Quantification of black carbon in soils and sediments

Thomas Bucheli

October 28, 2014
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- Introduction to BC
  - Environmental relevance
  - What is it?
  - Global emission estimates?
  - Where does it end up?
- How do we measure it
  - Chemo-thermal oxidation
  - Wet-chemical oxidation
  - Other methods
  - Comparison of methods
- Carbon nanotubes – yet another challenge
  - MWCNT
  - SWCNT
Environmental relevance of BC

Influences:

Sequestration of:

- Carbon
- Carbon dioxide
- Org. pollutants
- Global warming
- Climate Change
- C-Availability
- C-Turnover
- Soil fertility
- Mobility
- Soil & sediment risk-assessment
- Bioavailability

Soil fertility
**BC terminology**

**Carbonaceous geosorbents**

- **Black carbon**
  - Residues of incomplete combustion
  - (By-)products of industrial fuel production

- **Geogenic origin**
  - Diagenesis & catagenesis

- **Atmospheric recondensates**
  - Soots
  - Carbon Nanotubes

- **Residues**
  - Chars
  - Charcoal

- **Activated Carbon**
  - Cenospheres
  - Coke
  - Lampblack

- **Graphite**

- **Coals**
  - Peat
  - Brown coal
  - Bituminous coal
  - Anthracite

- **Kerogens**
  - Type I-III

**Pics: Jonker & Koelmans 2002**
The BC continuum

Nomenclature
Black carbon
Soot
Physico-chemical properties
Particle size
Formation T
Formation phase
Plant residues
O to C-; H to C-ratio
Initial reservoir

Adapted from Elmquist et al. 2006; Masiello 2004
Global annual BC production

<table>
<thead>
<tr>
<th>BC-type</th>
<th>Amount [Tg/y]</th>
<th>Source</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Biomass [%]</td>
<td>Fossil fuel [%]</td>
</tr>
<tr>
<td>Total BC</td>
<td>50 - 200</td>
<td>80</td>
<td>-</td>
</tr>
<tr>
<td>Total BC</td>
<td>50 – 270</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aerosol BC</td>
<td>8</td>
<td>60</td>
<td>40</td>
</tr>
</tbody>
</table>
Global annual aerosol BC production: sources

Global distribution of BC

In the black. Masiello and Druffel (1) determined age differences of 2400 to 13,900 years between sedimentary organic carbon (SOC) and black carbon (BC). Thus, they conclude that sedimentary black carbon must have spent considerable time in an intermediate pool. Candidates are terrestrial soils and the oceanic dissolved organic carbon (DOC) pool [data from (5, 7, 10)]. All values are in petagrams (1 Pg = 10^{15} g) per year.

Bucheli | © Agroscope ISS
Quantification of BC | Strategische Übungen Anal. Chem.

Kuhlbusch 1998
### TABLE 2. BC/TOC Ratios (%) in Sediments and Soils

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>BC Quantification Method</th>
<th>Median</th>
<th>Quartile Range</th>
<th>Number of Sites</th>
<th>Ref</th>
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<tr>
<td><strong>Sediments</strong></td>
<td></td>
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<tr>
<td>Suwannee River DOM</td>
<td>CTO-375</td>
<td>0.34</td>
<td>n.a.</td>
<td>1</td>
<td>122</td>
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<tr>
<td>Mexican Margin and several lakes</td>
<td>Chemical + CTO-375</td>
<td>1.0c</td>
<td>0.2–2.0c</td>
<td>12</td>
<td>118</td>
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<tr>
<td>Boston Harbor, Gulf of Maine</td>
<td>CTO-375</td>
<td>4</td>
<td>3–7</td>
<td>17</td>
<td>130</td>
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<tr>
<td>Swedish fjord</td>
<td>CTO-375</td>
<td>6</td>
<td>5–9</td>
<td>25</td>
<td>121a</td>
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<tr>
<td>Slovenian Lakes</td>
<td>CTO-375</td>
<td>6b</td>
<td>5–6b</td>
<td>12</td>
<td>133</td>
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<tr>
<td>French lakes, Mediterranean Sea</td>
<td>chemical</td>
<td>7</td>
<td>5–15</td>
<td>11</td>
<td>123</td>
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<tr>
<td>Boston Harbor and EPA sediments</td>
<td>CTO-375</td>
<td>8</td>
<td>6–16</td>
<td>32</td>
<td>93</td>
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<tr>
<td>Dutch flood plain lakes</td>
<td>CTO-375</td>
<td>9</td>
<td>8.7–9.6</td>
<td>3</td>
<td>55</td>
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<td>Norwegian rivers and fjords</td>
<td>CTO-375</td>
<td>9</td>
<td>7–11</td>
<td>4</td>
<td>95</td>
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<td>Eurasian Arctic river mouths</td>
<td>CTO-375</td>
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<td>4–12</td>
<td>13</td>
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<td>Finnish and Dutch lakes</td>
<td>CTO-375</td>
<td>11</td>
<td>3–13</td>
<td>5</td>
<td>85</td>
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<tr>
<td>Dutch and Finnish sediments</td>
<td>CTO-375</td>
<td>15</td>
<td>7–24</td>
<td>11</td>
<td>131</td>
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<tr>
<td>Pacific Ocean</td>
<td>chemical</td>
<td>17</td>
<td>14–25</td>
<td>26</td>
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<td>Mississippi river, Gulf of Mexico</td>
<td>CTO-375</td>
<td>17</td>
<td>7–23</td>
<td>5</td>
<td>186</td>
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<td>bay near New York</td>
<td>CTO-375</td>
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<td>n.a.</td>
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<td>bay near New York</td>
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<td>19</td>
<td>n.a.</td>
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<td>USA Great Lakes</td>
<td>CTO-375</td>
<td>20b</td>
<td>15–25b</td>
<td>&gt;100</td>
<td>132</td>
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<tr>
<td>six seas around Europe</td>
<td>CTO-375</td>
<td>24</td>
<td>18–35</td>
<td>33</td>
<td>117</td>
</tr>
<tr>
<td>Chinese lacustrine sediments</td>
<td>chemical</td>
<td>33</td>
<td>26–37</td>
<td>3</td>
<td>107</td>
</tr>
<tr>
<td><strong>Soils</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>loam soil</td>
<td>CTO-375</td>
<td>0</td>
<td>n.a.</td>
<td>1</td>
<td>108</td>
</tr>
<tr>
<td>Australian Soils</td>
<td>chemical + CTO-375</td>
<td>0.11d</td>
<td>0.07–0.15d</td>
<td>5</td>
<td>118</td>
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<td>Swiss soils</td>
<td>CTO-375</td>
<td>2.3</td>
<td>1.7–4.9</td>
<td>23</td>
<td>106</td>
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<tr>
<td>EPA soils</td>
<td>CTO-375</td>
<td>5</td>
<td>n.a.</td>
<td>2</td>
<td>93</td>
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<tr>
<td>Tenerife soils</td>
<td>CTO-375</td>
<td>6b</td>
<td>3–13b</td>
<td>38</td>
<td>102</td>
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<tr>
<td>German chernozemic soils</td>
<td>microscopy + 13C NMR</td>
<td>9</td>
<td>3–15</td>
<td>9</td>
<td>140</td>
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<tr>
<td>Danish and American soils</td>
<td>CTO-375</td>
<td>12</td>
<td>6–15</td>
<td>7</td>
<td>131</td>
</tr>
<tr>
<td>Australian soils</td>
<td>UV photooxidation + coulometry</td>
<td>~20</td>
<td>~10–30</td>
<td>4</td>
<td>141</td>
</tr>
<tr>
<td>Chinese sandy soil</td>
<td>chemical</td>
<td>38</td>
<td>n.a.</td>
<td>1</td>
<td>107</td>
</tr>
</tbody>
</table>

| median weighted per data point$^d$       | 9                      | 4–18   | ~300$^f$       |     |
| median weighted per reference$^h$        | 9                      | 6–14   | 19$^f$         |     |

- $^a$ Partly unpublished data.  
- $^b$ Values approximated from graphical data representation.  
- $^c$ Higher values (median 8%) before extensive chemical pretreatment.  
- $^d$ Higher values (median 5%) before extensive chemical pretreatment.  
- $^e$ Not applicable.  
- $^f$ Number of data on which median and quartile range are based.  
- $^g$ Median where each soil/sediment sampling site has a weight of one.  
- $^h$ Median where each reference has a weight of one.
## Method compilation (Hammes et al. 2007) (Bold, presented in more detail)

<table>
<thead>
<tr>
<th>Method</th>
<th>Pretreatment</th>
<th>Oxidation</th>
<th>Posttreatment</th>
<th>Detection</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemo-thermal oxidation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CTO-375</td>
<td>(1 M HCl)</td>
<td>24 h @ 375 °C airflow</td>
<td>1 M HCl</td>
<td>Elemental analysis (CHN)</td>
<td>1,2,3,4</td>
</tr>
<tr>
<td>TOT/R</td>
<td>1st heating step (to 550 °C) with 100% He</td>
<td>2nd heating step (to 870 °C) with 100% He</td>
<td>3rd heating step (to 900 °C) with 10% O₂/90% He</td>
<td>He-Ne laser transmittance, FID</td>
<td>11,12</td>
</tr>
<tr>
<td>TG-DSC</td>
<td>Temperature gradient to 990 °C (200C/min) with 20%O₂/80% He</td>
<td></td>
<td></td>
<td>Mass difference, energy flux</td>
<td>13</td>
</tr>
<tr>
<td>Wet-chemical oxidation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BPCA</td>
<td>Digestion/Extraction (TFA 4 M)</td>
<td>65% HNO₃, 8 h, 170 °C</td>
<td>Removal of Fe³⁺, Al³⁺, Derivatization</td>
<td>GC-MS</td>
<td>5,6,7</td>
</tr>
<tr>
<td>Cr₂O₇</td>
<td>3-6 M HCl, 10-22 M HF</td>
<td>0.1-0.5 M K₂Cr₂O₇/2 M H₂SO₄</td>
<td></td>
<td>Elemental analysis</td>
<td>8,9,10</td>
</tr>
<tr>
<td>NaClO⁻¹³C-NMR</td>
<td>6 M HCl</td>
<td>3 x 4 h 25g/L sodium hypochlorite</td>
<td></td>
<td>Aromatic signal at 110-140 ppm solid-state ¹³C-NMR</td>
<td>14</td>
</tr>
<tr>
<td>UV-Photooxidation</td>
<td>2% HF</td>
<td>UV photooxidation at 2.5 kW in oxygen-saturated water (2 h @ 23 °C)</td>
<td></td>
<td>Washing, ¹³C-NMR, Elemental analysis, mass difference</td>
<td>15</td>
</tr>
</tbody>
</table>

Chemo-thermal oxidation @ 375 °C

- Oxidation of labile organic carbon for 24 h @ 375 °C under a constant air flow
- Removal of inorganic carbon by fumigation with 12 M hydrochloric acid (HCl)
- Washing with deionized water to remove HCl residues
- CHN elemental analysis
Chemo-thermal oxidation @ 375 °C

Soil/Sediment (200-40 mg)
dried, grounded (<100 µm)

Removal of organic material
Thermal oxidation
24 h @ 375°C in active air flow

Quantification
CHN Elemental Analysis

Removal of inorganic carbonates
Acidification
Fumigation with 12 M HCl for 4 hrs

Agarwal & Bucheli 2011
Thermograms of different BC

Fig. 1. Thermograms of the seven soot and char materials. The dots represent experimental data and the lines represent the best fitting of the data to Eq. (1). The vertical line indicates the combustion temperature of 375 °C.

Song et al. 2012
Chemo-thermal oxidation @ 375 °C

- Pros:
  - Specific for soots

- Cons:
  - Risk for charring (false positives)
  - Restricted to soots, doesn’t cover any form of char
Chemo-thermal oxidation @ 375 °C

Wet chemical oxidation to yield benzene polycarboxylic acids (BPCA)

- Extraction/digestion with 4 M trifluoroacetic acid (4 h, 105 °C) – rinsed with deionized water (to remove polyvalent cations/metals such as Fe³⁺, Al³⁺, which could interfere with/catalyze oxidation), dried
- Oxidation with 65% nitric acid (HNO₃, 8 h, 170 °C), filtered and washed with deionized water
- Removal of remaining polyvalent cations by cation exchange resins
- Freeze drying of eluate
- Derivatization of the BPCAs to trimethylsilyl derivatives
- Separation & Detection with GC-MS
- Conversion of BCPA to BC, based on factors obtained with standards (e.g. PAHs)
Wet chemical oxidation to yield benzene polycarboxylic acids (BPCA)

Fig. 3. Schematic of the oxidation products of phenanthrene using the BPCA method. One molecule of phenanthrene theoretically could produce either one molecule of B2CA (A or A') or one molecule of B4CA (B).

Fig. 5. A proposed reaction schematic for the high pressure, high temperature oxidation of anthracene to B2CA. The products initially formed reach thermodynamic equilibrium as nitrophthalic acid (see Fig. 6).
Wet chemical oxidation to yield benzene polycarboxylic acids (BPCA)

Fig. 1. Chemical structures of benzenecarboxylic acids (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.
Wet chemical oxidation to yield benzene polycarboxylic acids (BPCA)
Wet chemical oxidation to yield benzene polycarboxylic acids (BPCA)

- **Pros:**
  - Provides quantitative and qualitative information (degree of aromaticity)
  - Works for a rather broad range of BC

- **Cons:**
  - False positives; some forms of OC (e.g. shales, coals, lignites, melanoidin, aspergillin) may be converted to BPCA as well
  - Some BC may be lost in the rinsing/wetting process
  - Conversion factor BPCA → BC not clearly defined
  - not specific to soot
Wet chemical oxidation with benzene polycarboxylic acids (BPCA)

Thermal/Optical Transmittance and reflectance (TOT/R)

- Sample deposed on a filter
- He/Ne laser light (632 nm) reflected from/projected through the filter for continuous monitoring of reflectance/transmittance
- Stepwise increase of temperature in presence of 100% He, producing several OC thermal fractions
- Stepwise increase of temperature in presence of 10% O₂/90% He yields several elemental carbon fractions
- Volatilized and oxidized carbon gases oxidized to CO₂, reduced to CH₄, and detected with FID
Thermal/Optical Transmittance and Reflectance (TOT/R)

Char
Soot
Sediment

T: Temperature
FID: Flame Ionization Detector signal; last peak is CH$_4$ Calibration
LR: Laser reflectance signal
LT: Laser transmittance signal
Oc1-4: Organic Carbon
Ec1-3: Elemental (Black) Carbon

Han et al. 2007, 2007b
Thermal/Optical Transmittance and Reflectance (TOT/R)

- **Pros:**
  - No/little sample preparation for aerosols
  - Low intra-/inter-laboratory variability
  - OC/EC quantified in one method

- **Cons:**
  - Sample preparation can be tricky for soils/sediments
  - False positives (e.g. from melanoidin, coals)
  - Interferences of inorganic material (premature charring)
  - Higher loaded (darker) samples difficult to optically correct for
Thermogravimetry- Differential scanning calorimetry

- Sample (3 mg for pure samples, 40 mg for sediments and soils) loaded on a high-precision thermobalance
- Temperature programmed oxidation (TPO)
  - dry air, 100 mL/min
  - 10 min @ 80 °C, to 900 °C with 5 °C/min, 60 min hold
- Sample weight measured as a function of temperature

Thermogravimetry

Thermogravimetry-Differential Scanning Calorimetry

Weight loss (TG, dashed line) vs. Temperature (°C)

(a) NIST peach leaf

(b) IHSS Pahokee peat soil

(c) IHSS Elliot silt loam soil

(d) Activated charcoal

Differential scanning calorimetry (DSC, solid line)

Plante et al. 2009
Thermogravimetry-Differential Scanning Calorimetry

- **Pros:**
  - Operationally very simple
  - All carbon species detected within one sample

- **Cons:**
  - Mineral impurities (e.g. clays) will contribute to measured weight loss as they lose water on heating
  - Not very frequently applied this far
Chemical oxidation-\(^{13}\text{C}\)-NMR

- Chemical oxidation of organic carbon using sodium hypochlorite
- Solid-state cross polarization magic angle spinning \(^{13}\text{C}\)-NMR
- Elemental analysis to quantify total carbon
- Black carbon is deduced from organic carbon content by reduction of \(^{13}\text{C}\)-NMR signal in the range of 110-140 ppm
Solid-state cross polarization magic angle spinning $^{13}$C-NMR of sediment

Aromatic signal before oxidation

Aromatic signal after oxidation

[Graph showing aromatic signals before and after oxidation for different locations: Bayou Grande, Brown's Marina, Mahogany Landing.]
Chemical oxidation-\(^{13}\text{C}\)-NMR

- **Pros:**
  - Selective for soot
- **Cons:**
  - Hardly used
  - Expensive and special infrastructure needed
Different methods measure different BC – and not only BC...

Hexane soot (positive control I)

- CTO-375
- TOT/R
- TG-DSC
- BPCA
- Cr2O7
- NaClO
- UV

Wood char (positive control II)

- CTO-375
- TOT/R
- TG-DSC
- BPCA
- Cr2O7
- NaClO
- UV

Bituminous coal: negative control

- CTO-375
- TOT/R
- TG-DSC
- BPCA
- Cr2O7
- NaClO
- UV

Marine Sediment (real sample)

- CTO-375
- TOT/R
- TG-DSC
- BPCA
- Cr2O7
- NaClO
- UV

Hammes et al. 2007
Recoveries [%] of added BC-standards from different soils

<table>
<thead>
<tr>
<th>Soil</th>
<th>Standard</th>
<th>Role</th>
<th>CTO-375</th>
<th>BPCA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Haplic Arenosol</td>
<td>Diesel Particulate Matter (DPM)</td>
<td>Positive control</td>
<td>27 ± 37</td>
<td>69 ± 7</td>
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<tr>
<td></td>
<td>Charcoal</td>
<td>Positive control</td>
<td>n.d.</td>
<td>84 ± 2</td>
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<tr>
<td></td>
<td>Lignite</td>
<td>Negative control</td>
<td>n.d.</td>
<td>56 ± 3</td>
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<tr>
<td></td>
<td>Bituminous coal</td>
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<td>n.d.</td>
<td>90 ± 28</td>
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<tr>
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<td>Urban dust</td>
<td>Diluted positive control</td>
<td>n.d.</td>
<td>111 ± 136</td>
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<tr>
<td>Haplic Luvisol</td>
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<td>n.d.</td>
<td>74 ± 1</td>
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<td>93 ± 2</td>
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<td>81 ± 4</td>
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<td>n.d.</td>
<td>93 ± 2</td>
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<tr>
<td></td>
<td>Urban dust</td>
<td>Diluted positive control</td>
<td>n.d.</td>
<td>14 ± 14</td>
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<td>Albic Umbrisol</td>
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<td>n.d.</td>
<td>58 ± 7</td>
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<td>Charcoal</td>
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<td>n.d.</td>
<td>69 ± 2</td>
</tr>
<tr>
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<td>Lignite</td>
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<td>n.d.</td>
<td>53 ± 2</td>
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<td>n.d.</td>
<td>70 ± 8</td>
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<td>n.d.</td>
<td>97 ± 38</td>
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<td>18 ± 1</td>
<td>72 ± 7</td>
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<tr>
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<td>Positive control</td>
<td>n.d.</td>
<td>114 ± 8</td>
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<tr>
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<td>Lignite</td>
<td>Negative control</td>
<td>n.d.</td>
<td>116 ± 16</td>
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<tr>
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<td>Bituminous coal</td>
<td>Negative control</td>
<td>n.d.</td>
<td>87 ± 27</td>
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<tr>
<td></td>
<td>Urban dust</td>
<td>Diluted positive control</td>
<td>n.d.</td>
<td>182 ± 7</td>
</tr>
<tr>
<td>Quartz powder</td>
<td>DPM</td>
<td>Positive control</td>
<td>73 ± 1</td>
<td>101 ± 0</td>
</tr>
<tr>
<td></td>
<td>Charcoal</td>
<td>Positive control</td>
<td>n.d.</td>
<td>111 ± 27</td>
</tr>
<tr>
<td></td>
<td>Lignite</td>
<td>Negative control</td>
<td>n.d.</td>
<td>168 ± 9</td>
</tr>
<tr>
<td></td>
<td>Bituminous coal</td>
<td>Negative control</td>
<td>n.d.</td>
<td>139 ± 10</td>
</tr>
<tr>
<td></td>
<td>Urban dust</td>
<td>Diluted positive control</td>
<td>n.d.</td>
<td>332 ± 52</td>
</tr>
</tbody>
</table>

Roth et al. 2012
Standard additions of BC-standards to Swiss soils & quantification with CTO

Dashed lines & empty symbols: predicted concentrations
Solid lines & filled symbols: quantified concentrations

7 Different NABO soils:
Recoveries: 47%-86%
Intercepts met native contents

Agarwal & Bucheli 2011
Conclusions BC in soils & sediments

- BC is a continuum
- Different methods measure different fractions of this continuum
- There is not one «gold standard» method
- Critical evaluation needed
  - Positive and negative standards
  - «biogeochemical consistency»
Carbon Nanotubes – yet another challenge

FIG. 1. Electron micrographs of microtubules of graphitic carbon. Parallel dark lines correspond to the (002) lattice images of graphite. A cross-section of each tubule is illustrated. a. Tube consisting of five graphitic sheets, diameter 6.7 nm. b. Two-sheet tube, diameter 5.5 nm. c. Seven-sheet tube, diameter 6.5 nm, which has the smallest hollow diameter (2.2 nm).

FIG. 2. Clinographic view of a possible structural model for a graphitic tubule. Each cylinder represents a coaxial closed layer of carbon hexagons. The meaning of the labels V and H is explained in the text.

Iijima 1991
CNT: present commercial applications

Fig. 1. Trends in CNT research and commercialization. (A) Journal publications and issued worldwide patents per year, along with estimated annual production capacity (see supplementary materials). (B to E) Selected CNT-related products: composite bicycle frame [Photo courtesy of BMC Switzerland AG], antifouling coatings [Courtesy of NanoCyl], printed electronics [Photo courtesy of NEC Corporation; unauthorized use not permitted]; and electrostatic discharge shielding [Photo courtesy].

De Volder et al. 2013 Science 339, 535-539
FIG. 8. Size distribution of the imaged particles ($N = 2121$) by shape category. Size corresponds to RMS length parameter from TEM image analysis. (Color figure available online).

FIG. 4. CNTs and nanotube agglomerates from 3 different fuel–engine combinations: CNG/4-stroke (a and b); gasoline/4-stroke (c and d); CNG/2-stroke (e and f). All scale bars are 100 nm.
Fig. 3. Carbon nanotubes in ice core sample (a) and contemporary air (b). (a) Magnified view of microcrystalline aggregate in Fig. 2(a). (b) Typical carbon nanotubes collected from lean burning flame (methane plus air).
Survival of CNTs during CTO-375

A. MWNT 11 "as-grown", before CTO-375 treatment

B. MWNT 11 after CTO-375 treatment

Sobek & Bucheli 2009 Environ. Pollut. 157, 1065-1071
Survival of CNTs during CTO-375

Sobek & Bucheli 2009 Environ. Pollut. 157, 1065-1071
Recovery in environmental samples 68-187%
Thermogravimetry (TGA)-mass spectrometry

- Sample (3 mg for pure samples, 40 mg for sediments and soils) loaded on a high-precision thermobalance
- Temperature programmed oxidation (TPO)
  - dry air, 100 mL/min
  - 10 min @ 80 °C, to 900 °C with 5 °C/min, 60 min hold
  - Alternatively: hydrogen assisted thermal degradation (HATD)
- Sample weight measured as a function of temperature

TGA-TPO: SWCNTs and environmental matrices

TGA-HATD: SWCNTs and environmental matrices

TGA-Mass spectrometry

- Continuous mass spectral analysis of gases evolved during TGA
- Specific for CNT:
  - Depletion of H, O, N relative to C
  - No m/z = 18 (H₂O),
  - No m/z = 30 (NO, CH₂O)
  - (m/z = 44: CO₂)

Addition of SWCNT decreases mass fractions of O, N containing gases

Detection limit given by co-oxidizing carbonaceous material (producing CO$_2$)

Current detection limits: 100 µg SWCNT/g sediment

Detection of CNTs in plant roots through microwave-induced heating

Irin et al. 2012 Carbon 50, 4441-4449
Detection of CNTs in plant roots through microwave-induced heating

Continuous heating
30 W microwave power

Calibration curves (CNT injected into roots):
30 W microwave power for 10 s

SWCNT: Single walled CNT, Aldrich, $d = 0.7$-$1.3$ nm
MWCNT: Multi walled CNT, Cheap Tubes, $l = 10$-$20$ $\mu$m, $d = 30$-$50$ nm
SDBS: sodium dodecyl benzene sulfonate (for CNT dispersion)

Irin et al. 2012 Carbon 50, 4441-4449
Detection of CNTs in plant roots through microwave-induced heating

<table>
<thead>
<tr>
<th>Sample</th>
<th>Root mass [mg]</th>
<th>ΔT [°C]</th>
<th>Mass of MWCNT [µg]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alfalfa in 1000 mg/kg soil for 14 d</td>
<td>7.0</td>
<td>41</td>
<td>0.0</td>
</tr>
<tr>
<td>Alfalfa in 1000 mg/kg soil for 111 d</td>
<td>9.8</td>
<td>71</td>
<td>0.1</td>
</tr>
<tr>
<td>Alfalfa in 10000 mg/kg soil for 14 d</td>
<td>5.7</td>
<td>40</td>
<td>0.0</td>
</tr>
</tbody>
</table>

Irin et al. 2012 Carbon 50, 4441-4449
Detection of CNTs in earthworms through microwave-induced heating

Li et al. 2013 Sci. Total Environ. 445-446, 9-13
Differentiating CNTs and soot using aF4-MALS

Online-Detectors
- UV-Vis
- MALS
- DLS

Offline-Detectors
- SEM

\[ r_g = \rho = r_h \]

Carrier+sample flow in

aF4-Channel

Laminar flow profile

Cross flow (actively pumped)

Membrane

Calibration

Ph.D. Thesis A. Gogos
CNT-soot differentiation by aF4-MALS

CNT-soot differentiation by aF4-MALS: confirmation by electron microscopy

CNT in spiked soil analyzed by shape factor

Application to CNT-spiked soil pot experiments

<table>
<thead>
<tr>
<th>plant</th>
<th>Microwave induced heat [μg CNT/mg plant shoot]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control</td>
<td>-</td>
</tr>
<tr>
<td>3 μg/g soil</td>
<td>0.022</td>
</tr>
<tr>
<td>3 mg/g soil</td>
<td>0.014</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Soil + 3 mg/g CNT</th>
<th>CTO-375 [mg/g]</th>
<th>Delta-ρ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-5 cm</td>
<td>2.24 ± 0.26</td>
<td>0.078</td>
</tr>
<tr>
<td>5-10 cm</td>
<td>2.36 ± 0.16</td>
<td>0.141</td>
</tr>
<tr>
<td>10-15 cm</td>
<td>2.39 ± 0.50</td>
<td>0.094</td>
</tr>
<tr>
<td>control</td>
<td>0.31 ± 0.01</td>
<td>0</td>
</tr>
</tbody>
</table>

Moll et al. 2014 in prep.
Single walled CNT nomenclature

rollup vector \( C_h = n\mathbf{a}_1 + m\mathbf{a}_2 = (n, m) \)

- armchair \((n=m)\)
- chiral
- zig-zag \((n, 0)\)
SWCNT conformations: 8,0 → 8,8

http://education.mrsec.wisc.edu/pmk/pages/bucky.html
Raman spectroscopy

- Inelastic scattering of monochromatic light on molecules or particles
- Photons interact with molecular vibrations, resulting in the energy of the photon (and – conversely – the molecule) being shifted
- The shift energy provides information about the vibrational modes in the system

Raman shift:

\[ \Delta \omega = \left( \frac{1}{\lambda_0} - \frac{1}{\lambda_1} \right) \]

\(\Delta \omega\): wavenumber [cm\(^{-1}\)]
\(\lambda_0\): excitation wavelength
\(\lambda_1\): Raman spectrum wavelength

Infrared absorption

Rayleigh scattering (elastic)

Stokes/anti-Stokes Raman scattering
Typical raman frequencies of SWCNT

Raman shifts [cm$^{-1}$]

Fig. 2. Raman-active normal mode eigenvectors and frequencies for a (10,10) nanotube. The red arrows indicate the magnitude and direction of the appropriate C-atom displacements, and the eigenvectors shown correspond to the seven most intense modes (see Fig. 1). The unit cell (blue atoms) is shown schematically in the upper right-hand corner.

Rao et al. 1997 Science 275, 187-191
Raman spectra of CNTs

Radial breathing mode (RBM)

Hodkiewicz 2010 Thermo Fisher Scientific Inc.
Relationship of CNT diameter ($d$) with radial breathing mode frequency $\omega$

\[ \omega_{RBM} = \frac{204}{d} + 27 \]

\[ d = 0.142 \cdot \sqrt{3(n^2 + nm + m^2)/\pi} \]

Surface enhanced Raman scattering (SERS) spectroscopic determination of carboxylated single walled CNT

- Subsequent filtration of gold NP and carboxylated SWCNT from aqueous samples on an acetate cellulose membrane
- SERS with a portable Raman spectrometer

SERS spectroscopic determination of carboxylated single walled CNT

Calibration curve and standard addition experiment

Table 2
Recovery study of spiked river samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Added concentration (mg L(^{-1}))</th>
<th>Found concentration(^{a}) (mg L(^{-1}))</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5</td>
<td>4.5 ± 0.3</td>
<td>86.5–93.8</td>
<td>4.02</td>
</tr>
<tr>
<td>2</td>
<td>8</td>
<td>8.0 ± 0.6</td>
<td>96.1–105.1</td>
<td>4.50</td>
</tr>
<tr>
<td>3</td>
<td>10</td>
<td>10.3 ± 0.7</td>
<td>97.8–105.5</td>
<td>4.13</td>
</tr>
<tr>
<td>4</td>
<td>15</td>
<td>14 ± 1</td>
<td>91.2–100.5</td>
<td>5.16</td>
</tr>
</tbody>
</table>

\(^{a}\) Average of three independent spiked samples ± CI (\(p < 0.05\)).

Near infrared fluorescence spectroscopy of individual SWCNTs

(n, m): roll-up vectors: define conformation of individual SWCNTs

Liu et al. 2011 Nature Commun. 2:309, DOI: 10.1038/ncomms1313
Near-infrared fluorescence spectroscopy (NIRF): extraction of SWCNT from sediments

- Spiking of sediment: 0.1 – 50 µg SWNT to 0.6 – 0.8 g of sediment in 8 mL of synthetic sea water, shaken for 1 – 30 d at 4 ºC
- Centrifugation (15 min @ 1880 g) to remove water phase
- Extraction: various surfactants in combination with high power sonication (empty bars). Recoveries tested with 14C-labelled SWCNT and scintillation counting
- Best conditions: 2% sodium deoxycholate (SDC) @ 40 W

NIRF response

- Open symbols: SWCNT in 2% SDC
- Filled symbols: SWCNT in sediment extracts
- Different colours represent three different excitation wavelengths
- Instrument detection limit: 15 ng/mL in 2% SDC
- Method detection limit (after concentration/cleanup step): 62 ng/g sediment

**NIRF: sediment standard additions**

![Graph showing quantitative measurement of SWNT concentration](image)

**Figure 3.** Quantitative measurement of two types of CoMoCat SWNT (SG65 and SG76) with different coatings (SDC and GA) in two estuarine sediments (BBC and LIS) over a wide range of amended concentrations ($C_{SWNT, added}$). Sediment extraction was performed after 24 h incubation. The dashed line represents a 1:1 relationship, $C_{SWNT, quantified}$ represents the cumulative SWNT concentration measured in extracts after four sequential extractions. The error bars represent one standard deviation about the mean ($n = 3$).

NIRF: quantification of SWCNT individually

Extraction of (n,m)-SWCNT from sediment after a 28 d benthic meiofauna exposure experiment

Tracking and Quantification of SWCNT in Fish using NIRF

- Excitation at 808 nm (5 W output power)
- Stokes-shifted emission > 1000 nm transmitted to a two dimensional array detector
- Works in situ without the need for extraction

Tracking and Quantification of SWCNT in Fish using NIRF

A. White light control

B. NIRF before SWCNT dose

C. NIRF 0 h after SWCNT dose

D. NIRF 8 h after SWCNT dose

E. NIRF 8 h after SWCNT dose, overlaying filet removed/gut exposed

F. NIRF 8 h after SWCNT dose, intestines removed

G. Intestines under whitelight

H. NIRF of intestines

SWCNT in wetland ecosystems (mesocosms)

CoMoCat SWCNT 2.5 mg/L

Lowry et al. 2012 ES&T 46, 7027-7036
SWCNT in wetland ecosystems (mesocosms)

- Analysis of SWCNT in
  - Water:
    - 20 mL sample volume
    - Ultracentrifugation (@207’570 g, 5.5 hours)
  - Water, Sediment traps, Sediments, Plants, biofilm
    - Pellet/sample suspended in 2% sodium deoxycholate by ultrasonication
    - Surfactant-dispersed sample centrifuged (17’860 g, 30 min)
    - Supernatant analysed by NIRF spectroscopy (Schierz et al. 2012)
  - Fish:
    - NIRF tracking (Bisesi et al. 2014)
  - Analysis of Co and Mo metal catalyst residues
    - Combustion
    - Acid digestion
    - ICP-MS

SWCNT in wetland ecosystems (mesocosms): results

**Water**

![Graph showing SWCNT concentrations in water](image)

**Sediment traps**

![Graph showing SWCNT accumulation in sediment traps](image)

Fig. 1 SWCNT concentrations (± one standard deviation) within the water column (blue) followed over 1 month after SWNT amendment. Insets show near-infrared fluorescence emission spectra (NIRF spectra) for SWNTs extracted from water samples at 0.5 h (A), 3 days (B) and 7 days (c < DL; 5 μg L⁻¹) (C) after spiking, legend: 638 nm (black), 691 nm (red) and 782 nm (blue) excitation wavelength. (D) Fit of SWNT water column concentration data to a first-order decay model results in a calculated half life of $t_{1/2} \approx 7.4$ hours ($r^2 = 0.76$).

Fig. 2 SWNT accumulation in sediment traps in the SWNT-dosed mesocosm one month following SWNT amendment. The $m_{SWNT}$ mass ($n = 1$) is normalized to the total surface area of the sediment traps. Insets show representative near-infrared fluorescence emission spectra (NIRF spectra) for of CoMoCat SWNT extracted from sediment traps after 1 day (A) and 30 days (B).

SWCNT in wetland ecosystems (mesocosms): results

SWCNT and Mo in sediment profile after 10 months

Overall SWCNT mass balance: 7 – 48% in sediment

Bucheli | © Agroscope ISS
Quantification of BC | Strategische Übungen Anal. Chem.
NIRF: pros and cons

- **Pros:**
  - Excellent selectivity and sensitivity (unprecedented)

- **Cons:**
  - Restricted to SWCNTs, which may not be environmentally relevant
CNTs in soils & sediments

- Progress is made for SWCNTs
- MWCNT more difficult; currently restricted to spiked samples at high concentrations
- (Again) – one single method may not do the job
CNT analysis in environmental and biological samples: a review

Accepted Manuscript

Title: CHARACTERIZATION OF CARBON NANOTUBES AND ANALYTICAL METHODS FOR THEIR DETERMINATION IN ENVIRONMENTAL AND BIOLOGICAL SAMPLES: A REVIEW

Author: C.Herrero Latorre J.Álvarez Méndez J.Barciela García S.García Martín R.M.Peña Crecente

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Thank you for your attention!