On the Formation and Detection of (Nitrooxy-)Organosulfates in Organic Aerosol Particles

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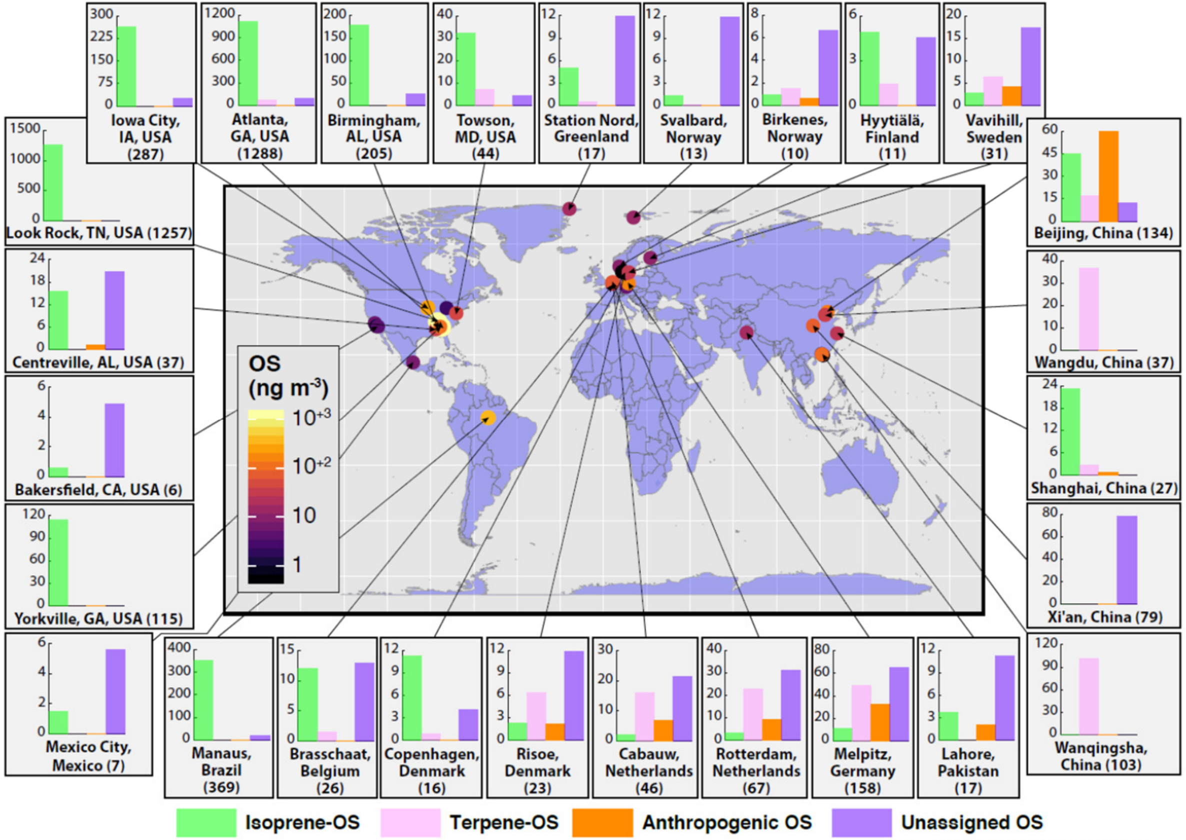
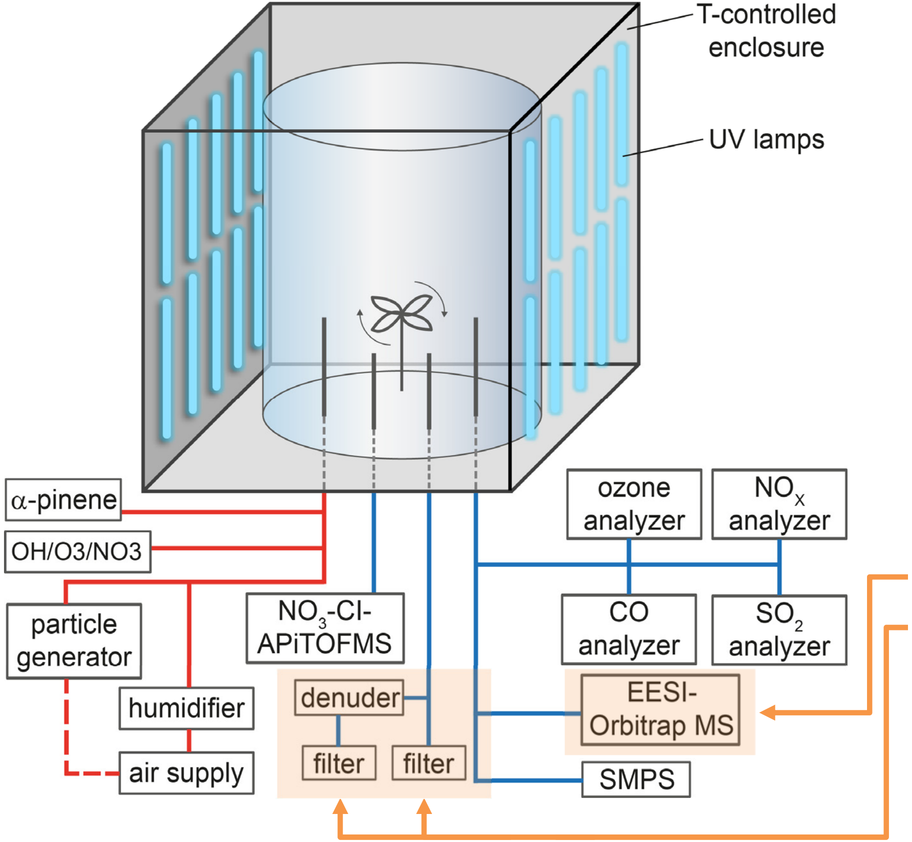
Organosulfates in Ambient Aerosol

- general formula: **R–OSO$_3$H**
- ubiquitously abundant in SOA
- formed via **acid-driven multiphase reactions** between reactive organic compounds (e.g., epoxides, carbonyls) and acidic sulfate aerosol (Iinuma et al., 2007b, 2007a, Surratt et al., 2008, 2010)
- recent reports suggest further **formation pathways via SO$_2$** (Ye et al., 2018, Wang et al. 2019, Yao et al., 2019)
- aerosol **acidity and liquid water content** were shown to play a key role in OS formation (McNeill, 2015; McNeill et al., 2012)



Brüggemann *et al.*, ES&T 2020: https://dx.doi.org/10.1021/acs.est.9b06751

Experimental

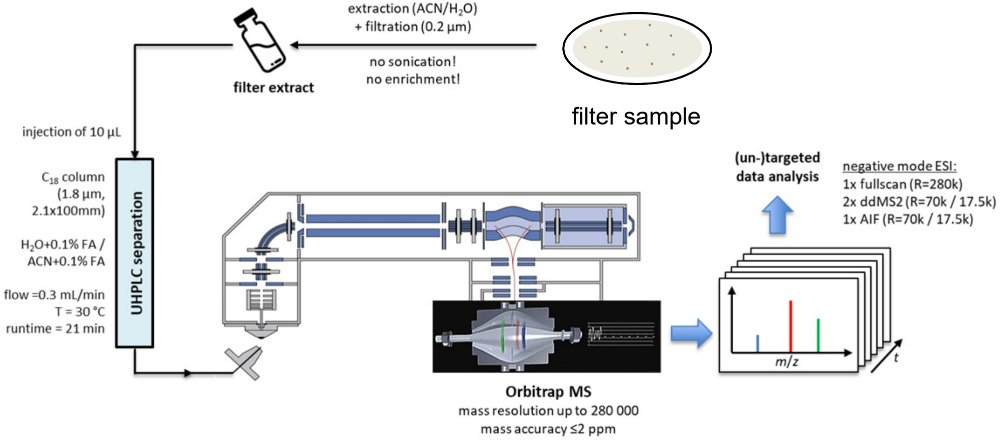


- experiments run in the TROPOS ACD chamber (ACD-C): Volume = 19 m^3; RH = 55%; T = 20 °C
- α-pinene = 60 ppb; SO_2 = 15 ppb; NO = 15 ppb
- daytime chemistry: ~4.2×10^6 OH cm^{-3}
- nighttime chemistry: ~1.8×10^9 NO_3 cm^{-3}
- ozonolysis: O_3 ~ 100 ppb
- seeds: $Na_2{}^{34}SO_4$ / H_2SO_4 in different ratios to vary pH (1.2 … 7)
- all experiments in continuous mode (flow = 190 LPM)

- **EESI-Orbitrap MS for online detection of (N)OSs**
- **parallel filter sampling with and without a denuder to remove gas-phase SO_2**

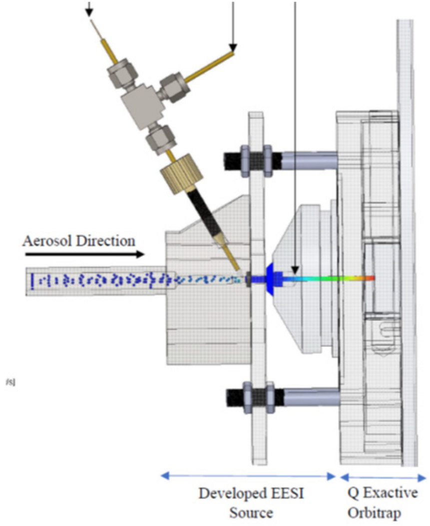
particle analysis by EESI-Orbitrap MS & LC-Orbitrap MS

LC-Orbitrap analysis of filter samples:



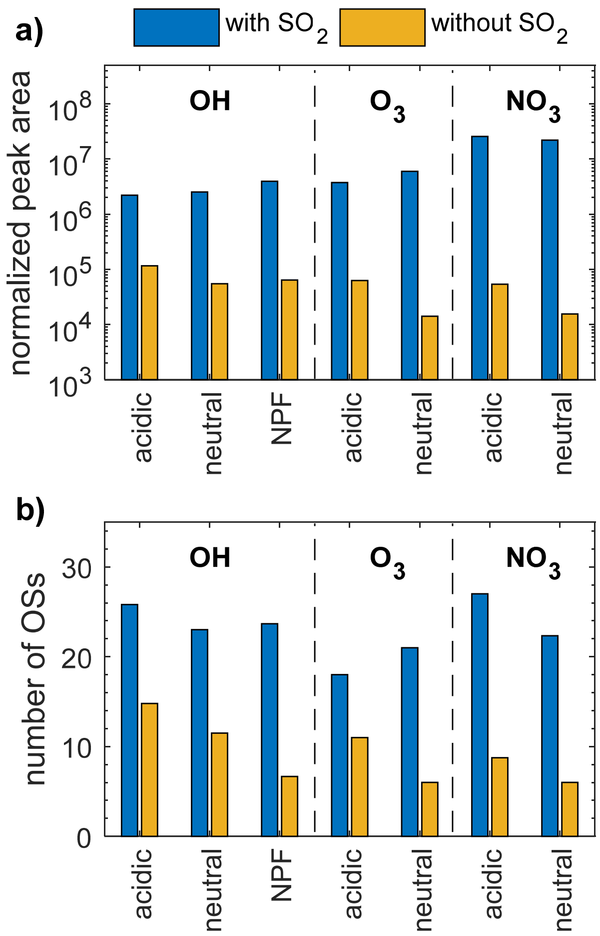
Brüggemann *et al.*, Environ. Chem. 2019,
https://doi.org/10.1071/EN19089

EESI-Orbitrap MS for online OS detection:



Lee *et al.*, ES&T 2020,
https://doi.org/10.1021/acs.est.9b07090

False Detection of OSs in the Presence of SO_2



- the **presence of gas-phase SO_2** strongly **enhanced OS abundance** by more than 3 orders of magnitude
- **upon removal of SO_2,** total number of detected OSs **decreased by ≤72%**
- **largest effect of SO_2** observed **for neutral seed particles**
- pH dependency indicates that that **S(IV) dissolves into the aqueous phase** on the filter substrate and **artificially enhances OS formation on the filter**

Figure 1. a) Total peak areas of detected OSs normalized to the total particle mass. Panel b) Average number of detected OSs including isomeric species (i.e., signals with identical *m/z* but different retention times).

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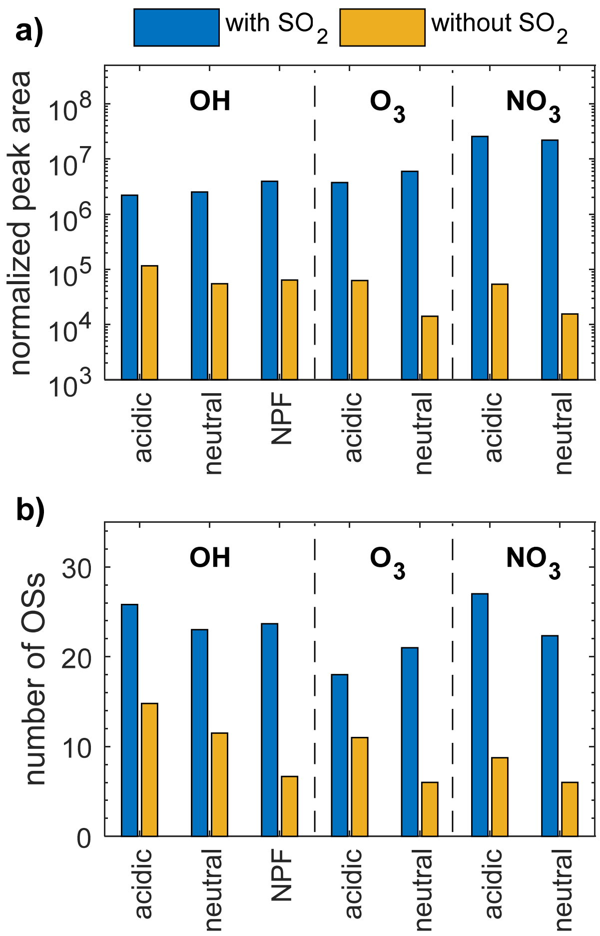
False Detection of OSs in the Presence of SO_2



- because neutral seed particles were isotopically labeled (i.e., ^{34}S), **all detected OSs must be derived, directly or indirectly, from gaseous SO_2**
- contributions of isotopically labeled OSs were not larger than the expected natural abundances of ^{34}S (i.e., about 4.3%)
- importantly, **OSs are not exclusively formed on the filter substrate** but must also form through heterogeneous chemistry in the particles

Figure 1. a) Total peak areas of detected OSs normalized to the total particle mass. Panel b) Average number of detected OSs including isomeric species (i.e., signals with identical *m*/*z* but different retention times).

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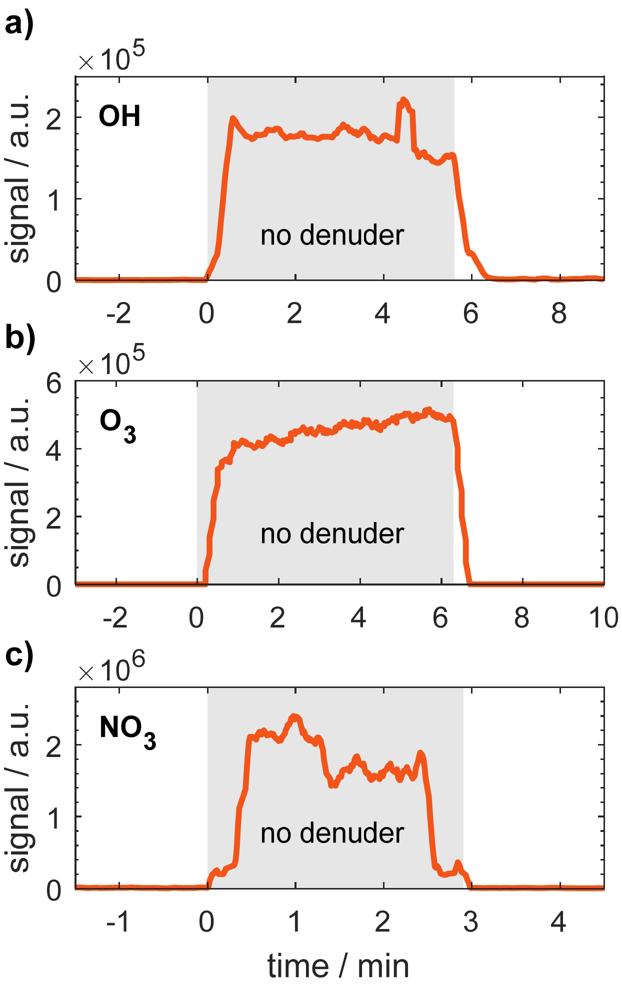
False Detection of OSs in the Presence of SO_2

Table 1. Enhancement factors for particle mass-normalized peak areas of single OS species in presence of SO_2. OSs that were only detectable in presence of SO_2 are denoted with “+“.

Oxidant	OH			O_3		NO_3	
Acidity / Formula	acidic	neutral	NPF	acidic	neutral	acidic	neutral
$C_{10}H_{18}O_5S$	7.95	602	495	31.0	+	10.2	+
$C_{10}H_{16}O_7S$	7.08	+	23.4	8.07	51.7	25.3	+
$C_{10}H_{18}O_7S$	39.7	37.9	79.7	30.2	136	32.0	+
$C_{10}H_{17}NO_7S$	**115**	**471**	**1400**	**1535**	**4930**	**1923**	**1880**
$C_8H_{14}O_{10}S$	1.64	1.73	2.42	1.44	1.60	2.44	3.09
$C_{10}H_{17}NO_8S$	5.57	102	+	+	+	48.1	76.6
$C_{10}H_{17}NO_9S$	+	+	+	+	+	+	92.3
$C_{10}H_{17}NO_{10}S$	**45.9**	**33.8**	**32.0**	**+**	**+**	**23.6**	**11.6**
$C_{10}H_{22}O_{13}S$	3.69	1.00	+	+	+	+	+
$C_{18}H_{37}NO_7S$	+	+	+	+	+	+	+
$C_{20}H_{32}O_8S$	+	+	+	+	+	+	+
$C_{19}H_{38}O_7S_2$	23.2	0.95	+	+	+	+	+
$C_{19}H_{31}NO_{10}S$	+	+	+	+	+	+	+
$C_{22}H_{40}O_{11}S$	+	+	+	+	+	+	+

- for almost all OS species strong enhancement factors were observed in all experiments
- **strong SO_2 enhancements observed for potential nitrooxy OSs (NOSs)** with the general formula $C_{10}H_{17}NO_xS$ (with x = 7–10)
- **SO_2 enhancements raise concerns on the actual abundance of (N)OSs** in atmospheric aerosol, as SO_2 is commonly not removed during filter sampling

False Detection of OSs in the Presence of SO_2



- without SO_2 removal, the number and abundance of OS signals rapidly increased

=> presence of gaseous SO_2 significantly affects the EESI

- SO_2 dissolution might play a key role
- kinetic accelerations are known to occur in ESI droplets, which might speed up artificial OS formation from SO_2

=> applying efficient reactive gas (i.e., SO_2, O_3, etc.) removal techniques are essential for EESI-MS detection of OSs

Figure 2. Total EESI-MS signal of *m/z* ratios corresponding to OSs formed in the ion source upon removal of the charcoal denuder during a) an OH oxidation experiment, b) an O_3 oxidation experiment, and c) a NO_3 oxidation experiment.

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NOS formation in different chemical regimes

NOS 295:

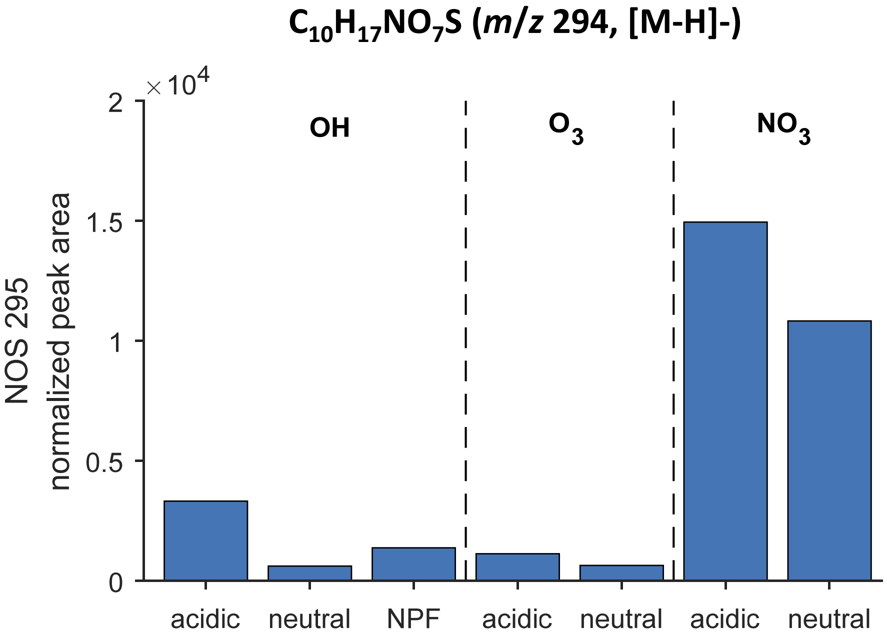


Figure 3. Particle mass-normalized peak areas of NOS 295 as determined from filter extracts by LC-Orbitrap MS. Gas-phase SO_2 was removed prior to particle sampling to avoid any sampling artifacts.

- **NOS 295 ($C_{10}H_{17}NO_7S$)** detected mainly during **NO_3 oxidation of α-pinene**
- largest total abundance of NOS 295 observed **under acidic conditions**

NOS formation in different chemical regimes

NOS 295:

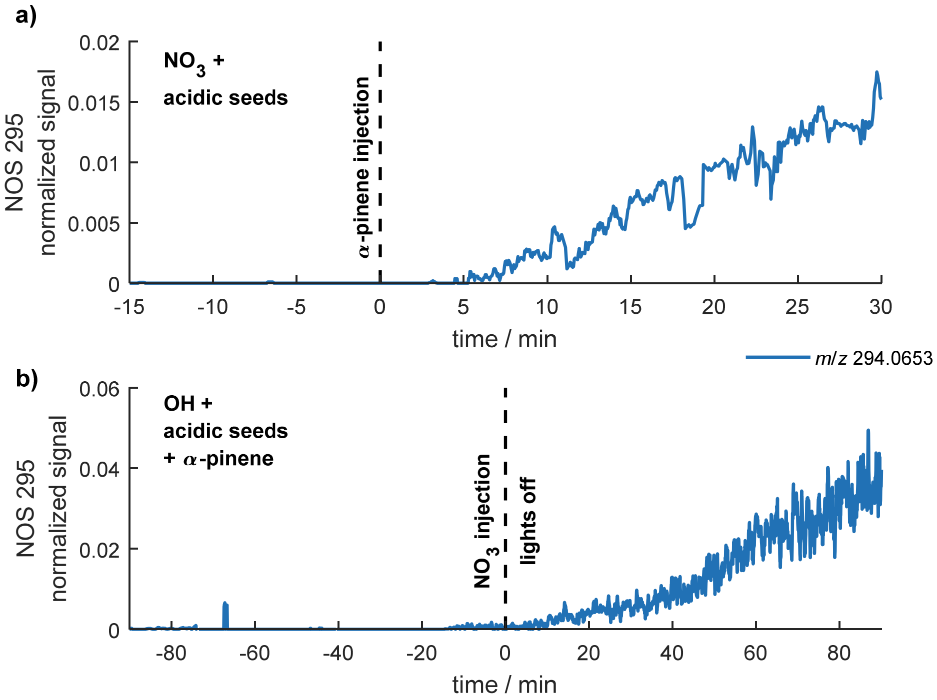


Figure 4. Online detection of NOS 295 by EESI-Orbitrap MS during OH and NO3 oxidation of α-pinene in the presence of acidic seed particles. The NOS 295 signal is normalized to HSO_4^- ion signals (*m/z* 96.9601), originating from the seed particles.

- NOS 295 observed online by EESI-MS
- ion signal immediately increases upon injection of α-pinene into NO_3 filled chamber
- ion signal immediately increases upon switching from daytime chemistry (OH) to nighttime chemistry (NO_3)
- no signals observable during O_3 and OH chemistry in any experiment

NOS formation in different chemical regimes

NOS 343:

$C_{10}H_{17}NO_{10}S$ (*m/z* 342, $[M-H]^-$)

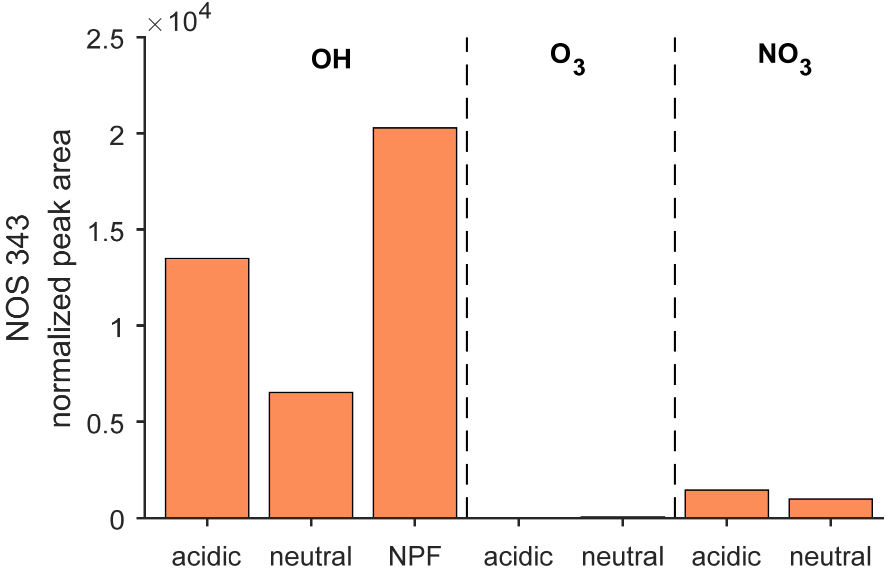
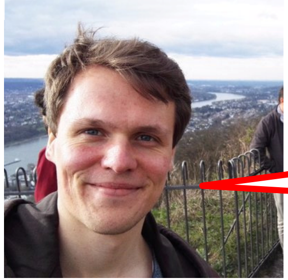


Figure 5. Particle mass-normalized peak areas of NOS 343 as determined from filter extracts by LC-Orbitrap MS. Gas-phase SO_2 was removed prior to particle sampling to avoid any sampling artifacts.

- **NOS 343 ($C_{10}H_{17}NO_{10}S$)** detected predominantly **during OH oxidation of α-pinene**
- largest total abundance of NOS 343 observed **for new particle formation**
- not detected online by EESI-MS probably because below detection limit

Summary

- the **presence of gas-phase SO_2** during particle sampling on filters **enhanced OS abundance** by more than three orders of magnitude
- pH dependency indicates that that **S(IV) dissolves into the aqueous phase** on the filter substrate and **artificially enhances OS formation on the filter**
- **SO_2 enhancements raise concerns on the actual abundance of (N)OSs**
- **presence of gaseous SO_2 significantly affects online detection of OSs by EESI-MS** => efficient removal of reactive trace gases essential
- **NOS 295** ($C_{10}H_{17}NO_7S$) detected predominantly during **NO_3 oxidation** of α-pinene
- **NOS 343** ($C_{10}H_{17}NO_{10}S$) detected predominantly during **OH oxidation** of α-pinene



Thank you for your attention!

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