Combustion Aerosol Emission Measurements

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Overview

- With the objective of highlighting sources of discrepancies and uncertainties…
  - Combustion sources of aerosols
  - Characteristics of combustion aerosols
  - Measured properties – Inventory vs. Climate Modeling
  - Form of Carbon?
  - Measurement Issues
  - Sampling Issues
  - Illustrative Examples of Results

Combustion Sources of PM

- Mobile Sources
  - On-road and off-road vehicles
    - Cars, trucks, equipment (construction, lawn and garden, agriculture)
  - Non-road
    - Marine, rail, aviation
- Stationary Sources
  - Residential and commercial heating and cooking (fossil fuel, biomass, food)
- Open or Area Sources
  - Forest fires, open biomass burning (grass, agriculture waste)

Non-Combustion Sources

- Resuspended and windblown dust
- Biogenic sources (detritus, mould, spores)
- Sea salt
- Tire and brake wear
- Secondary formation

Characteristics of Combustion PM

- Mobile Sources
  - Gasoline fueled vehicles (MPFI engines)
    - Mostly OC (>70%)
  - Diesel fueled vehicles
    - 2-stroke engines 40-60% OC
    - 4-stroke engines 5-20% OC
  - In both cases, with low sulphur fuel, PM is >95% carbon

Characteristics of Combustion PM

- Changes due to advanced combustion and aftertreatment systems
  - PM controls:
    - Oxidation catalysts
      - Reduce organic carbon content of PM
    - Diesel particulate filters
      - Virtually eliminate carbonaceous particle emissions
      - Nucleation particles (hydrocarbon or sulphate) form
  - NO_X Controls:
    - Selective Catalytic Reduction (urea or ammonia)
    - Lean NO_X catalysts ?
    - NO_X absorbers ?
  - Direct injection spark ignited engines:
    - Higher PM emissions compared to MPFI engines
    - Similar to diesel PM

Characteristics of Combustion PM

- Stationary Combustion Sources
  - Natural gas
    - Very low PM emissions
    - 62% OC, 6% EC [1]
  - Oil (light and heavy fuel oil) [2]
    - PM mostly sulphate (>40% by mass, depending on fuel sulphur)
    - Heavy metal content higher in HFO emissions
    - TC content low (long residence time in combustion zone)
    - OC and EC approximately equal, <15% total carbon
  - Coal [3]
    - Varies greatly by source, fuel type

[1] NYSERDA Report 04-05. [2] Lee et al. 2002 [3] Bond, 1999, 2002

Characteristics of Combustion PM

- Open Sources
  - Forest fires
    - Flaming and smoldering: Lower BC/OC ratio
  - Grasses
    - mostly flaming: Higher BC/OC ratio

Primary and Secondary PM

- Combustion sources emit both primary PM and precursors to atmospheric formation of secondary PM
  - Ammonia, SO_X, NO_X
  - VOCs, semivolatile organics
- In many cases, emissions of precursors are greater than primary PM emissions

Measured Properties

- Emission Inventory Measurements
  - PM mass by gravimetry with or without particle size cut (TPM, PM_{10}, $PM_{2.5}$, PM_1)
  - Chemical characterization
    - Organic and elemental carbon (TOR or TOT, variations)
    - Ions (sulphate, nitrate, inorganic and organic ions, ammonium) by ion chromatography or capillary electrophoresis
    - Detailed organic composition
    - Metals

Measured Properties

- Climate Relevant Measurements
  - Light Absorption at various wavelengths
    - Aethalometer, PSAP, Photoacoustic, Optical Extinction Cell, Integrating Plate, Soot Photometers, …
  - Light Scattering at various wavelengths
    - Nephelometer, …

- Measured optical properties depend on particle chemistry, particle size, relative humidity, matrix gases

Particle Size and Number

- Particle Size Distributions
  - Aerodynamic or mobility diameter depending on instrument
  - SMPS, PCASP, FSSP, ELPI, cascade impactors
- Number Concentrations
  - Condensation Particle Counter (CPC)
- Chemistry of particles changes with size
- Measured size distributions depend on sampling conditions
  - Temperature, relative humidity, residence time

What Form is the Carbon?

- BC, Soot and EC are used interchangeably and loosely BUT they are not the same thing!
- Black carbon (BC)
  - Light absorbing carbon, microcrystalline graphitic form of carbon
- Elemental Carbon (EC)
  - Operationally defined by instrument
  - Some forms of EC are "blacker" than others
- Soot
  - Carbonaceous PM formed by combustion processes
- Organic Carbon (OC)
  - Operationally defined by instrument
  - Not the same as organic matter (OM)
  - Evidence suggests it can either scatter or absorb light, depending on chemistry

Measurement Methods

- BC measured by light absorption methods
  - Results are to some extent instrument dependent.
  - A number of studies have been published comparing methods, identifying issues and proposing approaches to address issues.
- OC and EC usually measured by thermal-optical methods
  - Reflectance (DRI, IMPROVE)
  - Transmittance (Sunset Labs, NIOSH)
  - Methods agree for TC, OC/EC split differs due to method of correcting for pyrolysis
  - Neither TOR or TOT work well with very dark filters

Sample Collection

- Dilution sampling is the preferred approach to acquiring PM samples from mobile and stationary combustion sources.
- Samples from open burning sources are usually collected in-situ, in the smoke plume at a distance from the source.
- Most stationary source emission measurements are made "in-stack" not by dilution methods.

Dilution Sampling

- Goal is to obtain an aerosol sample from a hot, wet, corrosive exhaust gas
  - representative of the aerosol as it is emitted in the real world
  - on a filter or presented to an instrument
  - measure the mass emission rate of the aerosol.
- Extractive or total exhaust sampling
- Sampling conditions (residence time, relative humidity, temperature) influence measurements of mass, number concentration, size distributions

Filter Sample Collection

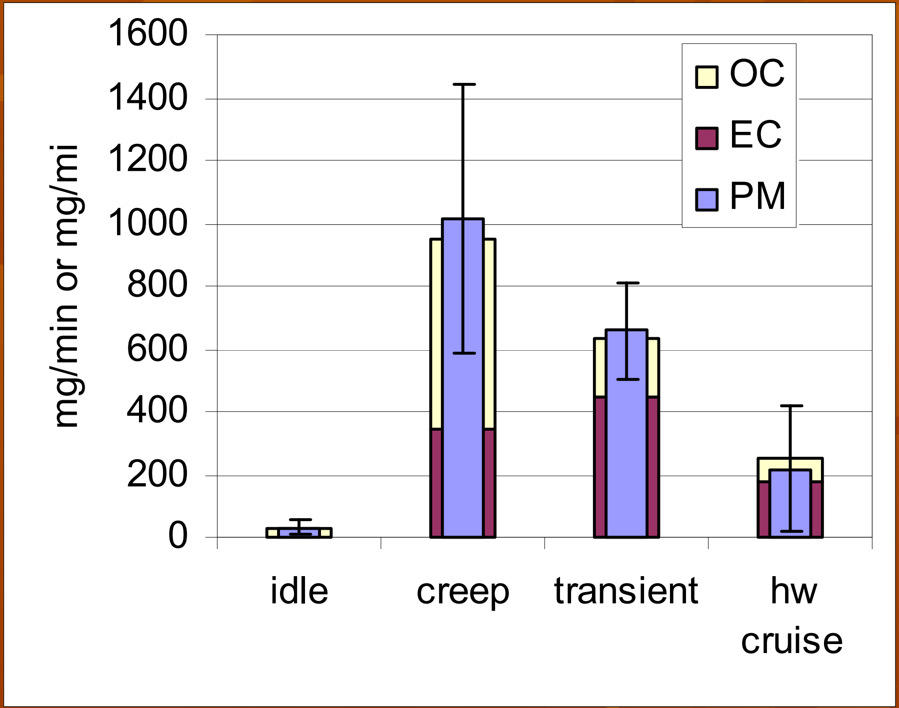
- Artifacts
  - Positive – adsorption of semivolatile material onto filter media or collected PM
  - Negative – loss of semivolatile material from filter media or collected PM
  - Depend on
    - type of filter media
    - sampling conditions (face velocity, pressure drop, sampling time)
    - Composition of sample stream
  - For mobile sources, many studies use regulatory prescribed sampling procedures
    - PM sample collection at 47 +/- 5 ^{o}C
    - How useful is this for atmospheric chemistry or climate modeling?

OC-EC Measurements

- TOR and TOT methods most common
- Sample collection on pre-fired quartz filters
- Primary filter collects PM, adsorbs semivolatile material from gas phase
- Artifact correction strategies
  - Ignore it
  - Assume a constant factor (based on what?)
  - Secondary quartz filter behind primary quartz filter
  - Secondary quartz filter behind a Teflon membrane filter
- Sample collection time is an important factor
  - Loss of material due to long sampling times and high pressure drops
- All these issues make integrating results from different studies into inventories very challenging.

Variability Within a Source

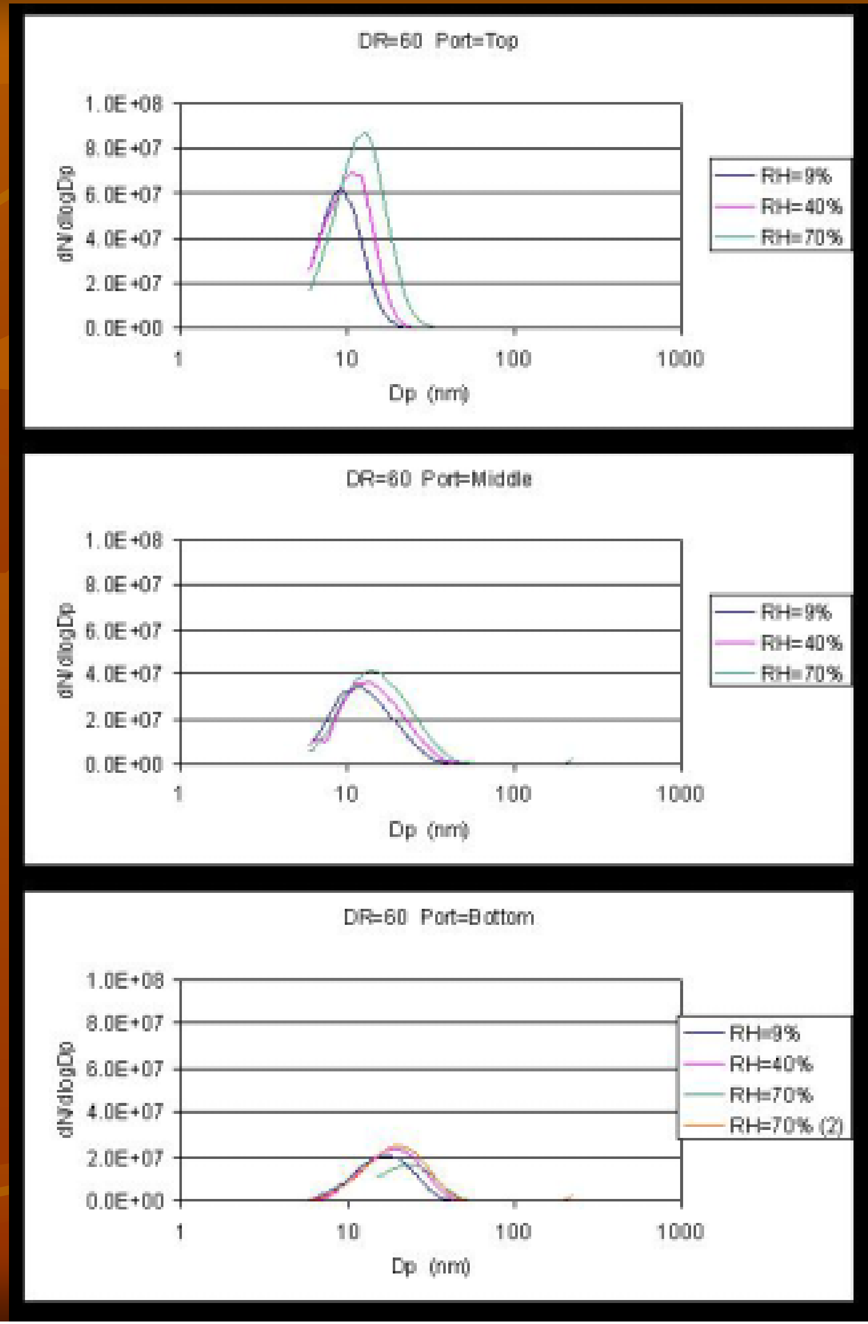
- Not all diesel engine combustion is the same
- HHDDTs operating in different driving conditions have very different emissions
  - EC/OC ratio varies from 0.2 to 4.5
- 4-stroke diesel generator EC/OC ratio relatively constant around 2.5
- 2-stroke diesel generator EC/OC ratio relatively constant at 0.75



Shah et al. ES&T 2004, 38, 2544-2550

Effect of Sampling Conditions

- Residence time and relative humidity affect measured size distributions and number concentrations
- Diluted PM emissions from small commercial boiler on #2 LFO.



What's Needed?

- Simultaneous measurements at the source of
  - PM mass emission rate ($PM_{2.5}$ or smaller)
  - Size resolved chemistry
  - Chemistry as complete as possible
    - EC, OC, ions, metals
    - Detailed OC characterization helps with source identification and apportionment
  - Optical properties: absorption and scattering at multiple wavelengths
  - Size distributions and number emissions
  - Other physical properties such as hygroscopicity
- Understanding of relative contribution of primary emissions and secondary formation in different regions
- Use of atmospheric chemistry and other models to take emissions from source to climate model grid input scale.

Recommendations

- Adoption of standardized protocols for OC/EC sample collection and analysis is critical to enabling integration of results from different studies to understand climate forcing, regional haze and air quality issues.
- A fundamental understanding of the relationship between optical and chemical properties of aerosols must be developed to support modeling activities to understand the role of aerosols in climate change.
- Support continued development of inventories that are technology-based to take advantage of information in air quality inventories and models and to better represent the variation of aerosol optical properties as a function source technology, chemistry and physical characteristics of aerosols.