MARGA: Chemical characterization and sources of inorganic gaseous and PM_{10} pollutants in Central Europe

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Umwelt Bundes Amt – Für Mensch und Umwelt

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Introduction

The online sampling system MARGA (Monitor for AeRosols & Gases in ambient Air), developed by Applikon Analytical, the Netherlands, quantifies hourly the particulate inorganic ions Cl^-, NO_3^-, SO_4^{2-}, Na^+, NH_4^+, K^+, Mg^{2+} and Ca^{2+} as well as the corresponding trace gases HCl, HONO, HNO_3, SO_2 and NH_3 [1].
With a flow of 1 m^3 per hour the air passes a Teflon coated PM_{10} inlet and enters a Wet Rotating Denuder (WRD) in which the water-soluble trace gases diffuse in an absorbance liquid. Because of the laminar flow within the WRD, the particles reach afterwards the Steam-Jet Aerosol Collector (SJAC). A supersaturation of water vapour within the SJAC leads to a growth of the particles into droplets. A cyclone collects these droplets containing the water-soluble inorganic ions. The liquid solutions of the WRD and the SJAC are analysed by an ion chromatography system which is continuously calibrated by an internal standard (LiBr). Since 2010 the MARGA operates at the background research station of the Leibniz Institute for Tropospheric Research in Melpitz, Germany (12˚56‘E, 51˚32‘N, 86 m a.s.l.) [2].

The main advantages are:
1. High-time resolution of one hour for the analysis of inorganic ions in the gas and particle phase
2. Artefacts like evaporation can be excluded in comparison to filter measurements
3. Online measurements with remote control

Longtime Measurement

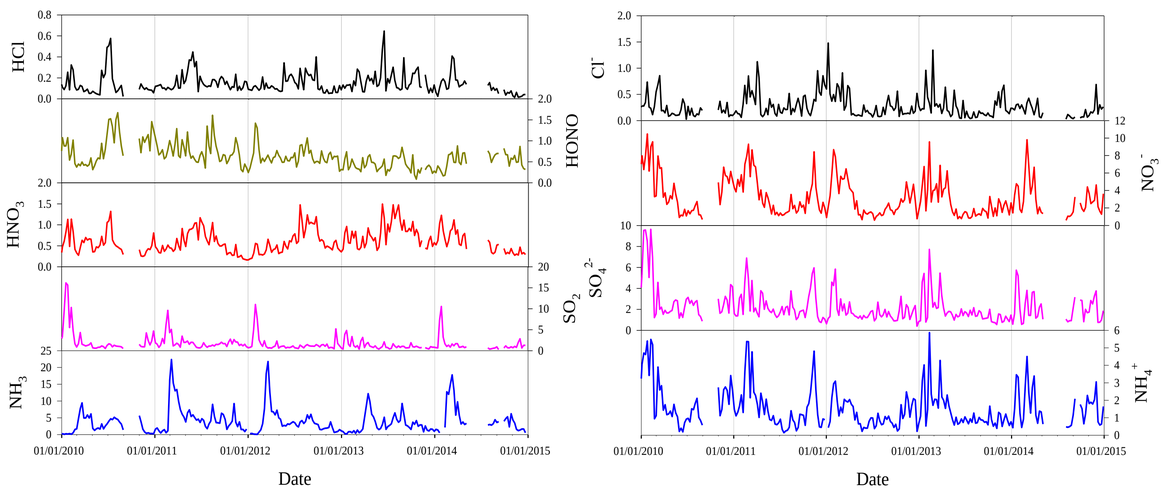

Fig. 1: The MARGA measurements in Melpitz yield a huge dataset for five years. Shown are the weekly averaged concentrations for the gases (left) and the main ions of the particle phase (right). Concentrations are given in µg m^{-3}.

Diurnal and Seasonal Variations

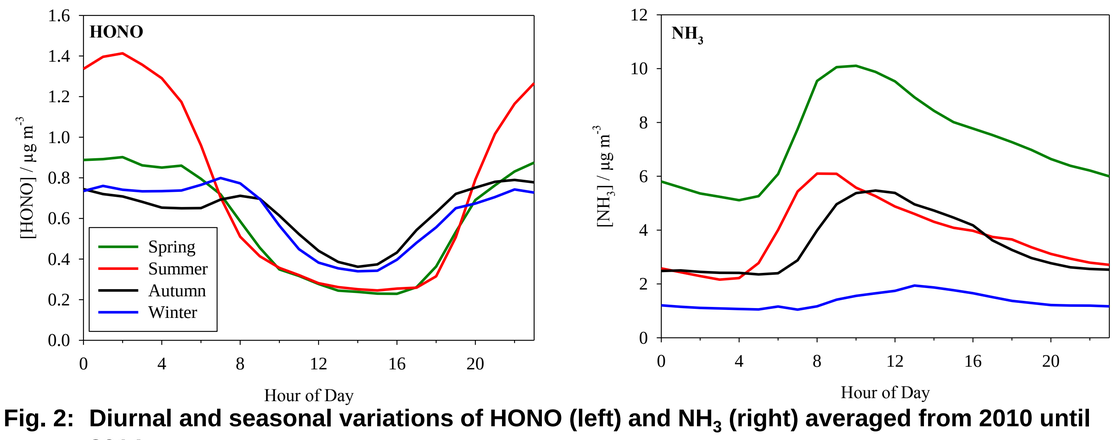

Fig. 2: Diurnal and seasonal variations of HONO (left) and NH_3 (right) averaged from 2010 until 2014.

- clear diurnal cycle for HONO but overestimations of the daytime HONO concentrations by the MARGA → probably due to wet chemical processes within the WRD
- significant increase of the NH_3 concentration in the morning → evaporation from surfaces
- highest values of NH_3 in spring → agricultural activities

Air Mass Origin

- source estimation of the individual pollutants due to combination of the hourly MARGA data with meteorological data or HYSPLIT 96h-backwards trajectories
- calculations of the most probable emission areas by the Potential Source Contribution Function (PSCF) [3] with the R package “Openair” [4]

Chloride

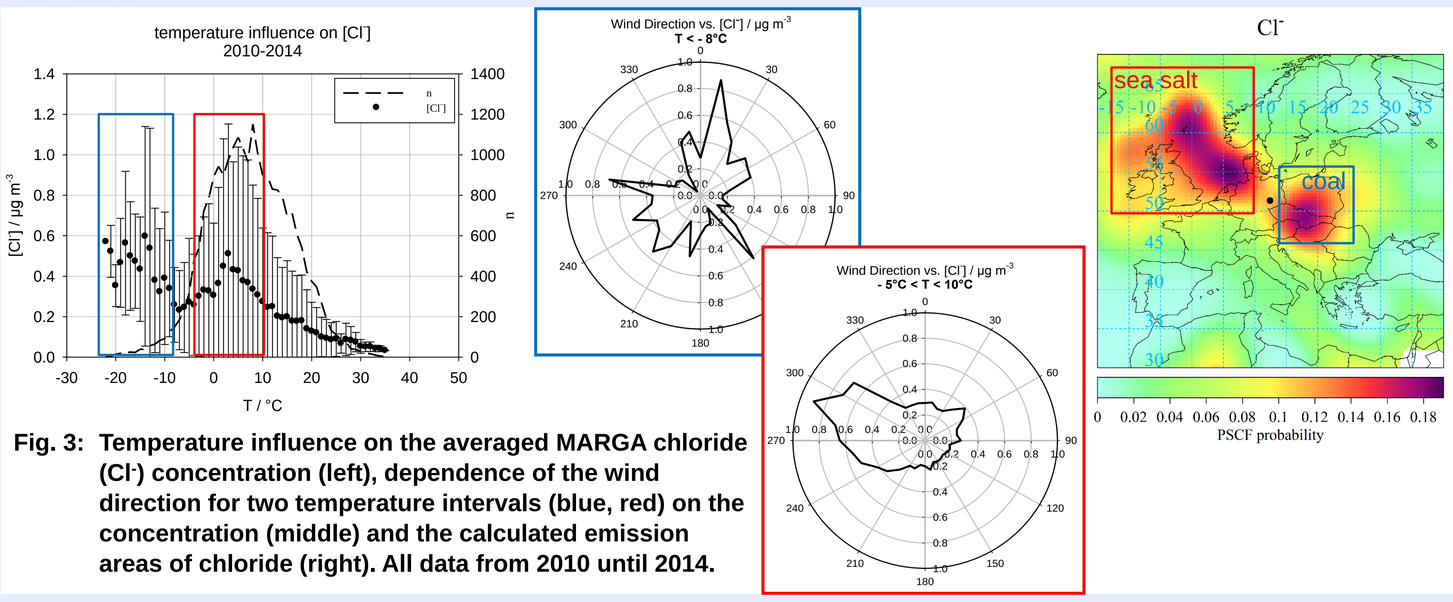

Fig. 3: Temperature influence on the averaged MARGA chloride (Cl^-) concentration (left), dependence of the wind direction for two temperature intervals (blue, red) on the concentration (middle) and the calculated emission areas of chloride (right). All data from 2010 until 2014.

- in winter, inversion layers accumlate chloride (emitted by coal burning and road salt) (no dominant wind direction) → blue colour
- transport of sea salt particles from the sea with air mass inflow from the west for temperatures between -5˚ and 10˚C → red colour

Anthropogenic Pollutants

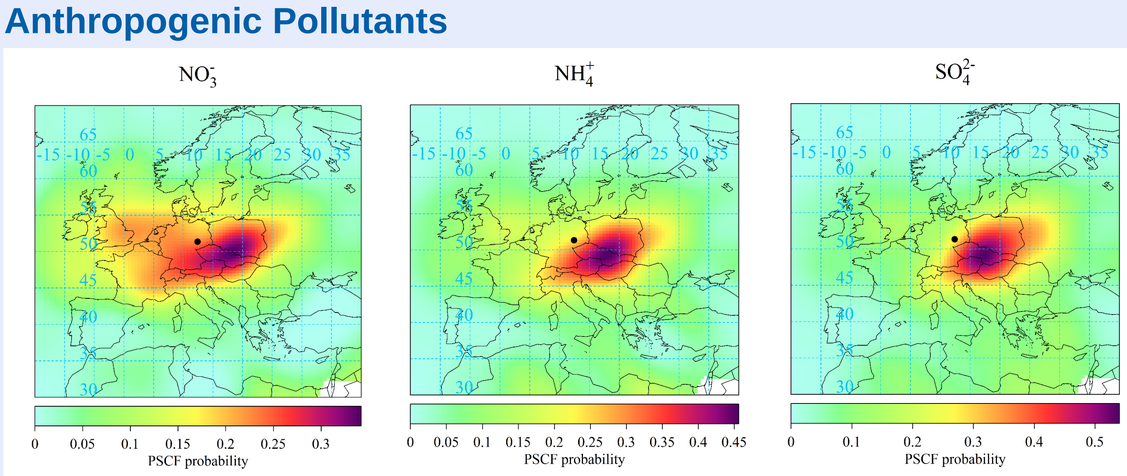

Fig. 4: Calculated PSCF for nitrate (NO_3^-) (left), ammonium (NH_4^+) (middle) and sulphate (SO_4^{2-}) (right) with Melpitz as black dot. Trajectories and MARGA data from 2010 until 2014.

- elevated concentrations of nitrate, sulphate and ammonium in Melpitz due to transport from East Europe
- have the same emission area → probably pollutants are transported as ammonium sulphate and ammonium nitrate to Melpitz

Comparisons with other Instruments

MARGA vs. ACSM

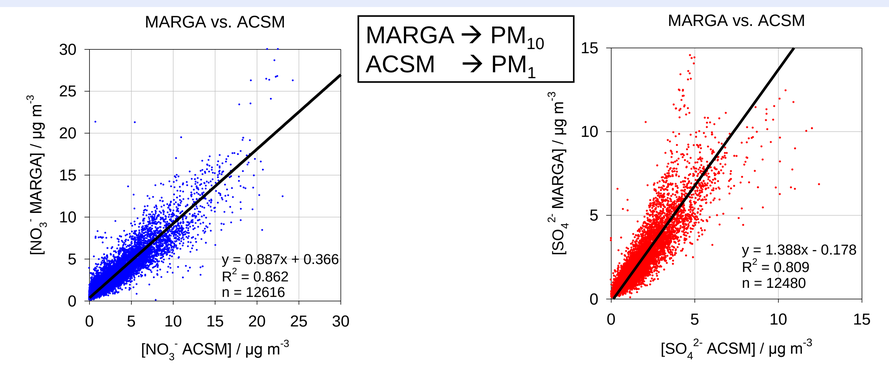

Fig. 5: Comparison between MARGA (PM_{10}) and the Aerosol Chemical Speciation Monitor (ACSM) (PM_1) in Melpitz from June 2012 until May 2014 with orthogonal regression for nitrate and sulphate.

- less nitrate measured by MARGA → ACSM measures organonitrates
- more sulphate measured by MARGA → measurement of course mode sulphate by MARGA

MARGA vs. PM_{10}-Filter

ion	slope	intercept	R^2	n
Cl^-	0.668	0.072	0.862	710
NO_3^-	0.694	0.509	0.877	1488
SO_4^{2-}	0.838	-0.016	0.906	1474
NH_4^+	0.828	-0.111	0.869	1452
Na^+	0.423	0.064	0.545	332
K^+	0.534	0.034	0.339	150
Mg^{2+}	0.716	0.063	0.656	108
Ca^{2+}	3.576	-0.348	0.182	342

Tab. 1: Orthogonal regression between MARGA and daily PM_{10}-Filter measurements in Melpitz from 2010 until 2014.

- good correlation with the main ions
- underestimation by the MARGA
→ possible adsorption of the corresponding trace gases on the filter
- weak correlations for metal ions
→ often under detection limits for the MARGA
- calcium overestimated due to accumulations within the sample loop

MARGA vs. HNO_3-Batchdenuder

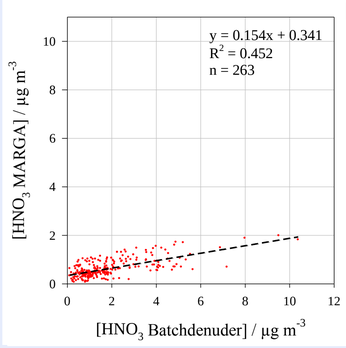

Fig. 6: Comparison between MARGA and an offline HNO_3-Batchdenuder for some days in August until October 2011 as well as for August and September 2012.

- HNO_3 concentration is strongly underestimated because of high wall adsorption in the inlet system of the MARGA

Summary

A MARGA system was used for measurements of water-soluble inorganic ions in the gas and particle phase in Melpitz. Since 2010 a data yield of over 80% was achieved for the main ions and gases.
The high data yield and the high-time resolution of one hour give excellent possibilities to study the air mass origin and the diurnal variations.
Comparisons with different measurement instruments show good correlations except for the metal ions due to concentrations under the detection limit as well as HNO_3 which is strongly underestimated by the MARGA.

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