J17.2 **Anthropogenic Perturbations of Biogenic Aerosols: Climate Impacts and Feedbacks**

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1. INTRODUCTION

Aerosols have been identified as a major uncertainty in climate forcing due to their direct and indirect effects on radiative balance. Both scattering and absorption of radiation is of concern in the direct effect, and aerosols acting as cloud condensation nuclei (CCN) leads to the indirect effect as the aerosols impact both cloud formation and type. Biogenic carbonaceous aerosol sources, as indicated by ^{14}C content, have been found to be major contributors in both primary and secondary organic aerosols on regional scales. The secondary organic aerosol precursors from biogenic emissions include isoprene, monoterpenes, and sesquiterpenes that react rapidly with OH, nitrate radical, and ozone. All of these oxidants are increased by the increased emissions of NOx from anthropogenic combustion sources. This chemistry will be reviewed and the evidence for these oxidized products contributing to enhanced aerosol absorption in both the UV and IR regions will be presented. The potential changes in these emissions due to climate change will also be addressed. These include earlier springs, longer growing seasons, and higher temperatures leading to enhanced emission rates anticipated with climate change. The biogenic secondary organic aerosols as sources of dissolved organic carbon in aqueous systems, including cloud droplets, will be discussed in terms of their surfactant properties. The potential for increased biogenic aerosols from agricultural activities (both directly and from burning of stubble) will also be briefly noted in terms of the possible development of larger bio-fuel production as an alternative energy source.

2. CARBON ISOTOPIC MEASUREMENTS

Radiocarbon measurements can distinguish between fossil fuel and non-fossil fuel carbon sources. All biogenic materials are labeled with a relatively constant initial $^{14}C/^{12}C$ ratio (Currie et al., 1982). The aerosols produced from fossil fuels contain no ^{14}C because their age is much greater than the 5730-year half-life of the ^{14}C. Therefore, the ^{14}C content in atmospheric aerosols provides a direct measure of the relative contributions of carbonaceous materials derived from fossil fuels and that derived from modern biomass sources. The ^{14}C content of atmospheric aerosols has been determined in samples collected in a number of areas over the years including recent papers from our group (Gaffney et al., 2008; Marley et al., 2009). A summary of these results, reported as the fraction of modern carbon contained in the aerosol samples, are summarized in Table I.

Table 1. The fraction of modern carbon in atmospheric aerosols reported for some urban areas (Marley, et al. 2009).

Location	Year	Modern C	Reference
Los Angeles	1982	0.3-0.5	Hildemann
Denver	1996-97	0.3-0.4	Klinedinst
Nashville	1999	0.7	Lewis
Houston	2000	0.5	Allen
Tampa	2002	0.8	Lewis & Stiles
Zurich	2002	0.6	Szidat
Launceston	2003-04	0.9	Jordan
Seattle	2004-05	0.6	Bench
Tokyo	2004-05	0.4-0.5	Takahashi
Phoenix	2005-06	0.5-0.6	Bench

The fraction of modern carbon in the Mexico City aerosol samples was found to be greater than 0.5 (> 50%) suggesting a large biogenic contribution to the carbonaceous aerosols even in this large urban area. Other measurements also have found significant biogenic sources particularly for the lower molecular weight and water soluble fractions of the carbonaceous aerosols (Aiken, et al., 2009). Thermal fractionation (OC/EC fractions) has indicated that elemental carbon, or higher molecular weight soots contain less modern carbon consistent with diesel soot being a major source in this megacity. Modern carbon aerosol content at the T1 (suburban/rural) site, located 18 miles north of Mexico City, was higher than observed in the city due to impacts from local grass fires. Biogenic impacts in these regions were measured up to 90%. These very high values may have been due to contributions from the burning of older trees that contained “bomb carbon” from nuclear testing in the 1950s. In any case data obtained from many areas, as indicated in Table 1, and other research that continues to be published is finding that we need to consider biogenic contributions to carbonaceous aerosols. Note that these organic aerosols have climate implications as they have significant enhanced absorption in the UV and IR that need to be considered.

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Table 1 also indicates that early measurements made in Los Angeles and Denver previous to the year 2000 showed lower modern carbon reflecting a higher percentage of fossil fuel derived materials (Hildeman *et al.,* 1994; Klinedinst and Currie, 1999). Later measurements have resulted in larger modern carbon fractions reflecting a lower percentage of fossil-derived absorbing carbon. This is also consistent with measurement taken on arctic haze in Barrow, AK that found values in the 0.3-0.4 range (Gaffney et al, 1984). Some reasons for this will be discussed in the next section on organic reactivity.

3. ORGANIC REACTIVITY AND AEROSOLS

It is important to recognize that the volatile organics that are emitted from fossil fuel sources and from biogenics have very different reactivity for OH, nitrate radical and ozone reactions. Since fossil fuel sources have been identified as “anthropogenic”, we have implemented control strategies for mobile and stationary sources of volatile organics and carbon monoxide in order to reduce ozone formation in urban regions. This has typically been through the use of catalytic converters for mobile sources and other methodologies for the reduction of aerosols and precursors. The sources of emissions for fossil and biomass fuels have been reviewed recently (Gaffney and Marley, 2009). With time, these control strategies have led to the reduction of reactive “anthropogenic” emissions that in the urban environments have led to the formation of indicator compounds such as peroxyacetyl nitrate (PAN). This has been found to lead to the reduction of PAN formation in Los Angeles, Mexico City, and other regions (Marley, et al., 2007). While the organic reactivity of motor vehicle emissions and energy related stationary sources has been reduced, the nitrogen oxide emissions have not been lowered. The result of the reduction in “anthropogenic” volatile organic carbon reactivity has led to slower production of ozone, reduced levels of PANs, and a transition from the formation of urban ozone to regional scale higher ozone concentrations.

A comparison of the reactivity for some common organics and natural hydrocarbons with OH is given in Table 2. The ozone and nitrate radical reactivity also follows the same general trend that isoprene (C5 hemiterpene), monoterpenes (C10), and especially the sesquiterpenes (C15) are very reactive and typically have lifetimes of minutes to hours in urban environments and hours to days in regional systems. The less reactive organic emissions tend to have hour to day lifetimes in urban environments, and day to month lifetimes on regional scales (Finlayson-Pitts and Pitts (2000).

In general, alkenes are more reactive than alkanes and aromatic hydrocarbons. This is due to the ability of OH radicals to add to the olefinic double bond. Also another trend is that groups that donate electrons to the double bond increase the reactivity. Thus, larger alkenes react faster than smaller ones. abstraction is the reaction mechanism for alkanes and those with more secondary and tertiary protons are more reactive. So again, larger molecules react faster. This same trend occurs in catalytic oxidation. Thus, the removal of reactive alkenes and larger alkanes predominates, yielding emissions of the much less reactive hydrocarbons than without catalytic converters. Note that isoprene, d-limonene and beta-caryophyllene are very, very reactive compared to the hydrocarbon emissions.

Table 2. Some OH reaction rates for hydrocarbons.

Alkenes	**rate x 10^{12} cm^{3} molecule^{-1} s^{-1}**
Ethene	8.5
Propene	26
1-butene	31
1-pentene	31
1-hexene	37
cis-2-butene	56
trans-2-butene	67
2-methyl-2-butene	87
2,3-dimethyl-2-butene	110
2-methylpropene	51
Cyclohexene	68
1,3-butadiene	67
2-methyl-1,3-butadiene(isoprene)	101
Limonene	171
beta-caryophyllene	collisional
Alkanes	
Ethane	0.03
n-Butane	2.5
Cyclohexane	7.4
Others	
Acetylene	0.08
Benzene	1.3

(Finlayson-Pitts and Pitts, 2000)

Oxidized organics are typically less reactive with OH, nitrate radical, and ozone, as in most cases they react by abstraction and are therefore more like small alkanes in terms of reactivity. Unless they are photochemically reactive, their lifetimes are typically longer. For comparison, at an OH radical concentration 1.0 x 10^{6} molecules per cc (typical of an urban environment) the lifetime of ethane is 43 days, ethene is 1.4 days, and cis-2-butene is 5 hours, while the biogenic hydrocarbons have lifetimes of minutes to hours. Indeed, the sesquiterpenes are so reactive with OH and ozone that they are typically very difficult to measure directly in the atmosphere and have to be inferred by monitoring the reaction products as marker compounds.

As we increase controls on the emissions from fossil fuel sources, we are lowering the overall atmospheric hydrocarbon reactivity. This has the effect of lowering ozone formation rates as well as yielding oxidized secondary organics at slower rates, thus lowering the secondary organic aerosol formation rates from these sources. At the same time the nitrogen oxide levels have not been reduced, so that the oxidation rates of the biogenics, which as noted are very reactive, will likely increase.

These considerations, as well as the fact that in many places the burning of biomass materials including wood, leaves, trash, and agricultural burning, is on the rise, all support an increasing fraction of biogenic carbon impacting the atmosphere in the formation of aerosols and atmospheric pollutants. These anthropogenic biomass burning practices are in many cases directly impacting the planet. While forest fires and biogenic hydrocarbon processes are natural, they also are likely being impacted indirectly by anthropogenic factors. These include the increases in carbon dioxide that act to “fertilize” plant growth and from climate change impacts including warming and precipitation changes that can lead to enhanced emissions of biogenic hydrocarbons, as well as earlier springs and longer growing seasons that lead to increases in brush and forest fires.

4. ORGANICS IN PRECIPITATION

Precipitation samples were collected at the University of Arkansas at Little Rock on the roof-top of the Science Lab Building during 2009 using a wet-dry collector with an automated sampler. Over 85 inches of rainfall occurred at the site during the year 2009. At the same time a seven wavelength aethalometer was operated to obtain Angstrom absorption exponents (AAEs) as well as aerosol black carbon concentrations. An AAE of 0.9 to 1.0 is typical for diesel soot (NIST standard). AAEs higher than 1.0 indicate the presence of UV absorbing compounds such as conjugated carbonyls or humic-like substances that are produced from biogenic volatile organic reactions with OH and ozone (Marley et al., 2009). The area near Little Rock is heavily forested with deciduous (isoprene emitting) and coniferous (monoterpene emitting) trees. Shown in Figure 1 are the aerosol AAEs, the total rainwater volume collected and an estimated aerosol black carbon concentration obtained using the 880 nm channel of a seven wavelength aethalometer.

Total dissolved carbon was measured using a Shimadzu DOC analyzer before and after the rainwater samples were filtered through a 0.45 micron membrane filter. The results are given in Figure 2. The comparison of unfiltered and filtered rainwater indicates that the organics in the rainwater samples are small colloidal or dissolved organic molecules. Analysis of the samples using mass spectrometry finds that the molecular weight of the dissolved organics is likely less than 500 daltons. A comparison of the reaction products of ozone with beta-caryophyllene with the dissolved organics have found them to be of similar molecular weight. These results indicate that a significant amount of the dissolved organics in the rainfall are due to low molecular weight oxidation products of biogenic hydrocarbons.

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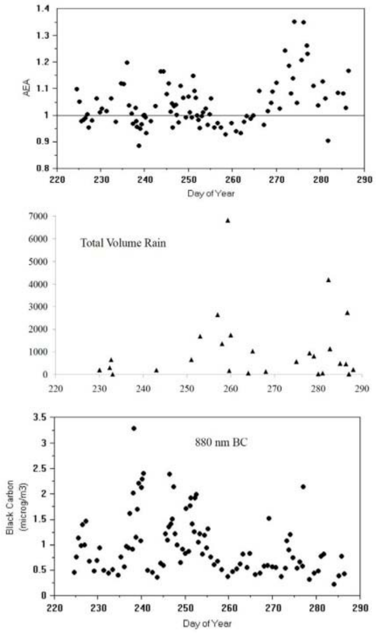

Figure 1. Angstrom absorption exponents (AAEs), rain water volume, and black carbon concentrations measured at UALR using a seven-wavelength aethalometer (Magee Scientific).

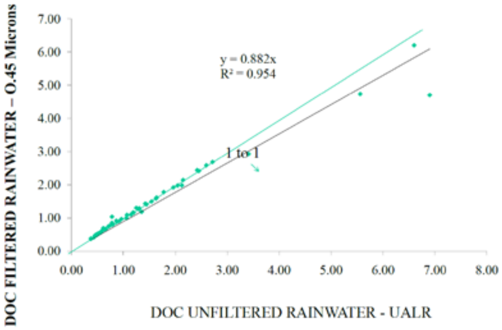

Figure 2. Relationship between total carbon and dissolved organic carbon (DOC) concentration less than 0.45 micron in rainwater samples. The green line is 1 to 1 line. Note that the high DOC values were for very light rainfall periods and may include some pollen.

The black carbon concentrations and the AAEs determined from aethalometer measurements show that there is significant carbon that remains in the atmosphere during rain events. Rain events clearly remove a significant amount of UV and blue region absorbing aerosols leaving behind the black carbon, as indicated from the AAE shifting from above 1 to 1 or below after rain events. Lower AAEs are anticipated for soots that have not been coated with secondary organics from biogenic or anthropogenic VOC oxidation.

A significant amount of the carbonaceous aerosols in the submicron region is not removed during the rain events and this will lead to longer lifetimes for these hydrophobic compounds (e.g. soots). It is likely that partitioning of semi-volatiles between the surfaces of aerosols and water droplets is occurring, thus allowing for the removal of the oxidized organics and the observed lowering of the AAEs to the base diesel values during rain events. It also indicates that the remaining black carbon would be expected to have longer lifetimes and be transported over much longer distances than the oxidized reaction products.

There are very few measurements of ^{14}C in DOC in rainwater (Avery et al., 2006). However, the few that have been reported in coastal North Carolina have found 76-96 % modern carbon. Again, this is consistent with a biomass source for the soluble organic compounds in the rainwater. These results indicate that these organics will likely impact rain and wet aerosols and may also act as surfactants, either increasing or decreasing uptake of other organics and water to aerosol surfaces. It should be noted that the organics produced from “quenched” fires or open burning will likely be a mix of oxidized compounds that will look chemically like those produced from the low temperature atmospheric oxidations by OH radical and other oxidants in the troposphere during transport. Thus, the levels of DOC species in rainwater also need to be examined in future studies.

5. BIOFUEL PRODUCTION IMPACTS

The production of biofuels anticipated by increased pressures to lower the use of foreign fossil fuels will likely have impacts with regard to biogenic aerosol formation and the presence of dissolved organics in rainwater. If ethanol use in motor vehicles is increased, the increased production of acetaldehyde, ethane, and formaldehyde emissions is likely (Gaffney and Marley, 2009). Both formaldehyde and acetaldehyde are air toxics and formaldehyde is quite water soluble and will likely distribute into rain and wet aerosols. Condensation reactions of this compound may also occur. These fuels also produce more NOx as they burn at higher temperatures. Higher levels of formaldehyde and NOx will enhance ozone production and that will in turn act to maintain or enhance regional ozone and natural hydrocarbon oxidation and secondary aerosol formation. These systems are linked and there will be feedbacks in the climate and air quality systems that may seem to be tied to natural sources but are indeed linked to anthropogenic fuel use.

If sugar cane is used for ethanol production the associated current agricultural burning practices need to be reexamined. The burning of sugar cane debris and other agricultural burning of crop debris for other biofuels would likely increase significantly if we are to rely on this as a fossil fuel substitute. There are also likely feedbacks into the water systems that may not currently be considered if increases in oxidized organics are added into our precipitation and water cycle.

6. FINAL COMMENTS

Future work on the organics in rain water along with radiotracers should allow for better estimates of semi-volatile oxidized organics and their role in aerosol absorption. The overall oxidation of organics from either biogenic or anthropogenic sources lead to the formation of smaller oxidized products and ultimately carbon dioxide and water. By using carbon isotope ratios (^{13}C/^{12}C and ^{14}C/^{12}C) important information can be obtained regarding the source of atmospheric hydrocarbons. There are also significant variations of biogenic emissions of volatile organics on a seasonal basis, and these can be very useful in examining the relative contributions of biogenic versus anthropogenic carbon sources since fossil fuel use should not have such a seasonal variation. Continued work is needed in this area along with the use of separations to size and chemically separate classes of compounds to evaluate the sources of various atmospheric hydrocarbons.

Climate change may lead to enhanced production of biogenic secondary aerosol and soluble organic compounds produced from the oxidations of isoprene, monoterpenes, and sesquiterpene emissions from deciduous and pine forests and in-turn these compounds have UV and IR absorption that may impact radiation balance on regional scales. The input of DOC from rainwater into surface waters can be important on regional scales. For example, for the data presented in Figure 1, the flux of these oxidized organics into Lake Maumelle (Little Rock water source) is estimated to be approximately one ton of C on an average rain event basis (assuming a 13.9 sq. mile surface area).

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5. REFERENCES.

Aiken, A.C., B. de Foy, C. Wiedinmyer, et al.,2009. Mexico City Aerosol Analysis during MILAGRO using High Resolution Aerosol Mass Spectrometry at the Urban Supersite (T0). Part 2: Analysis of the Biomass Burning Contribution and the Modern Carbon Fraction. Atmos. Chem. Phys. Discuss., 9, 29515-25981.

Allen, D., 2001. Gulf Coast Aerosol Research and Characterization Program (Houston Supersite). Progress Report, August 2001, Environmental Protection Agency Technology Transfer Network Ambient Monitoring Technology Information Center. Houston Supersite Project Information. http://www.epa.gov/ttnamti1/houprog.html.

Avery, G.B, Willey, J.D. and Kieber, R.J. 2006. Carbon isotopic composition of dissolved organic carbon in rainwater: Terrestrial and Marine Influences. Atm. Env. 40, 7539-7544.

Bench, G., Fallon, S., Schichtel, B., Malm, W., McDade, C., 2007. Relative contributions of fossil and contemporary carbon sources to PM 2.5 aerosols at nine Interagency Monitoring for Protection of Visual Environments (IMPROVE) network sites. Journal of Geophysical Research 112, D10205, doi:10.1029/2006JD007708,2007.

Currie, L.A., Klouda, G.A., and Gerlach, R.W., 1982. Radiocarbon: natures tracer for carbonaceous pollutants. In Cooper, J.A., Malek, D., (Eds.), Proceedings of the 1981 International Conference on Residential Solid Fuels: Environmental Impacts and Solutions. Oregon Graduate Center, Beaverton, OR pp 365-385.

Finlayson-Pitts, B.J. and Pitts, J.N. 2000. Chemistry of the Upper and Lower Atmosphere, Academic Press.

Gaffney, J.S., R.L. Tanner, and M. Phillips, 1984. Separating Carbonaceous Aerosol Source Terms Using Thermal Evolution, Carbon Isotopic Measurements, and C/N/S Determinations. The Science of the Total Environment, 36, 53-60.

Gaffney, J.S. and. Marley, N.A., 2000. Alternative Fuels, in Air Pollution Reviews: Volume 1. The Urban Air Atmosphere and Its Effects, P. Brimblecombe and R. Maynard, eds., Imperial College Press, London, U.K., Chapter 6, pp 195-246.

Gaffney J.S. and Marley, N. A. 2009. The Impacts of Combustion Emissions on Air Quality and Climate: From Coal to Biofuels and Beyond" Atmos. Env. 43, 23-36.

Gaffney, J.S., Marley, N.A., Tackett, M., Gunawan, G., Sturchio, N.C.. Heraty, L., Martinez, N., Hardy, K. 2008. Biogenic carbon dominance based on 13C/12C and 14C measurements of total carbon at T-0 and T-1 sites during MILAGRO. Paper J1.1 AMS National Meeting, New Orleans.

Hildemann, L.M., Klinedinst, D.B., Klouda, G.A., Currie, L.A., Cass, G.R., 1994. Sources of urban contemporary carbon aerosol. Environmental Science and Technology 28, 1565-1576.

Jordan, T.B., Seen, A.J., Jacobson, G.E., Gras, J.L., 2006. Radiocarbon determination of woodsmoke contribution to air particulate matter in Launceston, Tasmania. Atmospheric Environment 40, 2575-2582.

Klinedinst, D.B., Currie, L.A., 1999. Direct quantification of PM2.5 fossil and biomass carbon within the Northern Front Range Air Quality study's domain. Environmental Science and Technology 33, 4146-4154.

Lewis, C.W., Stiles, D.C., 2006. Radiocarbon content of PM2.5 ambient aerosol in Tampa, FL. Aerosol Science and Technology 40, 189-196.

Lewis, C.W., Klouda, G.A., Ellenson, W.D., 2004. Radiocarbon measurement of the biogenic contribution to summertime PM-2.5 ambient aerosol in Nashville, TN. Atmospheric Environment 38, 6053-6061.

Marley, N.A., Gaffney, J.S., Tackett, M., Sturchio, N.C., L. Heraty, Martinez, N., Hardy, K.D, Marchany-Rivera, A., Guilderson, T., MacMillan, A. and Steelman, K., 2009.The impact of biogenic carbon sources on aerosol absorption in Mexico City Atmos. Chem. Phys., 9, 1537-1549.

Marley, N.A., Gaffney, J. S., Ramos-Villegas, R. and Cárdenas González, B., 2007. Comparison of Measurements of Peroxyacyl Nitrates and Primary Carbonaceous Aerosol Concentrations in Mexico City Determined in 1997 and 2003. *Atmos. Chem. Phys.*, **7**, 2277-2285.

Marley, N.A., Machany-Rivera, A., Kelley, K. L., Mangu, A., Gaffney J.S., 2007: Aerosol Angstrom Absorption Coefficient Comparisons during MILAGRO. *Eos Trans. AGU, 88*(52), Fall Meet. Suppl., Abstract A43C-1421.