ALS Laboratory Group

ANALYTICAL CHEMISTRY & TESTING SERVICES

Environmental Division

Measurement of Hydrocarbons following Spill Events. Gathering Information Required for Human Health and Environmental Risk Assessments

Right solutions….

….Right partner

D.A. Birkholz, Research & Development

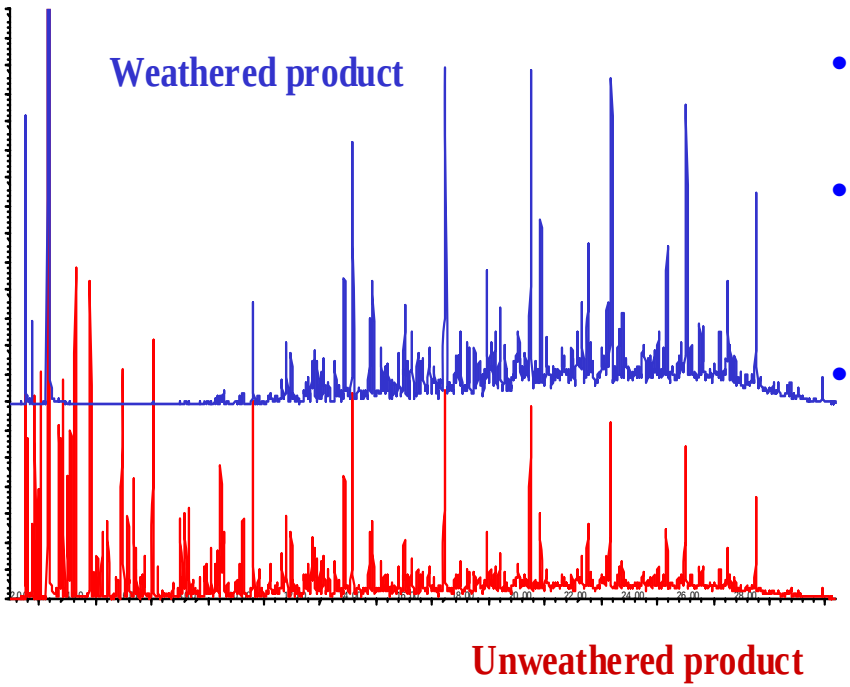
Fuel Oils

- Complex mixtures comprised of:
- n-alkanes
- iso-alkanes
- cycloalkanes
- olefins
- aromatics

- polycyclic aromatic hydrocarbons
- polycyclic aromatic nitrogen heterocyclics
- polycyclic aromatic sulfur heterocyclics
- polycyclic aromatic oxygen heterocyclics

Fate in the Aquatic Environment

Gas Chromatograms of Product and Weathered Product



- Following a spill event into the aquatic environment a number of processes occur to change or “weather” the spilled product. These events include:
- evaporation (10-40% for crude oil)
- dissolution (1-3% for crude oil)
- microbial degradation
- photolysis
- adsorption to suspended sediment
- water-in-oil emulsion, “mousse” and or tar ball formation
- Given enough time the chromatogram on the left would be reduced to a “UCM” due to resins and asphaltenes
- ref: Oil in Freshwater: Chemistry, Biology, Countermeasure Technology, Pergamon Press, 1987

Evaporation and Dissolution Properties of Selected Hydrocarbons at 25°C

Chemical	Vapor Pressure (Pa)	Solubility g/m^3	Te (h)	Td (h)
n-pentane	68400	40	0.012	2.0×10^3
n-heptane	6110	2.5	0.14	3.2×10^4
n-decane	175	0.05	4.7	1.6×10^6
n-dodecane	16	0.003	5.2 x 10	2.6×10^7
Benzene	12700	1780	0.065	4.5 x 10
p-xylene	1170	180	0.71	4.4×10^2
naphthalene	11	32	7.5 x 10	2.5×10^3
phenanthrene	0.02	1.2	4.2×10^4	6.7×10^4
anthracene	0.001	0.04	8.3×10^5	2.0×10^6
pyrene	0.001	0.14	8.3×10^5	5.7×10^5
Fuel Oil No. 5	282 (21°C)	~5.0	2.9	1.6×10^4
Fuel Oil No. 5	3519 (21°C)		0.24	
Fuel Oil No. 6	>500 (20°C)	4.5 (20°C)	< 1.7	1.8×10^4

For a 1 mm thick surface slick of volume 1 m^3 and area 1000 m^2. Te loss of half the hydrocarbons by evaporation.
Td lossof half the hydrocarbons by dissolution
Ref: D. Mackay In: Oil in Freshwater: Chemistry, Biology, Countermeasure Technology, Pergamon Press, 1987

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Relative abundances of selected compounds in untreated crude oil and in a lake microcosm

Compounds	South Louisiana crude oil	New Fork Lake – weathered oil		
		Day 7	Day 104	Day 362
Aliphatics expressed as % of $<C_{17}/\geq C_{17}$	45.5	35.4	6.3	7.2
Aromatics expressed as % of dibenzothiophenes and phenanthrenes				
Dibenzothiophene				
Methyl substituted	9.9	13.5	7.0	6.4
Phenanthrene	8.4	7.8	5.8	4.2
Methyl substituted	37.3	40.5	26.0	27.8
C_2-substituted	22.1	21.1	27.3	28.8
C_3-substituted	22.2	17.1	34.0	32.8
Naphthalene	54.5	1.4	1.2	<0.5
Methyl substituted	90.1	2.1	2.2	<0.5
C2-substituted	133.9	16.6	6.4	1.9
C3-substituted	78.6	25.1	7.7	3.4
Fluorene	4.9	1.6	0.5	<0.5
Methyl substituted	15.8	12.0	4.9	4.2
Biphenyl	28.1	1.1	1.2	<0.5
Methyl substituted	29.0	5.2	1.4	0.6

Ref: Oil in Freshwater (1987)

Percentage composition of major constituents of No. 2 fuel oil and their water-soluble fractions (WSF) 0.5 and 17 h after preparation

Product	WSF Product	Percent of total	
		0.5 h	17 h
No. 2 Fuel Oil			
Alkanes + cycloalkanes	48.0	trace	
Benzene + substituted benzenes	4.5	25.8	19.4
Naphthalene + substituted naphthalenes	32.4	73.4	79.7

Prepared by agitating 1 mL oil for 3 h with 1 L tap water (wrist action shaker) in uncapped bottles. Phases were allowed to separate for 30 min. Aqueous phase was sampled for analysis after further 0.5 h and 17 h equilibrium
Ref: Oil in Freshwater (1987)

Bioconcentration factors for selected petroleum hydrocarbons in cutthroat trout exposed for 90 days to Wyoming crude oil (520 ug/L)

Petroleum Compounds	Factor
Combined aliphatics	8X
Combined aromatics	163X
Non-alkylated compounds, tri-aromatics	18 – 163x
$(CH)_n$-mono & di-cyclic aromatics	148 – 447x

Bioconcentration of PAH by Daphnia Pulex from freshwater

Compound	Molecular weight	Ring Number	Bioconcentration factor (24 h)
Naphthalene	128	2	131 ± 10
Phenanthrene	178	3	325 ± 56
Anthracene	178	3	917 ± 48
9-methylanthracene	192	3	4583 ± 1004
Pyrene	202	4	2702 ± 1126
Benz(a)anthracene	228	4	10,109 ± 507
Perylene	252	5	7,191 ± 804

Ref: Oil in Freshwater (1987)

Chronic toxicity of PAHs

Chemical	Test Organism	Endpoint	Result
Naphthalene	Bass	7d-LC_{50}	0.68
Phenanthrene	Bass	7-d-LC_{50}	0.25
Naphthalene	Trout	27-d-LC_{50}	0.12
Phenanthrene	Trout	27-d-LC_{50}	0.03
Naphthalene	Selenastrum	Radius zone of inhibition @ 10 ppt	1.0 mm
2,6-diMe-naphthalene	Selenastrum	Radius zone of inhibition @ 10 ppt	2.7
1-Me-naphthalene	Selenastrum	Radius zone of inhibition @ 10 ppt	3.8
2,3-diMe-naphthalene	Selenastrum	Radius zone of inhibition @ 10 ppt	4.7
2,3,5-triMe-naphthalene	Selenastrum	Radius zone of inhibition @ 10 ppt	9.8
1,4-diMe-naphthalene	Selenastrum	Radius zone of inhibition @ 10 ppt	15
Phenanthrene	Selenastrum	Radius zone of inhibition @ 10 ppt	36

Ref: Oil in Freshwater (1987)

Metabolism and DNA-adducts

- Alkanes P-450 mediated oxidation to form alcohols, e.g. hexane forms 1-, 2-, and 3-hexanol.
- Unsaturated hydrocarbons P450 mediated oxidation to form glycols and alcohols via epoxidation
- PAHs P450 mediated oxidation to form alcohols, diols, phenols, quinones. For compounds having a 4 or more rings can form intermediate epoxide diol which forms DNA adducts.
- Fractionation of coal tar to separate PAHs and subsequent testing using Salmonella/microsome assay, CHEST assay and GJIC demonstrated that many PAHs are mutagenic with high potential for carcinogenicity
- ref: Reeves et al, Env. Sci. Tech., 35: 1630-1636, (2001)

Summation

- Following an oil spill the WSF is dominated by PAHs
- These are:
- relatively persistent
- demonstrate acute and chronic toxicity
- bioconcentrate
- some are mutagenic/carcinogenic and have been correlated to cause tumors and neoplasms in fish
- differences in toxicological responses from petrogenic sources can be related to the aromatic and PAH concentrations and distributions
- Many agencies recommend monitoring for PAHs following spill events because of these considerations

Agency Response

Water Quality Guidelines for Protection of Freshwater Aquatic Life

Compound	CCME Criteria ug/L	BC ug/L
Acenaphthene	5.8	60
Anthracene	0.012	1
Benz(a)anthracene	0.018	1
Benz(a)pyrene	0.015	0.1
Chrysene	NA	1
Fluoranthene	0.04	2
Fluorene	3.0	120
Naphthalene	1.1	10
Phenanthrene	0.4	3
Pyrene	0.025	0.2
Quinoline	3.4	34
Total PAHs	11	11

Partitioning sediment benchmarks

- US-EPA and States develop programs for protecting the chemical, physical and biological integrity of US waterways
- Auspices of Clean Water Act
- Benchmarks for 65 toxic pollutants or toxic pollutant categories
- Toxic contaminants in bottom sediments of lakes, rivers, wetlands and coastal waters create the potential for continued environmental degradation even where water column contaminant levels meet applicable water quality standards
- Contaminated sediments can lead to water quality impacts, even when direct discharges to the receiving water have ceased.

US EPA Benchmark values

- Risk from sediment PAHs to benthic organisms
- based on the number of PAH toxic units (TU) freely dissolved in the sediment pore water
- all PAHs assumed to have the same toxicity (on a molar basis) - narcosis model
- differ only in their tendency to partition from sediment to pore water
- For sediment PAHs, K_{OC}, K_{lipid}, and K_{OW} are used to calculate the concentration of each PAH that represents one toxic unit

Ref: Procedures for the Derivation of Equilibrium Partitioning Sediment Benchmarks (ESBs) for the Protection of Benthic Organisms: PAH mixtures (2003). EPA-600-R-02-013

Polycyclic aromatic hydrocarbon (PAH) toxic units and detection limits

Compound	Conc for one toxic unit (ug/g OC)	Target detection limit (ug/g sediment)	Method detection limit (ug/g sediment)
Naphthalene	385	0.11	0.001
Methylnaphthalenes	444	0.13	0.001
C2-naphthalenes	510	0.15	0.005
C3-naphthalenes	581	0.17	0.01
C4-naphthalenes	657	0.19	0.01
Acenaphthylene	452	0.13	0.001
Acenaphthene	491	0.14	0.001
Fluorene	538	0.16	0.001
C1-fluorenes	611	0.18	0.005
C2-fluorenes	686	0.20	0.01
C3-fluorenes	769	0.23	0.03
Phenanthrene	596	0.18	0.001
Anthracene	594	0.17	0.001
C1-phenanthrenes/anthracenes	670	0.20	0.005
C2-phenanthrenes/anthracenes	746	0.22	0.01
C3-phenanthrenes/anthracenes	829	0.24	0.02
C4-phenanthrenes/anthracenes	913	0.27	0.03
Fluoranthene	707	0.21	0.001

Compound	Conc for one toxic unit (ug/g OC)	Target detection limit (ug/g sediment)	Method detection limit (ug/g sediment)
Pyrene	697	0.21	0.001
C1-fluoranthenes/pyrenes	770	0.23	0.005
Benz(a)anthracene	841	0.25	0.002
Chrysene	844	0.25	0.002
C1-benz(a)anthracenes/chrysenes	929	0.27	0.01
C2-benz(a)anthracenes/chrysenes	1008	0.30	0.03
C3-benz(a)anthracenes/chrysenes	1112	0.33	0.05
C4-benz(a)anthracenes/chrysenes	1214	0.36	0.08
Benzo(b+k)fluoranthene	980	0.29	0.002
Benzo(e)pyrene	967	0.28	0.002
Benzo(a)pyrene	965	0.28	0.002
Perylene	967	0.28	0.002
Indeno(1,2,3-cd)pyrene	1115	0.33	0.002
Dibenz(a,h)anthracene	1123	0.33	0.002
Benzo(ghi)perylene	1094	0.32	0.002

Example calculation of ESBs

- **Concentration of naphthalene in sediment = 0.0894 ug/g d.w.**
- **TOC of sediment = 0.81%, f_{OC} = 0.0081**
- **Concentration of naphthalene on OC basis = 0.0894/0.0081 = 11 ug/gOC = C_{OC} (ug/g_{OC})**
- **Conc for one toxic unit of naphthalene (ug/g OC) = 385 = C_{OC},PAHi,FCVi (ug/g_{OC})**
- **$ESBTU_{FCVi}$ = 11 ug/gOC naphthalene / 385 ug/g OC = 0.0287 toxic units**

Example calculations of ESBs for PAH mixtures: sediment (TOC=0.81%; foc=0.0081)

PAH	COC, PAHi, ug/gOC	COC,PAHi, Max ug/gOC	Conc ug/g dw	COC ug/gOC	ESBTU
Naphthalene	385	61700	0.0894	11	0.0287
Acenaphthylene	452	24000	0.0348	4.29	0.0095
Acenaphthene	491	33400	0	0	0
Fluorene	538	26000	0.0722	8.91	0.0166
Anthracene	594	1300	0.628	77.6	0.1306
Phenanthrene	596	34300	0.139	17.1	0.0287
Pyrene	697	9090	0.171	21.1	0.0303
Fluoranthene	707	23870	0.0806	9.96	0.0141
Benz(a)anthracene	841	4153	0.0709	8.75	0.0104
Chrysene	844	826	0.157	19.4	0.023
Benzo(a)pyrene	965	3840	0.164	20.3	0.021
Benzo(b)fluoranthene	979	2169	0.139	17.2	0.0175
Benzo(k)fluoranthene	981	1220	0.139	17.2	0.0175
ΣESBTU					**0.3479**

Relative distribution of $\Sigma ESBTU_{FCV,TOT}$ to $\Sigma ESBTU_{FCV,13}$ and $\Sigma ESBTU_{FCV,23}$ for the combine EMPA dataset (N=488)

Percentile	$\Sigma ESBTU_{FCV,TOT}/\Sigma ESBTU_{FCV,13}$	$\Sigma ESBTU_{FCV,TOT}/\Sigma ESBTU_{FCV,23}$
50	2.75	1.64
80	6.78	2.8
90	8.45	3.37
95	11.5	4.14
99	16.9	6.57

Total PAHs required for deriving the ESB for PAH mixtures is defined as the sum of the $ESBTU_{FCV}$ values for a minimum of 34 PAHs (18 parents and 16 alkylated homologues).

The use of fewer than 34 PAHs may greatly underestimate the total toxicological contribution of the PAH mixtures

The problem with monitoring for parent PAHs only

The toxicological contribution of all 34 PAHs must be considered if the ESB is to be protective of benthic organisms, some assumption must be made regarding the contribution of the unmeasured PAHs

For a confidence level of 95%, the uncertainty factor is 11.5

If we multiply the $\Sigma ESBTU_{FCV,13}$ (0.348) by 11.5 we get $\Sigma ESBTU_{FCV,34}$ of 4.00

Since this value is greater than one, it suggests the potential for adverse effects from PAHs.

Measuring Parent PAHS

The application of uncertainty factors is dangerous. The uncertainty factor of 11.5 was applied in order to relate the data for 13 PAHs to an estimated ΣESBTU for 34 PAHs.

If the value for 50% confidence was selected (2.75), the estimated $\Sigma ESBTU_{FCV,34}$ drops to 0.957 which is much lower than the value predicted for the 95% confidence interval.

This difference illustrates the importance of measuring all 34 PAH compounds in order to eliminate unnecessary uncertainty in applying the PAH ESB

Do Sediment Benchmarks Work?

- $ESBTU_{FCV,34}$ was determined for 34 PAHs for a sediment. The value was 4.4 which exceeds the ESB ($\Sigma ESBTU_{FCV} > 1.0$).
- Examination of the data suggested it was contaminated with primarily petrogenic PAHs.
- The ratio $\Sigma ESBTU_{FCV,13}$ (which contains no alkylated PAHs) to $\Sigma ESBTU_{FCV,34}$ for the 34 PAHs is low, approximately 0.1
- Chemical analysis of the interstitial water for the 34 PAHs indicated in contained 5.6 TU
- Ten day toxicity showed 64% mortality of *R. abronius*
- Spiked sediment at $\Sigma ESBTU_{FCV,34} = 3.68$ also demonstrated similar toxicity with *R. abronius*
- This suggests the narcosis-based ESB is appropriate to the sediment

	ug/kg dw	ug/g dw	COC (ug/gOC)	COC,PAHi,FCVi	ESBTU	
	Freshwater		assume TOC = 0.81%			
Acenaphthene	48	0.048	5.93	491	0.012	
Acenaphthylene	67	0.067	8.27	452	0.018	
Anthracene	150	0.15	18.52	594	0.031	
Fluorene	83	0.083	10.25	538	0.019	
Naphthalene	210	0.21	25.93	385	0.067	
2-methylnaphthalene	110	0.11	13.58	444	0.031	
Phenanthrene	310	0.31	38.27	596	0.064	
benz(a)anthracene	210	0.21	25.93	841	0.031	
Benzo(a)pyrene	410	0.41	50.62	967	0.052	
Chrysene	460	0.46	56.79	844	0.067	
dibenz(a,h)anthracene	71	0.071	8.77	1123	0.008	
Fluoranthene	1230	1.23	151.85	707	0.215	
pyrene	460	0.46	56.79	697	0.081	
				ESBTU-FCV13	**0.697**	
				95% confid level	11.5 x 0.697 = 8.01	
				50% confid level	2.75 x 0.697 = 1.92	
Generic Sediment Quality Criteria (2002) BC MWLAP P3 Draft						

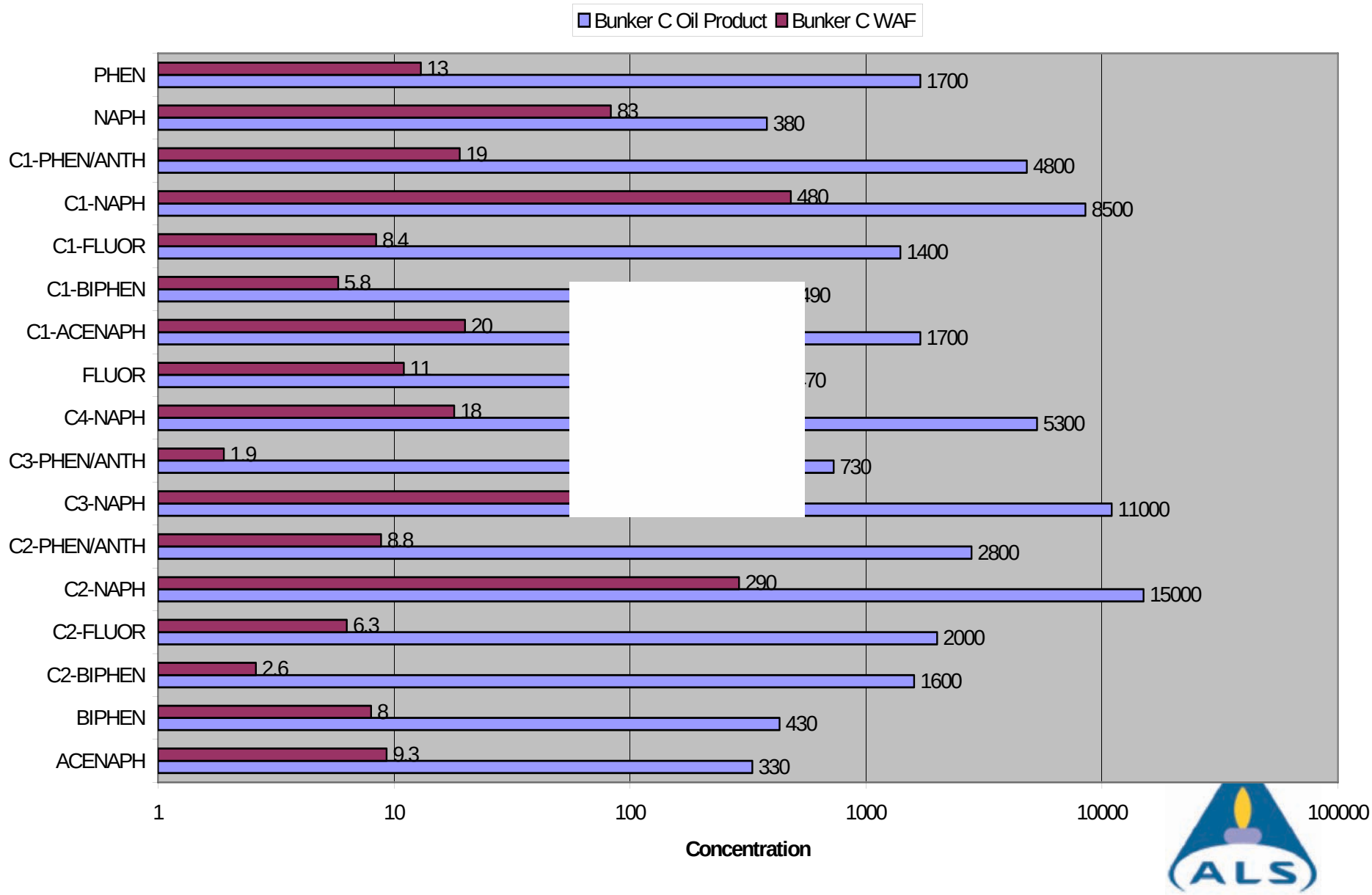
Application of model to waterfowl and piscivorous mammals

- An equilibrium partitioning-based bioaccumulation model is used to estimate total PAH concentrations in aquatic organisms consumed by wildlife
- Starting point is sediment PAH data on dry weight basis normalized to carbon content.
- Monte Carlo simulation
- Assessment endpoints survival and maintenance of the benthic invertebrate community, and survival, growth, and reproduction of wildlife.
- HQ = [exposure]/toxicity reference values
- TRVs obtained from studies on mallards and mink
- HQ = (mg PAH/kg prey)/ (TRV mg PAH/kg diet)

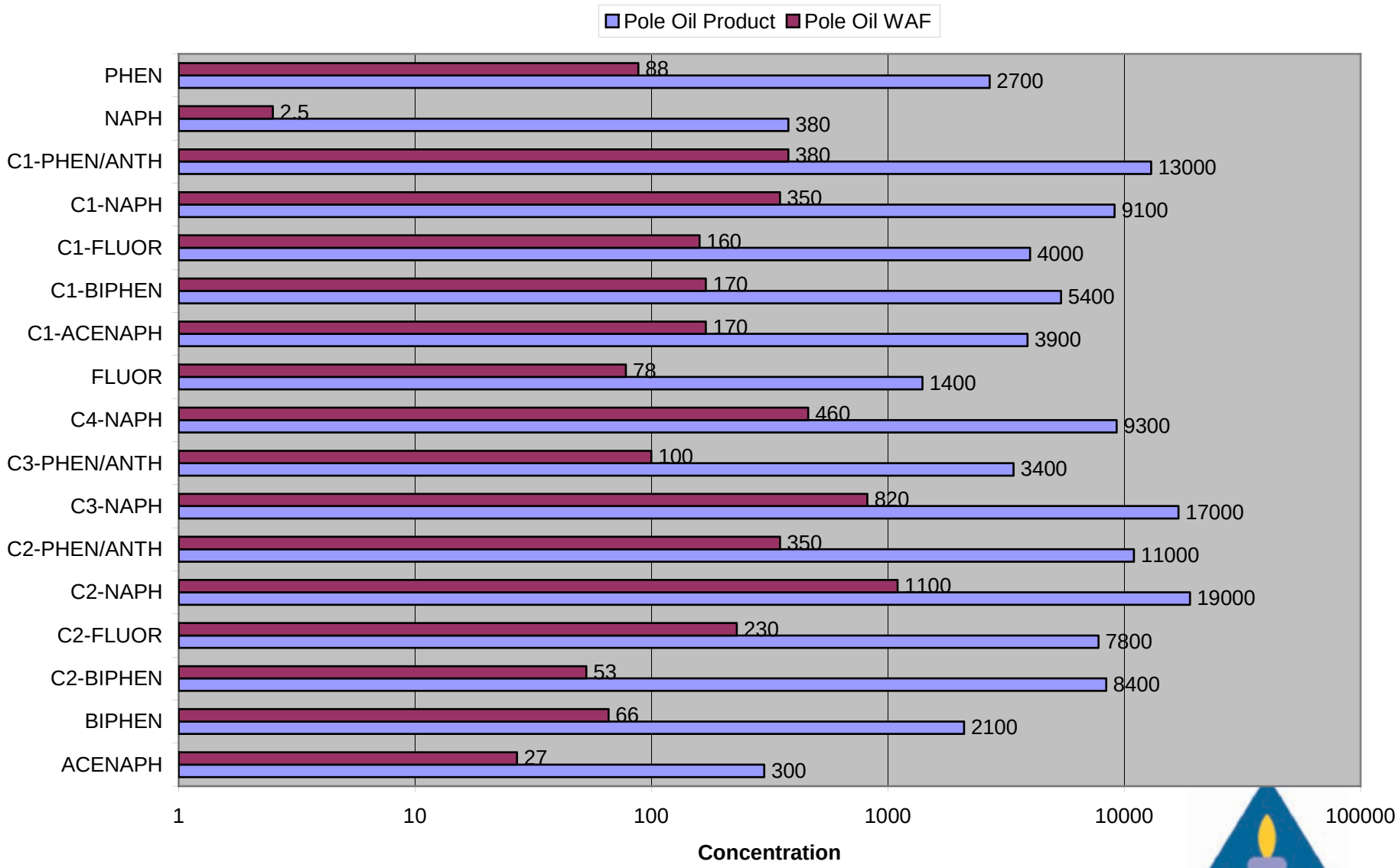
Exposure and risks of tPAH to benthic invertebrates and wildlife exposed at a Wyoming refinery pond

Receptor	Risk analysis	Parent PAHs	Estimated tPAH	Measured tPAH
			2.75 x FCV_{13}	
Benthic invertebrates	Sediment tPAH (mg/kg sediment)	4.7	13.0	44.8
	HQ range	0.2 – 1.5	0.7 – 4.1	2.3 – 1.4
	Probablity of risk	8%	59%	100%
Wildlife mink	Prey tPAH	0.05 – 5.3	0.1 – 13	0.5 - 47
	HQ range	0.002 – 1.8	0.007 – 4.0	0.02 - 16
	Probability of risk	1%	8%	44%
Waterfowl	Aquatic Plant tPAH (mg/kg plant)	2.3	6.2	26.8
	HQ range	0.1 – 1.1	0.2 – 3.1	1.3 - 13
	Probablity of risk	1.4%	23%	100%
Barron and Holder (2003): Human and Ecological Risk Assessment, 9: 1533-1545				

Comparison of Bunker C Product to WAF



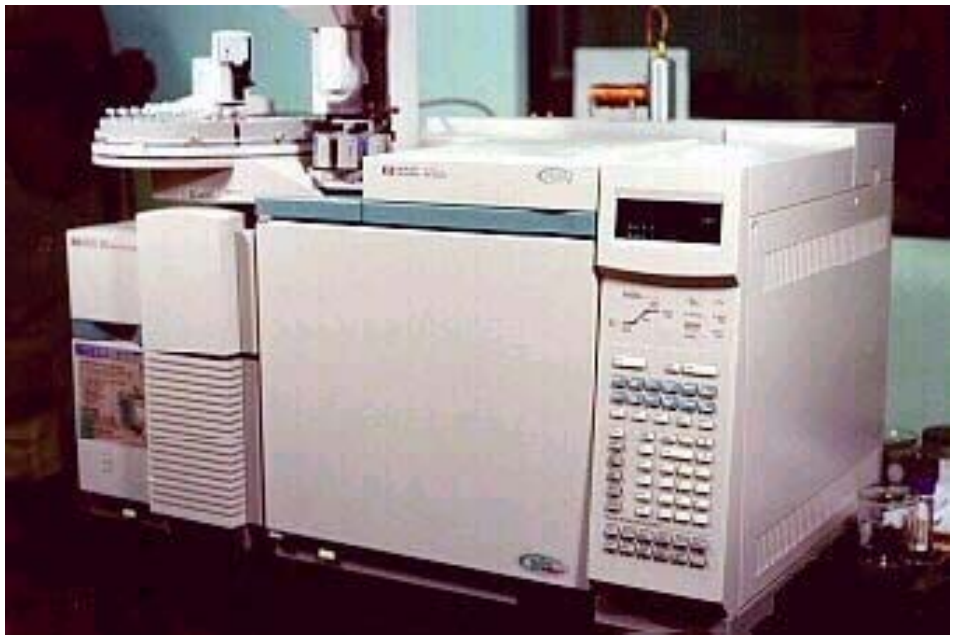
Pole Oil Product and WAF



EPA PAHs/Total PAHs

- Bunker C = 5.0%
- WAF Bunker C = 10.8%
- Pole Oil = 4.1%
- WAF Pole Oil = 4.3%

GC/MS Analysis of PAH Alkyl-homologues

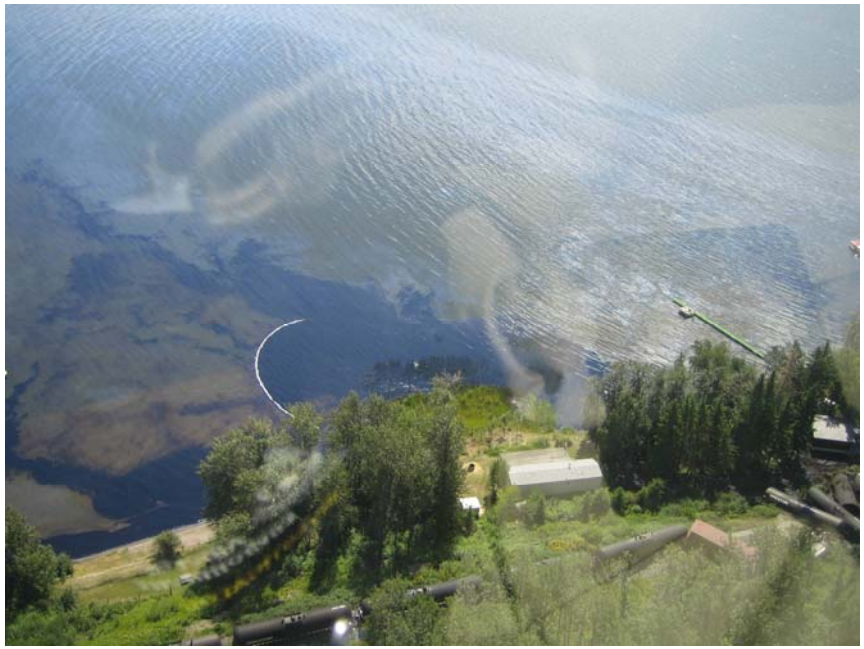


- Not straight forward
- Response factors for parent and alkyl homologues are different
- Obtaining all the standards necessary is a challenge and expensive
- Window setting for the homologues is a challenge
- Overlap of PASH and Alk-PAH
- Overlap of deuterated internal standards with Alk-PAH

GC/MS Response Factors Parent PAH vs Alkylated Homologue

Compound	GC/MS RRF vs parent
Naphthalene	1.00
C1-naphthalene	0.54
C2-naphthalene	0.34
C3-naphthalene	0.31
C4-naphthalene	0.25
Fluorene	1.00
C1-fluorene	0.49
C2-fluorene	0.40
C3-fluorene	0.40
Phenanthrene/anthracene	1.00
C1-phenanthrene/anthracene	0.40
C2-phenanthrene/anthracene	0.16
C3-phenanthrene/anthracene	0.15
C4-phenanthrene/anthracene	0.14
Hawthorne et al (2006) Env Tox & Chem 25: 287-296	

Conclusions



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- differences in toxicological responses from petrogenic sources can be related to the aromatic and PAH concentrations and distributions
- Many agencies recommend monitoring for PAHs following spill events because of these considerations

Conclusions

- Toxicology and various models (e.g. narcosis model) suggest that both alkylated and parent PAHs should be measured
- Supported by Monte Carlo simulations for wildlife
- Application of correction factors to EPA priority pollutant or CCME PAHs does not work – depending on HC distribution can underestimate or overestimate risk.
- Analysis for both parent and alkyl-homologues are analytically challenging and not straight forward (i.e. no SW-846 method).

Conclusions

- Recognizing the importance of adequate data in risk analyses Golder and ALS generated parent and alk-PAH data for all samples analyzed
- Because of the timely need for data in site decision making many analyses were performed within 12 h of receipt of samples