# Size-Resolved Concentrations of Carbonaceous Aerosol in Marine and Urban Sites in Puerto Rico

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## Introduction

**Atmospheric particles are of environmental significance since they can cause reduction and distortion of visibility, degradation of buildings/monuments, climatic effects and health effects. Health problems are associated with the fine mode of aerosols (diameters, $D_p$, < 1 um in diameter) because they can penetrate deeper and are retained in the lungs for a longer period. One of the most problematic effects is in the climate because they alter the radiative balance of the planet. This effect is divided in two: direct and indirect effect. The direct effect is associated with the scattering and absorption of radiation by the particles. The indirect effect refers to the influence these particles have on cloud radiative properties. To understand the impact that atmospheric particles can have in the environment information is needed in terms of their physical (size, concentration) and chemical properties (composition) and of its sources. This study is focused in the size-resolved characterization of carbonaceous particles, organic (OC) and elemental carbon (EC) which compose a significant fraction of the submicron aerosol mass. OC mainly scatters solar radiation and contributes to a negative climate forcing (cooling). EC, the principal light-absorbing aerosol species, produces a positive climate forcing (warming).**

## Experimental

### Sampling Sites

**1. Facundo Bueso (FB), Río Piedras – Urban Site**

This site is located in the campus of the University of Puerto Rico – Río Piedras and it is representative of an anthropogenic affected location.

**2. Cabezas de San Juan (CSJ), Fajardo – Marine Site**

This location is exposed to the trade winds from the Atlantic Ocean about 80% of the year and is free of major land masses upwind, minimizing the effects of anthropogenic pollution.

### Instrumentation

**1. Aethalometer (Magee Scientific)**

This instrument measures BC concentrations in real time using a wavelength of 850 nm (10 minutes sampling frequency in Marine site; 5 minutes sampling frequency in Urban Site)

**2. Condensation Particle Counter (CPC) (TSI Inc., Model 3022A TSI)**

Aerosol online instrument that measures aerosol particle number concentration in air ($D_p$ 0.01 – 3 μm).

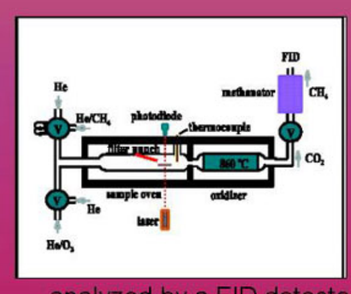
**3. Dekati Low-Pressure Impactor, DLPI**

A 13-stage cascade impactor that separates particles by size ($D_p$ from 10 um to 30 nm).

**4. OC/EC Analyzer (Sunset Lab Inc)**

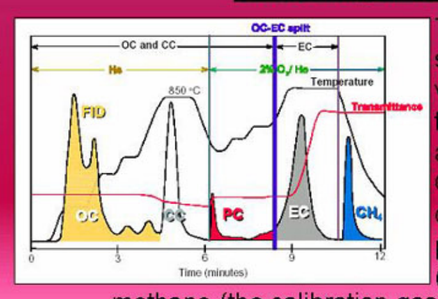
This instrument uses thermo/optical analysis for the determination of the aerosol concentrations of total carbon (TC), organic carbon (OC) and elemental carbon (EC). The method used is NIOSH 5040.

**1. Instrument Function**




The instrument uses He as the carrier gas in the first part of the analysis. With this, only OC is oxidized. Then using He/Ox as the carrier gas, the EC is then oxidized and analyzed by a FID detector. The filter is monitored during the analysis by a laser to correct for pyrolysis.

**2. Thermogram Analysis**



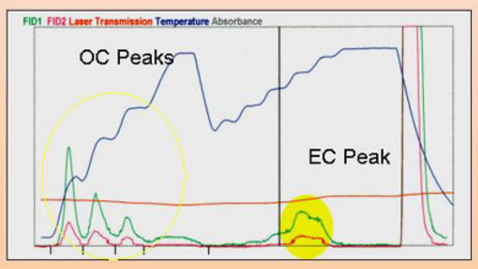

Thermograms show the more volatile species first. The peaks associated with OC, carbonate carbon (CC), pyrolyzed carbon (PC), EC and methane (the calibration gas) are shown in their designated region.

## Results

### Thermograms

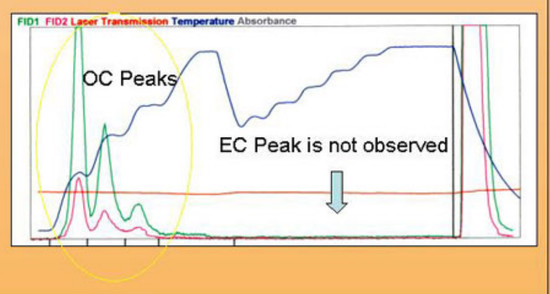
**In these thermograms the blue line represents temperature. In this representation the two temperature ramps are clearly shown by the different steps made by the instrument. The red line represents the laser signal. When the laser signal increases to the initial signal, the instrument designates the division between OC and EC signals. The green and pink lines represent the FID signal. The pink is the same as the green but at a lower frequency.**

#### Urban site (FB)




Typical thermogram of an urban site, in this case, FB. Defined by the green line, two areas are highlighted. At the beginning (left side of the graph), three distinctive peaks (most volatile ones) are observed. These represent the concentration of OC in the filter. The other area is composed of a broad peak. This is a typical signal for EC concentration.

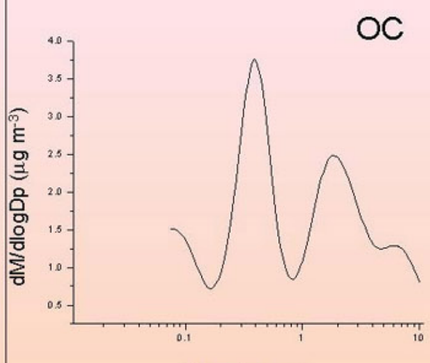
#### Marine site (CSJ)



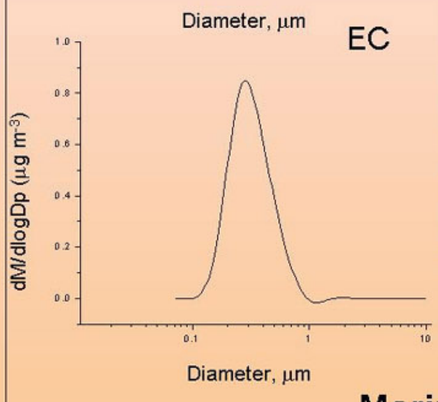

Representative thermogram of our marine site, CSJ. Here, the EC peak is not observed. Only OC concentrations are detected. This clearly show that under our sampling conditions this site was not affected by anthropogenic emissions (EC is a tracer for combustion).

### Size Distributions

OC




EC

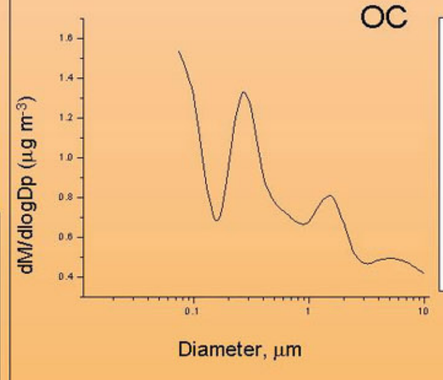


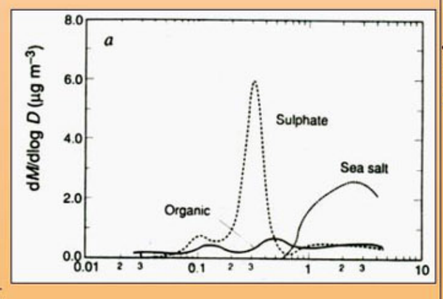

#### Urban Site

These are typical size-resolved concentrations in the urban site. The concentrations of OC show two modes in the coarse fraction and one in the fine. EC and OC in the fine mode have a similar size distribution with a maximum in the same diameter (~0.4 μm). The EC concentrations are always found in the fine mode. These similarities in the fine mode of both OC and EC concentrations suggests that they were produced by the same source (combustion). The OC in the coarse mode could come from primary biogenic particles and/or secondary organic aerosols.

#### Marine Site

OC

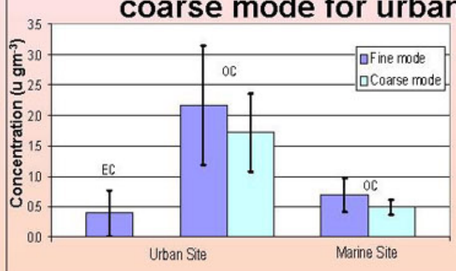



Only OC was found in the marine site (EC was absent). The size-resolved concentrations of OC represent the TC content in the sample. Comparing these results with a study performed in Puerto Rico in 1993 (*Novakov & Penner 1993*), we observe similar size distributions with OC being predominantly in the fine mode. In our sample displayed here, there is a peak in the fine mode larger than the peak in the coarse mode. The predominant mode for OC (fine vs coarse) was variable between samples. Meteorological data are needed for interpretation of these results.

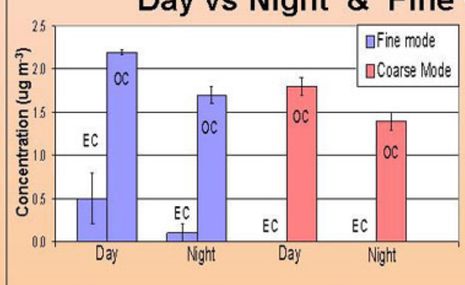
### Differences between Marine and Urban Sites

#### Average concentrations of EC and OC in fine and coarse mode for urban and marine sites



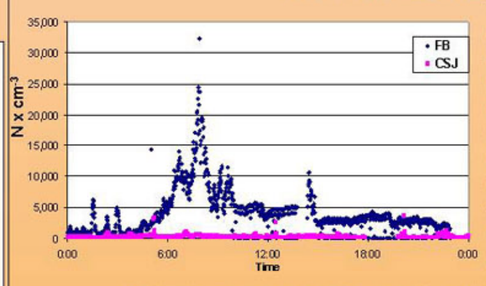

Differences between urban and marine sites are observed for EC and OC concentrations. EC concentrations are only observed in the urban site. Concentrations in the urban site are larger than in the marine site (TC urban: 4.3 μg $m^{-3}$; TC marine: 1.2 μg $m^{-3}$). Fine mode concentrations are larger in the urban site than in the marine site (2.6 μg $m^{-3}$vs 0.7 μg $m^{-3}$).

#### Average Urban Concentrations of EC and OC Day vs Night & Fine vs Coarse Mode



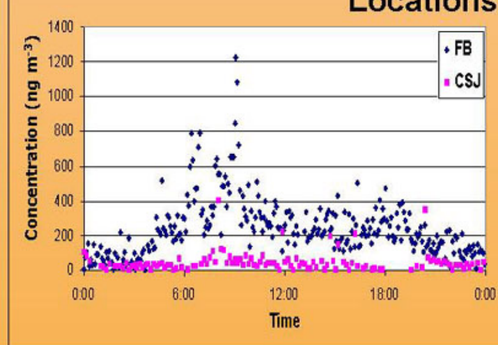

Daytime concentrations of EC and OC are larger than nighttime concentrations. Concentrations in fine mode are larger than in coarse mode for both day and nighttime cases. In the marine site, there was no significant difference between fine and coarse modes, but OC concentrations were higher during daytime.

#### Particle Number Concentrations in Urban and Marine Locations




The blue line shows the typical profile for particle number concentrations (24 h) at our urban location. The highest concentrations (33000 $cm^{-3}$) are observed around 6-9am (high traffic). Daytime concentrations are on average 5500 $cm^{-3}$ and 10400 $cm^{-3}$ during the traffic hours. Nighttime concentrations are on average 2000 $cm^{-3}$. CSJ average concentrations are 370 $cm^{-3}$.

#### BC Concentrations in Urban and Marine Locations




These results show the BC concentrations measured with the aethalometer for a 24-h period. As shown in the previous graph, the highest concentrations (1200 ng $m^{-3}$) are observed during the hours when the traffic is the highest (6-9am). Daytime concentrations are on average 330 ng $m^{-3}$ and during the traffic hours 470 ng $m^{-3}$. Nighttime concentrations are on average 130 ng $m^{-3}$ . CSJ average concentrations are 40 ng $m^{-3}$ .

## Conclusions

- The anthropogenic activity in Cape San Juan (marine site), based on the EC concentrations, was at low-to-non detected levels showing the suitability of this site for the measurement of aerosols of natural origin (marine) during trade wind conditions.
- CSJ OC concentrations showed no significant differences between day and night (average results in μg $m^{-3}$, Day = 1.3, Night = 1.1). The OC size distributions at CSJ were variable; therefore, it is not possible at this stage to determine the size fraction that contributes the most to this aerosol (meteorological data is been acquired to help in the interpretation of these results).
- The concentrations of OC in CSJ were lower than the concentrations of OC found in the urban location (urban: fine = 2.2 μg $m^{-3}$, coarse = 1.7 μg $m^{-3}$; marine: fine = 0.7 μg $m^{-3}$, coarse = 0.5 μg $m^{-3}$). The presence of EC (only in the fine mode) in significant concentrations, as high as 1.0 μg $m^{-3}$, is an indicator of the anthropogenic activity in the urban area under study. In the urban location, there were significant differences in EC and OC concentrations between day and night (Day: EC = 0.5 μg $m^{-3}$, OC = 4.6 μgm$^{-3}$; Night: EC = 0.1 μg $m^{-3}$, OC = 3.1 μg $m^{-3}$). EC was found with a consistent unimodal size distribution, peaking at 0.3 μm diameter. OC was found in both the fine and the coarse modes, showing that there was more than one source contributing to this species. The fine mode of both EC and OC comes probably only due to incomplete combustion of fossil fuel, the coarse OC mode due to biogenic material and/or secondary organic aerosols. The averaged concentrations of EC were greatest during day time (day = 0.5 μg $m^{-3}$; night = 0.1 μg $m^{-3}$).
- The ratio for EC/TC average concentrations is 0.16, typical number for an urban location *(U.S. EPA, 1996).*

## References

Novakov, T., C.E. Corrigan, J.E. Penner, C.C. Chuang, O. Rosario, O.L. Mayol-Bracero. Organic aerosols in the Caribbean trade winds: A natural source?, *J. Geophys.Res.102*(D17)21307-21313.1997.

Novakov, T. and J.E. Penner. Large contribution of organic aerosols to cloud condensation nuclei concentrations, *Nature, 365, 823-826. 1993*

United States Environmental Protection Agency, 1996, "Air quality criteria for particulate matter", EPA/600/P-95/001

## Acknowledgements

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## Future Outlook

- **Meteorological data will be used to interpret the results at both locations.**
- **Samples from both sites are going to be treated to determine the water-soluble organic content (WSOC). WSOC represents an important part of the aerosol water-soluble fraction. It can influence the surface tension of cloud droplets therefore affecting cloud condensation nuclei activity and thus having an impact on climate.**
- **Samples will also be analyzed using SEM/EDS to gain information in terms of the morphology and the elemental composition of the particles.**
- **The results that will be obtained from this study will provide insight regarding the possible sources of the aerosol under study and its impact on the environment (climate, health).**