OC and EC analyzed in PM by thermographic or thermo-optical method: A two year comparison for the central European site Melpitz, Germany

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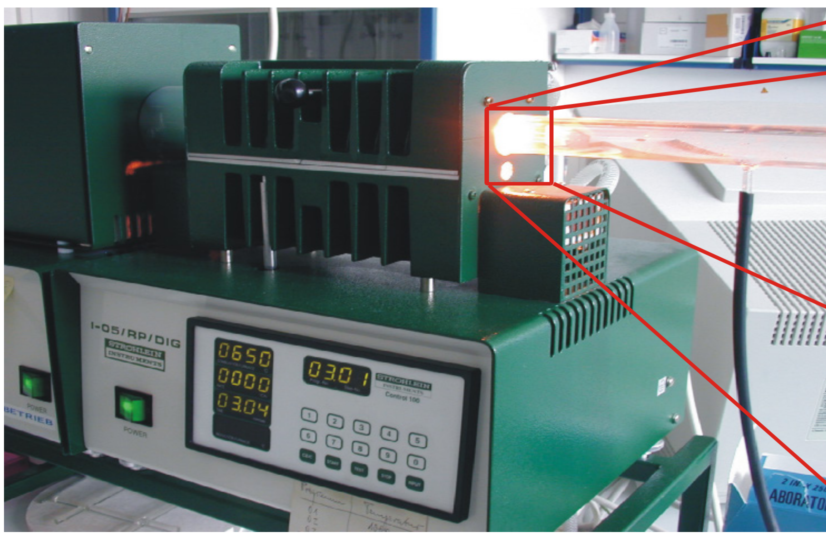
TROPOS Leibniz Institute for Tropospheric Research

Previous method for OC/EC-Determination at TROPOS

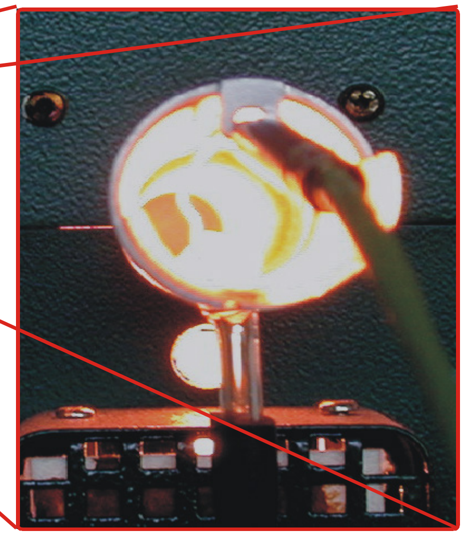
Thermographic OC/EC separation, oxidation to CO_2 and quantification by NDIR (modification of VDI 2465, part 2)

1st step : Volatilization of **OC** fraction (N_2-Atmosphere 650 °C ,8 min)
OC is oxidized by CuO contact at 850°C to CO_2

2nd step: Combustion of the remaining **EC** fraction (O_2-Atmosphere 650 °C, 8 min) to CO_2



Carbon-Analyzer C/Smax

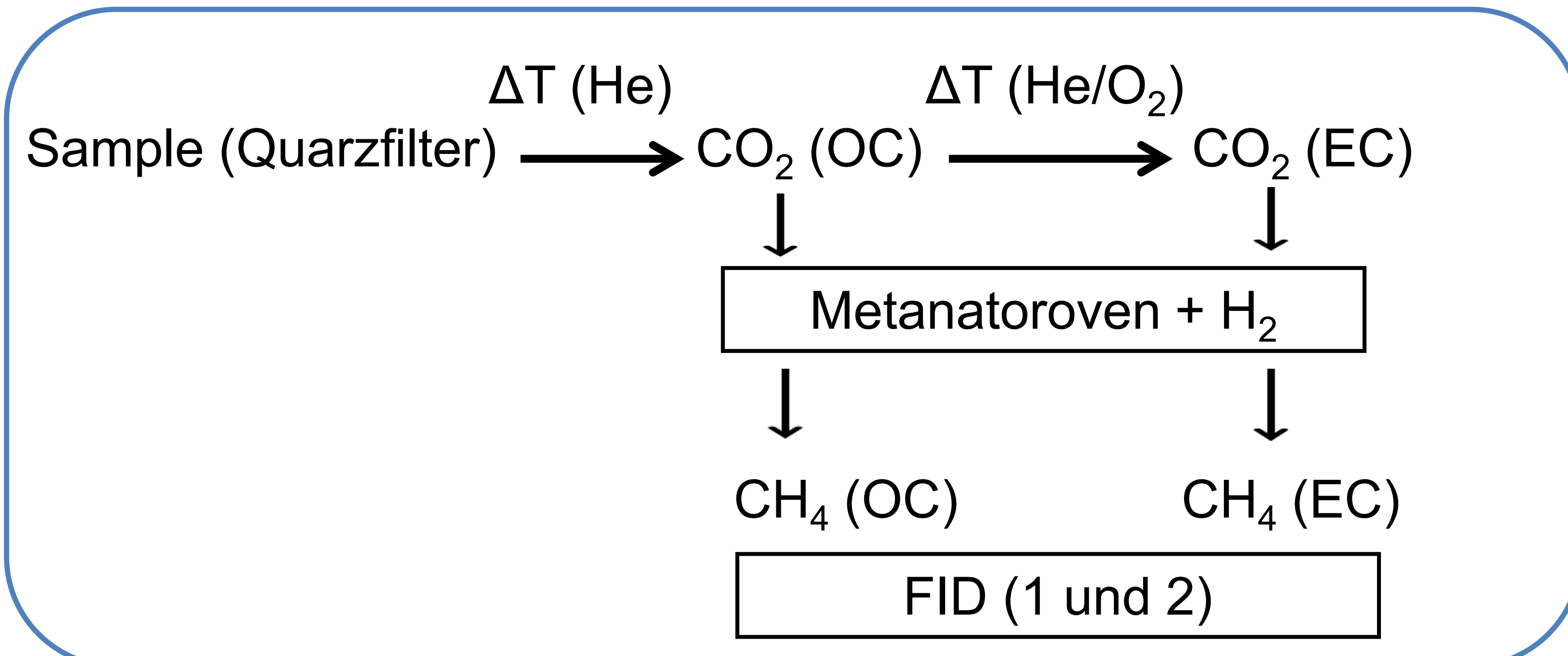


View in the quartz tube with burning section

Application since 2003 (C-mat 5500 and C/S MAX) for **quartz filters** and **Al-foils**.

Reasons to introduce the thermo-optical method at TROPOS

- Harmonizing of OC/EC detection using thermo-optical Method with an normalized temperature program (EUSAAR2) for samples in European networks (ACTRIS, EMEP).
- Optical correction for charring processes. Charring should lead by EC artifact formation to lower OC but in contrast to more EC. The correction value for „pyrolytic carbon“ originates from measurement of transmission or reflectance of the sample using a laser.



Thermo-optical instrument at TROPOS

O_2 air N_2 He H_2 5% methane or 10% O_2 in He

OCEC Lab Instrument
Sunset Laboratory Inc.
www.sunlab.com

ECM Processanalytic GmbH
Equipment for Continuous Monitoring of Process

Application since 2012 for **quartz filters**.

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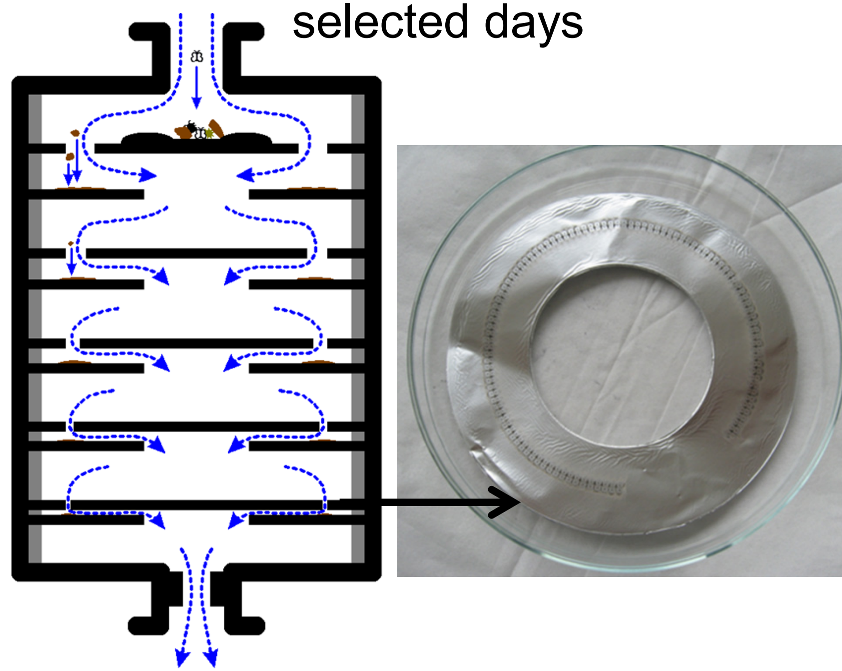
Situation at TROPOS since 2003

Digitel DHA-80, PM_{10}, $PM_{2.5}$, PM_1
at Melpitz site (long-time measurements)

five-stage BERNER impactor for selected days

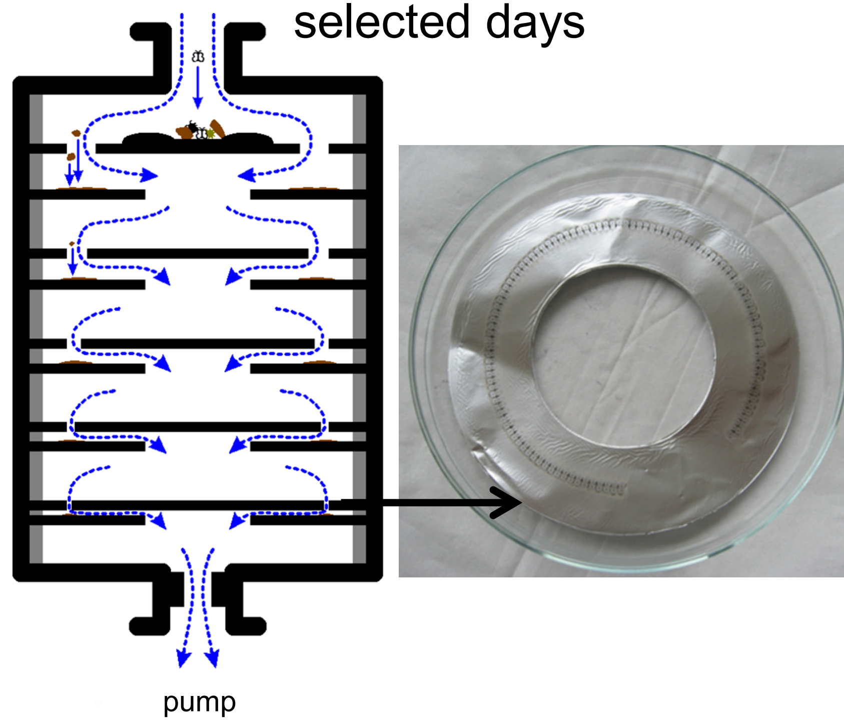


Thermographic OC/EC separation allows comparable results for **Quartz-filters** from long time measurements and daily measurements for sample spots on **Al-foils** used in five-stage BERNER impactors.

Situation at TROPOS now

Digitel DHA-80, PM_{10}, $PM_{2.5}$, PM_1
at Melpitz site (long-time measurements)

five-stage BERNER impactor for
selected days



Since 2003 Thermographic OC/EC Method (VDI)

+

Since 2012 thermo-optical Method with an normalized temperature program (EUSAAR2), Transmittance

Thermographic OC/EC Method (VDI)

Thermo-optical Method not possible
Al melting point 659°C, samples as Spots, Transmittance and Reflectance not possible

Empirical factors F for Melpitz site

The dataset:

Daily HV samples on quartz filters for PM_{10} and $PM_{2.5}$ and samples every six days for PM_1 from Melpitz site (January 2012 until December 2013, 24 month), analyzed.

with **thermographic Method** (VDI, modification of VDI 2465, part 2)

TG VDI

and **thermo-optical Method,** Transmittance, Temperature protocol EUSAAR2

TO T EUSAAR2

in parallel.

$$[OC;\ EC;\ TC]_{TG\ VDI} = F \times [OC;\ EC;\ TC]_{TO\ T\ EUSAAR2}$$

OC, **EC** and **TC** in PM_{10}, $PM_{2.5}$ and PM_1

Black Carbon (BC) in PM_{10} is also available for Melpitz site (Multiangle Absorption Photometer, MAAP, 637 nm), calculated from the particle light absorption coefficient σ_{ap} using a constant Mass Absorption Cross Section α_C of 6.6 m^2g^{-1}.

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Calculation of F for OC, EC and TC in PM_{10}, $PM_{2.5}$ and PM_1 (January 2012 until December 2013):

for all days

for days in winter (November until April) and summer (May until October),

for days with air-mass inflow from a sector West or East
(selection using 96h backward-trajectories, *Spindler et al. 2012 and 2013*)

for different ranges of daily OC, EC and TC (for all sizes)

for days of month (for all sizes)

$$[OC; EC; TC]_{TG\ VDI} = F \times [OC; EC; TC]_{TO\ T\ EUSAAR2}$$

Additional Calculation of Mass Absorption Cross Section α_C for PM_{10} (January 2012 until December 2013) using the absorption coefficient σ_{ap}:

for all days (whole time) and for days of month

$$[BC], [EC]_{TGVDI;TOTEUSAAR2} = \alpha_{C[TGVDI;\ TOTEUSAAAR2]} \times \sigma_{ap}$$

Nordmann et al. 2013

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The questions:

Can we derive correction factors for OC, EC (and TC)?

How they depend from particle size?

Are there differences for seasons?

Are there differences for source regions?

Are there differences for absolute content (OC, EC TC)?

Can we use correction factors to transform between the methods (TOTEUSAAR2 and TGVDI)?

Are there hints, which method is the better compromise?

What is the derived Mass Absorption Cross Section α_C for TGVDI and TOTEUSAAR2 for the whole time
and how is the variation over the month?

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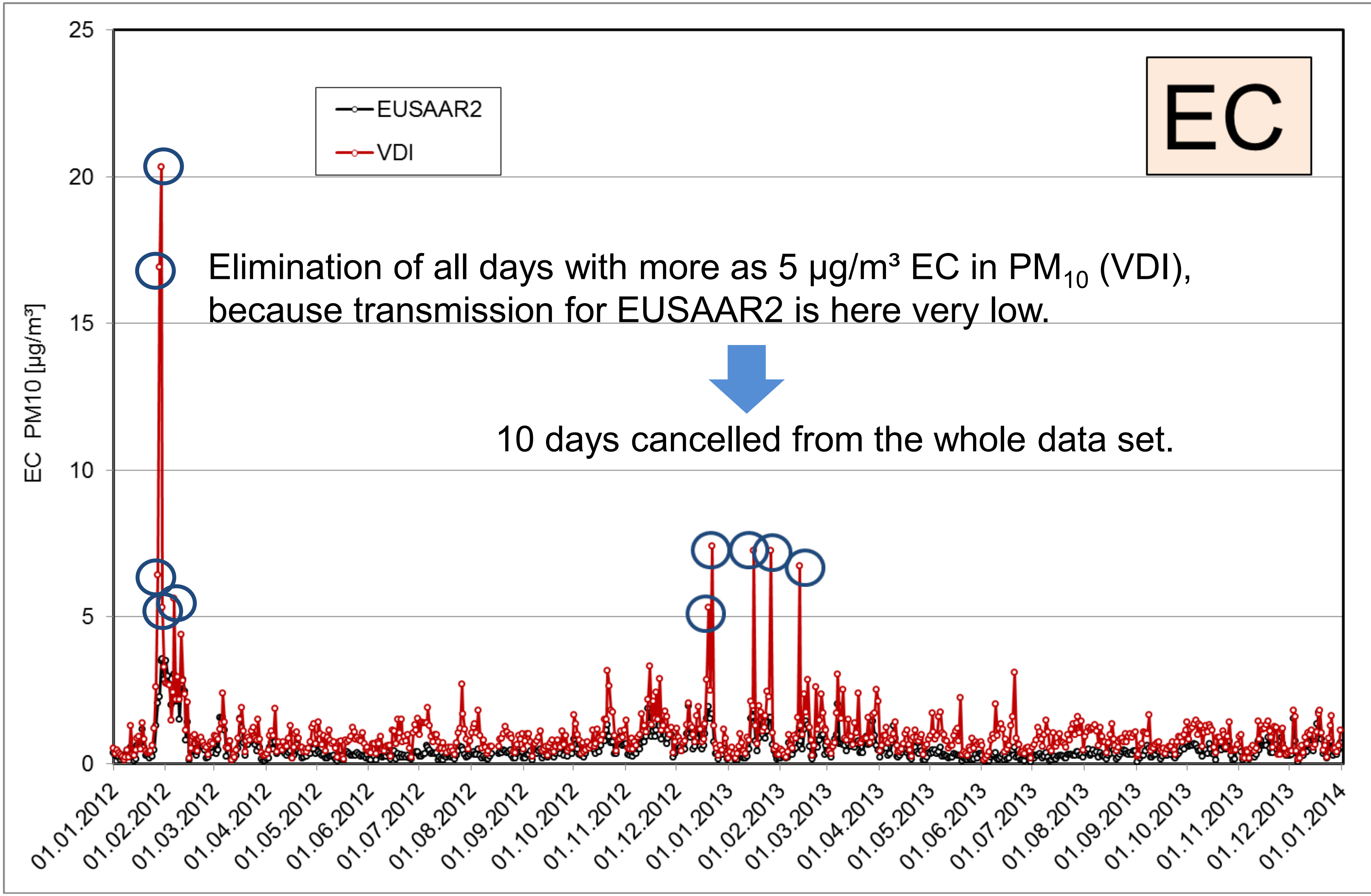
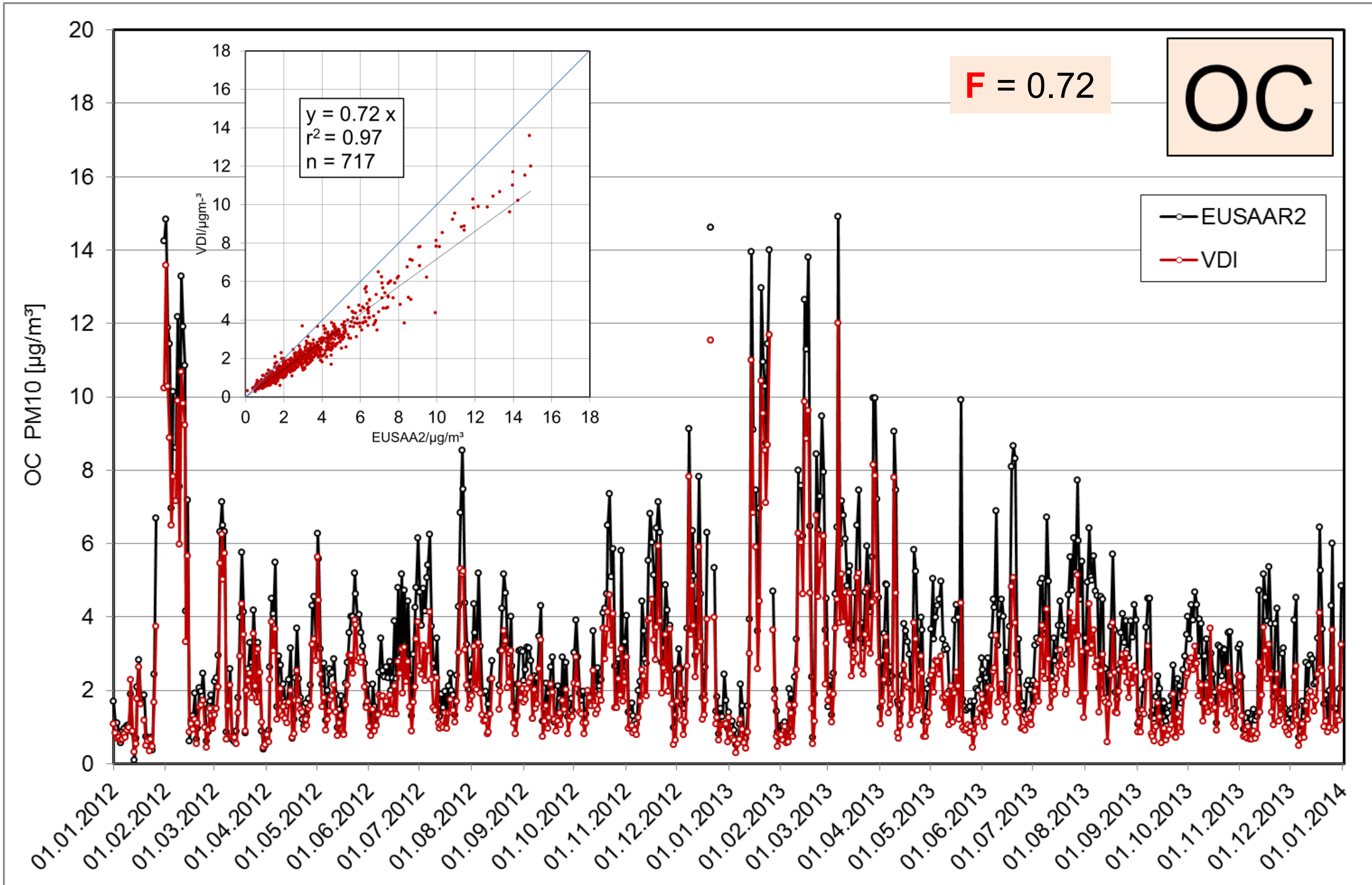
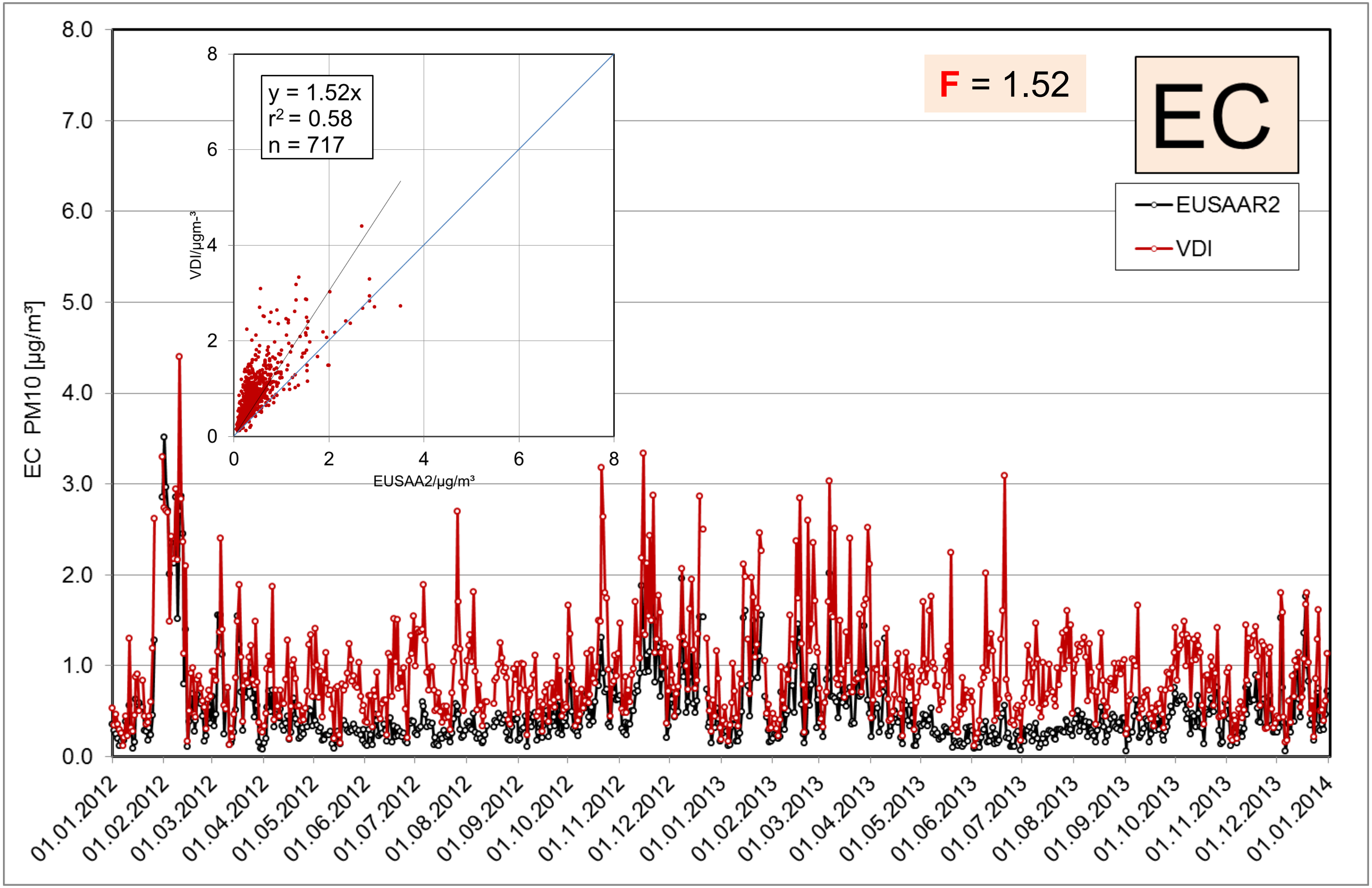
Preparation of dataset



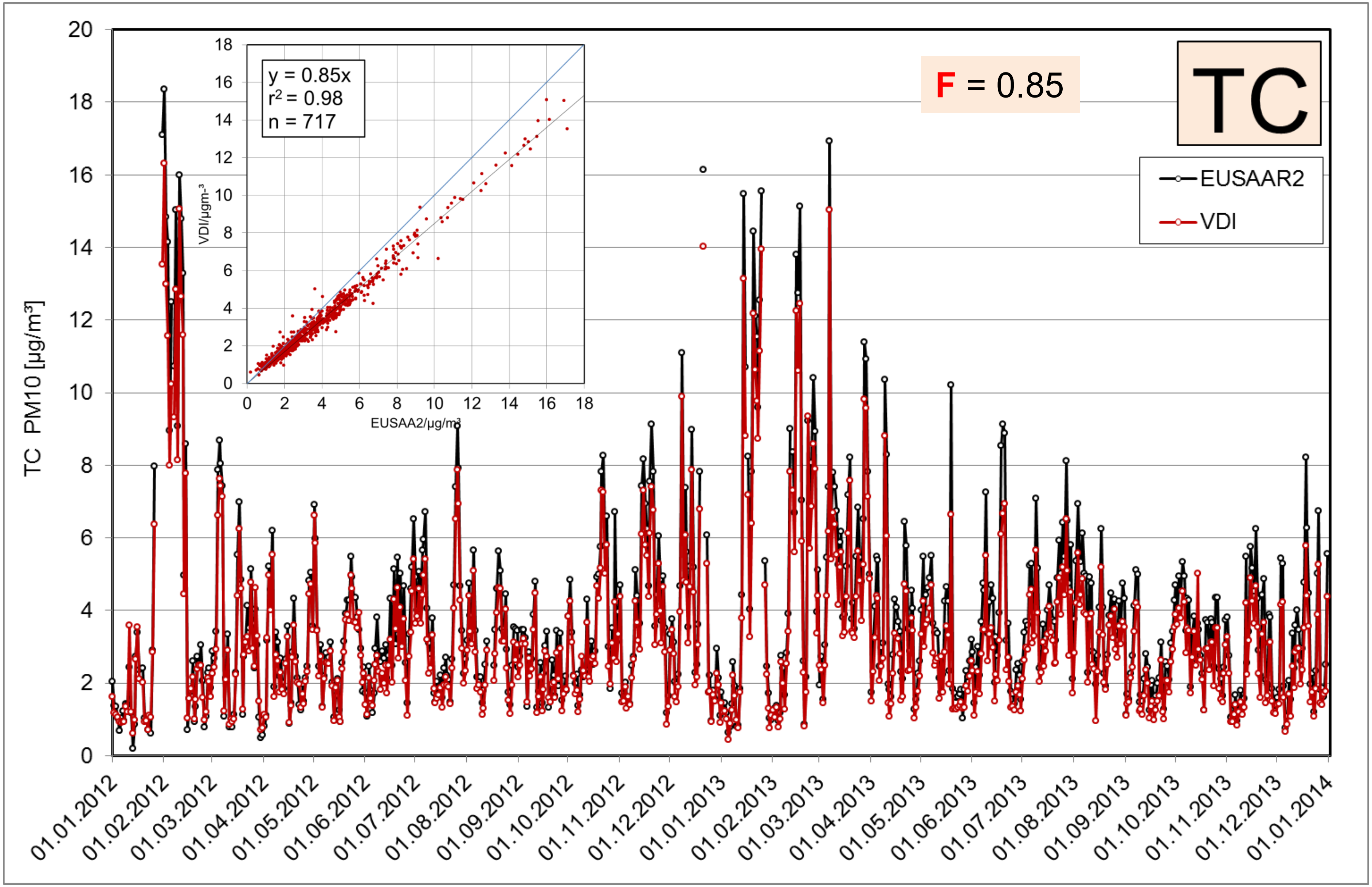
Calculation for PM_{10}, OC, (January 2012 until December 2013), all



Calculation for PM_{10}, EC, (January 2012 until December 2013), all



Calculation for PM_{10}, TC, (January 2012 until December 2013), all



Results – empirical factors (Melpitz site), F for all days

$$[OC; EC; TC]_{TG\ VDI} = F \times [OC; EC; TC]_{TO\ T\ EUSAAR2}$$

		F			
OC	PM_{10}	0.72	$r^2 = 0.97$	n = 717	
	$PM_{2.5}$	0.71	$r^2 = 0.96$	n = 718	**mean all sizes**
	PM_1	0.72	$r^2 = 0.93$	n = 218	**0.715 $r^2 = 0.98$**
					n=1653
EC	PM_{10}	1.52	$r^2 = 0.58$	n = 717	
	$PM_{2.5}$	1.60	$r^2 = 0.59$	n = 718	**mean all sizes**
	PM_1	1.58	$r^2 = 0.65$	n = 218	**1.557 $r^2 = 0.59$**
					n=1653
TC	**PM_{10}**	**0.85**	**$r^2 = 0.98$**	**n = 717**	
	$PM_{2.5}$	**0.83**	**$r^2 = 0.98$**	**n = 718**	**mean all sizes**
	PM_1	**0.84**	**$r^2 = 0.96$**	**n = 218**	**0.843 $r^2 = 0.99$**
					n=1653

We can derive mean correction factors for OC, EC and TC.
These factors depend not from particle size (range PM_{10} to PM_1).

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Results – empirical factors (Melpitz site), F
for winter and summer days

$$[OC; EC; TC]_{TG\ VDI} = F \times [OC; EC; TC]_{TO\ T\ EUSAAR2}$$

		F winter/summer	winter/summer	winter/summer
OC	PM_{10}	0.76/0.65	r^2 = 0.97/0.87	n = 352/365
	$PM_{2.5}$	0.74/0.62	r^2 = 0.98/0.86	n = 353/365
	PM_1	0.74/0.66	r^2 = 0.96/0.66	n = 94/124
EC	PM_{10}	1.35/2.33	r^2 = 0.69/0.40	n = 352/365
	$PM_{2.5}$	1.48/2.13	r^2 = 0.66/0.35	n = 353/365
	PM_1	1.51/1.89	r^2 = 0.68/0.29	n = 94/124
TC	**PM_{10}**	**0.86/0.83**	**r^2 = 0.99/0.94**	**n = 352/365**
	$PM_{2.5}$	**0.84/0.81**	**r^2 = 0.99/0.92**	**n = 353/365**
	PM_1	**0.84/0.84**	**r^2 = 0.98/0.78**	**n = 94/124**

There are small differences for seasons in the correction factors, especially for EC. The factors depend marginal from particle size (range PM_{10} to PM_1), especially in summer for EC.

Results – empirical factors (Melpitz site), F for WEST and EAST days

$$[OC; EC; TC]_{TG\ VDI} = F \times [OC; EC; TC]_{TO\ T\ EUSAAR2}$$

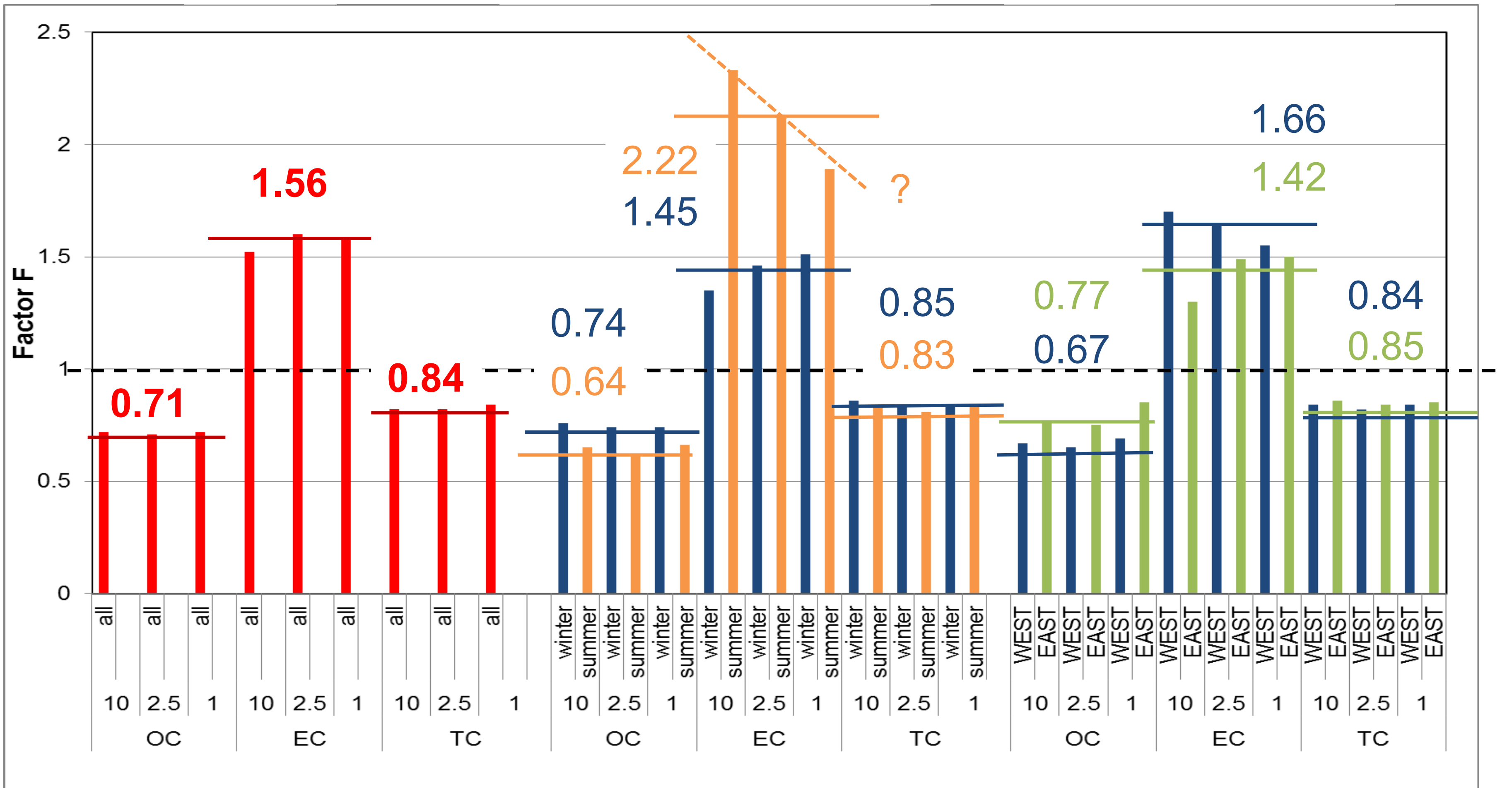
		F WEST/EAST	WEST/EAST	WEST/EAST
OC	PM_{10}	0.67/0.77	r^2 = 0.91/0.97	n = 450/110
	$PM_{2.5}$	0.65/0.75	r^2 = 0.91/0.97	n = 451/110
	PM_1	0.69/0.85	r^2 = 0.78/0.98	n = 130/47
EC	PM_{10}	1.70/1.30	r^2 = 0.53/0.62	n = 450/110
	$PM_{2.5}$	1.64/1.49	r^2 = 0.54/0.55	n = 451/110
	PM_1	1.55/1.50	r^2 = 0.61/0.55	n = 130/47
TC	**PM_{10}**	**0.84/0.86**	**r^2 = 0.95/0.99**	**n = 450/110**
	$PM_{2.5}$	**0.82/0.84**	**r^2 = 0.96/0.99**	**n = 451/110**
	PM_1	**0.84/0.85**	**r^2 = 0.87/0.98**	**n = 130/47**

There are small differences in the correction factors between air mass inflow WEST and EAST.
The factors depend not from particle size (range PM_{10} to PM_1).

Results – empirical factors (Melpitz site), F

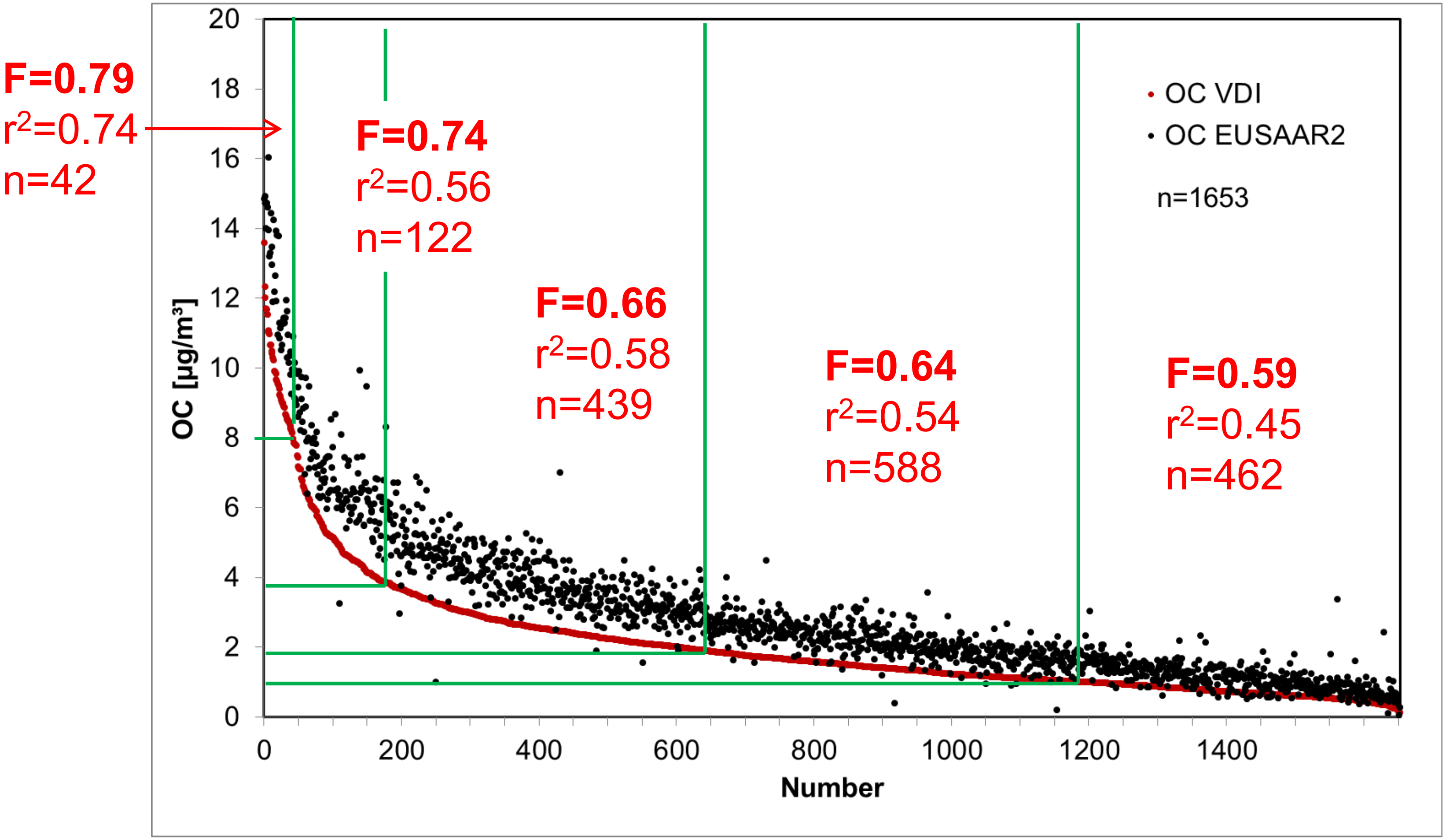
$$[OC; EC; TC]_{TG\ VDI} = F \times [OC; EC; TC]_{TO\ T\ EUSAAR2}$$

all days | winter and summer days | WEST and EAST days



Results – empirical factors (Melpitz site), F
Dependence from the absolute OC amount (TG VDI), all days, all sizes

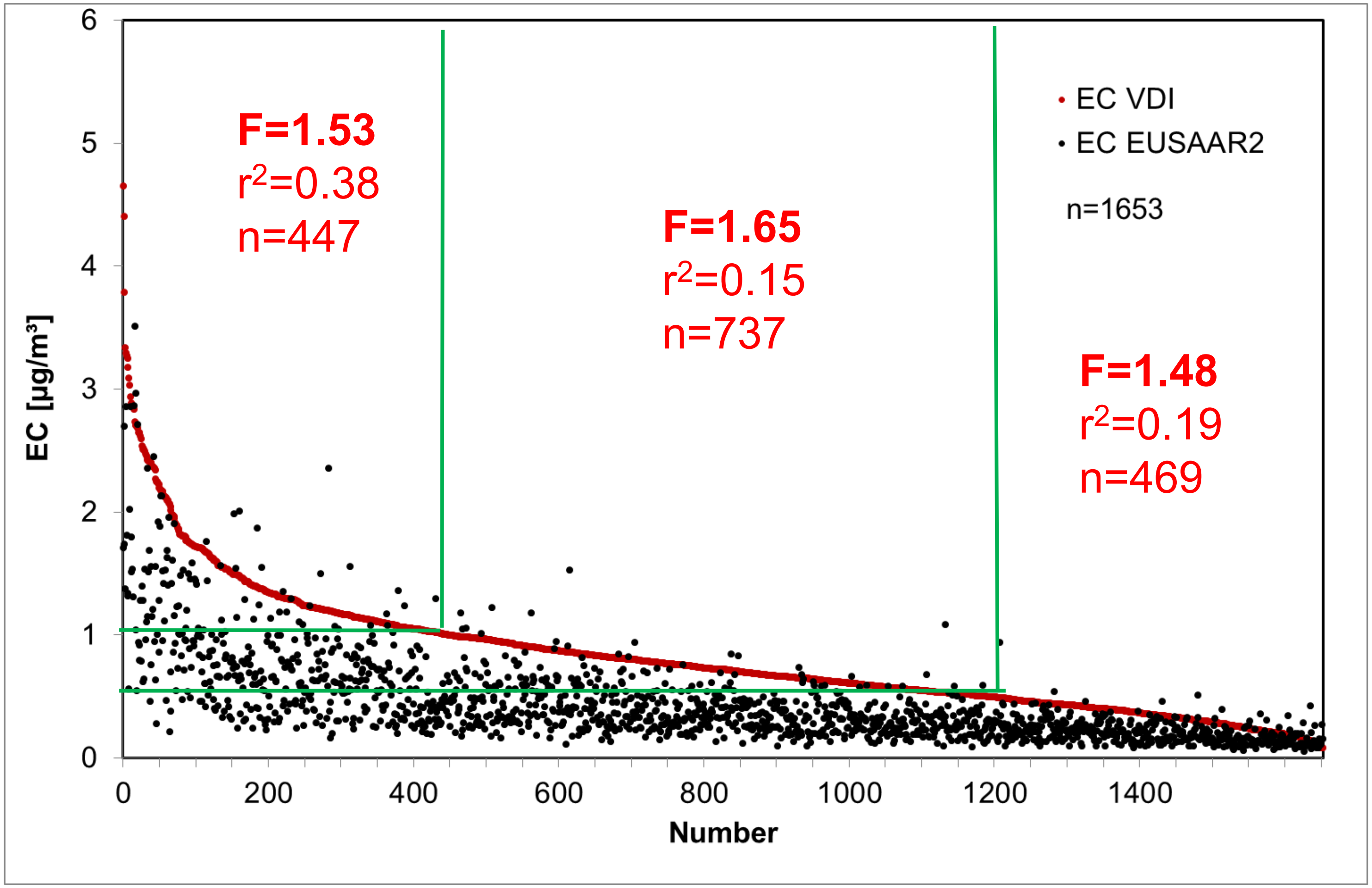
$$[OC; EC; TC]_{TG\ VDI} = F \times [OC; EC; TC]_{TO\ T\ EUSAAR2}$$



Higher OC content means a slightly higher factor F.

Results – empirical factors (Melpitz site), F
Dependence from the absolute EC amount (TG VDI), all days, all sizes

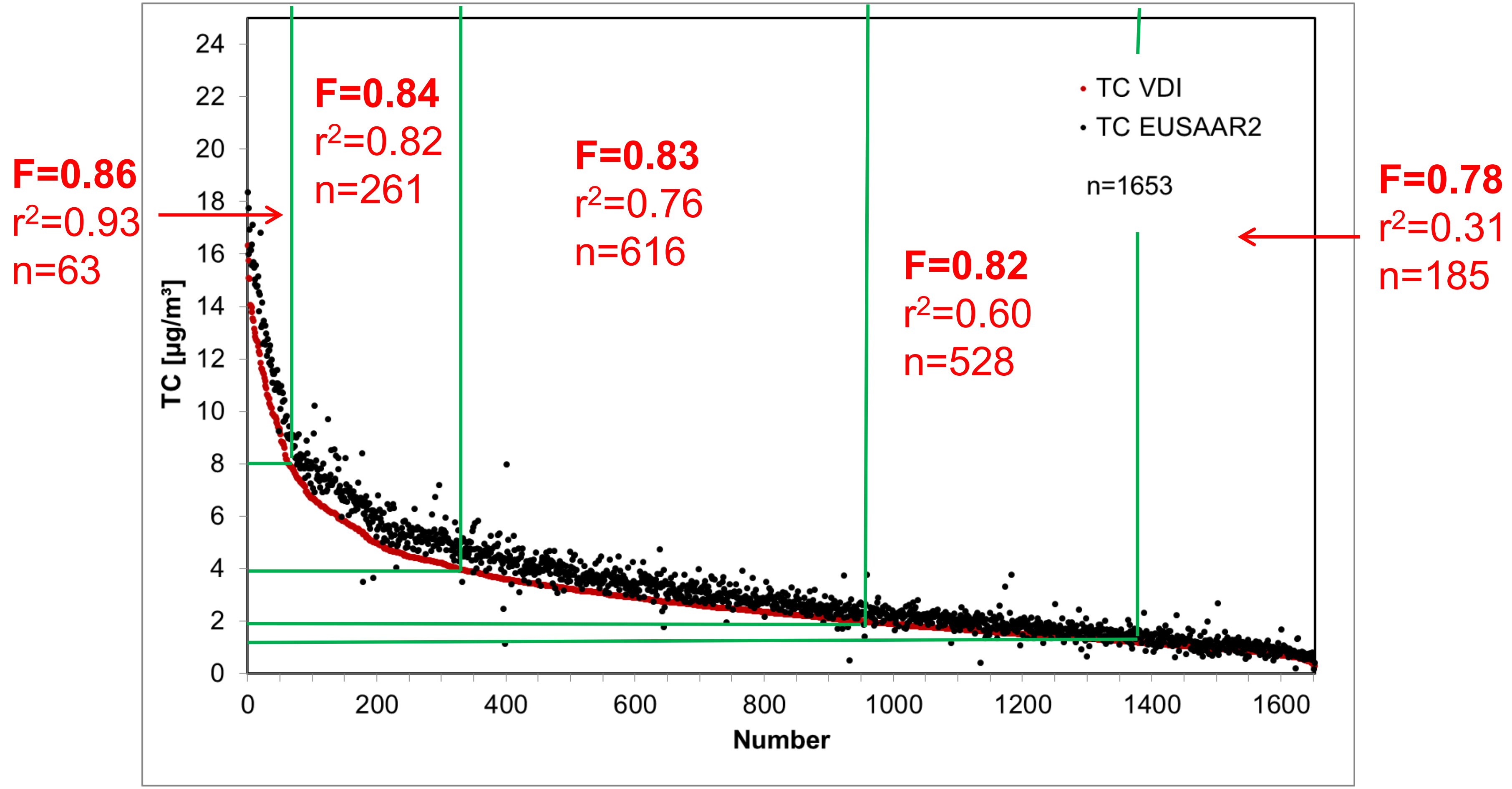
$$[OC; EC; TC]_{TG\ VDI} = F \times [OC; EC; TC]_{TO\ T\ EUSAAR2}$$



The EC content has no clearly influence on factor F.

Results – empirical factors (Melpitz site), F
Dependence from the absolute TC amount (TG VDI), all days, all sizes

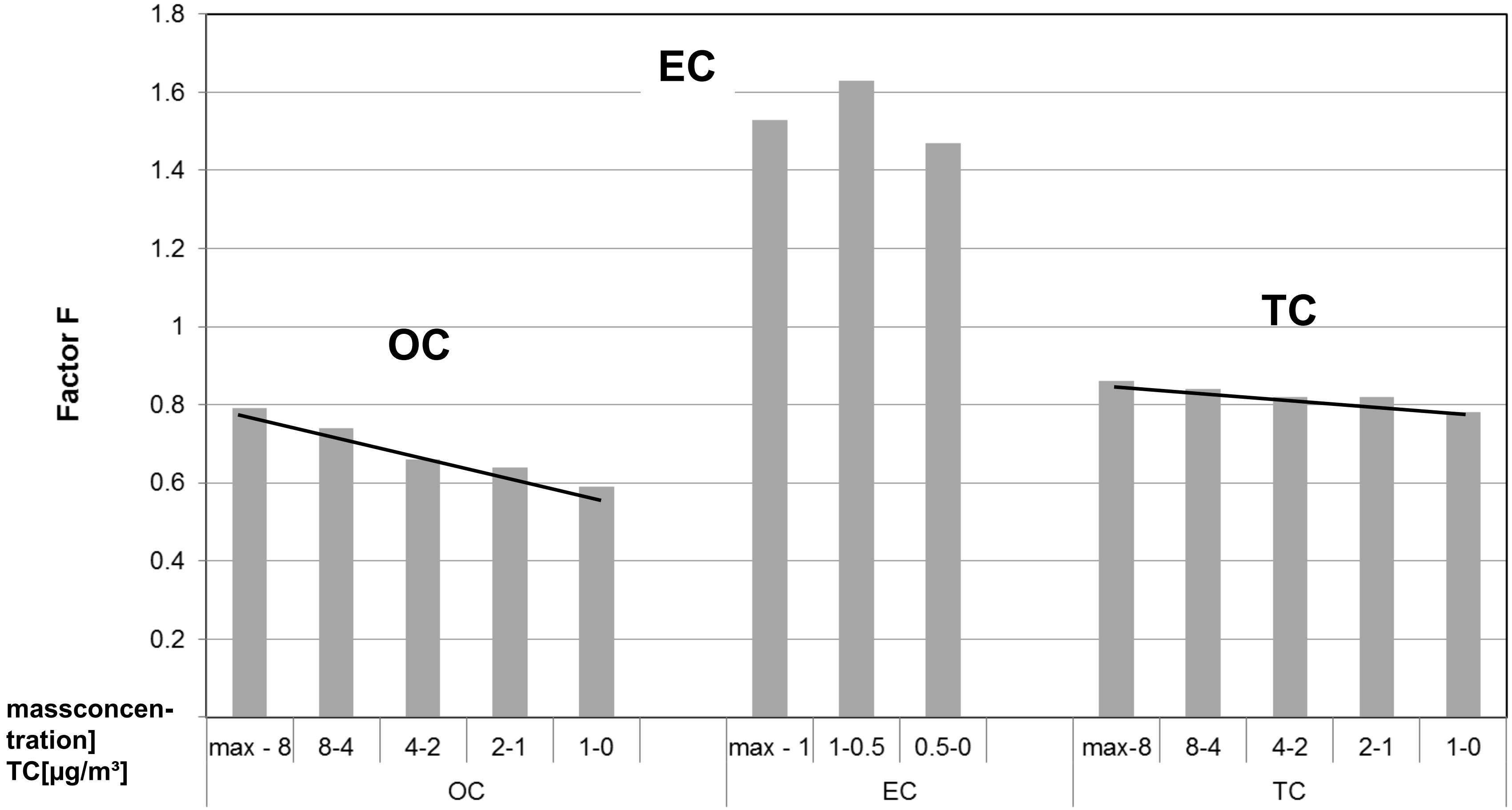
$$[OC; EC; TC]_{TG\ VDI} = F \times [OC; EC; TC]_{TO\ T\ EUSAAR2}$$



A high TC content means a hardly higher factor F.

Results – empirical factors (Melpitz site), F

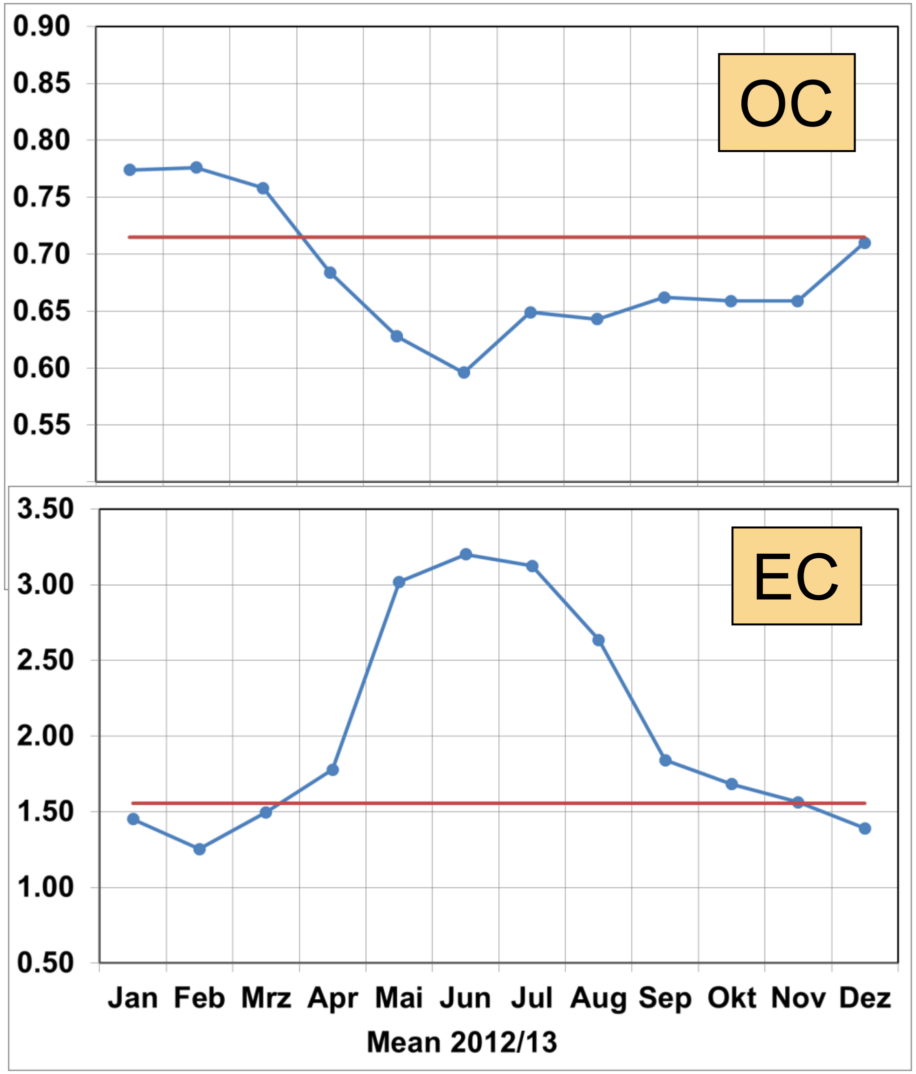
$$[OC; EC; TC]_{TG\ VDI} = F \times [OC; EC; TC]_{TO\ T\ EUSAAR2}$$

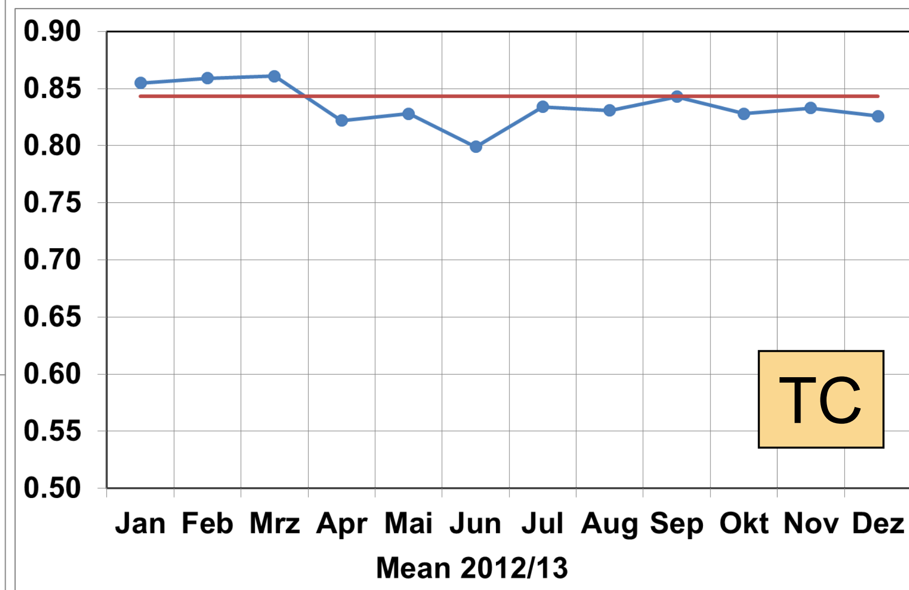


A higher OC content means a slightly higher factor F for all days and sizes
OC range 0.59 to 0.79 (TC range 0.78 to 0.86).

Estimated correction factors F to transform TOTEUSAAR2 to TGVDI (all sizes)

$$[OC; EC; TC]_{TG\ VDI} = F \times [OC; EC; TC]_{TO\ T\ EUSAAR2}$$





factor for all days (all sizes)

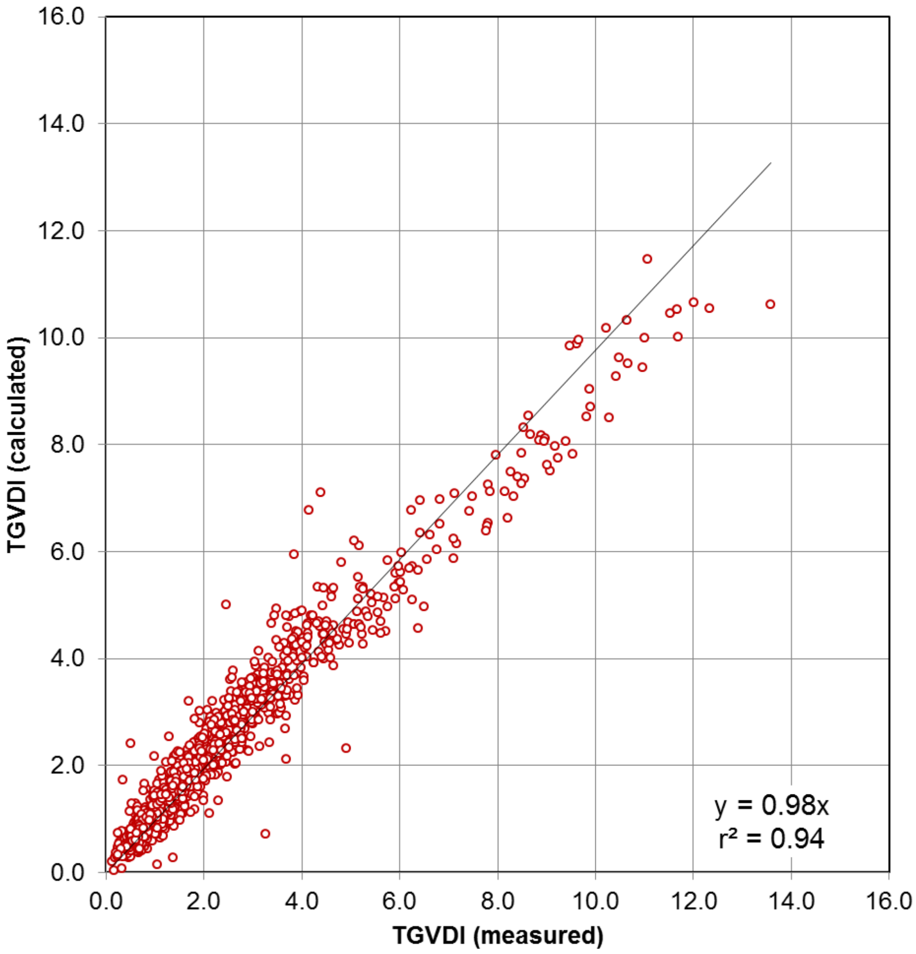
factor for all days in month (all sizes)

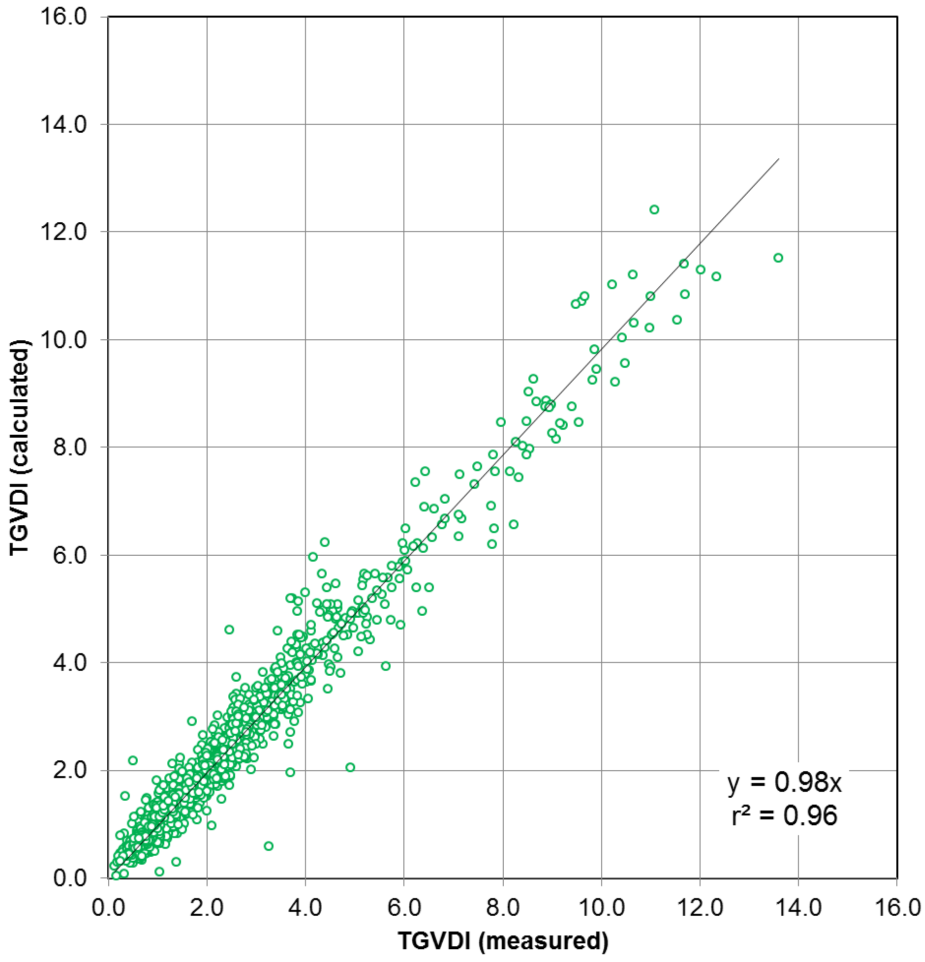
as an practicable approximation

Comparison of measured values TGVDI with re-calculated values TGVDI (from TOTEUSAAR2) using estimated correction factors

OC

factor for all days (all sizes) → factor for all days in month (all sizes)

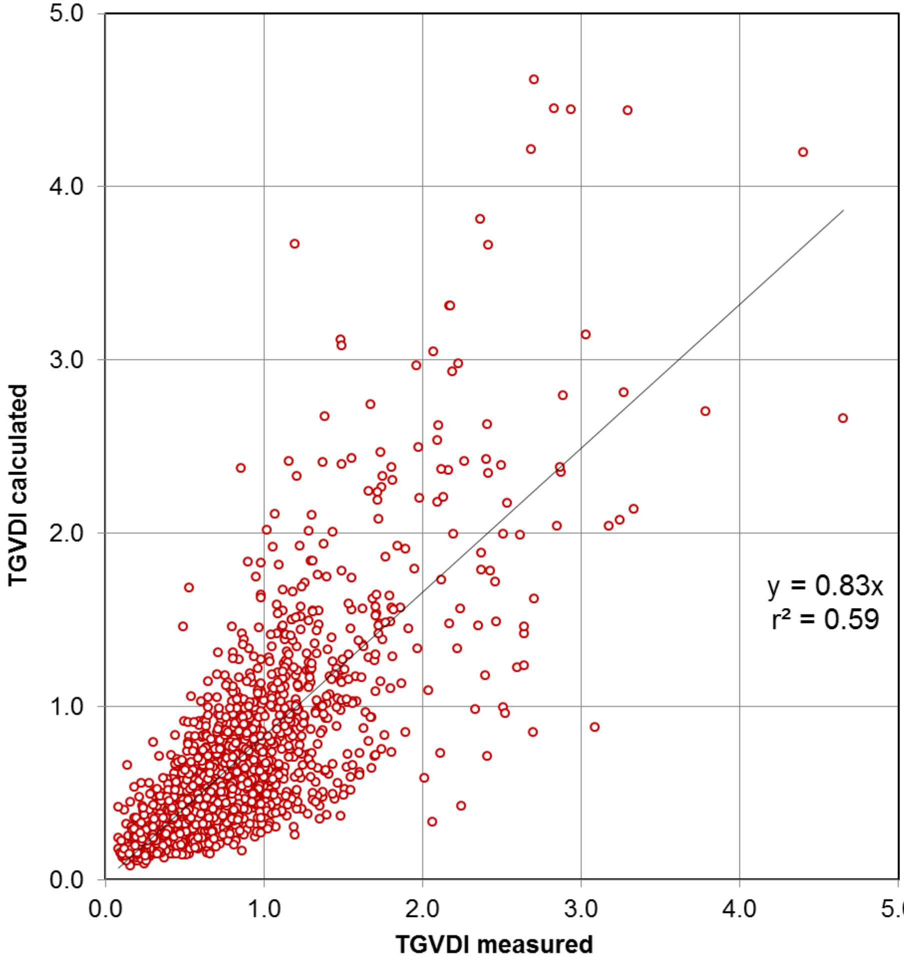


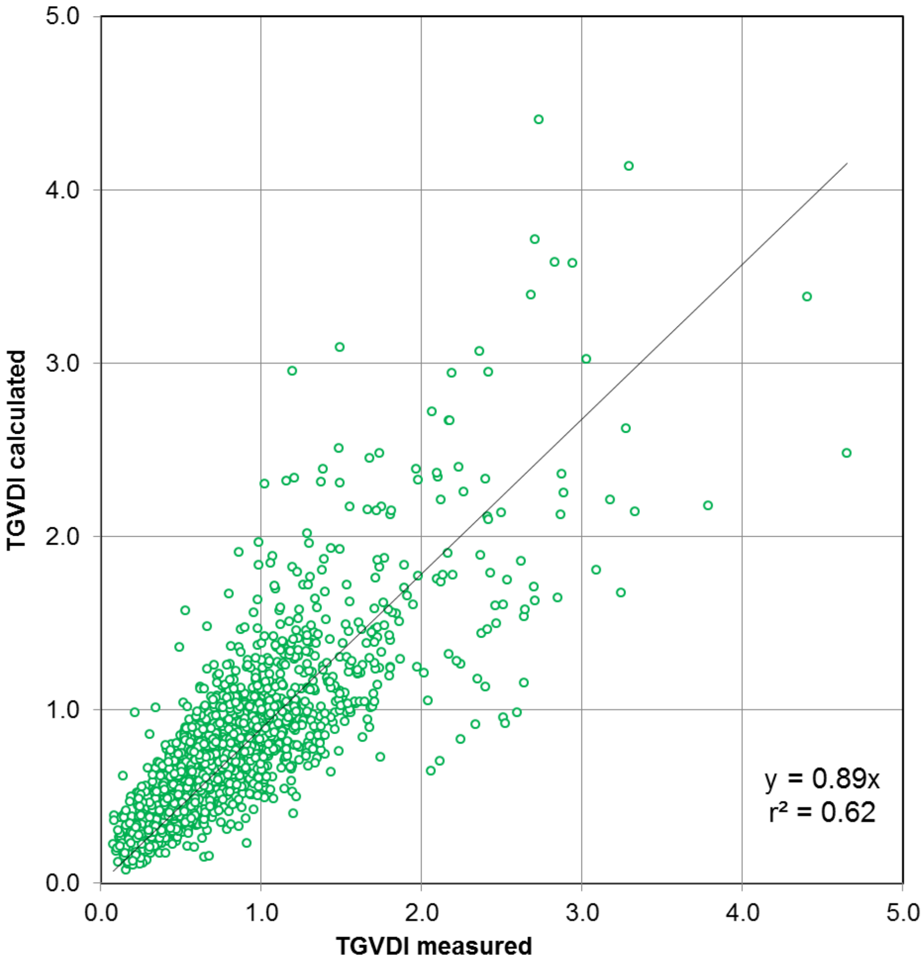


Comparison of measured values TGVDI with re-calculated values TGVDI (from TOTEUSAAR2) using estimated correction factors

EC

factor for all days (all sizes) → factor for all days in month (all sizes)

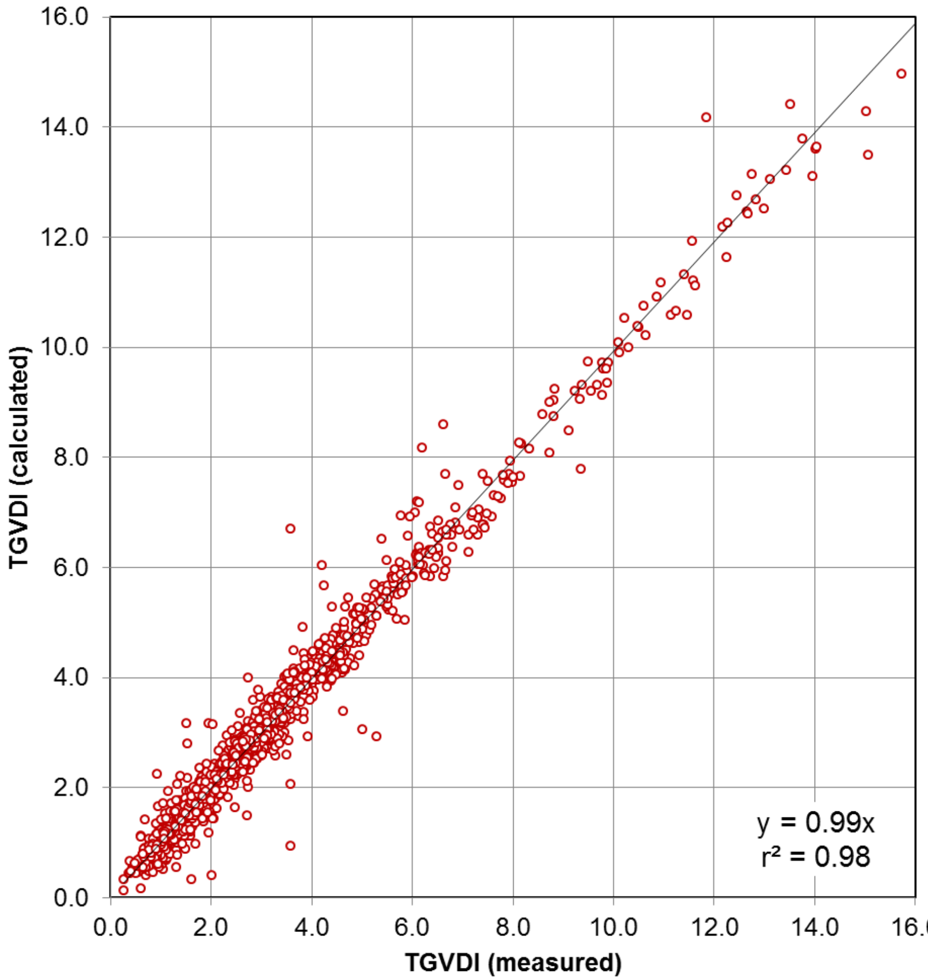


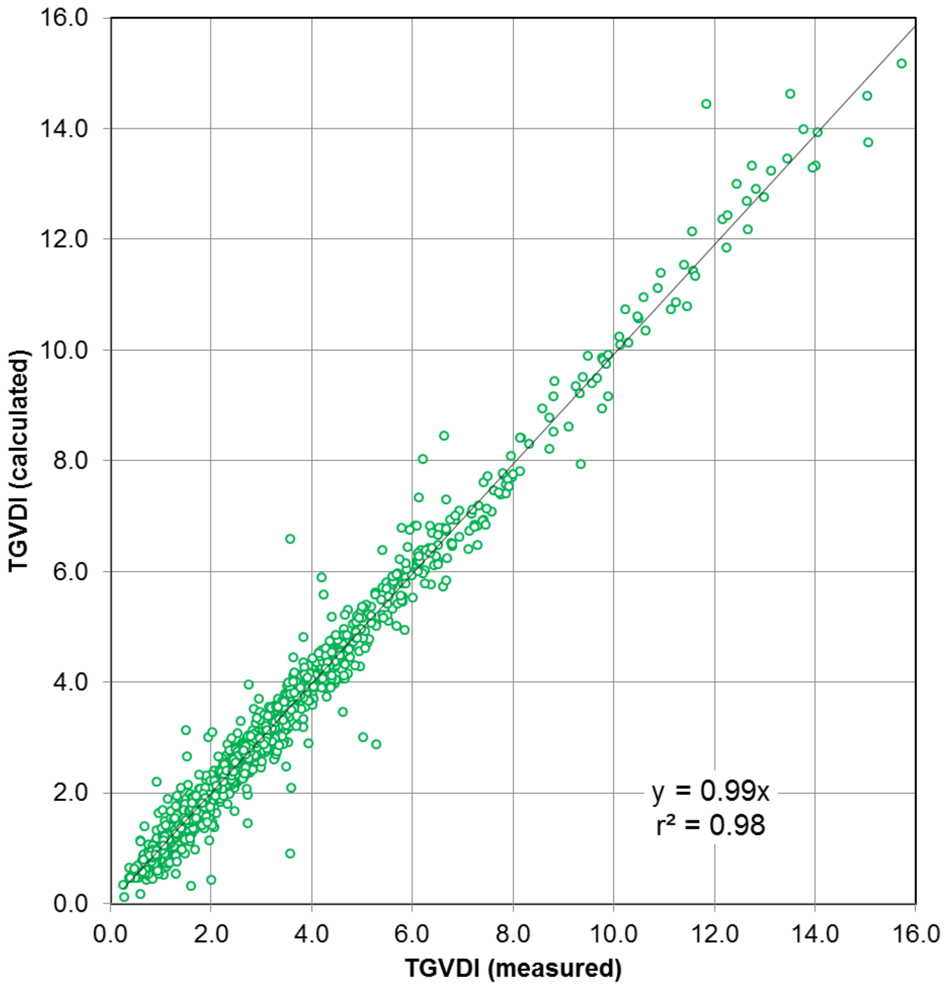


Comparison of measured values TGVDI with re-calculated values TGVDI (from TOTEUSAAR2) using estimated correction factors

TC

factor for all days (all sizes) → factor for all days in month (all sizes)

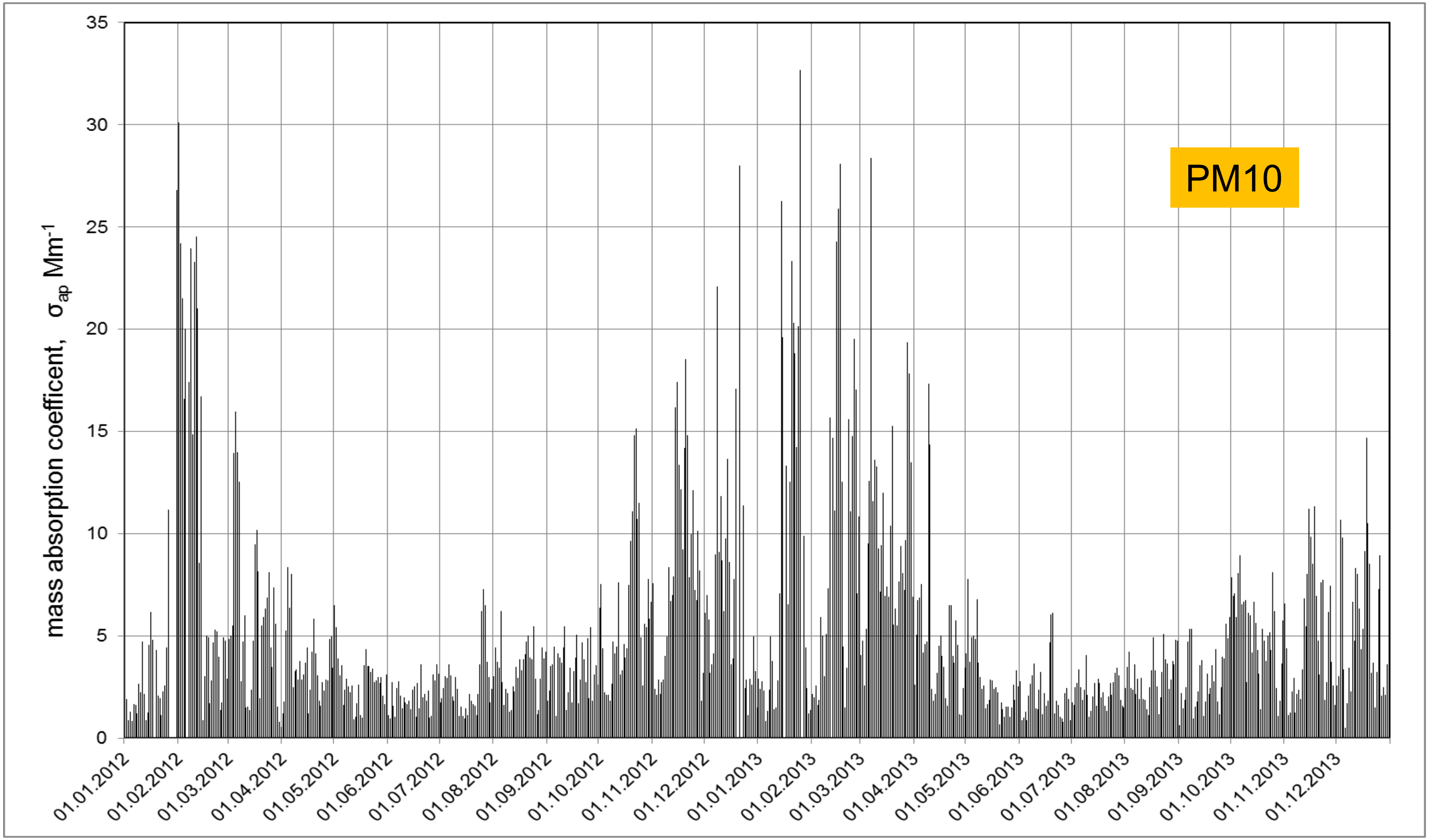




Comparison of measured values TGVDI with re-calculated values TGVDI (from TOTEUSAAR2) using estimated correction factors

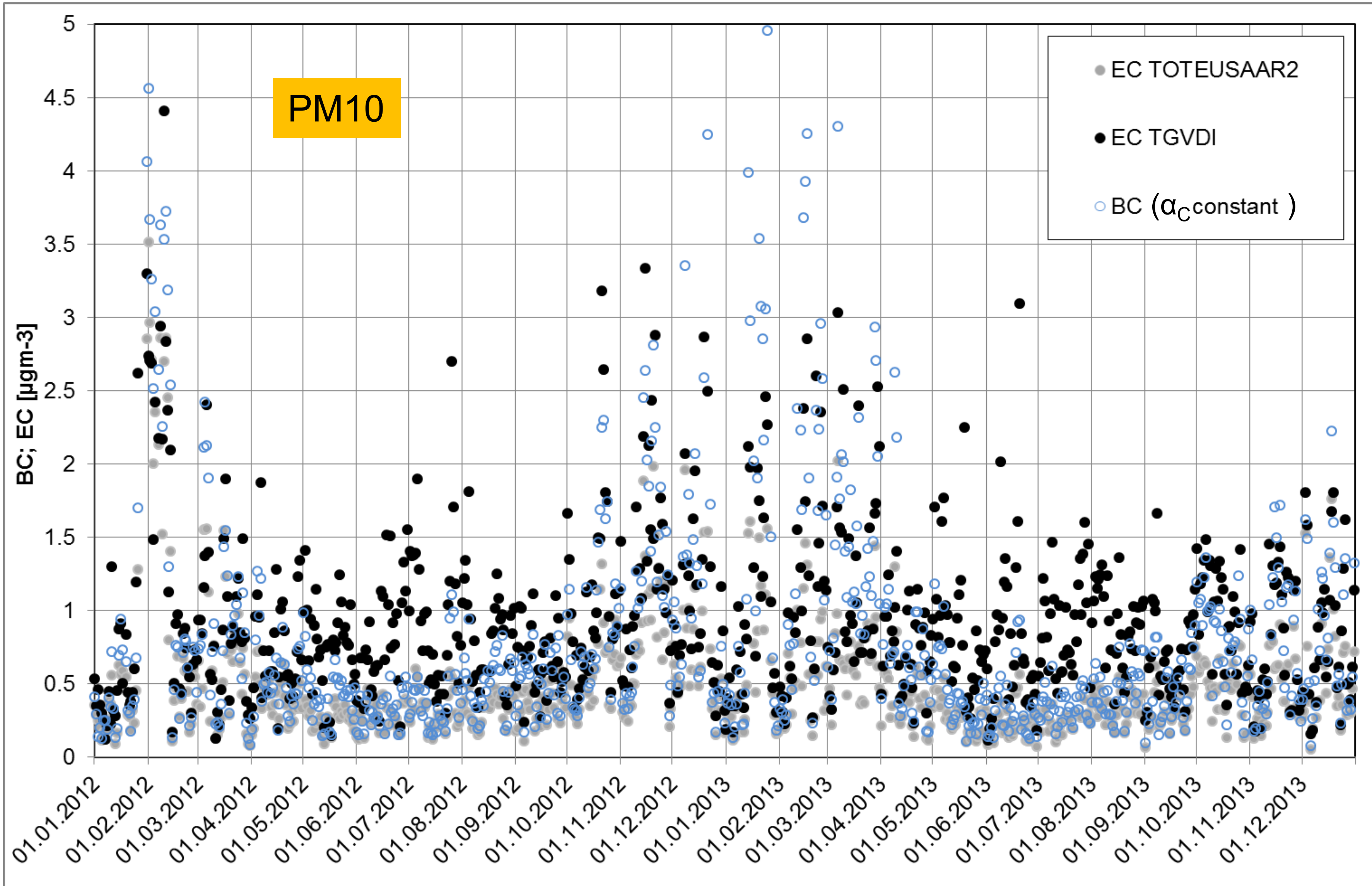
	factor for all days (all sizes)	factor for all days in month (all sizes)	
OC	$y = 0.98\,x$ $r^2 = 0.94$	$y = 0.98\,x$ $r^2 = 0.96$	n = 1653
EC	$y = 0.83\,x$ $r^2 = 0.59$	$y = 0.89\,x$ $r^2 = 0.62$	n = 1653
TC	$y = 0.99\,x$ $r^2 = 0.98$	$y = 0.99\,x$ $r^2 = 0.98$	n = 1653

Measured particle light absorption coefficient σ_{ap}, MAAP (637 nm), PM_{10} Melpitz 2012 and 2013 (daily means)



$$[BC], [EC]_{TGVDI;TOTEUSAAR2} = \alpha_{C[TGVDI;\ TOTEUSAAR2]} \times \boldsymbol{\sigma}_{\mathbf{ap}}$$

Comparison measured EC with BC
(BC calculated from absorption coefficient σ_{ap}, $\alpha_C = 6.6\ m^2g^{-1}$)



Calculation of different mass absorption cross sections

- ***constant mass absorption cross section***

  $[BC] = \alpha_{C\ constant} \times \sigma_{ap}$,

  $\alpha_{C\ constant} =$ **6.6 m^2g^{-1}**

- ***mass absorption cross section from correlation*** σ_{ap} ***with measured*** $EC_{TGVD,\ TOTEUSAAR2}$ ***(whole time)***

  $[BC] \triangleq [EC]_{TGVDI}$

  $[EC]_{TGVDI} = \alpha_{C\ TGVDI} \times \sigma_{ap}$

  $\alpha_{C\ TGVDI} =$ **5.917 m^2g^{-1}** $r^2 = 0.81$ $n = 717$

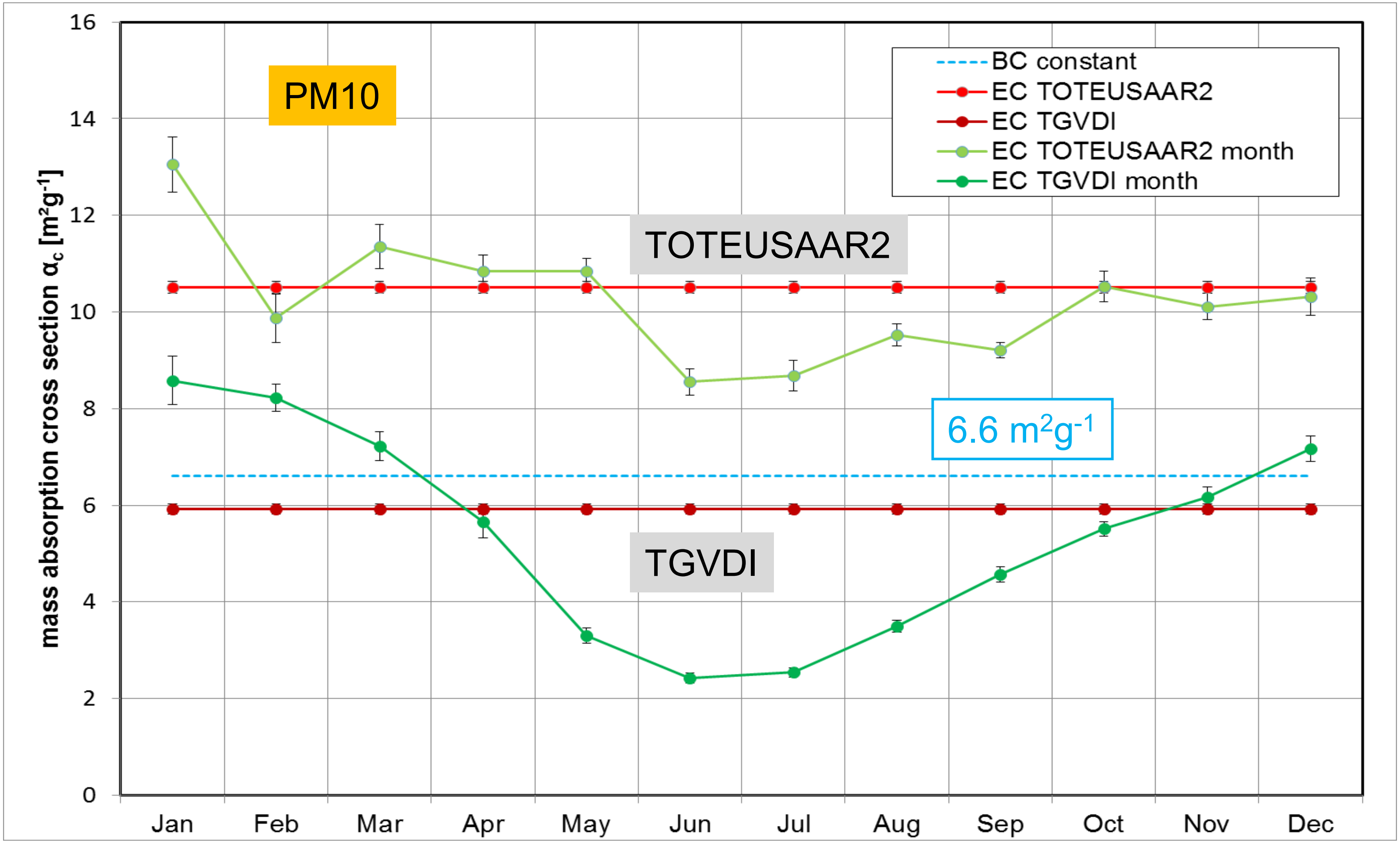
  $[BC] \triangleq [EC]_{TOTEUSAAR2}$

  $[EC]_{TOTEUSAAR2} = \alpha_{TOTEUSAAR2} \times \sigma_{ap}$

  $\alpha_{C\ TOTEUSAAR2} =$ **10.507 m^2g^{-1}** $r^2 = 0.91$ $n = 717$

- ***mass absorption cross section from correlation*** σ_{ap} ***with measured*** $EC_{TGVD,\ TOTEUSAAR2}$ ***(separate for the month)***

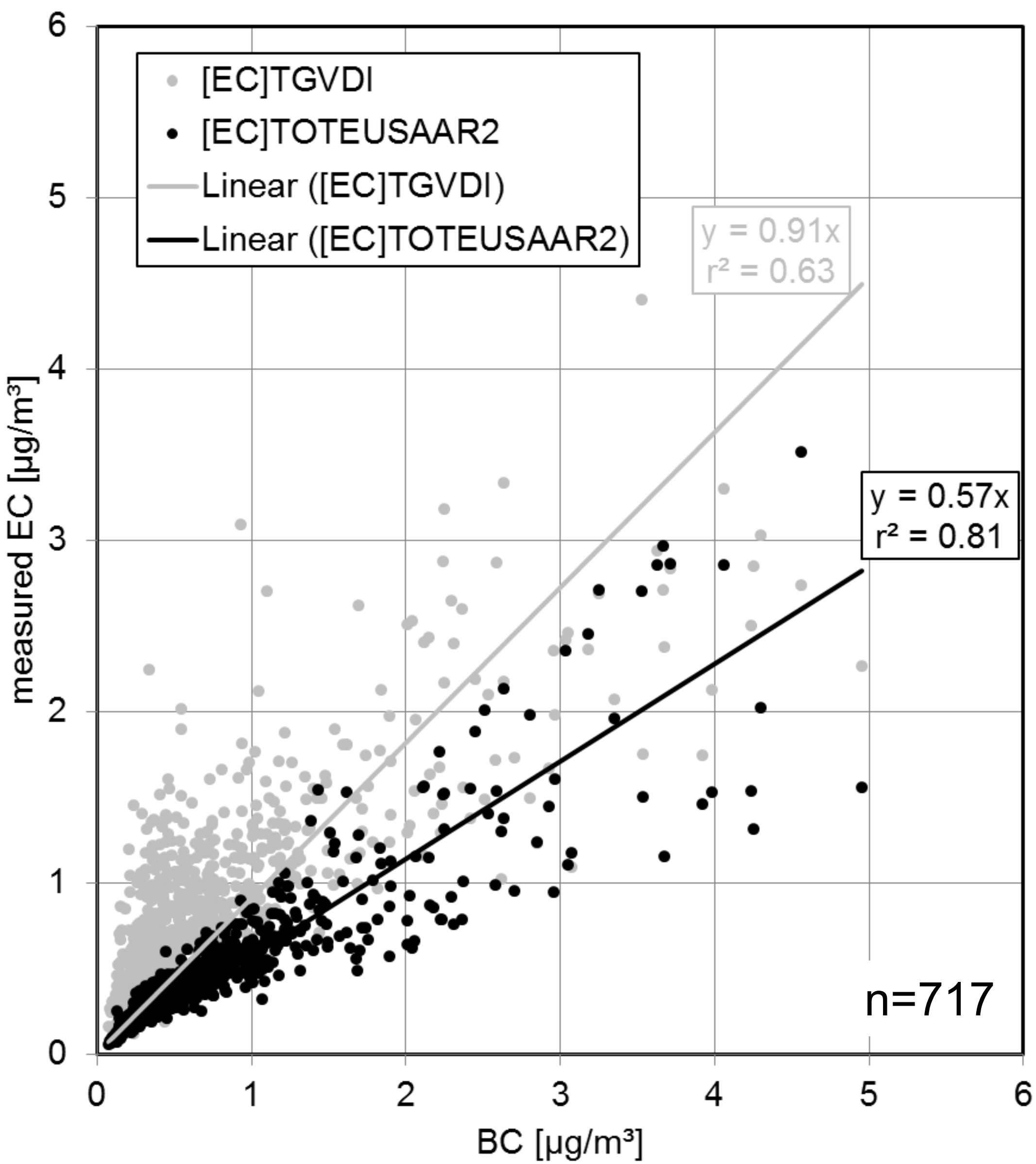
Different mass absorption cross sections, α_C



$[BC], [EC]_{TGVDI;TOTEUSAAR2} = \alpha_{C[TGVDI;\ TOTEUSAAAR2]} \times \sigma_{ap}$

Error α_C

Comparison BC and measured EC



$[EC]_{TGVDI;TOTEUSAAR2} = m_{BC} \times [BC]$

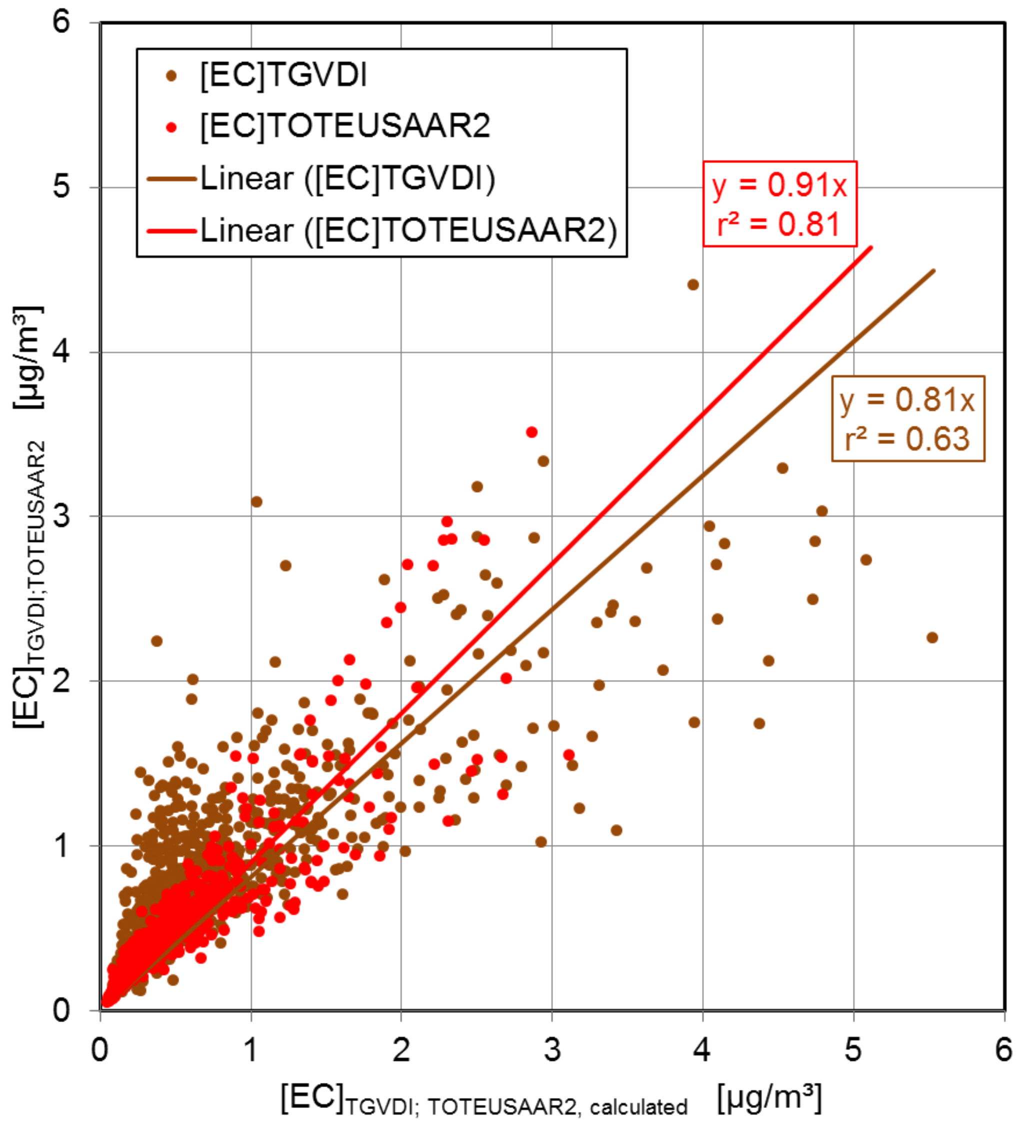
PM10

mass absoption cross section
$\alpha_C = 6.6\ m^2g^{-1}$

Comparison calculated EC (α_C = const) with measured EC

$[EC]_{TGVDI;TOTEUSAAR2} = m_{wt;TGVDI;TOTEUSAAR2} \times [EC]_{TGVDI;TOTEUSAAR2,calculated}$

$[EC]_{TGVDI;\ TOTEUSAAR2,calculetd} \triangleq [BC]$



PM10

mass absoption cross section

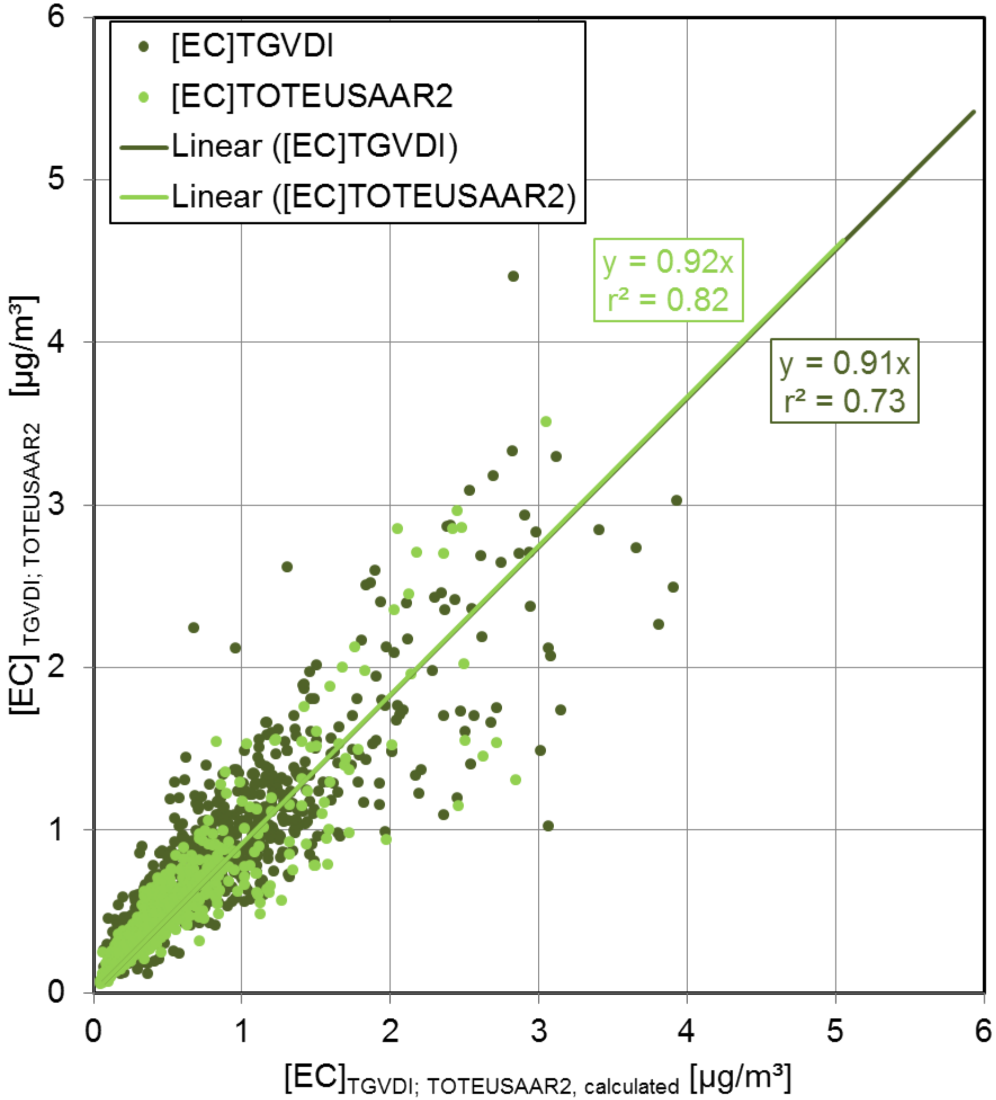
$\alpha_{C;\ TGVDI}$ = 5.9 m^2g^{-1}

$\alpha_{C;\ TOTEUSAAR2}$ = 10.5 m^2g^{-1}

Comparison EC (α_C = calculated for month) with measured EC

$$[EC]_{TGVDI;TOTEUSAAR2} = m_{wt;TGVDI;TOTEUSAAR2} \times [EC]_{TGVDI;TOTEUSAAR2,calculated}$$

$$[EC]_{TGVDI;\ TOTEUSAAR2,calculetd} \triangleq [BC]$$



PM10

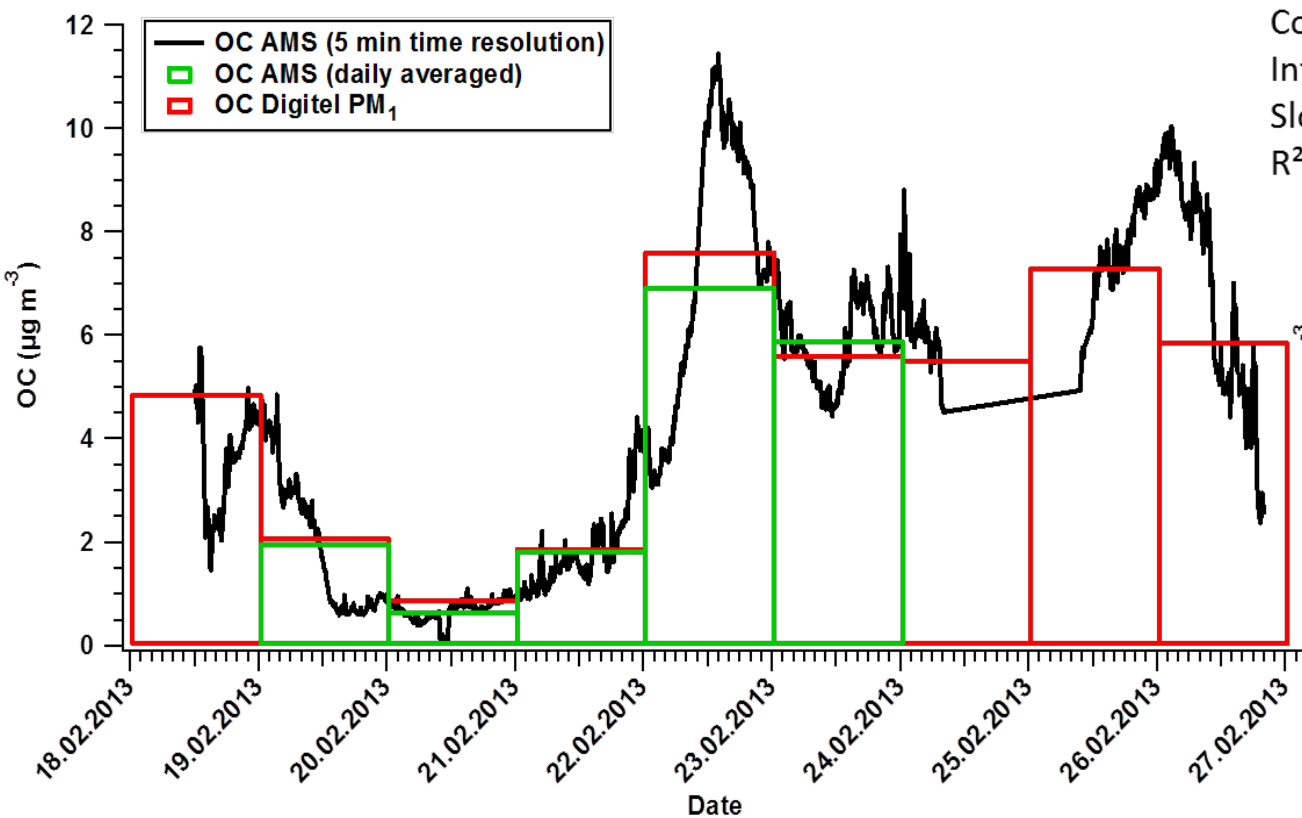
mass absoption cross section

$\alpha_{C;\ TGVDI}$ and $\alpha_{C;\ TOTEUSAAR2}$ calculated separate for month

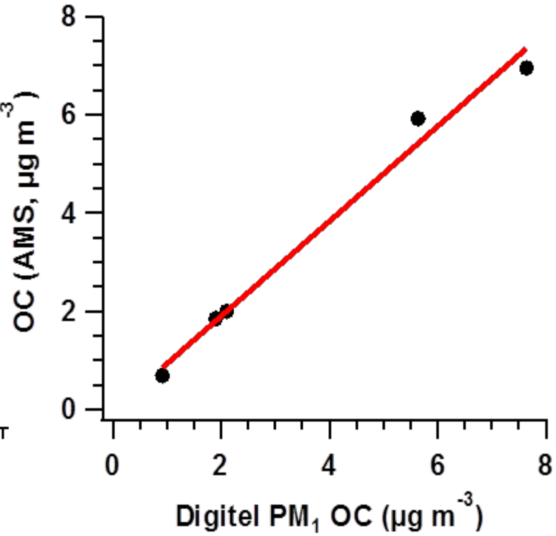
Which method (TGVDI or TOTEUSAAR2) is the better compromise? (I)

OC PM1 off-line (EUSAAR2) vs. on-line measurements (AMS)

AMS provides OM and ratio OM/OC based on the elemental analysis of the high resolution mass spectra.



Fit Type: least orthogonal distance fit
Coefficient value +/- one std dev.
Intercept = -0.039 +/- 0.301
Slope = 0.967 +/- 0.067
R^2 = 0.98



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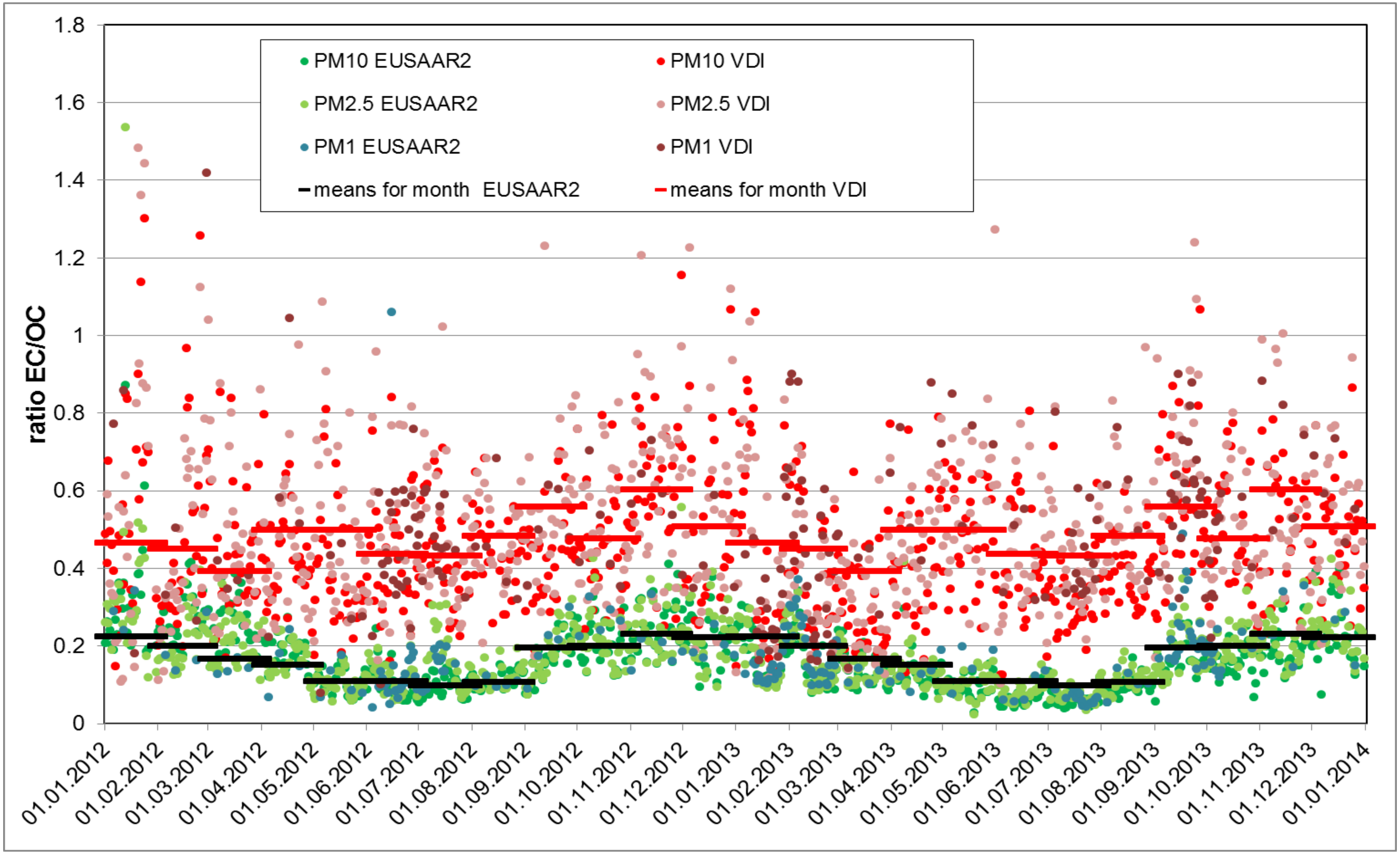
Which method is the better compromise? (II)



Daily ratios EC/OC for PM_{10}, $PM_{2.5}$ and PM_1
Method TG VDI and TO T EUSAAR2

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Results – empirical factors, F (TGVDI, TOTEUSAAR2) (summary)

- The mean factors depend not from particle size (range PM_{10} to PM_1) for all days.
- There are small differences for seasons in the mean correction factors, especially EC has higher factors in summer depending marginal from particle size (PM_{10} > $PM_{2.5}$ > PM_1).
- There are very small differences in the mean correction factors between air mass inflow WEST and EAST. The factors depend not from particle size.
- Higher TC content means a slightly higher factor F for all days and sizes for OC range 0.59 to 0.79 and for TC range 0.78 to 0.86.
- With monthly factors (derived for all days in month 2012,13, PM_{10}, $PM_{2.5}$, PM_1) OC_{TGVDI} can re-calculated from $OC_{TOTEUSAAR2}$ for 98% (r^2=0.96), EC for 89% (r^2=0.62) and TC for 99% (r^2=0.98)
- The thermo-optical method can give a more stable split for OC and EC.

Open Question: Depends the factors from the measurement place?
Depends the OC/EC split from the carrier material (TG VDI)?

Results – Comparison EC and BC for PM_{10} (summary)

- The measured absorption coefficient σ_{ap} (daily mean), MAAP (637 nm), PM_{10}, Melpitz 2012 and 2013 shows a diurnal variation between 0.2 and about 30 Mm^{-1}.
- For a constant mass absoption cross section of α_C = 6.6 m^2g^{-1} the measured EC_{TGVDI} represents 97% (r^2=0.63) of BC and the measured $EC_{TOTEUSAAR2}$ represents 57% (r^2=0.81) of BC.
- For a calculated mass absoption cross section over the whole time of α_C = 5.9 m^2g^{-1} (TGVDI) and α_C = 10.5 m^2g^{-1} (TOTEUSAAR2) the measured EC_{TGVDI} represents 81% (r^2=0.63) of $EC_{TGVDI,calculated}$ and the measured $EC_{TOTEUSAAR2}$ 91% (r^2=0.81) of $EC_{TOTEUSAAR2,calculated}$, respectively.
- For a separate over the month calculated mass absoption cross section for TGVDI and TOTEUSAAR2 the measured EC_{TGVDI} represents 91% (r^2=0.73) of $EC_{TGVDI,calculated}$ and the measured $EC_{TOTEUSAAR2}$ 92% (r^2=0.82) of $EC_{TOTEUSAAR2,calculated}$, respectively.
- The mass absorption cross section depends mostly from method and season.

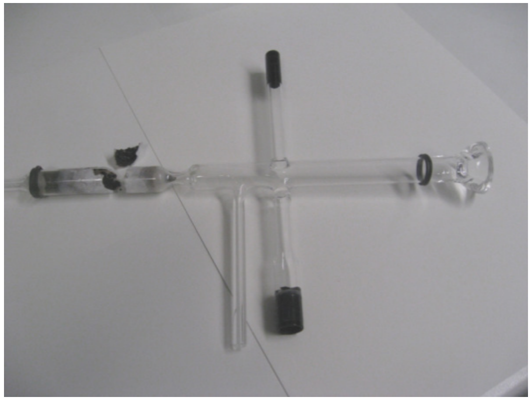
Sistine Chapel

Ship diesel

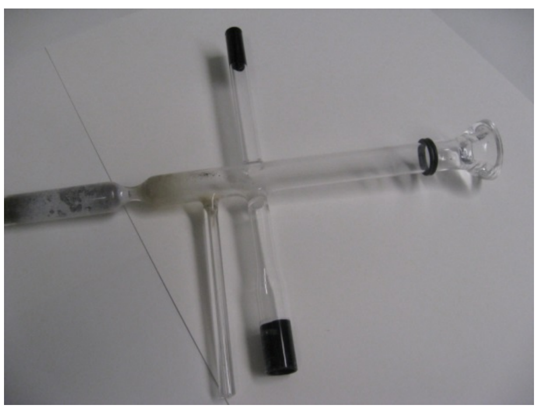
Thank you for attention!

TROPOS

Disturbances of the Sunset device

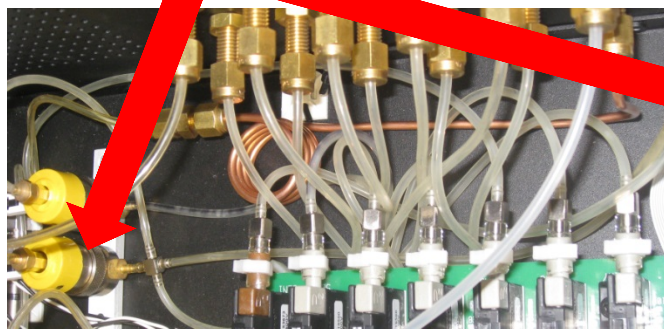


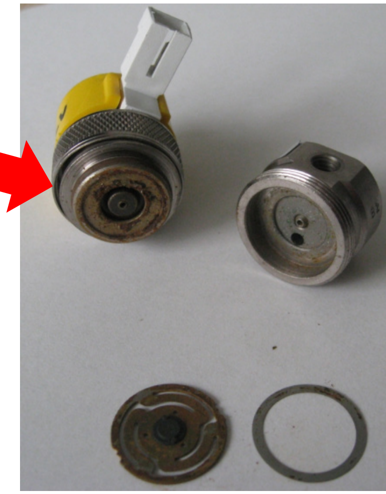
Main ofen defect (broken)

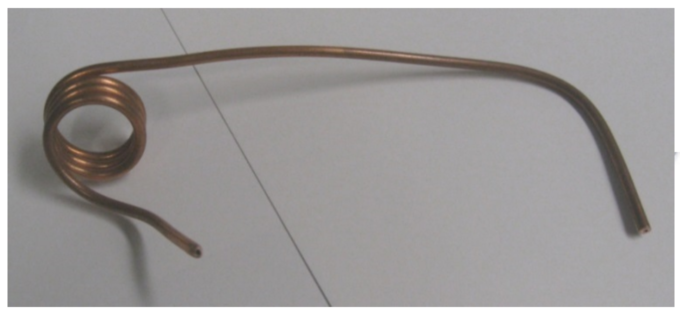


Main ofen „exhausted“

Corrosion ventil 2







Copper line

Corrosion of glow plug (FID)

Verwendete Temperaturprotokolle

	EPA/NIOSH[b]	NIOSH 5040	IMPROVE[c]	EUSAAR_1 short	EUSAAR_1 Long	He4-550	He4-750	He4-850	EUSAAR_2
STEP	T, duration °C, s	T, duration °C, s	T, duration °C, s	T, duration °C, s	T, duration °C, s	T, duration °C, s	T, duration °C, s	T, duration °C, s	T, duration °C, s
He1	310, 60	250, 60	120, 150–580	200, 120	200, 180	200, 180	200, 180	200, 180	200, 120
He2	475, 60	500, 60	250, 150–580	300, 150	300, 240	300, 240	300, 240	300, 240	300, 150
He3	615, 60	650, 60	450, 150–580	450, 180	450, 240	450, 240	450, 240	450, 240	450, 180
He4	900, 90	850, 90	550, 150–580	650, 180	650, 240	550, 240	750, 240	850, 240	650, 180
$He/O_2$1[a]	600, 45	650, 30	550, 150–580	550, 240	550, 300	550, 300	550, 300	550, 300	500, 120
$He/O_2$2	675, 45	750, 30	700, 150–580	850, 150	850, 180	850, 180	850, 180	850, 180	550, 120
$He/O_2$3	750, 45	850, 30	800, 150–580						700, 70
$He/O_2$4	825, 45	940, 120							850, 80
$He/O_2$5	920, 120	∑ 480 s							∑ 1020 s

[a] A mix of 2% oxygen in UHP helium.
[b] The temperature program for the EPA/NIOSH method is reported in Peterson and Richards (2002).
[c] The residence time at each temperature in the IMPROVE protocol depends on when the flame ionization detector (FID) signal returns to the baseline to achieve well-defined carbon fractions.

"Among the various protocols we tested, those with a maximum temperature in He set at 650 °C, yield the lowest LAC (light absorption carbon) pre-combustion and the minimum unevolved OC remaining and therefore, the most accurate estimation of EC. … EUSAAR 2 resulted as the best compromise for the analysis of OC and EC in different types of carbonaceous aerosol mixtures encountered across regional background sites in Europe."

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

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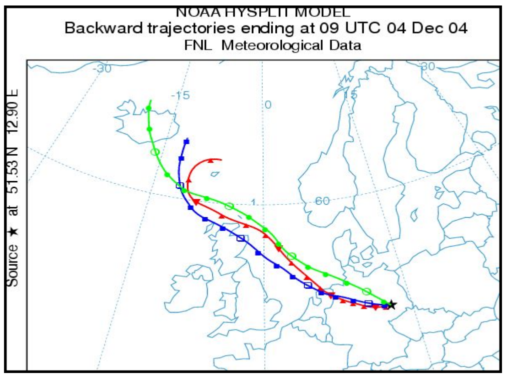
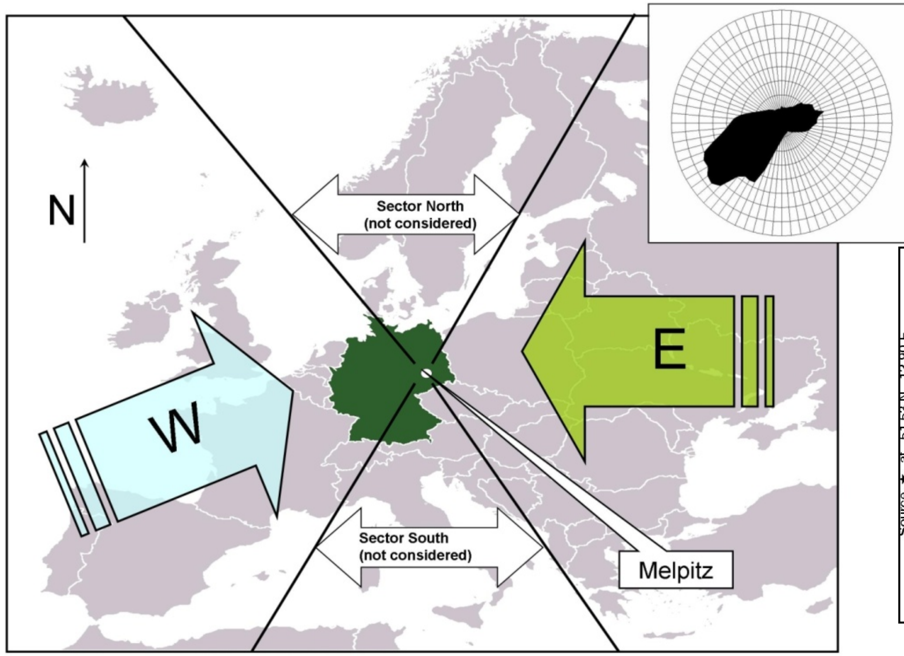
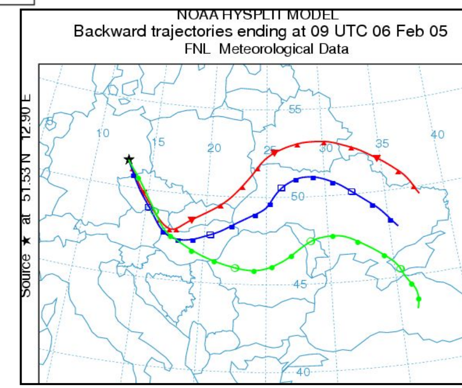
Categorization of measurement days for air mass origin

Example sector
WEST 210°-320°





Example sector
EAST 35°-140°



96-hour backward trajectories for two times(10 and 18 o'clock MEZ), for 200, 500 und 1500 m over ground were used.

source: http://www.arl.noaa.gov/ready/hysplit4.htm

Days with a strong change in transport direction, low wind velocity (more local influences) and with air mass transport from outside the two sectors were not considered.

Spindler et al.: J. Atmos.Chem (2012) 127-157 and (2013) 165-195

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