Long-term trend of EC and OC at rural Melpitz site in Germany – analysed with thermographic and thermo-optical method

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Leibniz-Gemeinschaft

TROPOS
Leibniz-Institut für Troposphärenforschung

Symposium „Soot and its climatic, environmental and health impacts“
Sino-German Science Center, 26 June to 1 July 2016, Peking University

Content

- The Melpitz site – location and filter sampling
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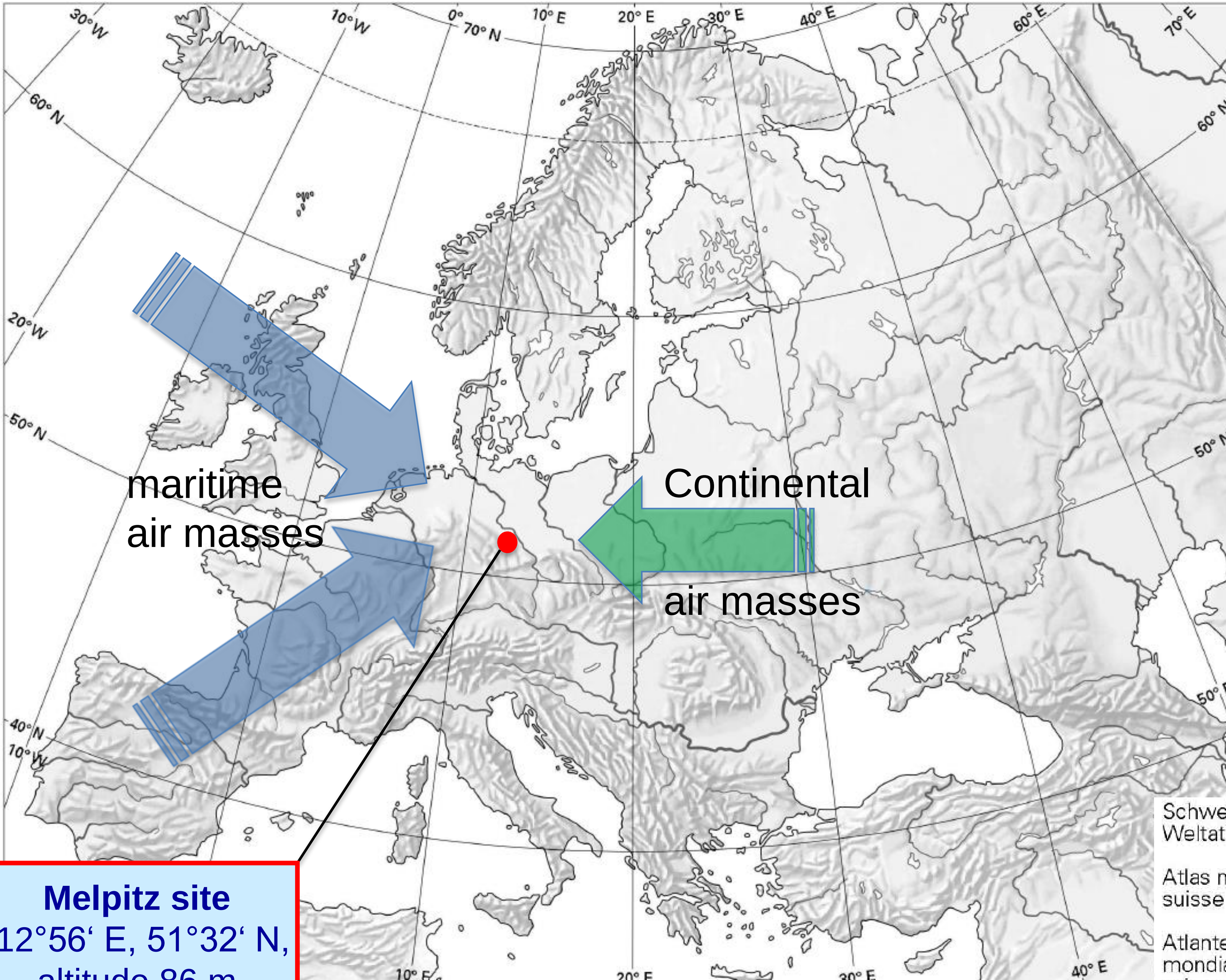
Location and integration of the TROPOS research site in Europe



Melpitz site
(12°56‘ E, 51°32‘ N,
altitude 86 m
above sea level)

Schweizer Weltatlas

Atlas mondial suisse

Atlante mondiale svizzero

© EDK

ACTRIS

REG KLAM

LANDESAMT FÜR UMWELT, LANDWIRTSCHAFT UND GEOLOGIE | Freistaat SACHSEN

Umwelt Bundesamt

German
Ultrafine
Aerosol
Network
(GUAN)

MARGA

emep

Europa fördert Sachsen.

EFRE
Europäischer Fonds für regionale Entwicklung

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PM High Volume (HV) Samplers, Quartz-filters

Sierra Andersen
Sammler 1000 l/min^{-1}

Digitel DHA-80
Sammler 500 l/min^{-1}

PM_{10} 11/1992-12/2002

PM_{10}, $PM_{2.5}$, PM_1 01/2003-12/2015 → 8461 days

	11/1992	2002|2003	12/2015	availability
PM_{10}	daily	daily		94.2 %
$PM_{2.5}$		daily		96.4 %
PM_1		every 6th day		23.0 %

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Gravimetric mass

Weighing with micro-balances (Mettler Toledo, Switzerland).
(50±5)% relative humidity and temperature (20±1) °C (conditioning time 72 hours).

Water soluble ions

Determination by standard ion chromatography after an aqueous extraction.

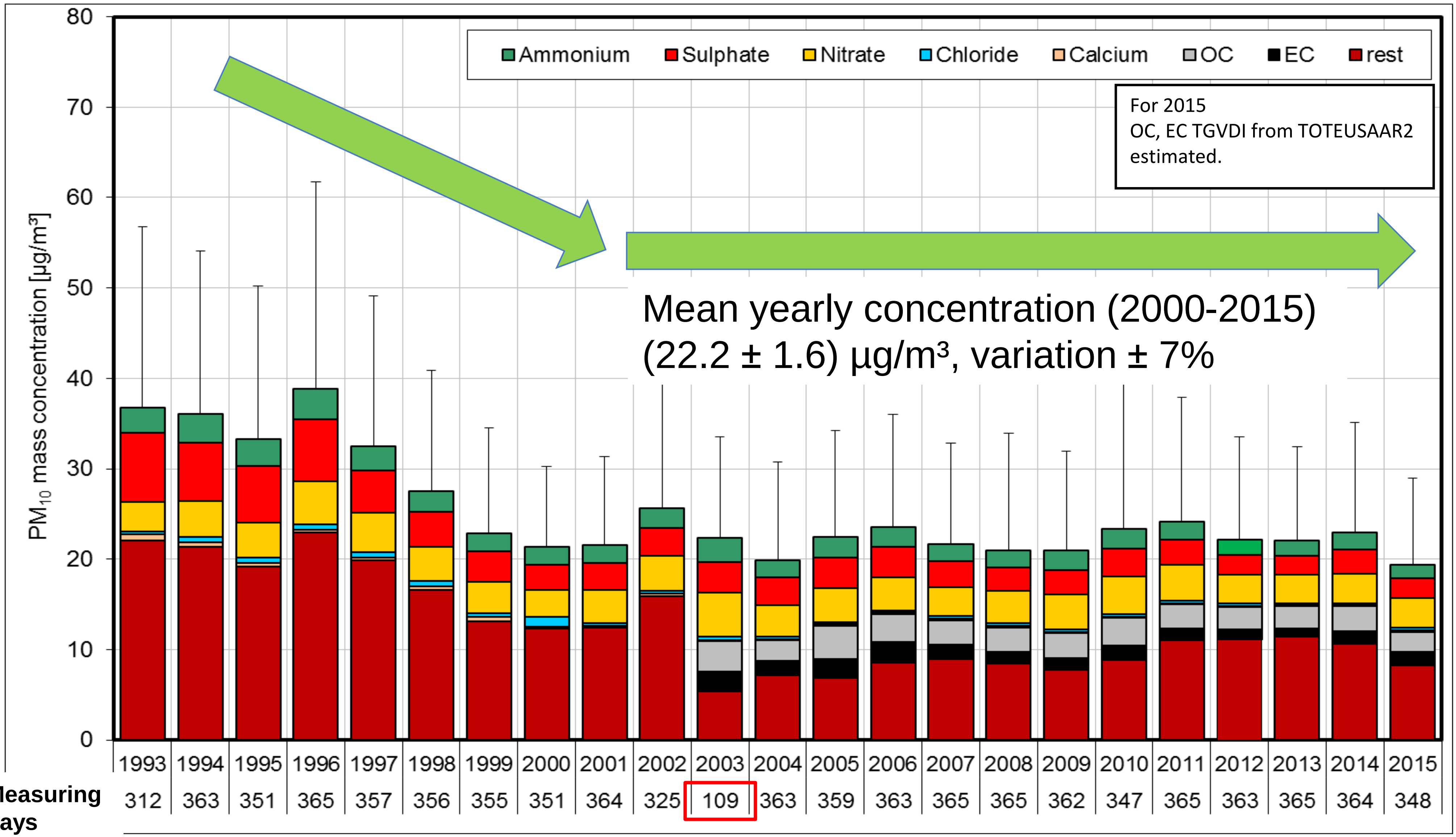
2003-2014 modified thermographic two-step-method
(VDI 2465, page 2), **TGVDI**
step: N_2-atmosphere 650 °C ⇒ organic carbon OC
step: O_2-atmosphere 650 °C ⇒ elemental carbon EC
Detection as CO_2 (IR) oxidation of C on a CuO-catalytic converter (850 °C)

Both methods for three years (2012, 13 and 149) used in parallel.

Since **2012** thermo-optical analysis, (Labanalyser Sunset Laboatory Inc., U.S.A.)
Temperature protocol EUSAAR2, Transmittance **TOTEUSAAR2**

(European Committee of Standardization (CEN) (CEN/TC 264/WG 35 prEN16909:2016)

PM_{10} concentration, content of main water soluble ions and carbon since 1993 (yearly means)



12.02.2003 until 09.10.2003 no sampling for PM10

The error bars are the positive standard deviation of daily particle mass concentration means.

HV-filter-sampler

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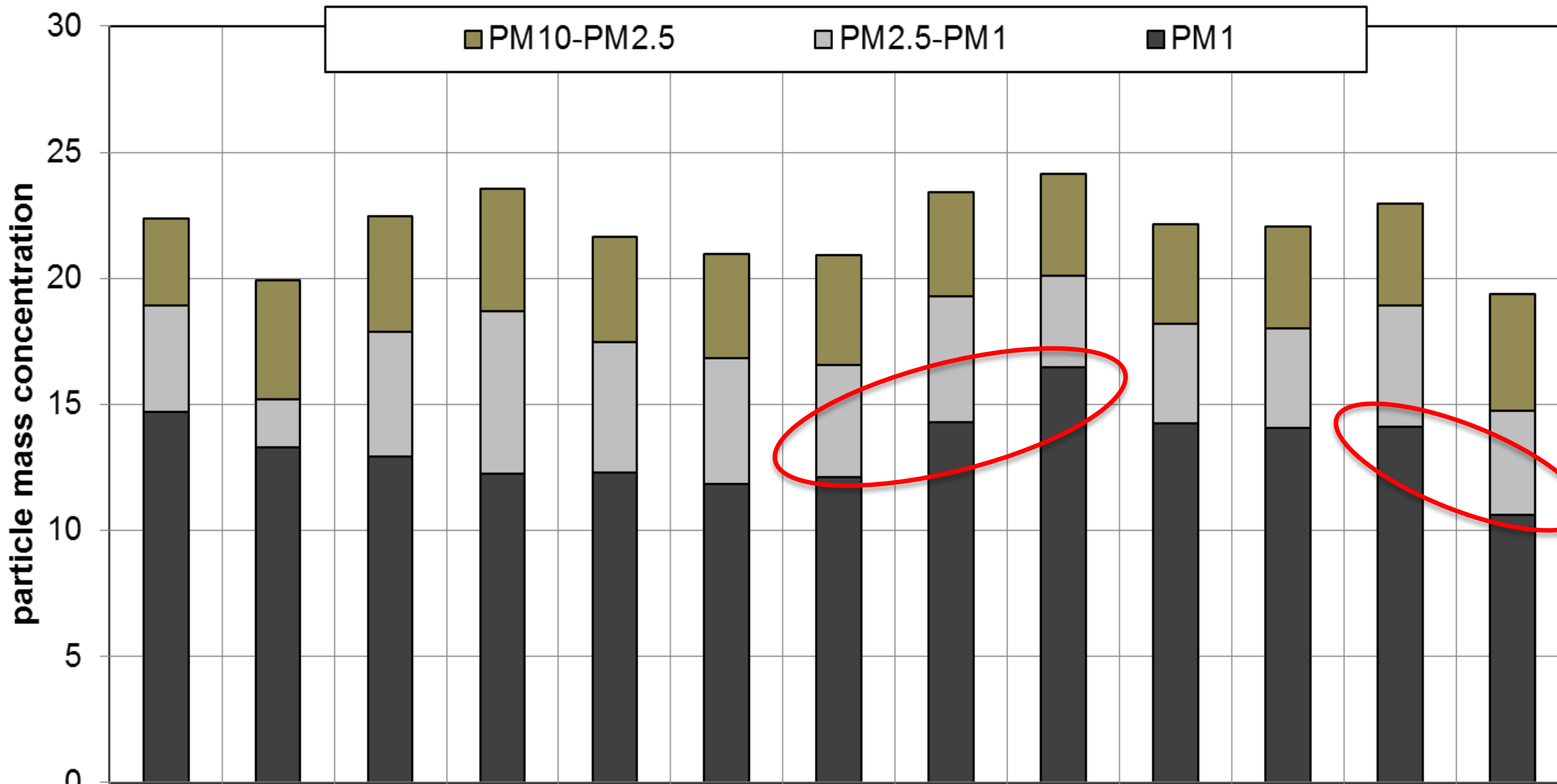
PM_{10}, $PM_{2.5}$ and PM_1 concentration 2003 - 2015 (yearly means)



	2003	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
PM_1/PM_{10}	0.66	0.67	0.58	0.52	0.57	0.56	0.58	0.61	0.68	0.64	0.64	0.61	0.55
$PM_{2.5}/PM_{10}$	0.85	0.76	0.80	0.79	0.81	0.80	0.79	0.82	0.83	0.82	0.82	0.82	0.76

HV-filter-sampler

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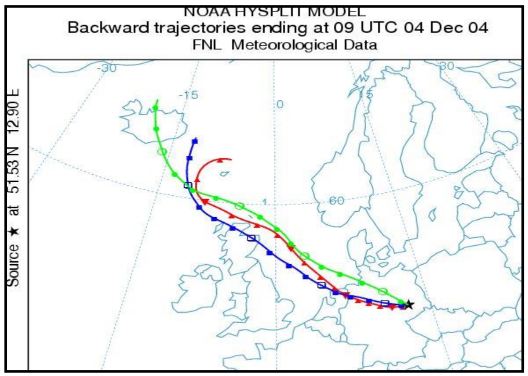
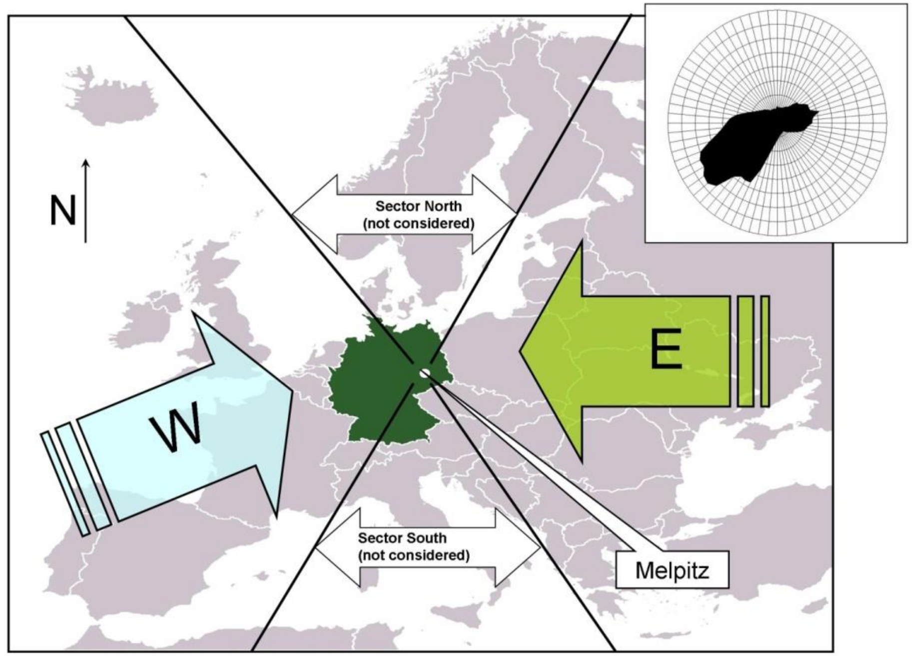
Categorization of measurement days for air mass origin and season

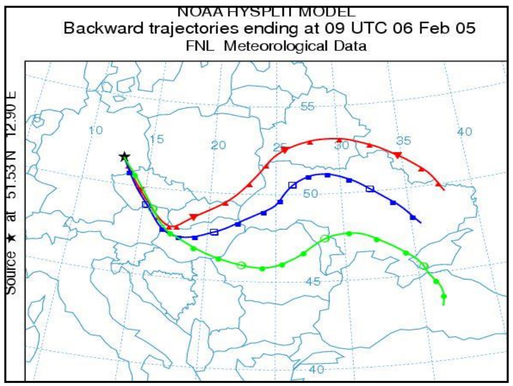
air mass origin

Example sector **W**EST
210°-320°





Example sector **E**AST
35°-140°



96-hour backward trajectories for two times (10 and 18 o‘clock CET), for 200, 500 und 1500 m over ground

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

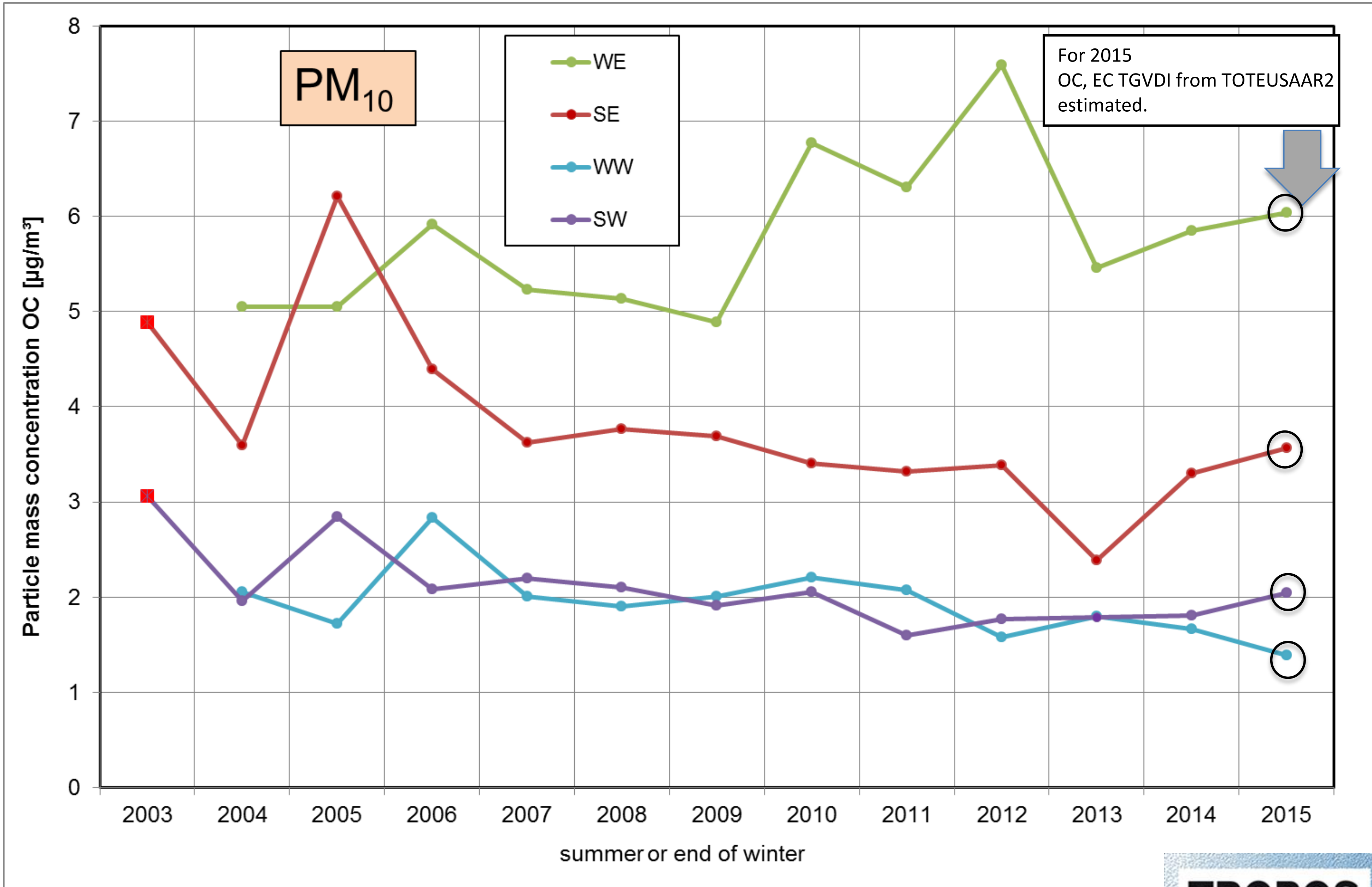
season

Winter: November – April
Summer: May - October

72.7 % of days in both categories
(11/1992 until 12/2015)

WW	WE
SW	SE
56.7%	16.0%

OC mass concentration TGVDI at Melpitz site 2003 – 2015
(yearly means for air-mass inflow West or East in summer and winter)



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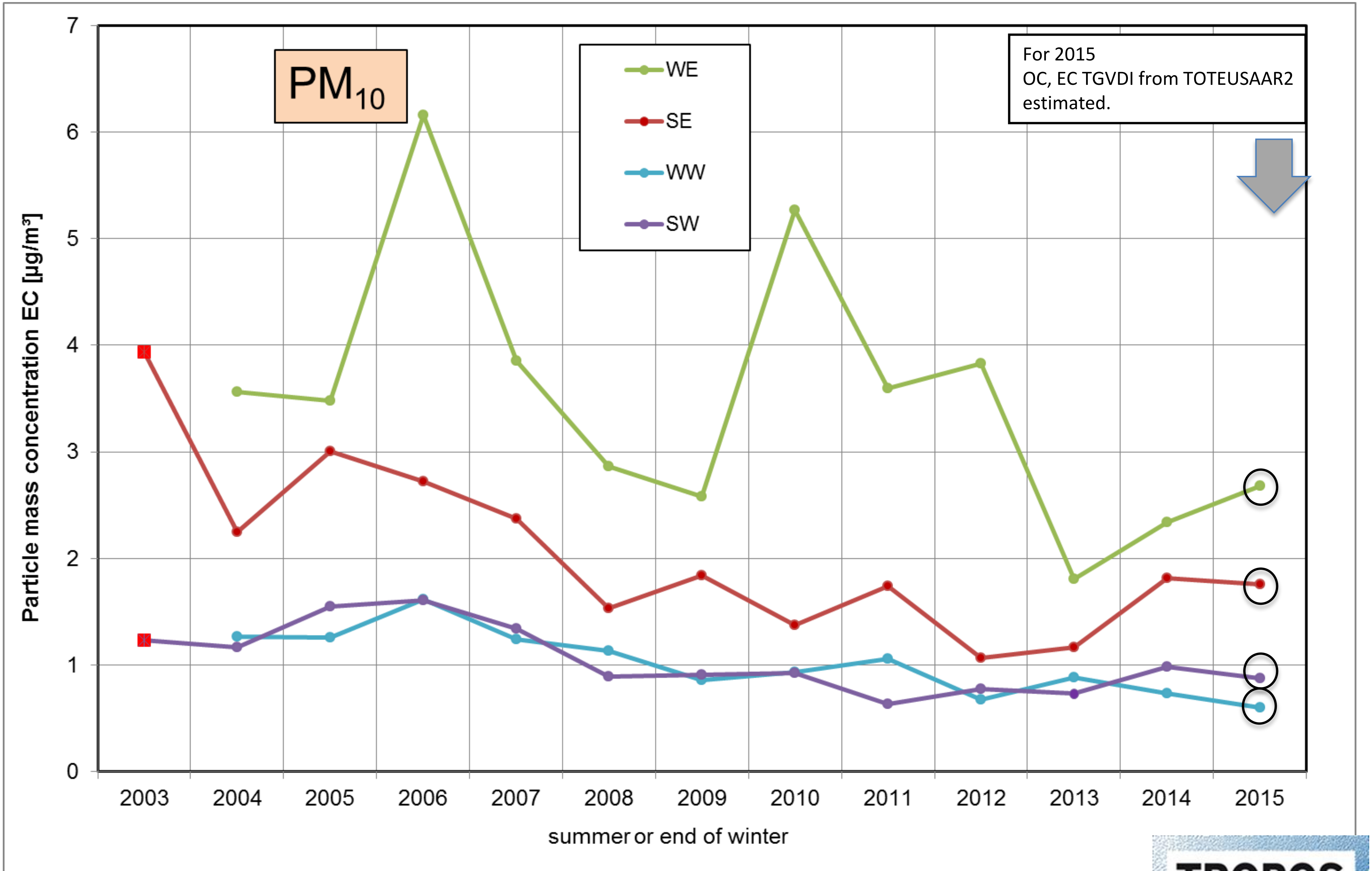
EC mass concentration TGVDI at Melpitz site 2003 – 2015

(yearly means for air-mass inflow West or East in summer and winter)



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Comparison of both methods for Melpitz site
calculation of conversion equations (orthogonal regression)

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 2014, 36 month), analyzed with both methods in parallel for OC, EC and TC.

thermographic Method
(VDI, modification of VDI 2465, part 2) **TGVDI**
and **thermo-optical Method,** Temperature protocol EUSAAR2
Transmittance (T) and Reflectance (R), **TOx EUSAAR2.**

x ≙ Transmittance, T or Reflectance, R

$$[OC; EC; TC]_{TGVDI} = m_x \times [OC; EC; TC]_{TOx\ EUSAAR2} + n_x$$

TOTEUSAAR2 is now recommended by CEN for $PM_{2.5}$ for rural sites in EUROPE

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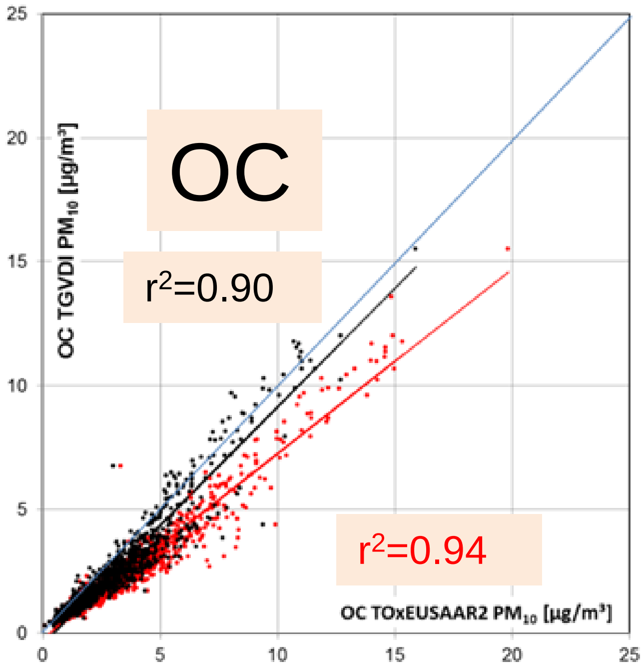
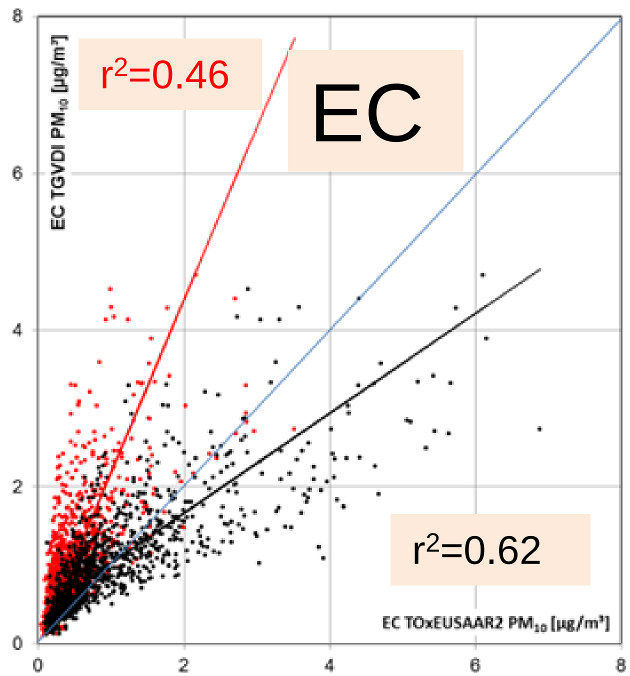
Scatterplots for determination of conversion equation (orthogonal regression)

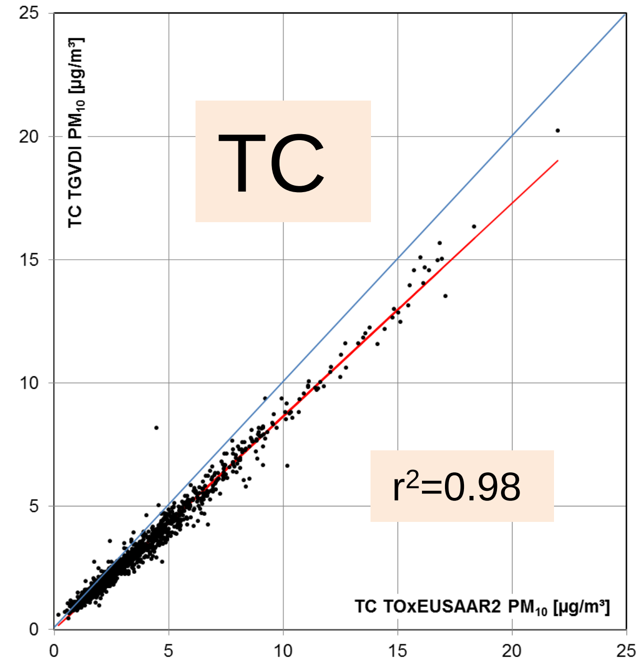
Overview for example PM_{10} (reflectance and transmittance), all days



TOR y=0.958x-0.428 n=1072
TOT y=0.746x-0.206 n=1072



TOR y=0.637x+0.394 n=1072
TOT y=2.204x-0.016 n=1072



TOx y=0.864+0.008 n=1072

The calculations show no reasonable differences for the particle size. Differences for m_x, was mainly found between summer and winter and between air-mass inflow West and East. Therefore monthly means for m_x were calculated for all sizes at all days in the three years.

14 days with more as 5 µg/m³ EC in PM_{10} (TGVDI) were cancelled.

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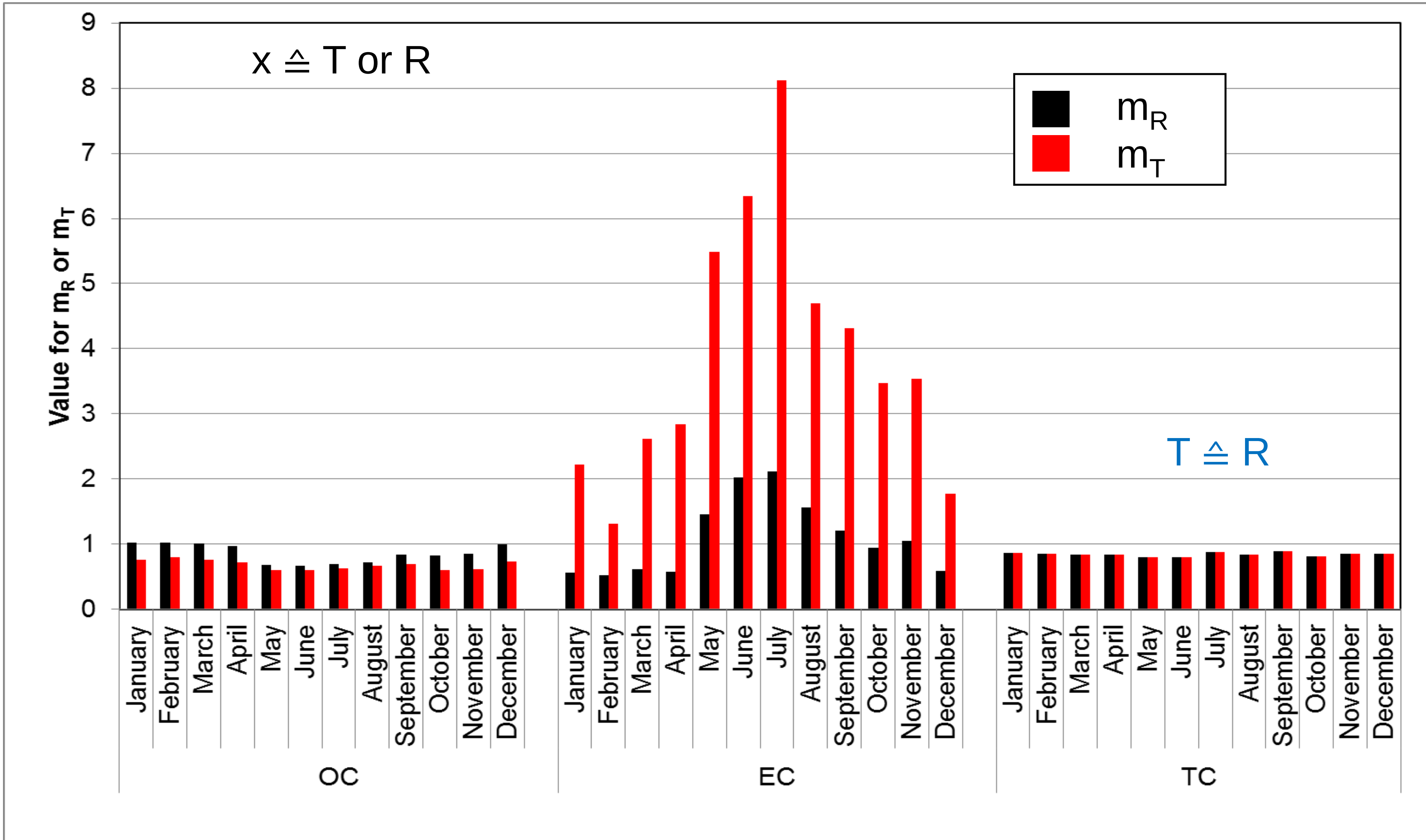
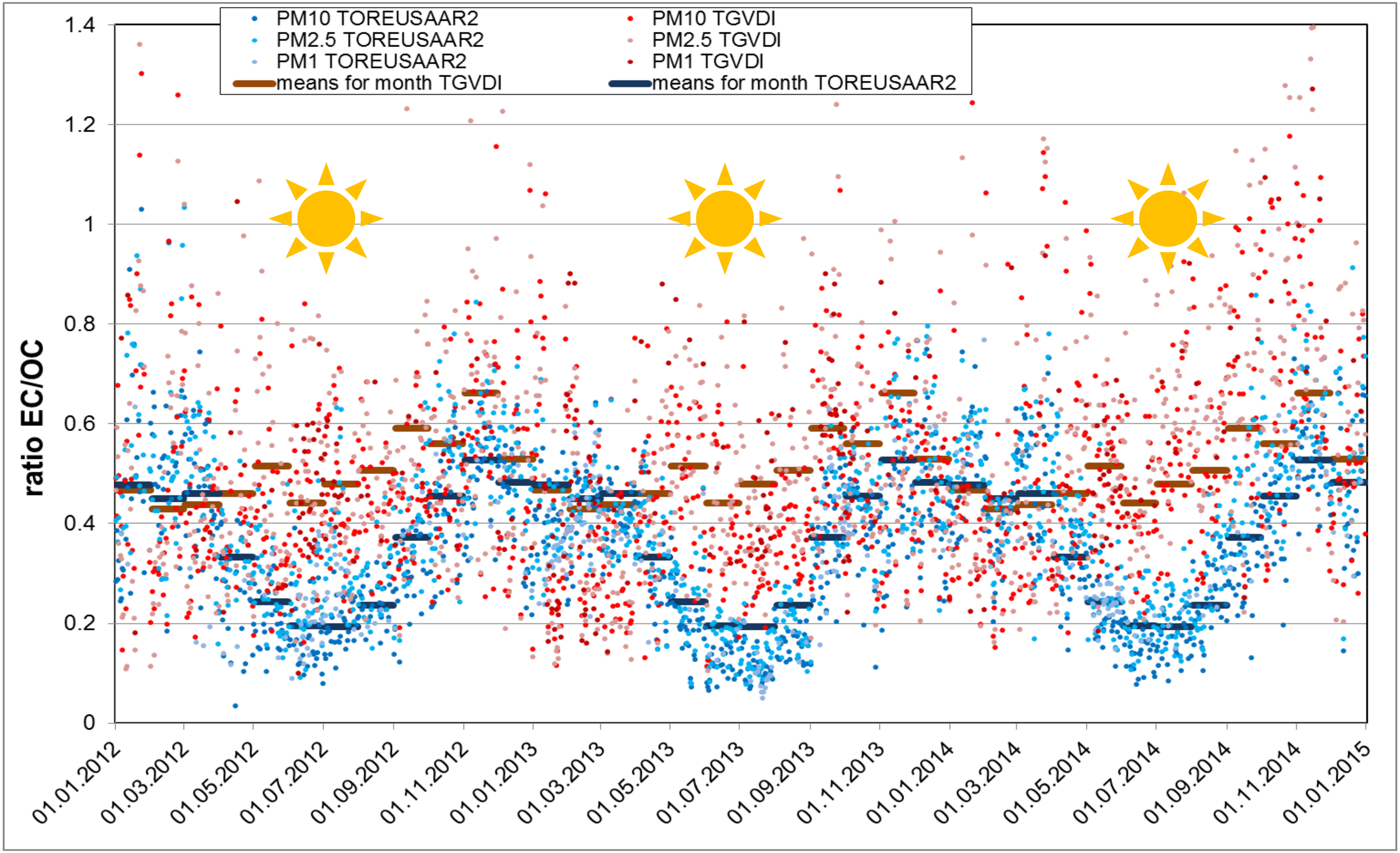
Results for all sizes (graphical overview m_x) for the twelve month

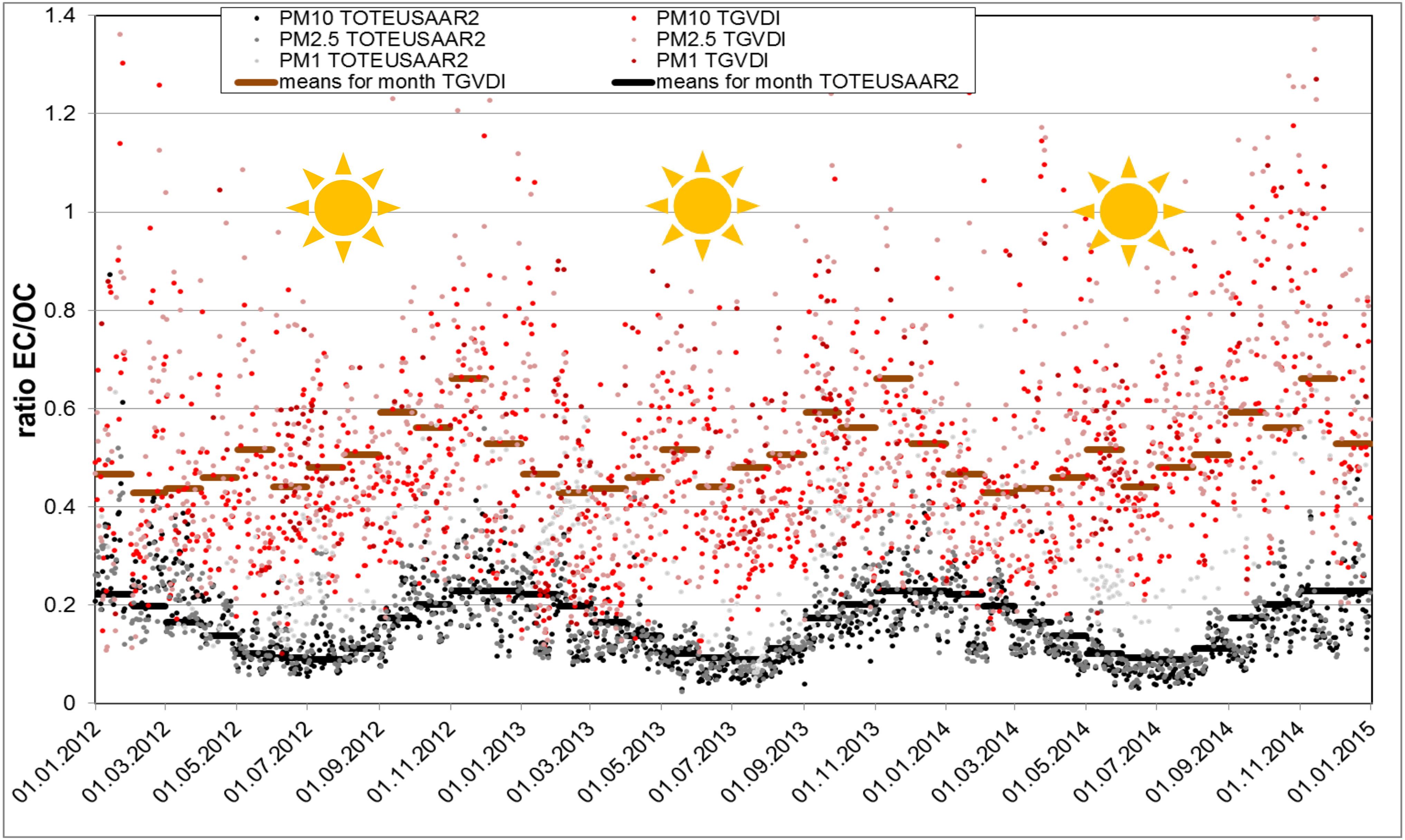
$$[OC; EC; TC]_{TGVDI} = m_x \times [OC; EC; TC]_{TOx\ EUSAAR2} + n_x$$



Daily ratios of EC/OC in 2012, 2013 and 2014 for PM_{10}, $PM_{2.5}$ and PM_1
Method TGVDI and TOREUSAAR2

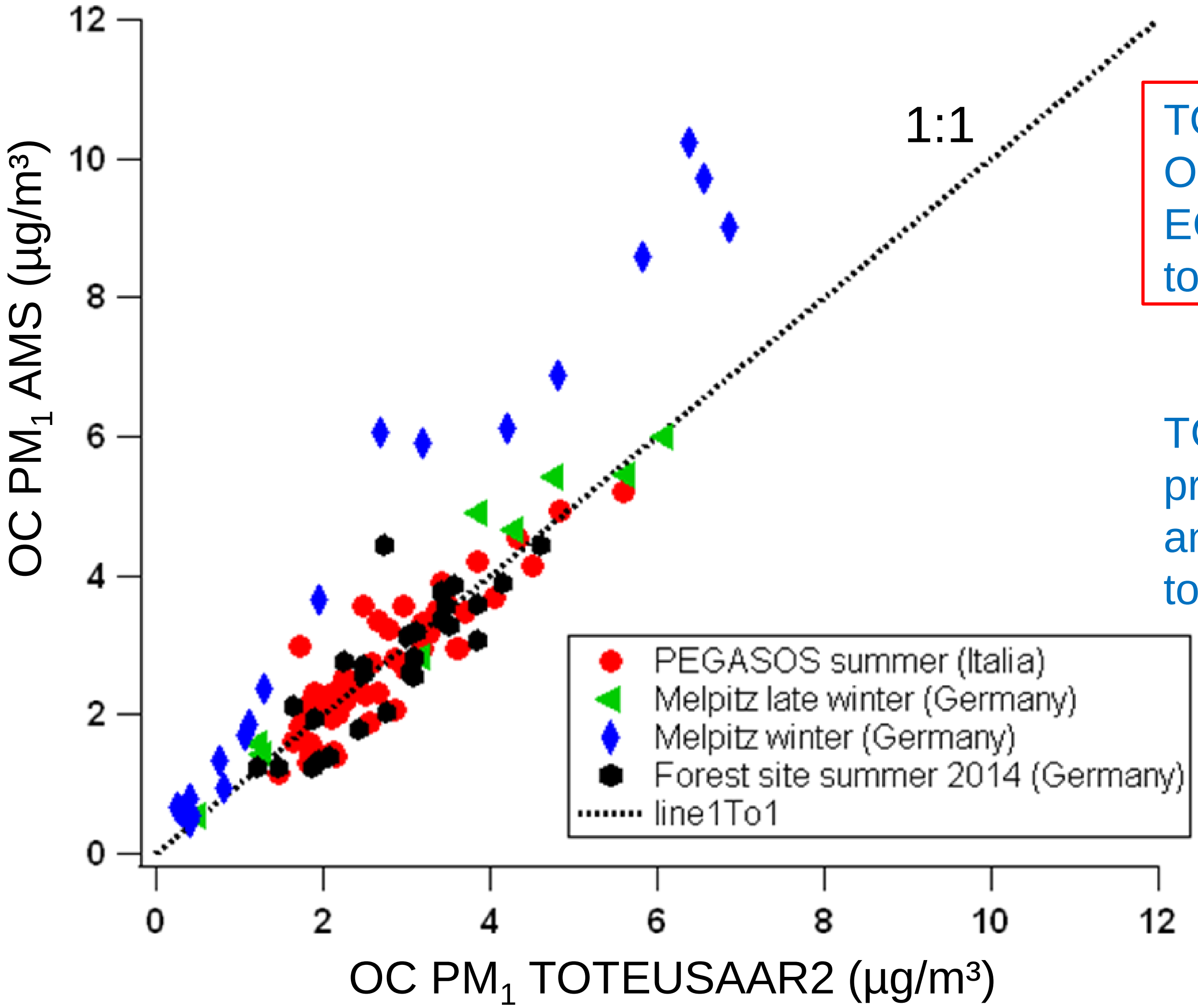


Daily ratios of EC/OC in 2012, 2013 and 2014 for PM_{10}, $PM_{2.5}$ and PM_1
Method TGVDI and TOTEUSAAR2



OC PM1 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 (Canagaratna et al. 2015).



TOTEUSAAR2 provides the highest OC concentrations and a lower EC/OC ratio compared to TOREUSAAR2.

TGVDI without charring correction provides the lowest OC concentrations and the highest EC/OC ratio compared to TOxEUSAAR2.

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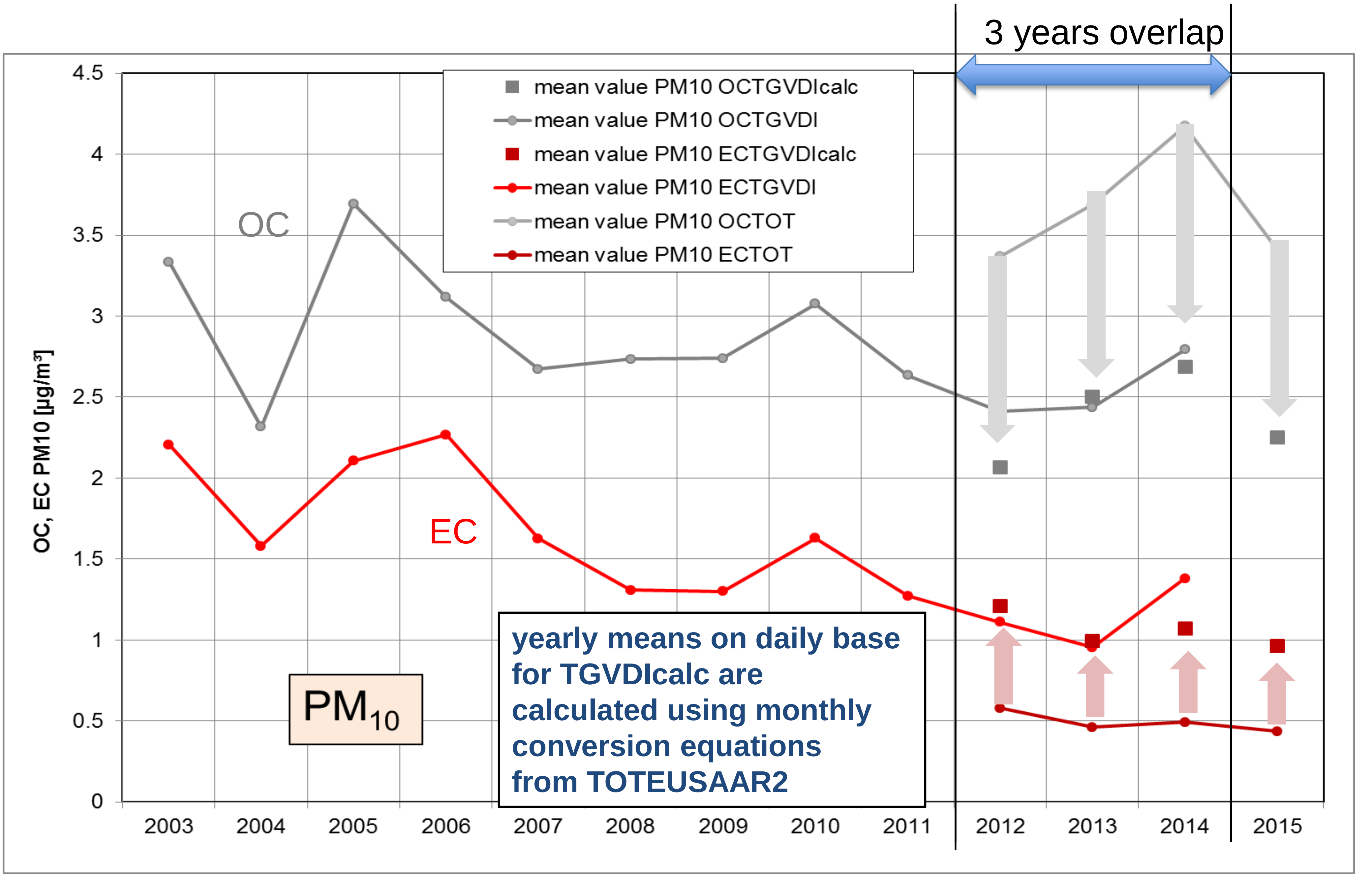
OC and EC in PM_{10}, yearly means TGVDI and TOTEUSAAR2



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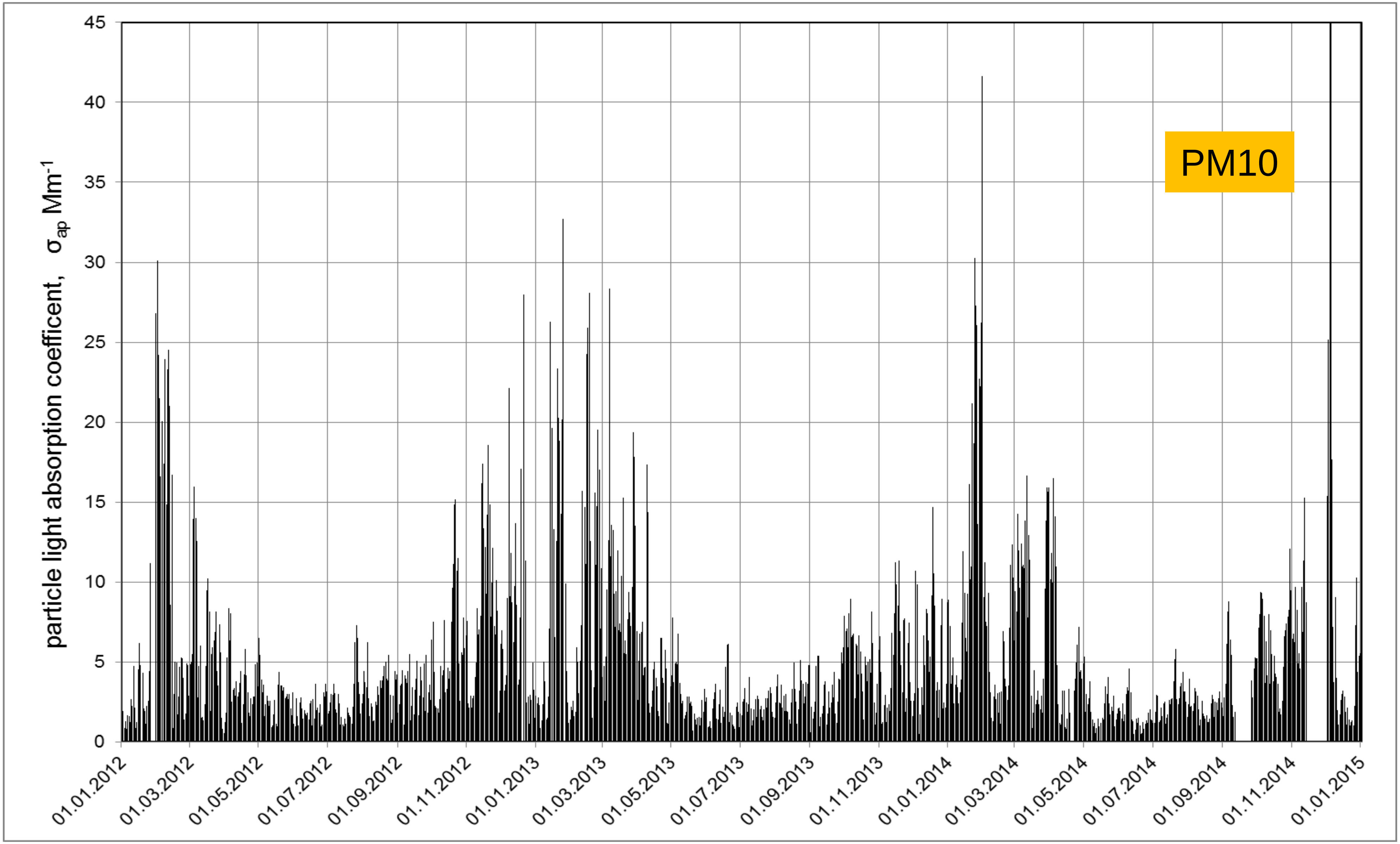
Measured particle light absorption coefficient σ_{ap}, MAAP (637 nm), PM_{10} Melpitz 2012, 2013 and 2014 (daily means)



$$\sigma_{ap} = \alpha_{C[TGVDI;\ TOxEUSAAAR2]} \times [BC], [EC]_{TGVDI;TOxEUSAAR2}$$

Calculation of different mass absorption cross sections α_C, PM_{10} mean for 2012, 13 and 14

constant mass absorption cross section

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

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

Nordmann et al. 2013,
J. Geophys. Res. Atmos. 118, 12075-12085

mass absorption cross section from correlation σ_{ap} with measured $EC_{TGVD,\ TOxEUSAAR2}$ (whole time)

[BC] ≙ $[EC]_{TGVDI}$

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

$\alpha_{C\ TGVDI} = 6.64\ m^2g^{-1}$ $r^2 = 0.55$ n = 1036

[BC] ≙ $[EC]_{TOxEUSAAR2}$

$\sigma_{ap} = \alpha_{C\ TOxEUSAAR2}$ x $[EC]_{TOxEUSAAR2}$

$\alpha_{C\ TOREUSAAR2} = 5.13\ m^2g^{-1}$ $r^2 = 0.94$ n = 1036

$\alpha_{C\ TOTEUSAAR2} = 12.12\ m^2g^{-1}$ $r^2 = 0.81$ n = 1036

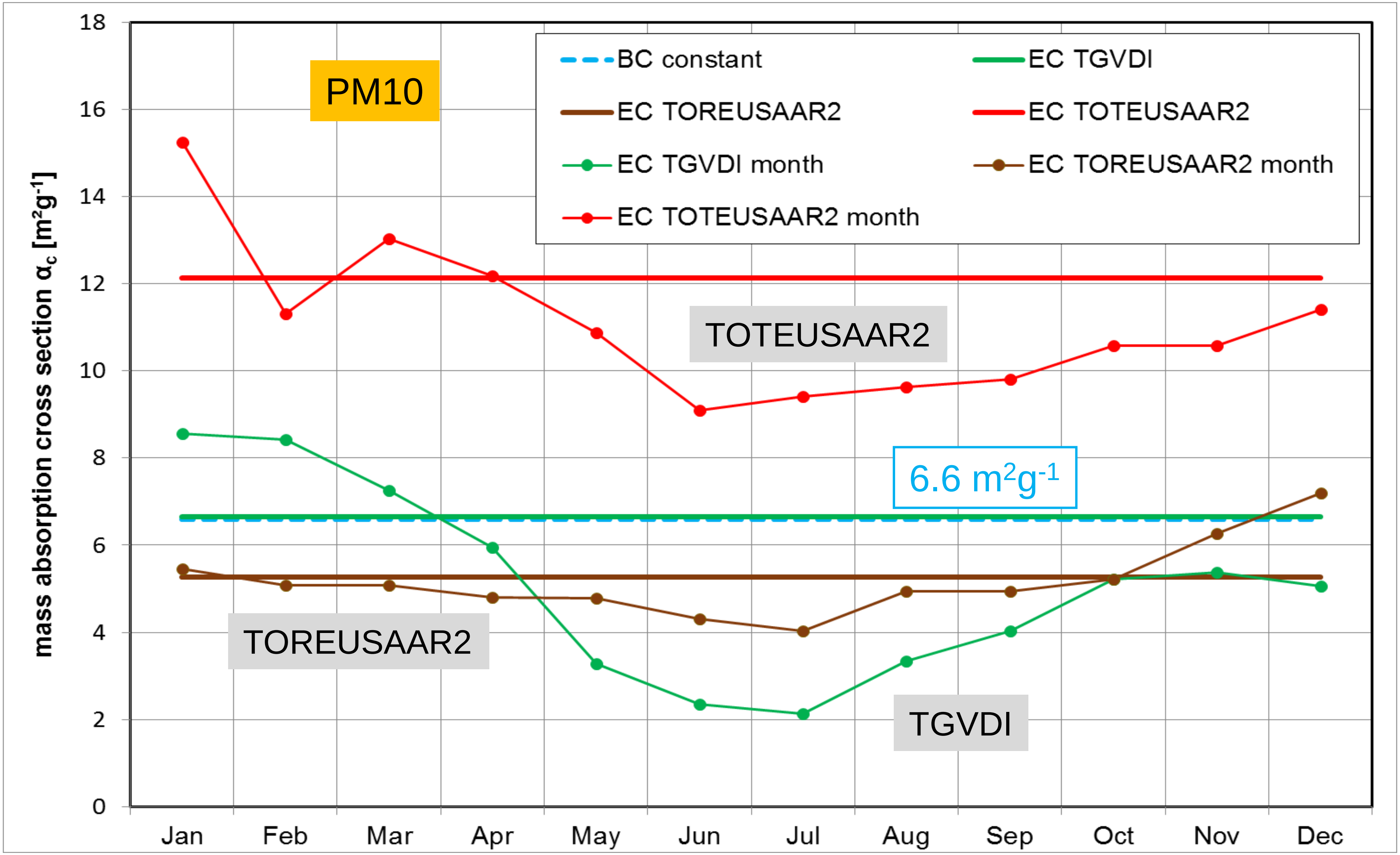
x ≙ T or R

mass absorption cross section from correlation σ_{ap} with measured $EC_{TGVD,\ TOxEUSAAR2}$

(separate calculated for all days of the twelve month in three years)

Different mass absorption cross sections, α_C

mean for 2012, 13 and 14



$$\sigma_{ap} = \alpha_{C[TGVDI;\ TOxEUSAAAR2]} \times [BC], [EC]_{TGVDI;TOxEUSAAR2} \qquad x \triangleq T \text{ or } R$$

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Summary

The particle mass concentration PM_{10} decreases since 1993 and remains constant over the last 16 years around 22.2 µg/m³ (± 7%).

The highest OC and EC concentration were found for WE.
EC shows generally a decreasing trend, also for westerly air-mass inflow.

Conversion equations could be derived for Melpitz site between thermographic and thermo-optical method. The slopes depend not on particle size (range PM_{10} to PM_1).

A comparison with AMS give hints for more realistic OC measurements using transmittance.

A comparison on daily base (PM_{10}, 2012 – 2014) between particle light absorption coefficient (σ_{ap}) and different chemical thermographic and thermo-optical EC measurement methods allows to calculate mass absorption cross sections: α_C(TGVDI) = 6.64 m^2g^{-1},
α_C(TOREUSAAR2) = 5.13 m^2g^{-1} and
α_C(TOTEUSAAR2) = 12.12 m^2g^{-1}, respectively.

The monthly derived mass absorption cross sections are lower in summer and higher in winter.

Some suggestions for future joint activities

Comparison of trends for OC and EC measured in China and Germany.

Exchange of experiences in using the thermo-optical devise for chemical determination of OC and EC on quartz filters.

Exchange of filters for method-intercomparison -
Linkage to the inter laboratory comparisons for TC and EC measurements among ACTRIS[1)] partners and EMEP[2)] laboratories in EUROPE (thermo-optical method, temperature protocol EUSSAR2, transmission).

Calculation of MAC-values from optical BC measurements and chemical EC measurements in parallel (with different methods) for China and Germany

---

1) Aerosols, Clouds, and Trace gases Research InfraStrukture Network
2) Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

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Thank you for attention!

Steam lokomotives of the Harz Mountain Light Railway
(Saxony-Anhalt, Germany), 23th January 2016

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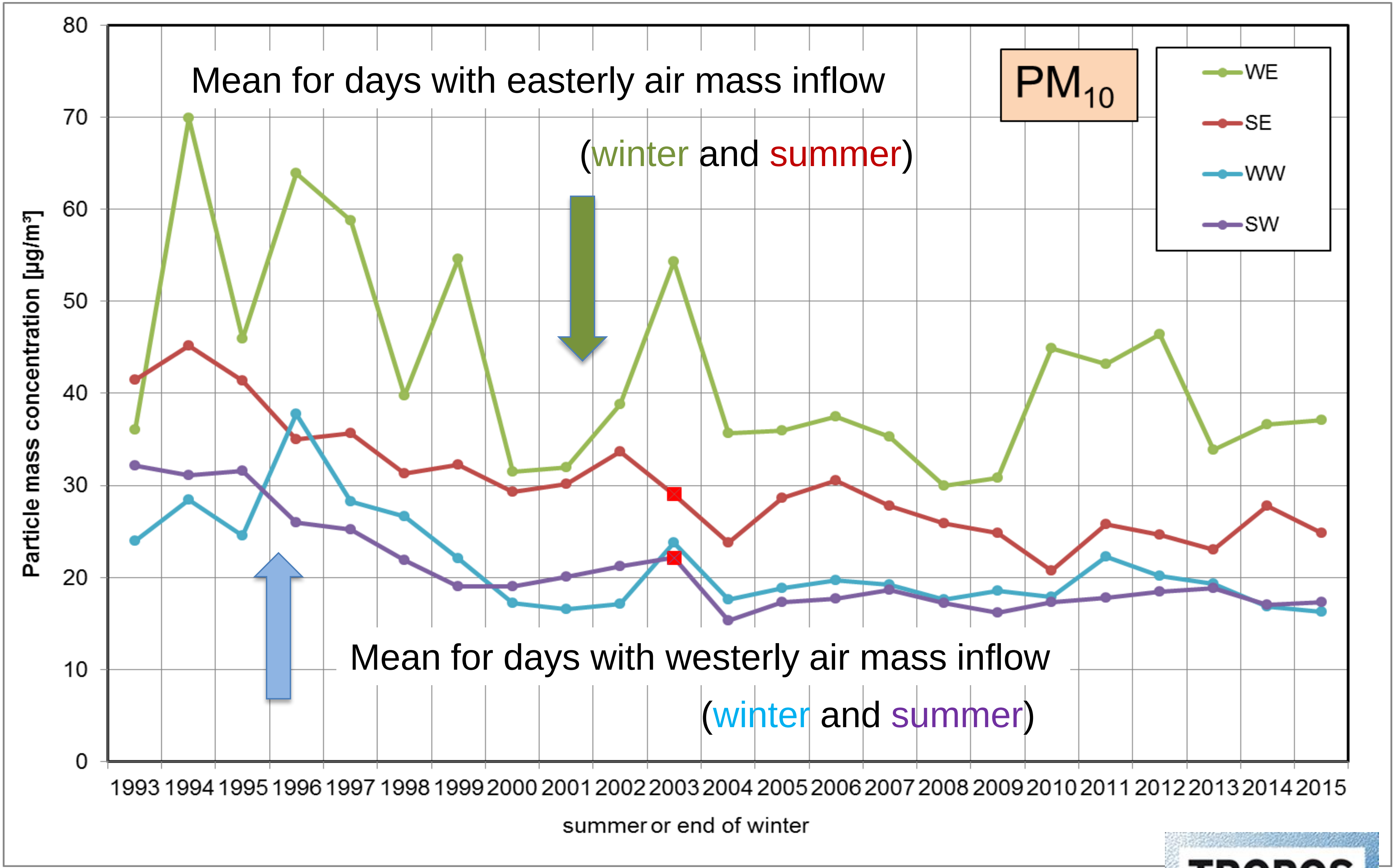
For discussion

PM$_{10}$ mass concentration at Melpitz site 1993 - 2015



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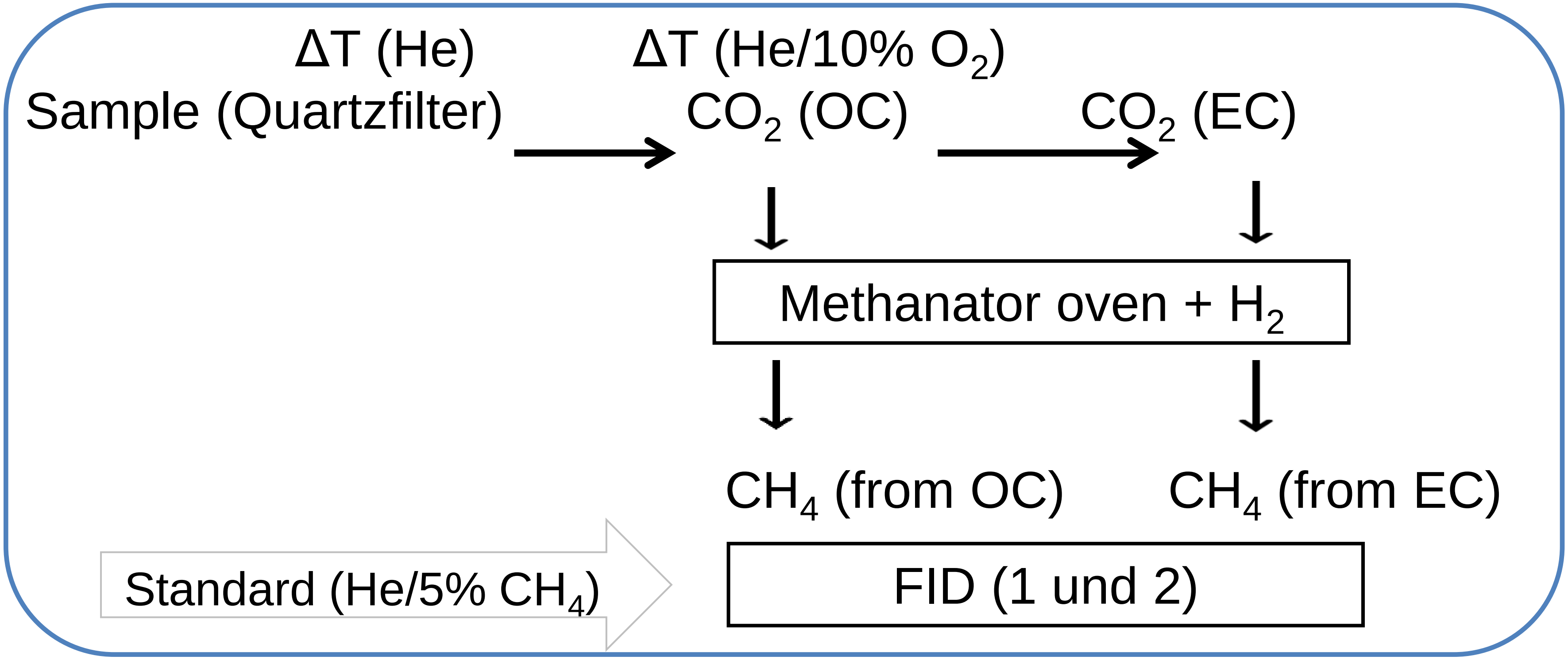
Reasons to introduce thermo-optical method with harmonized temperature protocol in EUROPE

- Harmonizing of OC/EC detection on quartz-filters.
- Using of a harmonized temperature program (EUSAAR2) for filter samples in European networks (ACTRIS, ACTRIS2, EMEP and other).
  Optical correction for charring processes using a laser (678 nm, 5 mW).
  Different correction value for „pyrolytic carbon" - transmittance or reflectance of the sample. Transmittance is recommended now.



Main Reasons for Variations of the Quantity of OC and EC

Variation based mainly:
- on the nature of sample, analysis protocols and instrumentation applied
- often TC (OC+EC) results with lower variation

Results from the thermo-optical method are influenced by:

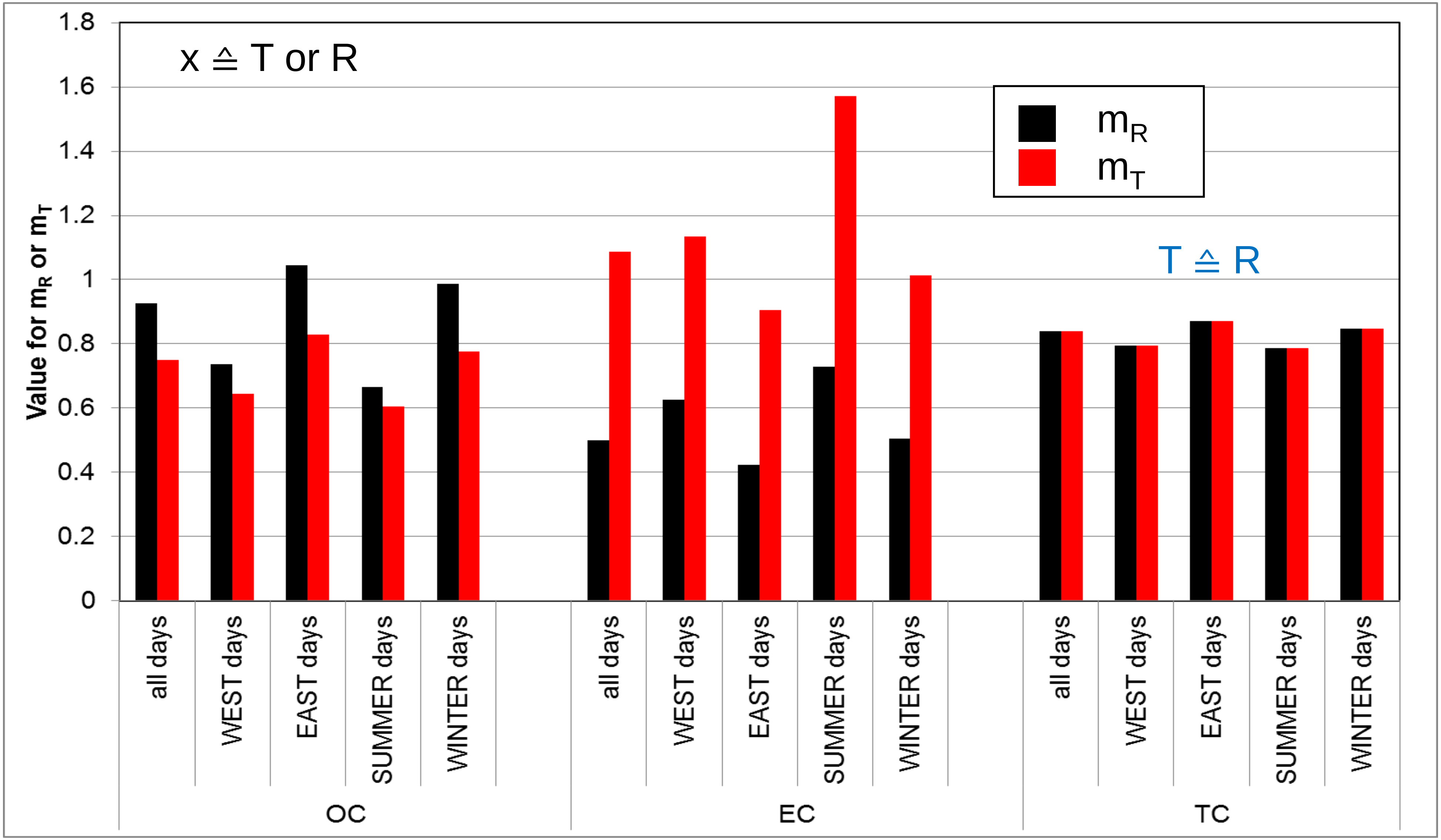
- temperature plateaus and ramps / residence time at each plateau
- charring correction by transmittance or reflectance
- optical monitoring configuration and wavelength
- combustion atmosphere / carrier gas flow
- location of temperature sensors in the quartz oven
- quantity of EC (to light or to dark sample influences reflectance or transmittance differently)

Chow, J.C. et al., Environ. Sci. Technol. 2004, *38*, 4414-4422
Bautista VII, A.T. et al., Atmospheric Pollution Research 2015, *6*, 334-342

Intercalibration measurements take place yearly (ACTRIS, ACTRIS2 and EMEP) for control of the comparability of OC and EC measurements.
The EUSAAR2 temperature protocol was mostly used in EUROPE.
Transmittance was chosen. TROPOS participate four times successfully.

Results for all sizes (graphical overview m_x) for all days, air-mass inflow direction and season

$$[OC; EC; TC]_{TGVDI} = m_x \times [OC; EC; TC]_{TOx\ EUSAAR2} + n_x$$



Thermo-optical instrument – recommended temperature program for EUROPE (ACTRIS)

	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

Since March 2015 recommended by CEN for EUROPE

∑ 17 Minutes

[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 a standardised thermal-optical protocol for measuring atmospheric organic and elemental carbon: the EUSAAR protocol. Atmos.Meas.Tech. *3*, 79-89, 2010

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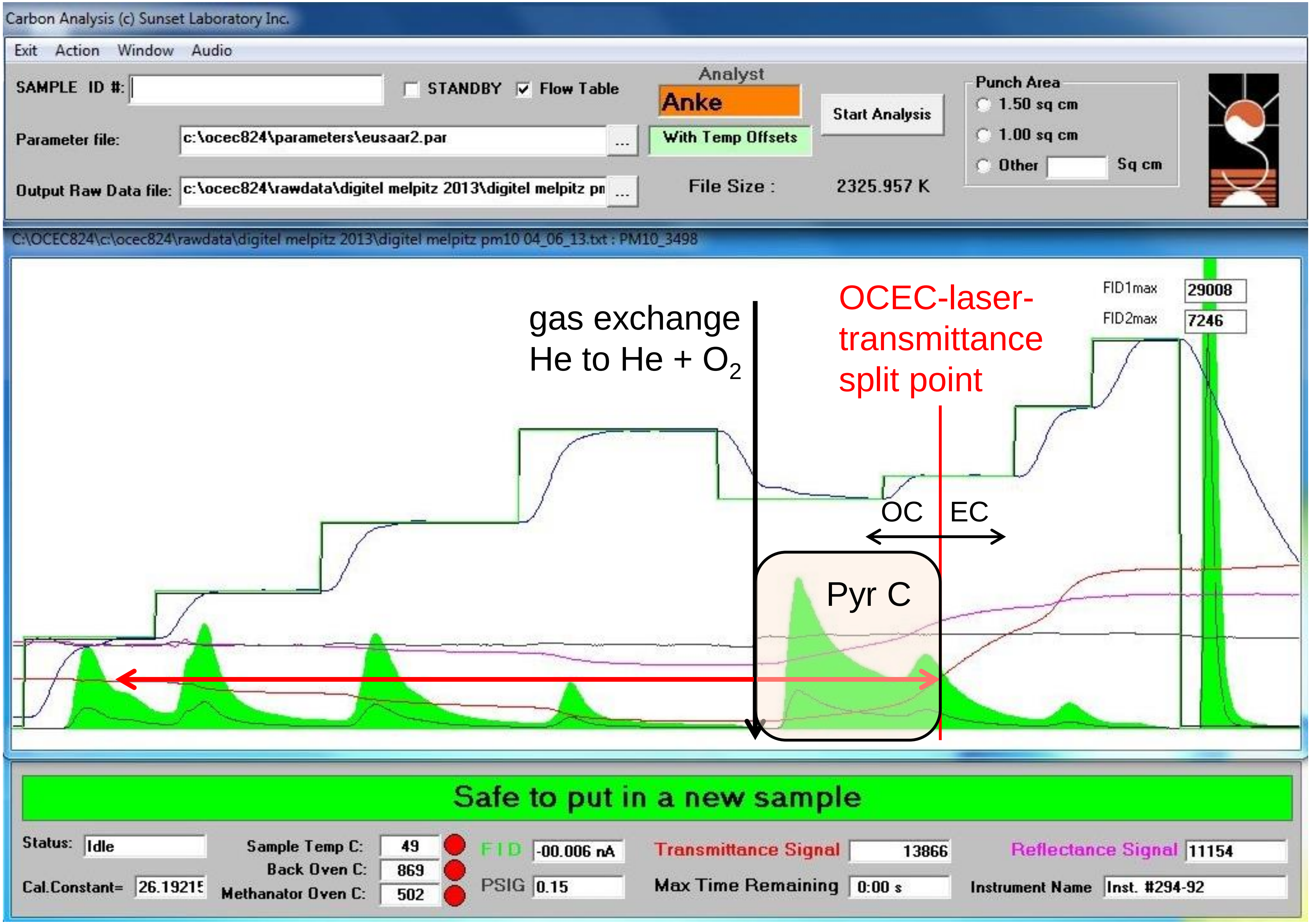
Pyrolytic carbon from thermo-optical instrument (Transmittance)



PM_{10}, 2013 and 2014, Comparison EC_VDI and (EC_EUSAAR2T+PyrCT)