

**Atmospheric Organic Carbon in the Hudson River and York River
Watersheds: Quantities, Character, Sources, and Fates**

A Final Report to the Hudson River Foundation

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Field work and laboratory analyses for the funded research have been ongoing since summer of 2006 and are nearing completion as detailed below. In addition to research activities, I have passed the Virginia Institute of Marine Science Ph.D. qualifying exam (January 2007) and been accepted as an official Ph.D. candidate (summer 2007). My Ph.D. coursework will be complete upon completion of a final paper from the spring semester 2007. I expect to submit 2 manuscripts from this work for peer-review publication within the next year, and am on schedule to defend the research for my dissertation in the fall semester of 2008 or spring semester of 2009.

Field Sampling Program

Preliminary air samples were collected in June and July 2005 in the Hudson River and York River watersheds (Figure 1), respectively. Primary field collections (conducted on approximately 3-4 month intervals in New York, and twice monthly in Virginia) related to the project began in May 2006 and will end in August 2007. High volume (24 h, $\sim 1000 \text{ m}^3$ of air filtered) aerosol ($>0.6 \mu\text{m}$) samples were collected from the Hudson River watershed site in Millbrook, NY May 21-26, August 16-21, and December 1-6 of 2006, and March 5-10 of 2007 to represent spring, summer, fall, and winter time periods respectively. Additional high volume aerosol samples were collected May 11-16 and August 10-14 of 2007 to support analyses to be performed at the Woods Hole Oceanographic Institution in Sept.-Oct. 2007 that will characterize the quantities and isotopic signatures ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$) of various operationally-defined fractions and compound classes of aerosols (see below). Soil, sediment, and river samples were collected concurrently during selected sampling periods, while in March of 2007 snow samples were collected in place of sediment and soil samples due to the river and ground being frozen. In the York River watershed, air samples were collected biweekly from May 2006 through mid-summer 2007.



Figure 1. Map of eastern United States showing study areas and in relation to several eastern U.S. cities.

Preliminary Findings

Mean atmospheric aerosol organic carbon (OC) concentrations during May and August 2006 sampling periods were higher in the York River watershed than in the Hudson River watershed ($7.12 \pm 1.28 \mu\text{gC m}^{-3}$ vs. $4.96 \pm 0.29 \mu\text{gC m}^{-3}$, respectively $p < 0.05$, student's t-test, Figure 2), a reversal of the trend observed for 2005 when the Hudson River watershed showed higher concentrations than the York ($11 \pm 0.95 \mu\text{gC m}^{-3}$ vs. $5.4 \pm 0.57 \mu\text{gC m}^{-3}$, respectively; $p < 0.05$, student's t-test - data not shown). The

reversal in this trend is indicative of the natural variability of aerosol concentrations and may be linked to differences in air mass sources. Using these preliminary concentration data, mean dry deposition of aerosol OC to the Hudson River watershed were calculated to be $1.7 \text{ g C m}^{-2} \text{ yr}^{-1}$ and $0.78 \text{ g C m}^{-2} \text{ yr}^{-1}$ for 2005 and 2006 respectively, amounting to $5.8 \times 10^{10} \text{ g C yr}^{-1}$ (2005) and $2.62 \times 10^{10} \text{ g C yr}^{-1}$ (2006) when scaled to the entire watershed area ($33,500 \text{ km}^2$). The York River watershed (8470 km^2) on the other hand received $7.3 \times 10^9 \text{ g C yr}^{-1}$ in 2005 $9.5 \times 10^9 \text{ g C yr}^{-1}$ in 2006 based on dry depositions of $0.86 \text{ g C m}^{-2} \text{ yr}^{-1}$ (2005) and $1.12 \text{ g C m}^{-2} \text{ yr}^{-1}$ (2006). These estimates are equivalent to 24-81% and 86-113% of the total OC flux out of the Hudson ($7.2 \times 10^{10} \text{ g C yr}^{-1}$) and York Rivers ($8.4 \times 10^9 \text{ g C yr}^{-1}$), respectively (Figure 3).

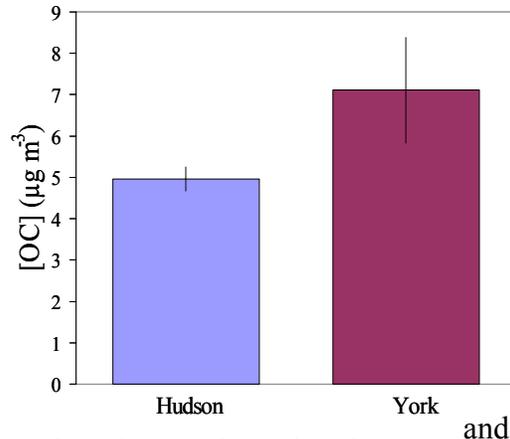


Figure 2. Aerosol organic carbon concentrations ($\mu\text{g m}^{-3}$) in the Hudson and York River watersheds. Error bars represent standard errors. $n=16$ for Hudson River; $n=7$ for York River.

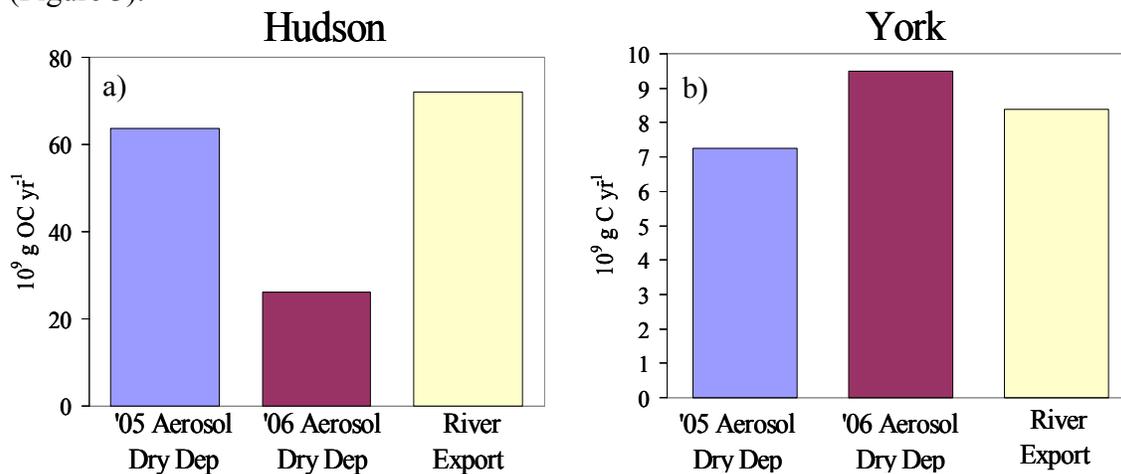


Figure 3. 2005 and 2006 dry deposition fluxes of atmospheric aerosols and mean annual river export to the a) Hudson River and b) York River watersheds.

Preliminary measurements of aerosol OC from the York River watershed in July 2005 (data not shown) indicated that the water soluble organic carbon (WSOC) component of aerosols accounts for nearly 50% of the OC in aerosols. In 2006, 58% of York River watershed aerosol OC was water soluble, while Hudson River watershed aerosols were 41% water soluble (Figure 4). Controlled laboratory experiments with Hudson watershed aerosols in May 2006 indicated that desorption of WSOC from aerosol OC is rapid and explained by first-order kinetics with half of the

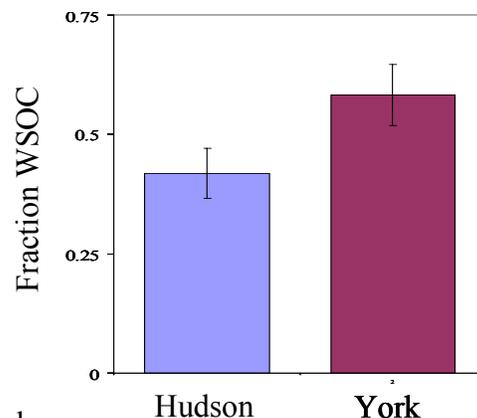


Figure 4. Fraction of aerosol OC that desorbs into the WSOC pool for the Hudson and York River watersheds. Error bars represent standard errors ($n=2$).

WSOC desorbing in less than 10 minutes and most of the WSOC desorbed within an hour (Figure 5).

Radiocarbon data for bulk aerosols collected from the Hudson and York River watersheds in 2006 are available for the May and August sampling periods and can be compared to preliminary data from 2005. The radiocarbon data show remarkably similar $\Delta^{14}\text{C}$ signatures for bulk aerosol OC both between the two watersheds and the two years of sampling (Figure 6). The fractions of modern and fossil OC are often calculated in studies of atmospheric aerosols as estimates of relative contribution of fossil fuel related activities (e.g.; Hildemann et al., 1994; Lewis et al., 2004; Tanner et al., 2004) using $\Delta^{14}\text{C}$ and $\delta^{13}\text{C}$ data as follows:

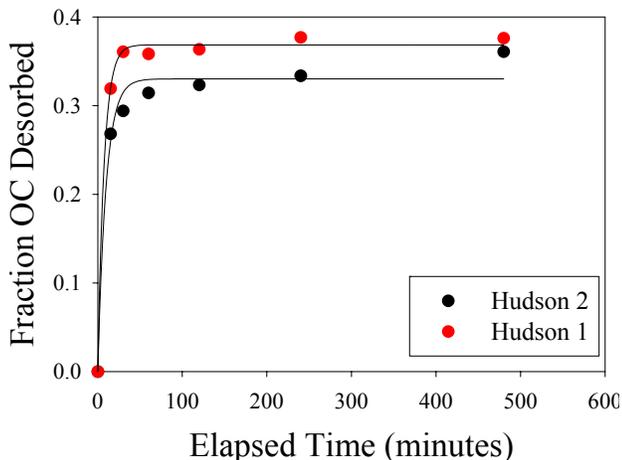


Figure 5. WSOC kinetics. The fraction of OC desorbed from total aerosol OC over time. The black and red dots represent replicates of the same experiment.

$$f_m = ({}^{14}\text{C}/{}^{13}\text{C})_{\text{sample}} / ({}^{14}\text{C}/{}^{13}\text{C})_{\text{Std}} \quad (\text{eqn. 3})$$

$$f_f = 1 - (f_m), \quad (\text{eqn. 4})$$

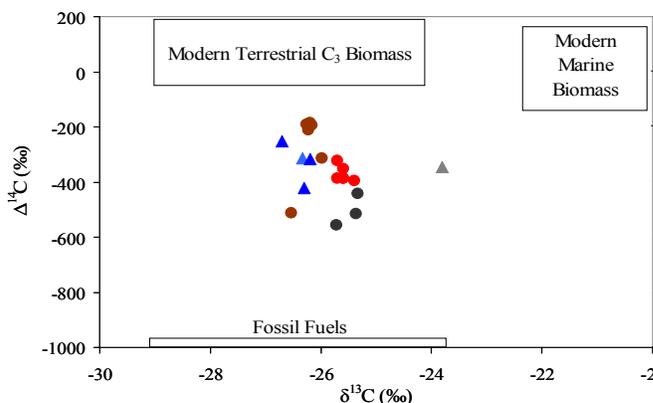


Figure 6. Isotopic signatures ($\Delta^{14}\text{C}$ vs. $\delta^{13}\text{C}$) of bulk aerosol OC collected in the Hudson River watershed (circles) in June 2005 (red), May 2006 (brown), and August 2006 (black) and in the York River watershed (triangles) in July 2005 (dark blue) and summer 2006 (light blue, grey).

aerosols, the WSOC sub-fraction of aerosol OC was also measured for $\Delta^{14}\text{C}$, and these data indicate that the WSOC is composed of a younger sub-fraction of compounds likely to be largely derived from contemporary C₃ plant biomass (Figure 7). The isotopic signatures of the water insoluble component of aerosol OC were calculated by isotopic mass balance of the two measured components (i.e., total bulk aerosol OC and WSOC) and early estimates suggest that the water insoluble aerosol OC shows a greater influence

where f_m is the fraction of modern carbon in the sample, f_f is the fraction of fossil carbon in the sample, $({}^{14}\text{C}/{}^{13}\text{C})_{\text{sample}}$ is the ratio of ${}^{14}\text{C}$ to ${}^{13}\text{C}$ in the sample, and $({}^{14}\text{C}/{}^{13}\text{C})_{\text{Std}}$ is the ratio of ${}^{14}\text{C}$ to ${}^{13}\text{C}$ in a near-modern standard. Radiocarbon signatures of Hudson River watershed aerosols showed 37% and 34% fossil contribution for 2005 and 2006 respectively, while 33% of aerosol OC could be attributed to fossil sources in the York River watershed both years (Figure 6). In addition to bulk

of fossil fuel derived OC (Figure 7). These results further indicate that much of the fossil-derived aerosol OC is likely to remain in the particulate phase.

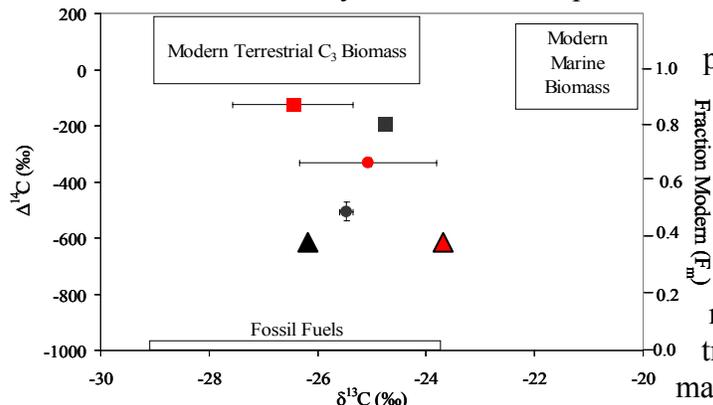


Figure 7. Isotopic ($\Delta^{14}\text{C}$ vs. $\delta^{13}\text{C}$) signatures of bulk aerosol OC (circles), aerosol WSOC (squares), and aerosol water insoluble OC (triangles) collected in the York (red) and Hudson (black) River watersheds from summer 2006 plotted with potential sources of aerosol OC.

for these experiments is so far inconclusive, but future experiments will include isotopic mass balances to allow for the determination of the reactive components of aerosol WSOC.

Preliminary microbial and photochemical incubations of Hudson River watershed WSOC were conducted in August of 2006. These initial experiments show a greater than 20% loss of WSOC after less than two weeks for both microbial and photochemical treatments illustrating that this material is both microbially and photochemically reactive. Isotopic signatures were monitored for pre- and post-incubations and allowed for an estimation of the isotopic signature of starting material. Isotopic information

Other Accomplishments and Future Work

The results from this study continue to be updated through additional analyses of bulk OC, WSOC, and their isotopic ($\delta^{13}\text{C}$, $\Delta^{14}\text{C}$) signatures for samples collected from September 2006 through summer 2007. Measuring these parameters over the course of a full year will provide an estimate of annual aerosol OC dry deposition fluxes to the two watersheds as well as provide some insight into some of the seasonal variability in these parameters. I have also begun measuring black carbon, the carbonaceous product of natural and anthropogenic combustion of biomass and fossil fuels, in my aerosol filters and will include these measurements in the analyses of the remaining samples in order to explore the extent to which black carbon is present in aerosols from the study regions. Concentrations of polycyclic aromatic hydrocarbons (PAHs) will be measured in the aerosol, soil, sediment, and river particulate samples in an attempt to track the fate of aerosol OC into these other organic matter pools. Additional WSOC desorption experiments will be conducted to understand the kinetics of WSOC desorption from aerosol OC. Microbial and photochemical incubation experiments will also be repeated to further elucidate the reactivity of aerosol WSOC. In these experiments, an additional microbial + photochemical treatment will be added to explore the combined effects of both microbial activity and photochemistry.

The preliminary research conducted during my tenure with the Hudson River Foundation Fellowship has also afforded me the opportunity of additional significant collaborations that will help to further characterize aerosols in the Hudson River and York River watersheds. I was recently awarded an internship with the Woods Hole Oceanographic National Ocean Sciences Accelerator Mass Spectrometry (NOSAMS) facility where I will undertake radiocarbon analyses on various sub-fractions of aerosol

OC in Sept-Oct 2007, as well as possible future dates. The NOSAMS facility is one of the few in the world where these detailed and analytically challenging analyses can be carried out. Briefly, aerosol OC will be extracted to isolate water-soluble, a total organic, aliphatic, and aromatic fractions. Concentrations and isotopic signatures of these aerosol OC sub-fractions will be measured using accelerator mass spectrometry (AMS) for ^{14}C and isotope ratio mass spectrometry (IRMS) for ^{13}C to i) obtain a mass balance of the distribution of these operationally-defined sub-fractions to the pool of total bulk aerosol OC and ii) determine how modern and fossil sources of OC are distributed amongst these sub-fractions. I have also established collaborative efforts to analyze aerosol WSOC samples on a Fourier Transform Ion Cyclotron Resonance Mass Spectrometer (FT-ICR MS) in the lab of Dr. Pat Hatcher at Old Dominion University. This particular FT-ICR MS provides extremely high resolution and mass accuracy allowing for a broad molecular-level characterization of natural and fossil fuel-derived compounds in the water-soluble components of aerosol OC. In particular, this work will examine whether and to what extent the WSOC contains black carbon, as well as other major components as established by its elemental and molecular weight characteristics.

Recent Presentations

- Wozniak, A. S., J. E. Bauer, R. M. Dickhut, and E. E. Keesee. 2007. Deposition and characteristics of aerosol-derived organic carbon in temperate watersheds. American Society of Limnology and Oceanography Aquatic Sciences Meeting, Santa Fe, NM.
- Wozniak, A. S., J. E. Bauer, R. M. Dickhut, and E. E. Keesee. 2007. Deposition and reactivity of aerosol-derived organic carbon in temperate watersheds. Virginia Institute of Marine Science, Department of Physical Sciences Seminar, Gloucester Point, VA.

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- Hildemann, L. M., D. B. Klinedinst, G. A. Klouda, L. A. Currie, and G. R. Cass. 1994. Sources of urban contemporary carbon aerosol. Environmental Science and Technology 28:1565-1576.
- Lewis, C. W., G. A. Klouda, and W. D. Ellenson. 2004. Radiocarbon measurement of the biogenic contribution to summertime PM-2.5 ambient aerosol in Nashville, TN. Atmospheric Environment 38:6053-6061.
- Tanner, R. L., W. J. Parkhurst, and A. P. McNichol. 2004. Fossil sources of ambient aerosol carbon based on ¹⁴C measurements. Aerosol Science and Technology 38(S1):133-139.