

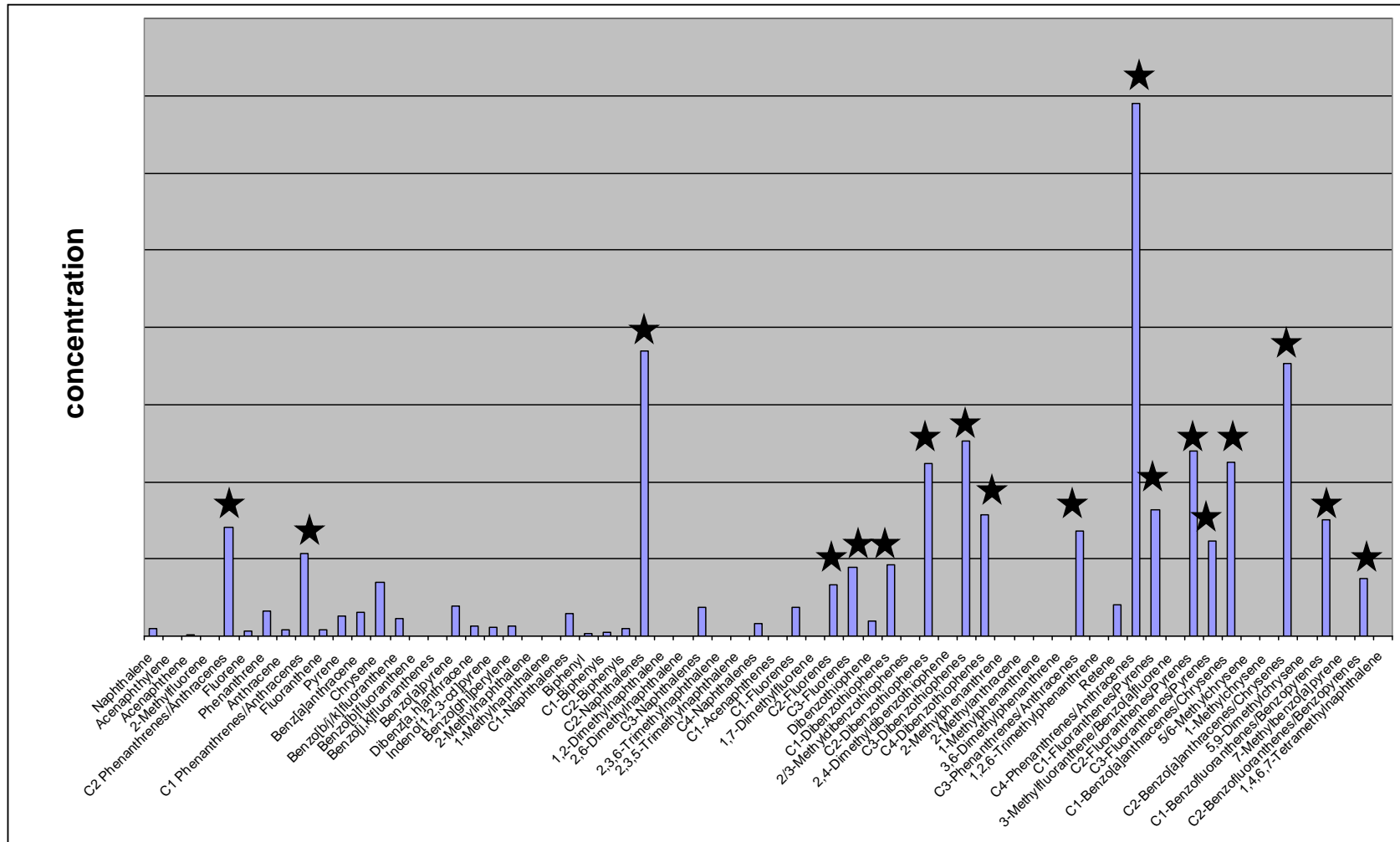
# **Analysis of Low Concentrations of PAH and Alkyl PAH in Environmental Samples**

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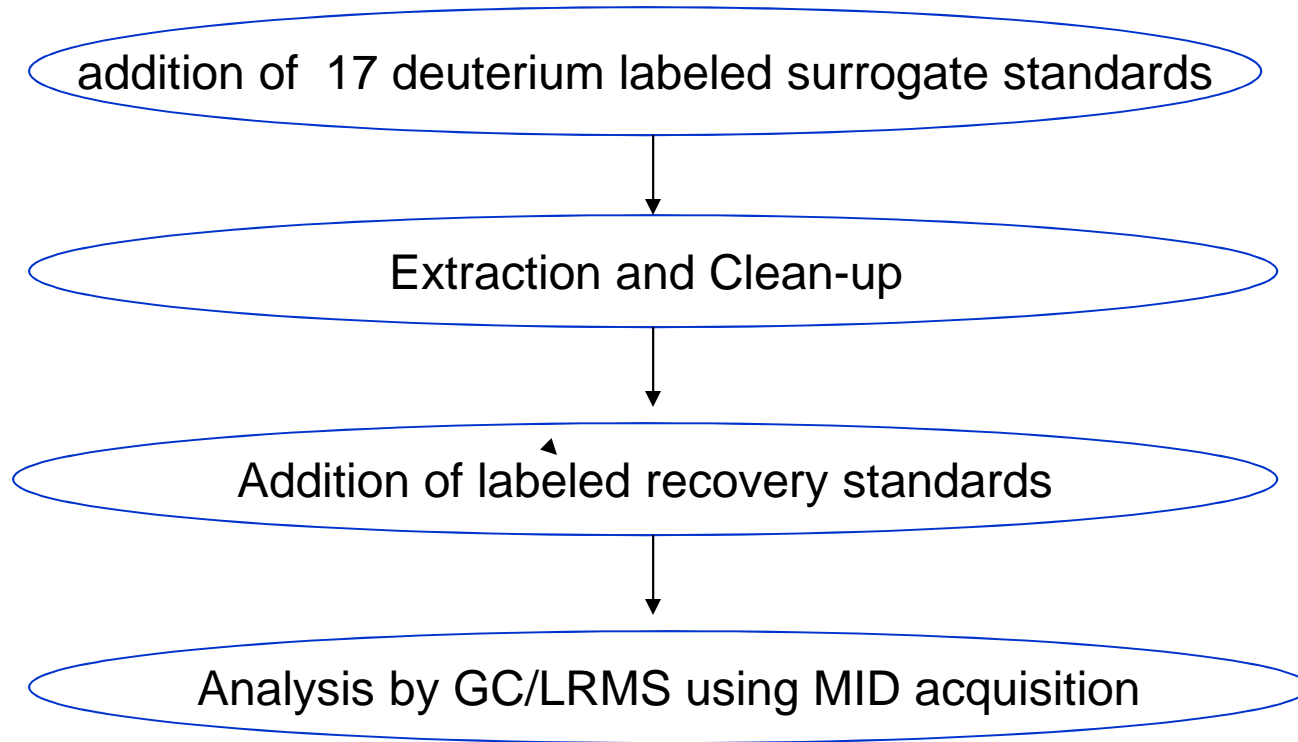
**May 2013**

# Low ng/sample detection limits, PAH + wide suite of alkyl PAH

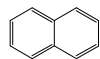
## Oil sands region monitoring



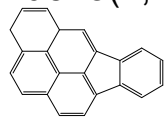
## Performance based method



## Parent PAH



Naphthalene  
Acenaphthylene  
Acenaphthene  
Fluorene  
Phenanthrene  
Anthracene  
Fluoranthene  
Pyrene  
Benz(a)anthracene  
Chrysene  
Benzo(b)fluoranthene  
Benzo(j/k)fluoranthenes  
Benzo(e)pyrene  
Benzo(a)pyrene  
Perylene  
Dibenzo(ah)anthracene  
Benzo(ghi)perylene  
Indeno(1,2,3-cd)pyrene



**Biphenyl**

**Dibenzothiophene**

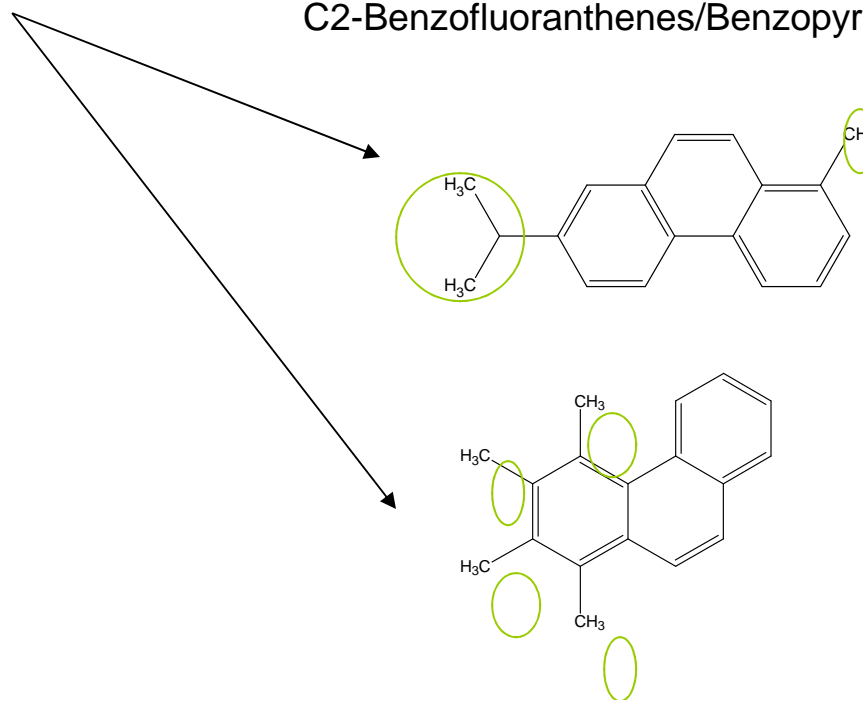
## Alkyl PAH

1-Methylnaphthalene  
2-Methylnaphthalene  
1,2-Dimethylnaphthalene  
2,6-Dimethylnaphthalene  
2,3,5-Trimethylnaphthalene  
2,3,6-Trimethylnaphthalene  
1,4,6,7-Tetramethylnaphthalene  
1-Methylphenanthrene  
2-Methylphenanthrene  
3-Methylphenanthrene  
9/4-Methylphenanthrenes  
2-Methylantracene  
7-Dimethylphenanthrene  
1,8-Dimethylphenanthrene  
2,6-Dimethylphenanthrene  
3,6-Dimethylphenanthrene  
1,2,6-Trimethylphenanthrene  
Retene (7-isopropyl-1-methylphenanthrene)  
2-Methylfluorene  
1,7-Dimethylfluorene  
2/3-Methyldibenzothiophene  
2,4-Dimethyldibenzothiophene  
3-Methylfluoranthene/Benzo(a)fluorene  
1-Methylchrysene  
5/6-Methylchrysenes  
5,9-Dimethylchrysene  
7-Methylbenzo(a)pyrene

## Alkyl Group Totals

C1-Naphthalenes  
C2-Naphthalenes  
C3-Naphthalenes  
C4-Naphthalenes  
C1-Phenanthrenes/Anthracenes  
C2-Phenanthrenes/Anthracenes  
C3-Phenanthrenes/Anthracenes  
C4-Phenanthrenes/Anthracenes  
C1-Biphenyls  
C2-Biphenyls  
C1-Acenaphthenes  
C1-Fluorenes  
C2-Fluorenes  
C3-Fluorenes  
C1-Dibenzothiophene  
C2-Dibenzothiophene  
C3-Dibenzothiophene  
C4-Dibenzothiophene

C1-Fluoranthenes/Pyrenes  
C2-Fluoranthenes/Pyrenes  
C3-Fluoranthenes/Pyrenes  
C4-Fluoranthenes/Pyrenes  
C1-Benz(a)anthracenes/Chrysenes  
C2-Benz(a)anthracenes/Chrysenes  
C3-Benz(a)anthracenes/Chrysenes  
C4-Benz(a)anthracenes/Chrysenes  
C1-Benzofluoranthenes/Benzopyrenes  
C2-Benzofluoranthenes/Benzopyrenes



# Extract Clean-up

## Minimum

Silica, 5% deactivated, removes:

- compounds of differing polarity- aliphatics, phthalate esters

## Additional

GPC (Biobead SX-3), removes

- lipid & other large molecules

Alumina, 2% deactivated, removes

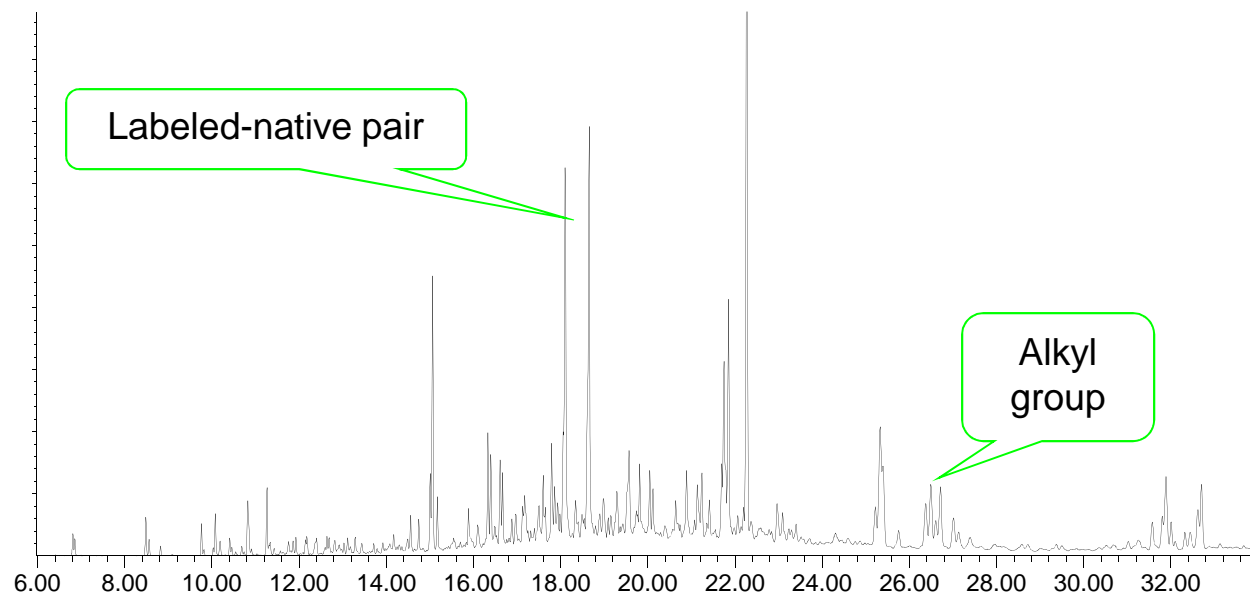
- polar compounds

Base Wash, 0.1 M NaOH, removes:

- acidic compounds

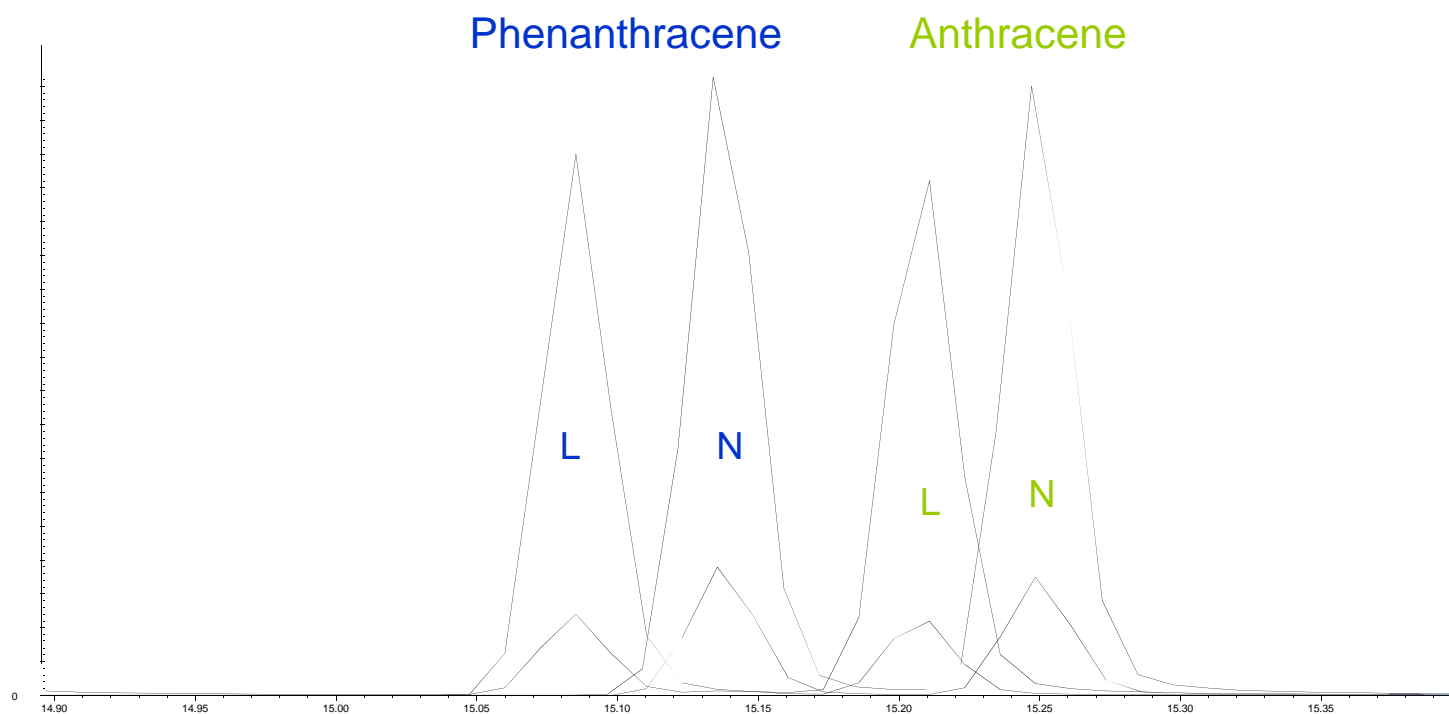
# Instrumental Analysis

Split/splitless injector, 30m Restek Rtx-5 column, 60-325 °C  
Electron impact ionization, unit mass resolution  
MID acquisition for sensitivity with 2 ions for specificity



# Identification: PAH, Alkyl PAH

**S:N, RRT window, 2 ions co-maximize, ion ratio within 20%**





# Identification: Alkyl Group Totals

## S:N, group RRT window

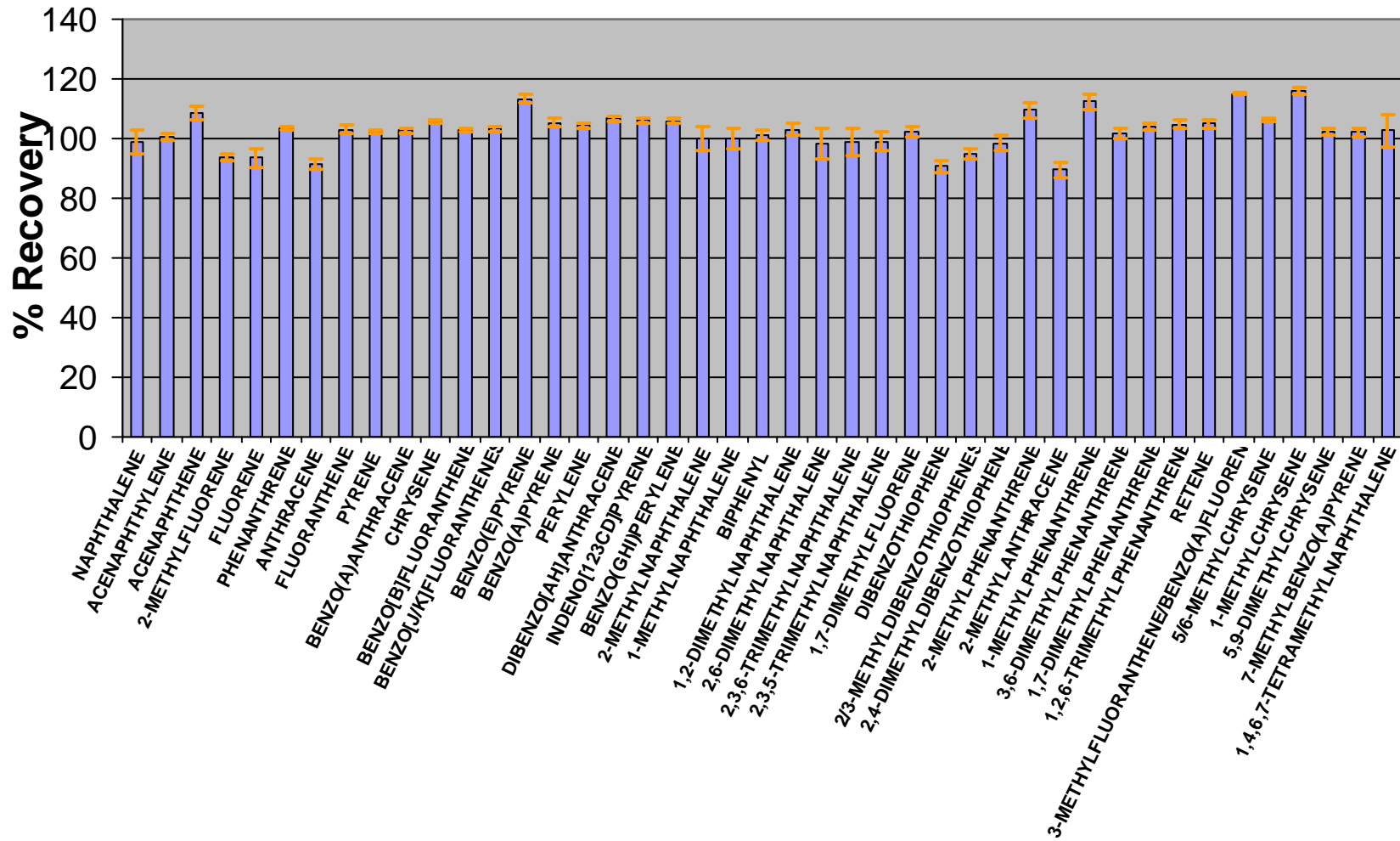


# Quantification

- RRFs, RRTs, & ion ratios from calibration (natives and labelled)
- multi-level calibration for PAH
- alkyl PAH use multi-level or single level calibration
- verification of calibration every 12 hours and at end
- quantification against labeled surrogates added prior to analysis
- results recovery corrected, little or no bias.
- sample specific DLs account for any matrix elevation of DL
- RRF of most similar compound used for alkyl group totals

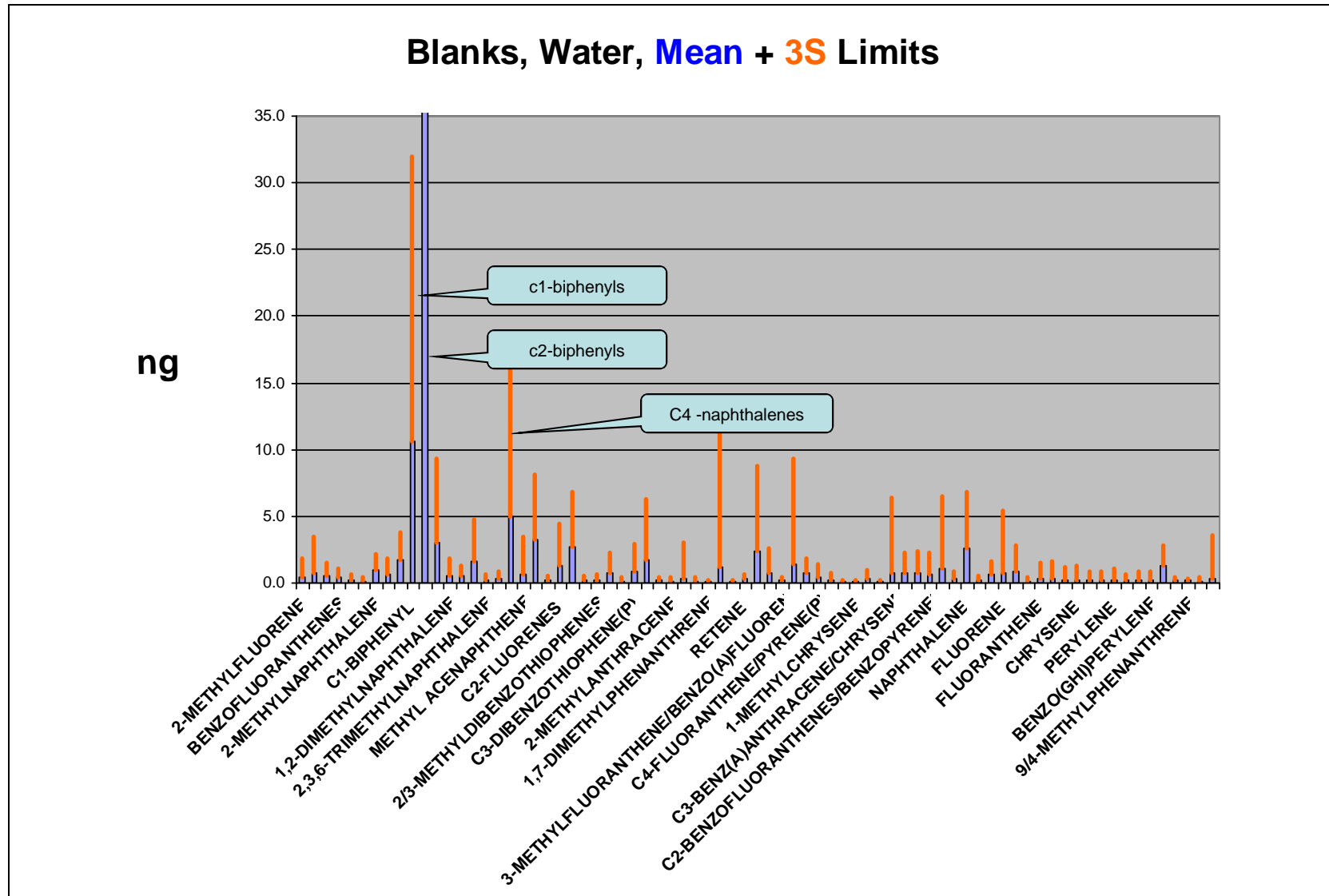
# Isotope dilution

## Intra-batch Trueness and Precision, Water



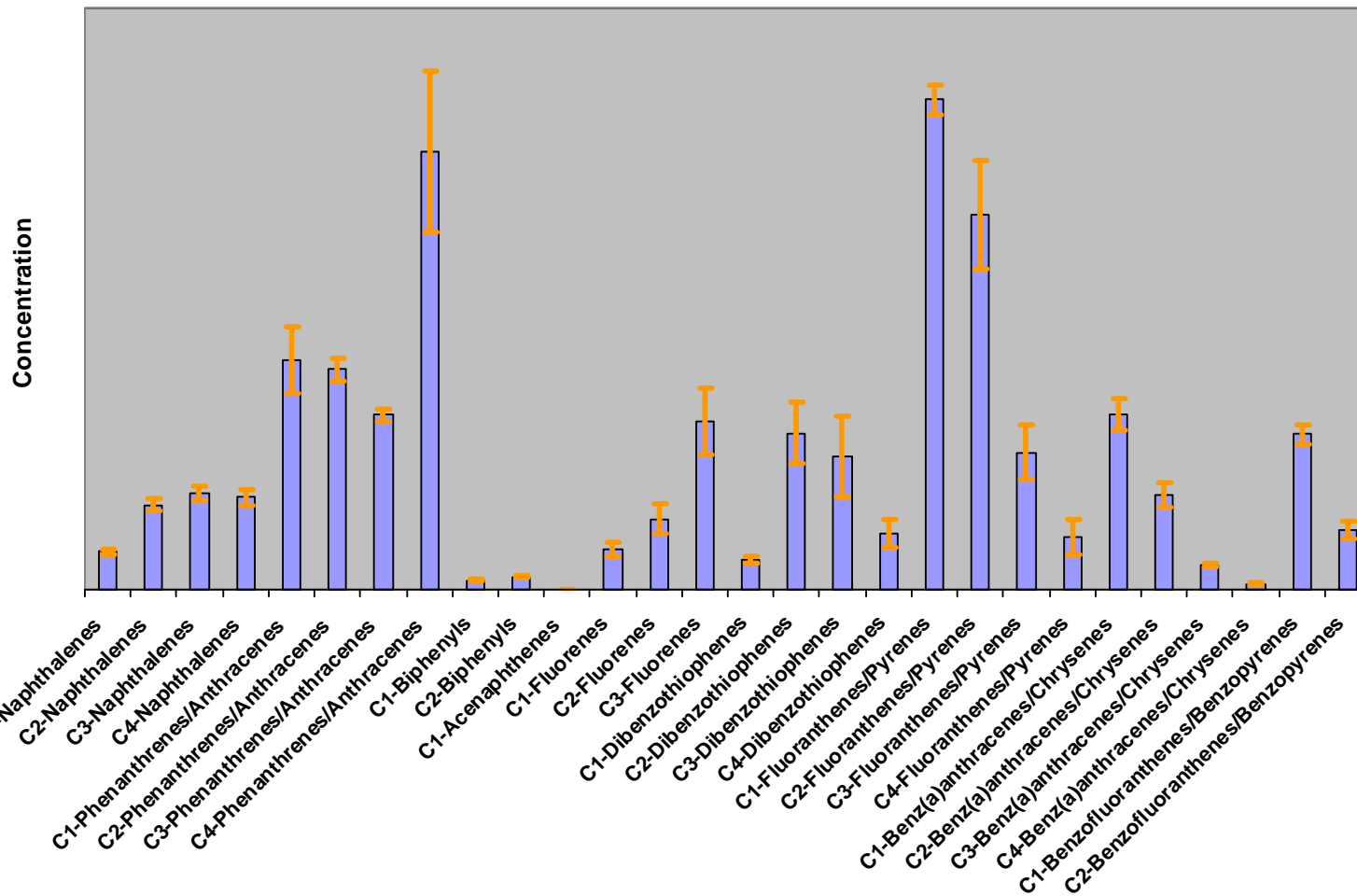


# Blanks



# Alkyl Group Precision

SRM 1944 Sediment, Inter-batch Precision



# Interlaboratory Comparison Exercises

- 2011, NIST Deepwater Horizon NRDA- marine sediment, 33 labs
- 2011 NIST Deepwater Horizon NDRA -mussel tissue, 34 labs
  - wide suite of PAH, alkyl PAH and alkyl PAH group totals
  - alkyl PAH group total study consensus value RSDs higher than for PAH, alkyl PAH
  - overall analytical issues noted by study authors:
    - choice of representative compound used for quantification of alkyl PAH
    - different alkyl PAH RFs depending on substitution
    - choice of peaks included in summation
    - (DL effect not examined)
  
- 2011 Deepwater Horizon NRDA- solution, spiked blood, spiked plasma, 6 labs
  - 4 PAH, 6 alkyl PAH
  - study results within reasonable range of gravimetric for most compounds
  - agreement for solution and plasma better than for blood
  - methylnaphthalenes in blood more variable, perhaps handling losses

# Conclusions

- Reliable low ppb or ppt concentration data can be obtained by careful application of standard analytical techniques.
- Determination of PAH plus wide suite of alkyl PAH compounds for oil sands monitoring applications.
- Critical components include a focus on clean blanks, labeled standards, effective interference removal and multiple ion monitoring identification.



# Questions