BC properties and its measurement techniques
An overview
1. Introduction and overview
   • some definitions

2. BC properties and how to measure them
   a. Light absorption
   b. Thermal stability
   c. Insolubility
   d. Morphology

3. Synopsis
EMISSION / IMMISSION DEFINITION

- **Emission:**
  
  “Emissions” as used herein shall mean *any air pollution*, noise, vibration, light, heat, radiation and similar phenomena *originating from an installation*.

- **Immission:**
  
  “Immissions” as used herein shall mean *any air pollution*, noise, vibration, light, heat, radiation and similar effects on the environment which affect human beings, animals and plants, soil, water, *the atmosphere* as well as cultural objects and other material goods.

Source: Federal Immission Control Act - BImSchG Section 3 Definitions
EMISSION / IMMISSION ILLUSTRATION

Source: http://www.ubz-stmk.at/
**Non-road mobile machinery**

- **Definition:**
  
  "non-road mobile machinery" shall mean any mobile machine, transportable industrial equipment or vehicle with or without body work, *not* intended for the use of passenger- or goods-transport *on the road*, in which an internal combustion engine ... is installed.

Source: DIRECTIVE 97/68/EC
Source: VDMA, Exhaust emission legislation
Diesel and gas engines
Examples for “non-road” emission regulations

Seagoing ships
- IMO MARPOL Annex VI
- EU Non-road Directive 97/68/EC 2004/26/EC
- Rhine vessel inspection regulation (RheinSchUO)

Inland waterway vessels
- Lake Constance shipping ordinance (BSO)
- USA Marine Engines

Rail
- EU – Rail
- UIC International Union of Railways
- USA (EPA i.e. 40 CFR 89, …)

Air traffic
- Turkey
- ICAO

Turkey
Various regulations limiting particulate mass

Particle Mass (PM)
- Aviation: no regulations on PM
- Seagoing ships: No values required
- Inland waterway vessels: EU 0.2-0.5 g/kWh, USA 0.04-8 g/kWh (depending on vessel size)
- Rail: EU 0.025-0.2 g/kWh, UIC 0.25 g/kWh, USA 0.022 – 0.19 g/kWh
- Road Transport (heavy duty trucks): EU 0.01 g/kWh, PN: 6-8 10^{11}

Source: VDMA, Exhaust emission legislation Diesel and gas engines
Introduction for BC measurement techniques

- Black carbon is defined by four properties (Bond et al.), that can not be measured simultaneously by one system
- There are several measurement systems in use and commercial available
- Some techniques can measure continuously (transient), others need a sample from a filter
- There are just a few standardised
- Every measurement technique / principal gains other results
- Studies which compare the different measurement principals show a dependency on the analysed aerosols
Basics for BC / PM emission measurements

- The aim of measurements are:
  - Quantify the emission of BC / PM

- Where measurements can be conducted:
  - on engine test bed
  - on-board ships according to standards (i.e. ISO 8178, or other defined protocol)
  - analysing ship emission plumes from distance (by planes carrying equipment or exhaust plumes reaches shore based equipment)

- Every measurement application has different requirements, challenges and options
The four properties of BC*

- **Light absorption**
  "It strongly absorbs visible light with a mass absorption cross section of at least 5 m²/g at a wavelength of 550 nm."

- **Thermal stability (refractory)**
  "It is refractory; that is, it retains its basic form at very high temperatures, with a vaporization temperature near 4000K."

- **Insolubility**
  "It is insoluble in water, in organic solvents including methanol and acetone, and in other components of atmospheric aerosol."

- **Morphology**
  "It exists as an aggregate of small carbon spherules."

*according to Bond et al. (2013)
Overview on measurement techniques according BC properties

- **Property: Light absorption**
  - Filter-based extinction measurement
  - Extinction-minus-scattering
  - Photo-acoustic technique
  - Interferometric technique

  A Mass Absorption Coefficient (MAC), which is instrument dependent, is applied to obtain *equivalent BC* (eBC).

- **Property: Morphology**
  - Raman spectroscopy (*Elemental Carbon*)
  - TEM/SEM (*nano-spherical (NS)-Soot*)
  - Mass spectrometry (*refractory BC or Elemental Carbon*)

- **Property: Thermal stability**
  - Laser induced incandescence (LII) (*refractory BC*)
  - Thermal-optical methods (*Elemental Carbon*)
    - Thermal optical transmittance (TOT)
    - Thermal optical reflectance (TOR)
    - VDI 2465 Blatt 2

- **Property: Insolubility**
  - VDI 2465 Blatt 1 (*Elemental Carbon*)

*recommendations accord. Petzold et al.*
Light absorption
Introduction

- Black Carbon consists of small spheres with many delocalized electrons (sp2 orbital hybridization), which leads to a broad-band light absorption.

- Mass absorption/attuention coefficient (MAC) of black carbon is comparable high. Freshly emitted BC has a MAC of 7.5+/- 1.2 m²/g at 550 nm.

- Linking BC morphology with optical properties has been a challenge, BC agglomerates do not show simple “Rayleigh” or “Mie” scattering behaviour.

- Overall, Filter-based and in-situ-techniques (for transient measuring) exists.

- Many scientists argue for the declaration of the measurement results in optical units.

- There are many challenges...
  Indications exists that the measurement of fresh combustion products delivers less bias than on aged filter materials.

- Interactions with sulphur!

- No commonly accepted reference material for calibration exists.
Filter-based extinction measurement 1/4

- Most traditional measurement technique
- Sample air flows through a filter
- The particles accumulate on and within the filter
- The light transmission (and attenuation) or reflection of the filter is measured continuously
- Collected black carbon leads to a higher light attenuation

- The mass is calculated with empirical mass attenuation coefficients, which are subject to on-going discussions
- There are some methods in use by the industry, e.g. filter smoke number, which is based on the same measurement principle.
Filter-based extinction measurement 2/4

Challenges

- Scattering within the filter
- Differentiate between Black Carbon and other light absorbing aerosols e.g. Brown Carbon
- Filter loading
- Scattering (increase of attenuation by direct scattering and increasing absorption)
- Humidity can alter filter scattering

A. Petzhold et al. (2005)
Filter-based extinction measurement 3/4

Challenges

- Scattering within the filter
- Differentiate between Black Carbon and other light absorbing aerosols e.g. Brown Carbon
- Filter loading
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Solutions

- Filter with refractive index close to atmospheric particles
- Measurement at different wavelengths. Black Carbon will absorb light at all wavelengths (Angstrom exponent of 1), other materials will show a wavelength depending absorption.
- Correction factor for scattering and filter loading (Aethalometer, PSAP)
- Measurement of the scattering (MAAP)
- Keep humidity low

Filter transmission measurements for industrial application usually don’t cover above mentioned aspects!
Filter-based extinction measurement 4/4

- Filter-based extinction measurements for industrial applications are usually not built to cater for above mentioned capabilities / circumstances as they should be:
  - **small, cheap and portable instruments**
  - easy to operate and maintain (automatic filter changes)
  - Resolution time: minutes to seconds
  - There are some doubts regarding the accuracy of differentiating BC from other light absorbing and scattering materials when time for filter loading and extinction measurement is more than days (from loading to analysing), “fresh” combustion particles and direct extinction measurement show improved comparable behaviour.
Extinction-minus-scattering technique

- A light beam is lead through an air sample
- The extinction and the scattering is measured
- The scattering is subtracted from the extinction

- Resolution: seconds
- Would be presumably easy and cheap technology
- Long path ways needed (mirrors) which make it sensitive towards mechanical vibration
- No instruments commercially available yet
- Sensitive towards humidity
Photo-acoustic techniques

- Photo-acoustic techniques are based on the photo-acoustic effect:
  - Light is sent through an air sample
  - The intensity of the light is changed rapidly
  - The air and aerosols are absorbing the electromagnetic energy (light) and are locally heated, depending on their optical properties and the wavelength of the light
  - The local heating and cooling leads to small thermal expansion and constriction, resulting in pressure waves which are detected as sound
  - A photo-acoustic spectrum can be recorded by varying the wavelength

- Corrections for scattering needed, but usually implemented in the measurement system
- Photo-acoustic measurements are used widely e.g. in medical research or to determine concentrations of trace gases (consider wavelength)

H. Moosmüller et al. (2009)
Challenges with Photo-acoustic techniques

- Interferences with noise and vibrations from the ship / engine? Although, measurements are conducted.
- Conversion factors to quantify the black carbon, which may not be appropriate due to variable amounts of Organic Carbon (OC)
- Sensitive towards semi-volatile compounds like water and coatings
- It is a “standard” technique for accurate measurements of aerosol light absorption
- There are several instruments available
- Time resolution: seconds
- BC-particles > 2.5µm would cause challenges
Interferometric techniques 1/2

- One probe laser is splitted into two beams, which travel the same path length and are detected afterwards.
- One of the beams passes through a sample volume, which is affected by a pump laser.
- If there is BC in the sample volume it is heated by the pump laser and will heat the air around, too.
- The heated air results in a different refractive index and a short optical path length.
- This leads to a observable phase shift between the two beams.
Interferometric techniques 2/2

- Time resolution: high (seconds)
- Commonly used to measure particle absorption
- Sensitive towards mechanical vibration
- Development on-going
- Not really usable today
Thermal stability (refractory)
The measurements techniques for the property of thermal stability can be distinguished into two techniques:

- Techniques to measure refractory black carbon
- Thermal-optical methods to measure elemental carbon

The most important difference is the temperature used. For refractory black carbon measurements 4000K are used, while the thermal-optical methods (elemental carbon) use just about 1000K.
**Refractory Black Carbon (rBC) / laser induced incandescence (LII)**

- Developed in the 70es for in situ investigation of soot
- Particles are heated by a high power density laser beam up to 4000k using the light absorbing and refractory properties of black carbon
- Black carbon starts glowing, vaporizes and emits blackbody radiation
- The blackbody radiation is used for identification and its magnitude for mass determination
- This measurement technique is commonly used
- Time resolution: seconds
- It is possible to gain many other information from this process e.g. particle size
- Lower particle size threshold is about 10 nm volume equivalent diameter
- There are two types of laser used:
  - Pulsed laser
  - Continuous laser
Refractory Black Carbon (rBC) / laser induced incandescence (LII)

**Pulsed laser**
- Measuring a group of particles
- Commonly used in motor engineering
- LII signal is proportional to the volume of BC
- Particle size can be gained by the cooling behaviour
- Measurement systems commercially available* and used for e.g. engine ECU settings (R&D)

**Continuous laser**
- Measuring single particles
- Determination of particle size by scattering
- Less stringent safety restrictions
- Two measurement systems commercially available (SP2, LII 200) and widely used in the atmospheric research

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*Commercially available does not imply that it is as well suitable for the purpose!
Thermal-Optical Methods

- PM collected on a filter, heated to a fixed temperature to exhale all volatile components and than the remaining EC is quantified
- There are a lot of different temperature protocols and methods
- Sensitive towards charring (coking)
- Result: Elemental Carbon
- Aging dependence!
- Long-standing reliance on these methods
- Many observational data
- Interferences with metal oxides
- Different methods gain different results, but seems for diesel engine exhaust suitable
- Time resolution: hours

J. Watson et al. (2005)
Thermal-optical transmittance (TOT) 1/2

NIOSH* 5040

- Standard for gaining the elemental carbon concentration of diesel particulate matter for occupational health and safety, especially in mining operations
- Filter based
- Used by several atmospheric scientists, too.
- A filter sample is heated to 870°C in helium atmosphere to remove the organic matter
- Filter transmittance is used to correct the charring effect
- The organic matter is catalytically oxidized, reduced to methane and measured with a flame ionization detector (FID)

*National Institute for Occupational Safety and Health
Thermal-optical transmittance (TOT) 2/2

- After removal of OC a oxygen-helium-mix is used to burn the remaining material
- The CO2 is reduced to methane and quantified by the FID

- It is a well-known and commonly used method, but it is just measuring EC and OC and does not fulfil the requirements of the BC-definition
- Measurement system commercially available*
- There are some doubts regarding the correction by laser
- Time-resolution: hours
- Sample will be transferred to shore

*Commercially available does not imply that it is as well suitable for the purpose!
Thermal-optical reflectance (TOR)

IMPROVE

- Interagency Monitoring of Protected Visual Environments (IMPROVE) was developed by several US agencies
- Purpose: Monitoring ambient air quality
- Similar to NIOSH 5040, but other temperature and optical monitoring protocols
- Using Laser reflectance
- Differencing the sample in seven fractions
- The comparability with the TOT-results depends on the analysed material (factor 4) but good for diesel
- There are some doubts regarding the correction by laser
Method for the EC immission quantification

Filter sample

Time resolution: hours

Desorption of OC by heating in an helium atmosphere

Burning of the EC with helium / oxygen-mixture

Quantification of CO₂ by a non-dispersive infrared detector (NDIR)

No correction for charring!
Insolubility
Overview

- This property is more or less ignored by the scientific community
- There are some methods to gain OC and the VDI 2465 Blatt 1 for EC
- Apple et al. made one proposal for a two-step extraction process
- Germanischer Lloyd developed a combination of VDI 2465 Blatt 1 and 2

- Filter-based technique
- Time resolution: hours
- Sample will be transferred to shore
**Insolubility – VDI 2465 Blatt 1**

- Method for the EC immission quantification
- Filter sample
- Liquid extraction by 50:50 vol.% mixture of toluene and 2-propanol
- Heating to 500° C in nitrogen atmosphere and cooling to 200° C
- Burning of the remaining EC by oxygen at 650° C
- Removal of sulphur oxides with silver wool and perhydrit
- Estimation of the produced CO₂ by Ba(ClO₄)₂-solution and titration
- High correlation to results of VDI 2465 Blatt 2
Morphology
Introduction

- Even though the other three properties of black carbon are results of the morphology of black carbon there are just a few techniques to investigate it directly due to several difficulties
- Electron microscopy has shown onion-like layers of graphitic platelets in a disordered and wrinkled structure
- Possibly ‘good’ instruments and techniques for fundamental research (i.e. combustion optimisation) but not useful for practical / field application
- Three measurement techniques
  - Raman spectroscopy
    (sometimes referred as regarding the light absorbing property)
  - Transmission / Scanning Electron Microscopy
  - Mass spectrometry
Raman spectroscopy

- Raman scattering is the inelastic scattering of a photon
- A small amount of photons are scattered inelastic when interacting with a solid or liquid
- The scattered photons have another frequency
- The Raman scattering depends on several properties of the measuring object, which can be investigated by Raman spectroscopy, e.g. chemical bonds and symmetry of molecules.
- Raman spectroscopy is very selective towards hexagonal lattice structures of SP2- orbital hybridization

- Result: Elemental Carbon!
- It needs a comparable big quantity of sample (filter collection)
- Time resolution: hours
Transmission / Scanning Electron Microscopy

- TEM or SEM images can be used to gain further information about the structure e.g. by the nested square method or the ensemble method
- Expensive and complicated measurement technology
- Not portable
- Filter samples
- Time resolution: hours
- Result: nano spherical-Soot (NS–Soot)
Mass spectrometry

- There are several types of mass spectrometer in use by the atmospheric scientists e.g.
  - Aerosol Mass Spectrometer (AMS / SP-AMS)
  - Aerosol time-of-flight mass spectrometer (ATOMFMS)
- Vaporising non-refractory components by heat (LII) and low pressure
- Expensive and not easy to maintain
Synopsis
Synopsis

The first analysis of measurement techniques has shown:

- There are many techniques available
- Every technique has its bias
- The measurement result depends on the measurement technique, measurement protocol and calibration method used
- The measurement system has to be chosen according to the intended use and measurement place
- Correlation from one measurement technique to others is hardly or even not possible.
- High sensitivity on sulphur exists!
- For any intended regulatory purpose, a standard measurement technique, a test protocol and (a) calibration material has to be defined
Thank you for your attention!

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