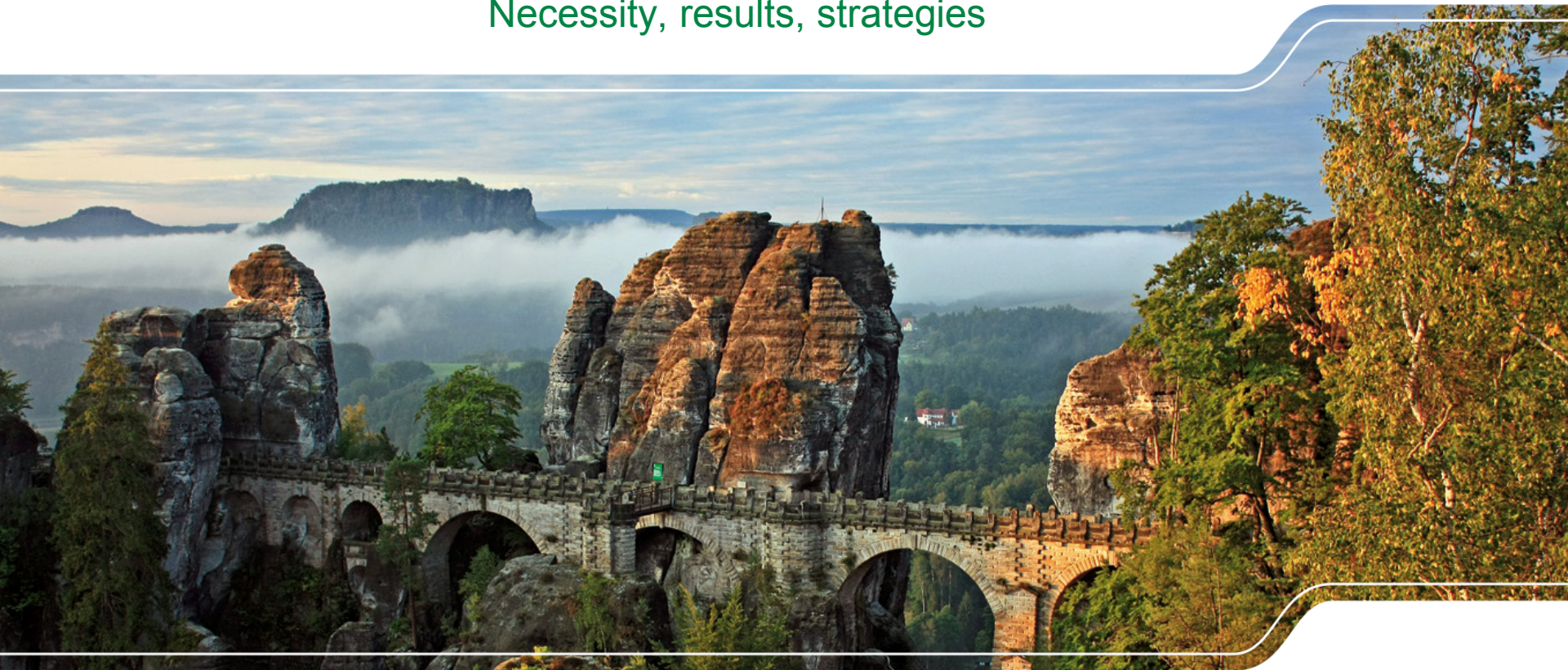


# Soot measurements in Saxon air monitoring sites with the thermal-optical method and the EUSAAR- II - Programme

## Necessity, results, strategies



# Overview

- **1. Measurement methods**
- **2. Legal regulations**
- **3. Measurement history Saxon air monitoring network**
- **4. Procedures of other departments for monitoring air quality in Germany**
- **5. The problem of quality assurance**
- **6. The approach of the Saxon air monitoring network**
- **7. Some results from limited data**
- **8. Work that remains to be done**

# 1.Measurement methods

## ■ *Discontinuously*

VDI 2465 Blatt 1.; removal of the organic carbon by solvent desorption with toluene / isopropanol , combustion of the remaining elemental carbon in oxygen at 650 ° C , coulometric measurement of the carbon dioxide produced by combustion . Result of elemental carbon (soot ) . Combustion of a non-extracted sample filter provides under the same conditions the amount of total carbon . For total carbon shall apply :

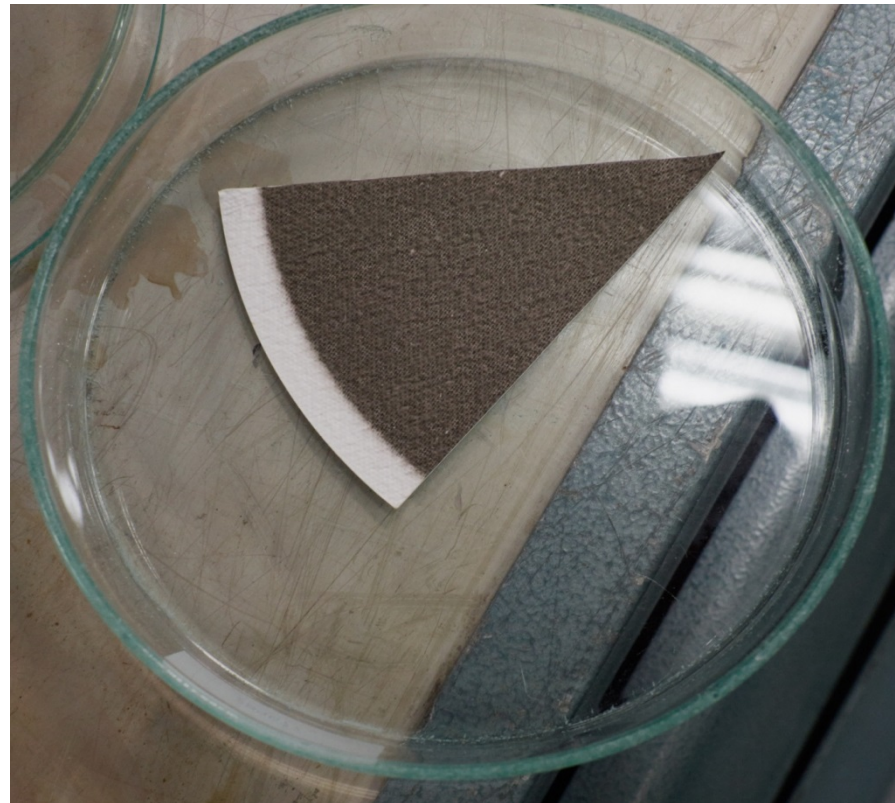
■  $TC = EC + OC.$

■ Method is described in 23. BImSchV

# 1.Measurement methods



# 1.Measurement methods



# 1.Measurement methods

## I VDI → 2465 Blatt 2 Thermography

Ramp step	1	2	3	4	5	6	7	8
Temperature	80	350	620	620	400	300	700	80
Hold time	0,2 min	1,2 min	1,2 min	0,6 min	0,3 min	0,5 min	0,9 min	Ende
Process gas	He					He / O <sub>2</sub>		
Process name	Thermodesorption OC					Combustion EC		

The carbon dioxide formed during the combustion is measured by NDIR.

# 1.Measurement methods

- I *continuous (only BC):*
- I Aethalometer : measuring the light absorption of the deposited suspended particulate matter on a filter belt
- I MAAP (Multi Angel Absorption Photometer): measurement of the light absorption of the deposited particulate matter PM1 or PM10 on a filter belt supported by existing filter reflectance at two different exit angles .

## 2. Legal regulations

- **23. BImSchV** from 1996-12-16, limit value for elemental carbon has been canceled in 2004. Until 2004 there was a limit value of  $10 \mu\text{g}/\text{m}^3$  at the beginning, lately  $8 \mu\text{g}/\text{m}^3$ .
- **39. BImSchV** from 25.01.2010: General formulations for PM<sub>2.5</sub> and EC / OC - measurements

### 3. Measurement history Saxon air monitoring network

- discontinuously: **EC (soot)** and **TC / EC / OC** according to VDI 2465 Bl.1 from PM10-samples deposited on a quartz fibre filter since 2010, red color = measurement has been stopped in 2010

Monitoring sites: **Zwickau**, **Chemnitz Nord**, **Chemnitz Leipziger Straße**, **Freiberg**, **Dresden Nord**, **Dresden Bergstraße**, **Dresden Winkelmannstraße**, **Görlitz**, **Leipzig Mitte**, **Leipzig Lützner Straße**, **Leipzig West**, **Borna**, **Radebeul Wahnsdorf**, **Collmburg**

- continuous: **BC** (Aethalometer with TSP from 2001 to 2008), **BC** (MAAP 5012 mit PM10) from 2008 to 2010), **BC** (MAAP with PM1 size selective inlet since 2010)

Monitoring sites: **Dresden Nord**, **Dresden Nord**, **Dresden Nord**, **Dresden Winkelmannstraße**, **Annaberg Buchholz**

## 4. Procedures of other departments for monitoring air quality in Germany

- Measurements of EC until 2004 (limit value for soot has been canceled) using filter devices according to VDI 2465 Bl. 1 or 2
- Since 2004 stop or comprehensive reduction for monitoring soot by filter devices
- Use of aethalometer / soot photometer to analyse BC, introducing of different hardware news
- Since 2008 also use of MAAP-2012 (Thermo Fisher) for monitoring BC
- Since 2012 testing of a new methode of thermography with optical detection for the volatile fraction of soot (TOT / TOR; TO = thermal optical procedure, T = transmission, R = reflection)

## 5. The problem of quality assurance

### I Standardization

- I For discontinuously estimation of EC and OC:  
VDI 2465 Blatt 1: December 1996, production of equipment has been finished 10 years ago, there is no support available  
VDI 2465 Blatt 2: Mai 1999
- I New European design for a standard method using TOT / TOR and EUSAAR II programme to ramp process temperatures and gases(CEN/TR 16243)
- I Continuous Determination of BC:
- I No standard procedure available, but some different optical methods in use

## 5. The problem of quality assurance

### I Reference materials

- I For VDI 2465 Blatt 1 and 2 and for TOT / TOR synthetic standards without reference to environmental and aerosol sampling ( oxalic acid, sugar, methane...)
- I No reference materials for continuous optical determination by light absorption available. Initial studies of the TROPOS with Printex as black carbon reference material by quantification using Raman spectroscopy has been published

### I Reference methods

- I By definition of 23. BImSchV : VDI 2465 Blatt 1 for estimating EC
- I Reference methods BC : temporary not available. (replacement)solution : Round Robin Test

## 6. The approach of the Saxon air monitoring network

- Procurement of a Sunset EC - OC - analyzer with optical mapping of the volatile fraction by a simultaneous reflection and transmission measurement path using the EUSAAR II temperature programme
- Installation of the equipment in order lab at the expense of BfUL
- Parallel measurement of samples from the monitoring network operation using VDI 2465 Blatt 1 and TOT / TOR for about 12 months
- Analysis of the data for determining a transfer function that allows an exchange of the old data in measuring value by TOT / TOR and vice versa
- Comparison of the results with the findings from other monitoring networks and TROPOS

## 6. The approach of the Saxon air monitoring network

- I Release of TOR - proceedings by the LfULG for the Saxon air monitoring network
- I No release of TOR - proceedings by the LfULG : Continuation of the VDI method is not secure

Temperature and process gas programme for TOT / TOR – method using EUSAAR II

Ramp step	1	2	3	4	5	6	7	8
Temperature	200	300	450	650	500	550	700	850
Hold time	120 s	150 s	180	180 s	120 s	120 s	70	80 s
Process gas	He				He / O <sub>2</sub>			
Process name	Thermodesorption OC					Combustion EC		

## 6. The approach of the Saxon air monitoring network



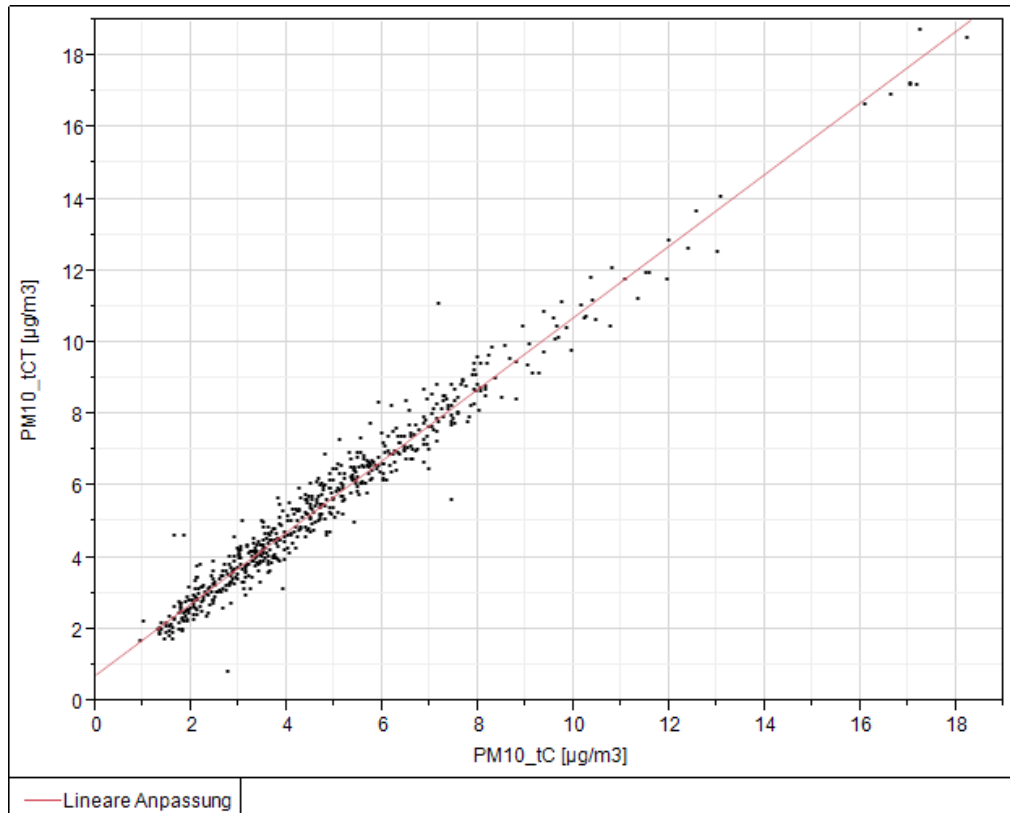
## 6. The approach of the Saxon air monitoring network



## 7. Some results from limited data

all data measured in reflection!

$$tCT = f(tC)$$



### Lineare Anpassung

$$PM10\_tCT [\mu g/m^3] = 0,7477254 + 0,9977351 * PM10\_tC [\mu g/m^3]$$

### Übersicht der Anpassung

$r^2$	0,966892
$r^2$ korrigiert	0,966837
Wurzel der mittleren quadratischen Abweichung	0,486766
Mittelwert der Zielgröße	5,631581
Beobachtungen (oder Summe Gewichte)	601

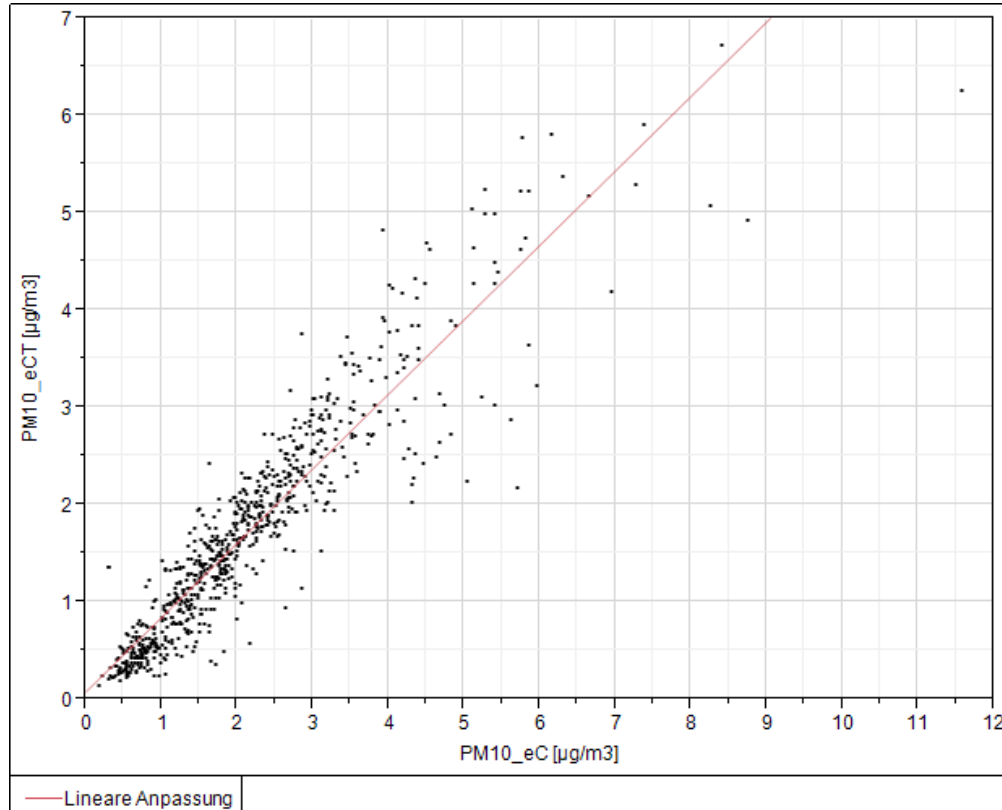
### Parameterschätzer

Term	Schätzer	Std.-Fehler	t-Wert	Wahrsch.> t
Achsenabschnitt	0,7477254	0,041925	17,83	<,0001*
PM10_tC [µg/m³]	0,9977351	0,007544	132,26	<,0001*

linear adjustment :  $tCT [\mu g/m^3] = 0,997 * tC [\mu g/m^3] + 0,748$

## 7. Some results from limited data

$$eCT = f(eC)$$



### Lineare Anpassung

$$PM10\_eCT [\mu g/m^3] = 0,0782117 + 0,7655737 * PM10\_eC [\mu g/m^3]$$

### Übersicht der Anpassung

$r^2$	0,853911
$r^2$ korrigiert	0,853716
Wurzel der mittleren quadratischen Abweichung	0,424574
Mittelwert der Zielgröße	1,720719
Beobachtungen (oder Summe Gewichte)	751

### Parameterschätzer

Term	Schätzer	Std.-Fehler	t-Wert	Wahrsch.> t
Achsenabschnitt	0,0782117	0,029262	2,67	0,0077*
PM10_eC [µg/m3]	0,7655737	0,01157	66,17	<,0001*

linear adjustment :  $eCT [\mu g/m^3] = 0,766 * eC [\mu g/m^3] + 0,078$

## 7. Some results from limited data

### I Transfer function for TC to the Saxon monitoring sites

Site name	typ	Slope	intersection	quality
Collmberg	background	1,004	0,644	0,978
Dresden-Bergstr.	hot spot	0,964	1,054	0,963
Dresden-Nord	urban	1,026	0,751	0,939
Dresden-Winckelmannstr.	Background	0,987	0,743	0,963
Leipzig West	Background	0,969	0,779	0,950
Leipzig-Lützner Str.	hot spot	0,974	0,871	0,962
Leipzig-Mitte	urban	0,984	0,741	0,951
Radebeul-Wahnsdorf	background	0,999	0,865	0,967

## 7. Some results from limited data

### I Transfer function for EC to the Saxon monitoring sites

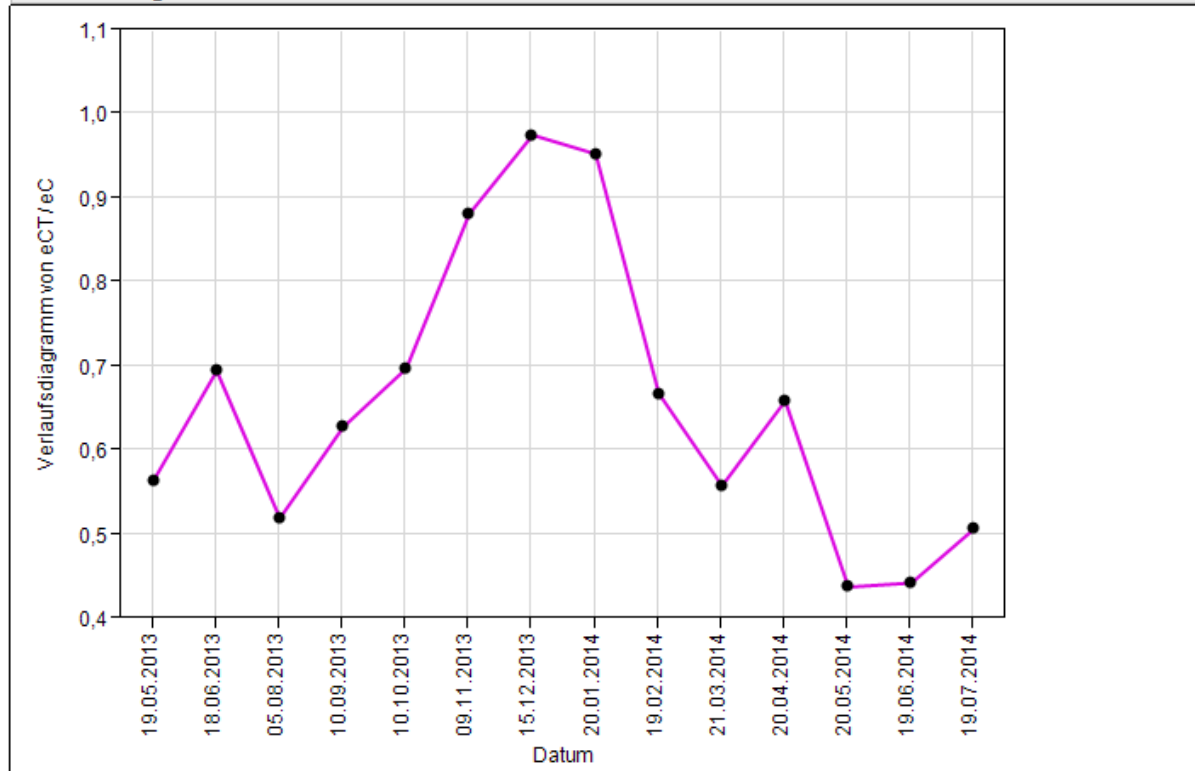
Site name	typ	Slope	intersection	quality
Chemnitz Leipziger Str.	hot spot	0,709	0,323	0,842
Collnberg	background	0,732	-0,081	0,868
Dresden-Bergstr.	hot spot	0,719	0,488	0,697
Dresden-Nord	urban	0,695	0,372	0,712
Dresden-Winkelmanstr.	background	0,661	0,155	0,849
Görlitz	urban	0,572	0,589	0,841
Leipzig West	background	0,784	-0,165	0,894
Leipzig-Lützner Str.	hot spot	0,715	0,176	0,716
Leipzig-Mitte	urban	0,747	0,262	0,840
Radebeul-Wahnsdorf	background	0,819	-0,046	0,838

## 7. Some results from limited data

Monthly average for the ratio TOR / VDI eC - Examples

Verlaufdiagramm Station=Collm

Verlaufdiagramm von eCT / eC

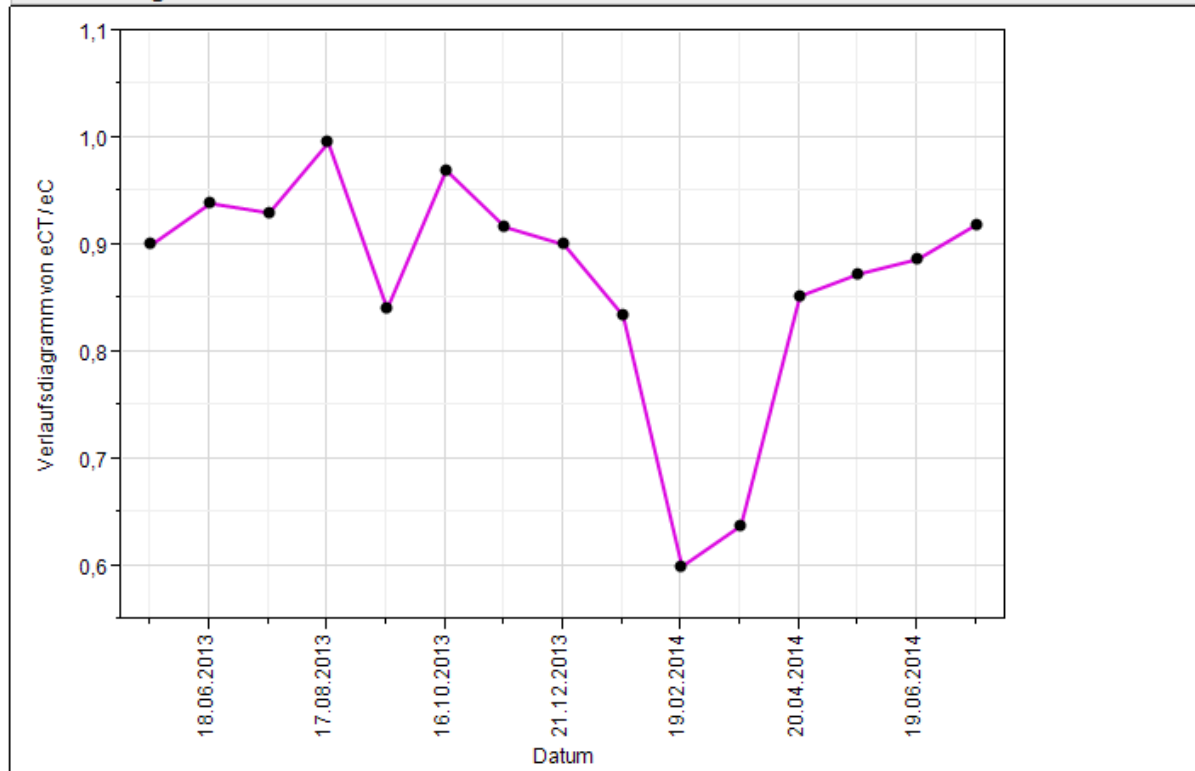


## 7. Some results from limited data

Monthly average for the ratio TOR / VDI eC - Examples

Verlaufdiagramm Station=DD-Bergstraße

Verlaufdiagramm von eCT / eC

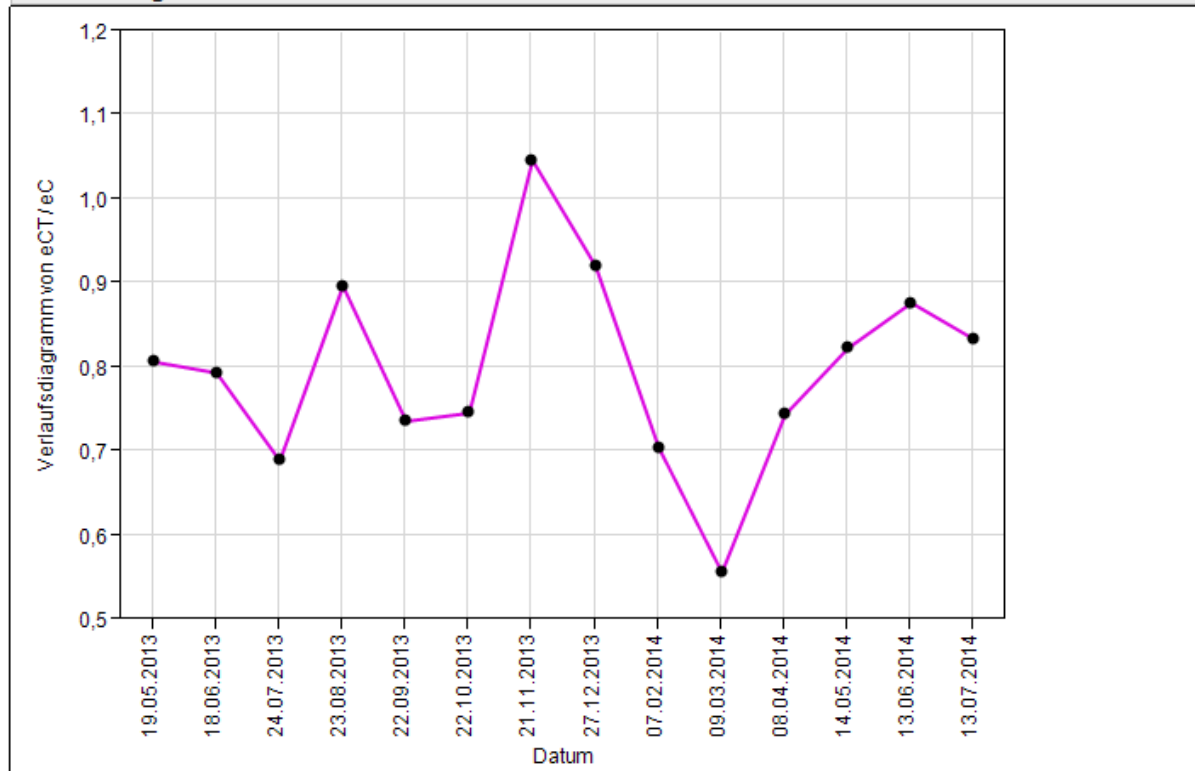


## 7. Some results from limited data

Monthly average for the ratio TOR / VDI eC - Examples

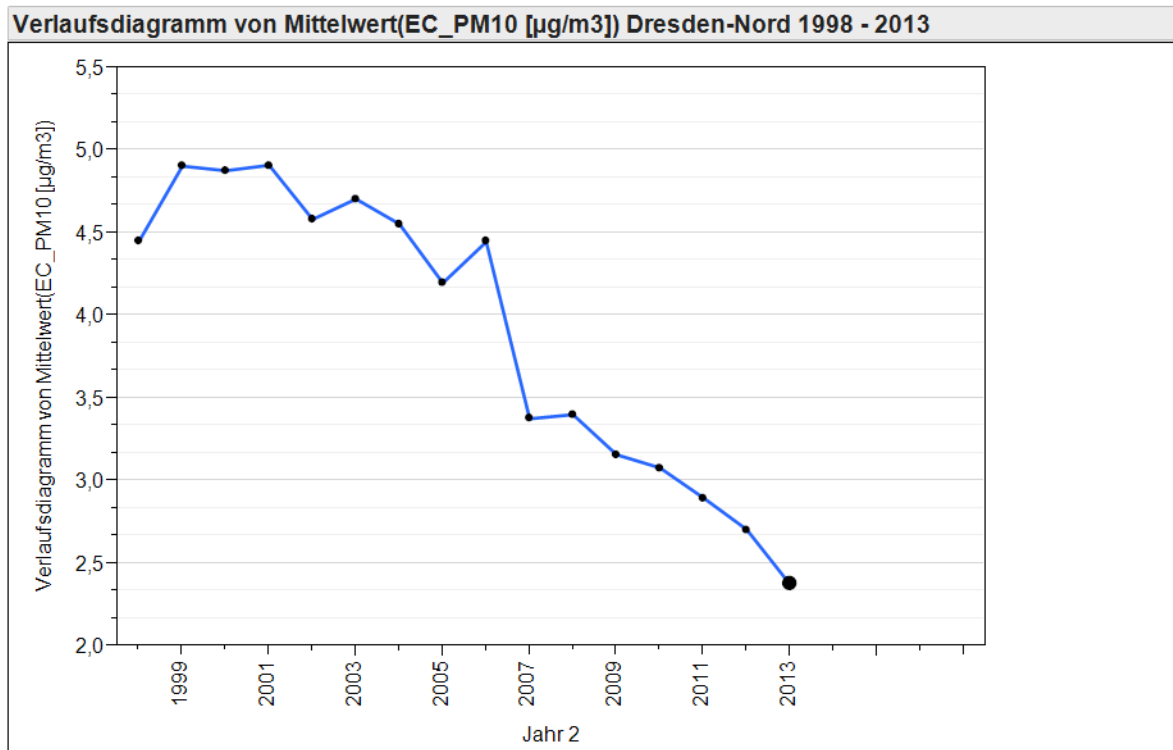
Verlaufdiagramm Station=Leipzig L.

Verlaufdiagramm von eCT / eC



## 8. Work that remains to be done

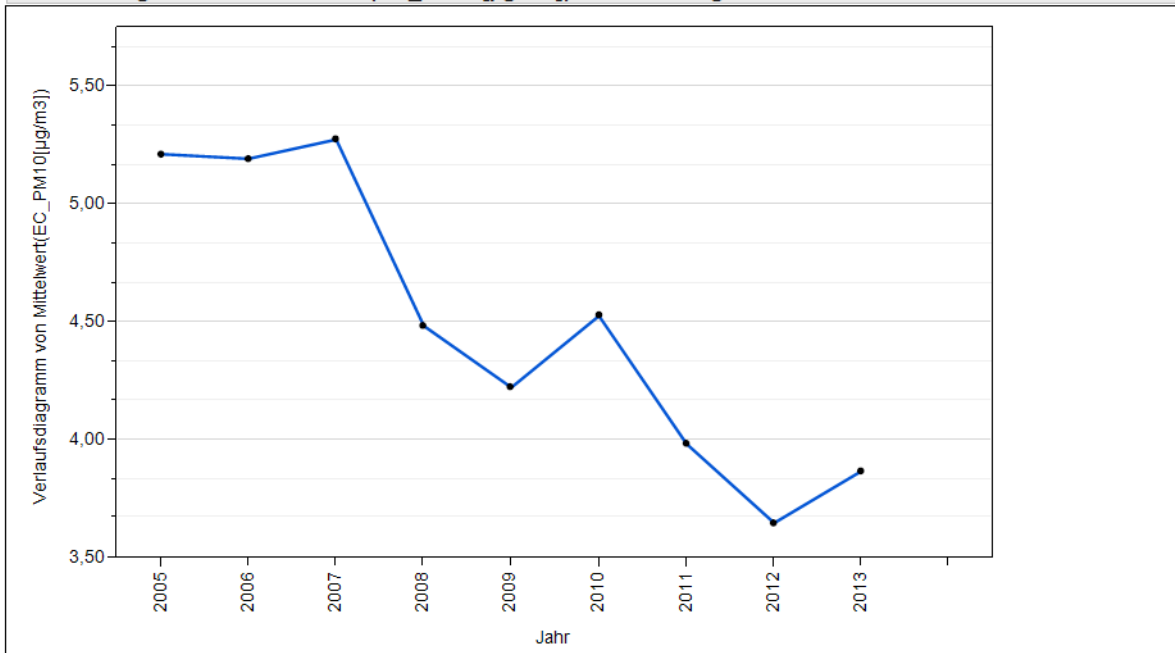
- I Development of air quality situation in relevant Saxon monitoring sites
- I Dresden Nord:



## 8. Work that remains to be done

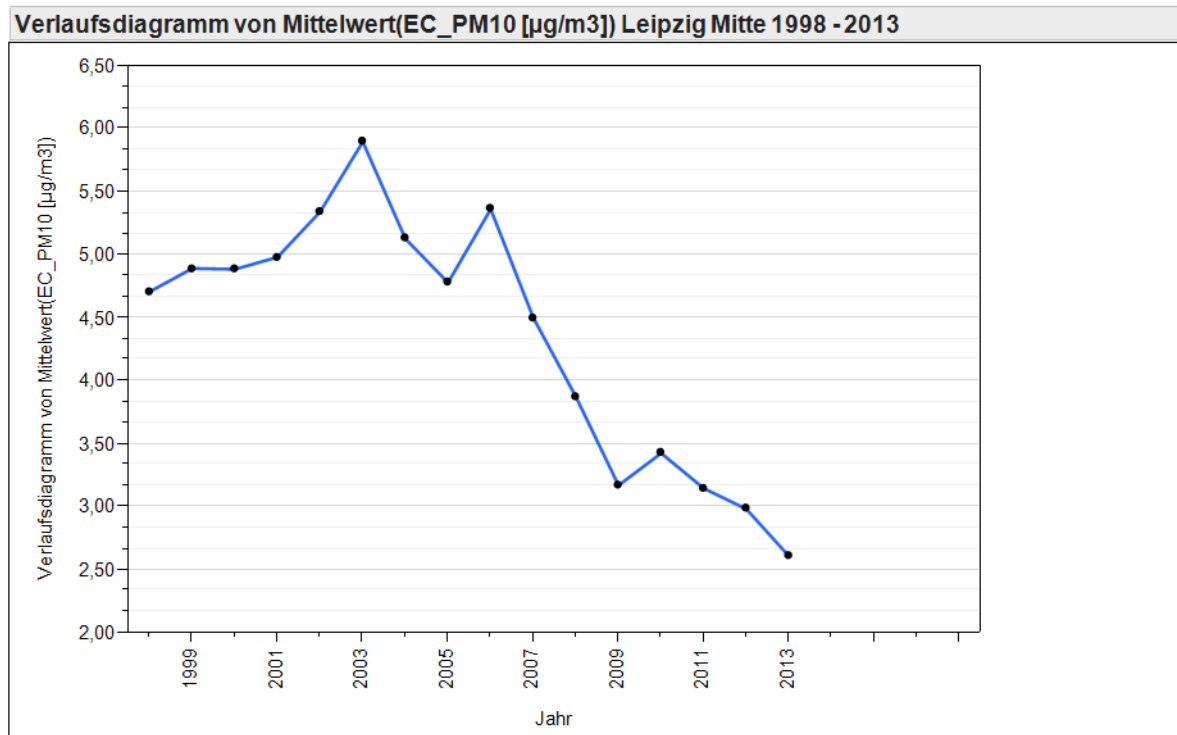
- I Development of air quality situation in relevant Saxon monitoring sites
- I Dresden Bergstraße:

Verlaufdiagramm von Mittelwert(EC\_PM10[ $\mu\text{g}/\text{m}^3$ ]) Dresden Bergstraße 2005 - 2013



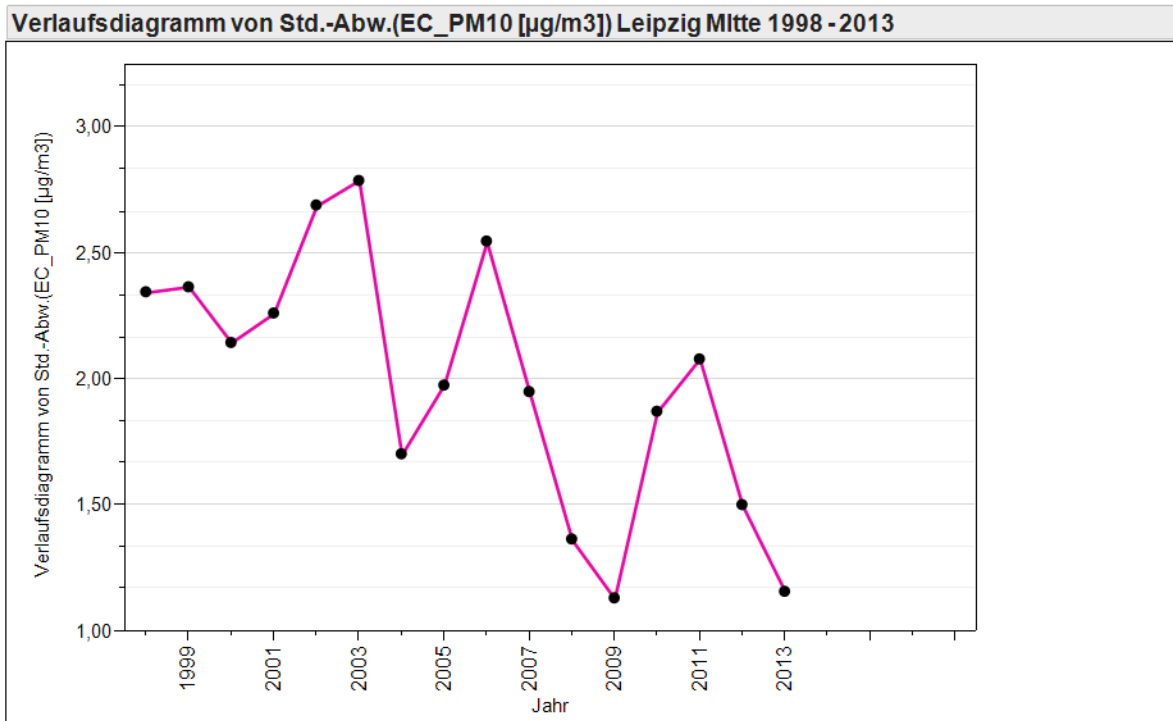
## 8. Work that remains to be done

- I Development of air quality situation in relevant Saxon monitoring sites
- I Leipzig Mitte:



## 8. Work that remains to be done

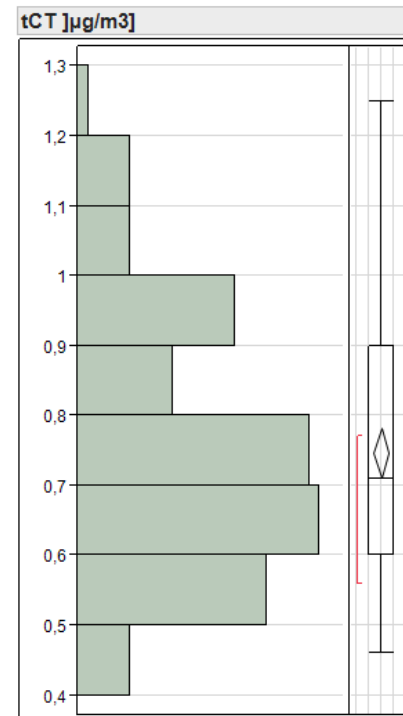
- Development of air quality situation in relevant Saxon monitoring sites
- Leipzig Mitte:



## 8. Work that remains to be done

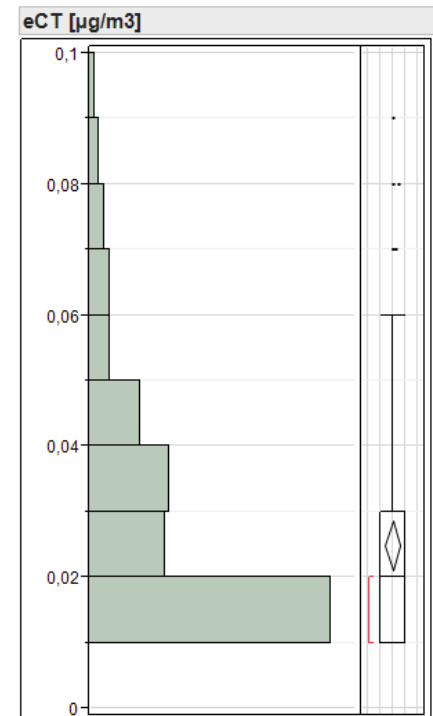
Field blank values for TOR eC and tC

- High entry through storage in the station, transport and handling for tC 90 % quartile of approximately  $1,0 \mu\text{g}/\text{m}^3$  !
- lower contribution field blank value for eC 90 % quartile of  $0.06 \mu\text{g}/\text{m}^3$
- Filter-based tC measurement seems to be difficult for expected values less than  $2.5 \mu\text{g}/\text{m}^3$



Quantile		
100.0 %	Maximum	1,25
99.5 %		1,25
97.5 %		1,174
90.0 %		1,018
75.0 %	Quartil	0,9
50.0 %	Median	0,71
25.0 %	Quartil	0,6
10.0 %		0,52
2.5 %		0,48
0.5 %		0,46
0.0 %	Minimum	0,46

Statistische Kenngrößen	
Mittelwert	0,7467961
Std.-Abw.	0,1834966
Std.-Fehler Mittelwert	0,0180805
95% KI oben Mittelwert	0,7826586
95% KI unten Mittelwert	0,7109336
N	103



Quantile		
100.0 %	Maximum	0,09
99.5 %		0,09
97.5 %		0,08
90.0 %		0,056
75.0 %	Quartil	0,03
50.0 %	Median	0,02
25.0 %	Quartil	0,01
10.0 %		0,01
2.5 %		0,01
0.5 %		0,01
0.0 %	Minimum	0,01

Statistische Kenngrößen	
Mittelwert	0,0248544
Std.-Abw.	0,0191927
Std.-Fehler Mittelwert	0,0018911
95% KI oben Mittelwert	0,0286054
95% KI unten Mittelwert	0,0211033
N	103

## 8. Work that remains to be done

- Continuation of the series of measurements with the methods currently used
- Decision to the monitoring network analysis for the Saxon air monitoring network
- Abreast of developments in the field of standardization
- Participation in nationwide workshops and working groups on the issue of measurement of TC , EC, OC , BC