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Chemical Characterization of Biogas from Varied Organic Feedstocks: Air Quality Implications

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ICCE Oslo

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California's Renewable Energy Future

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By 2050 California has pledged to cut greenhouse gas emissions by 80% below 1990 levels

- Renewable methane sources are essential to achieving the goal
- Need to confirm that biomethane use does not create other air quality or health issues

Objectives: Characterize trace organic constituent composition of raw biogas, upgraded biomethane, and combustion byproducts from different biogas sources using GC- and LC-high resolution mass spectrometry techniques

Raw Biogas Sampling

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Sources tested:

- Food waste digesters (2)
- Dairy waste (2; one lagoon, one digester)
- Landfill (newer and older zones)

Each tested ≥3 times

Biogas Upgrading System

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HELEE membrane unit tested for removal of CO_2 and trace constituents

Stove Appliance Testing

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Atmospheric Aging Experiments

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Field Deployment of Aging System

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Organics Collection and Analysis

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Collection	Instrumental Analysis	Analyte Classes	Representative Compounds
Tedlar bag	GC-TCD	Fixed gases C3-C5 hydrocarbons	CH_4, CO_2 Butane, pentane
	TD-GC-MS	Volatile sulfur TO-15 / halocarbons	Methyl mercaptan, carbon disulfide Chloropropanes, chlorobenzenes
	GC-FPD	Volatile sulfur	H_2S
Charcoal sorbent tube	GC-QTOF-MS	Extended hydrocarbons Siloxanes	Cyclohexane, C3 benzenes Tetramethyl disiloxane
XAD sorbent tube	GC-QTOF-MS	SVOCs / PAHs Pesticides / PCBs	Nitroanilines, pyrene Methoxychlor, PCB-53
DNPH sorbent	LC-QTOF-MS	Aldehydes / ketones	2-butanone, acetone

Nontarget Analysis Approaches

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DNPH coated sorbent tubes

Impingers pH 10

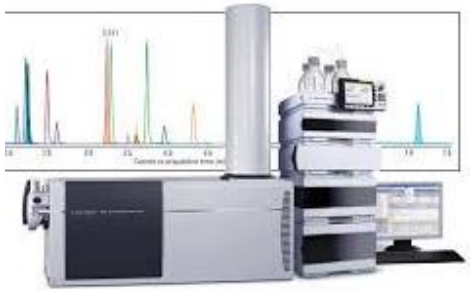
Collection
Concentrate or Solvent Extract

↓

LC-QTOF-MS

↓

Zorbax Eclipse Plus C 18
ESI+: H_2O+FA / ACN+FA
ESI-: H_2O+NH_4F / ACN
Data Acquisition:
All-Ion CE 0, 10, 20, 40 (target + suspect)
Full scan MS (non-target)



Agilent 6530

100's-1000's of constituents detected on each platform

Collection
Extract w/ DCM

↓

GC-QTOF-MS

↓

HP-5MS (30m x 0.25mm, 025µm)
Temp gradient: linear increase 35-325˚C in 80 min
Data Acquisition:
EI (target + suspect + non-target)

Small fraction of mass spectra in database

XAD-2 and charcoal sorbent tubes

Agilent 7200B

Instrument pictures: www.agilent.com

Representative VOC Target Results

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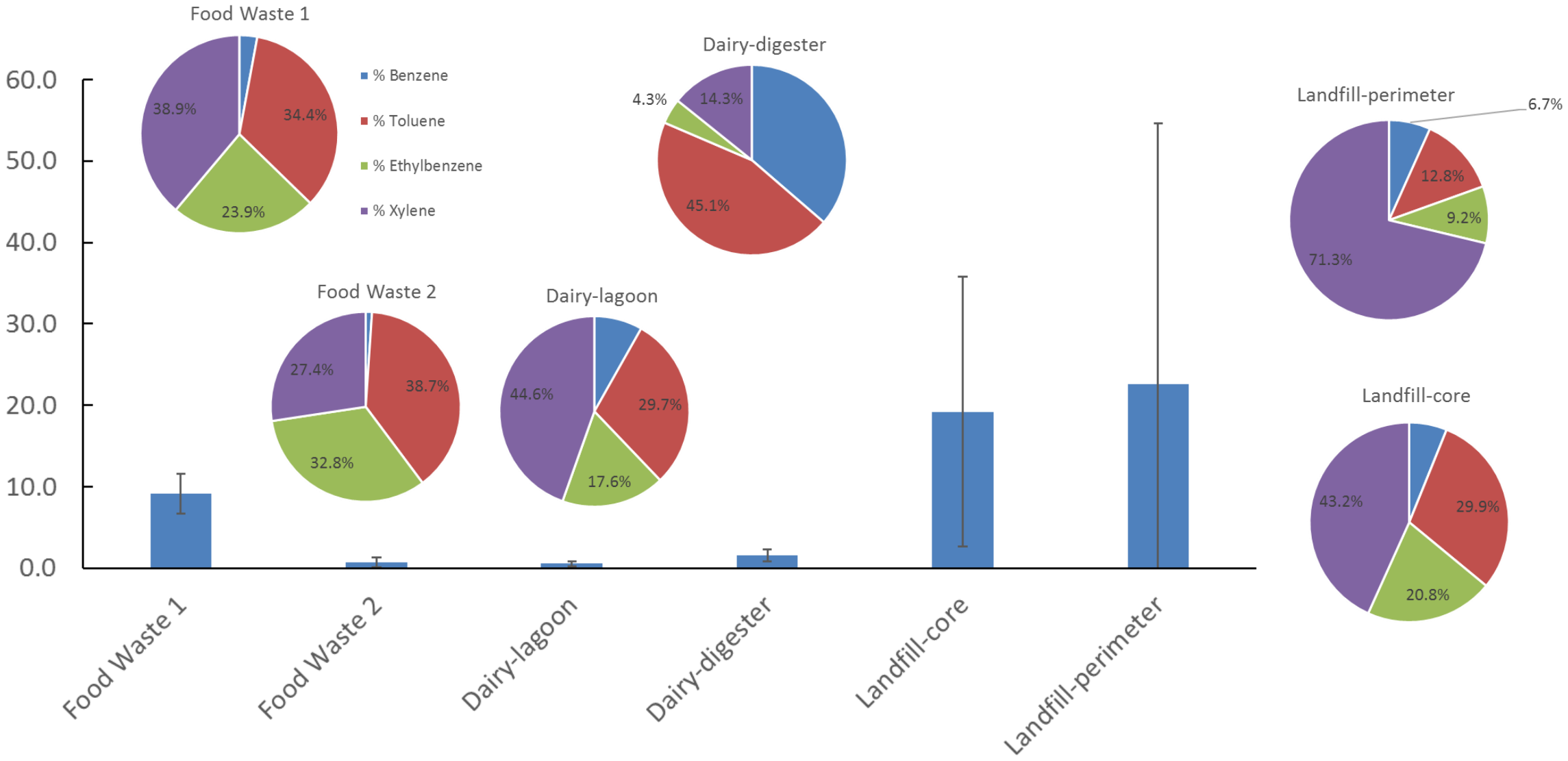

Temperature Effect on Landfill BTEX

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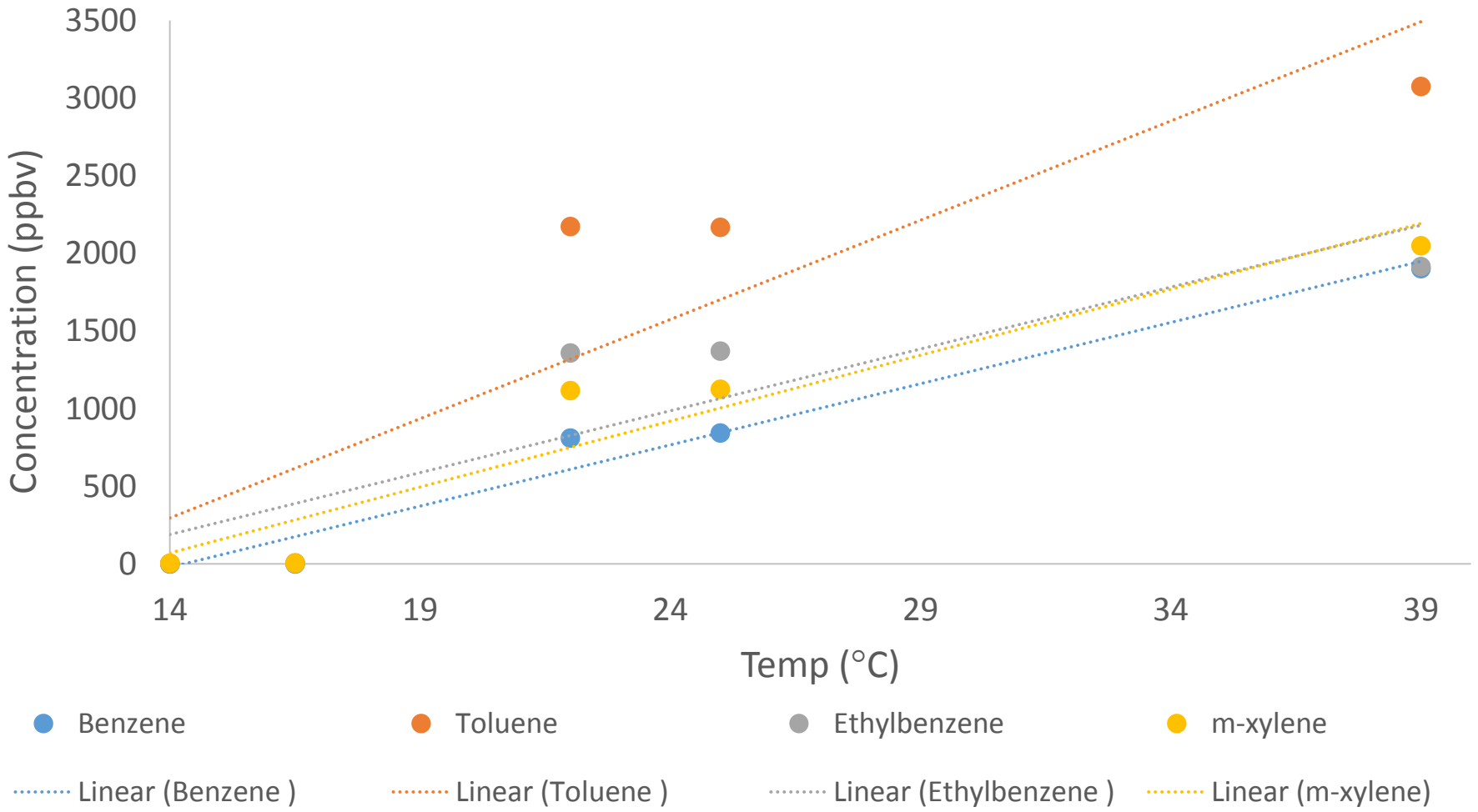
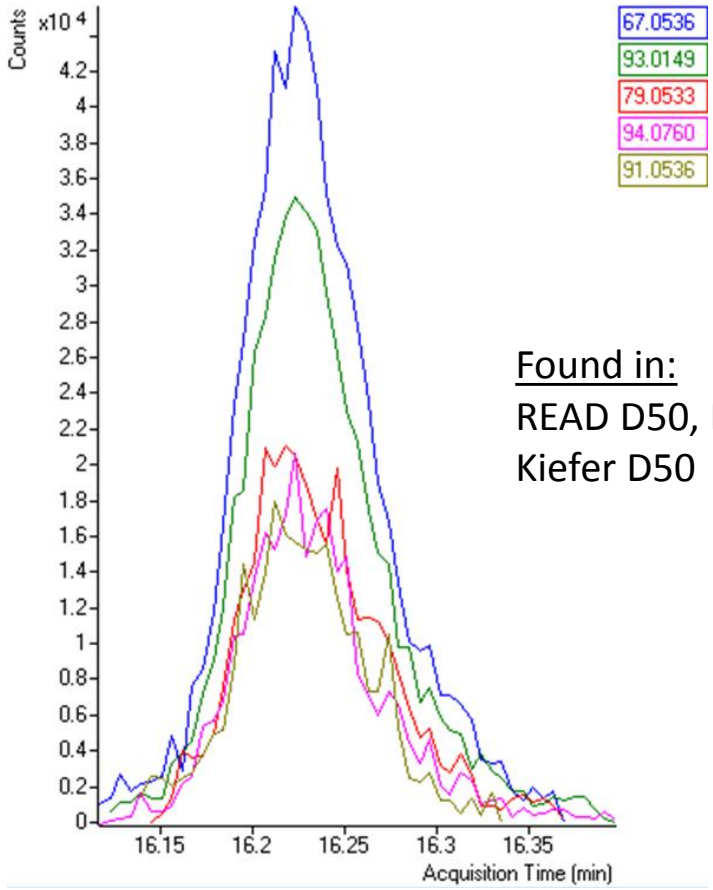
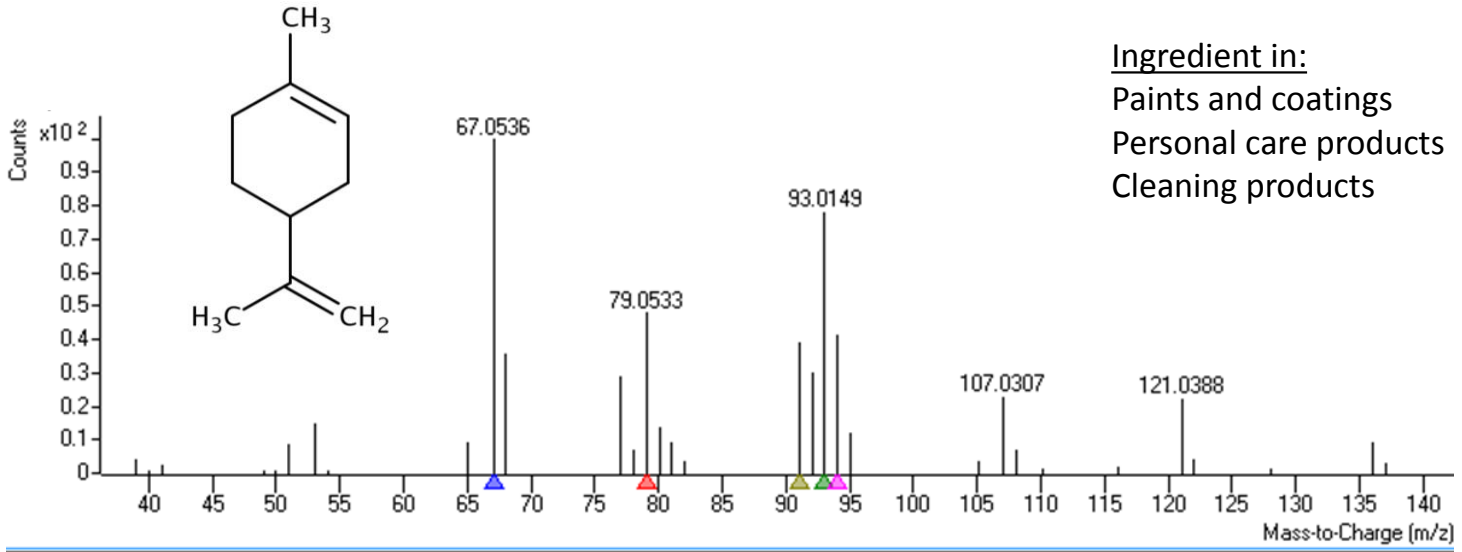
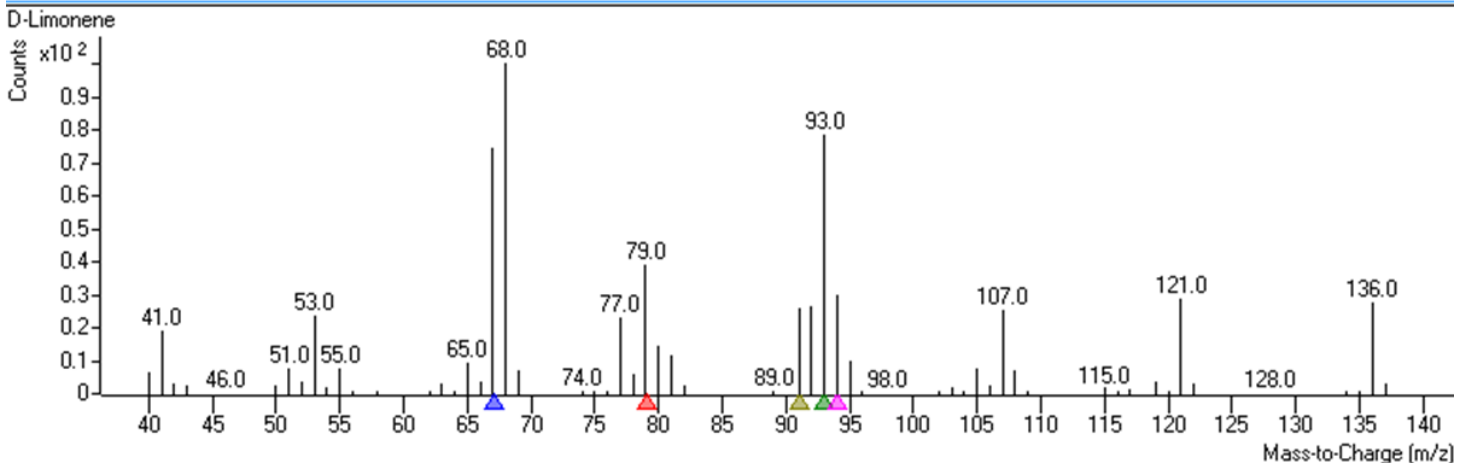


Example Unknown: Limonene



Found in:
READ D50, D500, L500
Kiefer D50





Ingredient in:
Paints and coatings
Personal care products
Cleaning products

Multi-halogen Benzene Derivatives

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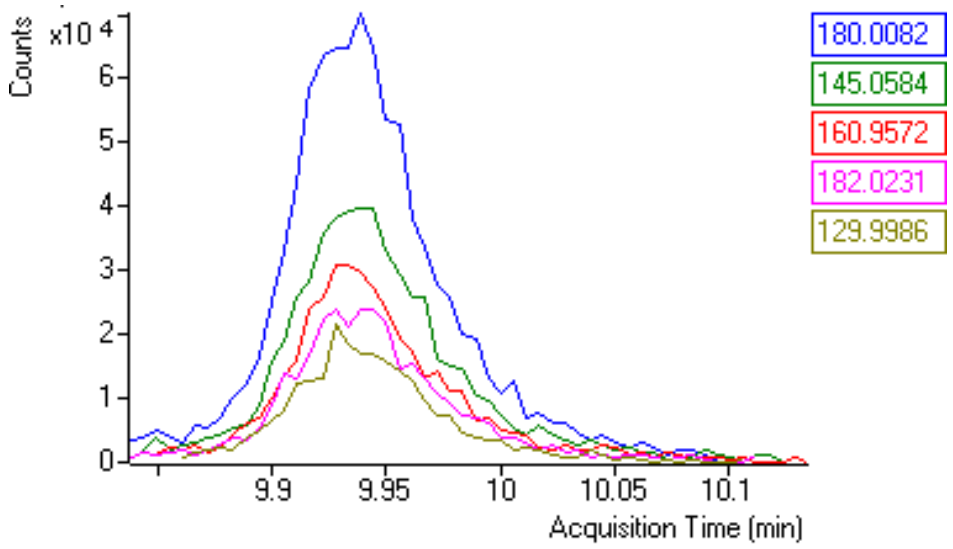
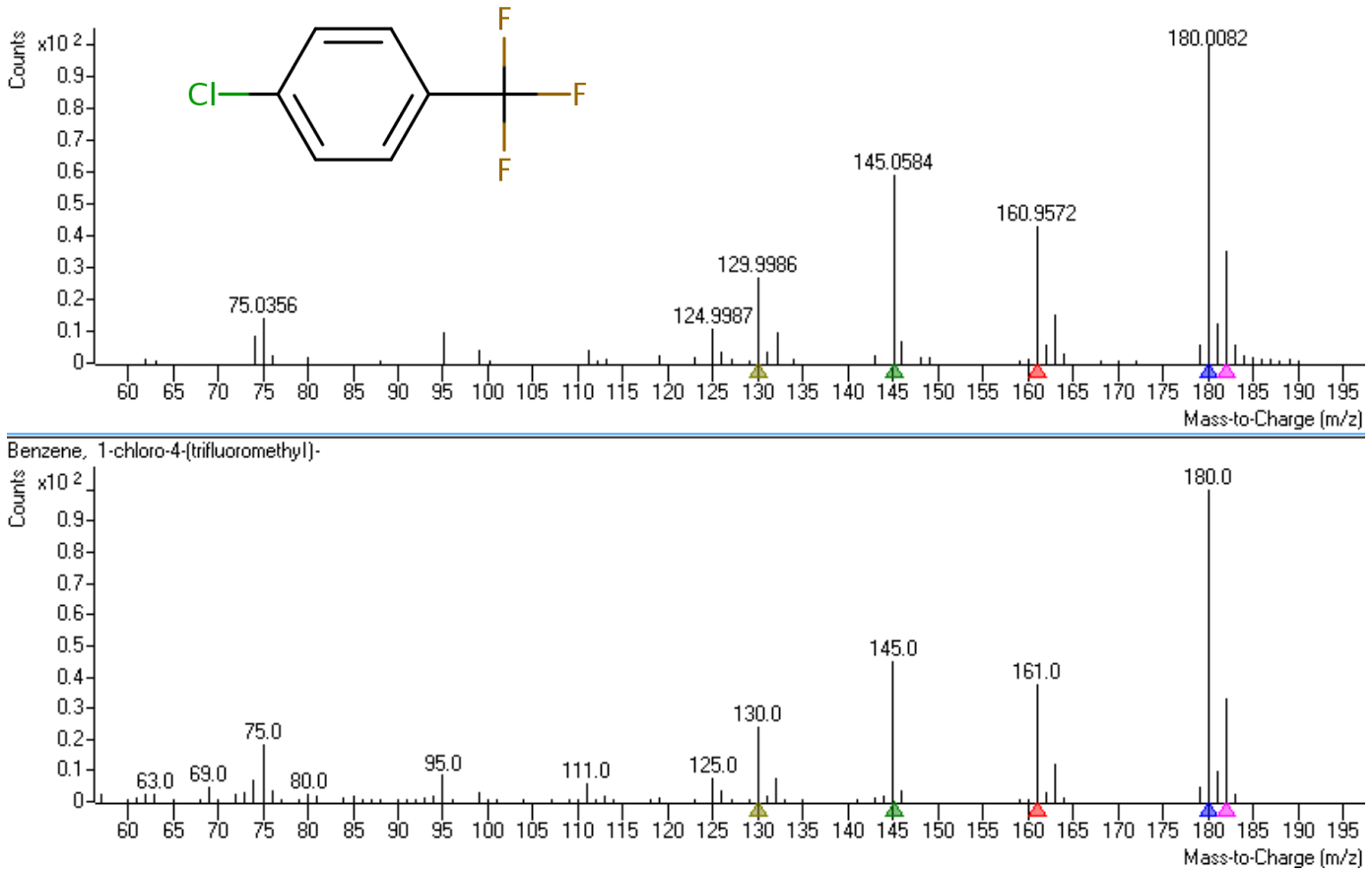
Found in:
Kiefer D500. L500





Unique Features: Food Waste

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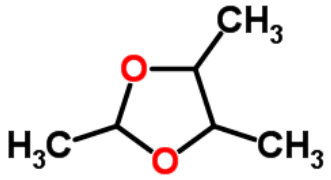
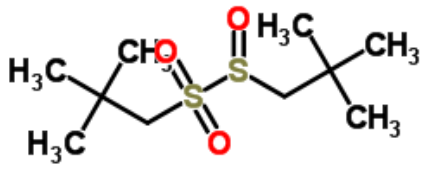
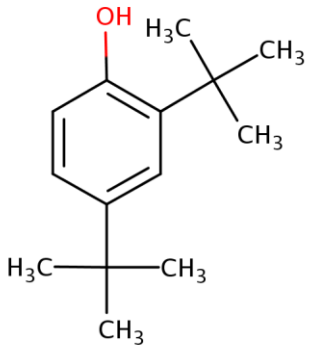
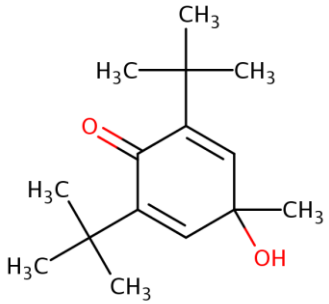
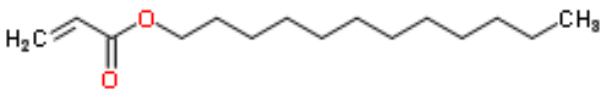


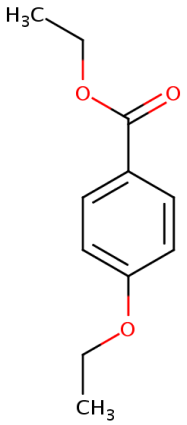


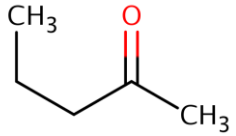


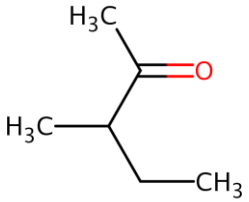


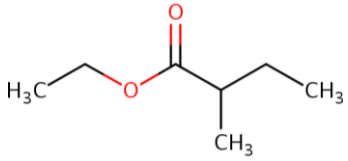
1,3-Dioxolane, 2,4,5-trimethyl-
2,2-Dimethyl-propyl 2,2-dimethyl-propanesulfinyl sulfone
2,4-Di-tert-butylphenol
2,5-cyclohexadien-1-one, 2,6-bis(1,1-dimethylethyl)-4-hydroxy-4-methyl-
2-Pentanone
2-Pentanone, 3-methyl-
Benzoic acid, 4-ethoxy-, ethyl ester
Butanoic acid, 2-methyl-, ethyl ester
Dodecyl acrylate
Tris(2,4-di-tert-butylphenyl) phosphate











Landfill: Diverse Benzene Derivatives

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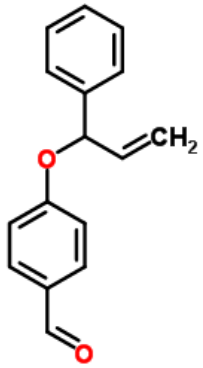
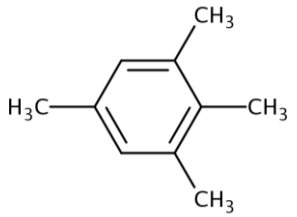
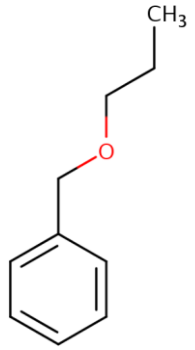
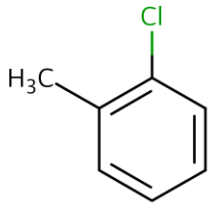
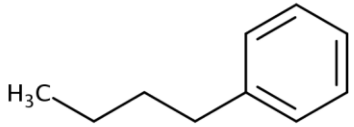
Benzene, (1-methylethyl)-
* Benzene, (propoxymethyl)-
* Benzene, 1,2,3,5-tetramethyl-
Benzene, 1,2,4-trimethyl-
Benzene, 1,2-dichloro-
* Benzene, 1-chloro-2-methyl-
* Benzene, 1-chloro-4-(trifluoromethyl)-
Benzene, 1-ethenyl-3-ethyl-
Benzene, 1-ethyl-2-methyl-
Benzene, 1-ethyl-4-methyl-
Benzene, 1-methyl-3-(1-methylethyl)-
* Benzene, 1-methyl-3-propyl-
* Benzene, 1-methyl-4-propyl-
* Benzene, n-butyl-
Benzene, propyl-

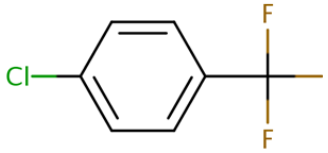


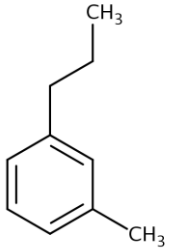


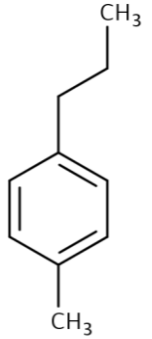












* Found only in Kiefer samples

DNPH Method for Target Carbonyls

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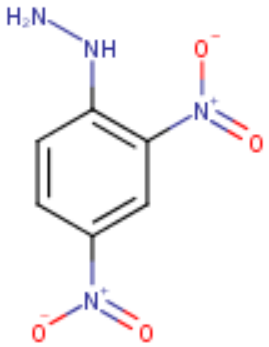
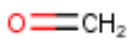
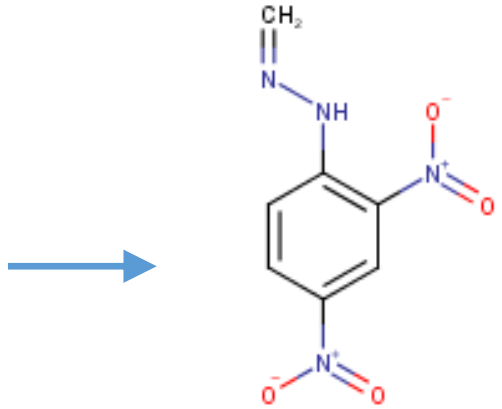


2,4-Dinitrophenyl hydrazine (DNPH)

+



Formaldehyde

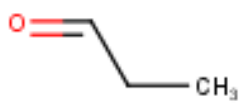


2,4-dinitrophenylhydrazone product

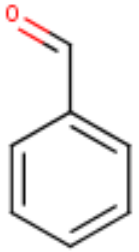
17 compounds on target list

All molecular formulas $C_aH_bO_c$

Representative target carbonyl compounds

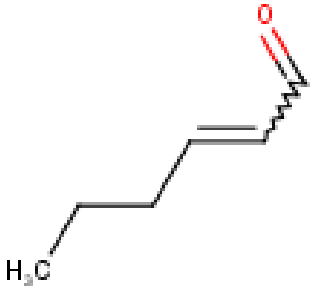


propionaldehyde

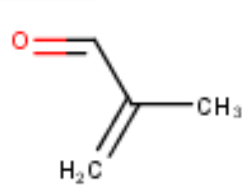


benzaldehyde

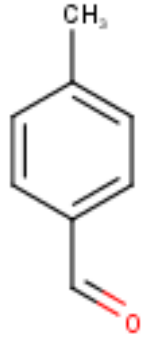
crotonaldehyde



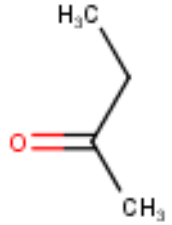
hexanaldehyde



methacrolein



P-tolualdehyde



2-butanone

Target Carbonyl Results

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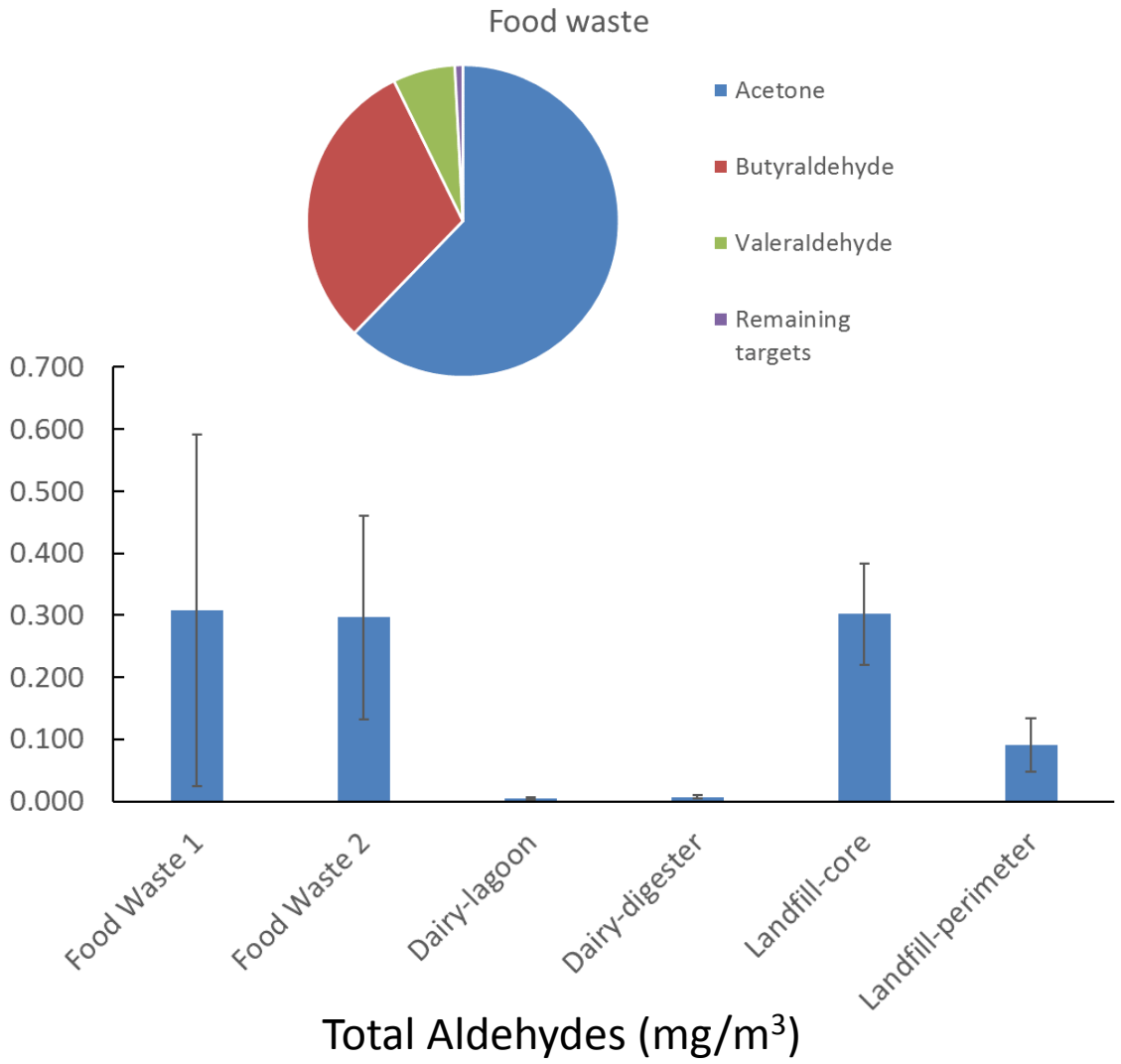
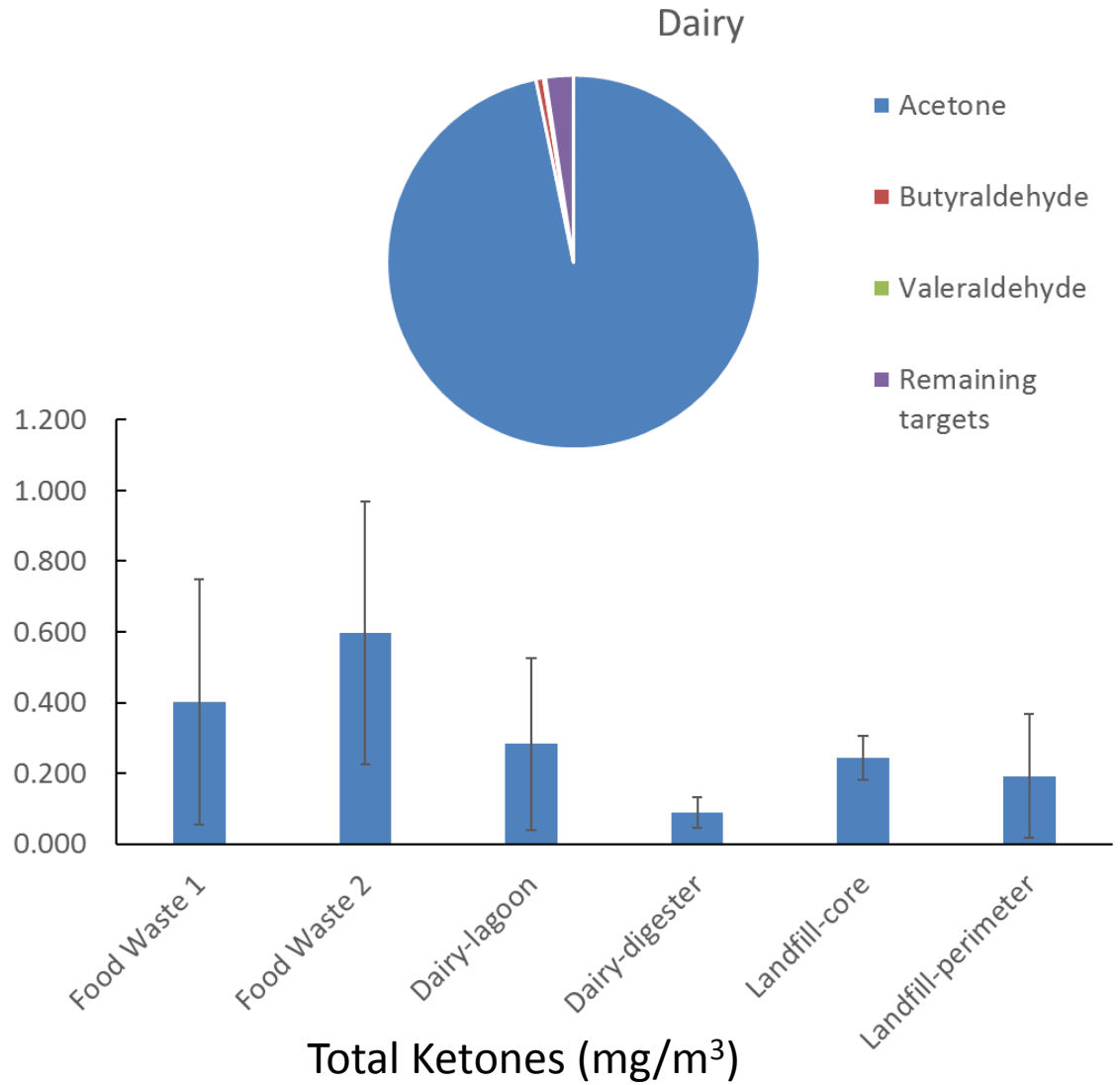


Total Aldehydes (mg/m^3)



Total Ketones (mg/m^3)

Finding Nontarget Carbonyls

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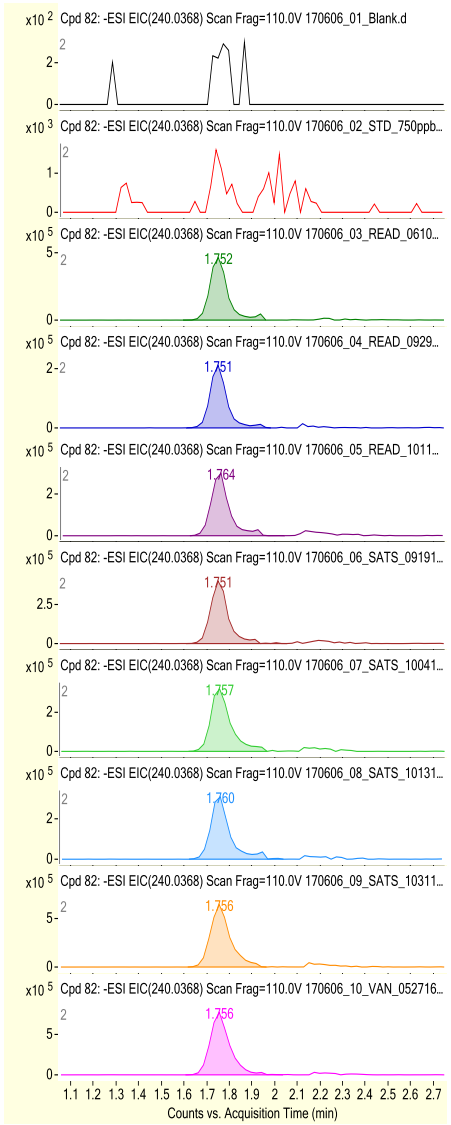

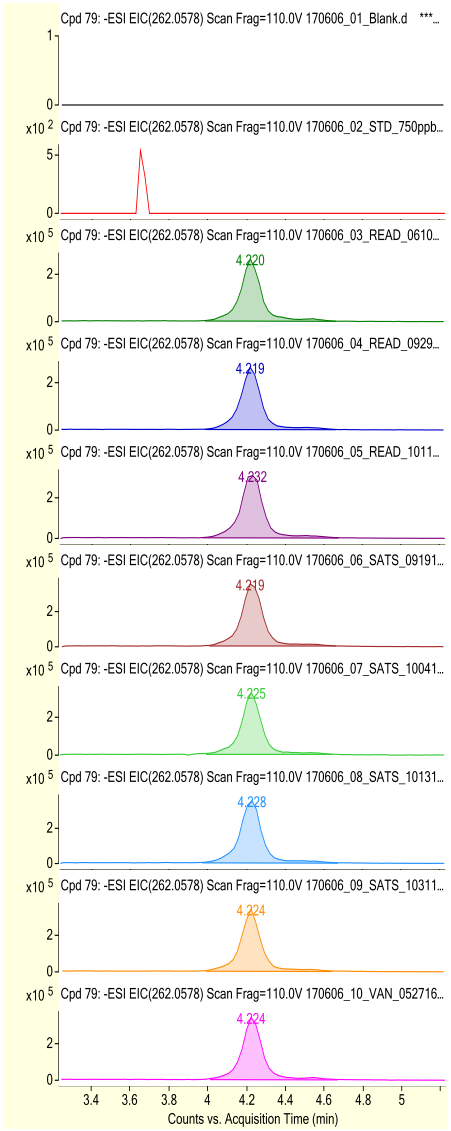

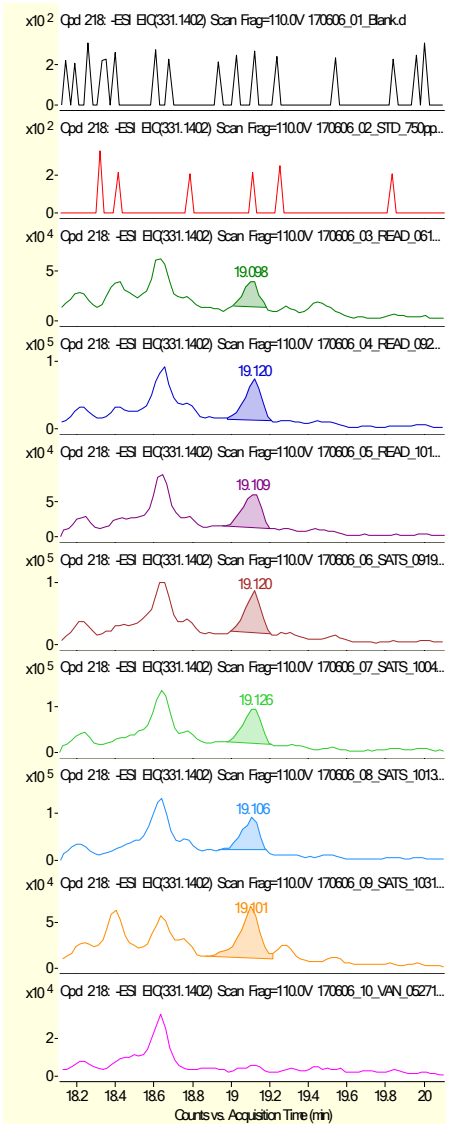

- Carbonyl species important because of atmospheric reactivity
- Peaks aligned across all samples using Agilent Profinder B08
- 517 features met criteria:
  - ✓ Not in blank
  - ✓ Not on target list
  - ✓ Target score>95
- Export features to Mass Profiler Professional 14 for formula generation and statistical analysis

Formula Generation Examples

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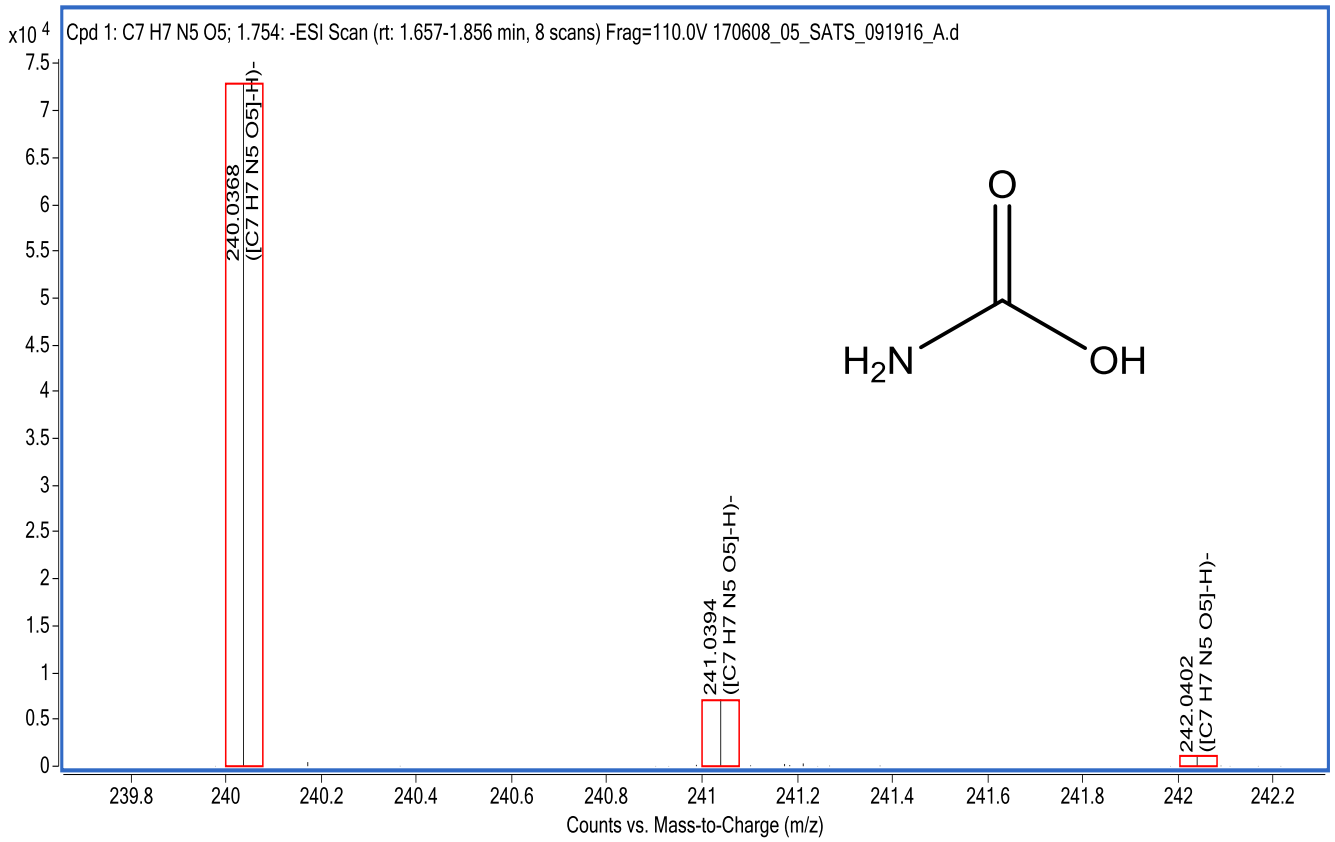

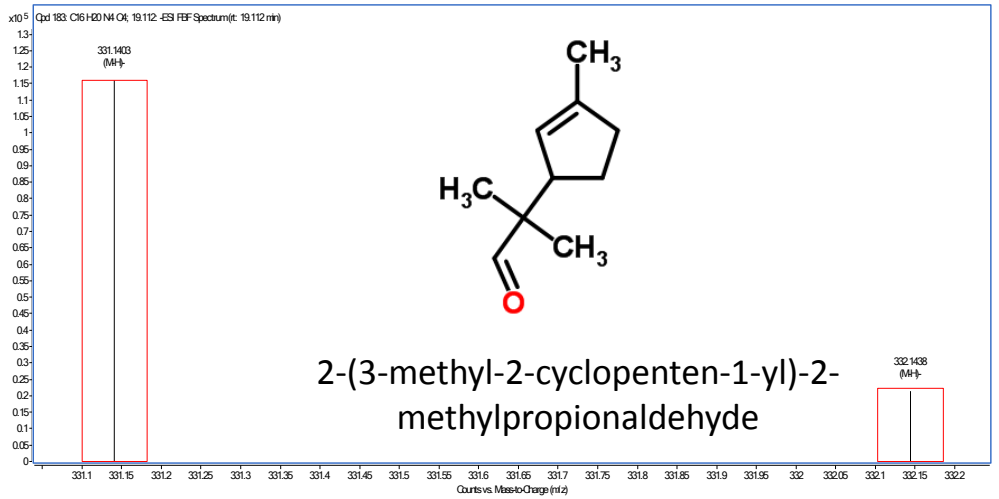

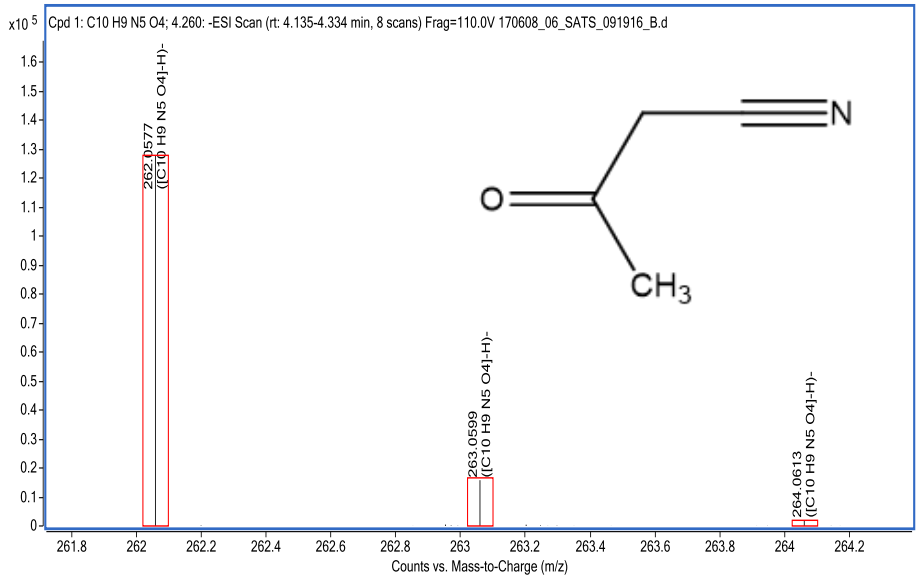

Cluster Analysis of Nontarget Carbonyls

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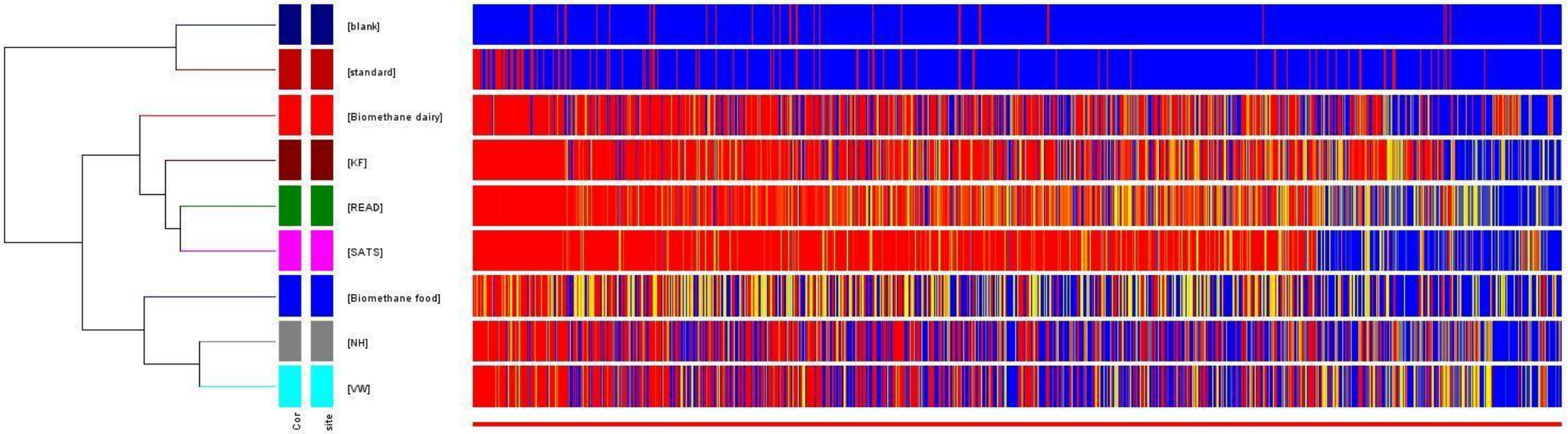

PCA of Nontarget Carbonyls

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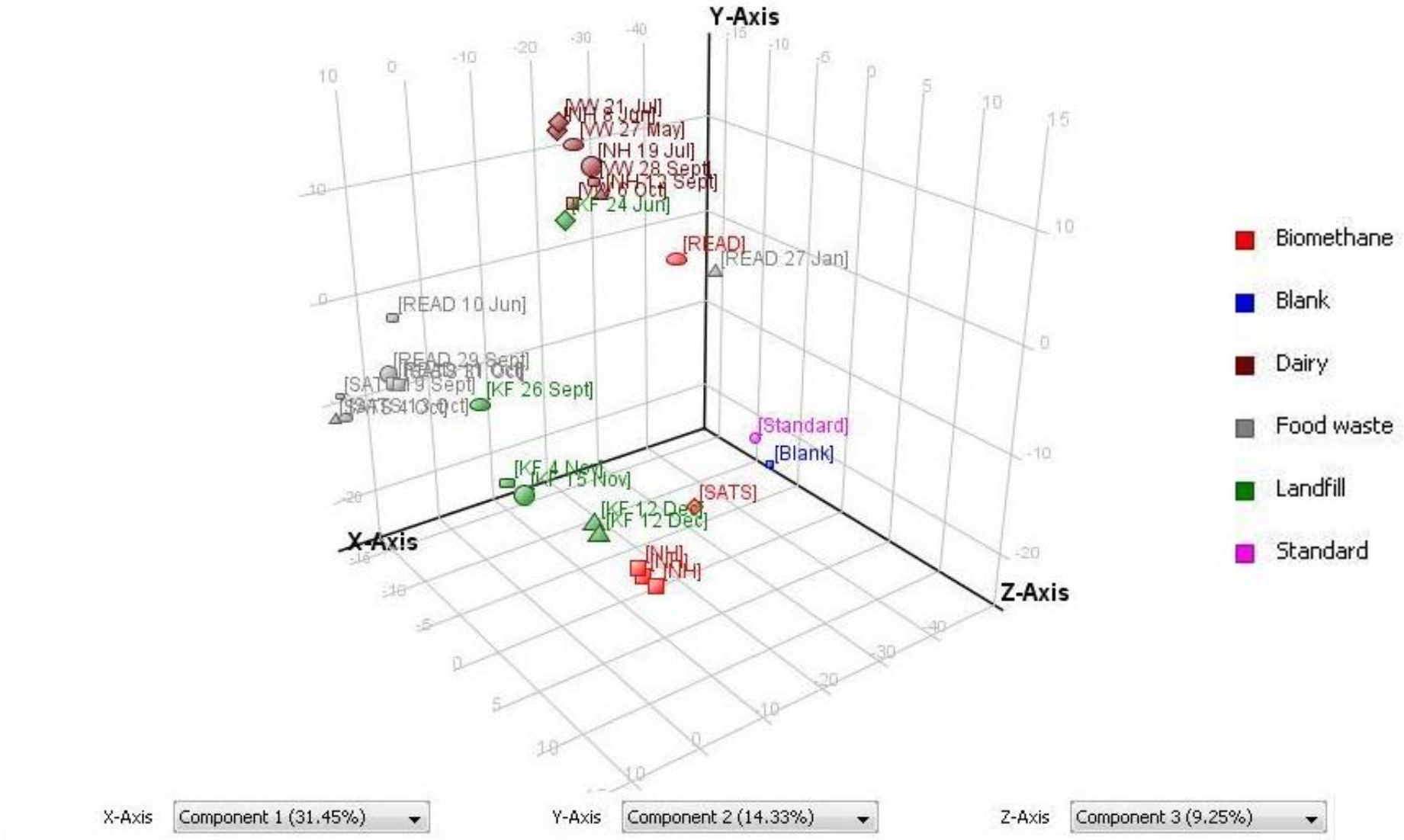

Unique Carbonyl Source Markers

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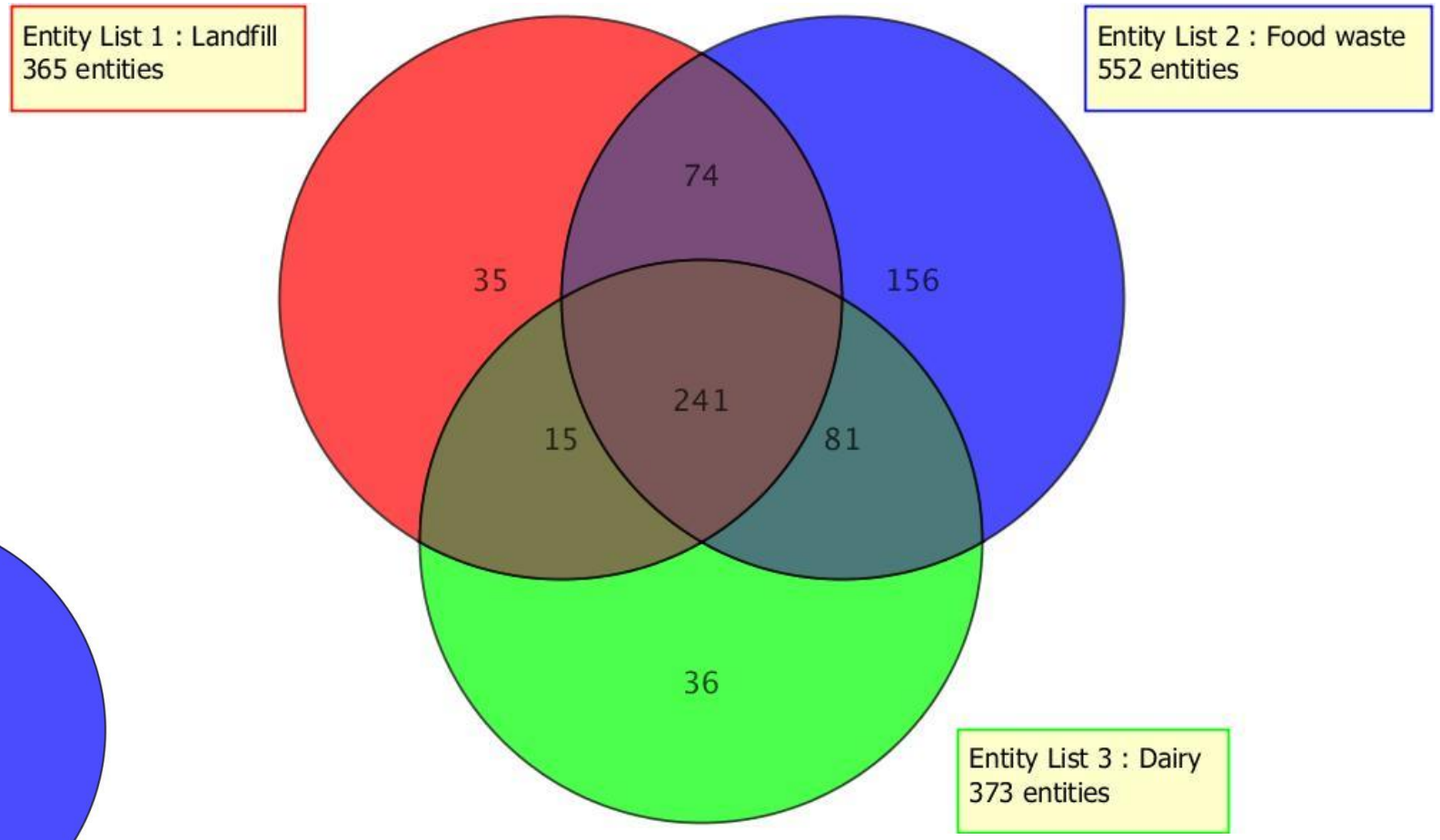
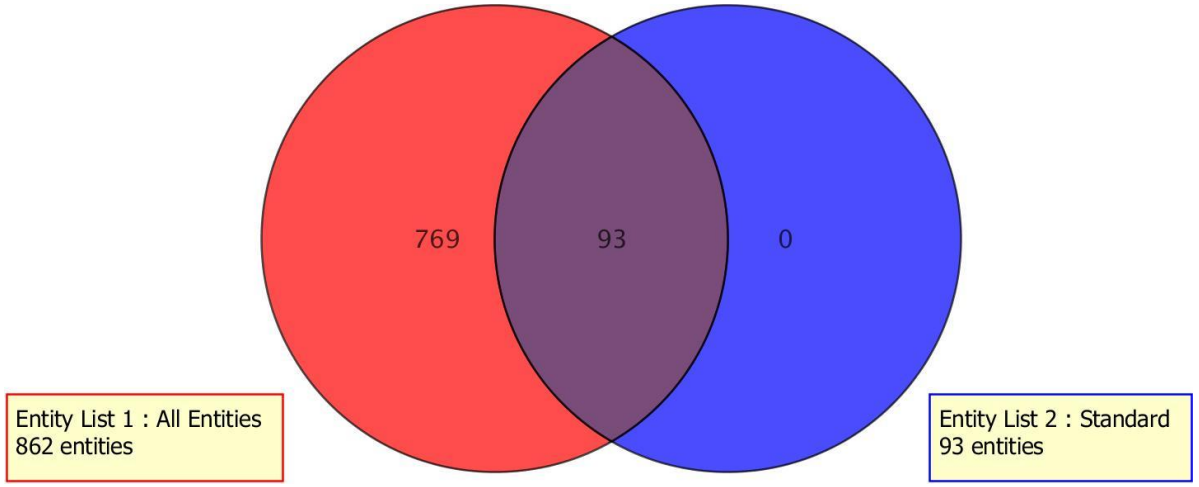
- Biogas samples have far more diverse carbonyl signatures than the target compounds
- Roughly 40% of ion abundance is associated with compounds present in the standard





Conclusions and Future Directions

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- Nontarget fraction of carbonyl compounds appears significant
- Characterizing the complex carbonyl compounds in biogas is a priority
- Tracking atmospheric reaction products of carbonyls provides a focus for nontarget analysis of chamber experiments
- Understanding sources and signatures of trace VOCs in different biogas sources and their combustion products is another future direction
- Combining nontarget results with bioassays (ongoing) will further focus identification efforts

Acknowledgements

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Thanks:

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