SoBRA

The Chemistry of PAHs

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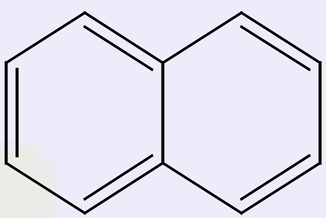
Outline

- What are PAHs
- Sources
- Which PAHs & Why
- Phys-chem Properties
- Composition in contaminated land
- Conclusions/recommendations

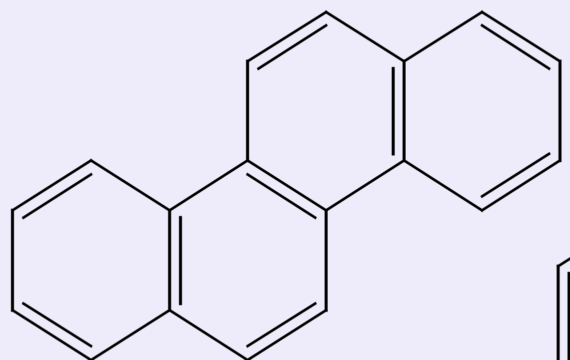
PAHs

- Polycyclic Aromatic Hydrocarbons (several hundred of ‘em)
- C + H only
- 2 or more fused aromatic rings (sometimes starts at 3!)
- Non-substituted PAHs are planar
- PAHs occur as complex mixtures **!**

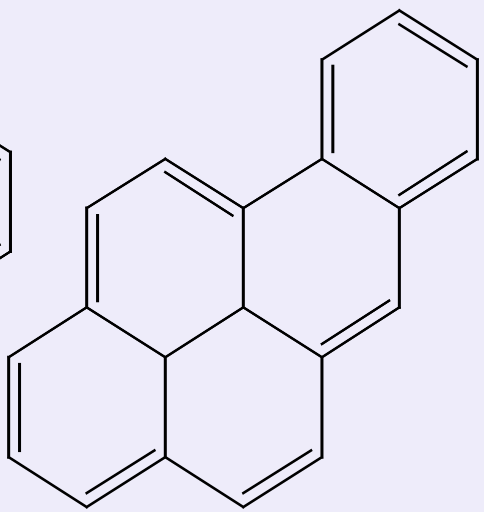
PAHs



Naphthalene



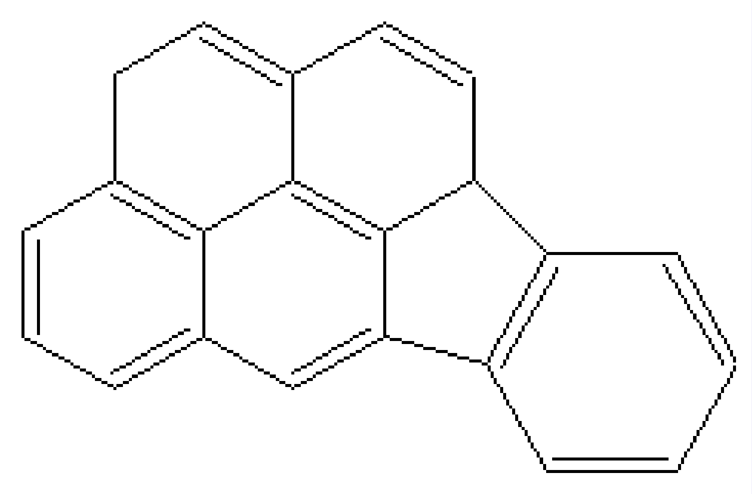
Chrysene



Benzo[a]pyrene

	Naphthalene	Chrysene	Benzo[a]pyrene
MW:	128	228	252
EC no.	11.7	27.4	31.3

PAHs



Indeno[1,2,3-cd]pyrene

MW = 276
EC# ~ 34

Definition of PAHs

- 'Polynuclear aromatic hydrocarbons' have more than two fused benzene rings (TPHCWG, 1998)
- ...two or more benzene rings fused together or to other hydrocarbon rings (HPA, 2008)
- two or more fused benzenoid rings (CCME, 2010)

➢ Naphthalene generally included……. but is considered as a specific priority contaminant

Sources of PAHs

- Incomplete combustion or pyrolysis of any organic matter
  (largely anthropogenic with natural contribution)

- Fossil fuels such as coal, crude oil, tar deposits (primarily anthropogenic)

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Sources of PAHs in ‘contaminated land’

- Atmospheric deposition of combustion particles (‘background concentration’)
- Ash fill and clinker from industrial processing (common in made ground)
- Coal tar from gas works (*fossil fuel and combustion source)
- Fuel oil (diesel, heating oil, lube oil*)
- Asphalt (crude oil derived)
- Industry processing oil and coal tar derivatives

o PAH composition/profile varies with source

Petroleum Source

PAH	% Composition of Fuel (ratio to BaP)		
	Diesel	Heating Oil	Lube Oil
Chrysene	4.5 x10^{-5} (0.2)	6.9 x10^{-2} (16)	3.5 x10^{-3} (2.1)
Benzo(a)pyrene	2.2 x10^{-4}	4.4 x10^{-3}	1.7 x10^{-3}
Benzo(a)anthracene	9.6 x10^{-5} (0.44)	5.5 x10^{-2} (12.5)	6.3 x10^{-3} (3.7)
Benzo(b)fluoranthene	3.1 x10^{-5}* (0.14)	4.4 x10^{-2}* (10)	1.5 x10^{-3} (0.88)
Benzo(j)fluoranthene			
Benzo(k)fluoranthene	3.1 x10^{-5}* (0.14)	4.4 x10^{-2}* (10)	
Dibenzo(ah)anthracene			
Benzo(g,h,i)perylene	1.2 x10^{-5} (0.05)		2.8 x10^{-3} (1.6)
Indeno[1,2,3-cd]pyrene	1.6 x10^{-5} (0.05)	1.0 x10^{-2} (2.3)	4.0 x10^{-3} (2.4)
Total	0.36 (PAHs)	34 ('total aromatics')	22 ('total aromatics')
%BaP (rel to G9)	**52**	**2.4**	**10**

TPHCWG (1998) Volume 2:

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Combustion Source (residue)

PAH	Composition (ratio to BaP)			
	Coal Tar 1 (mg/kg, Culp et al)	Coal Tar 2 (mg/kg, Culp et al)	Combustion Ash 1 (% of PAHs, Joa et al)	Combustion Ash 2 (% of PAHs, Joa et al)
Chrysene	2379 (1.3)	2960 (1.1)	8 (0.9)	10 (1.0)
Benzo(a)pyrene	1837	2760	9	10
Benzo(a)anthracene	2374 (1.3)	3340 (1.2)	10 (1.1)	8 (0.8)
Benzo(b)fluoranthene	2097 (1.1)	2890 (1.1)	10* (1.1)	8* (0.8)
Benzo(j)fluoranthene				
Benzo(k)fluoranthene	699 (0.4)	1010 (0.4)	10* (1.1)	8* (0.8)
Dibenzo(ah)anthracene	267 (0.15)	370 (0.13)		
In[1,2,3-cd]pyrene	1353 (0.74)	1990 (0.72)	8 (0.89)	8 (0.80)
Total PAHs				
%BaP (G8)	**17**	**18**	**20**	**23**

Selection of PAHs for risk assessment

- Considerations:

➢ Analytical methodology (what can the labs offer)
➢ Toxicology (focus on genotoxic PAHs)
➢ Occurrence in soil/contaminated land
➢ Fate and behaviour (relevant exposure pathways)

PAH Selection

PAH	USEPA 16	RIVM 10	DEPA	CCME	UK Haz Waste Regs	CLEA ?
Naphthalene	✓	✓		✓		✓
Acenaphthylene	✓					
Acenaphthene	✓					
Fluorene	✓					
Phenanthrene	✓	✓				
Anthracene	✓	✓		✓		
Fluoranthene	✓	✓	✓	✓		✓
Pyrene	✓					✓
Benzo(a)anthracene	✓	✓		✓	✓	✓
Chrysene	✓	✓			✓	✓
Benzo(b)fluoranthene	✓		✓	✓	✓	✓
Benzo(k)fluoranthene	✓	✓	✓	✓	✓	✓
Benzo(a)pyrene	✓	✓	✓	✓	✓	✓
Indeno(1,2,3-cd)pyrene	✓	✓	✓	✓	✓	✓
Dibenzo(a,h)anthracene	✓		✓	✓	✓	✓
Benzo(g,h,i)perylene	✓	✓		✓		✓
Benzo(j)fluoranthene				✓	✓	**Prob**

Rationale for PAH Selection

- USEPA 16 (Keith & Telliard, 1979)
- All compounds specifically named in the original Toxic Pollutant List were automatically included in the Priority Pollutant List.
- The availability of chemical standards was also considered mandatory, i.e. each representative compound had to be listed in at least one chemical supply catalogue.
- Frequency of occurrence of the representative compound in water was an important consideration
- Chemical production data were used as a guide for prioritising choices when they were available.
- Questionable relevance to PAH composition in contaminated land or toxicology

Additional PAHs to consider

- Not included in USEPA 16 & current UK risk assessment
- Benzo(j)fluoranthene (co-elutes with B(b)F)
  - known genotoxin & commonly occurring
- Benzo(e)pyrene
  - potential genotoxic carcinogen?
- Dibenzo(a,l)anthracene
  - more potent genotoxic carcinogen than BaP

- Heterocyclic (N- and S-), esp. in asphalt/tar
- Branched/alkyl-substituted PAHs (especially in diesel) - captured by PHC aromatic fractions

PHC Fractions

- PHC fraction approach considers non-carcinogenic endpoints
- Majority of EPA16 PAHs are Aromatic fraction EC>21-35

PHC Aromatic Fractions	**PAHs included in fraction**
Aro EC>10-12	NA
Aro EC>12-16	AC, ACL
Aro EC>16-21	AN, FL,PHE, PY(4R)
Aro EC>21-35	BaA, BaP, BeP, BbF, BjF, BkF, DBahA, FA, BghiP & IP

Phys-Chem Properties

PAH	Rings	MW	Sol (mg/L)	VP (Pa)	K_{aw}	Log K_{ow}
Naphth	2	128	19	2.3	6.6×10^{-3}	3.3
Phen	3	178	1.1	0.11	1.3×10^{-3}	4.4
Pyrene	4	202	0.13	1.5×10^{-5}	5.6×10^{-5}	5.1
Chrysene	4	228	0.002	4.5×10^{-8}	3.2×10^{-6}	5.7
BaP	5	252	0.0038	2×10^{-8}	1.8×10^{-6}	6.2
In(1,2,3-cd)py	6	276	2×10^{-4}	2×10^{-9}	2×10^{-6}	6.0

- EA(2009) Compilation of Data for Priority Organic Pollutants for Derivation of Soil Guideline Values. Science Report SC050021/SR7

Phys-Chem Properties

- With increasing MW:
  - Decreasing sol, VP & Kaw
  - Increasing hydrophobicity (Kow, Koc)
- Cut-off point within 4 ring PAHs between low and high MW = 228 (RIVM, 1995)
- All genotoxic PAHs are ≥4 ring AND MW ≥228

➢ Similar phys-chem props for all genotoxic PAHs (hydrophobic, non-volatile and strongly bound to soil OM)
  - implicit in a marker approach?

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Env Fate & Exposure Pathways

Ring Class	Environmental Summary	Most Significant Pathways
2 rings (Naphthalene)	Significant aqueous solubility, vapour phase in atmosphere, relatively mobile in soil & higher bioavailability (plants/microbes)	- Vapour inhalation - Soil/dust ingestion - Dermal exposure - Plant uptake
3 ring PAHs		
4 ring PAHs	Low solubility, vapour phase **&** particulate in atmosphere, relatively immobile in soil	- Soil/dust ingestion - Dermal exposure - Plant uptake?
≥5 ring PAHs	Insoluble, non-volatile, associated with particulates in atmosphere and very strongly sorbed to soil	- Soil/dust ingestion - Dermal exposure - Dust inhalation

- Plant uptake (huge variability in measured data)
  - CLEA modelling (LQM GACs) indicates % contribution ranging from 78% for ACL (3R) to 2.2% for BghiP (6R)

Soil half-lives (aerobic)

PAH	Rings	Mackay et al (mean half-life)	TR1 EA (2003)
Naphth	2	~2 months	<1-108 d
Phen	3	~8 months	10-35 d
Pyrene	4	~24 months	48-2000 d
Chrysene	4	~24 months	20-1400 d
BaP	5	~24 months	57-530 d
In(1,2,3-cd)py	6	-	290 d

- Soil half-lives increase with MW from weeks to months to years
- Leads to enrichment with higher MW PAHs (POPs)

PAH Composition of 'contaminated soil'

- Dependent on source and fate & behaviour (influenced by phys-chem and soil environment)
- %BaP in relation to gentoxic PAHs appears relatively constant

		» BaP/G8-9 ratio:
1.	Ashy/tarmac fill	15%
2.	PFS	12-17%
3.	Combustion	15-18%
4.	Landfill (ash MG)	13-18%
5.	Gasworks	7-17%
6.	Rural (SHS)	5-11% (av. 7.5%)

Conclusions

- Selection of PAHs for analysis and risk assessment should depend on both phys-chem & tox
- Differing phys-chem properties and environmental behaviour across PAH congeners but high MW genotoxic PAHs all have similar properties

➢ BaP appears suitable as marker for Genotoxic 8/9

- not for lower MW, non-genotoxic PAHs
- & may not be appropriate for fresh fuel/oil spills (some variance in PAH profile with source)

Conclusions

- Need to consider approach for 3 & 4 ring PAHs (non-carcinogens)

  - marker compounds; or

  - groups/fractions (ring class or PHC fractions)

  - Potential double-counting if assessing aromatic PHC fractions as well

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