18th Task Force on Measurement and Modelling Meeting

MARGA at the TROPOS/EMEP site Melpitz (Germany) – long-time measurements, validation, source apportionment and further developments since 2010

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Umwelt Bundesamt

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MARGA measurement site and principle

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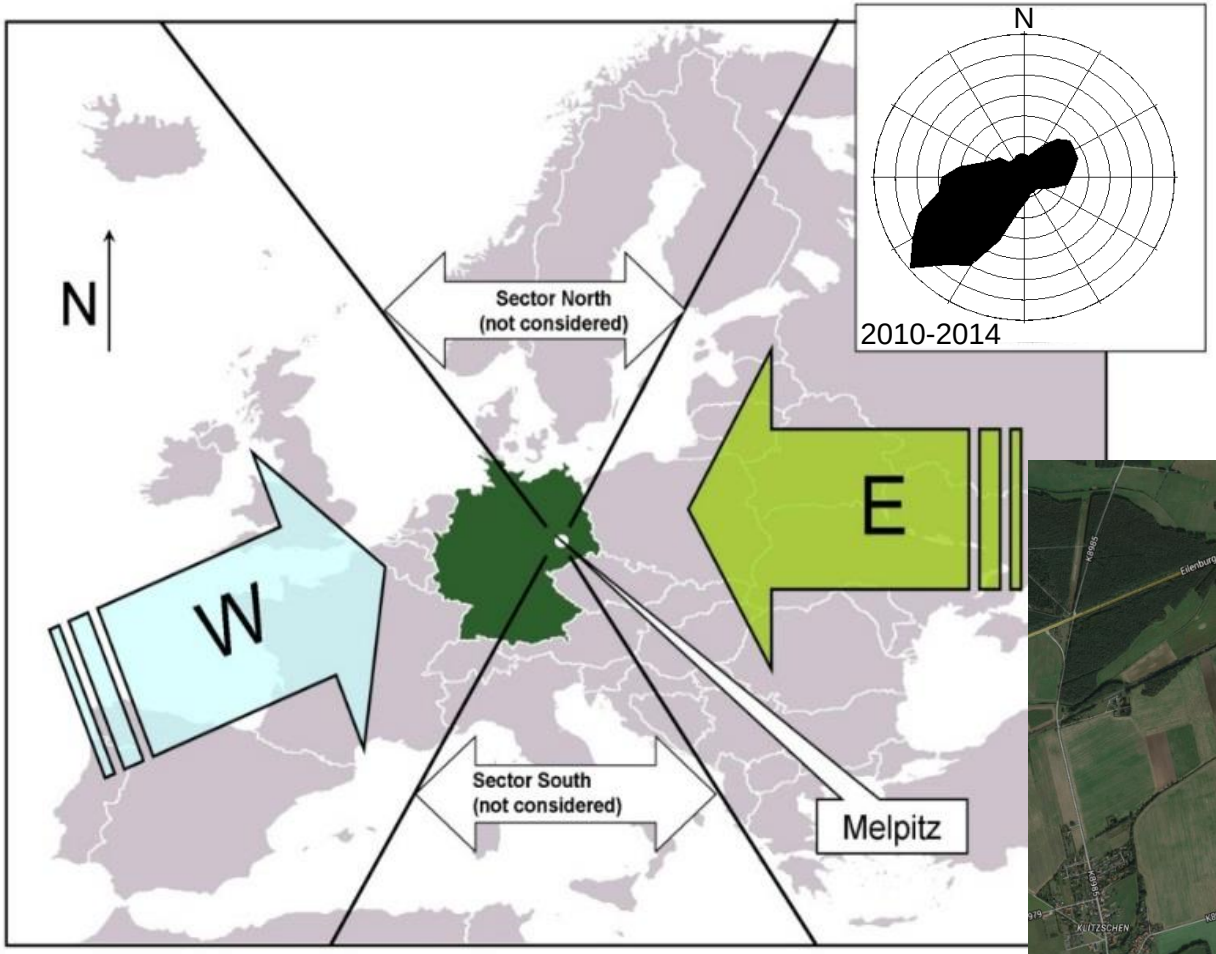
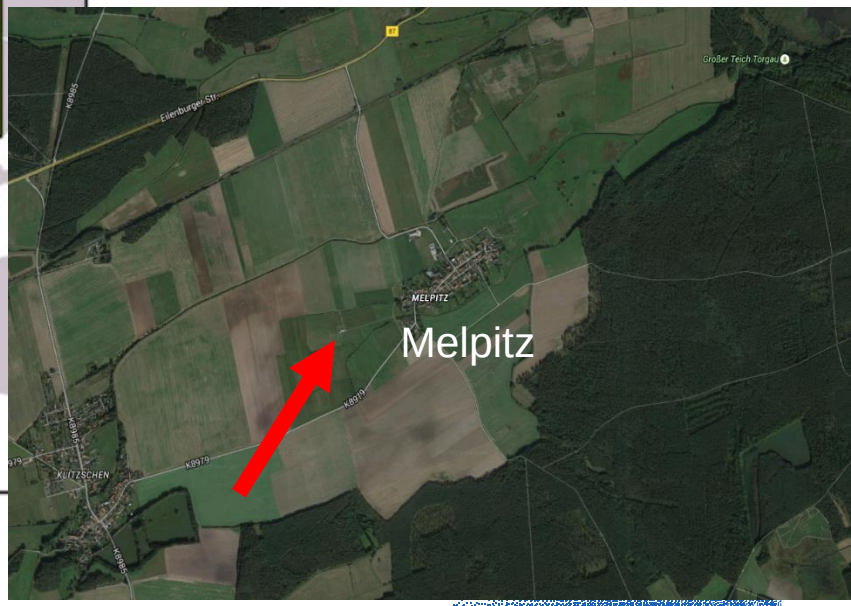
Measurement site Melpitz



- Rural site (atmospheric background measurements)
- Influenced by different air masses
- MARGA measurements in Melpitz since 2010



(12˚56‘ E, 51˚32‘ N, 86 m a.s.l.)

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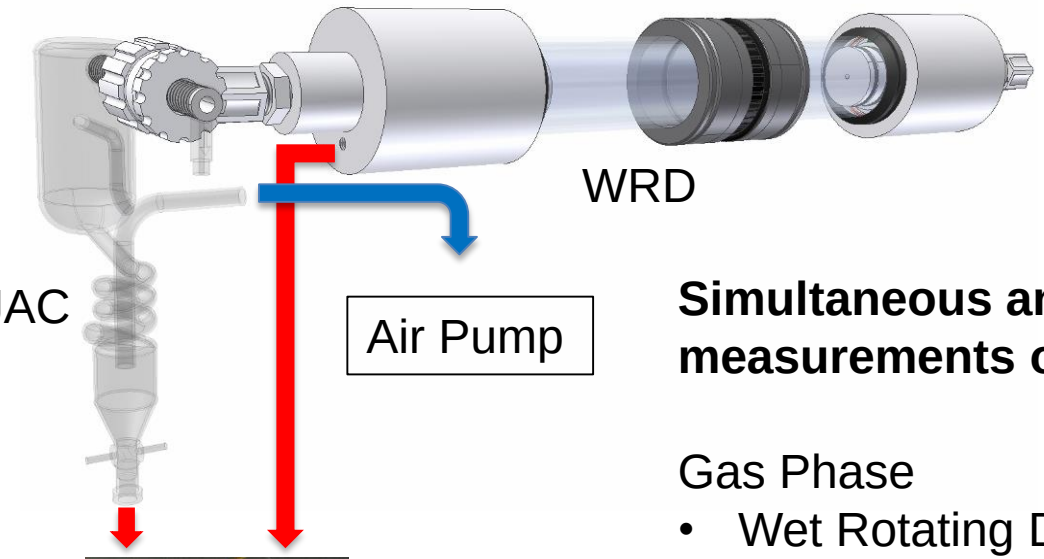
MARGA measurement principle – Sampling

MARGA – Monitor for AeRosols and Gases in ambient Air



Simultaneous and continuous measurements of the gas and particle phase

Gas Phase
- Wet Rotating Denuder (WRD)

Particle Phase
- Steam Jet Aerosol Collector (SJAC)
  - Particles grow to droplets in supersaturated environment

Sampling of 25 mL h^{-1} for WRD and SJAC

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applikon ANALYTICAL

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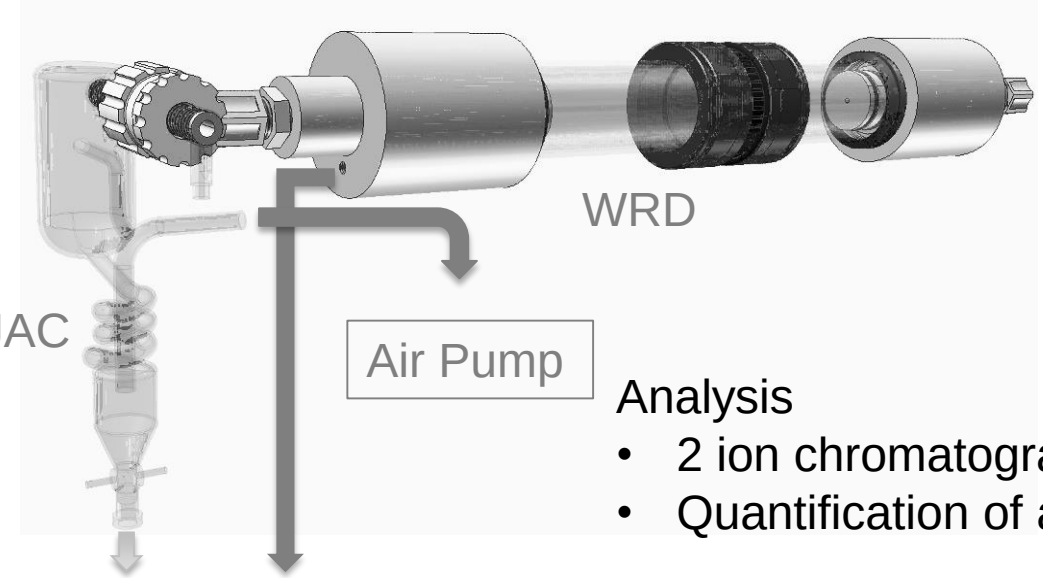
MARGA measurement principle – Analysis

MARGA – Monitor for AeRosols and Gases in ambient Air

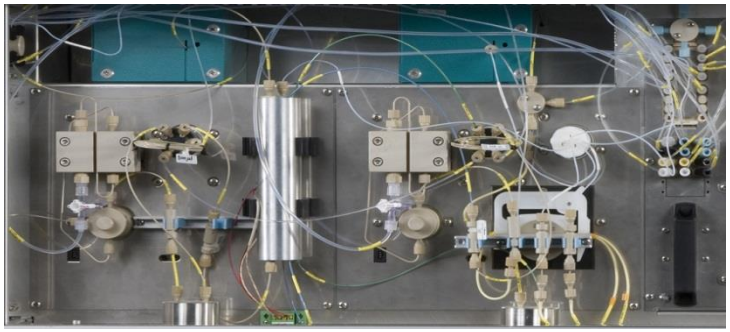


Air (1 m^3 h^{-1})

Analysis

- 2 ion chromatography systems (anions, cations)
- Quantification of aerosol and gas phase within 1 hour

Ion Chromatography System



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MARGA measurement principle – Analytes

gas phase	particle phase
hydrochloric acid (HCl)	chloride (Cl^-)
nitrous acid (HONO)	nitrate (NO_3^-)
nitric acid (HNO_3)	sulphate (SO_4^{2-})
sulphur dioxide (SO_2)	sodium (Na^+)
ammonia (NH_3)	ammonium (NH_4^+)
	potassium (K^+)
	magnesium (Mg^{2+})
	calcium (Ca^{2+})

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Gas phase comparison

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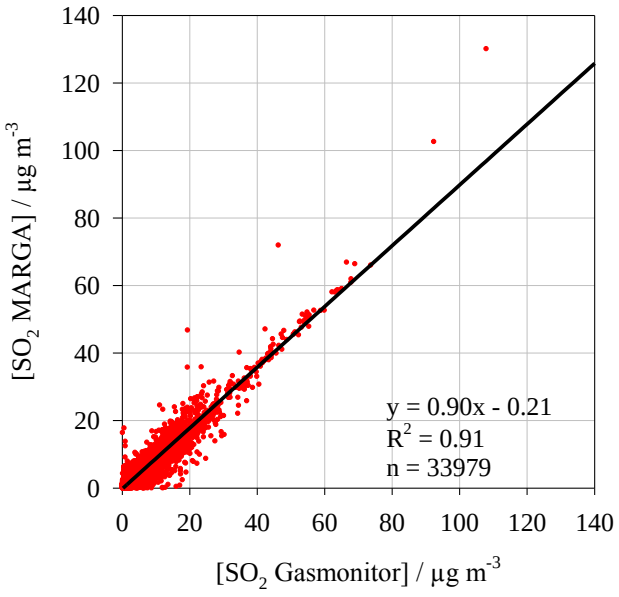
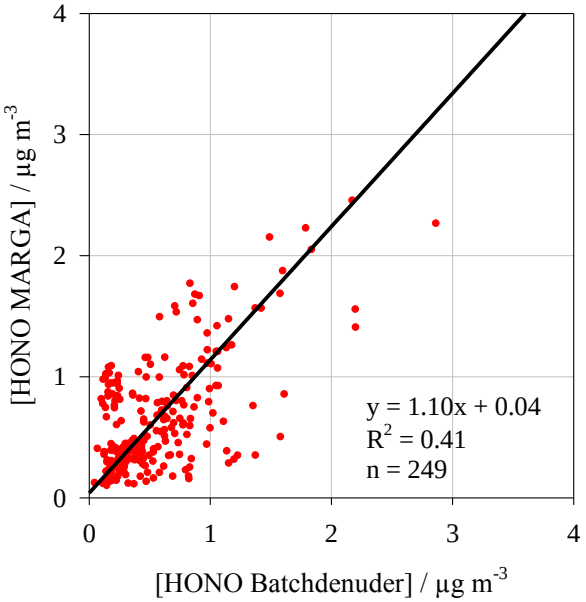
MARGA gas phase comparison

MARGA vs. SO_2-Gasmonitor



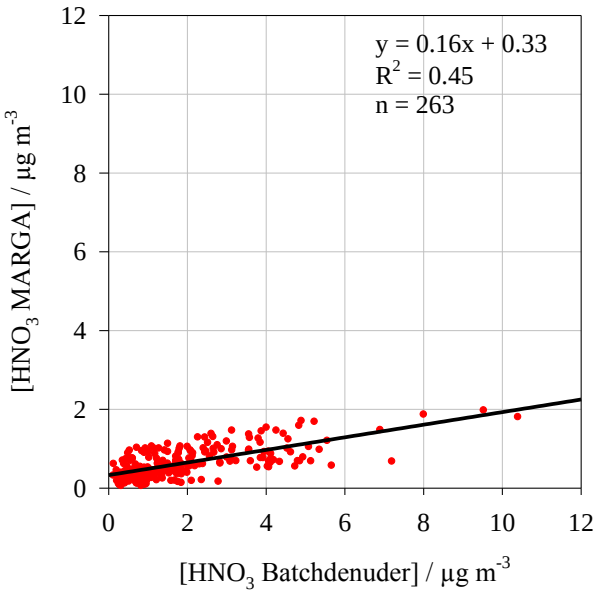
- Very good for SO_2

MARGA vs. HONO-Batchdenuder



- Large scattering for HONO

MARGA vs. HNO_3-Batchdenuder



- Bad for HNO_3

→ Sticky gas

→ Interactions with MARGA inlet

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Particle phase comparison

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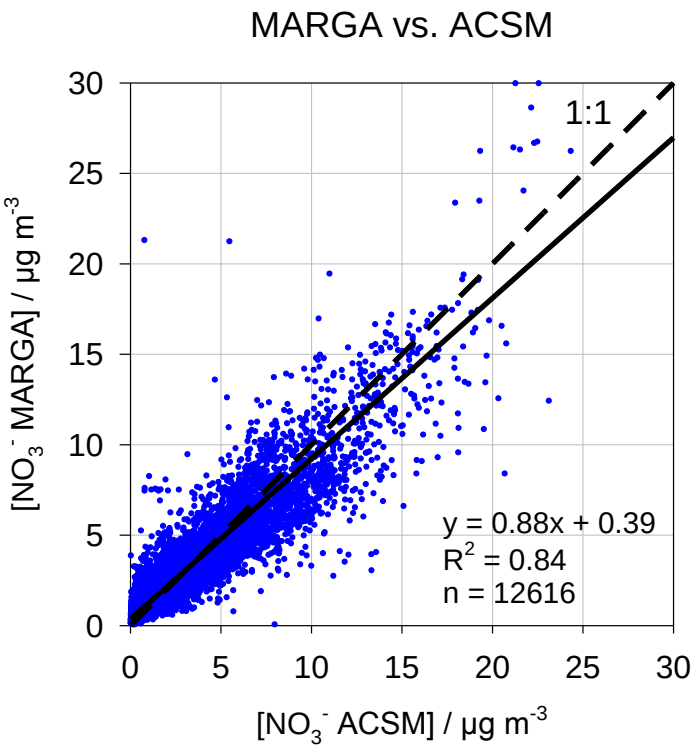
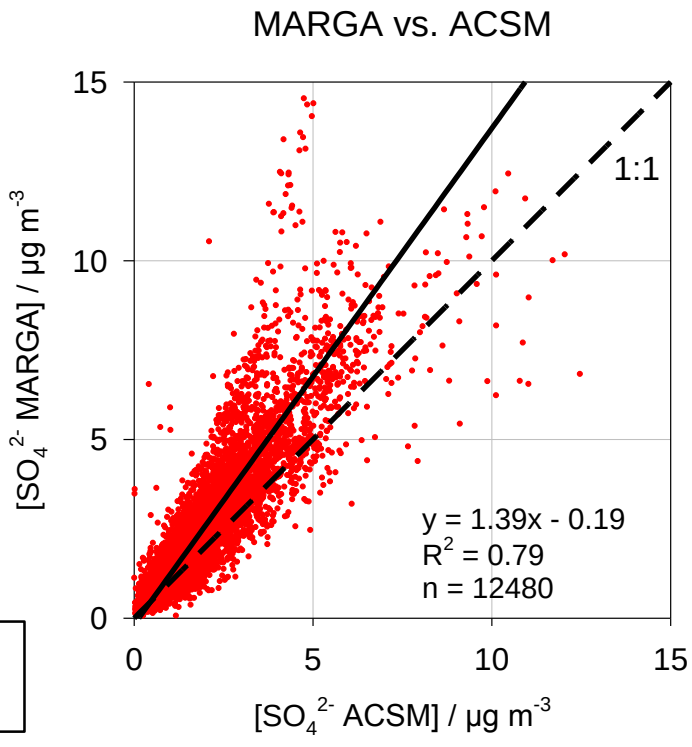
MARGA vs. ACSM

ACSM – Aerosol Chemical Speciation Monitor

MARGA → PM_{10}
ACSM → PM_1





comparison
Jun 2012 - May 2014

- Less nitrate measured by MARGA

→ Possible reason: measurement of organonitrates by ACSM

- More sulphate measured by MARGA

→ The same for ammonium

- Measurement of coarse mode aerosol (sea salt) with MARGA

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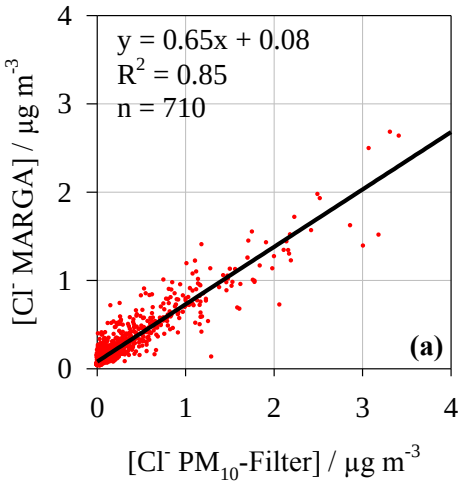
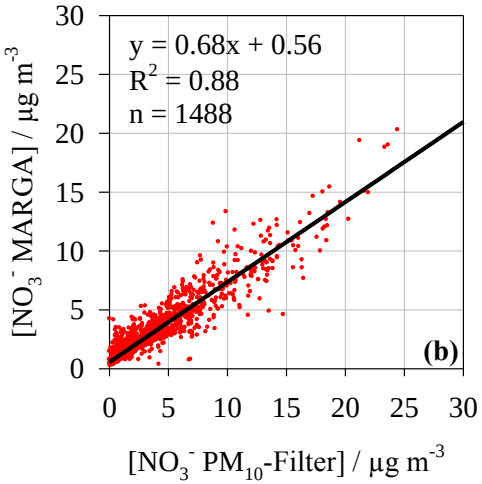
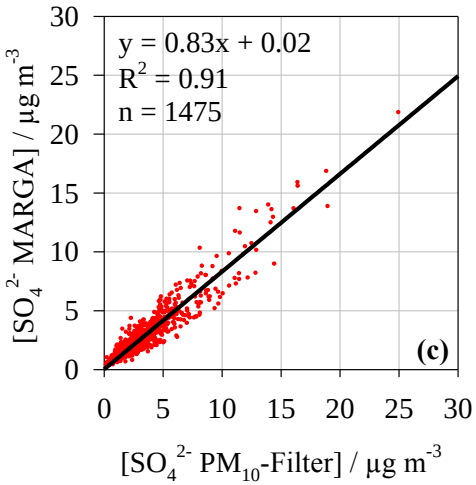
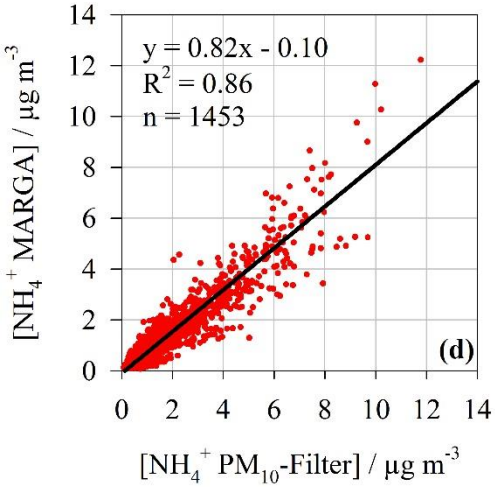
MARGA vs. PM_{10} filter

- Filter measurements offer widespread analysis of particle phase
- Only daily values for main inorganic compounds









- slightly higher concentrations on filter
  - ➢ Filter measure gas and particle phase

- Occurance of artifacts for filter measurements
  - ➢ Evaporation of volatile ammonium nitrate in summer

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MARGA measurements

a) Long-time series

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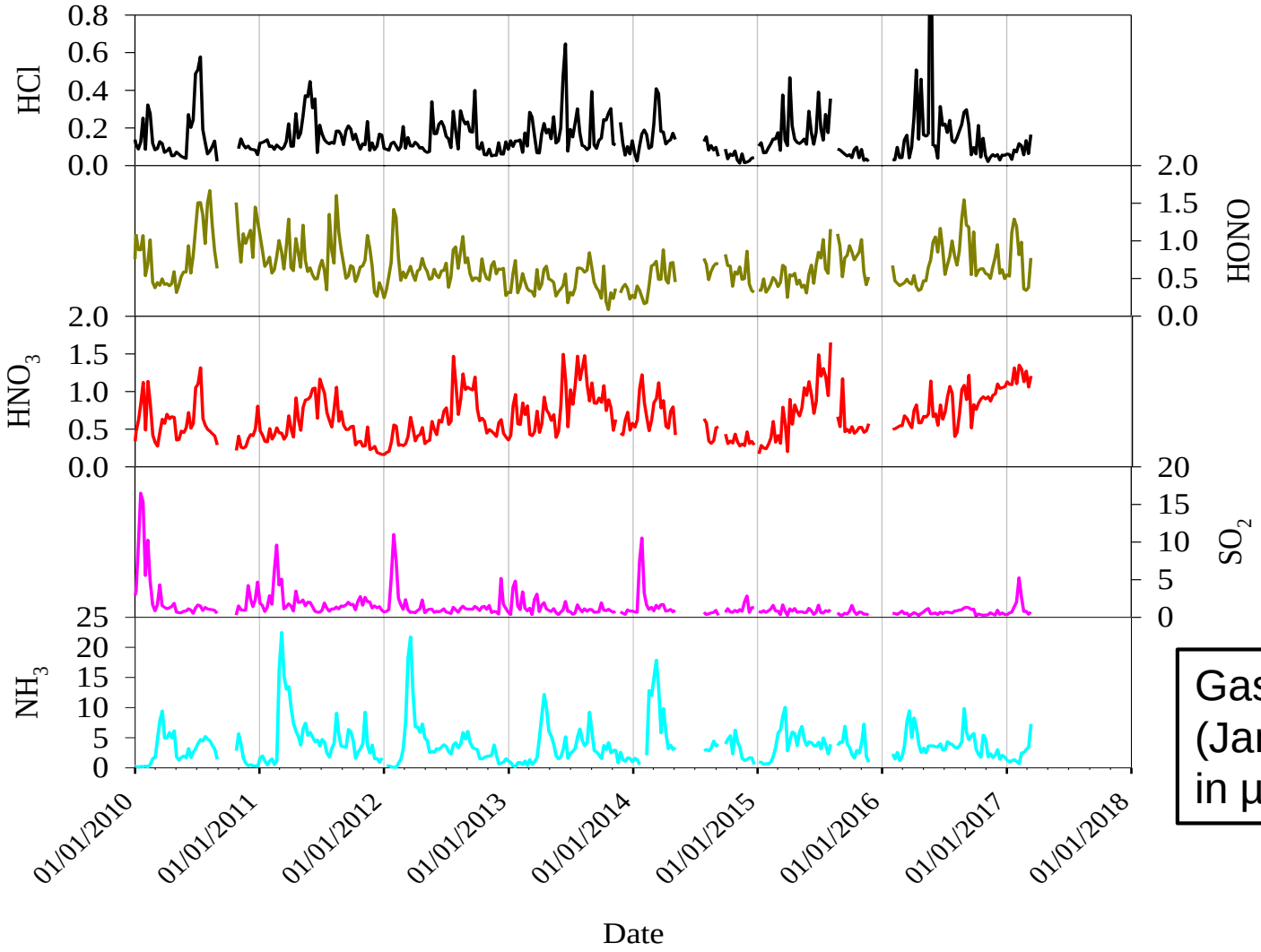
Long-time series - Gases



Gas measurements (Jan 2010 – Mar 2017) in µg m^{-3}

Weekly averages

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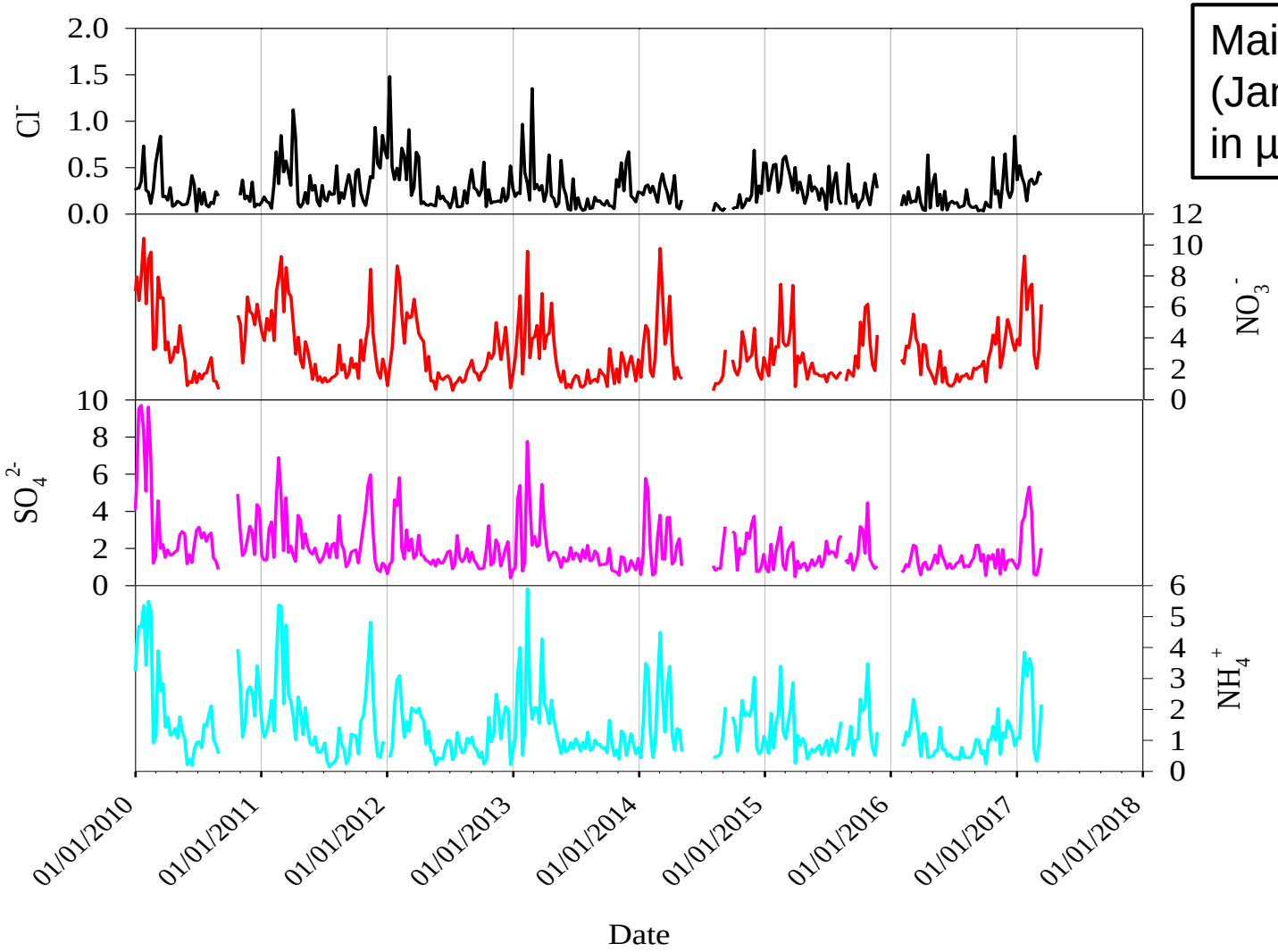
Long-time series – Main PM ions



Main PM ions
(Jan 2010 – Mar 2017)
in µg m^{-3}

Weekly averages

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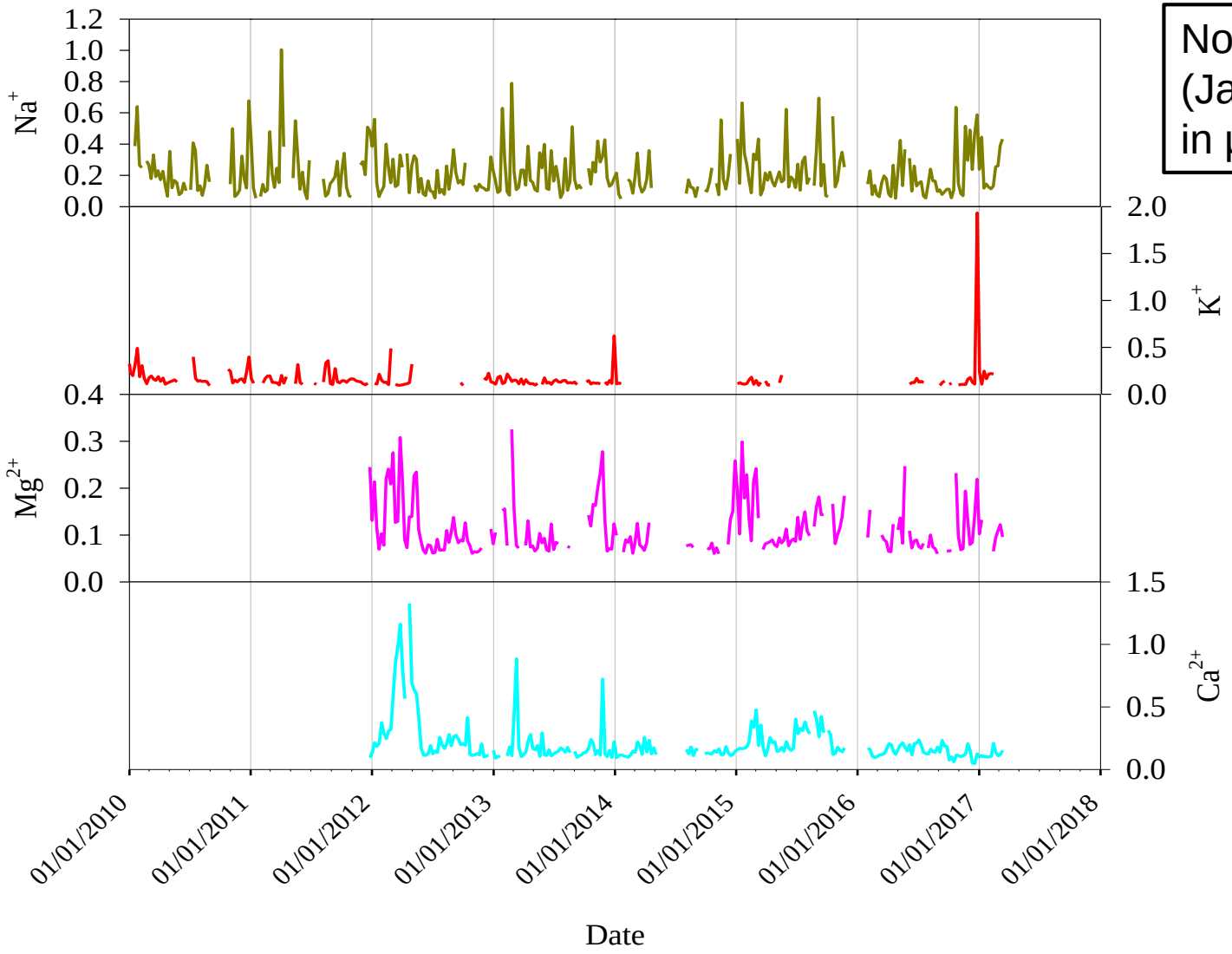
Long-time series – Non-NH_4^+ cations



Non-NH_4^+ cations
(Jan 2010 – Mar 2017)
in µg m^{-3}

Weekly averages

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MARGA measurements

b) Temporal variations of gases

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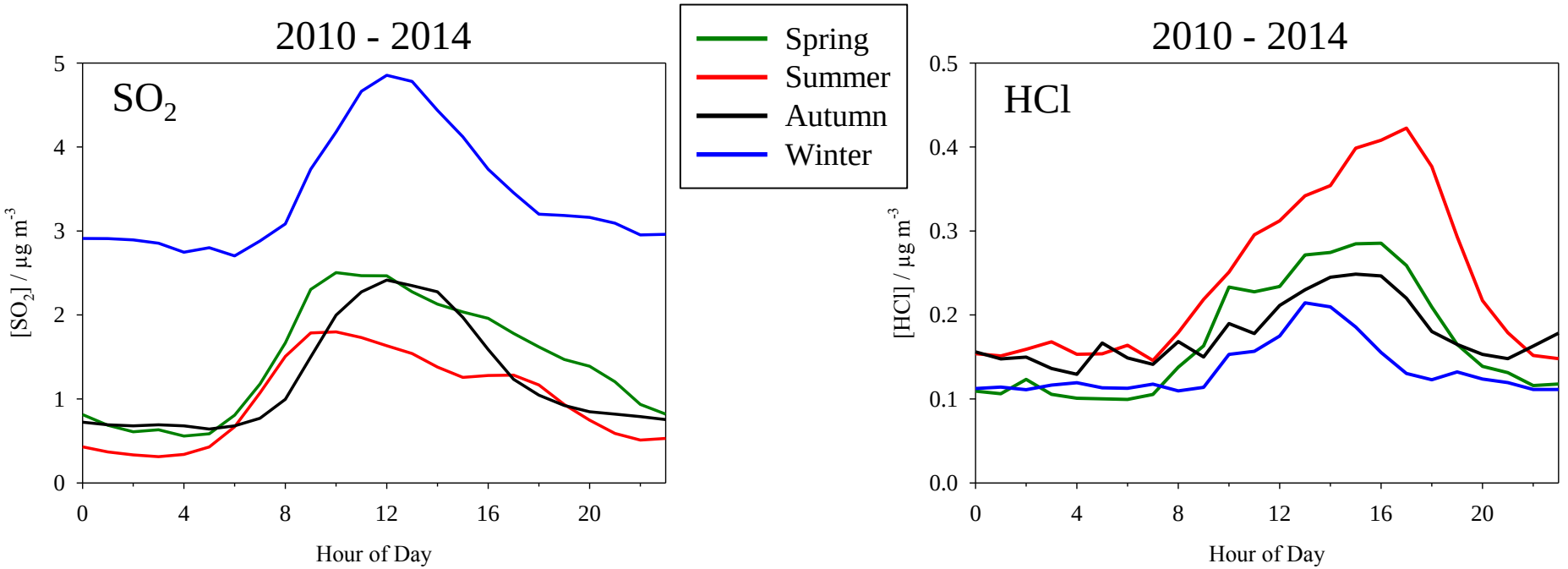
Temporal variations of gases – SO_2 and HCl



- Highest concentrations in winter

→ Anthropogenic origin

- Noontime peak

→ Transport in higher layers + down-mixing in the morning

- Source are surface reactions of H_2SO_4 and HNO_3 on sea salt aerosol
- Evaporation of volatile ammonium chloride for high temperutes

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MARGA measurements

c) Source apportionment of particulate ions

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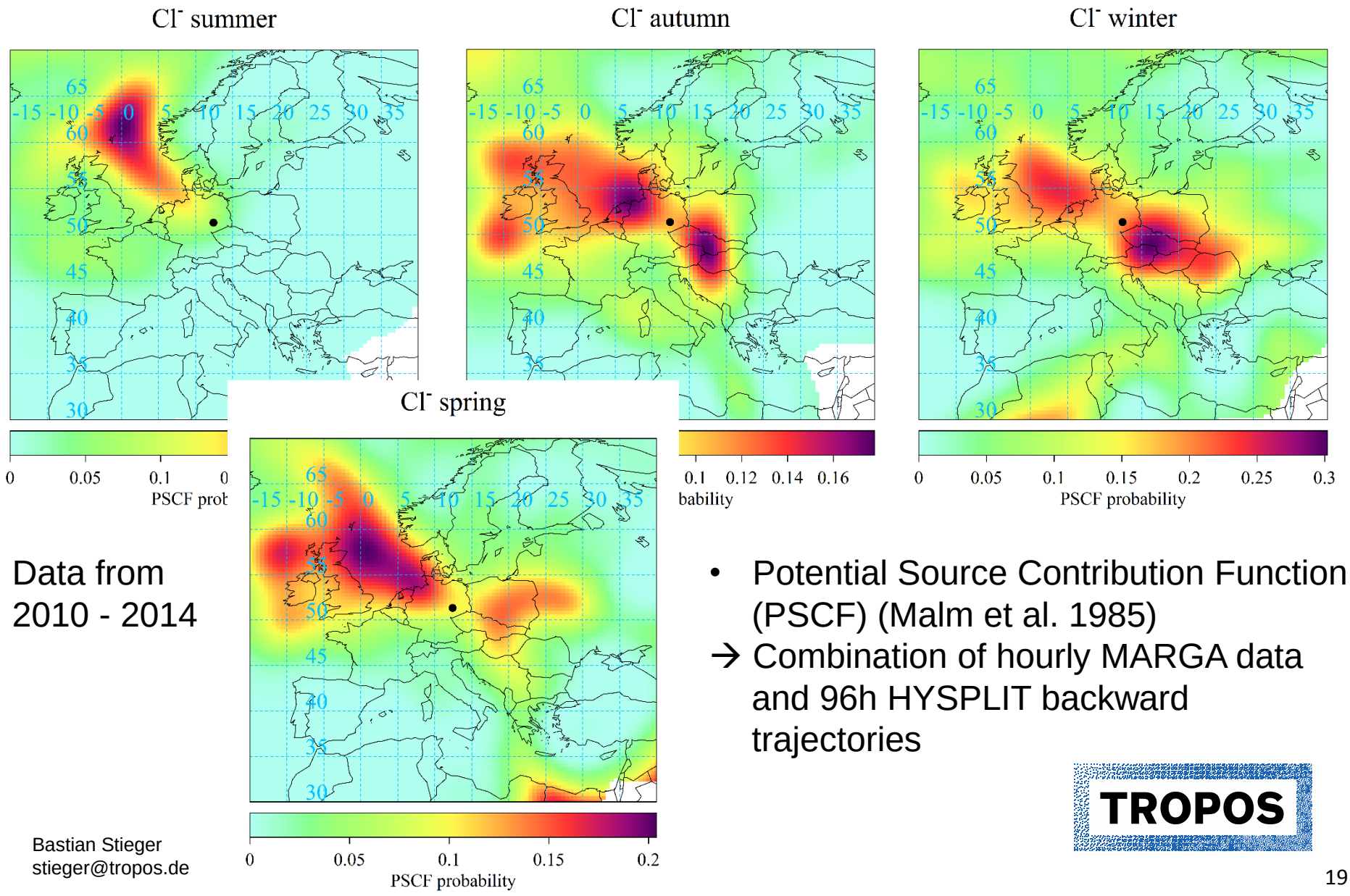
Sources of the PM ions - chloride



Data from 2010 - 2014

- Potential Source Contribution Function (PSCF) (Malm et al. 1985)

→ Combination of hourly MARGA data and 96h HYSPLIT backward trajectories

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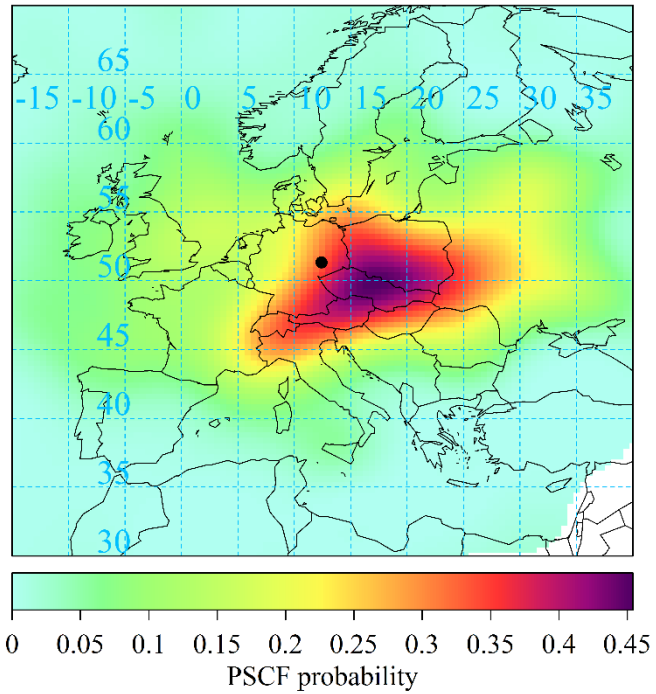
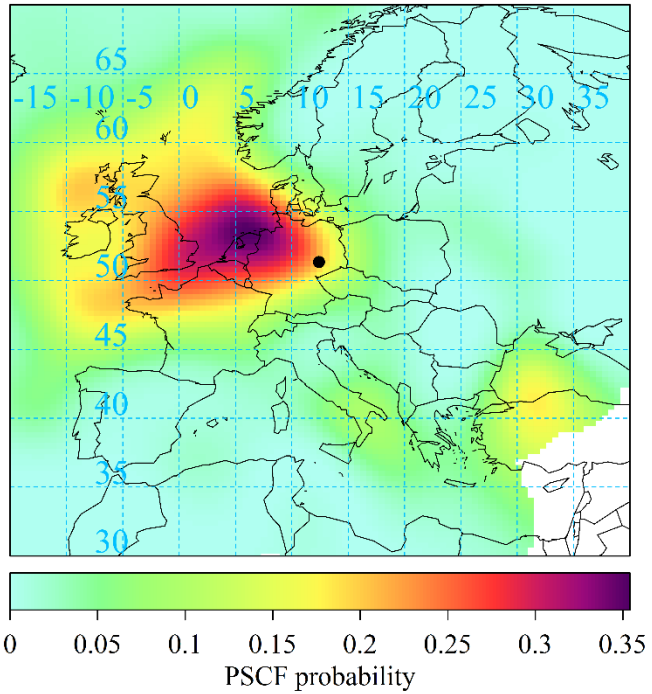
Sources of the PM ions – nitrate

NO_3^- winter



NO_3^- summer



- Anthropogenic source in winter

- Anthropogenic source
- Chloride-nitrate-exchange in sea salt particles

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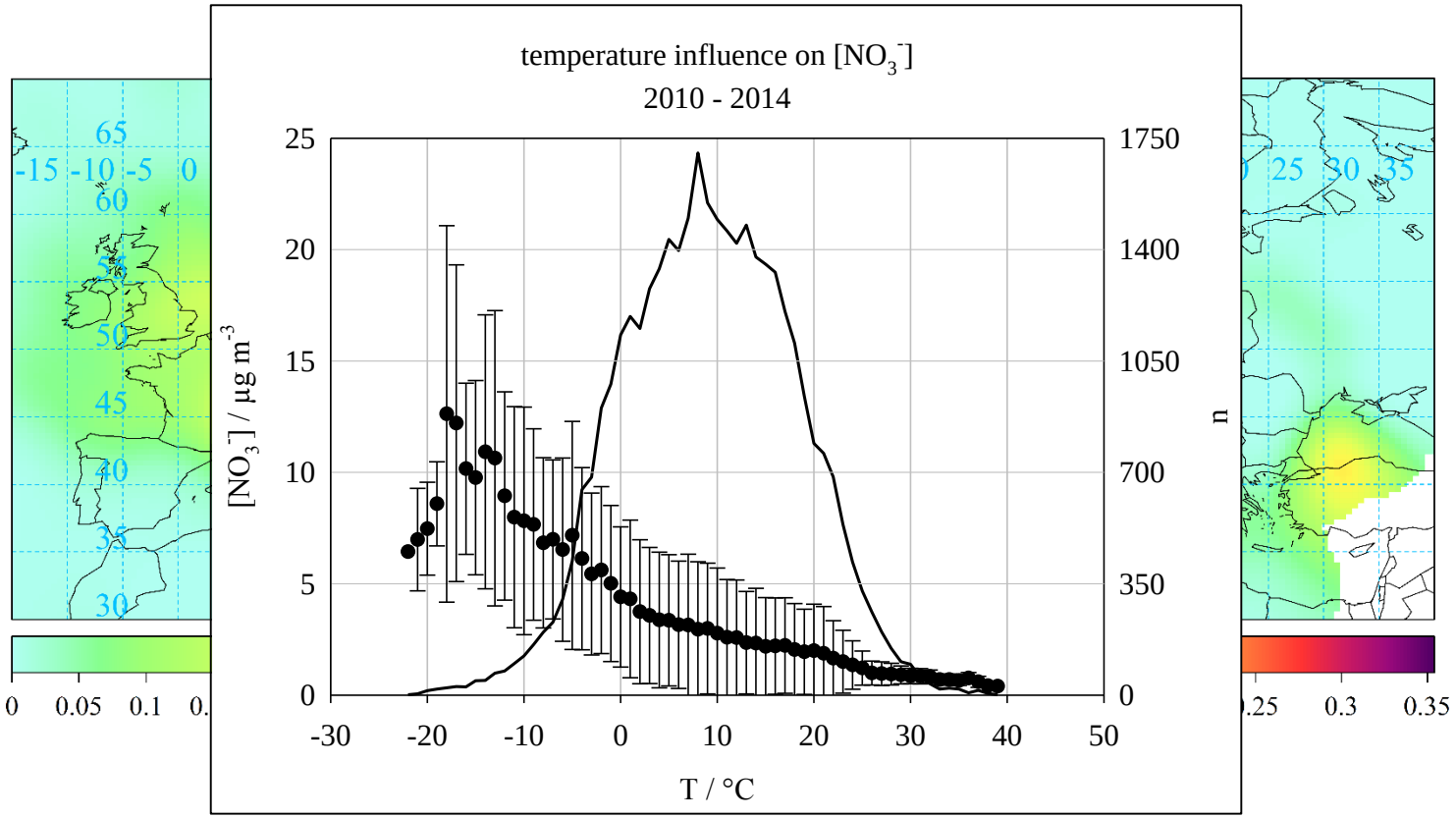
Sources of the PM ions – nitrate



- Anthropogenic source in winter
  - Highest concentrations for cold temperatures (combustion)
  - Volatilization for high temperatures (ammonium nitrate)
- Anthropogenic source
  - Chloride-nitrate-exchange in sea salt particles

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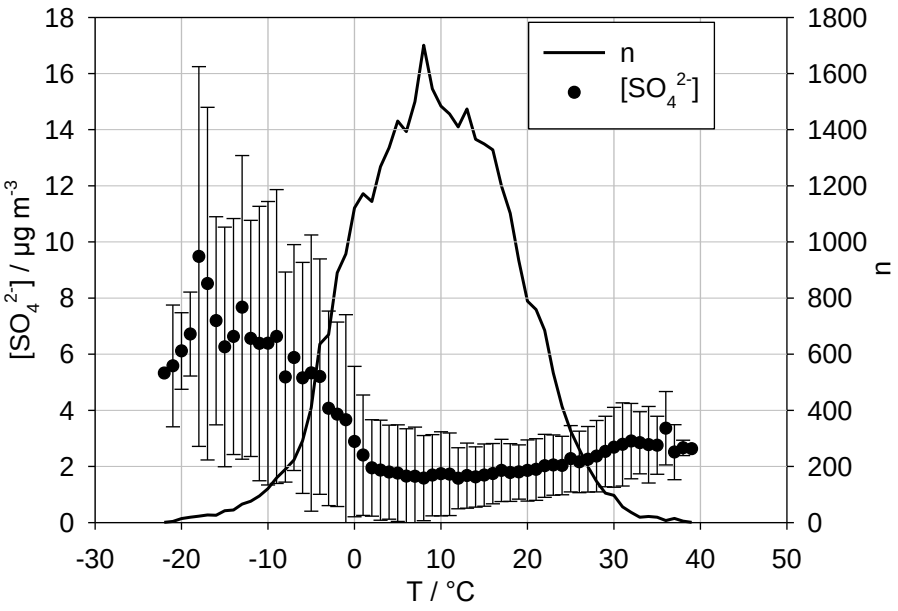
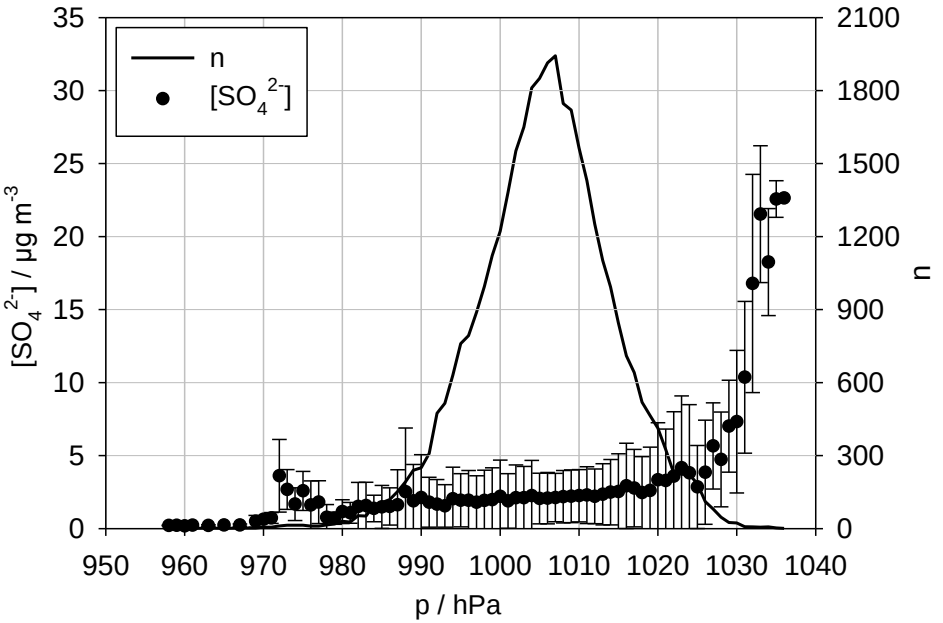
Sources of the PM ions – sulphate

sulphate → anthropogenic pollutant

temperature influence on $[SO_4^{2-}]$
2010-2014



pressure influence on $[SO_4^{2-}]$
2010-2014



- Highest concentration for low temperatures

→ Domestic heating in winter

- More sulphate for high pressure

→ High pressure favours the formation of an inversion layer (enrichment)

→ Sibirian high pressure system (winter) leads to transport from east to west

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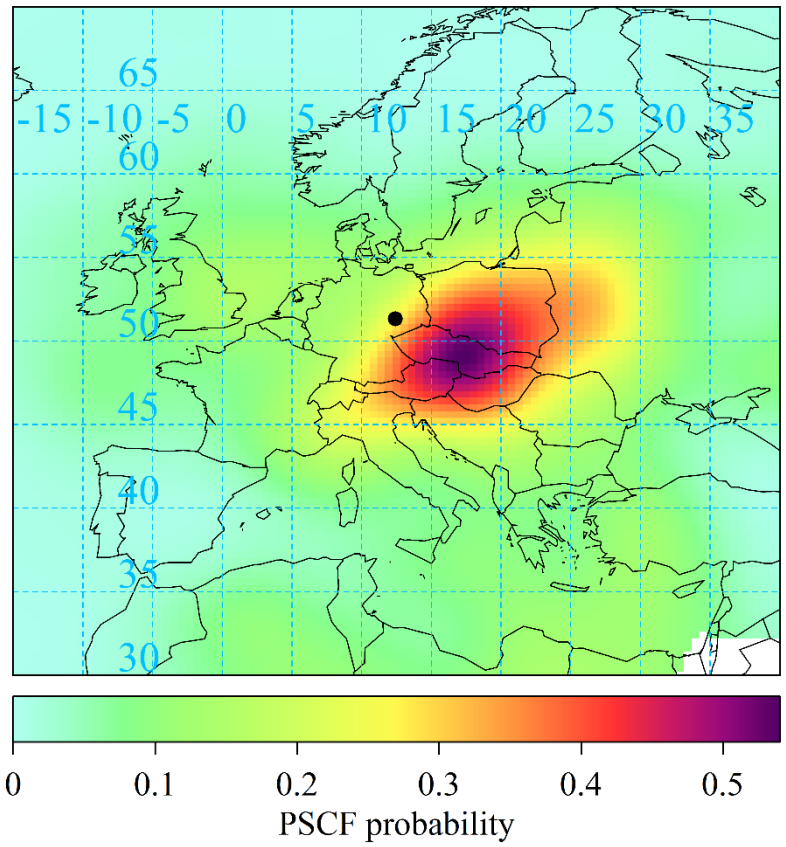
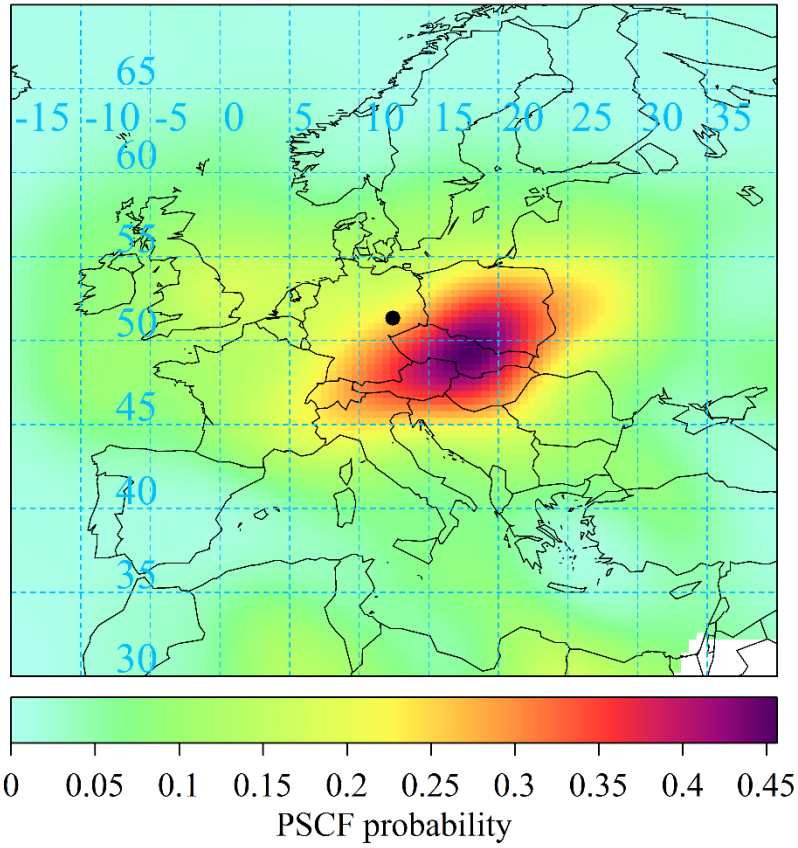
Sources of the PM ions – sulphate

SO_4^{2-}



NH_4^+



- Transport of sulphate in form of ammonium sulphate from east europe

→ Thermically stable salt

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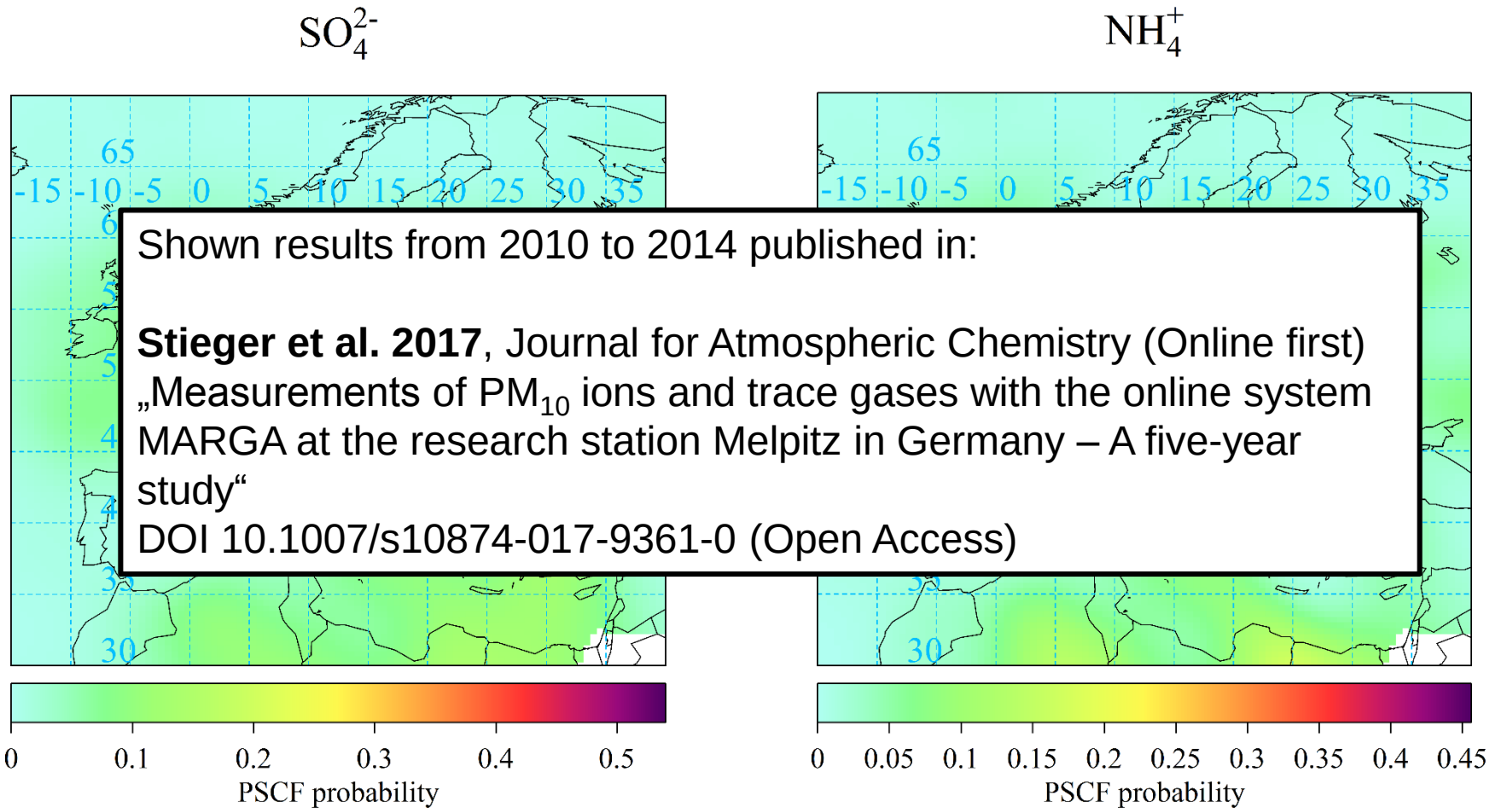
Sources of the PM ions – sulphate



Shown results from 2010 to 2014 published in:

Stieger et al. 2017, Journal for Atmospheric Chemistry (Online first) „Measurements of PM_{10} ions and trace gases with the online system MARGA at the research station Melpitz in Germany – A five-year study“
DOI 10.1007/s10874-017-9361-0 (Open Access)

- Transport of sulphate in form of ammonium sulphate from east europe

→ Thermically stable salt

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Analytical extension for carboxylic acid measurements

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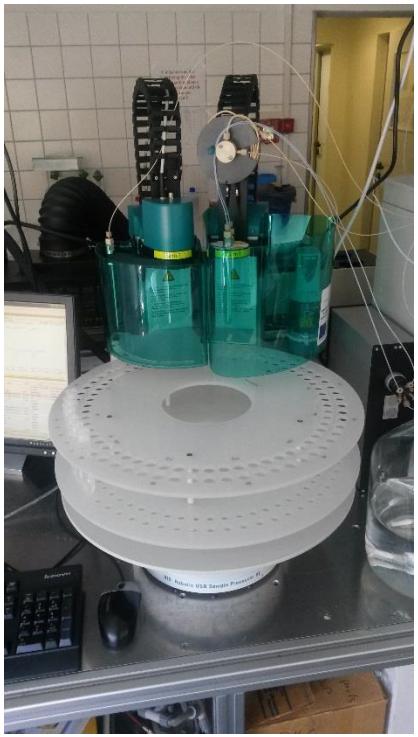
Detection of carboxylic acids - Extension

MARGA

Take the gas and particle phase solutions

+

Autosampler



1. Sample of gas and particle phase solutions
2. Injection to the IC

+

Compact-IC

Carboxylic acid analysis after inline pre-concentration

→ Time resolution of 2 hours

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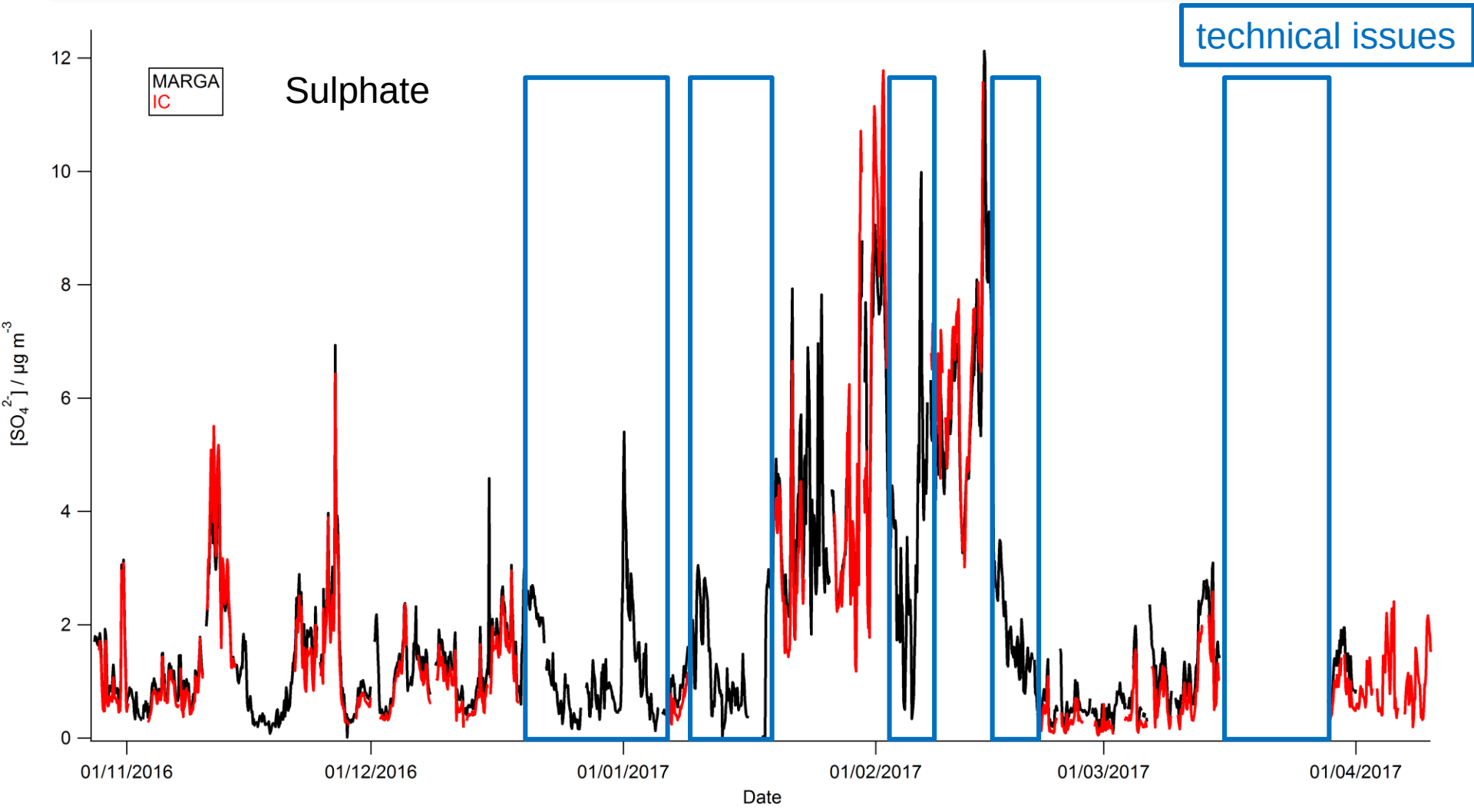
System evaluation



measurements since 28th October 2016

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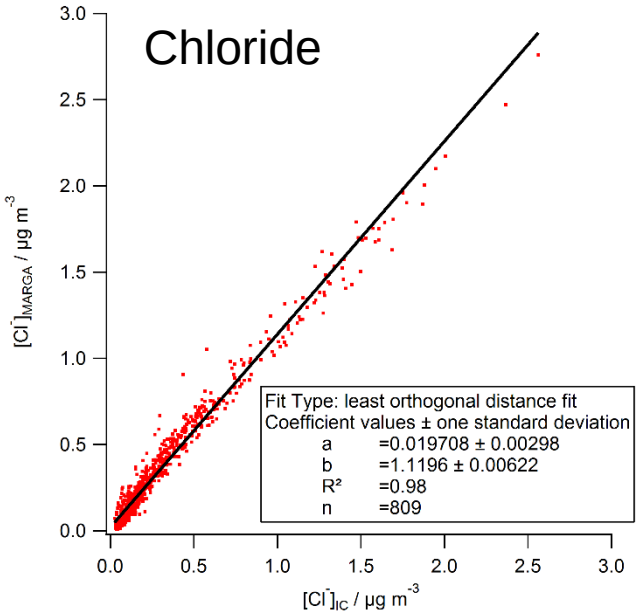
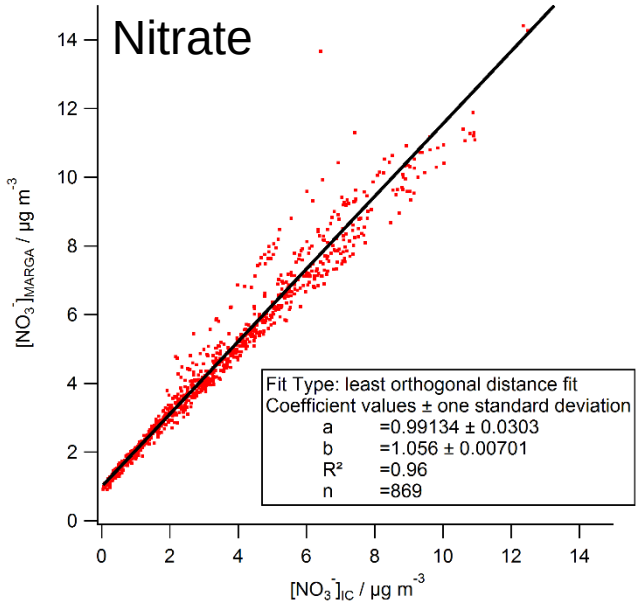
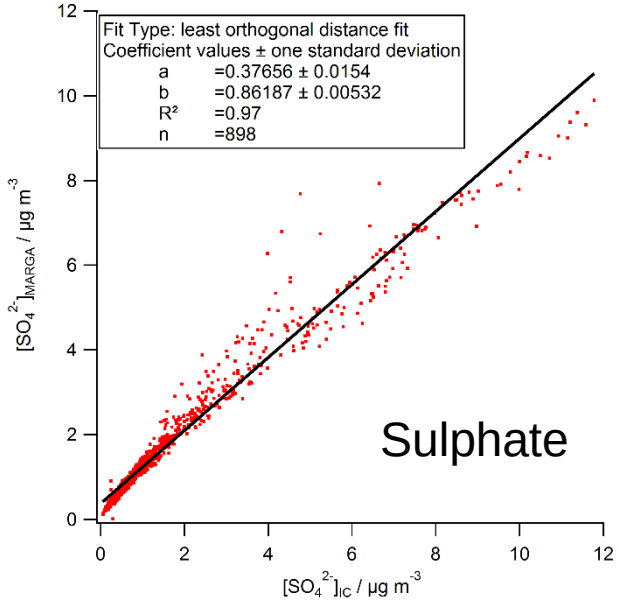
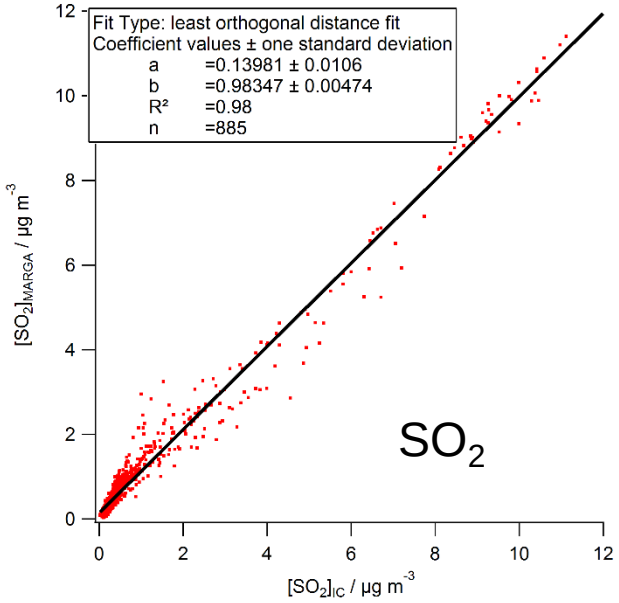
System evaluation





Very good correlations for main inorganic ions





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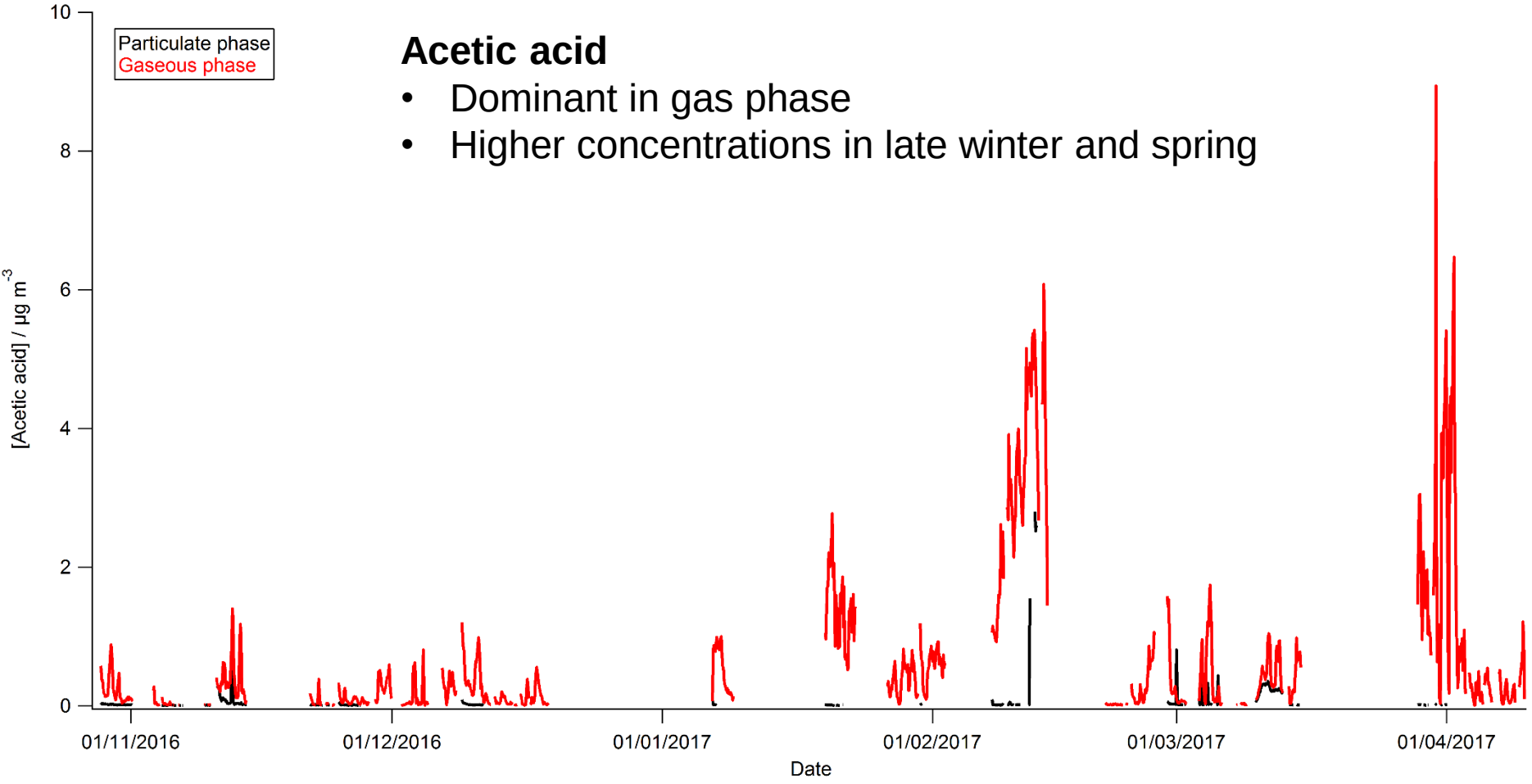
Acetic acid



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Carboxylic acids – First results and outlook

- In autumn and winter only formic, acetic and glycolic acid detectable
  - Formic and acetic acid dominant in gas phase
  - Glycolic acid in autumn and winter in particle phase
  - Glycolic acid in spring predominantly in gas phase (temperature influence?)
- Since spring more monocarboxylic acids (pyruvate, propionate, butyrate)
  - Possibly influenced by biological activity and photochemistry
- Rarely detection of oxalic acid in particle phase
  - Only detected during anthropogenic pollution events in winter

- Further measurements in spring and summer 2017
- Investigation of gas-particle-distribution
- Investigate reaction mechanism

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Summary

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Summary

- Monitor for AeRosols and Gases in ambient Air (MARGA)
  - → In Melpitz, Germany, since 2010
  - → Continuously measurements of inorganic ions in the gas and particle phase

- Advantages towards the standard PM_{10} filter measurements (higher time resolution, online system, gas measurement) and the ACSM
- Agreement with PM_{10} filter, ACSM and SO_2 gas monitor measurements in Melpitz

- Local sources for gases
- Investigations on sources of the particulate ions
  - Input: combination of MARGA data, meteorological data and HYSPLIT backward trajectories
  - → Transport as an important contributor to the measured concentrations of the main particulate ions

- Extension for the investigation of short-chain mono- and dicarboxylic acids
  - Measurements since autumn 2016
  - Investigation of gas-particle-distribution and reaction mechanism

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Thank you for your attention