# Quantification of known and unknown organosulfates in $PM_{10}$ using LC-HRMS/MS: Contrasting summertime rural Germany and the North China Plain

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## (1) Summary


- **Organosulfates (OS; R–$OSO_3H$)** account for a substantial fraction of ambient secondary organic aerosol (SOA), however, **remain an analytical challenge** due to missing authentic standards and an **incomplete identification of OS species**
- Here **we quantified known and unknown terpenoid OS in summertime $PM_{10}$** from Germany (Melpitz, MEL) and the North China Plain (NCP) using liquid chromatography in combination with **high-resolution Orbitrap mass spectrometry** (LC-HRMS; R 70k–280k, $\Delta m/z \leq 3$ ppm) **in a target/non-target approach**
- At each site **>50 monoterpene OS (MT-OS)** were detected, **13 of which were found at both sites**, contributing >55% to the average MT-OS concentrations
- **Main MT-OS contributor was a $C_9H_{16}O_7S$** isomer (*m/z* 267.0547, $[M-H]^-$), giving mean concentrations of 2.23 and 6.38 ng $m^{-3}$ for MEL and NCP, respectively
- MT-OS concentrations correlated with MT oxidation products at MEL; however, for NCP, a potential **suppression of carboxylic acid formation** was observed
- **40 and 17 sesquiterpene OS (SQT-OS) were identified at NCP and MEL**, respectively, 5 of which were present at both sampling locations
- SQT-OS concentrations were ~5-10 times larger at NCP, suggesting **insufficient particle acidity at MEL for efficient SQT-OS formation**


## (2) Overall composition of $PM_{10}$ samples

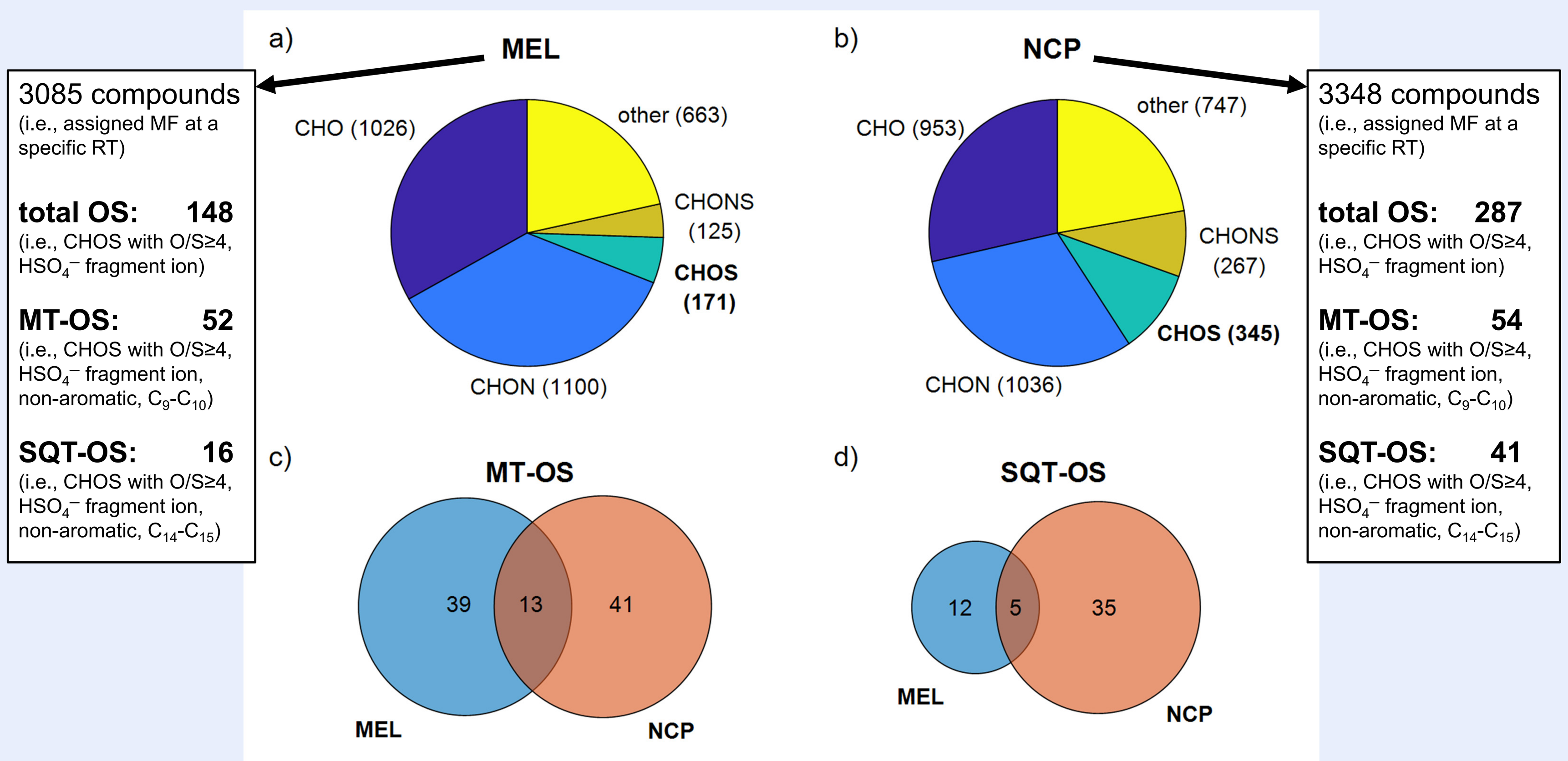


**Fig. 1: General organic composition of the $PM_{10}$ samples from MEL and NCP: (a) Elemental composition of all assigned MFs for MEL, (b) elemental composition of all MFs for NCP (other = compounds made of CH, CHN, or phosphorous- and halogen-containing). (c) Number of unique and common MT-OS detected at MEL and NCP, (d) number of unique and common SQT-OS observed at MEL and NCP.**

## (3) Concentrations of terpenoid OS

### diurnal MT-OS concentrations

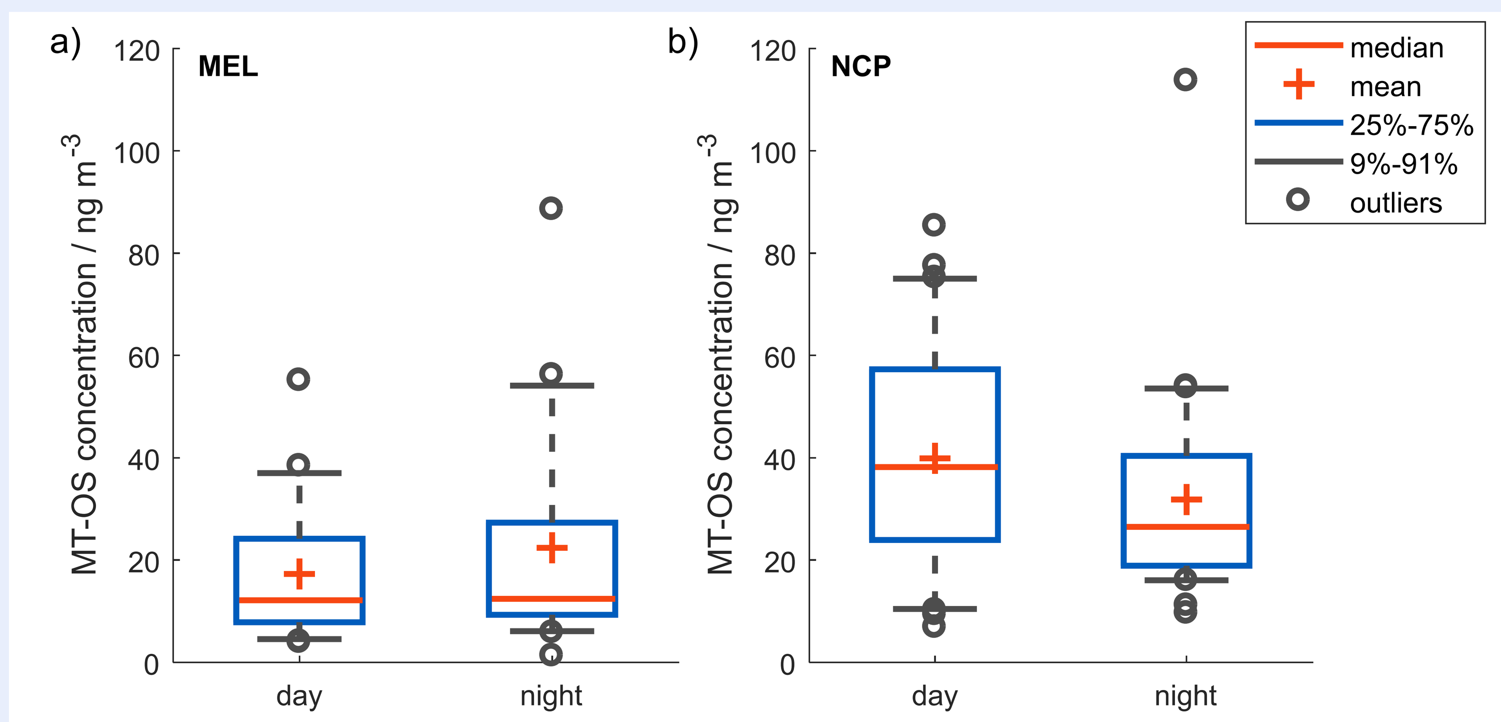


**Fig. 2: Diurnal total concentrations of all MT-OS determined in $PM_{10}$ samples from (a) MEL and (b) NCP. For MEL, median concentrations of 12.15 and 12.42 ng $m^{-3}$ were observed for day and night, respectively. For NCP, concentrations were ~2-3 times larger, giving median concentrations of 38.19 and 26.49 ng $m^{-3}$ for day and night, respectively.**

### diurnal SQT-OS concentrations

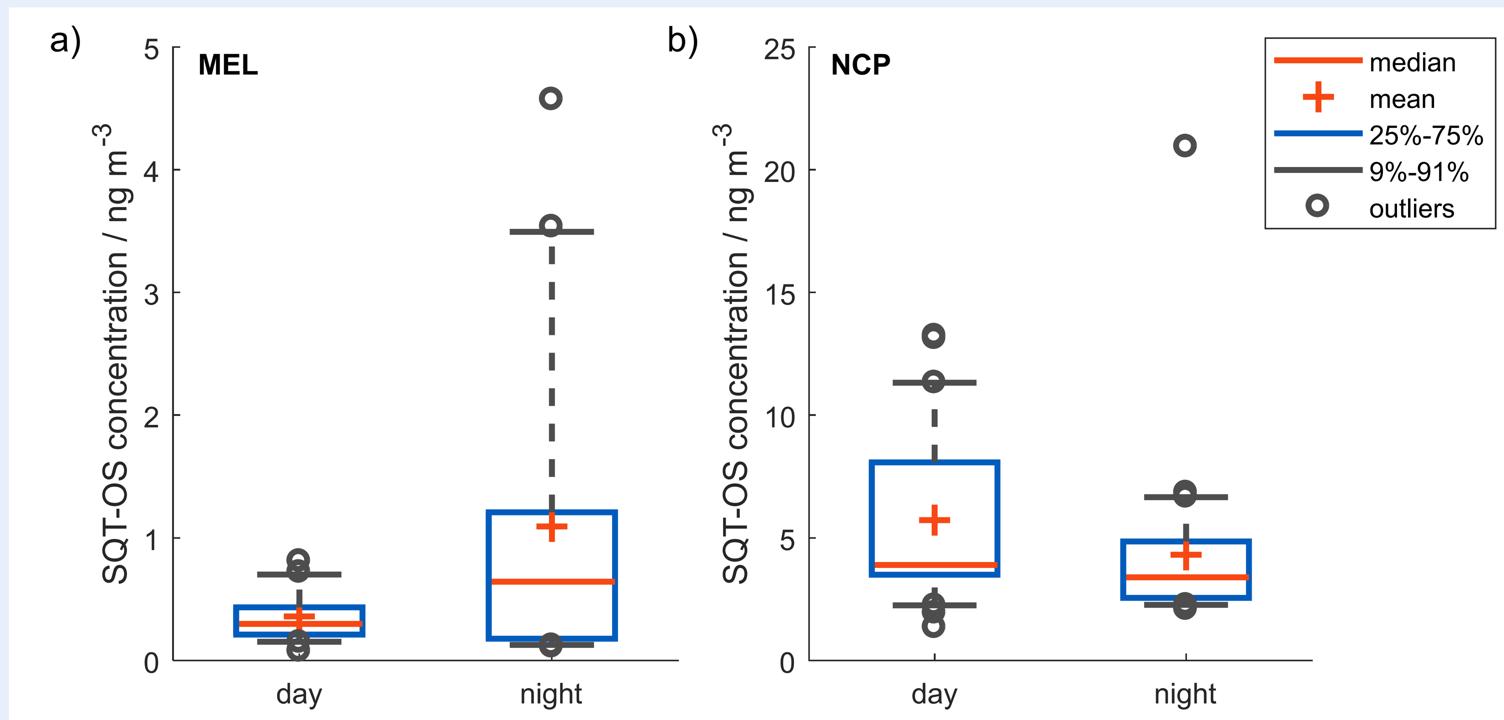


**Fig. 3: Diurnal total concentrations of all SQT-OS determined in $PM_{10}$ samples from (a) MEL and (b) NCP. For MEL, median concentrations of 12.15 and 12.42 ng $m^{-3}$ were observed for day and night, respectively. For NCP, concentrations were ~2-3 times larger, giving median concentrations of 38.19 and 26.49 ng $m^{-3}$ for day and night, respectively.**

### concentrations of common MT-OS and SQT-OS

**Table 1: Overview on the 13 common MT-OS and 4 SQT-OS detected in PM10 from MEL and NCP.**

*common MT-OS:*

| Name | Molecular Formula | *m/z* ($[M-H]^-$) | RT / min | $c_{avg}$ / ng $m^{-3}$ MEL | $c_{avg}$ / ng $m^{-3}$ NCP | fraction of MT-OS MEL | fraction of MT-OS NCP | previous studies | proposed precursors* |
|---|---|---|---|---|---|---|---|---|---|
| 231 | $C_{10}H_{16}O_4S$ | 231.0696 | 9.90 | 0.14 | 0.02 | 0.71% | 0.05% | p | - |
| 249 | $C_{10}H_{18}O_5S$ | 249.0806 | 5.90 | 0.59 | 0.01 | 2.98% | 0.04% | a, b, c, e, f, j, k, l, m, n, p, q, s, t, u | MT[a,b,c,l,m,n] |
| 251 | $C_{10}H_{20}O_5S$ | 251.0961 | 9.63 | 1.20 | 0.18 | 6.03% | 0.49% | m, o, q, u | alk[o] |
| 265a | $C_9H_{14}O_7S$ | 265.0393 | 1.07 | 0.68 | 1.57 | 3.43% | 4.37% | i, m, p, q | - |
| 265b | $C_{10}H_{18}O_6S$ | 265.0752 | 1.07 | 0.29 | 0.48 | 1.47% | 1.33% | l, m, o, q | MT[l,m], alk[o] |
| 267 | $C_9H_{16}O_7S$ | 267.0547 | 1.07 | 2.23 | 6.38 | 11.18% | 17.78% | b, c, i, j, k, m, o, p, q, s, u | MT[b,c,m], alk[o] |
| 279 | $C_{10}H_{16}O_7S$ | 279.0542 | 1.07 | 1.58 | 1.60 | 7.92% | 4.45% | b, c, d, e, f, g, h, j, k, l, m, n, o, p, q, s, u | MT[b,c,m,n], alk[o] |
| 281 | $C_9H_{14}O_8S$ | 281.0338 | 1.07 | 1.79 | 1.93 | 8.99% | 5.38% | i, m, n, p, q, s | isop[m], MT[n] |
| 283 | $C_{10}H_{20}O_7S$ | 283.0855 | 1.07 | 0.27 | 0.68 | 1.37% | 1.89% | l, q, r, u | diesel[r] |
| 295 | $C_{10}H_{16}O_8S$ | 295.0490 | 1.07 | 1.03 | 1.53 | 5.17% | 4.27% | m, o, u | alk[o] |
| 297a | $C_9H_{14}O_9S$ | 297.0284 | 1.07 | 0.99 | 1.72 | 4.98% | 4.80% | m, n, q, s | isop[m], MT[n] |
| 297b | $C_{10}H_{18}O_8S$ | 297.0648 | 1.07 | 0.85 | 1.55 | 4.26% | 4.32% | b, n, o, q, s, u | MT[b,n], alk[o] |
| 309a | $C_{10}H_{14}O_9S$ | 309.0286 | 1.07 | 0.30 | 0.54 | 1.53% | 1.49% | q | - |
| | | | **total:** | 11.94 | 18.19 | 60.02% | 50.68% | | |

*common SQT-OS:*

| Name | Molecular Formula | *m/z* ($[M-H]^-$) | RT / min | $c_{avg}$ / ng $m^{-3}$ MEL | $c_{avg}$ / ng $m^{-3}$ NCP | fraction of SQT-OS MEL | fraction of SQT-OS NCP | previous studies | proposed precursors* |
|---|---|---|---|---|---|---|---|---|---|
| 293 | $C_{14}H_{30}O_4S$ | 293.1793 | 12.31 | 0.007 | 0.011 | 0.89% | 0.22% | m, q | - |
| 309b | $C_{14}H_{30}O_5S$ | 309.1736 | 14.98 | 0.346 | ≤0.004‡ | 44.01% | - | m, q, r | diesel |
| 315 | $C_{15}H_{24}O_5S$ | 315.1271 | 10.28 | 0.005 | 0.035 | 0.60% | 0.68% | - | - |
| 317 | $C_{15}H_{26}O_5S$ | 317.1428 | 10.45 | ≤0.004‡ | 0.013 | - | 0.25% | v | β-caryop |
| 323 | $C_{14}H_{28}O_6S$ | 323.1531 | 10.83 | 0.051 | 0.255 | 6.53% | 5.01% | m, q | - |
| | | | **total:** | 0.409 | 0.314 | 52.03% | 6.16% | | |

* alkane (alk); isoprene (isop); monoterpenes (MT), β-caryophyllene (β-caryop)

‡ limit of quantification for SQT-OS

(a) Iinuma et al., 2007, (b) Surratt et al., 2007, (c) Surratt et al., 2008, (d) Altieri et al., 2009, (e) Kristensen and Glasius, 2011, (f) Yttri et al., 2011, (g) LeClair et al., 2012, (h) Lin et al., 2012, (i) Nguyen et al., 2012, (j) Stone et al., 2012, (k) Lin et al., 2013, (l) Ma et al., 2014, (m) Tao et al., 2014, (n) Mutzel et al., 2015, (o) Riva et al., 2016a, (p) Vogel et al., 2016, (q) Wang et al., 2016, (r) Blair et al., 2017, (s) Brüggemann et al., 2017, (t) Wang et al., 2017a, (u) Wang et al., 2018, (v) Chan et al., 2011

## (4) Correlations of MT-OS and SQT-OS

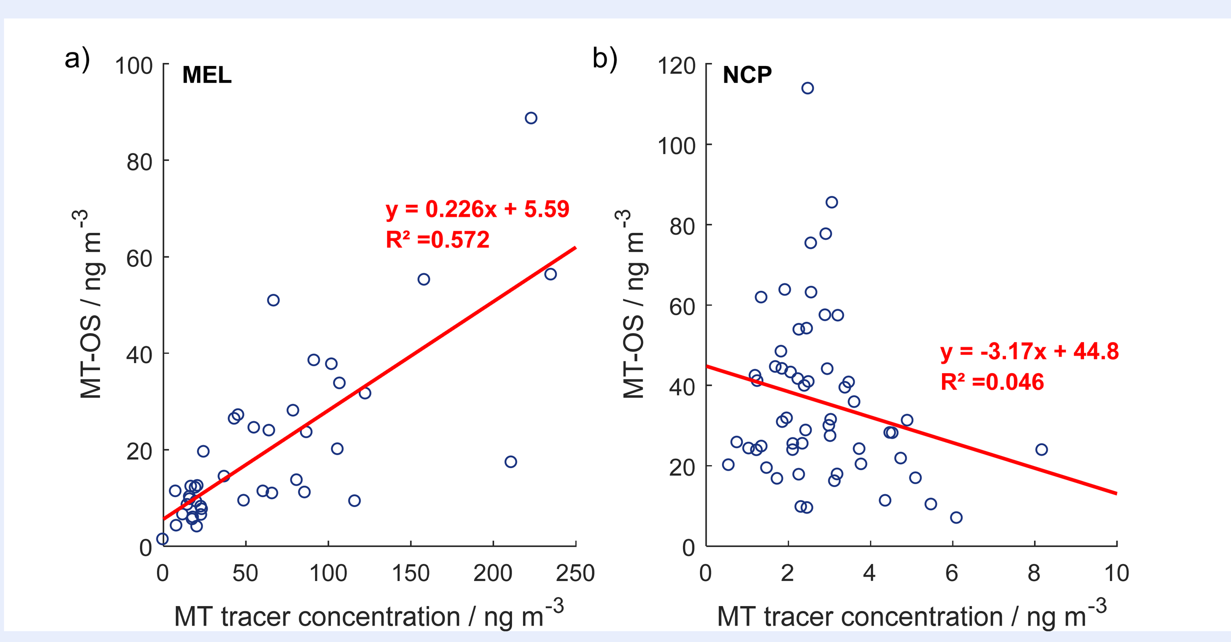


**Fig. 4: Linear regression applied to the total MT-OS concentrations as a function of the summed concentrations of eight common MT oxidation products (i.e., terebic acid, MBTCA, terpenylic acid, transnorpinic acid, pinic acid, DTAA, nor-pinonic acid, pinonic acid) for (a) MEL and (b) NCP.**

- linear correlation between MT oxidation products and MT-OS for MEL only
- same source for MT oxidation products and MT-OS => biogenic
- potential suppression of carboxylic acid formation under high $NO_X$ and particulate sulfate concentrations, favoring formation of OS and other functionalized S- and N-containing compounds

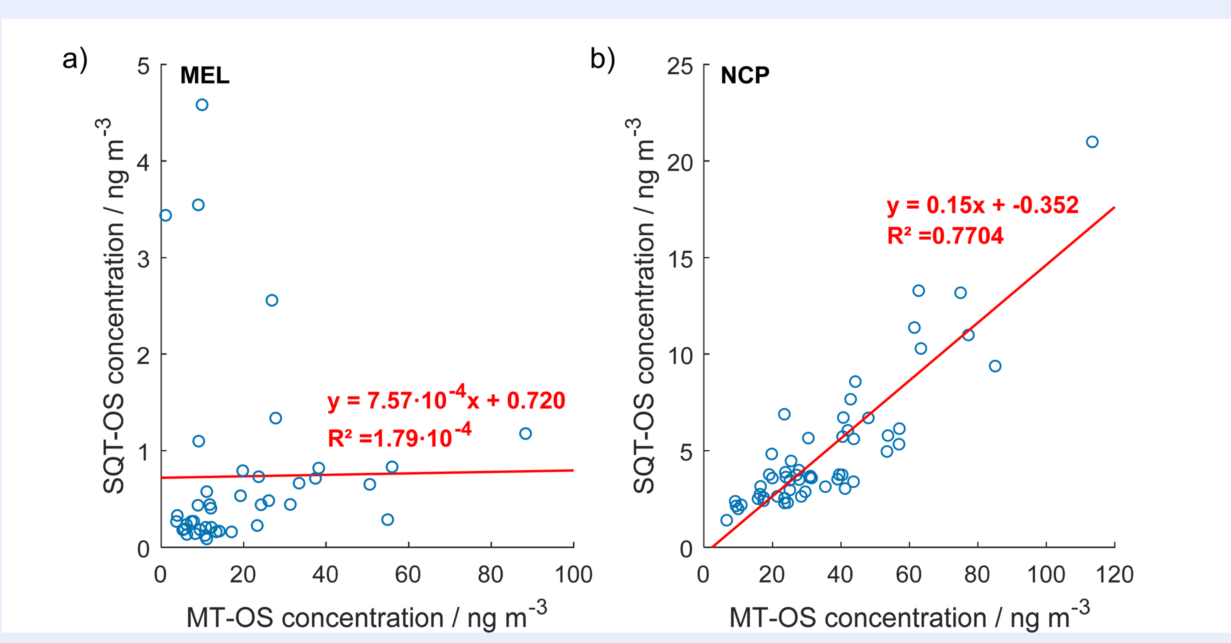


**Fig. 5: Linear regression applied to the total concentrations of SQT-OS as a function of the total concentrations of MT-OS for (a) MEL and (b) NCP.**

- linear correlation between SQT-OS and MT-OS concentrations for NCP only
- same source for MT-OS and SQT-OS => biogenic
- insufficient particle acidity at MEL (i.e., median neutralization ratio ~1) hampers SQT-OS formation (Chan et al., ACP 2011)
- particle acidity sufficiently large at NCP for SQT-OS formation (i.e., median neutralization ratio ~0.7)