"Light Absorbing Carbon"
Detailed Measurements from Houston Shipping

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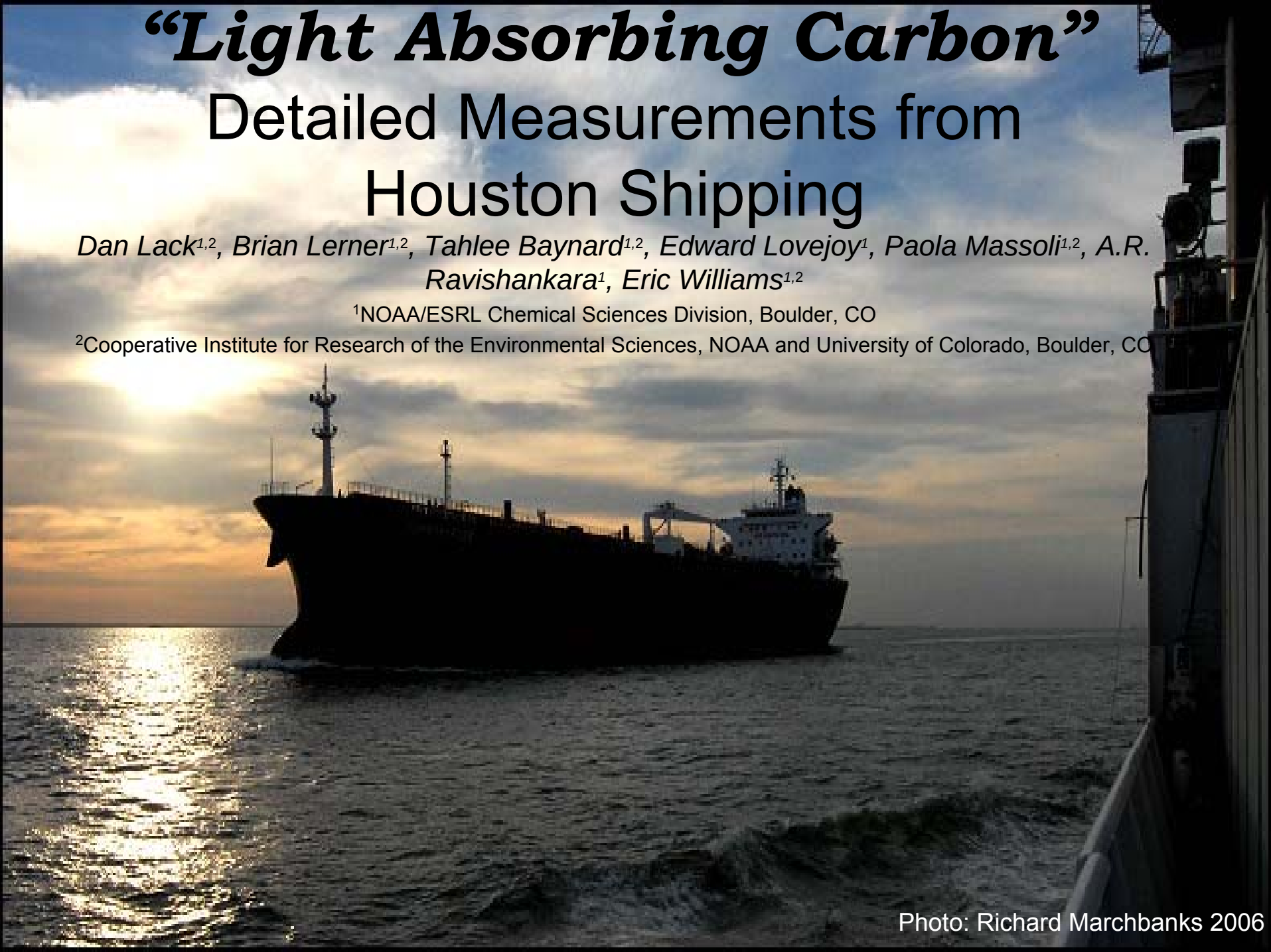


Photo: Richard Marchbanks 2006

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”

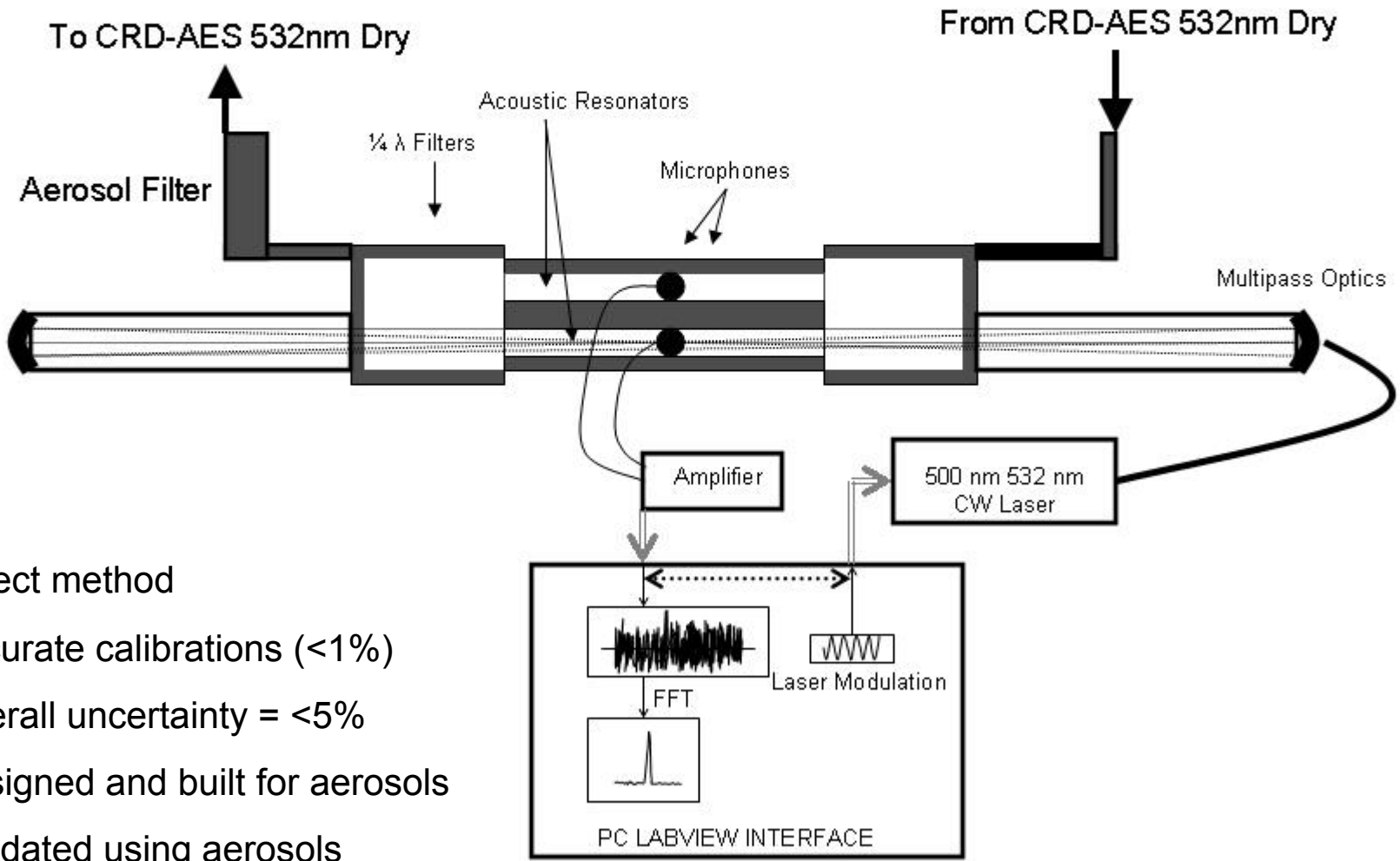
- Black Carbon, *elemental carbon*, **soot**, graphite, organic carbon, **organic matter**, light absorbing carbon, secondary organic aerosol, *brown carbon*, non-refractory carbon etc. etc. etc.

- 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

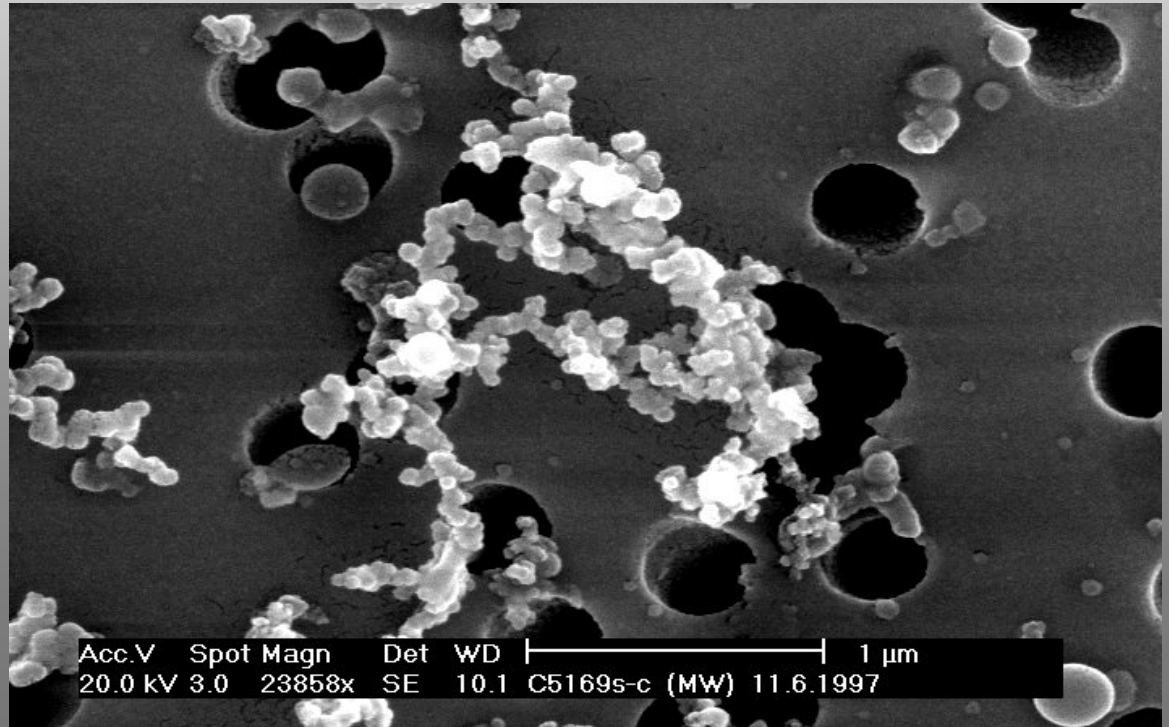
Converting Optical Absorption to Mass

- 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 ***$7.5 \pm 1.2\ m^2\ g^{-1}$***
  - Fresh LAC is a simpler aerosol
  - Most techniques of mass and optical absorption show good closure for this type of LAC

Bond, T. and R. W. Bergstrom (2006). "Light Absorption by Carbonaceous Particles: An Investigative Review." Aerosol Science and Technology **40**: 27-67.

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.



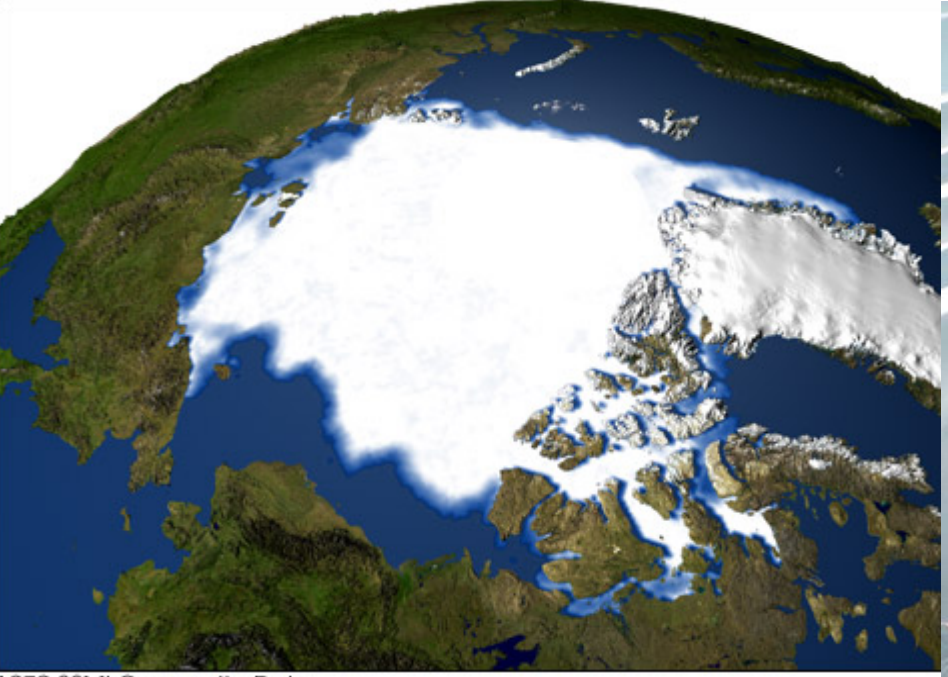
Emission Factors

- 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

Bond, T. C., D. G. Streets, K. Yarber, S. M. Nelson, J.-H. Woo and Z. Klimont (2006). "A Technology-Based Global Inventory of Black Carbon and Organic Carbon Emissions from Combustion." Journal of Geophysical Research **109**(D14203): doi:10.1029/2003JD003697.
Sinha, P., P. V. Hobbs, R. J. Yokelson, T. J. Christian, T. W. Kirchstetter and R. Bruintjes (2003). "Emissions of Trace Gases And Particles from Two Ships in the Southern Atlantic Ocean." Atmospheric Environment **37**(15): 2139-2148.

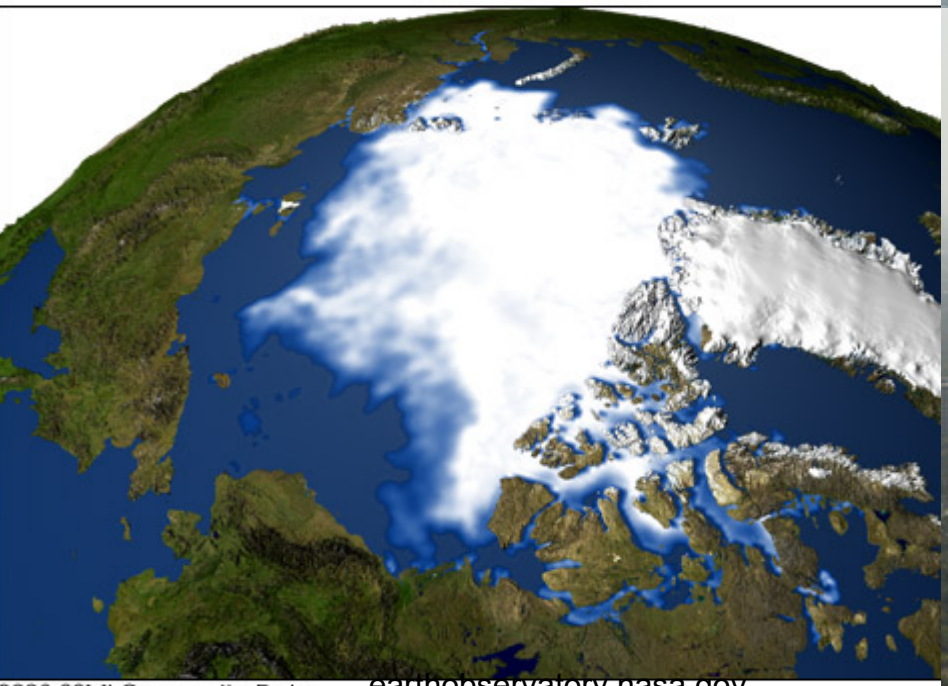
Emission Factors

- We need Emission Factors to know how much ***LAC*** there is!
  - Locally, regionally and globally.



1979 SSMI Composite Data

FirstPeople.us



2003 SSMI Composite Data

earthobservatory.nasa.gov

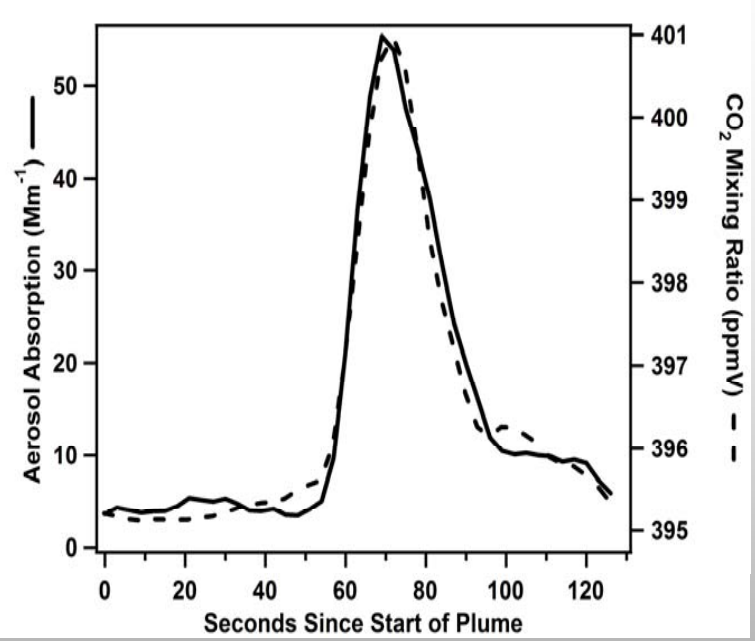
UCAR.edu

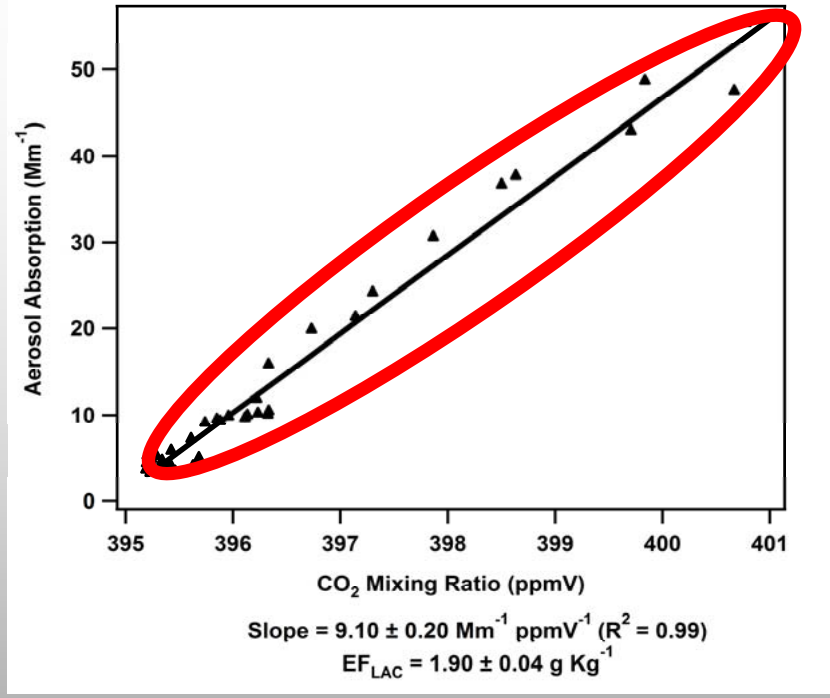
Shipping during TexAQS/GoMACCS

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

Photos: Richard Marchbanks & Dan Welsh-Bon

Calculating Emission Factors





1.62 :

CO_2 (ppmv) to mass of fuel

- assumes fuel is 86.5% C

$$EF_{LAC}(gkg^{-1}) = \frac{Absorption(Mm^{-1})}{CO_2(ppmV)} \times \frac{1}{MAC(m^2 g^{-1})} \times f_{fuel}$$

7.5 ± 1.2 m^2 g^{-1}

Bond et.at. 2006

Uncertainty in EF_{LAC}

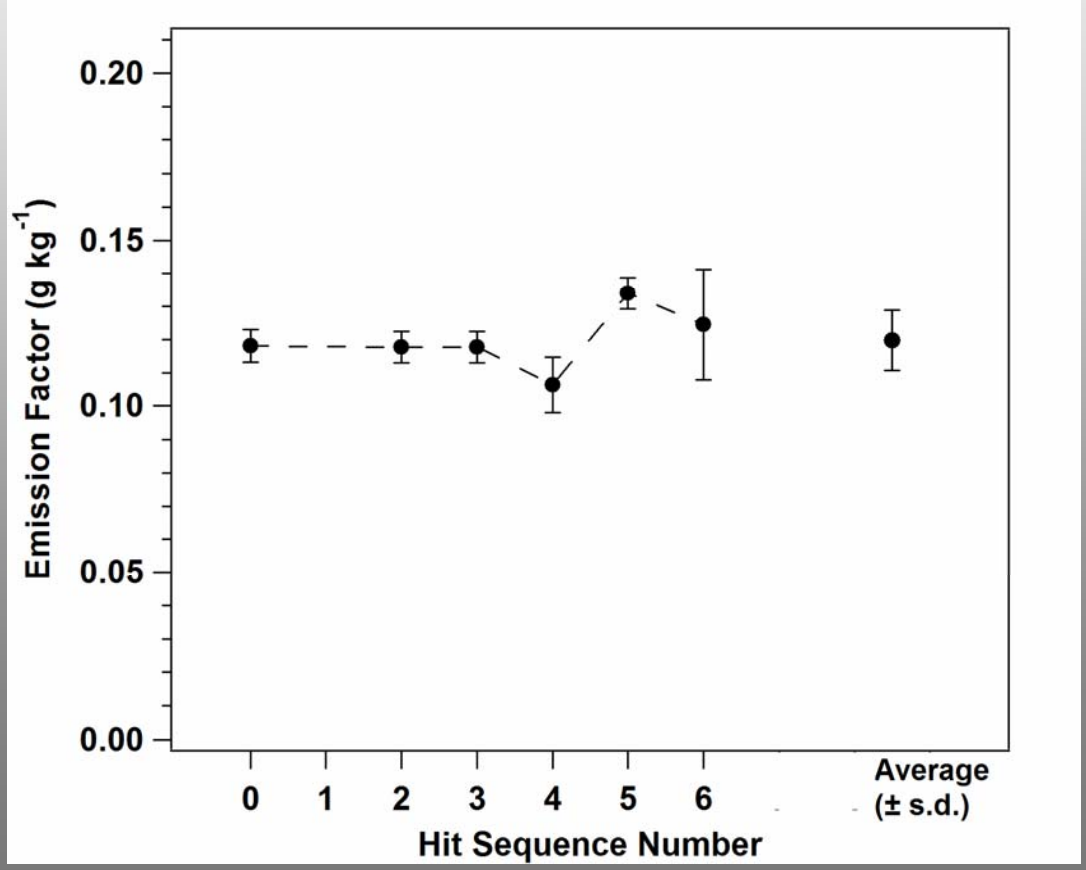
↓

± EF_{LAC} ~19%

- ± Absorption / CO_2 Slope: 7% (average)
- ± MAC: 15.5%
- ± Fuel Carbon Content: 1%
- ± Assumption that all fuel C → CO_2: 2%
- ± Precision of the EF_{LAC} Technique: 8% (will get to this)

Precision of the EF_{LAC} Method

- Patriot Encounter



Container ship at anchor

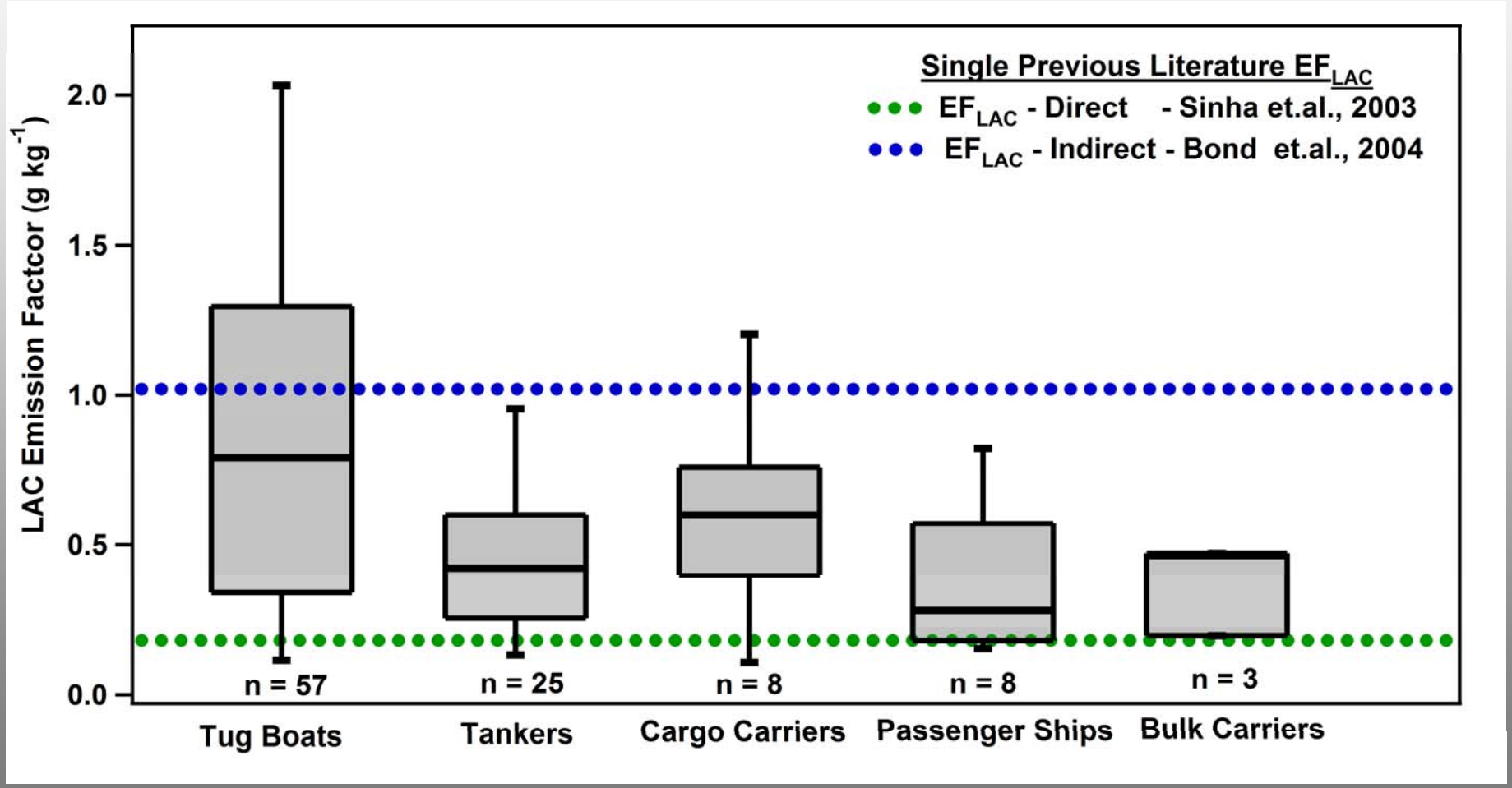
Assume constant output

8% precision:

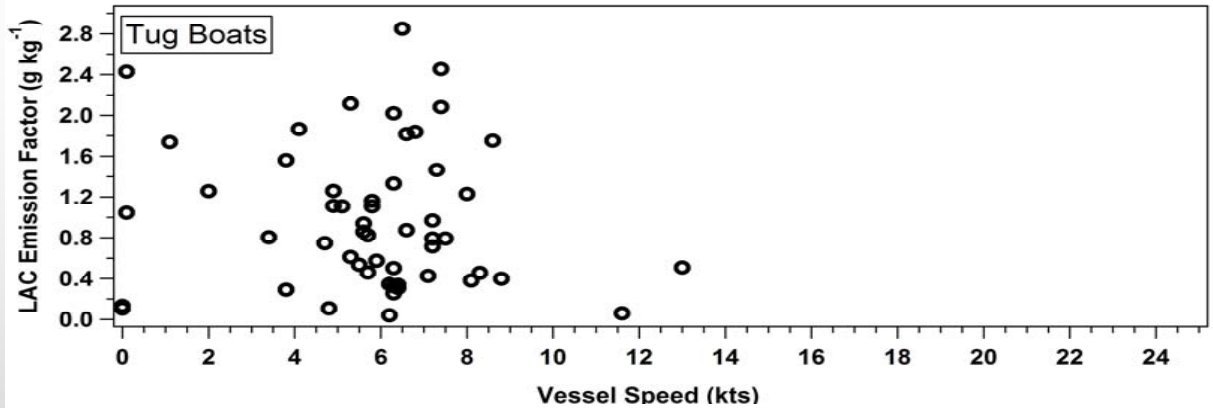
6 encounters, 150 minutes

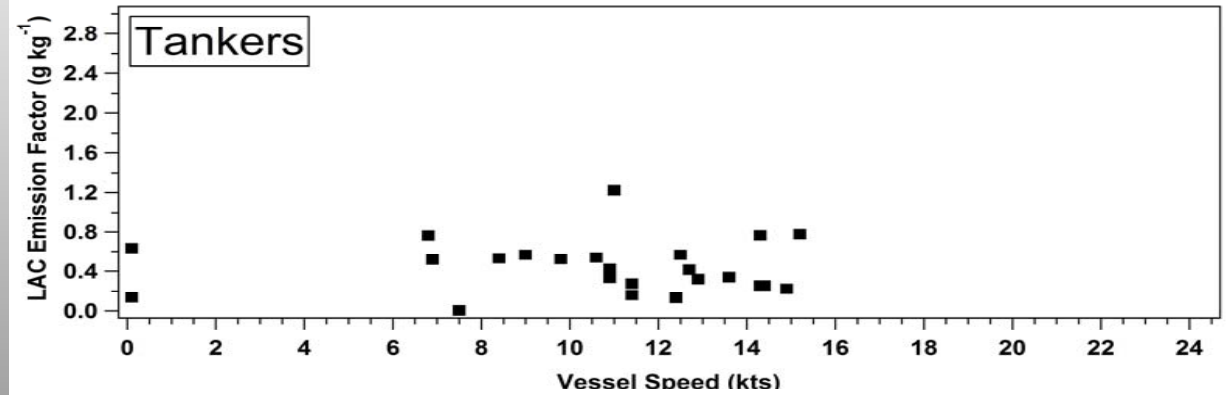
TexAQS LAC Emission Factors

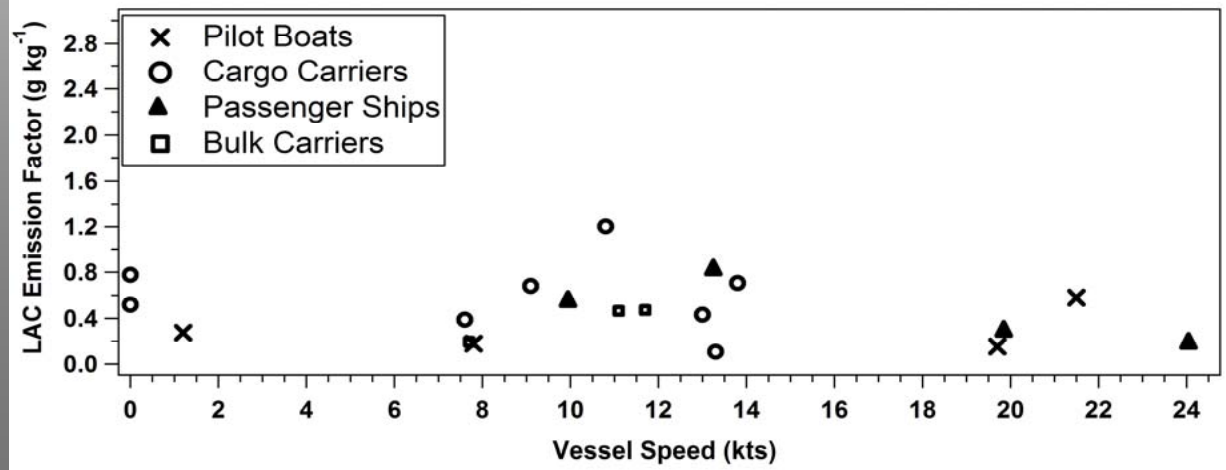
- 116 individual vessel plumes (15 yet to be identified)



EF_{LAC} vs Vessel Speed



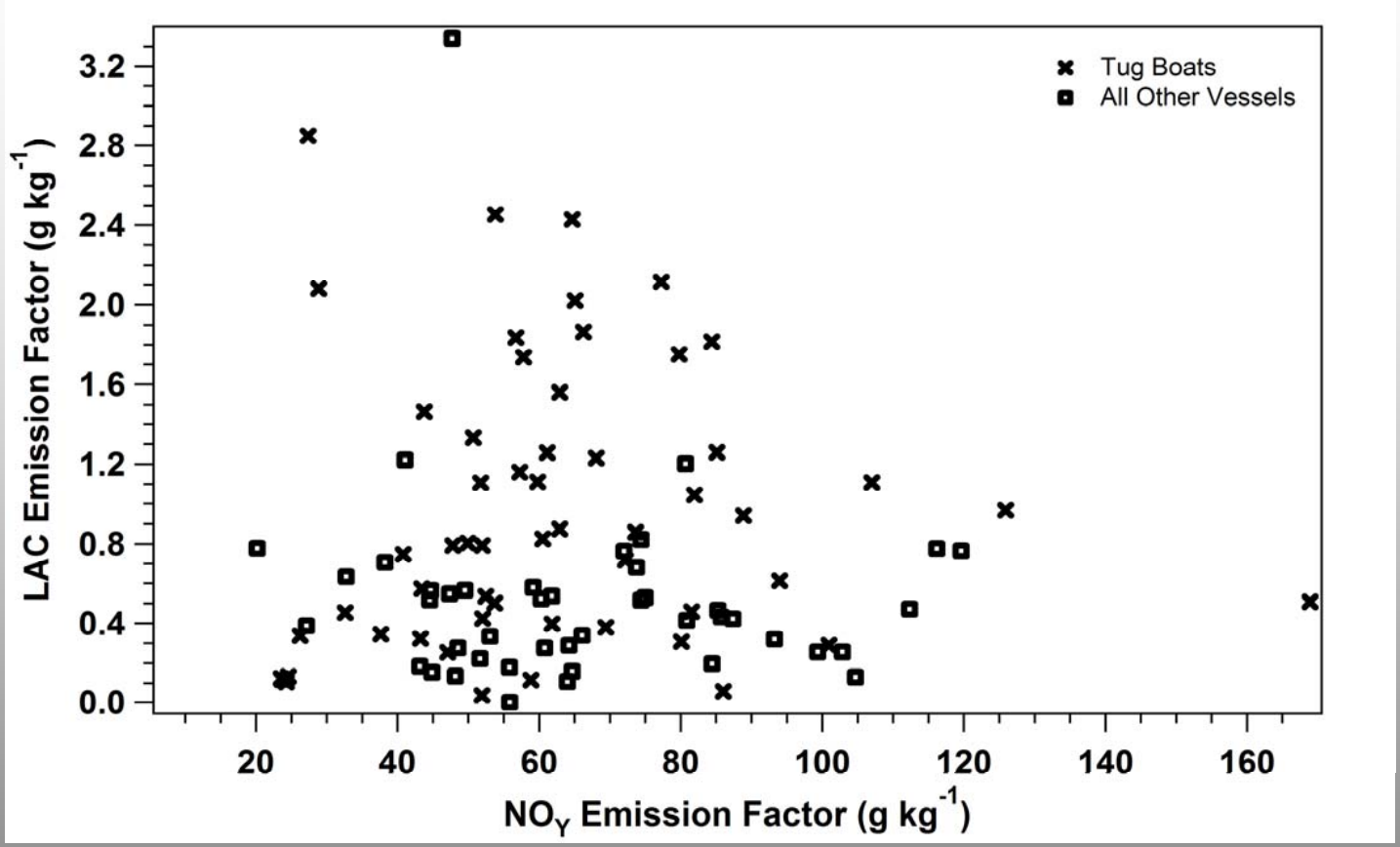




Lots of variability for Tug Boats.

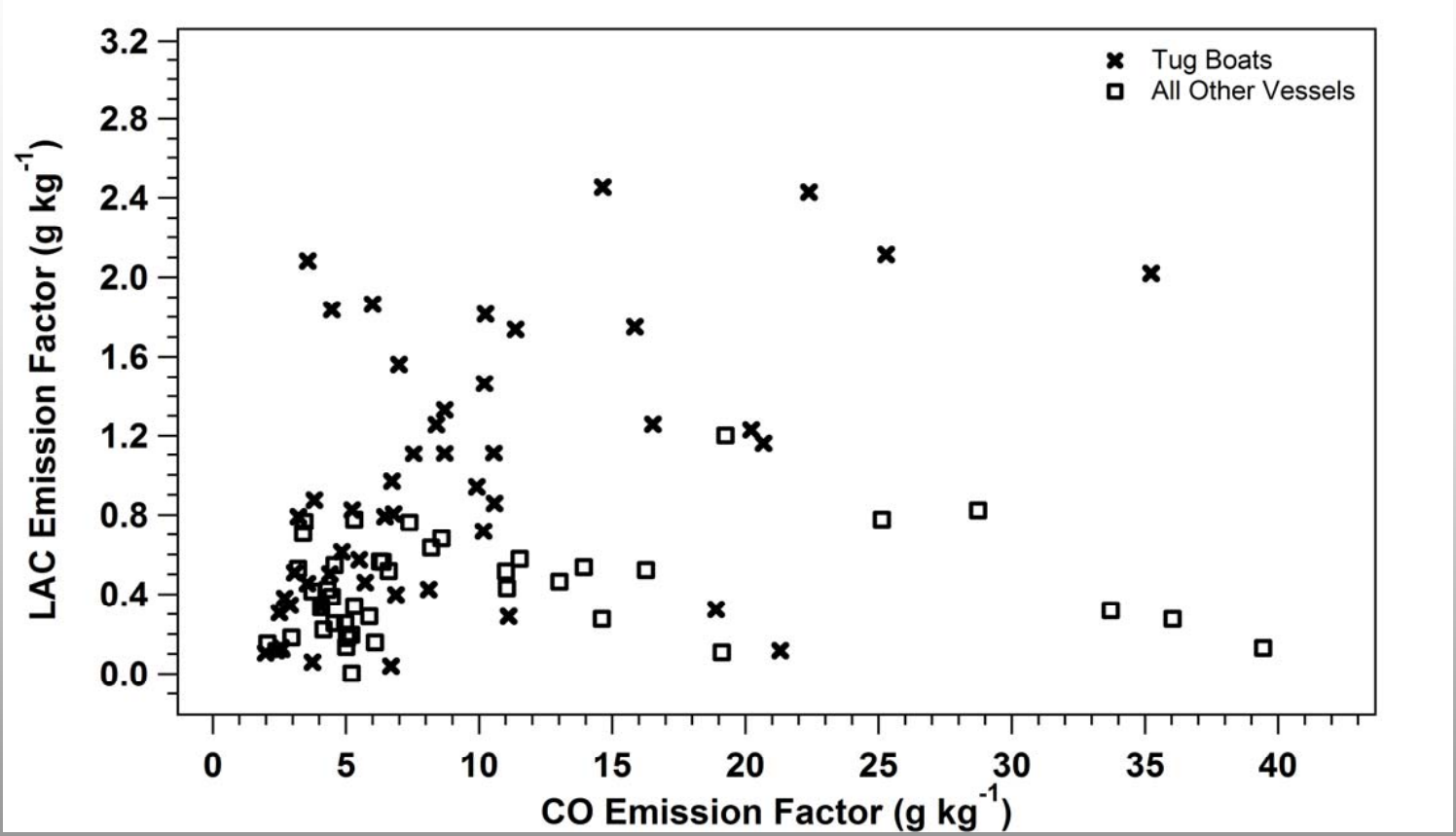
Less variability for other vessel classes.

EF_{LAC} vs Gas Phase EF_{NOY}



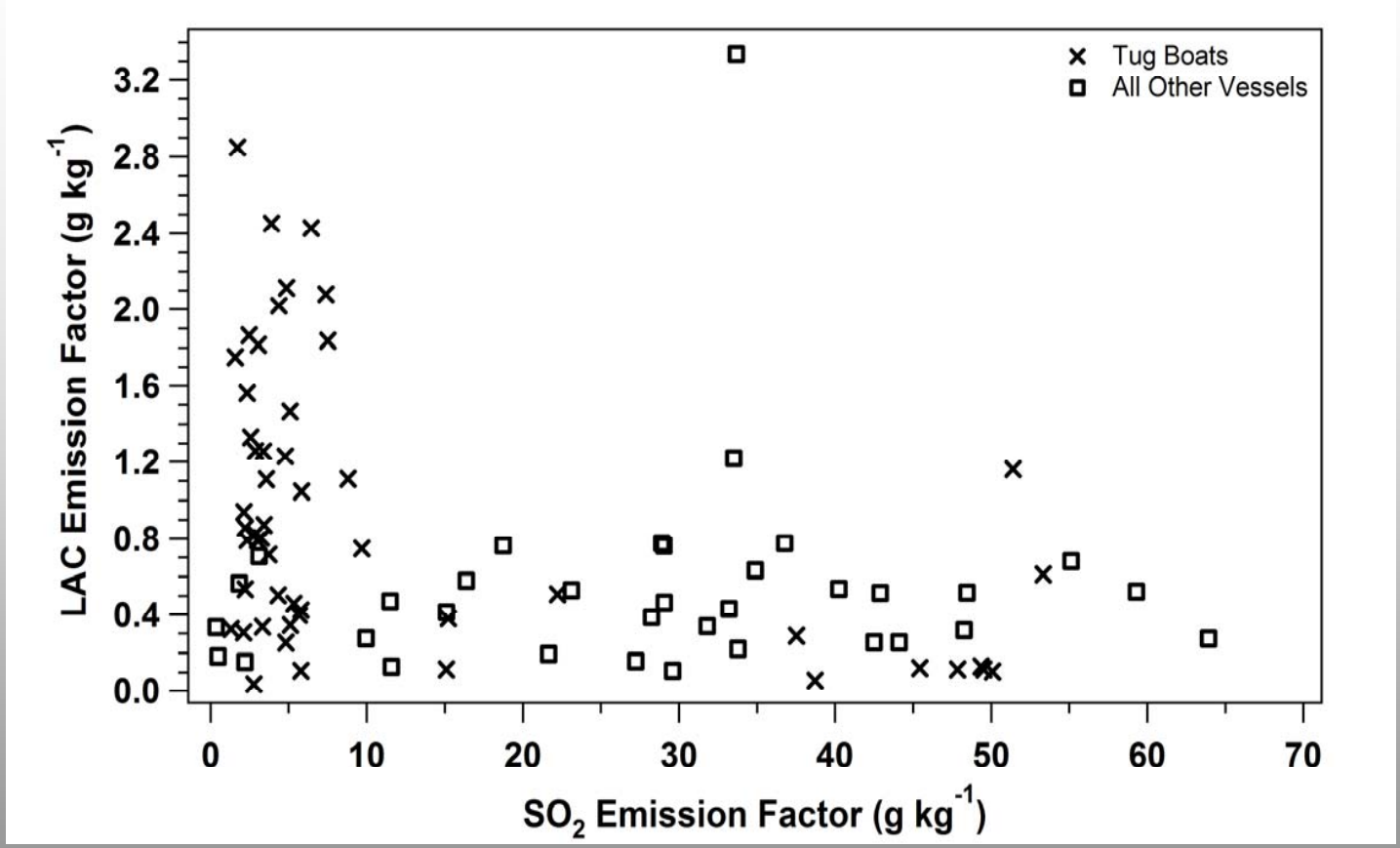
No Correlation

EF_{LAC} vs Gas Phase EF_{CO}



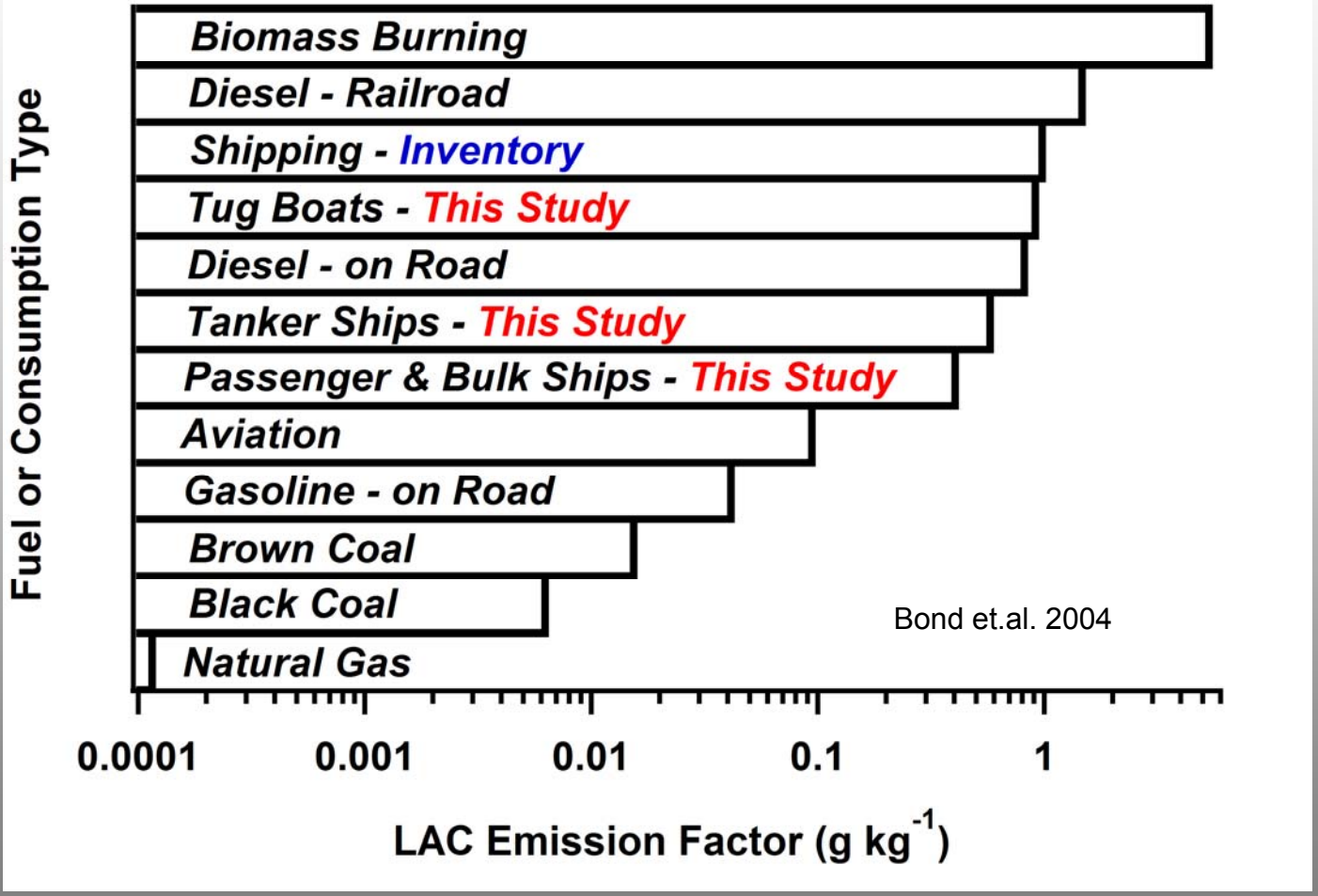
LAC Correlated to CO for Tugs

EF_{LAC} vs Gas Phase EF_{SO2}



Tug boats emitting lots of LAC with little SO_2

Comparisons to Other Fuels and Consumption Types



LAC in the Houston Area

- 2004 Fuel Usage : 0.13 Tg (from Eric Williams)
- Average EF_{LAC} = 0.85 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 → LOW μg g^{-1}(Docekal et.al., 1992)
  - Lead → HIGH μg 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

Docekal, B., Krivan, V., Pelz, N., 1992, Trace and Minor Element Characterization of Diesel Soot, Fresenius'Jounral of Analytical Chemistry, v343, #12

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