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A Larger Source of Secondary Organic Aerosol Precursors in Continental and Marine Air

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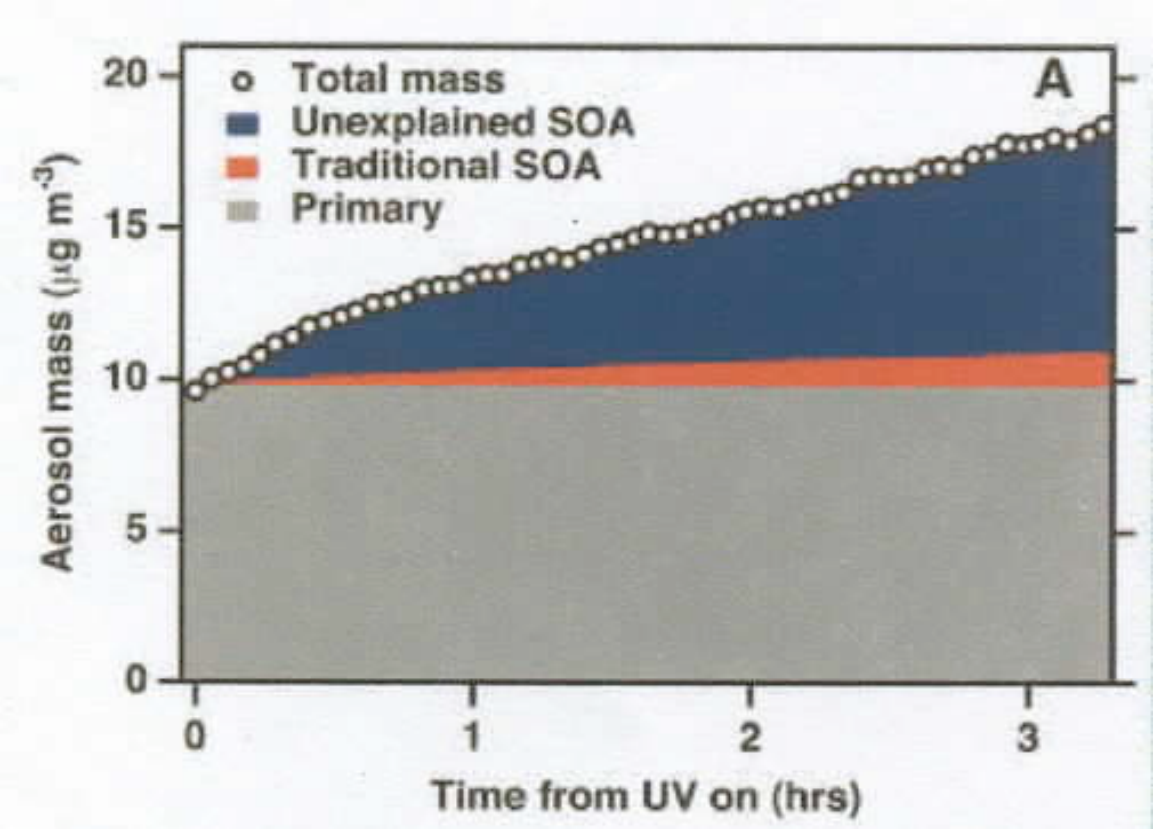
Unexplained SOA From Field Experiments

- ACE-Asia 2001 - "Our results suggest a large, sustained source of SOA in the free troposphere from oxidation of long-lived volatile organic compounds." (Heald et al., Geophys. Res. Lett., doi:10.1029/2005GL023831, 2005)
- NEAQS-2002 - "The increase in sub-μm POM could not be explained by the removal of aromatic precursors alone, suggesting that other species must have contributed and/or that the mechanism for POM formation is more efficient than previously assumed." (de Gouw et al., J. Geophys. Res., doi:10.1029/2004JD005623, 2005)
- MCMA-2003 - "…reactive anthropogenic VOCs produce much larger amounts of SOA than these models predict, even shortly after sunrise." (Volkamer et al., Geophys. Res. Lett., doi:10.1029/2006GL026899, 2006)

Unexplained SOA From Laboratory Experiments

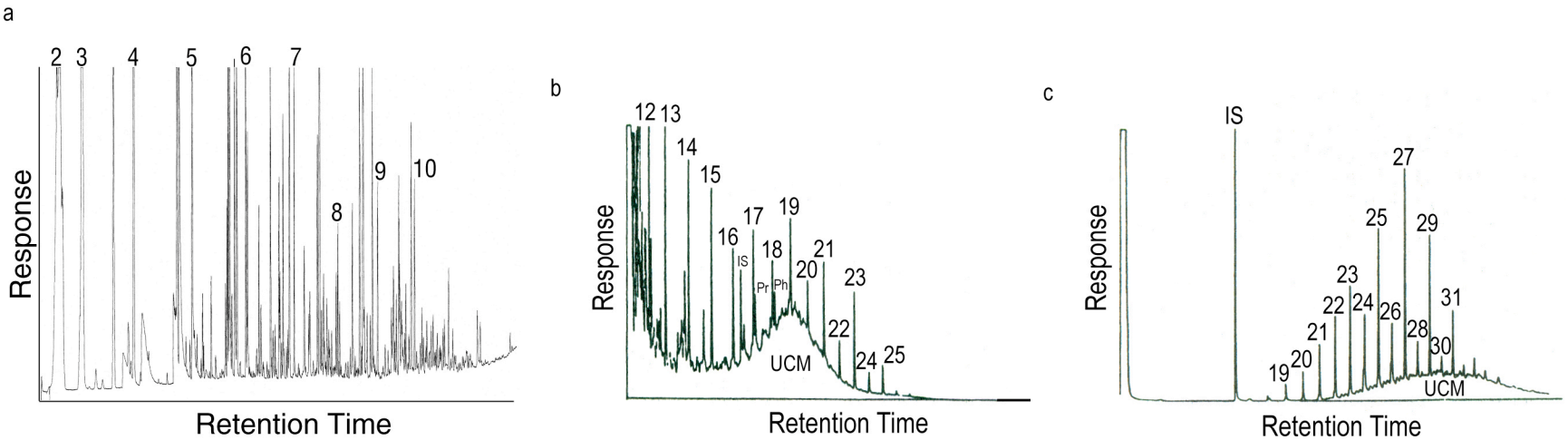


85% of the SOA yield from diesel exhaust was attributed to photochemical aging of semivolatile precursors less volatile than approximately an *n*-alkane with 12 carbon atoms (Robinson et al., Science, doi:10.1126/science.1133061, 2007).

Atmospheric Organic Matter C_2-C_{31}

Urban

Background Continental



n-C_2 – n-C_{10}
(20-80 ppbv)

n-C_{11} – n-C_{31}
(71 pptv)

n-C_{11} – n-C_{31}
(0.62 pptv)

Volatile Organic Compounds (VOCs)

Semivolatile Organic Compounds (SVOCs)

SVOCs in Diesel Exhaust*

- C_{11}-C_{29} *n*-Alkanes
- C_{14}-C_{20} Isoprenoids (norfarnesane, 2,6,10-trimethyl tridecane, farnesane, pristane, phytane)
- C_{11}-C_{25} *n*-Alkylcyclohexanes
- C_{11}-C_{13} *n*-Aldehydes
- C_{8}-C_{20} *n*-Alkanoic acids
- Polyaromatic hydrocarbons
- UCM - Unresolved complex mixture of branched and cyclic aliphatics

*Schauer et al., Environ. Sci. Technol., 33, 1578-1587, 1999; Schauer et al., Environ. Sci. Technol., 36, 1169-1180, 2002.

Gas/Aerosol Partitioning

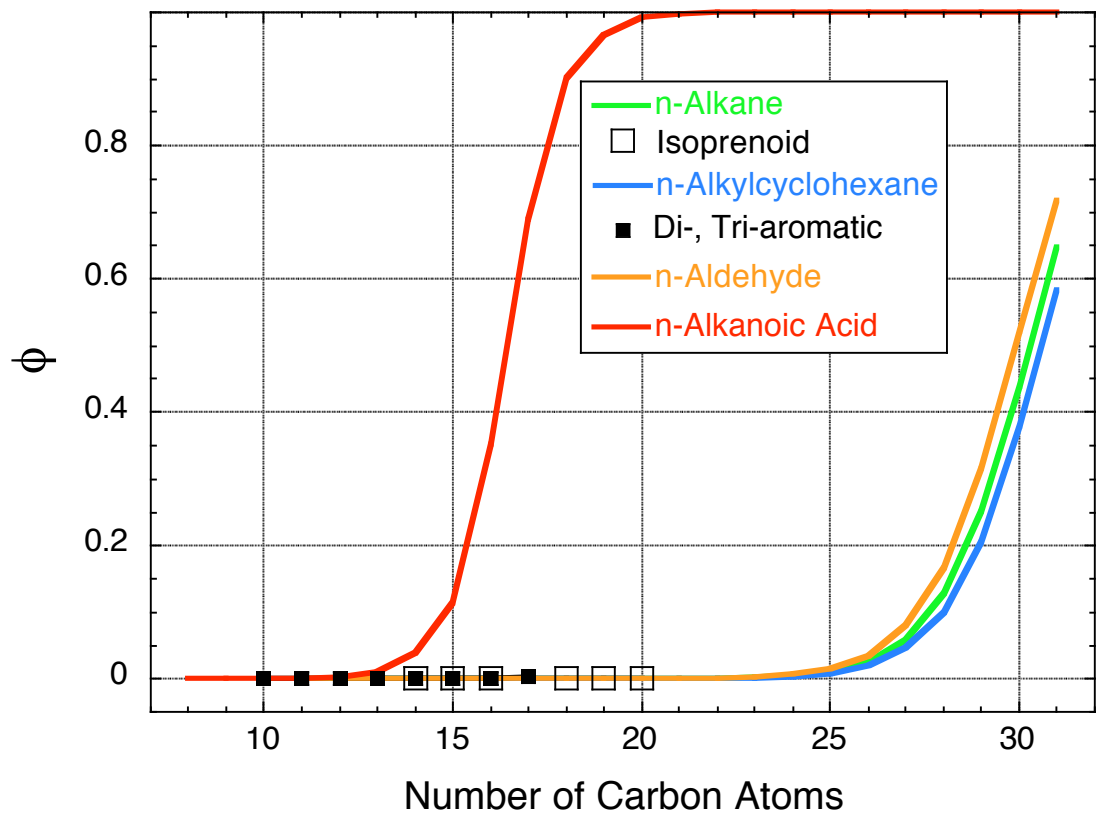
$$\phi = K_{pa}\,(TSP) \,/\, [1 + K_{pa}\,(TSP)]$$

$$\log K_{pa} = \log K_{oa} - 12.61$$

K_{pa} = Particle/Air partition coefficient

K_{oa} = Octanol/Air partition coefficient

TSP = Total suspended particle concentration ($\mu g\ m^{-3}$)

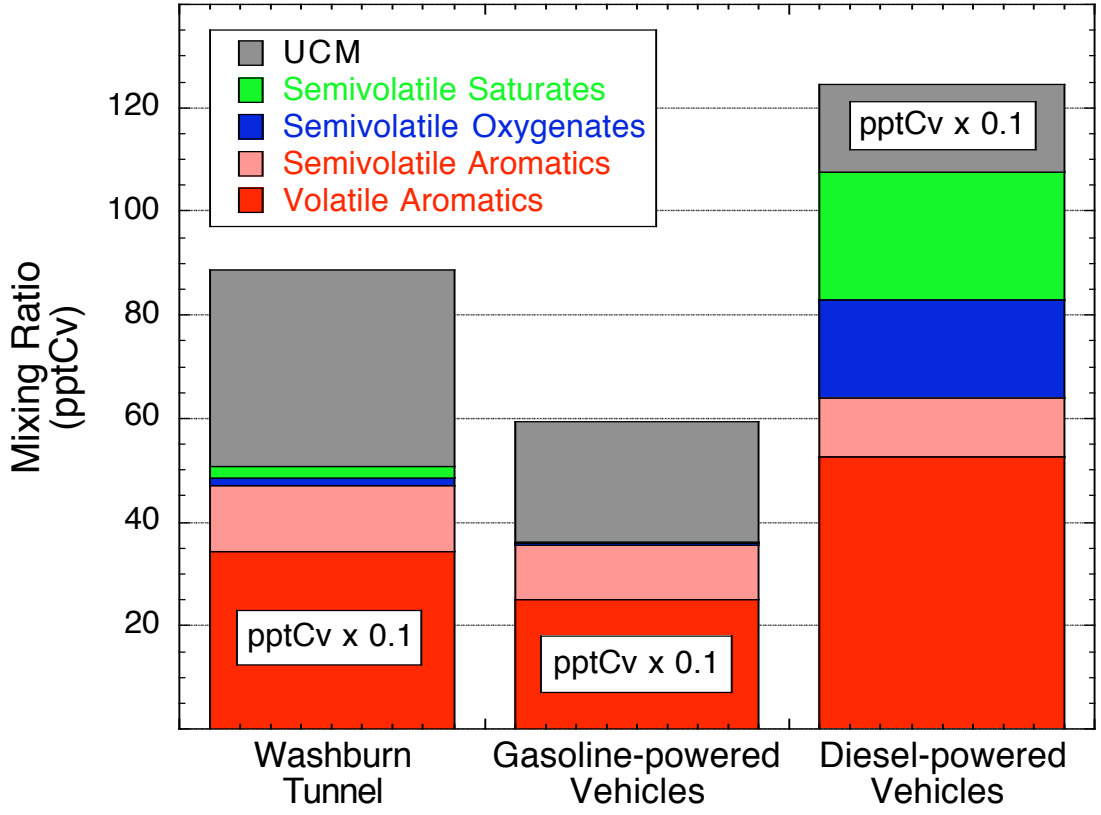


TSP = 32 $\mu g\ m^{-3}$

T = 25°C

SOA Precursors in Washburn Tunnel (Houston Texas)

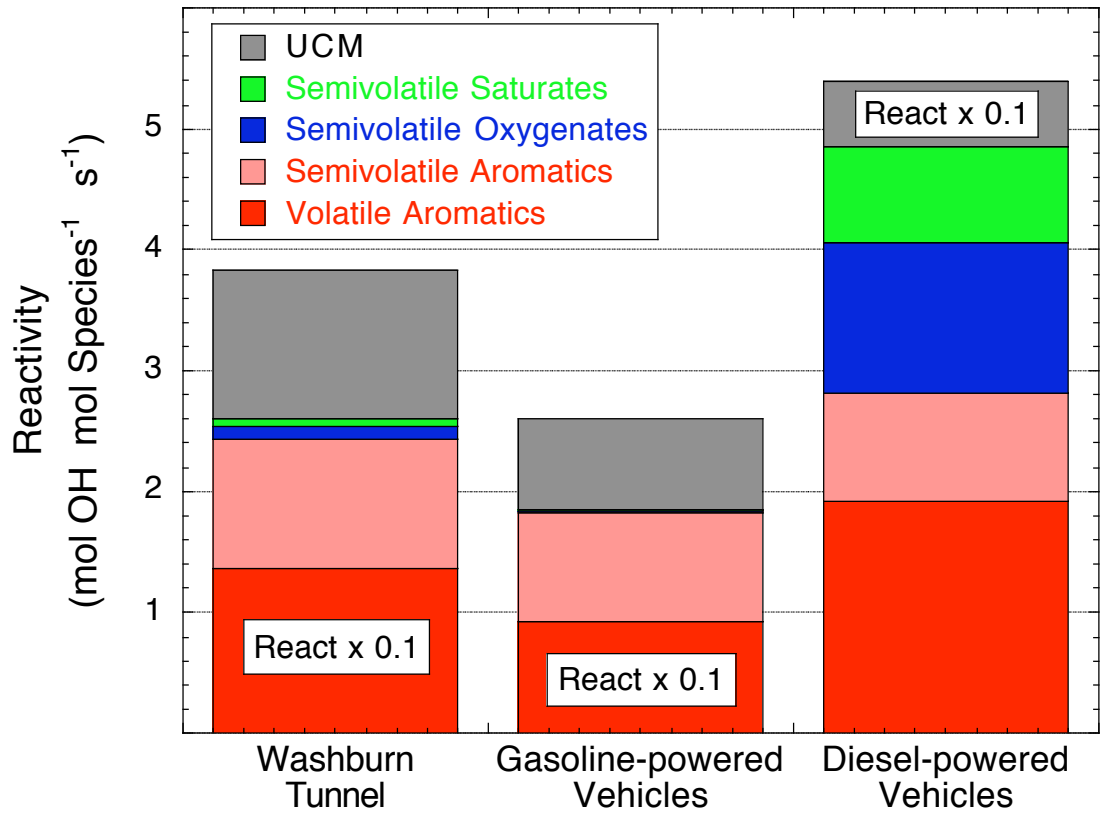
- 81% and 12% of SOA precursors emitted by DPV and GPV, respectively, are semivolatile.
- 14% of SOA precursors in the Washburn Tunnel sample are semivolatile, 30% can be resolved by 1DGC.



6% DPVs (Fraser et al., Environ. Sci. Technol., 37, 3904-3909, 2003)

OH reactivity of SOA Precursors in Washburn Tunnel (Houston Texas)

- 82% and 15% of the OH reactivity of SOA precursor emissions from DPVs and GPVs, respectively, is associated with SVOCs.
- 15% of the OH reactivity of SOA precursor emissions in the Washburn Tunnel sample is associated with SVOCs.
- DPV mileage in the U.S. represents 12% of the 2006 vehicle-miles.



6% DPVs (Fraser et al., Environ. Sci. Technol., 37, 3904-3909, 2003)

SVOCs in Forest Air

- Terrestrial plants, plankton, bacteria, fungi, and insects synthesize aliphatic hydrocarbons by a fatty acid elongation-decarboxylation pathway.
- Epicuticular waxes of terrestrial plants are abraded from leaves by wind and erosion, contain *n*-C_{21}–*n*-C_{35} with an odd carbon preference, and comprise a significant fraction of aerosol-phase *n*-alkanes observed in the atmosphere of forests.
- Gas-phase aliphatic hydrocarbons in forests exhibit a homologous series of *n*-alkanes with a slight odd-carbon preference indicative of a biogenic source, possibly microbial.
- Terpenes are quite likely the most important SOA precursors in semi-remote forests by virtue of large emission rates and rapid reaction with OH.

SVOCs in Marine Air

- Nonsiliceous plankton produce primarily *n*-C_{15}, *n*-C_{17}, and *n*-C_{19} but also produce *n*-alkanes over a broad range.
- Microbes synthesize *n*-alkanes over a broader range (*n*-C_{14}–*n*-C_{30}). Bacterial production of dissolved organic matter (DOM) in oligotrophic ocean waters can approach 23% of total primary production.
- Carbonyl compounds are produced in the ocean by photodegradation of DOM.
- In the coastal ocean of Mace Head, Ireland, the estimated volatilization rate of *n*-C_{15} was 21 pmol m^{-2} s^{-1}, which generated an atmospheric mixing ratio of 35 pptv, similar to observed values.
- In the coastal ocean of the U.K., the estimated volatilization rate of isoprene was 0.64 pmol m^{-2} s^{-1}.

OH Reactivity of SOA precursors in Marine Air*

SVOCs represent approximately 5% of the OH reactivity of SOA precursors in marine air.

Species	Mixing Ratio (pptCv)	OH Reactivity mol OH mol species^{-1} s^{-1}
Isoprene	240	1.2×10^{-1}
Monoaromatics	890	3.1×10^{-2}
n-C_{11}–n-C_{15}	260	7.5×10^{-3}

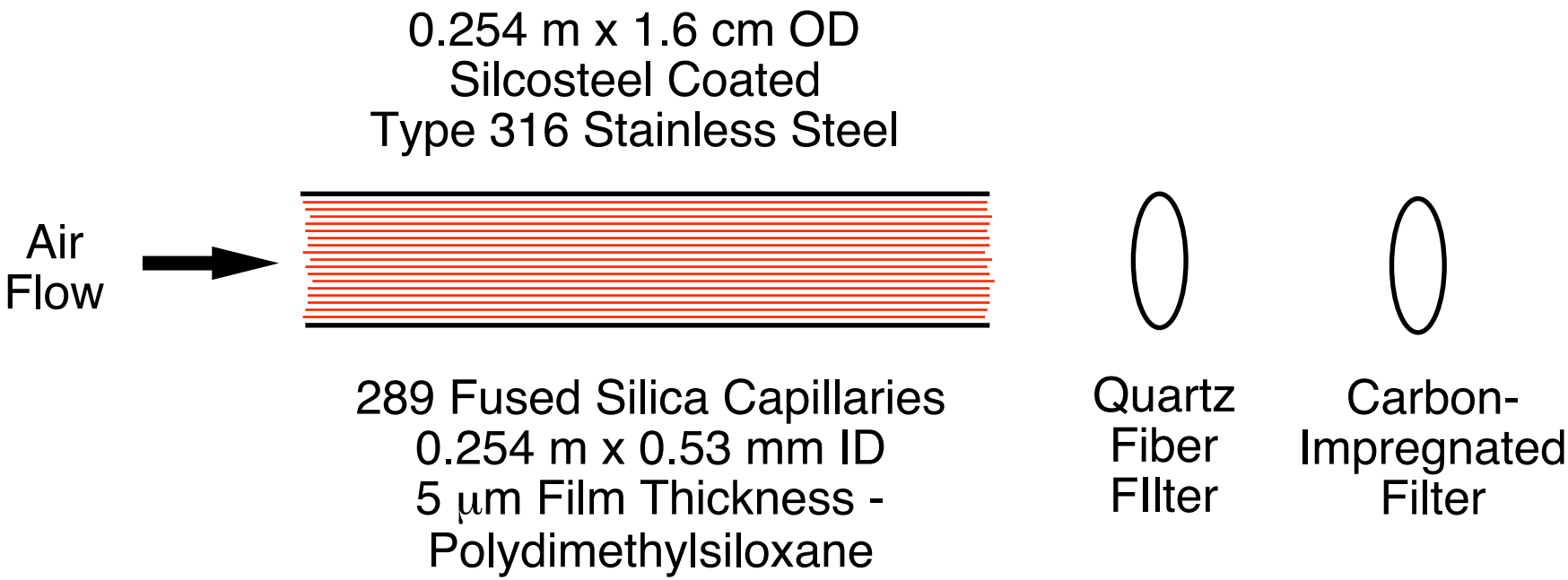
*Measurements in coastal ocean atmosphere of Mace Head, Ireland. (Lewis et al., J. Chem. Soc., Faraday Trans., 93, 2921-2927, 1997; Sartin et al., J. Geophys. Res., doi:10.1029/2000JD000232,2002)

Atmospheric Lifetime of SVOCs

Species	Continental Air[1]	Marine Air[2]	
	τ_{OH} (hr)	τ_{OH} (hr)	τ_{Cl} (hr)
Pentadecane	2	10	4
Pentadecanal	1	5	4

[1] OH = 7.5×10^6 molecules cm^{-3}
[2] OH = 1.5×10^6 molecules cm^{-3}, Cl = 1.3×10^5 atoms cm^{-3}

SVOC Sampling Approach



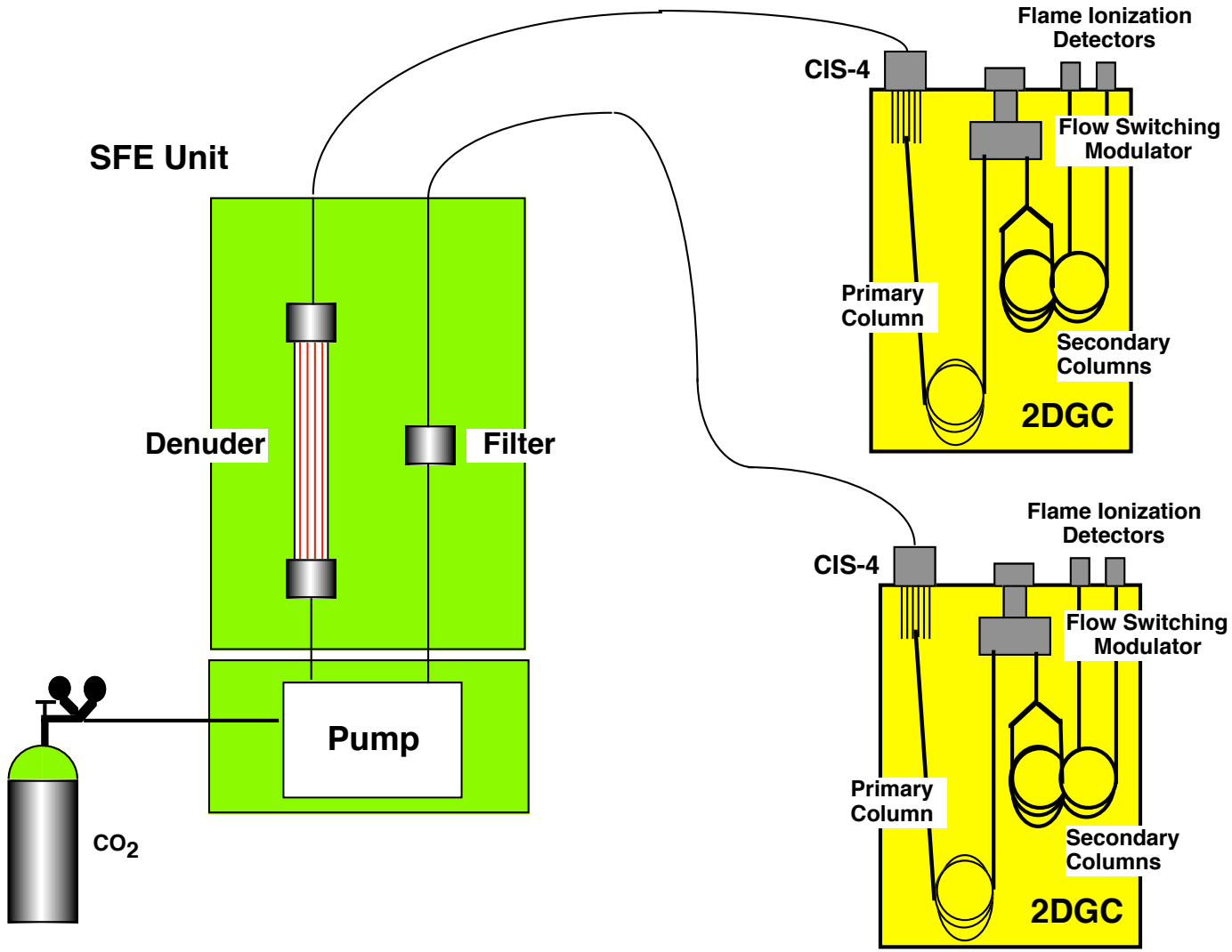
Gas-phase

- Aliphatics
- Oxygenated hydrocarbons
- Di- and Tri-aromatics

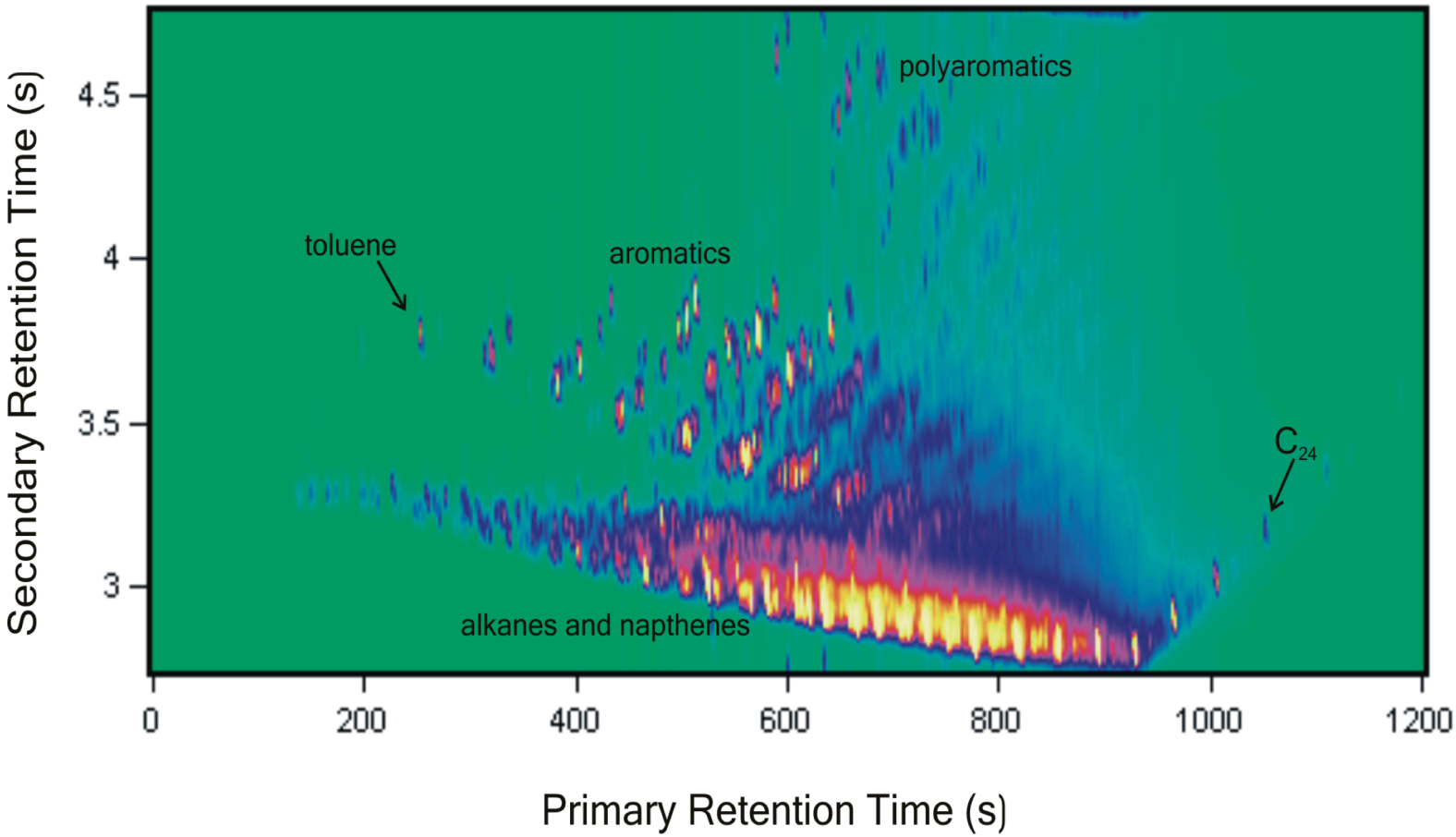
Aerosol-phase

- δ-Hydroxynitrates
- Dinitrates
- Hydroxydinitrates

SVOC Analytic Approach



Two-dimensional Gas Chromatography*/Time-of-Flight Mass Spectrometry (2DGC-TOFMS)



*Seeley, J.V., personal communication, Oakland University, Rochester, MI, 2008.