Diurnal profiles of summertime secondary organic aerosol constituents in Melpitz, Germany

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Introduction

- **Secondary organic aerosol (SOA)** formation and composition remain one of the most intensively investigated but also most poorly understood topic in atmospheric science.
- Up to 100,000 different organic substances can be present in SOA,[1] where the composition is highly variable over time depending on the present photochemical conditions and transported air masses.
- Organic acid functionalities often form during atmospheric transformation processes therefore their detection is of particular interest, to trace atmospheric ageing.

Methodology

Field campaign

07. July – 12. August 2021 collection of **$PM_{2.5}$ filter** samples in **4 h intervals** at TROPOS research station Melpitz, Germany (51.54 °N, 12.93 °E).

Trajectory analysis

Calculation of 96 h air mass back-trajectories with HYSPLIT 4.9 for every sample. Statistical trajectory analysis to evaluate crossed land classes.[4]

Sample preparation & chemical analysis

- 15x 6 mm spots per filter sample + 500 µL ultrapure water in 96-well filter plate.
- 60 min at 400 min^{-1} in an orbital shaker and transfer into deep well plates via vacuum filtration.
- Ion chromatography high mass resolution spectrometry (**IC/MS**)[2] and **LC/MS**[3] measurements to quantify **46** different organic and inorganic **compounds.**

Diurnal profiles of organic constituents

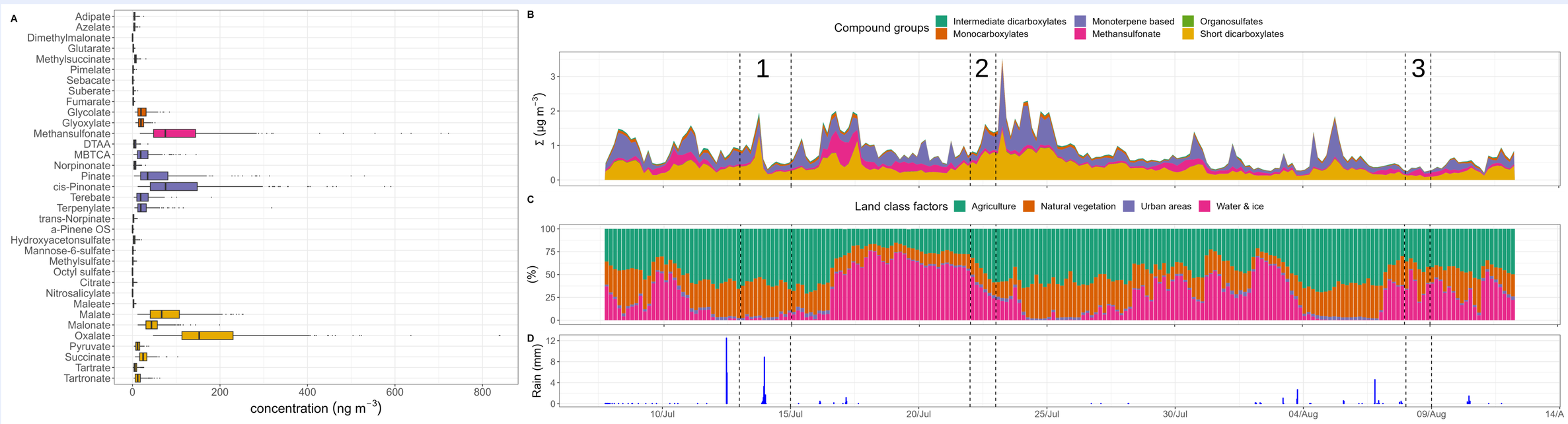

Fig. 1: Box-plot for all determined analytes and their group assignment (A), sum of all organic analyte groups (B), contribution of crossed land classes of trajectories per sample (C), and amount of precipitation at Melpitz (D).

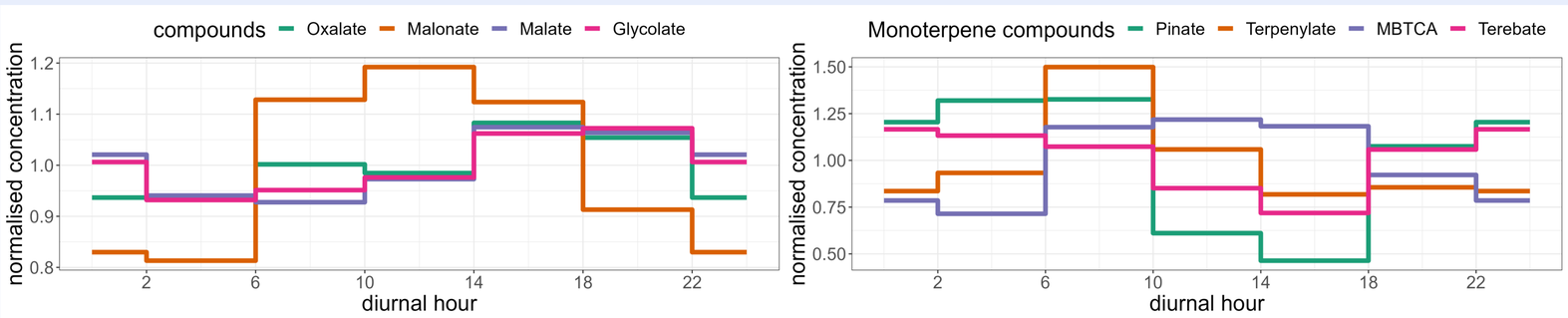

Fig. 2: Normalized concentration profiles for selected compounds over the entire campaign.

MBTCA: 3-Methyl-1,2,3-butanetricarboxylate

- All values are z-normalized.
- Early monoterpene products maximum in morning and night, late products stable during day.
- Short dicarboxylates have concentration maximum in the afternoon.
- Clear difference between Malonate (C_3) and Oxalate (C_2).

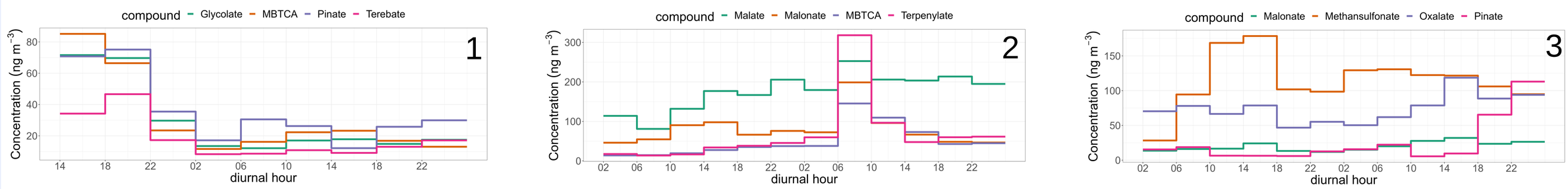

Fig. 3: 4-hourly concentration profiles of selected analytes during the three marked periods of the measurement campaign.

Heavy rain events over Central Europe after 20:00 cause wet deposition.

→ Observation of new formation processes

- General concentration maxima before rain event.
- Pinate as early oxidation product has concentration peak after sunrise (6-10).
- Glycolate increases stepwise

Period with constant trajectory origin, no precipitation, and almost localized calm.

→ Observation of local transformation processes.

- Malate is an important intermediate product, as its concentration increases constantly.
- MBTCA triples concentration after sunrise, possible precursor enrichment during the night.

Constant air mass origin in the Atlantic Ocean and crossing France with no local precipitation.

→ Observation of marine influenced air masses.

- High methansulfonate concentrations prove marine influence, daily maxima could indicate further formation pathways.
- Oxalate and Malonate show same profiles.

Summary

- Sample preparation allows batch processing and LOQs down to 0.015 ng m^{-3}, which is essential for low mass loaded but numerous filter samples.
- Short dicarboxylates and monoterpene based oxidation products contribute most to the total organic PM.
- Long-range transport and local formation mechanisms play different roles depending on the origin of the air masses and the local weather conditions.
- Important local sources of monoterpene emissions due to high concentration of first generation products.
- For many compounds, there is a clear correlation between concentration and the start of photochemistry in the morning.

References

[1] Spranger et al. (2019), Environ. Sci. Technol. 53 (19), 11353–11363;
[2] Kwiezinski et al. (2021), J. Sep. Sci., 1-15;
[3] Brüggemann et al. (2019), Environ. Chem. 16 (5), 333;
[4] van Pinxteren et al. (2010), J. Atmos. Chem. 67 (1), 1-28