Long-term size-segregated particle (PM_{10}, $PM_{2.5}$, PM_1) characterization study in the rural background of Germany – influence of air mass inflow and season

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Figure 1: Measuring field of the TROPOS research site Melpitz (view to south-east). The HV-filter-samplers for daily samples on quartz fibre filter with inlets for PM_{10}, $PM_{2.5}$ and PM_1 are shown in the middle of the picture.

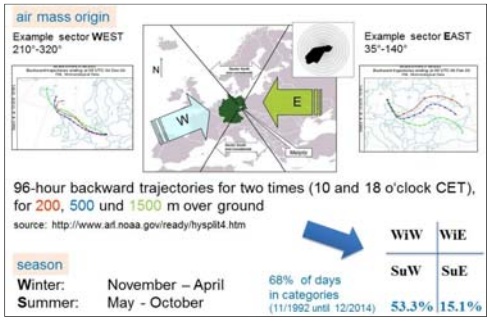


Figure 2: Location of the Melpitz site in Europe and evaluation of sampling days for PM for spatial and seasonal discrimination in four categories.

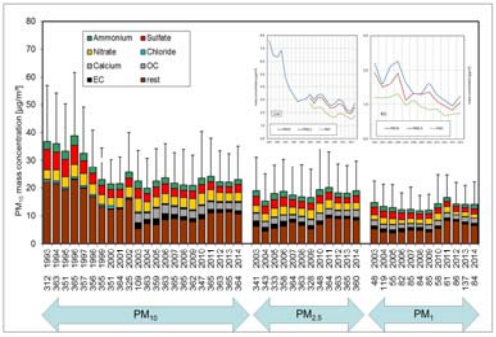
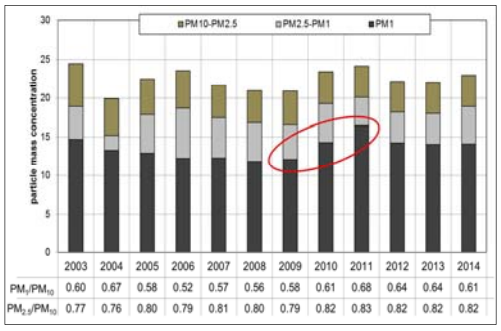


Figure 3: Yearly mean values of particle mass concentration, content of main water-soluble ions, OC and EC for PM_{10} (1993-2014), $PM_{2.5}$ and PM_1 (2003-2014). The error bars are the positive standard deviation of daily particle mass concentration means. The two small diagrams show the particle mass concentration for sulfate and EC in the three size fractions (PM_{10}, $PM_{2.5}$ and PM_1).



	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014
PM_1/PM_{10}	0.60	0.67	0.58	0.52	0.57	0.56	0.58	0.61	0.68	0.64	0.64	0.61
$PM_{2.5}/PM_{10}$	0.77	0.76	0.80	0.79	0.81	0.80	0.79	0.82	0.83	0.82	0.82	0.82

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

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 and long-range transport. The TROPOS research site Melpitz is located in the rural-background in Germany in the Saxon lowlands near Torgau in the glacial valley of the river Elbe (12° 56' E, 51° 32' N, 86 m asl., **Figure 1**) *(Spindler et al. 2013)*. The Melpitz station is integrated in ACTRIS[1)] and EMEP[2)] and representative for a large area in central Europe.
High-Volume (HV) quartz filter samples for particles < 10 µm aerodynamic-diameter (PM_{10}) were collected daily (since November 1992). Particles $PM_{2.5}$ and PM_1 were collected daily respective every six days (since January 2003). The determination of the particle mass was done 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) performed by a two-step thermographic method (according to VDI 2465 part 2). PAH (Polycyclic Aromatic Hydrocarbons) and n-alkanes were determined by CPP-GC-MS (Curie point 510° C) for PM_{10} samples in 2012. Daily samples were evaluated at first as yearly means and at second for spatial and seasonal discrimination days were sorted for air mass transport from a western sector (W, 210-320° , mostly maritime influenced) and a broad eastern sector (E, 35-140° , continentally influenced) using backward trajectories (96 h) Days with a strong change in transport direction (often more local influenced by inversion) were excluded here. A seasonal discrimination was done for winter (Wi, November-April) and for summer (Su, May-October). The result are four categories WiW, WiE, SuW and SuE in which 68% of the whole time (November 1992 until December 2014) can be sorted (53.3% for W, 15.1% for E). The principle for the spatial and seasonal selection is explained in **Figure 2** *(Spindler et al. 2012)*.

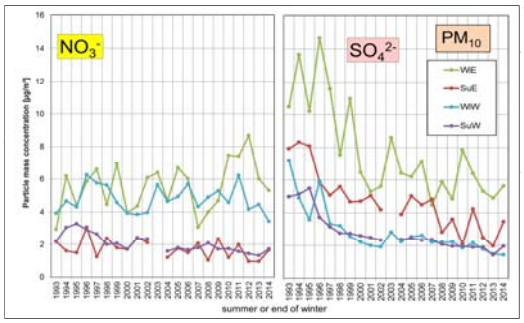


Figure 5: Nitrate and sulfate particle mass concentration PM_{10} at Melpitz site distinguished for summer and winter and air-mass inflow West and East (yearly means 1993-2014). For the summer 2003 mean values are not given, because the number of measuring days is to low.

Results and Discussion

PM_{10} shows a decreasing trend (1993-2000) followed by a second period without clear trend (2001-2014) with a mean mass concentration of about 22.3 ± 2.9 µg/m³ (variation 13%), compare **Figure 3**. The absolute sulphate and calcium concentration (PM_{10}, 1993-2014, $PM_{2.5}$ and PM_1 2003-2014) and the EC-concentration (PM_{10}, $PM_{2.5}$ and PM_1, 2003-2014) decrease since 1993 by about 75 and 50%, respectively. Sulphate shows a weaker decrease until 2000. Reasons are fast emission reductions in the region and since 2000 also continuous emission reductions in Europe, especially for petrol and coal combustion (*EMEP, 2012*).
Figure 4 shows the concentrations and the ratios of particle mass concentrations PM_1 and $PM_{2.5}$ in PM_{10}. The relative high PM_{10} concentrations in the years with relative cold winters (2010 and 2011) caused mainly by an increase of PM_1. The reasons for this higher PM_1 concentrations could be found in higher anthropogenic caused 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.
Figure 5 shows the yearly means for sulfate and nitrate distinguished for summer and winter and air-mass inflow West and East (compare Figure 2). The lowest concentrations were detected during maritime air-mass inflow west and the highest during continental air-mass inflow east. The nitrate concentration remains in comparison to sulfate more constant all the time, because the emission of NOx from traffic does not decrease significantly. The trends for the seasonal mean concentrations of OC and 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 6**. The mean concentration shows for the four cases no trend for OC and a decreasing trend for EC. The highest EC-concentration was found for a continental air-mass inflow. The reason is long-range transport also of emissions from individual coal fired ovens. 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 concentration sum of 19 PAH, the concentration of benzo(a)pyrene and the CPI (carbon preference index, *Pietrogrande et al. 2011*) for n-alkanes with C-Atom-numbers 20-33 are shown for 2012 in **Figure 7 and Figure 8**. The PAH concentrations are much higher in winter as in summer. Especially during cold winter periods with air-mas inflow East (long-range transport of particles from coal combustion) the concentrations are extremely high. The Benzo(a)pyrene concentrations in this period results more from local emissions (e.g. diesel combustion). The Benzo(a)pyrene concentrations during these typical winter period are lower as in December.
The CPI is high during summer. A source for n-alkanes with odd numbers of C-atoms is plant wax abrasion. A difference between air-mass inflow West or East was not found.

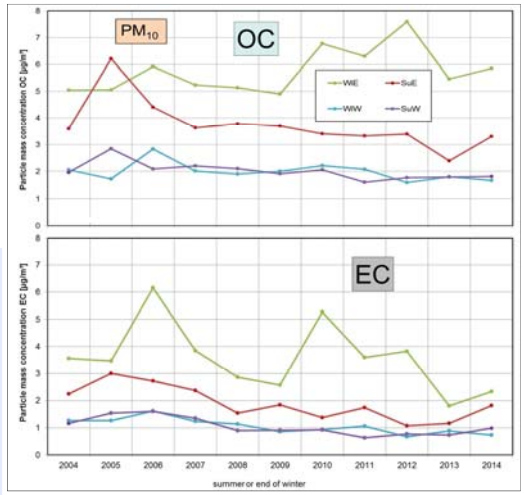


Figure 6: Mean seasonal particle mass concentrations PM_{10} of OC and EC in summers and winters distinguished for an air-mass inflow from a sector West or East (2004-2014).

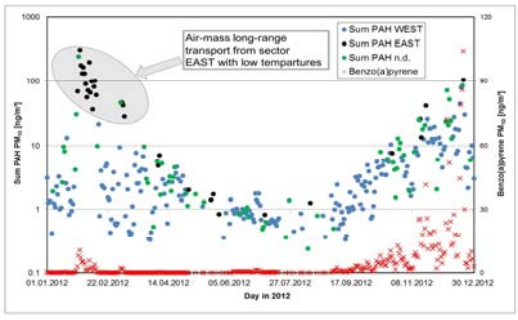


Figure 7: Sum PAH particle mass concentration (daily means, logarithmic scale) and particle mass concentration of Benzo(a)pyrene (daily means, linear scale) in PM_{10} in 2012 distinguished for air-mass inflow West and East. n.d. means air-mass inflow undefined.

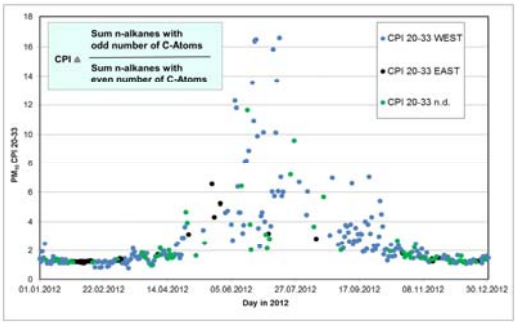


Figure 8: CPI in PM_{10} in 2012 distinguished for air-mass inflow West and East. n.d. means air-mass inflow undefined.

Summary

- **The particle mass concentration PM_{10} decreases since 1993 and remains constant in the last 15 years around 22.3 µg/m³ (± 13%).**
- **For sulfate the particle mass concentration decreases. For nitrate the particle mass concentration remains more constant.**
- **The highest EC concentration were found for WE. EC shows generally a decreasing trend, also for westerly air-mass inflow.**
- **The highest PAH concentrations were found in winter during air-mass inflow EAST. The CPI is highest in summer (biogenic sources).**

References

EU-Commission, Council Directive 1999/30/EC
EMEP Transboundary particulate matter in Europe Status report 2012 NILU Reference: O-7726. ISSN 1504–6192 Contributors: Yttri, K.E., Aas, W., Tørseth, K., Kristiansen, N.I., Myhre, C.L., Tsyro, S., Simpson,D., Bergström, R., Marečková, K., Wankmüller, R., Klimont, Z., Amann, M., Kouvarakis G.N., Laj, P.,Pappalardo, G., Prévôt, A.
http://www.nilu.no/projects/ccc/reports/emep4-2012.pdf
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
Pietrogrande, M.C., Abbaszada, G., Schnelle-Kreis, J., Bacco, D., Mercuriali, M., Zimmermann, R.: Seasonal variation and source estimation of organic compounds in urban aerosol of Augsburg, Germany. Environ. Pollut. 159, 1861–1868, 2011

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

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