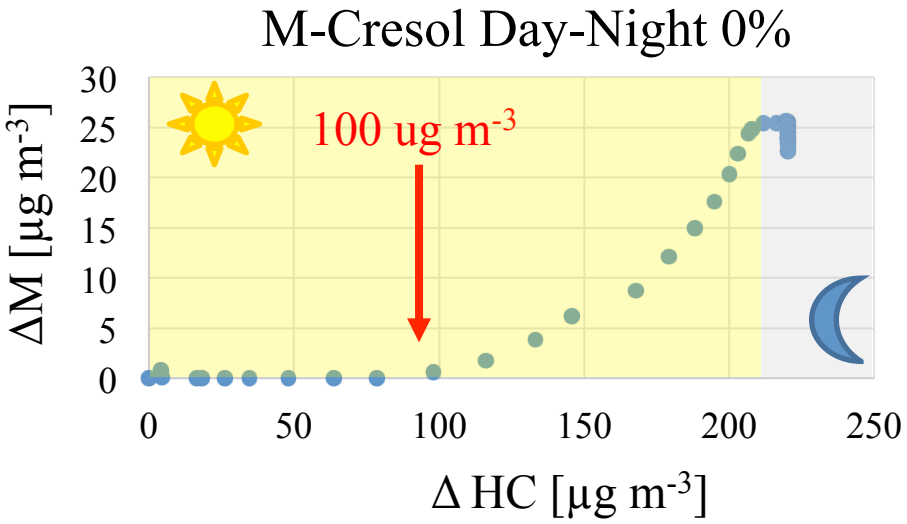
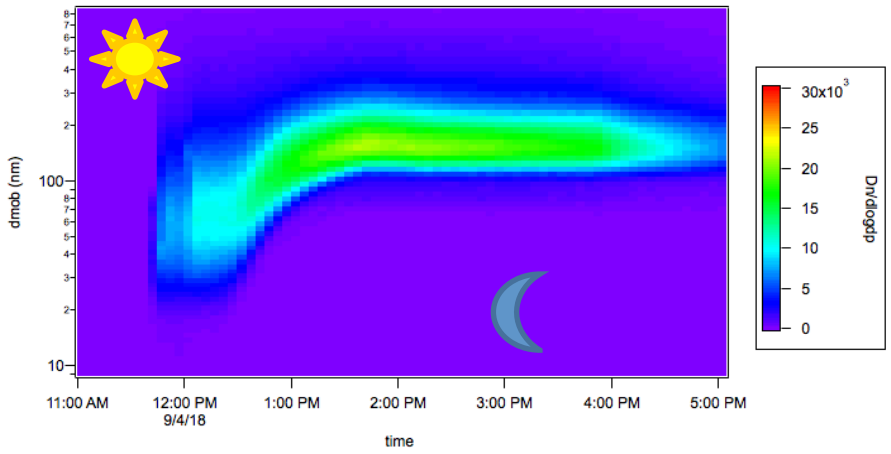
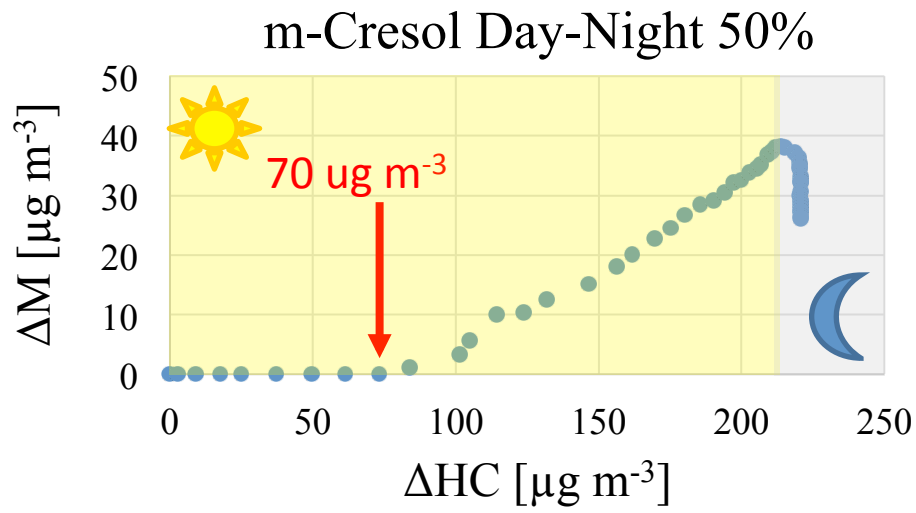
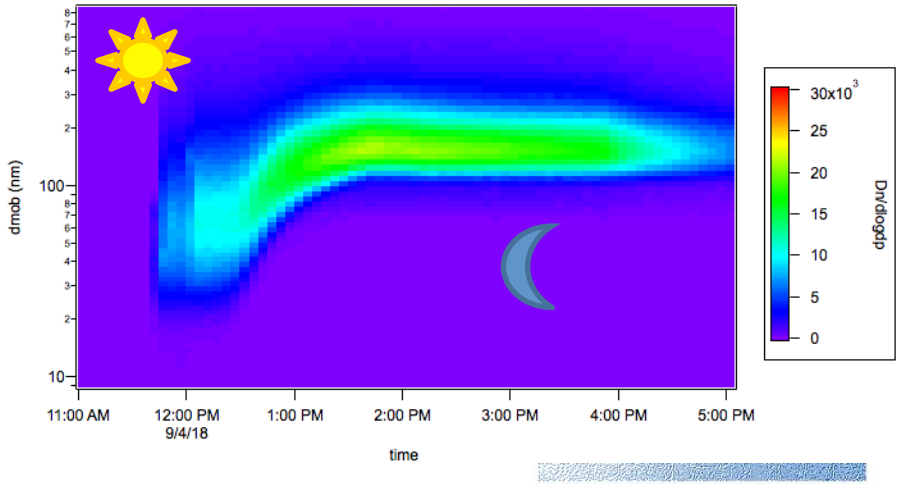
SOA formation DAY-NIGHT

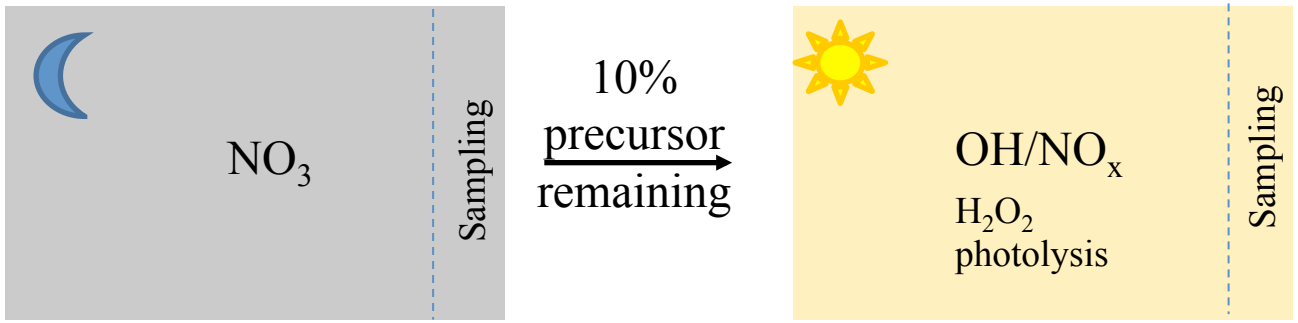


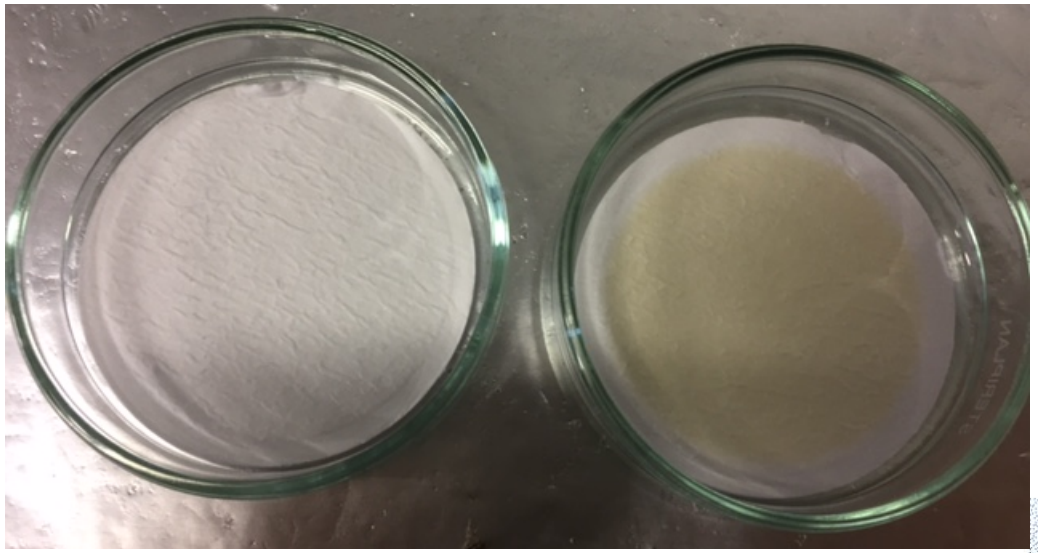






Typ B


NO_3
Sampling
10%
precursor
remaining
OH/NO_x
H_2O_2
photolysis
Sampling



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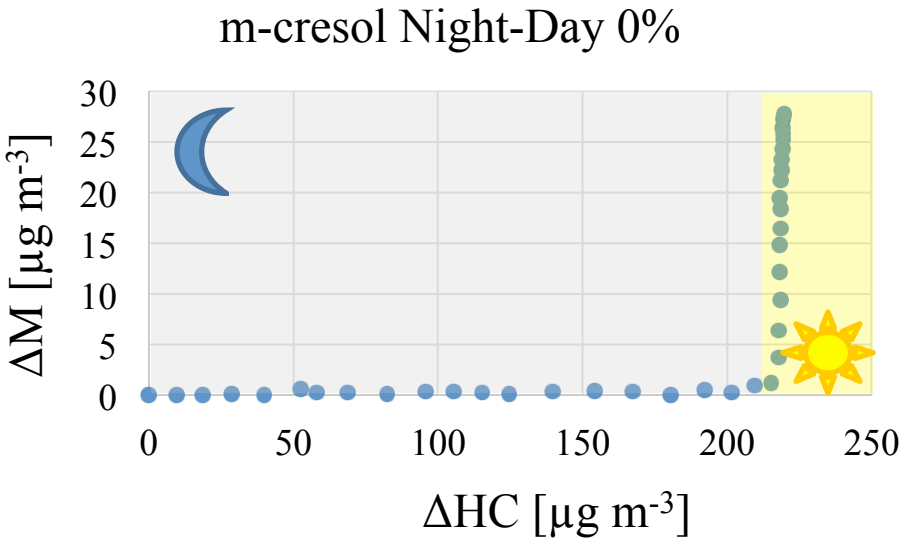
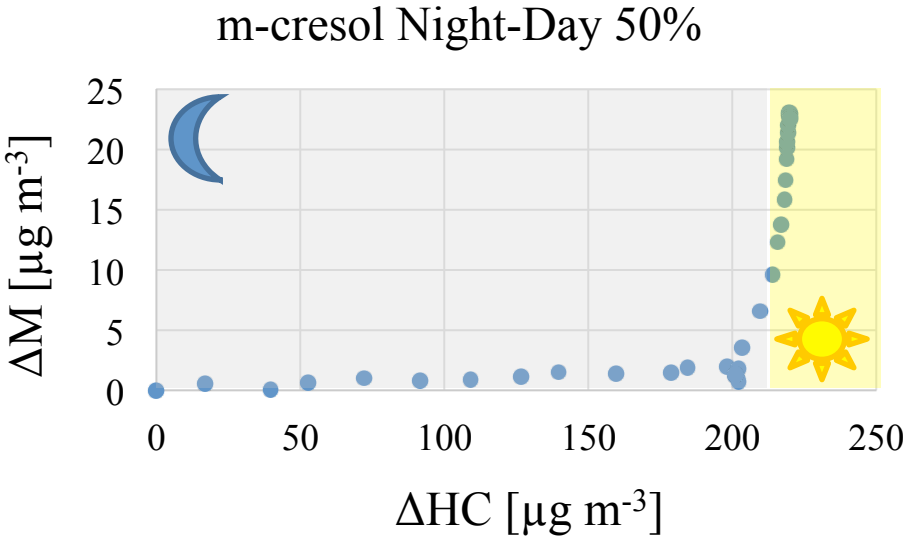
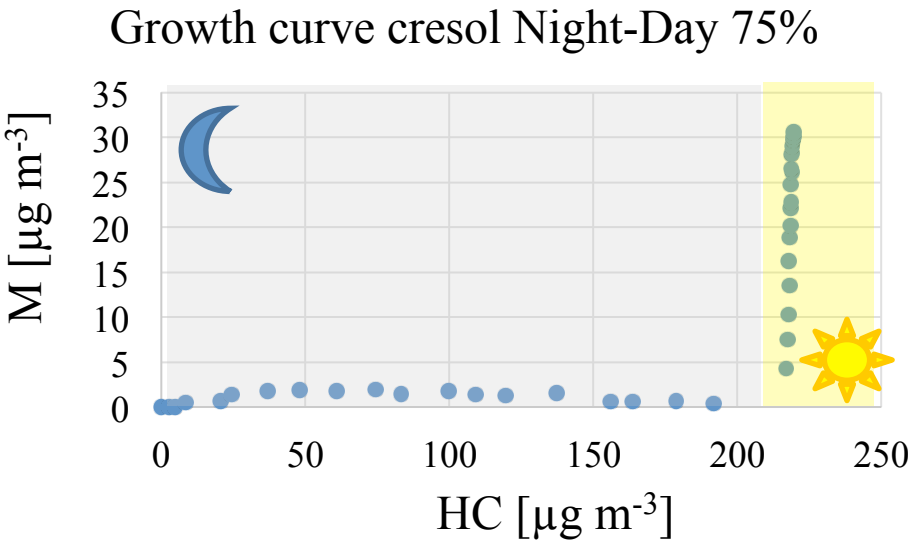
SOA formation NIGHT-DAY







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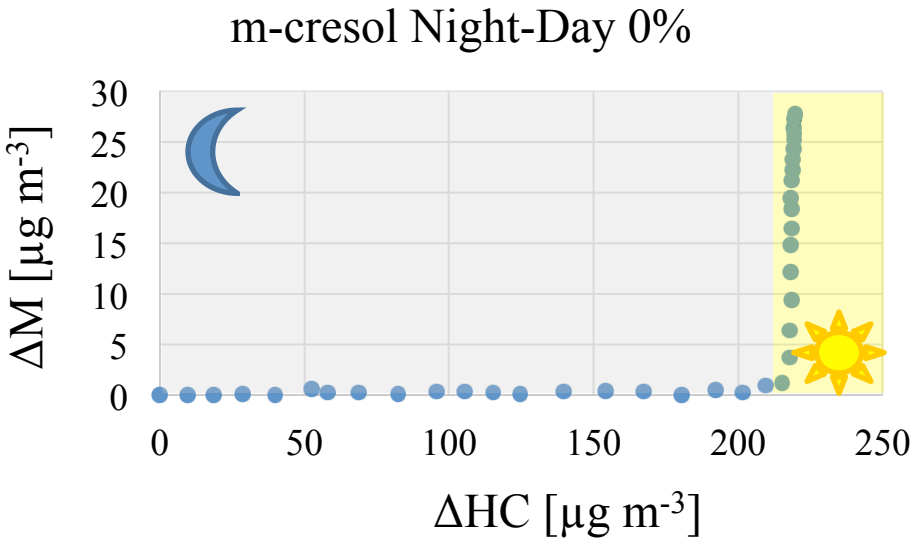
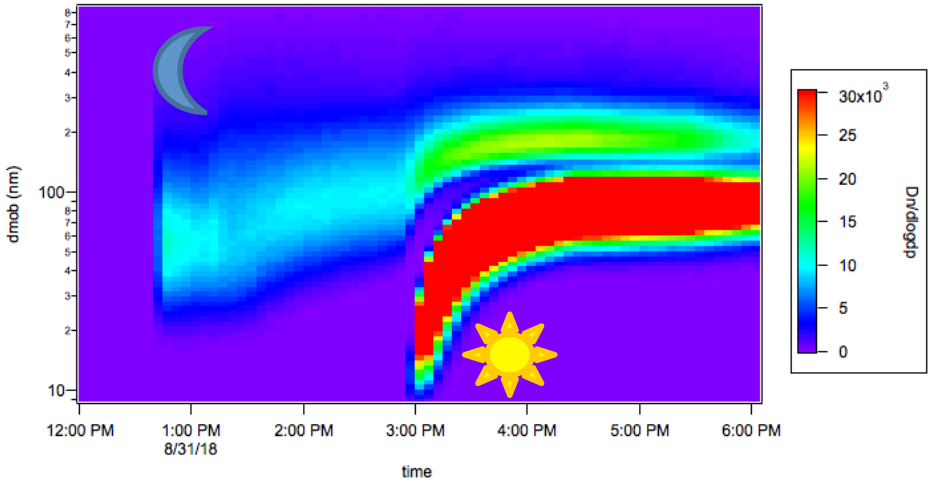
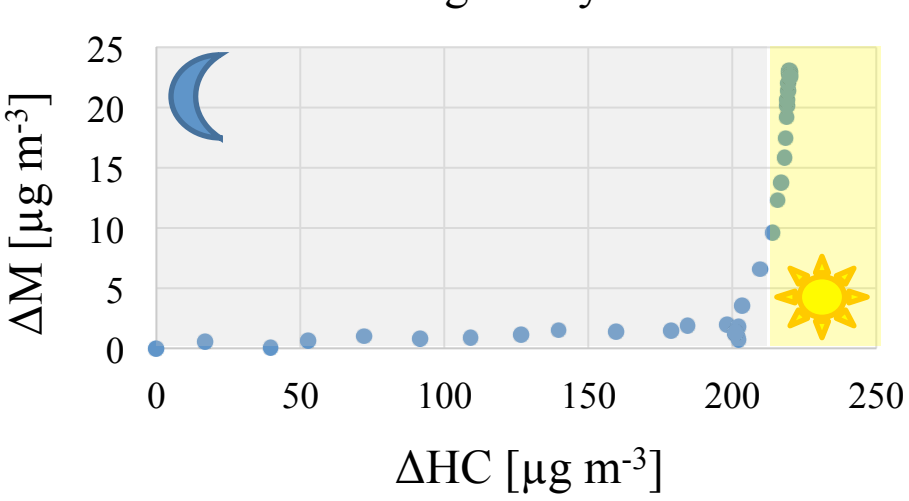
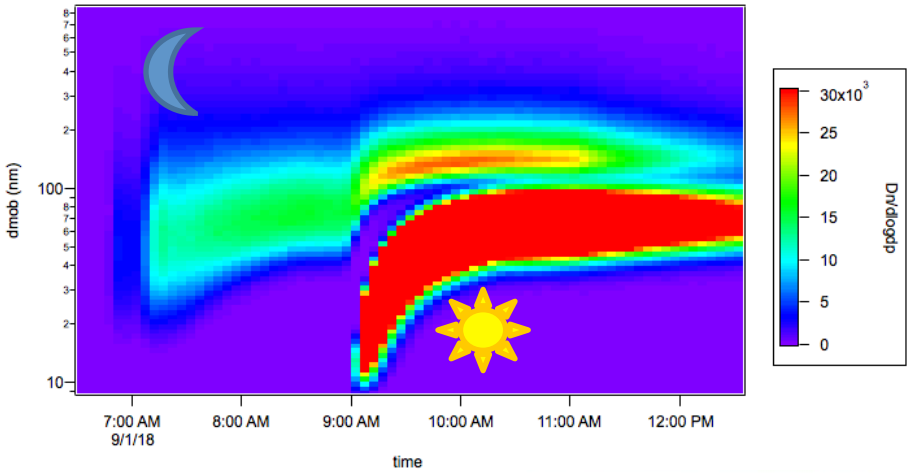
SOA formation NIGHT-DAY

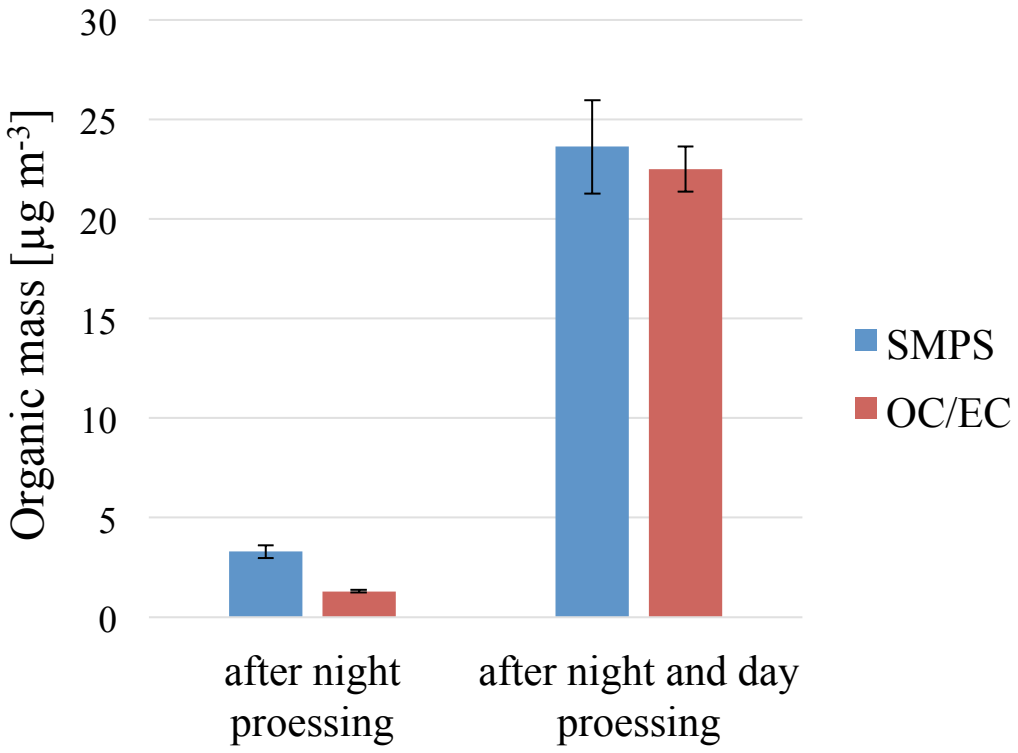








OM from OC/EC vs. SMPS



- Only small differences between SMPS and OC/EC measurements
- Contribution of inorganic NO_3 should be very small (<3%)
- Increase of ΔM is caused by partioning of organic compounds

Gas-phase chemical composition → **PTR-TOF/MS**
CI-APi-TOF/MS

Particle-phase chemical composition → **HPLC/(-)-ESI-TOF/MS**
Iodometric peroxide test
UPLC/HR-MS

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Results from CI-APi-TOF

Analysis of C-TOF data 150 m/z

→

Check temporal profiles
Apply selection criteria

→

44 Signals for data analysis

↓

7 signals show a strong correlation to ΔM (*m/z* 168, 169, 194, 197, 198, 231, 263)

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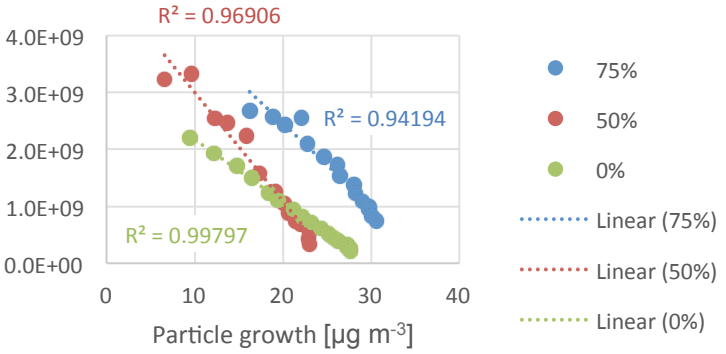
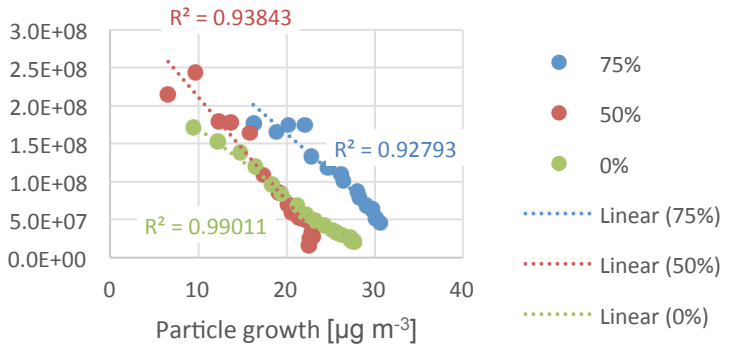
Correlation between gas-phase compounds and particle growth

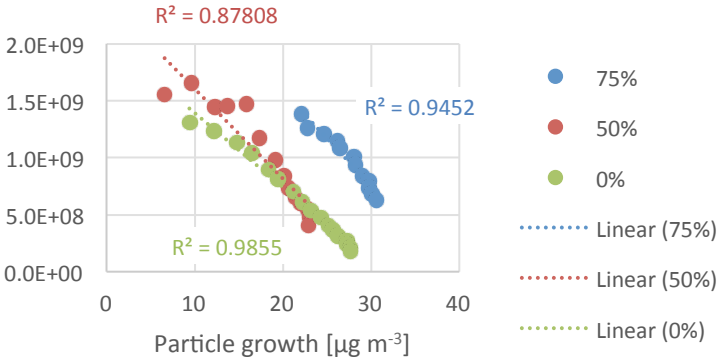
m/z 168



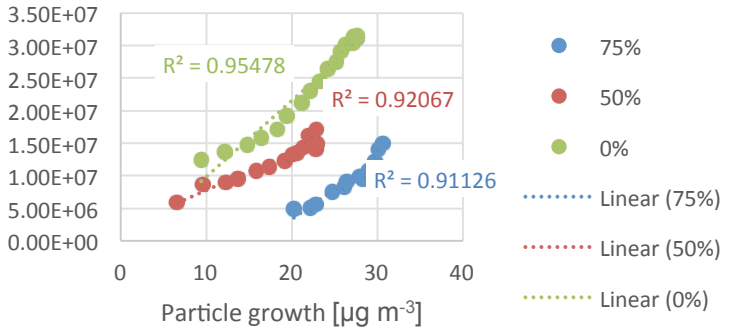
m/z 197



m/z 231



m/z 263



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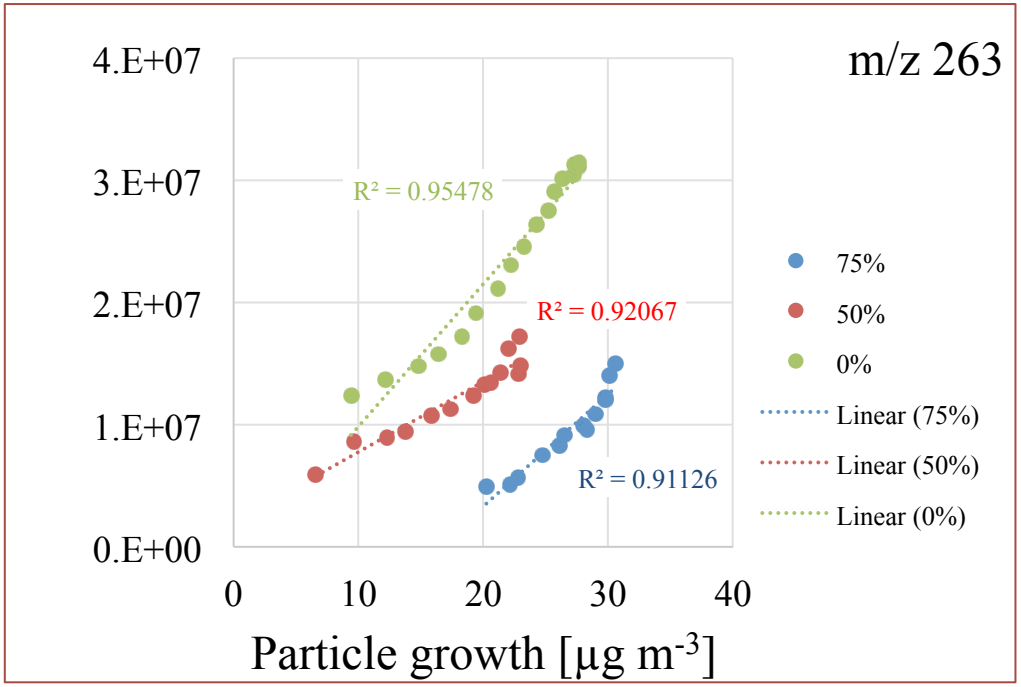
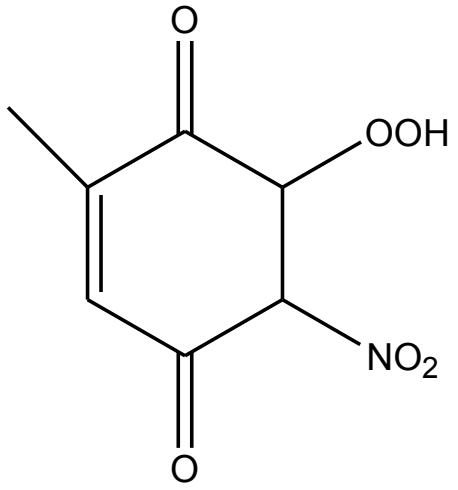
m/z 263 – $C_7H_7O_6N$



Adopted from Schwantes et al., 2017



$C_7H_7NO_6$
Exact Mass: 201.03

- *m/z* 263 -> $C_7H_7O_9N_2$ as NO_3 cluster
- Assuming a mono cluster -> the mass would correspond to $C_7H_7O_6N$ (Organonitrate)
- This seems to be solely formed from OH/NO_x system
- Methyl-benzoquinone has to be the precursor
- Several masses seems to correlate -> related structure

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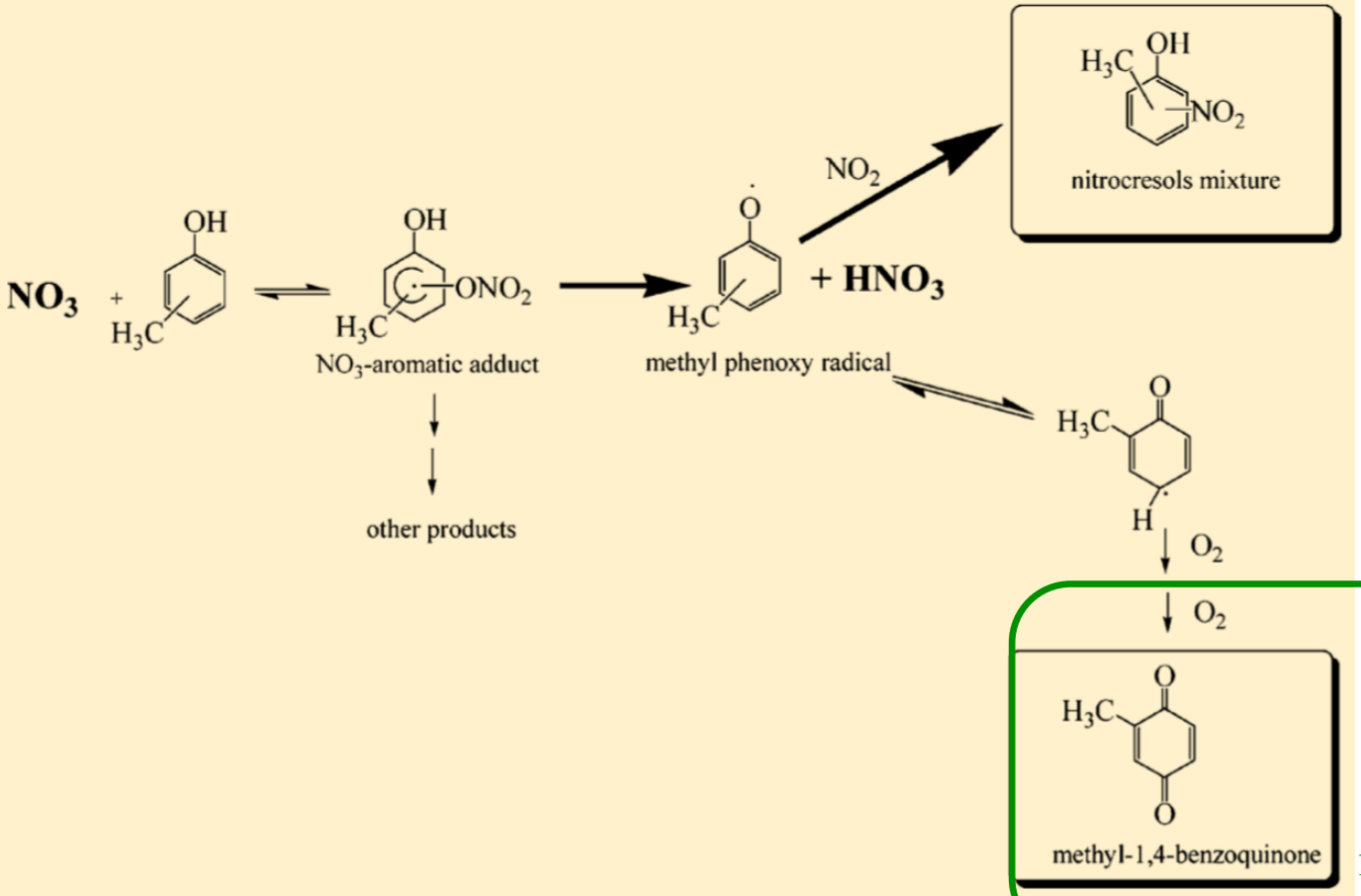
Generalized mechanism

Benzoquinone formation described by Olariu et al., 2013 and Schwantes et al., 2017



PTR-TOFMS
m/z 123 $[M+H]^+$
$C_7H_6O_2$
Only cdetected from night-day processing

Olariu et al., 2013

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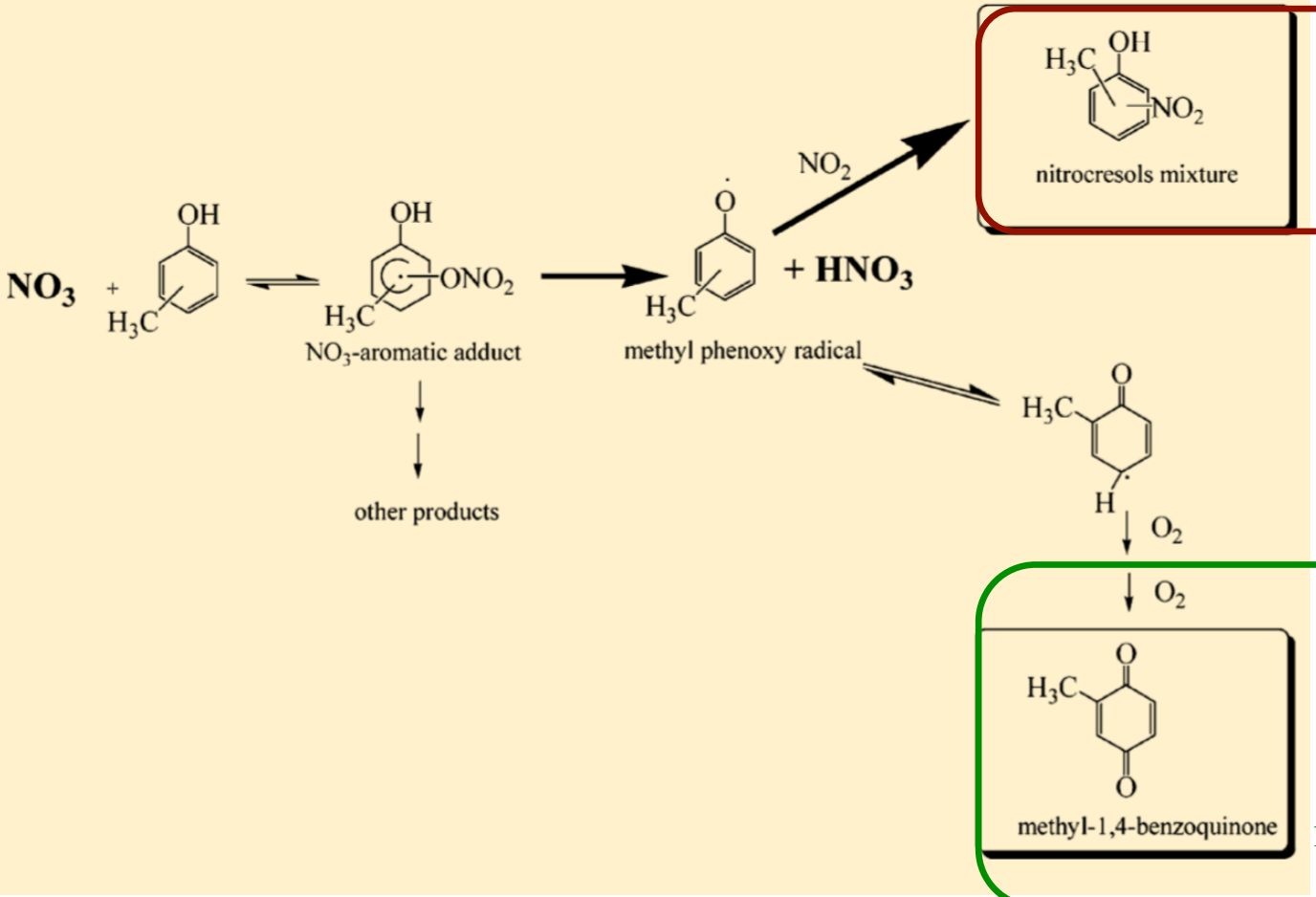
Generalized mechanism

Benzoquinone formation described by Olariu et al., 2013 and Schwantes et al., 2017



Products detected related to the cresol structure?

PTR-TOFMS
m/z 123 $[M+H]^+$
$C_7H_6O_2$
Only cdetected from night-day processing

Olariu et al., 2013

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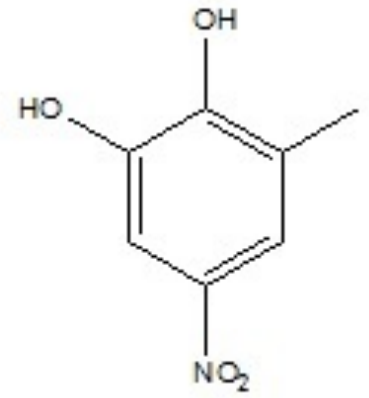
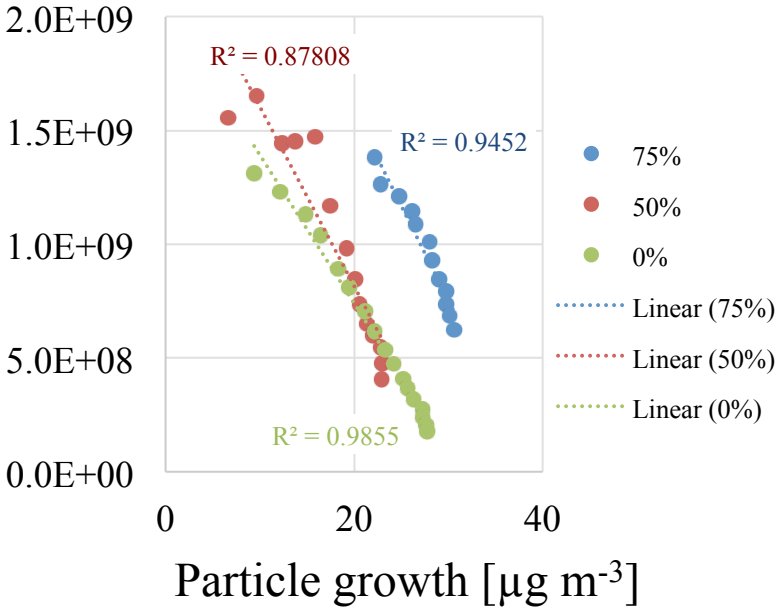
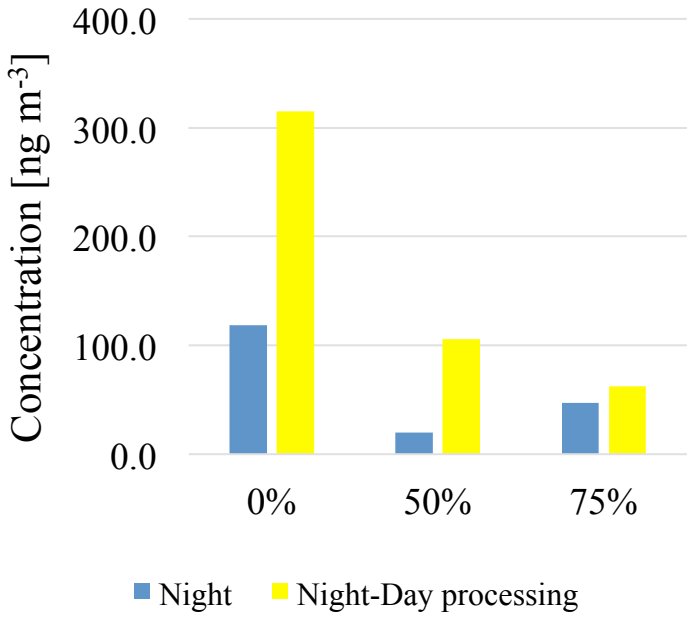
m/z 231 – $C_7H_7NO_4$

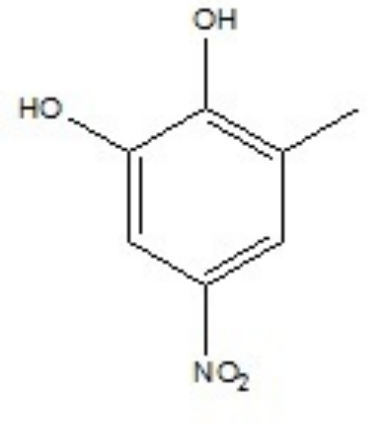


- *m/z* 231 - $C_7H_7NO_4$
- Strong correlation to particle growth
- Detected from filter analysis
- Concentration increases during processing
- BUT: much lower than from day-night processing (1600 ng m^{-3})



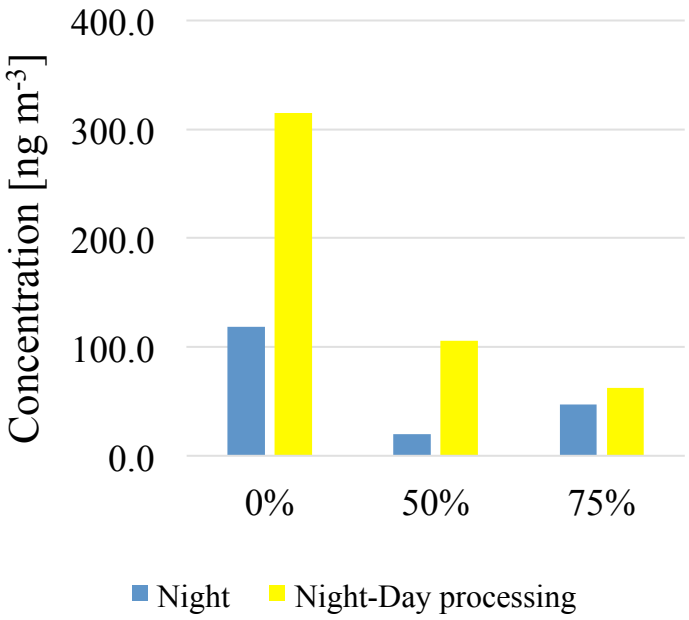


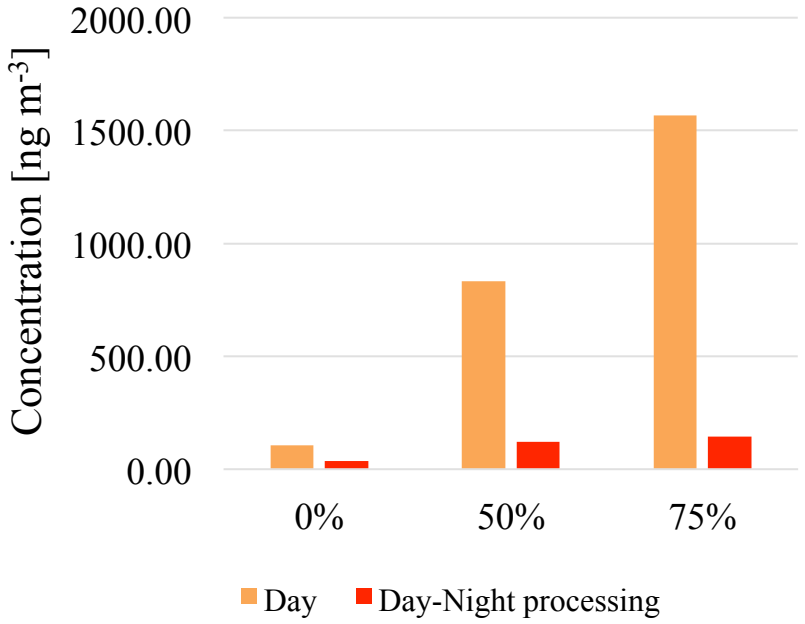
m/z 231 – $C_7H_7NO_4$



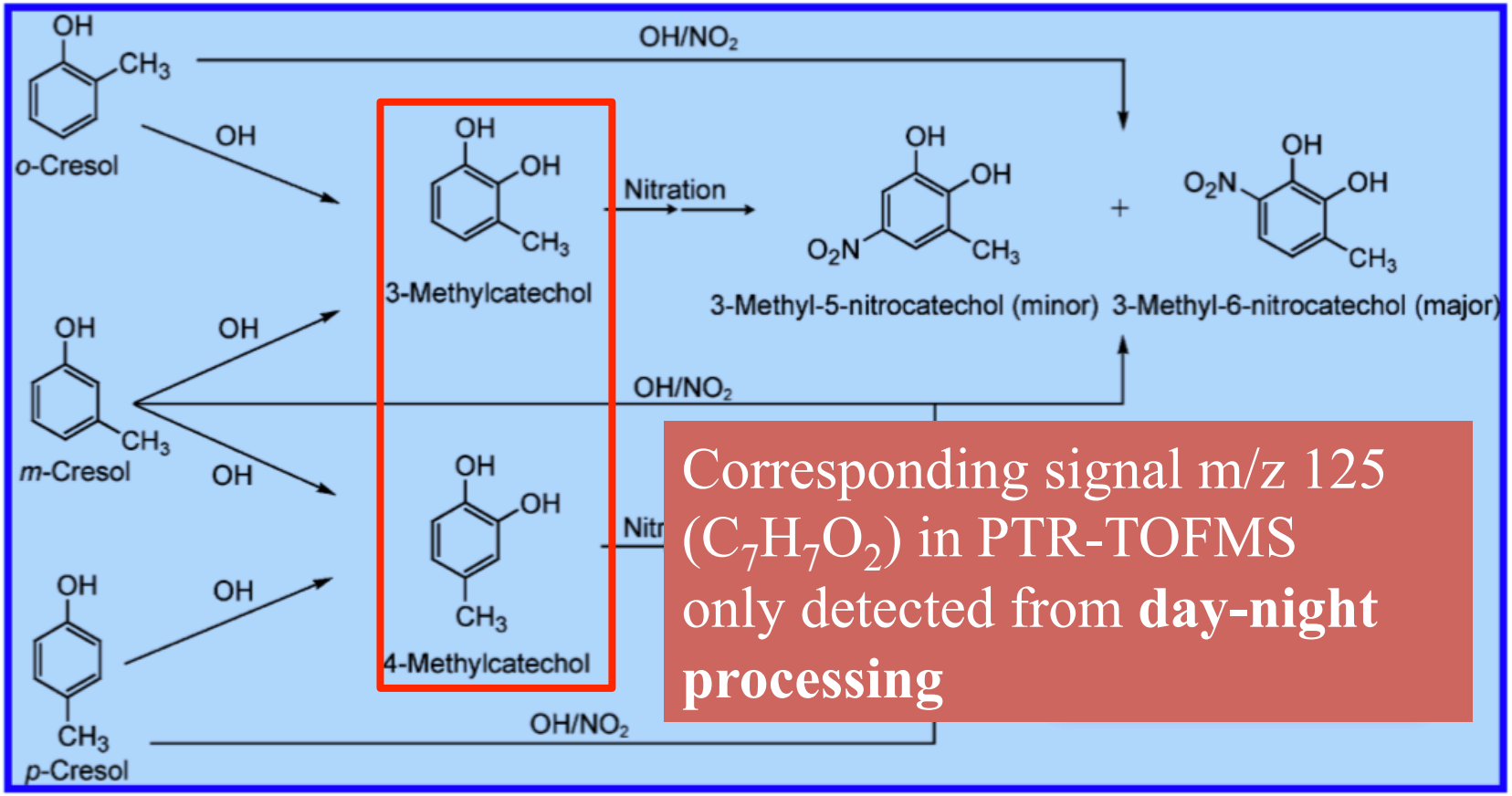
Methyl-nitro-catechol

- m/z 231 - $C_7H_7N_2O_7$
- Strong correlation to particle growth
- Detected from filter analysis
- Concentration increases during processing
- BUT: much lower than from day-night processing (1600 ng m^{-3})





Methyl-Catechol as precursor



Corresponding signal m/z 125 ($C_7H_7O_2$) in PTR-TOFMS only detected from **day-night processing**

Iinuma et al., 2013

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Summary

Compounds derived from **nitro-cresol structure**

- Correlate to particle growth
- Concentration after **day-night** processing much larger
- tentative precursor methyl-catechol only observed from day-night prossing

  ➔ cannot explain nucleation events as formation is more pronounced under day-night-processing

Compounds with **benzoquinone structure**

- Methyl-benzoquinone detected in gas-phase from **night-day** processing
- Under night conditions an Organonitrate ($C_7H_7O_6N$) is detected that strongly correlates with particle growth

  ➔Methyl-benzoquinone acts as reservoir compound for ON that might initalize a massive secondary formation of organic mass while changing from night to day time processing

Conclusion

- Day-Night simulation within one chamber run conducted for the first time
- Secondary formation of organic mass during night-day processing of m-cresol
  - ➔ Methyl-benzoquinone might act as reservoir compounds that is formed during NO_3 radical reaction and further processed under day time conditions
  - ➔ might be related to the occurence of $C_7H_7NO_6$

- Observed secondary mass production might be highly relevant as anthropogenic VOCs are often emitted in the evening hours

Outlook

- Oxidize methyl-benzoquinone with OH/NO_x and NO_3
  - ➔Formation of $C_7H_7NO_6$
  - ➔Nucleation event?
  - ➔confirm data with AMS

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Thank you for your attention!

DFG Deutsche Forschungsgemeinschaft
German Research Foundation
HE 3086/25-1

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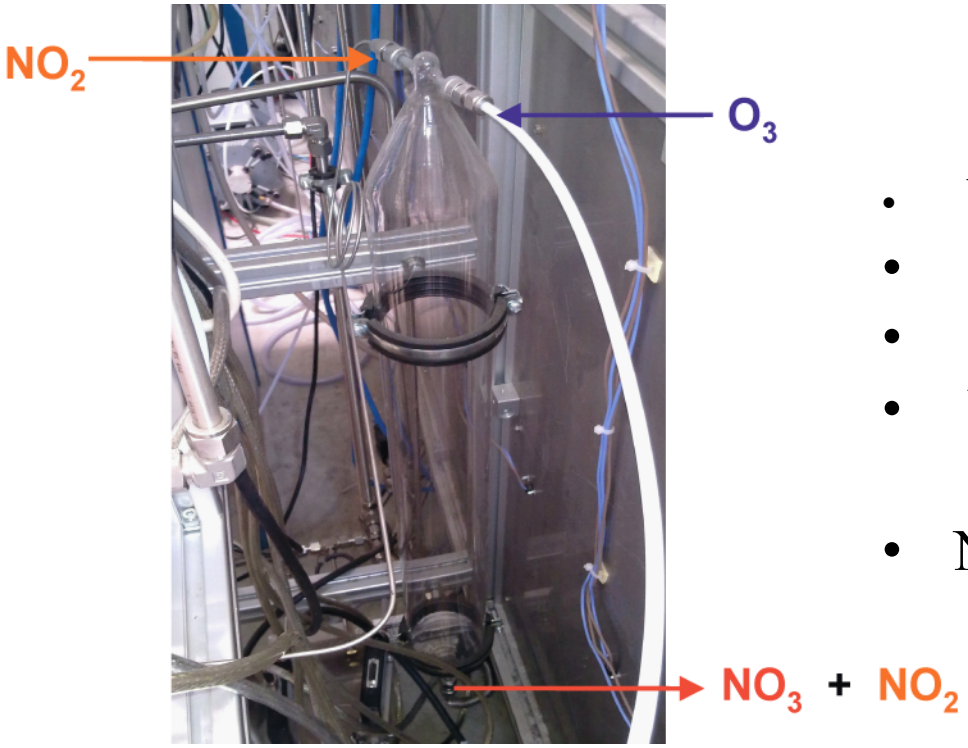
NO_3-Radical Production at LEAK



- NO_3 generation in a pre-reactor
- Volume of the reactor ~ 6.5 L
- Residence time ca. 12 min
- NO_3 / N_2O_5 production rate in chamber: ~ 30 ppb/h
- No O_3 in LEAK

Pre-reactor for the generation of nitrate-radicals at LEAK.

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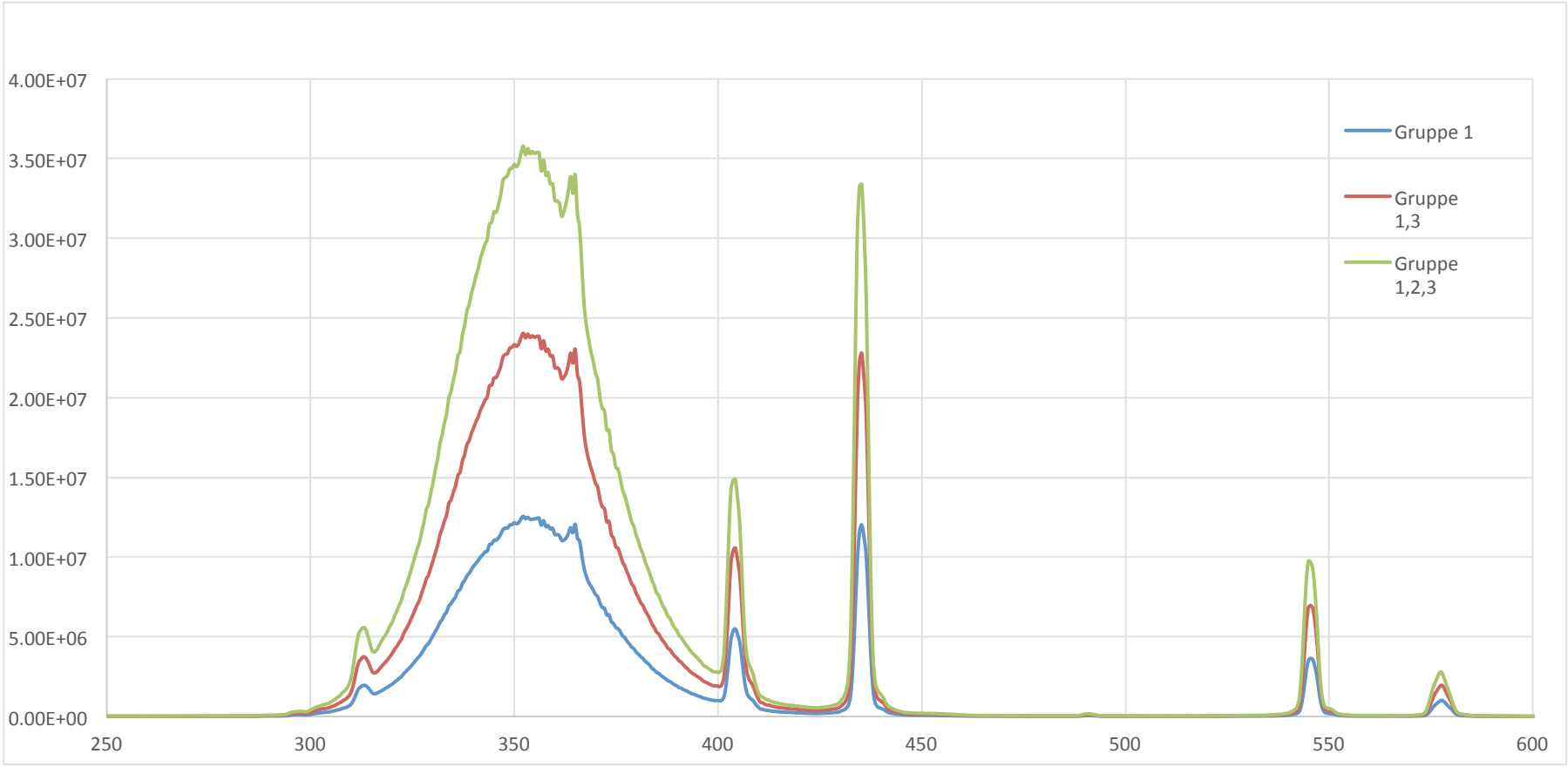
4.00E+07
3.50E+07
3.00E+07
2.50E+07
2.00E+07
1.50E+07
1.00E+07
5.00E+06
0.00E+00
250
300
350
400
450
500
550
600
Gruppe 1
Gruppe 1,3
Gruppe 1,2,3

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