OC and EC analyzed in PM using thermo graphic or thermo-optical method at Melpitz site in Germany – a comparison for 2012-13

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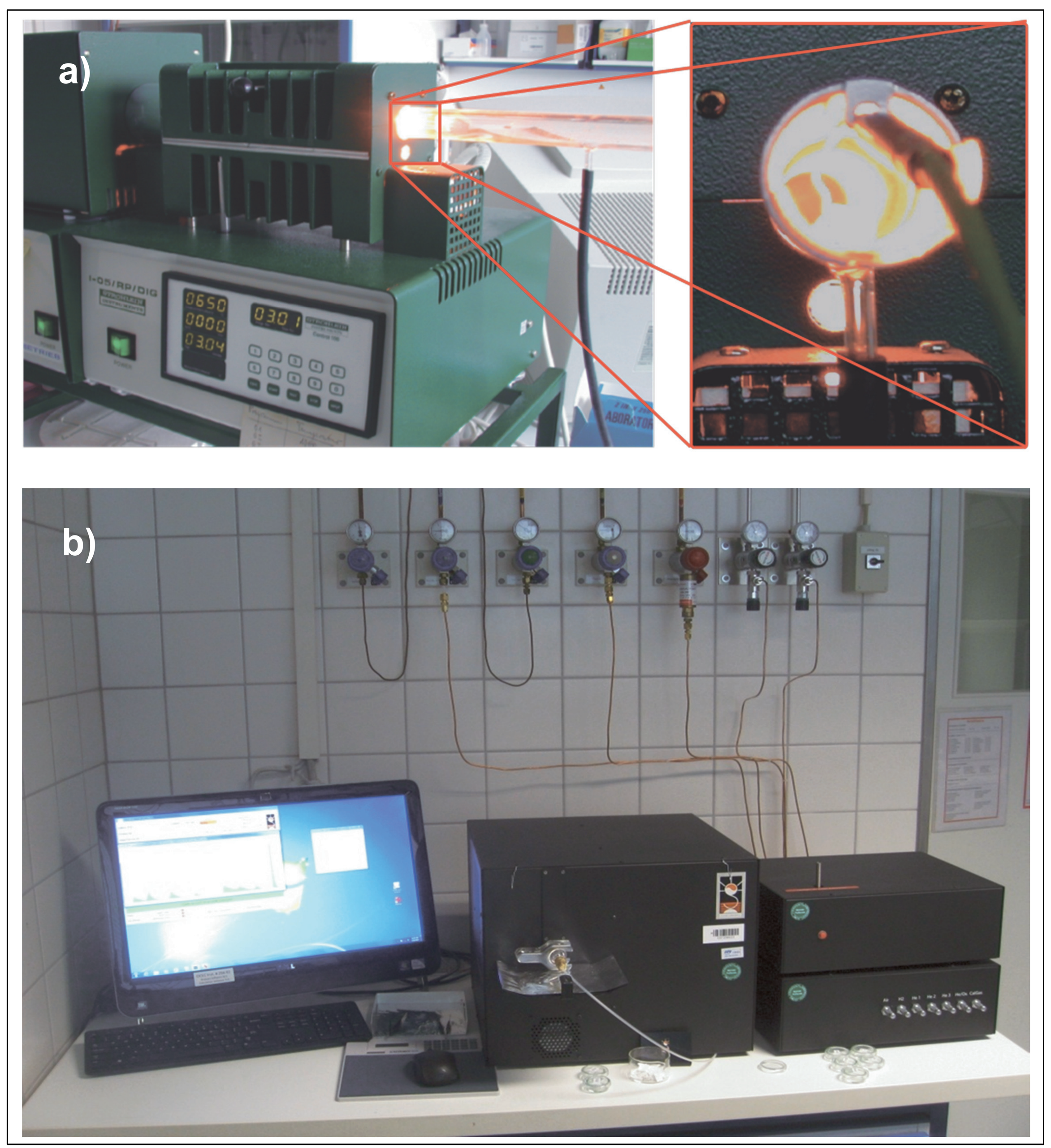

Figure 1: a) OCEC analyzer C/Smax with quartz oven, thermographic method
b) OCEC analyzer by Sunset Laboratory Inc., thermo-optical method

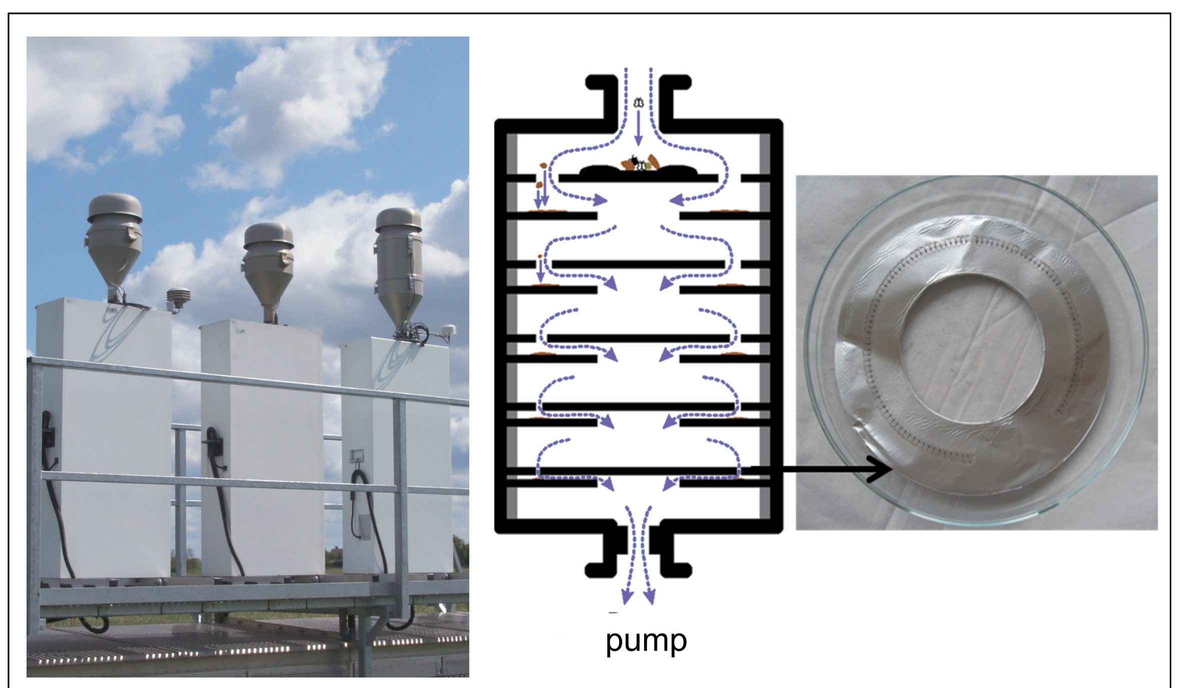

Figure 2: The HV-filter-samplers for PM_{10}, $PM_{2.5}$ and PM_1 at Melpitz site for daily samples on quartz fibre filters and the five stage BERNER-impactor for sampling on Al-foils for several days. The Al-foil for stage 5 is shown (particles with 0.05 to 0.14 µm aerodynamic diameter.

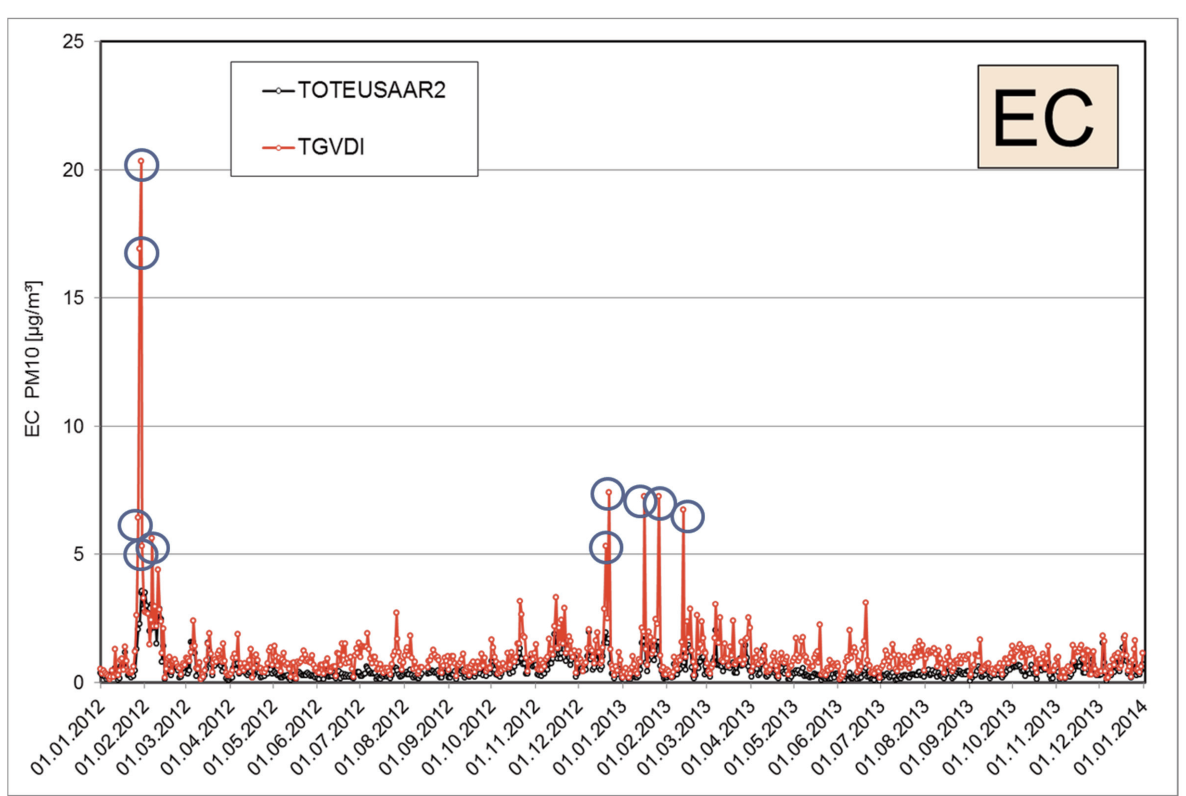

Figure 3: The two year data-set (daily HV-samples) for EC analyzed with both methodsTGVDI and TOTEUSAAR2. 10 days with high EC concentration were eliminated from the whole dataset.

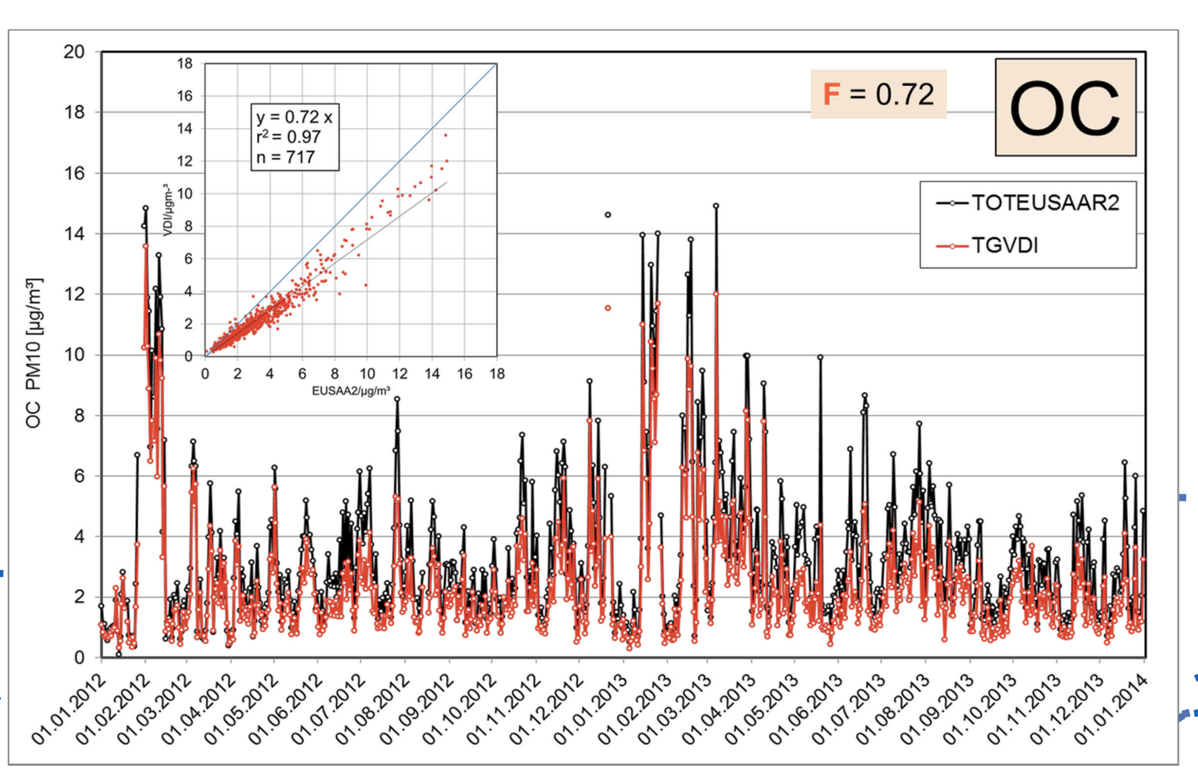

Figure 4: Example for the calculation of the empirical factor F for OC over the whole time (2012 and 2013).

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Motivation

Since 2002 organic carbon (OC) and elemental carbon (EC), in sum total carbon (TC), were quantified at TROPOS with a commercial carbon analyzer (C/Smax, Seifert Laborgeräte, Germany, Figure 1a) using the two-step thermo-graphic VDI-method (TGVDI), a modified VDI 2465 (Part 2) for quartz-filters (high-volume-sampler, HV) and for Al-foils (five stage BERNER-impactor-samples, IP), compare *Neusüß et al. 2002.*

In 2012 the thermo-optical method (TO) was introduced in parallel using the OCEC analyzer by Sunset Laboratory Inc., U.S.A., Figure 1b. This step was necessary to provide comparable results for the daily PM_{10}, $PM_{2.5}$ and PM_1 samples from Melpitz site for international networks (e.g. ACTRIES, EMEP). Therefore also the most common temperature protocol in Europe EUSAAR2 in combination with transmission of the laser-beam was used (TOTEUSAAR2), compare *Cavalli et al. 2010.*

To avoid future parallel analysis we derive empirical factors (F) to recalculate OC, EC and TC from two years TGVDI and TOTEUSAAR2 analysis (equation 1) for the Melpitz HV-samples. Furthermore a comparison with IP results can be done on this way, because the analysis of Al-foils with the TO is impossible.

Experimental and results

All daily HV samples on quartz fibre filters (every day for PM_{10} and $PM_{2.5}$ and every six days for PM_1) were taken at Melpitz site using three HV samplers DIGITEL DHA-80 (Walter Riemer Messtechnik, Germany). At Melpitz also IP samples with five stage BERNER-impactors (Hauke, Austria) were taken at several days in special projects (Figure 2).

The Melpitz site is operated by TROPOS and located in the lowlands of Eastern Germany (12°56'E, 51°32'N, 86 m a.s.l.). The place represents the regional background in Central Europe (*Spindler et al. 2012 and 2013*).

The quartz fibre filters were analysed with two different techniques:

For **TGVDI** OC was vaporized at 650° C under N_2 and catalytically converted to CO_2 and the remaining EC was than combusted with O_2 to CO_2. The formed CO_2 was quantitatively determined by a non-dispersive infrared detector (NDIR).

For **TOTEUSAAR2** the EUSAAR2 temperature-protocol (*Cavalli at al. 2010*) was used and a charring correction was realized. The correction value for „pyrolytic carbon“ is achieved from measurement of transmission of the sample using a laser (wavelength 678 nm).The samples are thermally desorbed from the filter medium under an inert He-atmosphere followed by an oxidizing O_2/He-atmosphere using carefully controlled heating ramps. A flame ionization detector (FID) is used to quantify the methane, resulting from catalytic methanation of CO_2.

From the two year data set 10 days with more than 5 µ/m³ EC (TGVDI) in PM_{10} were eliminated because the transmission for TOTEUSAAR2 is here very low, Figure 3. The calculation of factors F follows equation 1 (compare the example in Figure 4):

$$[OC;EC;TC]_{TGVDI} = F \times [OC;EC;TC]_{TOTEUSAAR2} \qquad (1)$$

The mean factors F were calculated for OC, EC and TC for the size classes PM_{10}, $PM_{2.5}$ and PM_1 for all days. To show a possible influence of season and air mass origin a separate calculation of the mean factor F was done for the group of winter days (November – April) and summer days (May – October) and for days with air mass inflow West and East (Spindler et al. 2013). The result is given in Figure 5. TGVDI deliver TC results which are in the mean about 85% than that of TOTEUSSAAR2. The reason is the lower maximum temperature of 650°C for TGVDI in comparison to the final temperature of the EUSAAR2-protocoll of 850°C. The TGVDI without charring correction provides in the mean lower OC values and higher EC values in comparison to TOTEUSAAR2. Factors F show low variation with air mass inflow and appreciable variation for season. The reason can be found in the variability of the EC/OC ratio over the year (Figure 7). F depends also from the absolute particle mass concentration, especially for OC respective TC (Figure 6).

The result of a recalculation for the whole time period is given in Figure 8. The determined mean F for all sizes reproduce TC perfect and OC good. For TC only an estimation is possible, because the spreading especially for TGVDI is to high. A comparison for OC in PM_1 with AMS-measurements give a hint for a more realistic OC/EC split realized with TOTEUSAAR2. This method give results with a lower spreading for the EC/OC-ratio in comparison to TGVDI for Melpitz site, definitely (compare Figure 7). However with TOTEUSAAR2, considering charring correction, only quartz-fibre filters with a homogeneous distribution of particles can by analyzed. An detection of particles on Al-foils from IP is impossible.

Summary

- We can derive mean correction factors for OC, EC and TC. They do not depend from particle size (range PM10 to PM1) for all days.
- There are small differences for seasons in the mean correction factors, especially EC shows higher factors in summer depending marginal from particle size (PM10 > PM2.5 > PM1).
- Higher TC content corresponds to a slightly higher F (all days and sizes).
- The thermo-optical method can give a more stable split for OC and EC.

References

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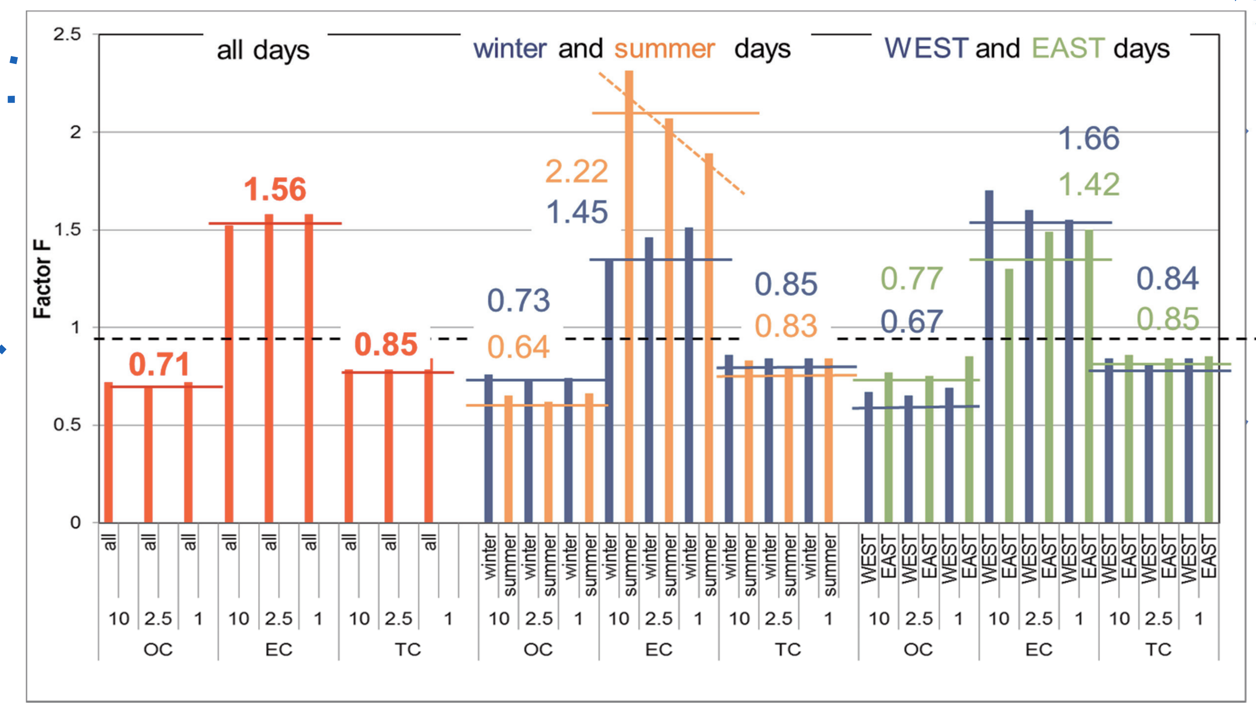

Figure 5: Factors F for a recalculation of OC, EC and TC in PM_{10}, $PM_{2.5}$ and PM_1, for different groups of days, derived from the two year dataset (compare Figures 3 and 4). The mean factors for all sizes are given as numbers.

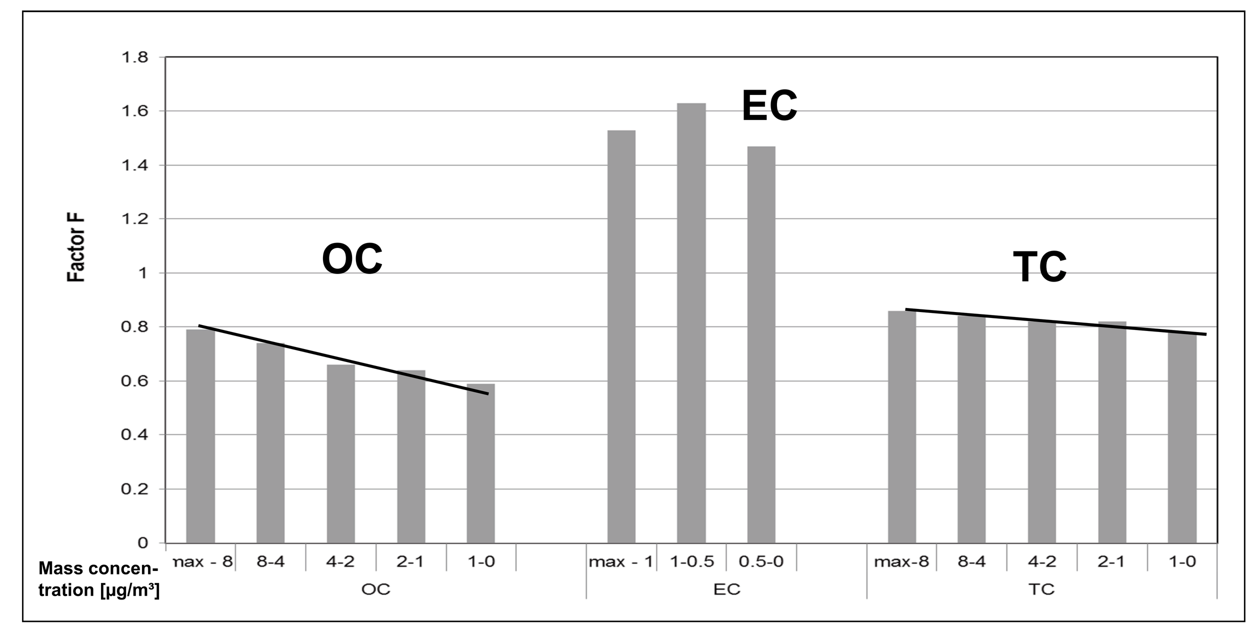

Figure 6: Dependency for factors F from the determined mass concentration for OC, EC and TC (for all samples PM_{10}, $PM_{2.5}$ and PM_1, TGVDI).

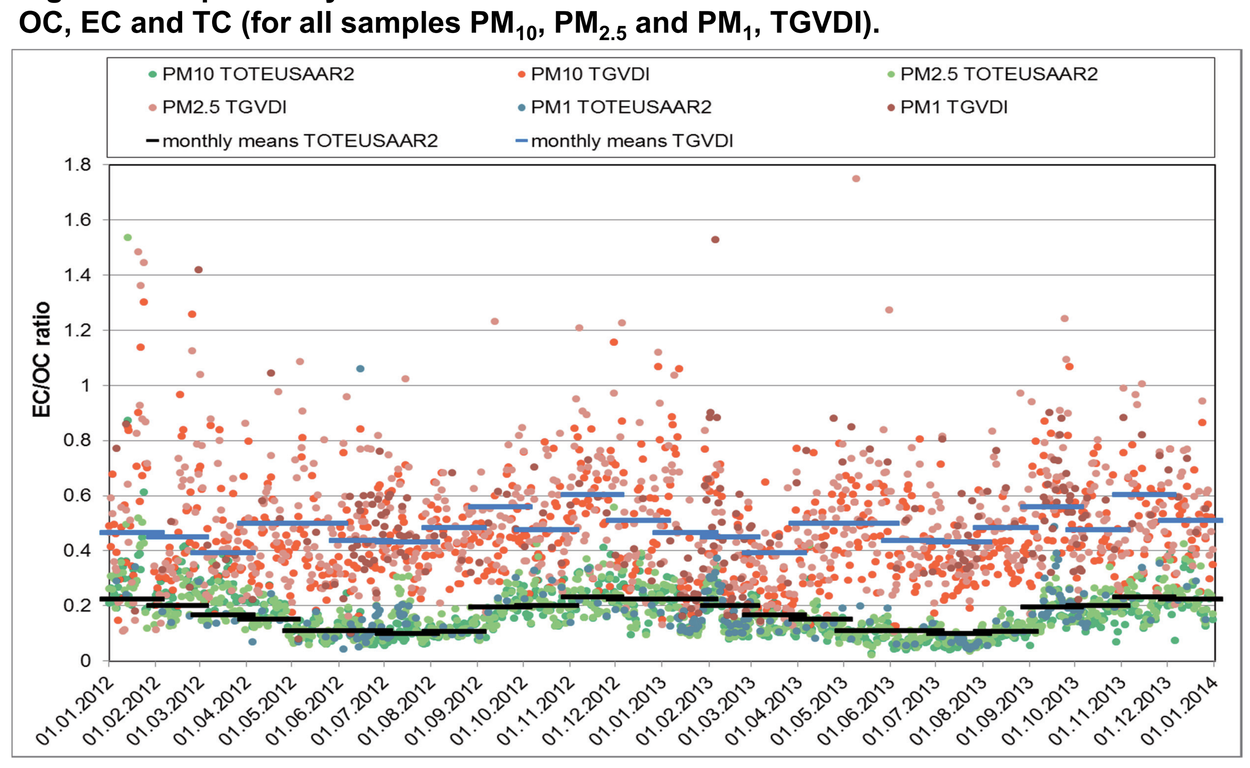

Figure 7: Daily ratios EC/OC for PM_{10}, $PM_{2.5}$ and PM_1, method TGVDI and TOTEUSAAR2. The blue and black lines are means for the month in the year, calculated from 2012 and 2013.

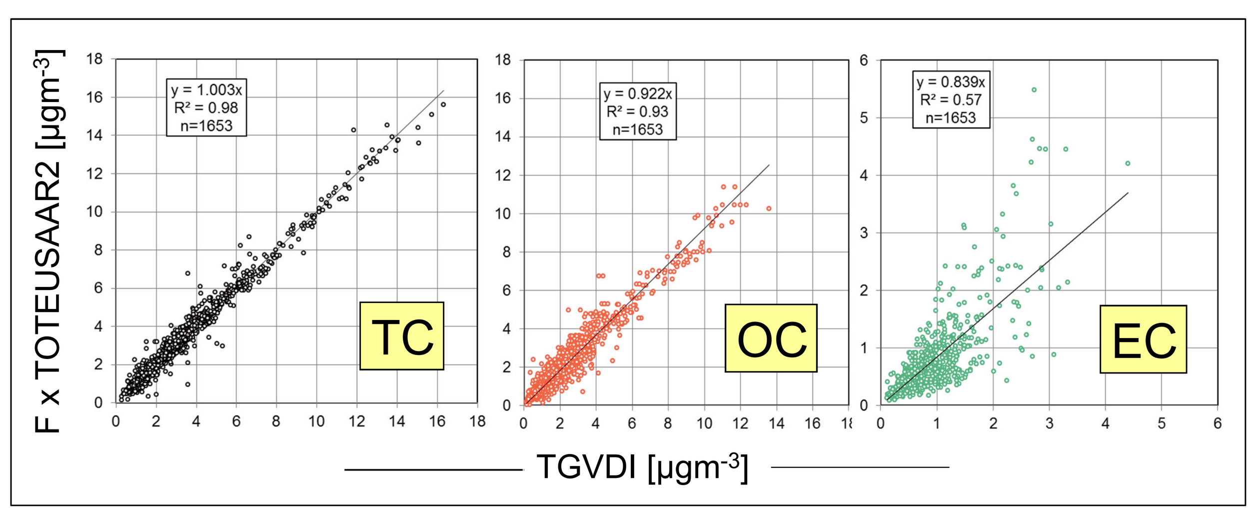

Figure 8: Comparison of results of recalculation of daily values for TC, OC and EC for method TGVDI from TOTEUSAAR2 using mean factors F for PM10, PM2.5 and PM1 derived from two year dataset (compare Figure 5).

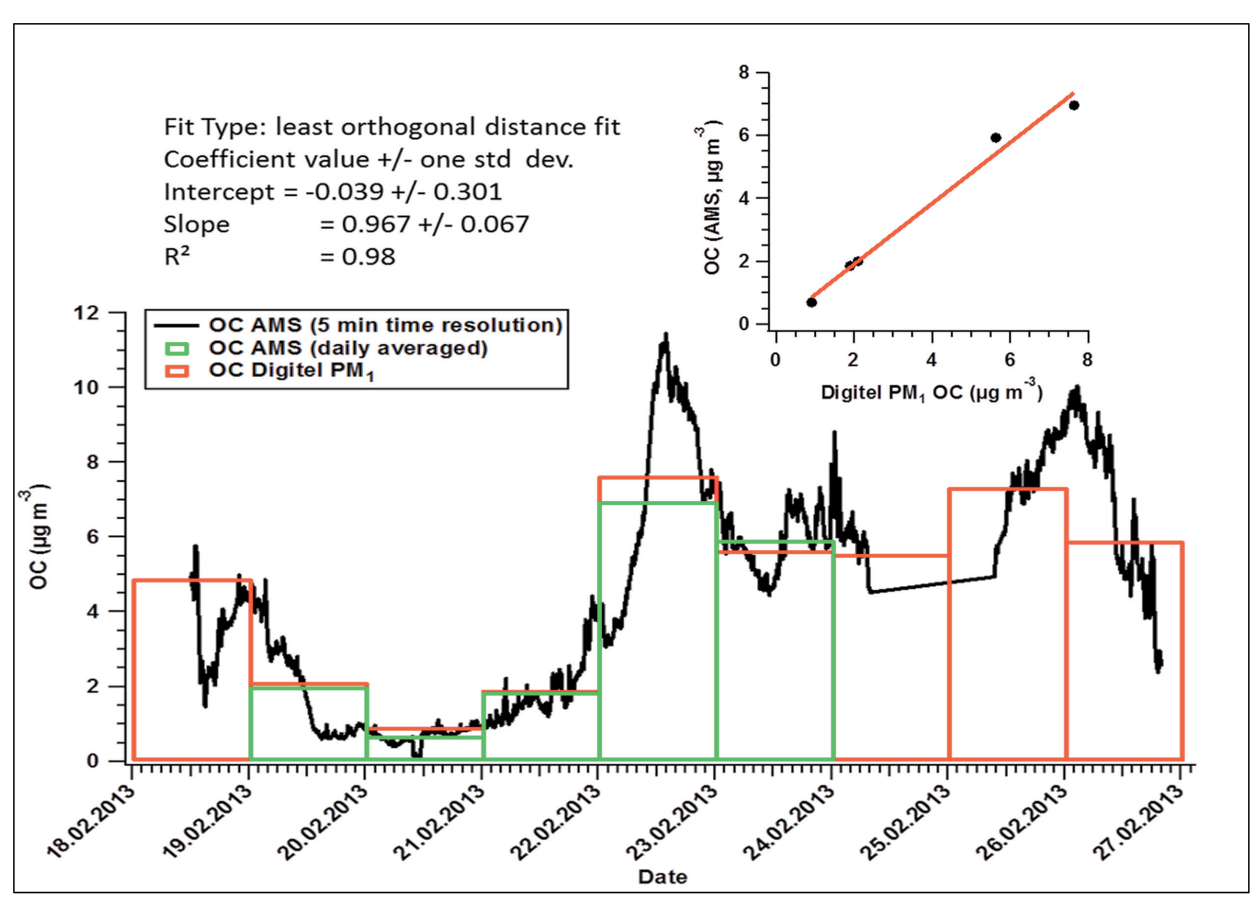

Figure 9: OC PM_1 off-line (TOTEUSAAR2) vs. on-line measurements (AMS). AMS provides OM and ratio OM/OC based on the elemental analysis of the high resolution mass spectra (only days with a complete dataset for AMS were compared).

Open questions:

Depends the factors on the measurement place?

Depends the OC/EC split from the carrier material (TGVDI for HV and IP)?