Black Carbon in the Atmosphere

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Lectures

- Lecture 1: Introduction to Atmospheric Aerosols
- Lecture 2: Aerosol Measurements and Monitoring Networks
- Lecture 3: Aerosols and Climate
- Lecture 4: Black Carbon in the Atmosphere
Outline

• What is Black Carbon (BC)?
• Measurement methods
• Recommendations for reporting results
• What are the sources of BC?
  • Natural
  • Anthropogenic
• How does BC impact climate?
  • Perturbation of the Earth’s radiation balance
• BC in the Arctic
• Shipping
What are the Issues?

- **Black carbon (BC) has important effects on climate and health**
  - Recently identified as #2 most important climate forcing agent (+1.1 W m\(^{-2}\), 90% bounds +0.17 to +2.1 W m\(^{-2}\), Bond et al., 2013).
  - Associated with asthma and other respiratory problems, heart attacks and lung cancer.

- **BC is poorly defined in the scientific literature**
  - Carbonaceous matter does not appear in atmospheric aerosols as a pure substance.
  - Measurements may refer to the same quantity with different names, or to different quantities with the same name.
  - Models may use emissions inventories based on one analytical method and verified with atmospheric observations made with a different analytical method.

- **BC measurements depend on the method used**
  - Current methods respond to different properties of BC.
  - Correlations between methods are frequently high, but relationships vary among sites, seasons and aerosol types.
What is Black Carbon?
What is Black Carbon (BC)?

Black carbon is a component of atmospheric particulate material (PM) and comes primarily from the incomplete combustion of C-rich fuels.

- Fossil fuels
- Wood, Biomass
- Paper
- Wax
- Other (e.g., plastics, organic materials, flammable gases)

Figure 2-2. BC Images. (a) High resolution transmission electron microscopy (TEM) image of a BC spherule (Pósfai and Buseck, 2010). (b) TEM image of a representative soot particle. Freshly emitted soot particles are aggregates of soot spherules (Alexander et al., 2008).
Terminology for "soot"

• Graphitic (GC) vs. Organic carbon (OC)
  – defined by molecular form of carbon

• Elemental carbon (EC)
  – based on refractory properties of carbon
  – also called particulate elemental carbon (PEC)

• Black carbon (BC)
  – based on optical properties of carbon
  – characterized by $1/\lambda$-dependence of absorption

• Brown carbon
  – light absorbing carbon that is not "black“ (HULIS, etc.)
What is Black Carbon?

Nanometer scale → Meter scale

Ogren & Charlson 1983

Soto, 2008

Coalhaye, 2009
Morphology of Graphitic Elemental Carbon

- $\Pi$ orbitals of planar graphite molecule are the cause of the strong, broadband light absorption of EC
- Coatings affect EC lifetime and optical properties

Source: Ogren et al., 1983
What is Black Carbon?

Defined by five essential characteristics

- Composition
- Morphology
- Volatility
- Solubility
- Light absorption
<table>
<thead>
<tr>
<th>Property</th>
<th>Characteristics</th>
<th>Consequences</th>
</tr>
</thead>
<tbody>
<tr>
<td>Composition</td>
<td>graphitic-like structure containing a high fraction of sp²-bonded carbon atoms</td>
<td>low chemical reactivity in the atmosphere; slow removal by chemical processes; strong optical absorption</td>
</tr>
<tr>
<td>Morphology</td>
<td>Aggregates of small spherules, each typically 10-50 nm diameter</td>
<td>high specific surface area; high capacity for sorption of other species</td>
</tr>
<tr>
<td>Volatility</td>
<td>refractory material with a volatilization temperature near 4000K; gasification is possible only by oxidation at T &gt; 340°C</td>
<td>high stability in the atmosphere; longer atmospheric residence time</td>
</tr>
<tr>
<td>Property</td>
<td>Characteristics</td>
<td>Consequences</td>
</tr>
<tr>
<td>-------------------</td>
<td>----------------------------------------------------------------------------------</td>
<td>------------------------------------------------------------------------------</td>
</tr>
<tr>
<td>Solubility</td>
<td>insoluble in water, in organic solvents including methanol and acetone, and in the other components of the atmospheric aerosol</td>
<td>Slow removal by clouds and precipitation, unless coated with water-soluble compounds; longer atmospheric residence time</td>
</tr>
<tr>
<td>Light absorption</td>
<td>uniformly absorbing in the spectral range of visible light; characterized by a significant, non-zero and wavelength-independent imaginary part of the refractive index over VIS and NIR spectral regions</td>
<td>Reduction of the albedo of clouds, snow, and ice; atmospheric heating; surface cooling – all of which lead to effects on solar radiation and climate</td>
</tr>
</tbody>
</table>
Blind Men and the Elephant

It’s a Fan!

It’s a Wall!

It’s a Rope!

It’s a Spear!

It’s a Snake!

It’s a Tree!
Interpreting “BC” Measurements

It's Black

It's BC!

It's a Chain Aggregate

It's Carbon

It's Insoluble

It's Refractory
What is Black Carbon?

Black carbon (BC) is carbon that is black. The formation process is excluded from this definition because of the variety of potential processes. While BC is mostly formed in incomplete combustion, it can be a product of pyrolysis of carbonaceous matter, dehydration of sugar, or heating of wood in an oxygen-free atmosphere.

Elemental carbon (EC) is formally defined as a substance containing only carbon. The formal term “elemental carbon” refers to a set of materials with different optical and physical properties instead of a given material with well-defined properties. Examples of “true” EC are diamond, carbon nanotubes, graphite or fullerenes.
What is Black Carbon (to summarize)?

• Carbonaceous particulate matter
  – a high fraction of which is sp\(^2\)-bonded carbon

• Consists of aggregates of spherules
  – Individually, from <10 to (typically) 50 nm in diameter

• Refractory

• Insoluble in water

• Strongly absorbs light at all visible wavelengths
  – when freshly emitted, has a mass absorption efficiency of at least 5 m\(^2\) g\(^{-1}\) at the mid-visible wavelength of 550 nm
Recommended Terminology
(from Petzold et al. (2014))

• No current method combines all five essential characteristics of BC
• Consequently, no current method can justifiably claim to provide a quantitative measurement of BC
• Recommendations
  • Use “BC” as a qualitative term referring to any of the quantitative methods
  • Use terms associated with the measurement methods when reporting quantitative results
Recommended Quantitative Terminology

Equivalent black carbon (EBC)
Data derived from *optical absorption methods*.
Report the optical measurements primarily as light absorption coefficient, and secondarily as EBC, along with the mass absorption efficiency used to convert absorption to EBC.

Refractory black carbon (rBC)
Data derived from *incandescence methods*.

Elemental carbon (EC)
Data derived from methods that are specific to the *carbon content* of carbonaceous matter (evolved carbon, aerosol mass spectrometry, Raman spectroscopy).

Petzold et al. (2014)
Black Carbon and Light Absorption

- Optical methods for determining BC really measure $\sigma_{ap}$ (PSAP, aethalometer, MAAP, photoacoustic, ...)

- $BC = \sigma_{ap} \times f_{ap} / MAE$
  - $f_{ap}$ = fraction of light absorption due to BC
  - $MAE =$ mass absorption efficiency of BC (m$^2$ g$^{-1}$)

- Climate forcing calculations require $\sigma_{ap}$

- Typical MAE used for BC in recent literature $\Rightarrow$ 5-10 m$^2$ g$^{-1}$

- Empirical relationships, like the one show above for the Indian Ocean, are required to determine BC from $\sigma_{ap}$ (WMO/GAW report #153)
<table>
<thead>
<tr>
<th>Thermochemical Classification</th>
<th>Molecular Structure</th>
<th>Optical Classification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Elemental Carbon (EC)</td>
<td>Graphene Layers (graphitic or turbostratic)</td>
<td>Black Carbon (BC)</td>
</tr>
<tr>
<td>Refractory Organics</td>
<td>Polycyclic Aromatics, Humic-Like Substances, Biopolymers, etc.</td>
<td>Colored Organics</td>
</tr>
<tr>
<td>Non-Refractory Organics (OC)</td>
<td>Low-MW Hydrocarbons and Derivatives (carboxylic acids, etc.)</td>
<td>Colorless Organics (OC)</td>
</tr>
</tbody>
</table>

Classification and molecular structure of carbonaceous aerosol components (Andreae and Gelencser, 2006)

Light-absorbing aerosol components

<table>
<thead>
<tr>
<th>VIS + IR</th>
<th>black carbon</th>
<th>brown carbon</th>
</tr>
</thead>
<tbody>
<tr>
<td>&quot;green&quot;</td>
<td>Fe$_2$O$_3$, mineral dust</td>
<td></td>
</tr>
<tr>
<td>near IR</td>
<td>H$_2$O</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(NH$_4$)$_2$SO$_4$</td>
<td></td>
</tr>
</tbody>
</table>

In the VIS, only graphitic-like black carbon and refractory organics (brown carbon) absorb light efficiently.
Measurement Methods for BC
“BC” Measurement Methods

Evolved Carbon
- CO$_2$ evolved from thermal or thermo-optical methods: IMPROVE / EUSAAR
- BC properties: composition, volatility

Light Absorption
- Filter-based: Aethalometer, PSAP, MAAP, CLAP/TAP, COSMOS
- In situ: photo-acoustic, ext. minus scat., retrievals from sun/sky radiances
- BC properties: light absorption

Laser Incandescence
- Laser heating of particles, e.g., SP2, LII
- BC Properties: volatility, composition
“BC” Measurement Methods

Aerosol Mass Spectrometry
- Vaporization and detection of carbon ion clusters in mass spectra: ATOFMS, SP-AMS
- BC properties: composition

Raman Spectrometry
- Detection of graphite-like ordered and disordered carbon
- BC properties: composition

Electron microscopy
- Detection of particle microstructure and morphology, e.g. TEM
- BC properties: morphology, composition
Measurements of Light Absorption Coefficient

• Filter-based
  – PSAP (particle/soot absorption photometer)
  – CLAP/TAP
  – Aethalometer
    • broadband
    • spectral
  – MAAP (multi-angle absorption photometer)

• "Direct"
  photoacoustic
  photothermal interferometer
Photoacoustic Absorption Measurement

- Laser light is power modulated by the chopper.
- Light absorbing aerosols convert light to heat, producing a sound wave. No response to light scattering.
- Microphone signal at chopper frequency is a measure of the light absorption.
- Calibrated by absorption by gases (NO$_2$, O$_3$), monodisperse particles, or light extinction
Aethalometer response vs. time

Separate runs with pure soot ($\sigma_{\text{ext}} \sim 800 \text{ Mm}^{-1}$) and ammonium sulfate ($\sigma_{\text{ext}} \sim 450 \text{ Mm}^{-1}$). Photoacoustic wavelength 532 nm, aethalometer wavelength 521 nm.
What are the Sources of Black Carbon?
History of US BC Emissions

- Coal replacing wood
- Dirty coking (for steel)
- Great Depression
- Rapid growth of transportation
- Regulations offset growth

Source: Bond, 2010
What are the Sources of BC?
Measurements of BC in Greenland Ice

• The shaded region represents the portion of BC attributed to industrial emissions, not boreal forest fires

• Large, short-lived increases in nss-S result from explosive volcanism

Source: McConnell et al., 2007
Are all Sources of BC Equal?

Short Answer: No.

- Soot mixtures can vary in composition,
- Have different ratios of organic carbon (OC) to BC,
- Usually include inorganic materials such as metals and sulfates.

The average OC:BC ratio among global sources:
- Diesel exhaust is ~ 1:1
- Biofuel burning is ~4:1
- Biomass burning is ~ 9:1
Black Carbon and Climate
Black Carbon and Climate

• Black carbon (a.k.a. elemental carbon, refractory carbon, soot) is the dominant light absorbing species in the atmospheric aerosol
• Light absorption by BC heats the atmosphere and decreases the reflectivity of clouds, snow, and ice
• These processes combine to cause a positive (warming) climate forcing that is claimed to be second only to CO$_2$
• Aerosol light absorption is commonly used as a proxy for BC
How BC Impacts Climate

- Black carbon has an atmospheric residence time of a few weeks
- Remains on surfaces like ice and snow until covered or transported via melt
- Ranks with CO2 and CH4 as strongest climate forcers

Figure 2-1. Effects of BC on Climate, as Compared to GHGs. (Source: U.S. EPA)

Removal Mechanisms of BC

• Aerosol light scattering is dominated by particles that are readily-scavenged by clouds, such as sulfates and water-soluble organics
• Aerosol light absorption is dominated by less readily-scavenged particles, such as graphitic carbon (soot)
• Cloud droplets are therefore enriched in light scattering particles relative to light absorbing particles
• When precipitation falls, it removes more of the light scattering particles than the light absorbing ones
• The resulting aerosol after the precipitation is relatively enriched in light absorbing particles (i.e., BC) → BC can have a longer residence time in the atmosphere than other types of aerosols
• Cloud scavenging therefore systematically decreases aerosol single-scattering albedo
Terminology: Mixtures

• External mixture
  – individual particles have different chemical composition
  – e.g., BC and sulfate are in separate particles

• Internal mixture
  – multiple chemical species in each particle
  – e.g., BC and sulfate are in the same particles

• Implications of mixing state for lifetime and radiative properties
  – hygroscopic coatings enhance BC removal
  – coatings enhance BC light absorption
<table>
<thead>
<tr>
<th>Location</th>
<th>Effects</th>
<th>Forcing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free Troposphere</td>
<td>Absorbs solar radiation, warms upper atmosphere</td>
<td>Negative (cooling at surface)</td>
</tr>
<tr>
<td>Free Troposphere</td>
<td>Absorbs solar radiation, dissipates clouds</td>
<td>Positive (warming at surface)</td>
</tr>
<tr>
<td>Free Troposphere</td>
<td>Decreases reflectivity of clouds</td>
<td>Positive</td>
</tr>
<tr>
<td>Boundary Layer</td>
<td>Absorbs solar radiation, warms lower atmosphere</td>
<td>Positive</td>
</tr>
<tr>
<td>Boundary Layer</td>
<td>Absorbs solar radiation, dissipates clouds</td>
<td>Positive</td>
</tr>
<tr>
<td>Boundary Layer</td>
<td>Decreases reflectivity of clouds</td>
<td>Positive</td>
</tr>
<tr>
<td>Deposit on Dark Surfaces</td>
<td>Lowers surface albedo</td>
<td>Minimal positive</td>
</tr>
<tr>
<td>Deposit on Light Surfaces</td>
<td>Lowers surface albedo</td>
<td>Positive</td>
</tr>
</tbody>
</table>
Aerosols and Clouds and Climate

- Black carbon absorbs solar radiation
- Heats the air in and around clouds
- Warmer temperature $\rightarrow$ lower relative humidity
- Decreased cloud lifetime

Less cloud $\rightarrow$ less cloud scattering $\rightarrow$ more incoming solar radiation $\rightarrow$ warmer climate

‘Semi-direct effect’
Aerosol Location, Darkness and Surface Albedo

Dark surface absorbs a large portion of the solar radiation

\[ \text{Absorbing aerosols will thus have a small effect.} \]

\[ \text{Scattering aerosols increase reflected solar radiation and have a cooling, since the solar radiation would otherwise be absorbed at the surface.} \]

Bright surface reflects incoming solar radiation

\[ \text{Scattering aerosols have a minimal effect.} \]

\[ \text{Absorbing aerosols reduce the outgoing radiation and have a warming effect} \]

From Myhre et al 2013
Black Carbon in the Arctic
Black carbon emissions contribute to Arctic warming

- The Arctic is warming at twice the global average rate and is three times more sensitive to the BC warming due to albedo effects
- Vessel activity continues to increase as summer ice diminishes
Arctic BC also comes from outside the Arctic

Emissions above 40N can significantly impact climate in the Arctic

Conservative estimates of vessel traffic show a doubling over 2013 numbers
- 420 vessels; 877 transits
Potential global BC contribution from shipping

Possibility of growing to 19% or as much as 35% by 2030 depending on a number of variables

2016-7-14
How can we reduce BC from shipping?

<table>
<thead>
<tr>
<th>Technology</th>
<th>PM</th>
<th>BC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diesel Oxidative Catalyst (DOC)</td>
<td>20-30%</td>
<td>Unknown</td>
</tr>
<tr>
<td>Diesel Particulate Filters (DPF)</td>
<td>70-95%</td>
<td>95-99%**</td>
</tr>
<tr>
<td>Exhaust Gas Scrubbers</td>
<td>60-80%</td>
<td>0-80%**</td>
</tr>
<tr>
<td>Slide Valves</td>
<td>10-50%</td>
<td>Not reported</td>
</tr>
<tr>
<td>Low Sulfur Diesel (from HFO)</td>
<td>up to 80%</td>
<td>30-80%**</td>
</tr>
<tr>
<td>Emulsified Diesel Fuel</td>
<td>50-60%</td>
<td>Not reported</td>
</tr>
<tr>
<td>LNG</td>
<td>99%</td>
<td>99%</td>
</tr>
<tr>
<td>Shore Power</td>
<td>Depends on auxiliary engines</td>
<td></td>
</tr>
</tbody>
</table>

Actual Reductions from different approaches are still uncertain

** Best estimates representing high degree of uncertainty and debate

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Will changes to fuel “fix” BC?

Short answer: We don’t know

There are significant gaps in emission factors (the amount of BC emitted by the engine) for ships.

Emissions can vary by engine load, speed, age, and maintenance

Changes to fuel and engine timing needed to improve combustion may have tradeoffs (e.g. increases in NOx)

Changing fuels may enable other technologies that can reduce BC
Summary

• Black Carbon (BC) has important effects on health and climate
• Recently identified as the second most important climate forcing agent
• Use “BC” as a qualitative term referring to any of the quantitative methods; use terms associated with the measurement methods when reporting quantitative results (e.g., EBC, rBC, EC)
• Most BC aerosols contain significant amounts of organic carbon also
• The climate effects of BC depend on its location in the atmosphere and the reflectivity of the underlying surface, but in general a strong surface warming effect (positive forcing)
• BC emissions have contributed to Arctic warming
• BC emissions from shipping and transportation are projected to increase, especially in the Arctic
Thank you for your attention!
Unused slides
Measurement of BC + Coatings using the Single Particle Soot Photometer (SP2)

- Data recorded at edge of laser represent “unperturbed” aerosol.
- Extrapolate scattering signal for optical size (requires information about the position of the particle in the laser).
- Clear reduction in optical size as particle is heated is used to identify internally mixed BC.

Source: J. Schwarz, personal communication
Summary of Filter-based Absorption

- Filter spot size and flow rate must be individually calibrated for each instrument
- Corrections are required for non-ideal responses of instrument to
  - scattering by particles (requires scattering measurement)
  - attenuation of light by deposited particles ("shadowing")
- Correction schemes
  - PSAP: Bond (1999, AS&T)
  - Aeth: Collaud Coen (2010, AMT)
  - improvements are coming
Filter Methods for Light Absorption

- Particles are deposited on the filter, which is a light-diffusing, multiple scattering substrate.
- Light absorbing particles reduce the light power at the photodetector.
- Ideally, light scattering particles don't reduce power.
- Variants:
  - Time-integrated: integrating plate method, integrating sphere, integrating sandwich
  - Continuous: aethalometer, PSAP, MAAP, CLAP, TAP
PSAP Optical Configuration

Light Source (LED)

Opal glass

O-Rings

Filter holder (clamped when running; shown open for clarity)

Particle deposit

Pallflex filter

Detectors

sample reference

Reference signal

Source: Bond et al. (1999)
"MAAP"

Simultaneously measures light (670 nm) transmitted and reflected by aerosol deposit on filter

A two-stream radiative transfer model is used to derive the aerosol absorption coefficient, accounting for light scattering by particles and filter.

Detection limit ~ 1 Mm\(^{-1}\) for 2-minute average at 16.7 lpm flowrate.

Source: A. Petzold\(^1\), M. Schönlinner\(^2\), H. Kramer\(^2\) and H. Schloesser\(^2\)

\(^1\)German Aerospace Center, Oberpfaffenhofen, Germany
\(^2\)ESM Andersen Instruments, Erlangen, Germany
MAAP Optical Configuration

Source: A. Petzold¹, M. Schönlinner², H. Kramer² and H. Schloesser²
¹German Aerospace Center, Oberpfaffenhofen, Germany
²ESM Andersen Instruments, Erlangen, Germany
Arctic vessels in D17 area of concern
2008 = 120
2009 = 130
2010 = 160
2011 = 190
2012 = 250
2013 = 240
2014 = 250
2015 = 300

Bering Strait Transits
2008 = 220
2009 = 280
2010 = 430
2011 = 410
2012 = 480
2013 = 440
2014 = 340
2015 = 540

Source: MXAK Marine Exchange of Alaska, AIS, Internet blogs.
Let’s talk about fuels

Two basic types of marine fuels - **distillate** and **residual**

**Distillate** fuel is composed of petroleum fractions of crude oil that are separated by "distillation" process. **Residual** fuel or "residuum" is the fraction that did not boil

Heavy fuel oil (HFO) or bunker fuel can mean:

- Residual RMA-RML Fuel Oil or Residual Fuel Oil, Intermediate Fuel Oil (IFO)
- Low sulfur fuel is usually some type of:
  - Distillate DMX, DMA, DMB, DMC Gas Oil or Marine Gas Oil

**LNG**: has the potential to reduce all PM emissions, but comes with tradeoffs and the requirement of landside infrastructure.
Will changes to fuel “fix” BC?

Short answer: We don’t know

There are significant gaps in emission factors (the amount of BC emitted by the engine) for ships.

Emissions can vary by engine load, speed, age, and maintenance.

Changes to fuel and engine timing needed to improve combustion may have tradeoffs (e.g. increases in NOx).

Changing fuels may enable other technologies that can reduce BC.
What about technologies?

- Technologies like scrubbers and diesel particulate filters (DPF) are promising.
- Limited marine application of both, and limited data on actual reductions.
- DPF require the use of low sulfur, low ash fuels or a combo of technology for successful operation.