Functionalised carboxylic acids in atmospheric particles: An annual cycle revealing seasonal trends and possible sources

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Motivation

Carboxylic acids in atmospheric particles:

- major fraction of water soluble organic carbon (WSOC)
- straight-chain monocarboxylic acids (MCA) and dicarboxylic acids (DCA) with 2-10 carbon atoms have extensively been studied in the past
- only a few studies exist dealing with functionalised carboxylic acids, i.e. having additional hydroxyl-, oxo- or nitro-groups
- Functionalised carboxylic acids supposed to be formed during atmospheric oxidation processes, e.g. through radical reactions

└> Studying functionalised carboxylic acids can provide insights into tropospheric multiphase chemistry.

Sampling and Experimental

- 256 quartz filter samples taken in 2010 at the rural research station Melpitz (Saxony, Germany) with a PM_{10} Digitel DHA-80 filter sampler
- 96-h backward trajectories from HYSPLIT (Draxler and Rolph 2003) for determining air mass origin
- Quantitatively determination of 28 carboxylic acids: 4 functionalised aliphatic MCAs, 5 aromatic MCAs, 3 nitro aromatic MCAs, 6 aliphatic DCAs, 6 functionalised aliphatic DCAs, 4 aromatic DCAs
- Preconcentration of water extract by *hollow fibre liquid-phase micro extraction* (HF-LPME) according to van Pinxteren et al. 2012:
  - Three-phase-extraction:
    Donorphase (watery filter extract; 1800 µL)
    Acceptorphase (50 mM $NH_{3\,(aq.)}$; 15 µL)
    Liquid membrane phase
    (Dihexyl ether containing 10% Trioctylphosphine oxide)
  - Organic solvent is immersed in the pores of the hollow fibre forming the liquid membrane
  - Acceptorphase is introduced into the hollow fibre
  - Extraction time: 2 h

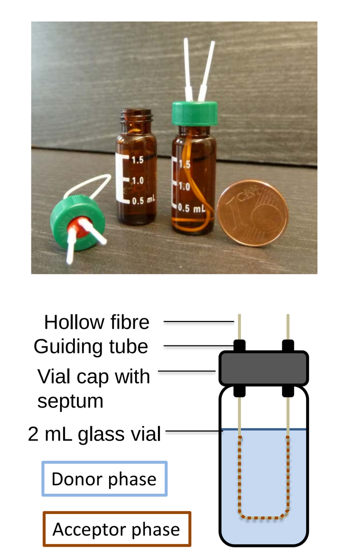


Fig. 1: HF-LPME device.

- Analysis of hollow fibre extract with *capillary electrophoresis* coupled with *mass spectrometry* (CE-MS)

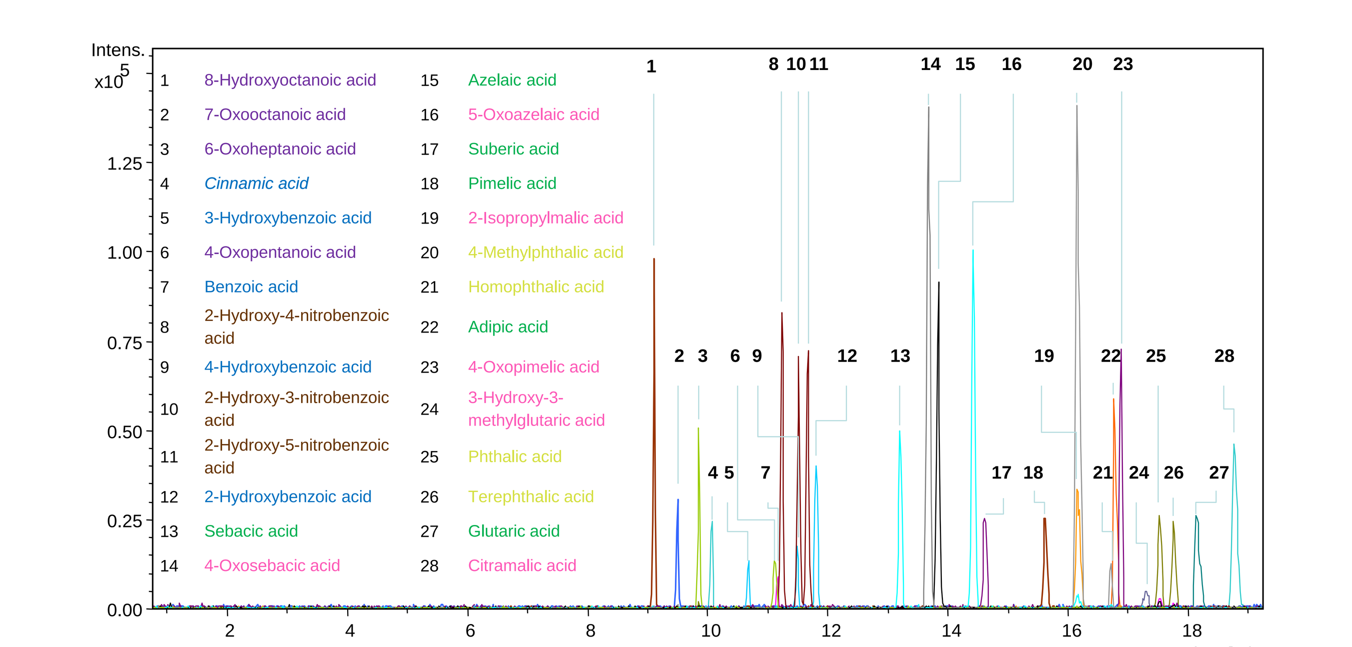
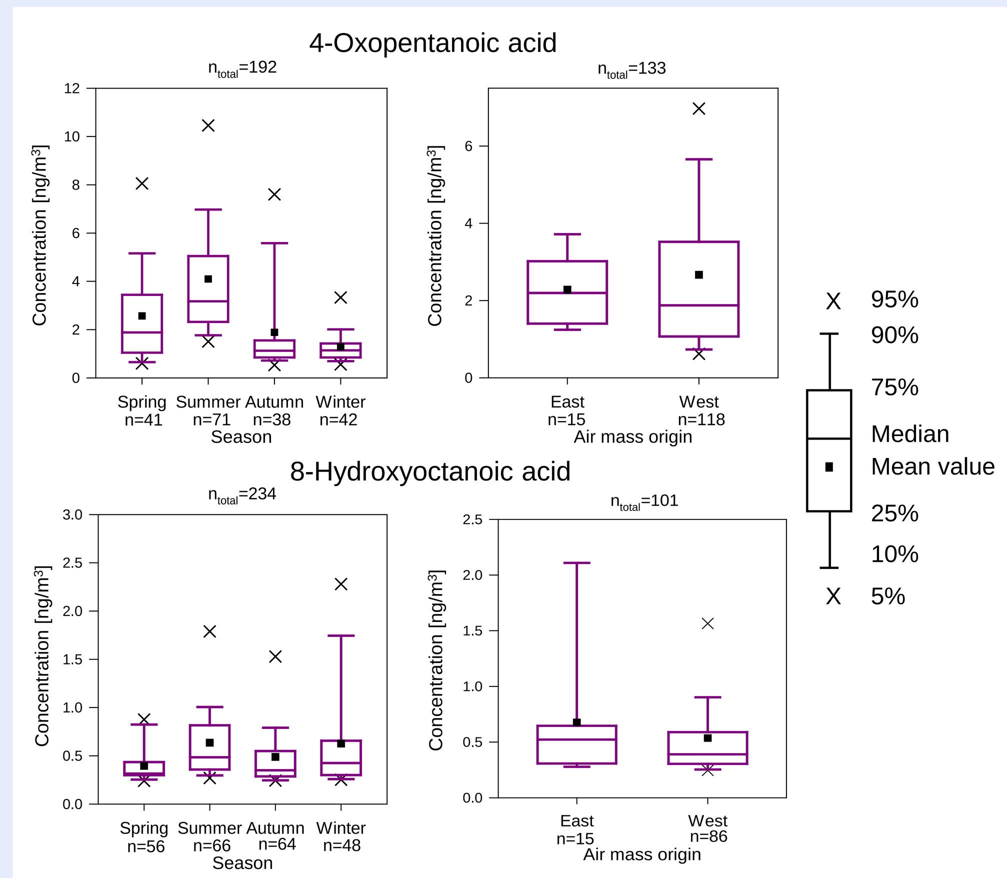


Fig. 2: Example of an electropherogram of a standard solution containing target species.

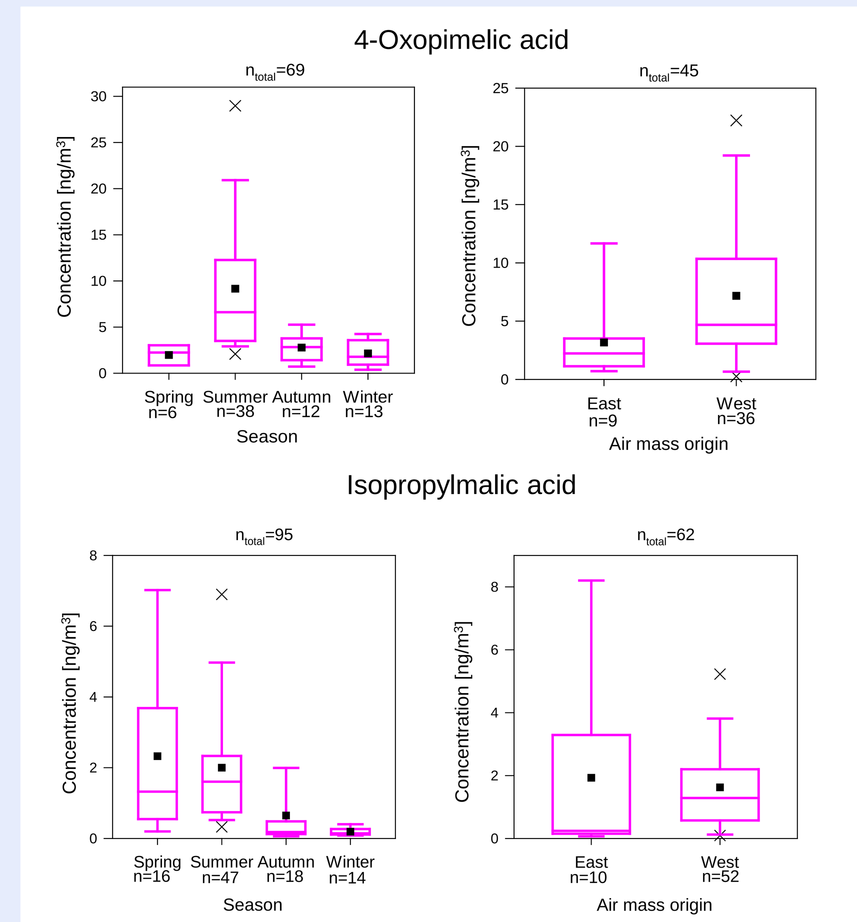
Results

Functionalised aliphatic MCAs



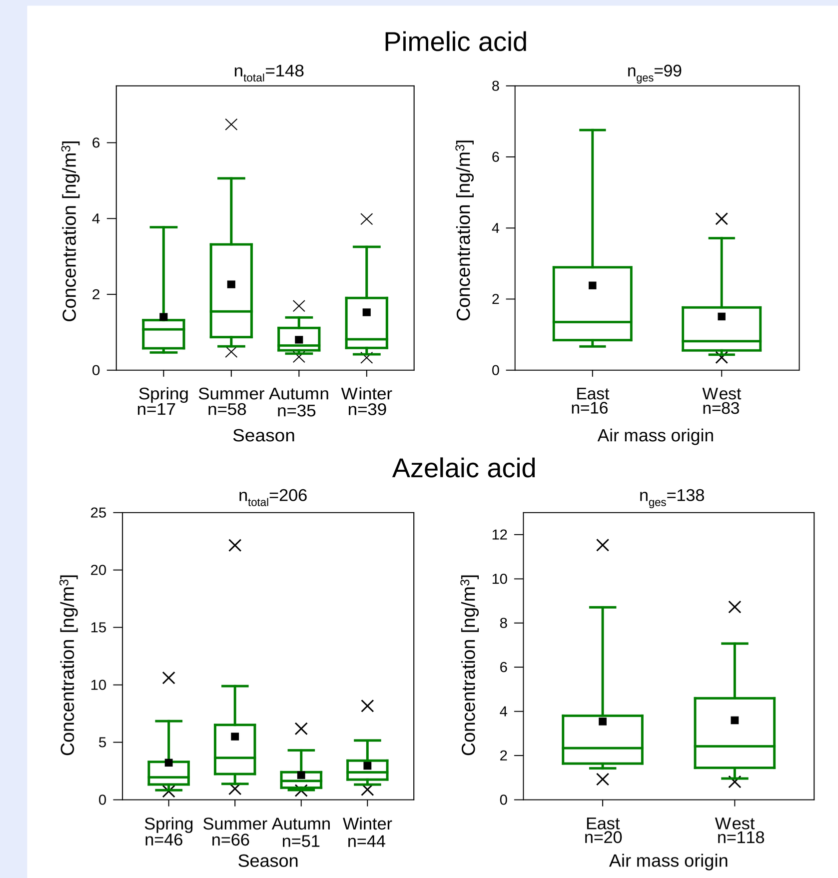
- In average highest concentration measured for 4-Oxopentanoic acid
- Seasonal variation tends to have higher concentrations in summer than in winter
- Concentrations considering the air mass origin are comparable

Functionalised aliphatic DCAs



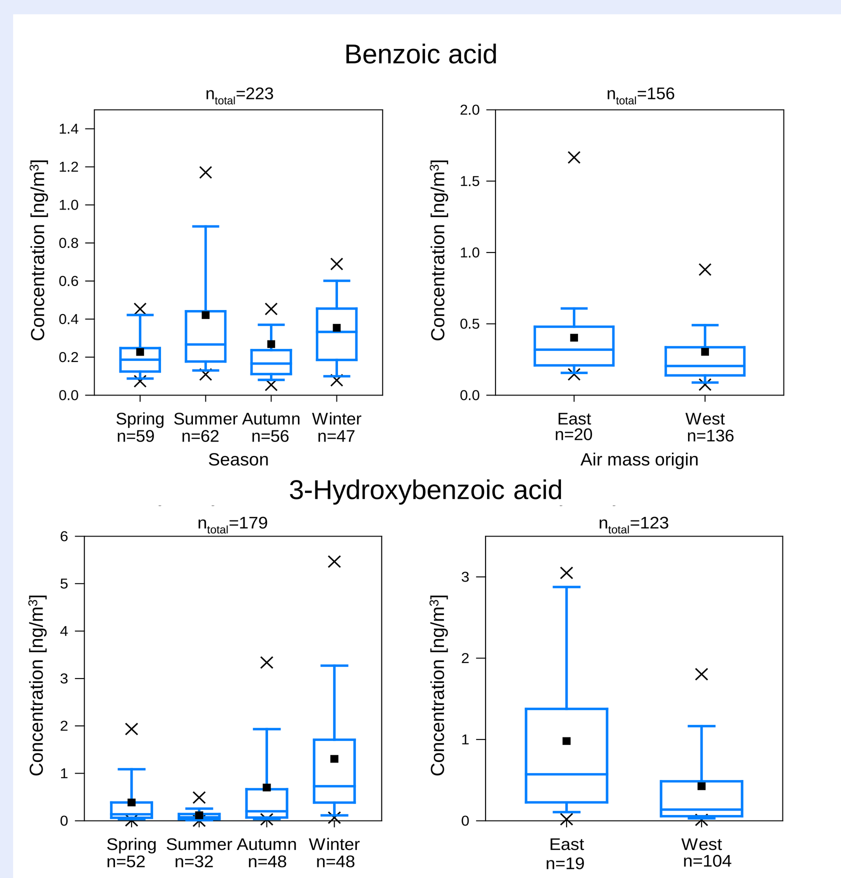
- Concentrations are highest in summer, except for 2-isopropylmalic acid
- Higher concentrations during western inflow or no tendency observable

Aliphatic DCAs



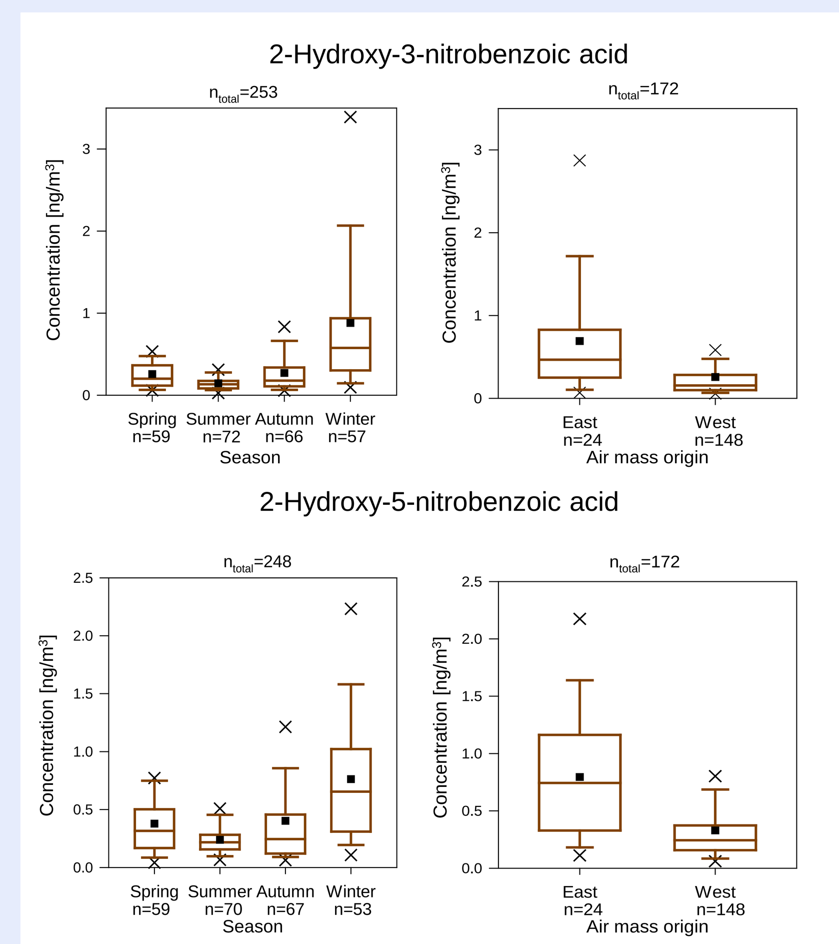
- Concentrations of C5-C10 acids show one maximum in summer and a lower maximum in winter
- Among this group the highest concentrations was determined for adipic acid (7.84 ng m^{-3} annual average)
- Higher concentrations during eastern inflow for C5-C7 acids
- Concentrations similar for eastern and western inflow for C8-C10 acids

Aromatic MCAs



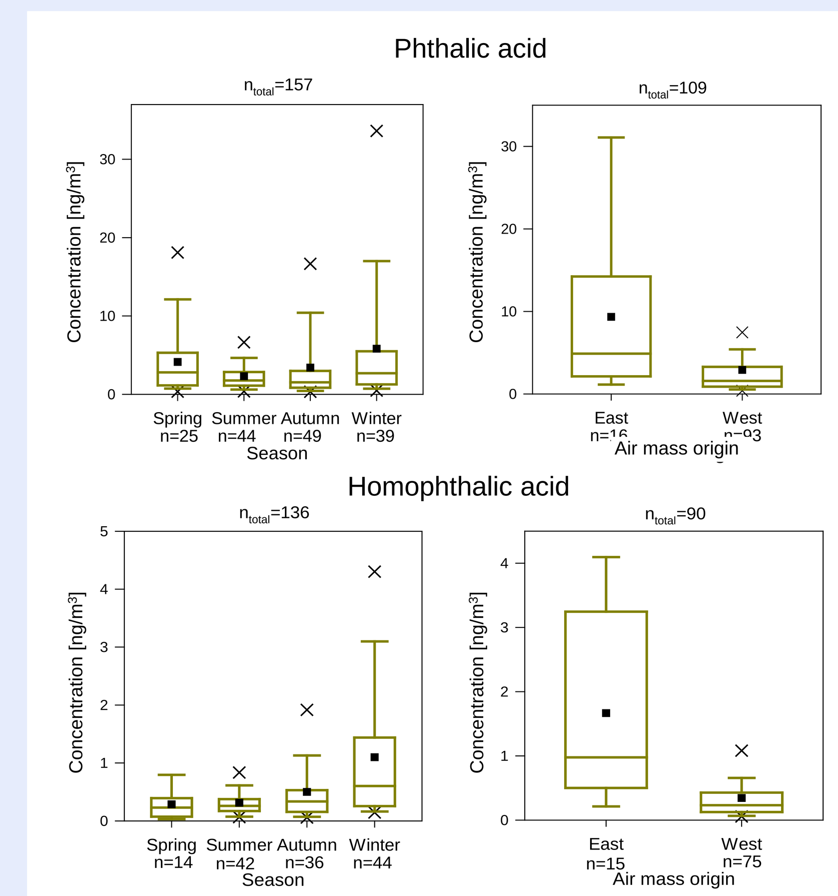
- Concentrations are highest in winter and lowest in summer
- Benzoic acid is an exception
- Benzoic acid concentration has two maxima
- Higher concentrations during eastern inflow

Nitro aromatic MCAs



- Highest concentrations are found to be in winter and if the air mass is transported from East

Aromatic DCAs



- Concentrations are highest in winter
- A second maximum is found in spring for phthalic acid and terephthalic acid
- Eastern inflow yields to higher concentrations

References

- Draxler, R.R., Rolph, G.D., **2003.** HYSPLIT (HYbrid Single-particle Lagrangian Integrated Trajectory) Model Access via NOAA ARL READY Website. NOAA Air Resources Laboratory, Silver Spring, MD. http://www.arl.noaa.gov/ready/hysplit4.html
- van Pinxteren, D., Teich, M. and Herrmann, H. **2012.** Hollow fibre liquid-phase micro extraction of functionalised carboxylic acids from atmospheric particles combined with capillary electrophoresis/mass spectrometric analysis. *Journal of Chromatography A*, 1267:178–188.

Conclusions

- High concentrations of aliphatic functionalised MCA and DCA in summer → photochemical formation processes
- Concentrations of functionalised DCAs are exceeding these of the corresponding n-DCAs → alphatic DCAs as precursors of functionalised DCAs
- Aromatic MCAs and aromatic DCAs show a concentration maximum in winter and higher concentrations during eastern inflow → Anthropogenic sources
- Aromatic acids show distinctly different seasonal behaviour than aliphatic acids → different sources (anthropogenic emission vs. photochemical formation)

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