Benzo[a]Pyrene Update - A Game Changer for Environmental Remediation and Property Revitalization?

April 28, 2017

WENCK

Responsive partner.
Exceptional outcomes.

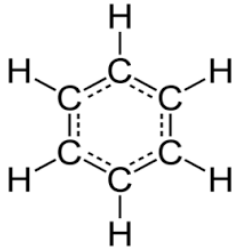
Air & Waste Management Association
GEORGIA CHAPTER

Presented by

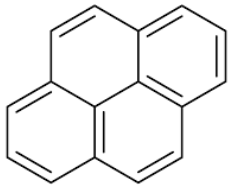
Kristen Rivera

What is Benzo[a]Pyrene (BaP)?

- Polycyclic aromatic hydrocarbon
- Ubiquitous compound
- CAS Number: 50-32-8
- $C_{20}H_{12}$
- Aka: 3,4-Benzopyrene
- A benzene ring fused to pyrene



Benzene
C_6H_6

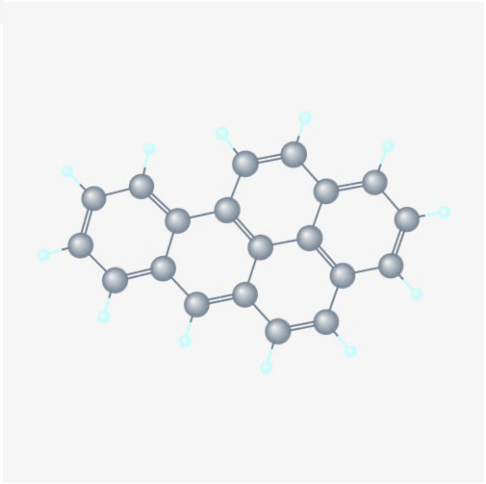


Pyrene
$C_{16}H_{10}$

2D Structure

3D Conformer*

*any of the spatial arrangements that the atoms in a molecule may adopt and freely convert between, especially by rotation about individual single bonds.



Images: PubChem

What is *a Polycyclic Aromatic Hydrocarbon?*

- One class of chemicals that occur naturally in coal, crude oil, and gasoline

Polynuclear Aromatic Hydrocarbons (PAHs)	CAS NO.
~Acenaphthene	83-32-9
~Anthracene	120-12-7
~Benz[a]anthracene	56-55-3
~Benzo[b]fluoranthene	205-99-2
~Benzo[a]pyrene	50-32-8
~Benzo[k]fluoranthene	207-08-9
~Benzo[j]fluoranthene	205-82-3
~Chloronaphthalene, Beta-	91-58-7
~Chrysene	218-01-9
~Dibenz[a,h]anthracene	53-70-3
~Dibenzo(a,e)pyrene	192-65-4
~Dimethylbenz(a)anthracene, 7,12-	57-97-6
~Fluoranthene	206-44-0
~Fluorene	86-73-7
~Indeno[1,2,3-cd]pyrene	193-39-5
~Methylnaphthalene, 1-	90-12-0
~Methylnaphthalene, 2-	91-57-6
~Naphthalene	91-20-3
~Nitropyrene, 4-	57835-92-4
~Pyrene	129-00-0

What is Benzo[a]Pyrene (BaP)?

- Pale yellow, crystalline solid or powder with a faint aromatic odor
- Odorless, silver-gray to black solid.
- Boiling point: 923°F (495°C)
- Density: 1.24 g/cm³
- Solubility in water: 0.2 to 6.2 µg/L
- Molar mass: 252.32 g·mol^{-1}

How does BaP form?

- Forms as a result of incomplete combustion at temperatures between 300 °C (572 °F) and 600 °C (1,112 °F)
- Forms as a gaseous by-product when certain carbon substances burn
- The main source of atmospheric BaP is residential wood burning
- Synthesis from pyrene and succinic anhydride ($C_4H_4O_3$)

Where is BaP found?

- In its pure form - used as a laboratory reagent
- Adhesives and sealant chemicals
- Fuels and fuel additives
- Found in coal tar
- Automobile exhaust fumes (diesel engines*)
- Present in all smoke resulting from the combustion of organic material - including cigarette smoke
- Grilled meats and charbroiled food

Where is BaP found?

- February 2014, NASA announced an upgraded database for tracking polycyclic aromatic hydrocarbons (PAHs), including BaP, in the universe
- More than 20% of the carbon in the universe may be associated with PAHs
- Possible starting materials for the formation of life
- PAHs seem to have been forming "only a couple of billion years after the Big Bang"
- Are widespread throughout the universe
- And are associated with new stars and exoplanets

Why do we care about BaP?

- 18th Century - Chimney Sweeps' Carcinoma
  - Young British chimney sweeps who climbed into chimneys suffered from a scrotal cancer peculiar to their profession
- 1775 - Scrotal cancer first connected to the effects of soot
  - **First work of occupational cancer epidemiology and also the first connection of any chemical mixture to cancer formation
- 19th Century - Frequent skin cancers were noted among fuel industry workers in the
- 1933- BaP was determined to be the compound responsible for these cases
- BaP's carcinogenicity was demonstrated when skin tumors occurred in laboratory animals repeatedly painted with coal tar
- BaP has since been identified as a prime carcinogen in cigarette smoke

Why do we care about BaP?

-NJ Dept of Health Right-to-Know Haz Substance Fact Sheet

- Benzo(a)pyrene can affect you when inhaled and by passing through the skin
- Benzo(a)pyrene may damage the developing fetus
- Contact can irritate and burn the eyes
- Benzo(a)pyrene can irritate the skin causing a rash or burning feeling on contact
- Repeated exposure can cause thickening and darkening of the skin
- There is some evidence that is causes stomach, skin, lung, blood, spleen, pancreas, and mammary cancer in animals

What happened?

- January 19, 2017 –EPA's Integrated Risk Information System (IRIS) program released its final assessment of BaP
- Process took about six years to complete
- BaP is now considered less toxic by the oral route
- New toxicity factors are also included that address carcinogenicity via inhalation as well as the potential for non-cancer health effects
- The more conservative cancer toxicity values will most likely dominate site management

New BaP Toxicity Values

	IRIS Toxicity Values	
	Previous	2017 Final
Cancer		
Oral Cancer Slope Factor $(mg/kg/dy)^{-1}$	7.3E+00	1E+00
Inhalation Unit Risk $(ug/m^3)^{-1}$	--	6E-04
Non-cancer		
Oral Reference Dose (mg/kg/dy)	--	3E-04
Inhalation Reference Concentration (mg/m^3)	--	2E-06

-- = No IRIS value

https://cfpub.epa.gov/ncea/iris2/chemicalLanding.cfm?substance_nmbr=136

What does that mean for us?

- With this new toxicity criteria, you can expect residential screening levels and resulting cleanup levels to be less conservative

EPA RSLs	Current RSLs [1]	Projected RSLs	Change
Residential Soil (mg/kg)			
cancer [2]	0.015	0.11	~7x Increase
non-cancer [3]	--	17.9	--
Industrial Soil (mg/kg)			
cancer [2]	0.29	2.1	~7x Increase
non-cancer [3]	--	220	--

[1] The RSLs are typically updated on a semi-annual basis. The last RSL update was in May 2016. The EPA RSL website currently indicates that the next RSL update is "*in development and should be released soon.*"

[2] RSLs based on the cancer endpoint are calculated using a 1E-6 (1 in 1 million) target risk level.

[3] No previous non-cancer toxicty values for BaP.

Something to note….

Dermal Slope Factor Omitted

- One of the most significant aspects of the final BaP assessment
- Absence of a controversial dermal cancer slope factor (DSF)
- When EPA's first public comment draft of the BaP assessment in 2013 included this DSF that created interest and controversy
- First time a skin-specific toxicity value had been developed by IRIS
- The stringency of the DSF proposed value would have resulted in risk-based screening levels that were well below background concentrations commonly found in the environment
- Due to the substantial amount of public comments and the novelty of the DSF, EPA agreed to solicit an external peer-review conducted by members of its Science Advisory Board, supplemented with scientists with expertise in topics relevant to the BaP assessment

Other things to note…

Regional Screening Level (RSL) Tables

- EPA's website states "The spring update is in development and should be released soon."
- However, RSL Calculator has been updated with new toxicity data
  - Message on EPA website "The RSL semiannual update is currently in progress. Calculator results may differ from the values in the download tables."
- Default variables HAVE been updated in RSL Calculator
  - BW updated from 70 kg to 80 kg
  - IRw (daily water ingestion rate) updated from 2 L/day residential to 2.5 L/day

Let's take a look at the RSL Calculator…

- **Residential Soil**
- **Residential Tap water**
- **Soil to Groundwater**

What does this mean for HSRA?

Current HSRA Soil RRS (mg/kg)			
Type 1	Type 2	Type 3	Type 4
1.64	1.25	1.64	7.84

Current HSRA Groundwater RRS (mg/kg)			
Type 1	Type 2	Type 3	Type 4
2.00E-04	3.00E-05	2.00E-04	3.92E-04

Projected* HSRA Soil RRS (mg/kg)			
Type 1	Type 2	Type 3	Type 4
1.64	4.72	1.64	57.23

Projected* HSRA Groundwater RRS (mg/kg)			
Type 1	Type 2	Type 3	Type 4
2.00E-04	8.52E-04	2.00E-04	2.86E-03

Brownfields

*EPA has not published Spring 2017 RSL Tables – these values are projected, but are subject to change and per EPD approval.

Projected Soil HSRA RRS

Type 1 Soil RRS				
Item 1 (i)	Item 1 (ii)	Item 1 (iii)	Item 2	Item 3
Appendix I	Type 1 GW	SSL for Migration	RAGS (Equ 7)	RAGS (Equ 6)
Concentration	Criteria x 100	to Groundwater	Non-Carcinogenic	Carcinogenic
1.64	0.02	nc	192.11	14.94

Type 2 Soil RRS				
Item 1	Item 2	Item 2	Item 3	Item 3
SSL for Migration	RAGS (Equ 7)	RAGS (Equ 7)	RAGS (Equ 6)	RAGS (Equ 6)
to Groundwater	Non-Carc Adult	Non-Carc Child	Carc Adult	Carc Child
4.72	192.11	23.46	17.03	9.13

Type 3 Soil RRS				
Item 1 (i)	Item 1 (ii)	Item 1 (iii)	Item 2	Item 3
Appendix I	Type 1 GW	SSL for Migration	RAGS (Equ 7)	RAGS (Equ 6)
Concentration	Criteria x 100	to Groundwater	Non-Carcinogenic	Carcinogenic
1.64	0.02	nc	735.84	57.23

Type 4 Soil RRS		
Item 1	Item 2	Item 3
SSL for Migration	RAGS (Equ 7)	RAGS (Equ 6)
to Groundwater	Non-Carc Adult	Carc Adult
67.55	735.84	**57.23**

Projected Groundwater HSRA RRS

- Type 1 and 3 Groundwater (2.00E-04 ug/L) found in: Appendix (391-3-19) III. Media Target Concentrations and Standard Exposure Assumptions

Type 2 RRS (ug/L)				
Item 1	Item1	Item 2	Item 2	Table 1, App III or
RAGS (Equ 2)	RAGS (Equ 2)	RAGS (Equ 1)	RAGS (Equ 1)	Background, or
Non-Carc Adult	Non-Carc Child	Carc Adult	Carc Child	DL
1.22E+05	5.21E+04	**8.52E-04**	1.83E-03	na

Type 4 RRS (ug/L)	
Item 1	Item 2
RAGS (Equ 2)	RAGS (Equ 1)
Non-Carc Adult	Carc Adult
3.41E+05	**2.86E-03**

In Summary

- EPA has released new toxicity values for BaP
- The Spring 2017 RSL Tables have not been published yet
- RSL calculator has been updated with new toxicity data
- It appears screening levels and clean up values will increase by an order of magnitude
- RCRA – less conservative screening level for developing CPOC list
- HSRA – appears T2 and T4 default RRS will be less conservative
- Brownfields – appears T2 default RRS will be less conservative

Example

Brownfields Site
Certify to T1 RRS
1.64 mg/kg

Projected type
residential T2 RRS
4.72 mg/kg

Benzo(a) pyrene	fl
1.64	
1.64	
1.25	
BRL	
2.66	
3.07	
0.0519	
BRL	
BRL	
BRL	
BRL	
0.508	
BRL	
BRL	
5.69	
BRL	
BRL	
0.922	
1.57	
BRL	
0.0407	
BRL	
11.3	
BRL	
0.926	
BRL	
0.0642	
BRL	
BRL	
5.57	
1.6	
BRL	
2.14	
0.189	
0.746	
NA	

Benzo(a) pyrene
1.64
1.25
NA
NA
NA
NA
NA
NA
NA
NA
470
NA
NA
BRL
NA
NA
BRL
BRL
NA
NA
2,400
BRL
NA
NA
NA
NA
NA
NA
NA
NA
NA
NA

Example

Emergency removal cleanup site

Delineated to Soil RSL of 0.015 mg/kg

w/new Bap Tox Factors: Soil RSL of 0.11 mg/kg

Tap Water RSL of 0.0251 ug/L

CONSTITUENT		Type 1 RRS (mg/Kg)	RSL (mg/Kg)	ANALYTICAL RESULTS (mg/Kg)			
				AS-SED	SED-1	SED-5	SED-6
SVOCs/ PAHs	Benz(a)anthracene	5	0.15	**230**	**35**	**150**	**2.5**
	Benzo(a)pyrene	1.64	0.015	**280**	**42**	**140**	**3**
	Benzo(b)fluoranthene	5	0.15	**330**	**68**	**220**	**4.3**
	Benzo(g,h,i)perylene	500	--	190	35	96	2.6
	Benzo(k)fluoranthene	5	1.5	**120**	BRL	BRL	**1.7**
	Chrysene	5	15	**200**	**35**	**130**	2.6
	Dibenz(a,h)anthracene	2.05	0.015	**53**	BRL	BRL	BRL
	Fluoranthene	500	2300	300	65	310	4.7
	Indeno(1,2,3-c,d)pyrene	5	0.15	**170**	**27**	BRL	**2.1**
	Phenanthrene	110	--	50	20	100	.94 J
	Pyrene	500	1700	260	50	250	3.5

mg/kg	Milligrams per kilogram
RRS	GA EPD Residential Type 1 Risk Reduction Standard for Soil
RSL	USEPA Regional Screening Level for Resident Soil (Nov 2014)
BRL	Below Reporting Limit
--	No RSL calculated
J	Estimated value detected below reporting limit
Bold	Result exceeds RRS and/or RSL

CONSTITUENT		ISWQS (mg/L)	RSL (mg/L)	SW-1 (mg/L)
SVOCs/ PAHs	Acenaphthene	0.99	0.53	0.01
	Benz(a)anthracene	0.000018	0.000034	**0.034**
	Benzo(a)pyrene	0.000018	0.0000034	**0.029**
	Benzo(b)fluoranthene	0.000018	0.000034	**0.035**
	Benzo(g,h,i)perylene	0.000018	--	**0.016**
	Benzo(k)fluoranthene	0.000018	0.00034	**0.015**
	Chrysene	0.000018	0.0034	**0.035**
	Fluoranthene	0.14	0.8	**0.12**
	Indeno(1,2,3-c,d)pyrene	0.000018	0.000034	**0.015**
	Phenanthrene	--	--	**0.032**
	Pyrene	4	0.12	**0.071**

mg/L	Milligrams per liter
ISWQS	GA EPD Instream Water Quality Standard
RSL	USEPA Regional Screening Level for Tap Water (Nov 2014)
DL	Detection Limit
--	Not provided/calculated in respective publication
Bold	Results exceeds ISWQS and/or RSL

Questions ?