**Primary and Secondary Environmental Tobacco Smoke Droplet Growth: Part 1 – Effects of composition for CCN activation and droplet growth**

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## Introduction

Secondhand or environmental tobacco smoke (ETS) is a significant source of human exposure to fine particles (Klepeis et al., 2003). ETS is the combination of "sidestream" smoke (released between puffs from the lit end of the cigarette) and "mainstream" smoke (exhaled by a smoker).
Dry cigarette smoke has the potential to grow to larger droplet sizes and effect deposition rates. In this work we quantify the sueprsaturation conditions and provide a model framework to characterize the growth of these particles. The goal of this study is to further characterize cigarette smoke, with an emphasis on droplet formation properties.

## Experimental Methods

A Walton Smoking Machine, WSM produced mainstream and sidestream ETS. Two types of reference cigarettes, 1R5F and 3R4F (College of Agriculture, University of Kentucky), were tested with the WSM. The cigarettes were lit and smoked in 1 minute intervals. Sidestream ETS was funneled and diluted with compressed air into an ejector pump to simulate second hand smoke. Mainstream ETS was sampled from a 350 $cm^3$ stainless steel chamber, as shown in Figure 1.

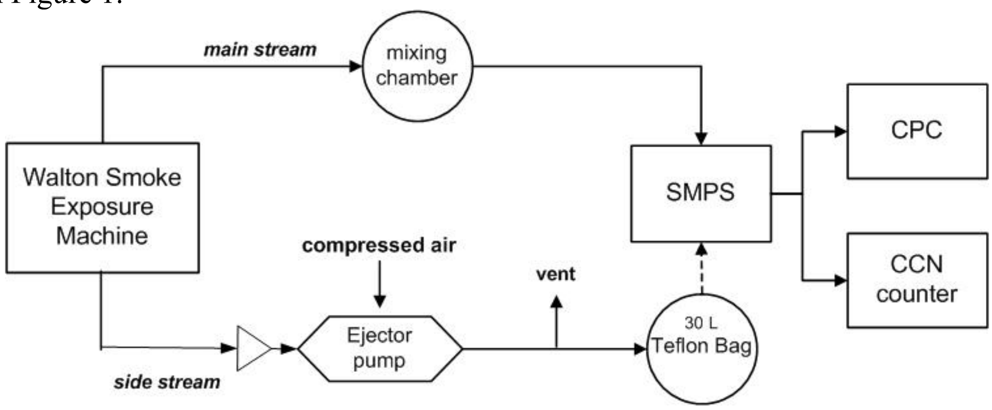


Figure 1 Schematic of Experimental setup

## Results and Discussion

Main and sidestream ETS produce well-mixed and stable particle size distributions. 3R4F ETS forms smaller particles than 1R5F ($D_{p,\mathrm{mode}}$ ~88 nm, in main and sidestream ETS). Mainstream smoke is diluted > 35 times more than sidestream smoke but the gas to aerosol phase partitioning forms similar aerosol distributions. 1R5F ETS forms aerosol distribution with larger modes, $D_{p,mode}$ = 113 ± 4.1 nm and $D_{p,\ mode}$ = 88.2 ± 3.2 nm in side and main stream modes, respectively.

The majority of 3R4F and IR5F particles in main and sidestream ETS are organic and semivolatile. The EC/OC fraction constitutes less than 1% of the aerosol mass fraction. Catalytic stripper dates supports EC/OC measurements and shows that less than 1% of the organic material is non-volatile (evaporates > 300ºC) and in the range of 60 to 100 nm. The differences in size distribution of 1R5F and 3R4F are attributed to changes in volatility as seen in the differences in organic chemical composition.

All experiments show abundance in the UMR *m/z* 43 fragmentation ion. HR analysis indicates that both oxidized ($C_2H_3O$+) and non-oxidized ($C_3H_7$+) species exist in the *m/z* 43 ion fragment. The fraction of *m/z* 43 ion in the total organic signal, $f_{43}$ = 8.5 ± 0.1% in both 3R4F to 1R5F mainstream ETS. Significant differences are observed in the UMR and HR AMS data. For example, the ratio of 3R4F to 1R5F mass spectra mainstream ETS at *m/z* 29 ion, $R_{29} = 1.6$; 3R4F forms 60% more aerosol fragments at *m/z* 29 (Formyl radical, CHO). The majority of $R_x$ < 0.95 and > 1.10 are at *m/z* ions > 43. 3R4F aerosol forms larger molecular weight fragments and aerosol than 1R5F.

HR data shows key fragments have significantly more oxidized components. In 3R4F main and sidestream smoke, the oxidized contribution to UMR *m/z* 44 differs; the relative contribution of $C_2H_3O$+ and $C_3H_7$+ ions is less in mainstream ( value ± ) versus side stream ( value ± ) 3R4F smoke. The CO2+ ion is the only contribution to the 3R4F mainstream smoke. However, 3R4F *m/z* 44 side stream ion fragments contain less oxidized $C_2H_4O$+ and $C_3H_8$+.
The smoke formed in main and side stream smoke of 3R4F cigarettes are of similar distribution and hygrosocopicity ($\kappa_{eff}$~0.15) (Fig 1 and Table 1). The change in oxidative state of the aerosol composition has little or no effect on overall aerosol hygrosocpicity.

Because the activation diameter for both cigarette types produce aerosol of similar hygrosocopicity ($\kappa_{eff}$~0.15), 1R5F cigarettes will produce more aerosol that activate and form droplets. At 0.54% and 0.85% s, 58% and 79% of the 3R4F and 68% and 78% of the 15RF respective dry aerosol distributions shown will form droplets at larger µm sizes.

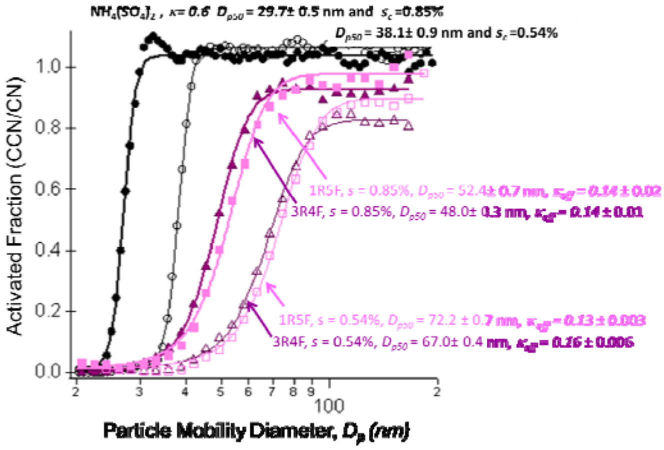


Figure 2 Activated fraction vs. particle mobility diameter of mainstream ETS for $s_c$ at 0.85% (closed) and 0.54% (open).

## References


Klepeis, N.E., Apte, M.G., Gundel, L.A., Sextro, R.G., Nazaroff, W.W., 2003. Determining size-specific emission factors for environmental tobacco smoke particles. *Aerosol Science and Technology*, 37.

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# CCN Activity and AMS Mass Spectra of Tobacco Smoke

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## Introduction

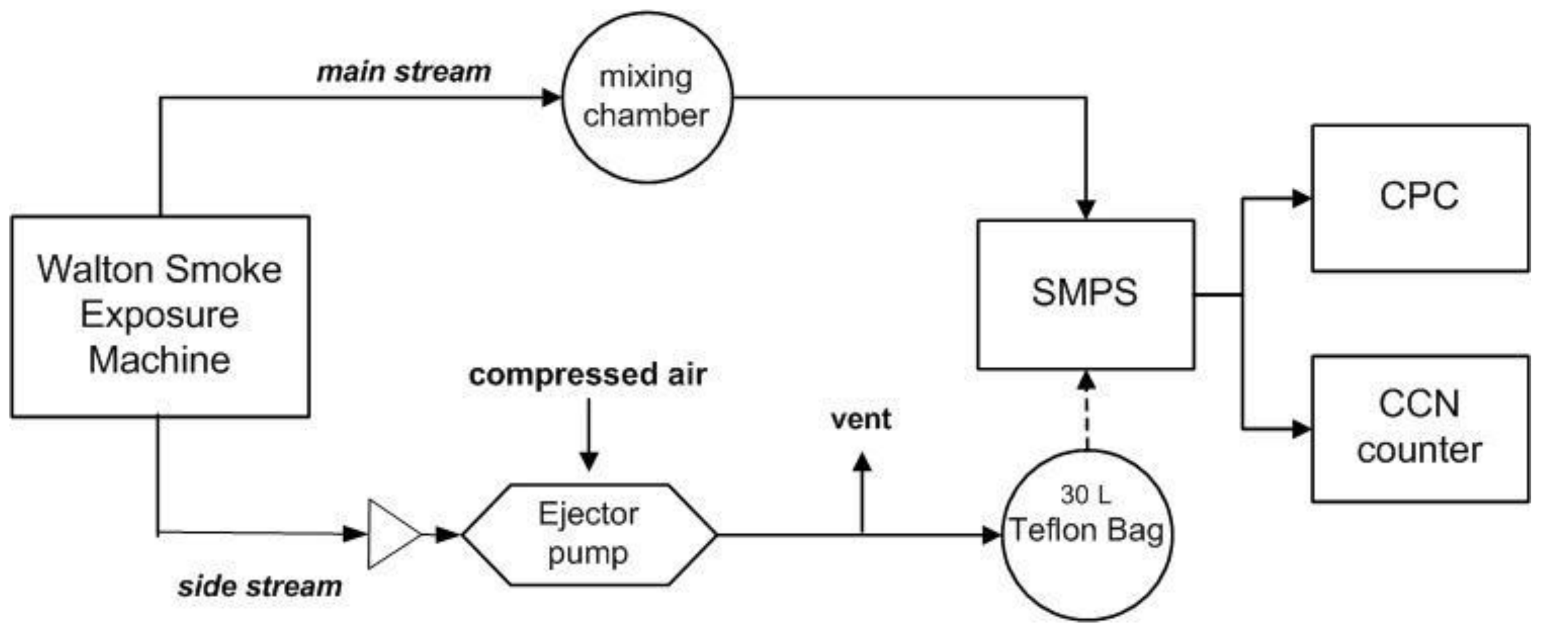
- Secondhand or environmental tobacco smoke (ETS) is a significant source of human exposure to fine particles (Klepeis et al., 2003).
  - ✓ ETS is the combination of "sidestream" smoke (released between puffs from the lit end of the cigarette) and "mainstream" smoke (exhaled by a smoker).
- Cigarette smoke is an aerosol of liquid droplets suspended in a mixture of gases and semi-volatile compounds (Ingebrethsen, 1986). More than 4700 components have been identified in tobacco smoke.
- Adverse health effects from PM air pollution are caused by the deposition of aerosol particles in the respiratory tract during inhalation.
  - ✓ The water vapor uptake by hygroscopic particulate components can alter dry PM size and deposition efficiencies (Broday and Georgopoulos, 2001; Varghese and Gangamma, 2009; Londahl et al., 2009, Schroeter et al., 2010).
  - ✓ The dose and deposition site of these aerosols are influenced by the growth of the particles.
- Dry cigarette smoke has the potential to grow to larger droplet sizes and effect deposition rates (Kousaka et al (1981) .

## Motivation and objective

- Characterize the particle size distribution of cigarette smoke with an emphasis on droplet formation properties.
- Explore the aerosol composition of inhaled cigarette smoke in relation to CCN properties.

## Experimental

### setup




### Material

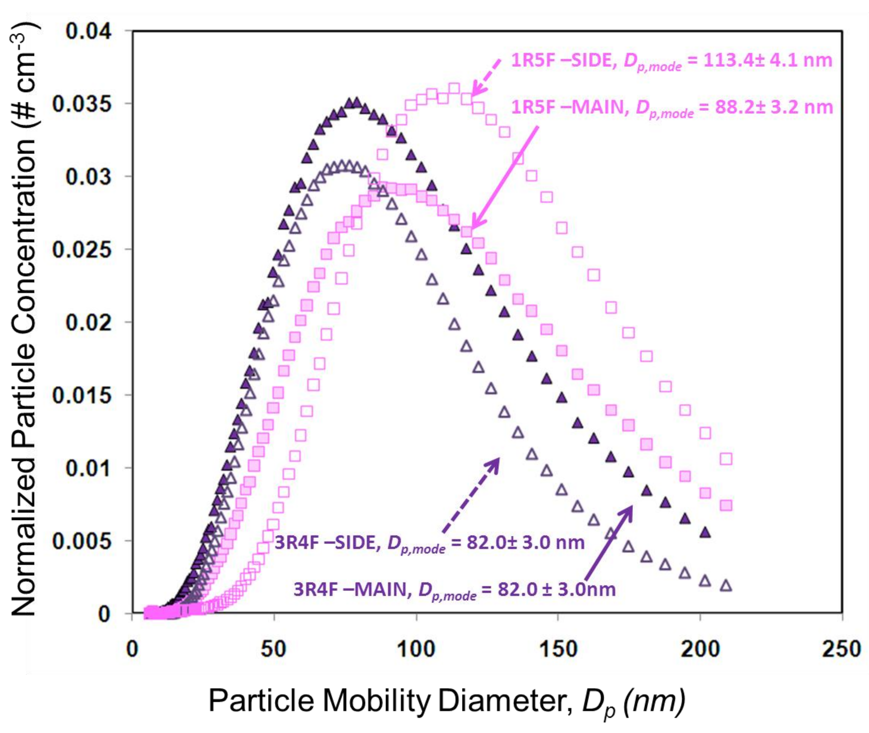
The cigarettes used in this study were research cigarettes purchased from University of Kentucky. Selected properties of the cigarettes used are summarized in the table shown below.

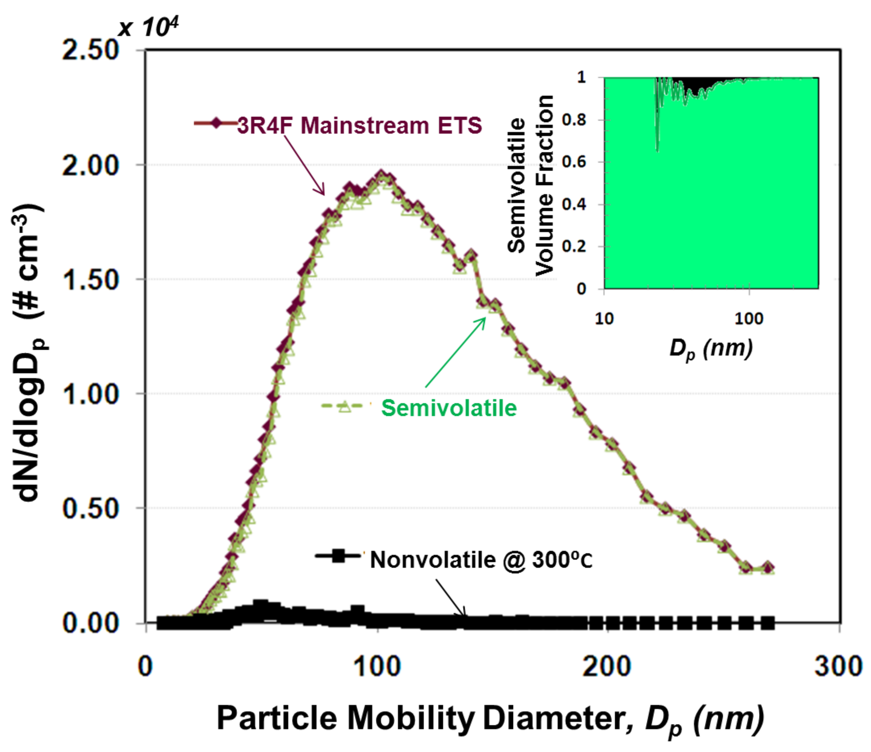
## Results

### Aerosol Composition Characteristics of Cigarette Smoke

| Type | TPM[a] [mg per CIG] | Tar[a] [mg per CIG] | Nicotine[a] [mg per CIG] | stream | O/C | N/C | OM/OC | EC/OC |
|---|---|---|---|---|---|---|---|---|
| 1R5F | 2.08 | 1.67 | 0.17 | main | 0.224 ±0.001 | 0.291 ±0.001 | 1.786 ±0.073. | BDL |
| | | | | side | 0.091 ±0.001 | 0.031±0.001 | 1.299 ±0.005 | 0.007 |
| 3R4F | 10.9 | 9.4 | 0.73 | main | 0.212 ±0.019 | 0.163±0.013 | 1.616 ±0.062 | 0.01 |
| | | | | side | 0.136 ±0.003 | 0.038±0.003 | 1.369 ±0.007 | 0.01 |

### Particle size distributions

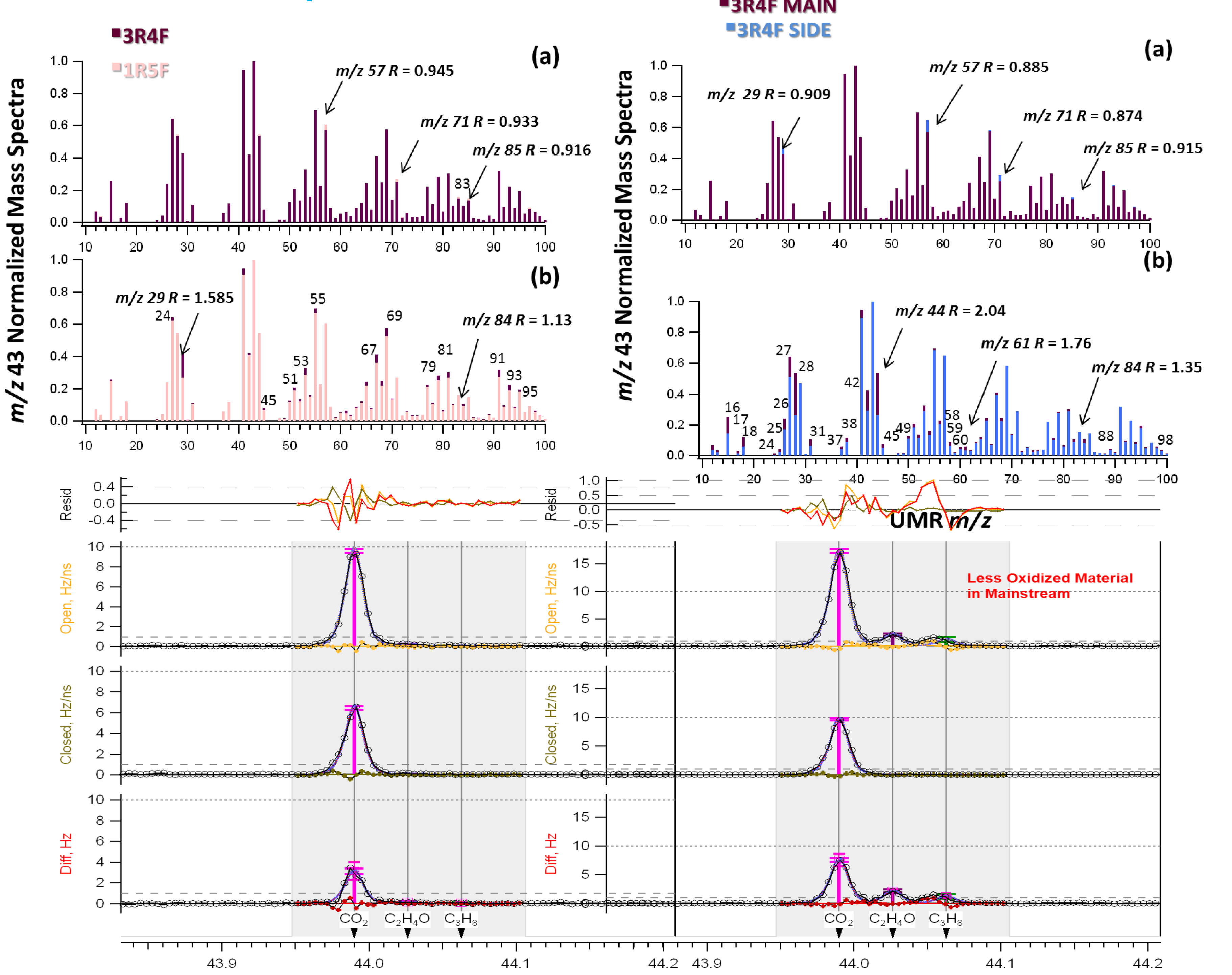



- 1R5F forms larger particles than 3R4F for both main and sidestream ETS
- The majority of 3R4F and 1R5F particles in both main and sidestream ETS are organic and semivolatile.

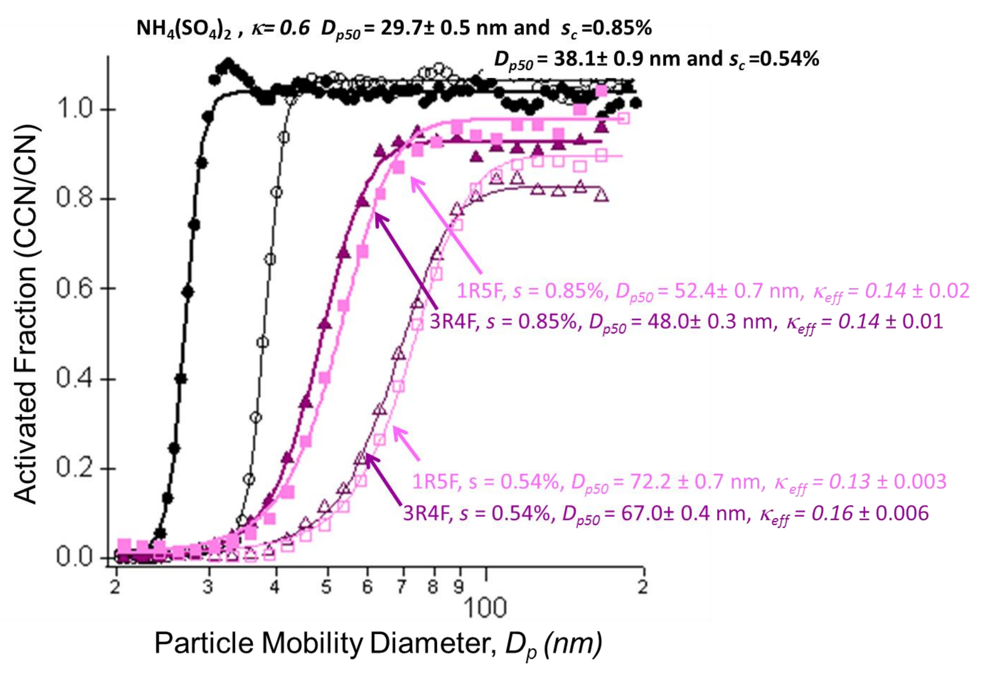
## Aerosol Mass Spectra

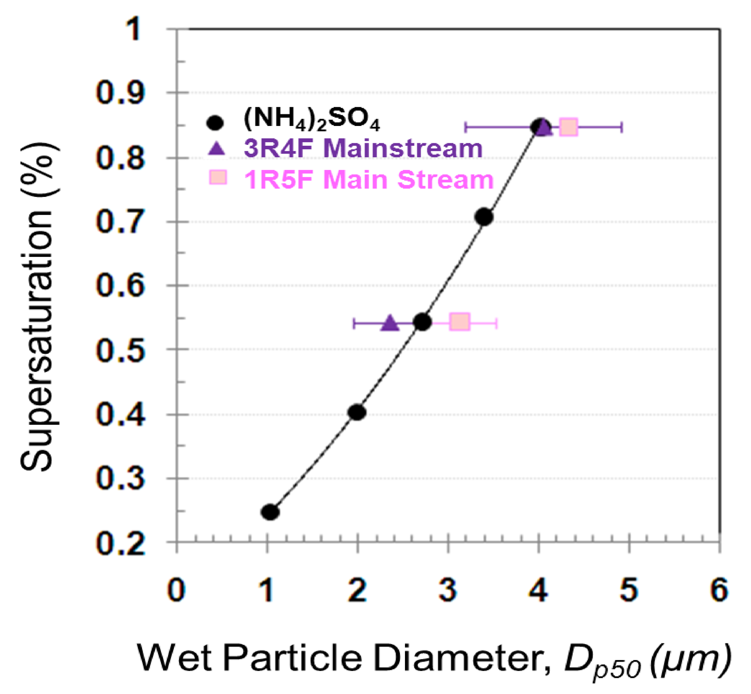
*m/z* 43 Normalized UMR Mass Spectra




- The *m/z* 43 is the most abundant fragment and comprise on average 8.5 ± 0.1% of the total organic signal in both cigarette types.
- 3R4F aerosol forms larger molecular weight fragments and aerosol than 1R5F.
- The side stream smoke likely contains more N products, as the presence of its fragmentation pattern (m/z 29,43,57,71,85) suggests the higher presence of N containing species favors the presented fragmentation pattern.
- Mainstream aerosol forms more oxidized products.
  - ✓ UMR data suggests twice as much m/z 44 is produced in main stream.
  - ✓ HR data shows that the C02+ ion is the only contribution m/z 44 of main stream, where as sidestream contains both CO2+ and less oxidized C2H4)and C3H8 ions.

## CCN Activity




- 3R4F (triangles) have smaller activation diameters, Dp50 compared to IR5F (squares) aerosol.
- $\kappa_{eff}$ (~0.15) of both cigarette types are indicative of partially soluble organic materials.

Both 3R4F and IR5F aerosol grow to similar sizes as $(NH_4)_2SO_4$ at activation. Despite being less hygroscopic ($\kappa_{eff}$ < 0.6), organic ETS have the same droplet growth rates as soluble $(NH_4)_2SO_4$ particles.

## Conclusions and implications

- Smoke particles are mostly semivolatile.
- MS shows side stream particle likely contain more N compounds.
- 3R4F has smaller activation diameter than 1R5F, while both cigarette types have $\kappa_{eff}$ ~ 0.15.
- *At larger supersaturation (< 0.6%), up to 90% of particles greater than 100 nm will form droplet in the lung airways.*

## References

Broday, D. M., and Georgopoulos, P. G.: Growth and deposition of hygroscopic particulate matter in the human lungs, Aerosol Sci Tech, 34, 144-159, 2001.
Ingebrethsen, B. J.: Evolution of the Particle-Size Distribution of Mainstream Cigarette-Smoke during a Puff, Aerosol Sci Tech, 5, 423-433, 1986.
Klepeis, N. E., Apte, M. G., Gundel, L. A., Sextro, R. G., and Nazaroff, W. W.: Determining size-specific emission factors for environmental tobacco smoke particles, Aerosol Sci Tech, 37, 780-790, 2003.
Londahl, J., Massling, A., Swietlicki, E., Brauner, E. V., Ketzel, M., Pagels, J., and Loft, S.: Experimentally Determined Human Respiratory Tract Deposition of Airborne Particles at a Busy Street, Environ Sci Technol, 43, 4659-4664, 2009.
Schroeter, J. D., Garcia, G. J. M., and Kimbell, J. S.: A computational fluid dynamics approach to assess interhuman variability in hydrogen sulfide nasal dosimetry, Inhal Toxicol, 22, 277-286, 2010.
Varghese, S. K., and Gangamma, S.: Particle deposition in human respiratory system: Deposition of concentrated hygroscopic aerosols, Inhal Toxicol, 21, 619-630, 2009.

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