Novel measurement technologies for ambient and combustion source aerosols

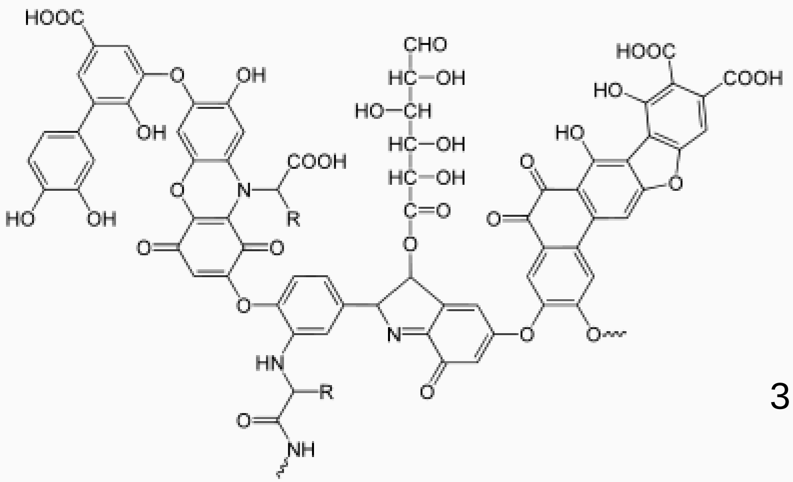
Michael D. Hays

Outline

I. Focus on (organic) aerosol particle composition
II. A brief history and review of select past studies
III. A look at newer developments and technology applications
IV. Possible new directions tied to health-related research directions
V. Wrap-up

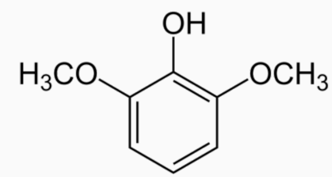
Aerosol chemical fractions

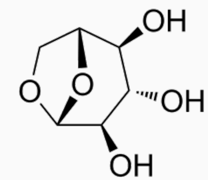
- organic carbon (OC); elemental carbon (EC); black carbon (BC); brown carbon (BrC);
- humic-like substances (HULIS);
- water-soluble organic carbon (WSOC);
- oxygenated organic aerosol (OOA) (Aerosol MS)
- molecular weight and size
- functional group-based chemistry (FT-IR)
- volatility and thermal-chemical fractions
- elemental and ionic (K^+ with some chloride, nitrate, and sulfate)
- water (hygroscopicity)

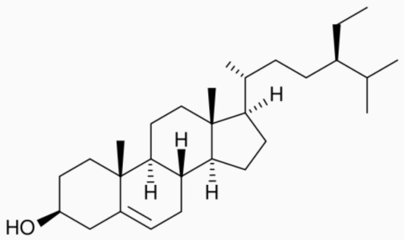


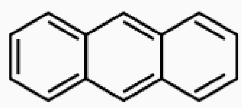
Examples of major organic compound classes

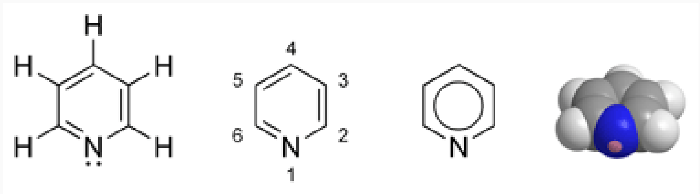
- carbohydrates and derivatives (anhydro-sugars)
- lignin derivatives (methoxyphenols)
- diterpenoids and triterpenoids
- phytosterols
- carboxylic acids
- alkanols, alkanals, and alkanoates
- alkanes and alkenes
- **polycyclic aromatic hydrocarbons (PAH)**
- **dioxins and furans**
- **organic nitrogen compounds (indoles, nitriles))**
- **Heterocyclics (thiophenes, organometallics)**







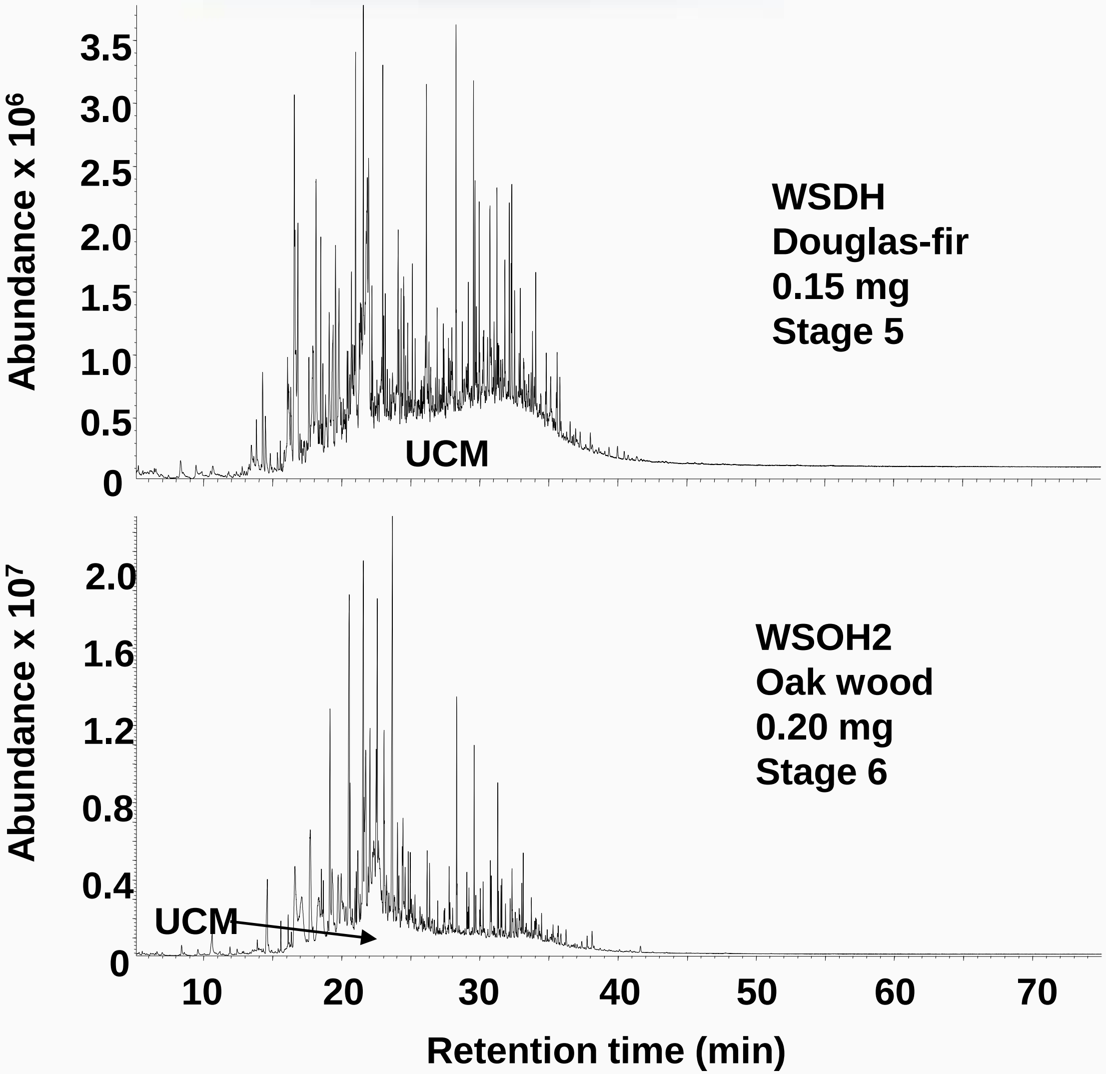




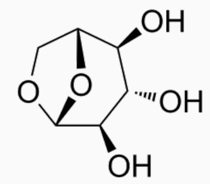
- GC-MS identified compounds
- Relative proportions and class change with atmospheric conditions and combustion source

Medeiros and Simoneit, ES&T, **2008** (*42*) p. 8310

GC-MS (biomass burning example)



- SVOC chemistry grounded in GC-MS
- GC-MS limited by:
- temperature or volatility (300 °C)
  - thermal degradation
- polarity
  - derivatization
- resolution (column space)



Resolution and temp. limits of GC-MS

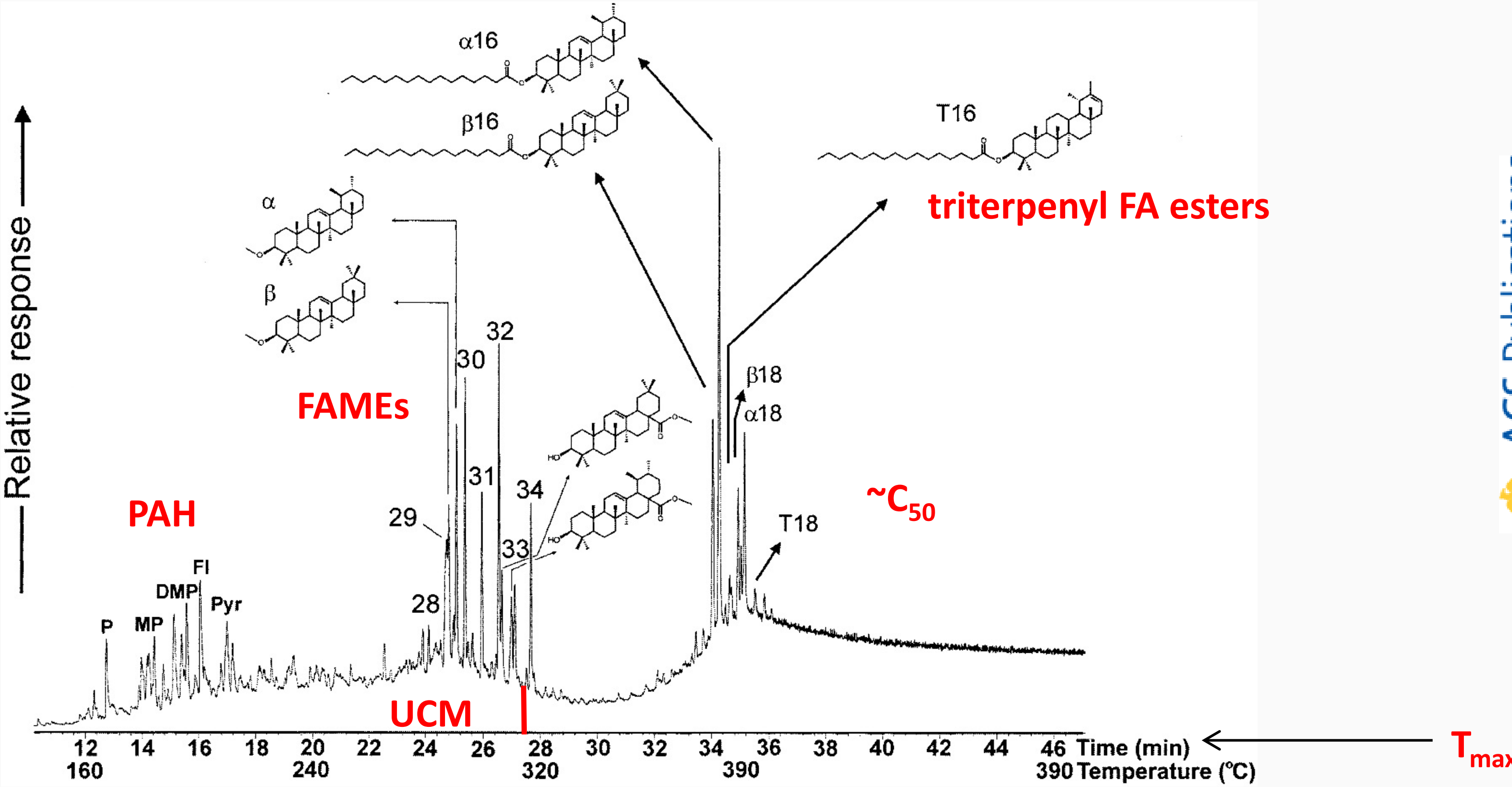
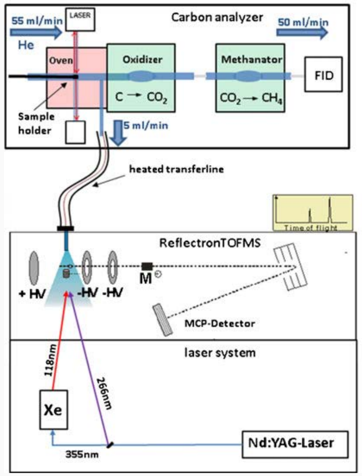


Figure 5. Representative total ion current trace (HTGC–MS) of the ester fraction from the smoke extract from burning of Castanha-do-Pará. Numbers refer to the carbon chain length of free fatty acids (analyzed as the methyl esters): P = phenanthrene; MP = methylphenanthrenes; DMP = dimethylphenanthrenes; Fl = fluoranthene, and Pyr = pyrene. α, β, and T are the esterified triterpenols α-amyrin, β-amyrin, and taraxasterol, respectively.

Published in: Vladimir O. Elias; Bernd R. T. Simoneit; et al.; *Environ. Sci. Technol.* **1999,** 33, 2369.

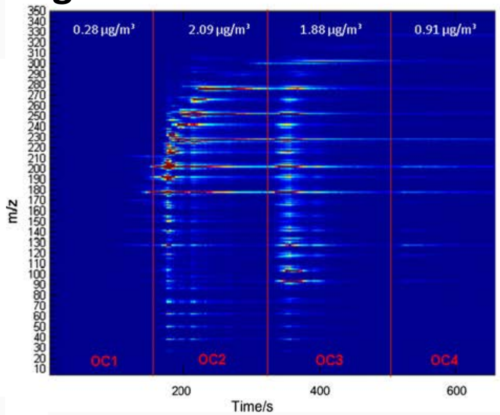
Carbon analyzer and PI-MS analysis

Chemistry changes with volatility:

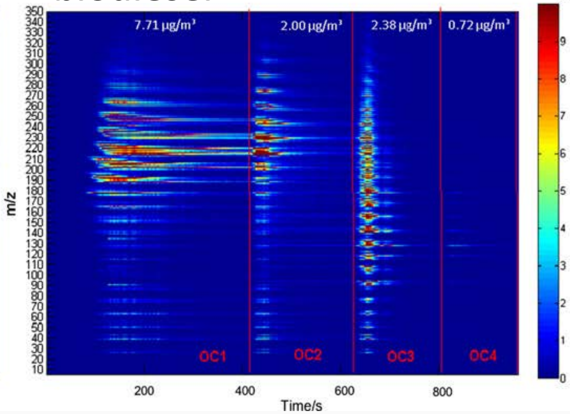


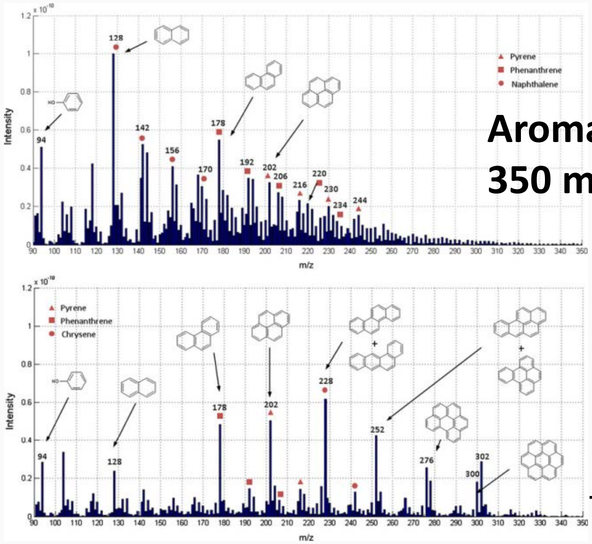
Pure Helium		Helium / 2 % O_2	
OC1	120°C	EC1	550°C
OC2	250°C	EC2	700°C
OC3	450°C	EC3	800°C
OC4	550°C		

gasoline



biodiesel





Aromatics 350 m/z

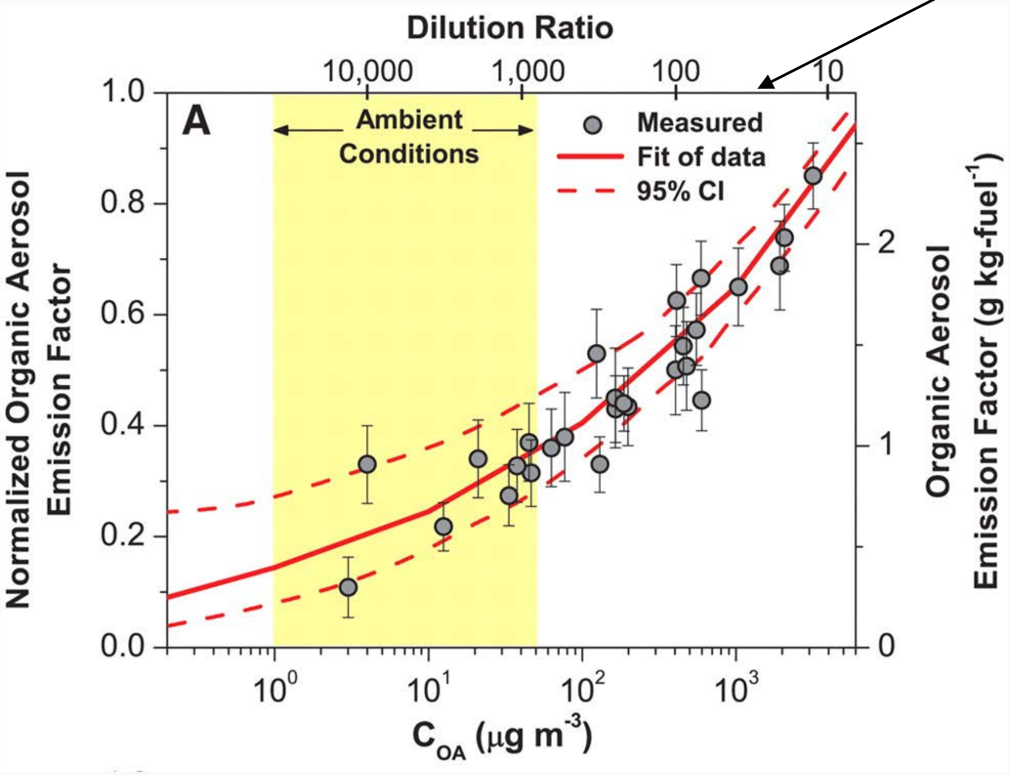
How do we develop a volatility-based toxicology model?

Grabowsky et al., (**2011**), *Anal. Bioanal. Chem.*, 401, pp. 3153-3164

Why is volatility distribution important?

Diesel exhaust at 300 ºK

typical emissions collection

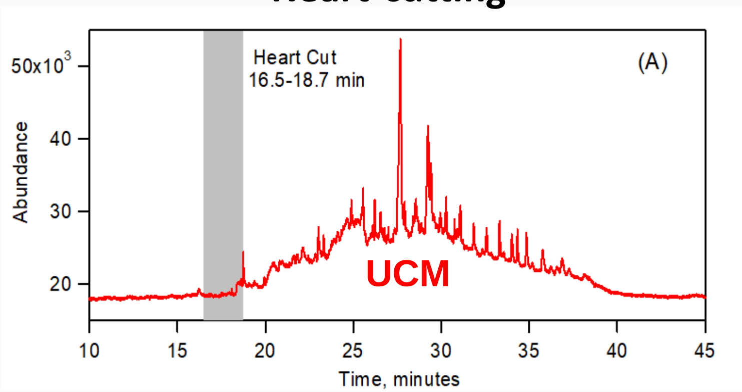


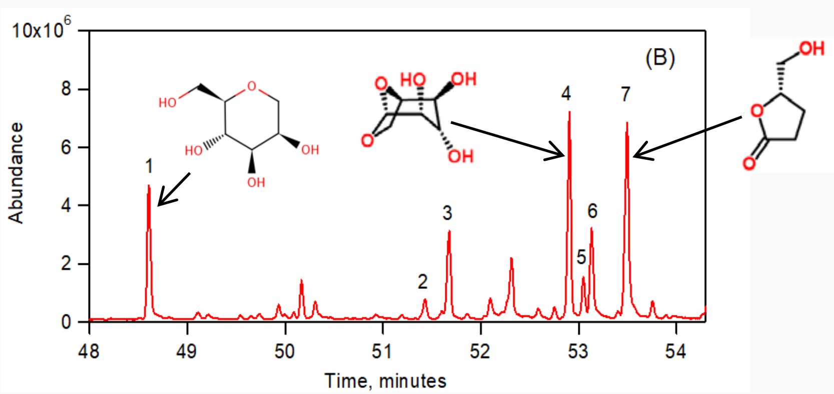
- produce more realistic chemical exposure scenarios
- there is more anthropogenic SOA than primary OA
    - reactive byproducts will be important

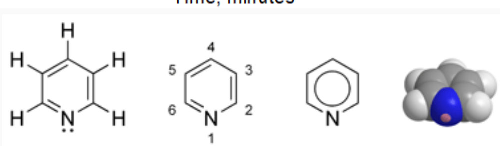
Robinson *et al.*, *Science*, **315** (5816): 1259-1262

2D-GC-MS (GC-GC and GCxGC)

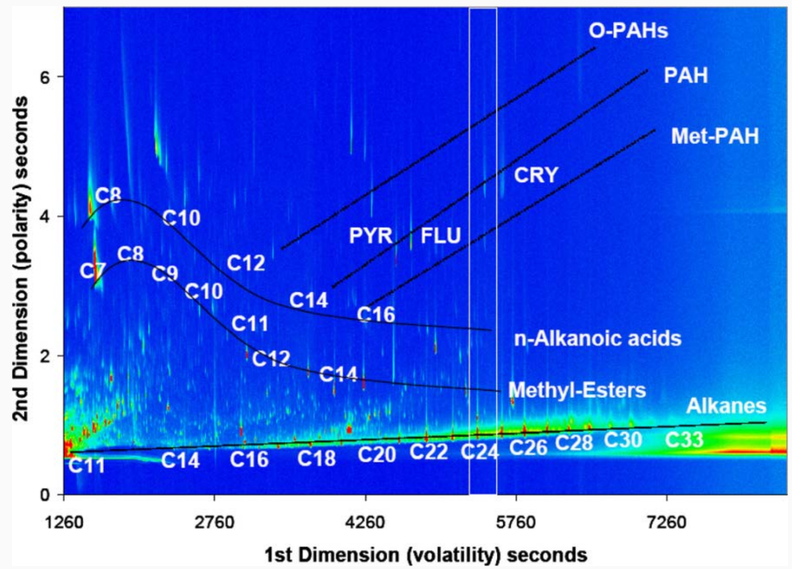
Heart-cutting







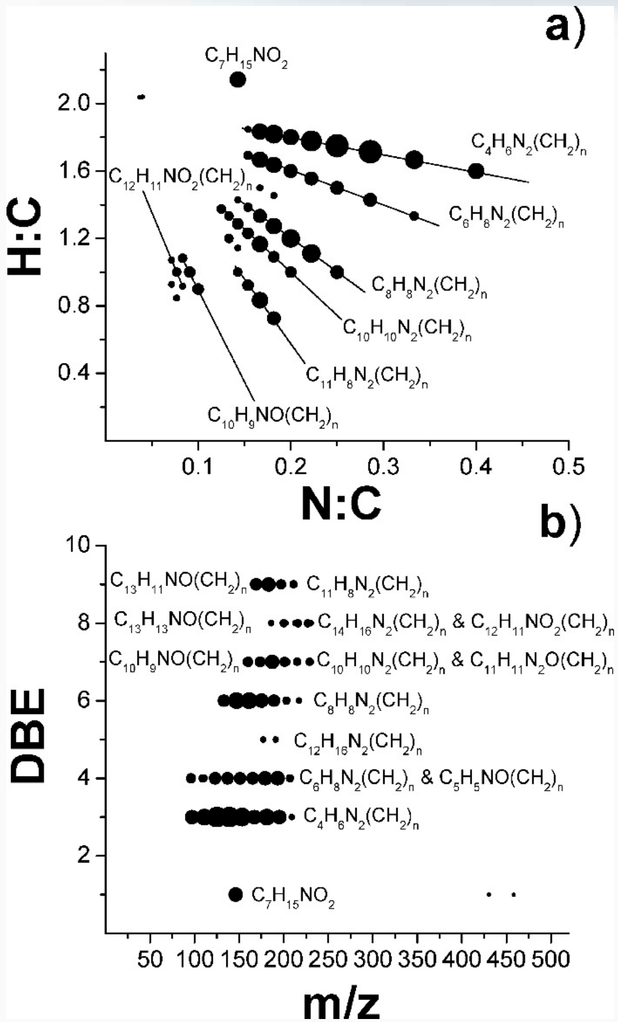
Comprehensive (fixed, fast modulation)



Published in: Schnelle-Kreiss et al; *J. Sep. Sci.* **2005,** 28, 1648.

2D-GC methods can overcome resolution and polarity challenges but not the temperature ones (yet)

LC-MS applications



ESI-(HR)MS

- van Krevelen diagram, PPNS sample
- chemical formulas are resolved with HR-MS
    - advanced fingerprinting
    - no chemical structure

- N proportional to H
- negative slope increases with C no.
- alkaloids were observed
    - new compound detection possible

Compositional knowledge is primarily based on solvent chemistry

The size of the data points is proportional to the logarithm of the peak intensity.

ACS Publications High quality. High impact.

Published in: Laskin et al; *Environ. Sci. Technol.* **2009,** 43, 3764-3771.

Solvent extraction

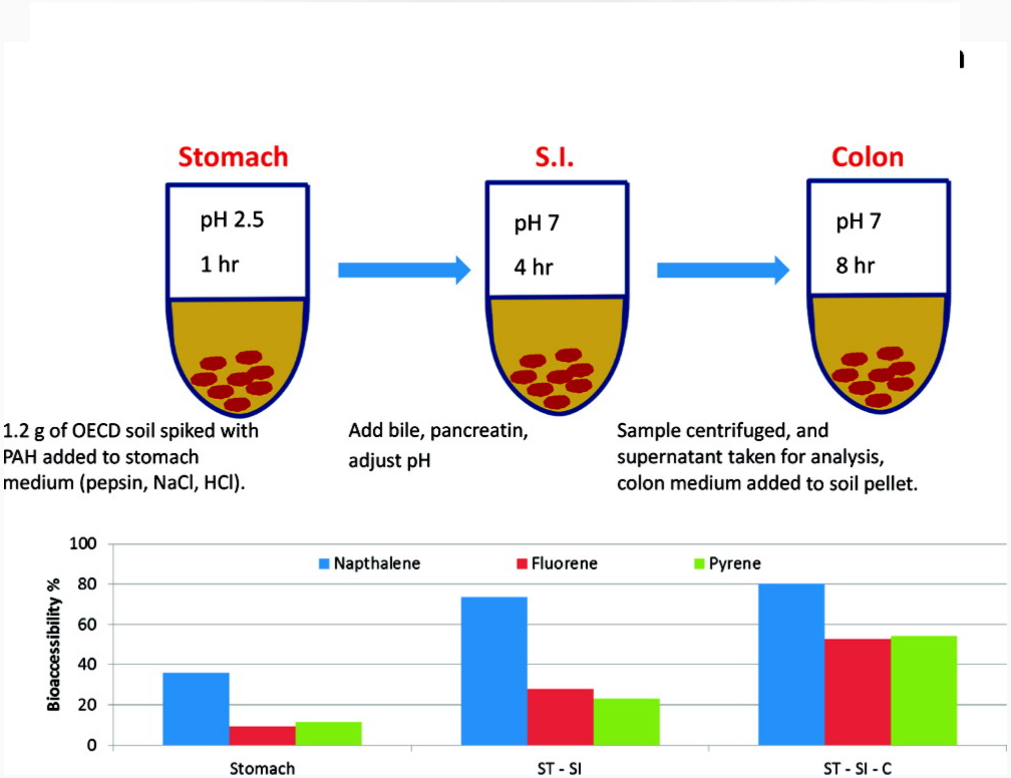
- goal is to extract as much and as many **organic** compounds as possible
- determine a maximum possible exposure
- **there can be organic solvent bias (dosimetry)**

What about bioavailability?

According to WEB OF SCIENCE^{TM}.

- since 1985, 518 papers have focused on “particulate matter” *AND* “bioavailability”
- more than half of those focused on “metals”
- minimal focus on organic compounds
- cell response/expression was covered (e.g.; ascorbate oxidation, glutathione depletion)

Physiological-based fluid extractions



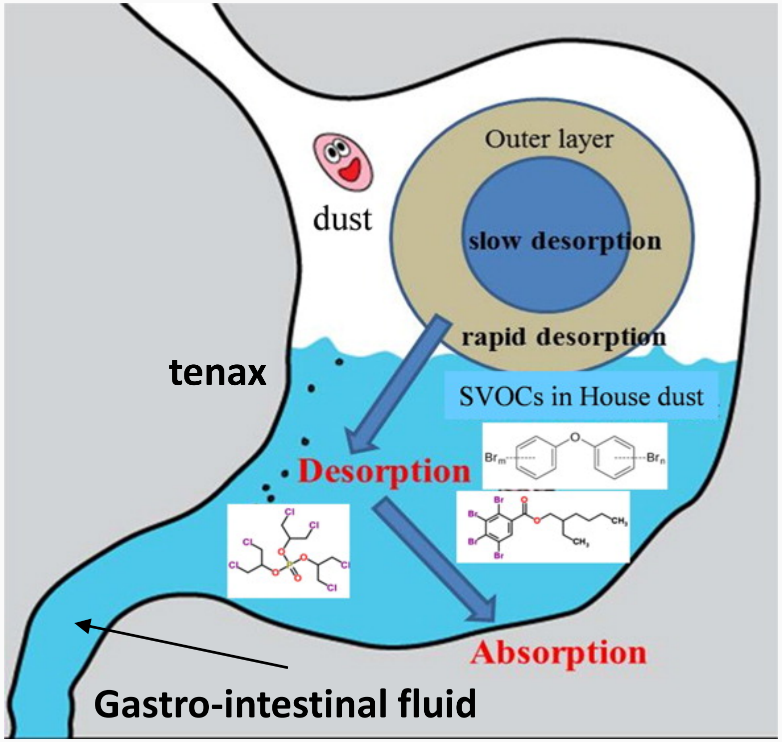
- Experiments
  - PAH in soil in the gastro-intestinal system
  - sequentially or in batch, time
  - differences in PAH bioaccessibility observed
  - GC-MS

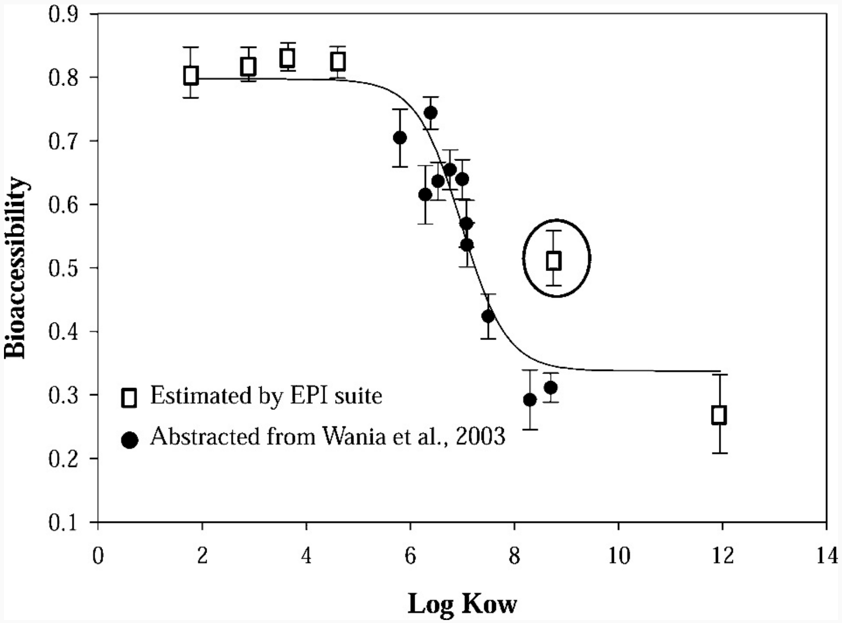
- Results
  - PBET underestimates [PAH] in soil
  - desorption of PAH is controlled by many factors
  - biological environment, K_{OW}
  - colon media aggressively desorbed PAH.

Precedent for particle extractions with lung fluid

E. L. Tilston; G. R. Gibson; C. D. Collins; *Environ. Sci. Technol.* **2011,** 45, 5301-5308.DOI: 10.1021/es2004705

Physiological-based fluid extractions





Flame retardants-PBDE and organophosphates

Published in: Mingliang Fang; Heather M. Stapleton; *Environ. Sci. Technol.* **2014,** 48, 13323-13330. DOI: 10.1021/es503918m

Simulated lung fluids

Gamble's solution - deep lung

ALF – following macrophage phagocytosis

SLF2 – extracellular fluid interaction

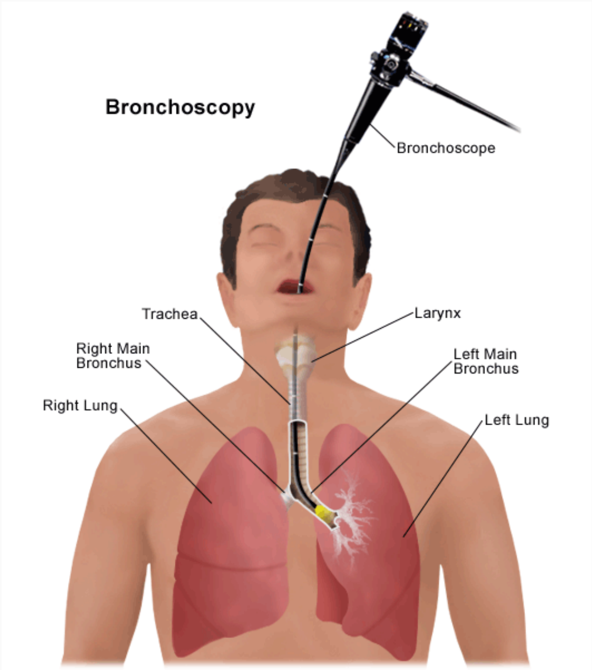
Table 11. Simulated Lung Fluid (SLF)

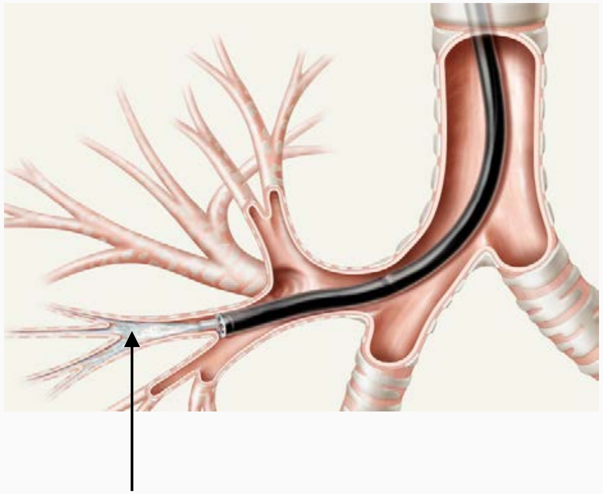
	SLF1		SLF2	SLF3	SLF4	SLF5
Composition	**ALF (g/L)**	**Gamble's Solution (g/L)**	**(mg/L)**	**(g/L)**	**(g/L)**	**mMol/L**
magnesium chloride	0.050	0.095	-	0.2033 (hexahydrate)	$MgCl_2$ hexahydrate 0.2033	-
sodium chloride	3.21	6.019	6800	6.0193	6.0193	116
potassium chloride	-	0.298	-	0.2982	0.2982	-
disodium hydrogen phosphate (Na_2HPO_4)	0.071	0.126	1700 (monohydrate)	-	-	-
sodium sulfate	0.039	0.063	-	0.0710 (anhydrous)	0.0710 (anhydrous)	-
calcium chloride dihydrate	0.128	0.368	290	0.3676	0.3676	0.2
sodium acetate	-	0.574	580	0.9526 (trihydrate)	0.9526 (trihydrate)	-
sodium hydrogen carbonate ($NaHCO_3$)	-	2.604	2300	2.6043	2.6043	27
sodium citrate dihydrate	0.077	0.097	-	0.0970	0.0970	0.2
sodium hydroxide	6.00	-	-	-	-	-
citric acid	20.8	-	420 (monohydrate)	-	-	-
glycine	0.059	-	450	-	-	5
sodium tartrate dihydrate	0.090	-	-	-	-	-
sodium lactate	0.085	-	-	-	-	-
sodium pyruvate	0.086	-	-	-	-	-
ammonium chloride	-	-	5300	-	-	10
phosphoric Acid	-	-	1200	-	-	-
sodium carbonate	-	-	630	-	-	-
potassium acid phthalate	-	-	200	-	-	-
sulfuric acid	-	-	510	-	-	0.5
sodium citrate dihydrate	-	-	590	-	-	-
sodium phosphate monobasic monohydrate	-	-	-	0.1420	0.1420	1.2
L-cystine hydrochloride	-	-	-	-	-	1.0
DPPC[a]	-	-	-	-	0.02% (w/v)	-
DTPA[b]	-	-	-	-	-	0.2
ABDCB[c]	-	-	-	-	-	50
Properties						
pH	4.5	7.4	7.4	7.4	7.4	-

[a]*DPPC: dipalmitoylphosphatidylcholine.*
[b]*DTPA: diethylenetriaminepentaacetic acid.*
[c]*ABDCB: alkylbenzyl dimethyl ammonium chloride 50% by volume.*

- Respiratory mucous contains
  - Glycoproteins, proteins, and lipids.
  - Varies with disease states
- Lung is generally difficult to simulate
  - Due to surfactant and aqueous fluid
- Salts can precipitate
- Stability of organic compounds in fluids is unknown
- work-up is required to perform a chemical analysis

Possible new research directions





Bronchial lavage with saline wash

- Lavage allows the collection of lung fluid, cells, and other materials inside the air sacs
- This fluid will be collected and used to perform PM extractions, assess bioavailability
- Potential to reduce animal use and save time compared with tissue measurements

Courtesy of Dr. Andy Ghio of the U.S. EPA

Wrap-up

- Combustion and ambient aerosol is chemically complex,
  - requires multiple analytical approaches
- Different chemical entities are commonly associated (OC, HULIS, WSOC, etc.)
- links between POA and SOA need to be explored further using thermodynamics
  - generational chemistry
- thermodynamics-based toxicology will emerge and are important for source-to-effect research
- It is time for physiological-based extractions of PM using lung fluids
  - This will improve our understanding of bioavailability of specific PM components