

# Utilization of Atmospheric Pressure Ionization Coupled to Triple Quadrupole Mass Spectrometry for the Analysis of Mixed-Halogenated Dioxins and Furans

Kari Organtini, Eric Reiner, Karl Jobst, Anne Myers, Adam Ladak, Doug Stevens, and Frank Dorman

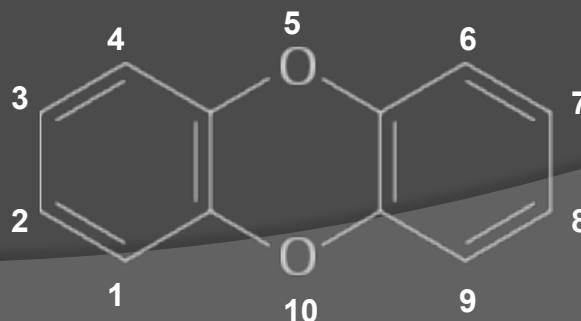
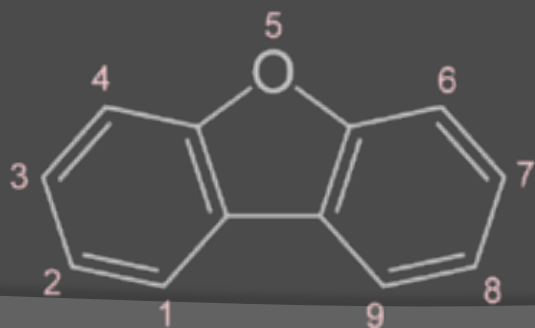
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# Dibenzo-p-dioxin/Dibenzofuran in fire debris

- Persistent environmental pollutants
  - 17 polychloro- congeners monitored by WHO
- Unintentional combustion byproducts
  - Municipal waste incinerators
  - Generation from brominated flame retardants during fires?
- Many studies performed on polychloro's (PCDD/Fs)
- Few analytical and biochemical studies of the mixed halo congeners have been performed (PXDD/Fs and PBDD/Fs)



# Analytical Challenges:

- Complex matrix
- Complex separation
  - 5000 possible PXDD/F, PCDD/F, and PBDD/F congeners
    - 421 2,3,7,8-substituted congeners
- Limited availability of commercially available standards
- Trace level concentrations



GCxGC-TOFMS



APGC-MS/MS

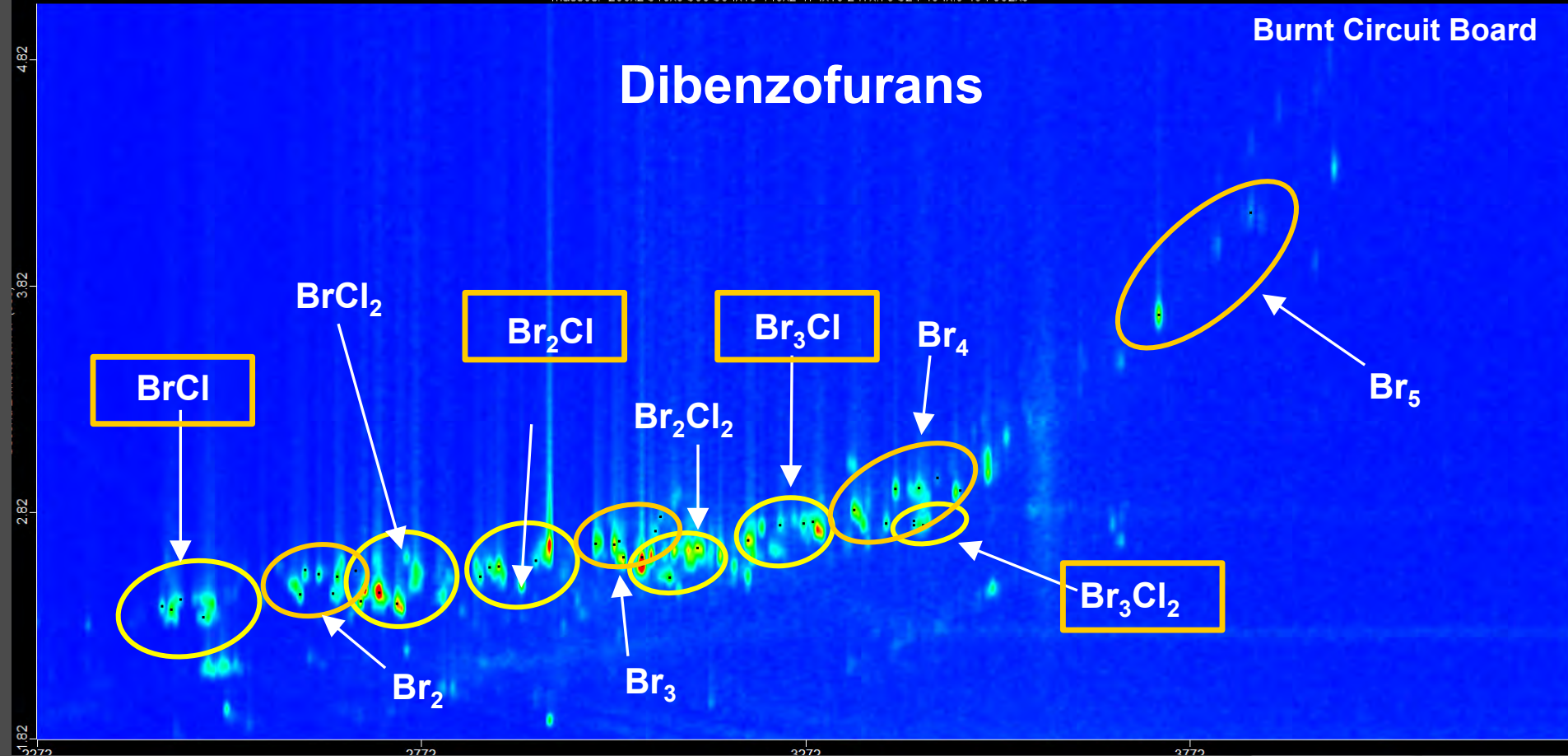
# GCxGC-TOFMS Analysis

## Electronics Fire Simulation Sample

Masses: 280x2 316x6 360 394x10 440x2 474x10 247x.75 324 404x.5 484 562x3

Burnt Circuit Board

### Dibenzofurans



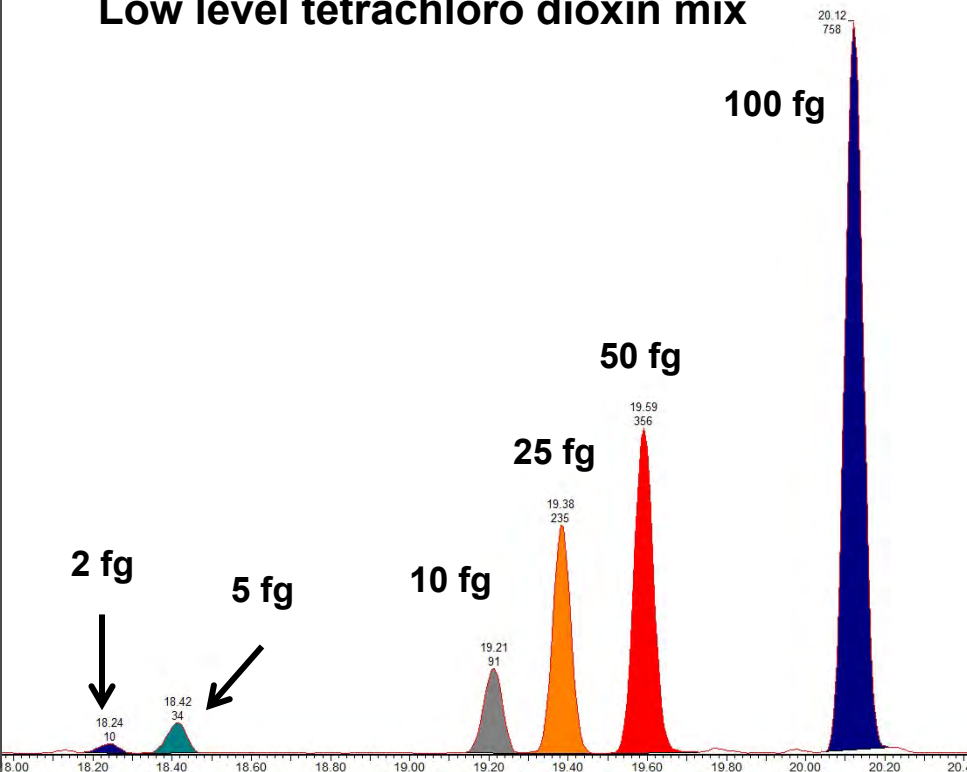
- Household fire generated a variety of PBDFs
- Electronics fire generated a variety of PBDFs and PXDFs
- No dioxin compounds identified
- Congener profiles very heterogeneous between samples



# APGC-MS/MS Analysis

- Instrumentation is highly sensitive (fg level)
- We qualified APGC-MS/MS as a dioxin instrument
  - Historically GC-HRMS is used
- APGC-MS/MS MDLs are 2-20 times lower than GC-HRMS in multiple matrices for dioxins

## Low level tetrachloro dioxin mix

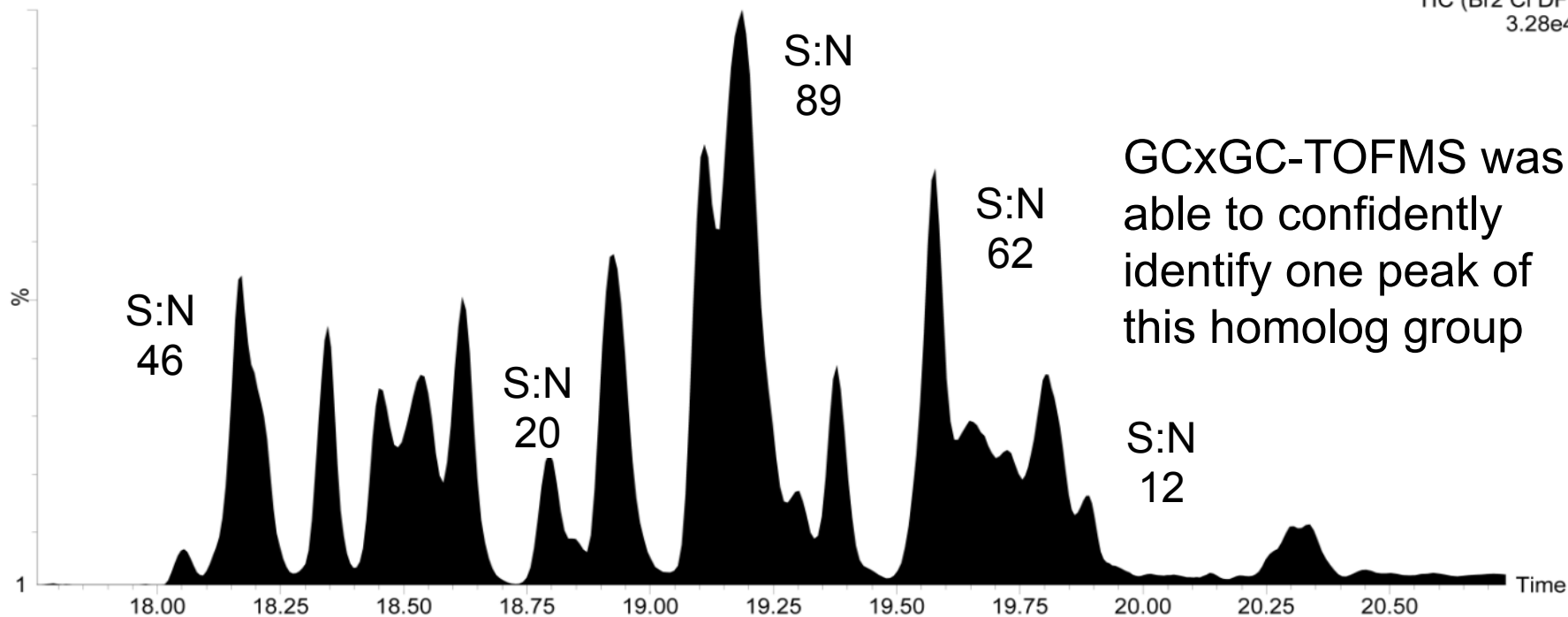


Compound	units	Soil matrix (n=10)	
		APGC-MS/MS MDL	GC-HRMS MDL
2,3,7,8-TCDF	pg/g	0.17	0.68
2,3,7,8-TCDD	pg/g	0.15	0.80
1,2,3,7,8-PeCDF	pg/g	1.32	2.64
2,3,4,7,8-PeCDF	pg/g	0.48	2.22
1,2,3,7,8-PeCDD	pg/g	0.39	3.85
1,2,3,4,7,8-HxCDF	pg/g	0.78	2.28
1,2,3,6,7,8-HxCDF	pg/g	0.54	1.01
1,2,3,7,8,9-HxCDF	pg/g	0.41	2.21
2,3,4,6,7,8-HxCDF	pg/g	0.37	2.30
1,2,3,4,7,8-HxCDD	pg/g	0.62	3.79
1,2,3,6,7,8-HxCDD	pg/g	0.40	3.01
1,2,3,7,8,9-HxCDD	pg/g	0.35	4.28
1,2,3,4,6,7,8-HpCDF	pg/g	0.28	3.36
1,2,3,4,7,8,9-HpCDF	pg/g	0.56	4.87
1,2,3,4,6,7,8-HpCDD	pg/g	0.41	1.62
OCDF	pg/g	0.74	4.85
OCDD	pg/g	1.42	4.49

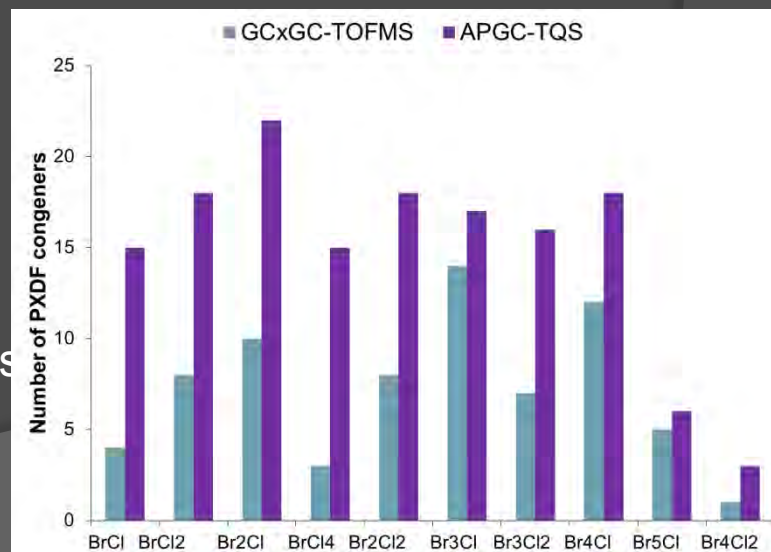
# APGC-MS/MS Analysis

PXDDF\_DryWall\_d10 Sm (Mn, 2x1)

6: MRM of 4 Channels AP+  
TIC (Br2 Cl DF)  
3.28e4



- APGC-MS/MS was considerably more sensitive than both GCxGC-TOFMS and GC-HRMS
- APGC-MS/MS analysis confirmed the GCxGC data but identified many more compounds in the samples
- Polyhalogenated dioxins were identified in samples
- Congener profiles were more homogeneous between samples



# Overall Conclusions and other studies

- Multiple analytical approaches have identified the generation of PXDD/Fs in fire debris
  - Semi-quantification has been completed to determine homolog group concentrations
  - Congener identity is not possible...yet
    - Ion mobility mass spectrometry
- Initial toxicity studies have shown these compounds behave similarly to 2,3,7,8-TCDD
  - Using a human cell culture system
- Fire fighters are being exposed to a complex mixture of PXDD/Fs through inhalation and contact
  - Better/increased regulation needed
  - Reconsider fire fighter safety procedures and standards

# Thank you for your attention!

klo5013@psu.edu

