

Monitoring ambient air

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

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Context: PM pollution, an increasing concern

The European Regulation for PM₁₀ and PM_{2.5}

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

After 2005: limit values for PM₁₀

Annual average value: 40 $\mu\text{g m}^{-3}$

35 exceedances of 50 $\mu\text{g m}^{-3}$ (24 h – average) not to be overstep

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

- PM_{2.5}: Limit annual average value for 2015: 25 $\mu\text{g m}^{-3}$

- 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

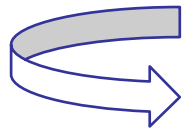
-PM_{2.5} chemical speciation on rural sites since june 2010

- **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 French network organisation for
PM episodes comprehension*

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

the CARA network

- Based on the confrontation of CHIMERE modelling outputs and PM₁₀ and PM_{2.5} chemical speciation to improve our comprehension of PM episodes and better anticipate them



*CARA: The French network
organisation for PM episodes
comprehension*

The CARA network organisation

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

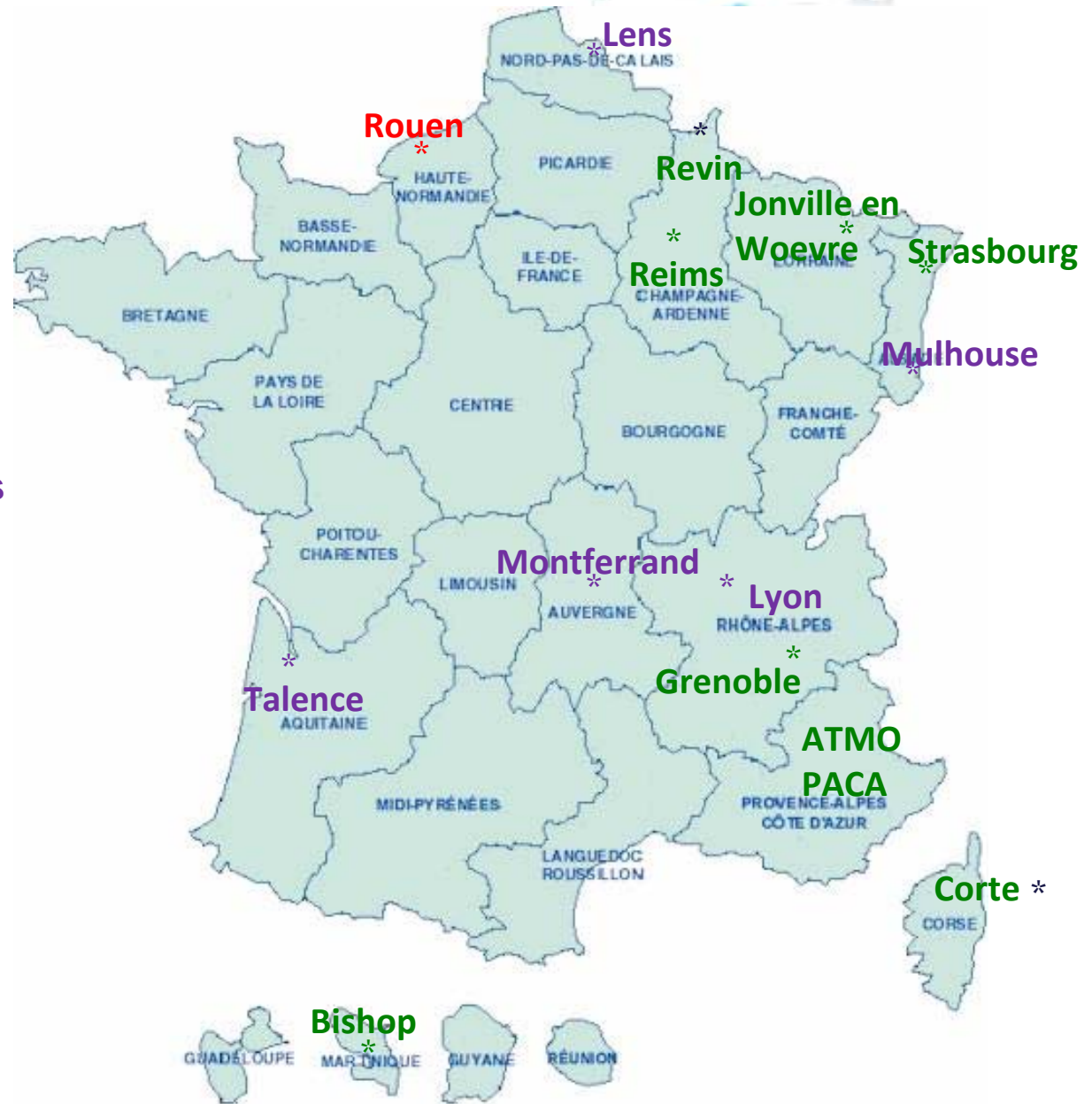
CARA: The French network organisation for PM episodes comprehension

The CARA network organisation

« Continuous » site

« Pseudo-continuous » sites

« Punctual » sites



*CARA: The French network
organisation for PM episodes
comprehension*

The CARA network organization

- PM₁₀ and PM_{2,5} regularly sampled on different sites
- « Routine » chemical speciation: EC/OC, anions (Cl⁻, SO₄²⁻, NO₃⁻ and cations (Ca²⁺, Na⁺, Mg²⁺, K⁺, NH₄⁺) ↔ 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 PM₁₀ episodes (PM₁₀ concentration above the limit value of 50 $\mu\text{g m}^{-3}$ 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.

The CARA network objectives

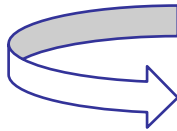
- 1-** Understanding PM_{10} and $PM_{2.5}$ origin and specially during PM_{10} episodes (PM_{10} concentration above the limit value of $50 \mu\text{g m}^{-3}$ set by the European Directive)
- 2-** **Setting up harmonized PM sampling and chemical speciation methods in concordance with European Directive (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.



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

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- 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

French EC/OC interlaboratory comparison

Organization

- 5 participants
- 3 protocols
- 2 charring corrections
- 2 types of reference materials:
 - Glucose solutions
 - 3 PM₁₀ CARA urban sites samples, N1, N2, N3


	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

- PM₁₀ samples homogeneity


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

French EC/OC interlaboratory comparison

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

French EC/OC interlaboratory comparison

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.

On the influence of the EC loading

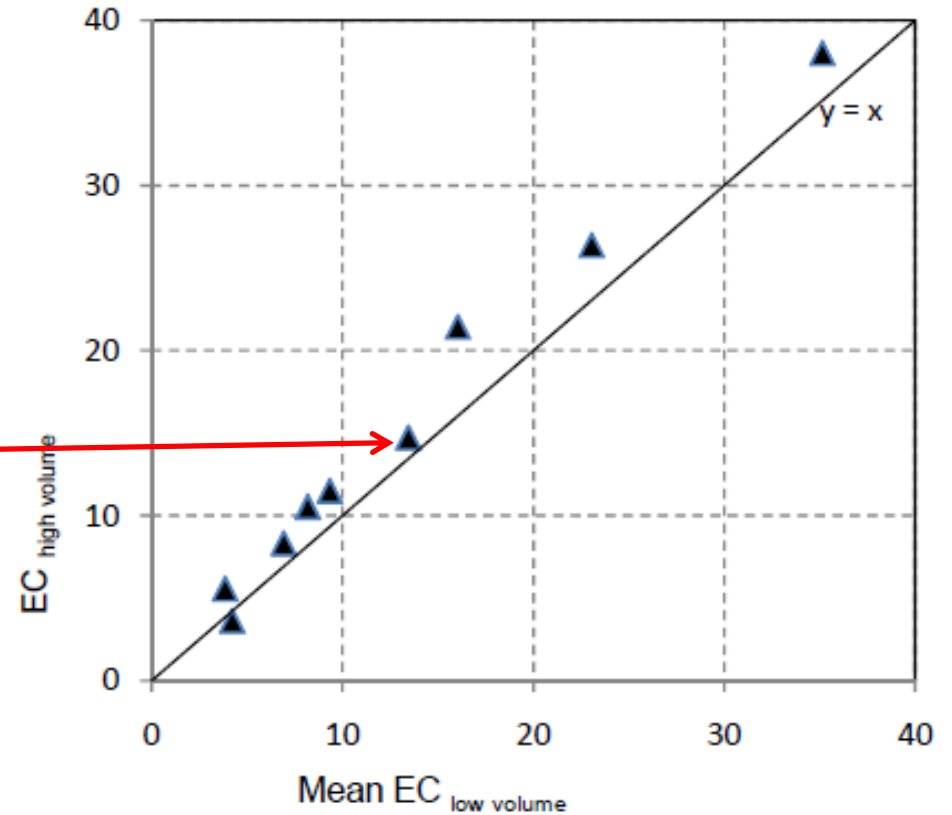
Organization

- 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 $\mu\text{g}/\text{cm}^2$ deposited on the filter) has been spiked on the filter punches.
- EC levels from 4 to 38 $\mu\text{g cm}^{-2}$ have been tested

On the influence of the EC loading

Results

The difference between the high volume EC measurement and the reference seems to become significant when the EC filter loading is above $15 \mu\text{g}/\text{cm}^2$



On the influence of reflectance and transmittance correction

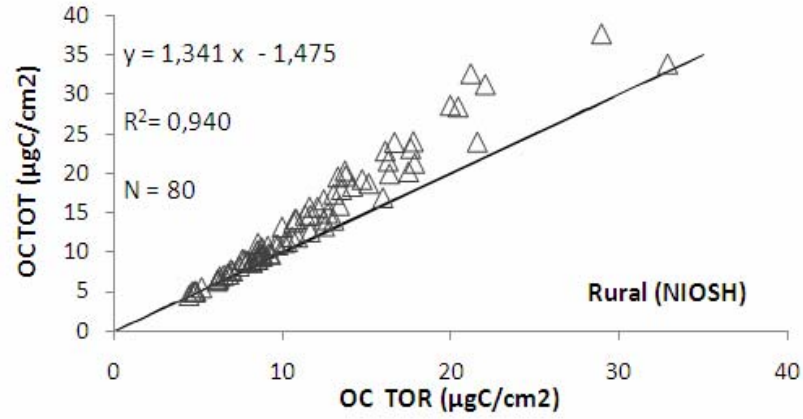
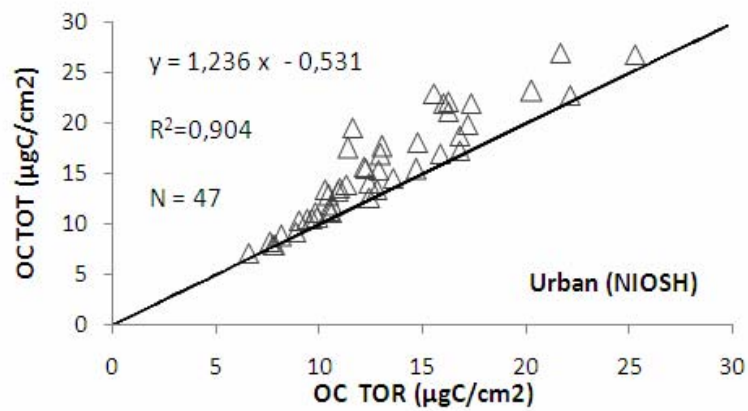
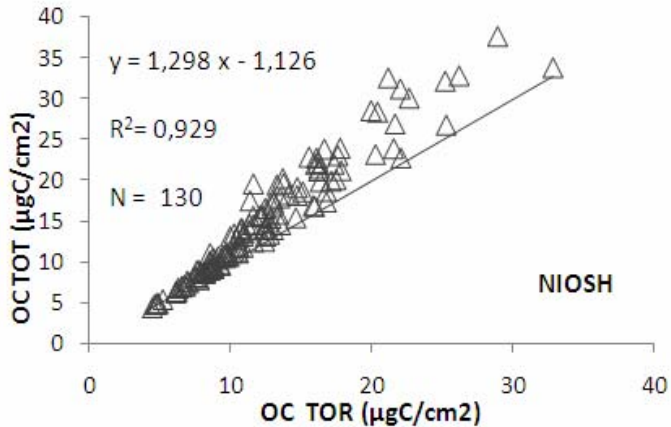
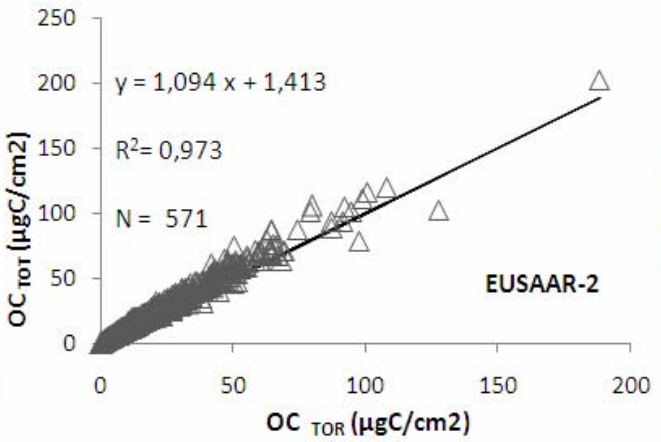
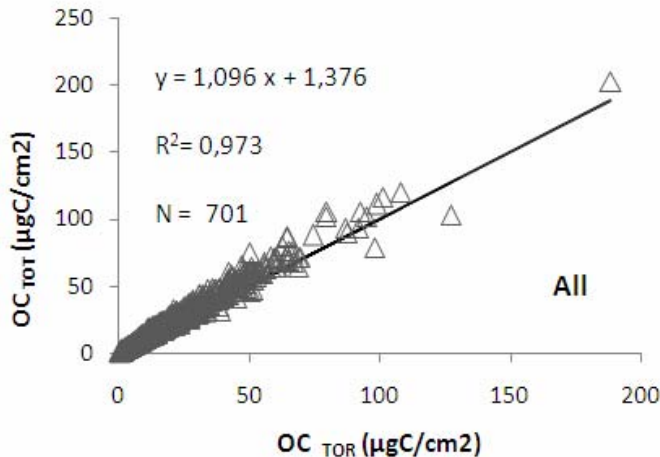
Organization

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

On the influence of reflectance and transmittance correction

Results: OC




On the influence of reflectance and transmittance correction

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.

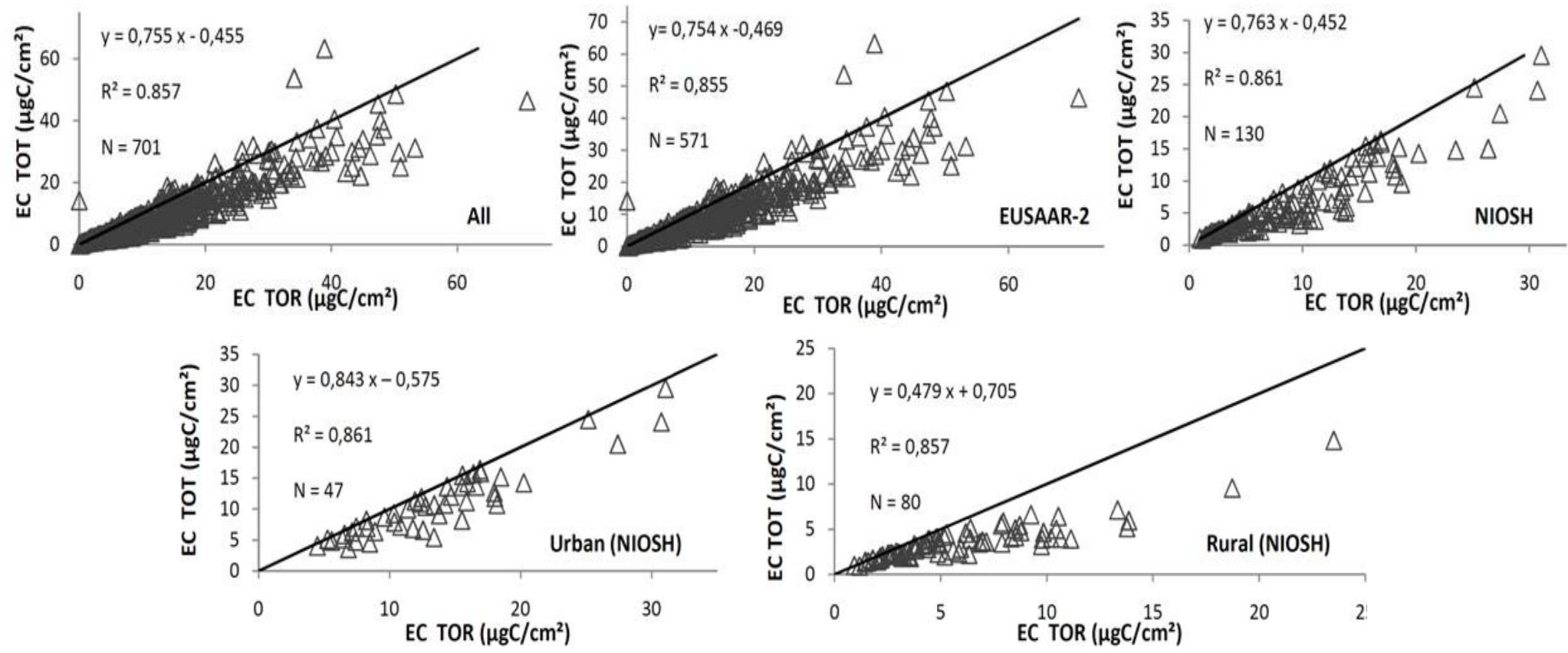
Hypothesis: last temperature step in the inert mode (850 °C for NIOSH, 650 °C for EUSAAR-2) defining the split point between EC and OC (Subramanian 2006). Peak inert mode too low  OC underestimation

- 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  $0.904 < R^2 < 0.997$

On the influence of reflectance and transmittance correction

Results: EC



On the influence of reflectance and transmittance correction

Results: EC

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

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

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

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

Hypothesis: PM chemical composition / “brown carbon” \leftrightarrow biomass combustion “tar balls” (Chakrabarty 2010).

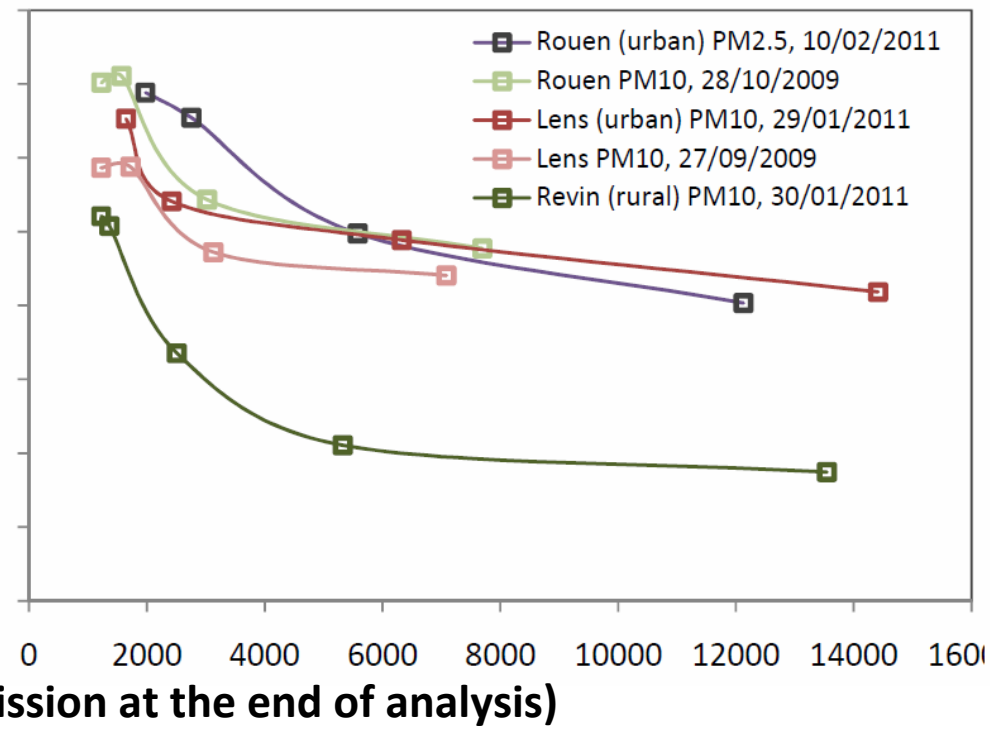
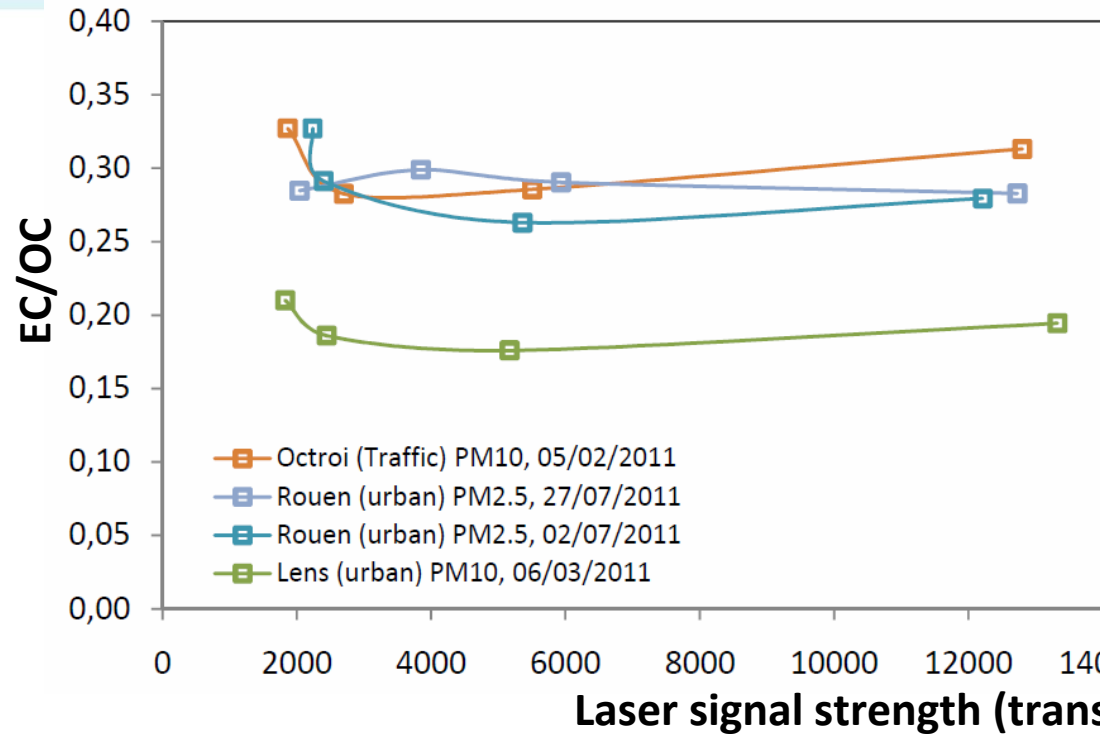
On the influence of laser signal

Organization

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

	Site	PM $\mu\text{g m}^{-3}$	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 ($\mu\text{g cm}^{-2}$)	OC ($\mu\text{g cm}^{-2}$)	PM ($\mu\text{g m}^{-3}$)
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 ($\mu\text{g cm}^{-2}$)	OC ($\mu\text{g cm}^{-2}$)	PM ($\mu\text{g m}^{-3}$)
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 exercises
- 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 ($EC > 15 \mu\text{g}/\text{cm}^2$)
- 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

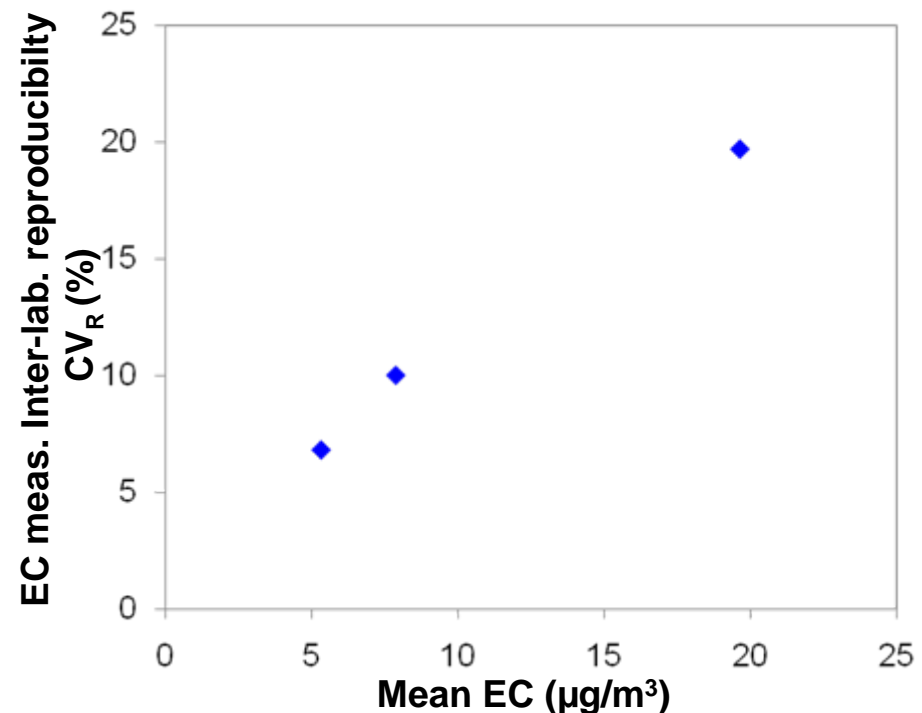
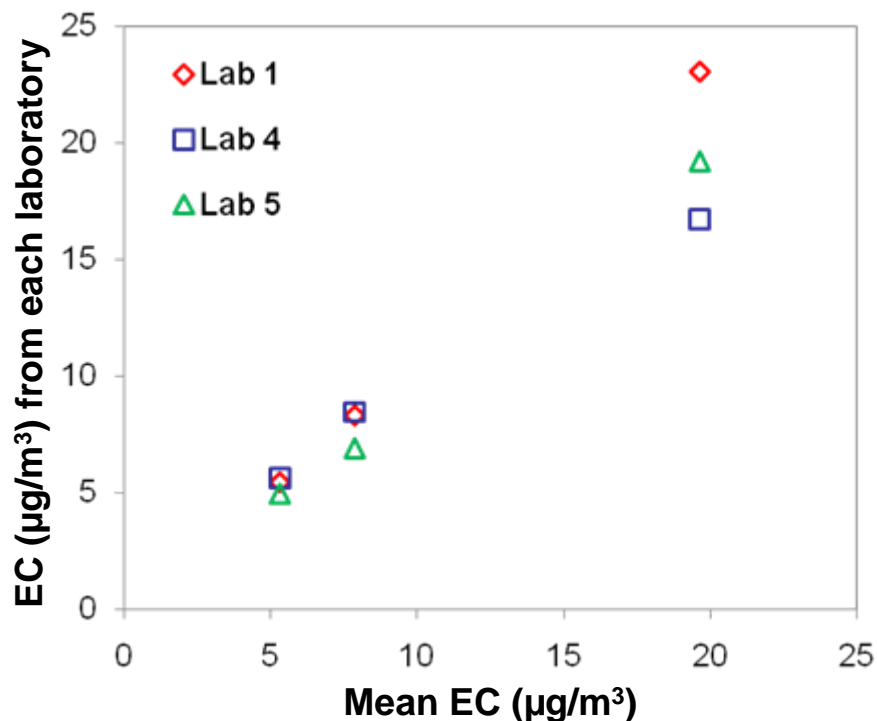
The French Ministry of Environment for air quality policy

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:



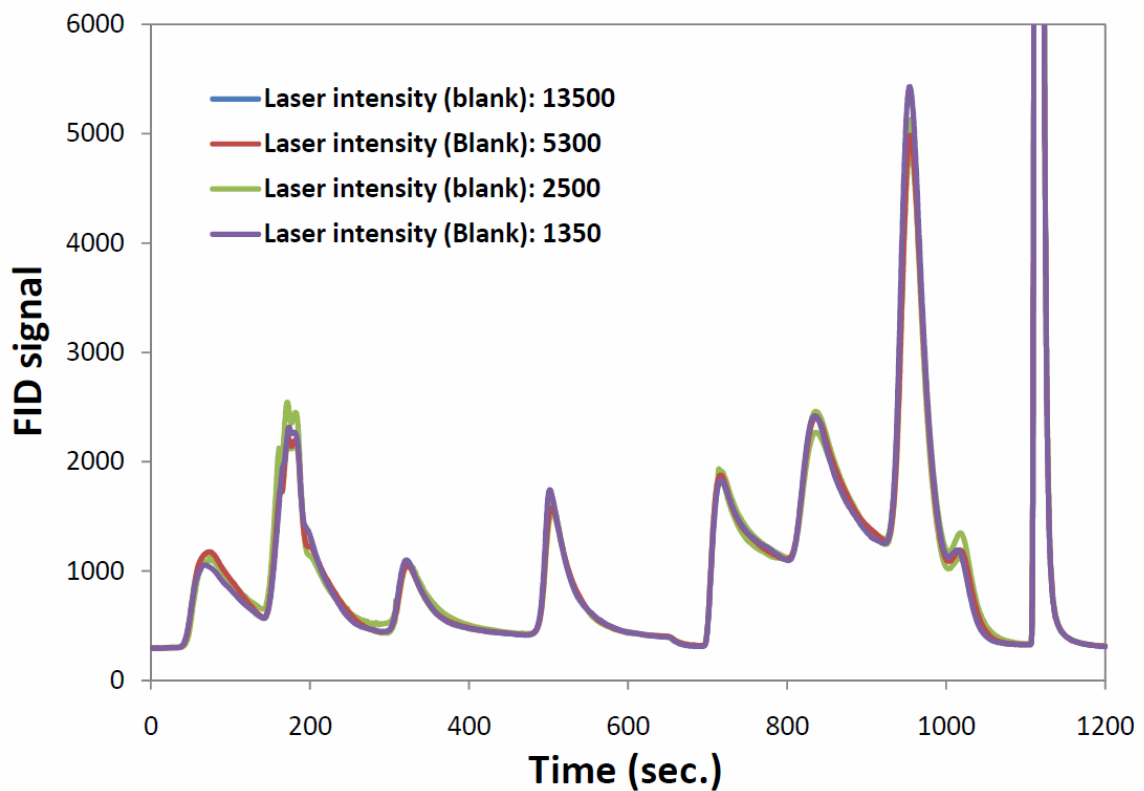
⇒ The higher the EC content, the worse the inter-laboratory reproducibility
Some more studies needed to decide on a max. EC level

On the influence of laser signal

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

Example, Revin (rural background), PM₁₀, January 2011:

No influence on FID trends

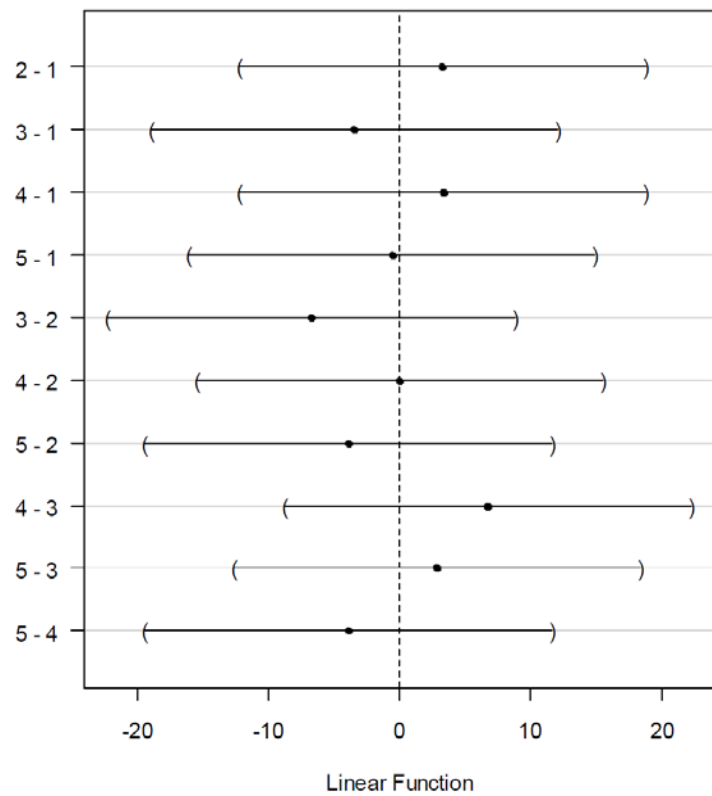


Influence on the OC/EC split point

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

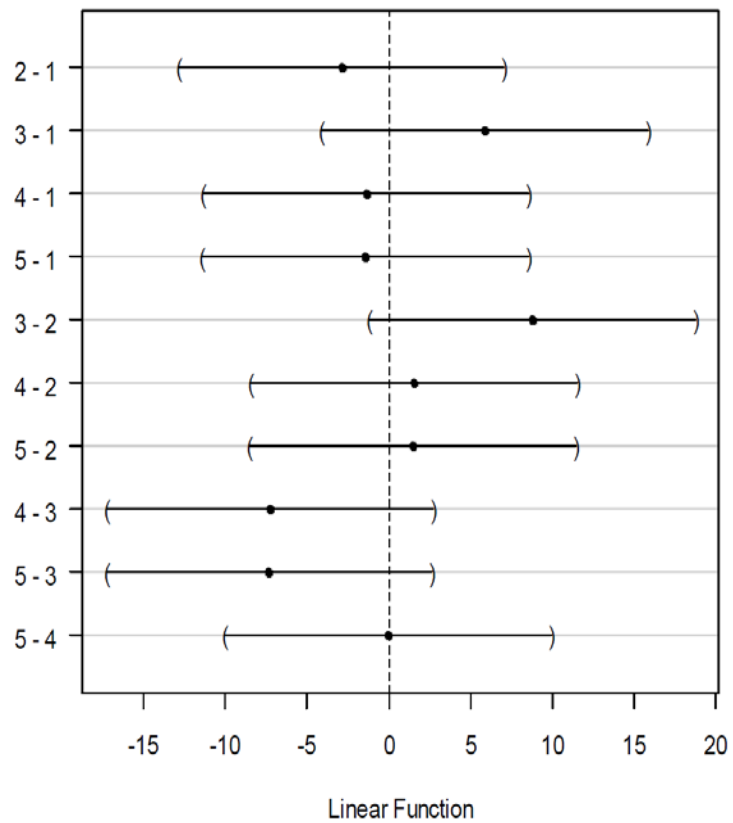
95% family-wise confidence level

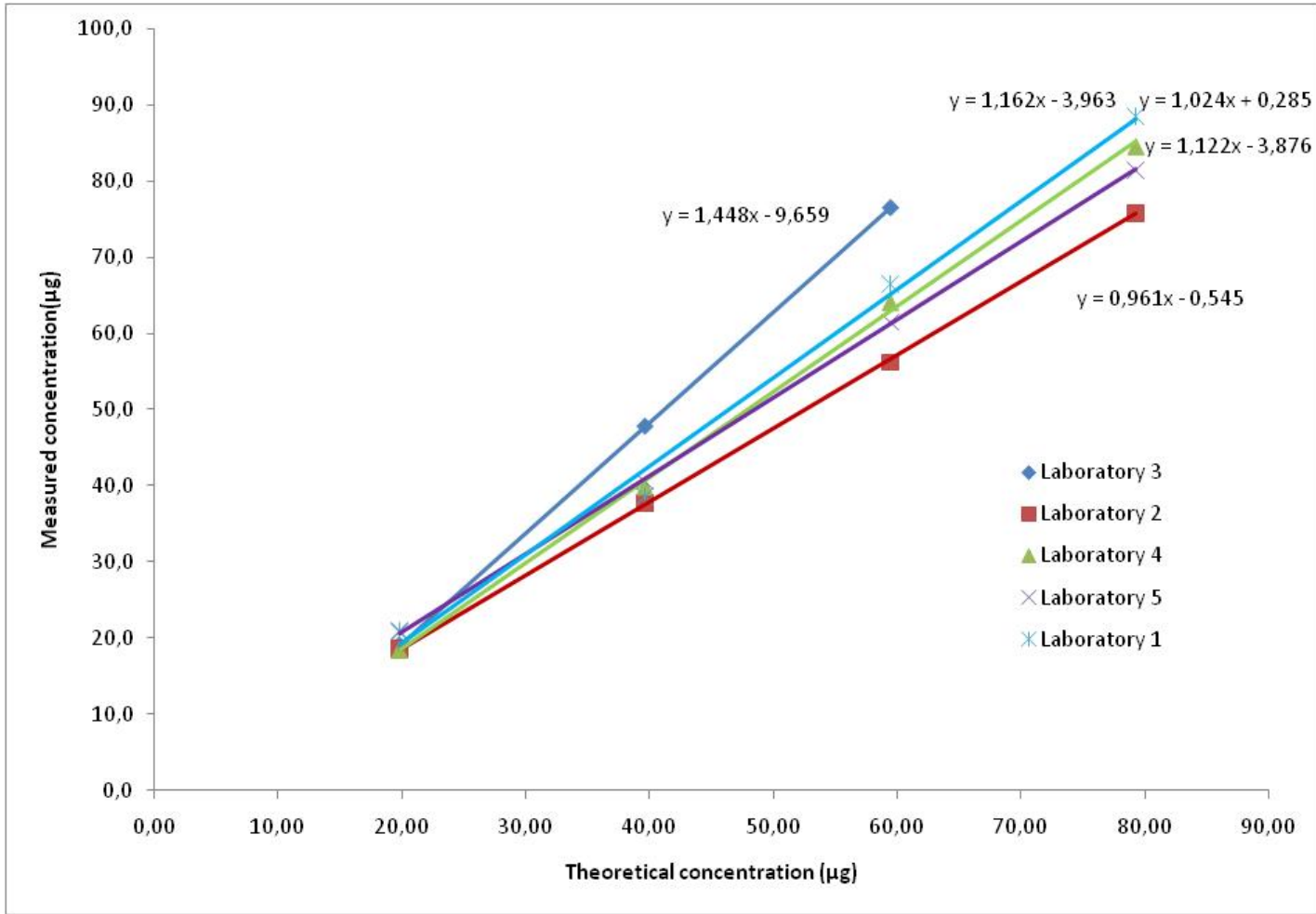
OC

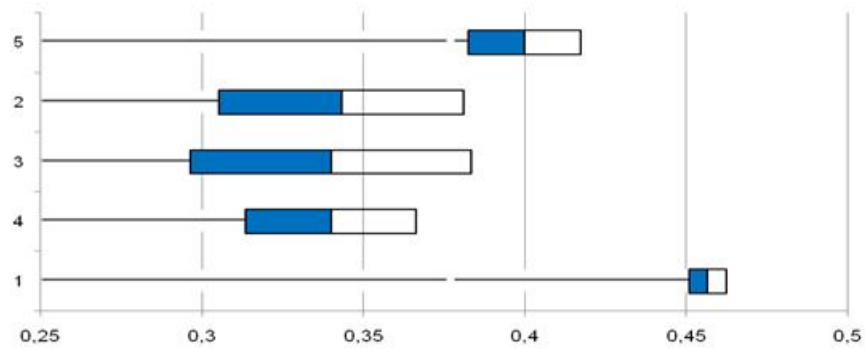
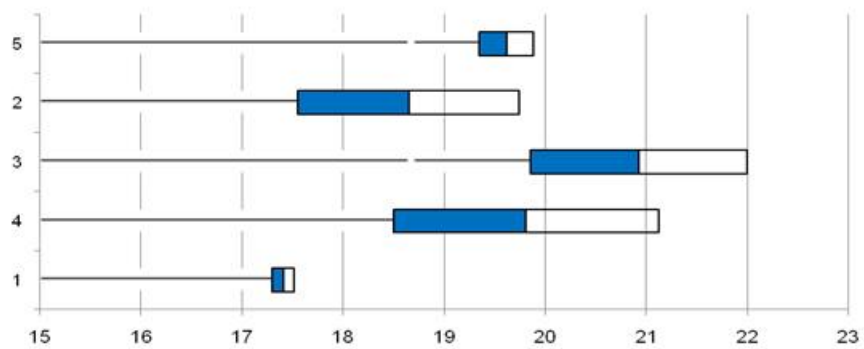


95% family-wise confidence level

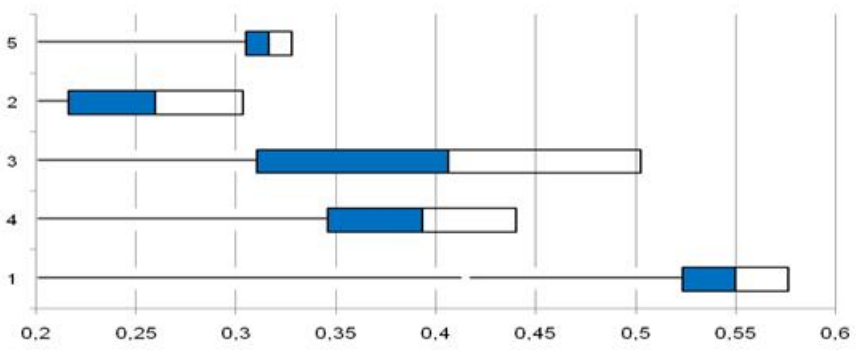
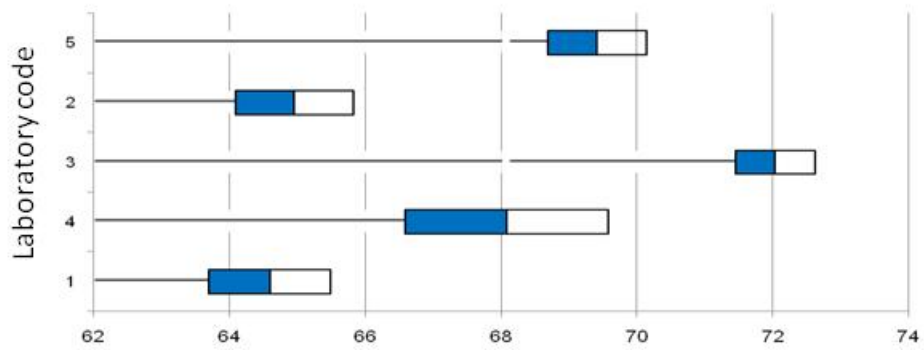
EC



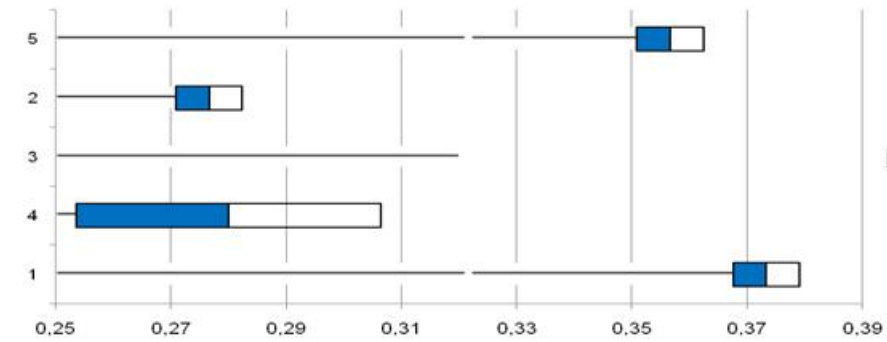
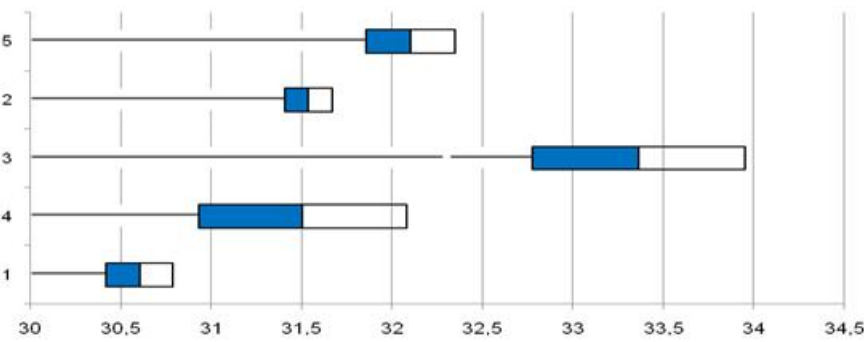




N1



N2



N3

Mean TC \pm 3 SD ($\mu\text{g cm}^{-2}$)

Mean EC/OC \pm 3 SD

