

Summary

AMS Data was used to evaluate the speciated transport efficiencies of submicron aerosol from the BL/FT to the outflow of convective systems. Transport was significant in most of the flights studied (about 20-100% of the relative transport efficiency of HCHO for the same flight) and comparable for all species, ie most of the transported aerosol was organics (OA).

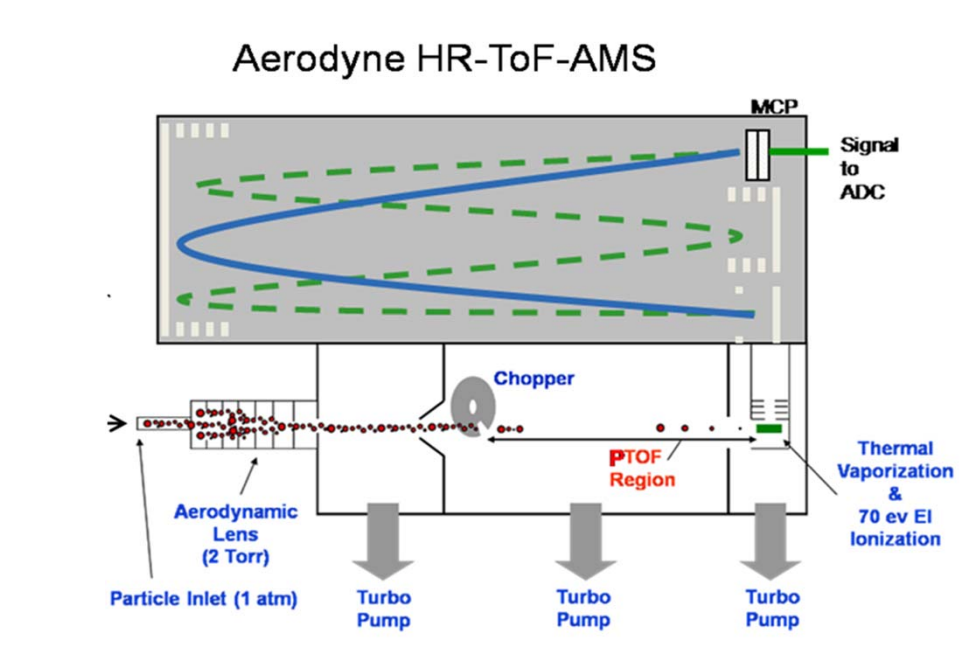
In some cases, a significant increase of the O/C of the OA in fresh outflow was observed relative to the inflow, although often it is not clear to what extent higher oxidized OA from the FT not sampled during the flight might have contributed.

Relatively high concentrations of OA were found on some Day 2 flights (~1 µg/sm³), with O/C ratios in line with fresh outflow. Interestingly, almost always there was a long lived OA background present in the UT exhibiting sometimes extreme O/C ratios (>1), often associated with biomass burning (BBOA) markers.

Nitrate was found both in the BL at higher concentrations close to agricultural sources, as well as often in the anvil outflow. In most cases, the nitrate in the anvil does not seem to be ammonium nitrate, we suggest it could be organic nitrate, although the quantification is still a work in progress. Nitrate and OA was also found during a nucleation event in the remains of an MCS.

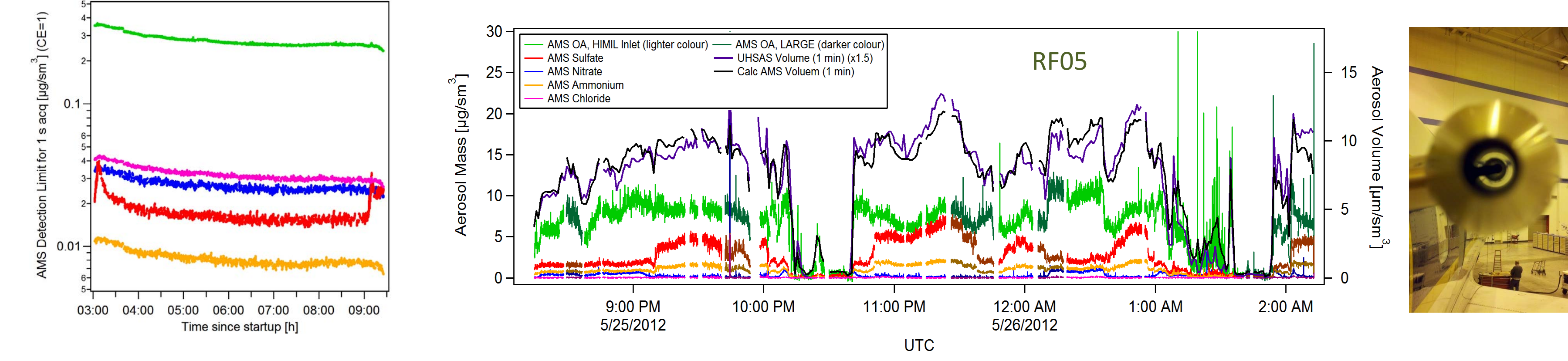
BBOA was found often during DC3, at very different aging stages and there is tentative evidence that the aging mechanism in the UT might be different from the one observed elsewhere. During a smoke plume penetration in the last flight, significant (100 ng/sm³) amounts of particulate mercury were detected both in the smoke plume and in the outflow of the storm above.

AMS Deployment during DC3



A custom Aerodyne Aerosol Mass Spectrometer (AMS), developed at CU by NCAR/NSF was flown on the NASA DC-8. Ambient aerosols in the AMS are analyzed by impact/vaporization of the aerosol on a porous tungsten vaporizer at 600 C and subsequent ionization of the gas plume by electron impact; ions are mass analyzed by a high-resolution time-of-flight mass spectrometer. The AMS quantifies non-refractory submicron aerosol, which includes organic species and most inorganic salts, but not black carbon.

The AMS was operated at 1 s time resolution, alternating with 5 s in aerosol size segregated mode. This fast time resolution allowed for chemical speciation under all circumstances, but for detailed chemical information such as O/C and H:C ratios the raw data was averaged in 1 min cycles to improve the accuracy of the high-resolution ion fitting.



The AMS was outfitted with a cryopump that improved DLs, especially at the beginning of the flight and at higher m/z, ie detection of BBOA at f60

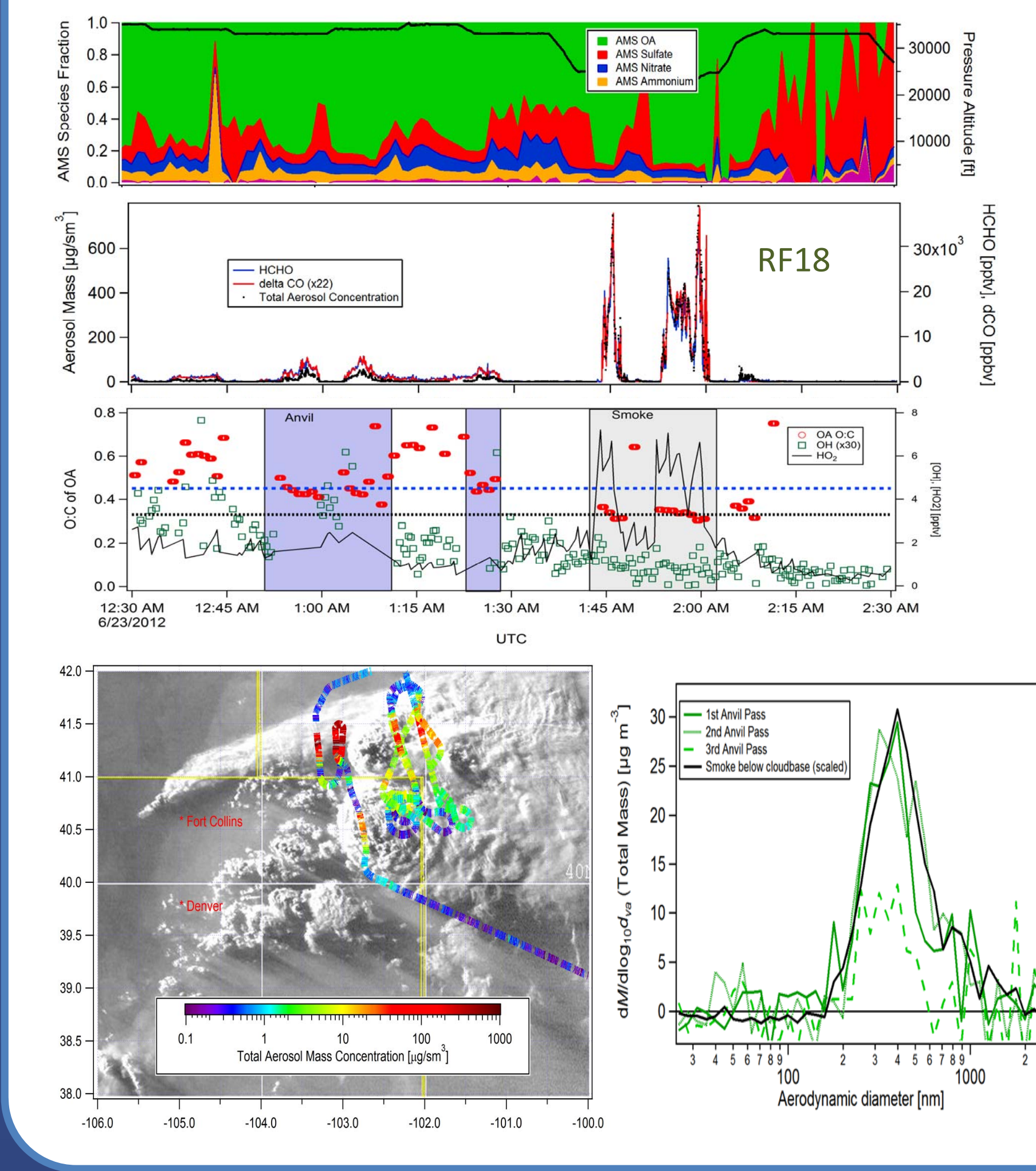
In order to reduce evaporative losses, for DC3 the AMS used a dedicated inlet located next to the instrument. A NCAR designed HIMIL inlet was lengthened to account for the DC-8 boundary layer and fitted with a secondary diffused for improved larger particle performance. Alternate sampling from the LARGE aerosol inlet showed no significant losses. The new inlet allowed for sub-1s residence times in the inlet line

Convective Transport: Two case studies

The flight on 6/22 (RF18) provides the most clear cut case of direct transport of smoke sampled in the FT at 25 kft to the anvil of a storm above at 33 kft. Aerosol mass concentrations were huge, hence eliminating potential issues with chemical analysis close to the detection limit.

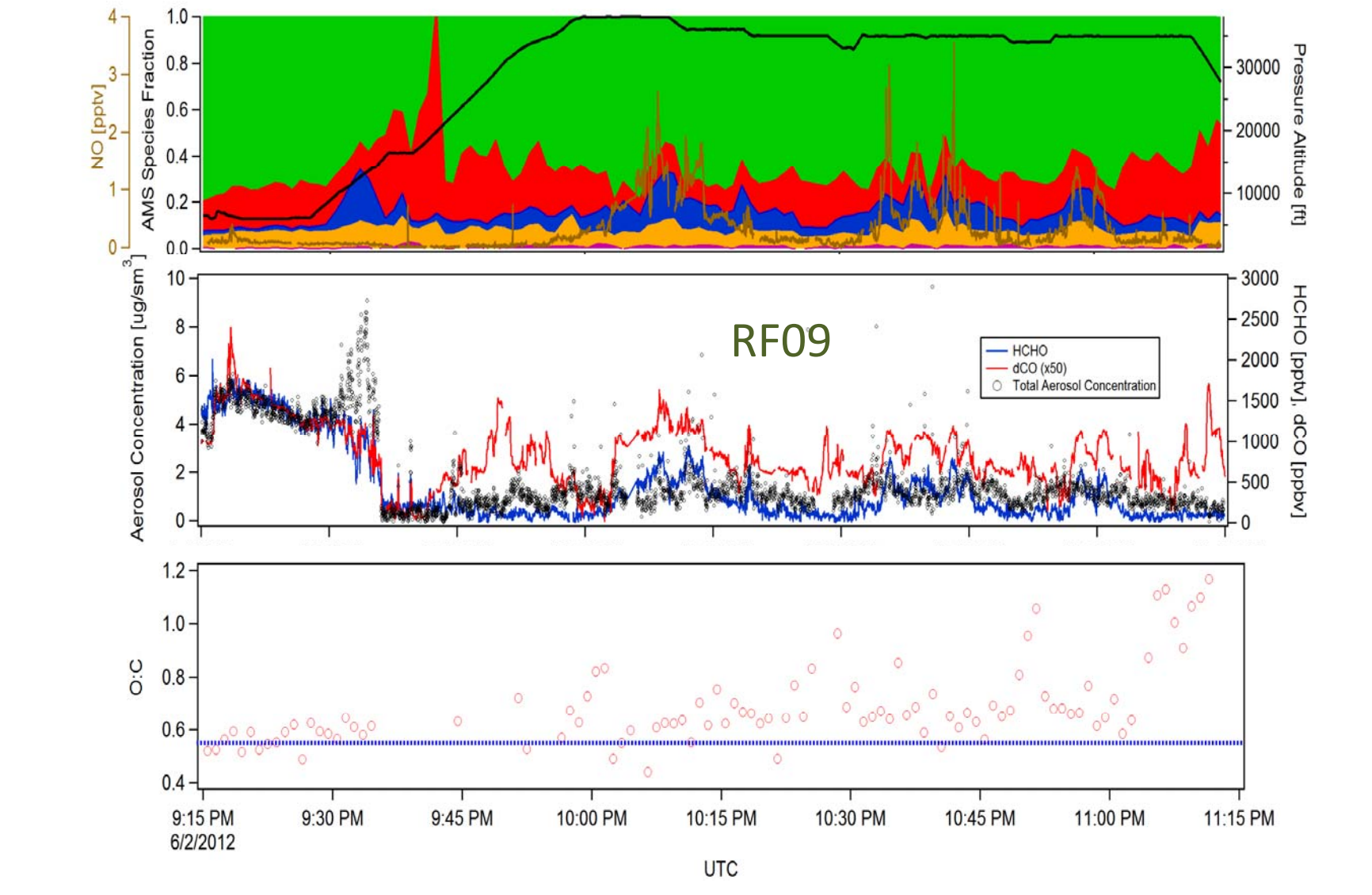
Both HCHO and CO were used to scale the efficiency of the aerosol transport. Relative to HCHO, about 50-60% of the aerosol was transported to the anvil. While sulfate and nitrate relative concentrations increased somewhat, the bulk of the transported aerosol was OA.

Despite the likely very short transport time, the O/C of the transported aerosol increased significantly (0.15), equivalent to several days of tropospheric aging



Another good, more typical example of convective transport of BL aerosol to a storm anvil was the flight on 6/2 (RF09). While the anvil pattern is harder to discern due to background aerosol (likely from previous convection, as seen in the delta CO pattern), for the actual anvil passes total aerosol mass closely follows the HCHO and NO outflow patterns.

In this case, relative species concentrations are conserved (except nitrate), ie there is no selective scavenging of OA. Interestingly, aerosol nitrate concentration increases compared to the BL. This is a feature seen in all storm transport cases and in most of the Day 2 outflow flights.



Total aerosol concentration is pretty much conserved relative to HCHO, and about 20% of delta CO. This was a flight with no aerosols between 15 and 30 kft, so while the UT background might distort things somewhat, the aerosol sampled should be BL aerosol.

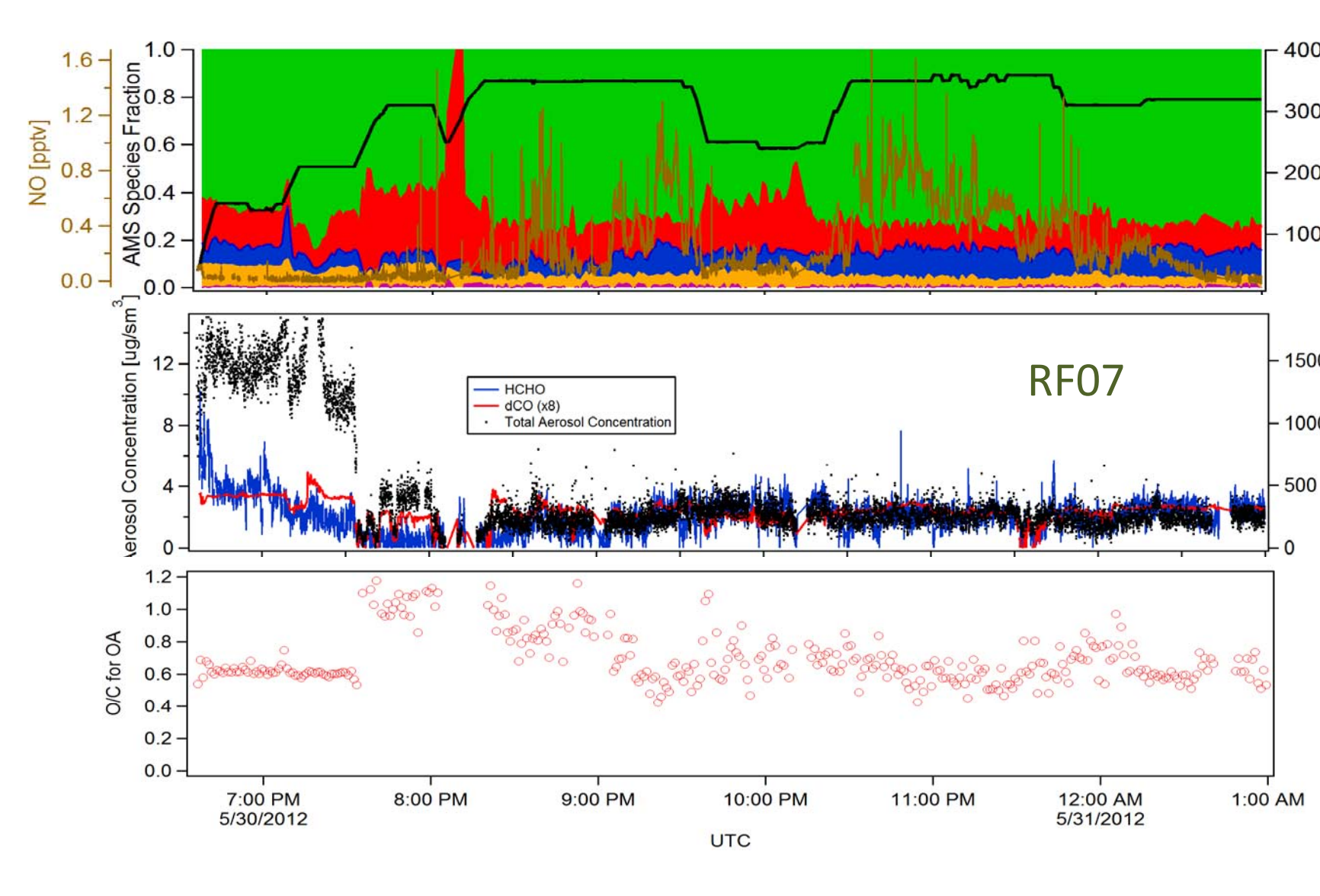
Other flights (RF01, RF02, RF08) show efficient convective transport to the anvil, with efficiencies (relative to HCHO) ranging between 20-100%. In some cases the BL has several layers and hence an accurate assessment of the source of the aerosol is problematic (RF02, RF12, RF14), or high FT concentrations and strong previous convection make comparisons untenable (ie RF11). So much more work is needed to quantify the extent of transport.

While much noisier, this flight also showed a slight increase of O/C in the anvil on the order of 0.1. Such increases are seen in about half of the workable cases. It remains to be seen how much of this is aging and how much is scavenging of lower O/C aerosol (which is sort of counterintuitive, but certainly possible).

Day 2 Outflow

The outflow flight on 5/30 where an 800 km triangle was repeatedly sampled provides a good illustration of the pattern seen also in other Day 2 flights, namely that:

- OA is always at least 50% of total submicron aerosol mass, even under smoky conditions (higher sulfate) and often up to 80%.
- Total aerosol concentrations are considerable (~1 µg/sm³) and in many cases, such as RF07, very stable for long sampling periods
- In general, delta CO predicts the total aerosol mass better than more short-lived tracers such as NO or HCHO, which implies that lifetimes of OA in the UT, once transported, are fairly long.
- OA in air masses were only dCO is observed have sometimes fairly extreme O/C values, up to 1.2, which is almost unheard of in the troposphere. So either aging in the UT is faster than in the troposphere or the OA lifetimes are indeed on the order of CO (ie 3-4 weeks)
- AS RF07 illustrates, a constant aerosol concentration can mask very different chemistries. The aerosol sampled at around 8:50z is very likely from a different source than the one sampled 2 h later, despite the similarity in the gas phase tracers.
- Lastly, some outflow flights such as RF07 and also RF16 showed the presence of aerosol nitrate, in similar concentrations as seen in the storm anvil (~0.1 µg/sm³)



References

- M.J. Cubison et al, Effects of Aging on Organic Aerosol from Open Biomass Burning Smoke in Aircraft and Laboratory Studies. ACP, 11, 12049-12064, doi:10.5194/acp-11-12049-2011, 2011
- J.R. Kimmel et al, Real-time Aerosol Mass Spectrometry with Millisecond Resolution. International Journal of Mass Spectrometry, 303(1), 15-26, 2011. DOI:10.1016/j.ijms.2010.12.004
- J.L. Fry, et al. Observations of gas- and aerosol-phase organic nitrates at BEACHON-RoMBAS 2011. ACPD, 13, 1979-2034, doi:10.5194/acpd-13-1979-2013, 2013.

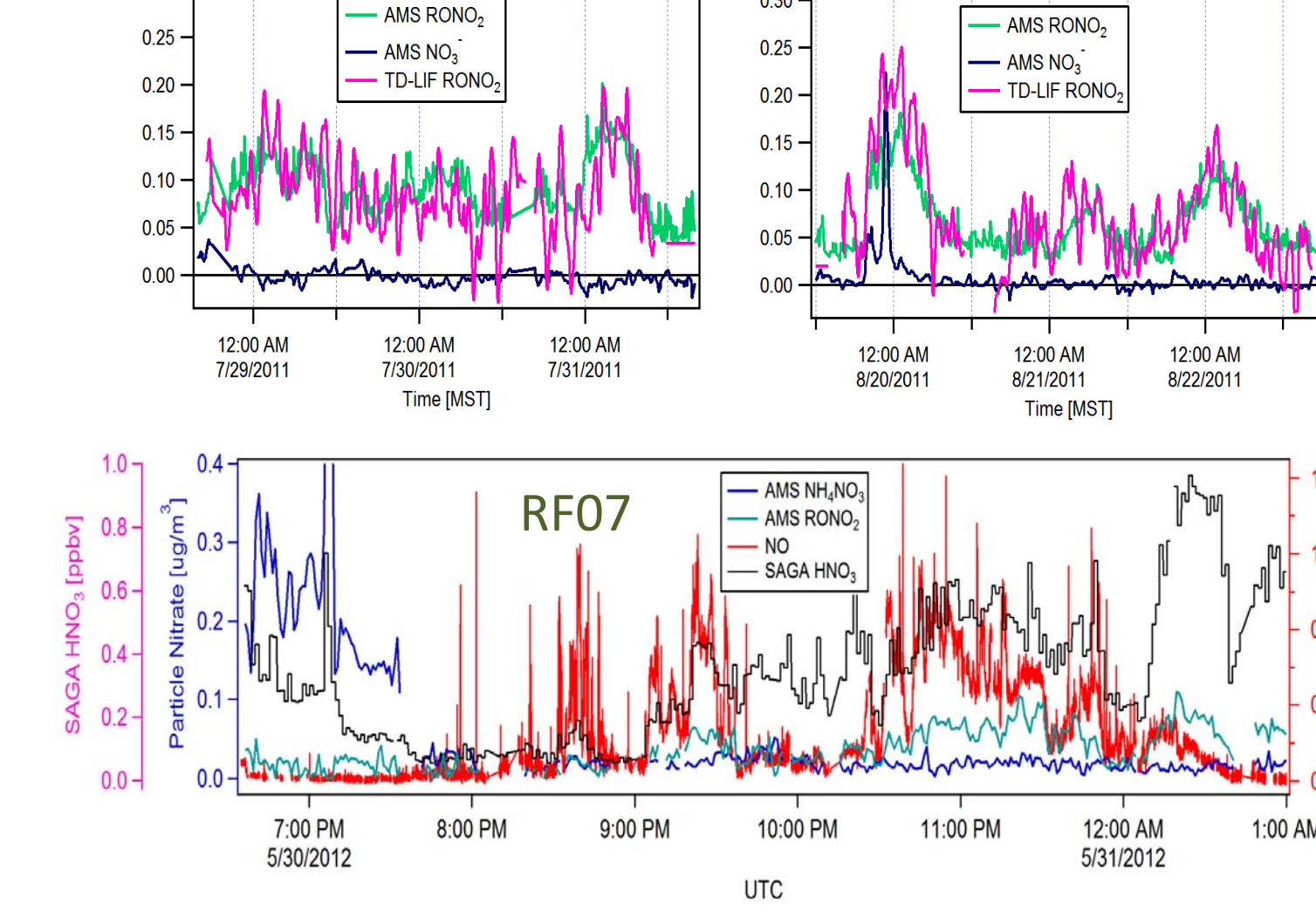
Acknowledgments

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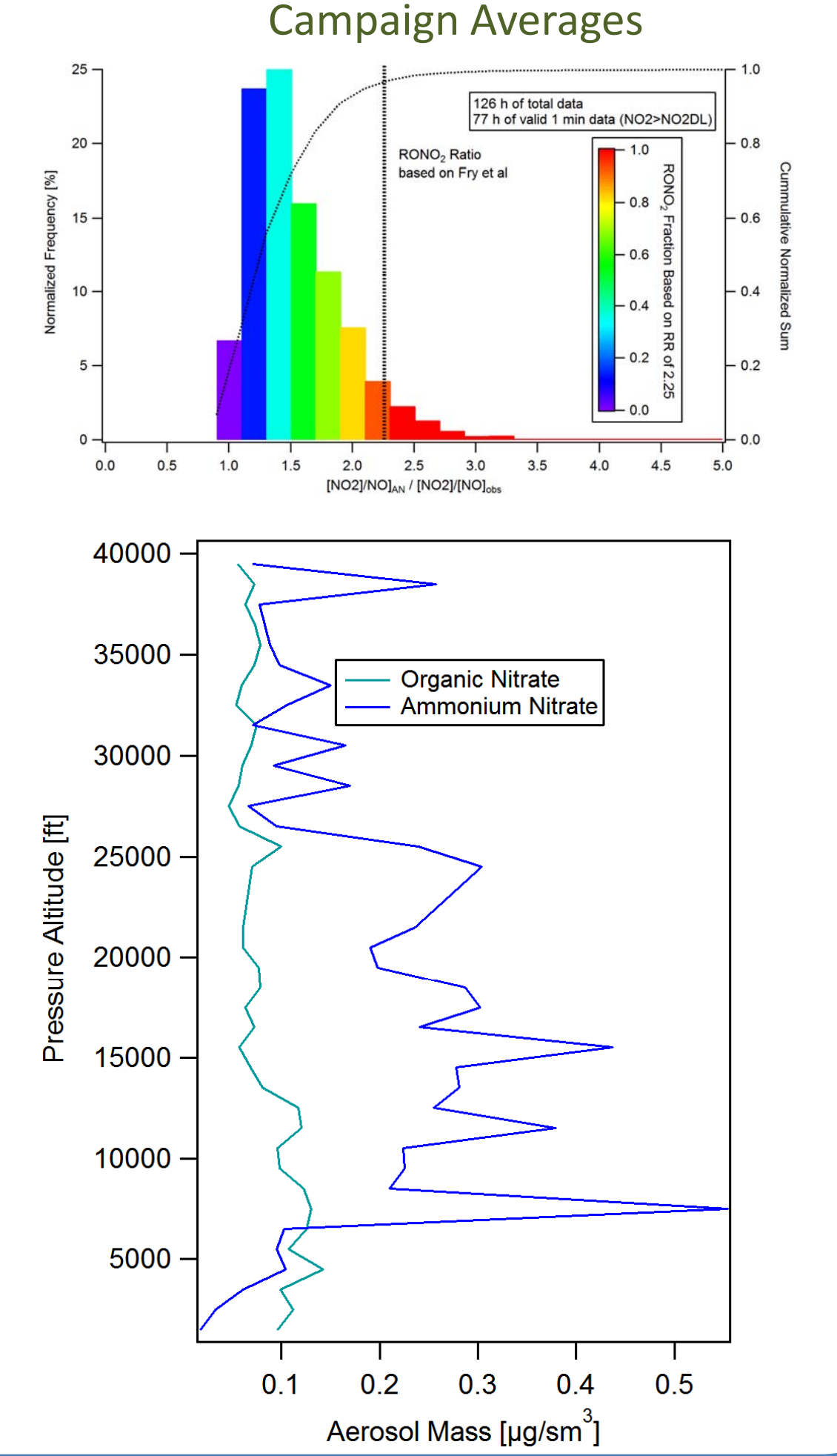
Aerosol Nitrate in the Outflow

Nitrate was routinely detected in the outflow of storms, but seldom in the inflow. There are two main exceptions: feeding lots (especially RF01) and strong BBOA emissions (RF14, RF18). The nitrate in the outflow of most storms did not show the typical fragmentation pattern of NH₄NO₃ (this pattern, ie the NO₂⁻/NO⁺ ion ratio is recorded during each AMS calibration). Significant deviations from this ratio indicate that the nitrate is bound in a different inorganic salt, such as NANO₃ (marine MBL), KNO₃ (biomass burning plumes) or Ca(NO₃)₂ (dust), or it can also be indicative of organic nitrates (RONO₂), which thermally dissociate in the AMS prior to ionization and can therefore not be identified as such.

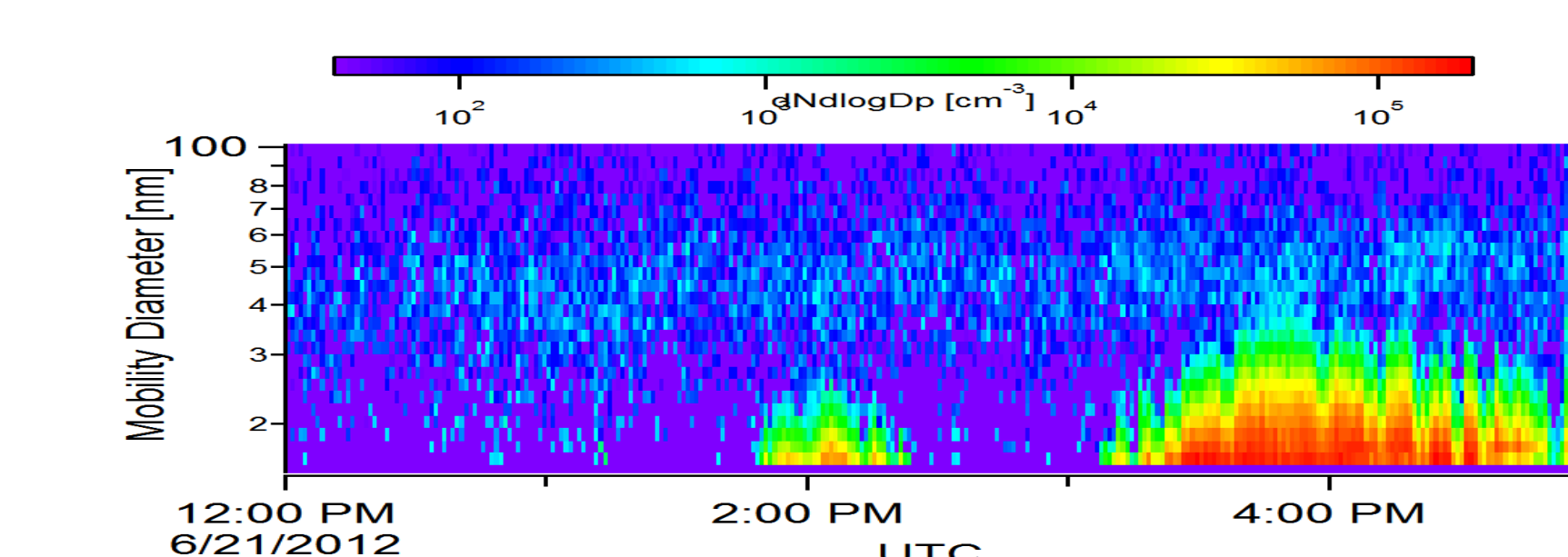
Recently Fry et al have shown that during the BEACHON-RoMBAS campaign using an extrapolated value for the ion ratio of RONO₂ and linearly interpolating between both ratios was able to predict the relative concentrations of RONO₂ as measured by TD-LIF.



The same formalism has been applied to the DC3 data. With the exception of strongly influenced BBOA plumes, inorganic interferences should be negligible. This analysis suggests that indeed most of the detectable nitrate in outflow is probably organic nitrate, and that about 40% of all particulate nitrate detected during DC3 was organic. It also shows that despite a very different NO₂⁻/NO⁺ ratio for NH₄NO₃, the extrapolated value for seems reasonable, ie only 10% of recorded values were higher (likely due to DLs)



Special case: Nucleation in MCS remains



The flight on 6/21 (RF17) crossed a fresh MCS "plume" several times as photochemistry set in. After the storm there was absolutely no OA left in the UT at 36 kft, but by the beginning of the flight very small concentrations of acidic ammonium sulfate could be detected. While the concentrations were way too small to size in the AMS, the calculated volumes are consistent with a small accumulation mode detected by the UHSAS at 250 nm.

During the third pass the LARGE SMPS showed the beginning of an aerosol nucleation process, which was fully ongoing by the fourth pass (15:30z to 16:30z). At the same time, the AMS picked up an increase in both OA and nitrate, while the ammonium sulfate signal stayed constant.

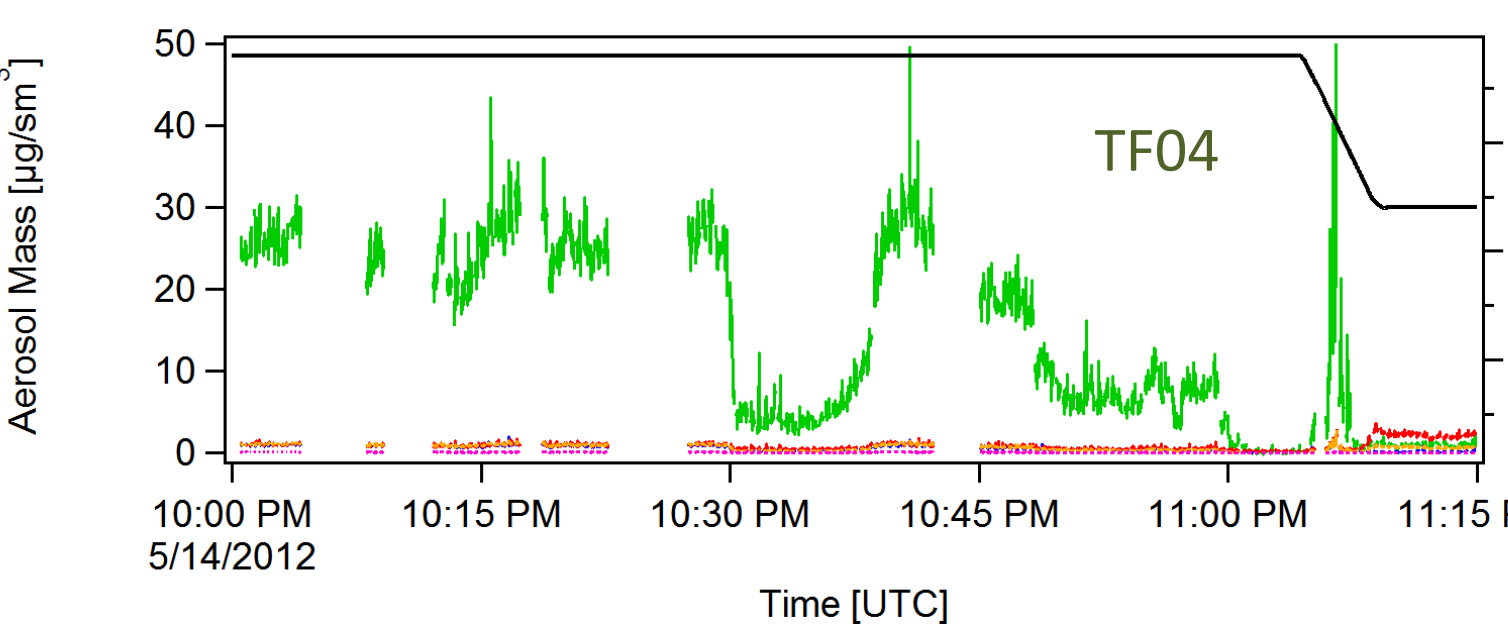
While most of the mass detected by the SMPS is below the AMS size range (~25 nm), there is a striking correlation between the SMPS detected volume and the mass detected by the AMS, so it seems likely that the AMS was sampling at least the upper part of this mode, and that OA and nitrate were main species in the nucleation mode.

As shown above, the fragmentation pattern of the aerosol nitrate can be examined in comparison to the ammonium nitrate pattern, and for this flight it was not consistent with NH₄NO₃. The correlation of nitrate and OA is suggestive, so it could be RONO₂. Note however that we are too close to the detection limit for proper quantification and that it is also possible that some of the HNO₃ detected by SAGA (with a very similar pattern to AMS nitrate) condensed on the particles at these low temperatures and did not evaporate prior to AMS analysis.

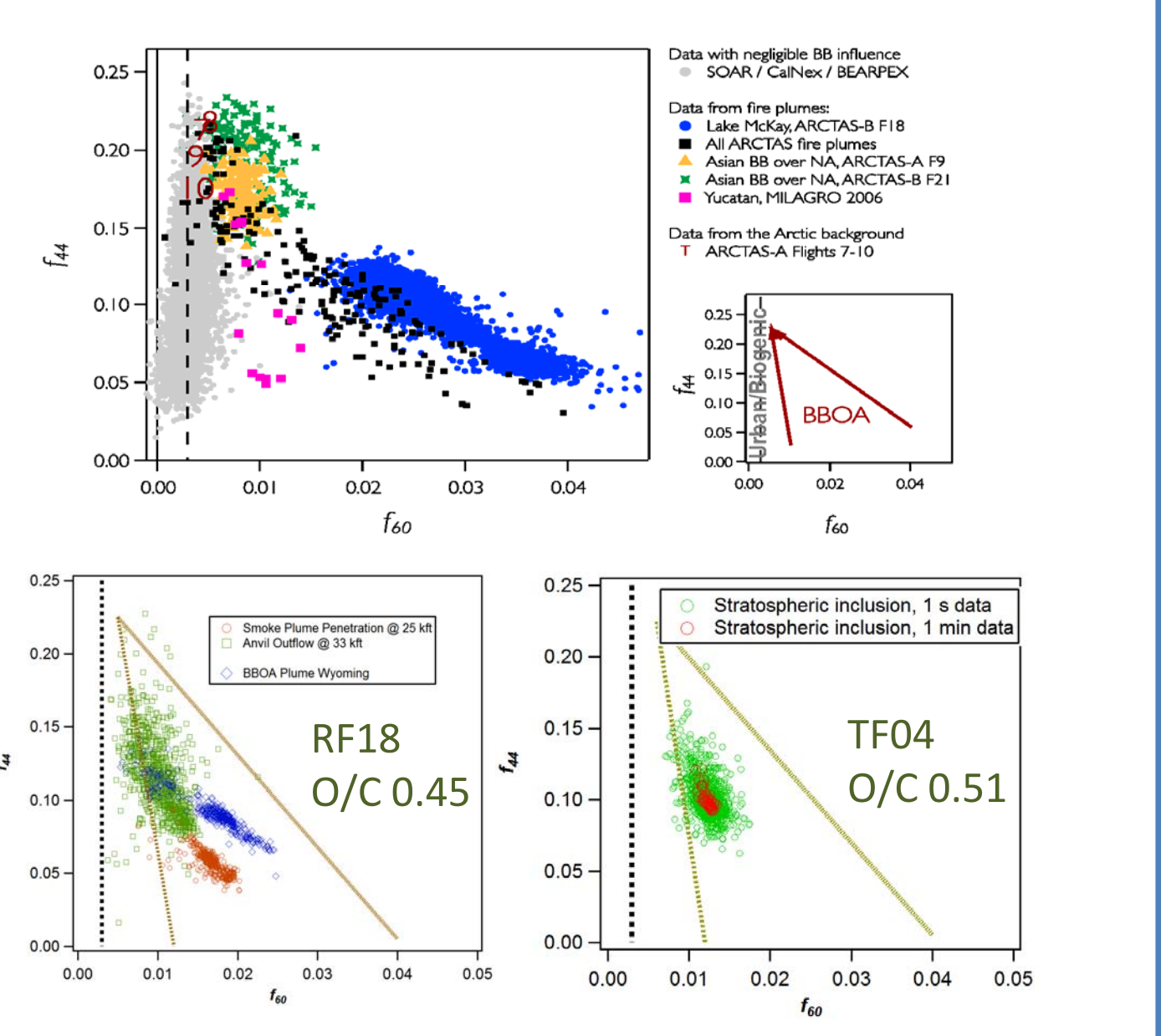
BBOA Aging: 15 min vs 8 days

The second largest BBOA plume during DC3 was sampled in the stratosphere during the 5/14 flight (TF04). About 30 µg/m³ of submicron OA were measured over a fairly large area. As the nearly constant values of the oxidation marker f44 and (biomass marker) f60 show, this was a chemically very homogenous air mass. Knapp et al have shown that its likely origin was a fire in Siberia 8 days prior, and that the plume was injected into the stratosphere within the first 12 hours of convective transport.

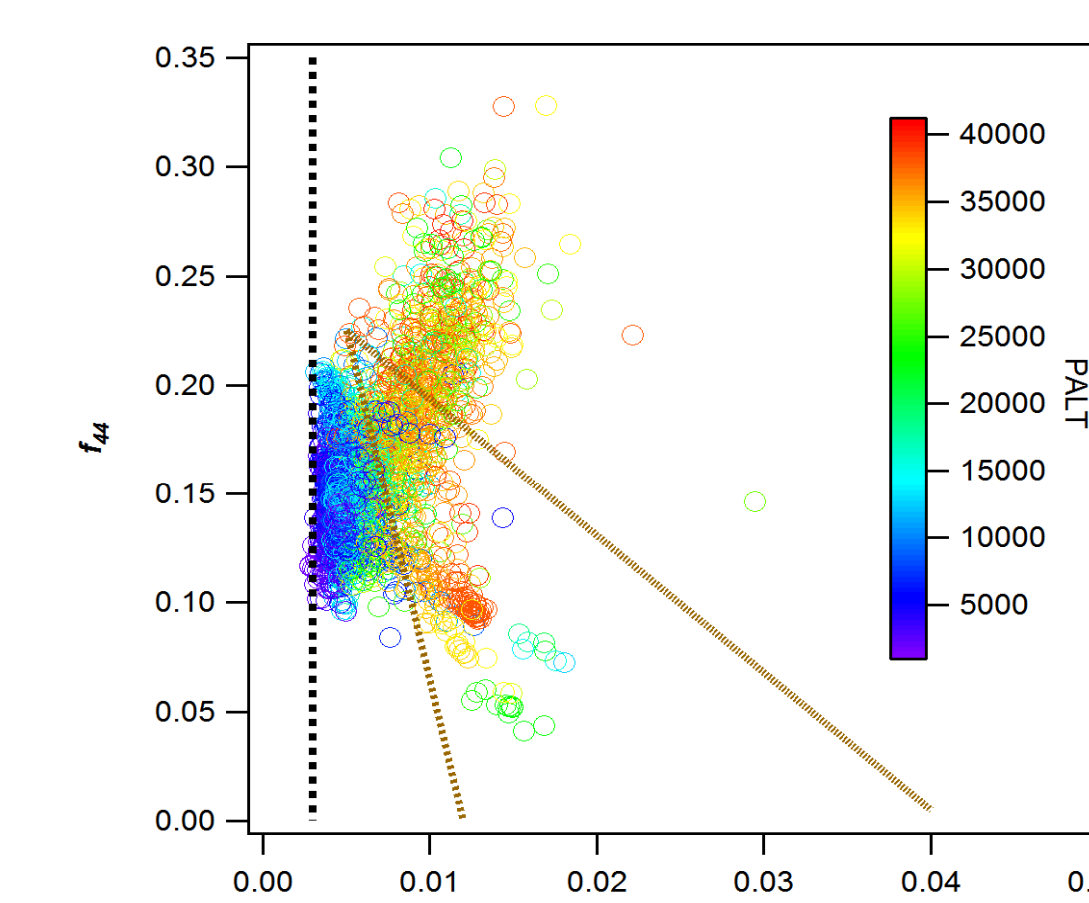
This provides the opportunity to compare the extent of aging of this BBOA with the smoke lofted to the anvil during RF18 (cf. opposite). Using the BBOA aging triangle of Cubison et al., which describes how fast levoglucosan is oxidized to a carboxylic group, it becomes apparent that the anvil BBOA was



Almost as oxidized after 15 min transport than the stratospheric BBOA, something that is also reflected in their fairly comparable O/C ratios.



Extent of BBOA oxidation observed in the UT



While 8 days in the stratosphere seem to contribute little to BBOA aging, this was not the case for the BBOA found in the UT over Colorado, Oklahoma and Texas in June 2012. For about 10% of the total campaign flight time OA with an appreciable levoglucosan signal (ie to the right of the first triangle line) was sampled. Aside from four distinct fresh plumes in the bottom of the triangle, most of the BBOA sampled was near the top, ie very aged, with typical O/C ratios of 0.7-0.8.

Intriguingly, a significant portion of the aged BBOA lies above the triangle, suggesting an alternative oxidation path where levoglucosan is conserved while other functional groups are oxidized. While potential interferences have to still be considered, the degree of oxidation of this subset of BBOA, as indicated by the f44 value is substantial, with O/C ratios up to 1.2. As noted opposite, it is yet unclear if this high O/C values are a function of a special, UT specific chemistry or rather due to very long residence times of the OA, compared to the troposphere.

Particulate mercury in both smoke and convective outflow

The shorter inlet transit time made it possible to detect particulate mercury both in the direct smoke as well as in the anvil during RF18. While confirming the presence of such a trace element in the presence of 600 µg/m³ of OA is challenging, the quality of the fit and the reproducible isotopic ratios seem to confirm that indeed mercury was detected. Using the same calibration factors as for aerosol nitrate, we calculate peak concentrations of 100 ng/sm³ in the smoke plume. Since the ionization efficiency of mercury is likely lower (TBD), and some mercury might still have evaporated in the inlet, this value is likely a conservative estimate.

A linear regression with total aerosol mass yields a value of 100 ppm particulate Hg per mass of fresh BBOA, which seems to indicate that the contribution of biomass burning to particulate mercury is very substantial. Small amounts of mercury were also found in TF04, and the ratio was comparable.

Particulate mercury is often thought to be bound as HgBr₂. Bromine was in fact detected as well during RF08. Again, calibration factors for Br are TBD, but assuming that the detection efficiency of Br is not lower than for Hg, the amounts detected result in a stoichiometry of only 0.6 Br : 1 Hg. It should be noted, however, that there is plenty of excess chloride that could potentially bind some mercury.

