Carbon Research Update:
Microplastic and biomass burning profiles with a Photoionization Time-of-Flight Mass Spectrometer (PI-TOFMS)

John G. Watson
Judith C. Chow
Patrick Martens
Xiaoliang Wang
Patrick Myers
Matt Claassen

Presented at IMPROVE Steering Committee,
Socorro, New Mexico

October 29, 2024

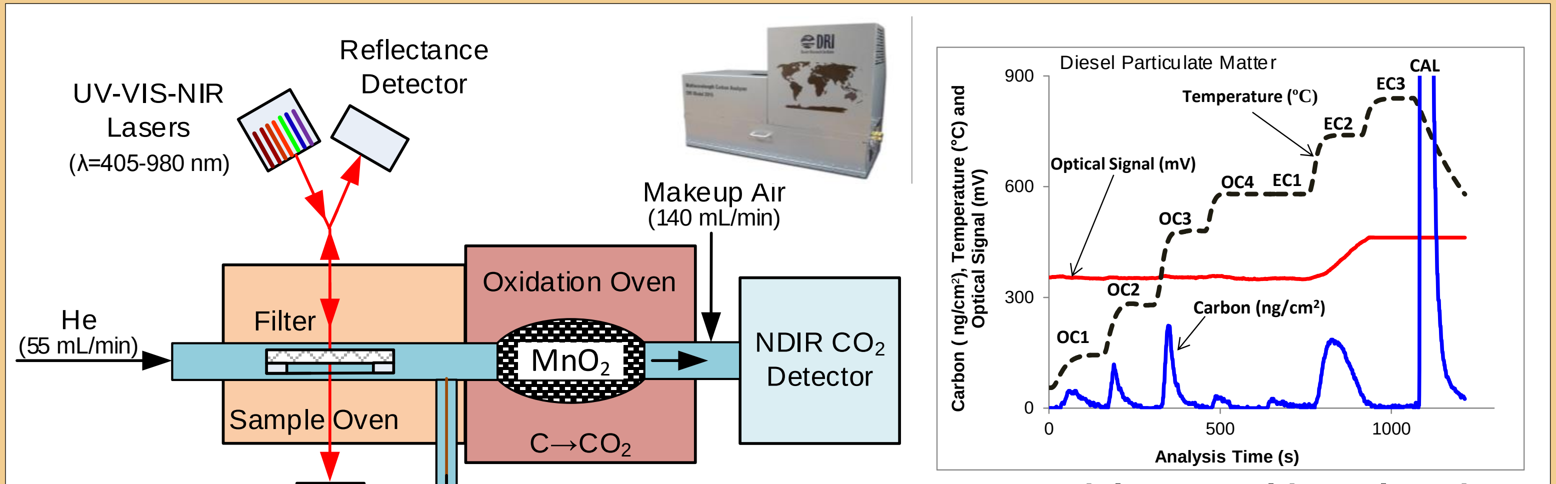
DRI

PI-TOFMS system arrived in June, 2024 and was interfaced to the DRI 2015 Carbon Analyzer, Patrick Martens recruited

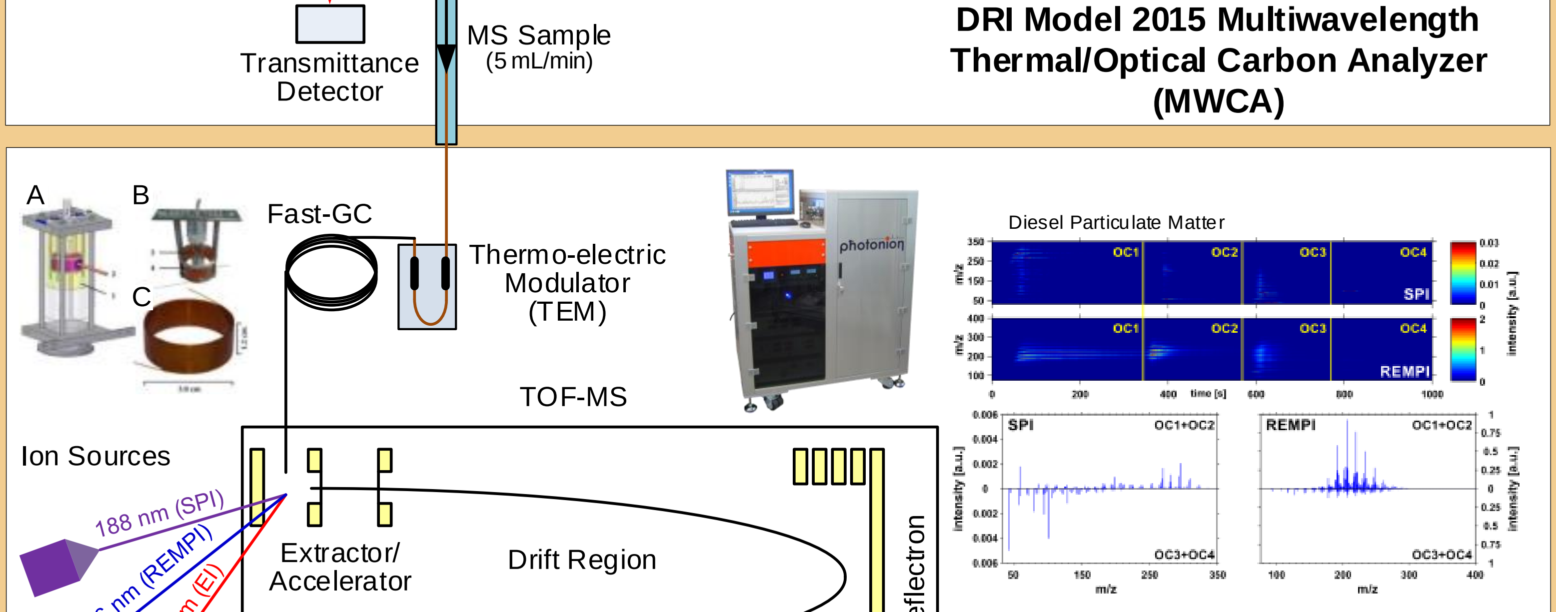
Patrick Martens, Dr. rer. nat.
Recently graduated in Analytical Chemistry/ Environmental Science from the University of Rostock, Rostock, Germany
Previous research focused on combustion aerosols and their toxicological effects
Now broadening scope to microplastic research and post-wildfire soil water repellency

DRI

The(PI-TOFMS) uses high intensity lasers for soft ionization of volatilized molecules from the carbon analyzer

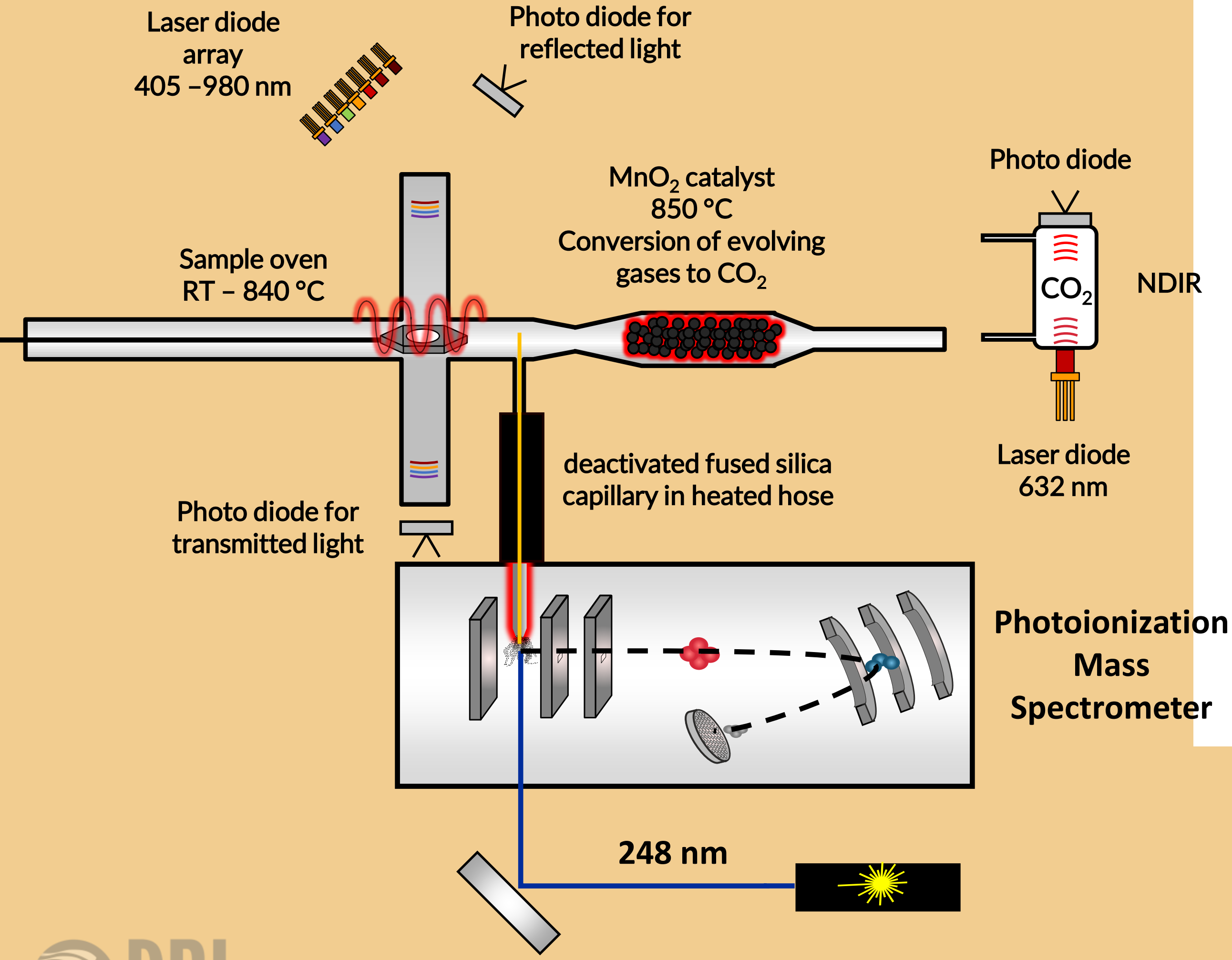


DRI Model 2015 Multiwavelength Thermal/Optical Carbon Analyzer (MWCA)

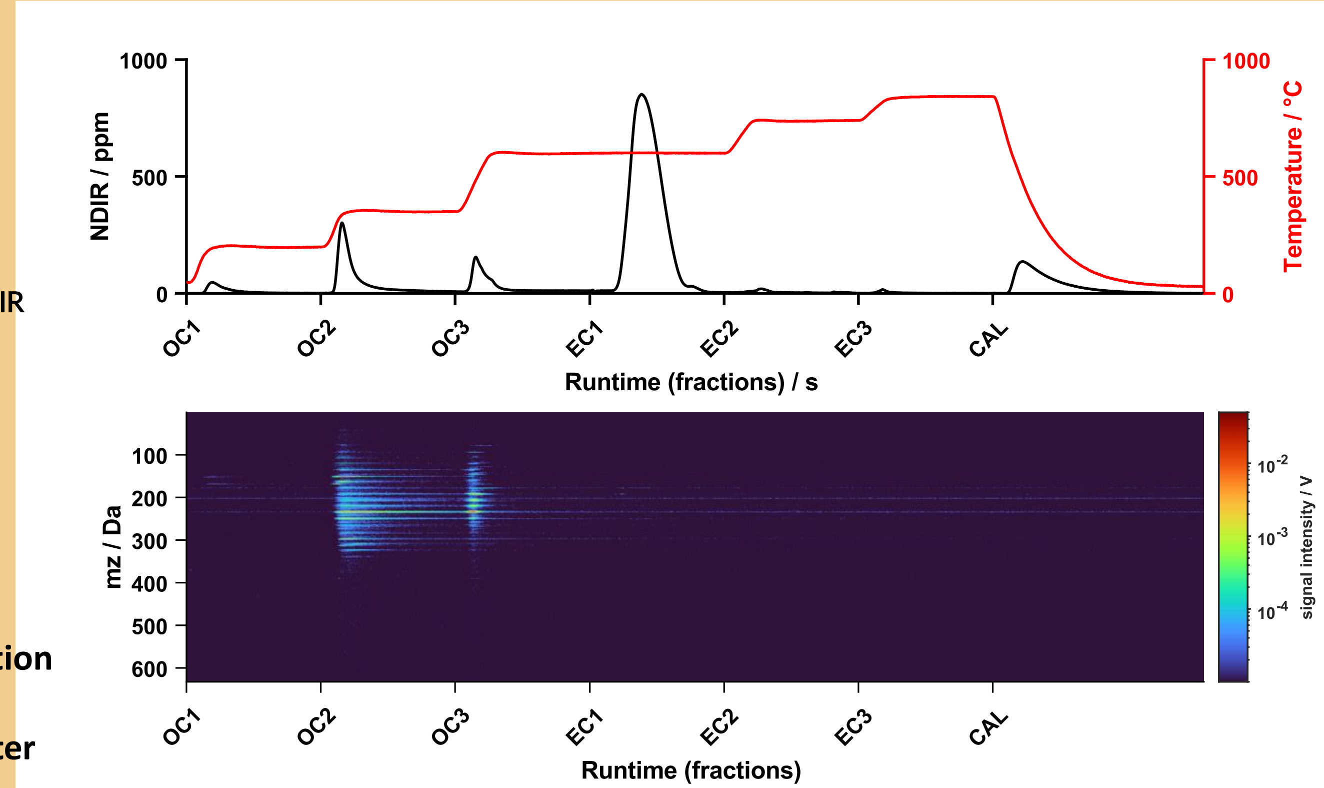


Photonion Photo-Ionization-Time of Flight Mass Spectrometer (PI-TOFMS)

The output consists of mass to charge ratios for different temperature fractions



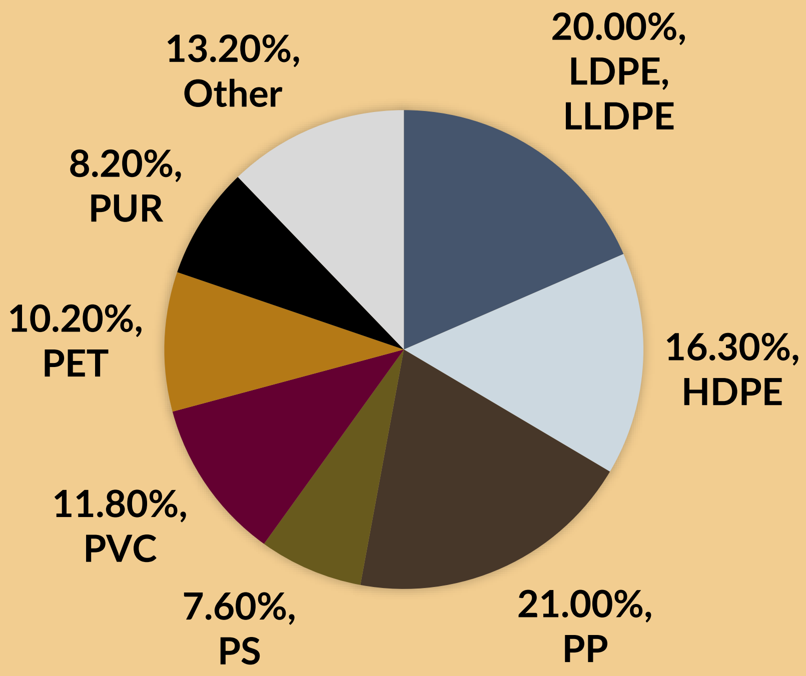
Carbon analyzer thermogram of lignin



Temperature dependent fingerprinting of the evolving gas mixture

Initial work is examining profiles for different microplastics

Plastic Production by Polymer in the USA, EU, China, and India in from 2002 -2014

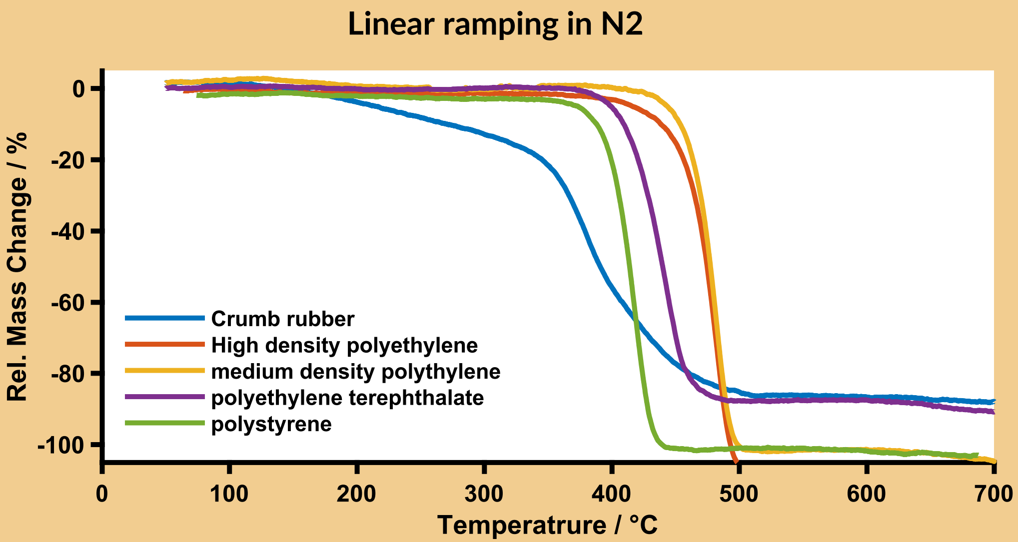


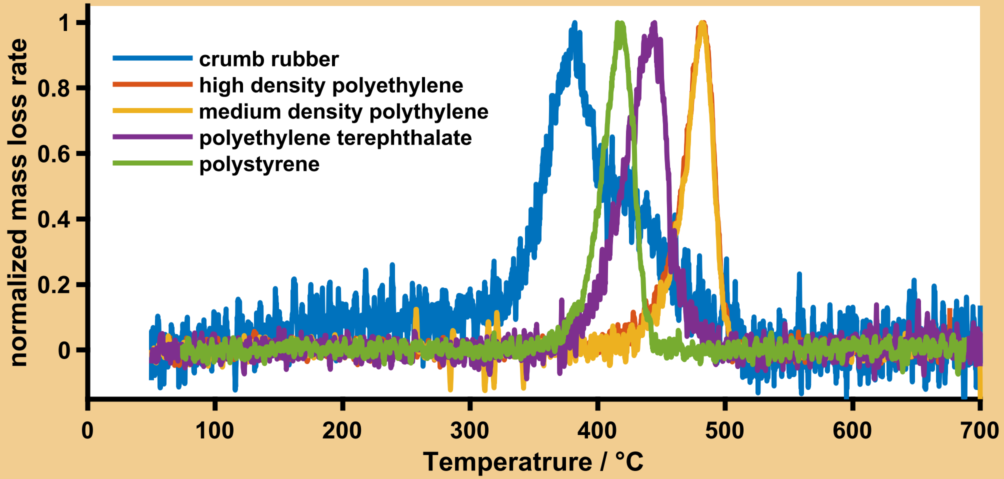
Geyer, R., Jambeck, J. R., & Law, K. L. (2017). Production, use, and fate of all plastics ever made. *Sci. Adv.*, *3*(7). https://doi.org/10.1126/SCIADV.1700782

Abbreviation	Material	Form
ULDPE	Ultra low density poltethylene	pellet
LDPE.1	Low-density polyethylene	pellet
LDPE.2	Low-density polyethylene	pellet
LLDPE.1	Linear low-density polyethylene	pellet
LLDPE.2	LLDPE made with metallocene catalyst	pellet
MDPE	Medium-density polyethylene	pellet
HDPE.1	High-density polyethylene	pellet
HDPE.2	High-density polyethylene	pellet
PP	Polypropylene	pellet
PEST	Polyester poplin fabric	fabric coupons
PET.1	Polyethylene terephthalate	pellet
PET.2	Recycled Polyethylene terephthalate	pellet
EVA	20% Ethylene-vinyl acetate	pellet
ABS	Acrylonitrile-Butadiene-Styrene	pellet
EPS	Expanded polystyrene foam	foam beads
PS	Polystyrene	pellet
PA6	Nylon 6	pellet
PA66	Nylon 6,6	pellet
PVC.1	Polyvinyl chloride	pellet
PVC.2	Polyvinyl chloride with phthalates	pellet (flexible)
CR	Crumb rubber from used tires	crumbed particles
CA*	Cellulose acetate	powder*

DRI

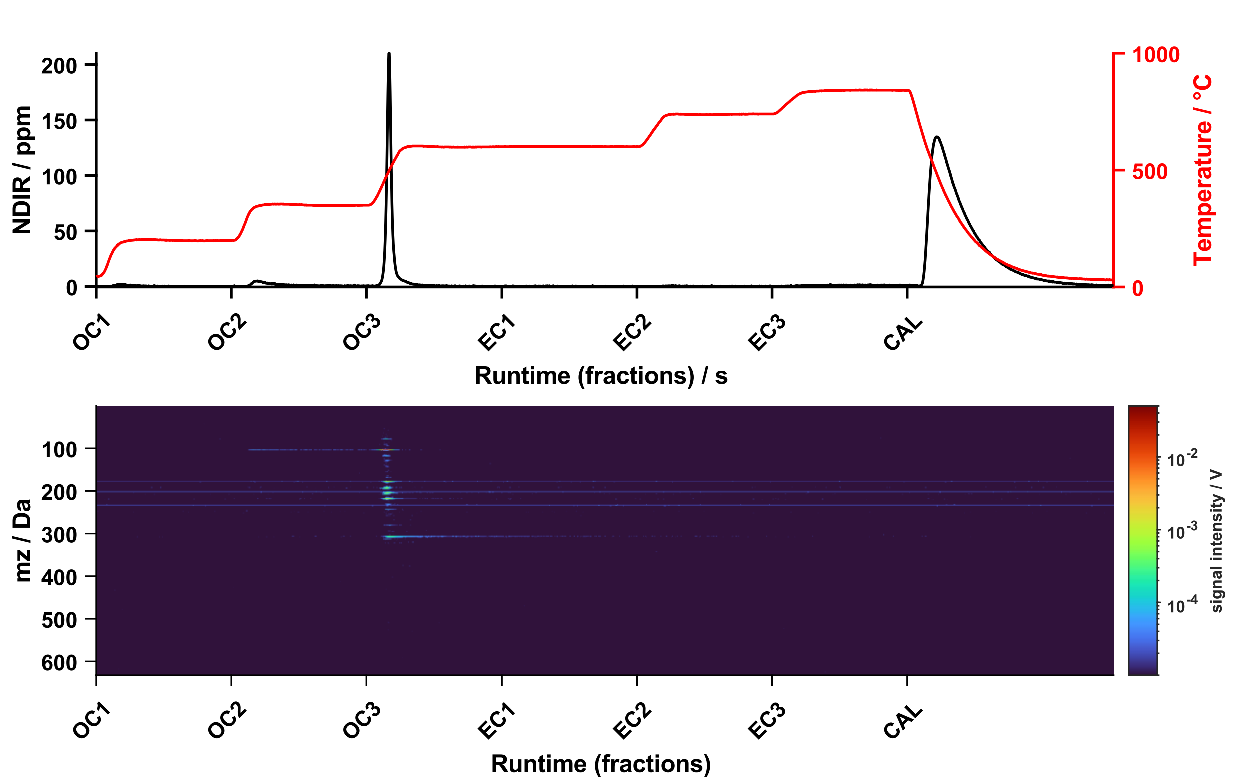
Initial tests show vaporization at different temperatures for different plastics, but these are within the OC3 fraction for the most part. OC3 needs finer fractions for improved discrimination

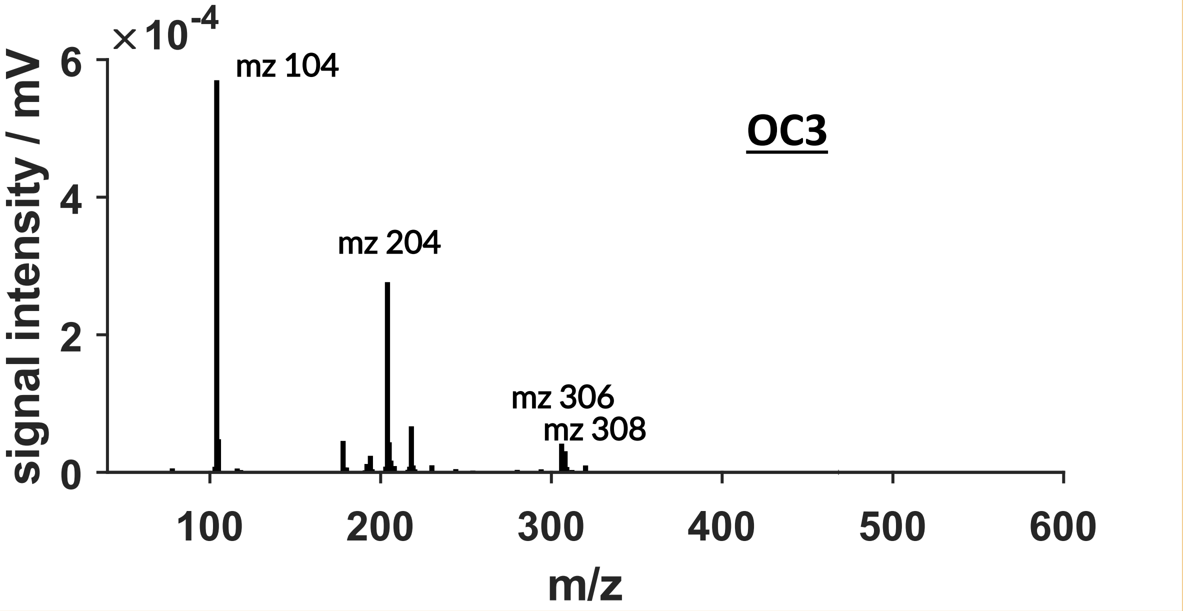




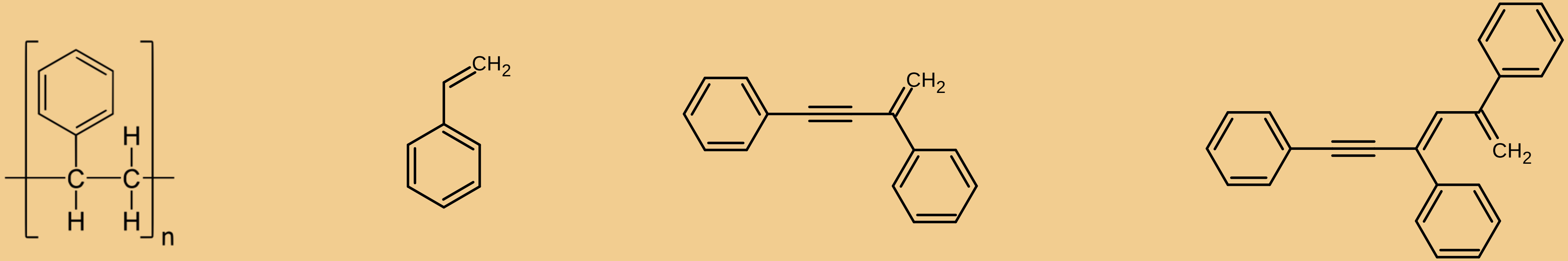
- Thermal decomposition occurs in a single mass loss step for most materials (e.g., polystyrene PS, polyethylene terephthalate PET)
- Some materials degrade almost completely (99%) others form char (e.g., PET and crumb rubber)
- No major differences in thermal decomposition temperatures between similar plastics, see medium and high-density polyethylene
- Plastics from different polymer types can be separated by their thermal decomposition temperature
  - Peak decomposition for different plastic types
    - PS: ca. 420 °C
    - PET: ca. 440 °C
    - HDPE + MDPE: ca. 480 °C
    - Crumb rubber (tire particles): ca. 380 °C
- What about natural materials that may cover particles as, for example, a biofilm?

Polystyrene profile is in OC3





- Cleavage of bond into differently sized oligomers



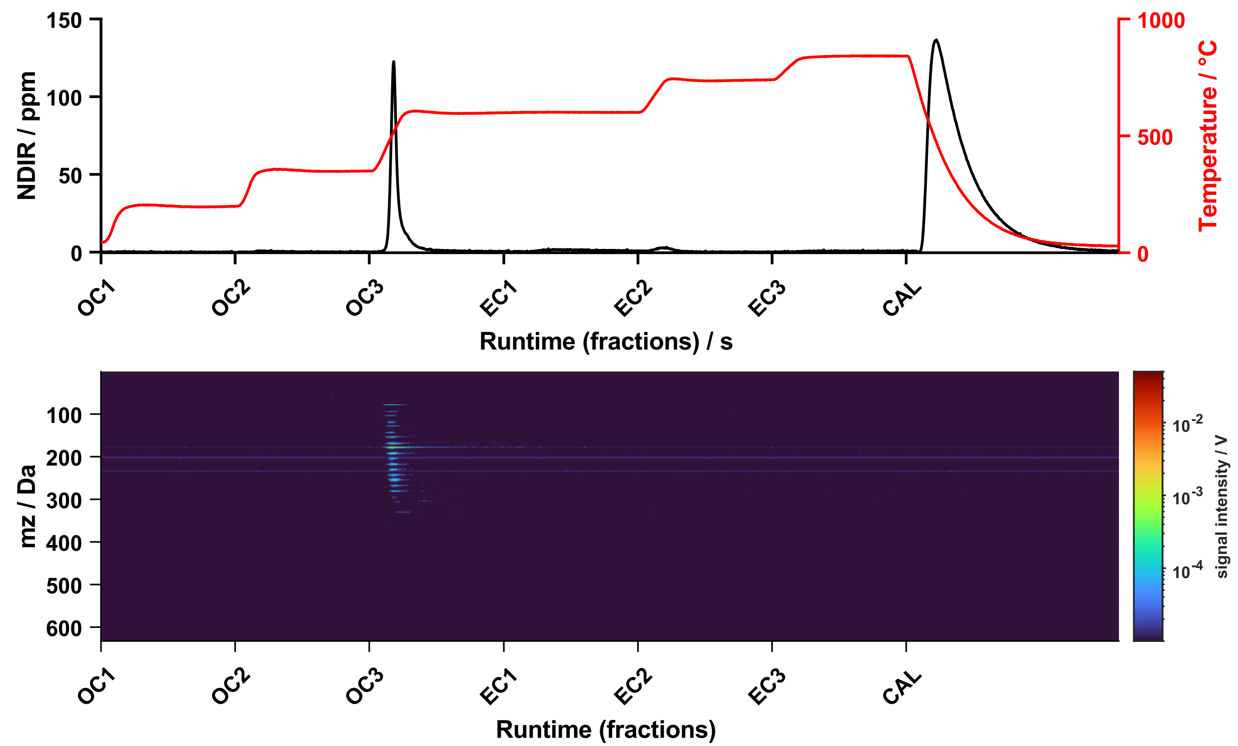
Polymer: mz 104

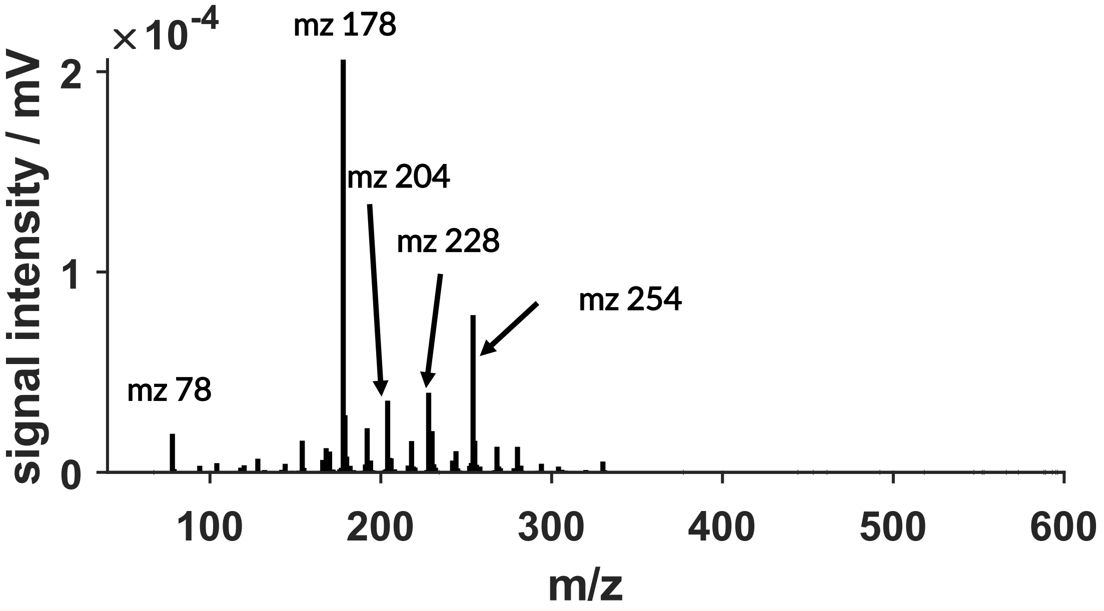
Monomer: mz 104

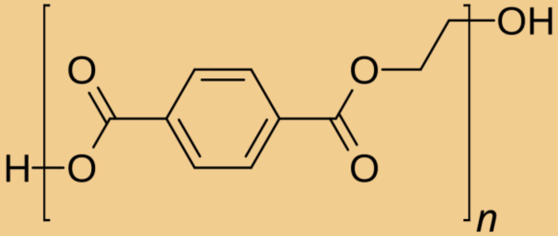
Dimer: mz 204

Trimer mz 306

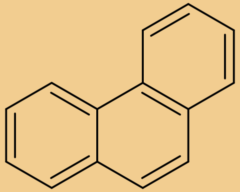
Polyethylene terephthalate profile is also OC3, but with a different molecular profile



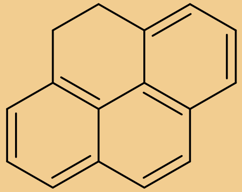




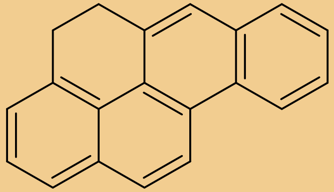
Polymer: mz 210



Polymer: mz 178

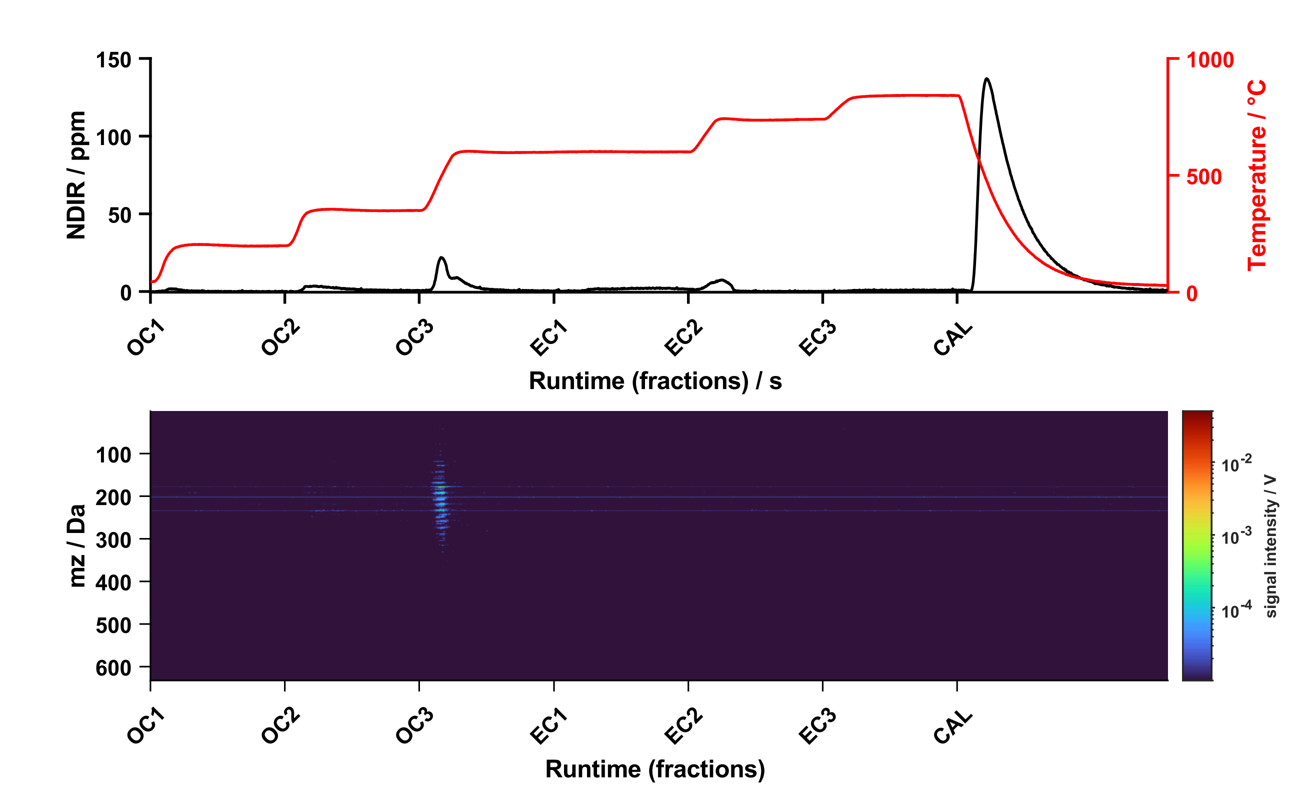


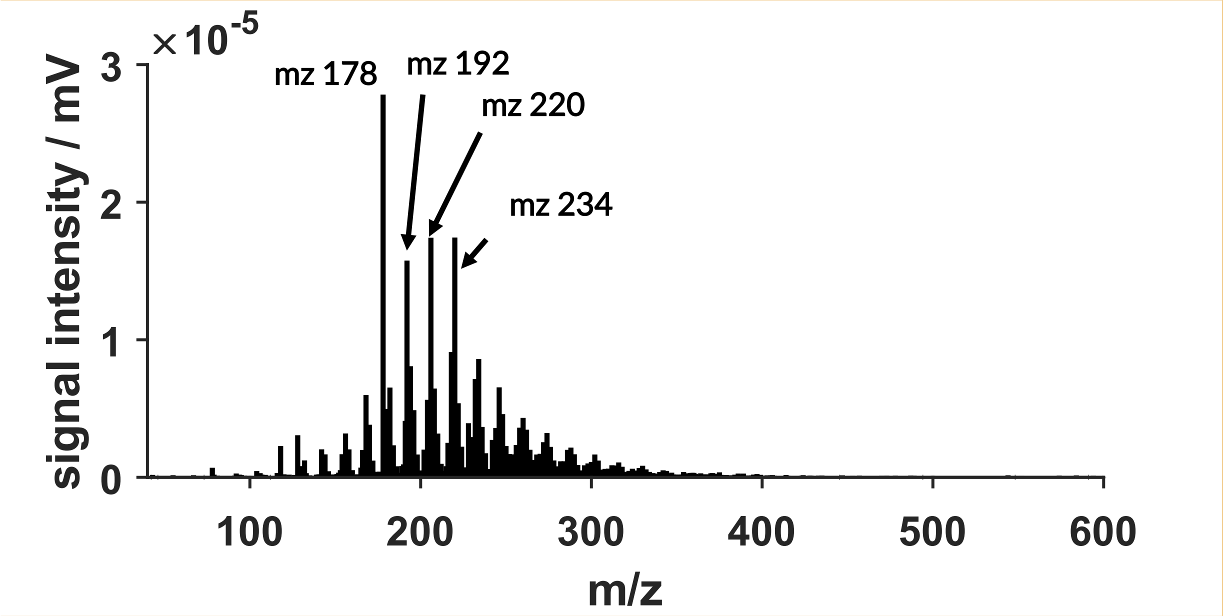
Polymer: mz 204

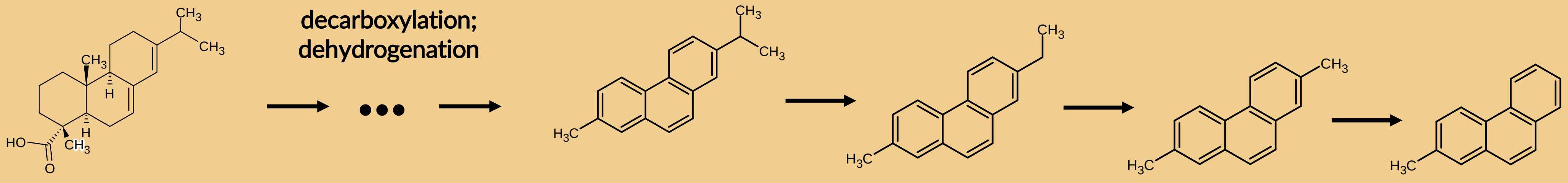


Polymer: mz 254

Tire dust has a more complex thermal and molecular profile







Resin acid like abietic acid in natural rubber

mz 234

mz 220

mz 206

mz 192

Biomass laboratory burning tests are examining profiles for fresh and aged emissions
Fresh and aged burn archived samples will be analyzed for comparison