Organic Aerosol is Formed in Unexpectedly Large Amounts in Urban Pollution Plumes

Joost de Gouw[(1)], C.A. Brock[(1)], C. Warneke[(1)], A.M. Middlebrook[(1)], W.C. Kuster[(1)], P.D. Goldan[(1)], B.M. Lerner[(1)], E.J. Williams[(1)], J.S. Holloway[(1)], F.C. Fehsenfeld[(1)], R.E. Peltier[(2)], A.P. Sullivan[(2)], R.J. Weber[(2)], T. Onasch[(3)], P.K. Quinn[(4)], T.S Bates[(4)], E.L. Atlas[(5)]

(1) Cooperative Institute for Research in Environmental Sciences, University of Colorado & NOAA Earth System Research Laboratory, Boulder, CO (2) Georgia Institute of Technology, Atlanta, GA (3) Aerodyne, Billerica, MA (4) NOAA Pacific Marine Environment Laboratory, Seattle, WA (5) University of Miami, Miami, FL

Introduction

The ICARTT study in 2004 (International Consortium for Atmospheric Research on Transport and Transformation) provided a good opportunity to study the sources of organic aerosol. Measurements were made in July and August from 2 different NOAA platforms operated in the northeastern U.S.:

A. The NOAA WP-3D research aircraft using:
1. AMS (Aerosol Mass Spectrometry)
2. PILS-TOC (particle in liquid sampling - total organic carbon) that measures water-soluble organic carbon (WSOC) [*Sullivan*, 2006]

B. The NOAA research ship Ronald H. Brown using:
1. AMS
2. PILS-TOC
3. Sunset Labs analyzer for EC/OC analysis

2. Strong WSOC growth is seen in urban plumes

Overall, the WSOC correlated very well with urban pollution tracers such as CO. An example from the aircraft measurements is shown in Fig. 1. On July 20 and 21 the plume from New York City was intercepted at 2 different distances (Fig. 1A). In both cases, the WSOC was well correlated with CO (Figs. 1B-C). Hydrocarbon measurements show that the plume on July 21 was much more processed (Figs. 1D-E). The ΔWSOC/ΔCO ratio increased from 8.9 μg C m^{-3} $ppmv^{-1}$ on July 20 to 23.1 μg C m^{-3} $ppmv^{-1}$ on July 21.

Figure 2 shows the ΔWSOC/ΔCO ratio for all urban plumes observed from the aircraft as a function of both the transport age (determined from the FLEXPART model and trajectory calculations) and the photochemical age (determined from measured benzene/toluene ratios). Three things to note:

A. Plumes with an age >1 day have much higher ΔWSOC/ΔCO ratios than younger plumes.

B. ΔPOC/ΔCO ratios from tunnel studies agree well with the ΔWSOC/ΔCO ratios close to urban sources.

C. ΔWSOC/ΔCO ratios agree well with a parameterization derived in an earlier paper [*de Gouw*, 2005].

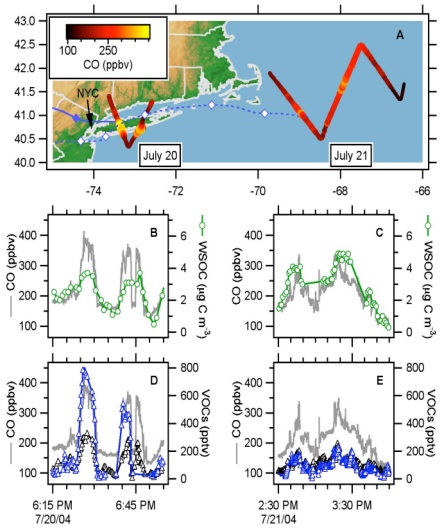


Figure 1: Growth of WSOC and removal of aromatic hydrocarbons in the plume from New York City on July 20 and 21, 2004.

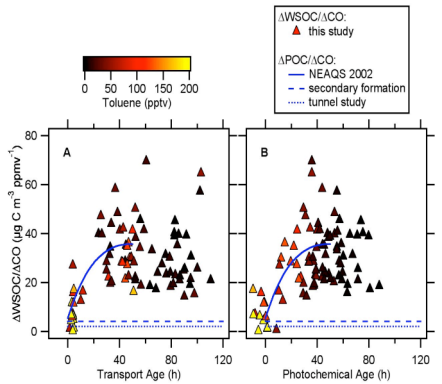


Figure 2: Growth of WSOC relative to CO in all urban plumes observed from the aircraft during ICARTT.

3. Growth is much higher than expected

Figure 3 summarizes the emission ratios relative to CO determined for all the hydrocarbons measured during ICARTT. Results are compared between two years and agree well. When multiplied with organic aerosol yields determined in the laboratory [Seinfeld and Pandis, 1998], we can estimate how much POM (particulate organic mass) can be formed relative to CO. Two things to note:

A. Toluene dominates as a precursor.

B. The contribution from all hydrocarbons adds up to 3.7 μg m^{-3} $ppmv^{-1}$ and is much smaller than the observed ratios in Fig. 2.

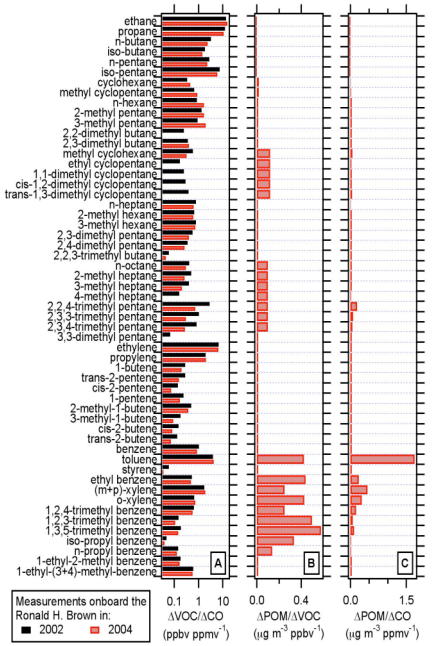
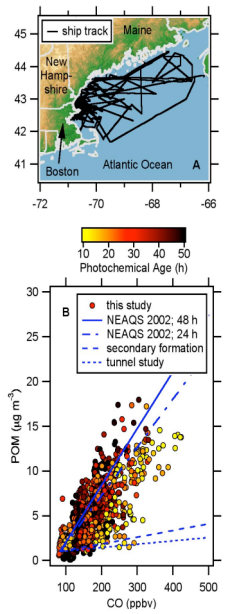


Figure 3: Emission ratios of all hydrocarbons measured during ICARTT and their potential to form POM (particulate organic matter) relative to CO.



4. Same findings from the ship data

A. POM correlated well with CO.

B. The higher the age, the higher the ΔPOM/ΔCO ratio.

Figure 4: Correlation between POM, measured by AMS, and CO during the ship cruise of the Ronald H. Brown during ICARTT.

5. What explains the discrepancies?

The answer is unknown but different factors may include:

A. WSOC is formed from different precursors: are there enough of those in the atmosphere?

B. WSOC formation is more efficient than laboratory simulations indicate.

C. WSOC formation from biogenic precursors is more efficient in urban plumes.

References

De Gouw (2005), Budget of organic carbon in a polluted atmosphere, JGR-Atmospheres 110, D16305, doi:10.1029/2004JD005623

Sullivan (2006), Airborne measurements of carbonaceous aerosol soluble in water over northeastern U.S., JGR-Atmospheres 111, D23S46, doi:10.1029/2006JD007072