Methods for PAH/Alkylated PAH and Naphthenic Acid Isomer Group Profile Analysis with Application to Background Monitoring and Fingerprinting Investigations

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Outline

- Routine methods for quantitative analysis:

  PAH and Naphthenic Acid

  Description of methods / quantification

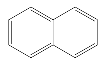
  Data Produced

- Examples of data from field samples - what can we learn?
  - Background Samples
  - Distinguishing background samples from industry influenced samples

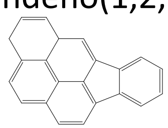
Key Aspects of PAH Monitoring

- Isotope dilution or Internal Standard quantification using SIM/GC/MS
- Low detection limits (< 1 ng/L) suitable for detecting ambient environmental levels
- Positive identification achieved by cleanup/fractionation of extracts, optimization of MS fragmentation conditions and monitoring of ratio of multiple ions

18 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

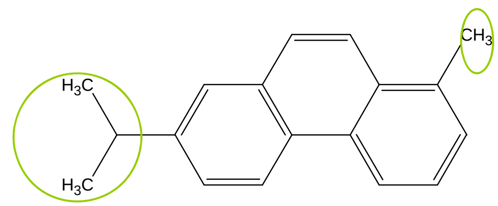
27 Individual Alkyl PAH

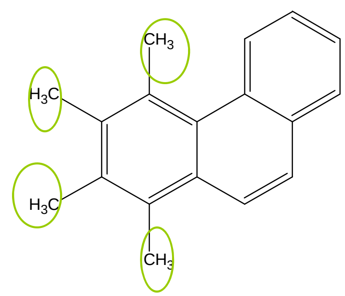
1-Methylnaphthalene
2-Methylnaphthalene
1,2-Dimethylnaphthalene
2,6-Dimethylnaphthalene
2,3,5-Trimethylnaphthalene
2,3,6-Trimethylnaphthalene
1,4,6,7-Tetramethylnaphthalene
1-Methylphenanthrene
2-Methylphenanthrene
3-Methylphenanthrene
9/4-Methylphenanthrenes
2-Methylanthracene
7-Dimethylphenanthrene
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

28 Alkyl Group Totals

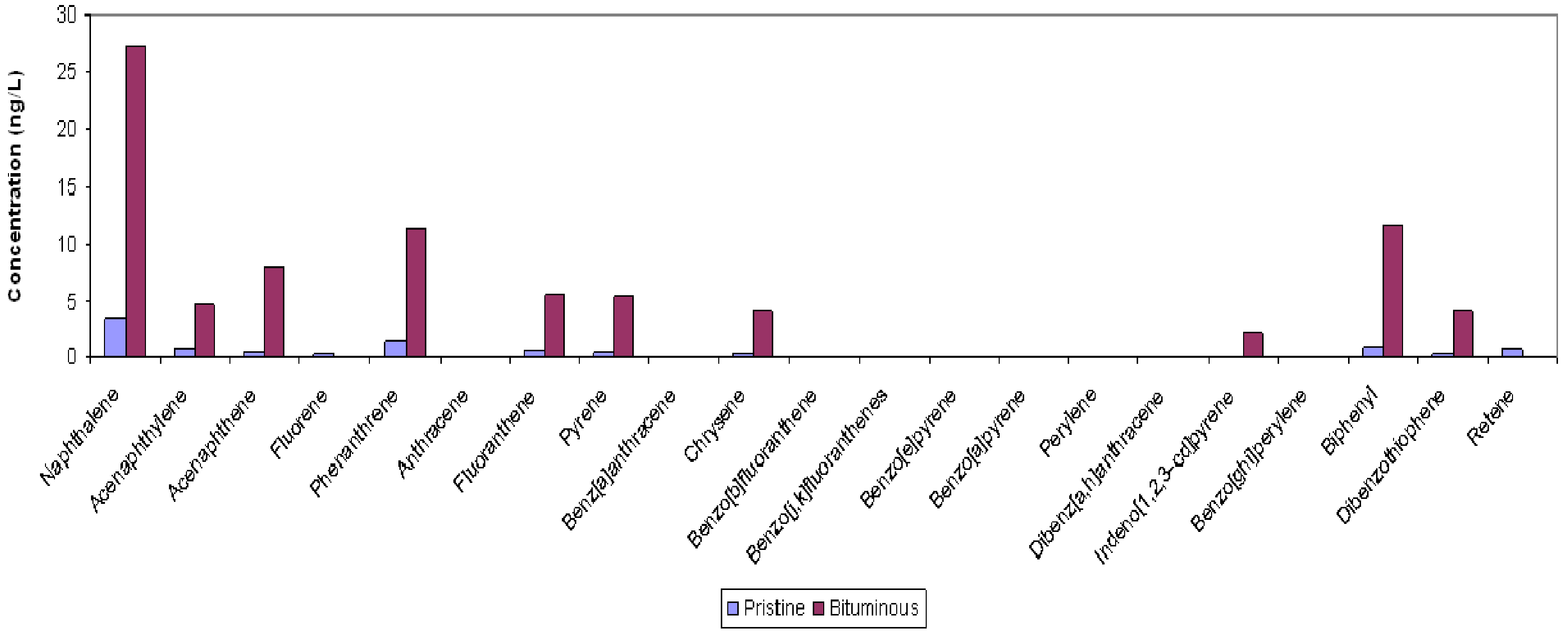
C1-Naphthalenes
C2-Naphthalenes
C3-Naphthalenes
C4-Naphthalenes
C1-Phenanthrenes/Anthracenes
C2-Phenanthrenes/Anthracenes
C3-Phenanthrenes/Anthracenes
C4-Phenanthrenes/Anthracenes
C1-Biphenyls
C2-Biphenyls
C1-Acenaphthenes
C1-Fluorenes
C2-Fluorenes
C3-Fluorenes
C1-Dibenzothiophene
C2-Dibenzothiophene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

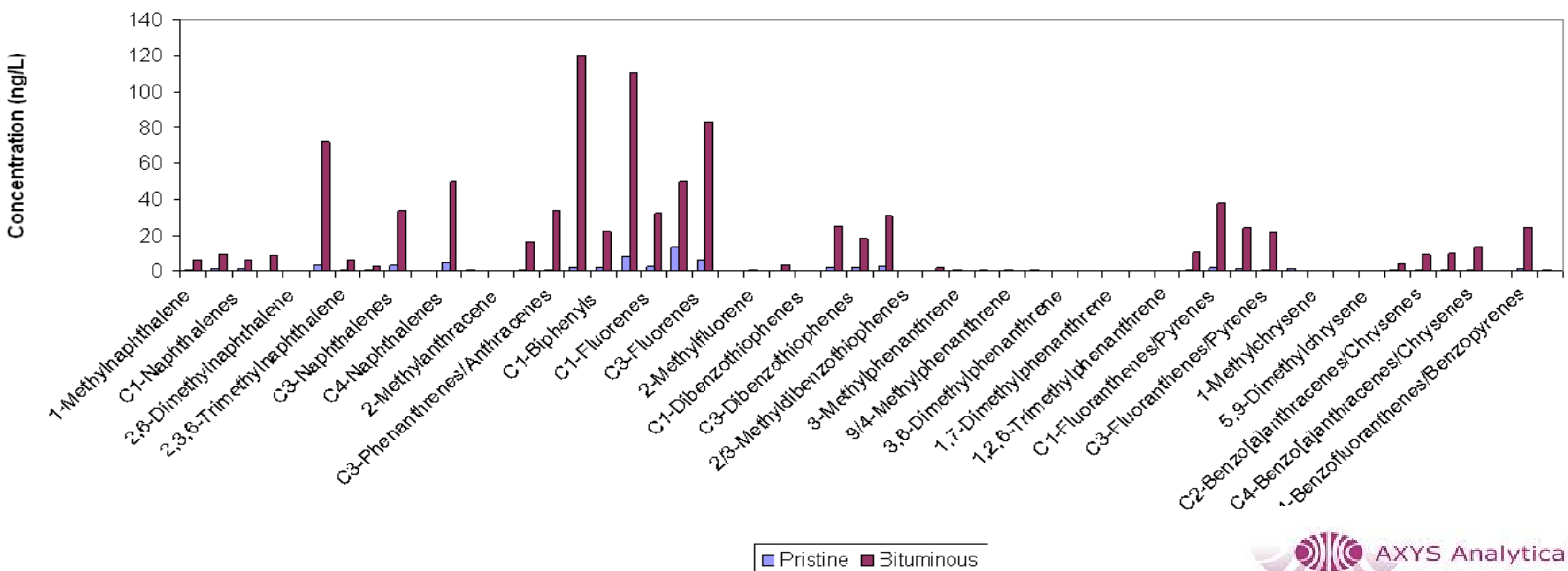




Parent PAHs in aqueous samples from pristine and bituminous site



Alkylated PAHs in aqueous samples from pristine and bituminous site



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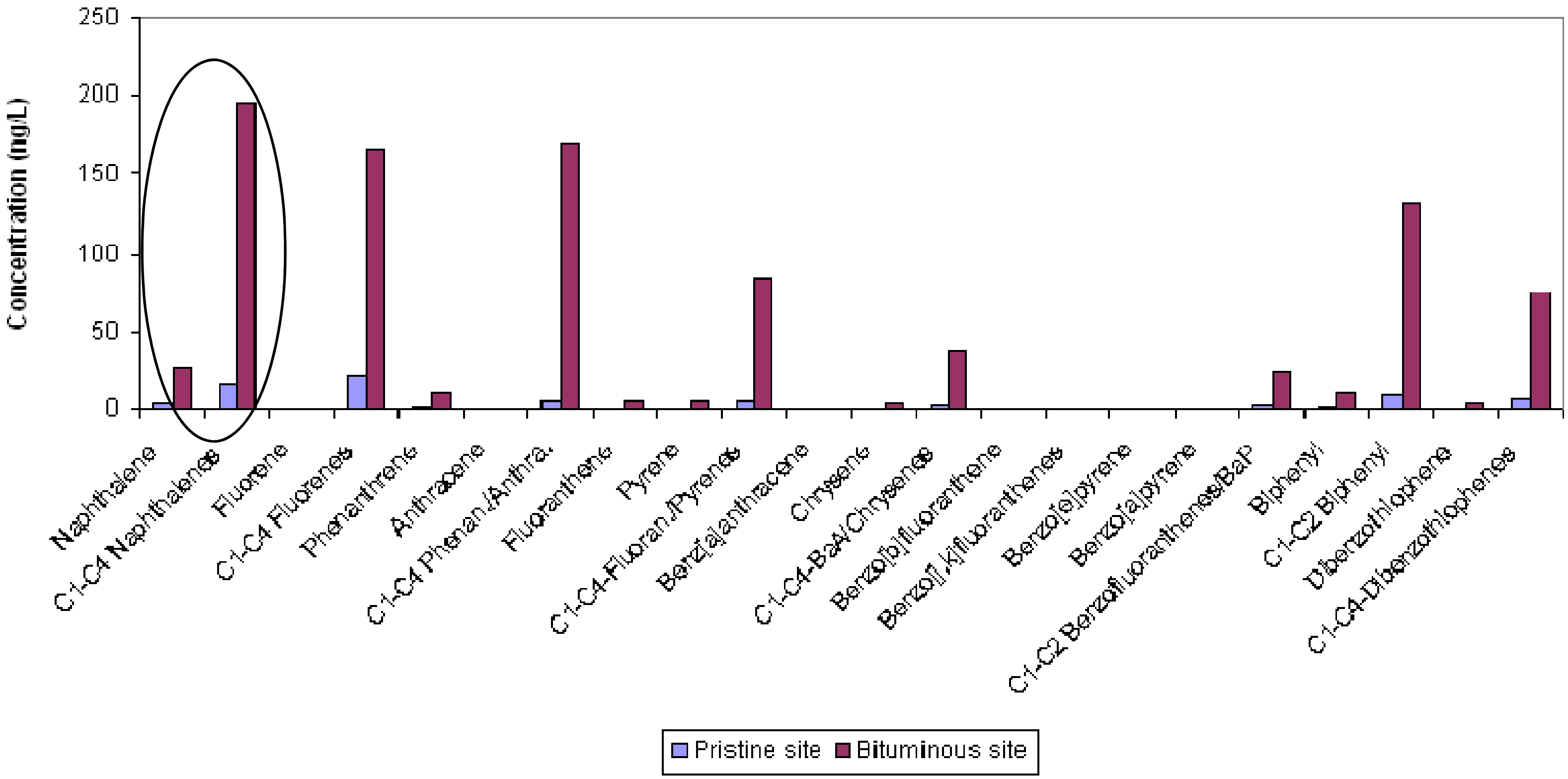
Comparison of concentrations for selected parent PAHs with total alkylated PAHs in water samples collected from pristine and bituminous sites.



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Key Aspects of NA monitoring $C_nH_{2n-z}O_2$

Sample + Labelled Standards

↓

Extraction: SPE or Soxhlet

↓

Derivatization with 1-EDC·HCl

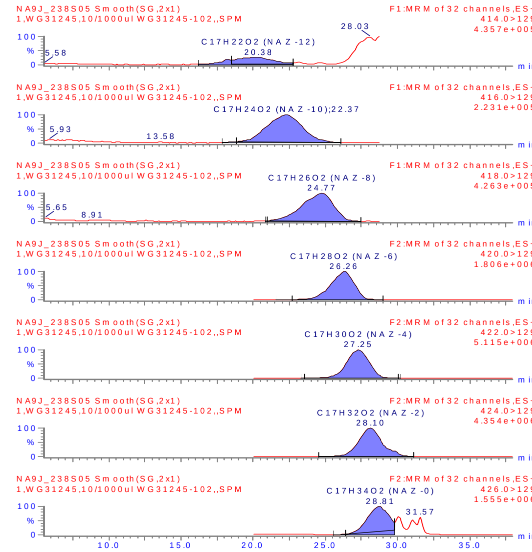
↓

LC/MS/MS-ESI+
Separation by Carbon number
and by extent of cyclization

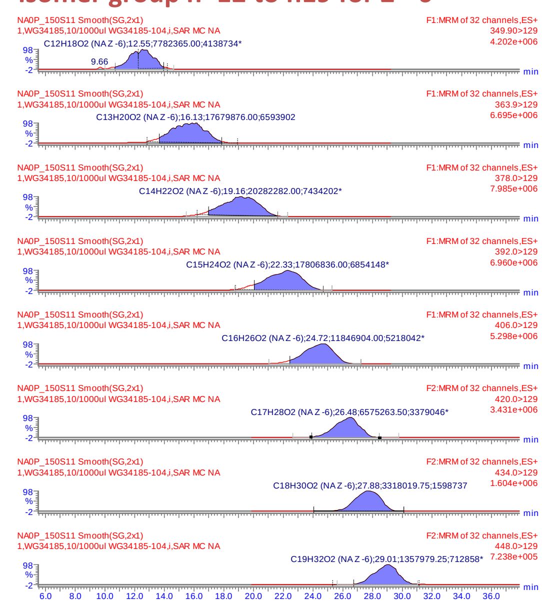
↓

Concentration
as pyrenebutyric acid equivalents

isomer group n=17, Z=-12 to 0



isomer group n=12 to n19 for Z=-6



Target NAs were selected based on prevalence in Northern Alberta surface water

% contribution of various NA to total NA in surface water sample

n	z=-12	z=-10	z=-8	z=-6	z=-4	z=-2	z=-0	Total
9	n/a	n/a	n/a	n/a	n/a	0	0.13	0.13
10	n/a	n/a	n/a	n/a	0	0	0	0
11	n/a	n/a	n/a	n/a	0.41	0.10	0	0.51
12	n/a	n/a	n/a	**0.62**	**1.50**	**0.28**	**0**	**2.40**
13	n/a	n/a	n/a	**2.13**	**3.33**	**0.53**	**0.02**	**6.01**
14	n/a	n/a	**0.68**	**5.25**	**5.07**	**0.77**	**0.04**	**11.8**
15	**1.28**	**1.09**	**1.86**	**7.59**	**5.48**	**0.90**	**0.05**	**18.3**
16	**2.58**	**1.54**	**2.70**	**7.47**	**4.45**	**0.68**	**0.06**	**19.5**
17	**3.52**	**1.70**	**2.60**	**4.92**	**2.77**	**0.46**	**0.05**	**16.0**
18	**3.43**	**1.59**	**1.80**	**2.68**	**1.47**	**0.32**	**0.02**	**11.3**
19	**2.32**	**1.10**	**1.15**	**1.42**	**0.81**	**0.15**	**0**	**6.95**
20	**1.85**	**0.71**	**0.54**	**0.60**	**0.35**	**0.06**	0	4.11
21	**0.97**	**0.39**	**0.24**	**0.29**	**0.15**	**0.02**	0	2.06
22	0.43	0.14	0.08	0.05	0.02	0	0	0.72
23	0.17	0.03	0.02	0.01	0	0	0	0.23

n/a = not applicable by structure

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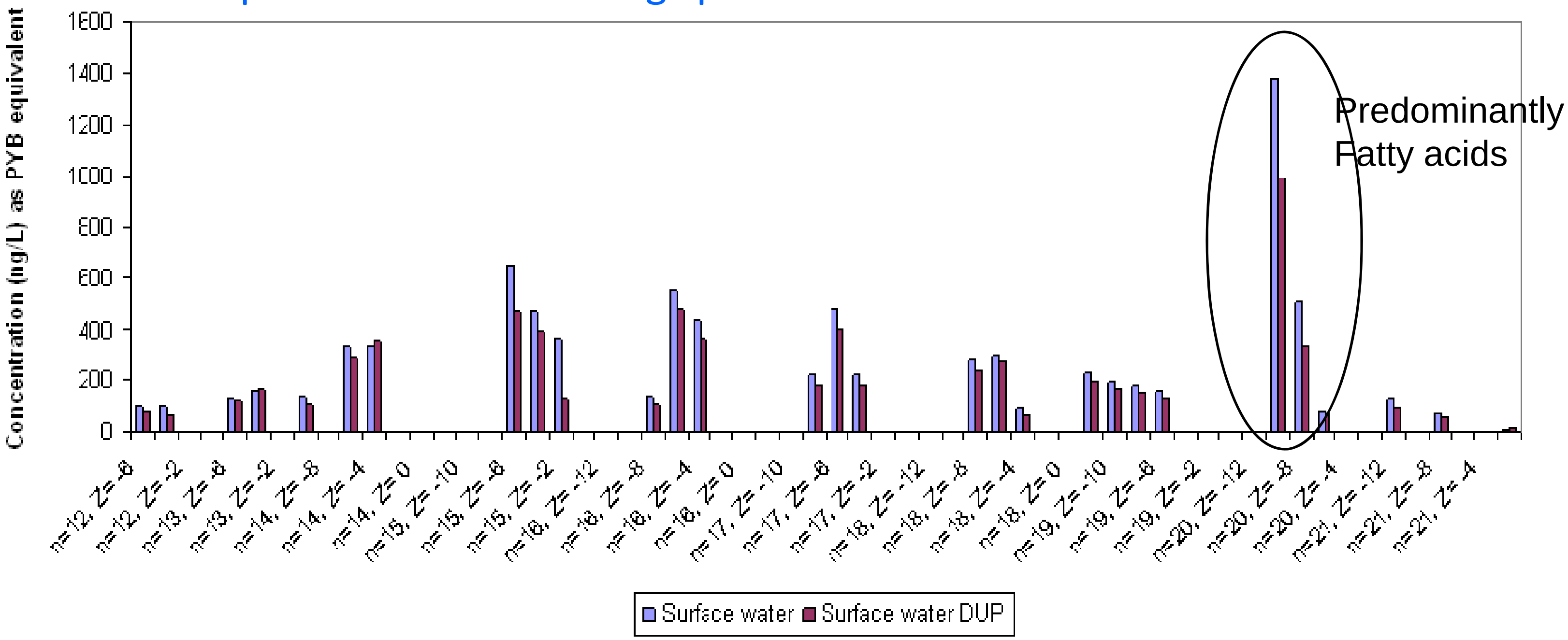
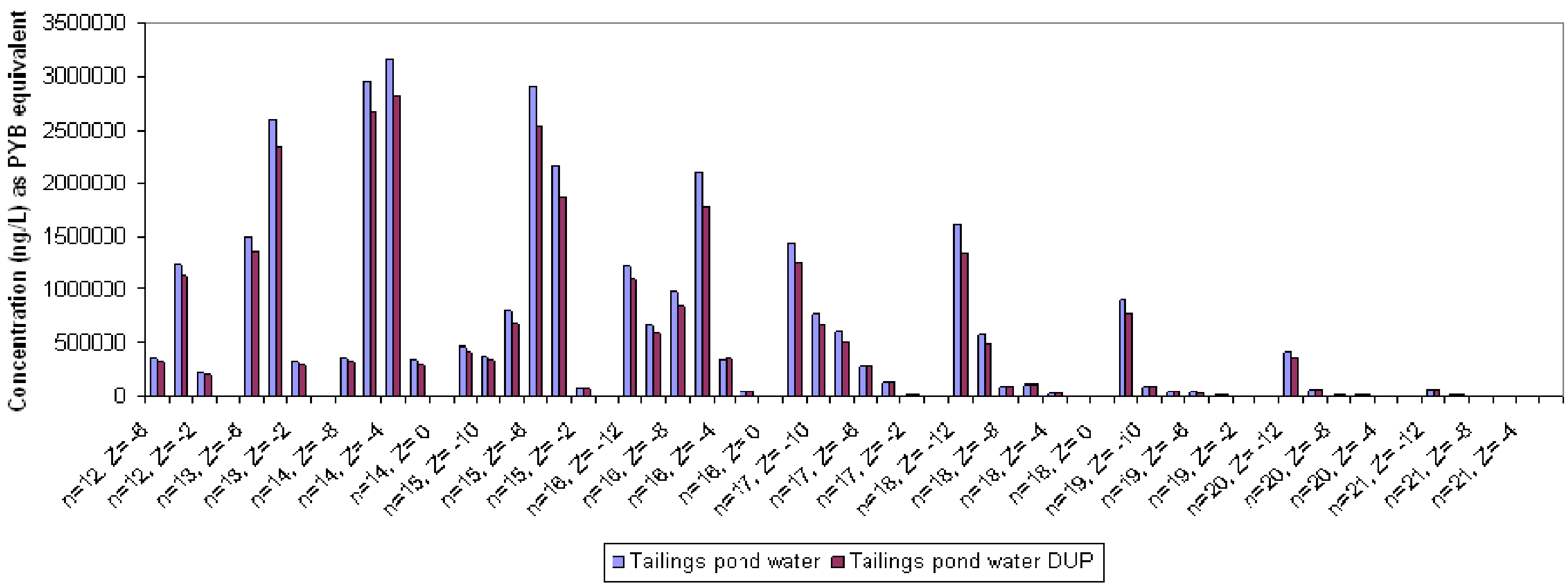
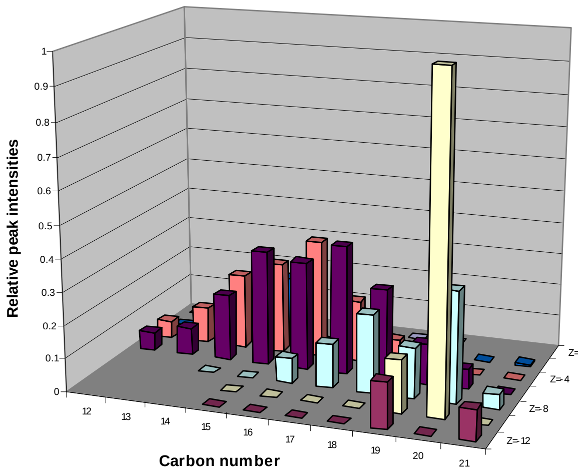
Comparison of NA patterns from a water samples collected from pristine surface water pristine site and tailings pond.



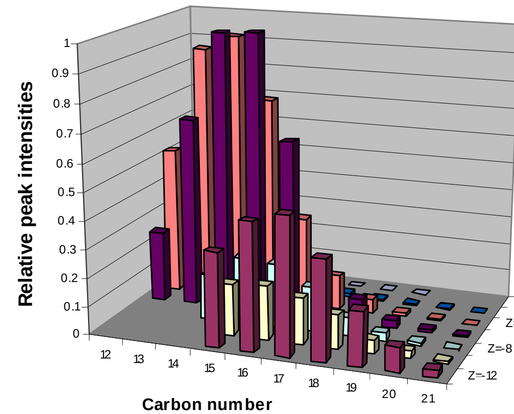


Analyte Patterns in Water Matrices and Standard

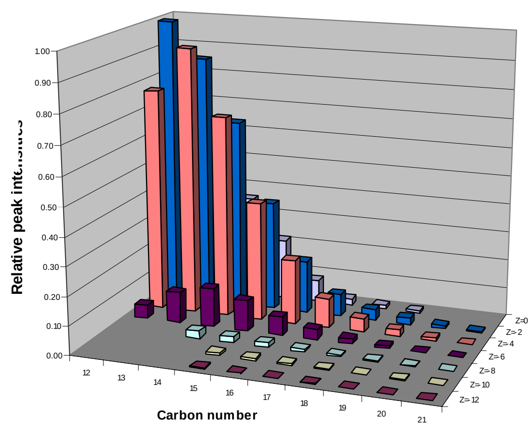
Surface water



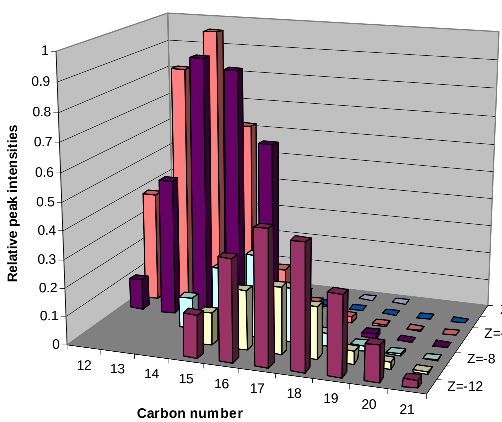
Process Water



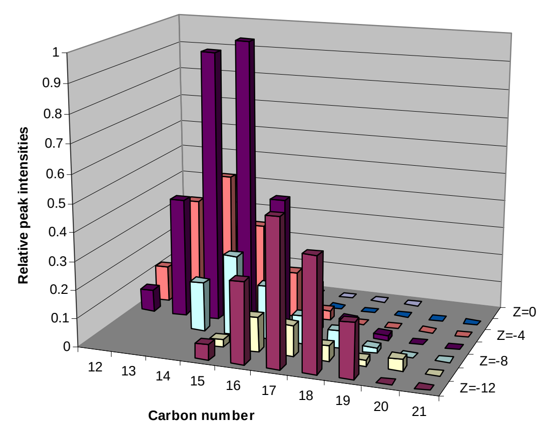
Merichem



Tailings pond water



Ground water



Research Question

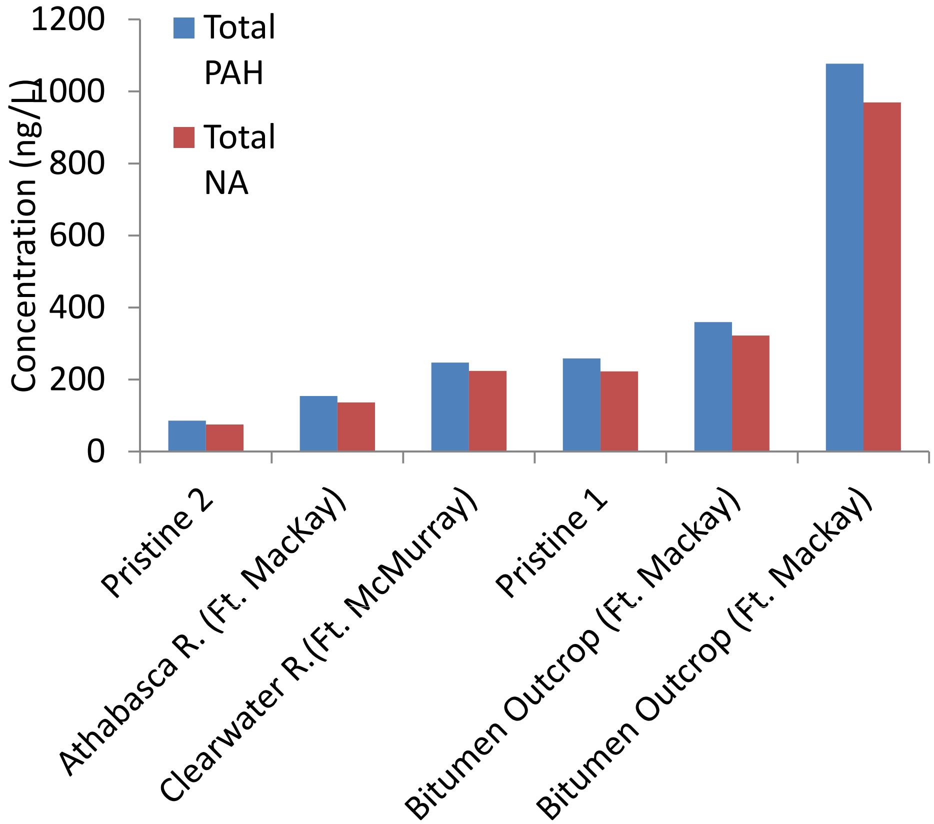
Can PAH and NA data be indicators of an ‘impacted’ site?

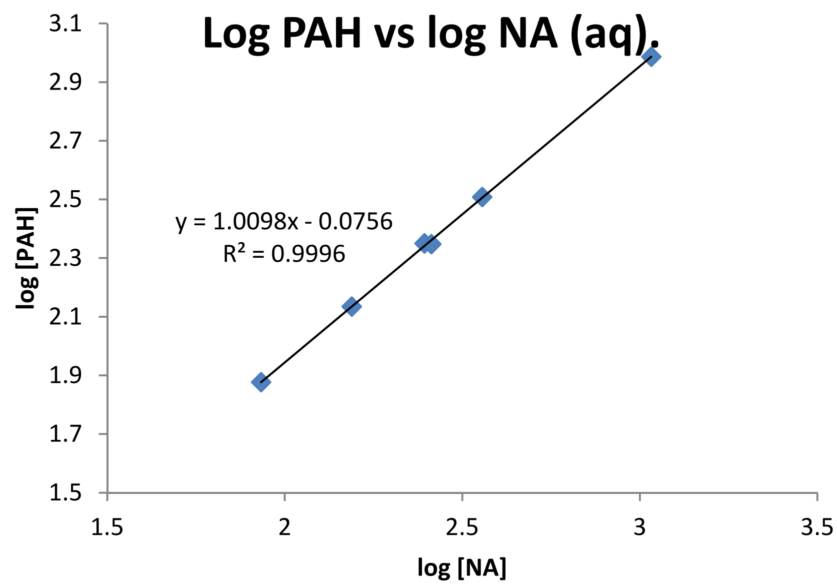
-Target class (NA vs PAH)? Total = Sum of individual targeted analytes

-Total concentration or compound/isomer group profiles?

-Matrix (solid or aqueous)?

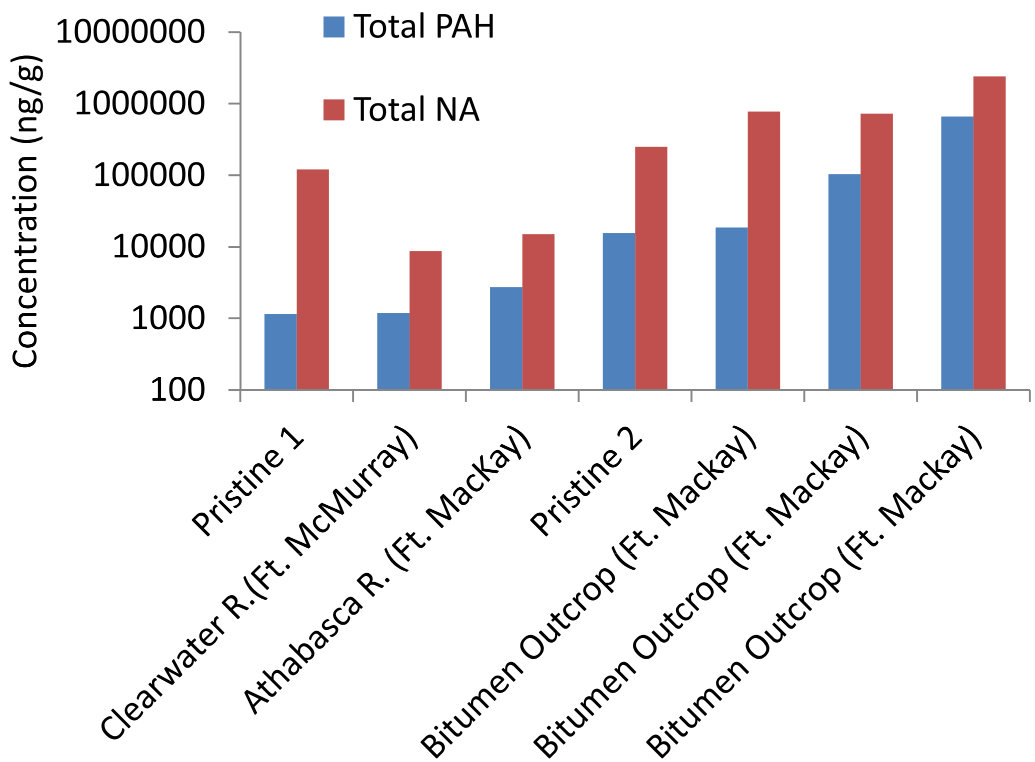
NA and PAH Aqueous Data

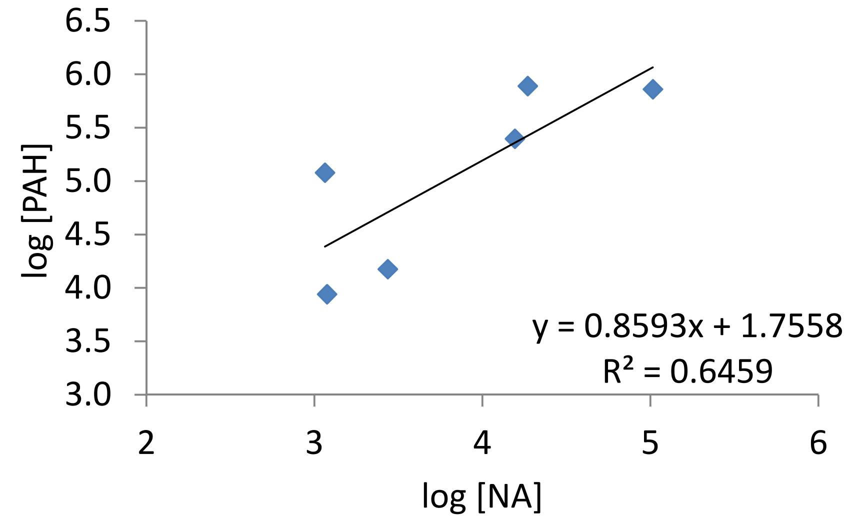




-Good relationship (R^2>0.99) between total PAH and total NA concentrations.
-While concentrations in samples near bitumen outcrops contained the highest concentrations of total PAH and NAs, 'pristine' locations had similar concentrations to those observed around oil sands locations.
-Total NA and total PAH concentrations were similar within a given site.

NA and PAH Solids Data





-Relationship between total PAH and total NA not as good in solids (R^2=0.65)
-While concentrations in solid samples near bitumen outcrops contained the highest concentrations of total PAH and NAs, 'pristine' locations had similar concentrations to those observed around oil sands locations.
-In contrast to AQ samples, in solid samples, total NA concentrations far exceeded total PAHs

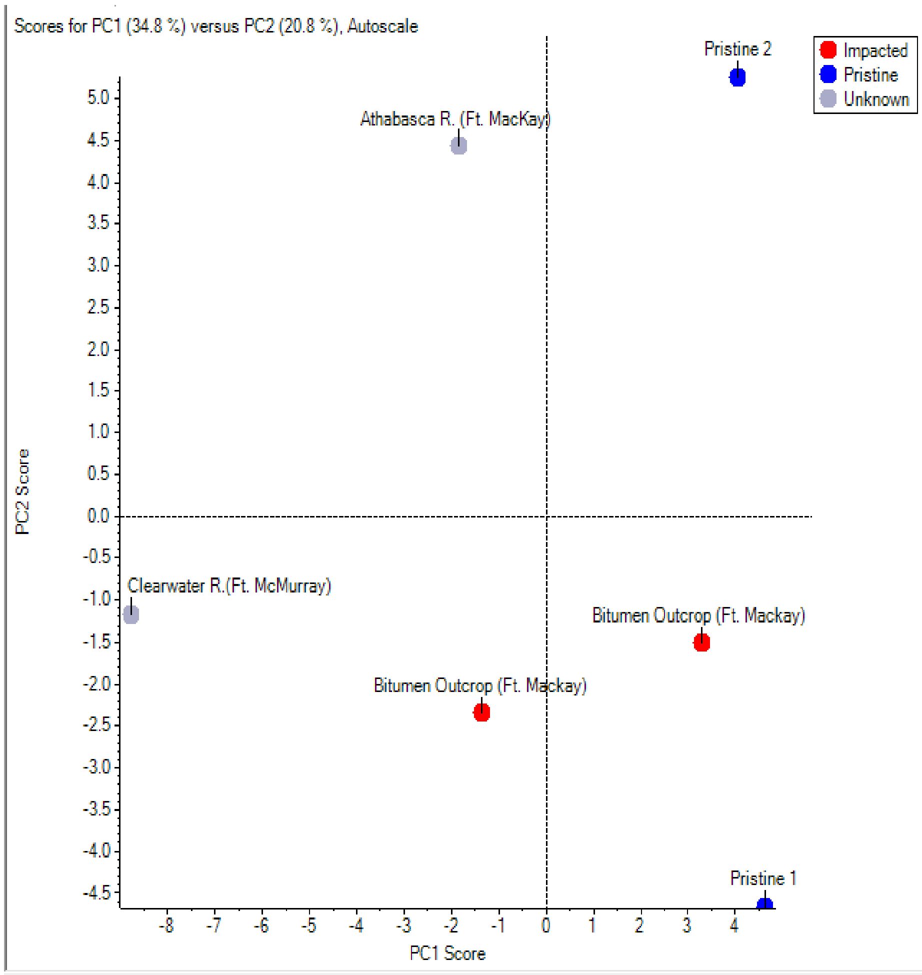
Take home message from 'total' data

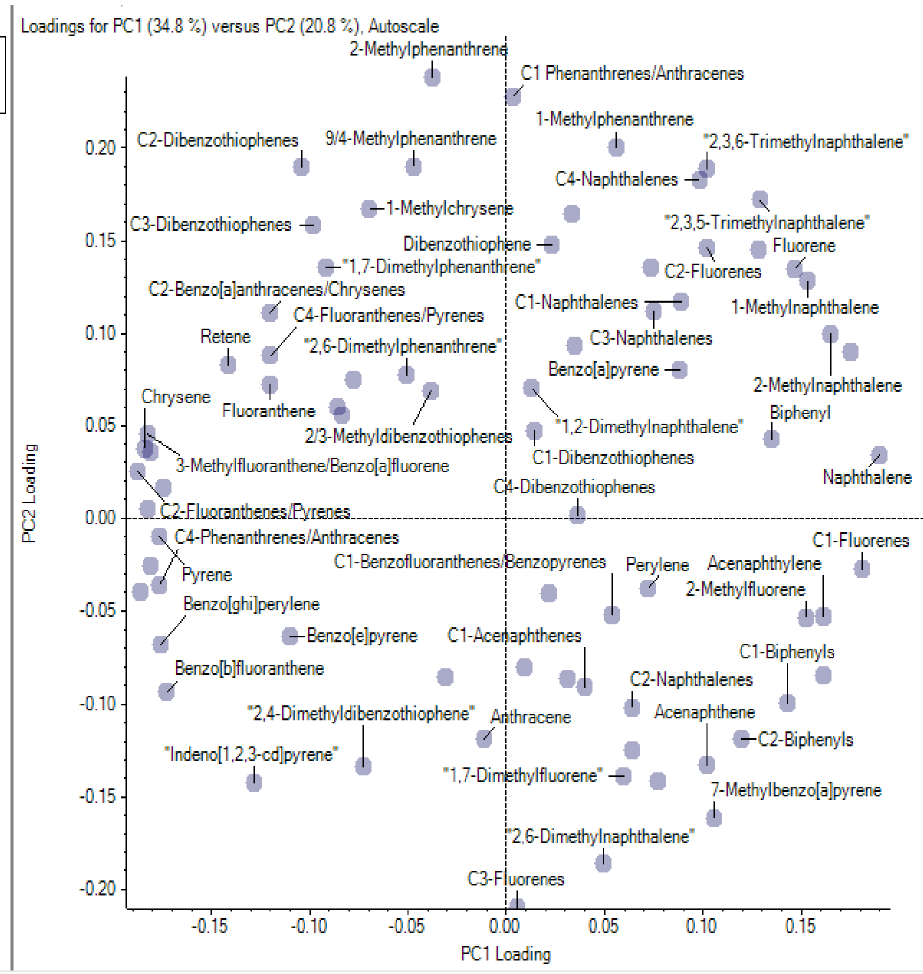
- Difficult to clearly differentiate samples collected in the immediate vicinity of bitumen outcrops, with 'pristine' areas and unknown (suspected to be impacted) samples using 'total' PAH or NA data.
- Need to look at patterns (fingerprinting) of individual PAH and NA isomer groups.

Apply PCA to the NA and PAH data
Use the same 'paired' data

- Note that samples confirmed to be impacted by industry were not included.
- First step is to see if we can differentiate a PAH or NA signature in a 'pristine' sample from an 'oil sands' signature (i.e. We're starting simply here -not trying to differentiate industry from non-industry).

Fingerprinting aqueous samples using PAHs





PAHs in AQ samples aren't great for fingerprinting in general.

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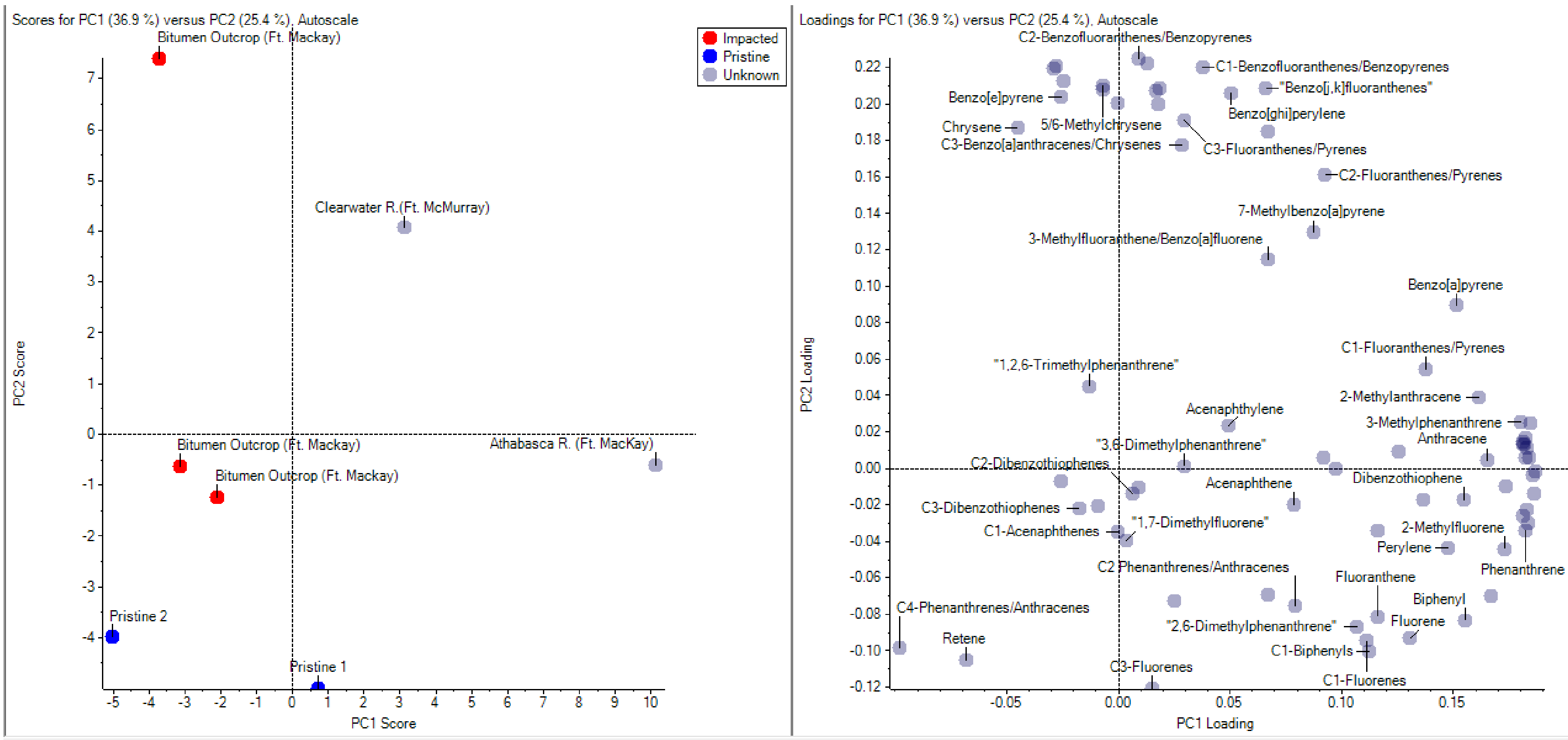
Fingerprinting solid samples using PAHs



PAH groupings also difficult to interpret from solids.

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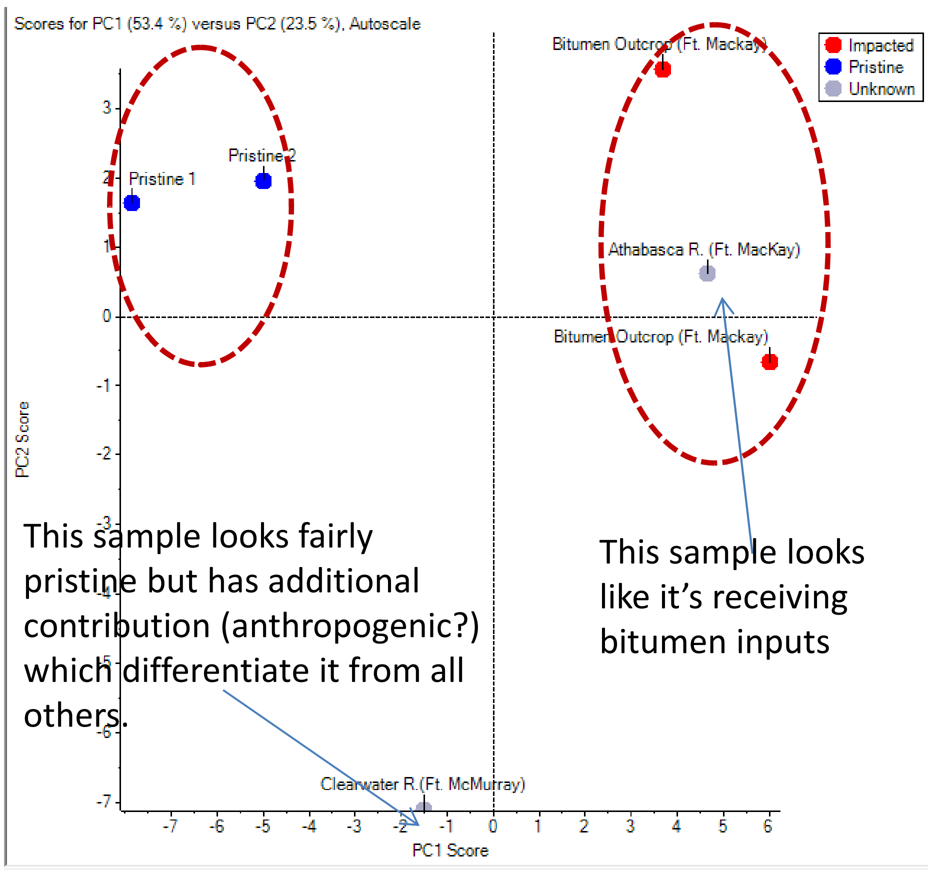
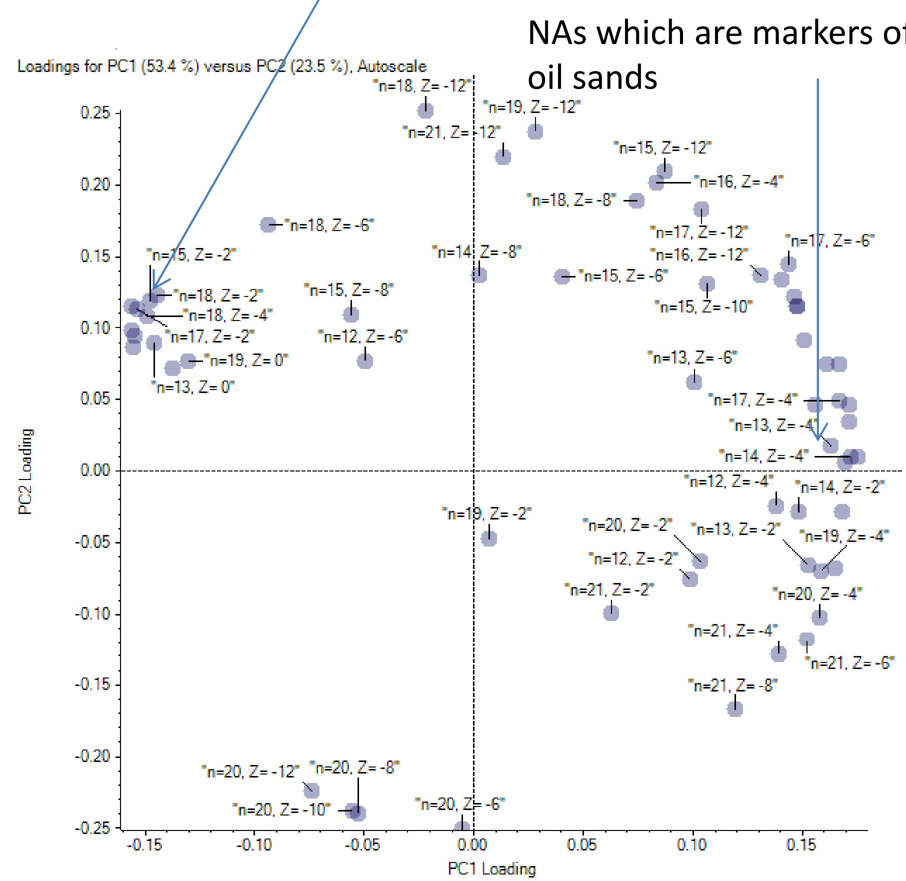
Fingerprinting aqueous samples using NAs

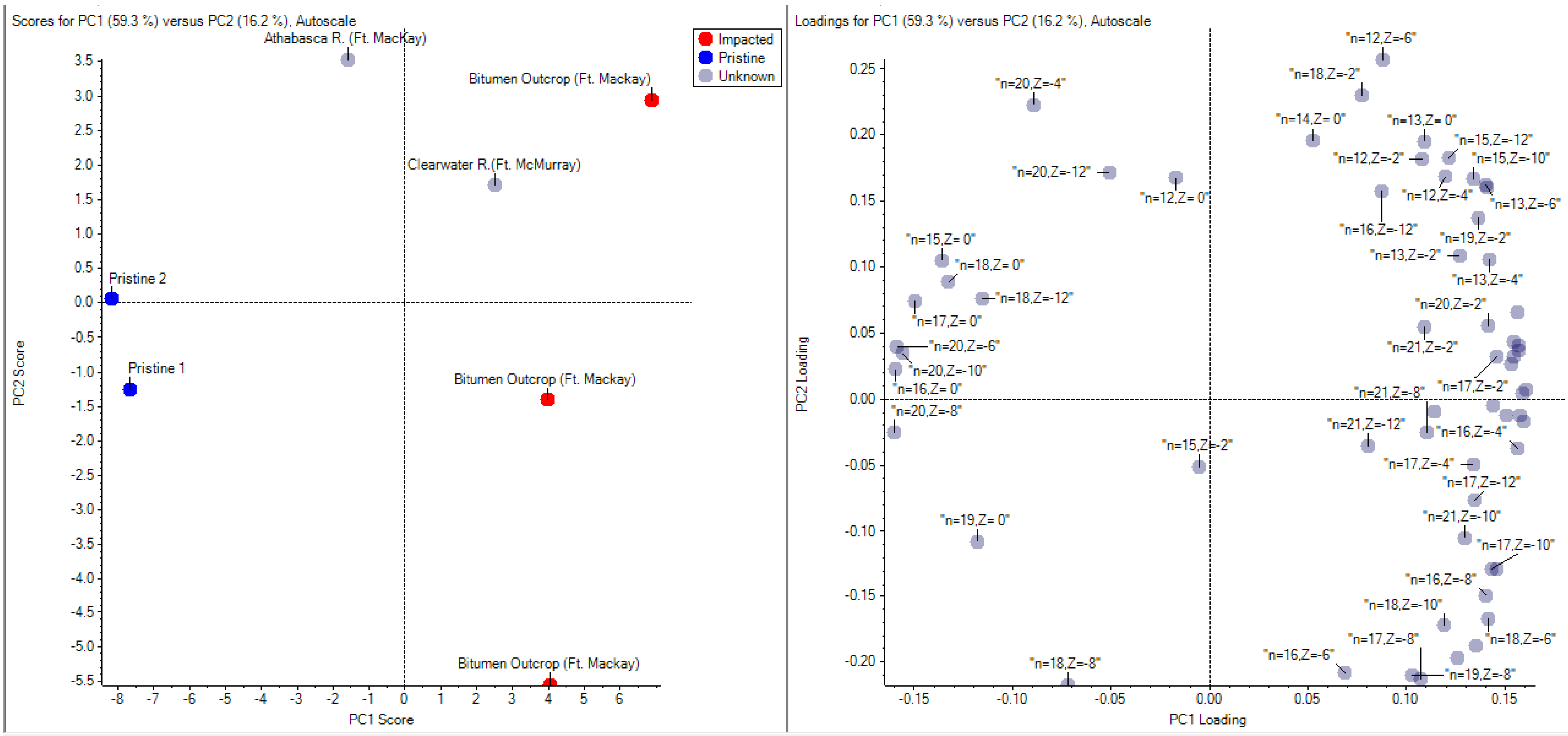
Consider groupings along PC 1

NAs which are markers of 'pristine' locations





Fingerprinting solid samples using NAs



Reasonable grouping along PC1, but lot's of spread on PC2.

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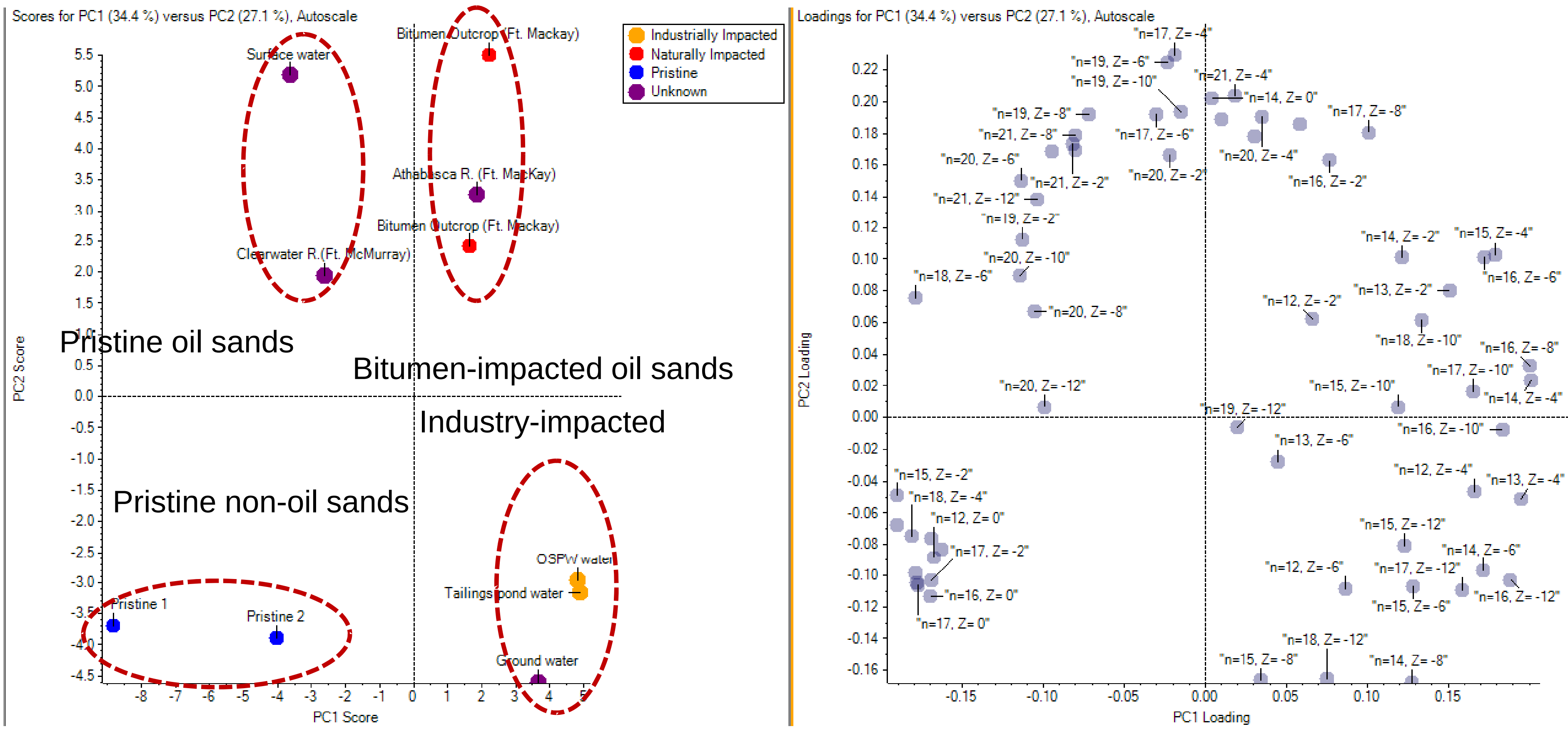
Take home message

- NA profiles in solid and aqueous samples were best for differentiating 'pristine' samples from oil sands samples.
- The next slides focus on NA profiles, with the addition of industry-impacted samples.

Inter-study fingerprinting



Conclusions

- Quantitative methods suitable for monitoring ambient levels of PAH and naphthenic Acids
- Higher concentrations of alkylated than parent PAH
- Total PAH and Total NA highly correlated in aqueous environmental samples, some correlation in sediment/soil samples.

More Conclusions

- PCA of PAH/alkylated PAH not useful for fingerprinting on small data set with only environmental samples.
- Inclusion of industry impacted PAH data may make PAH profiles more useful
- Small data set suggests that NA profiles in aqueous samples can be used to distinguish type of source
- Application to larger data set might reveal more detailed fingerprinting of sources

Acknowledgements

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