Quantification of black carbon in soils and sediments
What is Black Carbon (BC)?

- combustion continuum model
  - Goldschmitt conference 1999
  - not generally accepted

- Common characteristics
  - High carbon content
  - Chemically heterogeneous
  - Dominated by aromatic structure
  - terrestrial origin

- No clear boundaries
  - no inorganic salts
  - no organic molecules
  - no pure elemental carbon

- Different mechanism and factors during the incomplete combustion influence the BC

What is Black Carbon (BC)?

What is Black Carbon (BC)?
Why should we care about Black Carbon?

- Long environmental lifetime
  → Distribution over the globe (atmosphere, sediment, soil)

- Contributes to the Earth’s slow-cycling carbon pool
  = Significant fraction of the carbon

- Sorption of organic compounds or heavy metals

- Affect the earth’s heat balance

- Impact on the Human health

Problems for analytical analysis

Up to now there is independent literature with results that cannot be compared.

1. Lack of common definition

2. Underreporting of BC
   - failure to detect all BC

3. Over detection of BC
   - material not derived from combustion

4. Heterogeneity of samples

Define what has been measured by choice of method = operational definition

Eos, 2007, Vol. 88, No. 35
Analytical Standard

Consider:
- different compartments (aerosol, soil, marine sediment, dissolved organic matter)
- interfering material

• Prepare BC under defined conditions
• Operational definition

Global biogeochemical cycles, 2007, VOL. 21, 3016.
How can one analytically differentiate between different carbon pools, in particular, organic, inorganic and black carbon?
Get rid of organic and inorganic carbon

- Black carbon (BC) is more resistant to breakdown than other forms of organic matter
- Inorganic Carbon (Carbonates,..)
  - Oxidation by acid (HCl)
- Organic carbon (Hydro carbons,..)
  - Thermal treatment
  - Washing (deionised water)

- BC is left
Given that the black carbon is a continuum of carbonaceous materials, how can one differentiate between different forms of BC?
Different forms of BC

- As mentioned: Method leads to the different BC
  - Methods are optimized to detect a particular form
  - Comparison of different methods is not reasonable

- Atmosphere => optical methods
- Soil and sediments => resistance under degredation

- !! A lot of methods and modifications!!
Thermal oxidation methods

- Remaining BC after oxidation upon heating
  - Oxidize less refractory charcoal particles
  - Harsh conditions: only soot and graphite

- Oxidation of BC at higher temp.
  - Lose weight during heating (leads to the amount of BC)
Example – Thermogravimetry and Differential Scanning Calorimetry Analysis (TG-DSC)

- Thermogravimetry
  - Lose of weight during vaporisation of material is measured as a function of increasing temperature

- Differential scanning calorimetry (DSC)
  - technique for measuring the energy added to a sample and reference as a function of the temperature

Gélinas et al., 2001
Example – Thermogravimetry and Differential Scanning Calorimetry Analysis (TG-DSC)

- Pretreatment: No
- Oxidation: 20°C to 990°C (20°C/min)  
  20% O₂ / 80% He
- Detection: Mass difference during heating  
  Individual decomposition of components
Example – Thermogravimetry and Differential Scanning Calorimetry Analysis (TG-DSC)
Thermal methods - TG-DSC

Advantages

- Easy handling of temperature and gas flow
- Can detect all carbon species

Disadvantages

- Impurities lead to higher BC value
- Loss water on heating
Example – Thermal/Optical Transmittance and Reflectance (TOT/R)

- **Pretreatment**: No

- **Oxidation**:
  - 1. Heating step: 23°C to 550°C (in He)
  - 2. Hesting step up to 870°C (in He)
  - 3. Heating step up to 900°C (10% O₂ 90% He)

- **Detection**: He-Ne laser reflectance (632 nm)
  - FID (conversion to CO₂, reduce to CH₄)
Example – TOT/R

Huang et al. 2005
Fig. 3. Standardized thermogram for OC/EC separation and CO₂ collection methods. (A) (top panel) the protocol of total OC, POC+CC, and EC separation, used for isotopic measurements and (B) (bottom panel) the protocol of sub-divided OC fractions, total POC+CC and EC separation, used for thermal behavior characterizing.
Thermal methods – TOT/R

Advantages

- Easy handling of temperature and gas flow

Disadvantages

- Overdetection due to charring of non-BC
- Underdetection of charcoal
- Combusting may change the BC pore structure
- Diff. heating conditions lead to diff. results
Chemical methods

- Remaining BC after chemical extraction
- BC: material which survives treatment with:
  - Peroxide
  - Nitric acid
  - Dichromate and sulfuric acid
  - Hypochloride

Verardo, 1997
Example – Acid Dichromate Oxidation

- Pretreatment: Acid (HF, HCl), 24h
- Oxidation: Acid $K_2Cr_2O_7 + H_2SO_4$
- Detection: Elemental analysis
  - Mass difference before/between/after oxidation
Chemical methods

Advantages

- Least expensive
- Charring is avoided

Disadvantages

- Assumes that all carbon that survives is BC
- Losses of submicron-sized BC particles
- Diff. oxidating conditions lead to diff. results
Microscopic methods

- Measure/count the number of charcoal pieces
  - Optical microscopy
  - SEM (Scanning Electron Microscopy)
    - Secondary Electron Detector
    - images of a sample by scanning it with a focused beam of electrons
  - TEM (Transmitting Electron Microscopy)
    - Electron interaction by passing through a thin film of sample

- Preparation: Chemical Oxidation

*Clark, Peterson, 1997*
Microscopic methods

Figure 2a. Scanning electron microscope (SEM) pictures of Above: porous fly ash; Below: charcoal fragment (from Amazon forest fire).

Clark, Peterson, 1997
Chemothermal methods

Oxidation at 375°C (CTO-375)

- Pretreatment: Acid (HCl, HSO₃, HF,..)
- Oxidation: Temp. Programm (2.5-60°C/min) to 375°C
  18-24h, under air
- Detection: elemental analysis
  - (mass difference before/after oxidation)

CF-IRMS
  - Coulometric quantification of CO₂

Chemothermal methods

Advantages

- Best suited for quantifying the most condensed form of BC
- Differentiate between soot and chars

Disadvantages

- Not the whole BC continuum
- Higher conz. Possible
- Charring of material
Spectroscopic methods

- Pick characteristic IR-bands or NMR-regions
  - Conc. of BC based on the strength of these bands
  - Change of the intensity after removal of non-BC organic

- CP/MAS NMR
  - Cross Polarization Magic Angle Spinning nuclear magnetic resonance spectroscopy

- Focus on chemical signature of burning
  - Wide band of combustion continuum

*Skjemstad et al., 19995*
Spectroscopic methods - Example

- Pretreatment
  - Acid (HCl), 12h

- Oxidation
  - NaClO

- Detection
  - Before, between, after oxidation
  - NMR/CPMAS

Fig. 1 A comparison of solid-state NMR methods for an ancient char from the eruption of Mt. Vesuvius in Pompeii. Both direct detection (Bloch-decay MAS) and CPMAS $^{13}$C NMR produce similar spectra. After chemical oxidation, residual lignin is removed leaving behind only non-oxidizable aromatic carbon.
UV Photooxidation

Alternative oxidation method

- Pretreatment
  - Acid (2% HF)

- Oxidation
  - UV photooxidation at 2.5 kW in oxygen saturated water

- Detection
  - Before between and after oxidation
  - CPMAS NMR
UV Photooxidation

Advantages

● Detects BC across most of the BC continuum
● More gentle than the other oxidation methods

Disadvantages

● Time consuming
● Expensive
Molecular marker methods – BPCA

- E.g. Convert BC to BPCA (benzenecarboxylic acids)

\[
\text{benzoic acid} \quad \text{phthalic acid} \quad \text{isophthalic acid} \quad \text{terephthalic acid}
\]

Glaser et al., 1998

- Levoglucosan (trace contributions from vegetation combustion to sediments)

Elias, 2001
Molecular marker methods – BPCA

- Acid digestion
  - (e.g. 32% HCl for 4 h at 170°C, high pressure)
- Oxidation
  - (65% HNO₃ for 8 h at 170°C, high pressure)
- Sample clean up
  - Washing, ione removal, etc.
- Derivatization
  - converted to trimethylysilyl derivatives
- GC-FID (-MS,...)
Result - BPCA

- Several internal standards
  - Check the loss
- Identification
  - Comparison of retention time
- Quantification
  - Conversion factor (BC/BPCA)

Fig. 2. GC–FID chromatogram of benzenecarboxylic acids, citric acid and 2,2′-biphenyldicarboxylic acid. (1) Benzoic acid; (2) phthalic acid; (3) isophthalic acid; (4) citric acid; (5) terephthalic acid; (6) hemimellitic acid; (7) 2,2′-biphenyldicarboxylic acid; (8) trimellitic acid; (9) trimesic acid; (10) pyromellitic acid, (13) benzenepentacarboxylic acid; (14) mellitic acid.
BPCA

Advantages

- Best suited for BC in solutions
- Provides information on the nature of BC

Disadvantages

- Positive biases from non-BC material
- Incomplete conversion
  - Determination of the conversion factor (-> ?)
How can we quantify Carbon Nanotubes as separate specie?
Carbon Nano Tubes CNT

CNT-Applications

• Electrical cables and wires
• Solar cells
• Medical
• Optical power detectors
• Mechanical
• And many more
CNT isolation and quantification

- Programmed thermal analysis (PTA)
- Thermogravimetry – mass spectrometry (TGA-MS)
- Chemothermal oxidation (CTO)
- Asymmetric flow field-flow fractionation coupled to multi-angle light scattering (aF4-MALS)
Programmed Thermal Analysis

- Distinguish between thermally “weak” and “strong” CNT
- Optimized temperature programs
- Inert or oxidizing conditions
- Background elemental carbon interfered with weak CNT

K. Doudrick, Environmental Science & Technology, 2012, 46, 12246
Programmed Thermal Analysis

Heating to 870 °C
Inert Conditions

Heating to 910 °C
Oxidizing conditions

SW = Single-walled CNT
MW = Multi-walled CNT

K. Doudrick, Environmental Science & Technology, 2012, 46, 12246
Thermogravimetry – Mass Spectrometry

- Temperature programmed oxidation (TPO)
  Weight loss vs. temperature measured
- SWCNT widely diverse degradation temperatures
- Samples:
  - 40 mg for sediments / soil
  - 3 mg for pure substances
- Detection limits at 4 μg_{SWCNT} per sample (sediments)
- Hydrogen assisted thermal degradation (HATD) for better resolution
- Distinguish between incidental (e.g. soot) and engineered
- Produced gases measured by MS
- High carbon but low hydrogen and nitrogen content

Thermogravimetry – Mass Spectrometry

TPO

TPO - HATD

Thermogravimetry – Mass Spectrometry

- m/z 18 = H₂O
- m/z 30 = NO or CH₂O
- m/z 44 = CO₂

Chemothermal Oxidation (CTO)

- Mostly at 375 °C (CTO-375)

- Structure depending loss of CNT

Reflection electron microscope (REM) images of MWCNT before (A1, A2) and after CTO-375 (A3, A4).

Sobek, Bucheli, Env. Poll., 2009, 157, 1065
Asymmetric flow field-flow fractionation

- Gradient perpendicular to flow direction
  - Crossflow
  - Thermal gradient
  - Electric or magnetic field
  - Gravitation

- Separation by size and weight

Asymmetric flow field-flow fractionation

• Detection of MWCNT’s
• Shape factor depending
• Soot and soil
• Detection with multi-angle light scattering (MALS)
• Detection limit at 1.6 to 4 mg / g_{soil}

Thank you for your attention!

Questions