Black Carbon measurements with the Aethalometer

Spatial and temporal variations of black carbon, carbonaceous aerosols and co-emitted pollutants depend on the sources – results of Central European campaigns

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dr. Griša Močnik
Aerosol d.o.o.

grisa.mocnik@aerosol.si
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Mestna občina Maribor, Nova Gorica, Celje, Klagenfurt, PMinter - SI-AT 2007-2013
CEA-ARRS, bilateral project BI-FR/CEA/10-12-006.
Aerosol Black Carbon

- BC is a **primary** product of incomplete **combustion**
- BC **not** automatically related to CO₂ emission
- BC emissions can **not** be predicted: **must be measured**
- BC particles from **different sources** can have **different characteristics** that produce **different effects** in the atmosphere:
  (Coal/Diesel/Biomass, USA/Asia/Europe)
Health Effects

Two-pollutant models in time-series studies suggested that the effect of BCP was more robust than the effect of PM mass. The estimated increase in life expectancy associated with a hypothetical traffic abatement measure was four to nine times higher when expressed in BCP compared with an equivalent change in PM2.5 mass.

Jansen et al, 2011 EHP


<table>
<thead>
<tr>
<th>Mortality Ratio</th>
<th>Mortality</th>
</tr>
</thead>
<tbody>
<tr>
<td>Highest vs. Lowest PM</td>
<td></td>
</tr>
<tr>
<td>All causes</td>
<td>1.26</td>
</tr>
<tr>
<td>Lung cancer</td>
<td>1.37</td>
</tr>
<tr>
<td>Other cardiopulmonary</td>
<td>1.37</td>
</tr>
<tr>
<td>Non-cardiopulmonary</td>
<td>1.01</td>
</tr>
</tbody>
</table>
Climate Change Effects of Aerosols: BC vs. CO$_2$

What is the big deal with BC?
C mass emitted as BC is 0.1% of C mass emitted as CO$_2$!

... and its lifetime is small!

**BUT... BC absorbs sunlight extremely efficiently:**

1 g of BC absorbs as much as ~10 umbrellas!

truck: EF=10 g/kg → 1 umbrella/100 m

Bond 2012
Climate Change Effects of Aerosols

Haze over Asia: up to 40% of sunlight absorbed. Crop yields reduced; local rainfall changed. BC forcing is almost 1/3 of the total TOA GHG forcing! Heat redistribution → weather


Total BC forcing: direct + indirect

1.1 W/m²

(Bond et al 2013)
Climate & health!

Drew Shindell, et al.
Simultaneously Mitigating Near-Term Climate Change and Improving Human Health and Food Security
Science 335, 183 (2012);
Advantages / Attributes of Optical Analysis

Typical chemical speciation time resolution – hours, day!

Optical methods – minute!

• Instantaneous
• Non-destructive
• Mobile / Portable
• Added dimension - time
• Added dimension – wavelength
• Collect sample **continuously**.
• **Optical absorption** ~ change in ATN.
• Measure optical absorption **continuously** : $\lambda = 370$ to 950 nm.
• Convert **optical absorption** to **concentration of BC**:

$$BC (t) = \frac{b(t)}{\sigma}$$

• Real-time data: **5 minutes**
  – *Dynamical, real-time measurement, updated each period*
Aethalometer – Continuous rack mount instruments

AE31 Spectrum – Ambient Air Quality Monitoring

- Seven wavelength (370, 470, 520, 590, 660, 880, and 950 nm)
- Local source identification
- Regional, Continental, Global Atmospheric studies
- Particle size distribution, radiative transfer
- Climate change, albedo, cloud modification
The Aethalometer Model AE33

EUREKA/Eurostars FC Aeth E!4825
Aethalometer Model AE33

- **Multiple wavelengths**: absorption: UV-IR, quantitative source apportionment: fossil fuel vs. wood-smoke – BC and CM.
- **Dynamic loading compensation** eliminates filter loading artifacts.
- **Automated QA/QC** with zero, optical span checks and flow calibration.
- **Improved performance**: low noise, fast time resolution.
- Easily integrates into **networks**: ease of communication and maintenance.
Installations in monitoring stations

- fixed measurement sites
- analysis of *temporal* trends
- source apportionment

London, UK  Austria  China
Site and instrumentation

Aerosol light absorption:
Aethalometer AE31-ER

- 7 wavelengths: 370, 470, 520, 590, 660, 880, 950 nm
- flow 4 LPM
- absorption coefficient $b_{abs}$ - compensation for loading and scattering
- Angstrom exponent $\alpha$ from $b_{abs}(\lambda)$

OC / EC filter analysis:
Sunset T-O Carbon Aerosol analyzer

- 24 h quartz filters, 16,7 LPM
- EUSAAR-2 protocol

PM10:
EN 12341
reference gravimetric method

5 min time resolution  1 day time resolution
BC time-series, Nova Gorica

ng/m³
BC in Nova Gorica – diurnal variation

ng/m³

traffic

workday

Sunday

?
Traffic

Does traffic diurnal pattern match the BC pattern?

Trucks are all diesel and emit more than other vehicles.

What about cars?
Note the change in scale!
Wind

Does the wind diurnal pattern influence the BC pattern?

Wind does disperse the primary air pollution!
Composition of PM10 changes during the day!
From Black & White to Color
Biomass is globally a major energy source
Woodsmoke in cities?!

<table>
<thead>
<tr>
<th>PM2.5</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Paris, winter</td>
<td>20%</td>
<td>Favez 2009</td>
</tr>
<tr>
<td>Grenoble, winter</td>
<td>35%</td>
<td>Favez 2010</td>
</tr>
</tbody>
</table>

similar for Vienna, Graz, Salzburg (Caseiro 2009),
Zurich (Lanz 2008, Szidat 2006)...

and also:

| Milano, fall       | 30%              | Perrone 2012 |
| Milano, winter     | 25%              | Perrone 2012 |
Biomass-smoke vs. diesel - $7\lambda$

- measure attenuation with the Aethalometer
- absorption coefficient - $b_{abs}$
- for pure black carbon: $b_{abs} \sim 1/\lambda$
- generalize Angstrom exponent: $b_{abs} \sim 1/\lambda^\alpha$

**diesel:** $\alpha \approx 1$

**biomass-smoke:** $\alpha \approx 2$ and higher

Quantification

\[ b(\lambda) = b_{wb}(\lambda,\text{wood}) + b_{ff}(\lambda,\text{fossil}) \quad \lambda = 470 \text{ nm}, 950 \text{ nm} \]

\[ \frac{b_i(470 \text{ nm})}{b_i(950 \text{ nm})} = (470 \text{ nm} / 950 \text{ nm})^{-\alpha} \]

\[ \alpha = 1,0 \pm 0,1 (\text{fossil}) \quad \text{Bond & Bergstrom 2004} \]

\[ \alpha = 2,0 -0,5/+1,0 (\text{wood}) \quad \text{Kirchstetter 2004, Day 2006, Lewis 2008} \]
$\text{BC}_{ff}$, $\text{BC}_{wb}$ time series, Nova Gorica
Source apportionment: which sources to regulate?

![Graph showing aerosol concentrations for Zagorje workday with BC, BCff, and BCwb emissions. Traffic contributes 73% ± 8% and wood combustion contributes 27% ± 8%.]
Wood-smoke markers – levoglucosan

Levoglucosan - ion chromat. EARS
# Wood-smoke vs. Fossil fuel

<table>
<thead>
<tr>
<th></th>
<th>ug/m³</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CM</td>
<td>CMff</td>
</tr>
<tr>
<td>Maribor, SI</td>
<td>22,9</td>
<td>8,9</td>
</tr>
<tr>
<td>Vrbanski plato</td>
<td>23,8</td>
<td>3,5</td>
</tr>
<tr>
<td>Leibnitz, AT</td>
<td>35,5</td>
<td>10,7</td>
</tr>
<tr>
<td>Arnfels</td>
<td>6,4</td>
<td>1,1</td>
</tr>
<tr>
<td>Klagenfurt, AT</td>
<td>33,8</td>
<td>15,9</td>
</tr>
<tr>
<td>Voelkermarktstr</td>
<td>33,8</td>
<td>15,9</td>
</tr>
<tr>
<td>Limmersdorf</td>
<td>21,8</td>
<td>5,7</td>
</tr>
<tr>
<td>Zell</td>
<td>37,0</td>
<td>7,3</td>
</tr>
</tbody>
</table>

### Notes:
- **ug/m³** represents micrograms per cubic meter.
- **%** represents the percentage contribution of wood-smoke versus fossil fuel.
Maribor, SI

Ratio: city / background

MB center / Vrbanski plato

CM wood burning
CM fossil fuel
PAH – what is the source?

Zagorje

BaP (µg/m³)

BC_{wb} (µg/m³)

Y = A + B * X

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>0.36434994</td>
<td>0.05058862</td>
</tr>
<tr>
<td>B</td>
<td>190.39271329</td>
<td>10.72866021</td>
</tr>
</tbody>
</table>

R = 0.9527652
SD = 0.14331925
N = 34
P < 0.0001

BaP by GC-MS - EARS
Diurnal variation of $BC_{wb} = PAH$

$BC (\mu g/m^3)$

$PAH (ng/m^3)$

Zagorje workday
Conclusions

- we can measure **Black Carbon** from **Fossil Fuel** and **Biomass** combustion with the Aethalometer
- time resolution is 1 min
- we can investigate **time evolution** of BC and biomass smoke during the day, excellent correlation with markers, PAH source
- **quantitative biomass smoke determination** – 24 h TC, but Aethalometer high time resolution - minutes
- monitoring station pair: **regional and local behaviour**
- **woodsmoke is a regional pollutant**
Thank you for your attention!

Questions?

Aerosol d.o.o.
Kamniška 41
SI-1000 Ljubljana
Slovenia
tel: +386 59 191 220
fax: +386 59 191 221
grisa.mocnik@aerosol.si
Good agreement between thermal EC and optical BC!

mass absorption cross-section $\sigma = 7.6 \, m^2/g$

$y = 7.58x$

$R^2 = 0.88$
Milano, Italy

- Largest city in N Italy, in a valley
- 1.3 M inhabitants
- One of the most polluted cities in Europe
- Major traffic in the Po valley
- Traffic: 89,000 vehicles in the city center every day
- Traffic restriction in place since Jan 2008
Radial measurements

Each site:
ÂPM10, PM2.5, PM1
ÂBlack Carbon
ÂRH, T
08:30 ï 19:30

Summer:
July 2010

T = 30 C
Results

No difference!

Big difference!

PM

BC/PM
Carbonaceous matter

measure Total Carbon – 24 h resolution

\[ TC = OC + EC \]

\( \rightarrow \) carbonaceous matter CM

\[
CM = C_1 b(\text{fossil,950 nm}) + C_2 b(\text{wood,470 nm}) + C_3
\]

\( b \) \text{ absorbance}

fossil fuel combustion \( \text{BrC containing} \) – wood combustion -combustion sources

\[ CM = BC + OM \]
C_1, C_2, C_3 determination – some hand-waving

- C_1 is less variable than C_2 and C_3 and fixed to 290.000
- C_2 and C_3 determined from (CM-CM_{ff}) vs. CM
- determine CM_{ff} from

\[ CM_{ff} = BC_{ff} + OM_{ff} \]

\[ BC_{ff} / OC_{ff} = 1 \]

\[ OM_{ff} = 1.8 \cdot OC_{ff} \]

supported by ambient and emission studies, WSOC measured

Sandradewi 2008, Favez 2010
$C_2, C_3$ determination (2) – Nova Gorica

$CM = C_1 b_{(ff, 950 \text{ nm})} + C_2 b_{(wb, 470 \text{ nm})} + C_3$

$y = 0.67x + 1.05$

$R^2 = 0.79$
CM reconstruction using $C_i$ – Nova Gorica
## Wood-smoke vs. Fossil fuel

### Aethalometer model

<table>
<thead>
<tr>
<th>Location</th>
<th>CM (μg/m³)</th>
<th>CMff</th>
<th>CMwb</th>
<th>CMff %</th>
<th>CMwb %</th>
<th>TUW</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maribor</td>
<td>22.9</td>
<td>8.9</td>
<td>13.9</td>
<td>39%</td>
<td>61%</td>
<td>75%*</td>
</tr>
<tr>
<td>Vrbanski plato</td>
<td>23.8</td>
<td>3.5</td>
<td>20.3</td>
<td>15%</td>
<td>85%</td>
<td>82%</td>
</tr>
<tr>
<td>Leibnitz</td>
<td>35.5</td>
<td>10.7</td>
<td>24.7</td>
<td>30%</td>
<td>70%</td>
<td>62%</td>
</tr>
<tr>
<td>Arnfels</td>
<td>6.4</td>
<td>1.1</td>
<td>5.2</td>
<td>18%</td>
<td>82%</td>
<td>43%**</td>
</tr>
<tr>
<td>Voelkermktstr</td>
<td>33.8</td>
<td>15.9</td>
<td>17.9</td>
<td>47%</td>
<td>53%</td>
<td>54%</td>
</tr>
<tr>
<td>Limmersdorf</td>
<td>21.8</td>
<td>5.7</td>
<td>16.2</td>
<td>26%</td>
<td>74%</td>
<td>69%</td>
</tr>
<tr>
<td>Zell</td>
<td>37.0</td>
<td>7.3</td>
<td>29.7</td>
<td>20%</td>
<td>80%</td>
<td>77%</td>
</tr>
</tbody>
</table>

* reanalysis
** 31% other OM!

Good agreement!

Preliminary!
2010-11

80% ± 30%
20% ± 5%

CMwb
CMff

Zell

2011-12

78% ± 30%
22% ± 7%

CMwb
CMff

2010-11

55% ± 14%
45% ± 18%

CMwb
CMff

Klagenfurt

2011-12

69% ± 22%
31% ± 10%

CMwb
CMff