Optical, physical, and chemical characterization of marine Black Carbon

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Outline

- BC mass concentration measurement challenges
- instrument calibration verification
- BC/aerosol properties of interest and measurement methods
- sample conditioning
ICCT UCR linkage

- NRC Canada, with support from Transport Canada is contributing to the phase one of the ICCT UCR marine BC project
- The objective is to provide complementary data or support to the principle objectives of the ICCT UCR project
BC mass concentration measurement challenges

- All instruments measuring BC mass concentration do so indirectly, relying on knowledge of optical, physical, or chemical properties.
- Instruments are generally sensitive to interferences which depend on how they operate (underlying method and specific operating parameters).
- Manufacturers implement different calibration principles.
- A ‘bottled’ BC aerosol reference material does not exist.
- Impact of fuel type and engine load on BC characteristics and interferences not well known.
- Instrument contamination under harsh operating conditions possible (likely?)
Mitigating the measurement challenges

• instrument calibration verification before and after campaign using flame generated BC with known characteristics
• verification of BC optical, physical, and chemical properties as a function of fuel type and engine load
• quantification of co-emitted species
• explore exhaust condition strategies
Instrument calibration verification
Calibration verification against Thermal Optical Method

- Correlation to elemental carbon (EC) via thermo-optical method (NIOSH 5040)*

Production of BC
- miniCast burner
  - Multi-stage dilution
  - Size Cut and Splitting
    - cyclone

NIOSH 5040 filter collection
- Quartz Filter → MFC → Pump

Real-time mass measurement
- Real Time Instrument 1 → MFC → Pump
- Real Time Instrument 2 → MFC → Pump
- ...

Example of instrument comparison

- **NRC LII**: $y = 1.0916x$
- **AVL MSS**: $y = 1.1987x$
- **CU LII**: $y = 1.1026x$
- **CU MSS**: $y = 0.9314x$
- **CAPS (530nm)**: $y = 0.5277x$
- **CAPS (780nm)**: $y = 0.9164x$
Optical, physical, and chemical characterization
Characteristics of interest

- spectral variability of light absorbing properties
  - often expressed as Angstrom absorption exponent (AAE)
  - MEPC 67/INF.31 suggests AAE ~ 1 as a criteria for BC
- TEM ‘visual’ of particles
  - size, shape, compactness, maturity, coatings
- RAMAN spectroscopy
  - internal bond structures, graphitization, bound organics
- volatile coating mass
- composition of organic particles
- composition of all particles and gas phase
Spectral optical properties

- cavity attenuation phase-shift PM single-scattering albedo (CAPS PM$_{SSA}$)
  - extinction coefficient
  - total scattering coefficient
  - single-scattering albedo
  - 530, 660, 780 nm

- photoacoustic extinctioniometer (PAX)
  - absorption coefficient
  - total scattering coefficient
  - 375, 534, 870 nm

- angstrom absorption exponent
  - can be determined from multi-wavelength data
Quantitative TEM analysis

- primary particle size
- aggregate
  - size distribution
  - fractal structure
  - compactness
- internal structure
  - graphitic layer length and spacing
Qualitative TEM analysis

- particle maturity
- coatings
- other particles
  - solids
  - liquids
- particle collapse

SPA 45,000X

SP1 45,000X

SPA 50 nm

50 nm
microRaman surface analysis of BC particles

- spectroscopic technique used to observe vibrational, rotational, and other low-frequency modes in a material
- identifies internal structural features in carbon particles
  - bonding (sp² vs. sp³)
  - degree of graphitization
    - G – graphitic
    - D1-D4 – defects/disorders
- possible finger-print for different sources
Quantification of BC coating mass using DMA, CPMA, denuder, and CPC

• start with an aerosol of coated particles
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• start with an aerosol of coated particles
• size select particles using DMA
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• measure peak particle mass for size selected mass with CPMA and CPC
  o represents mass of particles with coating
Quantification of BC coating mass using DMA, CPMA, denuder, and CPC

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• strip particles of coating
Quantification of BC coating mass using DMA, CPMA, denuder, and CPC

- start with an aerosol of coated particles
- size select particles using DMA
- measure peak particle mass for size selected mass with CPMA and CPC
  - $o$ represents mass of particle with coating
- strip particles of coating
- measure peak particle mass for same size
- difference in mass is the coating mass
- can be done for a range of particle sizes
Sample conditioning
Sample conditioning

• brain storming ideas and looking for input from those with marine emission experience
  o dilution
  o heated dilution with evaporator tube
  o thermal denuder
  o thermal denuder with heated activated carbon
  o catalytic stripper
  o diffusion dryers/stripper which target particular gases that are problematic to instruments
Wrap up

• objective of this part of the campaign is to:
  o improve comparability of instruments
  o improve our understanding of marine engine generated BC particles and how they do or don’t change with fuel and load
  o help to understand any differences observed amongst BC mass concentration instrument
  o explore mechanisms to condition exhaust before measurement to improve measurement accuracy

• we welcome ideas, criticisms, reality checks!
Thank you

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