eurofins | Lancaster Laboratories Environmental

The Use of Advanced Instrumental Techniques to Address Emerging and Unique Circumstance Contaminants

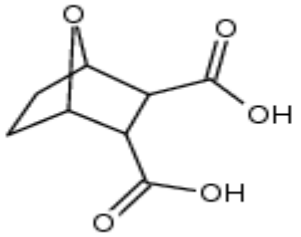
Charles Neslund, Scientific Officer, Eurofins Lancaster Laboratories Environmental, LLC

National Environmental Monitoring Conference, New Orleans, LA
August 6-10, 2018

Providing comprehensive scientific resources to environmental clients worldwide.

Case Study #1

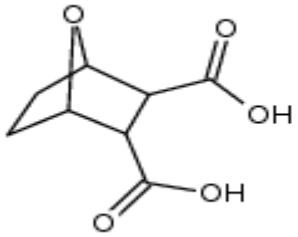
Endothall



- Widely used herbicide for control of aquatic weeds and algae
- Also used with sugar beets, hops, cotton and alfalfa.
- EPA has MCL of 100 ug/l in drinking water
- EPA Method 548.1 used for analysis in water

Case Study #1

Endothall

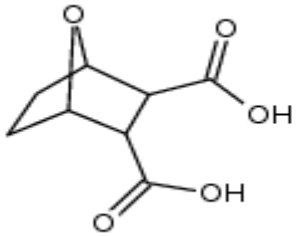


EPA Method 548.1

- Extract 100 mls of water with ion exchange SPE
- Derivatize with acidic methanol
- Analyze by GC/MS
- Method MDLs listed around 2 ug/l

Case Study #1

Endothall

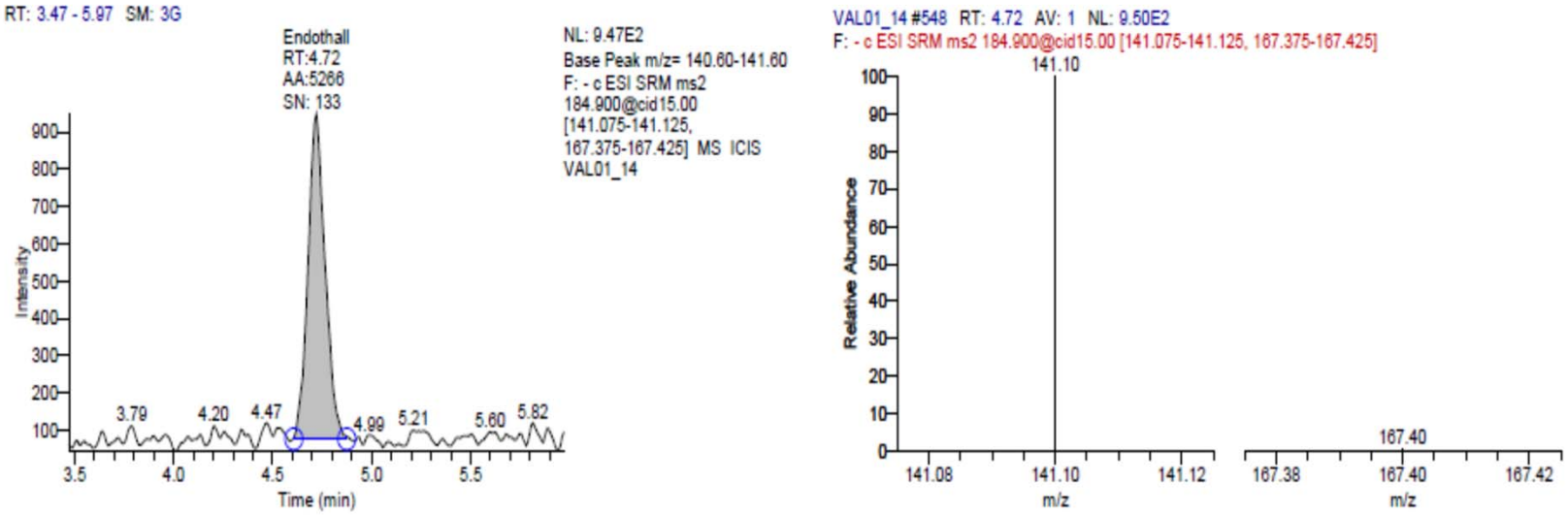


- Client needed soil samples analyzed in addition to waters
- No proven methodology for soil
- Dicarboxylic acid functionality looked suitable for LC/MS/MS approach
- Extract from soil? Optimally use water…maybe ion pairing reagent

Case Study #1

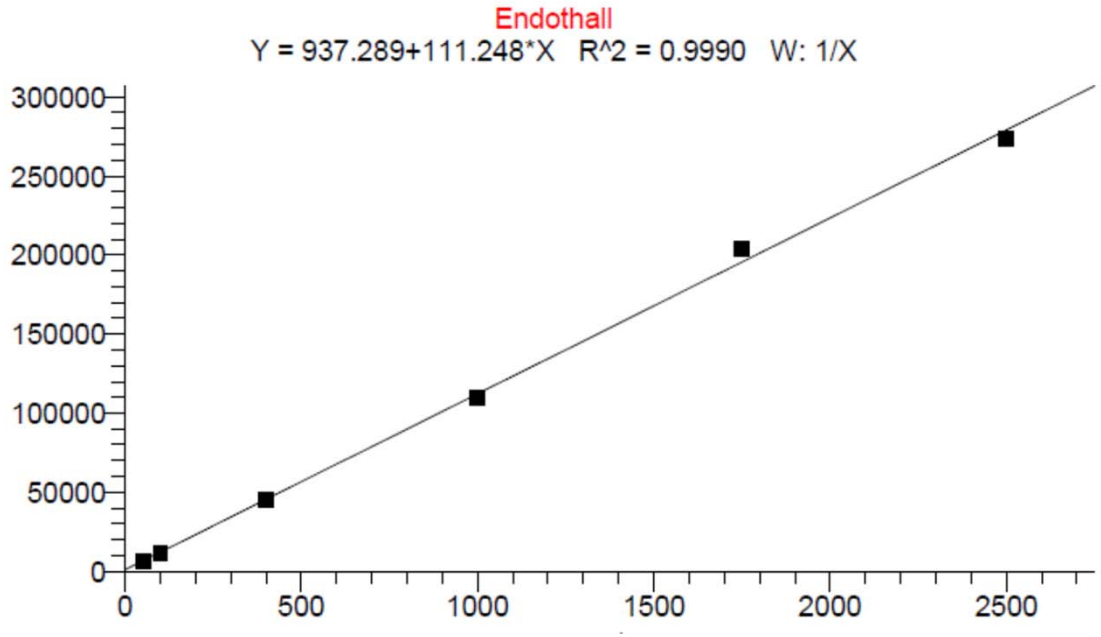
LOQ Level Standard for Endothall – 50 ng/g in soil

10 ng/ml in solution



Case Study #1

Calibration Curve for Endothall – 50 ng/g to 2500 ng/g in soil



Recoveries of 70-130

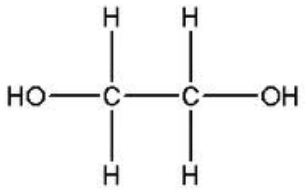
LOQ = 50 ng/g

MDL = 25 ng/g

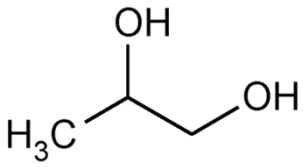
Case Study #2

Glycols

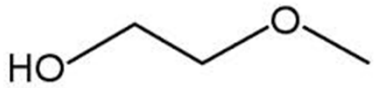
Ethylene Glycol



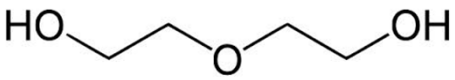
Propylene Glycol



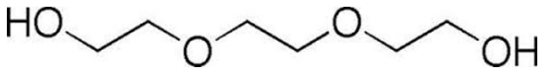
2-methoxy ethanol



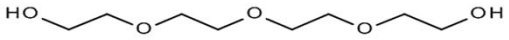
Diethylene Glycol



Triethylene Glycol



Tetraethylene Glycol



Case Study #2

Glycols

- Group of compounds is very water soluble which makes extraction and concentration difficult
- Typical approach has been to use a GC/FID method like SW-846 8015, with direct aqueous injection (DAI)
- Sample matrix can have significant impact on what is detected (false positives)
- Sensitivity not spectacular, 5-10 mg/l common, optimized systems may do a little better

Case Study #2

Glycols

- What about application of LC/MS/MS?
- Well suited for DAI, better selectivity and sensitivity?
- Concern about small size of molecules, particularly ethylene and propylene glycol
- How effectively would they ionize?

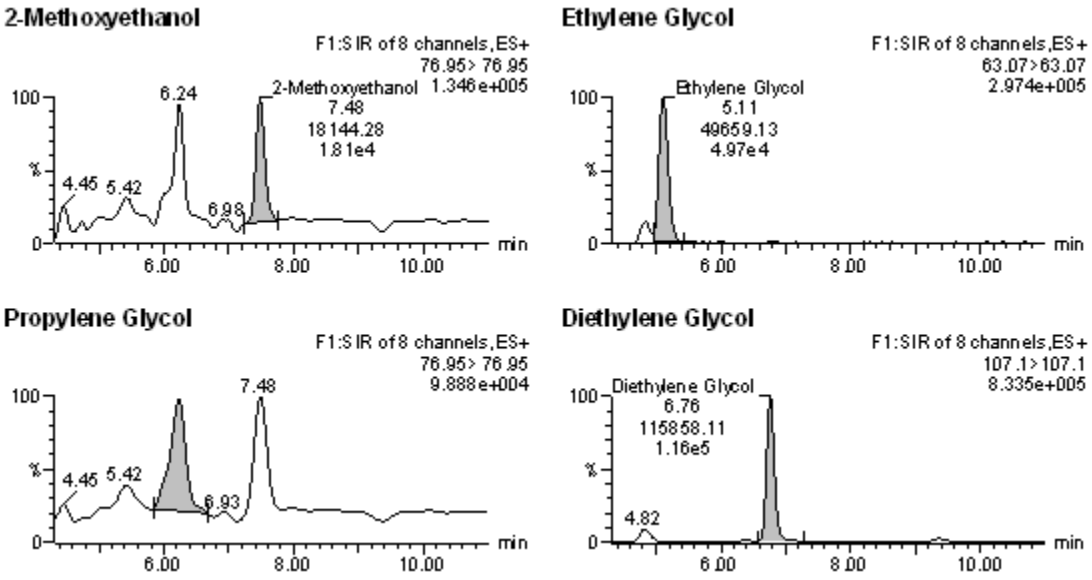
Case Study #2

Glycols

Resolution – split the analysis into two analytical runs

a. Selected Ion Reaction (SIR)

b. Multiple Reaction Monitoring (MRM)



Ethylene Glycol – 500 ug/l

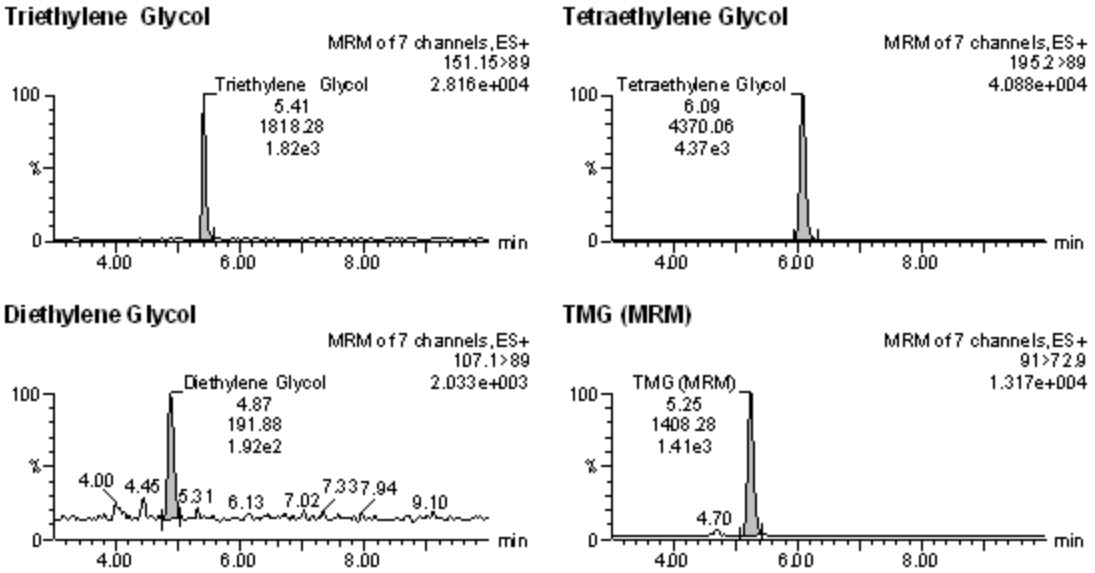
Propylene Glycol – 100 ug/l

2-methoxyethanol – 100 ug/l

Diethylene glycol – 25 ug/l

Case Study #2

Glycols



Diethylene glycol – 25 ug/l

Triethylene glycol – 25 ug/l

Tetraethylene glycol – 25 ug/l

Diethylene glycol can be reported from either mode

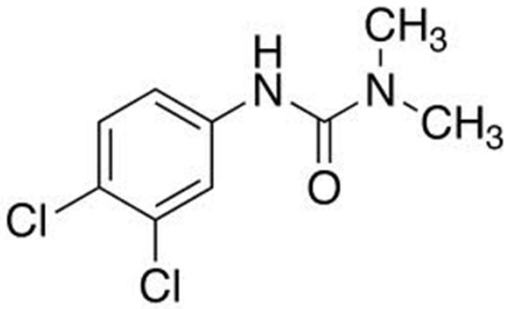
Note use of a surrogate, tetramethylene glycol

Limit for tetraethylene glycol improves

Case Study #3

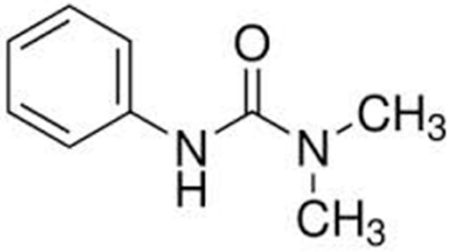
Phenyl Urea Herbicides

Diuron



Monuron

Fenuron



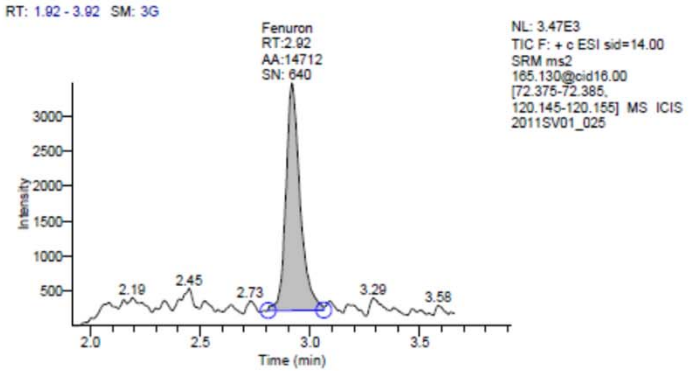
Case Study #3

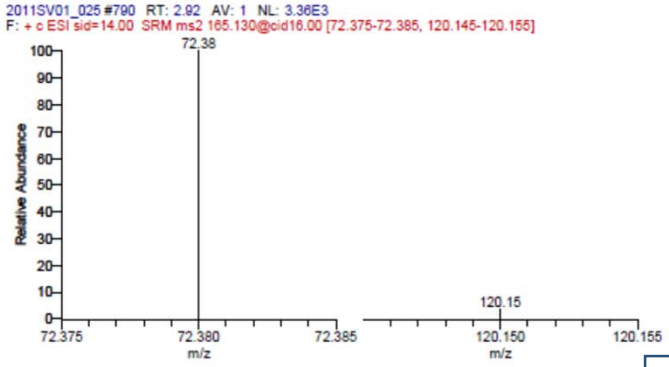
Phenyl Urea Herbicides

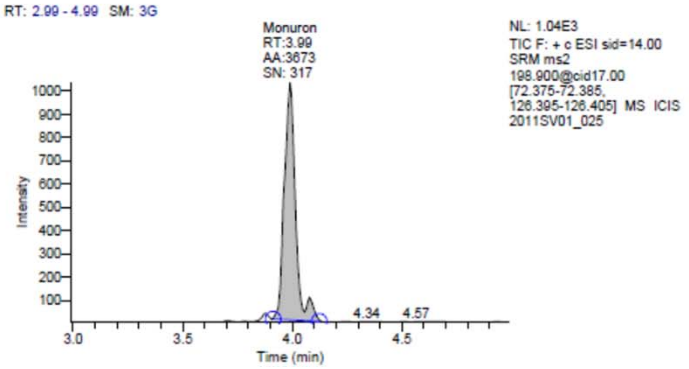
- Used for pre- and postemergent control of broadleaf and grassy weeds
- Also used on fruit and nut crops, grains, cotton, corn, etc.
- Analysis of compounds referenced in SW-846, Method 8321B
- Use of a generalized extraction resulted in sub-ppm limits
- Desire to optimize for low level detection

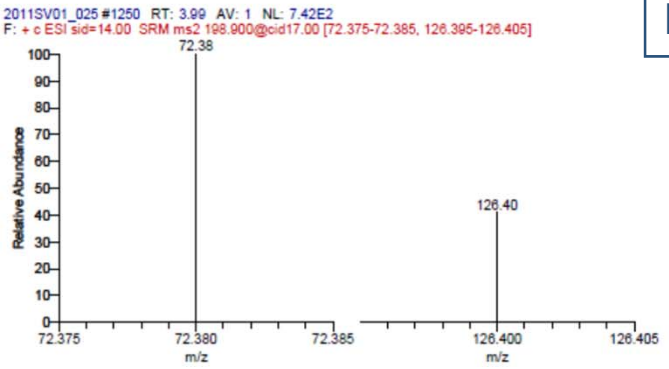
Case Study #3

Phenyl Urea Herbicides







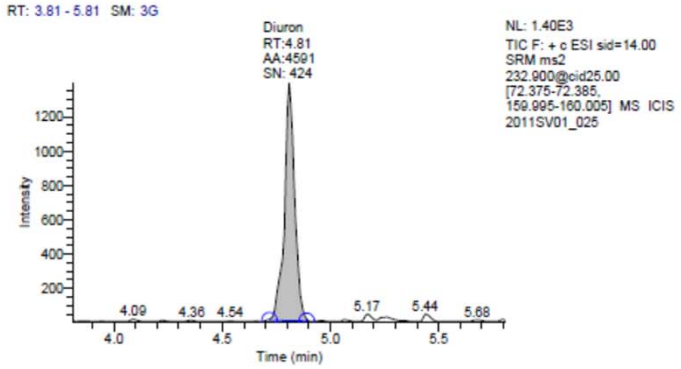


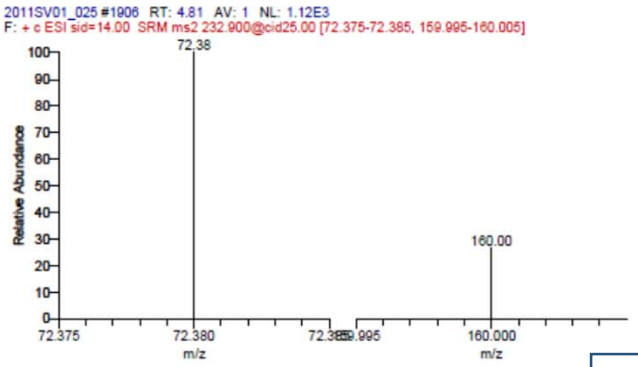
Fenuron – 1 ng/ml

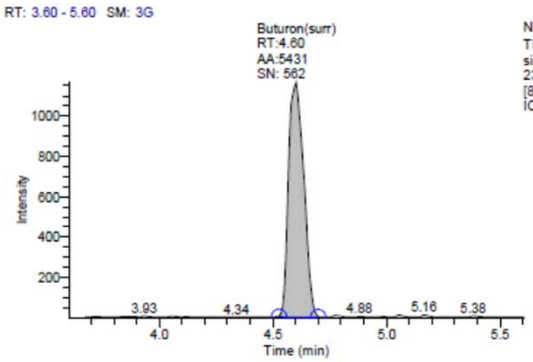
Monuron – 1 ng/ml

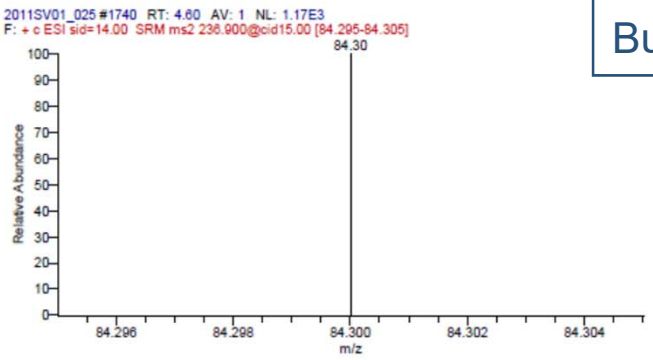
Case Study #3

Phenyl Urea Herbicides









Diuron – 1.5 ng/ml

Buturon – 1.5 ng/ml

Case Study #3

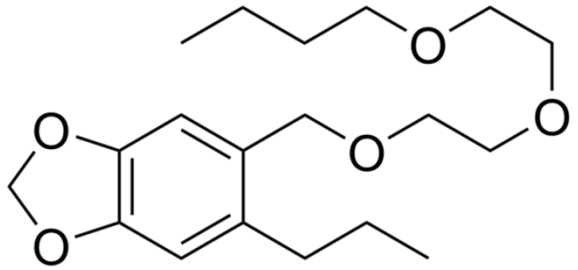
Phenyl Urea Herbicides

- 5 grams of soil blended with water and acetonitrile
- Extract cleaned up on SPE column
- Able to report low limits for analysis

	LOQ
Monuron -	0.2 ng/g
Fenuron -	0.2 ng/g
Diuron -	0.3 ng/g

Case Study #4

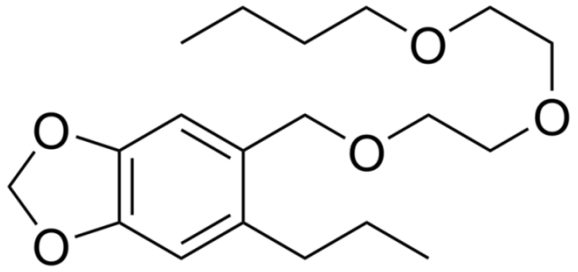
Piperonyl Butoxide



- Used as a synergist in pesticide formulations
- Enhances the potency of pesticide compounds like pyrethrins, pyrethroids and certain carbamates
- Used in over 1500 EPA registered products
- Home use and restaurants a significant consumer of products employing piperonyl butoxide

Case Study #4

Piperonyl Butoxide

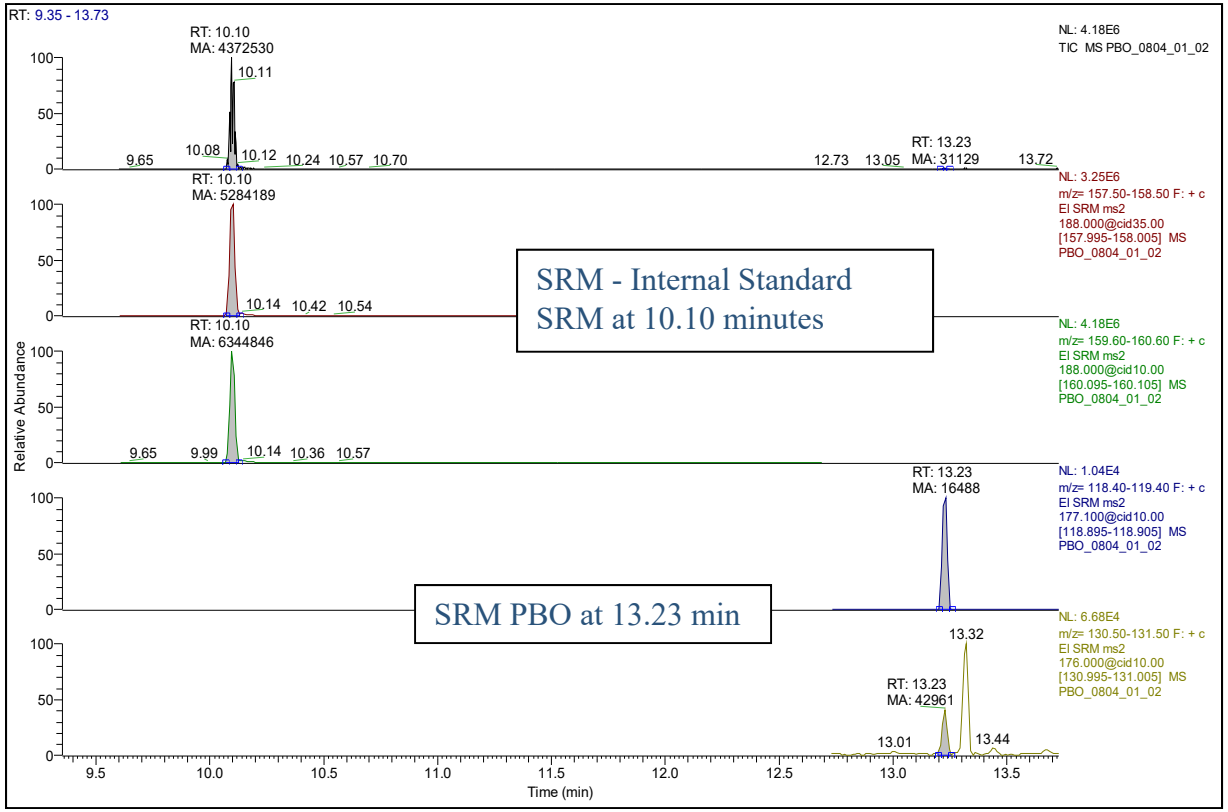


- Client with project to assess residual levels in WWTP sludges and biosolids
- Treatment of processes to degrade PBO, so need for low level analysis
- Extraction and clean-up of sludge extracts a challenge to meet low limits
- Take advantage of selectivity and sensitivity of GC/MS/MS to reach goals

Case Study #4

Piperonyl Butoxide

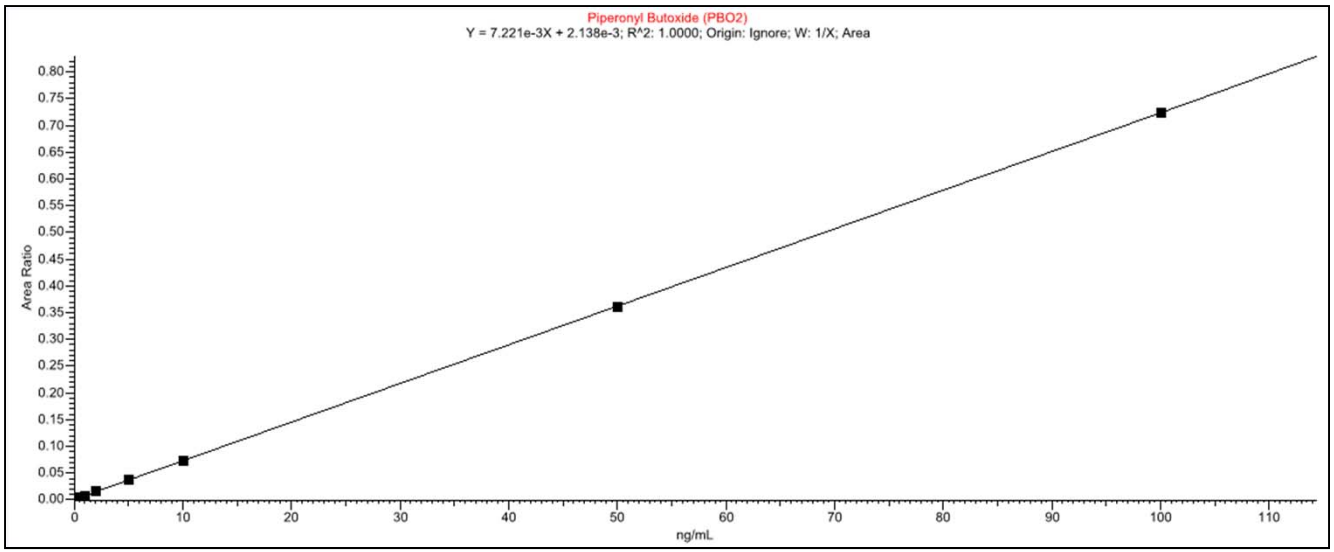
LOQ Level Standard at 0.5 ng/ml



Case Study #4

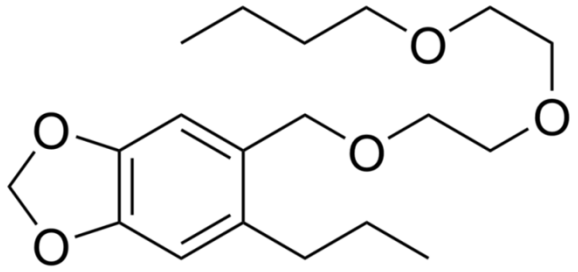
Piperonyl Butoxide

Calibration Curve - 0.5 ng/ml to 100 ng/ml



Case Study #4

Piperonyl Butoxide

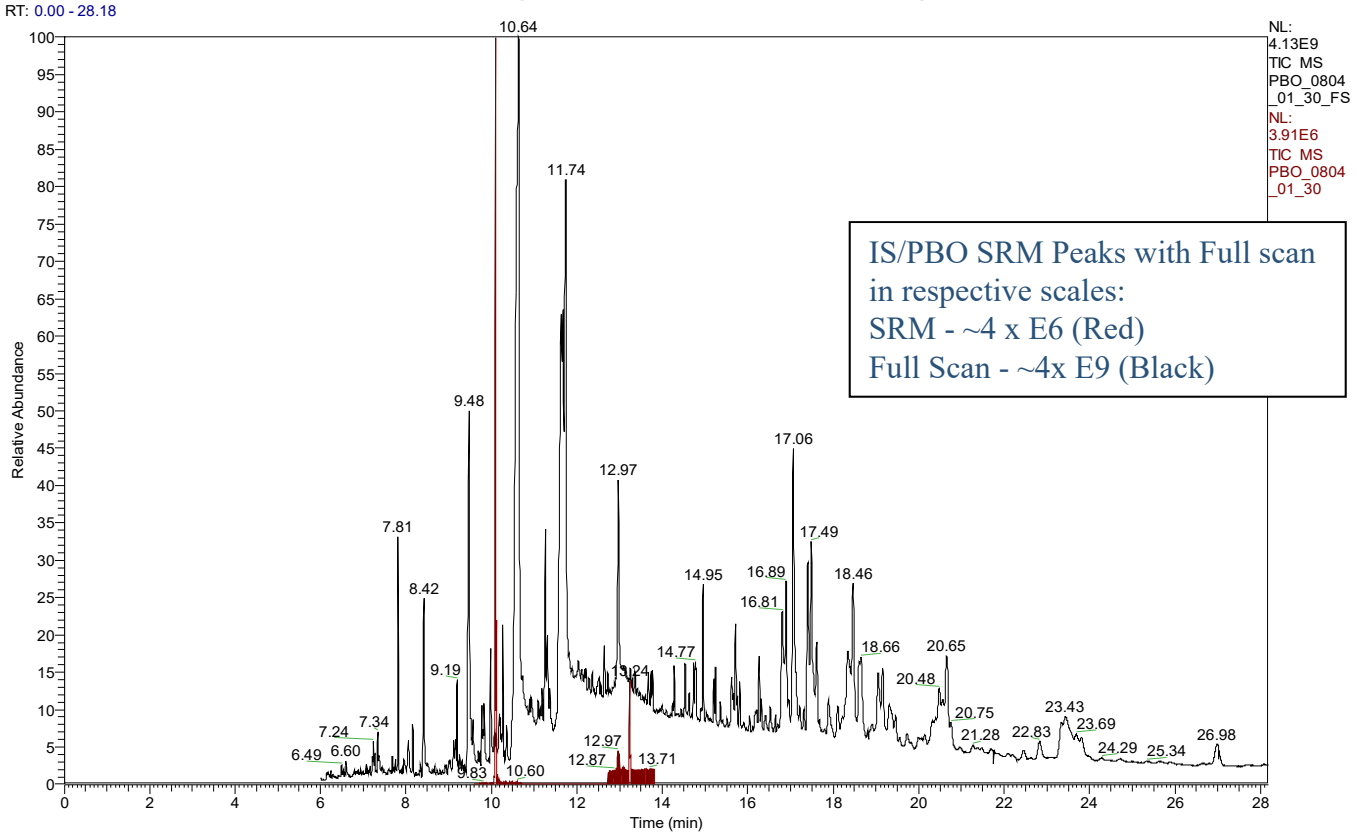


- Matrix present with the higher solids content presents problem
- Greater sensitivity and selectivity of GC/MS/MS allowed us to
  a. Use less sample for extraction (liq/liq extraction)
  b. Avoid use of column clean-ups that ultimately may have reduced recoveries.
- Under this scenario, still able to detect to 25 ng/l

Case Study #4

Piperonyl Butoxide

Full Scan Chromatogram vs SRM Chromatogram of Matrix



Conclusions

- While not exactly mainstream yet, the analytical techniques of LC/MS/MS and GC/MS/MS hold great promise
- Superior selectivity and sensitivity enable reporting in difficult matrices at lower levels
- Better sensitivity allows reduction in sample amounts and reduction in sample processing techniques
- Useful tools to consider for application to compounds not already well defined by the more standard analytical methods

Acknowledgement

- Meng Yu (Eurofins Lancaster Laboratories Environmental)
- Tim Trees (Eurofins Lancaster Laboratories Environmental).

Thank you

Charles Neslund

charlesneslund@eurofinsus.com

717-799-0439