Source apportionment studies and instrumental comparisons with the on-line system MARGA in Melpitz, Germany

Bastian Stieger[1], Gerald Spindler[1], Achim Grüner[1],Laurent Poulain[1],
Markus Wallasch[2], Hartmut Herrmann[1]

1 Leibniz Institute for Tropospheric Research, Leipzig, Germany
2 Federal Environmental Agency, Dessau-Roßlau, Germany

Introduction

The standard measurement method for the detection of particle mass is filter sampling. The main disadvantage of this analysis is the time resolution. Hence, the MARGA (Monitor for AeRosols and Gases in ambient Air, Metrohm Applikon, the Netherlands) provides an alternative. The concentrations of the particulate inorganic ions Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} can be quantified with an hourly time resolution. In addition, the water soluble and corresponding trace gases HCl, HONO, HNO_3, SO_2 and NH_3 are measured by the MARGA.
An air pump transports the ambient air through a Teflon coated PM_{10} inlet to a Wet Rotating Denuder (WRD). Therin, the water soluble trace gases diffuse in the absorbance solution. Because of inertia, particles follow the laminar flow within the WRD and enter the Steam-Jet Aerosol Collector (SJAC) where a supersaturation of water vapour leads to a growth into droplets. The liquid solutions of the WRD and the SJAC are transported via syringe pumps to two ion chromatography systems for the quantification of the anionic and cationic compounds in the samples for both phases [1].
Since 2010, the MARGA is located at the background research station of the Leibniz Institute for Tropospheric Research in Melpitz, Germany. Melpitz is predominantly influenced by westerly winds that transport marine and slightly anthropogenic processed aerosol to the station. Additionally, easterly winds can transport strongly anthropogenically polluted air to Melpitz [2].
The combination of hourly MARGA data, meteorological data and backward trajectories offers the possiblity to investigate the origin of the quantified inorganic compounds in the gas and particle phase.

Longtime Measurement

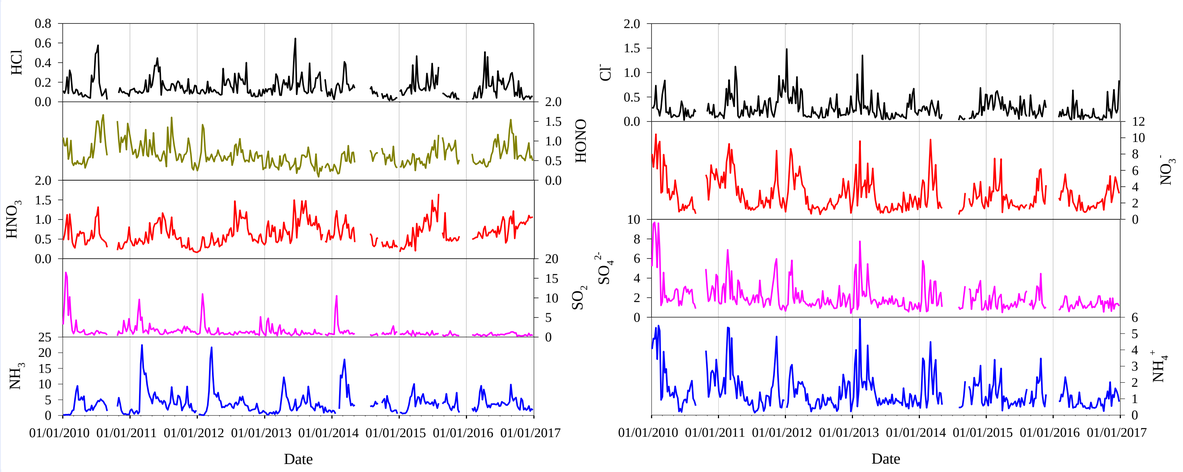

Fig. 1: The MARGA measurements in Melpitz yield a huge dataset from 2010 until 2016. Shown are the weekly averaged concentrations for the gases (left) and the main ions of the particle phase (right). Concentrations are given in µg m^{-3}.

Air Mass Origin

- Combination of the hourly MARGA data with meteorological data or backwards trajectory by calculating the Potential Source Conbtribution Function (PSCF) can give hints on probable source areas

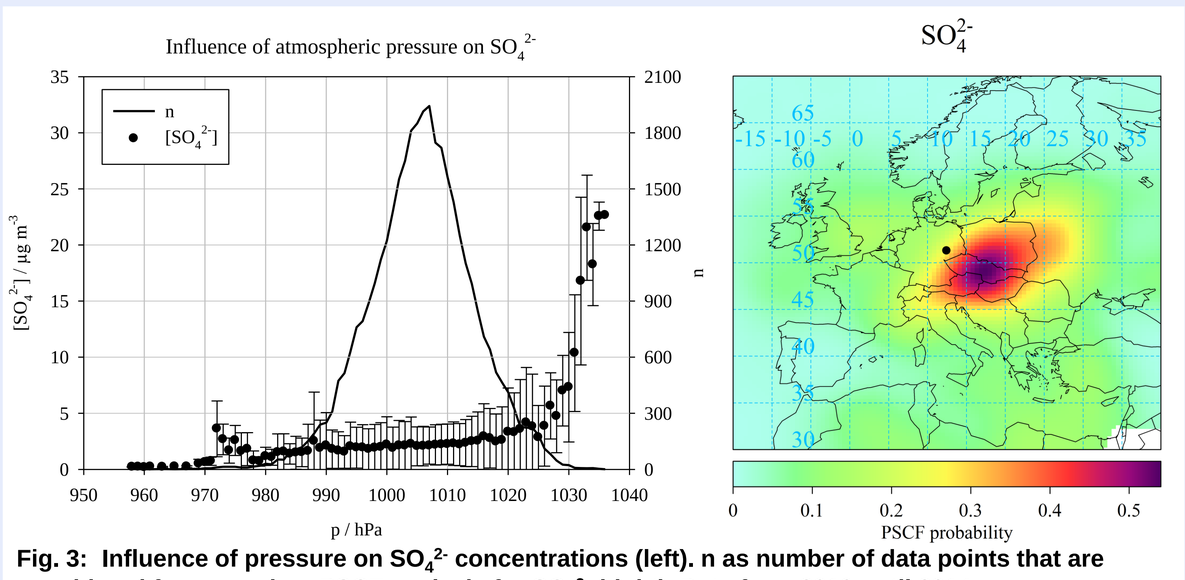

Fig. 3: Influence of pressure on SO_4^{2-} concentrations (left). n as number of data points that are considered for averaging. PSCF analysis for SO_4^{2-} (right). Data from 2010 until 2014.

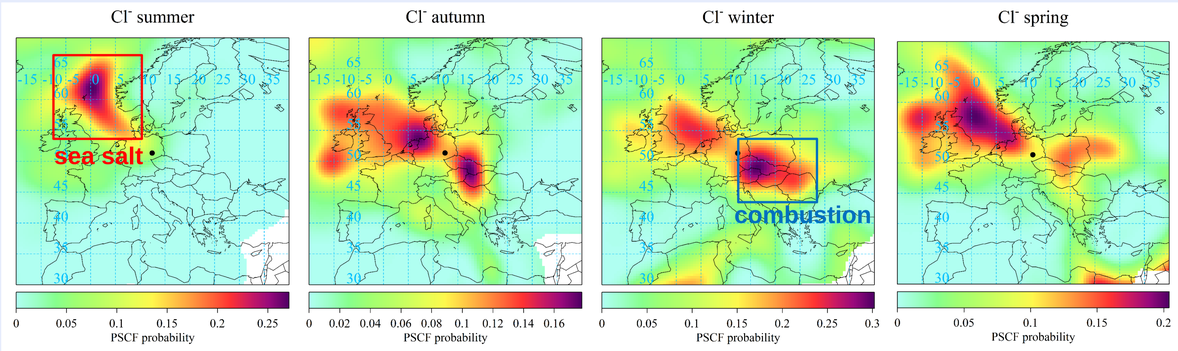

Fig. 4: PCSF analysis of Cl^- in summer, autumn, winter and spring (from left to right) using open access R package 'Openair'. Data are from 2010 until 2014. Melpitz as black point.

- Transport of SO_4^{2-} with easterly winds with a probable source area in East Europe (comparable with NH_4^+ and winter NO_3^-)
- Enrichment during episodes with high pressure (stable conditions especially in winter)

- Change of possible emission areas in the different seasons for Cl^-
- High Cl^- concentrations can be explained by sea salt in summer that is transported by westerly winds
- For colder seasons, there is an additional source because of coal combustion for domestic heating in East Europe

Summary

A MARGA system is used for measurements of water-soluble inorganic ions in PM_{10} and the corresponding trace gases in Melpitz since 2010.
The hourly time resolution provides an excellent possibility to study probable emission areas of species with higher tropospheric lifetimes. The anthropogenic pollutants SO_4^{2-}, NO_3^- and NH_4^+ have their main emission area in East Europe. The emission of Cl^- changes between summer (sea salt) and winter (anthropogenic domestic heating). Diurnal variations allow investigations of formation of the gaseous compounds.
Comparisons with different measurement instruments show good correlations except for the HNO_3 concentrations which is strongly underestimated by the MARGA because of inlet issues.

Temporal Variations

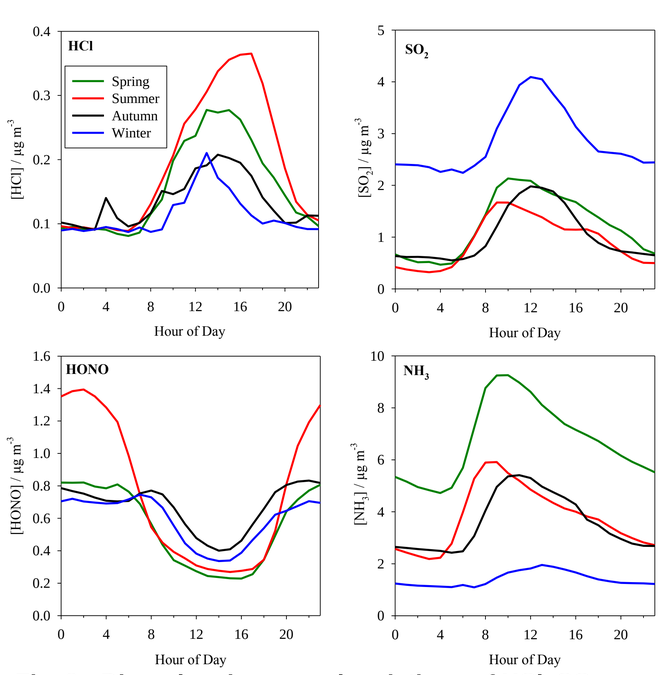

Fig. 2: Diurnal and seasonal variations of HCl, SO_2, HONO and NH_3 averaged from 2010 until 2016.

- MARGA provides possibility to investigate diurnal courses of the measured species
- Gases more sensitive for diurnal changes

- **HCl**: Peak in the afternoon
→ chloride containing particles react with gaseous H_2SO_4 and HNO_3 and form gaseous HCl (especially in summer)

- **SO_2** : highest concentrations in winter and during noon
→ anthropogenic pollution and labilization of the boundary layer

- **HONO**: Nighttime peaks and strong photolysis in the morning

- **NH_3**: Fertilization in spring lead to high concentrations; increase of NH_3 concentrations in the morning due to evaporation and tropospheric mixing processes

Comparisons with other Instruments

MARGA vs. ACSM

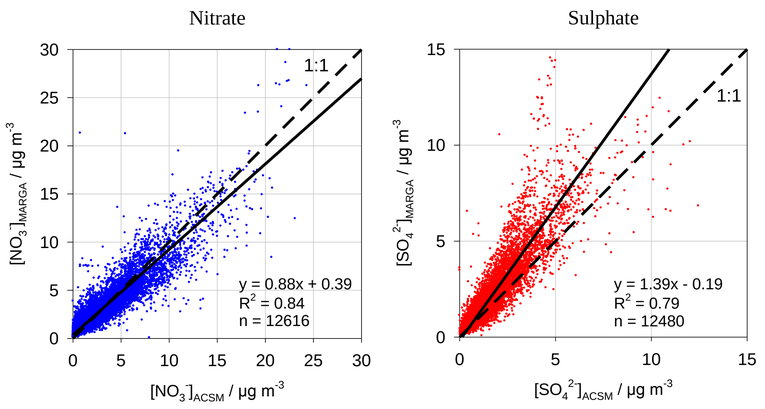

Fig. 5: Comparison between MARGA (PM_{10}) and ACSM (PM_1) for NO_3^- (left) and SO_4^{2-} (right) in Melpitz from 2012 until 2014.

MARGA vs. PM_{10}-Filter

Ion	Slope	Intercept	R^2	n
Cl^-	0.65	0.08	0.85	710
NO_3^-	0.68	0.56	0.88	1488
SO_4^{2-}	0.83	0.02	0.91	1474
Na^+	0.41	0.07	0.57	333
NH_4^+	0.82	-0.10	0.86	1453
K^+	0.56	0.02	0.41	151
Mg^{2+}	0.73	0.06	0.59	109
Ca^{2+}	2.83	-0.21	0.13	343

Table 1: Parameters of the orthogonal regression between MARGA and PM_{10}-Filter from 2010 until 2014 in Melpitz. Data are daily averages.

Gas comparison

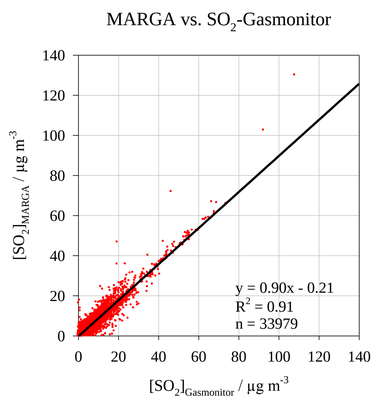

Fig. 6: MARGA comparison with SO_2-Gasmonitor (UV-Fluorescence) 2010 until 2014 as hourly data and offline HNO_3-Batchdenuder for selected days as daily averages.

- Good agreements with other instruments like the ACSM, the SO_2-Gasmonitor or PM_{10}-Filter measurements
- Higher NO_3^- concentrations for ACSM → ACSM can detect organonitrates
- Higher PM_{10} concentrations → Filter also sensitive for gaseous species (absorption/desorption)
- HNO_3 concentration
  1. is strongly underestimated because of high wall adsorption in the inlet system
  2. can be overestimated by high concentrations of N_2O_5 [3]

References

[1] Stieger, B., Spinder, G., Fahlbusch, B., Müller, K., Grüner, A., Poulain, L., Thöni, L., Seitler, E., Wallasch, M., Herrmann, H.: Measurements of PM_{10} and trace gases with the online system MARGA at the research station Melpitz in Germany - A five-year study. Journal of Atmospheric Chemistry (2017). doi10.1007/s10874-017-9361-0

[2] Spindler, G.; Brüggemann, E.; Gnauk, T.; Grüner, A.; Müller, K.; Herrmann, H. (**2010**): A four-year size-segregated characterization study of particles PM10, PM2.5 and PM1 depending on air mass origin at Melpitz. Atmospheric Environment, 44, (2), 164-173. doi:10.1016/j.atmosenv.2009.10.015

[3] Phillips, G. J.; Makkonen, U.; Schuster, G.; Sobanski, N.; Hakola, H.; Crowley, J. N. (**2013**): The detection of nocturnal N_2O_5 as HNO_3 by alkali- and aqueous-denuder techniques. Atmospheric Measurement Techniques, 6, (2), 231-237. doi:10.5194/amt-6-231-2013

Acknowledgements

Financial support from the Federal Environment Agency in Germany (grant no. 351 01 093 and 351 01 070), from EUSAAR (contract no. RII3-CT-2006-026140), as well as ACTRIS and ACTRIS-2 (grant no. 262254 and 654109) is gratefully acknowledged.
We would also like to thank our technical staff.