Monitoring ambiant air

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aamg

Intercomparison of thermal-optical protocols currently used in France and Europe for the assessment of ambient air organic and elemental carbon within PM.

L. Chiappini[1], O. Favez[1], S. Verlhac[1], W. Maenhaut[2], J. P. Putaud[3]

[1]INERIS (National Institut for Environment and Risks) - LCSQA (French Central Air Quality Surveillance Laboratory), France

[2]Ghent University (UGent), Belgium

[3]European Commission, Joint Research Centre, TP 050, I-21027 ISPRA, Italy

LCSQA INERIS JRC EUROPEAN COMMISSION UNIVERSITEIT GENT

The European Regulation for PM_{10} and $PM_{2.5}$

- **1999** : 1st daughter directive for PM (99/30/CE)

After 2005: limit values for PM_{10}
Annual average value: 40 µg m^{-3}
35 exceedances of 50 µg m^{-3} (24 h – average) not to be overstep

- **2008** – the integrated Directive 2008/50/CE:

- $PM_{2.5}$: Limit annual average value for 2015: 25 µg m^{-3}
- Average Exposure Indicator (AEI): 3 years average $PM_{2.5}$ concentrations in urban background sites to assess whether the national exposure reduction target is met
-$PM_{2.5}$ chemical speciation on rural sites since june 2010

- **2013**: Directive revision

The European Regulation application in France

- Strategic, technical and scientific support to the French Ministry of Environment for air quality policy

- Ensure quality and consistency to the data reported by the associations part of the French air quality monitoring network

The French organization for Air Quality management

The European Regulation application in France on a « PM point of view »

the CARA network

- Based on the confrontation of CHIMERE modelling outputs and PM_{10} and $PM_{2.5}$ chemical speciation to improve our comprehension of PM episodes and better anticipate them

The CARA network organisation

- PM_{10} and $PM_{2,5}$ regularly sampled at different sites by the regional French air quality monitoring networks

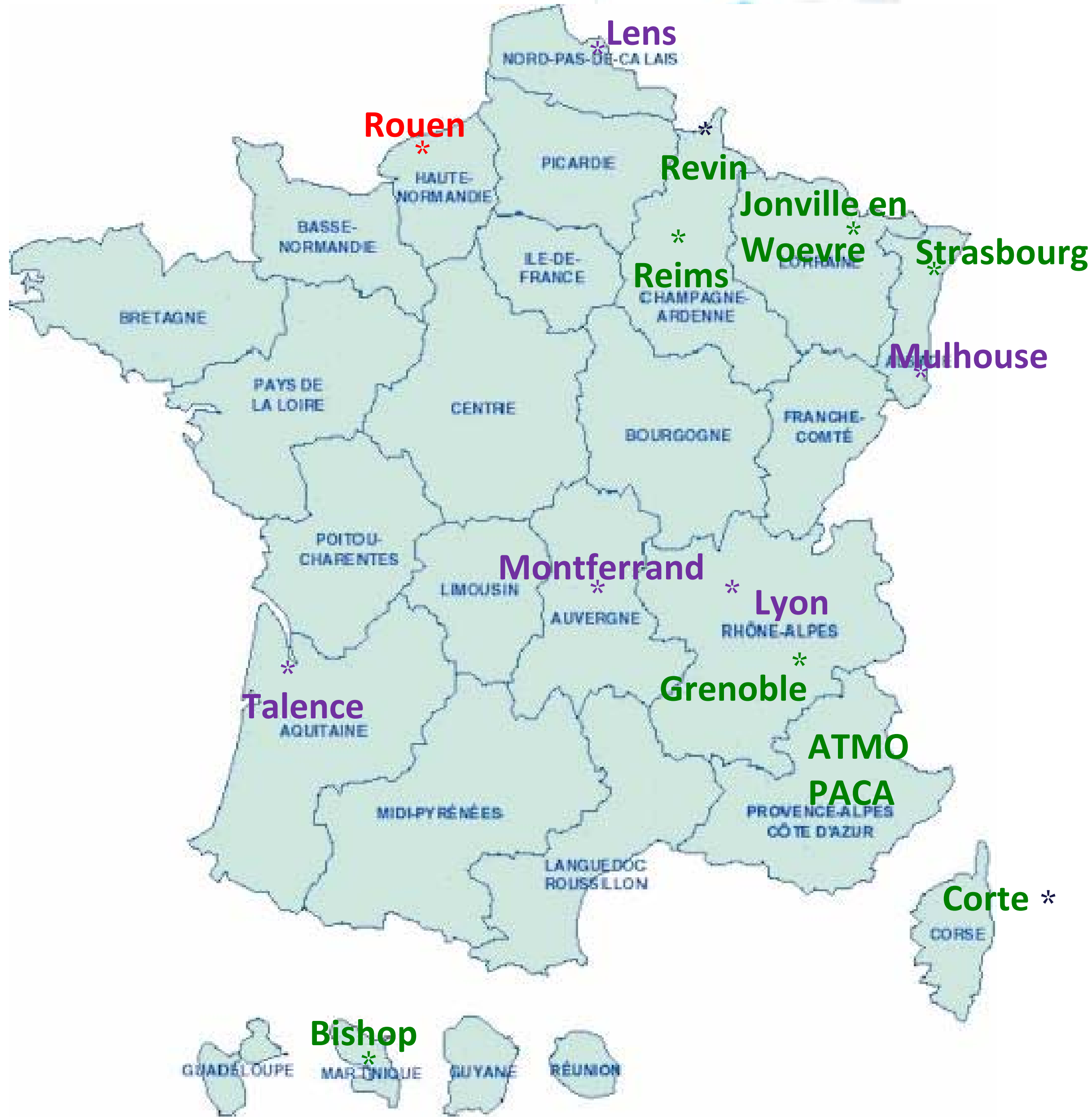
CARA: The French network organisation for PM episodes comprehension

The CARA network organisation

« Continuous » site

« Pseudo-continuous » sites

« Punctual» sites



The CARA network organization

- PM_{10} and $PM_{2,5}$ regularly sampled on different sites
- « Routine » chemical speciation: EC/OC, anions (Cl^-, SO_4^{2-}, NO_3^- and cations (Ca^{2+}, Na^+, Mg_2^+, K^+, NH_4^+) ⟺ normalisation WG 34 and 35
- More specific chemical speciation (wood burning, traffic…)
- Comparison to CHIMERE outputs

The CARA network objectives

1- Understanding particles origin specially during PM_{10} episodes (PM_{10} concentration above the limit value of 50 µg m^{-3} set by the European Directive)

2- Setting up harmonized PM sampling and chemical speciation methods in concordance with European Directive (2008/50/CE)

3- Improving PM CHIMERE modeling comparing model outputs and measurements results.

4- Apportioning sources on specific PM episodes using statistic models such as Chemical Mass Balance completed with a more specific chemical speciation.

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1- Understanding PM_{10} and $PM_{2.5}$ origin and specially during PM_{10} episodes (PM_{10} concentration above the limit value of 50 µg m^{-3} set by the European Directive)

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2- Setting up an harmonized PM sampling and chemical speciation methods in concordance with European Directive (2008/50/CE)

- Participation in normalization WG 34 (anions and cations) and 35 (EC/OC) in $PM_{2,5}$

- 2010: First interlaboratory comparison for EC and OC measurement organization in France

First interlaboratory comparison for EC and OC measurement organization in France

- Tests (involving a burner) on the influence of the EC loading

- Comparison of reflectance and transmittance results for OC and EC measured on ~ 700 filters sampled on rural, urban and suburban sites, in France, Belgium and Italy

- Tests on the influence of the laser attenuation

Organization

- 5 participants
- 3 protocols
- 2 charring corrections

	NIOSH 5040	IMPROVE	EUSAAR_2
Laboratory number	2	3	1, 4, 5
Step		T(°C), duration (s)	
He1	250, 60	120, 150-580	200, 120
He2	500, 60	250, 150-580	300, 150
He3	650, 60	450, 150-580	450, 180
He4	850, 90	550, 150-580	650, 180
He/O_2 1[a]	650, 30	550, 150-580	500, 120
He/O_2 2	750, 30	700, 150-580	550, 120
He/O_2 3	850, 30	800, 150-880	700, 70
He/O_2 4	940, 120		850, 80
Charring correction	Transmittance	Reflectance	Transmittance

- 2 types of reference materials:

- Glucose solutions

- 3 PM_{10} CARA urban sites samples, N1, N2, N3

- PM_{10} samples homogeneity

Filter	N'1			N'2			N'3		
	OC	EC	TC	OC	EC	TC	OC	EC	TC
					(µg/cm²)				
Mean (µg/cm²)	10,0	3,6	13,6	21,4	8,0	29,5	27,5	8,3	35,8
SD (µg/cm²)	0,6	0,1	0,7	0,5	0,3	0,5	0,6	0,2	0,7
RSD %	6,1%	3,3%	4,8%	2,2%	3,5%	1,9%	2,3%	2,7%	1,9%

Results

- Glucose solution stability demonstrated
- Glucose solution homogeneity ⇒ 1%

- **Glucose solutions**

Satisfactory calibration curves ⇒ analytical protocol and instruments are properly controlled

Necessity to work with freshly made solutions, kept under refrigerated conditions and with bactericidal

Results

- **Global result: repeatability**

Whatever the analytical protocol (NIOSH, IMPROVE, EUSAAR2), the repeatability for each laboratory is satisfactory ⇨ RSD< 10 %.

- **Global results: Reproducibility**

When considering laboratory 3 results in transmittance, the reproducibility remains above 20 % but under 40 % (similar to JRC intercomparison results).

- **Charring corrections**

Differences between results in transmittance and reflectance for the same thermal protocol are significant

- **Carbon filter loading**

Seems to play a role on the data quality: the higher the loading, the less satisfactory the data quality.

Organization

- Use of a propane burner to load filter with different EC amounts

- 2 samplers used simultaneously: a high volume and a low volume (several samplings performed to cover the whole high volume sampling time - reference).

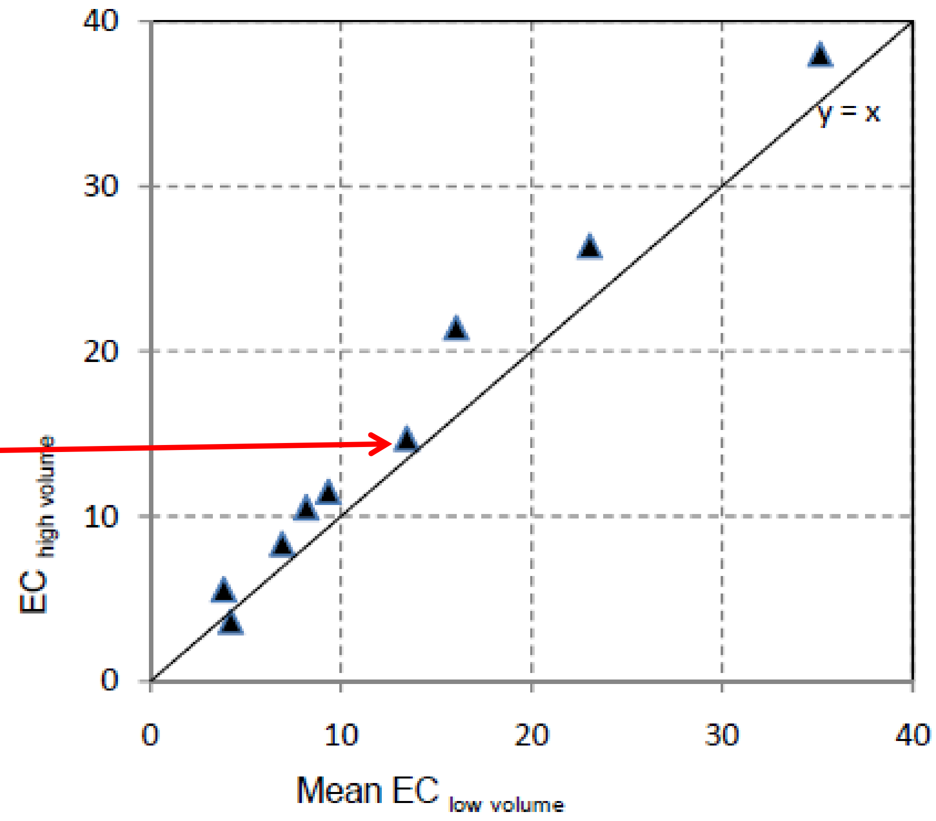
- Different EC filter loading generated changing sampling time

- To mimic real carbonaceous PM content, 10 µL of a 2 gC/L glucose solution (corresponding to 20 µg/cm2 deposited on the filter) has been spiked on the filter punches.

- EC levels from 4 to 38 µg cm^{-2} have been tested

Results

The difference between the high volume EC measurement and the reference seems to become significant when the EC filter loading is above 15 µg/cm2

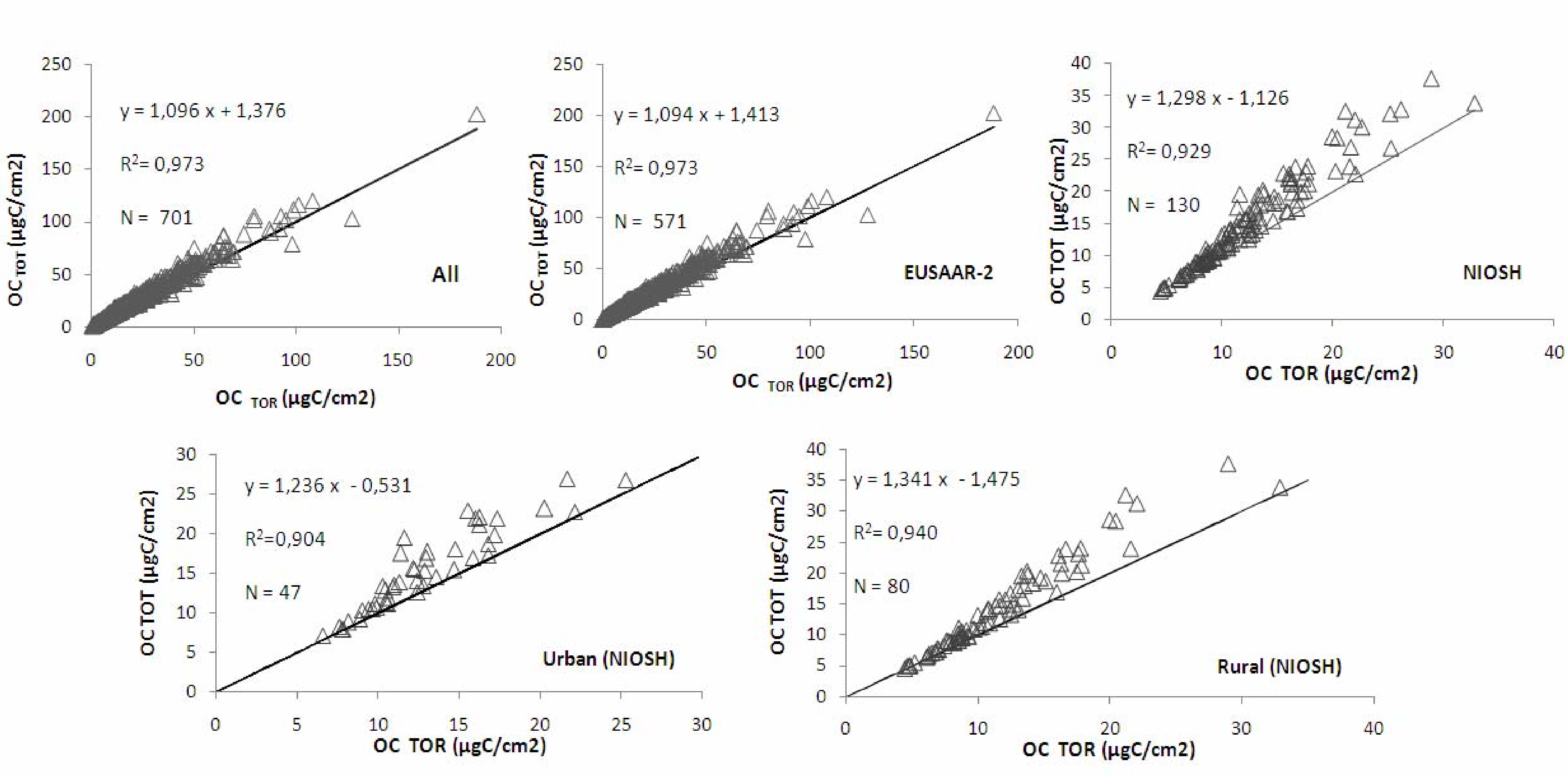


Organization

Differences of EC and OC measurements as a function of the optical correction studied on three batches of filters from:

Institute	Site	PM	Sampling period	Analytical method	Number of filters
LCSQA-INERIS CARA Network	Urban	PM10	2008-2009 whole year	EUSSAR 2	246
VMM - Ghent University	Urban / rural	PM10, PM2,5	2009, fall, winter	NIOSH	128
JRC	Sub urban	PM10	2009 whole year	EUSSAR 2	326

Results: OC


y = 1,096 x + 1,376
R2= 0,973
N = 701
All
OC TOT (µgC/cm2)
OC TOR (µgC/cm2)
y = 1,094 x + 1,413
R2= 0,973
N = 571
EUSAAR-2
OC TOT (µgC/cm2)
OC TOR (µgC/cm2)
y = 1,298 x - 1,126
R2= 0,929
N = 130
NIOSH
OC TOT (µgC/cm2)
OC TOR (µgC/cm2)
y = 1,236 x - 0,531
R2=0,904
N = 47
Urban (NIOSH)
OCTOT (µgC/cm2)
OC TOR (µgC/cm2)
y = 1,341 x - 1,475
R2= 0,940
N = 80
Rural (NIOSH)
OCTOT (µgC/cm2)
OC TOR (µgC/cm2)

Results: OC

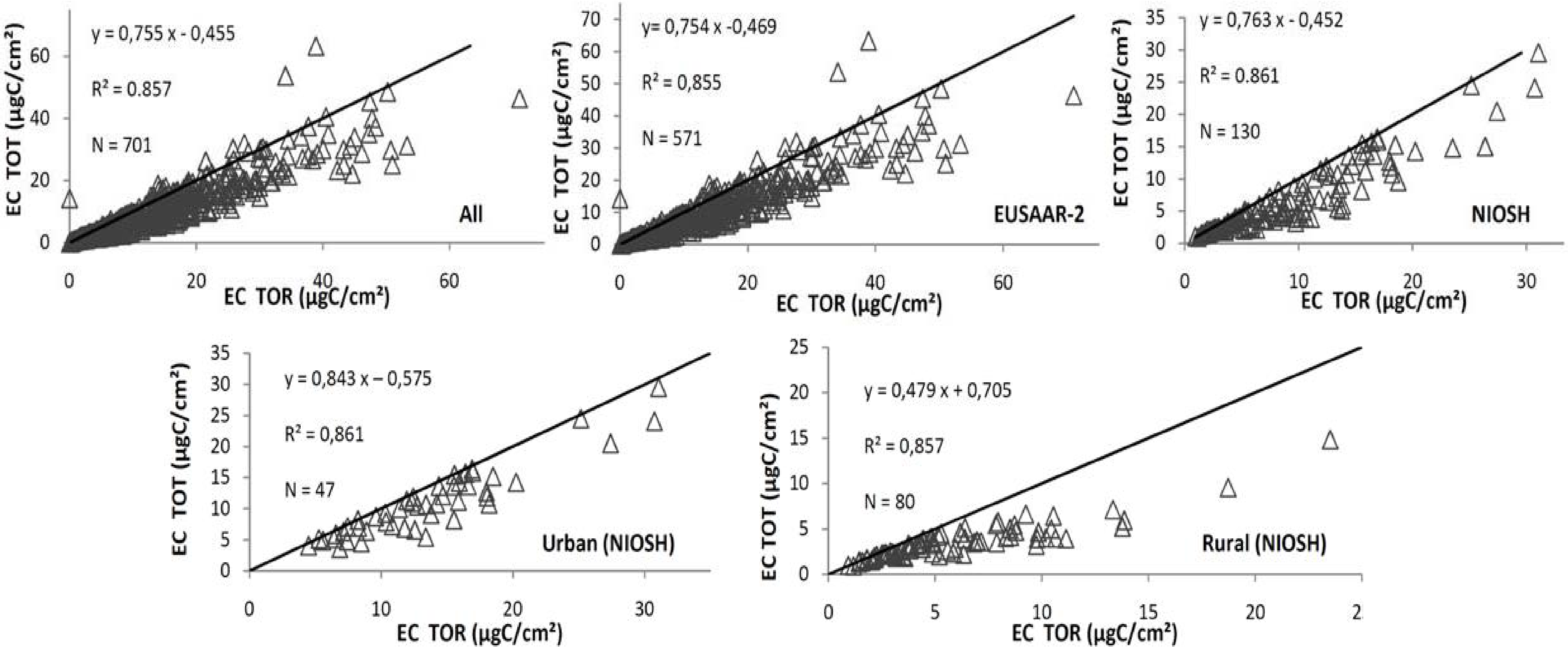
- Transmittance optical correction leads to higher OC than reflectance
  Hypothesis: charring within the filter

- Comparison between NIOSH and EUSAAR-2: higher differences between TOT and TOR for OC analyzed using the NIOSH protocol.
  Hypothesis: last temperature step in the inert mode (850 °C for NIOSH, 650 °C for EUSAAR-2) defining the split point between EC and OC (Subramanian 2006). Peak inert mode too low ⇒ OC underestimation

- Influence of the site: No significant differences (OC TOT and TOR ratio slightly higher for rural)

- Whatever the protocol or the site, correlation between TOR and TOT is good ⇒ $0.904 < R^2 < 0.997$

Results: EC


y = 0,755 x - 0,455
R² = 0.857
N = 701
All
EC TOT (µgC/cm²)
EC TOR (µgC/cm²)
y= 0,754 x -0,469
R² = 0,855
N = 571
EUSAAR-2
EC TOT (µgC/cm²)
EC TOR (µgC/cm²)
y = 0,763 x - 0,452
R² = 0.861
N = 130
NIOSH
EC TOT (µgC/cm²)
EC TOR (µgC/cm²)
y = 0,843 x – 0,575
R² = 0,861
N = 47
Urban (NIOSH)
EC TOT (µgC/cm²)
EC TOR (µgC/cm²)
y = 0,479 x + 0,705
R² = 0,857
N = 80
Rural (NIOSH)
EC TOT (µgC/cm²)
EC TOR (µgC/cm²)

Results: EC

- TOT leads to lower EC than TOR (oppositely to OC)

  Hypothesis: light absorbing carbon distribution at the filter surface (pyrolitic carbon comes out from the inside) ⇒ TOR signal returns earlier to its original value than TOT (Chow et al. 2004)

- Correlation TOR /TOT worst for EC than for OC ⇒ $0.851 < R^2 < 0.861$

- Rural results display the higher TOT/TOR ratio of about 0.5 (Cheng et al. 2011)

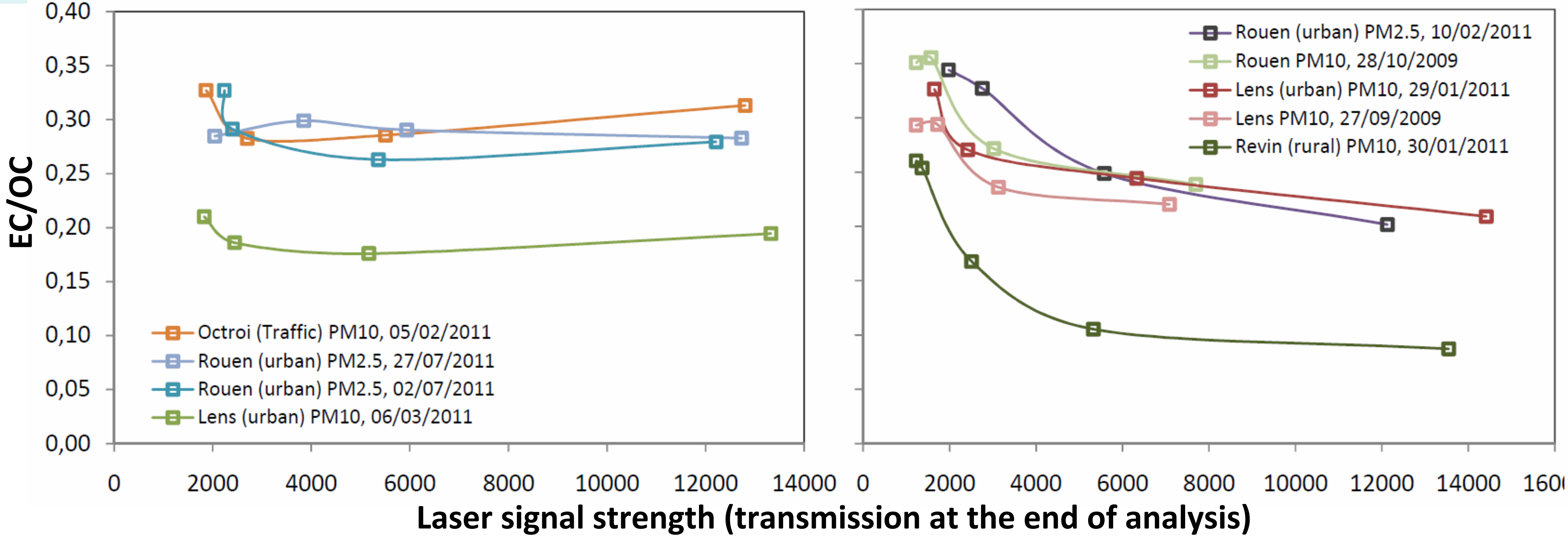
Hypothesis: PM chemical composition / "brown carbon" ⇔ biomass combustion "tar balls" (Chakrabarty 2010).

Organization

- Laser signal attenuation simulated piling up punches of blank filters underneath the sample filter punch.
- Nine samples studied:

	Site	PM µg m-3	EC (ug/sq cm)	OC (ug/sq cm)
F1	Rural	82	4,01	41,94
F2	Urban	49	11,04	41,74
F3	Urban	26	3,42	14,17
F4	Urban	34	7,78	30,79
F5	Urban	26	8,19	21,13
F6	Trafic	21	8,98	19,70
F7	Urban	18	2,97	7,53
F8	Urban	74	7,43	26,32
F9	Urban	44	6,99	22,31

On the influence of laser signal



	EC (µg cm^{-2})	OC (µg cm^{-2})	**PM (µg m^{-3})**
Octroi, 05/02/2011	9	19,5	**21**
Rouen, 27/07/2010	3	7,5	**18**
Rouen, 02/07/2010	8	21	**26**
Lens, 06/03/2011	3,5	14	**26**

	EC (µg cm^{-2})	OC (µg cm^{-2})	**PM (µg m^{-3})**
Rouen, 10/02/2011	8	31	**34**
Rouen, 28/10/2009	7	22	**44**
Lens, 29/01/2011	11	42	**49**
Lens, 27/09/2009	7,5	26,5	**74**
Revin, 30/01/2011	4	42	**82**

- EC/OC ratio tends to increase when the laser transmission signal decreases
- The variations seem to depend on the filter TC content

Conclusions

- Results of the interlaboratory comparison are satisfactory, comparable to previous exercices

- Influence of the optical correction (significant difference between TOT and TOR, in particular for EC measurements)

- Influence of PM chemical composition (unclear, needs investigation)

- Influence of the filter loading (EC>15 $\mu g/cm^2$)

- Influence of the laser intensity on the OC charring correction ⇒ necessity to watch out the laser signal decrease with time since it might lead to EC overestimation

Acknowledgments

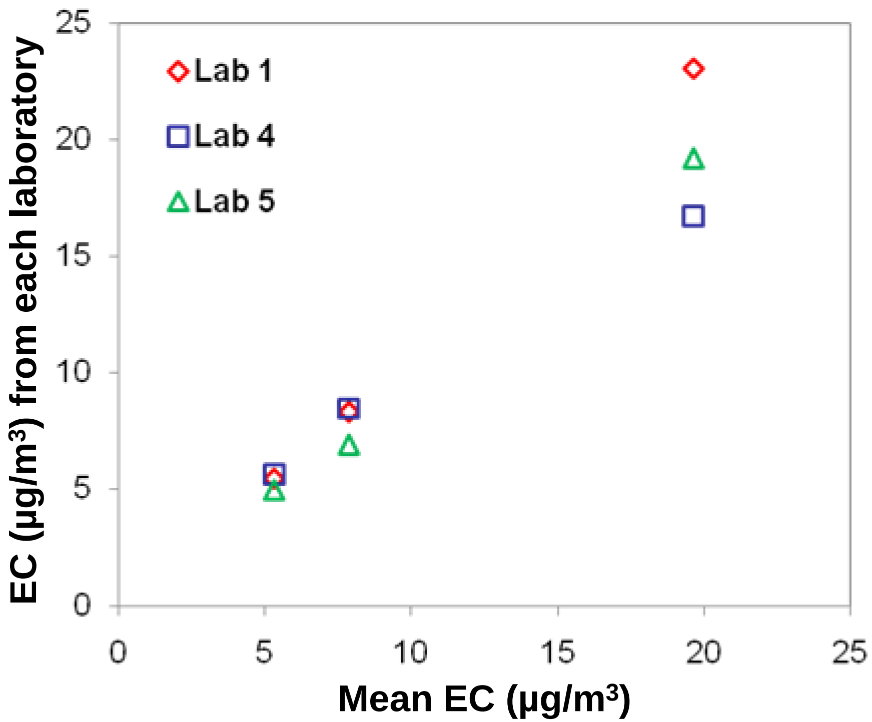
The French Ministry of Environment for air quality policy

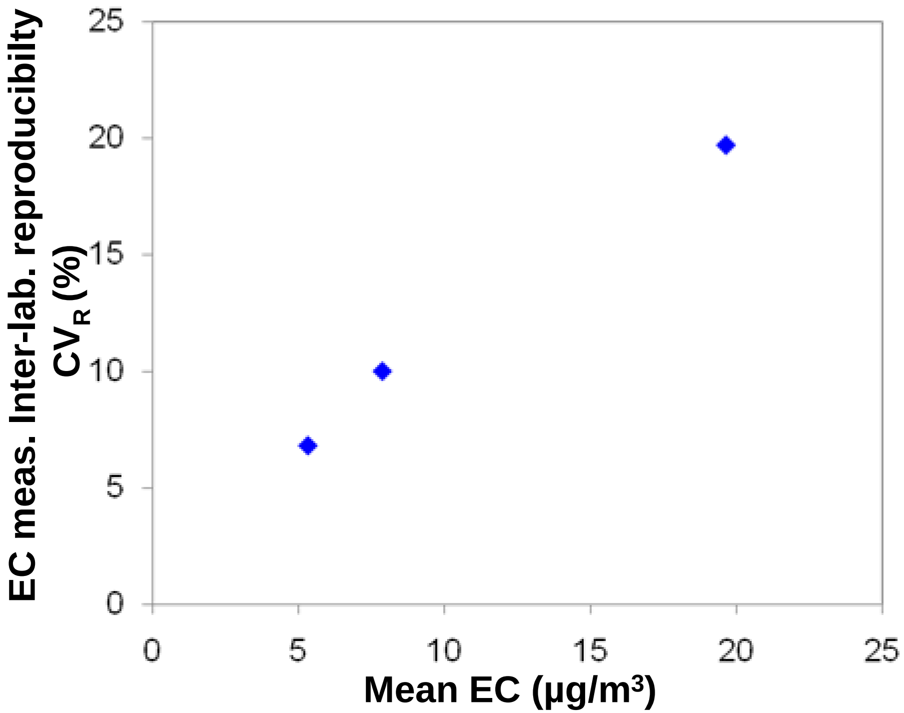
Regional French air quality monitoring networks

Thank you for your attention

On the influence of the EC loading

3 Sunset Lab. instruments, each of them using EUSAAR2:





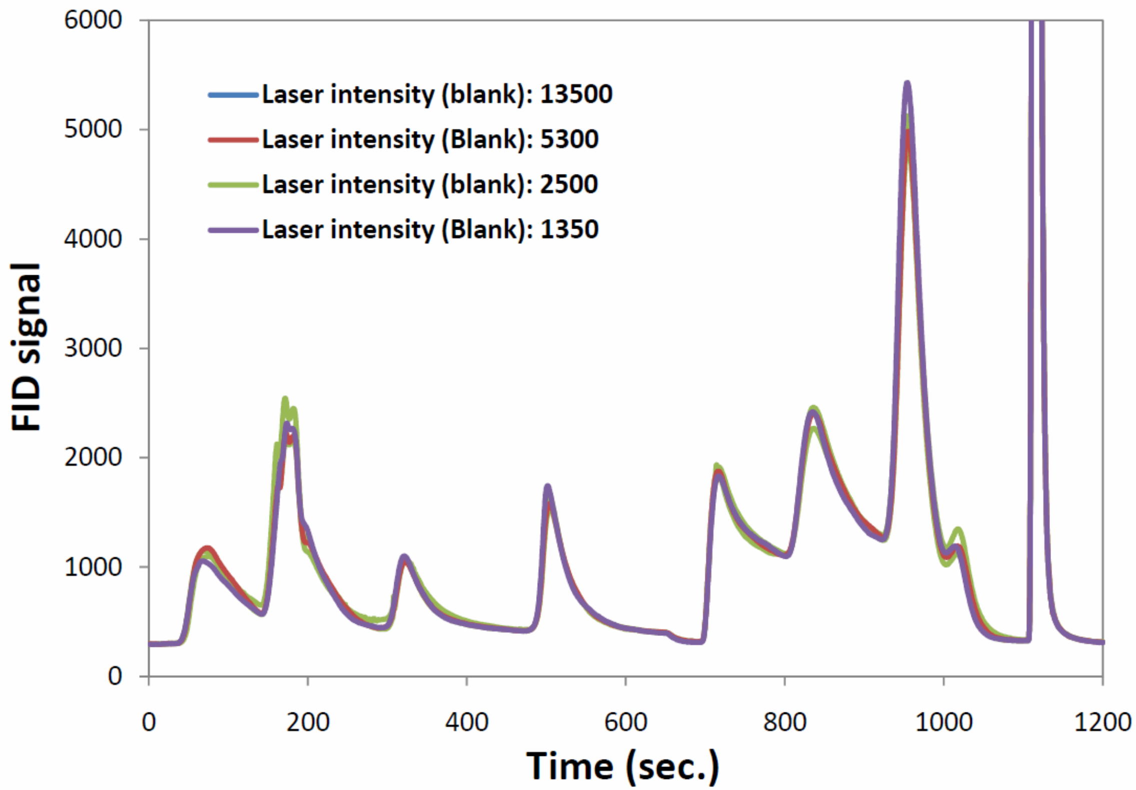
⇨ **The higher the EC content, the worse the inter-laboratory reproducibility**

Some more studies needed to decide on a max. EC level

Laser signal attenuation simulated by gradually piling up punches of blank filters underneath the sample filter punch.

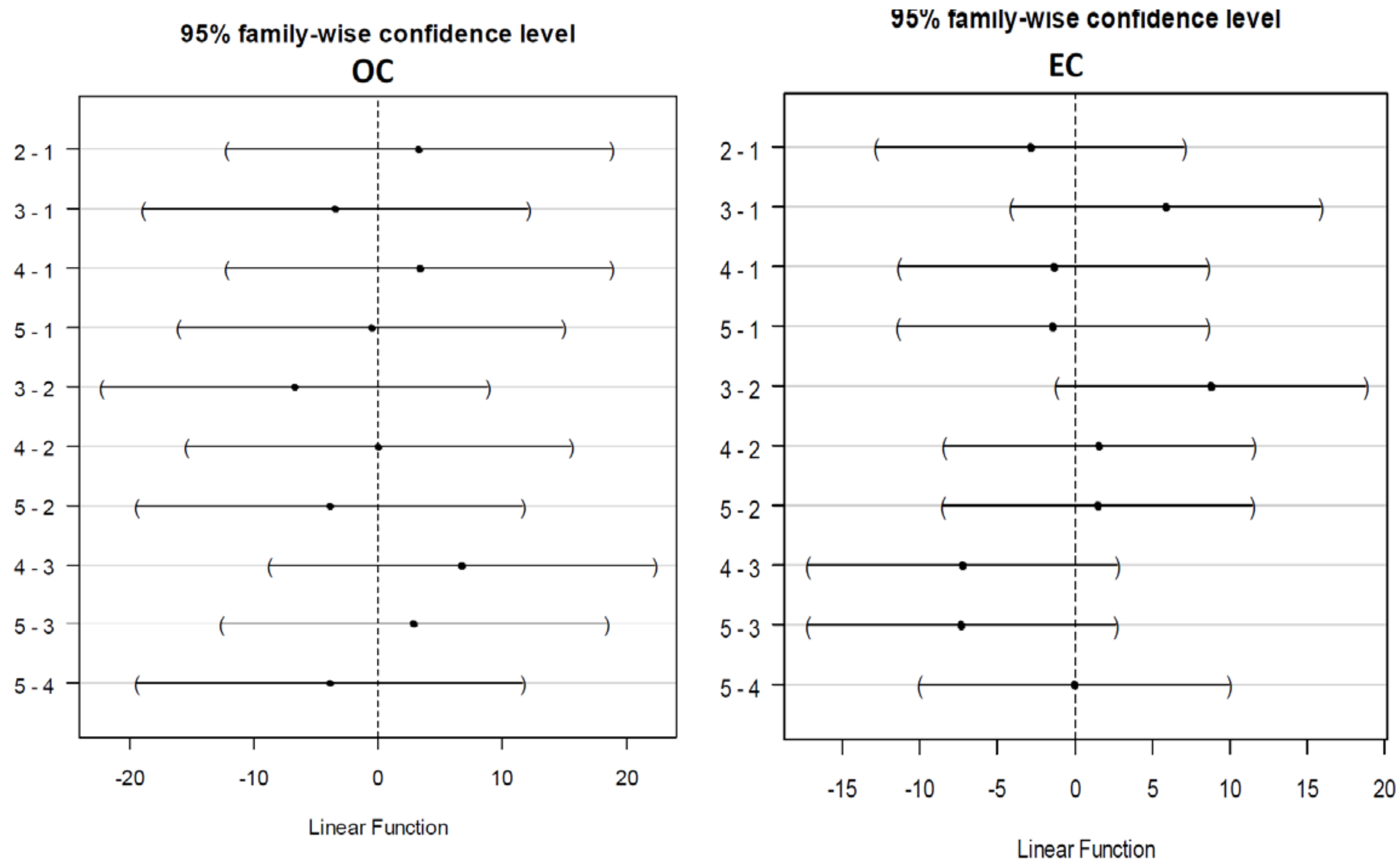
Example, Revin (rural background), PM_{10}, January 2011:

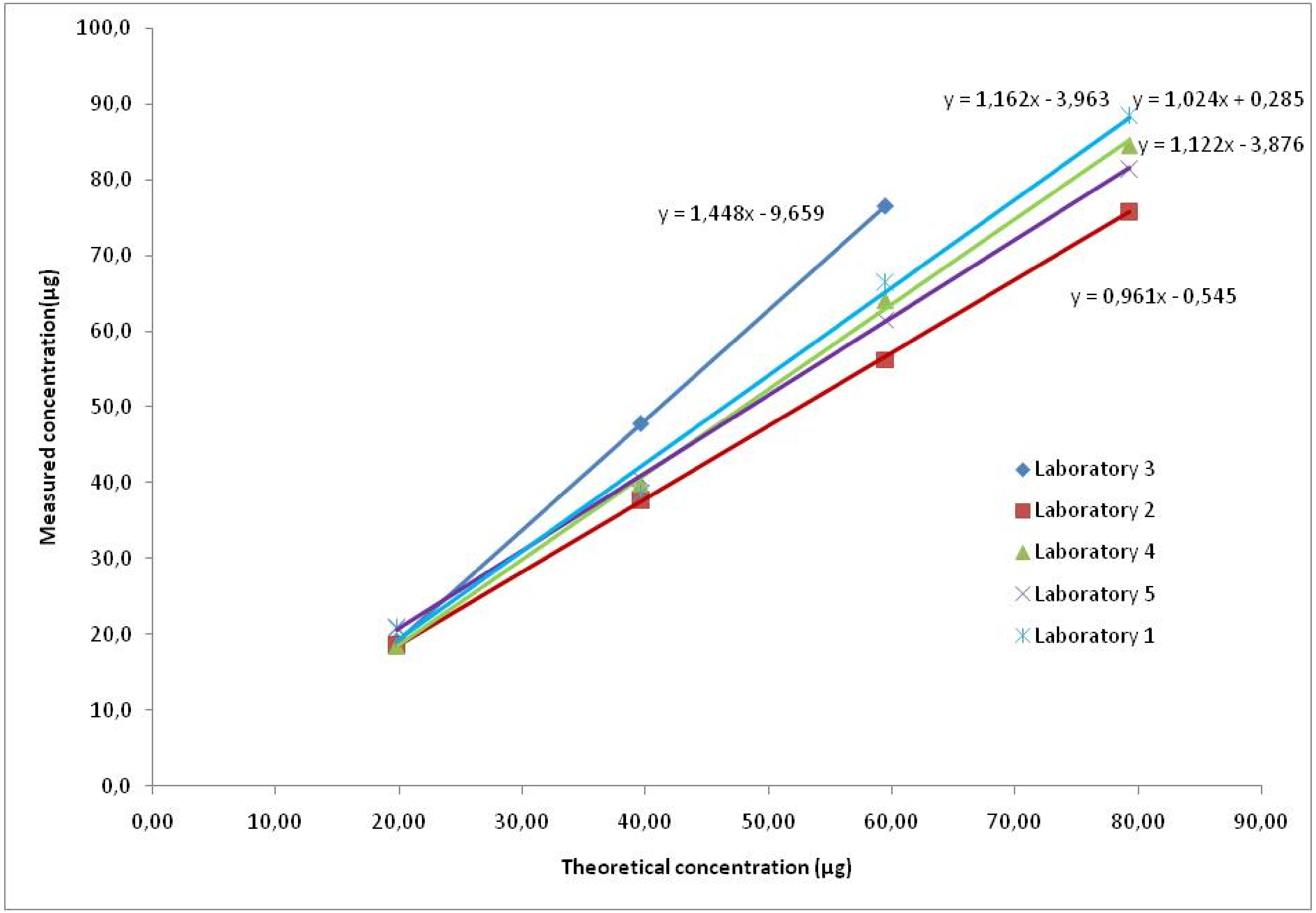
No influence on FID trends



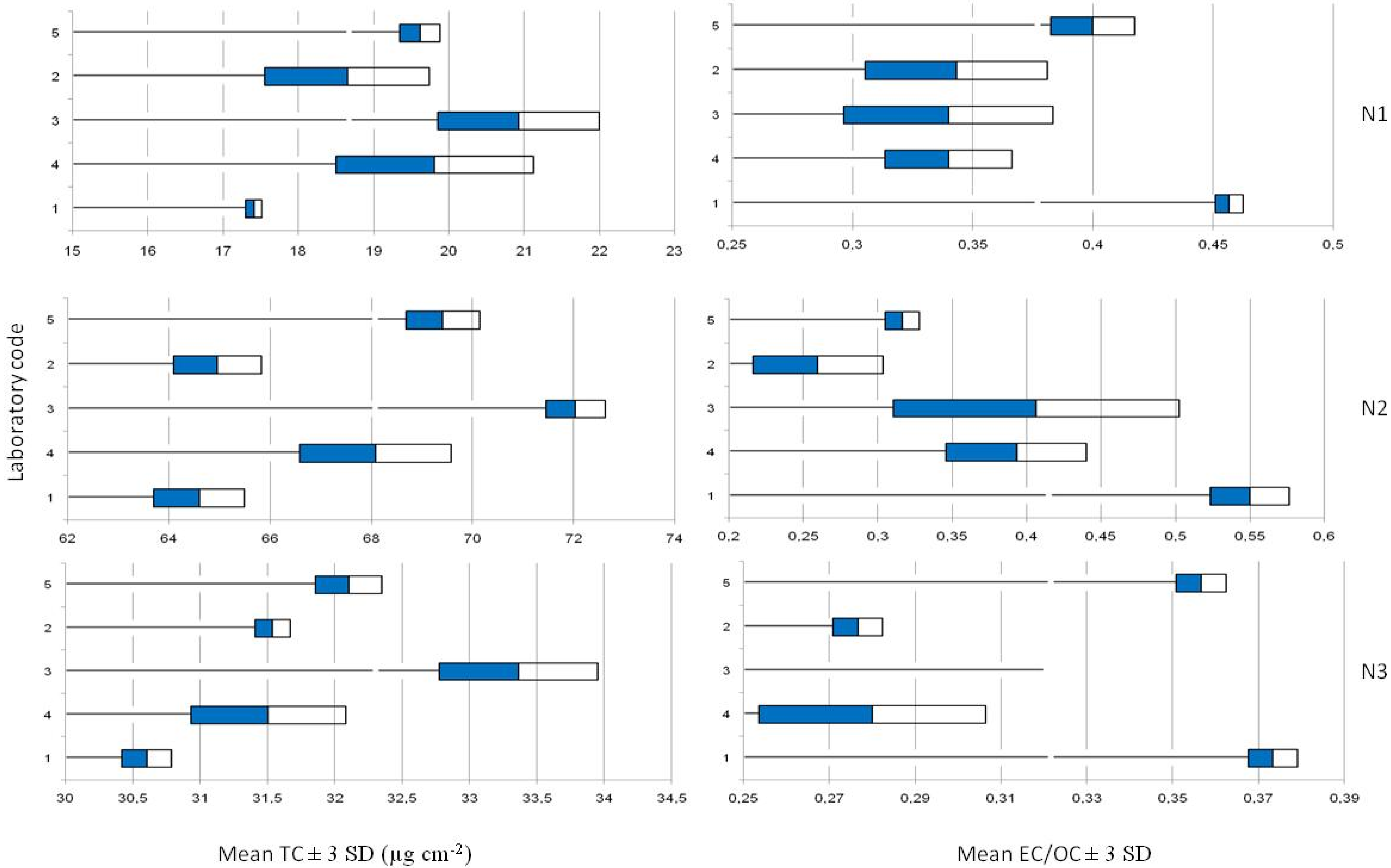
Influence on the OC/EC split point

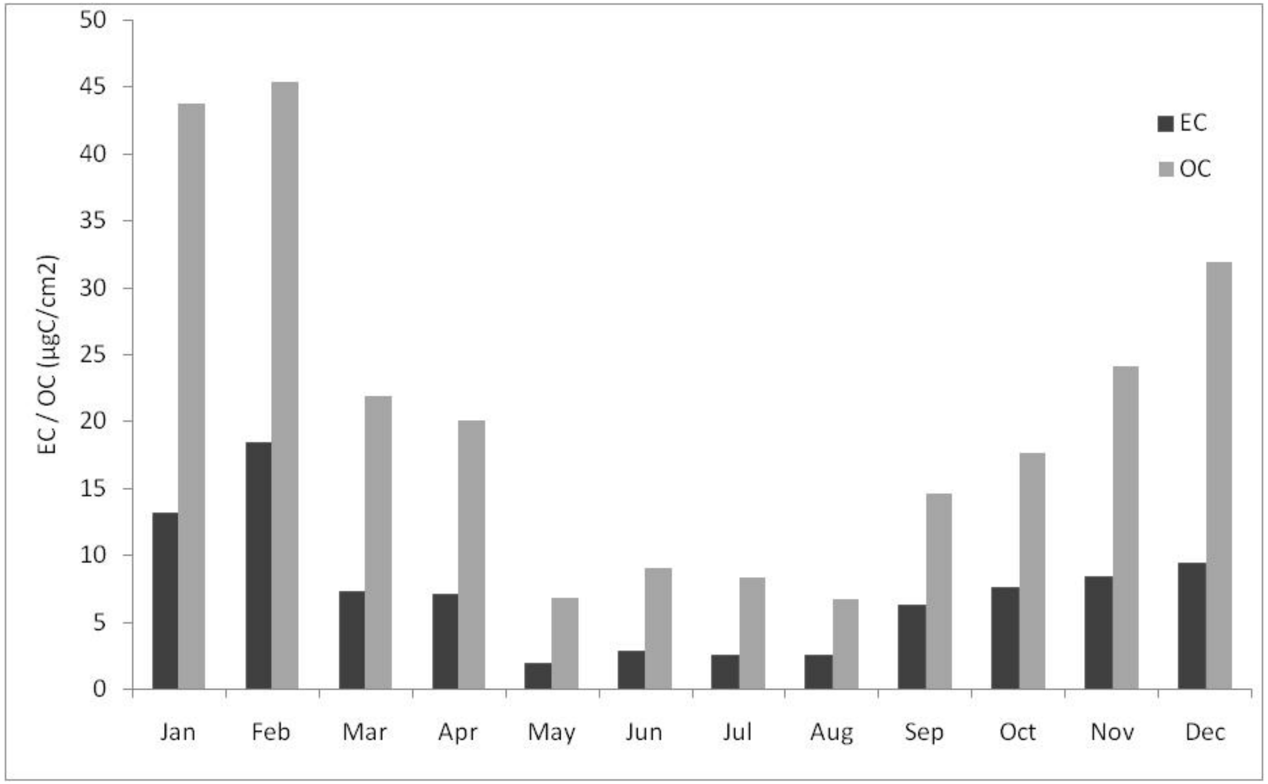
Laser intensity	Split time
13500	979
5300	970
2500	956
1350	943

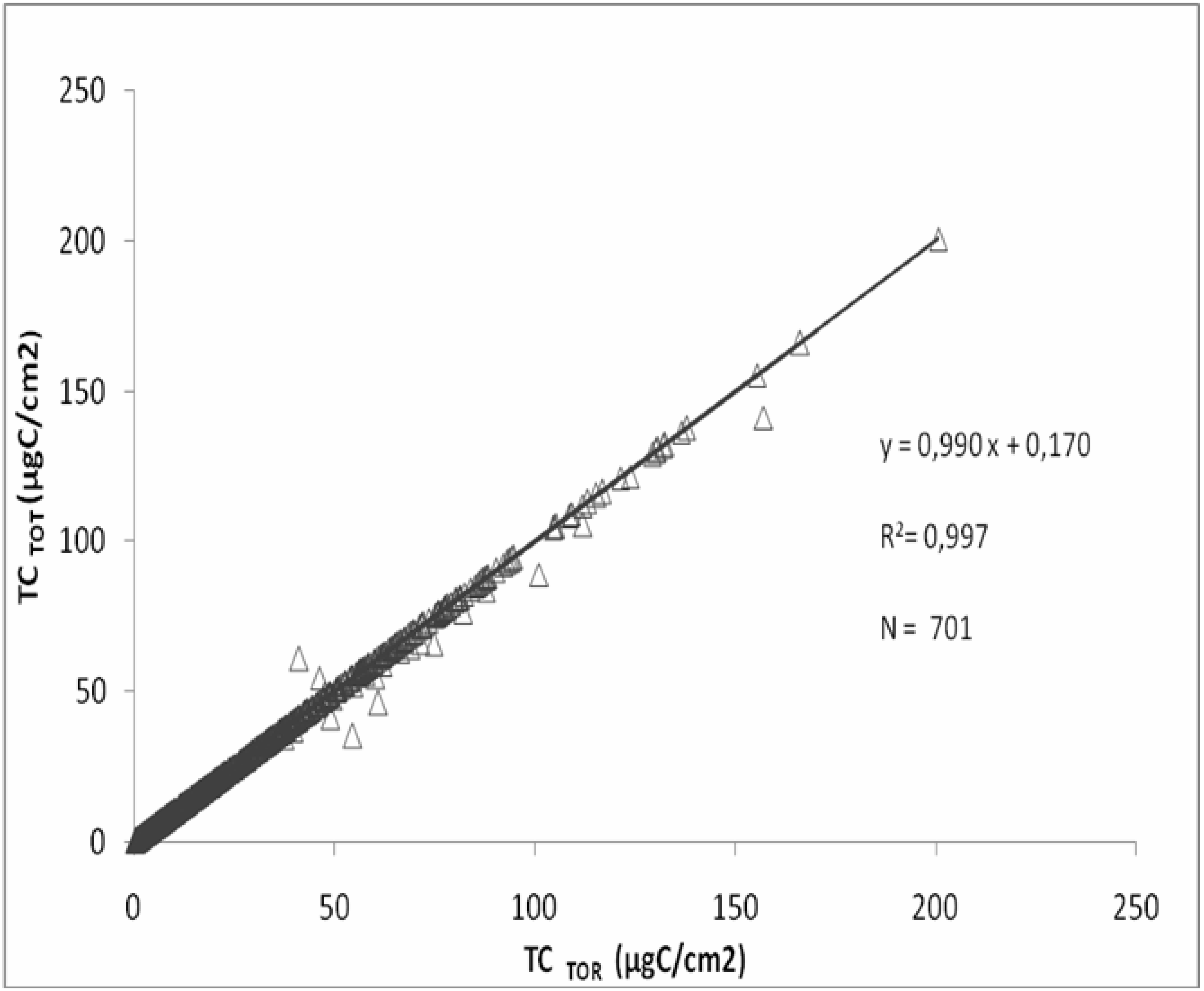

95% family-wise confidence level
OC
2 - 1
3 - 1
4 - 1
5 - 1
3 - 2
4 - 2
5 - 2
4 - 3
5 - 3
5 - 4
-20
-10
0
10
20
Linear Function
95% family-wise confidence level
EC
2 - 1
3 - 1
4 - 1
5 - 1
3 - 2
4 - 2
5 - 2
4 - 3
5 - 3
5 - 4
-15
-10
-5
0
5
10
15
20
Linear Function



100,0
90,0
80,0
70,0
60,0
50,0
40,0
30,0
20,0
10,0
0,0
Measured concentration(µg)
0,00
10,00
20,00
30,00
40,00
50,00
60,00
70,00
80,00
90,00
Theoretical concentration (µg)
y = 1,162x - 3,963
y = 1,024x + 0,285
y = 1,122x - 3,876
y = 1,448x - 9,659
y = 0,961x - 0,545
Laboratory 3
Laboratory 2
Laboratory 4
Laboratory 5
Laboratory 1


N1
N2
N3
Laboratory code
5
2
3
4
1
15
16
17
18
19
20
21
22
23
0,25
0,3
0,35
0,4
0,45
0,5
62
64
66
68
70
72
74
0,2
0,25
0,3
0,35
0,4
0,45
0,5
0,55
0,6
30
30,5
31
31,5
32
32,5
33
33,5
34
34,5
0,25
0,27
0,29
0,31
0,33
0,35
0,37
0,39
Mean TC ± 3 SD (µg cm-2)
Mean EC/OC ± 3 SD


EC / OC (µgC/cm2)
0
5
10
15
20
25
30
35
40
45
50
EC
OC
Jan
Feb
Mar
Apr
May
Jun
Jul
Aug
Sep
Oct
Nov
Dec


TC TOT (µgC/cm2)
TC TOR (µgC/cm2)
0
50
100
150
200
250
y = 0,990 x + 0,170
R²= 0,997
N = 701