Speciation of nitrogen heterocyclics in biomass burning aerosols using two-dimensional GC-MS with heart-cutting

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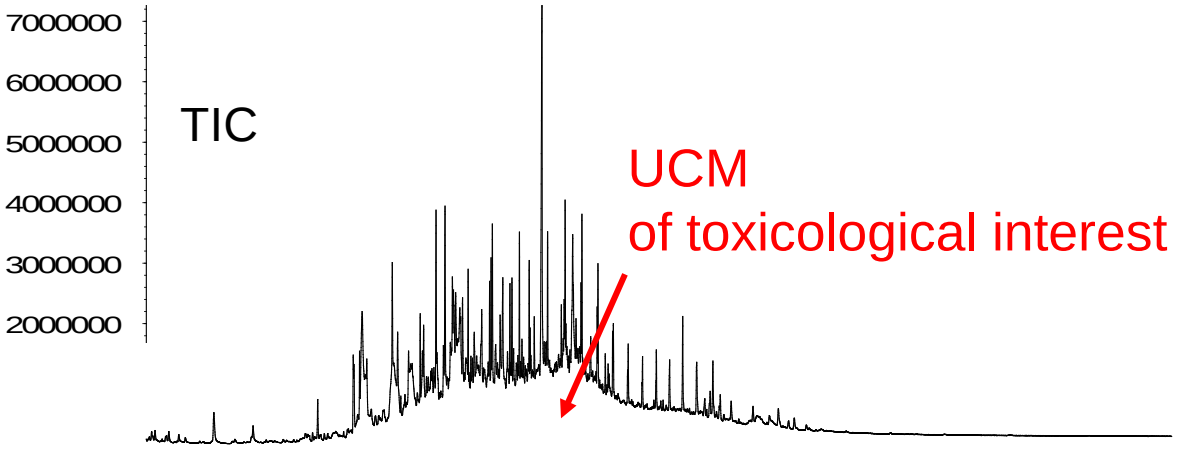
9th ICCPA, August 2008

Background and motivation

- Chemical characterization of carbonaceous aerosols is important.
- Conventional GC-MS is widely used
  - limited resolving power of single column
  - co-elution
  - unresolved complex mixture (UCM)
- Emerging two-dimensional GC systems
  - comprehensive (GC×GC)
  - heart-cutting (GC-GC)

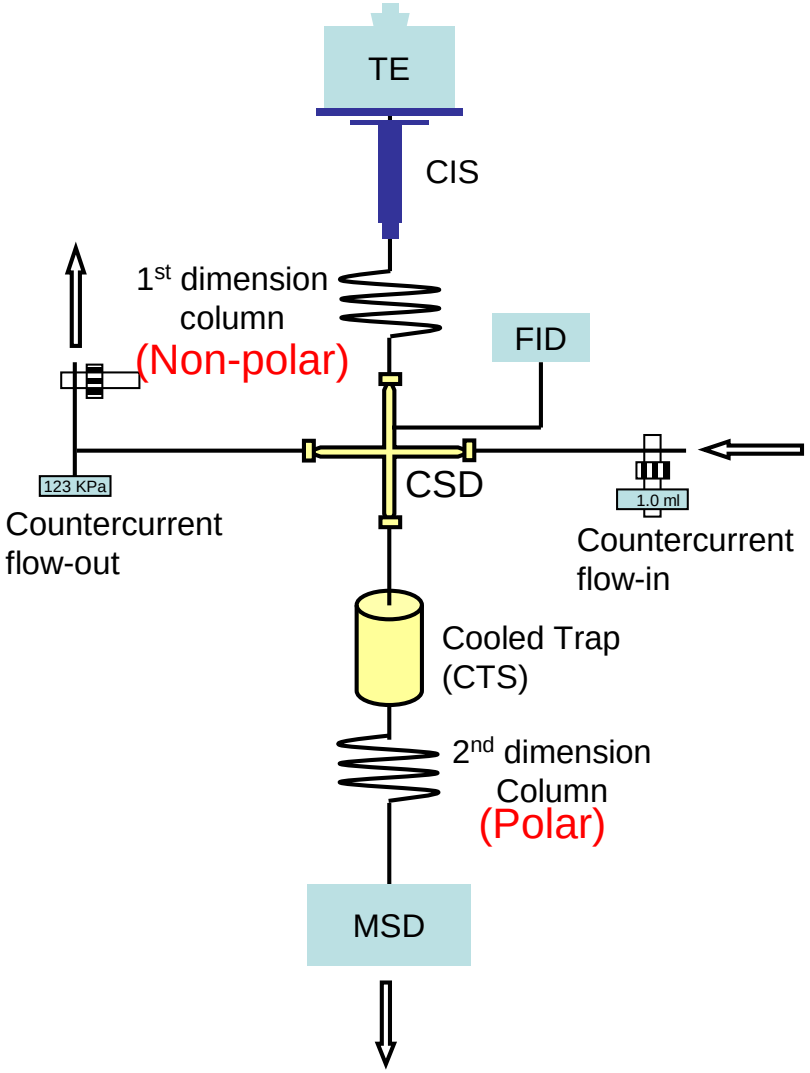


Objective

Develop and validate a novel thermal extraction (TE)-GC-GC-MS technique for a quantitative evaluation of heterocyclic nitrogen compounds in aerosols from emissions sources.

- Deconvolve UCM components.
- N-heterocyclics
  - can be toxic to the environment or essential to plant nutrient and biogeochemical cycling.
  - not reported before.
- Data obtained can be potentially used for the study of:
  - chemical emissions inventories;
  - pollutant exposure estimation;
  - source apportionment;
  - atmospheric processes.

TE-GC-GC-MS heart-cutting technique



TE – thermal extraction unit

CIS – cooled injection system

CTS – cryo-focusing system

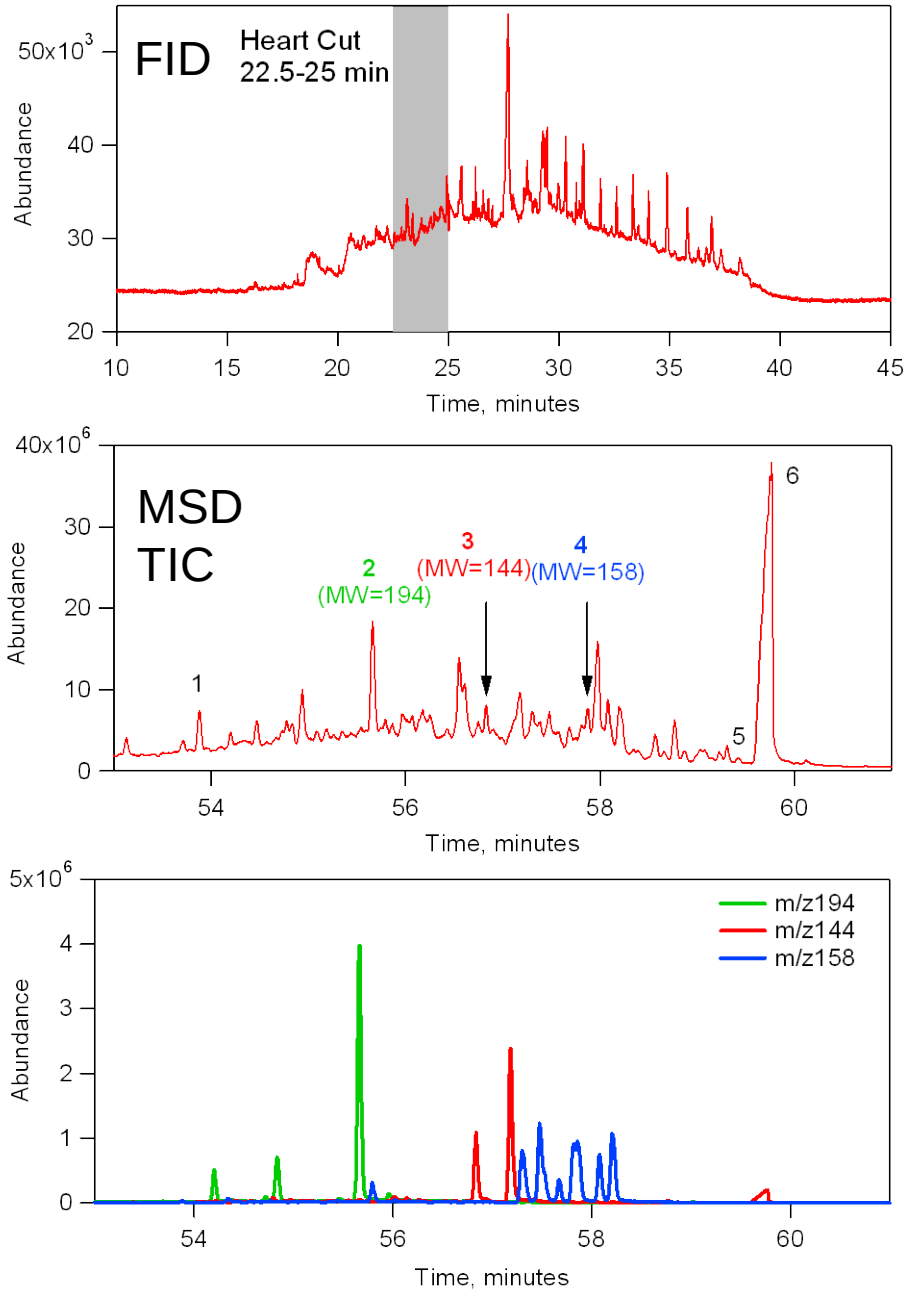
CSD – column switching device

FID – flame ionization detector

MSD – mass spectrum detector

MACH – modular accelerated column heater

Heart-cut within the UCM



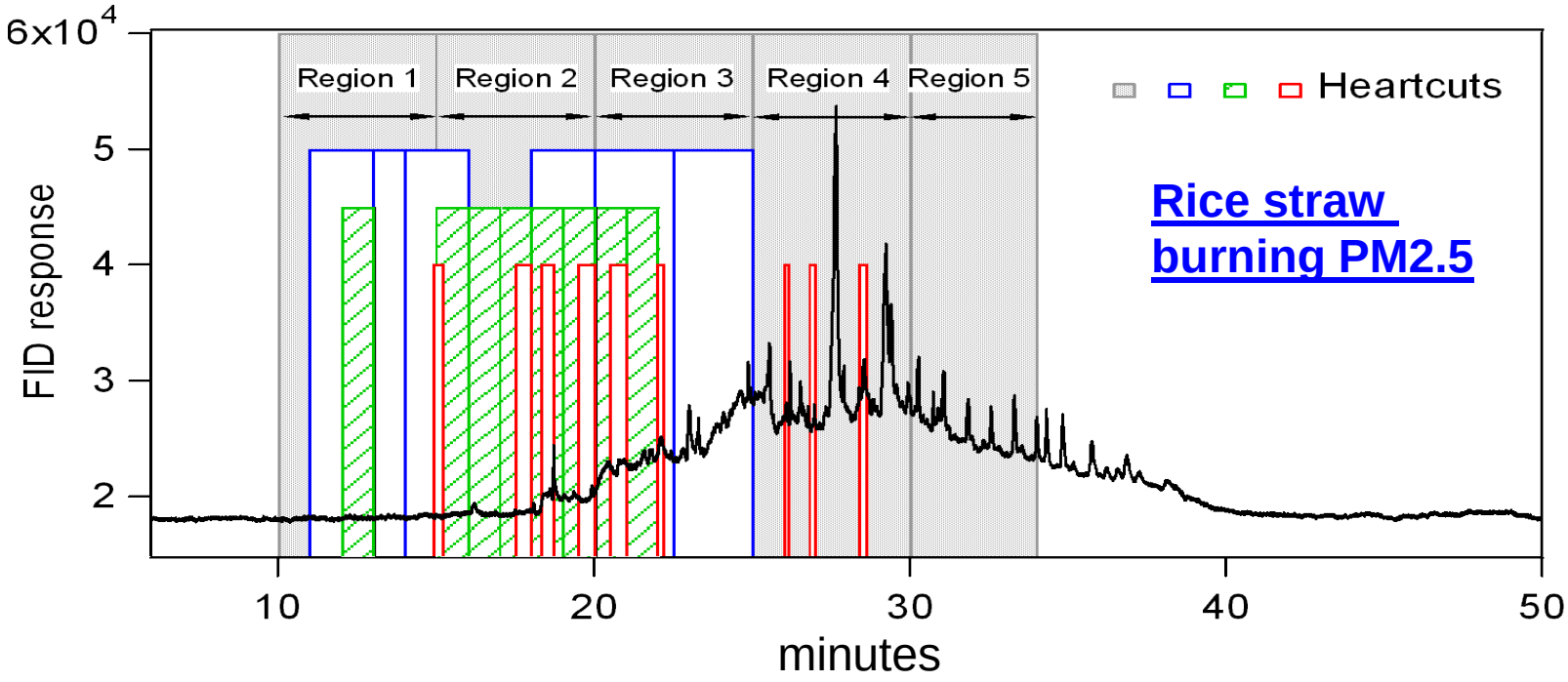
Rice straw burning PM2.5

- Lower background (baseline)
- Levoglucosan resolved
- Structural isomers resolved
- Direct identification feasible

Peak	Compounds	Match
1	dodecanoic acid	96
2	phenol, 2,6-dimethoxy-4-(2-propenyl),	93
3	1-naphthalenol	95
4	1-naphthalenol, 2-methyl	91
5	1,3-benzenediol, 4,5-dimethyl	94
6	**levoglucosan**	**90**

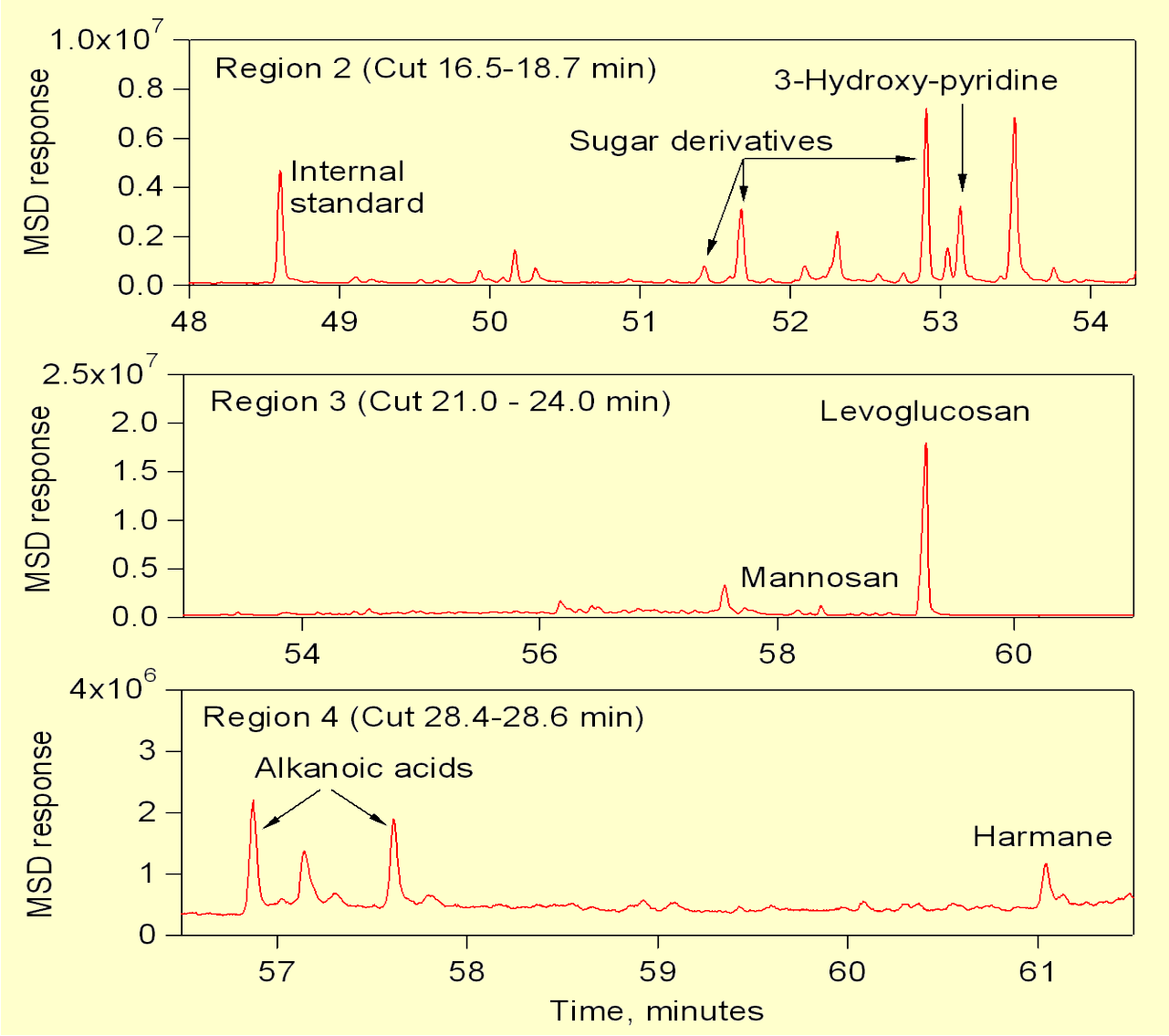
The identification of N-heterocyclics

Where to make the heartcuts?

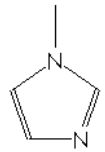


- Different cut regions are used to locate and identify the N heterocyclics.
- N heterocyclics are first tentatively identified using NIST MS library and AMDIS.
- Only the N-heterocyclics confirmed with authentic standards are chosen as target compounds for quantification.

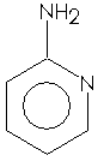
Examples of nitrogen heterocyclics within different cut regions



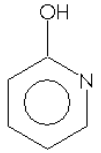
Target nitrogen heterocyclics



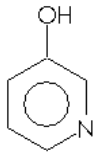
1-Methyl-imidazole (1MI)
$C_4H_6N_2$



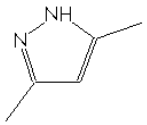
2-Amino pyridine (2AP)
$C_5H_6N_2$



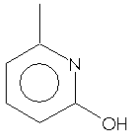
2-Hydroxy-pyridine (2HP)
C_5H_5NO



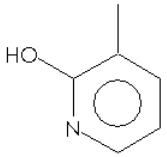
3-Hydroxy-pyridine (3HP)
C_5H_5NO



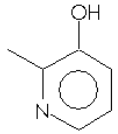
3,5-Dimethyl-pyrazole (35DP)
$C_5H_8N_2$



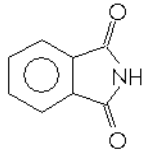
2-Hydroxy-6-methyl-pyridine (2H6MP)
C_6H_7NO



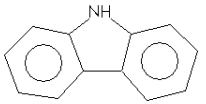
2-Hydroxy-3-methyl-pyridine (2H3MP)
C_6H_7NO



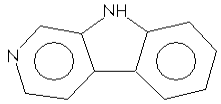
3-Hydroxy-2-methyl-pyridine (3H2MP)
C_6H_7NO



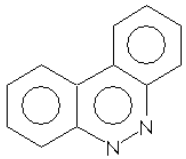
Phthalimide (PTL)
$C_8H_5NO_2$



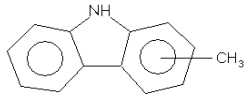
Carbazole (CBZ)
$C_{12}H_9N$



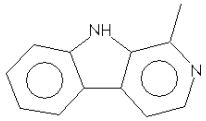
Norharmane (NHM)
$C_{11}H_8N_2$



Benzo [c] cinnoline (BCN)
$C_{12}H_8N_2$



2- Methyl-carbazole (2MC)
$C_{13}H_{11}N$



Harmane (HM)
$C_{12}H_{10}N_2$

Method's proficiency evaluation

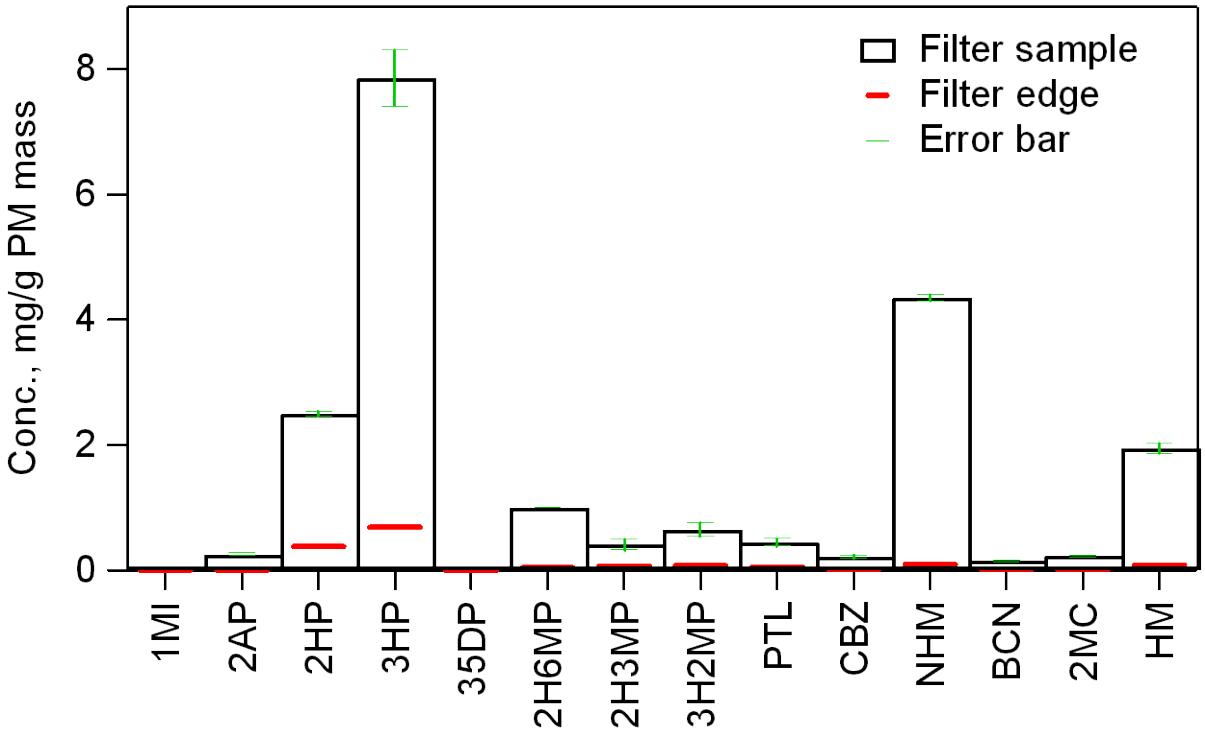
Method optimization

- Column selection, length, and temperature program
- Thermal extraction parameters
- CIS parameters
- CSD countercurrent flow rate
- Heart-cut parameters etc.

Overall Method's validation parameters

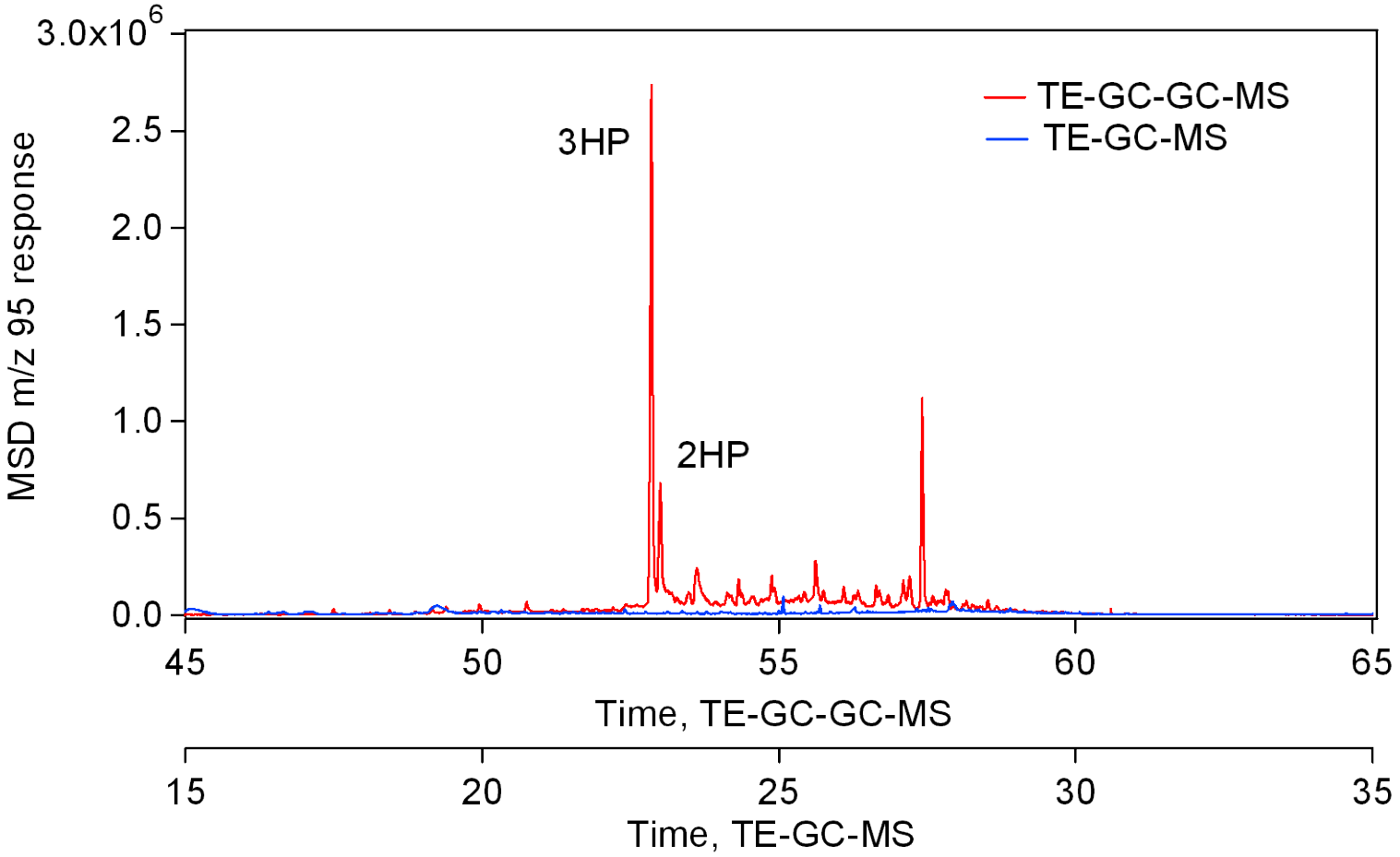
• Limit of detections	0.14 ng/µL
• Linearity range	0.5 ng/µL and 33.3 ng/µL
• Precision (standards)	5.9%
• Carry over	< 0.4 %
• Recovery	92.9 ± 5.7 %
• Overall method uncertainty	9.2%

N heterocyclics in rice straw burning PM2.5



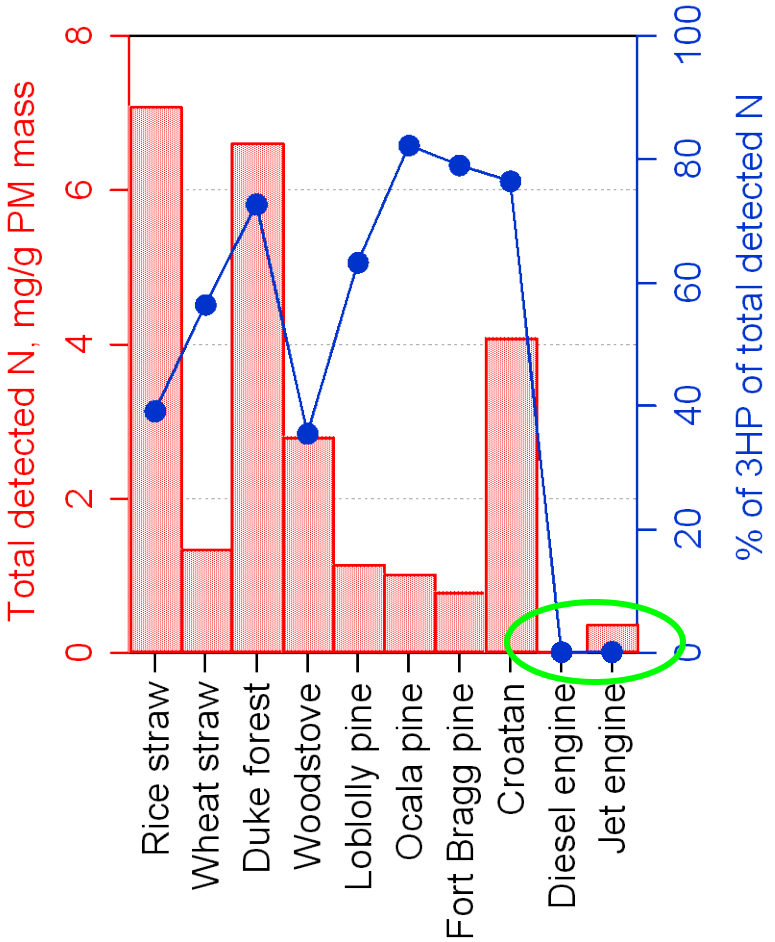
- Total detected N heterocyclics: ~7.1 mg/g of PM mass
- 3-hydroxy-pyridine & norharmane predominate, accounting for 39% and 22% of the total detected N.
- 1-methyl-imidazole & 3,5-dimethyl-pyrazole: <MDLs
- The unexposed edges of the same filter: <1% of those in aerosol sample.

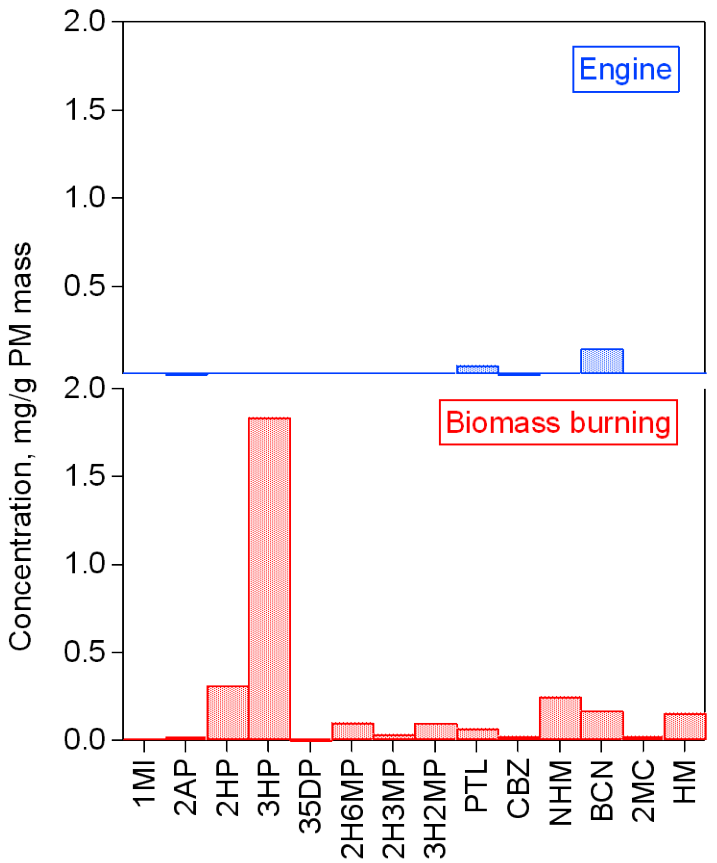
Comparison with conventional method



TE-GC-MS: unable to resolve and confirm the presence of N Heterocyclics

N heterocyclics in PM2.5 from source emissions



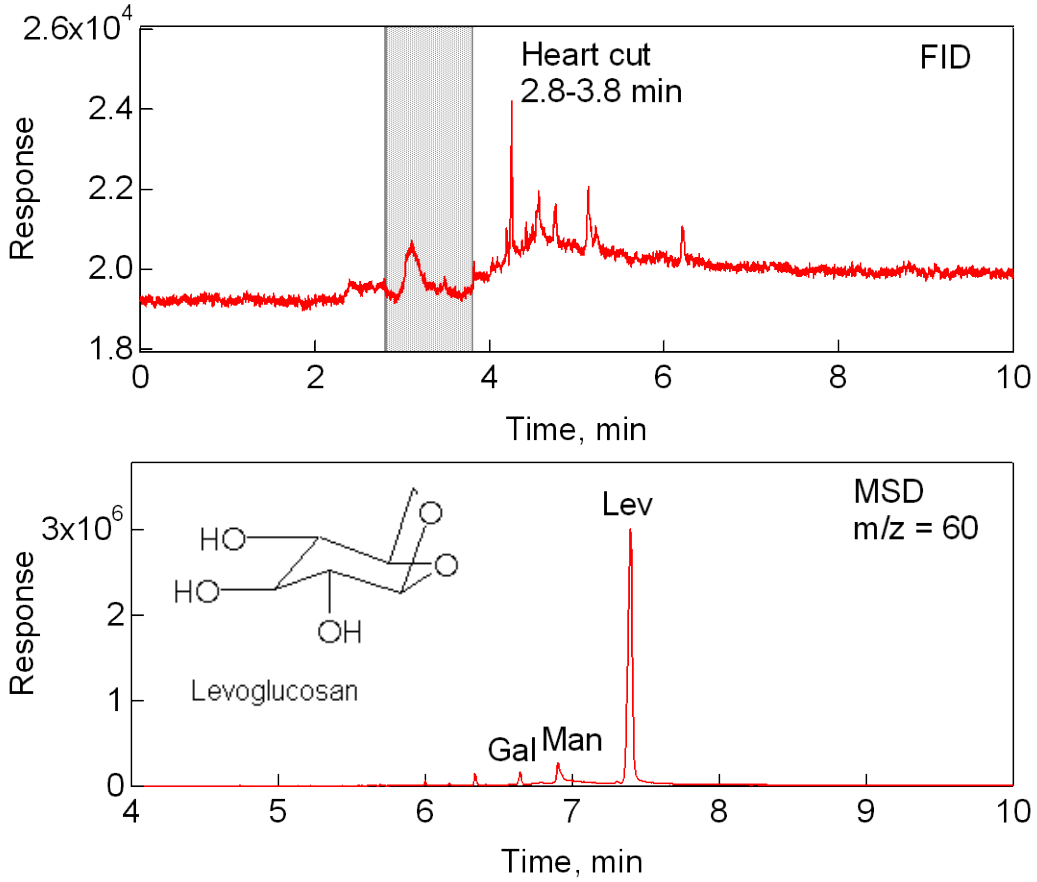


- Total detected N heterocyclics ranges from 0.8 to 7.1 mg/g PM mass for biomass burning aerosols.
- 3-hydroxy pyridine predominates, occupying 33-82% of Total detected N in biomass burning PM2.5.

- Most of the detected N heterocyclics are from biomass burning PM2.5 but not detectable from engine PM2.5.

Fast & direct determination of levoglucosan
and other anhydro-sugars

Levoglucosan: Biomass burning tracer for atmospheric aerosols



Ambient PM2.5 sample

- Analysis: within 10 minutes
- No sample pre-treatment
- Underivatized structure: m/z 60, narrow Gaussian peak
- Fully separated from isomers

More details can be found in poster 1011

Conclusions

- Analytical method for the identification and quantification of trace level nitrogen-containing heterocyclic compounds is developed and validated with TE-GC-GC-MS.
  - Acceptable proficiency, negligible carryover, reproducible performance, and picogram sensitivity.
  - Conventional TE-GC-MS is unable to resolve and thus confirm the presence of these compounds.

- Other important polar organic markers–anhydro sugars, organic acids, and substituted phenols–are identified with TE-GC-GC-MS method without derivatization.

- N heterocyclics in source emissions PM2.5 are resolved, identified and quantified with the above method.

This project was supported in part by an appointment to the Research Participation Program at the U.S. Environmental Protection Agency, administered by the Oak Ridge Institute for Science and Education through an interagency agreement between the U.S. Department of Energy and EPA.