Evaluation of Methods for Measuring Particulate Carbon in Precipitation

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1. INTRODUCTION

Black carbon (BC) and organic carbon (OC) affect the Earth's radiance balance and contribute to climate change. OC also contributes to the nutrient enrichment of surface water. The exact extent of these negative impacts is unknown because the life cycle of carbon aerosols and their removal process has not been studied extensively. Wet deposition is the major removal mechanism (~80%) of these aerosols. OC and BC are emitted from the same sources and their scavenging process could be linked. Some studies have focused on the monitoring of individual species but only one study has measured OC and BC in precipitation. The low concentration of BC in rain and the susceptibility of the OC analysis to contamination are the key challenges in developing a standard analytical method.

2. OBJECTIVE

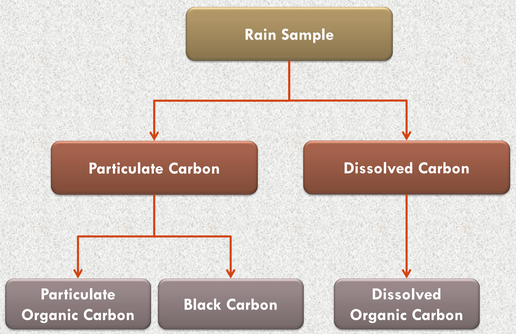
❖ Evaluate different analytical techniques to measure OC and BC in precipitation.

3. METHODS & RESULTS

❖ Carbon Fractionation
- BC and OC are separated in the particulate and dissolved fractions (Figure 1).

❖ Particulate carbon was measured using the following methods:
- UV/VIS Spectrophotometer
- Single Particle Soot Photometer (SP2)
- Thermo-Optical Analysis

Figure 1. Fractionation of Carbon in Rain



A. UV/VIS Spectrophotometer

- The light absorbance of the rain samples was measured and the BC concentration estimated using the absorbance of the laboratory-prepared reference material (Figures 2 and 3).
- The difference in the samples composition and low concentration of BC in rain make difficult to get accurate measurements.
- The uncertainty of this method is ±15 µg/L.

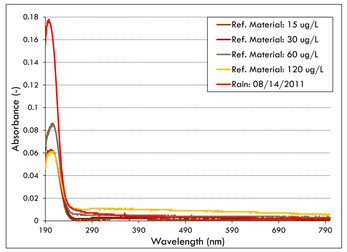


Figure 2. The light absorbance of the reference material and rain sample was measured from 190 to 790 nm. The absorbance of rain samples in the UV range is higher because it contains more OC. The absorbance of BC is almost constant in the visible range.

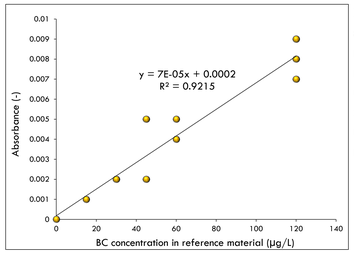


Figure 3. The absorbance of the reference material was measured at 550 nm. The uncertainty of the instrument is caused by the low concentration measurements.

B. Single Particle Soot Photometer (SP2)

- BC concentrations in rain samples and reference materials were measured with the SP2 by the Droplet Measurement Technologies Laboratory at Boulder, CO.
- The SP2 showed a good response to the BC mass in the reference material and rainwater; however, the results suggest losses during the analysis that have to be investigated (Figure 4).
- Particle size in the reference material is larger than in the rain sample (Figure 5).
- The low detection limit (10 ng/m^3 air), low sample volume, and rapid analysis are the major advantages of this method.

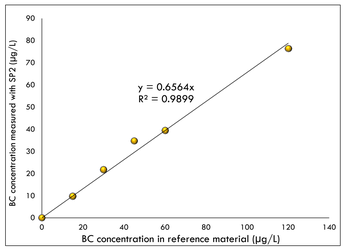


Figure 4. The response of the SP2 was evaluated by analyzing different concentrations of the reference material. The instrument was able to detect at least 66% of the BC mass.

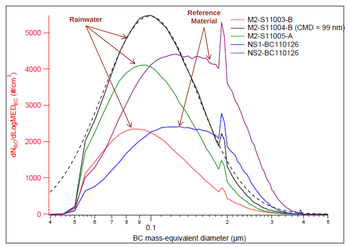


Figure 5. The BC mass-equivalent diameter was obtained from the SP2 analysis, assuming a density of 1.8 g/cm^3. The reference material shows most particles between 100-200 nm; the rainwater sample appears centered around 80-100 nm.

C. Thermo-Optical Method (OC/EC Analyzer)

- The OC/EC analysis requires filtration of the water samples through a series of quartz fiber filters.
- Filtration of reference materials showed that collection efficiency was lower than 20% (Figure 6).
- In order to make this method viable for water analysis, a coagulant aid must be added to the sample.
- Different compounds were evaluated considering the catalytic effects, organic contamination, and instrument damage.
- $NH_4H_2PO_4$ and $(NH_4)_2SO_4$ are the most suitable coagulant aids evaluated in this study (Figures 7 and 8).

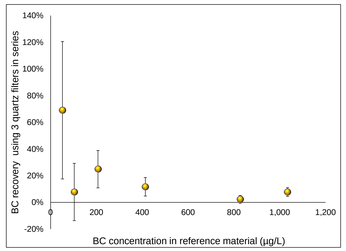


Figure 6. The collection efficiency of the 3 quartz fiber filters in series was less than 20%. The higher efficiency at low concentration could be caused by artifacts in the analysis.

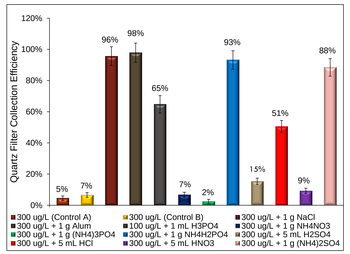


Figure 7. Evaluation of the quart filter collection efficiency and thermo-optical analysis using reference materials. The addition of ionic compounds and acids increased the efficiency compared with the control samples.

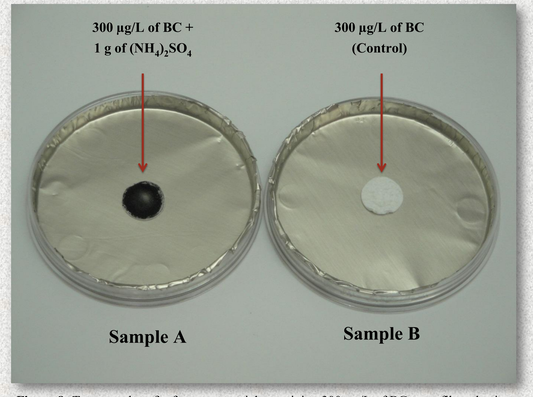


Figure 8: Two samples of reference material containing 300 µg/L of BC were filtered using a quartz fiber membrane. One gram of $(NH_4)_2SO_4$ was added to the sample A, but sample B contained no coagulant aid. The efficiency of collection of sample A was 88% compared with 5% for sample B.

4. KEY FINDINGS

❖ The UV/VIS spectrophotometer proved to respond to BC concentrations in water, but the resolution is not sufficient to get accurate concentrations.

❖ The SP2 is an excellent method for rainwater analysis because of its low detection limit and precision but the losses in the system have to be studied further.

❖ Thermo-optical analysis requires the addition of ionic compounds to increase particles size and collection efficiency.

❖ Published data using the Thermo-Optical analysis (without coagulant) may be suspect due to the low collection efficiency of the quartz filters.

5. ACKNOWLEDGMENTS

The author thanks the following institutions and individuals:
- The Illinois State Water Survey (National Atmospheric Deposition Program) for funding this research and provide precipitation samples.
- Odelle L. Hadley, U of California, Berkeley, for providing BC samples and suggestions for the analysis.
- R Subramanian, Droplet Measurement Technologies, for giving advise and performing the SP2 analysis.
- University of Puerto Rico at Mayaguez (UPRM)
- This poster was developed under the STAR Fellowship Assistance Agreement no. FP917370-01-0 awarded by the U.S. Environmental Protection Agency (EPA).