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EUR – Scientific and Technical Research series – ISSN 1018-5593,
ISBN 978-92-79-11294-2, DOI 10.2788/34791

ECN-O--09-042 November 2009

JRC Scientific and Technical Reports

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Report of the preparatory workshop for a future standard measurement method

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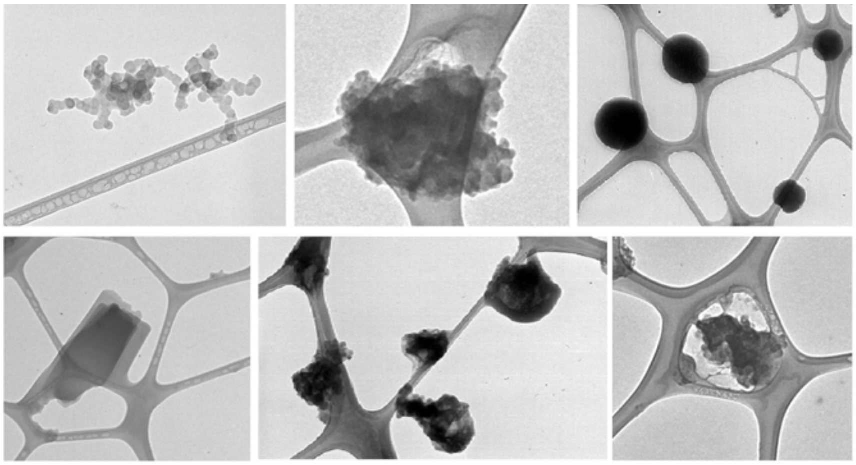

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EUR 23992 EN - 2009

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European Commission
Joint Research Centre
Institute for Environment and Sustainability

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JRC 54045

EUR 23992 EN
ISBN 978-92-79-11294-2
ISSN 1018-5593
DOI 10.2788/34791

Luxembourg: Office for Official Publications of the European Communities

Printed in Italy

Table of contents

1 Foreword

The EC/OC Workshop, a preparatory workshop for the future standard measurement method, was held in Ispra, Italy on 10th and 11th February 2008. More than 70 participants from 20 countries took part in this workshop and contributed to the discussion related to the main tasks:

- giving the general background on determination and quantification of elemental and organic carbon (EC + OC),
- collecting information on available measurement standards in Europe and worldwide,
- presenting and exchanging experiences in Europe related to the measurement of EC and OC,
- and discussing recommendation to be taken into account for the future measurement method.

The presentations on the first day covered all basic scientific and measurement technique relevant topics ranging from reference materials, discussion of optical and thermally based measurement methods, needs and design of round robin tests to assess uncertainties and reproducibility, artefacts during sampling and analysis, and their application at regional background sites within EMEP and EUSAAR.

The focus of the second day was more on national contributions and experiences which also covered a huge range of relevant information such as maintenance, reliability, temperature profiles, optical methods and the issue of brown carbon.

The organizers really thank all presenters but also all participants for their extremely valuable contributions to the success of this work shop which really helps to get a good kick-off for the standardisation work needed to be done.

Yours

Annette Borowiak and Thomas Kuhlbusch

Summaries of the Presentations

2.1 Introduction and Background to Measurement Techniques

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Introduction

Elemental and organic carbon (EC & OC) are two important components of airborne particulate matter. The importance is derived from their mass share of e.g. PM 10 and PM2.5, their property to absorb (EC) or scatter (EC and OC) light and their possible interference with human health. The latter point was the reason why the requirement of EC and OC measurements of PM was implemented for regional background stations in the new Air Quality Directive of the EU in 2008. The paper in combination with the slides of the presentation is intended to give a general background needed for the implementation of a WG for the standardisation of EC and OC measurements in PM in Europe.

What is EC and OC? Where does it come from?

In his seminal book "Black Carbon in the Environment" Goldberg (1985) points out:
There is no clear definition of black carbon. It often is defined by scientists on the basis of their techniques of isolation and measurement. Despite the highly variable nature of black carbon we may describe it as a combustion derived carbon fraction of black color.

This statement, even though stemming from 1985, is still valid. It also has to be noted that Goldberg uses the term Black Carbon (BC) implying optical properties of this carbon fraction while other terms used are Elemental Carbon (EC), implying chemical purity like in graphite, or soot, some kind of incompletely combusted organic matter.

The lack of a clear definition and terminology leads to the current discussion and partial confusion on 'elemental carbon', the term used here. This discussion on EC is directly linked to organic carbon since for simplicity OC is generally defined as the difference between total carbon and the sum of elemental and inorganic carbon (EC + IC):

OC = TC – (EC + IC)

Nevertheless, some general standard methods and protocols exist (e.g. VDI, US EPA, EMEP, EUSAAR). Their intercomparability is currently at least debatable and may in some cases be poor, based on the different basic principles used for the differentiation of EC and OC. Since we agree with the statement by Goldberg (1985) that EC "is defined by scientists on the basis of their techniques of isolation and measurement, definition may be based on:

- the thermal stability of EC,
- the chemical nature of EC,
- the basic structure of EC,
- the optical properties of EC.

Sources of EC are generally any incomplete combustion processes either of anthropogenic or natural origin. This includes emission from e.g. diesel engines, gas burners, coal fired power plants, domestic heating by e.g. wood combustion, or vegetation fires. This list can be extended, especially if "blackness" is used for the definition of EC, to degradation products of organic matter and vegetation fire residues.

Airborne organic particulate matter may be derived from direct, primary emission sources as well as from gaseous precursors while EC can only originate from primary emission. Direct particulate OC (POC) emission may be from incomplete combustion, (re)suspension of biological particles like spores, fungi, plant debris or abrasion products from e. g. tires and plastics. Similarly, anthropogenic and natural emissions also lead to particulate OC by the release of precursors (volatile organic carbon, VOC) and their subsequent conversion to POC. Sources here are e.g. incomplete combustion (diesel, vegetation fires etc.), biogenic emission (isoprenes etc.) and VOC from industry (refineries, dry cleaners etc.).

Why do we want to measure EC and OC?

The main reasons for the determination of airborne elemental and organic carbon are based on the possible health and climatic implications. Elemental carbon is one of the few aerosol components with strong light absorbing properties, while OC and other aerosol constituents mainly scatter light. It has to be noted that the ratio of light scattering to extinction determines the "particle albedo". The particle single scattering albedo linked with the atmospheric PM load and the surface albedo determines whether the aerosol leads to cooling or warming of the atmosphere.

The other important implication of EC and OC are their possible implication on human health. This also is the background of why the measurement obligation to determine EC and OC was implemented in the new Air Quality Directive and why this workshop was set up. The background to possible health effects by EC and OC is based on several toxicological and epidemiological studies. There is no doubt that EC and OC from e.g. incomplete combustion processes lead to negative health effects but the mechanisms on how EC and OC interact with humans and the quantitative link to health effects is still not clear. Does EC from diesel, gasoline, gas and vegetation fires have the same exposure – response ratio?

How can it be measured? What are the main principles?

Measurement methods for OC and EC must be based on their unique properties in comparison to the general matrix, here PM. Carbon in PM which can be determined by the measurement of e.g. CO_2 after thermal treatment and oxidation can be separated into inorganic, organic and elemental carbon. Inorganic carbon (i.e. carbonates) can be quantified by acidification which leads to the release of carbonate carbon as CO_2. The interference in the determination of EC and OC caused by IC depends on the method and has to be dealt with separately.

As already stated above, quantification of OC is mainly based on the difference of TC and EC. Total carbon can only be determined by chemical analysis and is normally done by a total combustion technique (elemental analysis). Comparability exercises of the measurements of total particulate carbon showed generally good agreements within an uncertainty range of ca. 20% while the uncertainties are much higher for the measurements of EC.

Unique properties of EC have to be used for the separation of TC from EC. These properties can be summarized to specific optical properties (light absorption) and thermal stability (low volatility and higher combustion temperature). This already summarizes the two main measurement approaches for EC:

- techniques based on the measurement of light absorption,
- techniques based on the measurement of thermal stability of carbon.

Beside techniques solely based on one of those approaches also combinations of both exist. The presentation gives examples and describes the main techniques currently in use in Europe for the quantification of airborne EC with indication of their advantages and disadvantages.

What are the measurement requirements?

The demands related to the measurement requirements are important to clarify which analysis method best fits the needs and where further tests are needed. The presentation therefore opened up the discussion on this topic. The summary of the results of the ongoing discussion is given in the Resume and recommendation section of this report. The questions raised with respect to standardisation were:

- on-line or off-line method?
- manual or automatic method?
- combined EC and OC method?
- optical or mass based method?
- comparability?
- repeatability?
- calibration / validation?
- artefacts during sampling

2.2 Atmospheric Soot Network: toward to development the EC/OC standard material

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Combustion carbonaceous aerosols, also known as soot, are one of the most important particulate species in the atmosphere because of its impact on climate on a global scale and health on a local scale. However, our current ability to predict environmental and health effects of soot emissions is strongly limited. There is no quantitative estimations of the soot exhaust effect from industry /commercial sources, transport, and domestic heating to compare it with natural sources from biomass burning and forest plumes.

There are many instruments to measure carbonaceous aerosols with various techniques but at the moment there is no standard reference material that can be use to calibrate these instruments. Therefore the uncertainty in measured combustion aerosols is estimated to be no better than ± 30-50% or even higher. At the moment, the users of these instruments rely upon the nominal calibrations provided by the manufacturer but that have not been commonly accepted. Lack of BC material for calibration instruments leads that many instruments in different laboratories are calibrated by different materials producing various results. Therefore, the technical challenge presently is to produce reference material of known composition and to be able to deliver it in a form that can be easily used in any of the various instruments that measure this quantity.

Combustion carbonaceous aerosols consist of a varying mixture of organic carbon and elemental carbon that depends upon the type of combustion and the age of the soot particles. The work of the EU commission on the EC/OC standardisation will soon start. Atmospheric Soot network (ASN) recommends a further task has to be considered, which is the development of standard material for the calibration of the standard EC/OC measurement method. The objective of this task proposes the manufacturing and testing reference material of precise elemental and organic carbon content for the purpose of calibrating instruments that measure soot for application air quality monitoring. There are currently no methods for producing soot particles of known characteristics, i.e. size, surface area, and composition. Hence, the development of atmospheric representative and accessible soot materials with reproducible “programmable” characteristics will ensure long-term intra and inter-laboratory data quality leading to a great progress by the entire environmental community in the measurement and monitoring soot aerosols.

ASN proposes to develop a Set of reference materials including graphitized soot as EC standard and OC tailored materials as EC/OC standards. They should be tested by many techniques for deriving soot mass concentrations, light absorption and EC/OC separation. The principle tasks to be performed are: 1) specification of characteristics for soot from various combustion sources, 2) manufacturer of test reference materials that meet the specifications, 3) development of soot delivery system, 4) round-robin testing of reference materials with instrumentation, 5) presentation of test results to the EC/OC standardisation commission.

To approach the objectives of CEN 264 activity ASN recommends the organization of the specially-oriented workshop on TC/EC/OC standards selection and preparation, which could support the commission on the EC/OC standardisation for prescribing the appropriate standards and intercomparison tests concerning the calibration technique of the standard EC/OC method and for potential equivalence testing.

The task of TC/EC/OC Reference Material preparatory workshop would be:
1. Presentation and identification of potential materials for TC/EC/OC testing and standardization (main requirements for standard materials),
2. Discussion of ways for preparing reference quartz fiber filters,
3. Arrangement of the intercomparison compaing on proposed standard materials using the EC/OC and light absorption measurement techniques,
4. Recommendations to the EC/OC standardisation commission.

2.3 Principles of thermal methods for the detection and differentiation of EC and OC, intercomparison results

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1. Introduction

Carbonaceous aerosols consist of organic carbon (OC), elemental carbon (EC) or black carbon (BC), and inorganic carbonate carbon (CC). EC and BC are used to denote roughly the same refractory and light-absorbing fraction of the carbonaceous matter; when this fraction is determined with a thermal method it is normally termed EC and when it is measured with an optical method it is normally denoted as BC. The distinction between OC and EC or BC is, however, not sharp; from a thermochemical point of view there is a transition region of refractory organic carbon in between OC and EC and from an optical viewpoint there is coloured organic carbon (or brown carbon) in between OC and BC [Pöschl, 2003]. Depending on the method of analysis or the operational parameters, different amounts of carbon from refractory and coloured organic compounds are included in OC and EC or BC. The distinction between OC and EC or BC is generally simpler for urban aerosol samples than for rural samples and it is especially difficult for aerosol samples that are impacted by biomass burning (e.g., wood smoke). However, also for urban samples, different methods can provide substantial differences for the EC (or BC) fraction of the carbonaceous matter, as was for example demonstrated in the aerosol carbon round robin exercise that was organised by TU Vienna 10 years ago [Schmid et al., 2001].

2. Thermal analysis of atmospheric particulate matter for OC and EC

For thermal analysis of atmospheric particulate matter (PM) one normally collects the aerosol with a filter sampler using quartz fibre filters or occasionally with a cascade impactor with aluminium foils or quartz fibre filters as impaction surfaces and the thermal analysis of the samples is carried out in the laboratory. However, there are also instruments such as the Rupprecht & Patashnick Series 5400 Aerosol Carbon Particulate Monitor (now not sold anymore) or the Sunset Laboratory Carbon Aerosol Analysis Field Instrument, which perform thermal analyses of aerosols for OC and EC in situ and in real time. The principles used in these thermal in-situ instruments are the same as in the thermal laboratory instruments and no further discussion of the in-situ instruments will be given here.

The thermal methods used in the laboratory instruments can be classified in three categories, i.e., (1) simple thermal methods, (2) two-step thermal methods, and (3) thermal-optical methods. Methods of all three categories were applied in the above-mentioned aerosol carbon round robin exercise of Schmid et al. [2001] and their principles and literature references for them are given in this publication. Here, one or two examples are given for each category of methods and the principles involved are briefly described.

As indicated above, carbonaceous aerosols contain in addition to OC and EC, also CC, so that total carbon (TC) = OC+EC+CC. Unless the CC is removed prior to the thermal analysis, it is generally included in either the OC or the EC measurement. For fine aerosols (e.g., PM2.5) CC is often small or negligible, but for PM10 and especially Total Suspended Particulate (TSP), it may be substantial.

2.1. Simple thermal methods

An example of a simple thermal method is that developed at TU Vienna [Puxbaum, 1979]. The sample (or a fraction of it) is subjected to a constantly increasing temperature (20°C min^{-1}) up to a maximum temperature of 800°C in a pure O_2 stream. The evolving carbonaceous vapours are converted into CO_2 by a MnO_2 catalyst (held at 700°C) and the CO_2 is measured with a non-dispersive infrared (NDIR) detector. The last peak(s) in the thermogram (thus at high temperature) is (are) considered to represent EC, whereas the earlier peaks are considered as OC. The quantification is done by determining the area under the peaks and the instrument is calibrated with samples of known amounts of carbon (e.g., sucrose).

Besides NDIR, also other detection methods can be used for measuring the CO_2 in simple thermal methods or in the other thermal methods. The CO_2 can be measured by coulometric titration [Cachier et al., 1989] or it can be converted into CH_4 and the latter can be measured with a flame ionisation detector (FID).

A first limitation of the simple thermal methods is that some of the organic matter may be converted into pyrolytic carbon (PC) by pyrolysis or charring and like the “real” EC only be converted into vapour at higher temperature and then erroneously be counted as EC. Incidentally, this limitation applies also to the two-step thermal methods. The artifact formation of PC is smaller in an oxidising atmosphere (O_2) than in an inert gas (He, N_2, Ar). A second limitation is that the presence of inorganic cations, such as K^+ or Na^+ (which are important components in biomass burning samples), has a serious influence on the thermal evolution of the carbonaceous vapours. As a result, the peaks come faster in the thermogram and the distinction of EC from OC may be quite difficult to make. In order to improve the determination of EC, the sample is often subjected to an aqueous extraction (which removes the water-soluble OC and the cations) prior to the thermal analysis.

2.2. Two-step thermal methods

A first example of a two-step thermal method is that developed by Cachier et al. [1989]. In this method, the samples are first subjected to a pretreatment in HCl vapour to remove the inorganic carbonates. For the measurement of EC, one part of the sample then subjected to a thermal pretreatment step (precombustion at 340°C for 2 h) in order to remove the organic component. The remaining EC is determined by combustion at 1100°C and coulometric titration of the evolved CO_2 in a carbon analyzer (Ströhlein Coulomat 702C). For another part of the sample, the combustion/titration is performed without any thermal pretreatment, so that the content of TC is obtained. The difference (TC - EC) then yields OC.

Another example is the VDI-2 method, as used at the Leibniz Institute for Tropospheric Research (IfT) in Leipzig, Germany [Neusüß et al., 2002; Plewka et al., 2004]. This method is a two-step thermographic method, which uses a commercial carbon analyser C-mat 5500 (Ströhlein, Germany); the analyser consists of a free programmable combustion furnace (IR 05) followed by a resistance oven (D03 GTE) holding the CuO catalyst at 850°C (to convert carbon quantitatively to CO_2) and a NDIR detector measuring the IR absorption of the CO_2 formed. In the first step, the sample is heated at 590°C (or 650°C) in nitrogen carrier gas for OC volatilisation and in the second step, EC is combusted at 650°C in an oxygen atmosphere. In between the two steps, the IR furnace is cooled down to 50°C to avoid EC losses during flushing with oxygen.

2.3. Thermal-optical methods

Examples of thermal-optical methods are those of Desert Research Institute (DRI) [Chow et al., 1993] and of Sunset Laboratory [Birch and Cary, 1996]. Traditionally, DRI makes use of a thermal-optical reflectance (TOR) correction and Sunset Laboratory of a thermal-optical transmission (TOT) correction, but both have now instruments where simultaneous TOR and TOT corrections are possible. Here, we describe the TOT instrument of Sunset Laboratory. A punch of 1.5 or 1.0 cm^2 of the quartz fibre filter sample is placed in the quartz oven of the instrument. In the first phase of the analysis, which takes place in a pure He gas stream, the filter punch is heated in 4 steps up to a temperature of 870°C (or 900°C); the desorbed carbonaceous vapours are catalytically oxidised into CO_2 (by a MnO_2 catalyst held at 870°C); the CO_2 formed is reduced to CH_4 (in a Ni-firebrick methanator, held at 500°C) and the latter is subsequently measured with an FID. Laser light (of 670 nm) is continuously passed through filter punch and the light transmission is continuously measured. During this first phase of the analysis, part of the OC is pyrolysed (charred) with formation of PC, so that the light transmission through the filter punch decreases. At the end of the first phase, the filter punch is slightly cooled. In the second phase, which takes place with a 98%He/2%O_2 mixture as carrier gas, the filter punch is in four (or more) steps further heated to e.g. 900°C and otherwise everything is the same as for the first phase. When the light transmission through the filter punch equals that seen at the beginning of the first phase, the OC/EC split is set; the CO_2 measured in the first phase and during the second phase prior to the split is considered as OC (it includes the PC) and the CO_2 measured after the split is considered as the “real” EC. The total CO_2 measured during the second phase (which represents the sum of PC + “real” EC) corresponds to the EC, which is measured without optical correction [Schmid et al., 2001]. After the end of the second phase, while still in a He/O_2 mixture, a known amount of CH_4 gas is injected through a loop; this serves for internal calibration. An example of a TOT thermogram (without the internal calibration peak) as obtained with the NIOSH protocol is shown in Figure 1.

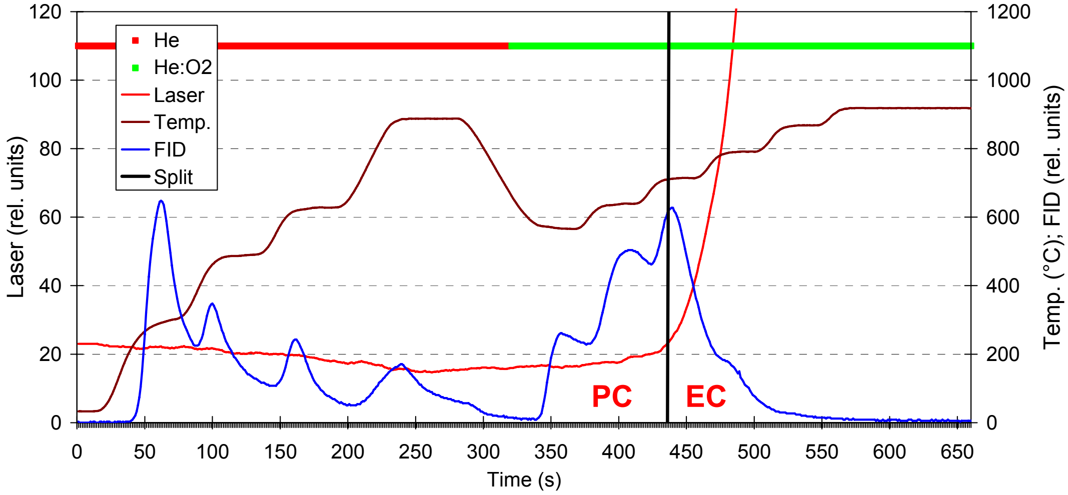

Figure 1. TOT thermogram, obtained with an instrument from Sunset Laboratory and the NIOSH temperature protocol, for an urban PM2.5 quartz fibre filter sample collected at Ghent.

3. Intercomparison results

3.1. Dependence on operational parameters. Intercomparison of four temperature protocols in TOT for five sample sets

At University Gent we have two TOT laboratory instruments from Sunset Laboratory. Our instrument A was acquired in December 1997 and instrument B in September 2002. It was examined to what extent the OC, EC, and TC data depend on the temperature protocol and whether the two instruments provide comparable results. This exercise was done for five sample sets and for four different temperature protocols, and each sample of each sample set was analyzed with each instrument and each of the protocols. The sample sets consisted of (1) TSP samples collected during 2003 in Beijing, (2) PM2.5 samples from a 2003 winter campaign in Ghent, (3) TSP samples from southern Austria taken in 1999, (4) PM2.5 samples from a 2003 summer campaign at K-puszta, Hungary, and (5) PM2.5 samples from a pasture site in Amazonia taken in 2002 during the dry (biomass burning) season. All samples had been collected on quartz fibre filters (pre-fired Pall filters in the case of the PM2.5 samples). The four analysis temperature programs were (1) our "standard" program (ST), which is the program that we used in the aerosol carbon round robin [Schmid et al., 2001], (2) a program called NIOSH2 (N2), which is very similar to the ACE-Asia base case program of Schauer et al. [2003] and identical to the NIOSH program used for Figure 1, (3) the EUSAAR 2 (E2) protocol, which has been developed within the EU project "European Supersites for Atmospheric Aerosol Research" (EUSAAR), and (4) a program called ACE-Asia alternate3 (A3), which is identical to the one used by Schauer et al. [2003] and is a proxy for the DRI IMPROVE program. The maximum temperatures during the first stage (in pure He) of the analysis for the four programs are 900, 870, 650, and 550°C, respectively, and the durations of the four programs, including the CH_4 internal calibration phase, are 620, 775, 1170, and 780 s, respectively. The ranges for TC (in μg/cm^2) and for the EC/TC ratio, as obtained with program ST and instrument B for each sample set, are given in Table 1; also the number of samples within each set is indicated in the Table.

Table 1. Ranges for TC and for EC/TC, obtained with our program ST, and mean ratios (and assoc. std. dev.) to program ST for EC/TC for programs N2, E2, and A3 for five series of aerosol filter samples and instrument B. The ratios to ST for EC/TC were calculated per sample and then averaged over all samples of the same series.

Sample series	no. of samples	Range TC (μg/cm^2)	Range EC/TC	Mean ratios to program ST for EC/TC N2	 E2	 A3
Beijing	5	71 –240	0.15 – 0.24	1.15± 0.05	1.72± 0.20	2.02± 0.45
Ghent	26	15 –110	0.084– 0.35	1.04± 0.14	1.70± 0.41	1.72± 0.26
Austria	16	18 – 40	0.076– 0.13		1.21± 0.25	1.53± 0.24
K-puszta	5	16 – 25	0.038– 0.056	1.38± 0.02	1.51± 0.15	1.92± 0.15
Amazon	5	57 – 98	0.021– 0.031	1.35± 0.07	2.67± 0.43	2.90± 0.31

It turned out that the TC data obtained with our two instruments agreed well (typically within better than 10%) and that the various protocols provided similar TC data; one major exception existed for our instrument A in combination with protocol E2, the TC data of this combination were substantially lower (by up to 40%) than those obtained with E2 and our instrument B or with both instruments and the other three programs. It was noted that, for actual aerosol filter samples, the time lag between the last peak in the thermogram and the CH_4 internal calibration peak was substantially shorter for E2 than for the other three protocols and that the valley in between that last peak and the CH_4 internal calibration peak did not come down deep enough for our instrument A. The calculation program that is provided by Sunset Laboratory calculates the area under the peaks in the thermogram by subtracting a linear sloped background (baseline). This background is obtained from a number of channels at the start of the thermogram and a number of channels before the CH_4 internal calibration peak. If the valley before the latter peak is not deep enough, as was the case for E2 with our instrument A, then the background is overestimated and TC is underestimated. We obtained a modified calculation program from Sunset Laboratory, whereby there is an option to keep the background linear and constant and to estimate it from the initial channels in the thermogram. By performing the calculations with this option and the modified program, correct TC data were obtained for E2 and our instrument A. It is clear that the last temperature step in E2 is not kept on long enough. It is suggested to extend the duration of this step by at least 50 s, and possibly by 100 s in order to avoid problems. This extension will unfortunately make that E2 will become even longer; it is now already by far the longest of the four protocols.

The EC/TC ratios obtained with the four protocols were compared with each other. This comparison was done in terms of ratios to the EC/TC ratios obtained with ST. The ratios (of EC/TC ratios) were calculated on a sample by sample basis and then averaged over all samples of same sample set (and separately for each of the two instruments). The results obtained with instrument B are included in Table 1. It is clear that the lowest EC/TC ratios were obtained with ST and that A3 provided the highest ratios. There was clearly an inverse relationship between the EC/TC ratio and the maximum temperature during the first phase of the analysis. This is illustrated in Figure 2, which shows for each of the five sample sets the average EC/TC ratio as a function of that maximum temperature. It is clear from both Table 1 and Figure 2 that the lowest difference in EC/TC ratios between the four protocols is obtained for the rural samples from Austria. The largest difference exists for the biomass burning impacted samples from Amazonia. The urban samples from Beijing and Ghent and the samples from K-puszta show a behaviour which is intermediate between that of the Austrian and Amazonian samples.

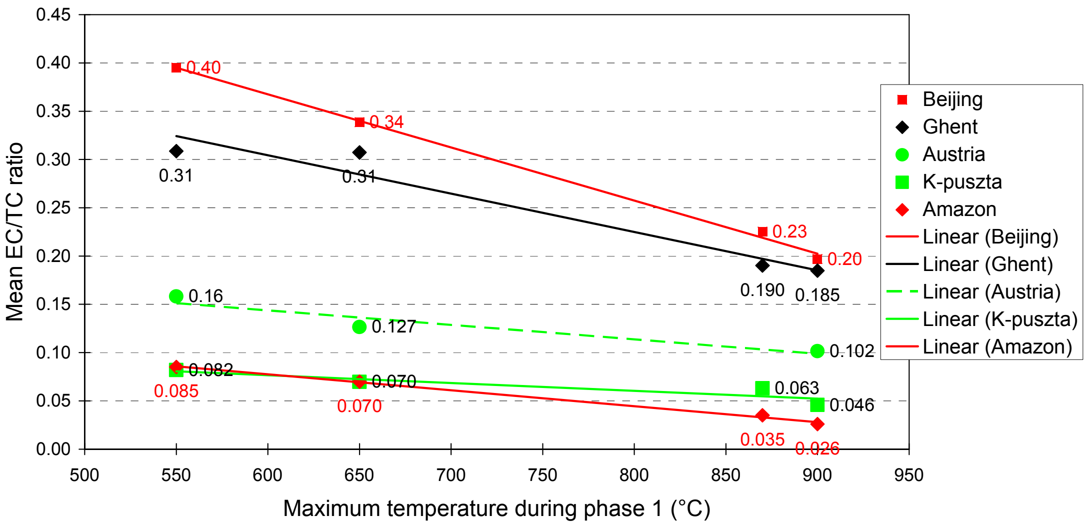

Figure 2. Average EC/TC ratio as a function of maximum temperature in the first phase (in pure He) of the analysis protocol. The average EC/TC ratios are indicated by the symbols and are also given in numeric form. The four analysis protocols from left to right are A3, E2, N2 and ST. All data were obtained with our instrument B.

It should be noted that the EC/TC ratio does not only depend on the analysis temperature protocol, but also on the type of optical correction used. For the same protocol, different EC/TC ratios are obtained with TOR and TOT; there is a tendency for larger EC/TC ratios in TOR than in TOT.

3.2. Intercomparison of EC and BC results from thermal and optical methods for a 2006 winter campaign in Vienna

Several thermal and optical methods for measuring EC and BC were compared during a 2006 winter campaign that took place from 7 February to 15 March on a rooftop of the University of Vienna. The results of this study are described in detail by Reisinger et al. [2008]. Here, only a brief presentation is given. Three optical methods for measuring BC and four thermal methods for measuring EC were used in the study; the optical methods were a light transmission method (LTM), the multi-angle absorption photometer (MAAP), and the integrating sphere (IS) method; the thermal methods were TOM-TU, the two-step method of Cachier et al. [1989], and TOT with the N2 and A3 protocols. TOM-TU is a modification of the simple thermal method described in section 2.1; it was extended with an optical transmission correction. The samples for the thermal methods were 24-hour PM10 quartz fibre filter samples, with filter change nominally at 13:00 UTC. On certain days, i.e., for the 4-day period from 23 to 27 February, very substantial differences were found between the EC data of the four thermal methods, with TOM-TU and the two-step Cachier method providing much larger data than A3 and N2. The 4-day period turned out to be a cold period in which 24-h averaged temperatures dropped to -4°C and in which wood burning for space heating was prominent in the surroundings of Vienna. By adapting the IS method so that it could differentiate between BC-brown, which is ascribed to the wood burning, and BC-black, which originates mainly from diesel fuel, it was found that the BC-brown levels were indeed enhanced in the 4-day period. The BC-black levels for these 4 days agreed well with the EC data obtained by A3.

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2.4 Artefacts in the sampling of OC

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INTRODUCTION

OC/EC is (typically) sampled with quartz fibre filters. There are two types of artefacts associated with this sampling:

1) The filters adsorb of volatile OC-components; the so-called positive artefact
2) Collected semi-volatile components evaporate; a "negative" artefact.

Adsorption and evaporation proceed at the same time because different OC-components are involved. A comprehensive review of the artefacts is provided by Turpin et al. (2000). As an introduction I recommend a presentation from which I took a number of sheets: ***gonzalo.er.anl.gov/ACP/2002presentations/Novakov02.pdf***

There are sophisticated ways to deal with the artefacts that e will discuss below. These show that the adsorption artefact is the most important. It is also seen that the amount of artefact OC does not follow the volume of air sampled. In other words, the relative contribution of artefact OC decreases with increasing sampling volume.

EN-12341 requires the use of quartz fibre filters for the determination of PM10-mass. Thus a large number of have been taken in the EU. The OC-artefact must have lead to an artificial increase in the amount of PM10. However, we could not find documentation on the importance of this artefact.

Field blanks

A minimum value for the adsorption artefact is found in the values in the so-called field blanks. These are filters that are put in the sample holders without being loaded. The filters take up OC via diffusion, that is, by just being passively exposed to ambient air. The networks in the US report field blanks that are large in comparison with the actual OC-data. Only some scattered data are available in Europe. We just finished a study in which sampling was performed with automated KFG-samplers. 150 field blanks were taken. The average OC-value of these field blanks corresponded to a concentration of **1.3** ug m-3.

Lot blanks

Filters received from the manufacturer often contain OC and they are therefore cleaned in scientific studies. This is done by pre-firing. Whatman-QMA filters are pre-fired in the factory. We analysed OC in a large number of such Whatman-QMA. These "lot"-blanks were unsealed only shortly before analysis. Filters from the top of a stack contained OC values higher than that of the average field blank. Further down the values rapidly decreased to often insignificant values.

ASSESSMENT AND AVOIDANCE OF THE ARTEFACTS

Lot-blanks should be tested before use. Filters may have to be pre-fired; cooling in a wet atmosphere pacifies the surface (advice of Puxbaum). A first indication of the magnitude of the sampling artefact is provided by the field blank.

For an assessment and quantification of the sampling artefacts there are several methods in use for which we also provide the name of the respective institute / scientist using these:

1. **Filter-pack** / tandem filters / 2 filters in series; the amount of OC in the 2d filter is a first measure for the sampling artefact in the first filter (*EMEP*, *Sillanpää*).
2. A gas-**denuder** to remove the adsorptive volatile OC (*Maenhaut / Viana*).
3. **Impregnation** of the second filter to collect the semi-volatile OC that evaporates from the first filter, to correct for the negative artefact (*Putaud*).

ad 1. **Teflon-quartz** filter-pack; in a parallel sampling line. The Teflon filter does not adsorb OC; the OC on the quartz back-up filter is a (better) measure for the adsorption artefact (*Vecchi*)

SUGGESTION FOR ISSUES TO BE ADDRESSED IN THE WORK-GROUP

1. **Filter type**: EN-14907 allows glass fibre; OC/EC analysis is possible
2. **Combination of mass-determination** and OC/EC-analysis for the same (quartz) filter

3. **Brand** of quartz-filter; there are different brands with possibly different blank characteristics
4. **Amount of air drawn** through the filters. This affects the ratio of artefact OC and real OC
5. **Filter-packs** to correct for the artefacts, specifically for source apportionment
6. **Denuders** to remove volatile OC
7. **Pre-firing** and, if so, what protocol.

Addendum: automated on-line instruments

Artefact formation can be easily checked in automated instruments. This is done by periodically placing an absolute filter in the sampling line. Own experience was not encouraging in this respect. The ACPM's (R&P 5400) tested had a large and irreproducible artefact.

Artefacts with filters can be avoided by collecting PM differently. There is an instrument for artefact-free sampling of the (semi-volatile) nitrate. The collection occurs via condensation of steam. The nitrate is analysed in the collected condense-water. In this water also OC can be measured.

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2.5 Towards a Standardised Method for Measuring Organic and Elemental Carbon within the EUSAAR network

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The current European Directive on ambient air quality (2008/50/EC) states that measurements shall be made at rural background locations for providing information on the chemical speciation of fine particulate matter ($PM_{2.5}$). Carbonaceous matter accounts for 45 ± 20 % of $PM_{2.5}$ (ref.?) across Europe. A reference method for monitoring this important PM constituent is however lacking. EUSAAR aims at improving the quality of the measurements of non-regulated aerosol properties of interest to air pollution and climate change issues. The analytical protocol for carbonaceous PM "EUSAAR_2" copes with a series of requirements that a reference method should meet, including:

1- A robust determination of the total carbon (TC) concentration.

TC can directly be determined using thermal methods: PM samples collected on e.g. quartz fiber filters are exposed to increasing temperature (up to 850°C) so that carbonaceous species are all volatilized and/or oxidized to CO_2, which is directly or indirectly detected. The analytical protocol EUSAAR_2 includes the determination of TC through a straightforward calibration using gases and solutions containing inorganic or organic carbon.

2- A pragmatic speciation of TC.

Atmospheric carbonaceous PM consists of hundreds of different molecules. Labor-intensive combinations of the most advanced analytical techniques can resolve and quantify up to ca. 30% of the TC mass. These techniques are therefore not suitable for monitoring. However, it is important to go for TC speciation, particularly to distinguish between elemental carbon (EC), directly emitted in the particulate form by combustion processes, and organic carbon (OC), that arises from both natural and anthropogenic [primary and secondary] sources. However, it is difficult to make a clear distinction between highly refractory organic molecules and pure EC.

Thermal analytical techniques split TC fractions according to their volatility. In an inert atmosphere (step 1), just OC volatilizes. EC is combusted to CO_2 during step 2 in an oxidizing atmosphere. The highest temperature reached during step 1 is critical. If it is too low (550°C like in the IMPROVE protocol), a fraction of OC (up to 40%) does not evolve during step 1 and could be detected as EC. If it is too high (850°C like in the NIOSH protocol), as much as 21.2±4.4% of EC could be combusted during step 1 and be detected as OC. The compromise (650°C) chosen in the EUSAAR_2 protocol ensures that a maximum of 2.5±2.4% of EC will be combusted during the analytical step 1, and a minimum of 80% of even high molecular mass organic molecules (humic-like substances) are volatilised or charred (see point 3) during step 1.

3- A correction for charring

Instead of volatilizing, some organic molecules polymerize and form a highly refractory black species during temperature ramps (charring). This pyrolitic carbon (PC) would be detected as EC. Not correcting for charring can lead to analytical errors in the determination of atmospheric EC larger than 400% (EUSAAR_2 intercomp'2007).

Thermal-optical analytical techniques monitor charring by recording the decrease in light transmission and/or reflection through the filter during the analysis. As O_2 is added to the carrier gas, refractory black PC and EC are combusted and light transmission and reflection gradually increase again. When light transmission or reflection reaches the value recorded before the analysis starts, it is considered that all PC formed from OC during the analysis has evolved and that all carbon evolving afterwards is atmospheric EC.

4- A limitation of charring

To discriminate between artificially formed PC and native atmospheric EC, thermal–optical methods assume that one of the following two hypotheses is correct:

(a) PC evolves from the filter before EC during the analysis.
(b) PC has the same specific light absorption cross section (σ) as EC.

However, none of these assumptions always holds: PC and EC have been shown to co-evolve, and PC's σ was found to be generally larger than EC's. Temperature programs should therefore aim at reducing the amount of charring to a minimum. Longer steps at low temperature (120 s @ 200°C, and 150 s @ 300°C) as in the EUSAAR_2 protocol reduce charring by 16% on average compared to e.g. the NIOSH protocol.

5- A low sensitivity of the EC value to the split point position

The transmission or reflection threshold value which is used to split between PC and EC is known with an uncertainty of ca. ±3%. To minimize the effect of this uncertainty on EC determination, the temperature protocol should be such that the amount of carbon evolving at the split point is as little as possible.

The EUSAAR_2 protocol includes three temperature plateaus in the analytical step 2, where the split point occurs, which increases the chance of having a smooth evolution of carbon around the split point. Over 9 samples collected in Ispra (semi-rural site in Italy), an uncertainty of ±3% in the determination of the laser signal threshold translated in an acceptable uncertainty of ±10 % in EC determination.

Conclusion

While alternative methods could be more precise, accurate, and/or rigorous on specific aspects of the determination of OC and EC in atmospheric PM, a thermal-optical method implementing the newly optimized temperature protocol EUSAAR_2 fulfills a series of requirements that makes it highly suitable for the monitoring of OC and EC concentrations in $PM_{2.5}$ in Europe.

A recent intercomparison demonstrated that 5 among 6 EUSAAR partners using this protocol could determine TC and EC/TC with relative errors <17 and 29%, respectively, a fraction of this difference being possibly due to filter heterogeneity. Furthermore, using EUSAAR_2, the amount of PC determined optically (integrating the laser signal) and thermal-optically (integrating the CO_2 signal up to the laser-determined split point) well agree ($R^2 = 0.75$, $n = 224$) for filter loads <25 µg/cm², which guarantees the accuracy of the EC (and therefore OC) determination.

2.6 OC/EC/TC analysis: the Spanish experience

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EC/OC Workshop, February 11th, 2009, Ispra

At present, OC and EC analyses are carried out in Spain at two research institutions:

- ISCIII (National Health Institute) in Madrid, where a TOT Sunset OCEC Analyzer was acquired and runs since May 2006 (using the quartz.par protocol)
- IJA/IDAEA-CSIC (Spanish Research Council) in Barcelona, where a TOT Sunset OCEC Analyzer was acquired and runs since July 2007 (currently using the EUSAAR2.par)

The acquisition of a third TOT Sunset OCEC Analyzer is currently in process at the Huelva University. In addition, numerous TC analysers (CHNS analyzers, etc.) are available in laboratories throughout Spain.

Prior to the use of Sunset instruments for OCEC determination, analyses were carried out at the laboratories of Prof. C. Pio at Aveiro University, Dr. JP. Putaud at JRC Ispra and Prof. W. Maenhaut at Ghent University. At these laboratories and since 2002, samples were run from various Spanish sites in order to obtain preliminary estimations of OC and EC concentrations as well as to assess the influence of sampling artefacts. The results obtained were published in a number of SCI papers (Rodríguez et al., 2007; Viana et al., 2006, 2007).

At IJA/IDAEA-CSIC, on average 1200-1500 samples are currently run per year originating from a large variety of monitoring environments: regional and urban background sites, as well as traffic and industrial hotspots. Therefore, the PM mixtures analysed significantly differ from each other with respect to PM loading and chemical composition. The samples originate from high- and low-volume samplers (with and without denuders), and they are collected on Munktell and Pallflex substrates.

Regarding the daily run of the instrument, since July 2007 the only major incidence registered at the IJA/IDAEA-CSIC lab refers to the combustion oven, given that a progressive increase in the pressure in the combustion oven was observed (PSIG increased from 1 to 3 in 9 months). As shown in Figure 1, this increase is slow at the start but grows exponentially after 3-4 months. Consequently, in our case the oven had to be completely removed and substituted by a new one, and this process was repeated 2 times in 1.5 years.

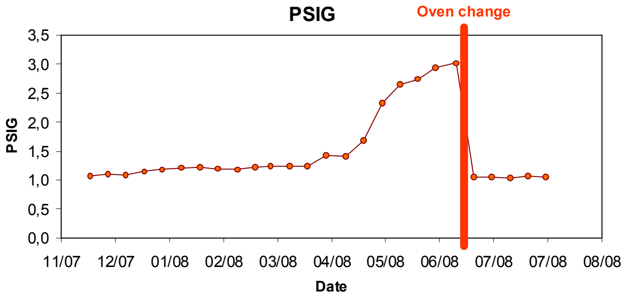

Figure 1. Progressive increase in the pressure in the combustion oven.

Potential causes of this incidence are the type of samples analysed (e.g., samples from a ceramic production area with high % of refractory material), and/or the use of HCl to eliminate carbonate carbon (which seemed to be extremely harmful to the instrument).

Another incidence observed was the increase in the variability of sucrose concentrations if the instrument is not run continuously. The standard deviation of the samples increased from

0.1 µg/µl when the instrument was run continuously, to 0.64 µg/µl after a 15-day analysis gap.

The analytical protocol used by the IJA/IDAEA-CSIC lab was the default Quartz.par from the installation of the instrument until April 2008, when preliminary tests were carried out using EUSAAR2.par. Given the good results obtained with the EUSAAR2.par protocol, evidenced by positive results obtained in 2 round robin exercises, since September 2008 all analyses are performed under the EUSAAR2.par protocol.

The abovementioned tests regarding the EUSAAR2 protocol pursued 3 aims:

1. Comparison between Quartz / NIOSH / EUSAAR2 and repeatability: 1 single PM sample was analysed 3 times with each of the protocols. TC levels obtained were similar for NIOSH and EUSAAR2 and differed slightly from Quartz, and the precision was highest with NIOSH. EC/TC ratios increased from Quartz to NIOSH and EUSAAR2.
2. Comparison between Quartz / EUSAAR2 for different PM mixtures: 5 different types of PM mixtures (episodes) were selected, and a total of 22 samples were analysed. The influence of the PM mixture seemed to be minor on OCEC results, given that EUSAAR2/Quartz ratios for OC did not vary significantly between PM episodes. EC/TC ratios were higher again for EUSAAR2 than for Quartz. The correlation between both methods for OC, EC and TC was high (>0.88).
3. Comparison between Quartz / EUSAAR2 thermograms: the following results were obtained: (a) a clearly better peak separation was observed with EUSAAR2; (b) combustion of light absorbing carbon (LAC) was minimal for both protocols (only detected for 2/11 samples); and (c) results were not optimal for either protocol regarding the split point, as in 7/11 samples for EUSAAR2 and 9/11 samples for Quartz the split point fell in the middle of a peak or close to it, inducing possible inaccuracy in the quantification of EC.

Further research is currently underway to test the performance of EUSAAR2 on urban aerosol mixtures, especially in comparison with the Quartz protocol and under the influence of different PM mixtures.

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2.7 MEASUREMENTOF CARBONACEOUS AEROSOL BY THERMO-OPTICAL METHODS: The Portuguese experience

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Summary

The University of Aveiro has more than 15 years of experience in the measurement of OC and EC by thermo-optical techniques. This presentation describes the evolution of equipment and thermal heating programs and the advantages and limitations of the different alternatives. Several tests were done in order to evaluate the importance of possible interferences in the correct separation between OC and EC, taking into account the pyrolization of OC. Carbonates evolution, the interference during EC/OC measurements and the effect of pre removal with HCl vapours is discussed.

There is a delay between the volatilization of carbon in the filter and the detection of the resulting CO_2 in the NDIR detector. Furthermore during the transport to the detector there is the dispersion of the emitted volatile carbon in the oven, tubing and detector. This delay / dispersion needs to be taken into account to minimize errors in the correct separation between OC and EC.

The variability in the intensity of the laser signal during thermal carbon evolution can be used to assess the optical characteristics of the pyrolysed OC and EC. Measurements show that, in urban aerosol samples, the pyrolitic OC and initial EC have similar optical absorbance characteristics. However, in rural samples, a clear variability in optical absorptivity is observed during the evolution of pyrolised OC and EC, with an initial low absorptivity coefficient value followed by a much higher coefficient during the burning of the last carbon material. This dual character of the pyrolitic OC plus EC may hinder a correct evaluation of EC in these rural samples.

The methodology used at Aveiro to measure OC and EC was tested with NIST standards and intercompared in international tests, showing EC results between those of the IMPROVE and NIOSH protocols, but more similar to the first one.

Fifteen years of aerosol measurements using the same analytical technique permitted the gathering of results that show a constant minimum OC/EC ratio value, along time and space. This is a good indication that the minimum OC/EC ratio in urban areas in winter can be safely used to determine the amount of primary OC from fossil fuel combustion, contributing to the correct source apportionment of the carbonaceous aerosol.

2.8 Measurements of Organic and Elemental Carbon in UK AirQuality Networks

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Analytical Science Team, National Physical Laboratory

This brief summary describes the monitoring of elemental and organic carbon (EC/OC) within UK Networks. It does not cover monitoring made at the EMEP site at Auchencorth Moss (which currently monitors Black Carbon by aethalometry) or short term campaigns.

There are two relevant Networks:

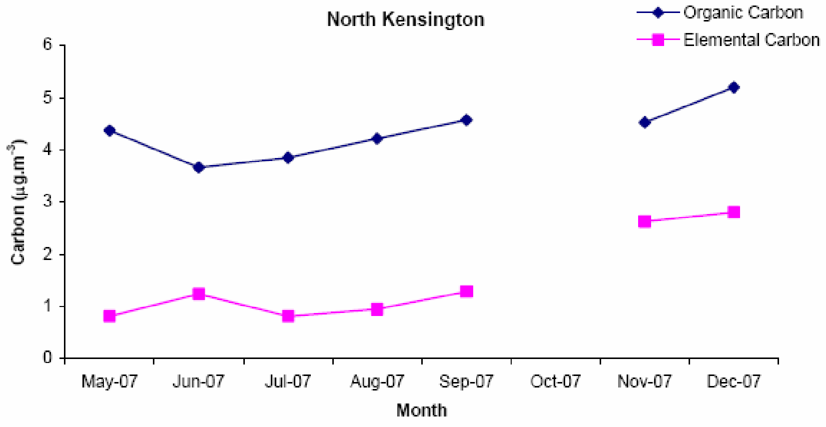
The Particles Network is currently managed and operated by NPL and King's College London. Apart from EC/OC it measures particle number concentration (currently at 4 sites), size distribution (3 sites), sulphate, nitrate and chloride (PM_{10}) daily (3 sites), nitrate ($PM_{2.5}$) hourly (3 sites).

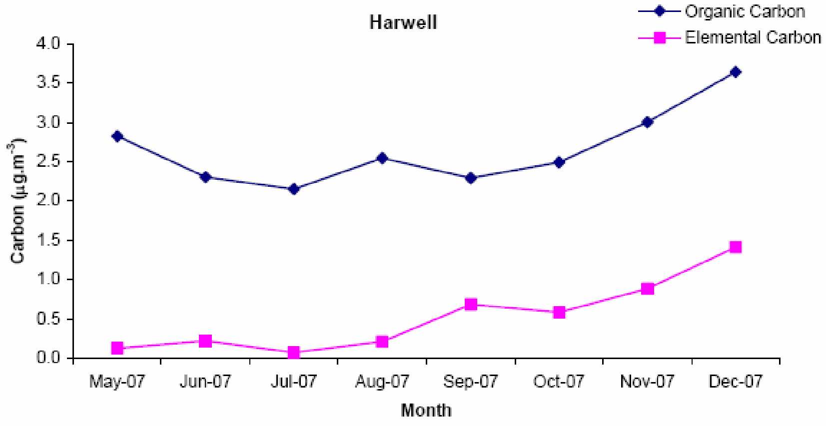
For EC/OC, from 2002 – 2007 hourly (or 3-hourly) measurements were made with 4 R & P (Thermo) 5400 analysers (4). These instruments are no longer available or supported. They had serious weaknesses in sample collection (impaction was used, and particles less than around 100 nm were not collected), in analysis (a thermal method with no charring correction was used), and in QA/QC (although the CO_2 monitor could be calibrated, it was not possible to do a "whole instrument" calibration).

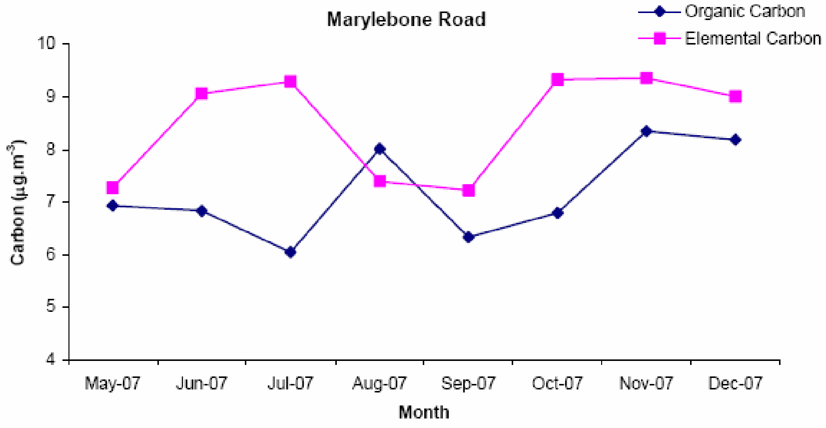
From 2007 EC/OC has been monitored at 3 sites (Marylebone Road (London kerbside), North Kensington (London background) and Harwell (SE England rural)) by daily filter sampling using a Partisol 2025 onto Pallflex Tissuquartz 47 mm filters, followed by with lab analysis at NPL on a Sunset Laboratories instrument using the "quartz" protocol. Monthly averages for 2007 (since the start of this method in the Network) are shown below.

The Black Smoke Network has measured Black Smoke Index for many decades using daily filters analysed manually with a reflectometer. In most cases, concentrations are too low to measure accurately with this method. In 2008 the instruments at the 21 sites were changed from the old samplers to aethalometers (Magee AE-21), which will provide a more precise measure of Black Carbon with much higher time resolution.

Results and further details are available through the Defra website www.airquality.co.uk by following "research" and "reports database".


North Kensington
Organic Carbon
Elemental Carbon
Carbon (µg.m^{-3})
0
1
2
3
4
5
6
May-07
Jun-07
Jul-07
Aug-07
Sep-07
Oct-07
Nov-07
Dec-07
Month


Harwell
Organic Carbon
Elemental Carbon
Carbon (µg.m^{-3})
0.0
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0
May-07
Jun-07
Jul-07
Aug-07
Sep-07
Oct-07
Nov-07
Dec-07
Month


Marylebone Road
Organic Carbon
Elemental Carbon
Carbon (µg.m^{-3})
4
5
6
7
8
9
10
May-07
Jun-07
Jul-07
Aug-07
Sep-07
Oct-07
Nov-07
Dec-07
Month

2.9 Swedish experience - Eusaar_2 and ^{14}C

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In Sweden there are two groups working with carbonaceous aerosol. My experience is only valid for the experience at Lund University. Lund has in contrast to most other institutes not a Sunset carbon analyser but a DRI 2001A OC/EC Thermal Optical Carbon Analyzer. In general the two instruments work in the same manner but the sample size (the filter punch) is smaller using the DRI. This smaller punch may put us in the position where the sample load is too small and give higher uncertainties. The analyser has been running well since November 2008 and is generally demonstrating an instrumentation blank at approximately 0.1 µg C.

In Lund, Eusaar_2 EC/OC protocol was tested in May 2008 and has ever since been used to analyse ambient samples from our background station Vavihill. Before, samples were analysed using the Improve method. The major differences between the methods are Eusaar_2's higher temperature of the last He-stage and the lower temperature at which oxygen is introduced. For samples collected in southern Sweden this new protocol has shown good results. Using the Improve method, the OC/EC split generally falls in the peak where oxygen is introduced at 550°C. Eusaar_2 has, with its lower temperature of 500°C (in Lund at 480°C and rising to 500°C), a wider peak and the split falls, in most cases, in the valley between the peak for 500°C and 550°C. The split of Eusaar_2 result in lowering the uncertainties of OC/EC separation. The temperature in the last OC stage in Eusaar_2 is set at 650°C which is 100°C higher than the Improve protocol. This temperature is enough to start combustion of charred substances (true or false EC). The length of this temperature stage has so far not been as long as required to restore the laser baseline for the transmission signal to its starting value. A temperature of 650°C is however not high enough to combust soot in pure helium gas. Collected pure soot, generated at Lund University, show practically no increase in laser transmission during the 650°C helium phase.

At Lund the split between OC and EC is of primary interest for climate research. The information is used, together with radiocarbon (^{14}C) measurements, to quantify the sources of the carbonaceous aerosol. This is possible since the naturally occurring carbon isotope ^{14}C is radioactive and has a half-life of 5730 years. Fossil fuel is therefore ^{14}C-free while biomass has ^{14}C concentration as the atmosphere of today. EC, originating from combustion, might by radiocarbon measurement be separated into fossil fuel and biomass burning. Known, or estimated, value of EC/OC from wood burning may be used to complete the source apportionment of OC into fossil fuel, biomass burning and biogenic sources.

To separate OC and EC prior to radiocarbon measurement two techniques are tested in Lund. The first and most promising is a method based upon the work of Sönke Szidat the University of Bern, Switzerland (Szidat et al. 2004, Radiocarbon, 46, 475-484). The water soluble OC is removed by water treatment and the filter is heated in 375°C in air for the time needed to remove all OC. Szidat found that 4 hours was needed to get a stable ^{14}C concentration in the remaining carbon. The carbon left on the filter is considered pure EC and may be analysed. The radiocarbon content of the OC fraction is in Lund determined by subtraction after measured ^{14}C in the total sample. This method is currently being verified using the Eusaar_2 protocol. Since OC/EC separation is user defined it is important that the separation of OC and EC prior radiocarbon measurement is comparable.

In the second considered method the gas flow from the carbon analyser is diverted and trapped it in a cold trap using liquid nitrogen. This would make it possible to use different gas mixtures and monitor the filter's optical properties during the analysis. Because of the small punch size of the DRI, several punches might be required before sufficient carbon has been collected to be able to perform the ^{14}C measurement.

It is necessary to extract the carbon from the aerosol samples and convert it into solid carbon prior to ^{14}C AMS measurement (Accelerator Mass Spectrometer) at Lund University. Carbon analysed with the first method is combusted to carbon dioxide. In both methods the carbon dioxide is collected and converted into solid graphite carbon. The carbon dioxide is mixed with hydrogen in a small volume with iron powder and converted into graphite by heat. The process is constantly monitored by measuring the pressure. In Lund the graphitisation system is capable of handling samples as small as 25 µg C, which makes analyses of aerosol samples possible. The use of radiocarbon content in aerosol fractions is not the only analysis needed but together with other parameters it is a valuable tool to create a total source apportionment of aerosol particles.

2.10 Résumé

The main outcomes from the presentations and discussions during the precious two days were discussed and summarised by all participants. The statements given below are meant to be recommendations for the standardisation of OC and EC measurements in Europe.

Rationale

The main focus of the new standard should go along with the intention of the new Air Quality Directive. Information related to health effects and mass closure for PM should take priority over the aim to derive information related to climate change (optical properties). Nevertheless, whenever possible combination of the different aims should be pursued.

Types of sites

It is stressed that the method should also be applicable to urban and roadside sites as well as rural sites, even though the Directive only specifies rural background sites. This is to ensure comparability in all relevant areas of use of the data such as of chemical composition, source identification and apportionment, exposure assessment.

Time resolution

The minimum time resolution of the method should allow daily values to be in accordance with those for PM. This does specifically not exclude shorter time resolution methods. Contrary, shorter time resolutions should be favoured if the data will be obtained with the same quality.

Sampling

There needs to be an explicit link to e.g. EN 14907 sampling for $PM_{2.5}$ without addressing sampling artefacts. Filter types will need to be more restricted than EN 14907. The method should not be linked to a specific size fraction.
The use of blank filters, filter handling, and use of blank filter results will need to be clearly addressed, e.g. more stringent than in EN 14907.

Parameter

The high data quality in determining TC (significant lower uncertainty than for EC and OC) should be considered when setting up a standard.

Analysis

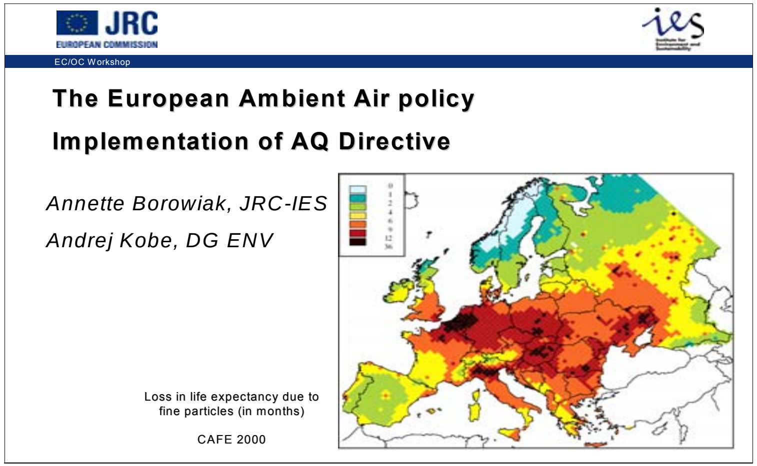
EC and OC data should allow / support mass closure of PM along with other PM constituent determined e.g. within the AQD framework.

Links to other standards and network protocols

The European standard should not be developed in isolation from relevant work in other communities especially EMEP, EUSAAR and the US.

Annex: The Presentations

A.1 The European Ambient Air policy Implementation of AQ Directive



The European Ambient Air policy

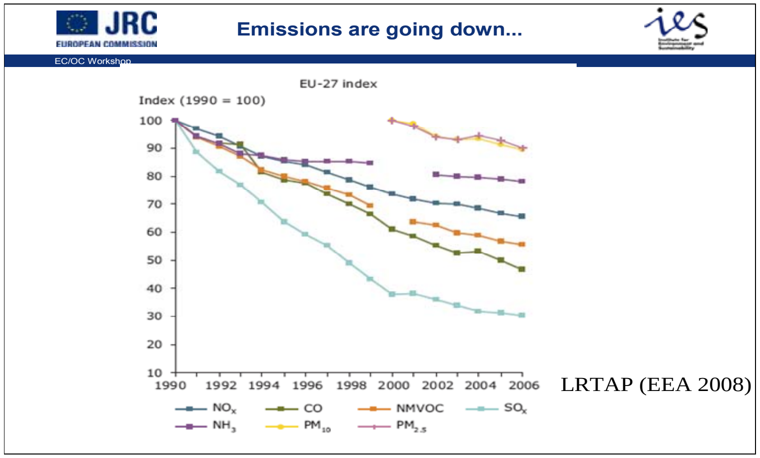
Implementation of AQ Directive

Annette Borowiak, JRC-IES

Andrej Kobe, DG ENV

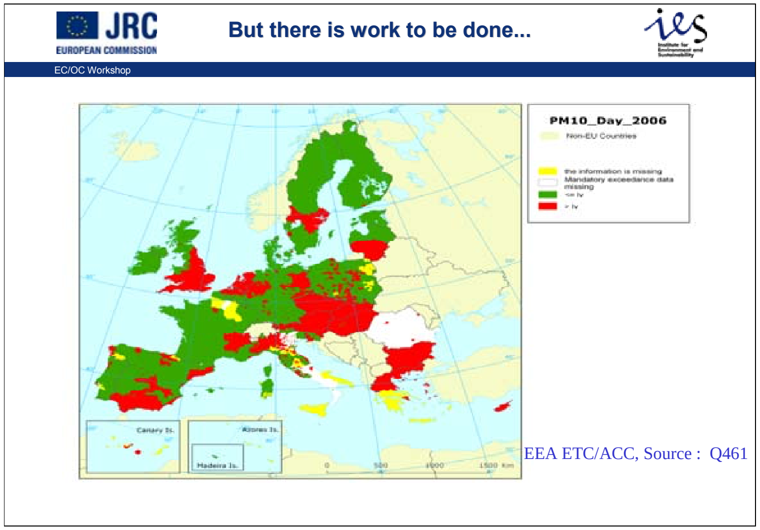
Loss in life expectancy due to fine particles (in months)

CAFE 2000



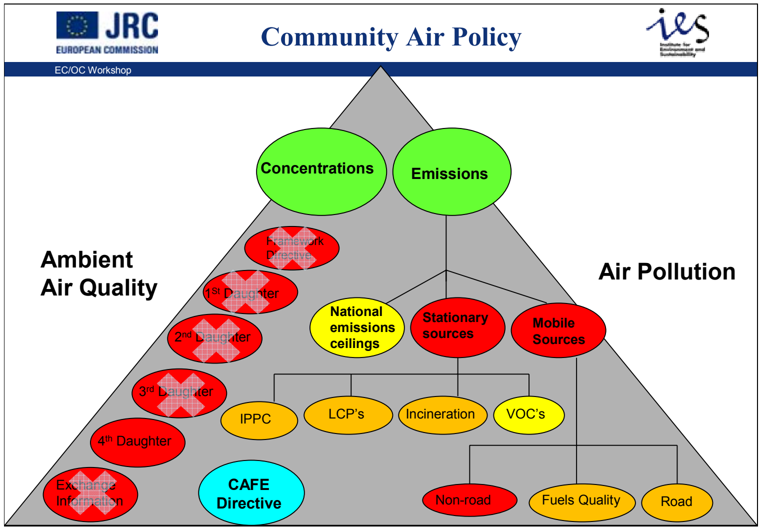
Emissions are going down...

LRTAP (EEA 2008)



But there is work to be done...

EEA ETC/ACC, Source : Q461



Community Air Policy

New Directive 2008/50/EC (I)

Streamlined provisions, more clarity in implementation

PM2.5 objectives, monitoring requirements

Focused , more coherent measures, better information for further policy development

New approach: exposure standard based on urban background monitoring in cities

More time for compliance, under conditions

Art. 22

Assessment of measures by Commission

New Directive 2008/50/EC (II)

Expanded concept of deduction of natural contributions

Better Assessment > better understanding of sources, more effective measures

Additional QA/QC provisions, reference methods…

higher quality data (monitoring & modelling)

New reporting provisions,

Faster availability, higher quality, spatial dimension of AQ

Updated guidance

Support to implementation and more harmonized approach

What's in for us?

Article 6 of the CAFE Directive

(5) (…) measurements shall be made, at rural background locations away from significant sources of air pollution for the purpose of providing (…) information on (…) the chemical speciation concentrations of fine particulate matter ($PM_{2.5}$) on an annual average basis (…).

Further criteria

- **One sampling point every 100.000 km².**
- **Agree with neighbouring Member States on common sampling stations.**
- **Where appropriate monitoring shall be coordinated with the monitoring strategy and measurement programme of EMEP.**
- **Data quality objectives of Annex I (PM measurement) and Annex IV apply.**
- **Member States shall inform the Commission of the chemical composition measurement methods used.**

Annex I (PM concentration measurement)

Data Quality Objectives

- Uncertainty 25%
- Further quality requirements: traceability (ISO 17025), established QA/QC system (incl. data collection and reporting), regular maintenance, participation to Community QA programmes.

Annex IV

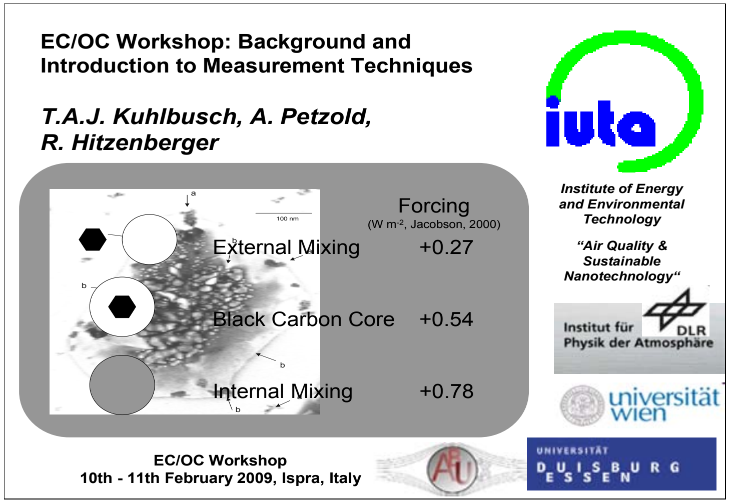
Measurements at rural background locations irrespective of concentration

Objectives:

- ensure information on background levels to judge enhanced levels in more polluted areas,
- assess contribution from long range transport,
- support source apportionment analysis,
- validation data for modelling.

Substances: NO_3^-, Cl^-, SO_4^{2-}, Na^+, K^+, NH_4^+, Mg^{2+}, Ca^{2+}, EC, OC

A.2 EC/OC Workshop: Background and Introduction to Measurement Techniques



EC/OC Workshop: Background and Introduction to Measurement Techniques

T.A.J. Kuhlbusch, A. Petzold, R. Hitzenberger

Forcing
(W m^{-2}, Jacobson, 2000)

External Mixing +0.27

Black Carbon Core +0.54

Internal Mixing +0.78

Institute of Energy and Environmental Technology

“Air Quality & Sustainable Nanotechnology“

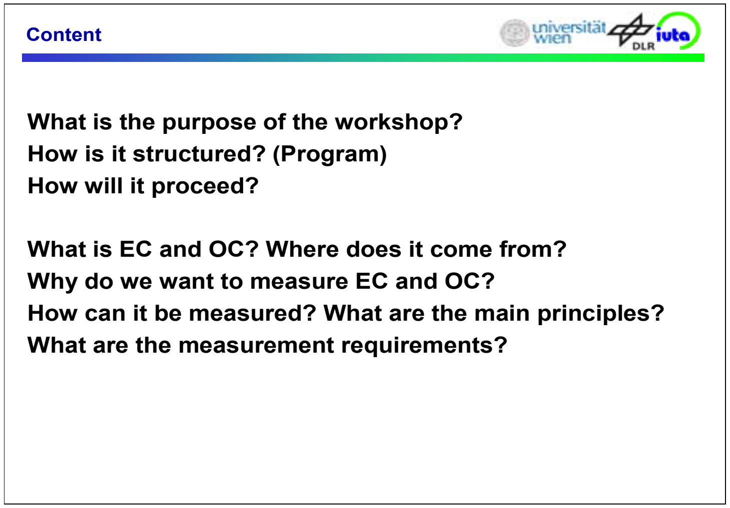
Institut für Physik der Atmosphäre

DLR

universität wien

UNIVERSITÄT DUISBURG ESSEN

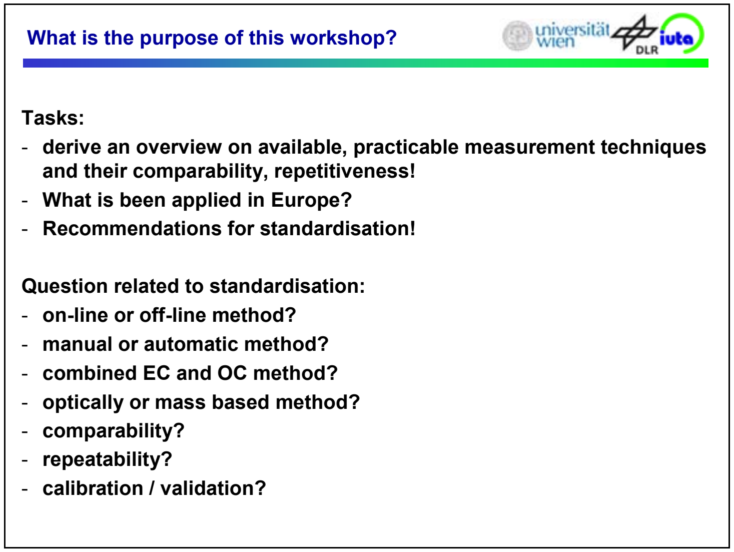
EC/OC Workshop
10th - 11th February 2009, Ispra, Italy



Content

What is the purpose of the workshop?
How is it structured? (Program)
How will it proceed?

What is EC and OC? Where does it come from?
Why do we want to measure EC and OC?
How can it be measured? What are the main principles?
What are the measurement requirements?



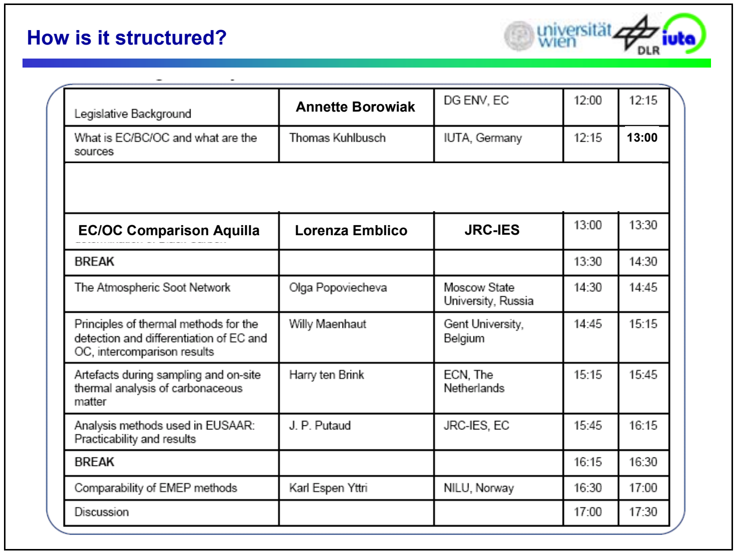
What is the purpose of this workshop?

Tasks:

- **derive an overview on available, practicable measurement techniques and their comparability, repetitiveness!**
- **What is been applied in Europe?**
- **Recommendations for standardisation!**

Question related to standardisation:

- **on-line or off-line method?**
- **manual or automatic method?**
- **combined EC and OC method?**
- **optically or mass based method?**
- **comparability?**
- **repeatability?**
- **calibration / validation?**



How is it structured?

Legislative Background	**Annette Borowiak**	DG ENV, EC	12:00	12:15
What is EC/BC/OC and what are the sources	Thomas Kuhlbusch	IUTA, Germany	12:15	**13:00**
EC/OC Comparison Aquilla	**Lorenza Emblico**	**JRC-IES**	13:00	13:30
BREAK			13:30	14:30
The Atmospheric Soot Network	Olga Popoviecheva	Moscow State University, Russia	14:30	14:45
Principles of thermal methods for the detection and differentiation of EC and OC, intercomparison results	Willy Maenhaut	Gent University, Belgium	14:45	15:15
Artefacts during sampling and on-site thermal analysis of carbonaceous matter	Harry ten Brink	ECN, The Netherlands	15:15	15:45
Analysis methods used in EUSAAR: Practicability and results	J. P. Putaud	JRC-IES, EC	15:45	16:15
BREAK			16:15	16:30
Comparability of EMEP methods	Karl Espen Yttri	NILU, Norway	16:30	17:00
Discussion			17:00	17:30

How is it structured?

Draft agenda Day 2

Current VDI standards	Dieter Gladtke	LANUV, Germany	9:00	9:15
Hungarian experience	Andras Gelenscer	AoS, Hungary	9:15	9:30
Spanish Experience	Mar Viana	CSIC, Spain	9:30	9:45
Portugese experience	Casimiro Pio	University Aveiro, Portugal	9:45	10:00
French experience	Jean Sciare	LSCE, France	10:00	10:15
UK experience	Paul Quincey	NPL, UK	10:15	10:30
Swedish experience	Johan Genberg	Lund University, Sweden	10:30	10:45
BREAK			10:45	11:15
Discussion			11:15	12:30
Conclusions			12:30	13:00

How will it proceed?

- **Collection of a summary of the presentations**
- **Preparation of proceedings:**
  Summaries of presenters and slides
  Summary of discussion
  List of recommendations
- **WG will meet in 28th-29th April, discuss and decide on the methods and procedures necessary for pursuing the standard.**

Content

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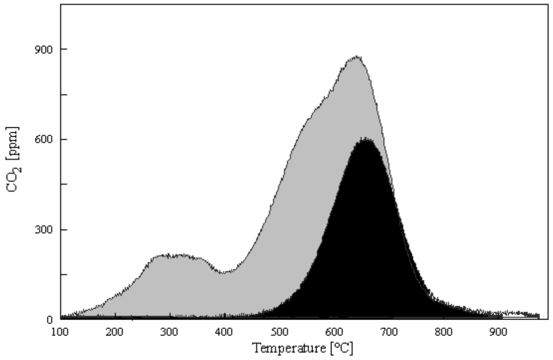
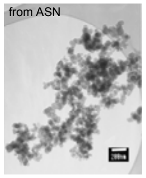
What are the measurement requirements?

What is EC and OC?



Defined by thermal stability?

What is EC and OC?


from ASN

Defined by
- its thermal stability?
- its chemical nature?
- its basic structure?
- its optical property?

In his seminal book "Black Carbon in the Environment" Goldberg points out:

There is no clear definition of black carbon. It often is defined by scientists on the basis of their techniques of isolation and measurement. Despite the highly variable nature of black carbon we may describe it as a combustion derived carbon fraction of black color.

➔ OC = TC – EC/BC?

Where does it come from?

EC:
Combustion processes (anthropogenic & natural)

BC:
Also degradation processes and fire residues

OC:
Industry (dry cleaner…)
Biogenic (isoprene, terpines…)
Biological (wax, pieces of plants….)

This already implies a definition!

Content

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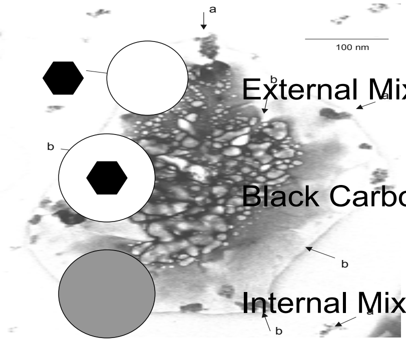
Mixing of Black Carbon



	Forcing (W m^{-2}, Jacobson, 2000)
External Mixing	+0.27
Black Carbon Core	+0.54
Internal Mixing	+0.78

The high uncertainty of both, the amount of absorbing carbon and the efficiency of absorption, lead to high uncertainties in climate simulations!

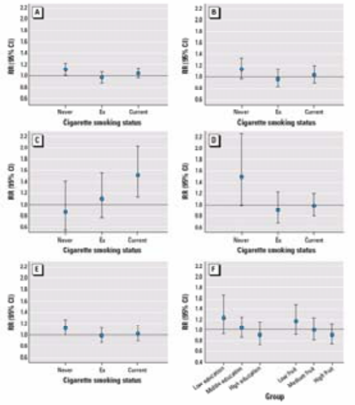


Figure 3. Association between black smoke overall concentration (1987–1996) and cause-specific mortality in subgroups for cigarette smoking status in the full cohort data set (A–E), and (F) by education and fruit consumption in the case–cohort data set. (A) Natural-cause (p = 0.15), (B) cardiovascular (p > 0.2), (C) respiratory (p = 0.11), (D) lung cancer (p = 0.14), and (E) other mortality (p > 0.2). (F) Education of the household coded as low = only primary school; middle = lower vocational education; and high = junior high school, senior high school, higher vocational education, and university (p > 0.2). Fruit consumption divided in tertiles: low, 0–96.8 g/day; medium, 96.8–191.8 g/day; and high, > 191.8 g/day. Adjusted for age, sex, smoking status, and area-level indicators of socioeconomic status (p > 0.2). p-Value, Cochran's Q test for heterogeneity.

Relative risks (95% confidence intervals) for a 10-µg/m3 increase in BS concentrations were 1.05 (1.00–1.11) for natural cause, 1.04 (0.95–1.13) for cardiovascular, 1.22 (0.99–1.50) for respiratory, 1.03 (0.88–1.20) for lung cancer, and 1.04 (0.97–1.12) for mortality other than cardiovascular, respiratory, or lung cancer. Results were similar for NO2 and PM2.5, but no associations were found for SO2.

Long-Term Effects of Traffic-Related Air Pollution on Mortality in a Dutch Cohort
Beelen et al., Env. Health Persp. **116, Number 2, February 2008**

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Basic techniques

EC

- Optical methods
- Photoacoustic method

} MAAPS, PSAP, Aethalometer, IS etc.

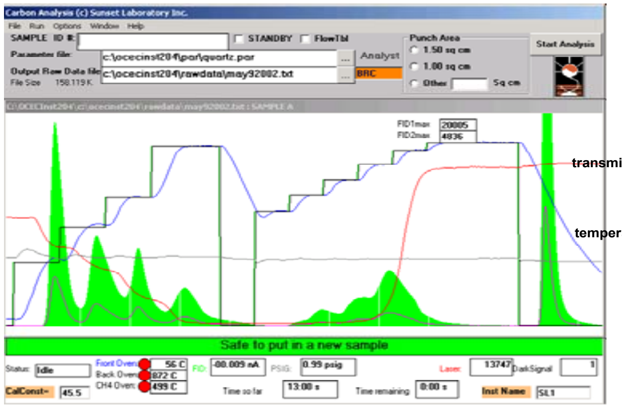
- Thermal methods

} VDI 2465, Cachier, DRI, NIOSH, etc.

OC

- Thermal methods
- GC – MS (3D MS) for speciation

Sunset analysis



Carbon Analysis (c) Sunset Laboratory Inc.

SAMPLE ID #:

Parameter file: c:\ocecinst204\par\quartz.par

Output Raw Data file: c:\ocecinst204\rawdata\may92002.txt

File Size 158.119 K

Analyst: BRC

C:\OCECInst204\c:\ocecinst204\rawdata\may92002.txt : SAMPLE A

FID1max 20005

FID2max 4836

Safe to put in a new sample

Status: Idle

Front Oven: 56 C

Back Oven: 872 C

CH4 Oven: 499 C

FID: -00.009 nA

PSIG: 0.99 psig

Laser: 13747

DarkSignal: 1

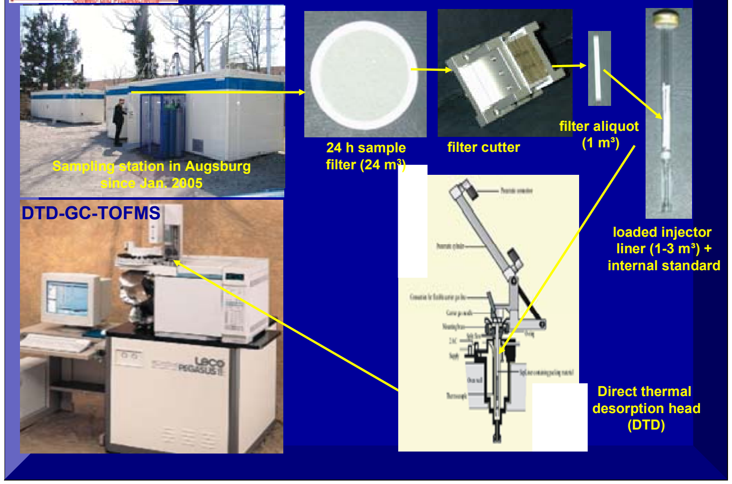
CalConst= 45.5

Time so far: 13:00 s

Time remaining: 0:00 s

Inst Name: SL1

DTD-GC-TOFMS - Method



Sampling station in Augsburg since Jan. 2005

24 h sample filter (24 m³)

filter cutter

filter aliquot (1 m³)

loaded injector liner (1-3 m³) + internal standard

Direct thermal desorption head (DTD)

DTD-GC-TOFMS

Basic techniques

EC

- Optical methods
- Photoacoustic method

} MAAPS, PSAP, Aethalometer, IS etc.

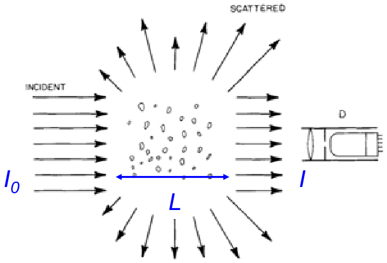
- Thermal methods

} VDI 2465, Cachier, DRI, NIOSH, etc.

OC

- Thermal methods
- GC – MS (3D MS) for speciation

Light extinction



The attenuation of light along the direction of propagation through a scattering and absorbing medium is a key process responsible for visibility degradation.

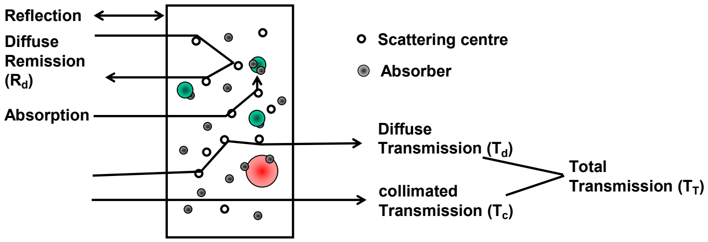
The light attenuation for a parallel beam of light of incident irradiance I_0 is given by the Lambert-Beer law

$$\frac{I}{I_0} = e^{-\sigma_{ext} L}$$

σ_{ext} = extinction coefficient in m^{-1} ; L = length of atmospheric column in m

---

Light scattering / Absorption



Extinction = Scattering + Absorption

$$\varepsilon = \sigma_S + \sigma_A$$

Mechanisms of interaction

- When a beam of light impinges on a particle, electric charges in the particle are excited into oscillatory motion.
- The excited electric charges reradiate energy in all directions (*scattering*) and may convert a part of the incident radiation into thermal energy (*absorption*).
- Conservation of energy requires that the light removed from the incident beam (extinction) by the particle is accounted for by scattering in all directions and absorption, i.e.
- $\sigma_{ext} = \sigma_{sp} + \sigma_{ap}$
- Coefficients for light extinction by particles (σ_{ep}), scattering (σ_{sp}) and absorption (σ_{ap}) are calculated for spherical particles by Mie theory.
- Efficiencies Q for extinction, scattering and absorption are defined as the ratio of the cross-section with respect to particle-radiation interaction and the geometrical particle cross-section
- $A_p = \pi D^2 / 4$

The extinction coefficient σ_{ext} for an aerosol consisting of *N* particles per unit volume of cross-sectional area A_p (spherical particle of diameter D_p) is

$$\sigma_{ext} = N A_p Q_{ext} = N \frac{\pi D_p^2}{4} Q_{ext}$$

The fraction of scattering to extinction is defined by the single-scattering albedo

$$\omega_0 = \frac{\sigma_{scat}}{\sigma_{ext}} = \frac{\sigma_{scat}}{\sigma_{scat} + \sigma_{abs}} = 1 - \frac{\sigma_{abs}}{\sigma_{scat} + \sigma_{abs}}$$

Key Parameters

- ratio of particle size to wavelength of light, or *size parameter* $\alpha = \frac{\pi D_p}{\lambda}$
- complex index of refraction $m = n + i k$

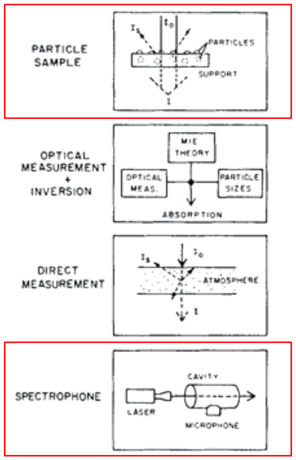
for non-absorbing particles is $k = 0$
and for absorbing particles is $k > 0$
***m* is determined by the chemical composition of the particle**

TABLE 22.2 Refractive Indices of Atmospheric Substances at $\lambda = 589$ nm (Unless Otherwise Indicated)

	$m = n - ik$	
Substance	n	k
Water	1.333	0 (see Table 22.1)
Water (ice)	1.309	
NaCl	1.544	0
H_2SO_4	1.426[a]	0
NH_4HSO_4	1.473[b]	0
$(NH_4)_2SO_4$	1.521[b]	0
SiO_2	1.55	0 ($\lambda = 550$ nm)
Carbon	1.96	0.66 ($\lambda = 550$ nm)
Mineral dust[c]	1.56	−0.006 ($\lambda = 550$ nm)

[a] Stelson (1990), assuming a 97% pure (by mass) mixture of H_2SO_4 with H_2O.
[b] Weast (1987).
[c] Tegen et al. (1996).

Aerosol Absorption Measurement Methods



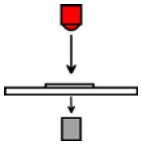
Sketches of the major categories of measuring light absorption by aerosol particles, the graph is taken from the Proceedings of the First International Workshop on Light Absorption by Aerosol Particles

(Gerber, H.E. and E.E. Hindman (1982) *Light Absorption by Aerosol Particles*, Spectrum Press, Hampton.).

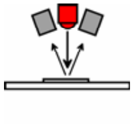
Filter-Based Absorption Measurement - Methods

- Sampling of particles on a fibrous filter matrix.
- Measurement of the modification of filter-optical properties by the collected aerosol particles.
- Assumption of Lambert-Beer type relationship for data analysis.

Transmission method



Reflectance method



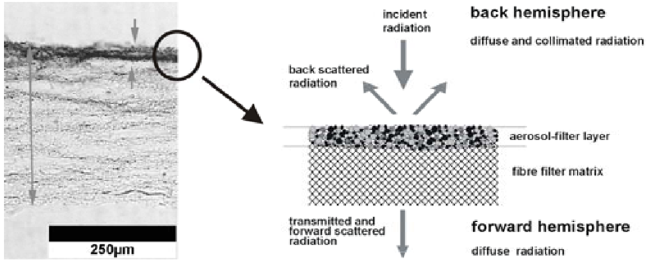
$$ATN = -100 \ \ln\left(\frac{T}{T_0}\right) = B_{ATN}\ S_{BC}$$

$$\sigma_{0\ (TRANS)} = \frac{A}{V}\ \ln\left(\frac{T_0}{T}\right)$$

$$\sigma_{0\ (REF)} = \frac{1}{2}\frac{A}{V}\ln\left(\frac{R_0}{R}\right)$$

filter surface area A , sampled volume V, mass-specific absorption coefficient B_{ATN} [$m^2\ g^{-1}$] , filter mass loading S_{BC} [μg/cm^2]

Interaction of Particles, Fibres and Radiation



Filter Matrix Effects

+ Multiple scattering of light by filter fibres and light-scattering aerosol particles tends to overestimate the absorption coefficient.

- „Shadowing" of collected particles inside the fibre matrix tends to underestimate the absorption coefficient .

Filter-Based Absorption Measurement - The Problem

Methods measure light transmission through a particle-loaded filter;

filter transmittance:

1.0 (“white”) ≥ *Tr* > 0 (“black”)

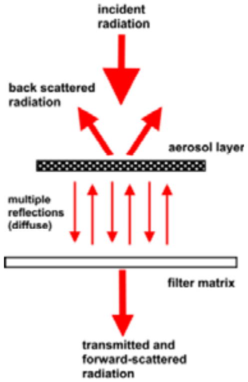
aerosol absorption coefficient:

σ_{ap} = - ln *I* (t + Δt) / *I* (t) · *A / V*

the response of any practical method depends on filter loading and interaction between radiation, particles and filter:

$\sigma_{ap} = \sigma_{ap}^{(0)} \cdot f\,(Tr\,;\,\sigma_{sp})$

f (*Tr* ; σ_{sp}) has to be known for each method, it requires knowledge on the aerosol scattering coefficient σ_{sp}.



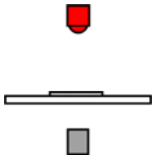
Filter-Based Absorption Measurement - Solutions

Transmittance Methods

Determine the response function *f* (*Tr* ; σ_{sp}) in calibration experiments;

perform parallel measurements of $\sigma_{ap}^{(0)}$ and σ_{sp};

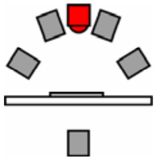
calculate $\sigma_{ap} = \sigma_{ap}^{(0)} \cdot f\,(Tr\,;\,\sigma_{sp})$.



Multi-Angle Absorption Photometry

Measure forward and back scattered radiation simultaneously;

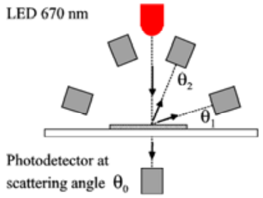
apply a radiative transfer scheme to the aerosol-filter system, which includes multiple scattering processes: $f\,(Tr\,;\,\sigma_{sp}) = 1.0$ (?)

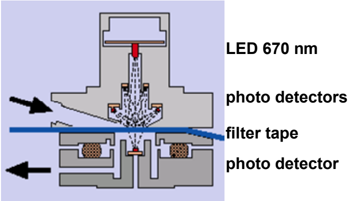


Aerosol Absorption Methods in Reno Aerosol Optics Study 2002 (RAOS)

Photoacoustic Spectroscopy			***in situ***
#1	532 nm, 1047 nm		
Particle/Soot Absorption Photometer PSAP			filter transmission;
#1	565 nm	(regular)	f (*Tr* ; σ_{sp}) applied
#2	471, 543, 659 nm	(modified 3-λ)	
Multi-Wavelength Aethalometer			filter transmission;
#1	370, 470, 521, 590, 660, 880, 950 nm		no corrections for
#2	370, 430, 470, 521, 565, 700, 950 nm		*Tr* and b_{sp} applied
Multi-Angle Absorption Photometer MAAP			filter-based;
#1	630 nm		f (*Tr* ; σ_{sp}) = 1 (?)
Reference method **Absorption = Extinction - Scattering** (Extinction Cell - Integrating Nephelometer)			***in situ***

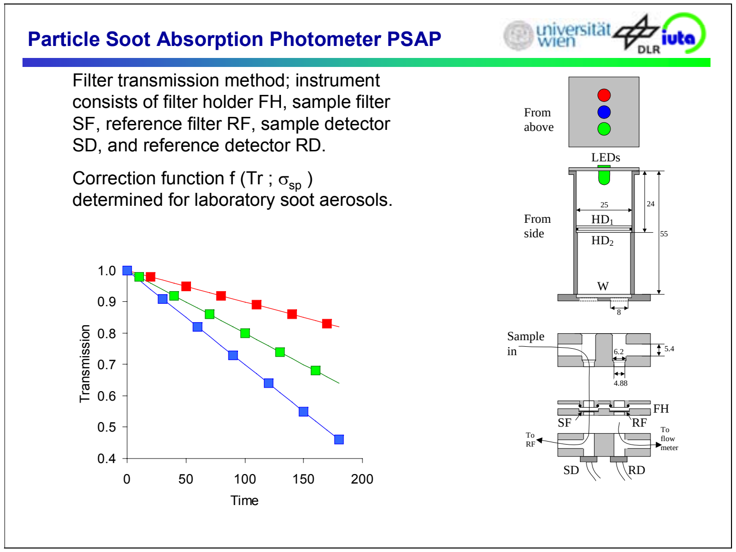
Multi-Angle Absorption Photometry





The MAAP sensor unit permits the simultaneous analysis of transmittance method, reflectance method and multi-angle absorption photometry from the same aerosol sample.

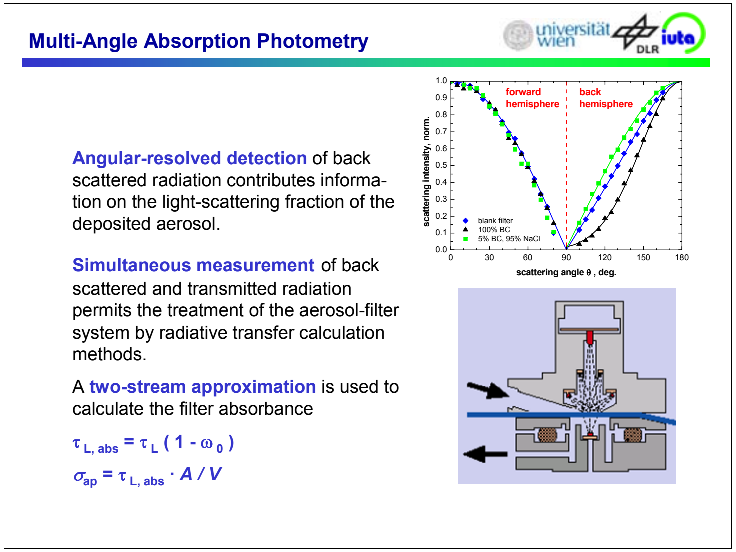
Petzold, A. and M. Schönlinner, *J. Aerosol Sci.*, 35, 421-441, 2004.



Particle Soot Absorption Photometer PSAP

Filter transmission method; instrument consists of filter holder FH, sample filter SF, reference filter RF, sample detector SD, and reference detector RD.

Correction function f (Tr ; σ_{sp}) determined for laboratory soot aerosols.



Multi-Angle Absorption Photometry

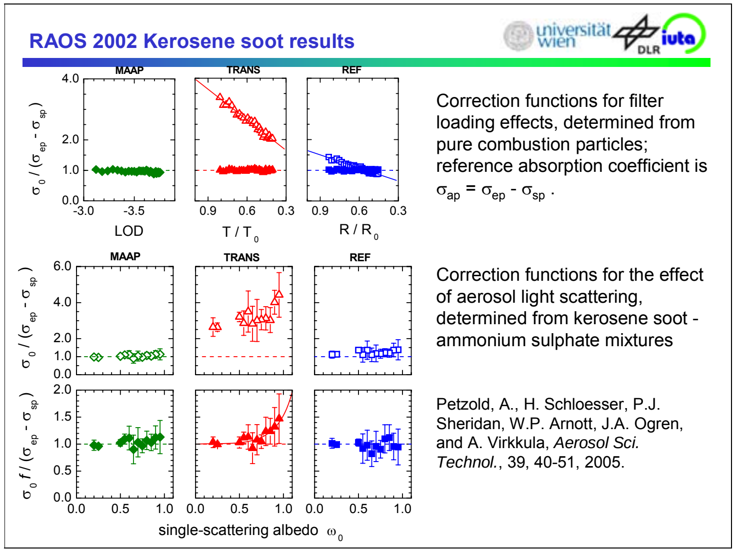
Angular-resolved detection of back scattered radiation contributes information on the light-scattering fraction of the deposited aerosol.

Simultaneous measurement of back scattered and transmitted radiation permits the treatment of the aerosol-filter system by radiative transfer calculation methods.

A **two-stream approximation** is used to calculate the filter absorbance

$\tau_{L,\,abs} = \tau_L\,(1 - \omega_0)$

$\sigma_{ap} = \tau_{L,\,abs} \cdot A / V$

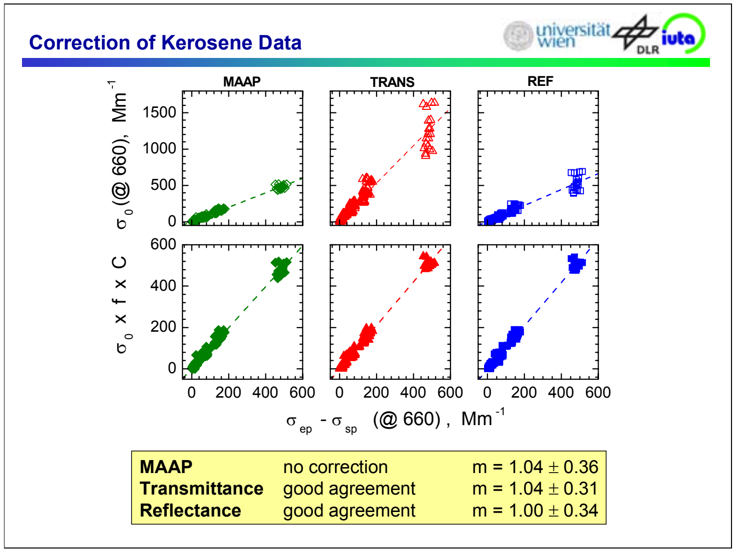


RAOS 2002 Kerosene soot results

Correction functions for filter loading effects, determined from pure combustion particles; reference absorption coefficient is $\sigma_{ap} = \sigma_{ep} - \sigma_{sp}$.

Correction functions for the effect of aerosol light scattering, determined from kerosene soot - ammonium sulphate mixtures

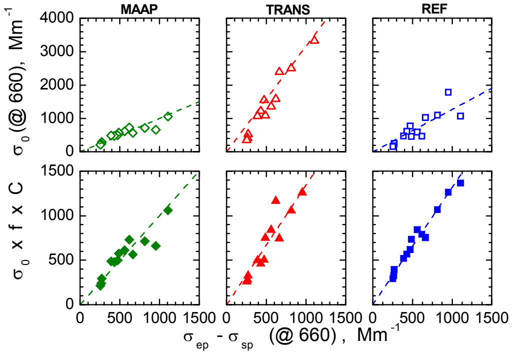
Petzold, A., H. Schloesser, P.J. Sheridan, W.P. Arnott, J.A. Ogren, and A. Virkkula, *Aerosol Sci. Technol.*, 39, 40-51, 2005.



Correction of Kerosene Data

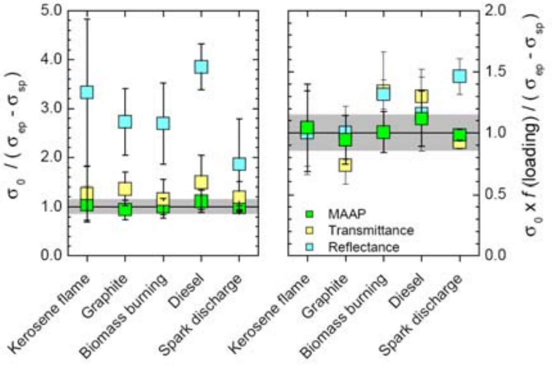
MAAP	no correction	m = 1.04 ± 0.36
Transmittance	good agreement	m = 1.04 ± 0.31
Reflectance	good agreement	m = 1.00 ± 0.34

Correction of Biomass Burning Data using Kerosene Functions



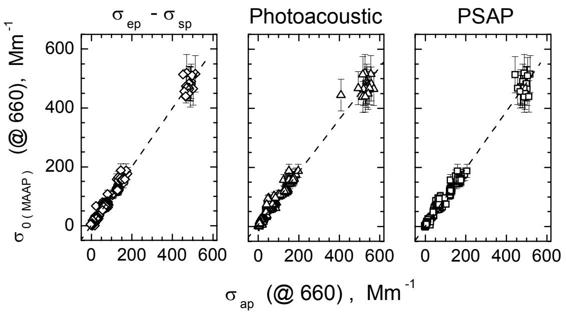
MAAP	no correction	m = 1.01 ± 0.17
Transmittance	over - estimation	m = 1.34 ± 0.32
Reflectance	over - compensation	m = 1.32 ± 0.12

Summary of Correction Functions



MAAP	no correction required
Transmittance	kerosene correction function deviates by more than 20% from reference data

RAOS 2002 Kerosene soot results



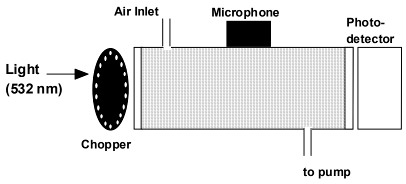
$$\sigma_{ext} = \sigma_{scat} + \sigma_{abs}$$

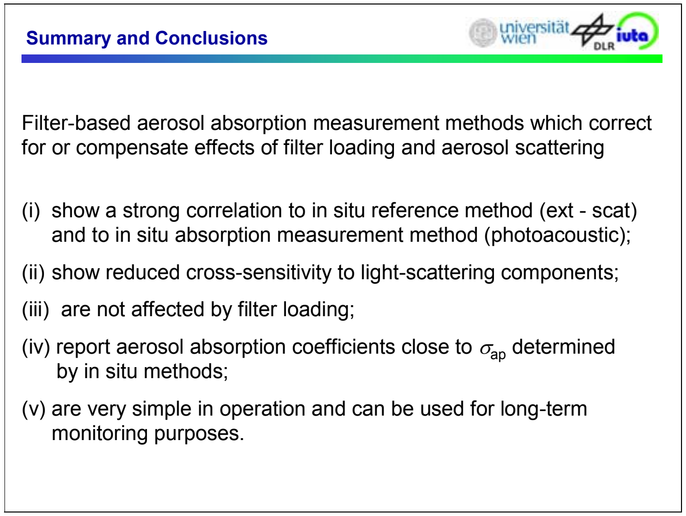
In-situ measurement of σap

Photoacoustic method	measures heat generated by absorbed radiation. The absorbed energy translates into a pressure change in a closed volume which is measured by a microphone.

$$\mathbf{PA} \propto \sigma_{ap} \times \mathbf{P}_{LASER}$$

artifact-free in-situ method ; high time resolution;
complex instrument set-up; applicability to long-term measurements not clear;
detection limit not suitable for clean air conditions (LOD > 100 ng / m³).





Summary and Conclusions

Filter-based aerosol absorption measurement methods which correct for or compensate effects of filter loading and aerosol scattering

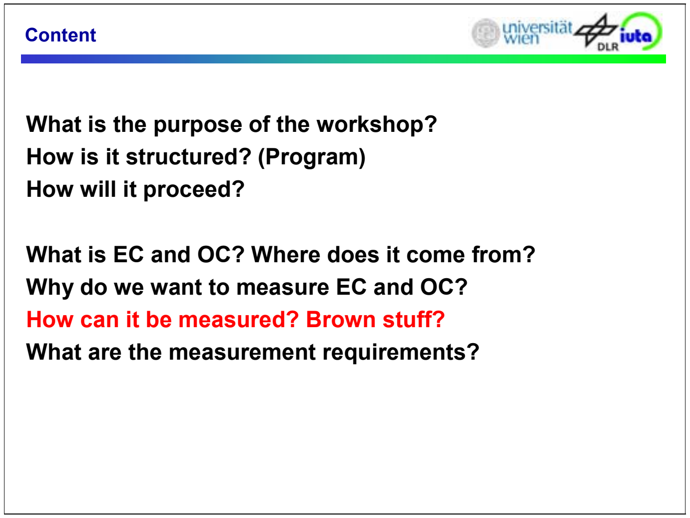
(i) show a strong correlation to in situ reference method (ext - scat) and to in situ absorption measurement method (photoacoustic);

(ii) show reduced cross-sensitivity to light-scattering components;

(iii) are not affected by filter loading;

(iv) report aerosol absorption coefficients close to σ_{ap} determined by in situ methods;

(v) are very simple in operation and can be used for long-term monitoring purposes.



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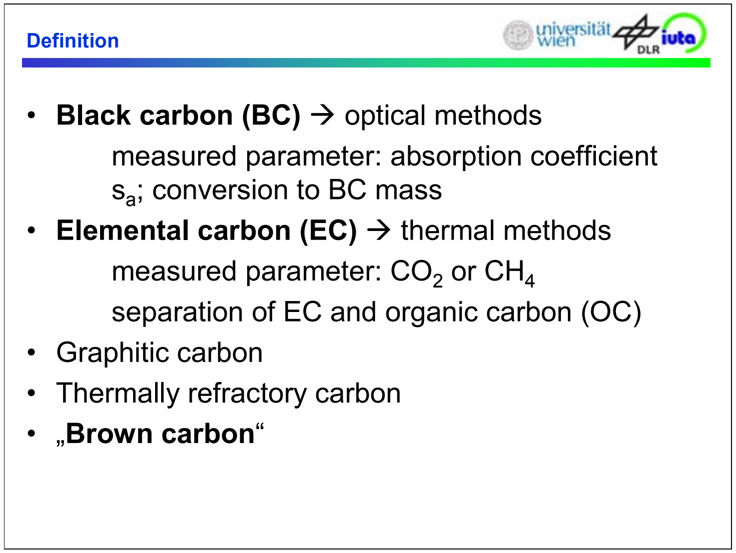
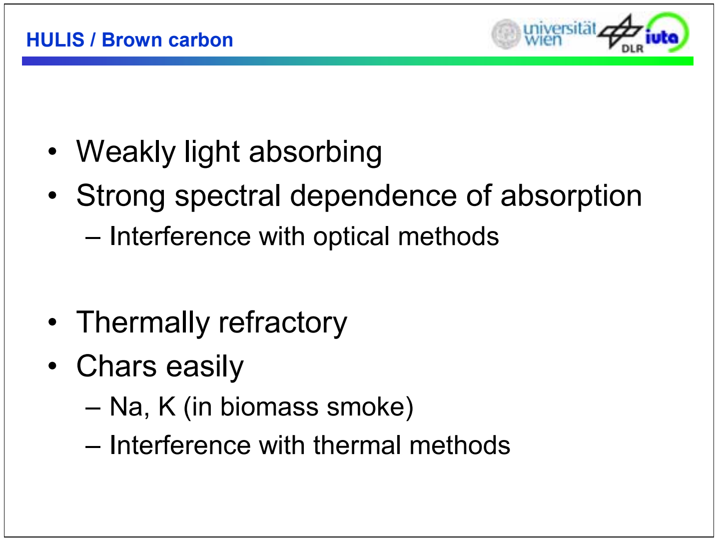


Definition

- **Black carbon (BC)** → optical methods
  measured parameter: absorption coefficient s_a; conversion to BC mass
- **Elemental carbon (EC)** → thermal methods
  measured parameter: CO_2 or CH_4
  separation of EC and organic carbon (OC)
- Graphitic carbon
- Thermally refractory carbon
- „**Brown carbon**“



HULIS / Brown carbon

- Weakly light absorbing
- Strong spectral dependence of absorption
  - Interference with optical methods

- Thermally refractory
- Chars easily
  - Na, K (in biomass smoke)
  - Interference with thermal methods

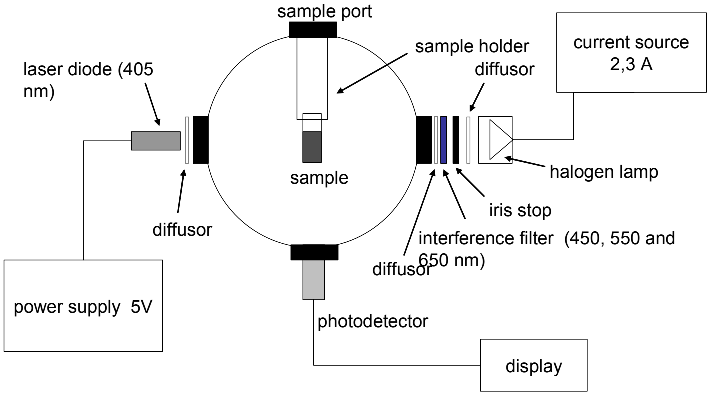
Optical methods (except MAAP and IS)

- Light transmission of clean and loaded filter
- Absorption coefficient s_a(l)
- Conversion to BC concentration via calibration constant or specific attenuation
- Aethalometer, Light transmission method:
  19 m²/g
- PSAP 10 m²/g

Integrating sphere method

- Polycarbonate filter; soluble in chloroform
- Suspension of dissolved filter + sample
- Reduction of light flux at 550 nm in sphere by absorbing material
- Conversion to BC concentration using calibration curve (Elftex 124, Cabot)

Integrating Sphere Technique



sample port

sample holder

current source
2,3 A

laser diode (405 nm)

diffusor

sample

halogen lamp

iris stop

diffusor

interference filter (450, 550 and 650 nm)

diffusor

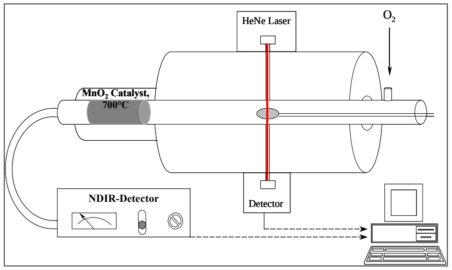
power supply 5V

photodetector

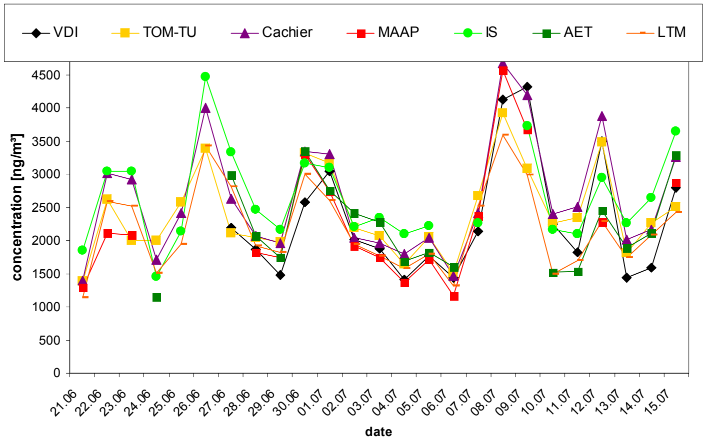
display

Thermal /thermo-optical methods

- Cachier method: Two step combustion
  2 hr 340°C, then 1000°C; O_2
- Thermo-optical: 20°C/min, T_{max} 800°C, O_2

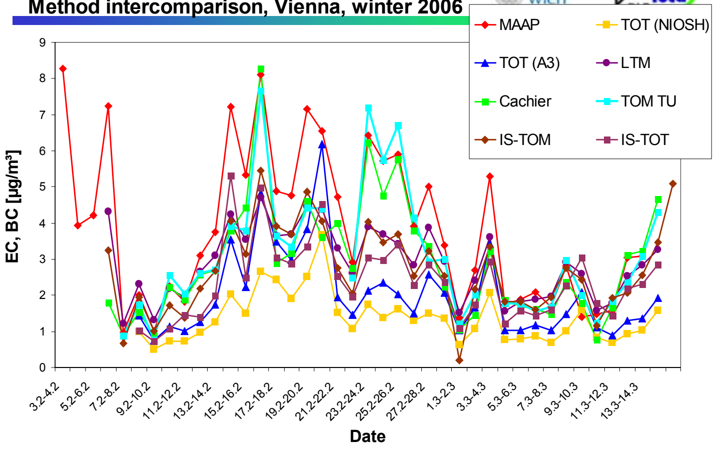


Method intercomparison, Vienna, summer 2004



Hitzenberger et al. (2006) ES&T 40, 6377-6383

Method intercomparison, Vienna, winter 2006



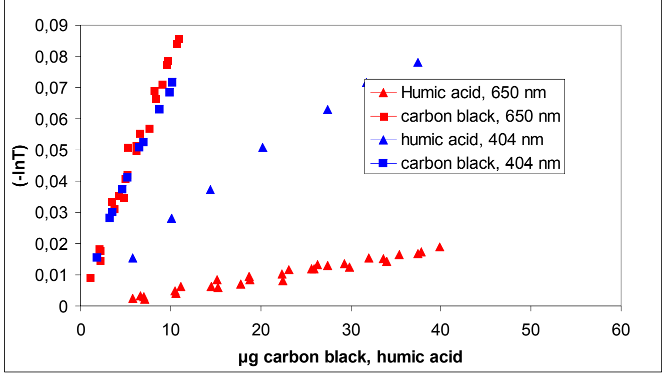
Reisinger et al.(2008) ES&T 42, 884–889

Calibration / Assumptions IS

- Proxy substances
  - Elftex 124 (Cabot Corp.)
  - Humic Acid Sodium Salt (Acros Organics)
- BC behaves like Elftex 124
- BrC behaves like Humic Acid Sodium salt

- → BC concentration
- → BrC concentration

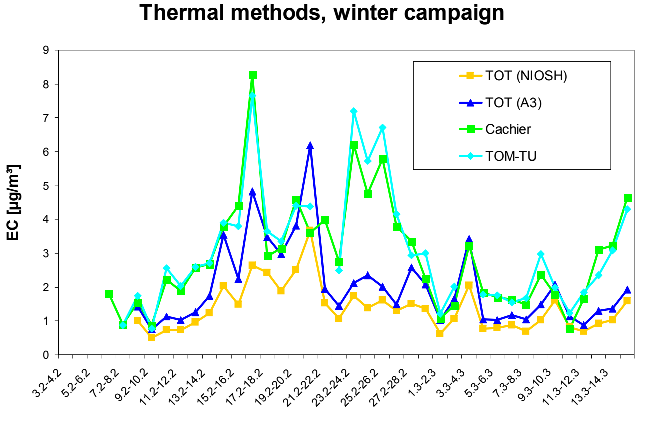
Calibration / Assumptions IS



Calibration curves,
Carbon black (squares) and Humic Acid (triangles)

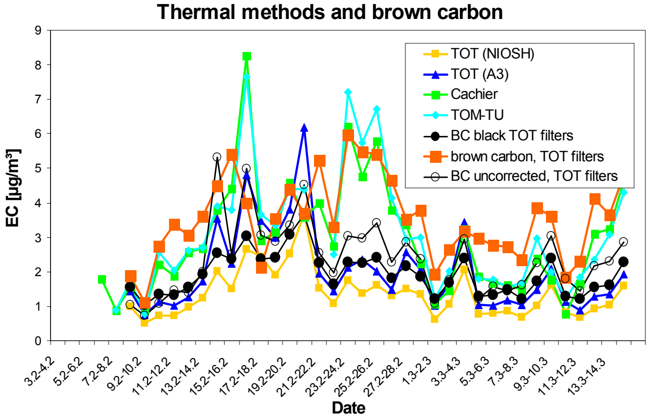
Wonaschütz et al., 2009 EST Accepted

Thermal methods, winter campaign



Reisinger et al.(2008) ES&T 42, 884–889

Thermal methods and brown carbon



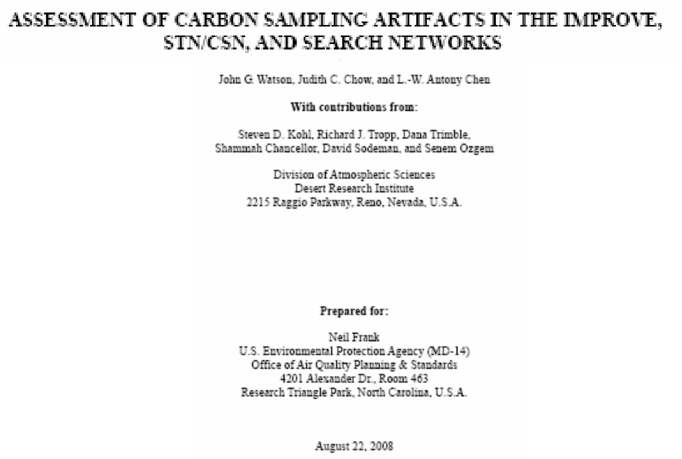
Reisinger et al.(2008) ES&T 42, 884–889

Conclusions

- BC from IS method can be corrected for influence of BrC
- Estimation of BrC concentration
- Effect of biomass smoke on EC or BC methods!!!
- What does this imply for the standard?

- But: depends on proxy substances

Artifacts



ASSESSMENT OF CARBON SAMPLING ARTIFACTS IN THE IMPROVE, STN/CSN, AND SEARCH NETWORKS

John G. Watson, Judith C. Chow, and L.-W. Antony Chen

With contributions from:

Steven D. Kohl, Richard J. Tropp, Dana Trimble,
Shammah Chancellor, David Sodeman, and Senem Ozgem

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August 22, 2008

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Measurement requirements

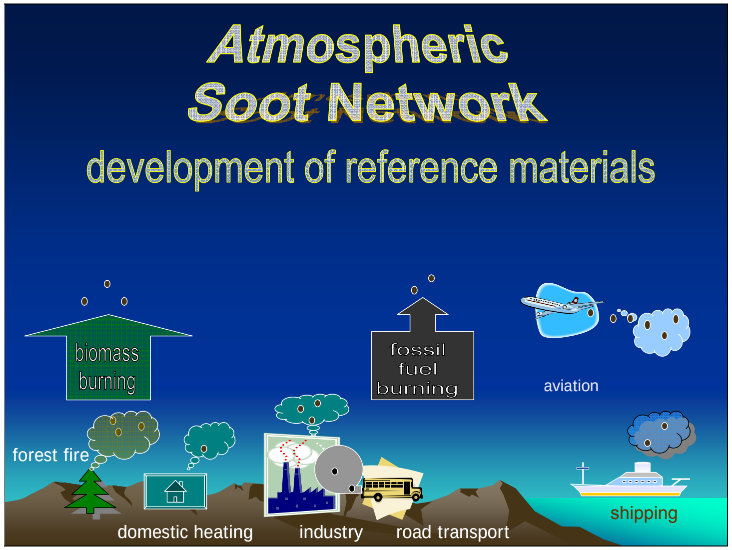
Tasks:

- derive an overview on available, practicable measurement techniques and their comparability, repetitiveness!
- What is been applied in Europe?
- Recommendations for standardisation!

Question related to standardisation:

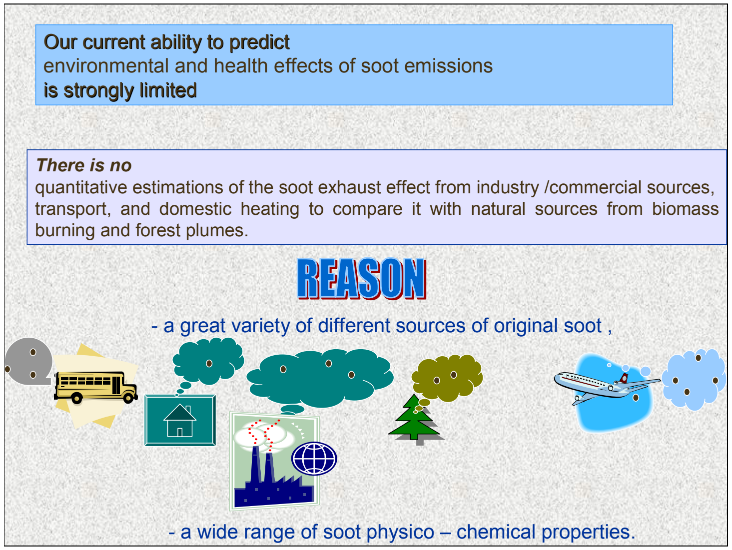
- on-line or off-line method?
- manual or automatic method?
- combined EC and OC method?
- optically or mass based method?
- comparability?
- repeatability?
- calibration / validation?

A.3 Atmospheric Soot Network development of reference materials



Atmospheric Soot Network

development of reference materials



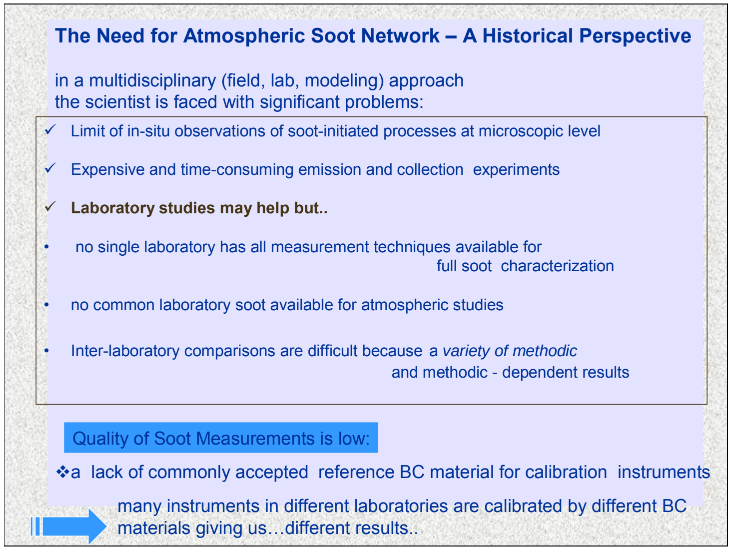
Our current ability to predict
environmental and health effects of soot emissions
is strongly limited

There is no
quantitative estimations of the soot exhaust effect from industry /commercial sources, transport, and domestic heating to compare it with natural sources from biomass burning and forest plumes.

REASON

- a great variety of different sources of original soot ,

- a wide range of soot physico – chemical properties.



The Need for Atmospheric Soot Network – A Historical Perspective

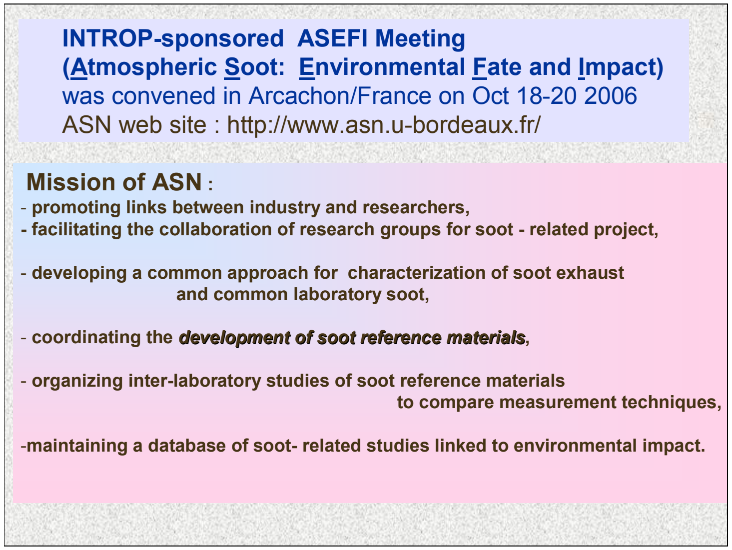
in a multidisciplinary (field, lab, modeling) approach
the scientist is faced with significant problems:

- ✓ Limit of in-situ observations of soot-initiated processes at microscopic level
- ✓ Expensive and time-consuming emission and collection experiments
- ✓ **Laboratory studies may help but..**
- no single laboratory has all measurement techniques available for full soot characterization
- no common laboratory soot available for atmospheric studies
- Inter-laboratory comparisons are difficult because a *variety of methodic* and methodic - dependent results

Quality of Soot Measurements is low:

❖a lack of commonly accepted reference BC material for calibration instruments

many instruments in different laboratories are calibrated by different BC materials giving us…different results..



INTROP-sponsored ASEFI Meeting
(Atmospheric Soot: Environmental Fate and Impact)
was convened in Arcachon/France on Oct 18-20 2006
ASN web site : http://www.asn.u-bordeaux.fr/

Mission of ASN :

- promoting links between industry and researchers,
- facilitating the collaboration of research groups for soot - related project,

- developing a common approach for characterization of soot exhaust and common laboratory soot,

- coordinating the *development of soot reference materials*,

- organizing inter-laboratory studies of soot reference materials to compare measurement techniques,

-maintaining a database of soot- related studies linked to environmental impact.

ASN: characteristics of reference calibration materials

- precisely- known properties, especially the content and nature of organic compounds
- reproducibility
- stability
- certification
- comparison Test campaigns

@RM Round Robin Test

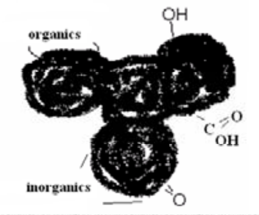
There are currently no controlled methods for producing soot of precisely-known properties, i.e. size, surface area, composition, organic coverage.

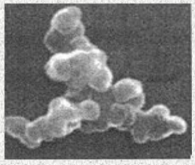
The development of atmospheric representative and accessible BC materials with reproducible “programmable properties” will ensure long-term intra and inter-laboratory data quality leading to a great progress of the entire environmental community in the BC measurement and monitoring.

Combustion particles in atmosphere: typical features

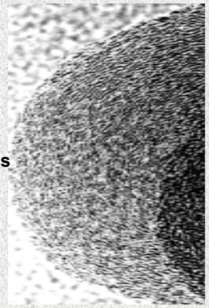
Soot is a product of incomplete burning of hydrocarbons

EC, OC + inorganic





morphology



microcrystallites of graphites

soot agglomerates of primary particles 30-100 нм

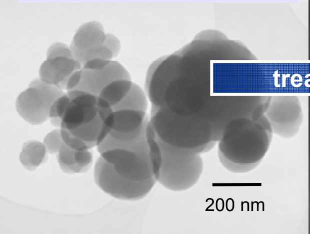
Combustion particles in atmosphere: typical features

fossil fuel burning

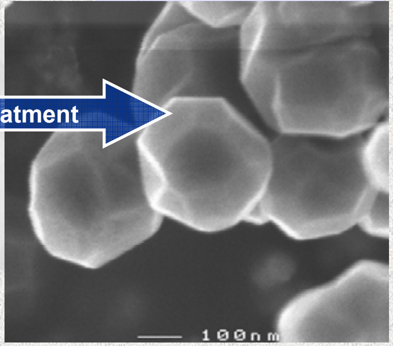
OC content:
alkanes, alkenes, PAHs,
organic aromatic and aliphatic acids,
ketons, esters, alkilbenzenes,
and derivaties

ASN: Elemental Carbon Reference Material

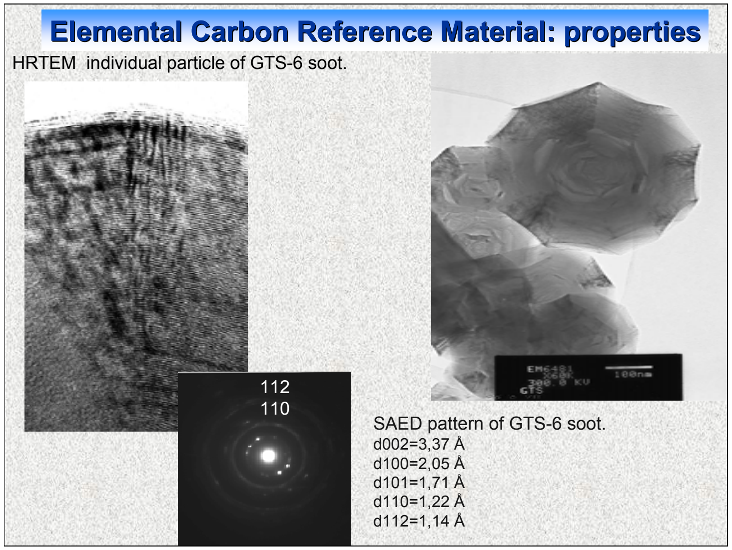
Thermal soot by gas pyrolysis



Graphitized Thermal soot GTS



- **cleaning from**
  - **- organic coverage,**
  - **- inorganics, ash.**
- **production of well-graphitized structure, perfect chemically uniform surface.**

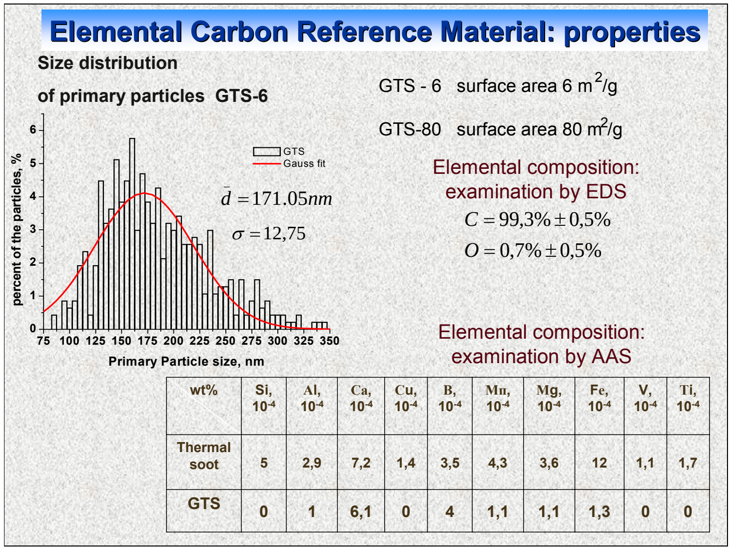


Elemental Carbon Reference Material: properties

HRTEM individual particle of GTS-6 soot.

SAED pattern of GTS-6 soot.

d002=3,37 Å
d100=2,05 Å
d101=1,71 Å
d110=1,22 Å
d112=1,14 Å



Elemental Carbon Reference Material: properties

Size distribution

of primary particles GTS-6

$\bar{d} = 171.05\,nm$

$\sigma = 12{,}75$

GTS - 6 surface area 6 m^2/g

GTS-80 surface area 80 m^2/g

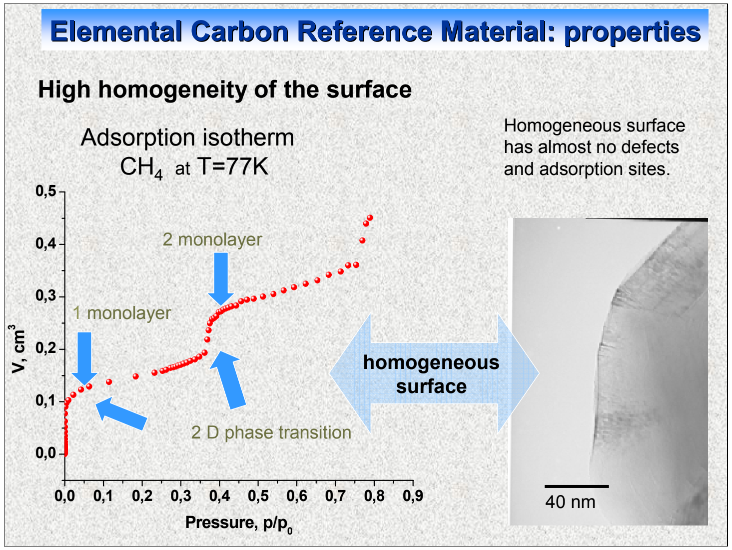
Elemental composition:
examination by EDS

$C = 99{,}3\% \pm 0{,}5\%$

$O = 0{,}7\% \pm 0{,}5\%$

Elemental composition:
examination by AAS

wt%	Si, 10^{-4}	Al, 10^{-4}	Ca, 10^{-4}	Cu, 10^{-4}	B, 10^{-4}	Mп, 10^{-4}	Mg, 10^{-4}	Fe, 10^{-4}	V, 10^{-4}	Ti, 10^{-4}
Thermal soot	5	2,9	7,2	1,4	3,5	4,3	3,6	12	1,1	1,7
GTS	0	1	6,1	0	4	1,1	1,1	1,3	0	0

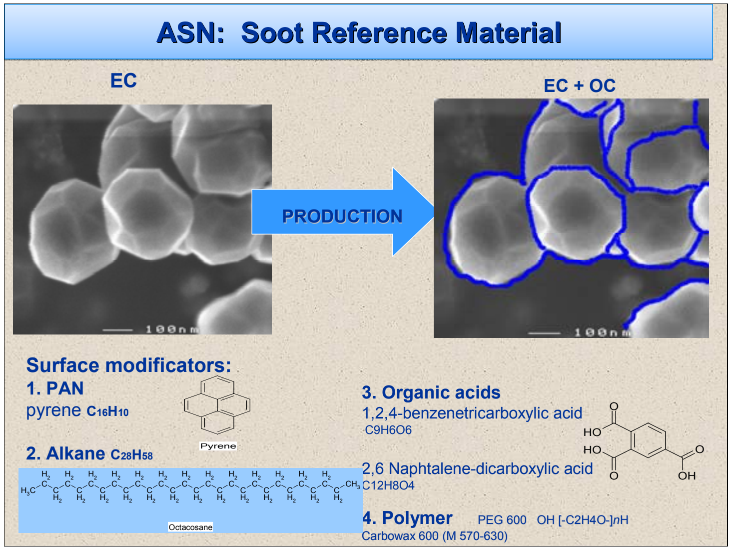


Elemental Carbon Reference Material: properties

High homogeneity of the surface

Adsorption isotherm
CH_4 at T=77K

Homogeneous surface has almost no defects and adsorption sites.



ASN: Soot Reference Material

Surface modificators:

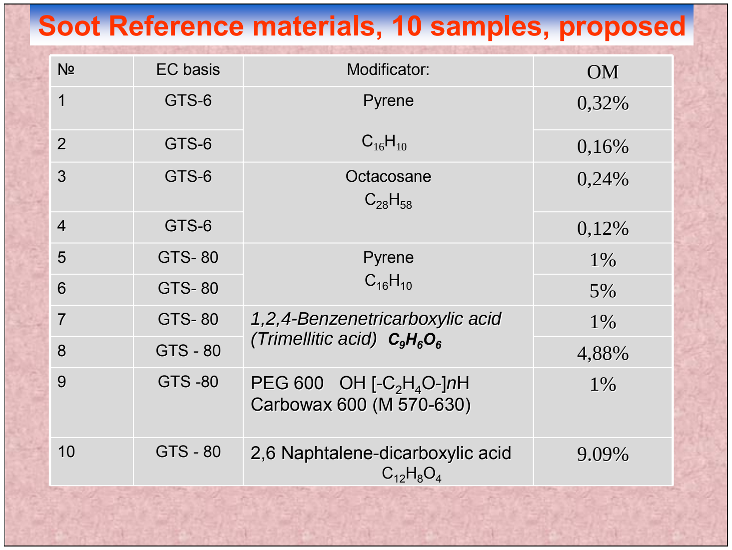
1. PAN
pyrene $C_{16}H_{10}$

2. Alkane $C_{28}H_{58}$

3. Organic acids
1,2,4-benzenetricarboxylic acid
C9H6O6

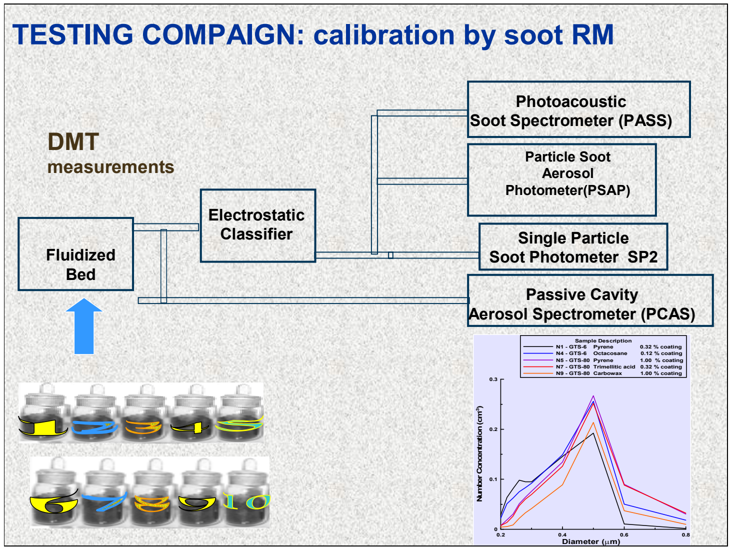
2,6 Naphtalene-dicarboxylic acid
C12H8O4

4. Polymer PEG 600 OH [-C2H4O-]*n*H
Carbowax 600 (M 570-630)



Soot Reference materials, 10 samples, proposed

№	EC basis	Modificator:	OM
1	GTS-6	Pyrene $C_{16}H_{10}$	0,32%
2	GTS-6		0,16%
3	GTS-6	Octacosane $C_{28}H_{58}$	0,24%
4	GTS-6		0,12%
5	GTS- 80	Pyrene $C_{16}H_{10}$	1%
6	GTS- 80		5%
7	GTS- 80	*1,2,4-Benzenetricarboxylic acid (Trimellitic acid)* $C_9H_6O_6$	1%
8	GTS - 80		4,88%
9	GTS -80	PEG 600 OH [-C_2H_4O-]*n*H Carbowax 600 (M 570-630)	1%
10	GTS - 80	2,6 Naphtalene-dicarboxylic acid $C_{12}H_8O_4$	9.09%



TESTING COMPAIGN: calibration by soot RM

DMT measurements

Fluidized Bed

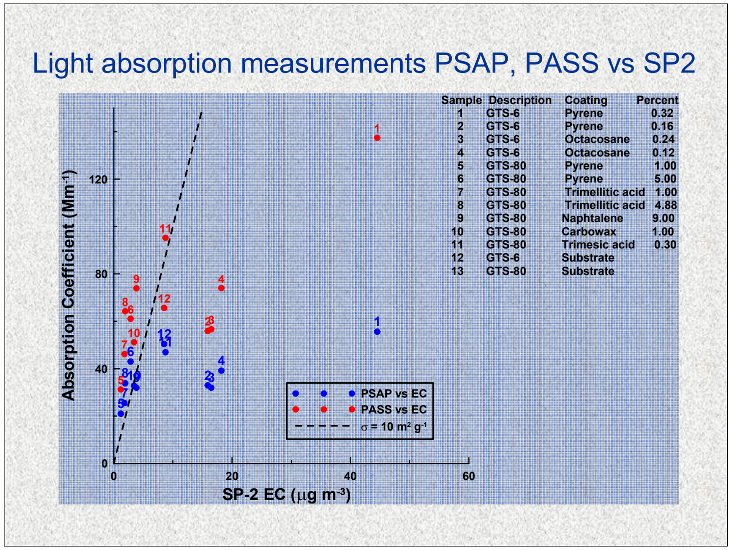
Electrostatic Classifier

Photoacoustic Soot Spectrometer (PASS)

Particle Soot Aerosol Photometer(PSAP)

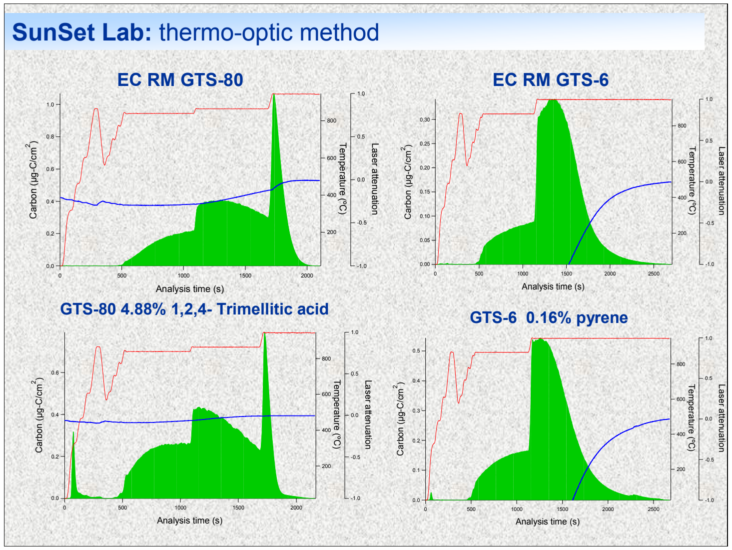
Single Particle Soot Photometer SP2

Passive Cavity Aerosol Spectrometer (PCAS)



Light absorption measurements PSAP, PASS vs SP2

Sample	Description	Coating	Percent
1	GTS-6	Pyrene	0.32
2	GTS-6	Pyrene	0.16
3	GTS-6	Octacosane	0.24
4	GTS-6	Octacosane	0.12
5	GTS-80	Pyrene	1.00
6	GTS-80	Pyrene	5.00
7	GTS-80	Trimellitic acid	1.00
8	GTS-80	Trimellitic acid	4.88
9	GTS-80	Naphtalene	9.00
10	GTS-80	Carbowax	1.00
11	GTS-80	Trimesic acid	0.30
12	GTS-6	Substrate	
13	GTS-80	Substrate	



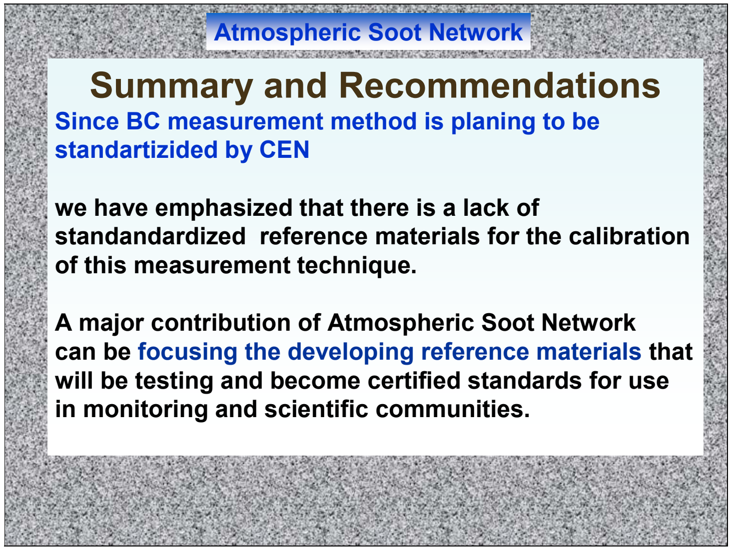
SunSet Lab: thermo-optic method

EC RM GTS-80

EC RM GTS-6

GTS-80 4.88% 1,2,4- Trimellitic acid

GTS-6 0.16% pyrene



Atmospheric Soot Network

Summary and Recommendations

Since BC measurement method is planing to be standartizided by CEN

we have emphasized that there is a lack of standandardized reference materials for the calibration of this measurement technique.

A major contribution of Atmospheric Soot Network can be focusing the developing reference materials that will be testing and become certified standards for use in monitoring and scientific communities.

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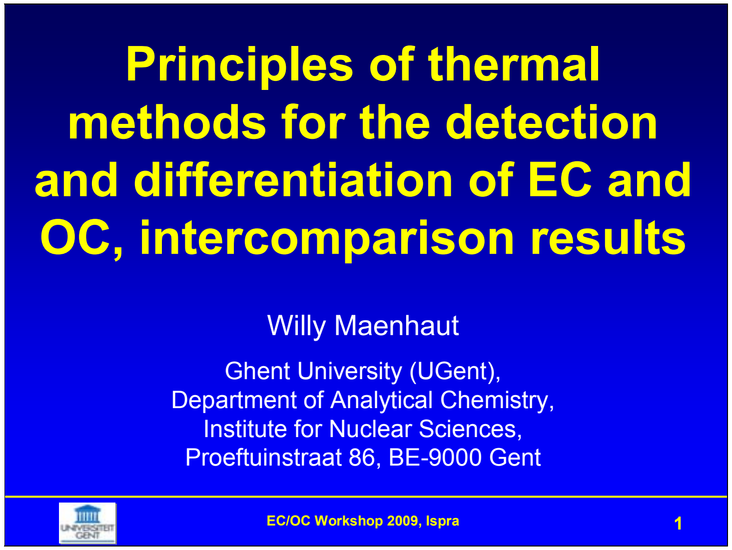
E. Vlasenko, T.Khokhlova

CINaM
B. Demirdjian, V. Tishkova

A.4 Principles of thermal methods for the detection and differentiation of EC and OC, intercomparison results



Principles of thermal methods for the detection and differentiation of EC and OC, intercomparison results

Willy Maenhaut

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Department of Analytical Chemistry,
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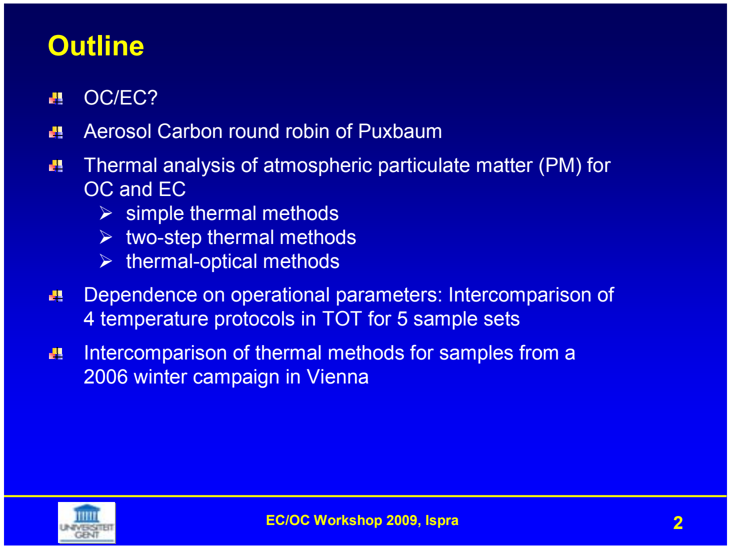

Outline

- OC/EC?
- Aerosol Carbon round robin of Puxbaum
- Thermal analysis of atmospheric particulate matter (PM) for OC and EC
  - simple thermal methods
  - two-step thermal methods
  - thermal-optical methods
- Dependence on operational parameters: Intercomparison of 4 temperature protocols in TOT for 5 sample sets
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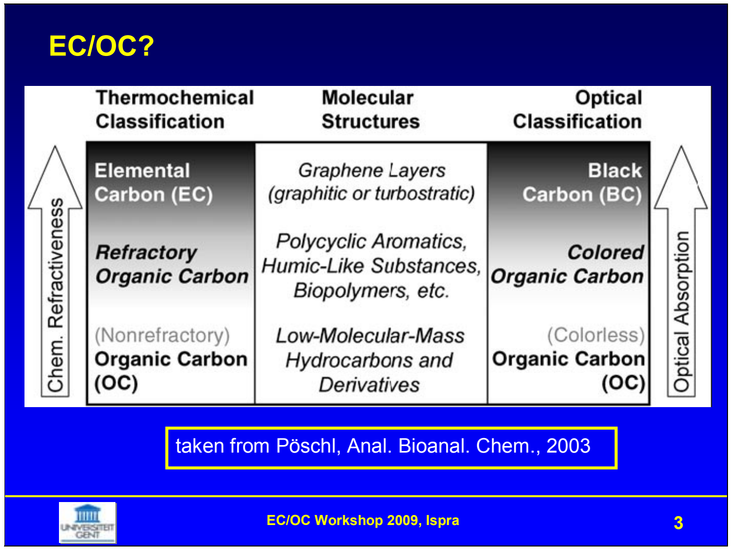
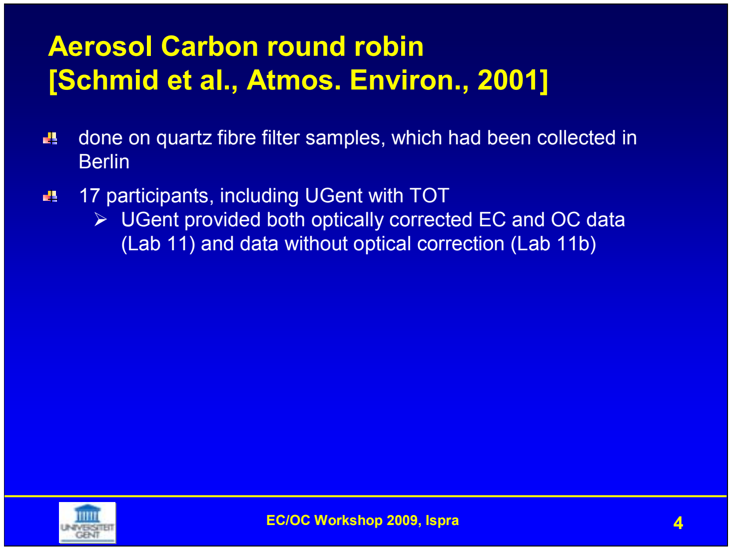


EC/OC?

Thermochemical Classification	Molecular Structures	Optical Classification
Elemental Carbon (EC)	*Graphene Layers (graphitic or turbostratic)*	**Black Carbon (BC)**
Refractory Organic Carbon	*Polycyclic Aromatics, Humic-Like Substances, Biopolymers, etc.*	***Colored Organic Carbon***
(Nonrefractory) **Organic Carbon (OC)**	*Low-Molecular-Mass Hydrocarbons and Derivatives*	(Colorless) **Organic Carbon (OC)**

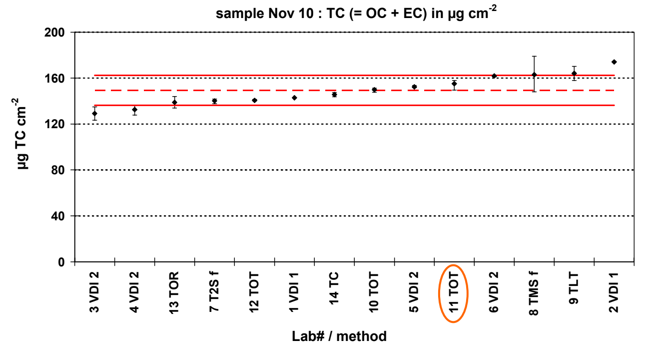
taken from Pöschl, Anal. Bioanal. Chem., 2003



Aerosol Carbon round robin [Schmid et al., Atmos. Environ., 2001]

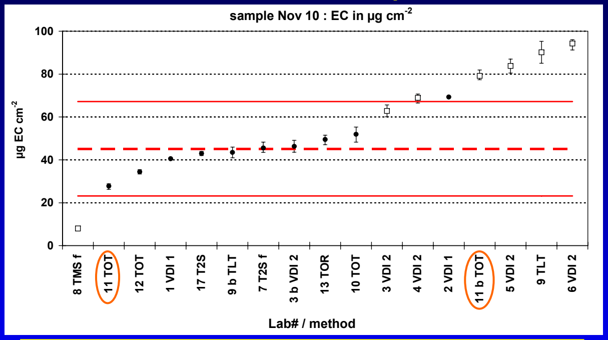
- done on quartz fibre filter samples, which had been collected in Berlin
- 17 participants, including UGent with TOT
  - UGent provided both optically corrected EC and OC data (Lab 11) and data without optical correction (Lab 11b)

TC values for a difficult sample



- determination of TC (= OC + EC) is no problem
- the red dashed line is the mean
- red full lines: mean ± 1 standard deviation

EC values for a difficult sample



- quite some difference between the EC data of the various participants
- filled black symbols are the data of the methods, which were considered as more reliable, e.g., those with optical correction
  - red dashed line is the mean of the more reliable data
  - red full lines: mean ± 2 standard deviations

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Thermal analysis of PM for OC and EC

- Total carbon (TC) = OC + EC + (CC)

- Analysis in the lab of collected aerosol samples
  - samples normally collected on quartz fibre filters

Thermal methods

1. Simple thermal methods
   - Evolved Gas Analysis (EGA) [Puxbaum, Novakov]
2. Two-step thermal methods
   - Cachier method [Tellus B, 1989]
   - VDI-2 method
3. Thermal-optical methods
   - thermal-optical transmission (TOT) technique with instrument of Sunset Lab
   - thermal-optical reflectance (TOR) technique with instrument of Desert Research Institute (DRI)

Evolved Gas Analysis (EGA)

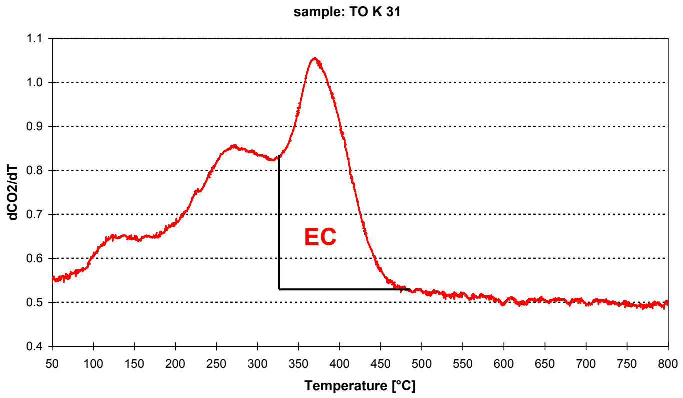
- heating in oxygen
- program with linear temperature ramp
  - from room temperature to 800°C
  - temperature ramp of 20°C min^{-1}
- carbonaceous vapours converted into CO_2 by MnO_2 catalyst (at 700°C)
  - CO_2 measured with NDIR detector
  - alternative detection methods for CO_2
    - coulometry
    - conversion into CH_4 and measurement of the latter with a flame ionisation detector (FID)
- thermogram obtained
  - CO_2 peaks at low temperature considered as OC
  - CO_2 peak at high temperature considered as EC
- quantification done by determining the area under the peaks
  - calibration with samples of known amount of carbon (e.g., sucrose)

Evolved Gas Analysis (EGA)

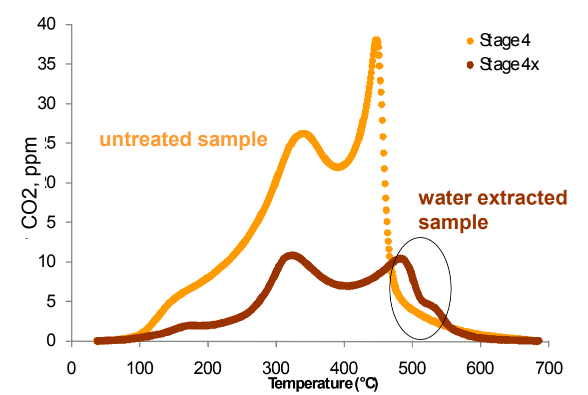
Limitation of the pure thermal methods

- some of the organic matter may be converted into pyrolitic EC (PEC) by pyrolysis or charring and like the “real” EC only be converted into vapour at higher temperature and then erroneously be counted as EC
  - this limitation applies also to the two-step thermal methods
  - the artifact formation of PEC is smaller in an oxidising atmosphere (O_2) than in an inert gas (He, N_2, Ar)
- the presence of inorganic cations, such as K^+ or Na^+ (which are important components in biomass burning samples), has a serious influence on the thermal evolution of the carbonaceous vapours
  - peaks come faster
  - distinction of EC from OC is often not easy
  - aqueous extraction of the sample often done to improve the determination of EC

Example of thermogram obtained by EGA



Thermograms for cascade impactor stage from SMOCC



Two-step thermal methods: Cachier

- Samples first subjected to a pretreatment (in HCl vapour) to remove the inorganic carbonates
- Measurement of EC [Cachier et al., Tellus B, 1989]
  - one part of the sample then subjected to a thermal pretreatment step (precombustion at 340°C for 2 h) in order to remove the organic component
  - the remaining EC is determined by combustion of the sample at 1100°C and coulometric titration of the evolved CO_2 in a carbon analyzer (Ströhlein Coulomat 702C)
- Measurement of OC
  - for another part of the sample, the combustion/titration performed without any thermal pretreatment, so that the content of TC is obtained
  - the difference (TC - BC) then yields OC

Two-step thermal methods: VDI-2

- As an example: Approach currently used at IfT, Leipzig [Neusüß et al., JGR, 2002; Plewka et al., J. Atmos. Chem., 2004]
- Two-step thermographic method using a commercial carbon analyzer C-mat 5500 (Ströhlein, Germany); consists of
  - free programmable combustion furnace (IR 05)
  - followed by a resistance oven (D03 GTE) holding the CuO catalyst (to convert carbon quantitatively to CO_2) at 850°C
  - and a NDIR detector measuring the IR absorption of the CO_2 formed
- First step: heating of the sample at 590°C (or 650°C) in nitrogen carrier gas for OC volatilisation
- Second step: EC combusted at 650°C in an oxygen atmosphere
- In between the two steps, the IR furnace cooled down to 50°C to avoid EC losses during flushing with oxygen

---

Thermal-optical transmission (TOT) technique

- e.g. TOT technique with instrument of Sunset Lab
  - for analysis of aerosol samples on quartz fibre filter
- in Dept. Anal. Chem., UGent: 2 Sunset Lab TOT instruments

1st phase [in pure He]

- filter punch, in quartz oven, in 4 steps heated to e.g. 900°C
- desorbed carbonaceous vapours catalytically oxidised into CO_2 (by MnO_2 held at 870°C)
- CO_2 reduced to CH_4 (in Ni-firebrick methanator, at 500°C)
- CH_4 measured with flame ionisation detector (FID)
- laser light (670 nm) continuously passed through filter punch
  - light transmission continuously measured

During 1st phase pyrolysis (charring) of part of the OC occurs with formation of PEC, so that the light transmission decreases

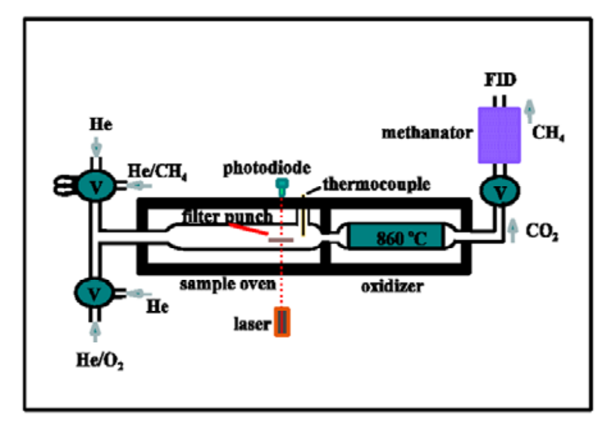
---

2nd phase [in 98%He/2%O_2 mixture]

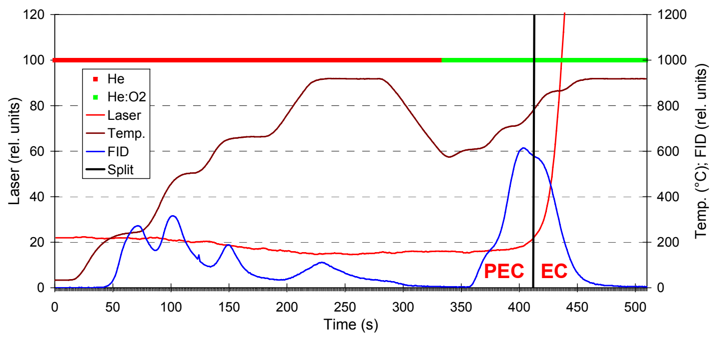
- after slight cooling, filter punch in four (or more) steps further heated to e.g. 900°C
- otherwise same as for 1st phase
- when the light transmission through the filter punch equals that seen at the beginning of the 1st phase, the OC/EC split is set
  - CO_2 measured in the 1st phase and during the 2nd phase prior to the split considered as OC (includes the PEC)
  - CO_2 measured after the split considered as the “real” EC

Total CO_2 measured during 2nd phase (sum of PEC + “real” EC) corresponds to the EC, which is measured without optical correction

Scheme of Sunset Lab TOT instrument (V = valve)



Thermogram for quartz fibre filter sample from Ghent, obtained with UGent standard temperature program (ST)



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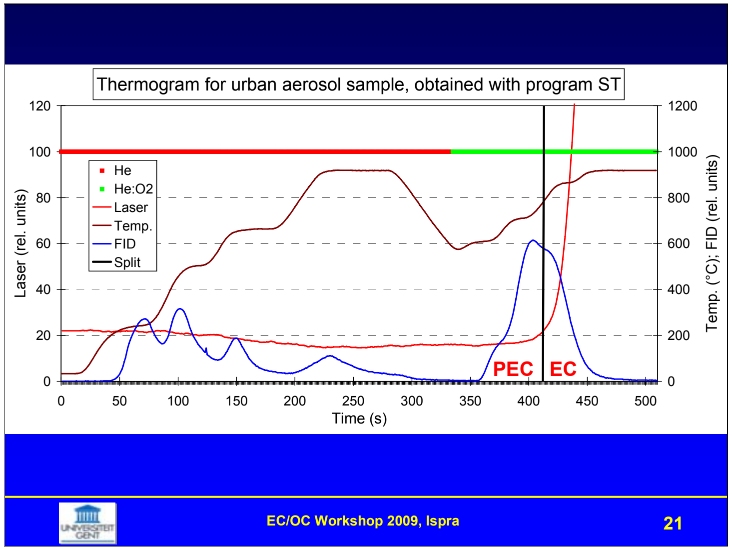
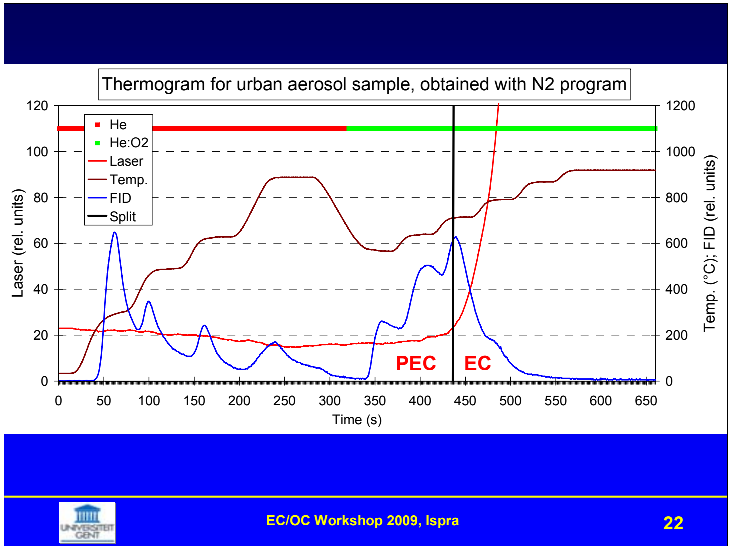
Dependence on operational parameters

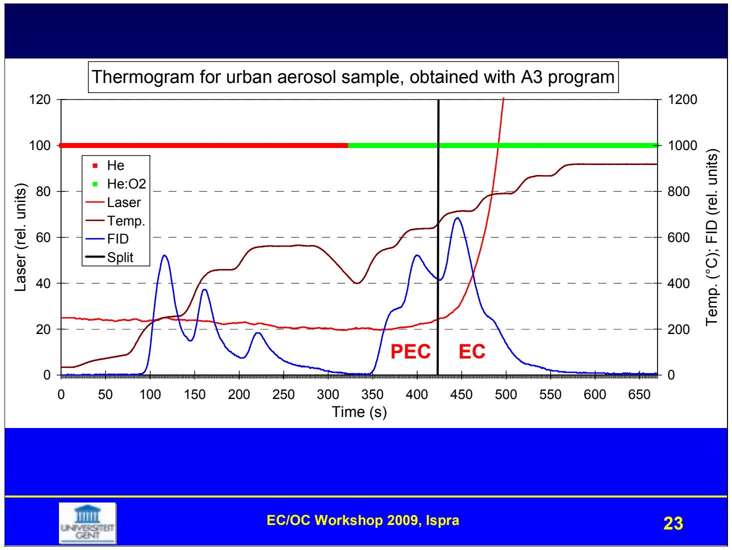
- For a single method, such as TOT, there is a strong dependence of the EC/TC ratio on the operational parameters and especially on the temperature program during the 1st phase of the analysis
- At UGent samples from 5 different locations analysed with 4 different temperature programs, with maximum temperature in 1st phase
  - UGent ST : 900 °C
  - NIOSH 2 (N2) : 870 °C
  - A3, proxy for temperature program used by DRI : 550 °C
  - EUSAAR 2 (E2) : 650 °C


Thermogram for urban aerosol sample, obtained with program ST

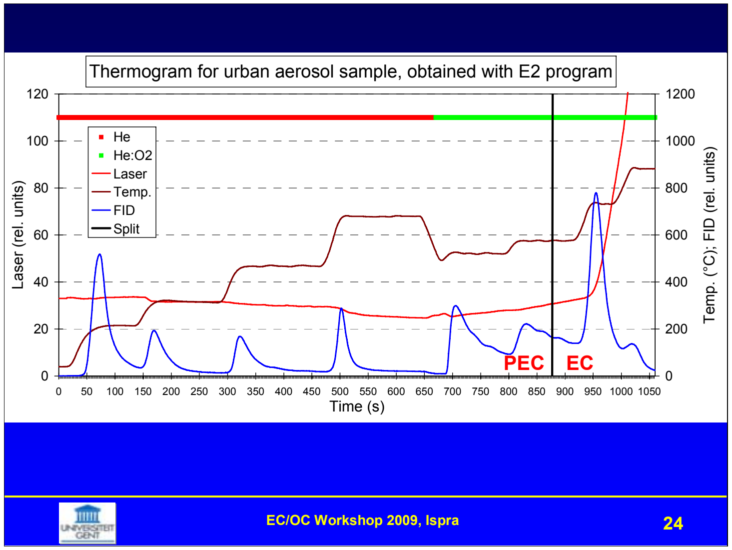
EC/OC Workshop 2009, Ispra


Thermogram for urban aerosol sample, obtained with N2 program

EC/OC Workshop 2009, Ispra


Thermogram for urban aerosol sample, obtained with A3 program

EC/OC Workshop 2009, Ispra

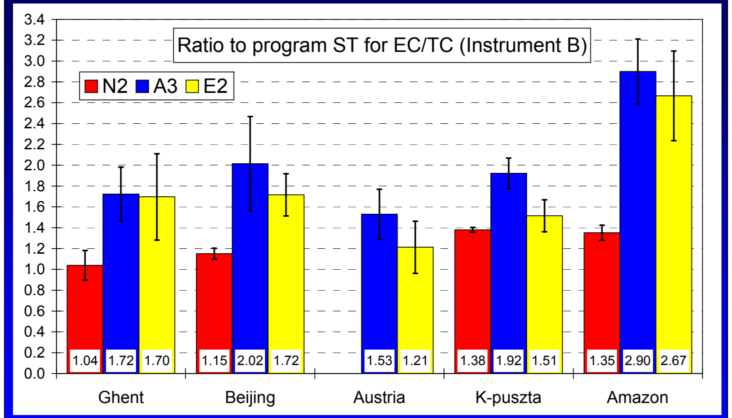

Thermogram for urban aerosol sample, obtained with E2 program

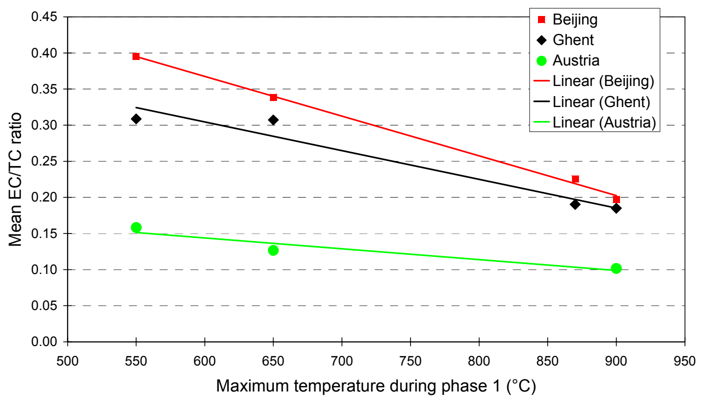
EC/OC Workshop 2009, Ispra

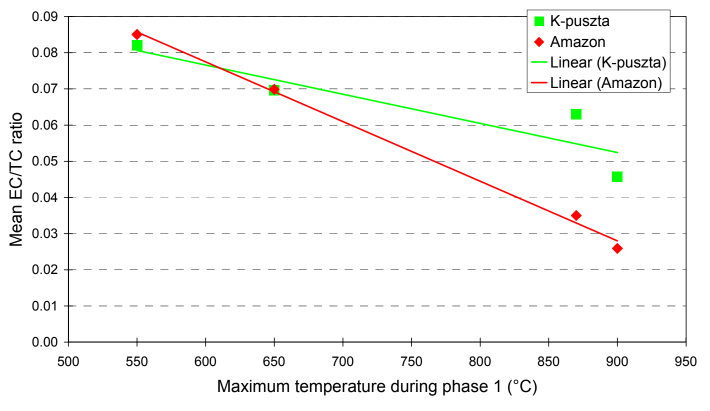
Table

Ranges for TC and for EC/TC, as obtained with the program ST and UGent instrument B, for 5 series of aerosol filter samples

Sample series	no. of samples	Range TC (µg/cm²)	Range EC/TC
Ghent	26	15 – 110	0.084 – 0.35
Beijing	5	71 – 240	0.15 – 0.24
Austria	16	18 – 40	0.076 – 0.13
K-puszta	5	16 – 25	0.038 – 0.056
Amazonia	5	57 – 98	0.021 – 0.031







Dependence on operational parameters

- For the same temperature program:
  - different EC/TC ratio for optical correction with TOT and with of TOR

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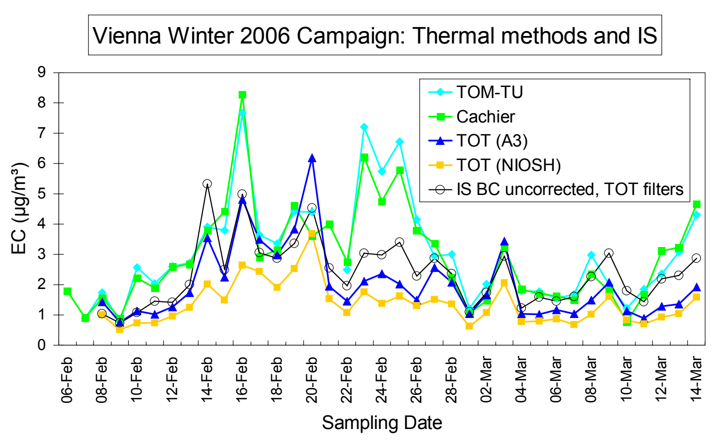
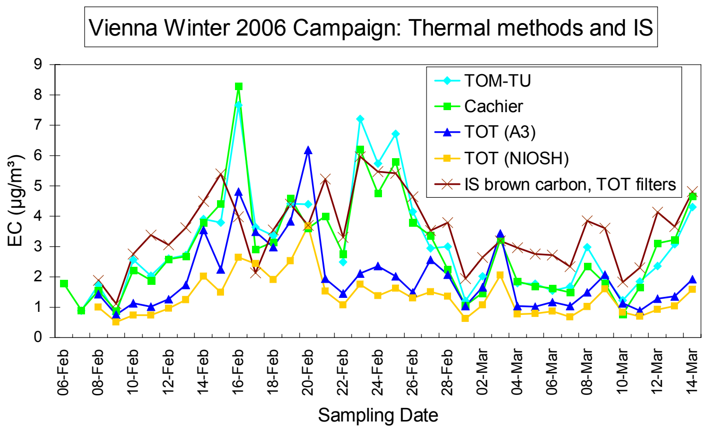
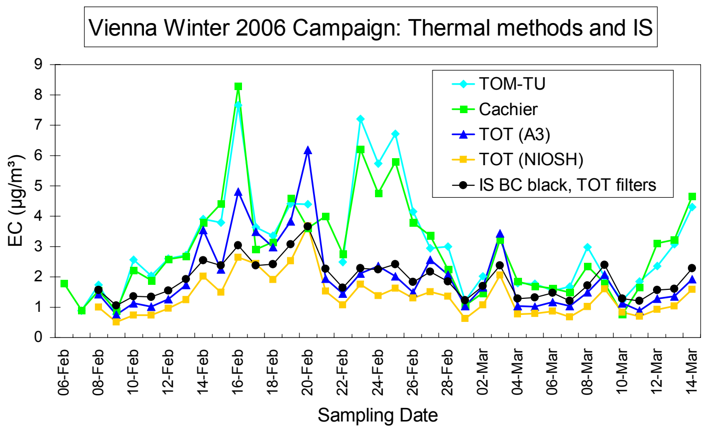
EC/BC intercomparison for aerosol samples collected in 2006 winter in Vienna [Reisinger et al., Environ. Sci. Technol., 2008]

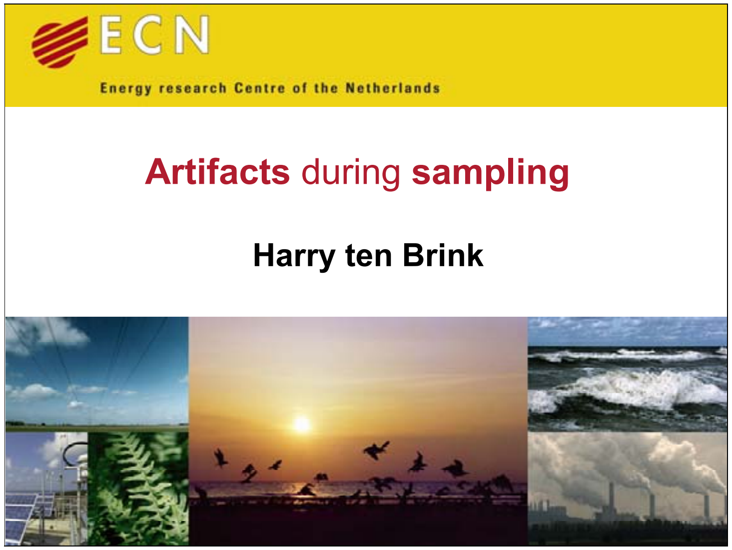
- samples of 24 hours collected on rooftop of Univ. of Vienna
- samples analysed by 3 optical methods and 4 thermal methods
  - optical (BC): LTM, MAAP, IS
  - thermal (EC): TOM-TU, Cachier, TOT-NIOSH, TOT-A3




Vienna Winter 2006 Campaign: Thermal methods and IS
EC (µg/m³)
0
1
2
3
4
5
6
7
8
9
TOM-TU
Cachier
TOT (A3)
TOT (NIOSH)
IS brown carbon, TOT filters
06-Feb
08-Feb
10-Feb
12-Feb
14-Feb
16-Feb
18-Feb
20-Feb
22-Feb
24-Feb
26-Feb
28-Feb
02-Mar
04-Mar
06-Mar
08-Mar
10-Mar
12-Mar
14-Mar
Sampling Date


Vienna Winter 2006 Campaign: Thermal methods and IS
EC (µg/m³)
0
1
2
3
4
5
6
7
8
9
TOM-TU
Cachier
TOT (A3)
TOT (NIOSH)
IS BC black, TOT filters
06-Feb
08-Feb
10-Feb
12-Feb
14-Feb
16-Feb
18-Feb
20-Feb
22-Feb
24-Feb
26-Feb
28-Feb
02-Mar
04-Mar
06-Mar
08-Mar
10-Mar
12-Mar
14-Mar
Sampling Date

A.5 Artifacts during sampling

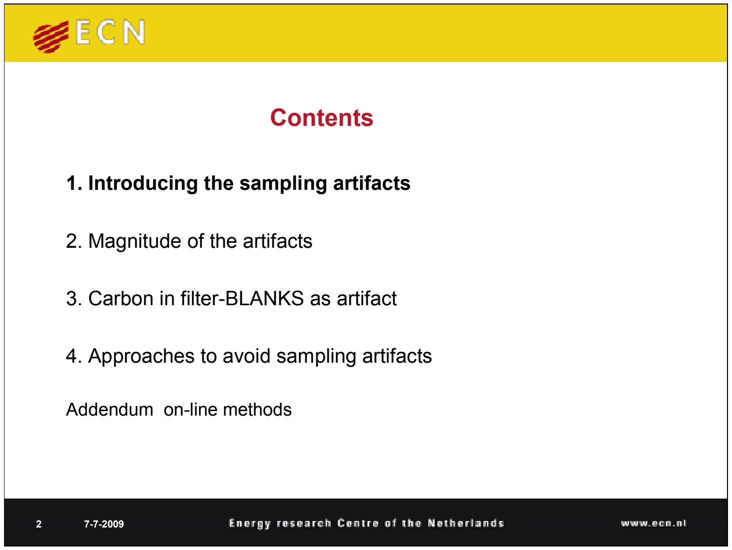


ECN

Energy research Centre of the Netherlands

Artifacts during sampling

Harry ten Brink



ECN

Contents

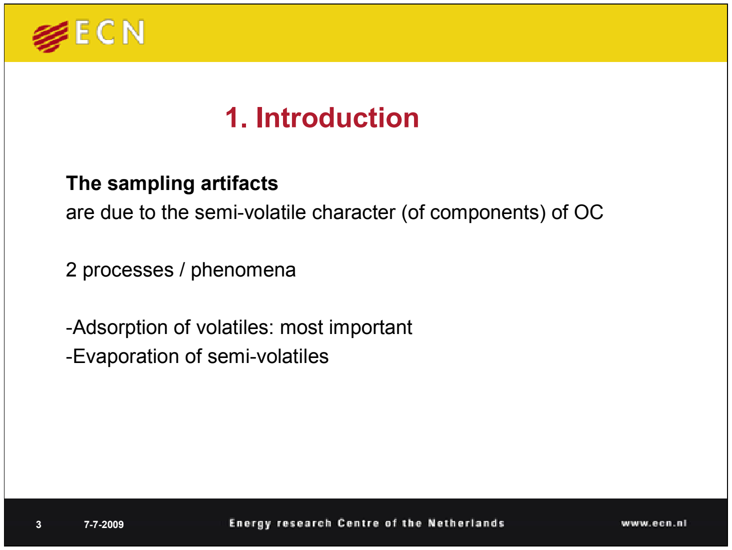
1. Introducing the sampling artifacts

2. Magnitude of the artifacts

3. Carbon in filter-BLANKS as artifact

4. Approaches to avoid sampling artifacts

Addendum on-line methods



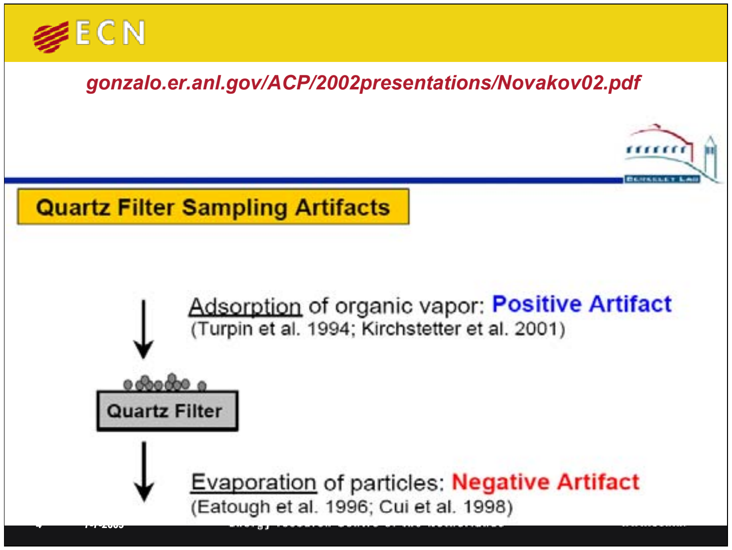
ECN

1. Introduction

The sampling artifacts
are due to the semi-volatile character (of components) of OC

2 processes / phenomena

-Adsorption of volatiles: most important
-Evaporation of semi-volatiles



ECN

gonzalo.er.anl.gov/ACP/2002presentations/Novakov02.pdf

Quartz Filter Sampling Artifacts

Adsorption of organic vapor: **Positive Artifact**
(Turpin et al. 1994; Kirchstetter et al. 2001)

Quartz Filter

Evaporation of particles: **Negative Artifact**
(Eatough et al. 1996; Cui et al. 1998)

Literature

Turpin et al., AE, 2000.

Dedicated laboratory investigations to quantify sampling artifacts like in case of nitrate are **not** possible.

Carbon compounds responsible for artifact are not known.

The next best approach is an intercomparison of collection methods

---

TC instead of OC

Investigation *should* focus on OC
However, amount of OC depends on analysis method
(Schmid / Puxbaum et al., 2001 round-robin)

Had a look at OC values in that study:

factor of 2 difference between institutes

Thus: there is a combined uncertainty in sampling and analysis of OC

Better: evaluation of data of **Total Carbon**

COMPARABILITY OF METHODS FOR MEASURING THE CARBON CONTENT IN AEROSOL IN EUROPE

HARRY TEN BRINK[1], ARJA EVEN[1]
K. MUELLER[2], TH. GNAUK[2], GER. SPINDLER[2]
X.CHI[3], W. MAENHAUT[3]
R. HITZENBERGER[4], A. BERNER[4]
H. BAUER[5], H. PUXBAUM[5]
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*1Energy Research Centre of the Netherlands (**ECN**), Petten, The Netherlands*
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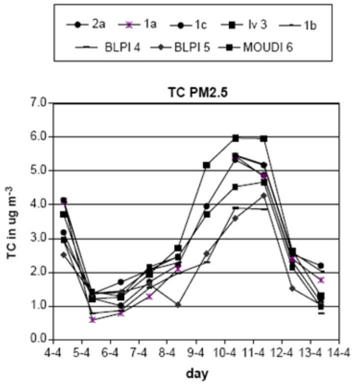
*3Gent University (**UGhent**), Institute for Nuclear Sciences, Gent, Belgium*
*4Institut fuer Experimentalphysik (**IEP**), Wien, Austria*
*5Institute for Analytical Chemistry, Vienna University of Technology (**TUV**), Austria*
*6National Institute of Chemistry (**NIC**), Ljubljana, Slovenia*
*7Joint Research Center (**JRC**), Ispra , Italy*



Scientific approach / experience in Europe

Filters in series Filter-pack
Sillanpää

Denuder preceeding the filter-pack
Maenhaut / Viana

Denuder filter/coated-filter
PTFE-filter followed by denuder and coated-filter
Putaud

Compare with US
•Networks with hundreds of stations
•scientific programs for 2 decades:

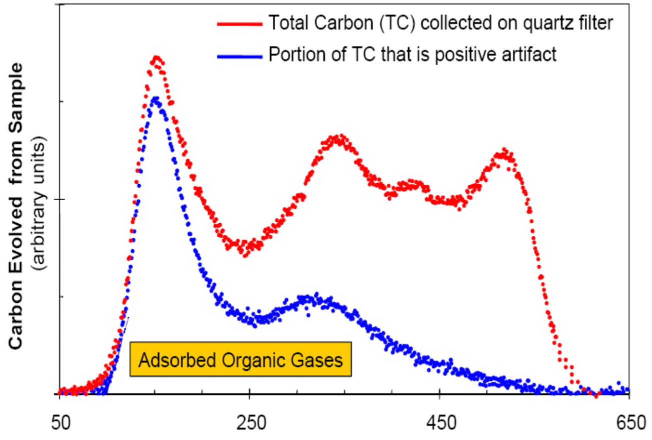
Turpin, Eatough, Chow, Kirchstetter/Novakov

Amount of air through filter and Carbon in 2d filter expressed as concentration

face velocity cm s^{-1}	**artifact**
20	4.6 µg C m^{-3}
40	2.9 µg C m^{-3}
80	1.8 µg C m^{-3}

Turpin *et al.*

Turpin *et al.* (1994) Atm. Env. 28, No 19, 3061 - 3071



How large is Positive Artifact?

Field Experiment	Back Quartz TC ÷ Front Quartz TC (%)
• CALSPAN (Smog chamber)	90 ± 34 (n = 34)
• CLAMS (UW CV-580)	77 ± 09 (n = 19)
• TARFOX (UW CV-580)	66 ± 07 (n = 28)
• SAFARI (UW CV-580)	54 ± 19 (n = 54)
• PRIDE (Tropical Trade Winds)	45 ± 16 (n = 04)
• ACE-2 (RV Vodyanitskiy)	30 ± 10 (n = 12)
• Berkeley, CA (LBNL)	30 ± 06 (n = 12)
• Fresno, CA (EPA Supersite, Oct 2000)	15 ± 06 (n = 20)

3. Carbon in filter-blanks: network-concern

In Europe little to no information on the amount of carbon in the filters **before sampling**

Filters are pre-fired: **all OC is combusted away**?!
but then: handling and exposure

For instance: filters are weighed before deployment in the field

Latest: Whatman-QMA filters are pre-fired in the factory!

Examples of blanks

Just finished year-long campaign in Netherlands

Analysis of filters used for equivalence tests for mass (EN 12341)

1500 filters
150 field blanks

Tens of stock-filters measured: “lot-blanks”

Evaluation so far

Example of field-blanks: filters in standard filter-carousel Rotterdam area, 2 sites

448-A-BL.L 20/09	**1.5**	DCMR-A-BL.L 20/09	**5.4**
448-A-BL.R 20/09	**1.3**	DCMR-A-BL.R 20/09	**4.0**
448-B-BL.L 20/09	**1.8**	DCMR-B-BL.L 20/09	**1.8**
448-B-BL.R 20/09	**1.9**	DCMR-B-BL.R 20/09	**1.3**

“Field blanks” in ug/m3

Field blanks versus actual values

Overall average of the field blanks

1.3 ug / m3
SD 0.6

This may be just acceptable versus the average of loaded filters:
5 ug/m3

The low blank is is due to the relatively high flow rate of 55 m3 / day.

Field Blanks in EMEP campaign

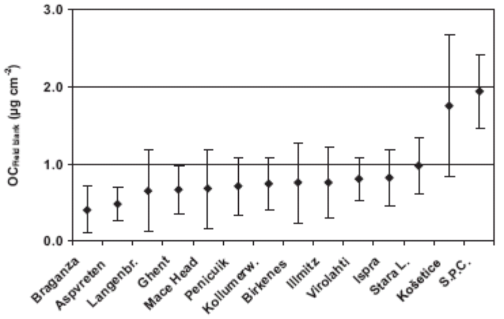


Fig. 2. Mean concentration of OC on field blanks. The size of the standard deviation is shown as error bars.

"Lot" Blanks; starting filters

Whatman-QMA filters, pre-fired in the factory

2 batches

	Per filter
	µg
Filter 1	112.6
Filter 2	19.4
Filter 3	105.8
Filter 4	38.6
Filter 5	116.2
Filter 6	36.2

Lot-blanks in more common unit

	TC in µg/cm^2
Filter 1	6.5
Filter 2	1.1
Filter 3	6.1
Filter 4	2.2
Filter 5	6.7
Filter 6	2.1

In red: typical values for filters from the top of a pile as received from manufacturer, contaminated by lid of the cassette!!

Carbon-blanks Kuhlbusch 1995

Filter	Treatment (°C, h)	Number of replicates	TC (µg/cm^{-2})	TH (µg/cm^{-2})	BC$_i$ (µg/cm^{-2})	BH (µg/cm^{-2})
From oven						
Borosilicate[a]	600/2	2	1.34 ± 0.18	6.44 ± 0.18	0.26 ± 0.01	1.33 ± 0.06
Quartz fiber[b,c]	n.t.	6	2.61 ± 1.01	ADL	0.39 ± 0.03	ADL
Quartz fiber[b,c]	n.t.	7	6.09 ± 0.58	ADL	0.92 ± 0.14	ADL
Quartz fiber[c]	600/6	4	1.33 ± 0.10	ADL	0.29 ± 0.05	6.44 ± 0.42
Quartz fiber[c]	800/1	4	1.63 ± 0.62	1.09 ± 0.88	0.58 ± 0.26	1.01 ± 0.05
Quartz fiber[c]	800/4	4	0.47 ± 0.07	0.21 ± 0.14	0.46 ± 0.69	0.26 ± 0.52
Quartz fiber[c]	850/4	8	0.54 ± 0.31	0.81 ± 0.76	0.43 ± 0.33	0.05 ± 0.07
From roof						
Quartz fiber[c]	600/6	3	1.35 ± 0.52	> 11.00	1.12 ± 1.10	4.11 ± 0.28
Quartz fiber[c]	850/4	7	1.01 ± 0.27	0.55 ± 0.23	0.14 ± 0.03	BDL
Sampled filters						
Quartz fiber[c]	Mixed[d]	~50	39 ± 22	7.8 ± 4.1	13.5 ± 6.9	0.80 ± 1.10

ECN

4. Avoiding **sampling artifacts** or quantifying these

1. **Filter-pack** (tandem filters): 2 filters in series -EMEP/Yttri

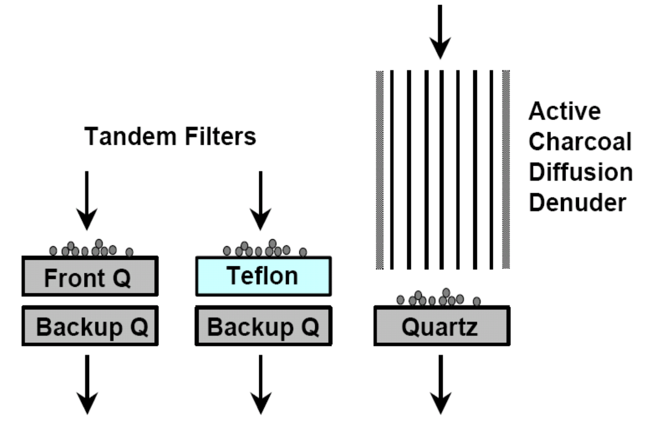
second filter is indicative of adsorption artifact

2. Gas-**denuder** before the filter-pack to remove adsorptive gases

3. Impregnated 2d filter to collect semi-volatiles from 1st filter

1b. Inert first filter (Teflon) : only volatiles on 2d

Sampling Methods to Correct for Adsorption Artifact



ECN

Which approach for CEN?

1. Face velocity
2. Filter-pack
3. Denuder filter-pack
4. Combination of OC/EC-analysis and mass-determination (weighing)?
5. Pre-firing
6. Filter brand

ECN

EAC2009 Artifacts

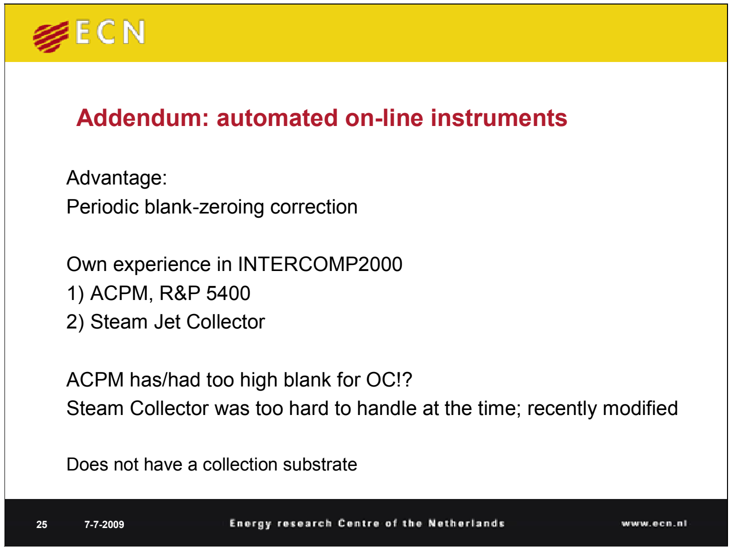
Subject of coming ANNUAL meeting of

Working-Group PM

European Aerosol Conference, EAC2009, Karlsruhe 5-9 September

Special Session on Artifacts

You can still submit contribution
on web-site EAC2009



ECN

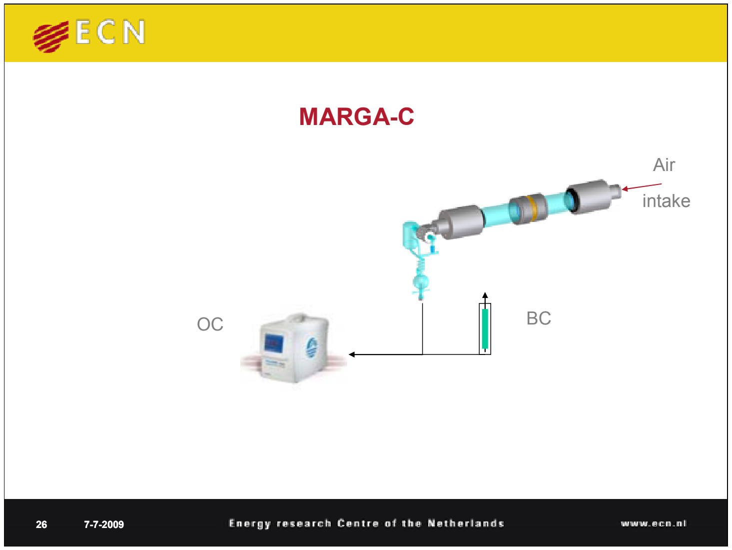
Addendum: automated on-line instruments

Advantage:
Periodic blank-zeroing correction

Own experience in INTERCOMP2000
1) ACPM, R&P 5400
2) Steam Jet Collector

ACPM has/had too high blank for OC!?
Steam Collector was too hard to handle at the time; recently modified

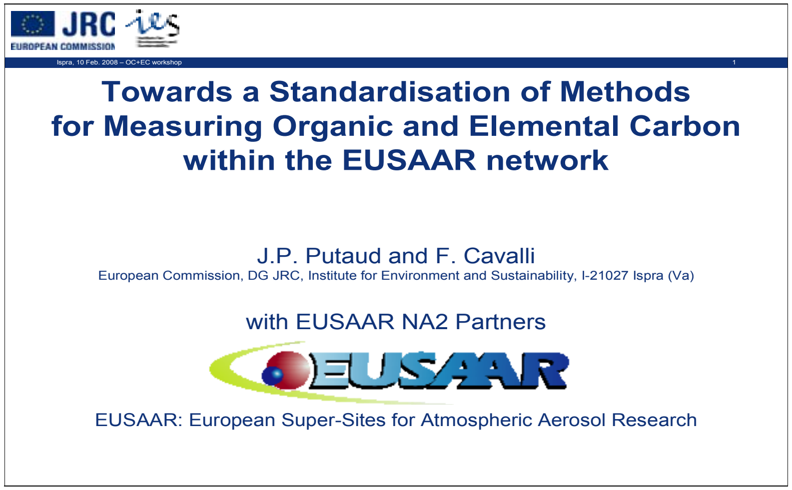
Does not have a collection substrate



ECN

MARGA-C

A.6 Towards a Standardisation of Methods for Measuring Organic and Elemental Carbon within the EUSAAR network



Ispra, 10 Feb. 2008 – OC+EC workshop 1

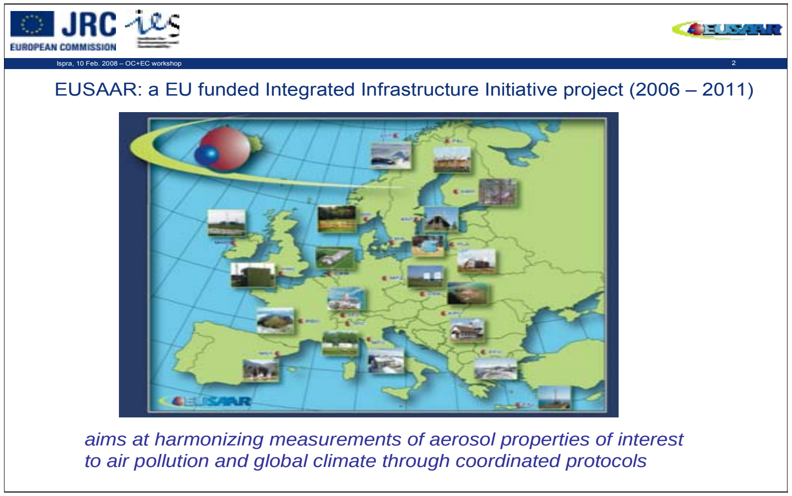
Towards a Standardisation of Methods for Measuring Organic and Elemental Carbon within the EUSAAR network

J.P. Putaud and F. Cavalli

European Commission, DG JRC, Institute for Environment and Sustainability, I-21027 Ispra (Va)

with EUSAAR NA2 Partners

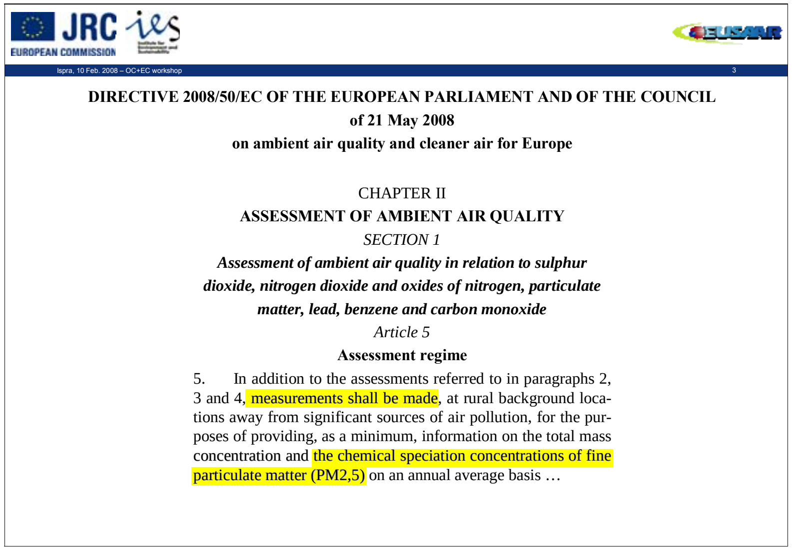
EUSAAR: European Super-Sites for Atmospheric Aerosol Research



Ispra, 10 Feb. 2008 – OC+EC workshop 2

EUSAAR: a EU funded Integrated Infrastructure Initiative project (2006 – 2011)

aims at harmonizing measurements of aerosol properties of interest to air pollution and global climate through coordinated protocols



Ispra, 10 Feb. 2008 – OC+EC workshop 3

DIRECTIVE 2008/50/EC OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

of 21 May 2008

on ambient air quality and cleaner air for Europe

CHAPTER II

ASSESSMENT OF AMBIENT AIR QUALITY

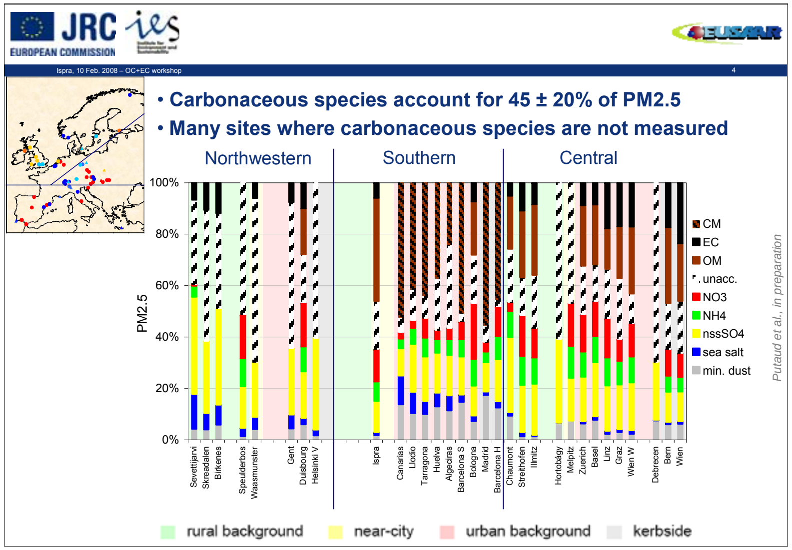
SECTION 1

Assessment of ambient air quality in relation to sulphur dioxide, nitrogen dioxide and oxides of nitrogen, particulate matter, lead, benzene and carbon monoxide

Article 5

Assessment regime

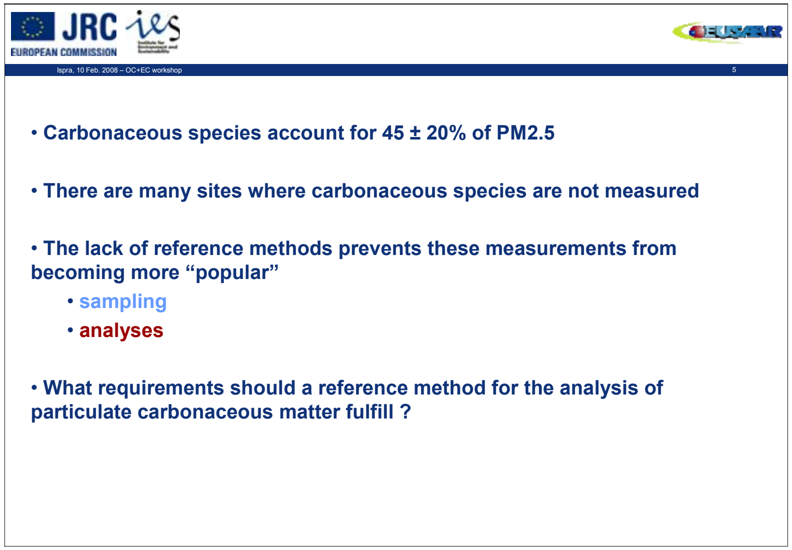
5. In addition to the assessments referred to in paragraphs 2, 3 and 4, measurements shall be made, at rural background locations away from significant sources of air pollution, for the purposes of providing, as a minimum, information on the total mass concentration and the chemical speciation concentrations of fine particulate matter (PM2,5) on an annual average basis …



Ispra, 10 Feb. 2008 – OC+EC workshop 4

- **Carbonaceous species account for 45 ± 20% of PM2.5**
- **Many sites where carbonaceous species are not measured**

Putaud et al., in preparation

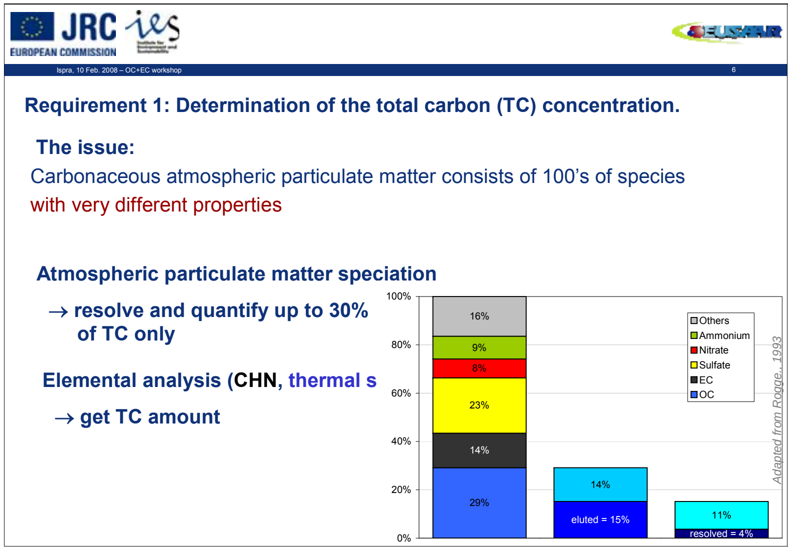


- **Carbonaceous species account for 45 ± 20% of PM2.5**

- **There are many sites where carbonaceous species are not measured**

- **The lack of reference methods prevents these measurements from becoming more “popular”**
  - **sampling**
  - **analyses**

- **What requirements should a reference method for the analysis of particulate carbonaceous matter fulfill ?**



Requirement 1: Determination of the total carbon (TC) concentration.

The issue:

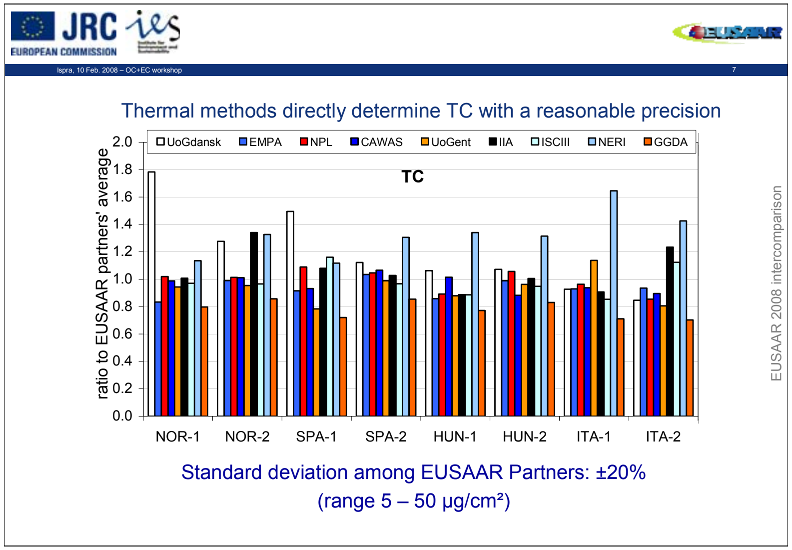
Carbonaceous atmospheric particulate matter consists of 100’s of species with very different properties

Atmospheric particulate matter speciation

→ resolve and quantify up to 30% of TC only

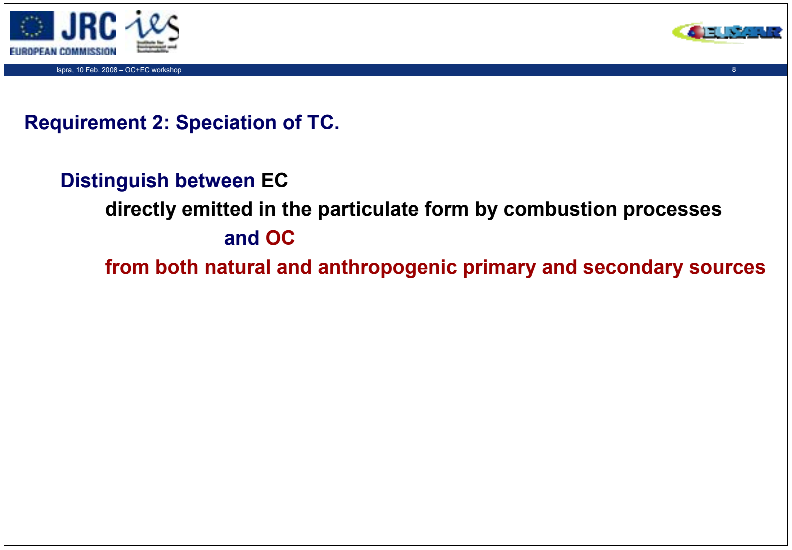
Elemental analysis (CHN, thermal s

→ get TC amount



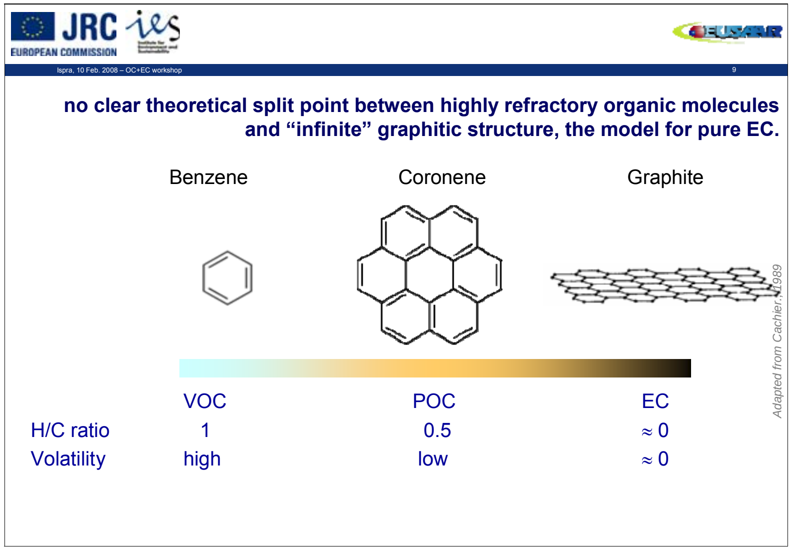
Thermal methods directly determine TC with a reasonable precision

Standard deviation among EUSAAR Partners: ±20%
(range 5 – 50 µg/cm²)



Requirement 2: Speciation of TC.

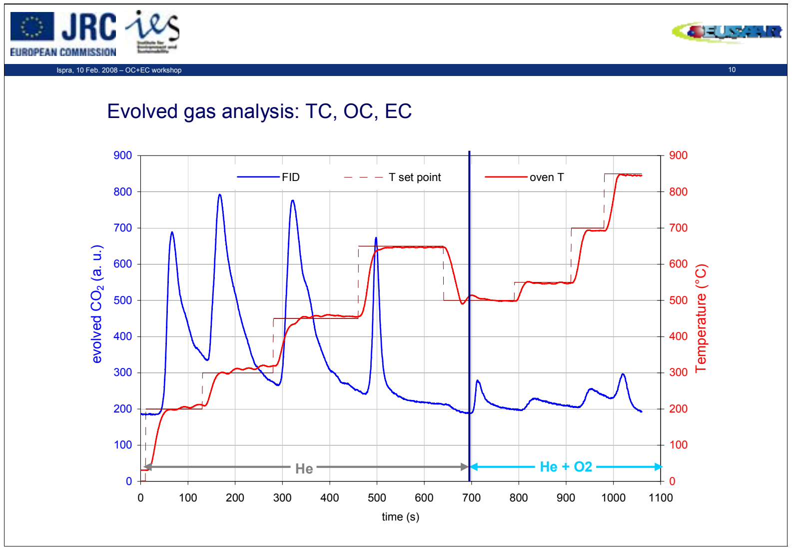
Distinguish between EC
directly emitted in the particulate form by combustion processes
and OC
from both natural and anthropogenic primary and secondary sources



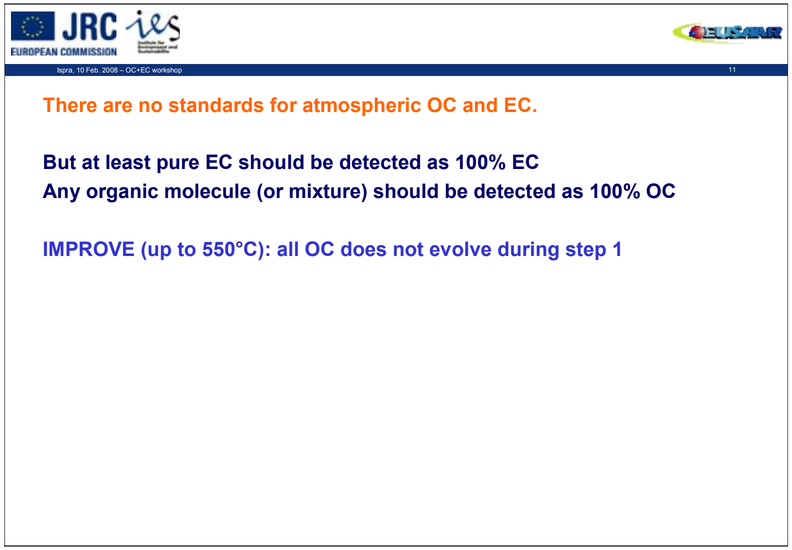
no clear theoretical split point between highly refractory organic molecules and “infinite” graphitic structure, the model for pure EC.

	VOC	POC	EC
H/C ratio	1	0.5	≈ 0
Volatility	high	low	≈ 0

Adapted from Cachier, 1989



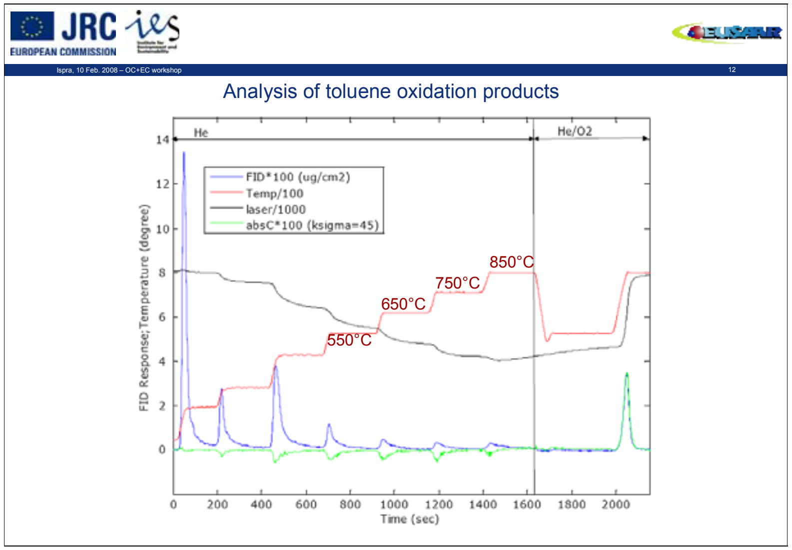
Evolved gas analysis: TC, OC, EC



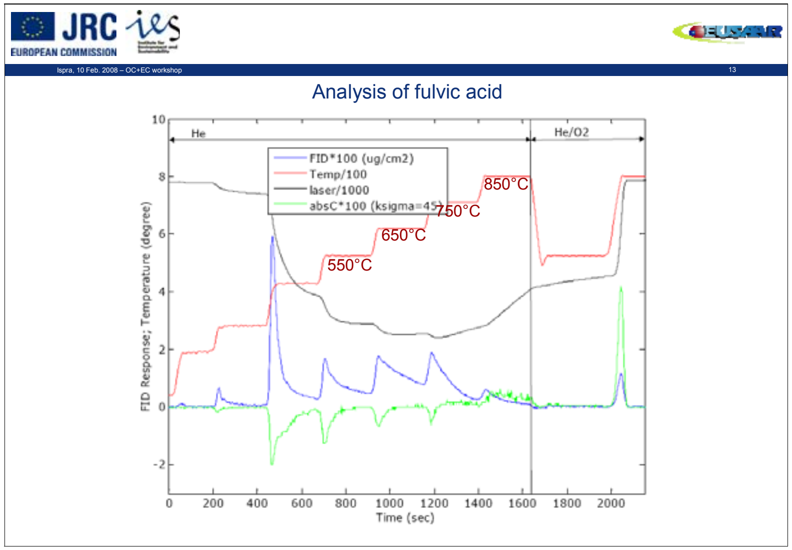
There are no standards for atmospheric OC and EC.

But at least pure EC should be detected as 100% EC
Any organic molecule (or mixture) should be detected as 100% OC

IMPROVE (up to 550°C): all OC does not evolve during step 1

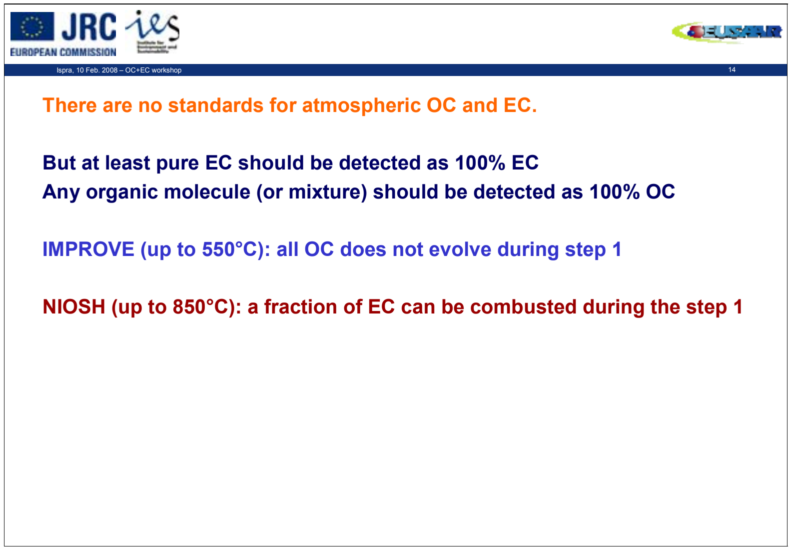


Analysis of toluene oxidation products



Ispra, 10 Feb. 2008 – OC+EC workshop 13

Analysis of fulvic acid



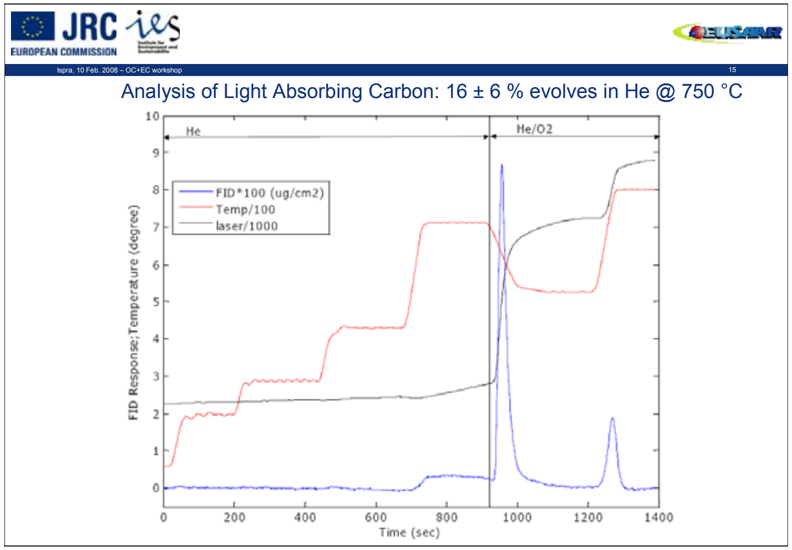
Ispra, 10 Feb. 2008 – OC+EC workshop 14

There are no standards for atmospheric OC and EC.

But at least pure EC should be detected as 100% EC
Any organic molecule (or mixture) should be detected as 100% OC

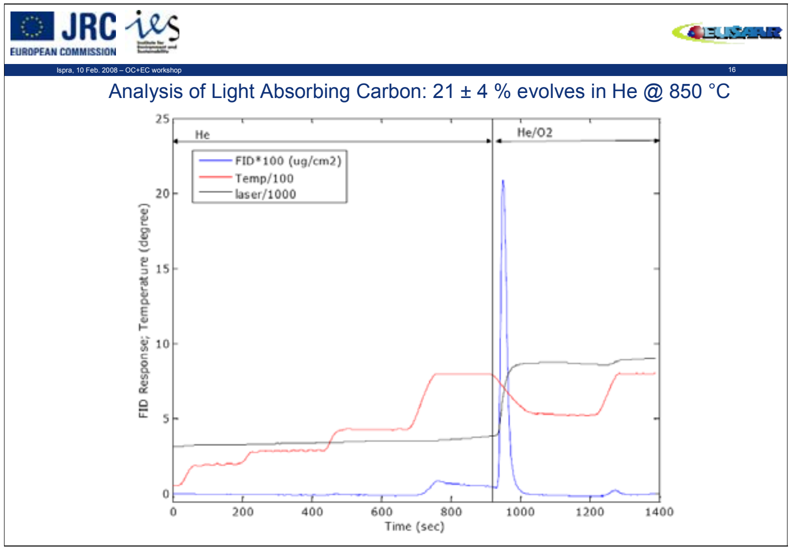
IMPROVE (up to 550°C): all OC does not evolve during step 1

NIOSH (up to 850°C): a fraction of EC can be combusted during the step 1



Ispra, 10 Feb. 2008 – OC+EC workshop 15

Analysis of Light Absorbing Carbon: 16 ± 6 % evolves in He @ 750 °C



Ispra, 10 Feb. 2008 – OC+EC workshop 16

Analysis of Light Absorbing Carbon: 21 ± 4 % evolves in He @ 850 °C

There are no standards for atmospheric OC and EC.

But at least pure EC should be detected as 100% EC
Any organic molecule (or mixture) should be detected as 100% OC

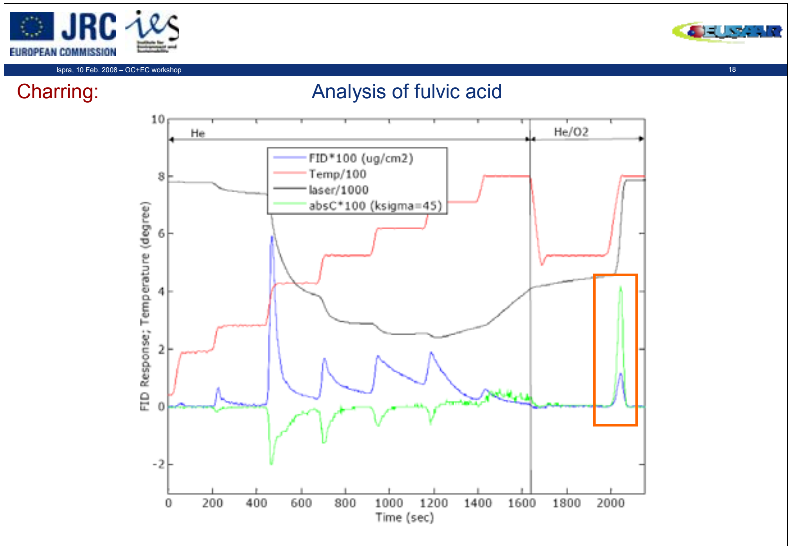
IMPROVE (up to 550°C): all OC does not evolve during step 1

NIOSH (up to 850°C): a fraction of EC can be combusted during the step 1

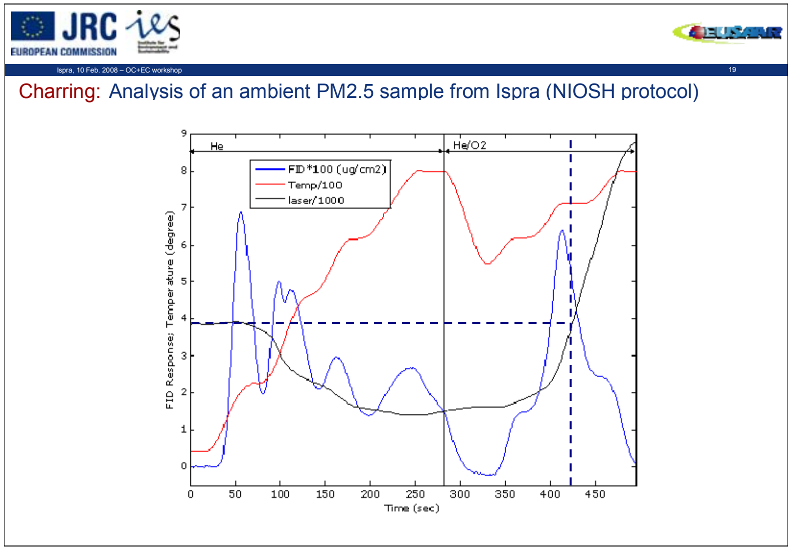
EUSAAR_2 (up to 650°C): best compromise
max 2.5 ± 24 % of EC evolves in He
min 80% of OC evolves in He

Carrier gas	Temp °C	Time s
OC1_He	200	120
OC2_He	300	150
OC3_He	450	180
OC4_He	650	180
EC1_He/O_2	500	120
EC2_He/O_2	550	120
EC3_He/O_2	700	70
EC4_He/O_2	850	80

Charring: Analysis of fulvic acid

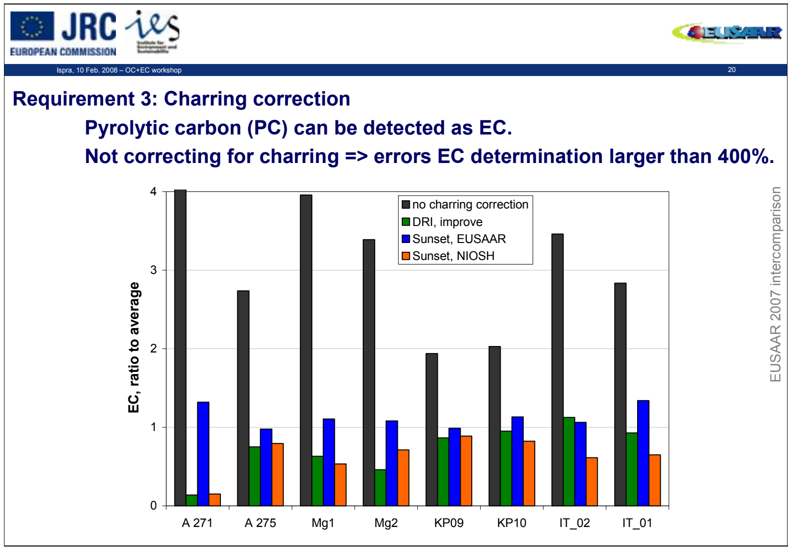


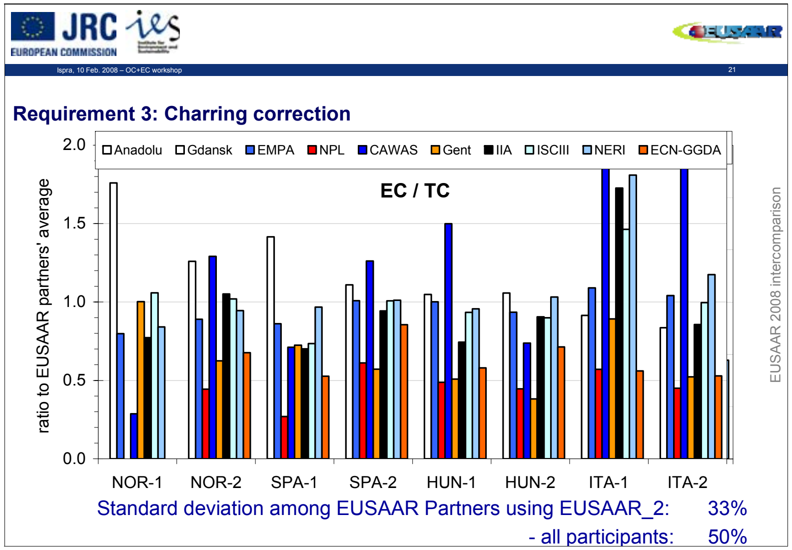
Charring: Analysis of an ambient PM2.5 sample from Ispra (NIOSH protocol)



Requirement 3: Charring correction

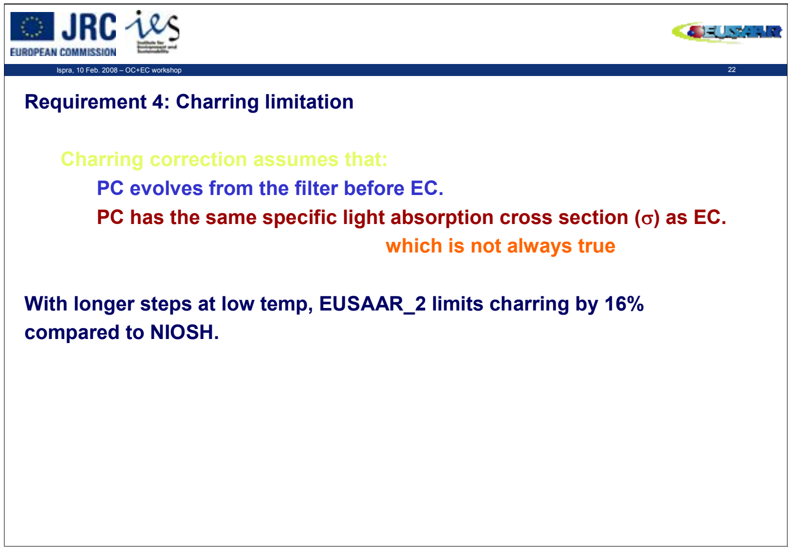
Pyrolytic carbon (PC) can be detected as EC.
Not correcting for charring => errors EC determination larger than 400%.





Requirement 3: Charring correction

Standard deviation among EUSAAR Partners using EUSAAR_2: 33%
- all participants: 50%



Requirement 4: Charring limitation

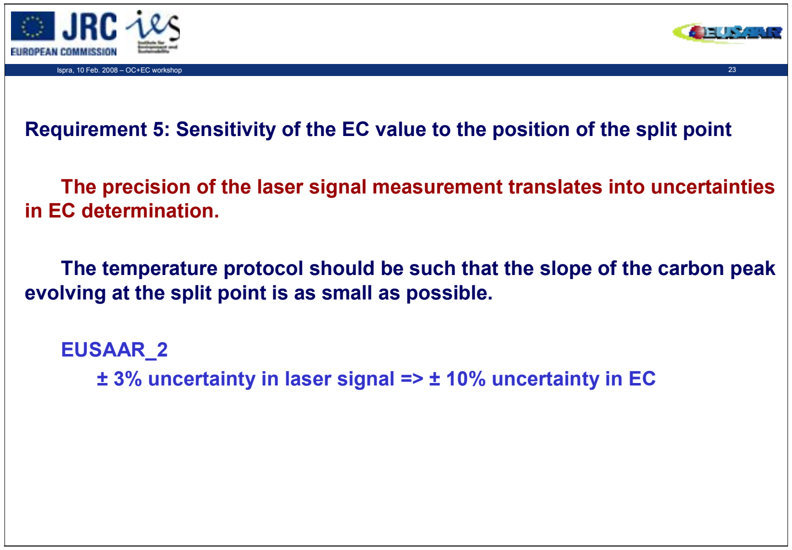
Charring correction assumes that:

PC evolves from the filter before EC.

PC has the same specific light absorption cross section (σ) as EC.

which is not always true

With longer steps at low temp, EUSAAR_2 limits charring by 16% compared to NIOSH.



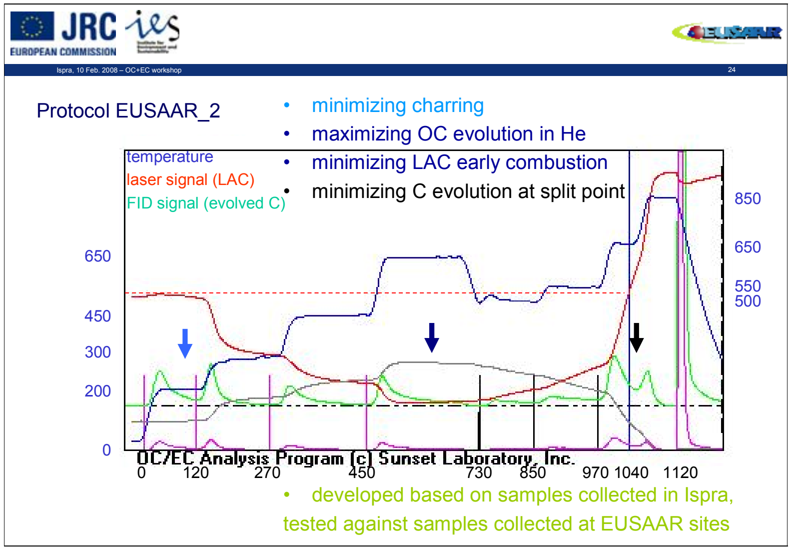
Requirement 5: Sensitivity of the EC value to the position of the split point

The precision of the laser signal measurement translates into uncertainties in EC determination.

The temperature protocol should be such that the slope of the carbon peak evolving at the split point is as small as possible.

EUSAAR_2

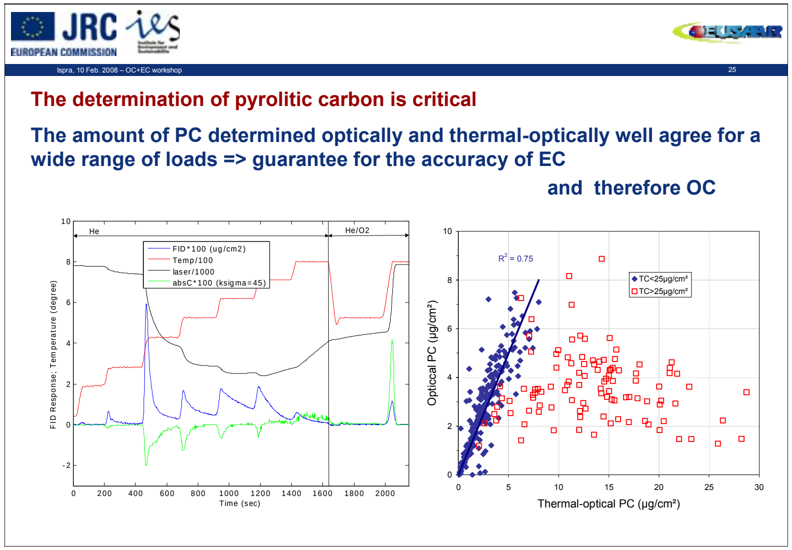
± 3% uncertainty in laser signal => ± 10% uncertainty in EC



Protocol EUSAAR_2

- minimizing charring
- maximizing OC evolution in He
- minimizing LAC early combustion
- minimizing C evolution at split point

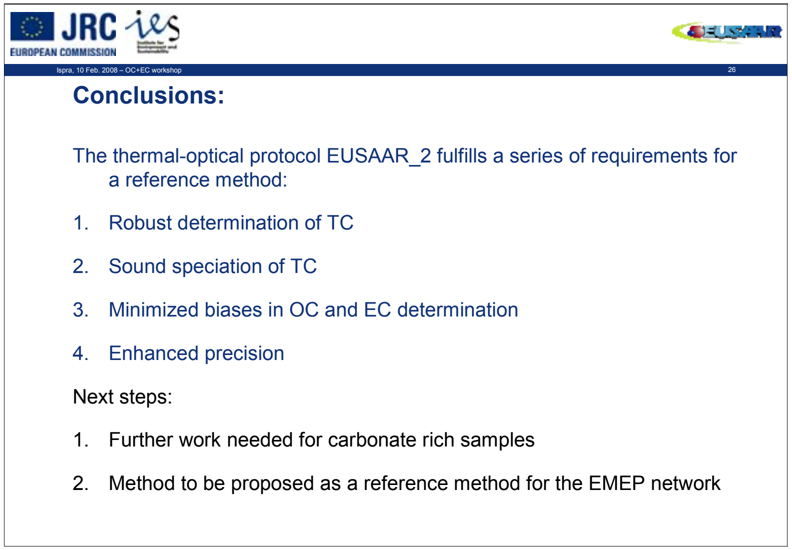
- developed based on samples collected in Ispra, tested against samples collected at EUSAAR sites



The determination of pyrolitic carbon is critical

The amount of PC determined optically and thermal-optically well agree for a wide range of loads => guarantee for the accuracy of EC

and therefore OC



Conclusions:

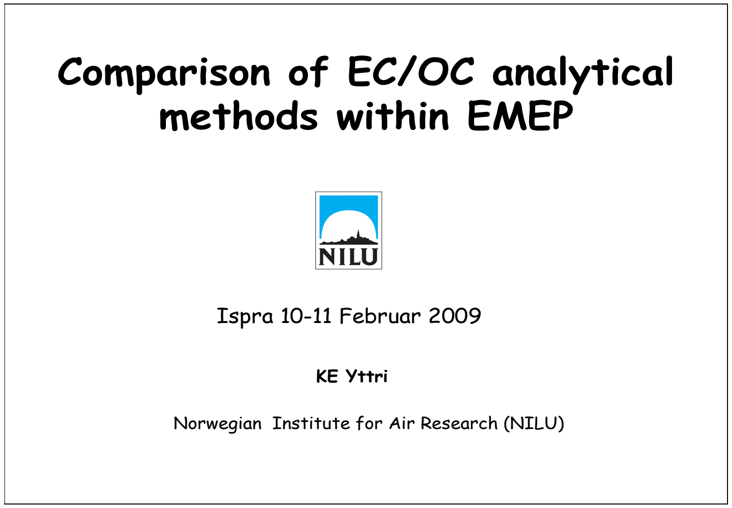
The thermal-optical protocol EUSAAR_2 fulfills a series of requirements for a reference method:

1. Robust determination of TC
2. Sound speciation of TC
3. Minimized biases in OC and EC determination
4. Enhanced precision

Next steps:

1. Further work needed for carbonate rich samples
2. Method to be proposed as a reference method for the EMEP network

A.7 Comparison of EC/OC analytical methods within EMEP



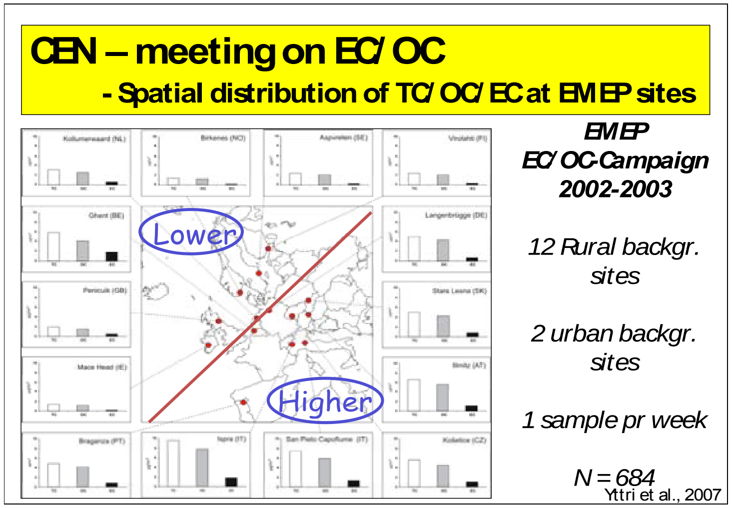
Comparison of EC/OC analytical methods within EMEP

NILU

Ispra 10-11 Februar 2009

KE Yttri

Norwegian Institute for Air Research (NILU)



CEN – meeting on EC/OC

- Spatial distribution of TC/OC/EC at EMEP sites

EMEP EC/OC-Campaign 2002-2003

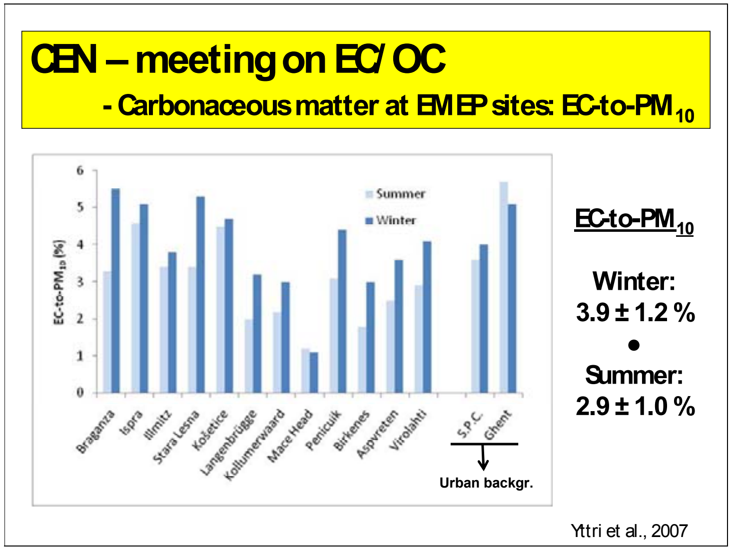
12 Rural backgr. sites

2 urban backgr. sites

1 sample pr week

N = 684

Yttri et al., 2007



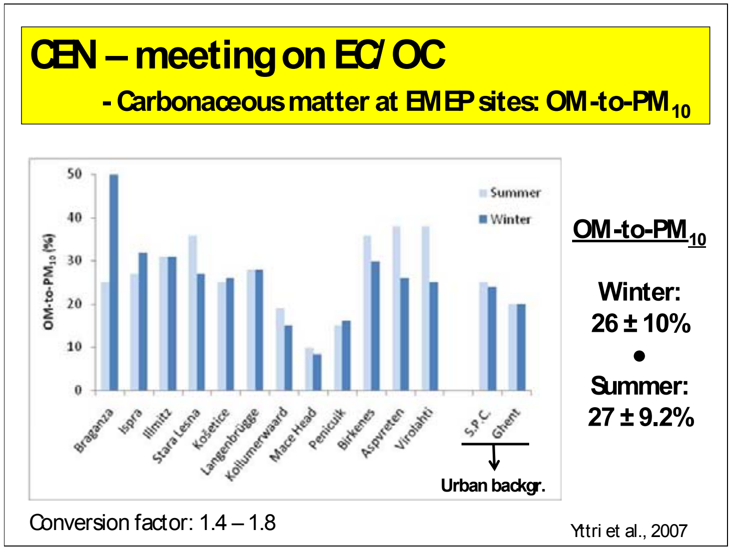
CEN – meeting on EC/OC

- Carbonaceous matter at EMEP sites: EC-to-PM$_{10}$

EC-to-PM$_{10}$

Winter:
3.9 ± 1.2 %
●
Summer:
2.9 ± 1.0 %

Yttri et al., 2007



CEN – meeting on EC/OC

- Carbonaceous matter at EMEP sites: OM-to-PM$_{10}$

OM-to-PM$_{10}$

Winter:
26 ± 10%
●
Summer:
27 ± 9.2%

Conversion factor: 1.4 – 1.8

Yttri et al., 2007

CEN – meeting on EC/OC

- European Monitoring and Evaluation Program - EMEP

Convention on Long-range Transboundary Air Pollution

emep

msc-w msc-e ccc ciam ceip

EMEP Home
EMEP Facts
EMEP Emissions
EMEP Measurements
EMEP Models
EMEP Model Results
EMEP Grid
Co-operation

Welcome to EMEP

NEWS AND UPDATES

2008-09-25 **21st meeting of TFEIP, Milan, Italy, 10-11 November 2008**

2008-08-27 **Technical Reports to the 32nd Session of the EMEP Steering Body meeting**

2008-08-27 **10th meeting of TFMM, Oslo, Norway, 14-15 October 2008**

2008-08-27 **1st EMEP Open Source Training Course, Oslo, Norway, 13 October 2008**

2008-04-10 **9th joint meeting of TFEIP and EIONET, Tallinn, Estonia, 26-27 May 2008**

2008-04-10 **9th meeting of the Task Force on Measurements and Modelling, Bordeaux, France, 23-25 April 2008**

2008-02-07 **Release of the Unified EMEP model as Open Source**

2008-01-16 **The new emission centre (CEIP) on-line**

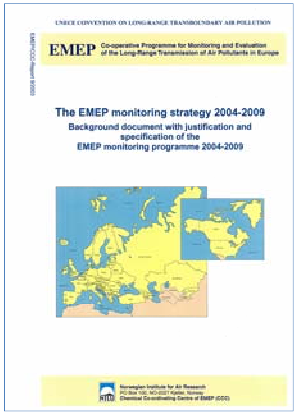
2007-11-21 **Initiation of the 2008 Emission Reporting Round**

The European Monitoring and Evalutaion program addresses the transboundary air pollution in Europe through emissions, modelling and monitoring

www.emep.int/

CEN – meeting on EC/OC

- EMEP monitoring strategy



UNECE CONVENTION ON LONG-RANGE TRANSBOUNDARY AIR POLLUTION

EMEP Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe

The EMEP monitoring strategy 2004-2009
Background document with justification and specification of the EMEP monitoring programme 2004-2009

Norwegian Institute for Air Research
Chemical Co-ordinating Centre of EMEP (CCC)

EMEP has an extensive monitoring program

- The current onitoring strategy is valid for the period 2004 – 2009
- A revised version of the new monitoring strategy will be presented
  - ✓to the steering body (SB) in September 2009
  - ✓to the executive body (EB) in December 2009
- There will only be minor changes in the new monitoring strategy, including that of carbonaceous particulate matter

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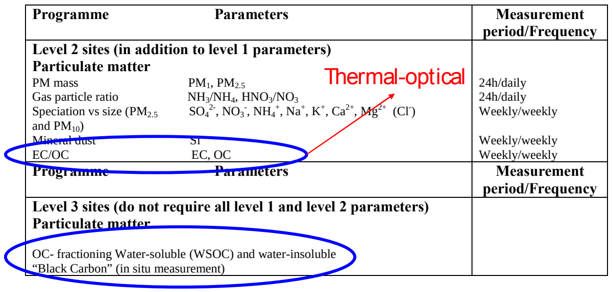
CEN – meeting on EC/OC

- Monitoring of EC and OC is EMEP level 2 activity

Table 2: Monitoring requirements for the various levels specified by the EMEP monitoring strategy.



Programme	Parameters	Measurement period/Frequency
Level 2 sites (in addition to level 1 parameters)		
Particulate matter		
PM mass	PM_1, $PM_{2.5}$	24h/daily
Gas particle ratio	NH_3/NH_4, HNO_3/NO_3	24h/daily
Speciation vs size ($PM_{2.5}$ and PM_{10})	SO_4^{2-}, NO_3^-, NH_4^+, Na^+, K^+, Ca^{2+}, Mg^{2+} (Cl^-)	Weekly/weekly
Mineral dust	Si	Weekly/weekly
EC/OC	EC, OC	Weekly/weekly
Programme	**Parameters**	**Measurement period/Frequency**
Level 3 sites (do not require all level 1 and level 2 parameters)		
Particulate matter		
OC- fractioning Water-soluble (WSOC) and water-insoluble “Black Carbon” (in situ measurement)		

Thermal-optical

The EMEP monitoring strategy 2004-2009. Background document with justification and specification of the EMEP monitoring programme, 2004-2009 Ed. by Kjetil Tørseth and Øystein Hov. EMEP/CCC-Report 9/2003

CEN – meeting on EC/OC

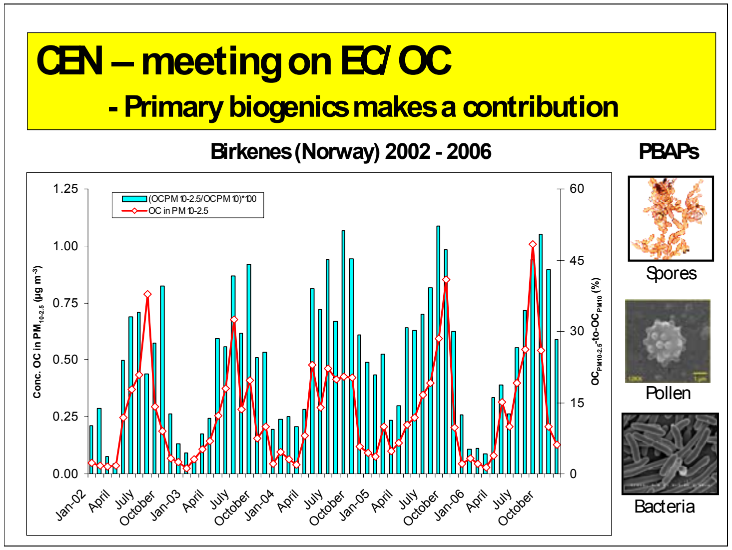
- Reporting status of EC and OC in EMEP

Table 1.5: Sites reporting EC and OC to EMEP, including PM size fractions and sampling period

Site (Country)	EC	OC	$PM_{2.5}$	PM_{10}	Period
Birkenes (Norway)	X	X	X	X	2001, 2002, 2003, 2004, 2004, 2005, 2006, 2007,
Illmitz (Austria)	X	X	X	X	1999, 2000, 2002[1)
Ispra (Italy)	X	X	X	X	2002[1), 2004, 2004, 2005, 2006[2), 2007,
Melpitz (Germany)	X	X	X	X	2006, 2007,

1. For PM_{10} only
2. EMEP EC/OC campaign

”Data from campaigns and periods shorter than one year are not included”



CEN – meeting on EC/OC

- Primary biogenics makes a contribution

Birkenes (Norway) 2002 - 2006

PBAPs

Spores

Pollen

Bacteria

CEN – meeting on EC/OC

- Sampling equipment and analytical approach

Table 1.6: Sampling equipment and analytical approach used at he various sites sites reporting EC and OC to EMEP

Site (Country)	Sampling time/Frequency	Filter face velocity	Sampling Equipment	Analytical approach
Birkenes (Norway)	Weekly/Weekly	53 cm s^{-1}	Single filter	Sunset TOT (quartz.par)
Illmitz (Austria)	Every 6th day	54 cm s^{-1}	Single filter	VDI 2465 part 1
Ispra (Italy)	24 hr, daily	20 cm s^{-1}	Denuder (positive corr.)	Multi-step flash heating1)2)
Melpitz (Germany)	24 hr, daily	54 cm s^{-1}	Single filter	VDI 2465 part 2

1. Two aliquots were analyzed: one from the plain filter, the other after baking for 2 hours in He/O_2 carrier gas at 340° C Charring-free EC from the latter.
2. Sunset dual optical analyzer from 2006.

CEN – meeting on EC/OC

- EUSAAR protocal for EC/OC measurments

Why is there not yet a reference method for EC/OC measurements in EMEP?

✓ Substantial difficulties associated with sampling and subsequent analysis of EC/OC e.g.

- Positive and negative sampling artefacts
- Analytical challenges in separating EC and OC

✓ EC/OC measurements was introduced to the monitoring strategy in 2004

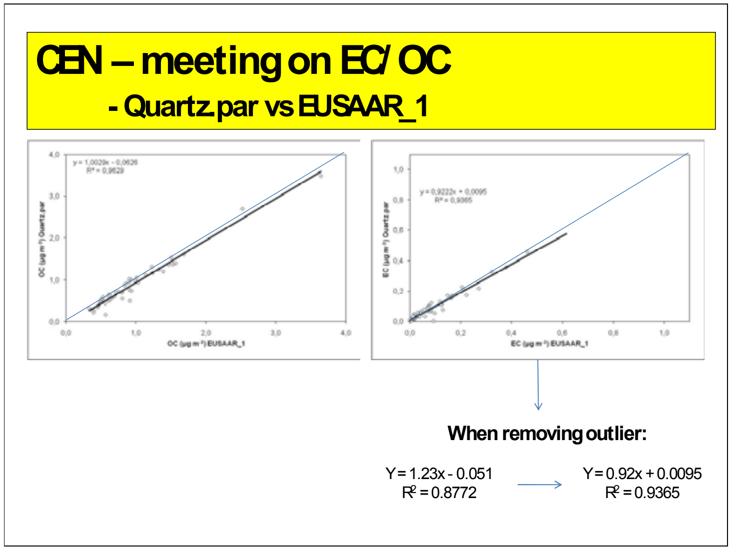
✓ Only a few thermal-optical instruments were available in Europe at the time (2004)

✓ Awaiting the EUSAAR unified protocol

When will the EUSAAR unified protocol be implemented in EMEP?

✓ The EUSAAR_2 temperature program is not yet officially included as the new protocol for EC/OC in EMEP but it is already beeing used, e.g. in the EMEP intensive measurements periods.

✓ 8 – 10 sites is expected to report EC/OC data to EMEP using EUSAAR_2 within next 1 – 2 years.



CEN – meeting on EC/OC

- Quartz.par vs EUSAAR_1

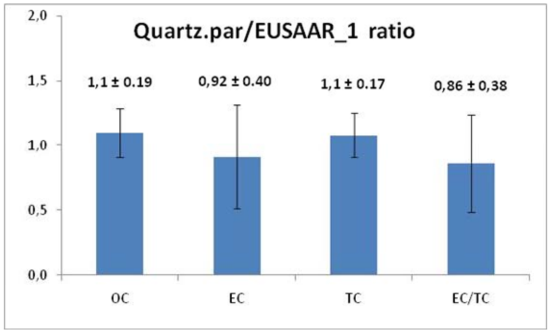
When removing outlier:

Y = 1.23x - 0.051
R^2 = 0.8772

Y = 0.92x + 0.0095
R^2 = 0.9365

CEN – meeting on EC/ OC

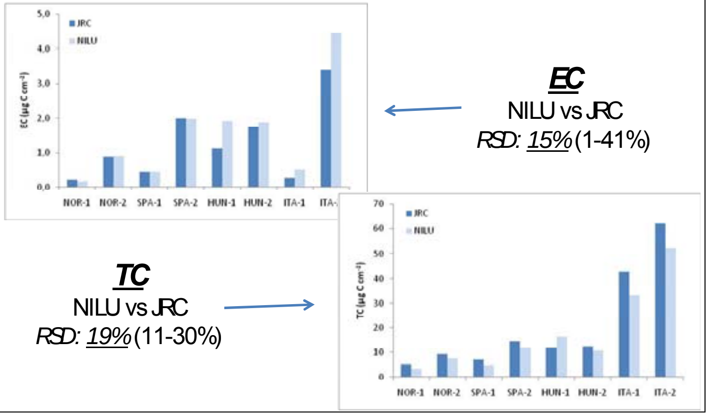
- Quartz. Par vs EUSAAR_1



In general: Good agreement for OC and TC, more pronounced difference for EC (higher RSD)
Remark: Change from NIOSH derived temperature programs to EUSAAR should be not be too great a problem for OC and TC, but perhaps somewhat more challenging for EC

CEN – meeting on EC/ OC

- Comparison of EMEP sites EUSAAR_2



EC
NILU vs JRC
RSD: 15% (1-41%)

TC
NILU vs JRC
RSD: 19% (11-30%)

CEN – meeting on EC/ OC

- Guidelines for EC/ OC measurements in EMEP


EMEP Manual for Sampling and Analysis

contents and revisions and preface

Download the Manual:

English
MS word (zipped 1.5 MB)
pdf (2.2 MB)

Russian
MS word (zipped 2.3 MB)
pdf (2.7 MB)

Chinese
pdf (13 MB)

To be included in the EMEP Manual:

- Draft protocol for EC/OC
- Protocol for Low cost denuder measurements (pdf 0.8 MB, MS Word 13 MB))

Other relevant manuals:

- WMO-GAW Aerosol Measurement Procedures, Guidelines and Recommendations (report No153, pdf, 1 MB)
- WMO-GAW Manual for the precipitation chemistry programme (report No160, pdf, 1.8 MB)

•No reference method for EC/OC, yet, but guidelines for EC/OC can be found on the EMEP/CCC homepage (http://tarantula.nilu.no/projects/ccc/manual/index.html)

- ✓ Introduction to the topic
- ✓ Sampling time/ frequency
- ✓ Sampling equipment
- ✓ Sampling substrate
- ✓ Correction for positive artefacts
- ✓ Calibration of TC with external standards
- ✓ EC/ OC split quality assurance using standards
- ✓ Every year intercomparison of EC/ OC
- ✓ Field blanks

EMEP Manual: http://tarantula.nilu.no/projects/ccc/manual/index.html

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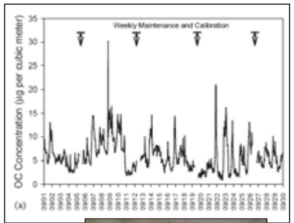
CEN – meeting on EC/ OC

- Some questionmarks: EC/ OC - monitors

EC/ OC monitors are likely to be taken into service on a broader scale than today

2-3 hour time resolution of EC and OC will improve our knowledge on e.g.:

- •Ambient levels
- •Variability of sources
- •Human exposure



Monitors can be less costly to operate, due to reduced sampling site visits and eliminated need of laboratory factilities and analyses costs


http://www.sunlab.com/

CEN – meeting on EC/ OC

- Some questionmarks: EC/ OC - monitors

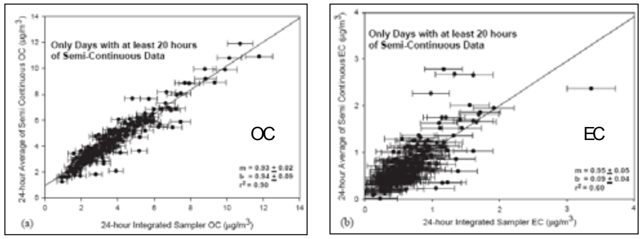


Fig. 5. Comparison of 24-h average semi-continuous analyzer and daily integrated sampler fine particle organic and elemental carbon at the St. Louis-Midwest Supersite for the year 2002 data set: (a) organic carbon; and (b) elemental carbon. The available hourly concentrations measured by the semi-continuous instruments for days with less than 24 valid measurements are used to estimate the 24-h average.

Correlation less good for EC than for OC

CEN – meeting on EC/ OC

- Some questionmarks

- Attempts made to run the EUSAAR_2 temperature program on the Sunset laboratories monitor have not been all successful, which is an drawback in order to obtain comparable data

  - Could other programs than the EUSAAR_2 protocol be preferred?

- The EC/ OC monitors also provide $EC_{optical}$ from which "$OC_{optical}$" can be derived

  - Are the optical EC/ OC comparable to the thermal-optical EC and OC?
  - Could $EC_{optical}$ and "$OC_{optical}$" be preferred due to their better detection limit (e.g. Saarikoski et al., 2008)

- Could BC derived from in situ measurements of the absorption coefficient (PSAP, MAAP) be preferred to thermal optical EC for BC.

CEN – meeting on EC/ OC

- Summary

1. Carbonaceous particulate matter account for a substantial fraction of PM in the European rural background environment

2. EC/ OC data reported to EMEP are based on a range of different methods which hampers the comparability

3. EMEP provides guidelines for how to perform sampling and analysis with respect to EC/ OC, while awaiting the finalization of the unified EUSAAR prototocol
4. Results obtained using the EUSAAR_2 temperature program looks promising. The transition from currently applied NIOSH derived thermal optical approaches to EUSAAR_2 ought to proceed rather smoothly

5. Some concern is caused by the difficulties of using the full length EUSAAR_2 temperature program in EC/ OC monitors, an instrument wich appears to grow in popularity

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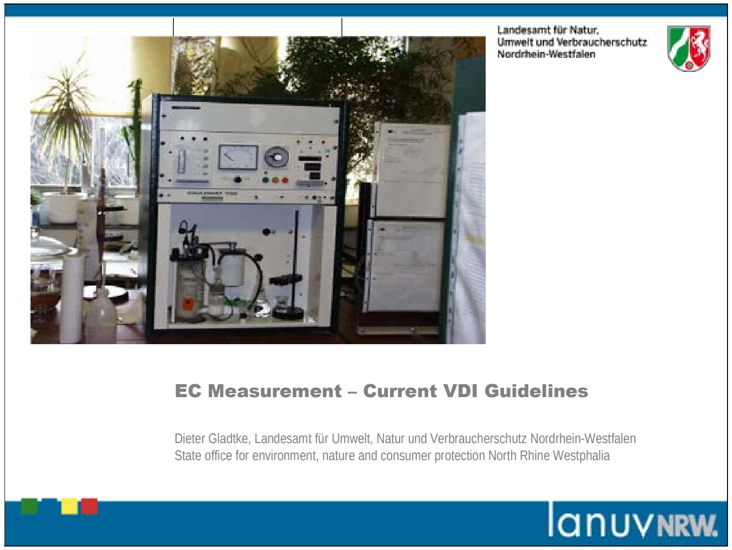
CEN – meeting on EC/ OC

- What does EMEP require?

- Comparability
- Cost Effective
- Availability
- Easy-to-operate

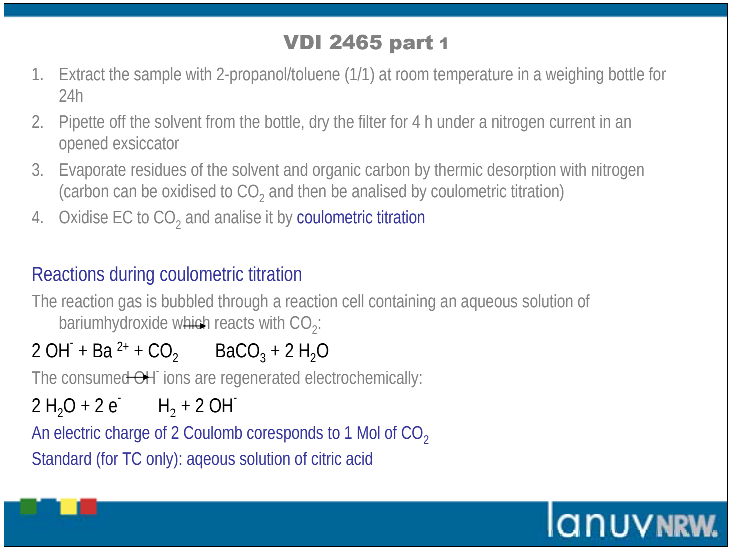
A.8 EC Measurement – Current VDI Guidelines



Landesamt für Natur,
Umwelt und Verbraucherschutz
Nordrhein-Westfalen

EC Measurement – Current VDI Guidelines

Dieter Gladtke, Landesamt für Umwelt, Natur und Verbraucherschutz Nordrhein-Westfalen
State office for environment, nature and consumer protection North Rhine Westphalia



VDI 2465 part 1

1. Extract the sample with 2-propanol/toluene (1/1) at room temperature in a weighing bottle for 24h
2. Pipette off the solvent from the bottle, dry the filter for 4 h under a nitrogen current in an opened exsiccator
3. Evaporate residues of the solvent and organic carbon by thermic desorption with nitrogen (carbon can be oxidised to CO_2 and then be analised by coulometric titration)
4. Oxidise EC to CO_2 and analise it by coulometric titration

Reactions during coulometric titration

The reaction gas is bubbled through a reaction cell containing an aqueous solution of bariumhydroxide which reacts with CO_2:

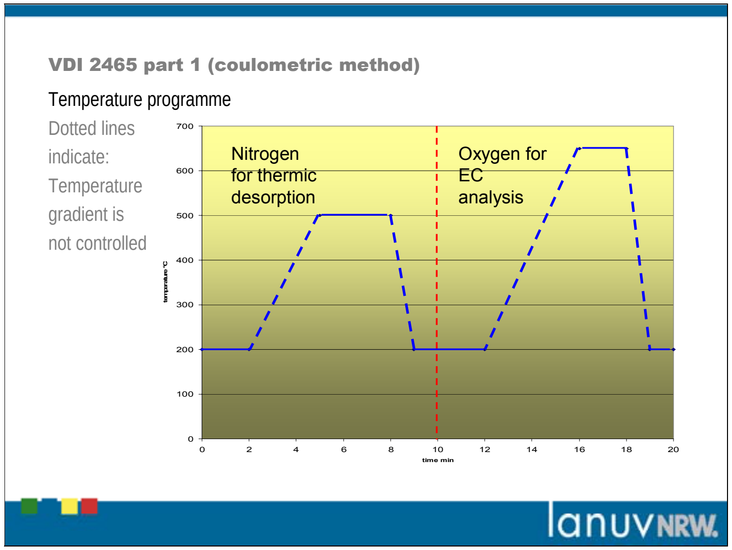
$$2\,OH^- + Ba^{2+} + CO_2 \rightarrow BaCO_3 + 2\,H_2O$$

The consumed OH^- ions are regenerated electrochemically:

$$2\,H_2O + 2\,e^- \rightarrow H_2 + 2\,OH^-$$

An electric charge of 2 Coulomb coresponds to 1 Mol of CO_2

Standard (for TC only): aqeous solution of citric acid



VDI 2465 part 1 (coulometric method)

Temperature programme

Dotted lines indicate: Temperature gradient is not controlled

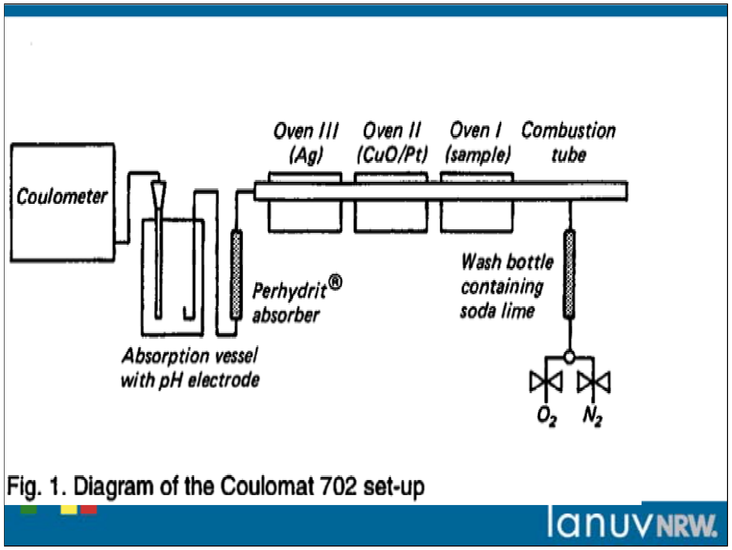


Fig. 1. Diagram of the Coulomat 702 set-up

Flow sheet for VDI 2465 part 1

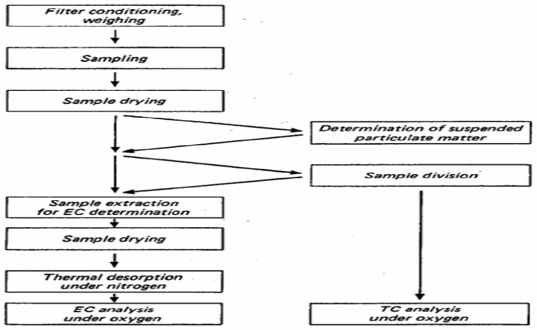


Fig. 2. Flow diagram of the overall method for the analysis of elemental (EC) and total (TC) carbon (immission)

Results after different techniques to remove organic carbon

Petzold, A.; Niessner, R.: Mikrochim. Acta 117, 215 – 237 (1995)

Sampling site: road with high traffic volume in Munich

Sampling time: November 1992 to April 1993

Removal method	Average fraction of toal carbon
Thermal desorption at 500 °C for 8 min with He	0,55 +/- 0,07
Solvent extraction with toluene/2-propanol	0,76 +/- 0,15
Solvent extraction followed by thermal desorption	0,40 +/- 0,08

Disatvantages of the method

- Apparatus is not computer-interfaced
- Indicated oven temperatures are wrong (construct a temperature sensor by yourself!)
- Extraction is difficult to handle (pipetting off the solvent), by far not complete (room temperature) and time consuming
- EC and OC cannot be analised in one step
- No automatic analysis possible

If analysis of EC and OC is recommended for every sample:

No more than 8 to 10 samples can be analised per day with one Coulomat-apparatus

Advantage of the method: Extraction with an organic solvent reduces charring; for traffic influenced sites the results are realistic

---

VDI 2465 part 2 (thermographic method)

Organic carbon is thermically desorbed with helium (oxidation of organic compounds to CO_2 with a CuO/CeO_2 catalyst is possible) at temperatures up to 600 °C (heating is performed in two steps)

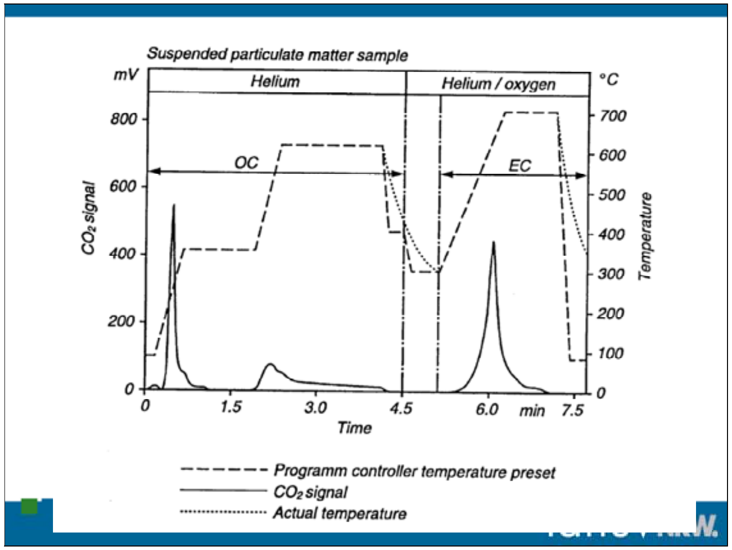
Elemental carbon is oxidised with 20% oxygen in helium at high temperatures (700 °C)

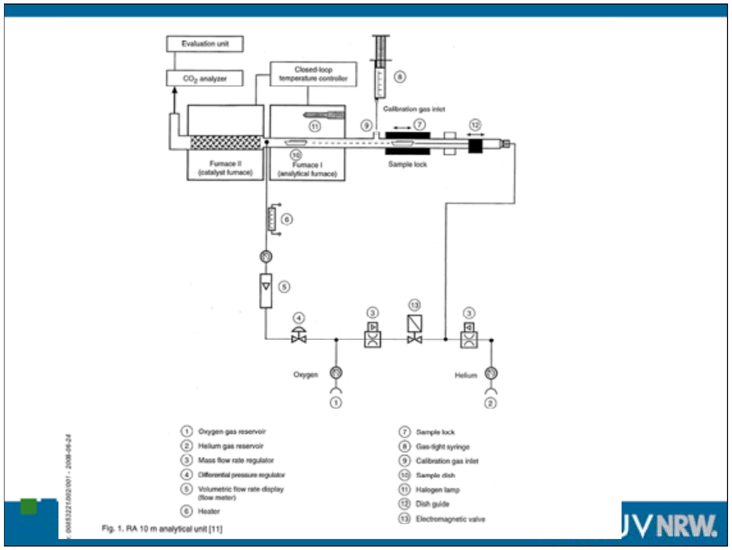
CO_2, formed by combustion of organic compounds and elemental carbon is analised by its infrared absorption

Method is fast, handling of samples is easy

Charring is not controlled results may be too high (see Niessner and Petzold)

Methane and polystyrene are used as standards for carbon and OC





① Oxygen gas reservoir
② Helium gas reservoir
③ Mass flow rate regulator
④ Differential pressure regulator
⑤ Volumetric flow rate display (flow meter)
⑥ Heater
⑦ Sample lock
⑧ Gas-tight syringe
⑨ Calibration gas inlet
⑩ Sample dish
⑪ Halogen lamp
⑫ Dish guide
⑬ Electromagnetic valve

Fig. 1. RA 10 m analytical unit [11]

Comparison of VDI 2465 part 1 and 2

PM10 Samples from a traffic influenced site and a remote site, parameters of regression

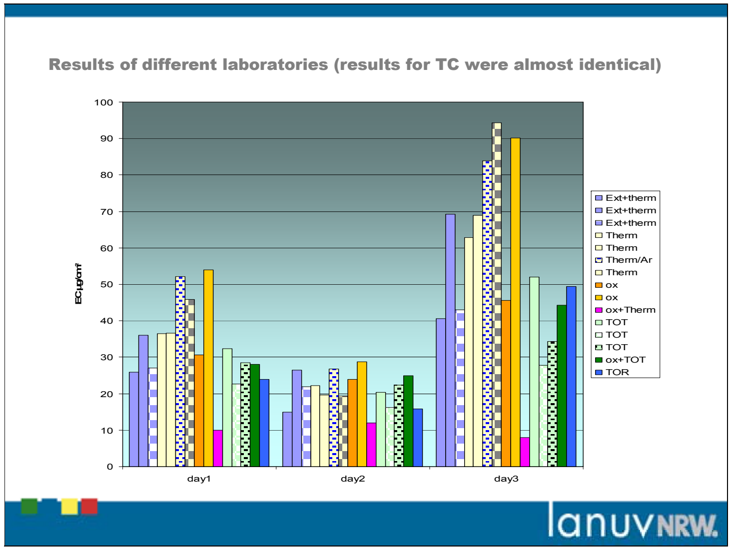
		EC	TC
Axis intercept $a \pm s_a$	µg/filter	−7 ± 10	−19 ± 22
Slope $b \pm s_b$		0.99 ± 0.02	1.00 ± 0.07
Correlation coefficient r		0.99	0.99
Mean of coulometry	µg/filter	408	809
Mean of thermography	µg/filter	397	789

Correlation is astonishing!!

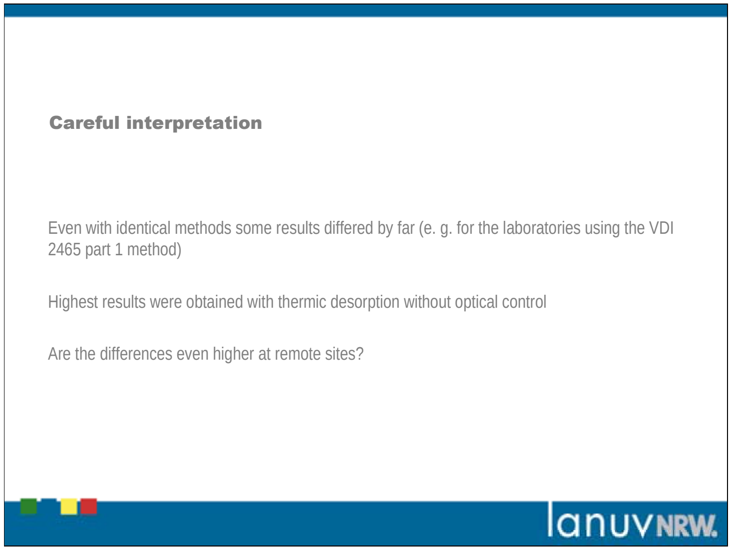
„Vienna intercomparison“ 1999 Atm. Env. 35, 2111-2121 (2001)

- Samples were taken at Frankfurter Allee, a narrow road with high traffic volume in Berlin, in November 1998
- A high volume sampler with a PM10 sampling head (DIGITEL DHA89) was used
- Dust was collected on pre-fired (850°C) quartz fibre filters
- Four filter cuts with a diameter of 1 cm of each sample were distributed to each laboratory
- 13 laboratories participated
- 15 results with 13 methods were reported

method	remarks
Ext+therm	VDI2465,1
Ext+therm	VDI2465,1
Ext+therm	extraction+thermic desorption
Therm	VDI2465,2
Therm	VDI2465,2
Therm/Ar	VDI2465,2 Ar as inert gas
Therm	OC: 590°C, 2x EC: 850°C,O_2
ox	OC: 340°C, O_2 EC: 650°C,O_2
ox+Therm	He/O_2 80/20 130, 230, 340°C, He 650°C for OC, He/O2 80/20 650°C for EC
ox	Temperature of OC/EC split not mentioned!
TOT	OC: He, 820°C, EC: 2%O_2, 850°C, optical transmission control
TOT	OC: He, 900°C, EC: 5%O_2, 900°C, optical transmission control
TOT	OC: He, 600°C, EC: He/air, 850°C, optical transmission control
ox+TOT	
TOR	OC: He, 550°C, EC: 2%O2, 800°C, optical reflectance control



Results of different laboratories (results for TC were almost identical)



Careful interpretation

Even with identical methods some results differed by far (e. g. for the laboratories using the VDI 2465 part 1 method)

Highest results were obtained with thermic desorption without optical control

Are the differences even higher at remote sites?

A.9 The “Hungarian” experience

Contribution to the EC/OC preparatory workshop The ”Hungarian” experience

András Gelencsér
Veszprém, HUNGARY

Outline

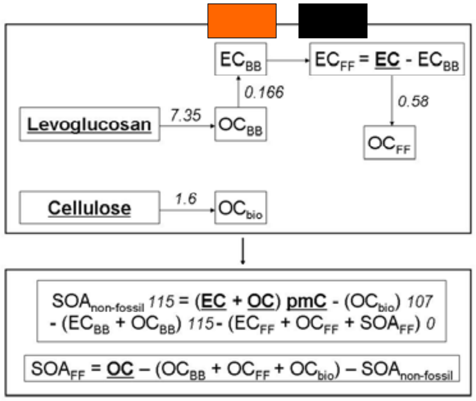
- Source apportionment studies of EC/OC based on 2-year aerosol observations at six European sites – CARBOSOL
- Studies on biomass burning brown carbon properties with MPI – SMOCC
- Studies on properties of tar balls in biomass smoke – SAFARI

The CARBOSOL project

Pio, C., Legrand, M., Oliveira, T., Afonso, J., Santos, C., Caseiro, A., Fialho, P., Barata, F., Puxbaum, H., Sanches-Ochoa, A., Kasper-Giebl, A., Gelencsér, A., Preunkert, S., Schock , M., **Climatology of aerosol composition (organic versus inorganic) at non-urban areas on a West-East transect across Europe**, *J. Geopys. Res.* 2007 doi:10.1029/2006JD008038

Gelencsér, A., May, B., Simpson, D., Sánchez-Ochoa, A., Kasper-Giebl, A., Puxbaum, H., Caseiro, A., Pio, C., Legrand, M, **Source apportionment of PM2.5 organic aerosol over Europe: primary/ secondary, natural/ anthropogenic, fossil/biogenic origin**, *J. Geopys. Res.* 2007 doi:10.1029/2006JD008094

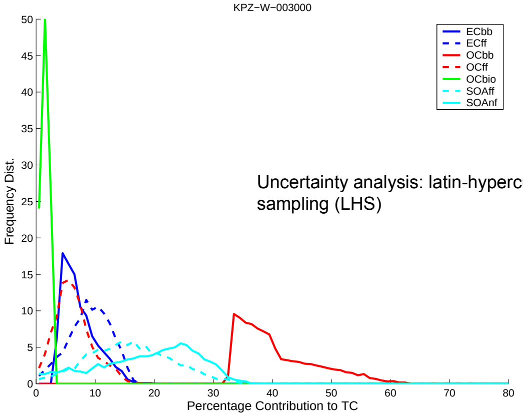
Scheme of the ^{14}C-based source apportionment



$SOA_{non\text{-}fossil}$ *115* = (**EC** + **OC**) **pmC** - (OC_{bio}) *107* - (EC_{BB} + OC_{BB}) *115* - (EC_{FF} + OC_{FF} + SOA_{FF}) *0*

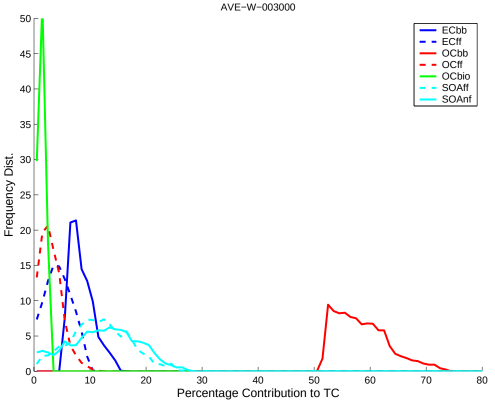
SOA_{FF} = **OC** – (OC_{BB} + OC_{FF} + OC_{bio}) – $SOA_{non\text{-}fossil}$

Estimated contributions of EC/OC subtypes to TC K-Puszta. winter

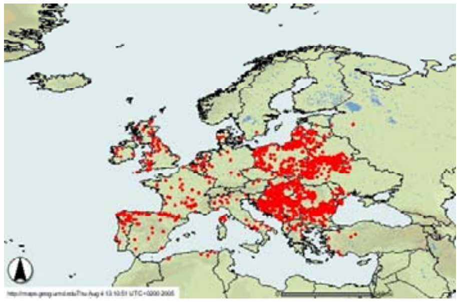


Uncertainty analysis: latin-hypercube sampling (LHS)

Estimated contributions of EC/OC subtypes to TC Aveiro, winter



Open fires in the period 20-27 March 2003



Large differences in EC sources between summer and winter

Site	Season	OC_{BB}	EC_{BB}	OC_{FF}	EC_{FF}	OC_{bio}	$SOA_{non-fossil}$	SOA_{FF}
		%	%	%	%	%	%	%
AVE	winter	64	11	1	2	1	5	16
	summer	7	1	7	13	2	63	7
KPZ	winter	40	7	6	10	1	21	15
	summer	6	1	5	9	5	69	4

A.10 OC/EC/TC analysis: the Spanish experience

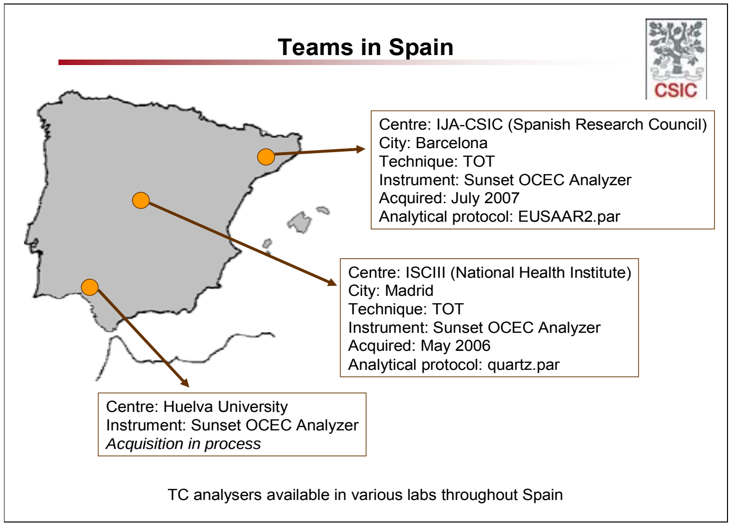
OC/EC/TC analysis: the Spanish experience

M. Viana, A. Alastuey, X. Querol

Institute for Environmental Assessment and
Water Research (IDAEA-CSIC)

mviana@ija.csic.es / mar.viana@idaea.csic.es

EC/OC Workshop, February 11th, 2009, Ispra



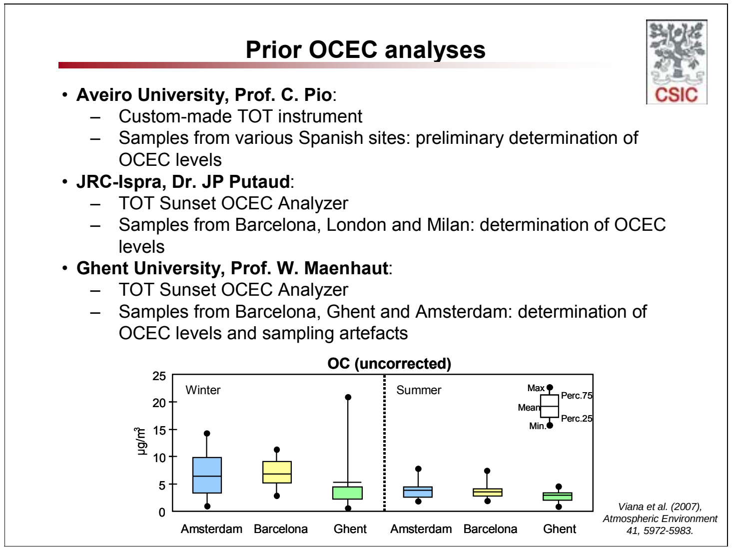
Teams in Spain

Centre: IJA-CSIC (Spanish Research Council)
City: Barcelona
Technique: TOT
Instrument: Sunset OCEC Analyzer
Acquired: July 2007
Analytical protocol: EUSAAR2.par

Centre: ISCIII (National Health Institute)
City: Madrid
Technique: TOT
Instrument: Sunset OCEC Analyzer
Acquired: May 2006
Analytical protocol: quartz.par

Centre: Huelva University
Instrument: Sunset OCEC Analyzer
Acquisition in process

TC analysers available in various labs throughout Spain



Prior OCEC analyses

- **Aveiro University, Prof. C. Pio**:
  - Custom-made TOT instrument
  - Samples from various Spanish sites: preliminary determination of OCEC levels
- **JRC-Ispra, Dr. JP Putaud**:
  - TOT Sunset OCEC Analyzer
  - Samples from Barcelona, London and Milan: determination of OCEC levels
- **Ghent University, Prof. W. Maenhaut**:
  - TOT Sunset OCEC Analyzer
  - Samples from Barcelona, Ghent and Amsterdam: determination of OCEC levels and sampling artefacts

OC (uncorrected)

Viana et al. (2007), Atmospheric Environment 41, 5972-5983.

Current situation (IJA-CSIC)

- 1200-1500 samples/year
- Large variety of monitoring environments:
  regional background, urban background, industrial hotspots
- High- and low-volume samplers (with and without denuders, within EUSAAR)
- Munktell and Pallflex filter substrates

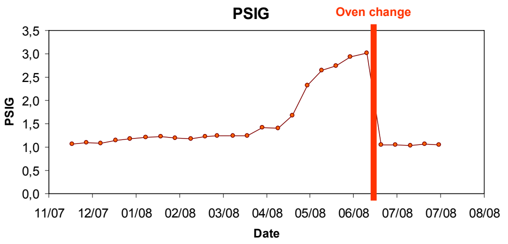
Problems / Incidences (IJA-CSIC)

1. Incidences refer mainly to the <u>combustion oven</u>:

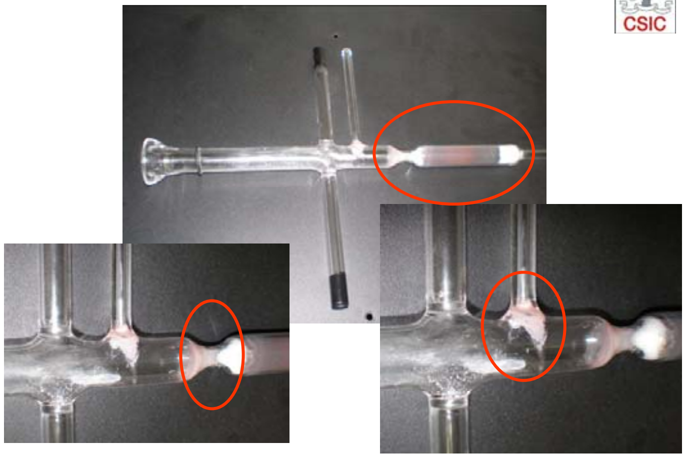
- Progressive increase in oven pressure (PSIG=1 to 3 / 9 months)
- Resulting in need to change the oven (2 times in 1.5 years)

Potential causes (we believe):

- Type of samples (ceramic area with high % of refractory material)
- Use of HCl to eliminate CC



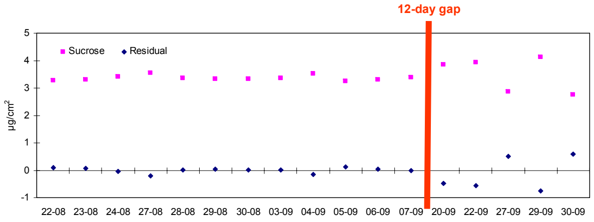
Problems / Incidences (IJA-CSIC)



Problems / Incidences (IJA-CSIC)

2. Increase in the variability of sucrose concentrations if instrument not run continuously:

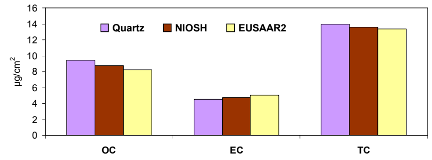
Sucrose standard (3,365 µg/µl)		
Instrument:	Conc.	Std. dev
Run continuously	3,36	0,10
After gap	3,51	0,64
Total	3,40	0,34



Analytical protocol tests (1/3)

(1) <u>Comparison Quartz / NIOSH / EUSAAR2:</u> 1 sample +2 blks

	Quartz			NIOSH			EUSAAR2		
Sample (3 runs)	**OC**	**EC**	**TC**	**OC**	**EC**	**TC**	**OC**	**EC**	**TC**
average (µg/cm²)	**10,6**	**4,5**	**15,1**	**9,7**	**4,8**	**14,5**	**9,3**	**5,1**	**14,5**
std dev	**0,6**	**0,1**	**0,7**	**0,3**	**0,05**	**0,3**	**0,8**	**0,3**	**1,0**
Blanks (2)									
average (µg/cm²)	**1,2**	**0,02**	**1,2**	**0,9**	**0,02**	**1,0**	**1,1**	**0,04**	**1,1**
std dev	**0,3**	**0,03**	**0,3**	**0,4**	**0,03**	**0,3**	**0,3**	**0,05**	**0,3**
EC/OC	**0,48**			**0,55**			**0,62**		
EC/TC	**0,32**			**0,35**			**0,38**		



Analytical protocol tests (2/3)

(2) Comparison Quartz / EUSAAR2: PM episodes

- 22 samples
  5 different PM episodes:
  - 🟦 Atlantic air mass transport
  - 🟨 Regional re-circulation
  - 🟧 African dust + stangant atmospheric conditions
  - ⬜ Stagnant atmospheric conditions
  - 🟨 African dust

	QUARTZ			EUSAAR2		
	OC	EC	TC	OC	EC	TC
MO320	1,3	0,0	1,4	1,3	0,0	1,3
MO347	2,2	0,2	2,4	2,0	0,2	2,3
MO224	2,7	0,2	2,9	2,4	0,3	2,7
MO273	3,7	0,2	3,9	3,3	0,2	3,5
MO303	2,4	0,1	2,6	2,3	0,2	2,5
MO287	2,4	0,1	2,5	2,2	0,2	2,4
MO255	2,4	0,2	2,6	2,5	0,3	2,7
MO388	2,8	0,2	2,9	2,6	0,3	2,9
MO390	2,7	0,3	2,9	2,4	0,4	2,8
MO191	3,3	0,4	3,7	3,2	0,5	3,7
MO193	4,2	0,3	4,5	3,8	0,5	4,4
MO170	3,4	0,2	3,6	3,5	0,3	3,8
MO184	3,6	0,4	4,1	3,6	0,6	4,2

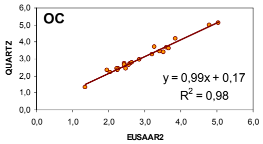
EUSAAR2/Quartz		EC/TC	
EC	OC	Quartz	EUSAAR2
1,10	0,95	0,06	0,07
1,45	0,93	0,06	0,08
1,51	0,94	0,08	0,12
1,27	0,99	0,09	0,11
1,20	0,96	0,05	0,06

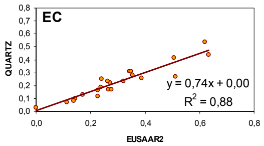
CSIC

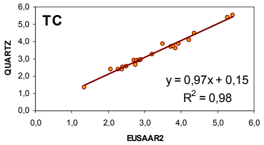
Analytical protocol tests (2/3)

CSIC

(2) Comparison Quartz / EUSAAR2: PM episodes





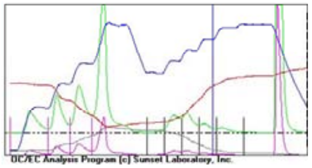


Analytical protocol tests (3/3)

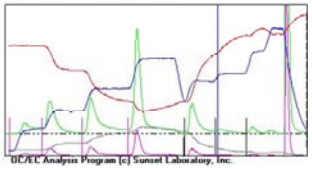
CSIC

(3) Comparison Quartz / EUSAAR2 thermograms: 11 samples

Quartz



EUSAAR2



EUSAAR2 results:

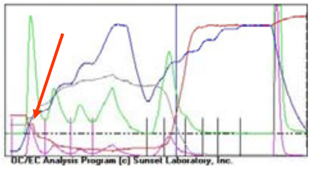
- Peak separation: very good. Certain overlap between peaks 1 and 2 from the He phase only for a small number of samples. For the rest of the peaks separation was excellent.

Analytical protocol tests (3/3)

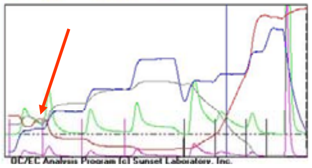
CSIC

(3) Comparison Quartz / EUSAAR2 thermograms: 11 samples

Quartz



EUSAAR2



EUSAAR2 results:

- Combustion of LAC: it seems to be minimal. Slight increase of transmittance during the He phase for 2/11 samples.

A.11 Measurement of Carbonaceous Aerosol by Thermo-Optical Methods: the Portuguese experience

EC/OC
Workshop
Ispra
10-11 Feb, 2009

MEASUREMENT OF CARBONACEOUS AEROSOL BY THERMO-OPTICAL METHODS: the Portuguese experience

Casimiro Pio

University of Aveiro; Portugal

Outline of presentation

- Historical
- Equipment Description and evolution
- Temperature Programs
- Discrimination PC/EC
- Calibration and Intercomparisons
- Carbonate interference and measurement
- Measurement of Optical Properties
- Application to Carbon Source Apportionment
- Conclusions

Historical

- First OC/EC measurements in 1988, with pure thermal method, on glass fiber filters

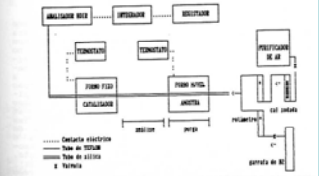


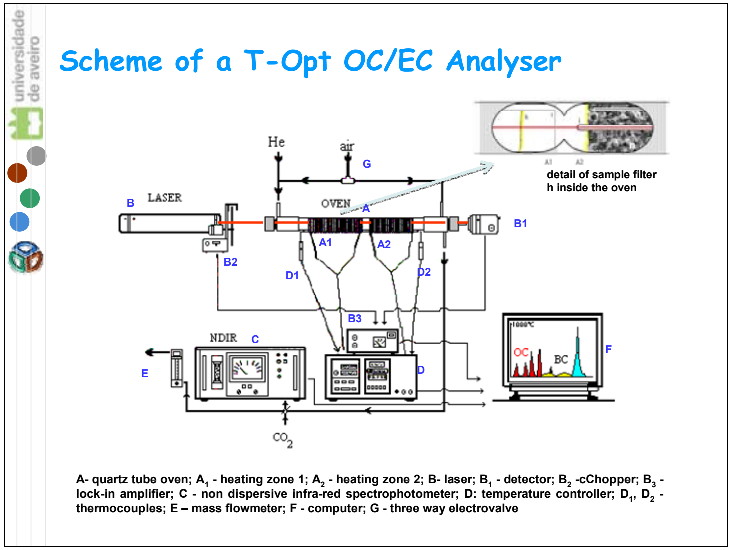
Figura 1 : Esquema da montagem para determinação do carbono em aerossois colhidos com filtros.

Pio and Jorge, 1990

- Thermo-Optical (T-Opt) OC/EC measurements started in 1992 with the building of an analyzer inspired in the work done at Ford Laboratories in the eighties.

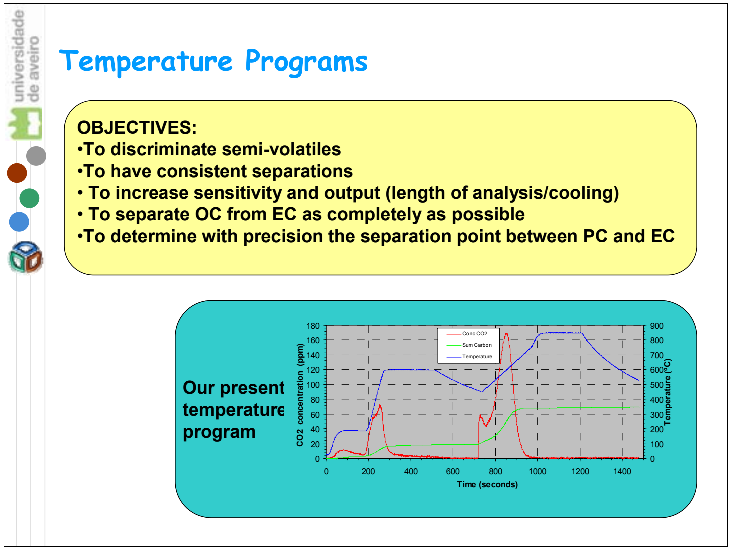
Home-made Thermo-optical OC/EC Analysers

- Three T-Opt OC/EC analyzers
- Two quartz ovens each
- Hardware or Software PID temp. control
- Red laser / chopper / lock-in amplifier
- Pulsed laser / software filtration
- Mass flow meters
- National Instr. acquisition interfaces
- Labview acquis. and control software
- NDIR Analyzer



Scheme of a T-Opt OC/EC Analyser

A- quartz tube oven; A_1 - heating zone 1; A_2 - heating zone 2; B- laser; B_1 - detector; B_2 -cChopper; B_3 - lock-in amplifier; C - non dispersive infra-red spectrophotometer; D: temperature controller; D_1, D_2 - thermocouples; E – mass flowmeter; F - computer; G - three way electrovalve

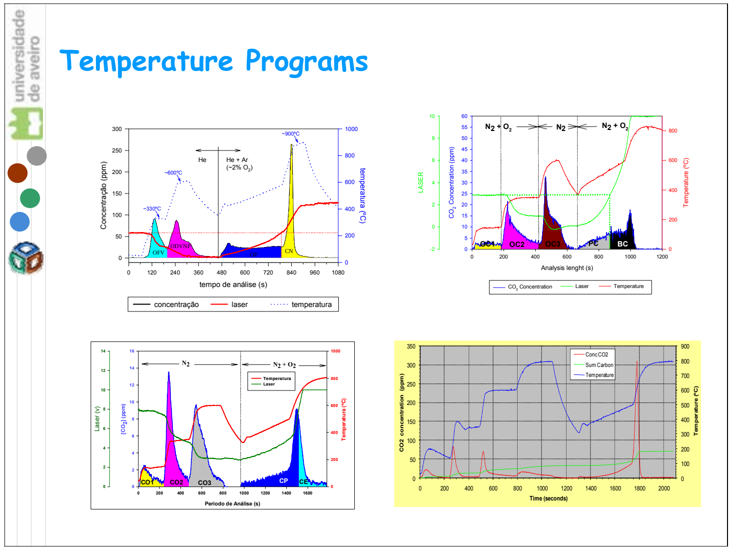


Temperature Programs

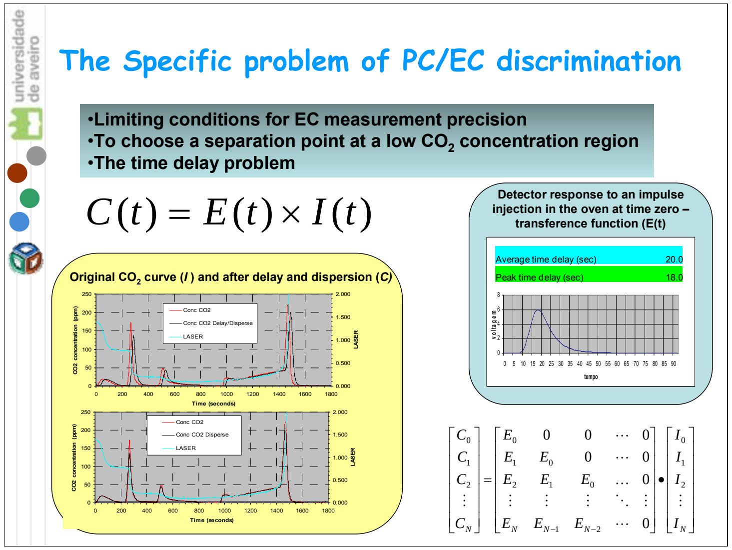
OBJECTIVES:

- To discriminate semi-volatiles
- To have consistent separations
- To increase sensitivity and output (length of analysis/cooling)
- To separate OC from EC as completely as possible
- To determine with precision the separation point between PC and EC

Our present temperature program



Temperature Programs



The Specific problem of PC/EC discrimination

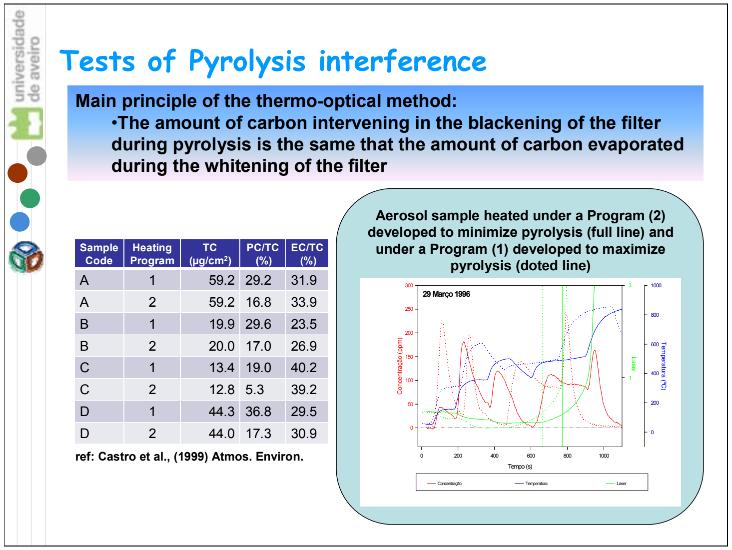
- Limiting conditions for EC measurement precision
- To choose a separation point at a low CO_2 concentration region
- The time delay problem

$$C(t) = E(t) \times I(t)$$

Original CO_2 curve (*I*) and after delay and dispersion (*C*)

Detector response to an impulse injection in the oven at time zero – transference function (E(t))

$$\begin{bmatrix} C_0 \\ C_1 \\ C_2 \\ \vdots \\ C_N \end{bmatrix} = \begin{bmatrix} E_0 & 0 & 0 & \cdots & 0 \\ E_1 & E_0 & 0 & \cdots & 0 \\ E_2 & E_1 & E_0 & \ldots & 0 \\ \vdots & \vdots & \vdots & \ddots & \vdots \\ E_N & E_{N-1} & E_{N-2} & \cdots & 0 \end{bmatrix} \bullet \begin{bmatrix} I_0 \\ I_1 \\ I_2 \\ \vdots \\ I_N \end{bmatrix}$$



Tests of Pyrolysis interference

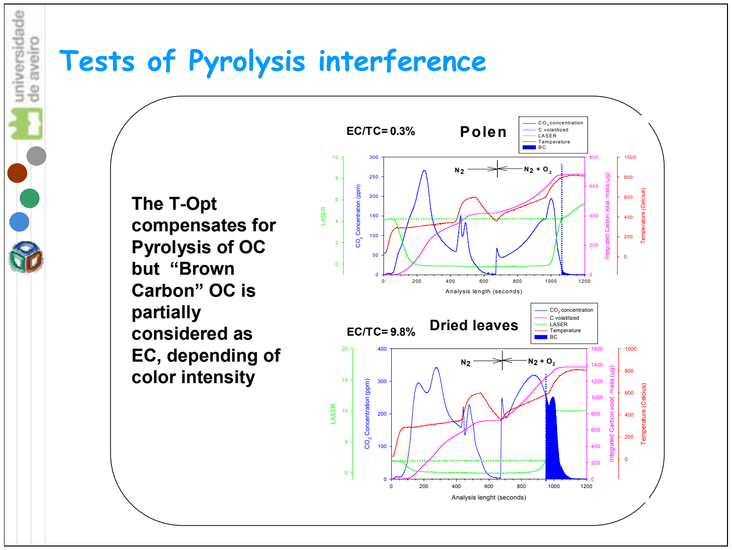
Main principle of the thermo-optical method:

- **The amount of carbon intervening in the blackening of the filter during pyrolysis is the same that the amount of carbon evaporated during the whitening of the filter**

Sample Code	Heating Program	TC (μg/cm²)	PC/TC (%)	EC/TC (%)
A	1	59.2	29.2	31.9
A	2	59.2	16.8	33.9
B	1	19.9	29.6	23.5
B	2	20.0	17.0	26.9
C	1	13.4	19.0	40.2
C	2	12.8	5.3	39.2
D	1	44.3	36.8	29.5
D	2	44.0	17.3	30.9

ref: Castro et al., (1999) Atmos. Environ.

Aerosol sample heated under a Program (2) developed to minimize pyrolysis (full line) and under a Program (1) developed to maximize pyrolysis (doted line)

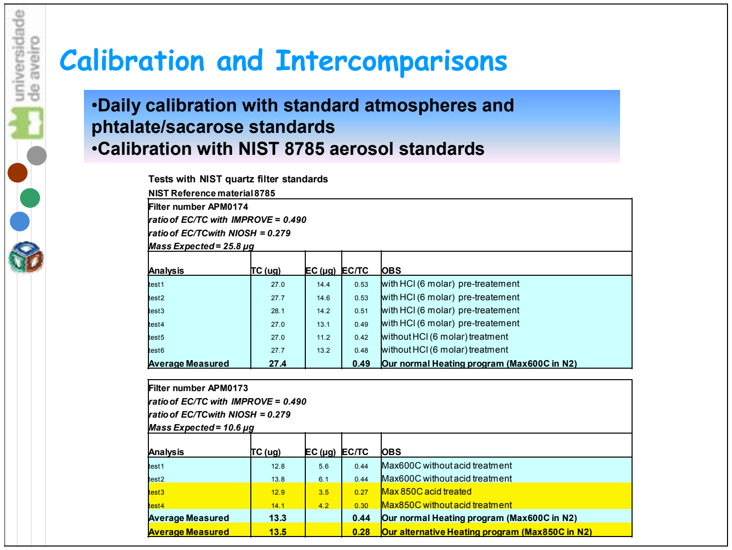


Tests of Pyrolysis interference

The T-Opt compensates for Pyrolysis of OC but "Brown Carbon" OC is partially considered as EC, depending of color intensity

EC/TC= 0.3% **Polen**

EC/TC= 9.8% **Dried leaves**



Calibration and Intercomparisons

- **Daily calibration with standard atmospheres and phtalate/sacarose standards**
- **Calibration with NIST 8785 aerosol standards**

Tests with NIST quartz filter standards

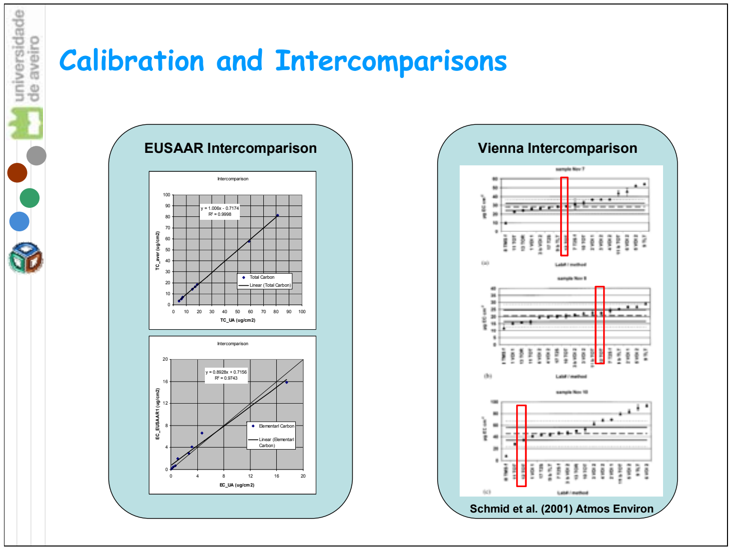
NIST Reference material 8785

Filter number APM0174
ratio of EC/TC with IMPROVE = 0.490
ratio of EC/TCwith NIOSH = 0.279
Mass Expected = 25.8 μg

Analysis	TC (ug)	EC (μg)	EC/TC	OBS
test1	27.0	14.4	0.53	with HCl (6 molar) pre-treatement
test2	27.7	14.6	0.53	with HCl (6 molar) pre-treatement
test3	28.1	14.2	0.51	with HCl (6 molar) pre-treatement
test4	27.0	13.1	0.49	with HCl (6 molar) pre-treatement
test5	27.0	11.2	0.42	without HCl (6 molar) treatment
test6	27.7	13.2	0.48	without HCl (6 molar) treatment
Average Measured	**27.4**		**0.49**	**Our normal Heating program (Max600C in N2)**

Filter number APM0173
ratio of EC/TC with IMPROVE = 0.490
ratio of EC/TCwith NIOSH = 0.279
Mass Expected = 10.6 μg

Analysis	TC (ug)	EC (μg)	EC/TC	OBS
test1	12.8	5.6	0.44	Max600C without acid treatment
test2	13.8	6.1	0.44	Max600C without acid treatment
test3	12.9	3.5	0.27	Max 850C acid treated
test4	14.1	4.2	0.30	Max850C without acid treatment
Average Measured	**13.3**		**0.44**	**Our normal Heating program (Max600C in N2)**
Average Measured	**13.5**		**0.28**	**Our alternative Heating program (Max850C in N2)**



Calibration and Intercomparisons

EUSAAR Intercomparison

Vienna Intercomparison

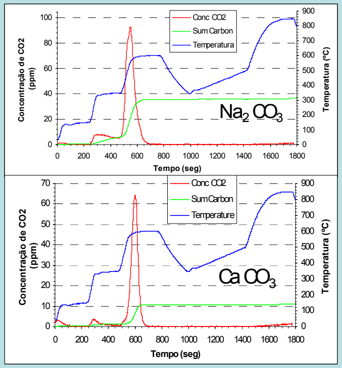
Schmid et al. (2001) Atmos Environ

Carbonate Interference and measurement

Thermal volatilization of carbonates happen within a wide range of temperatures, depending of the crystalline structure

natural carbonated material

Material	Initial Volat. Temperature (ºC)	Temperature of Max. Volatilisation (ºC)
Calcite (stalagnite)	643	841
Dolomitic limestone	661	803
Oolitic limestone	654	788
limestone (Candeeiros)	615	788
Limestone (Ançã)	644	800

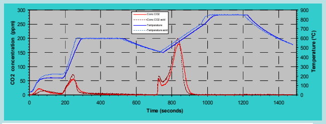


Carbonate Interference and measurement

Removal efficiency of sodium carbonate from filters, with HCl vapors

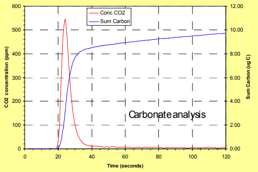
Time (hours)	HCl (Molar)	Carbon (µg)	Removal (%)
0	-	37.1	0
18	3	21.5	42
2	6	35.9	10
4	6	1.7	95

Analysis of an urban aerosol sample, with and without HCl pretreatment



	Sample F005	OCa	OCb	PC	EC	TC
Without treatment	Carbon Mass Analysed (µg)	4.7	12.2	5.5	38.1	60.5
Acid treated	Carbon Mass Analysed (µg)	3.9	13.5	4.6	39.0	61.0

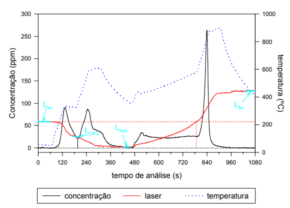
Analysis of carbonates in filters by immersion in concentrated phosphoric acid and CO_2 evolution

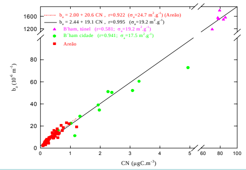


Measurement of Optical Properties

Comparison of EC with filter attenuation of LASER light L , using Beer Law:

$$\ln\frac{I_0}{I} = \ln\frac{L_{fin}}{L_{int}} = -b_a = -\sigma_a \times m/A$$





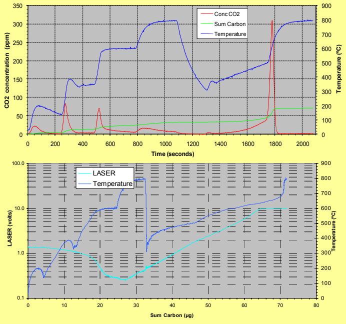
Average Mass absorptivity (extinction) of 20 m².g⁻¹

Measurement of Optical Properties

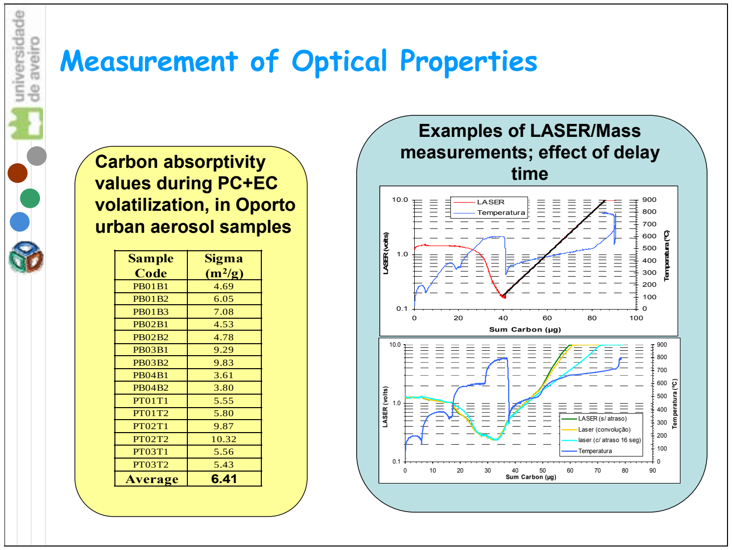
The slope of LASER intensity during PC+EC evolution relates with the specific absorptivity (extinction) of carbon being volatilized, in accordance with Beer Law:

$$\frac{d\ln L}{d(-m)} = -\sigma_a/A$$

	OC1	OC2	OC3	OC4	PC	EC	TC
Mass Analysed (µg)	4.3	9.2	11.1	8.4	10.8	28.1	71.8
Mass Filter (µg)	1388	2965	3571	2709	3483	9084	23201
Percentage (%)	6.0	12.8	15.4	11.7	15.0	39.2	100.0



-m

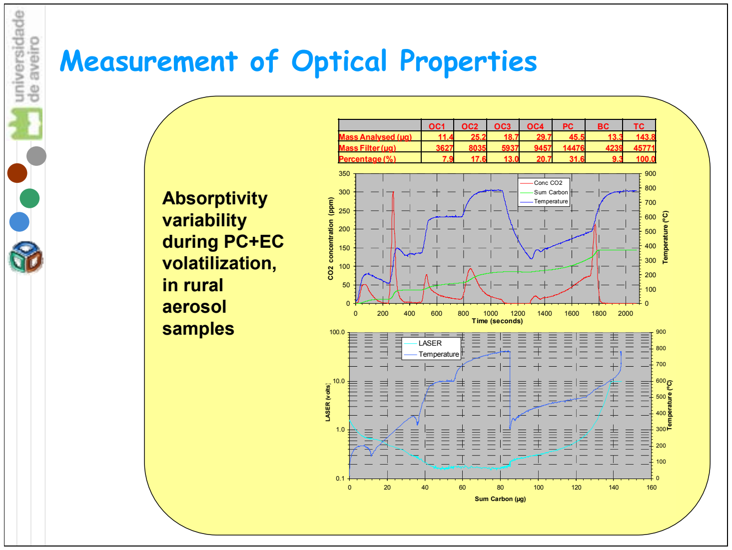


Measurement of Optical Properties

Carbon absorptivity values during PC+EC volatilization, in Oporto urban aerosol samples

Sample Code	Sigma (m^2/g)
PB01B1	4.69
PB01B2	6.05
PB01B3	7.08
PB02B1	4.53
PB02B2	4.78
PB03B1	9.29
PB03B2	9.83
PB04B1	3.61
PB04B2	3.80
PT01T1	5.55
PT01T2	5.80
PT02T1	9.87
PT02T2	10.32
PT03T1	5.56
PT03T2	5.43
Average	**6.41**

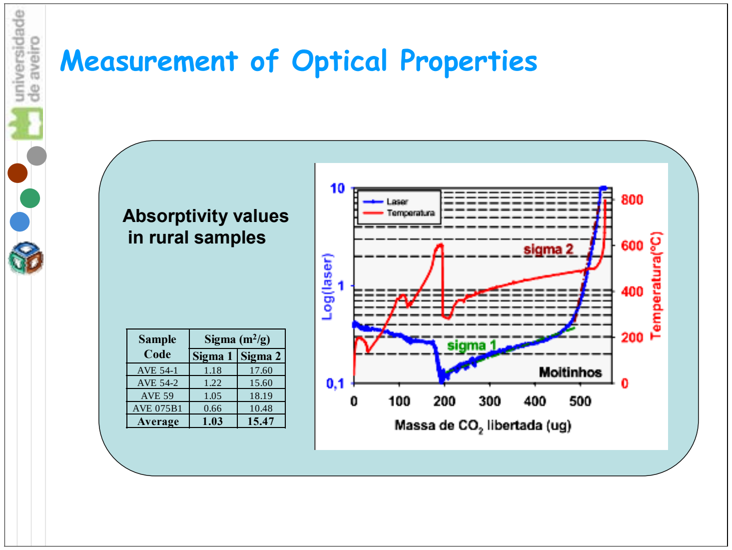
Examples of LASER/Mass measurements; effect of delay time



Measurement of Optical Properties

Absorptivity variability during PC+EC volatilization, in rural aerosol samples

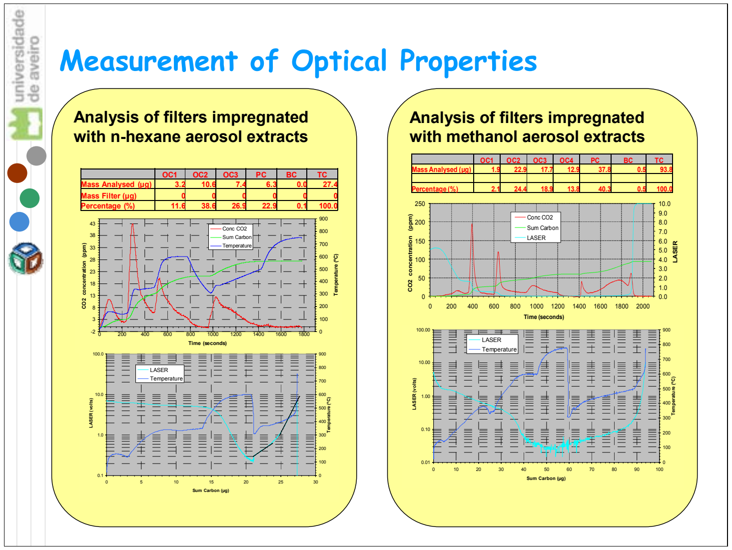
	OC1	OC2	OC3	OC4	PC	BC	TC
Mass Analysed (µg)	11.4	25.2	18.7	29.7	45.5	13.3	143.8
Mass Filter (µg)	3627	8035	5937	9457	14476	4239	45771
Percentage (%)	7.9	17.6	13.0	20.7	31.6	9.3	100.0



Measurement of Optical Properties

Absorptivity values in rural samples

Sample Code	Sigma (m^2/g)	
	Sigma 1	Sigma 2
AVE 54-1	1.18	17.60
AVE 54-2	1.22	15.60
AVE 59	1.05	18.19
AVE 075B1	0.66	10.48
Average	**1.03**	**15.47**



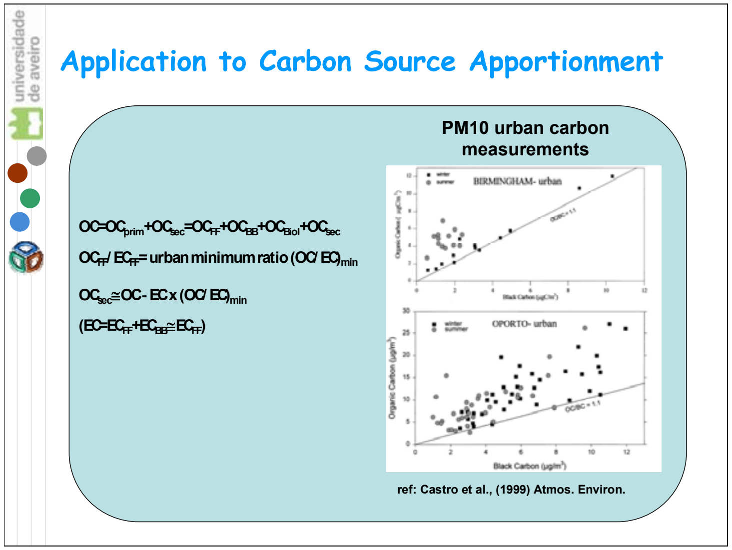
Measurement of Optical Properties

Analysis of filters impregnated with n-hexane aerosol extracts

	OC1	OC2	OC3	PC	BC	TC
Mass Analysed (µg)	3.2	10.6	7.4	6.3	0.0	27.4
Mass Filter (µg)	0	0	0	0	0	0
Percentage (%)	11.6	38.6	26.9	22.9	0.1	100.0

Analysis of filters impregnated with methanol aerosol extracts

	OC1	OC2	OC3	OC4	PC	BC	TC
Mass Analysed (µg)	1.9	22.9	17.7	12.9	37.8	0.5	93.8
Percentage (%)	2.1	24.4	18.9	13.8	40.3	0.5	100.0



Application to Carbon Source Apportionment

$OC = OC_{prim} + OC_{sec} = OC_{FF} + OC_{BB} + OC_{Biol} + OC_{sec}$

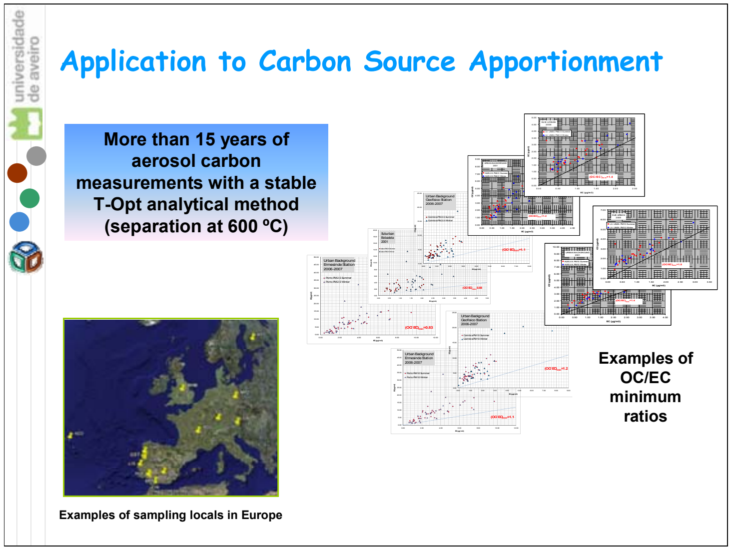
OC_{FF} / EC_{FF} = urban minimum ratio $(OC/EC)_{min}$

$OC_{sec} \cong OC - EC \times (OC/EC)_{min}$

$(EC = EC_{FF} + EC_{BB} \cong EC_{FF})$

PM10 urban carbon measurements

ref: Castro et al., (1999) Atmos. Environ.

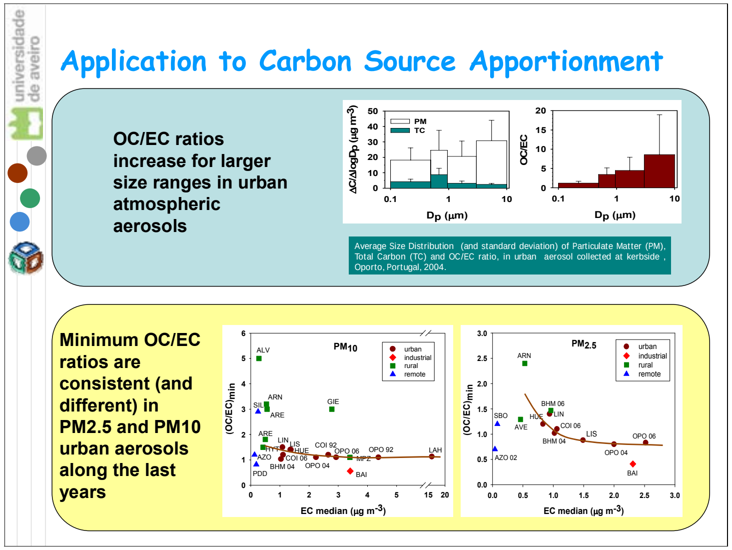


Application to Carbon Source Apportionment

More than 15 years of aerosol carbon measurements with a stable T-Opt analytical method (separation at 600 ºC)

Examples of sampling locals in Europe

Examples of OC/EC minimum ratios

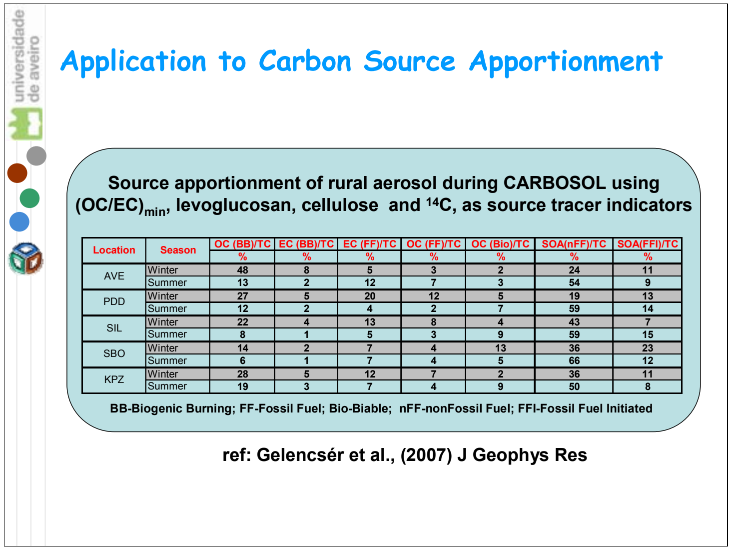


Application to Carbon Source Apportionment

OC/EC ratios increase for larger size ranges in urban atmospheric aerosols

Average Size Distribution (and standard deviation) of Particulate Matter (PM), Total Carbon (TC) and OC/EC ratio, in urban aerosol collected at kerbside, Oporto, Portugal, 2004.

Minimum OC/EC ratios are consistent (and different) in PM2.5 and PM10 urban aerosols along the last years



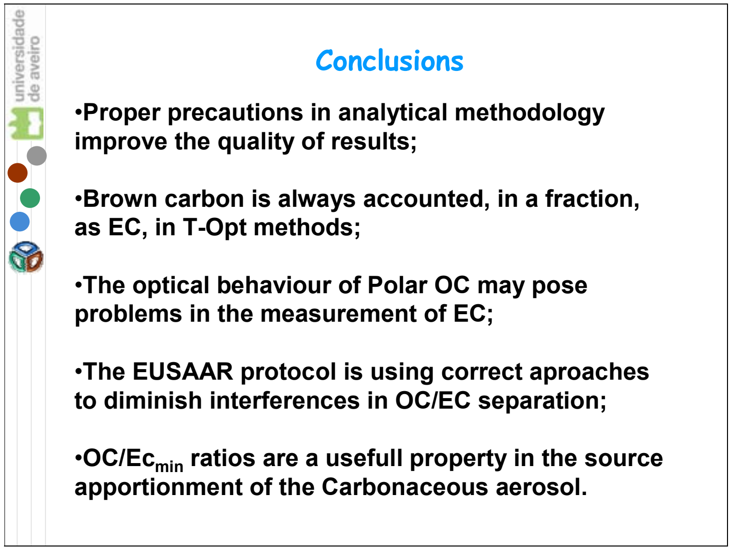
Application to Carbon Source Apportionment

Source apportionment of rural aerosol during CARBOSOL using $(OC/EC)_{min}$, levoglucosan, cellulose and ^{14}C, as source tracer indicators

Location	Season	OC (BB)/TC	EC (BB)/TC	EC (FF)/TC	OC (FF)/TC	OC (Bio)/TC	SOA(nFF)/TC	SOA(FFI)/TC
		%	%	%	%	%	%	%
AVE	Winter	48	8	5	3	2	24	11
	Summer	13	2	12	7	3	54	9
PDD	Winter	27	5	20	12	5	19	13
	Summer	12	2	4	2	7	59	14
SIL	Winter	22	4	13	8	4	43	7
	Summer	8	1	5	3	9	59	15
SBO	Winter	14	2	7	4	13	36	23
	Summer	6	1	7	4	5	66	12
KPZ	Winter	28	5	12	7	2	36	11
	Summer	19	3	7	4	9	50	8

BB-Biogenic Burning; FF-Fossil Fuel; Bio-Biable; nFF-nonFossil Fuel; FFI-Fossil Fuel Initiated

ref: Gelencsér et al., (2007) J Geophys Res



Conclusions

- Proper precautions in analytical methodology improve the quality of results;

- Brown carbon is always accounted, in a fraction, as EC, in T-Opt methods;

- The optical behaviour of Polar OC may pose problems in the measurement of EC;

- The EUSAAR protocol is using correct aproaches to diminish interferences in OC/EC separation;

- OC/Ec_{min} ratios are a usefull property in the source apportionment of the Carbonaceous aerosol.

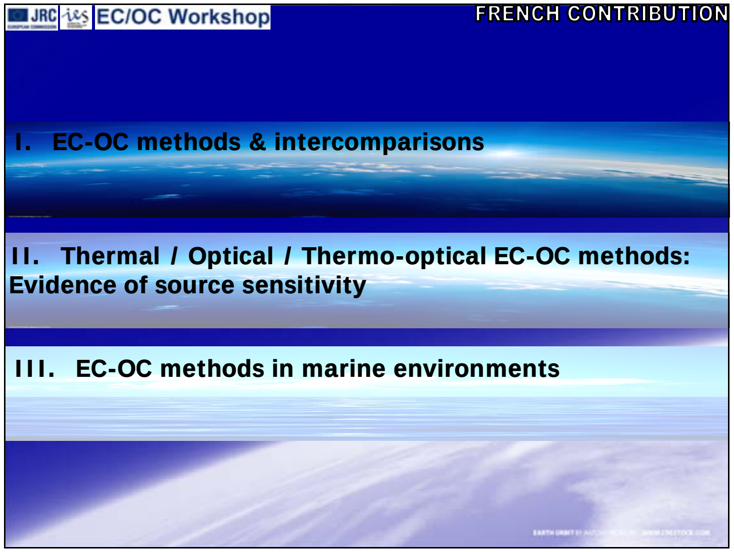
A.12 The French Contribution

EC/OC Workshop

A FRENCH CONTRIBUTION

Jean SCIARE, Hélène CACHIER, Olivier FAVEZ

LSCE, GIF/YVETTE, FRANCE



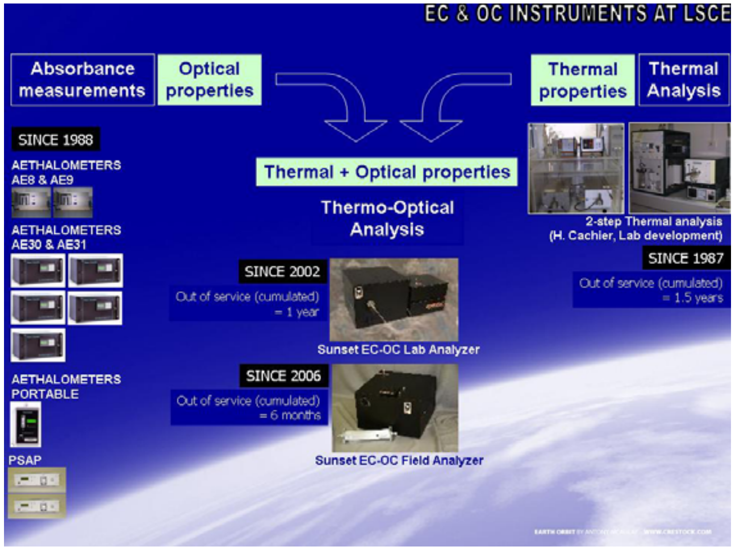
EC/OC Workshop

FRENCH CONTRIBUTION

I. EC-OC methods & intercomparisons

II. Thermal / Optical / Thermo-optical EC-OC methods: Evidence of source sensitivity

III. EC-OC methods in marine environments



EC & OC INSTRUMENTS AT LSCE

Absorbance measurements

Optical properties

Thermal properties

Thermal Analysis

Thermal + Optical properties

Thermo-Optical Analysis

SINCE 1988

AETHALOMETERS AE8 & AE9

AETHALOMETERS AE30 & AE31

AETHALOMETERS PORTABLE

PSAP

SINCE 2002

Out of service (cumulated) = 1 year

Sunset EC-OC Lab Analyzer

SINCE 2006

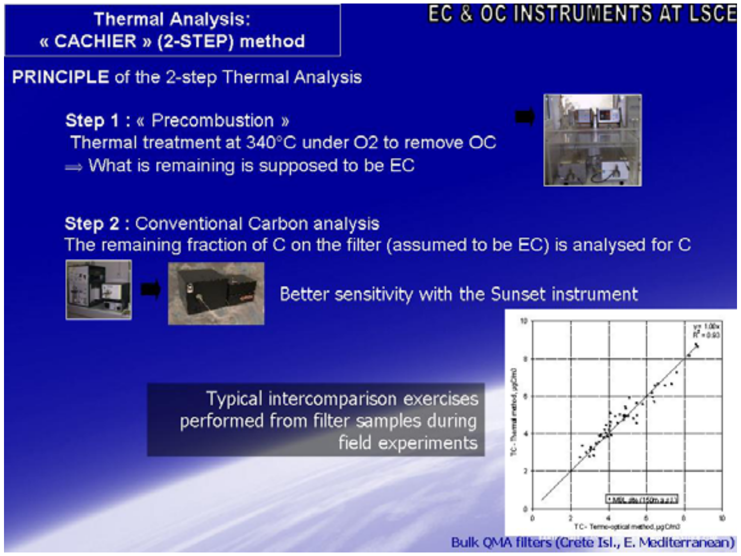
Out of service (cumulated) = 6 months

Sunset EC-OC Field Analyzer

2-step Thermal analysis (H. Cachier, Lab development)

SINCE 1987

Out of service (cumulated) = 1.5 years



Thermal Analysis: « CACHIER » (2-STEP) method

EC & OC INSTRUMENTS AT LSCE

PRINCIPLE of the 2-step Thermal Analysis

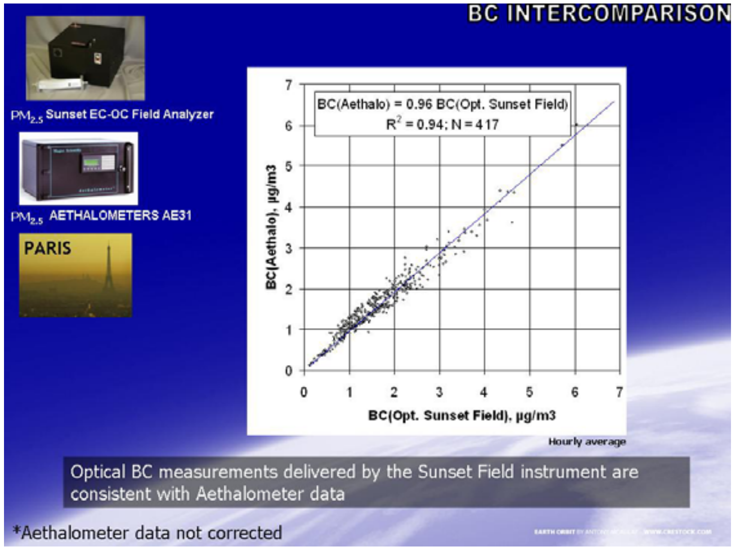
Step 1 : « Precombustion »
Thermal treatment at 340°C under O2 to remove OC
⟹ What is remaining is supposed to be EC

Step 2 : Conventional Carbon analysis
The remaining fraction of C on the filter (assumed to be EC) is analysed for C

Better sensitivity with the Sunset instrument

Typical intercomparison exercises performed from filter samples during field experiments

Bulk QMA filters (Crete Isl., E. Mediterranean)



BC INTERCOMPARISON

$PM_{2.5}$ Sunset EC-OC Field Analyzer

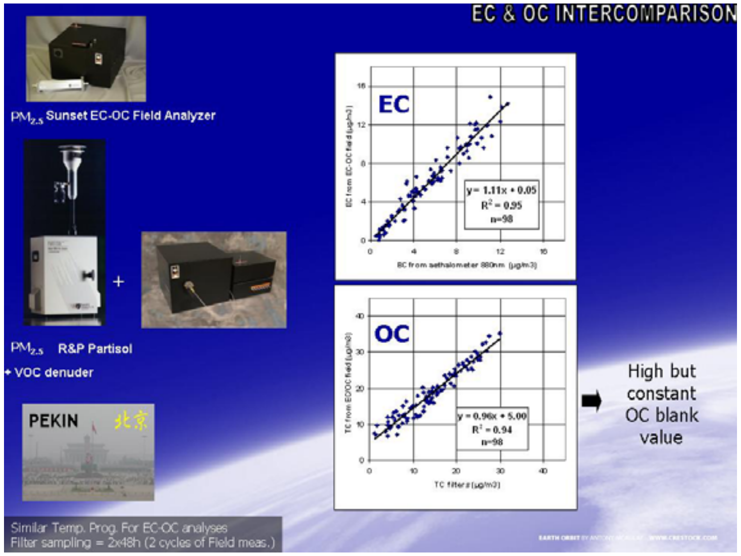
$PM_{2.5}$ AETHALOMETERS AE31

PARIS

Hourly average

Optical BC measurements delivered by the Sunset Field instrument are consistent with Aethalometer data

*Aethalometer data not corrected



EC & OC INTERCOMPARISON

$PM_{2.5}$ Sunset EC-OC Field Analyzer

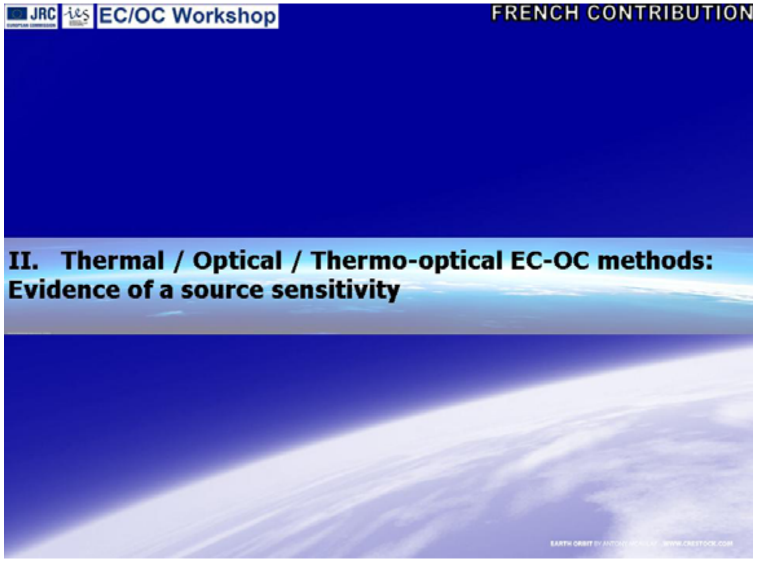
$PM_{2.5}$ R&P Partisol

+ VOC denuder

PEKIN 北京

➡ High but constant OC blank value

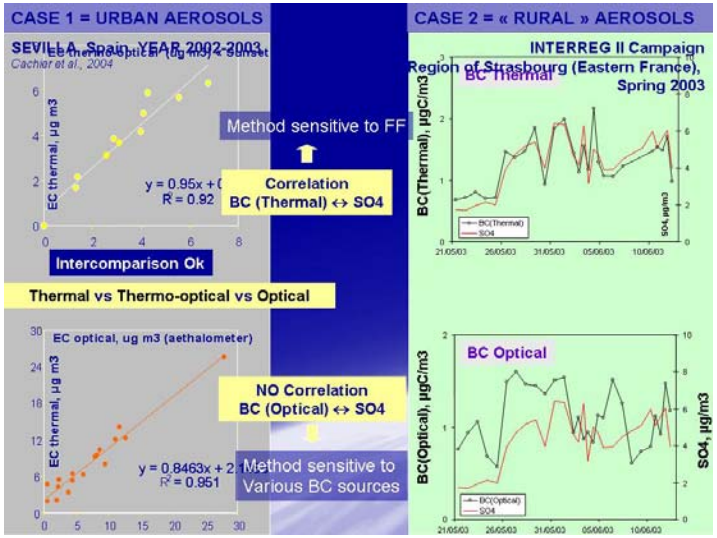
Similar Temp. Prog. For EC-OC analyses
Filter sampling = 2x48h (2 cycles of Field meas.)



JRC ies EC/OC Workshop

FRENCH CONTRIBUTION

II. Thermal / Optical / Thermo-optical EC-OC methods: Evidence of a source sensitivity



CASE 1 = URBAN AEROSOLS

SEVILLA, Spain, YEAR 2002-2003

Cachier et al., 2004

Intercomparison Ok

Thermal vs Thermo-optical vs Optical

Method sensitive to FF

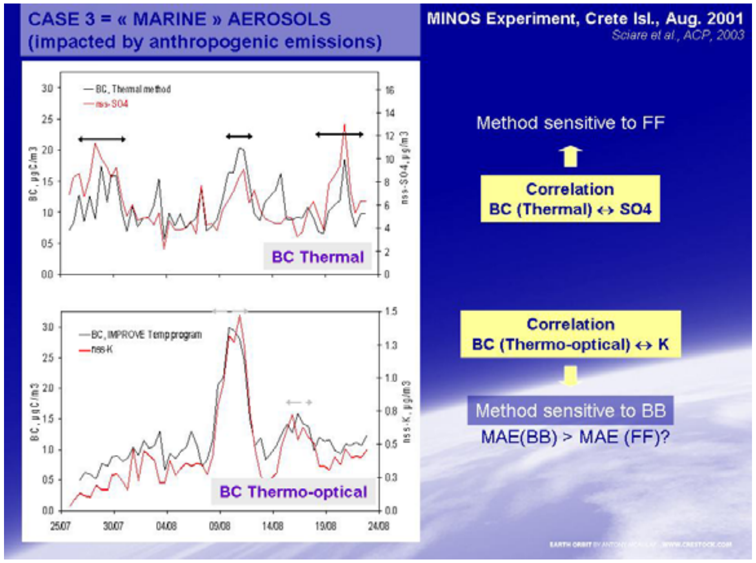
Correlation
BC (Thermal) ↔ SO4

NO Correlation
BC (Optical) ↔ SO4

Method sensitive to Various BC sources

CASE 2 = « RURAL » AEROSOLS

INTERREG II Campaign
Region of Strasbourg (Eastern France),
Spring 2003



CASE 3 = « MARINE » AEROSOLS
(impacted by anthropogenic emissions)

MINOS Experiment, Crete Isl., Aug. 2001

Sciare et al., ACP, 2003

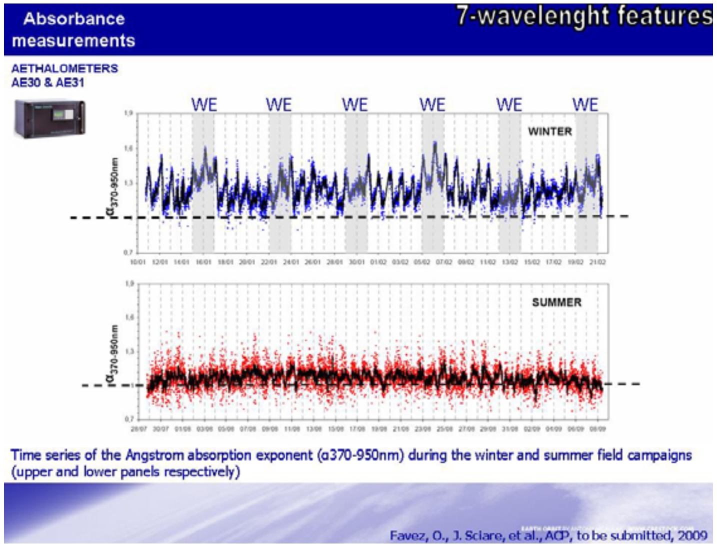
Method sensitive to FF

Correlation
BC (Thermal) ↔ SO4

Correlation
BC (Thermo-optical) ↔ K

Method sensitive to BB

MAE(BB) > MAE (FF)?



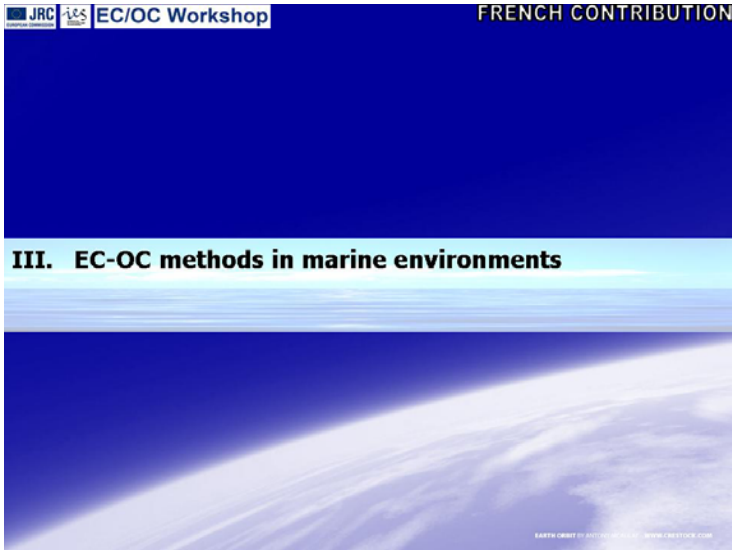
Absorbance measurements

7-wavelenght features

AETHALOMETERS
AE30 & AE31

Time series of the Angstrom absorption exponent (α370-950nm) during the winter and summer field campaigns (upper and lower panels respectively)

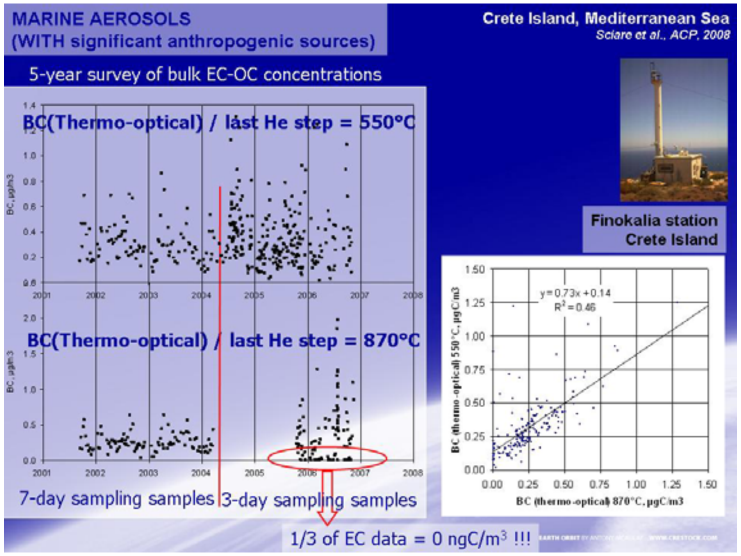
Favez, O., J. Sclare, et al., ACP, to be submitted, 2009



JRC ies EC/OC Workshop

FRENCH CONTRIBUTION

III. EC-OC methods in marine environments



MARINE AEROSOLS
(WITH significant anthropogenic sources)

Crete Island, Mediterranean Sea
Sciare et al., ACP, 2008

5-year survey of bulk EC-OC concentrations

BC(Thermo-optical) / last He step = 550°C

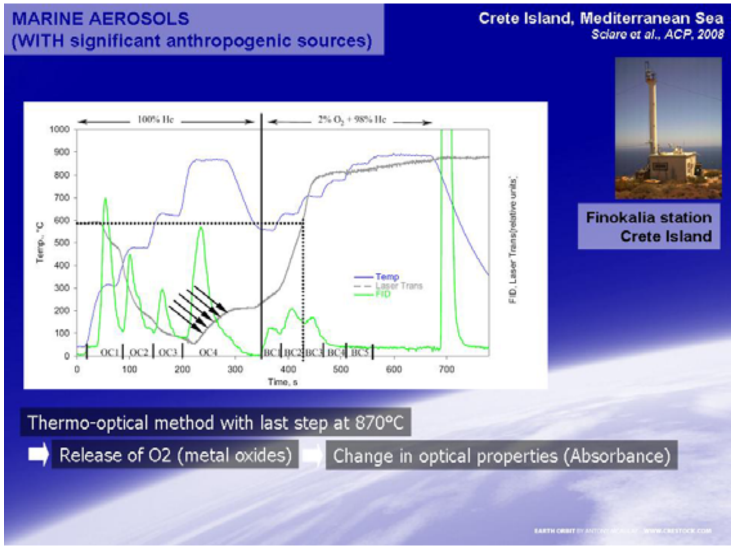
BC(Thermo-optical) / last He step = 870°C

7-day sampling samples

3-day sampling samples

1/3 of EC data = 0 ngC/m³ !!!

Finokalia station
Crete Island



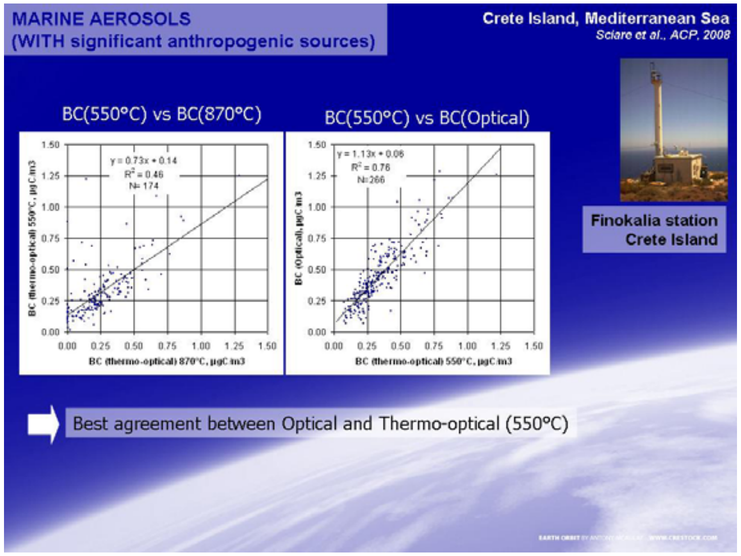
MARINE AEROSOLS
(WITH significant anthropogenic sources)

Crete Island, Mediterranean Sea
Sciare et al., ACP, 2008

Finokalia station
Crete Island

Thermo-optical method with last step at 870°C

➡ Release of O2 (metal oxides) ➡ Change in optical properties (Absorbance)



MARINE AEROSOLS
(WITH significant anthropogenic sources)

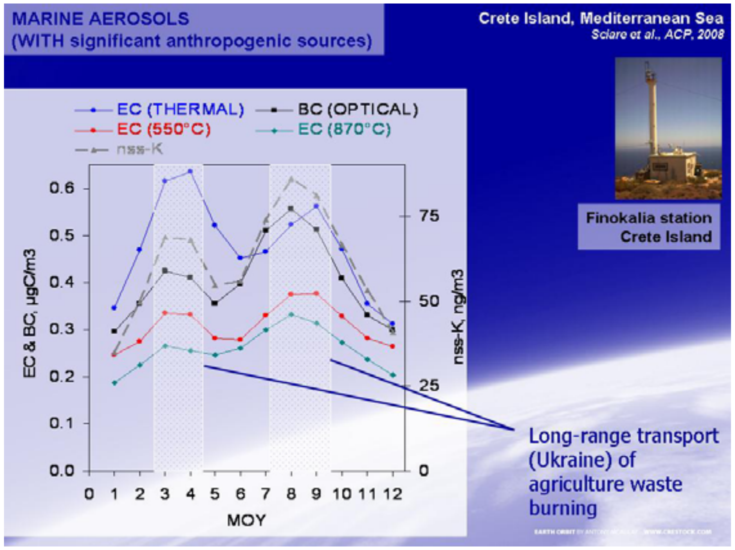
Crete Island, Mediterranean Sea
Sciare et al., ACP, 2008

BC(550°C) vs BC(870°C)

BC(550°C) vs BC(Optical)

Finokalia station
Crete Island

➡ Best agreement between Optical and Thermo-optical (550°C)

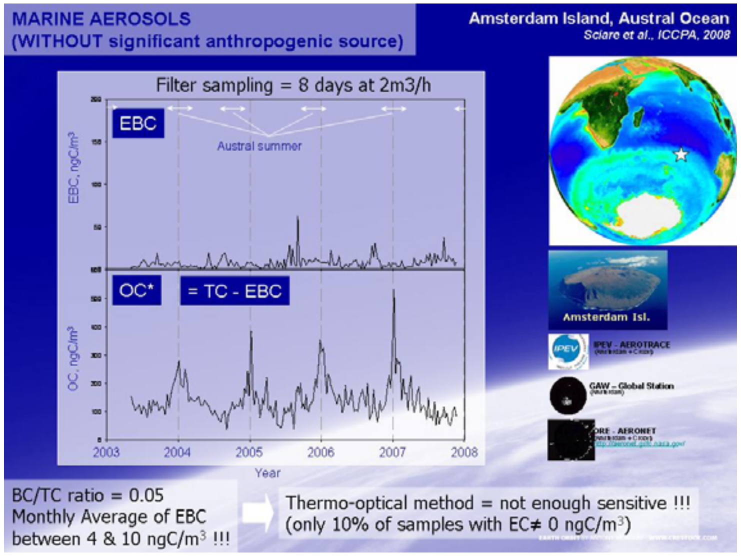


MARINE AEROSOLS
(WITH significant anthropogenic sources)

Crete Island, Mediterranean Sea
Sciare et al., ACP, 2008

Finokalia station
Crete Island

Long-range transport (Ukraine) of agriculture waste burning



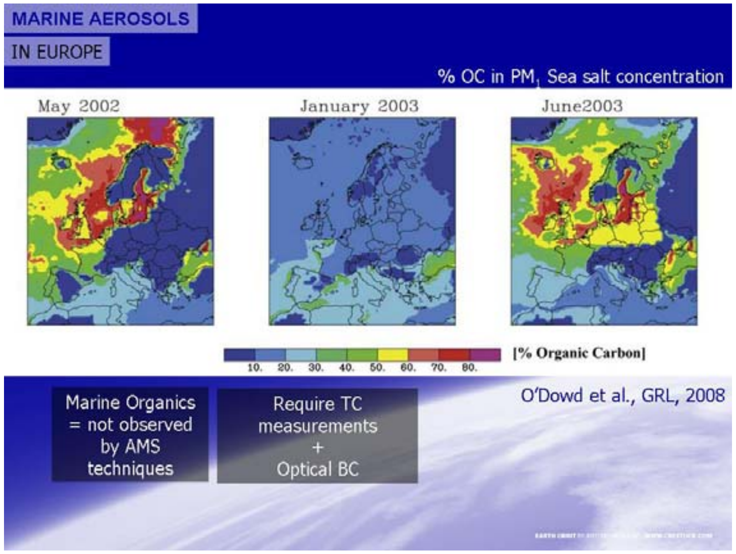
MARINE AEROSOLS
(WITHOUT significant anthropogenic source)

Amsterdam Island, Austral Ocean
Sciare et al., ICCPA, 2008

Filter sampling = 8 days at 2m3/h

BC/TC ratio = 0.05
Monthly Average of EBC
between 4 & 10 ngC/m³ !!!

Thermo-optical method = not enough sensitive !!!
(only 10% of samples with EC≠ 0 ngC/m³)



MARINE AEROSOLS

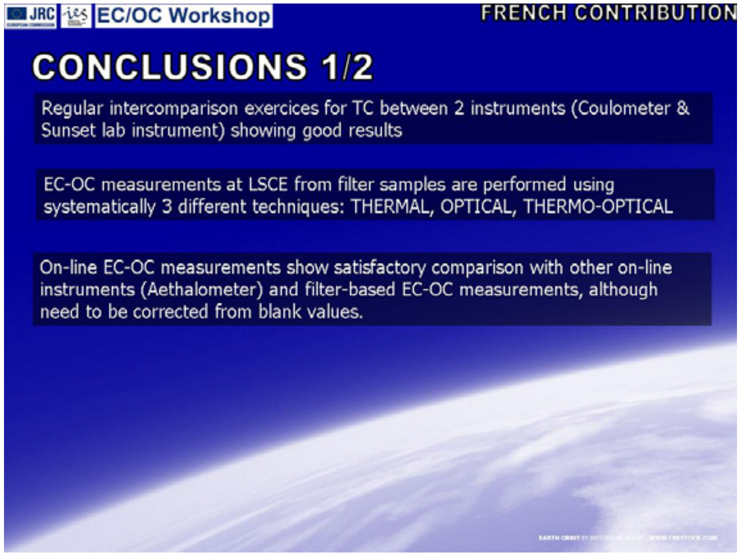
IN EUROPE

% OC in PM, Sea salt concentration

O'Dowd et al., GRL, 2008

Marine Organics
= not observed
by AMS
techniques

Require TC
measurements
+
Optical BC



JRC EC/OC Workshop

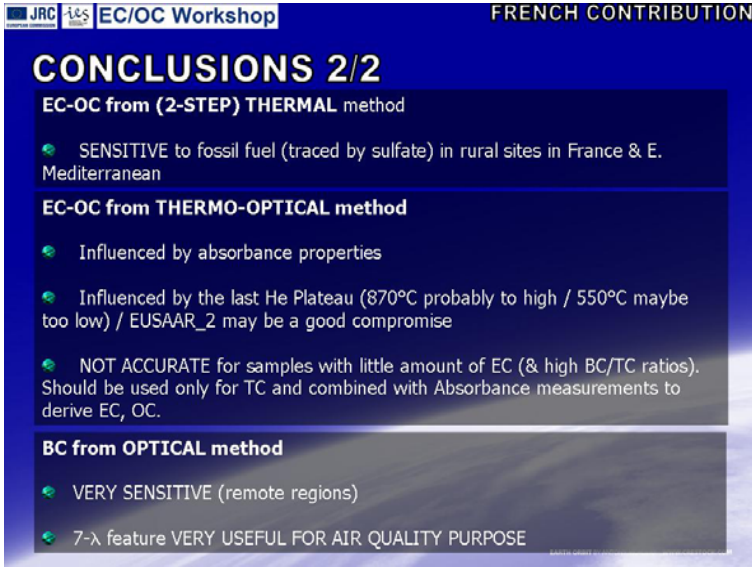
FRENCH CONTRIBUTION

CONCLUSIONS 1/2

Regular intercomparison exercices for TC between 2 instruments (Coulometer & Sunset lab instrument) showing good results

EC-OC measurements at LSCE from filter samples are performed using systematically 3 different techniques: THERMAL, OPTICAL, THERMO-OPTICAL

On-line EC-OC measurements show satisfactory comparison with other on-line instruments (Aethalometer) and filter-based EC-OC measurements, although need to be corrected from blank values.



CONCLUSIONS 2/2

EC-OC from (2-STEP) THERMAL method

- SENSITIVE to fossil fuel (traced by sulfate) in rural sites in France & E. Mediterranean

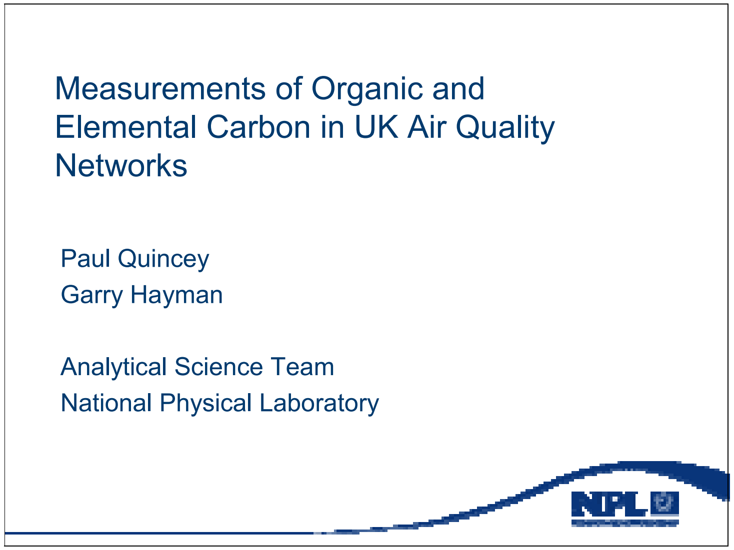
EC-OC from THERMO-OPTICAL method

- Influenced by absorbance properties
- Influenced by the last He Plateau (870°C probably to high / 550°C maybe too low) / EUSAAR_2 may be a good compromise
- NOT ACCURATE for samples with little amount of EC (& high BC/TC ratios). Should be used only for TC and combined with Absorbance measurements to derive EC, OC.

BC from OPTICAL method

- VERY SENSITIVE (remote regions)
- 7-λ feature VERY USEFUL FOR AIR QUALITY PURPOSE

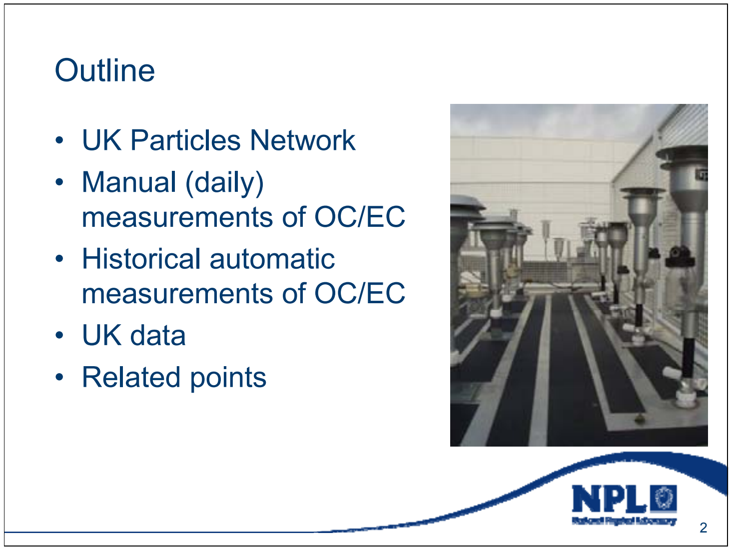
A.13 Measurements of Organic and Elemental Carbon in UK Air Quality Networks



Measurements of Organic and Elemental Carbon in UK Air Quality Networks

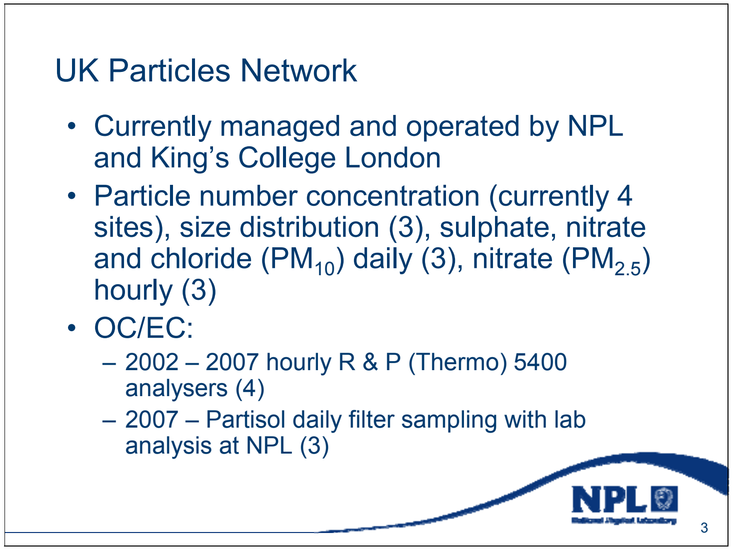
Paul Quincey
Garry Hayman

Analytical Science Team
National Physical Laboratory



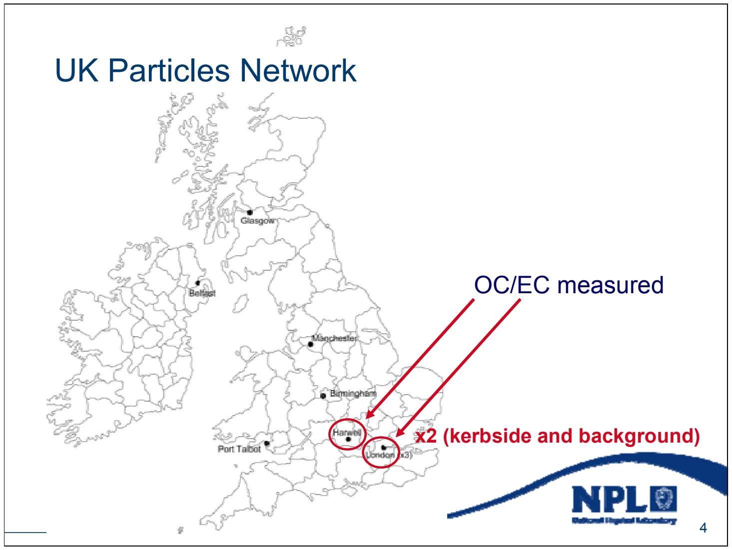
Outline

- UK Particles Network
- Manual (daily) measurements of OC/EC
- Historical automatic measurements of OC/EC
- UK data
- Related points



UK Particles Network

- Currently managed and operated by NPL and King's College London
- Particle number concentration (currently 4 sites), size distribution (3), sulphate, nitrate and chloride (PM_{10}) daily (3), nitrate ($PM_{2.5}$) hourly (3)
- OC/EC:
  - 2002 – 2007 hourly R & P (Thermo) 5400 analysers (4)
  - 2007 – Partisol daily filter sampling with lab analysis at NPL (3)



UK Particles Network

OC/EC measured

x2 (kerbside and background)

Measurement of OC/EC

- Harwell (rural site)
- North Kensington (urban background site)
- Marylebone Road (kerbside site)

- Daily PM_{10} samples (24 m^3) are collected using Partisol 2025 samplers onto quartz (Pallflex Tissuquartz) filters, and are then analysed at NPL using a Sunset Laboratory carbon analyser

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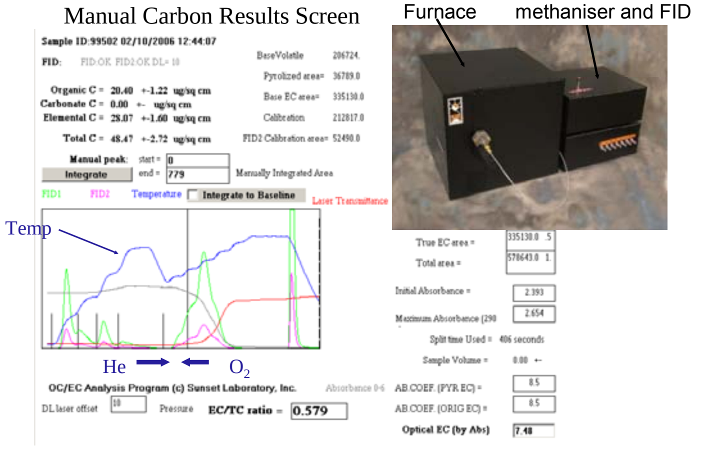


Sample ID:99502 02/10/2006 12:44:07

FID: FID:OK FID2:OK DL= 10

Organic C = 20.40 +-1.22 ug/sq cm
Carbonate C = 0.00 +- ug/sq cm
Elemental C = 28.07 +-1.60 ug/sq cm

Total C = 48.47 +-2.72 ug/sq cm

BaseVolatile 206724.
Pyrolized area= 36789.0
Base EC area= 335130.0
Calibration 212817.0
FID2 Calibration area= 52490.0

Manual peak: start = 0
end = 779
Manually Integrated Area

☐ Integrate to Baseline

OC/EC Analysis Program (c) Sunset Laboratory, Inc.

DL laser offset 10
Pressure
EC/TC ratio = 0.579

Absorbance 0-6

True EC area = 335130.0 .5
Total area = 578643.0 1.
Initial Absorbance = 2.393
Maximum Absorbance (290 2.654
Split time Used = 406 seconds
Sample Volume = 0.00 ←
AB.COEF. (PYR EC) = 8.5
AB.COEF. (ORIG EC) = 8.5
Optical EC (by Abs) 7.48

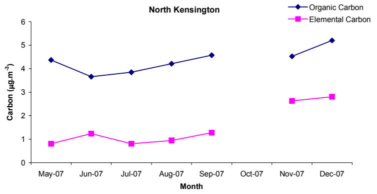
Green	FID Response (Amount of Carbon)
Magenta	Attenuated FID Response
Blue	Oven Temperature
Red	Amount of transmitted light
Grey	Absorbance of sampler

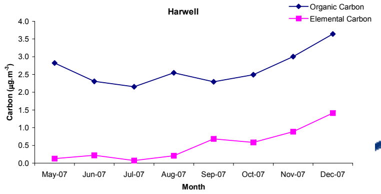
Protocol: "Quartz"

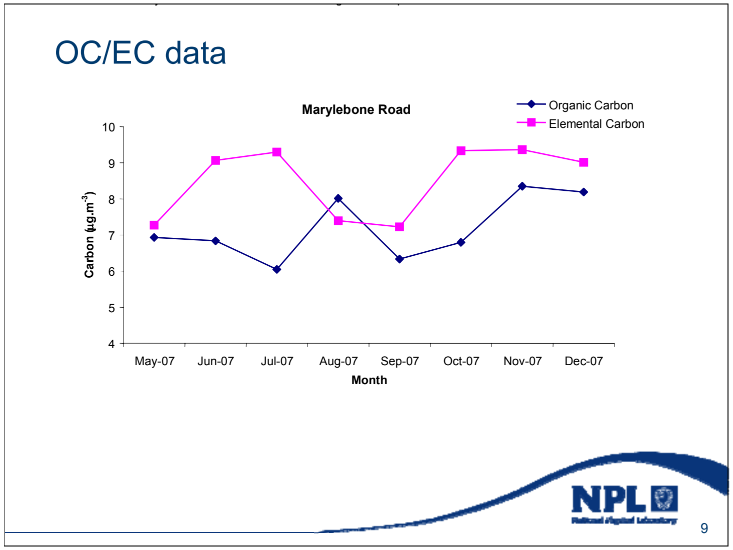
Carrier gas	Temperature plateau duration (s)	Temperature set point (°C)
Helium	70	310
	60	475
	60	615
	105	870
1% Ox in He	60	550
	60	625
	60	700
	60	775
	110	890
Charring correction	Transmittance	

Principal calibration with sucrose solution

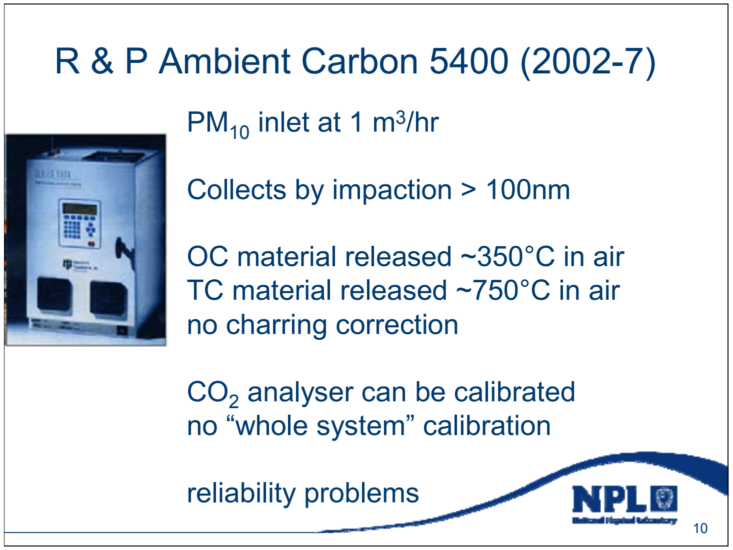
OC/EC data







OC/EC data



R & P Ambient Carbon 5400 (2002-7)

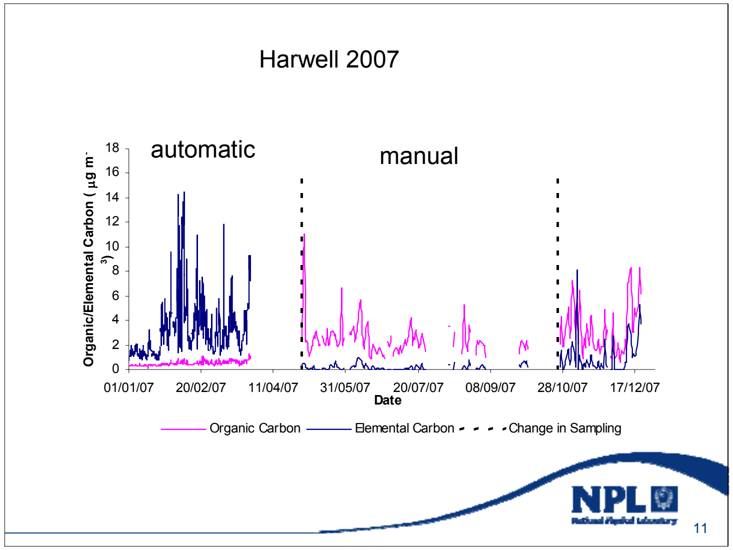
PM_{10} inlet at 1 m^3/hr

Collects by impaction > 100nm

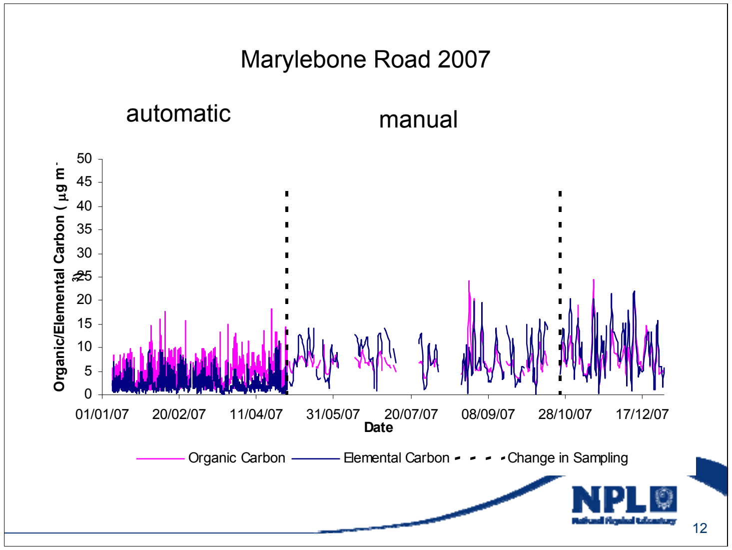
OC material released ~350°C in air
TC material released ~750°C in air
no charring correction

CO_2 analyser can be calibrated
no “whole system” calibration

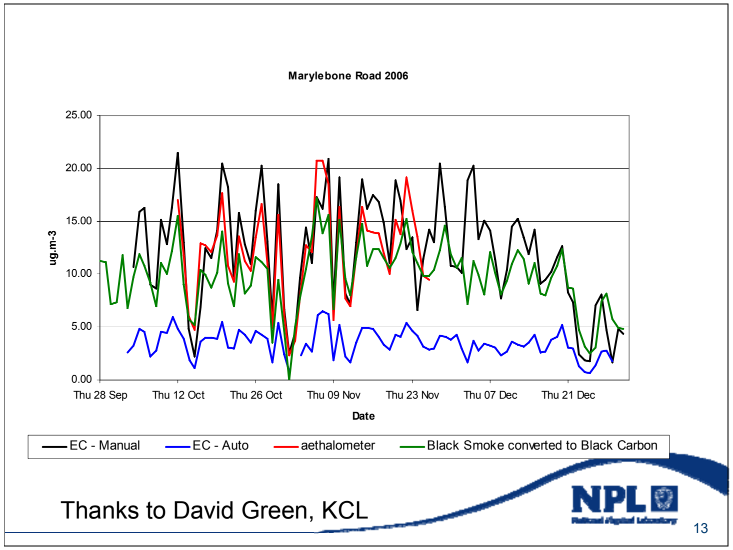
reliability problems



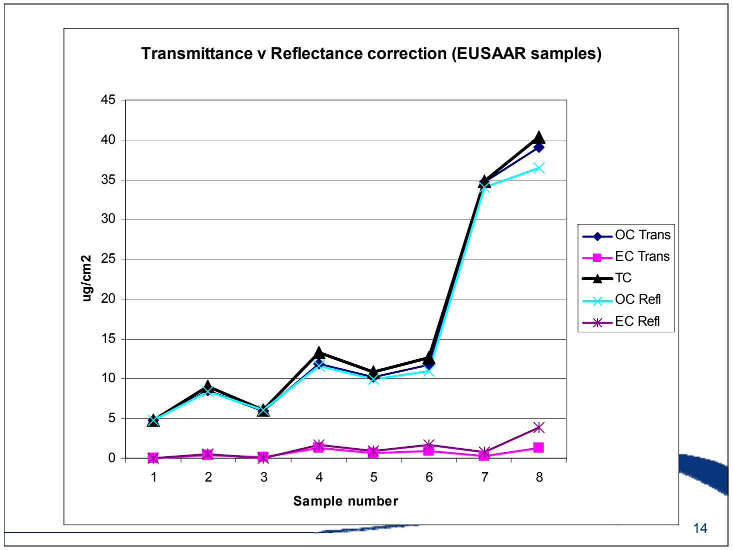
Harwell 2007

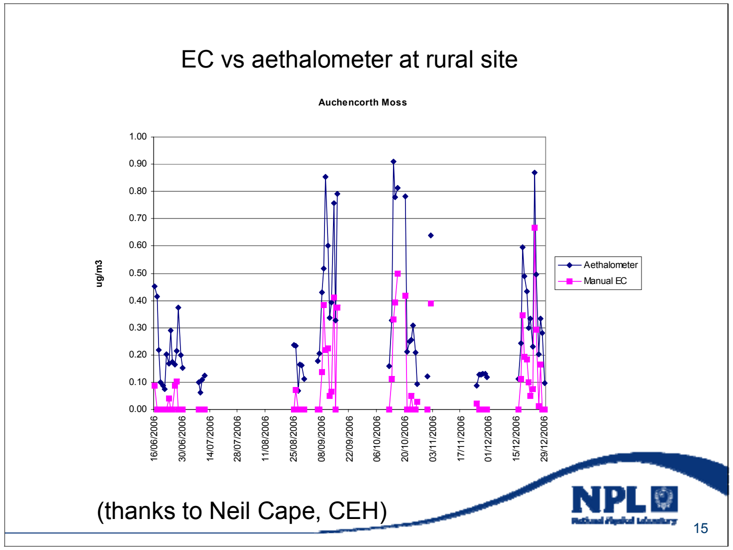


Marylebone Road 2007



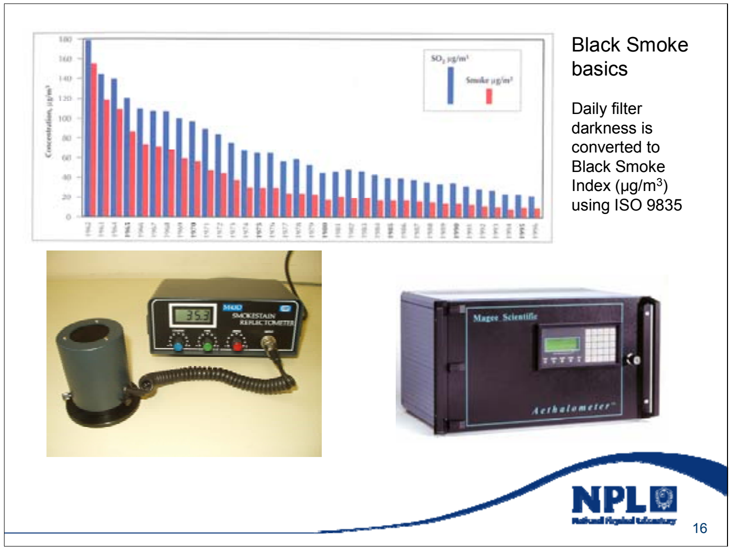
Thanks to David Green, KCL





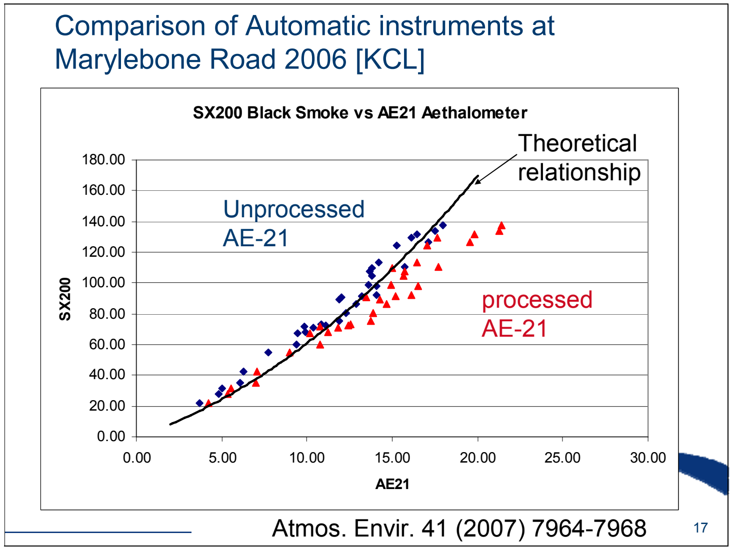
EC vs aethalometer at rural site

(thanks to Neil Cape, CEH)



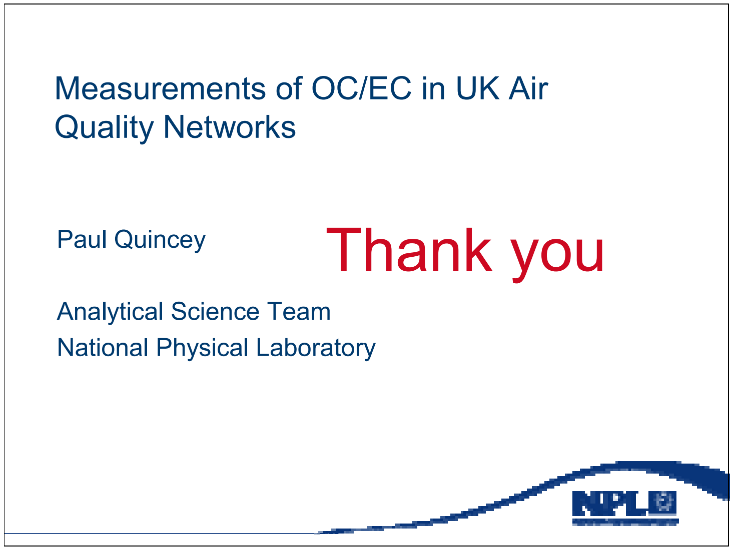
Black Smoke basics

Daily filter darkness is converted to Black Smoke Index (µg/m^3) using ISO 9835



Comparison of Automatic instruments at Marylebone Road 2006 [KCL]

Atmos. Envir. 41 (2007) 7964-7968



Measurements of OC/EC in UK Air Quality Networks

Paul Quincey

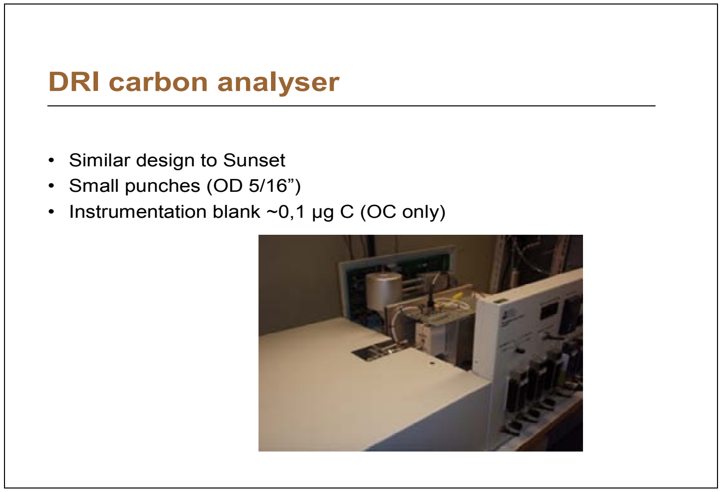
Thank you

Analytical Science Team
National Physical Laboratory

A.14 Swedish experience Eusaar_2 source apportionment

Swedish experience Eusaar_2 source apportionment

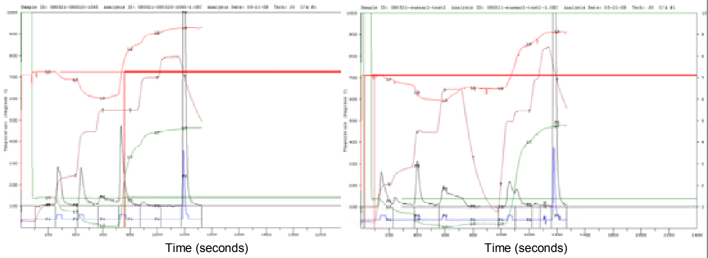
Johan Genberg, Lund University



DRI carbon analyser

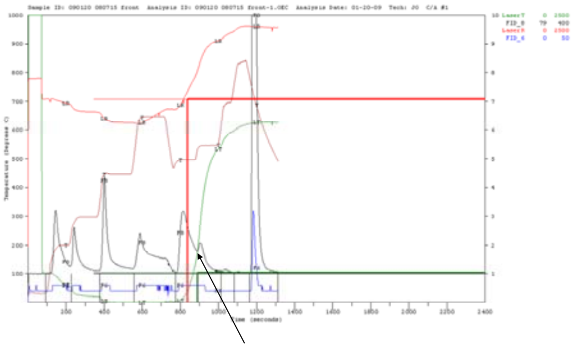
- Similar design to Sunset
- Small punches (OD 5/16”)
- Instrumentation blank ~0,1 µg C (OC only)

Eusaar_2 vs. Improve



⬛ F8 = FID signal
🟩 LT = laser transmission
🟧 signal
T = temperature

The ”perfect” split

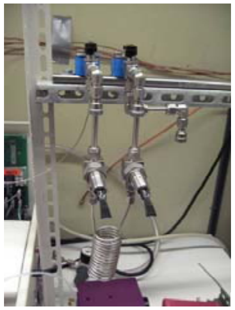


^{14}C in carbonaceous aerosol

- Reveals the source as fossil or contemporary
- EC originate from burning; fossil fuel
  biomass
- Known/estimated EC/TC values may split carbon into
  fossil fuel
  biomass burning
  biogenic carbon

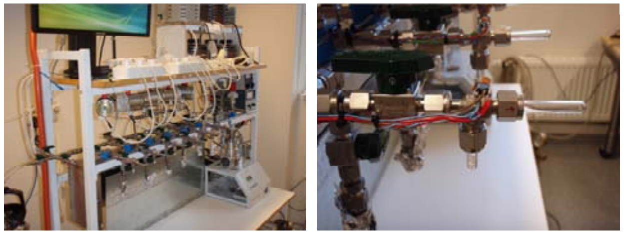
Separate OC from EC

- Remove water soluble components
  Remove OC in air, 375 C, four hours
  The remaining is EC
- Use the carbon analyser
  May use pure oxygen
  Trap CO_2 with LN_2



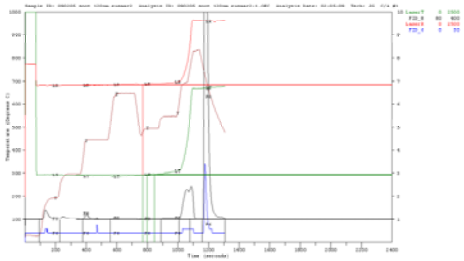
Grafitisation

CO_2 mixed with H_2 over iron catalyst.



Eusaar_2 and EC

650ºC removes EC even in pure helium but pure soot is left unharmed.



Co-workers

- Erik Swietlicki (supervisor)
- Kristina Stenström (supervisor)
- Erik Nilsson (PhD-student)

Thanks

European Commission

EUR 23992 EN – Joint Research Centre – Institute for Environment and Sustainability
Title: Measurement of Elemental and Organic Carbon in Europe
Author(s): Thomas A.J. Kuhlbusch, Annette Borowiak, Andras Gelenscer, Johan Genberg, Dieter Gladtke, Willy Maenhaut, Casimiro Pio, Olga Popoviecheva, Jean P. Putaud, Paul Quincey, Jean Sciare, Harry ten Brink, Mar Viana, Karl Espen Yttri
Luxembourg: Office for Official Publications of the European Communities
2009 – 117 pp.
EUR – Scientific and Technical Research series – ISSN 1018-5593
ISBN 978-92-79-11294-2
DOI 10.2788/34791

Abstract

The new Air Quality Directive 2008/50/EC is asking in Annex IX that elemental (EC) and organic (OC) carbon as well as soluble ions should be measured at selected background sites in each Member State. Several methods (thermal, optical or photo-acoustic methods) to determine elemental and organic carbon exist which do not always deliver comparable results. European experts in EC/OC measurements met at the JRC in Ispra on 10th and 11th February 2009 to discuss during a workshop the best suitable European method.

The main tasks of this workshop were

- to discuss the advantages and disadvantages of different methods for the determination of OC and EC,
- to get information from the Member States on existing methods or even standards being applied,
- to initiate discussions on a preferred basic method to be standardised by CEN within the scope of Directive 2008/50/EC.

The conclusions of this workshop will directly feed into CEN and the corresponding Working Group to clearly define their task for European wide standardisation and hence harmonisation.

The mission of the JRC is to provide customer-driven scientific and technical support for the conception, development, implementation and monitoring of EU policies. As a service of the European Commission, the JRC functions as a reference centre of science and technology for the Union. Close to the policy-making process, it serves the common interest of the Member States, while being independent of special interests, whether private or national.

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EUROPEAN COMMISSION

LB-NA-23992-EN-C

Publications Office
Publications.europa.eu

ISBN 978-92-79-11294-2
9 789279 112942