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Gaps and Uncertainties Associated with PAH Soil Quality Guidelines in Canada and Challenges with Human and Ecological Risk Assessment

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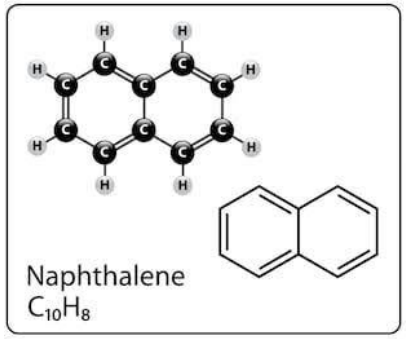
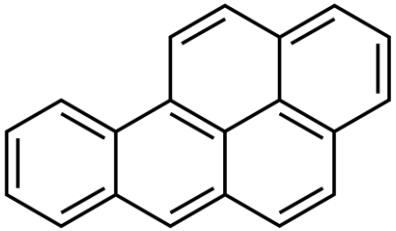
Outline

- What are PAHs & toxic limits?
- Ambient concentrations in soil.
- Guideline summary across Canada:
  - CCME
  - Alberta
  - Ontario
- Pathways and receptors:
- Examples
- Summary





Benzo(a)pyrene

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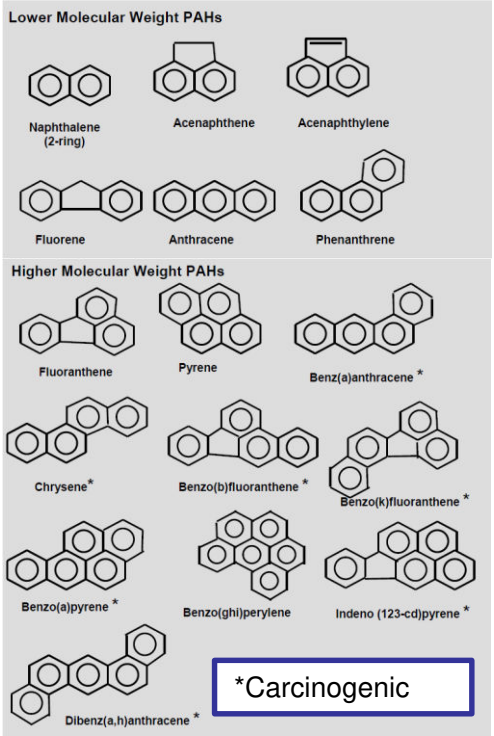
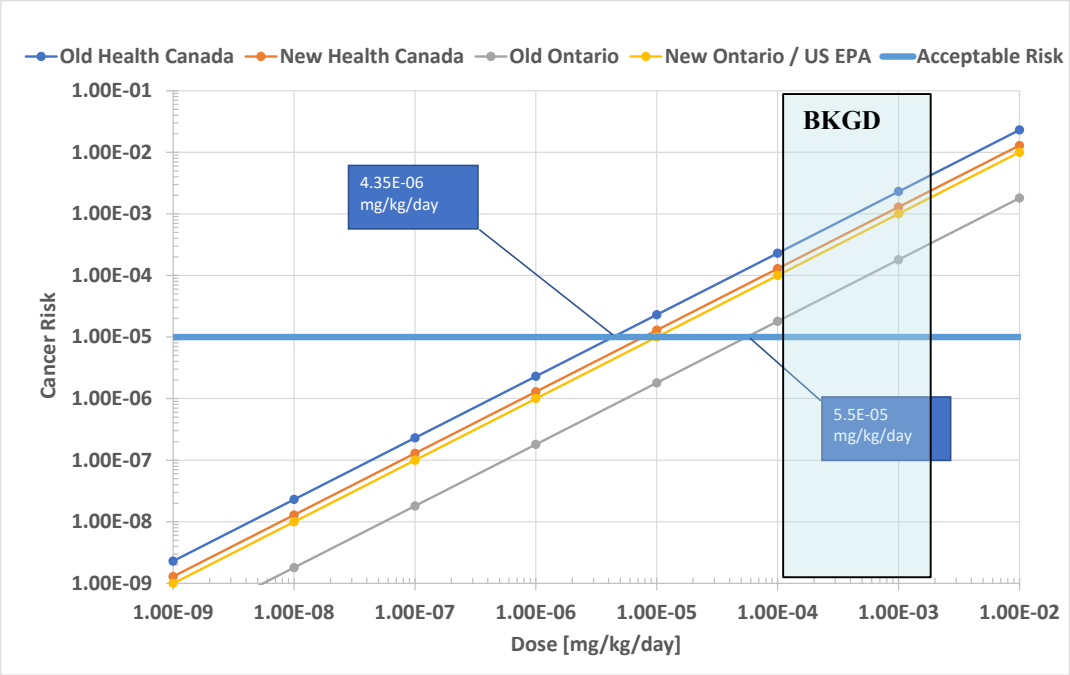
Polycyclic Aromatic Hydrocarbons (PAHs)

- Defined many ways:
  - Low molecular weight PAH
  - High molecular weight PAH
  - Non-carcinogenic
  - Carcinogenic
- Assessed:
  - Individually
  - Mixture - potency equivalence factors (PEFs) for carcinogenic PAHs



Toxic Limits for Oral Exposure

Non-cancer PAH	Limit [mg/kg/day]
Anthracene	0.3
Fluorene	0.02
Fluoranthene	0.04
Naphthalene	0.02
Pyrene	0.03



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Ambient Levels in Prairie Soil

- Native Grassland
- Saskatchewan to southern Texas
- Some exceed aquatic life guidelines "◀"

PAH	Concentration Range
Naphthalene	0.0063 – 0.179 ◀
Acenaphthene	0.0005 – 0.0041
Acenaphthylene	0.0003 – 0.0038
Fluorene	0.0010 – 0.0088
Phenanthrene	0.031 – 0.087 ◀
Anthracene	0.0004 – 0.0021
Fluoranthene	0.0047 – 0.029
Pyrene	0.0033 – 0.011
Benz[a]anthracene	0.0006 – 0.0027
Chrysene	0.0014 – 0.0083
Benzo[b+j+k]fluoranthene	0.0014 – 0.011
Benzo[a]pyrene	0.0002 – 0.0027
Indeno[1,2,3-c,d]pyrene	0.0004 – 0.0040
Dibenz[a,h]anthracene	0.0001 – 0.0008
Benzo[g,h,i]perylene	0.0005 – 0.0034

CCME 2010

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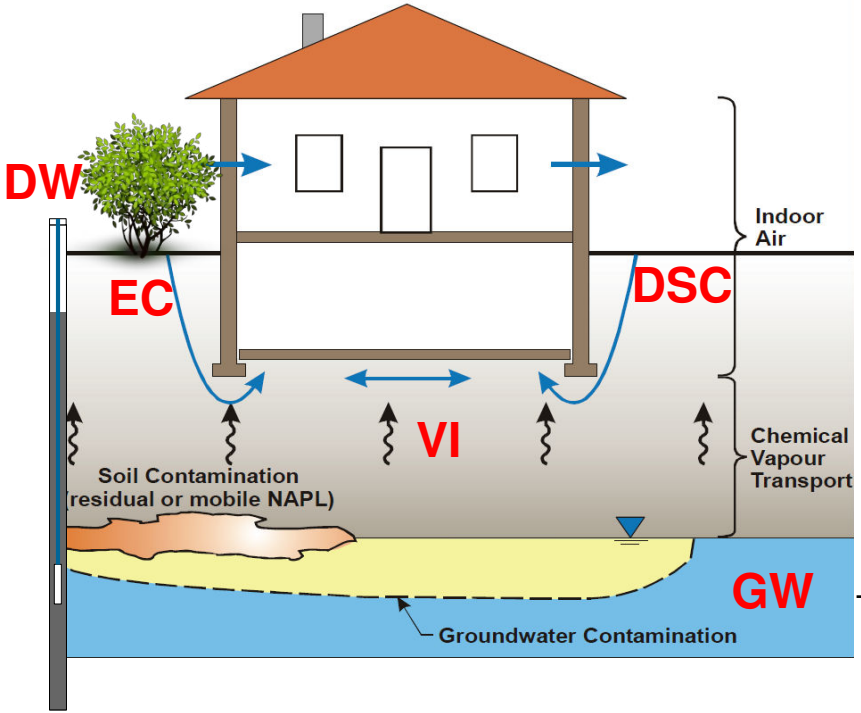
Pathways and Receptors of Concern



Interim Guidelines

10 meters:

- Dispersion
- Degradation

SW(FAL) / LW / WW / IW

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Guidelines – Interim Ones???

- Have a value of 0.5 mg/kg
- Typically applied where there is uncertainty or data gaps.
- Ancient (CCME 1991).
- Scientific basis mysterious and unknown.
- Difficult to surmise risk to human and ecological receptors.

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Guidelines in Canada – Human Soil Contact

Agency	Benzo[a]anthracene	Benzo[b+j+k]fluoranthene	Benzo[g,h,i]perylene	Benzo[a]pyrene	Chrysene	Dibenz[a,h]anthracene	Indeno(1,2,3-c,d)pyrene	B(a)P TPE	Acenaphthene	Acenaphthylene	Anthracene	Fluoranthene	Fluorene	Naphthalene	Phenanthrene	Pyrene
Potency Equivalency Factor (PEF)	0.1	0.1	0.01	1	0.01	1	0.1	--	--	--	--	--	--	--	--	--
AEP 2019 (mg/kg)	TPE	TPE	TPE	TPE	TPE	TPE	TPE	5.3	5,300	--	24,000	3,500	2,700	1,800	--	2100
CCME 2010 (mg/kg)	TPE	TPE	TPE	TPE	TPE	TPE	TPE	5.3	--	--	--	--	--	--	--	--
OMOE 2011 (ug/g)	5.7	--	57	0.57	57	0.57	5.7	0.57	570	57	57	57	720	360	--	540
US EPA (mg/kg)	11	4.2 - 110	--	1.1	1,100	1.1	11	--	3,600	--	18,000	2,400	2,400	38	--	1,800

B(a)P Toxic Potency Equivalent = ∑[PAH] x PEF

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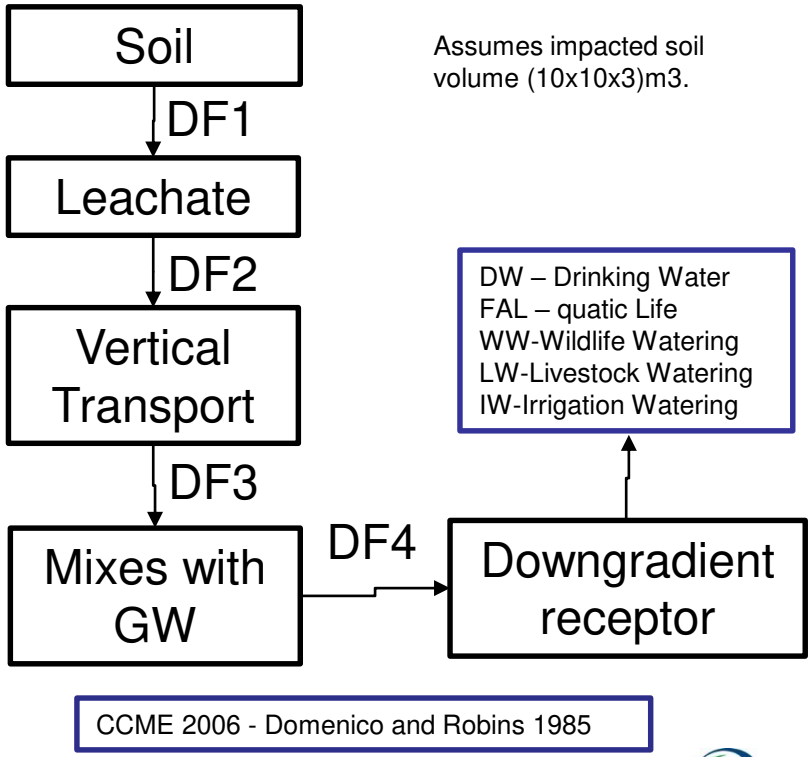
Example#1 – Human Soil Contact

- Good consensus and confidence in soil contact guidelines for carcinogens:
  - Low uncertainty with slope factor for incremental risks
  - Confidence with mode of action
  - Extensive investigation and broad agreement with PEF values for mixture evaluation
- Non-carcinogenic PAH risks are rarely a concern.
- Assumes PAHs 100% bio-accessible via soil ingestion but PAHs in soil are generally expected to be less than 50% (Ruby et al. 2016) and can be as low as 33% (Peters et al. 2016) bio-accessible.
- Reasonably conservative exposure point concentration (EPC) should be used, like a 95th upper confidence limit on the mean (95UCLM).
  - Collect enough surface soil samples to run the statistics!

Soil to Groundwater Transport

- DF1 - Partitioning of the contaminant between soil and soil pore water.
- DF2 - Leaching of the contaminant through the unsaturated zone to the groundwater table. (Typically = 1)
- DF3 - Mixing and dilution of leachate into groundwater.
- DF4 - Saturated zone horizontal transport of the contaminant to a down-gradient receptor.



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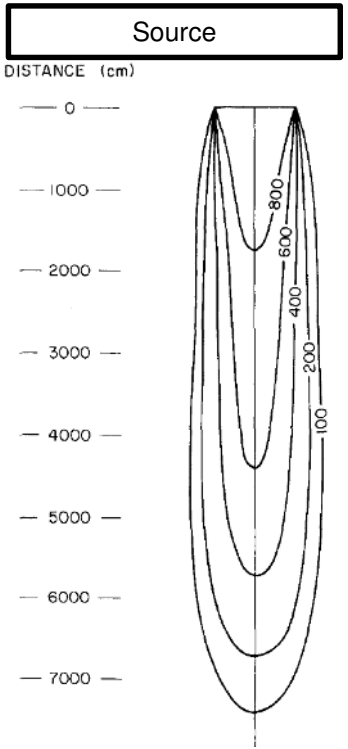
Groundwater (GW/DW/FAL) – DF4

- Default DF4=1 for DW guidelines
- DF4 for FAL, LW, WW assumes horizontal separation 10m
- DF4 estimates dispersion and biodegradation ($t_{1/2}$)
- PAH guidelines assume no degradation – DF4~1



Guidelines in Canada – Ecological (FAL)

PAH	AEP 2019 Guidelines – Coarse Soils (Similar as CCME)				
	Soil Quality Guideline [mg/kg]	Groundwater Quality Guideline [µg/L]	Surface Water Quality Guidelines[1]		
			SWQG [µg/L]	Basis	Safety Factor
Acenaphthene	0.38	5.8	5.8	96-hr LC50 of 580 µg/L for brown trout	multiplied by a safety factor of 0.01
Anthracene	0.0056	0.012	0.012	15 min LC50 of 1.2 µg/L for Daphnia pulex	multiplied by a safety factor of 0.01
Fluoranthene	0.055	0.057	0.04	1 hr LC50 of 4µg/L for D. magna	Multiplied by a safety factor of 0.01
Fluorene	0.34	3	3	14-day LOEC of 125 µg/L for Daphnia magna adjusted by a correction factor of 0.24	multiplied by a safety factor of 0.1
Naphthalene	0.017	1.1	1.1	LOEL of 11 µg/L for rainbow trout	multiplied by a safety factor of 0.1
Phenanthrene	0.061	0.4	0.4	LOEL of 4 µg/L for rainbow trout	multiplied by safety factor of 0.1
Pyrene	0.15	0.092	0.025	LC50 of 2.5 µg/L for A. aegypti	Multiplied by a safety factor of 0.01

[1] CCME 2010

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PAH Degradation Rates in GW

PAH	Maximum Half-life [Days]	Maximum Half-life [years]
Acenaphthene	204	0.6
Anthracene	913	2.5
Benzo(a)anthracene	1361	3.7
Benzo(b)fluoranthene	1219	3.3
Benzo(k)fluoranthene	4271	11.7
Benzo(a)pyrene	1059	2.9
Chrysene	2000	5.5
Fluoranthene	876	2.4
Fluorene	120	0.3
Naphthalene	258	0.71
Phenanthrene	2081	5.7
Pyrene	3796	10.4

Howard et al 1991; CCME 2000; Axiom 2011

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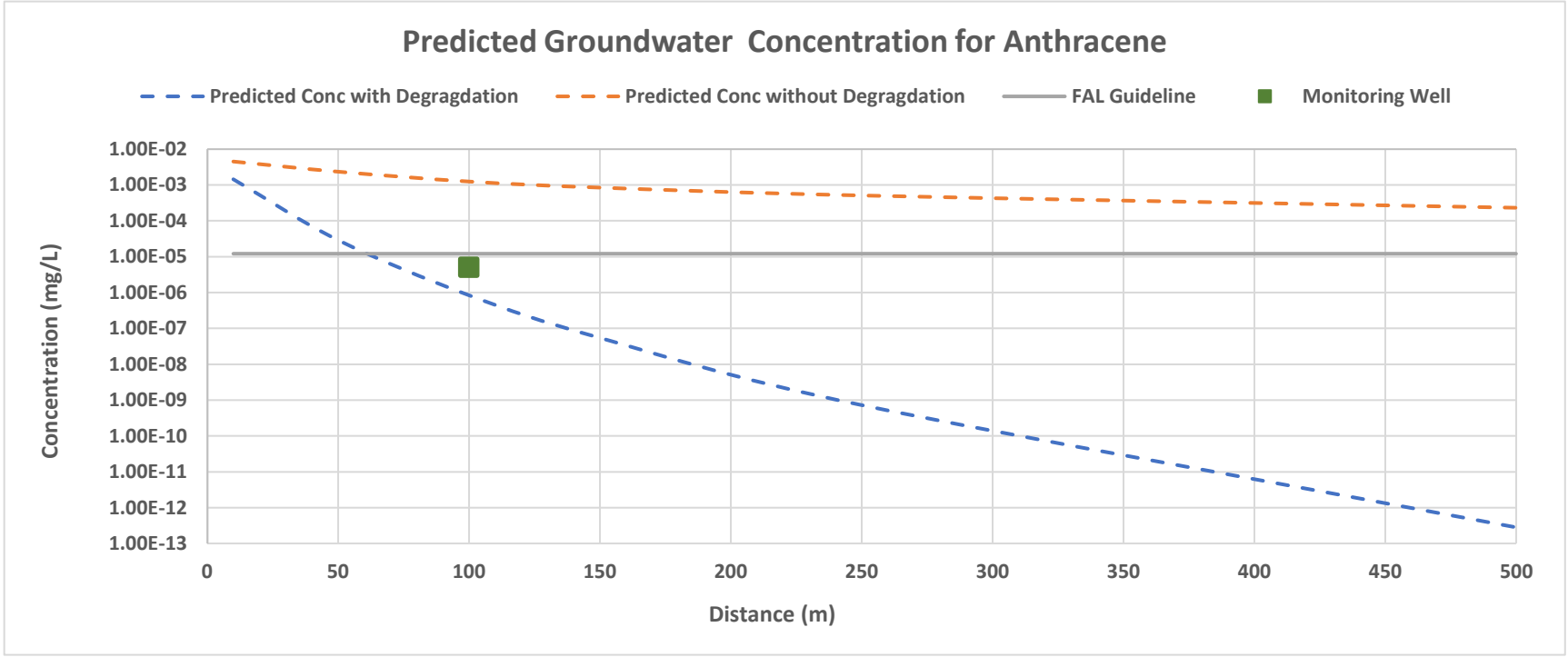
Example#2 – GW Modeling



Example#3 – GW Modelling

- Soil quality screening is required based on regulatory expectations.
- Using soil PAH concentrations as a proxy to assess FAL / DW risk has considerable uncertainty.
- Soil FAL or DW (i.e., IACR) exceedances should be followed by groundwater testing.
- PAHs don't like water but prefer to be bound to soil organic matrix/carbon.
- Often soil concentrations exceed DW or FAL PAH guidelines but groundwater concentrations are non-detect or impacts are limited in extent.
- Non-carcinogenic PAHs in soil don't exceed DW guidelines frequently.

Example#4 – GW Degradation

- The OMOE (2011) and CCME (2010) acknowledges that biodegradation is a site-specific factor and observed to be a highly variable process that does not occur consistently at every site.
- Usually, soil exceedances take priority over groundwater evidence when identifying risks or remediation volumes, which can be unnecessary.
- Often need to collect enough data to provide multiple lines of evidence and reduce uncertainty.

Guidelines in Canada – Ecological Contact

- What are the risks to plants and invertebrates from PAHs in soil?
- Limited data are available on the toxicity of PAHs in soil to plants and soil invertebrates.
- Sufficient data for benzo(a)pyrene and fluoranthene using a weight-of-evidence (WOE) approach are available.
- Effect/endpoints were reduction in growth or reproduction in plants (oats, ryegrass, bird rape, lupin) and invertebrates (springtail, earthworm, potworm).
- Anthracene lowest effect concentration.

PAH	Guideline for Coarse/Fine Soil [mg/kg]
Anthracene	2.5 (LOEC 5 / 2)
Benzo(a)pyrene	20
Fluoranthene	50

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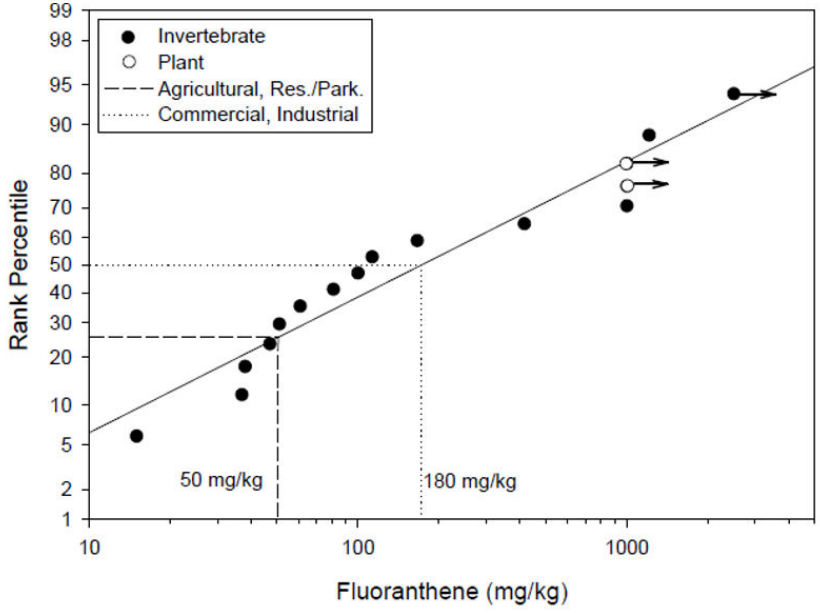
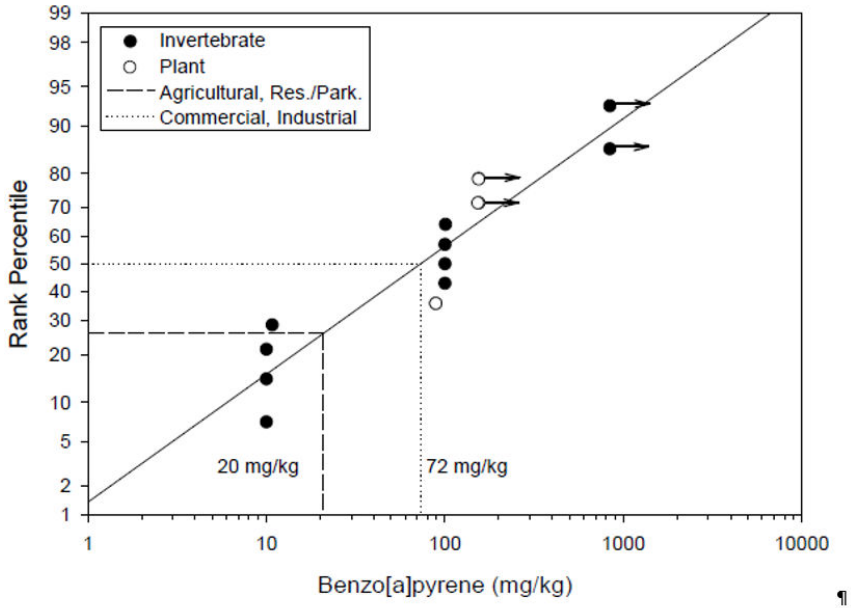
Guidelines in Canada – Ecological Contact



Figure·1→Ranked·Ecotoxicity·Data·for·the·Effects·of·Fluoranthene·on·Soil·Invertebrates·and·Plants¶



Figure·2→Ranked·Ecotoxicity·Data·for·the·Effects·of·Benzo(a)pyrene·on·Soil·Invertebrates·and·Plants¶

The figures highlight that some of the datapoints (i.e., arrow on data point directed to the right) were plotted at estimated concentrations as the actual effect concentration was higher but could not be measured

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Other Jurisdictions – Ecological Contact

- OMOE (2011) has more PAH guidelines
- But based on little to no plant and invertebrate toxicity data for these compounds.
- Based on aquatic species and/or quantitative structure-activity relationships (QSAR)

PAH [mg/kg]	OMOE 2011	CCME 2010
Anthracene	2.5-3.1*	2.5
Benz(a)anthracene	0.63	--
Benzo(a)pyrene	20-25*	20
Benzo(g,h,i)perylene	8.3	--
Benzo(k)fluoranthene	9.5	--
Chrysene	8.8	--
Fluoranthene	50-63*	50
Indeno(1,2,3-cd)pyrene	0.48	--
Naphthalene	0.75	--
Phenanthrene	7.8	--

*Adjusted with soil texture to get Medium/Fine Soil

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Example#5 - Caution

- Ontario (2011) developed guidelines based on Dutch Serious Risk Concentrations for the Ecosystem (SRCECO) values, developed by Lijzen et al. (2001).
- CCME (2010) states that PAH guidelines are often developed using very limited datasets, aquatic species toxicity with back calculation of soil concentrations from effect concentrations in water and partitioning relationships, or data identified through quantitative structure-activity relationships (QSAR).
- According to CCME (2010), “there is little support for using a QSAR approach, such as those used by Lijzen et al. (2011) and Verbruggen et al. (2001)”.

Other Jurisdictions – Ecological Contact

- US EPA Eco-SSLs (2007).
- Used similar data to CCME but grouped individual PAHs into two groups:
  - LMW
  - HMW
- Calculated guidelines for soil invertebrates and data insufficient for plants
- Also calculated limits for mammalian wildlife.

Pathway of Concern	Plants [mg/kg]	Inverts [mg/kg]	Avian Wildlife [mg/kg]	Mammalian Wildlife [mg/kg]
Low Molecular Weight (LMW) PAHs	NA	29	NA	350 (Herbivore) 100 (Insectivore) 110 (Carnivore)
High Molecular Weight (HMW) PAHs	NA	18	NA	39 (Herbivore) 1.1 (Insectivore) 1,200 (Carnivore)

NA (Not Available). Data were insufficient to derive an Eco-SSL.

LMW defined as PAHs with less than 4 rings.

HMW defined as PAHs with 4 or more rings.

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Other Jurisdictions – Ecological Contact

PAH		Test Organism	Soil pH	% Organic Matter	Endpoint		Concentration (mg/kg)
LMW PAHs							
Phenanthrene	springtail	Folsomia candida	6.0	10.0	Repro	MATC	175
Fluoranthene	springtail	Folsomia fimetaria L.	6.2	2.8	Repro	EC_{10}	37
Phenanthrene	springtail	Folsomia fimetaria L.	6.2	2.8	Repro	EC_{10}	23
Fluorene	springtail	Folsomia fimetaria L.	6.2	2.8	Repro	EC_{10}	8
Fluoranthene	potworm	Enchytraeus crypticus	6.2	2.8	Repro	EC_{10}	15
Phenanthrene	potworm	Enchytraeus crypticus	6.2	2.8	Repro	EC_{10}	40
Fluorene	potworm	Enchytraeus crypticus	6.2	2.8	Repro	EC_{10}	25
Phenanthrene	springtail	Folsomia fimetaria L.	6.2	2.8	Repro	EC_{10}	9
Fluoranthene	earthworm	Eisenia veneta	6.2	2.8	Growth	EC_{10}	113
Phenanthrene	earthworm	Eisenia veneta	6.2	2.8	Growth	EC_{10}	25
Fluorene	earthworm	Eisenia veneta	6.2	2.8	Growth	EC_{10}	31
						Geomean:	**29**
HMW PAHs							
Pyrene	earthworm	Lumbricus rubellus	n/a	10.0	Repro	MATC	80
Pyrene	springtail	Folsomia candida	6.0	10.0	Repro	MATC	10
Pyrene	springtail	Folsomia fimetaria L.	6.2	2.8	Repro	EC_{10}	10
Pyrene	potworm	Enchytraeus crypticus	6.2	2.8	Repro	EC_{10}	11
Pyrene	springtail	Folsomia fimetaria L.	6.2	2.8	Repro	EC_{10}	10
Pyrene	earthworm	Eisenia veneta	6.2	2.8	Growth	EC_{10}	38
						Geomean:	**18**

Notes:

EC_{10} = 10% effect concentration; MATC = Maximum acceptable toxicant concentration

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Guidelines in Canada – Livestock / Wildlife

- Consideration of soil and food ingestion by cows as a representative livestock species, and mule deer, meadow vole and American robin as representative wildlife species (CCME 2010).
- Similar approach to US EPA Eco-SSLs.
- Watch for “Note” at bottom of the table.

PAH	DTED ($mg \cdot kg^{-1} \cdot day^{-1}$)	Cow ($mg \cdot kg^{-1}$)	Mule Deer ($mg \cdot kg^{-1}$)	Meadow Vole ($mg \cdot kg^{-1}$)	American Robin ($mg \cdot kg^{-1}$)
Naphthalene	28.6	11,726	33,150	6,971	**8.8**
Acenaphthene	70	28,700	81,136	17,062	**21.5**
Fluorene	50	20,500	57,955	12,187	**15.4**
Anthracene	200	82,000	231,818	48,750	**61.5**
Phenanthrene	140	57,400	162,273	34,125	**43.0**
Fluoranthene	50	20,500	57,955	12,187	**15.4**
Pyrene	25	10,250	28,977	6,094	**7.7**
Benz[a]anthracene	20	8,200	23,182	4,875	**6.2**
Chrysene	20	8,200	23,182	4,875	**6.2**
Benzo[b+j]fluoranthene	20	8,200	23,182	4,875	**6.2**
Benzo[k]fluoranthene	20	8,200	23,182	4,875	**6.2**
Benzo[a]pyrene	2	820	2,318	487	**0.6**
Dibenz[a,h]anthracene	N/A	--	--	--	--

(Bolded SQG_I: lowest calculated values for different vertebrate receptors)
NOTE: According to the protocol (CCME, 2006), naphthalene was the only PAH that met the minimum data requirements for calculation of the SQG_I. Therefore, values presented for all other PAHs are considered “provisional”, and have not been used in determining the overall SQG_E.

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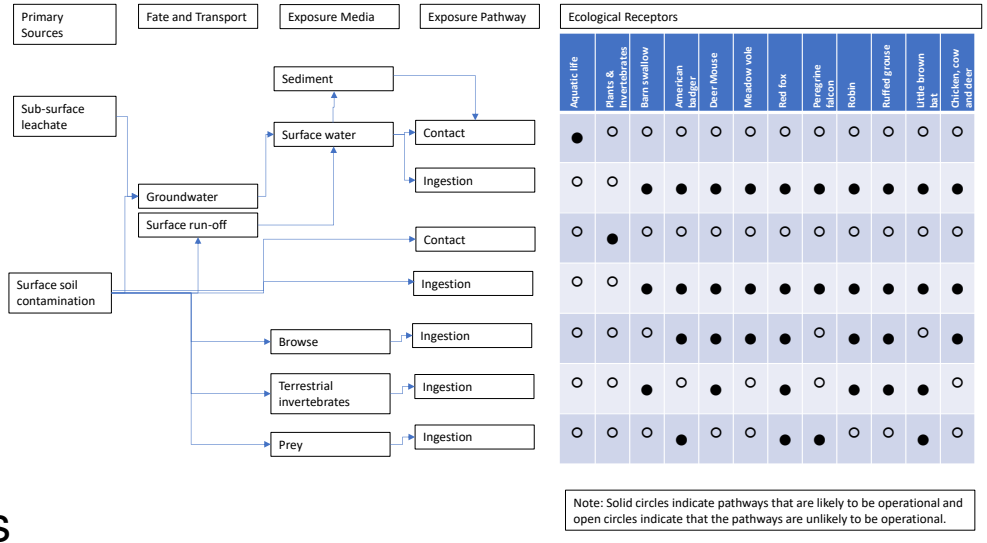
Example#6 – Livestock / Wildlife

- Use weight of evidence:
  - Screen soil data against CCME and Eco-SSL guidelines.
- Complete a site-specific ecological risk assessment (ERA) for target wildlife.
- Use measured PAHs in abiotic media to predict concentrations in biotic media.
- HQ values are typically predicted to be acceptable.



Summary

Contrā (Conservative / ↑ Uncertainty)

1. Interim guidelines should be resolved.
2. Conservative assumptions assumed for GW (e.g., FAL / DW):
   - PAHs partition to soil organic matrix
   - Groundwater degradation of PAHs
3. Eco-contact guidelines missing for most PAHs due to lack of toxicity data.
4. CCME (2010) & US EPA (2007) are dated.

Prō (Reasonable / ↓ Uncertainty)

1. Human soil contact
2. Vapour inhalation risks low
3. Livestock / wildlife
4. Existing eco-contact guidelines for B(a)P and FLUOR

Questions?

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