A long-term study for PM and trace gases at rural Melpitz site in Germany

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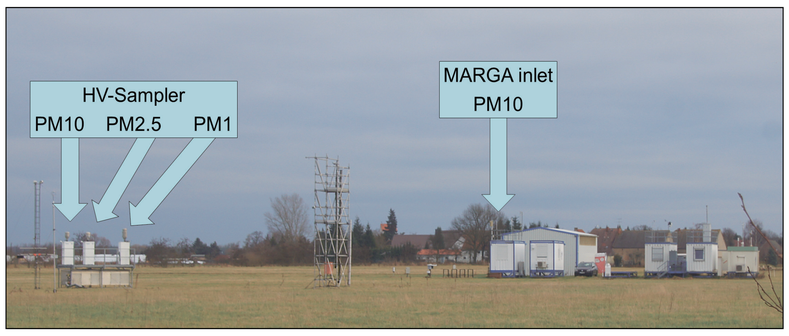

Figure 1: Measuring field of the TROPOS research site Melpitz (view to north-east). The HV-samplers for daily filter samples on quartz fibre with inlets for PM_{10}, $PM_{2.5}$ and PM_1 are shown on the left side, in the middle is the MARGA PM_{10} inlet placed on the rooftop of a container.

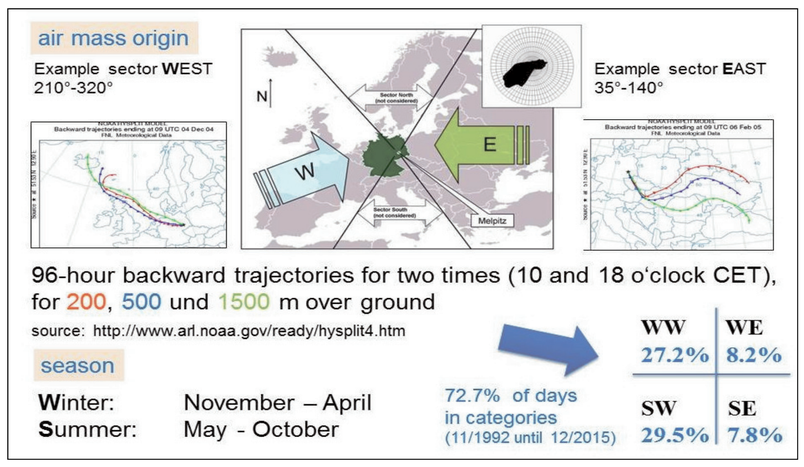

Figure 2: Location of the Melpitz site in Europe and subjective evaluation of sampling days for PM for spatial and seasonal discrimination into four categories.

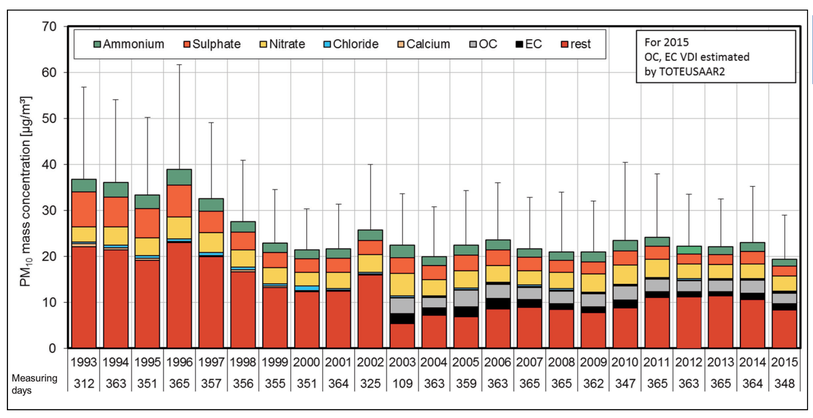

Figure 3: Yearly mean values of particle mass concentration (1993-2015), content of main water-soluble ions, OC and EC for PM_{10}. The error bars are the positive standard deviation of daily particle mass concentration means.

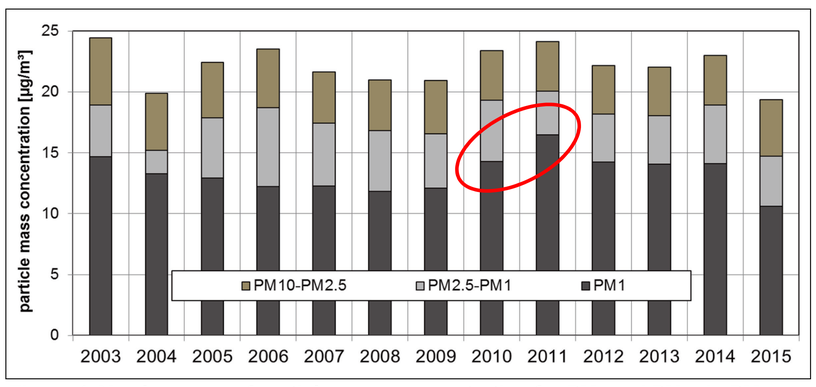

Figure 4: Yearly means of particle-mass-concentration for PM_1 and $PM_{2.5}$ in PM_{10} (2003-2015). The increase of PM_{10} results mainly by the increase of PM_1 in years with relative cold winters (2010 and 2011, red oval).

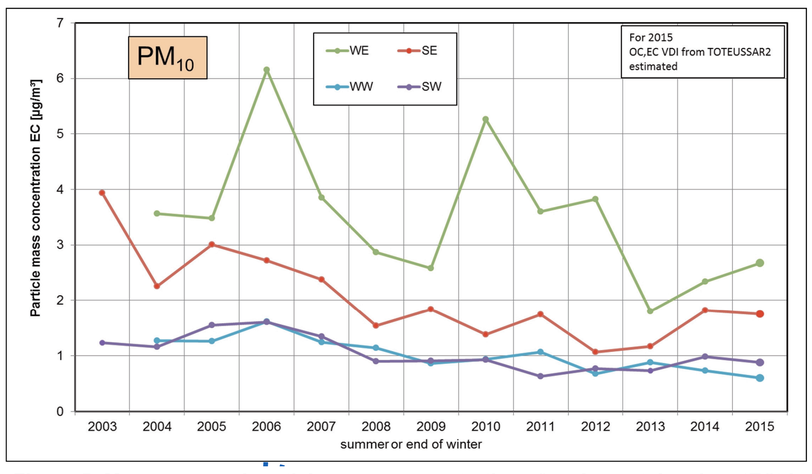

Figure 5: Mean seasonal particle mass concentrations for elemental carbon (EC) in PM_{10} (2003-2015) in summers (S) and winters (W) distinguished for an air-mass inflow from a sector West (W) or East (E).

Summary

- The particle mass concentration PM_{10} decreases since 1993 and remains constant in the last 15 years with an yearly mean about 22.2 µg/m³ (± 7%).
- For sulphate the particle mass concentration decreases (about 7.5 µg/m³ in 1993 to about 2.5 µg/m³ in 2008 - 2015)
  For nitrate the particle mass concentration remains constant (about 3.7 µg/m³).
- The highest EC concentration was found for WE. EC shows generally a decreasing trend, also for westerly air-mass inflow.
- Hourly time resolved online measurements of gases and particles allows to investigate diurnal cycles in different seasons and together with backward trajectories source identifications since 2010 .

Method and Motivation

Long-term studies allow quantifying the influence of decreasing emissions to the concentrations. The particle mass concentration is also influenced by particle formation from precursors, the air-mass-inflow (long-range transport) and season. **Figure 2** shows the simple subjective classification in two sectors for air-mass-inflow (West, W and East, E) and season (Winter, W and Summer, S). The TROPOS research site Melpitz (**Figure 1**) is located in the rural-background in Germany in the Saxon lowlands near Torgau in the post-glacial valley of the river Elbe (12° 56' E, 51° 32' N, 86 m asl.). The Melpitz station is representative for a large area in central Europe and integrated in ACTRIS2[1] and EMEP[2] (*Spindler et al., 2013*).
High-Volume (HV) quartz filter samples for particles < 10 µm aerodynamic-diameter (PM_{10}) were collected daily (since November 1992). $PM_{2.5}$ was collected also daily and PM_1 every six days (since January 2003). The particle mass was determinated gravimetrically. Main water-soluble ions (NO_3^-, SO_4^{2-}, Cl^-, Na^+, NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were analyzed by ion chromatography. The determination of organic (OC) and elemental carbon (EC) (available since 2003) was performed by a two-step thermographic method (according to VDI 2465 part 2). Since 2012 the thermo-optical method with detection by transmission and temperature protocol EUSAAR2 (*Cavallli et al., 2010*) was used (for 2012-2014 in parallel to the former method).
For the hourly quantification of water-soluble ions in PM_{10} (Cl^-, NO_3^-, SO_4^{2-},NH_4^+, Na^+, K^+, Mg^{2+}, Ca^{2+}) and their corresponding trace gases (HCl, HONO, HNO_3, SO_2, NH_3) a **M**onitor for **Ae**R**o**sols and **G**ases in ambient **A**ir (MARGA, Applikon, The Netherlands) is used in Melpitz and act in parallel with filter sampling since 2010. This instrument collects the gases with a Wet Rotating Denuder (WRD) and samples the particles via a Steam Jet Aerosol Collector (SJAC). The resulting liquids are analyzed on-line with ion chromatography (Metrohm, Switzerland) (*Stieger et al., 2016, submitted*).

Results and Discussion

PM_{10} shows a decreasing trend (1993-2000) followed by a second period without clear trend (2001-2015) with a mean mass concentration of about 22.2 ± 1.6 µg/m³ (variation 7%), compare **Figure 3**. The absolute PM_{10}-sulphate-concentration (1993-2015) and the PM_{10}-EC-concentration (2003-2015) decrease since 1993 by about 75 and 50%, respectively.
Sulphate shows a weaker decrease since 2000. Reasons are fast emission reductions in the region and also continuous emission reductions in Europe, especially for petrol and coal combustion (*EMEP, 2012*). **Figure 4** shows the yearly mean particle mass concentrations for PM_1, $PM_{2.5}$ and PM_{10}. The relative high PM_{10} concentrations in the years with colder winters (2010 and 2011) are caused mainly by an increase of PM_1. The reasons for these higher PM_1 concentrations could be found in higher anthropogenic emissions of small particles by combustion processes in the surroundings and in long-range transport of anthropogenic influenced air-masses. Such situations can increase the number of days with exceedances of the limit value for PM_{10} (EU-Commission 1999) significantly. The trends for the seasonal mean concentrations of EC in PM_{10} for summers (May-October) and winters (November-April) distinguished for an air-mass inflow from a sector West or East are shown in **Figure 5**. The mean EC-concentration shows decreasing trends for the four cases. The highest EC-concentration was found for a continental air-mass inflow. Long-range transports of industrial and domestic heating emissions are the most likely reasons. The strong pattern of the mean values in winter was triggered for the continental air-mass by the different "meteorological" character of the winters. The slightly decreasing trend of the EC-concentration in summer for an air-mass inflow from sector East can be caused by lower industrial EC-emissions year by year in the source regions. During maritime air-mass inflow the mean values are low and comparable for winter and summer and show a slightly decreasing trend.
The hourly time resolution of the MARGA is a benefit and allows the investigation of the diurnal cycles of measured species. Especially the gases show clear variations in **Figure 6**. SO_2 can be identified as anthropogenic pollutant with highest concentrations in winter due to combustion processes (e.g. domestic heating). The severe increase of and NH_3-concentrations in the morning can be explained by down-mixing processes. Agricultural activities lead to a general increase of NH_3 in spring. The HCl peak in the afternoon, especially in summer, is a result of the exchange reaction of sea salt and gaseous sulfuric and nitric acid. The low HONO-concentration during day-time is the result of photolysis.
The validation of the MARGA with the standard High-Volume (HV) quartz filter samples for particles bares a significant advantage for the MARGA. The NO_3^- concentrations differ in summer measurements between both instruments in **Figure 7**. The reason is the high volatility of particulate ammonium nitrate that can evaporate from the filter surface. In winter HV-samples can be influenced by positive sampling artefacts.
The combination of the hourly MARGA data with HYSPLIT backward trajectories can be used for the source identification. **Figure 8** shows as example the seasonal change of the emission areas for chloride identified by PSCF (Potential Source Contribution Function). The sea salt aerosol dominates from spring to autumn. In winter, there is another significant anthropogenic chloride source in the East. Due to the combustion of chloride-containing coal in East Europe, easterly winds can transport chloride containing particles to Melpitz.

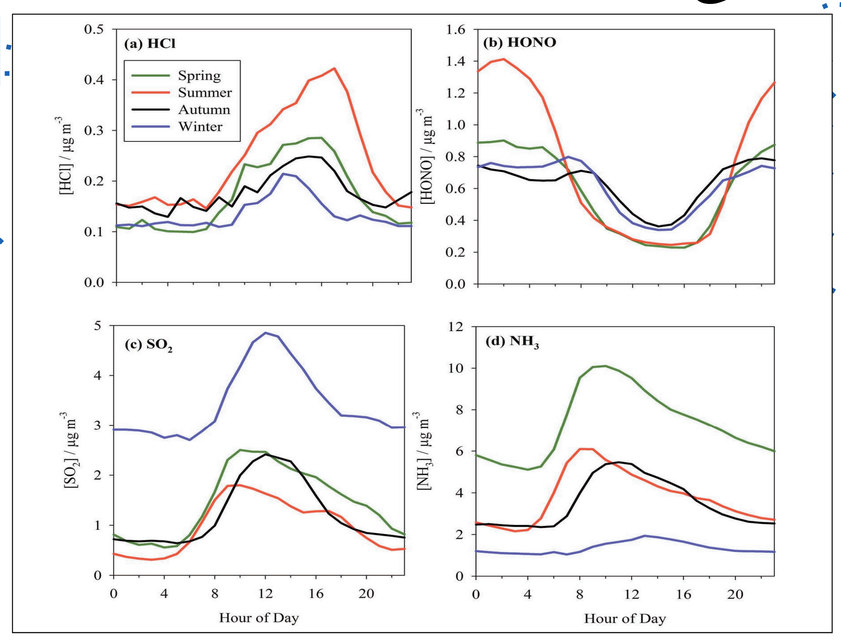

Figure 6: Diurnal cycles of (a) HCl, (b) HONO, (c) SO_2 and (d) NH_3 and their seasonal dependence for spring (green), summer (red), autumn (black) and winter (blue). Each average was calculated for the five year measurement period from 2010 to 2014.

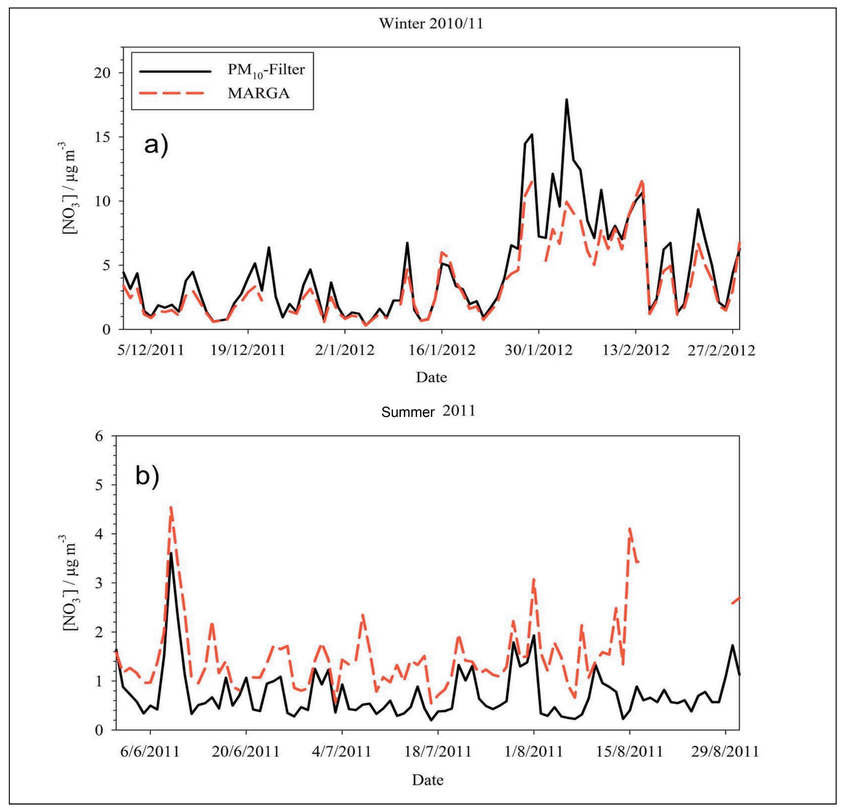

Figure 7: Comparison of NO_3^- measured with MARGA (red dotted line) and PM_{10} filter offline analysis (black line) during (a) winter 2010/2011 and (b) summer 2011. Data points are daily means.

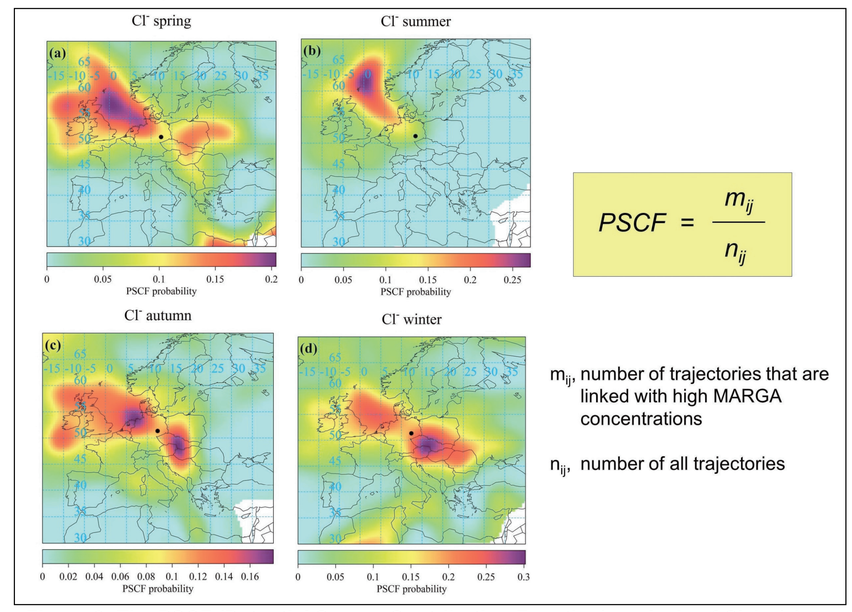

Figure 8: The PSCF (Potential Source Contribution Function) analysis of Cl^- in (a) spring, (b) summer, (c) autumn, and (d) winter over five years (2010-2014) was calculated using the open access R package 'Openair'. The colors correspond to the probability that the respective reason is the most likely emission area of the measured particulate ions in Melpitz (black point).

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1) **E**uropean **M**onitoring and **E**valuation **P**rogramme
2) **A**erosol, **C**louds, and **T**race gases **R**esearch **I**nfra**S**tructure Network

References

Alastuey, A., Querol, X., Aas W., Lucarelli, F., Pérez, N., Moreno, T., Cavalli, F., Areskoug, H., Balan, V., Catrambone, M. , Ceburnis, D., Cerro, J.C., Conil, S., Gevorgyan, L., Hueglin, Ch., Imre, K.,Jaffrezo, J.-L., Leeson, S.R., Mihalopoulos, N.,Mitosinkova, M., O'Dowd, C.D., Pey, J., Putaud, J.-P., Riffault, V., Ripoll, A., Sciare, J., Sellegri, K., Spindler, G., Yttri, K.E.: Geochemistry of PM10 over Europe during the EMEP intensive measurement periods in summer 2012 and winter 2013. Atmos.Chem.Phys 16, 6107-6129, 2016

Cavalli, F., Viana, M., Yttri, K.E., Genberg, J., Putaud J.-P.: Toward a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. Atmos.Meas.Tech. 3, 79-89, 2010

EMEP: Joint Report of the Task Force on Measurements and Modelling (TFMM), Air pollution trends in the EMEP region between 1990 and 2012. Chemical Co-ordinating Centre (CCC), Meteorological Synthesizing Centre-East (MSC-E), Meteorological Synthesizing Centre-West (MSC-W) , 2016

Stieger, B., Spindler, G., Fahlbusch, B., Müller, K., Grüner, A., Poulain, L. ,Thöni, L., Seitler, E.,Wallasch , M., Herrmann, H.: Measurements of PM10 and trace gases with the online system MARGA at the research station Melpitz in Germany – A 5-year study. J. Atmos. Chem. (submitted)

Spindler, G., Gnauk, T., Grüner, A., Iinuma, Y., Müller, K., Scheinhardt, S., Herrmann, H.: Size-segregated characterization of PM_{10} at the EMEP site Melpitz (Germany) using a five-stage impactor: a six year study. J. Atmos. Chem., 69, 127-157, 2012

Spindler, G., Grüner, A., Müller, K., Schlimper, S., Herrmann, H.: Long-term size-segregated particle (PM_{10}, $PM_{2.5}$, PM_1) characterization study at Melpitz – influence of air massinflow, weather conditions andseason. J. Atmos. Chem., 70, 165-195, 2013