Carbonaceous Aerosol Removal During Precipitation Events: Climate Implications

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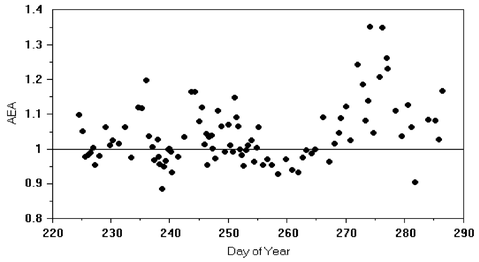
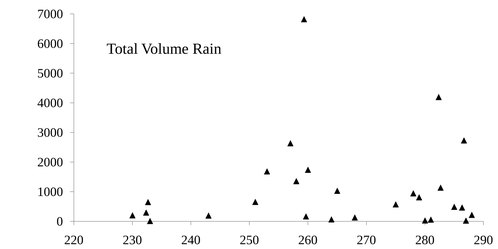
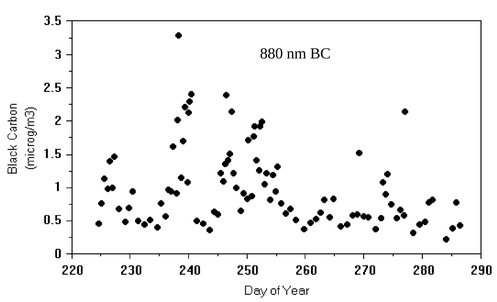
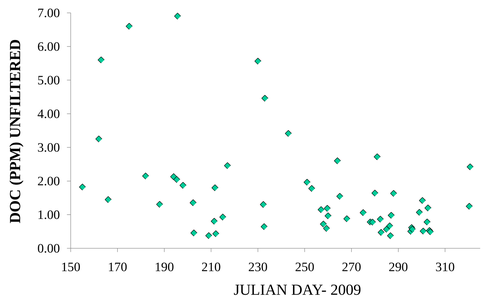
ABSTRACT

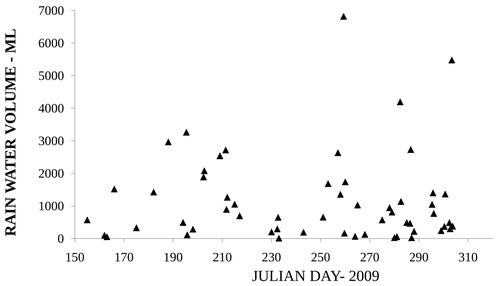
Atmospheric aerosols and their links to clouds are one of the main focus areas of the Department of Energy's Atmospheric Systems Research particularly as they affect regional climate. Aerosol lifetimes depend on the aerosol's ability to uptake water and grow to sufficient size to be either removed by gravitational settling, act as cloud condensation nuclei, or be removed by precipitation scavenging. The investigation of uv-visible absorbing aerosols is underway using a seven-channel aethalometer to evaluate the change in optical absorption during precipitation events. Angstrom absorption exponents (AAEs) are determined before, during, and after rain events to examine the changes in AAEs anticipated by removal of short-wave absorbing organic species (i.e. carboxylates) that are produced by the atmospheric oxidation of biogenic emissions (isoprene, monoterpenes, sesquiterpenes) or biomass buring. Black carbon data taken at the University of Arkansas at Little Rock and other sites clearly show that a significant amount of absorbing carbon is not removed during rain events, and that the organic matter removed is likely secondary organics from biogenic sources as indicated by lower AAEs. The determinations of dissolved organic carbon (DOC) and natural radionuclides in precipitation are also used to help examine the carbonaceous aerosol removal during rain events. This work suggests that carbonaceous aerosols will have different lifetimes depending on their aqueous solubilities (non-polar or polar) and their morphologies (i.e. organic coatings on non-polar materials or polar materials or as separate organic aerosol species). The work also indicates that equilibria may exist between the semi-volatile water soluble organics and aerosol surfaces that act to remove the oxidized organics while "black carbon" is not removed. The data are discussed in terms of the potential impacts of anthropogenic enhancement of secondary organic aerosols that are absorbing radiation and adding to atmospheric heating, and their anticipated lifetimes.

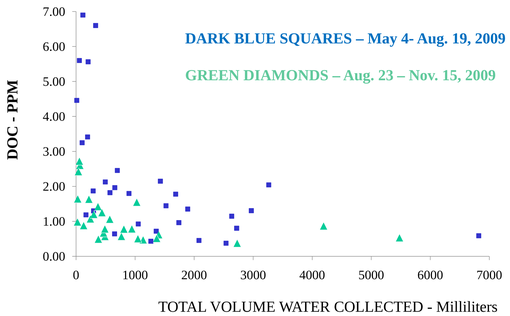






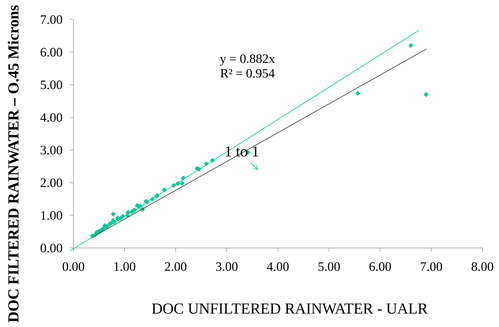




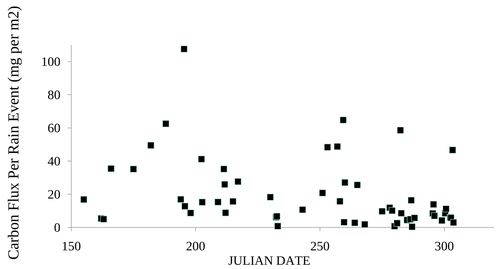


Angstrom Absorption Exponents – AAEs were determined every 12 hours using a seven wavelength aethalometer. The black carbon measurements reported by the aethalometer at (370, 470, 520, 590, 660, 880, and 950 nm) were converted to absorption (Mm^{-1}) by using the sigma values (A = σ * [BC]) reported by the manufacturer for the respective wavelengths (39.5, 31.1, 28.1, 24.8, 22.2, 16.6, and 15.4). The AAEs were calculated by an exponential fit for all 7 absorption measurements (ln A = - AAE * ln λ). An AEA of 1 (λ^{-1}) is an indication of diesel soots. An AAE greater than 1 indicates an enhanced absorption in the UV-blue region typically due to secondary organics or biomass burning derived compounds such as conjugated ketones, aldehydes, or carboxylic acids. An AAE less than one indicates enhanced absorption in the red or longer wavelengths and is typically due to inorganic dusts.

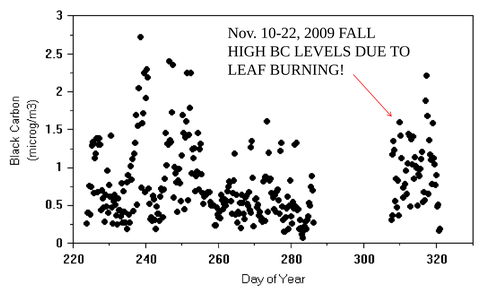
The data shown in the first three figures (left) show that AAEs are around 1 during periods of significant rain events, indicating that the aerosols were composed predominately of diesel or other forms of carbon soot. AAEs during dry periods tend to be greater than one indicating the presence of absorbing organics. This suggests that absorbing secondary organics that may be coating the soot aerosols are water soluble and are removed in the precipitation. Note that during rain events there is still a significant amount of black carbon remaining in the atmosphere. The three figures above show the amounts of DOC found in the rainfall collected during this period. Increased aerosol absorbance is seen during the fall due to aerosol production from local leaf burning practices in Saline and Pulaski Counties.



DOC in rainwater is found to be SMALLER THAN 0.45 microns in size. Ultrafiltration will be used to do further size fractionate the DOC to determine the molecular size distribution .

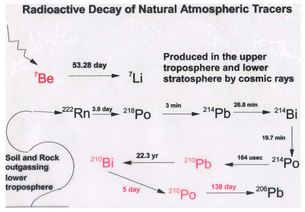


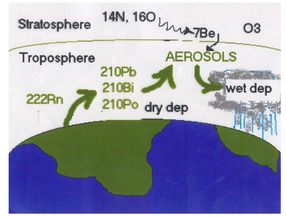
The mean flux of C in rainwater was 26 mg m^{-2} for the period May 15 – August 21, 2009 (Day 135-233). and 12 mg m^{-2} for the period of August 21, 2009 - November 15, 2009 (233-319) . This would account for about 1 ton of carbon deposited into the Lake Maumelle system during Spring/Summer precipitation events (assuming 13.9 square miles and a uniform deposition over that area). The reduction in rainfall DOC from Spring/Summer to late Summer/Fall is likely due to the reduction in biogenic emissions from the local deciduous trees. Carbon-14 determinations are planned to determine directly the contribution of biogenics to the rainwater DOC and the carbon deposition to surface waters.



ACKNOWLEDGEMENT

This work was conducted as part of the Department of Energy's Atmospheric Systems Research Program . This work was supported by the Office of Science (BER), U.S. Department of Energy, Grant No. DE-FG02-07ER64328 and Grant No. DE-FG02-07-ER64329 .





^{7}Be and ^{210}Pb in size fractionated aerosol samples collected at UALR.
^{7}Be and ^{210}Pb were determined using gamma counting at 477 keV and 46.5 keV, respectively. Blue text indicates data from rainy periods and red indicates dry periods . Activities are reported in mBq m-3.
Note that the all the activity for both of these species is in the submicron size range consistent with their attachment to 0.3 micron size particles as expected due to surface area considerations. Also note that no significant change in radionuclide size distributions was found for the rain events as compared to the non-rain events. The period of 212-215 and 216-219 showed some small growth. Rain samples examined for ^{7}Be on 209, 211, and 215 showed no detectable ^{7}Be in the samples. The sample on 217 showed some ^{7}Be activity (0.17 mBq per ml). There was no detectable ^{210}Pb.in any of the rain samples. Future work will include the use of samplers to collect larger rain volumes.

Date	July 27-30	July 31-Aug 3	Aug 4-7	Aug 7-10	Aug 10-13
Day of Year	208-211	212-215	216-219	219-222	222-225
7Be					
1 7.2-10	0.00	0.00	0.00	0.00	0.00
2 3.0-7.2	0.00	0.00	0.00	0.00	0.00
3 1.5-3.0	0.00	0.00	0.00	0.00	0.00
4 0.95-1.5	0.00	0.09	0.11	0.00	0.00
5 0.49-0.95	0.14	0.21	0.31	0.38	0.25
6 0.49-0.1	0.21	0.32	0.44	0.50	0.41
7 0.0-0.1	0.19	0.26	0.50	0.46	0.62
210Pb					
1 7.2-10	0.000	0.000	0.000	0.000	0.000
2 3.0-7.2	0.000	0.000	0.000	0.000	0.000
3 1.5-3.0	0.000	0.000	0.000	0.000	0.000
4 0.95-1.5	0.000	0.000	0.000	0.000	0.000
5 0.49-0.95	0.000	0.011	0.010	0.012	0.008
6 0.49-0.1	0.010	0.018	0.009	0.017	0.017
7 0.0-0.1	0.011	0.024	0.021	0.023	0.028
Ratios	**7Be to 210Pb**				
1 7.2-10	0.000	0.000	0.000	0.000	0.000
2 3.0-7.2	0.000	0.000	0.000	0.000	0.000
3 1.5-3.0	0.000	0.000	0.000	0.000	0.000
4 0.95-1.5	0.000	0	0.000	0.000	0.000
5 0.49-0.95	0.000	19.000	31.000	32.000	31.000
6 0.49-0.1	21.000	17.000	48.000	29.000	24.000

CONCLUSIONS

Significant amounts of DOC are found in rainwater samples collected using standard dry/wet deposition collectors at a roof top site at the University of Arkansas at Little Rock. Concurrent aerosol measurements indicate that some soluble aerosols are being taken up and removed by wet deposition. Low rainfall amounts can lead to significantly high DOC concentrations. Flux of DOC in rain waters vary significantly but mean values for Spring/Summer show a significant reduction in deposition when compared to late Summer/Fall likely due to the presence of soluble organic compounds produced from the oxidation of biogenic emissions (isoprene, monoterpenes, and sesquiterpene) from deciduous and pine forests in the region. The average flux of these oxidized organics into the local water shed is estimated to be approximately one ton of C to Lake Maumelle assuming a 13.9 sq. mile surface area. Comparison of unfiltered and filtered (0.45 micron) samples indicates that the organics in the rain water are small colloidal or dissolved organic molecules.

AAEs determined from aethalometer measurements show that there is significant black carbon that remains in the atmosphere during rain events. Rain events clearly remove a significant amount of UV and blue absorbing aerosols as indicated from the AAEs shifting from above 1 to 1 or below after rain events. Lower AAEs are anticipated for soots that have not been coated with absorbing organics. A significant amount of the aerosol in the submicron region not removed during rain events implies longer lifetimes for these hydrophobic compounds (e.g. soots). Coating of the aerosols with some hygroscopic materials leading to some water uptake and growth in particle size is indicated by the observation that some ^{7}Be is found in the larger size ranges during rainy periods,. However, this growth is clearly not leading to significant aerosol washout as indicated by the lack of ^{7}Be found in the rainwater. Future characterization of the organics in rain water along with the use of radiotracers should allow for better estimates of the semi-volatile oxidized organics and their role in aerosol absorption. The aerosol direct forcing will depend on their lifetimes and their removal by wet deposition needs to be assessed with regard to fractional aerosol removal per event. We will be pursuing aerosol "age" determinations and ^{14}C measurements on rain water DOC and aerosols in future work in CARES and GVAX.