“Light Absorbing Carbon”
Detailed Measurements from Houston Shipping

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Photo: Richard Marchbanks 2006
Outline

• What is ‘Light absorbing Carbon’ and why do we care?
• How is it measured? Mass and Optical
• Emission Factors
• TexAQS/GoMACCS Shipping Emission Factors
• Significant Findings
Measuring “Light Absorbing Carbon”

• Black Carbon, *elemental carbon*, *soot*, *graphite*, *organic carbon*, *organic matter*, *light absorbing carbon*, secondary organic aerosol, *brown carbon*, *non-refractory carbon* etc. etc. etc.

• LAC and air quality / health  
  – How much is there?  
  – Where is it?  
  – What is it? Carcinogens, heavy metals etc.

• LAC and climate?  
  – How much is there?  
  – How much light does it absorb?  
  – Where is it?  
  – What is it? Hydrophobic of hydrophilic? How long does it stay around?
Measuring ‘Light Absorbing Carbon’ - LAC

• Common:
  – Filter-based absorption
  – Measure change in filter transmittance
  – Uncertainties/corrections
  – Aerosol can be physically altered → not measuring atmospheric aerosol

• Newer Technology:
  – Photoacoustic technique measures absorption directly
- Direct method
- Accurate calibrations (<1%)
- Overall uncertainty = <5%
- Designed and built for aerosols
- Validated using aerosols
Converting Optical Absorption to Mass

• Mass absorption Coefficient (MAC)

• Absorption per mass of LAC aerosol

• MAC varies with particle size, composition and aging

• Bond & Bergstrom (2006) carefully reviewed MACs to find *freshly emitted* LAC (from fossil fuel combustion) has an **MAC of 7.5 ± 1.2 m² g⁻¹**
  – Fresh LAC is a simpler aerosol
  – Most techniques of mass and optical absorption show good closure for this type of LAC

Measuring Mass - Filters

- Gravimetric analysis
  - collect for many hours
  - other aerosol present.

- Thermal analysis
  - heat and oxidise aerosol to release CH$_4$
  - gas evolution regimes
  - conversion of measured CH$_4$ to ‘elemental’ or ‘organic’ carbon mass.
Emission Factors

• What is an EF?
  – g kg\(^{-1}\)

• Used to build emission inventories.

• For Global Shipping:
  • 1 directly measured EF\(_{LAC}\) (0.18 ± 0.02 g kg\(^{-1}\), Sinha et.al., 2003)
  • 1 indirectly measured EF\(_{LAC}\) (1.02 ± 1 g kg\(^{-1}\), Bond et.al., 2004)
  • ~2% of total LAC emissions


Emission Factors

• We need Emission Factors to know how much **LAC** there is!
  – Locally, regionally and globally.
Potential for arctic shipping to dramatically increase.

To assess the contribution of shipping to air quality and local climate in areas like Houston.
Shipping during TexAQS/GoMACCS

• Over 1100 individual plumes.
  – 116 where full data available for this study.

Photos: Richard Marchbanks & Dan Welsh-Bon
Calculating Emission Factors

\[ EF_{LAC} (\text{gkg}^{-1}) = \frac{\text{Absorption (Mm}^2)}{\text{CO}_2 \text{ (ppmV})} \times \frac{1}{\text{MAC} (\text{m}^3 \text{g}^{-1})} \times \text{f}_{fuel} \]

\[ 7.5 \pm 1.2 \text{ m}^2 \text{ g}^{-1} \]

*Bond et.al. 2006*

\[ \text{CO}_2 \text{ (ppmv) to mass of fuel} \]

*assumes fuel is 86.5% C*
Uncertainty in $\text{EF}_{\text{LAC}}$

$\pm \text{EF}_{\text{LAC}} \sim 19\%$

- $\pm$ Absorption / CO$_2$ Slope: 7% (average)
- $\pm$ MAC: 15.5%
- $\pm$ Fuel Carbon Content: 1%
- $\pm$ Assumption that all fuel C $\rightarrow$ CO$_2$: 2%
- $\pm$ Precision of the EF$_{\text{LAC}}$ Technique: 8% (will get to this)
Precision of the $\text{EF}_{\text{LAC}}$ Method

- Patriot Encounter

Container ship at anchor
Assume constant output
8% precision:
  6 encounters, 150 minutes
TexAQS LAC Emission Factors

- 116 individual vessel plumes (15 yet to be identified)
EF_{LAC} vs Vessel Speed

Lots of variability for Tug Boats.

Less variability for other vessel classes.
$\text{EF}_{\text{LAC}} \text{ vs Gas Phase } \text{EF}_{\text{NOY}}$

No Correlation
$E_{LAC}^F$ vs Gas Phase $E_{CO}^F$

LAC Correlated to CO for Tugs
$E_{\text{LAC}}$ vs Gas Phase $E_{\text{SO}_2}$

Tug boats emitting lots of LAC with little $\text{SO}_2$
Comparisons to Other Fuels and Consumption Types

- Biomass Burning
- Diesel - Railroad
- Shipping - Inventory
- Tug Boats - This Study
- Diesel - on Road
- Tanker Ships - This Study
- Passenger & Bulk Ships - This Study
- Aviation
- Gasoline - on Road
- Brown Coal
- Black Coal
- Natural Gas

LAC Emission Factor (g kg$^{-1}$)

Bond et.al. 2004
LAC in the Houston Area

- 2004 Fuel Usage: 0.13 Tg (from Eric Williams)
- Average \( \text{EF}_{\text{LAC}} = 0.85 \text{ g kg}^{-1} \)
- LAC emissions for 2004
  - 0.11 Gg
  - Compares to 140 Gg LAC for global shipping
- Highly uncertain calculation - fuel usage numbers
- Heavy metals are concentrated into Heavy Fuel Oils (HFO) used in shipping.
  - Arsenic, chromium, selenium \( \rightarrow \) LOW \( \mu g \text{ g}^{-1} \) (Docekal et.al., 1992)
  - Lead \( \rightarrow \) HIGH \( \mu g \text{ g}^{-1} \)
  - Particulate Mass from HFO contains \(~1\%\) Heavy Metals
  - “results suggest that exposure to metal-rich particles exacerbate existing asthma”, Gavett et.al., 2003

Gavet, S.H., Haykal-Coates, N., Copeland, L., B., Heinrich, J., Gilmour, M.I., 2003, Metal composition of Ambient PM2.5 Influences Severity of Allergic Airways Disease in Mice, Environmental Health Perspectives, v111, #12
Summary

• Correlations of $EF_{LAC}$ with $SO_2$ could have important air quality implications.

• Correlations of $EF_{LAC}$ with CO for Tug Boats reveal a relationship between engine efficiency and LAC emission.

• Lack of correlations between $EF_{LAC}$ and vessel speed in contradiction to predictions from indirect measurements.
Summary

• 116 EFs over 5 vessel classes compared to 1 direct and 1 indirect EF.
  – With some more work this could increase to over 200!
  – Previous Direct EF \( LAC \) = 0.18 ± 0.02 g kg\(^{-1}\)
  – This Study (excluding Tugs) = 0.5 ± 0.3 g kg\(^{-1}\)
  – This Study – Tug Boats = 0.95 ± 0.73 g kg\(^{-1}\)

• Will contribute to:
  • Global LAC emissions – global climate impacts
    – We calculate global LAC from shipping to be 2% of total.
  • Regional LAC emissions in high traffic areas – climate effects in regions like the Arctic.

• Regional and local emissions for air quality and health. A greater understanding of emission factors for LAC from shipping will contribute to better understanding of:
  – Areas of concentration of ship emissions
  – The largest emitters: e.g tugs operate 24hrs/day in a concentrated area
  – Emission of carcinogens and heavy metals associated with LAC