Do soil PAH guidelines represent true risk?

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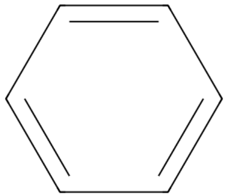
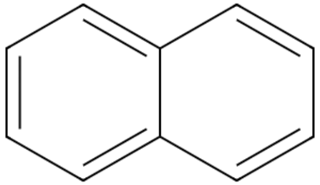
Chemistry 101

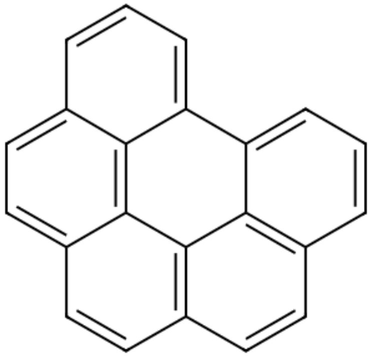
- What is a PAH anyway?
  - Polycyclic aromatic hydrocarbon
  - A group of hydrocarbons composed of two or more fused benzene rings
  - Found primarily within F2 ($C_{>10}$-C_{16}) and F3 ($C_{>16}$-C_{34})
  - PAHs are PHCs, but not every PHC is a PAH
  - Some are carcinogenic
  - Not super water soluble



Benzene (C_6H_6)



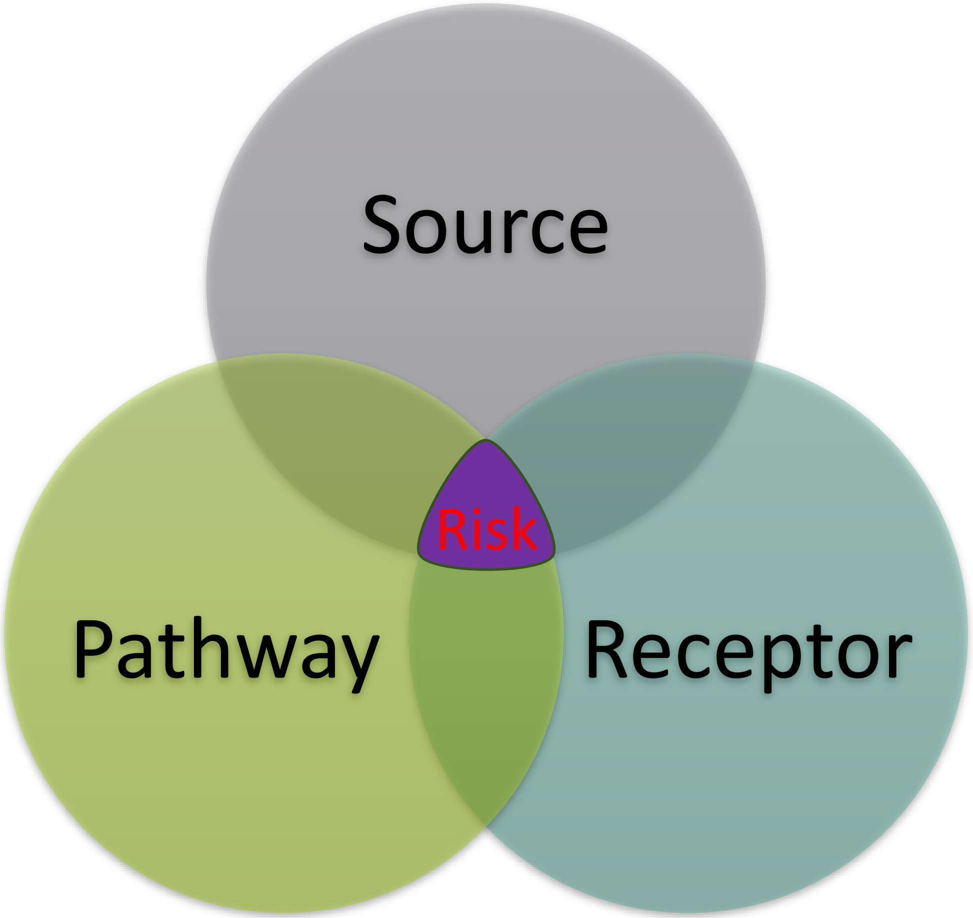
Naphthalene ($C_{10}H_8$)



Benzo[ghi]perylene ($C_{22}H_{12}$)

Risk Paradigm: Source → Pathway → Receptor

- Source
    - Contaminants of concern
- Receptor
    - Human and/or ecological
- Pathway
    - Describes how the contaminants get to the receptor
- For risk to exist, all three need to be present



What is a “source”?

- Think of source as

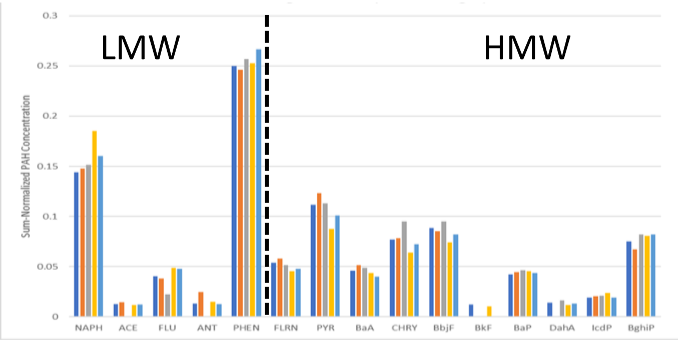
1. Origin: rather than assuming anthropogenic impact
2. Composition: identifiable features

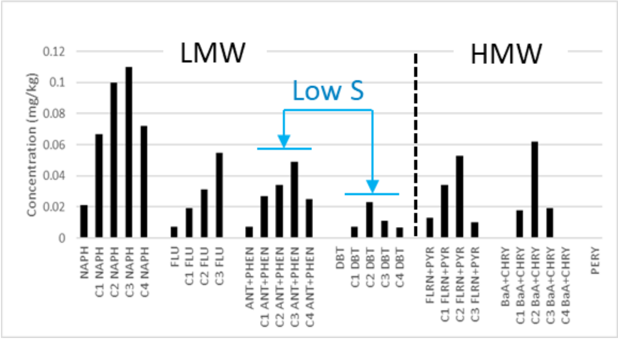
- ‘Contaminants’ have many possible origins:
  - **Biogenic** – Produced by biological systems
  - **Pyrogenic** - Forest fires, combustion residues, coal (oil) pyrolysis, black carbon
  - **Geogenic** - Oil, coal, shale

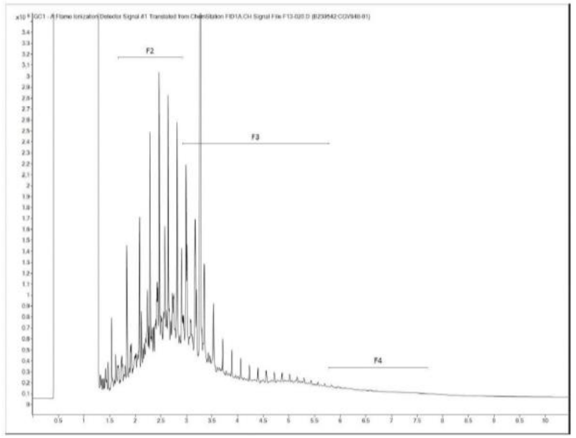
- Understand the composition = understand the ‘source’

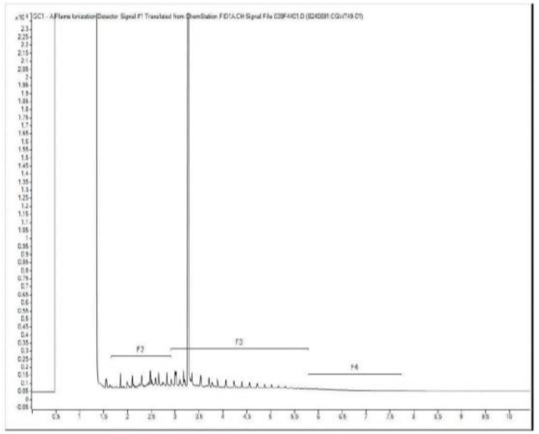
Determining the Source

- Application of Forensic Chemistry to differentiate between anthropogenic and natural sources
    - Site history and setting
    - Field observations
    - Borehole logs
    - PAH fingerprinting
    - PHC chromatograms
- Built on over 10 years of research and applied assessment









Why Does the Source Matter?

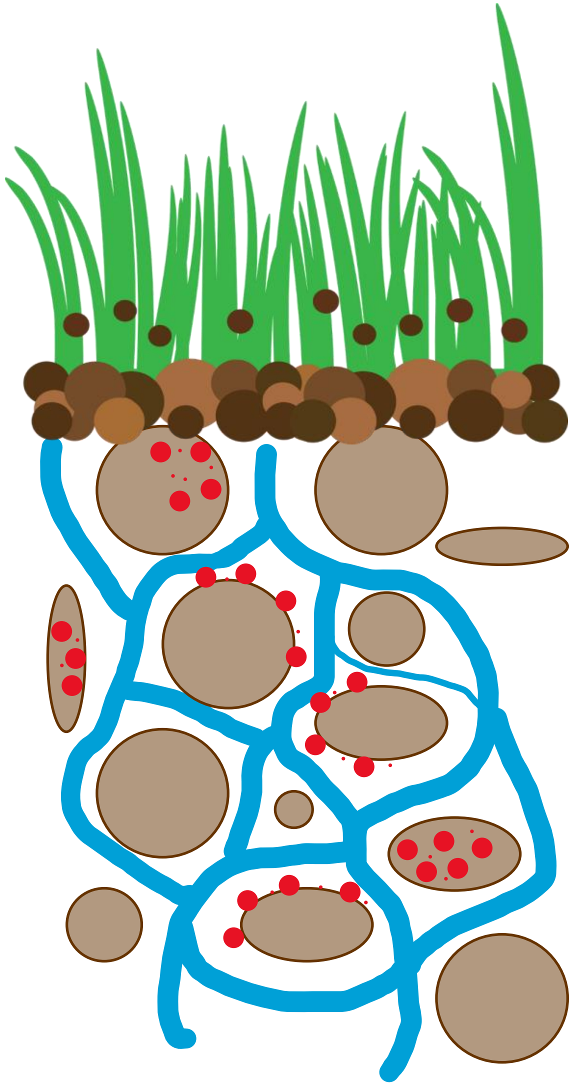
- The CCME guideline calculations assume that PAHs are from a petroleum source and will dissolve into soil pore water to some degree
- PAHs from natural sources, such as coal, will behave differently in the environment
- When we understand the source, we have a better understanding of the pathway

Pathway

- How does the source travel to the receptor?
    - Chemical fate and transport
    - Partitioning behaviour
- Applicable pathways for PAHs in surface and sub-surface soil include those protective of water users:
    - Potable Water (PW) and
    - Freshwater Aquatic Life (FAL),
- FAL is the most restrictive pathway for consideration for non-carcinogenic PAHs

Guideline Assumptions & Calculations

- Soil guidelines for the PW and FAL pathways are calculated using water-based guidelines
- Assumption that an organic chemical will partition in a predictable manner between the soil surface and the pore water
    - Assumes that PAHs are from oil
- In the CCME guidelines, this is applied using Dilution Factor 1 (DF1)



Dilution Factors

The CCME guidelines consider the hydrological links between soil and groundwater systems, which are the limiting pathways in many jurisdictions.

This is built into four steps, called Dilution Factors (DFs):

- DF1: Partitioning between soil and pore water as ‘leachate’ (K_d)
- DF2: Transport of ‘leachate’ from pore water to the water table
- DF3: Mixing of ‘leachate’ with groundwater
- DF4: Groundwater transport to aquatic receptor

Dilution Factor 1 (DF1): Partitioning to Groundwater

$$SQG_{FAL} = C_L \left\{ \boxed{K_d} + \left(\frac{\theta_w + H'\theta_a}{\rho_b} \right) \right\}$$

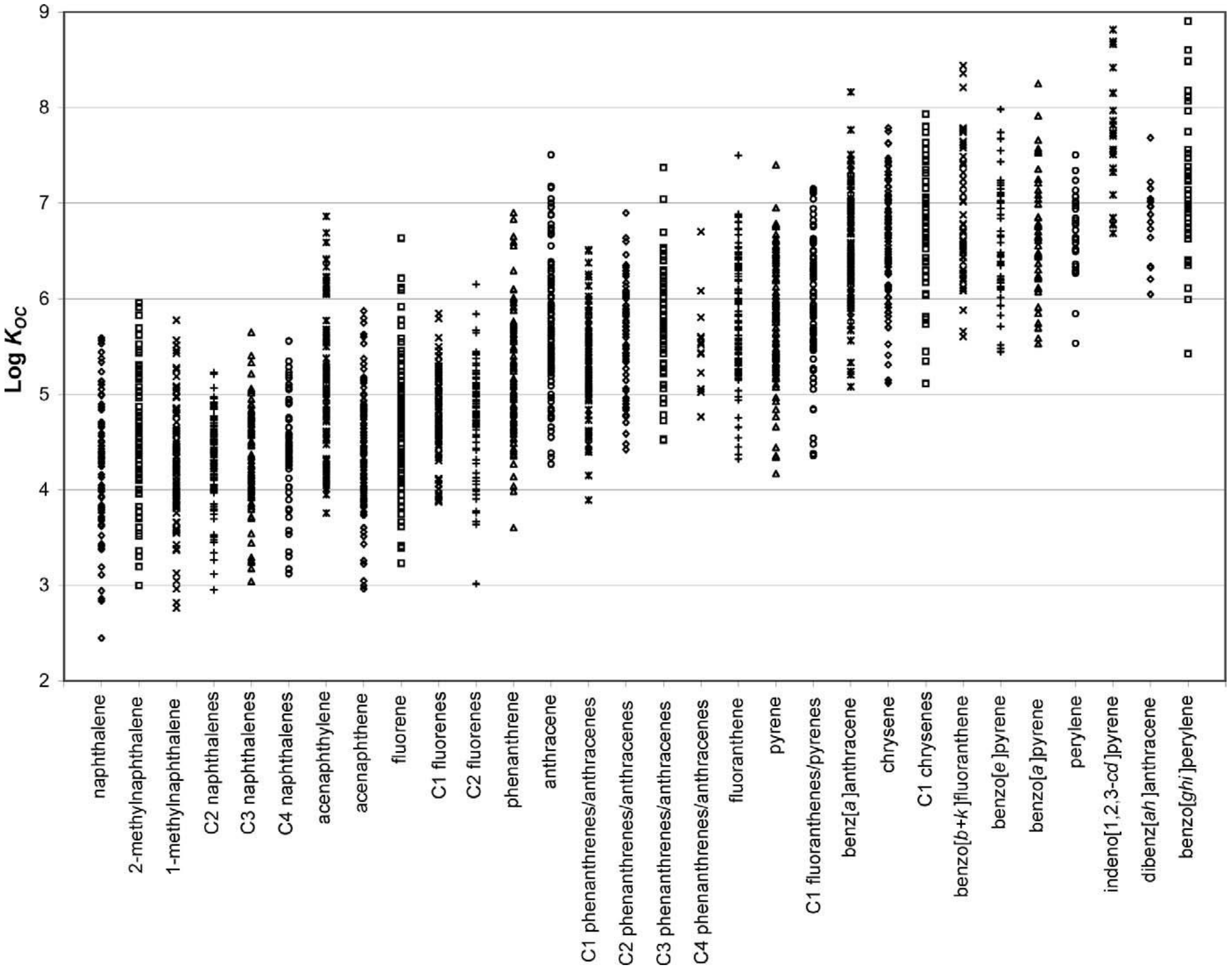
$$K_d = K_{OC} \times f_{OC}$$

$$K_d = \text{distribution coefficient}$$
$$K_{OC} = \text{organic carbon partitioning coefficient}$$
$$f_{OC} = \text{organic carbon fraction of soil}$$

- K_d is derived by multiplying the chemical-specific soil organic carbon partitioning factor (K_{OC}) with the fraction of organic carbon in the soil (f_{OC}).
- The default value for f_{OC} is 0.005 and can be adjusted to be site-specific

K_{OC} Values

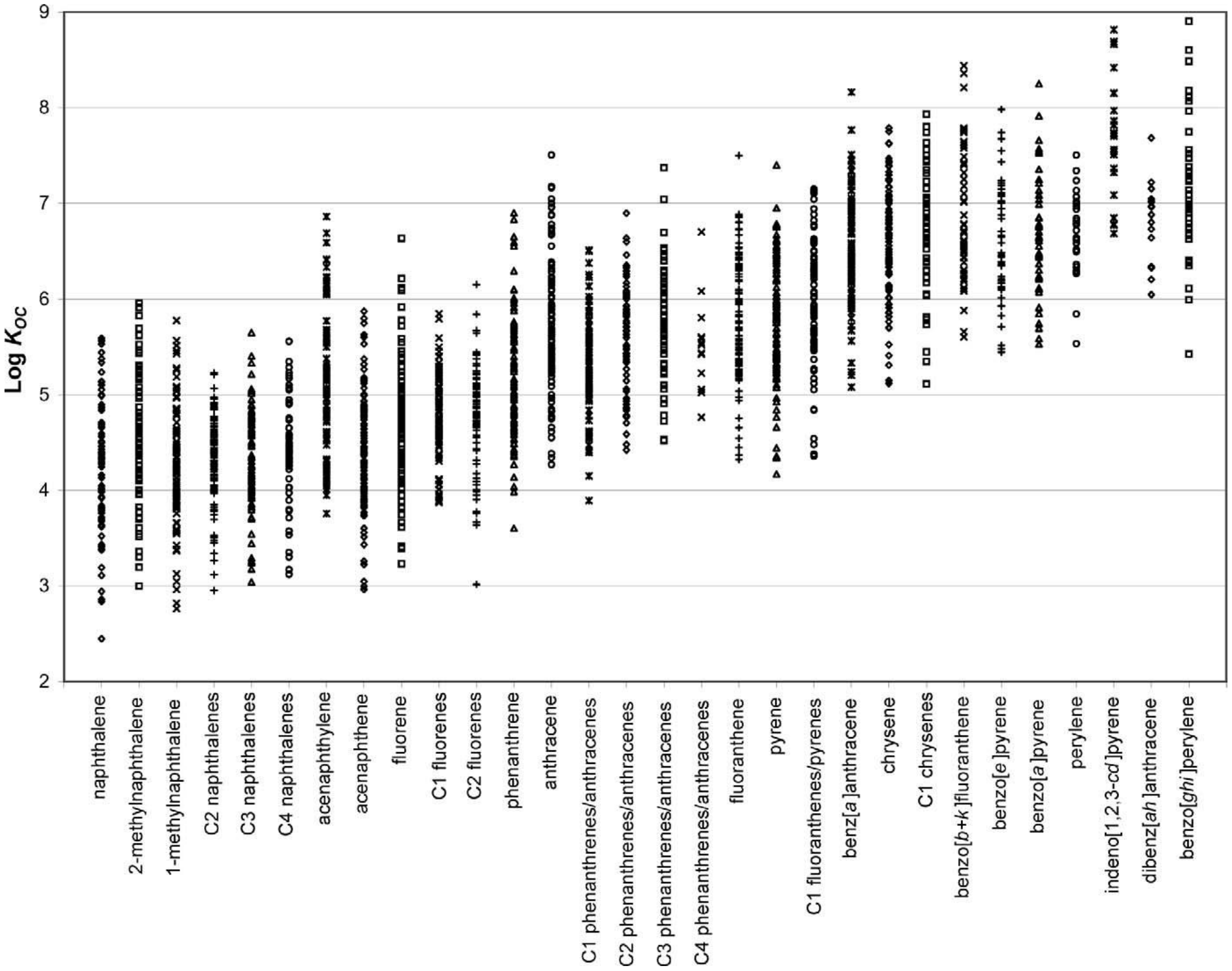
- The K_{OC} value describes how strongly a chemical will “stick” to organic carbon
    - K_{OC} values can be measured in a lab and/or estimated using modelling equations
- There is a wide range of literature K_{OC} values available for any given chemical
    - No single, “right”, answer
    - Source is a big driver of K_{OC} values



Hawthorne, S.B., Grabanski, C.B., Miller, D.J. (2006). *Measured partitioning coefficients for parent and alkyl polycyclic aromatic hydrocarbons in 114 historically contaminated sediments: Part 1. K_{OC} values*. Environmental Toxicology and Chemistry, 25(11), 2901-2911.

K_{OC} Values

- “These results clearly show that the use of a single K_{OC} value to predict the behavior of a particular PAH is not sufficiently accurate for the range of sediments and PAH partitioning behaviors that actually exist in field sediment sites.”



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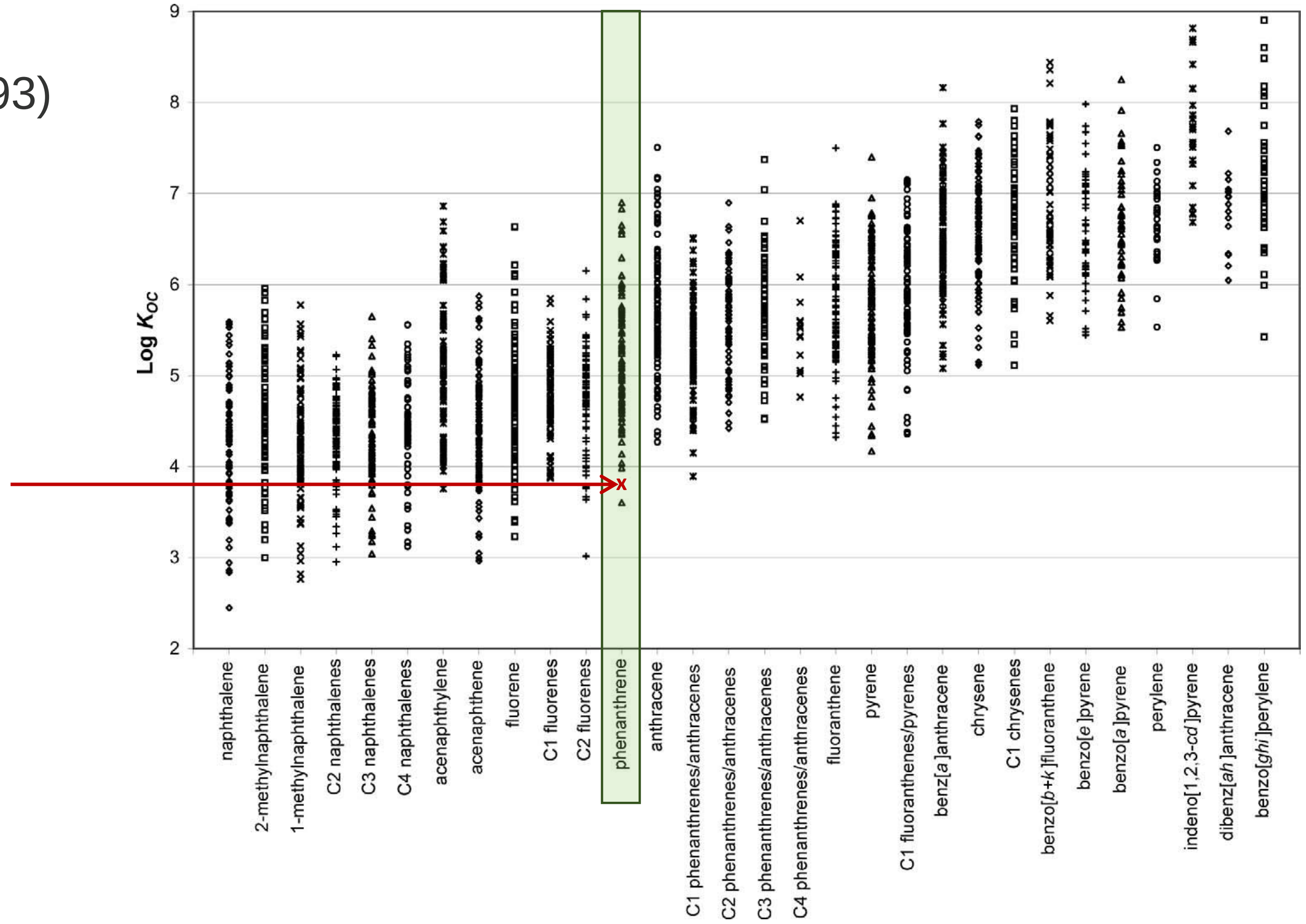
Range of K_{OC} Values – Phenanthrene

- Example of phenanthrene (n=93)
  - Min: 3.6
  - Mean: 5.2
  - Max: 6.9
  - CCME: 3.82



CCME Value

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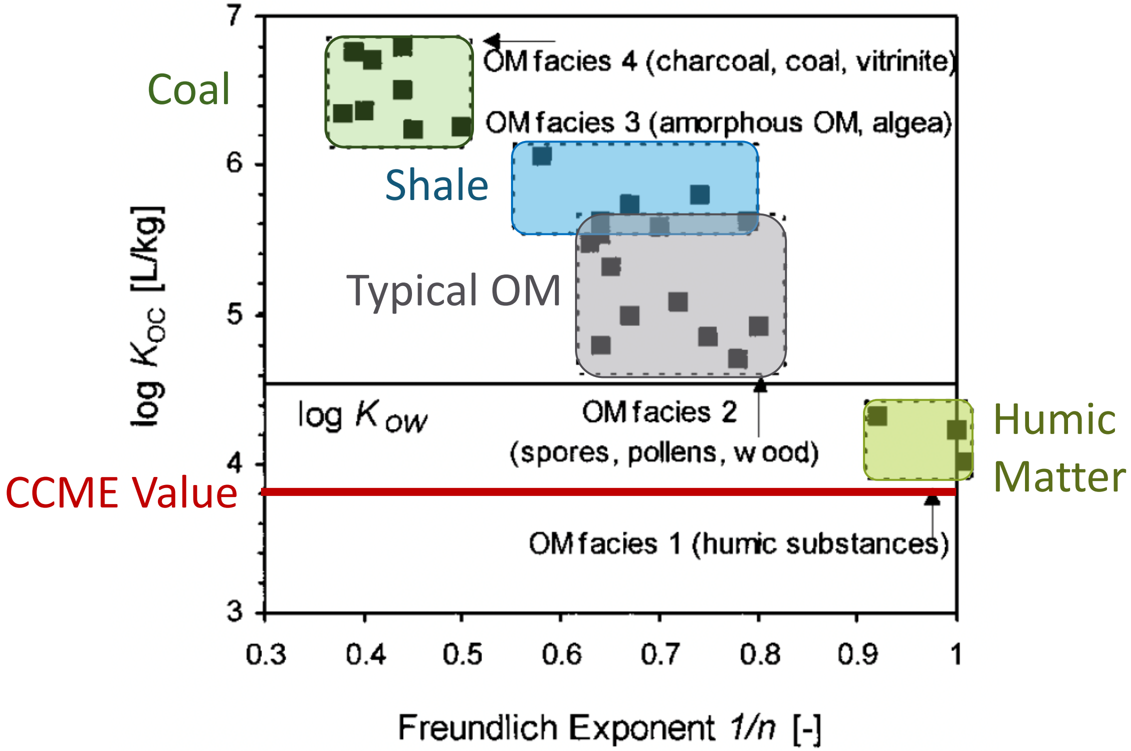
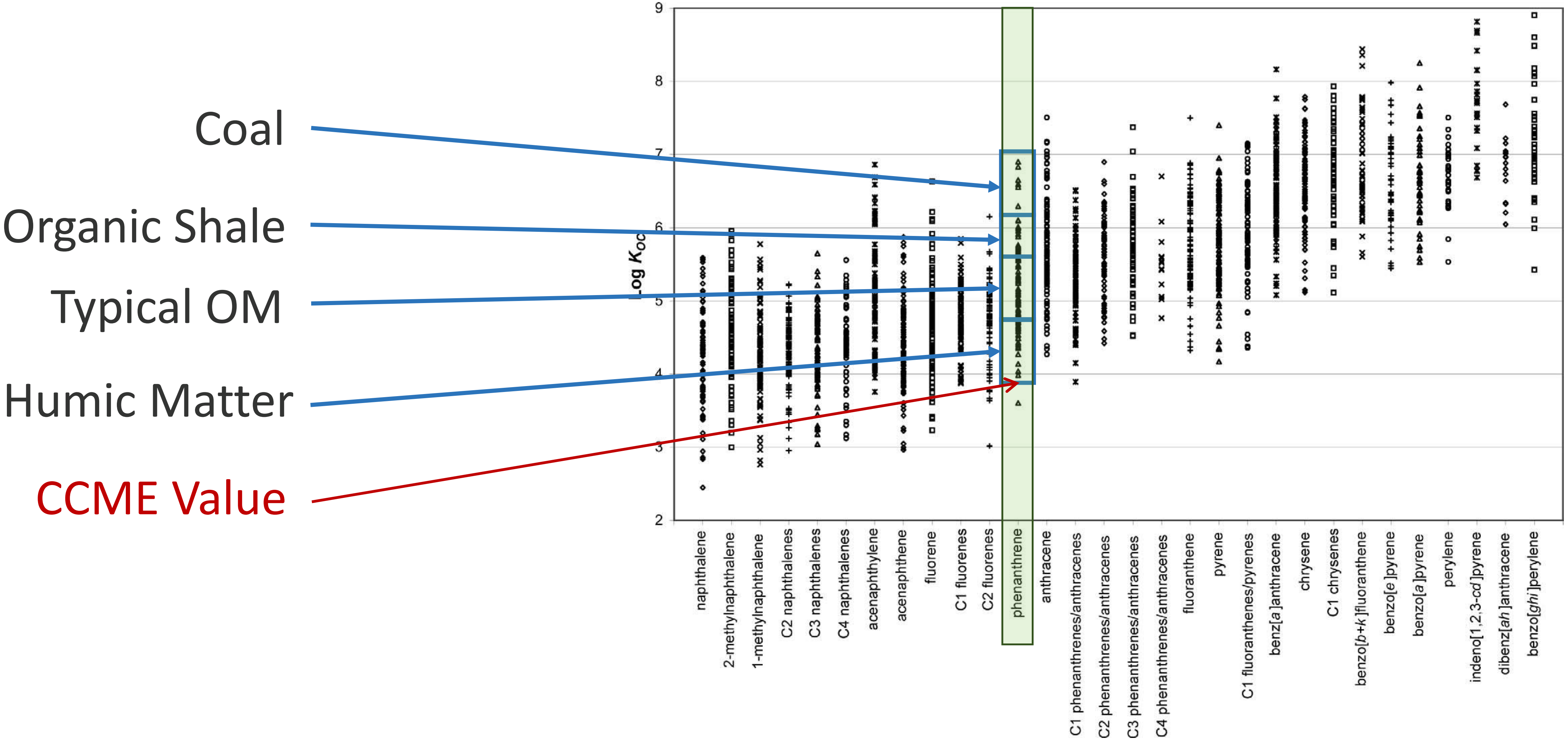
Effect of Source on K_{OC} Values

- Source-specific K_{OC} values were understood in 1999
- Broad range of K_{OC} values
- Example of phenanthrene
    - Min: 3.6
    - Mean: 5.2
    - Max: 6.9
    - CCME: 3.82
- Source is a big driver of K_{OC} values



Kleineidam, S., Rugner, H., Ligouis, B., Grathwohl, P. (1999). *Organic Matter Facies and Equilibrium Sorption of Phenanthrene.* Environmental Science and Technology, 33, 1637-1644.

Effect of Source on K_{OC} Values



Coal

Organic Shale

Typical OM

Humic Matter

CCME Value

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Effect of K_{OC} Values on Guidelines – Phenanthrene

$$\underset{\uparrow}{SQG_{FAL}} = C_L \left\{ \underset{\uparrow}{K_d} + \left(\frac{\theta_w + H'\theta_a}{\rho_b} \right) \right\}$$

$$\underset{\uparrow}{K_d} = \underset{\uparrow}{K_{OC}} \times f_{OC}$$

Phenanthrene				
	Literature Min	CCME	Literature Mean	Literature Max
LogK_{OC} Value	3.60	3.82	5.20	6.90
K_{OC} Value	3,981	6,607	158,489	7,943,282
Soil Guideline*	0.036 mg/kg	0.11 mg/kg	NGR	NGR
Governing Pathway	Freshwater Aquatic Life	Freshwater Aquatic Life	Exceeds Solubility Limit	Exceeds Solubility Limit

*Residential land use, fine-grained soil, Alberta-specific inputs for groundwater infiltration rates

Further Regulatory Guidance

- Solubility limits
  - When K_{OC} values are high, partitioning of PAHs from soil to groundwater is low
  - When partitioning from soil to groundwater is very low, no scenario may exist where groundwater concentrations could exceed a toxicity threshold and thus no guideline is required for that pathway.
  - For coal, this would occur at least two orders of magnitude lower with a coal-specific K_{OC}.
    - Min K_{OC} value of phenanthrene from coal = 1,995,262 L/kg
    - Solubility of phenanthrene maxes out with $K_{OC} \approx$ 11,800 L/kg
- If coal is the source of phenanthrene, no guideline should be required because solubility limits are exceeded.

CCME. (2010). *Canadian Soil Quality Guidelines. Carcinogenic and Other Polycyclic Aromatic Hydrocarbons (PAHs) (Environmental and Human Health Effects). Scientific Criteria Document (revised).*

Further Regulatory Guidance

- The CCME Scientific Criteria Document for PAH soil quality guidelines states:
    - It should be noted that the calculation of DF1 is highly sensitive to the K_{OC} value used.
    - The K_{OC} for a substance can also vary by as much as three orders of magnitude when determined in the field, depending on various site-specific conditions, such as the forms of organic carbon present in the soil which can vary in their sorption characteristics.
    - Soil-specific K_{OC} (and K_d) values are often higher than default values reported in the literature.
    - Therefore, users may wish to consider calculating Tier 2 SQG_{PW} values by using K_{OC} values derived on a site-specific basis as parameter values for the above equations.

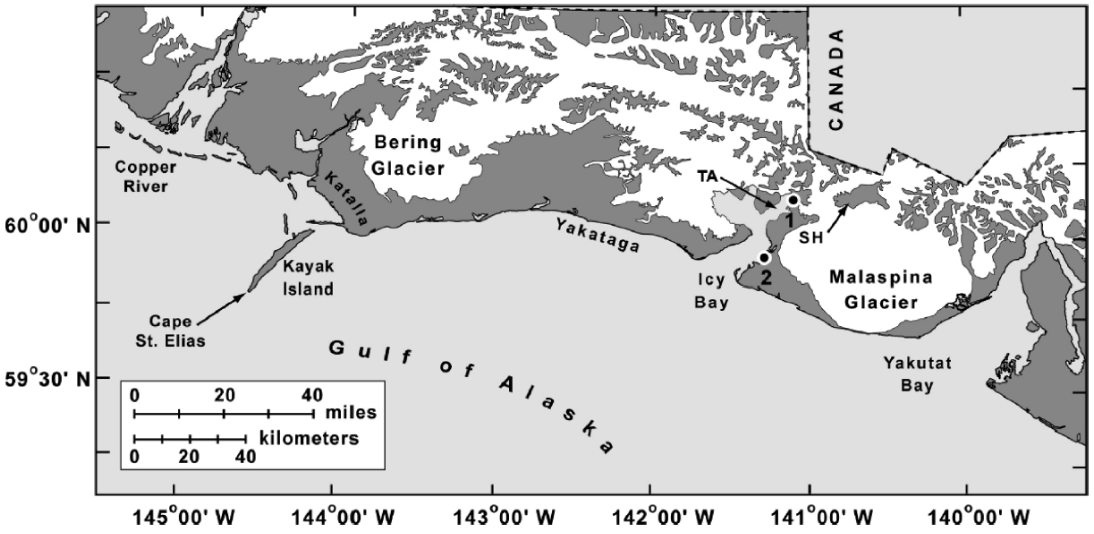
CCME. (2010). *Canadian Soil Quality Guidelines. Carcinogenic and Other Polycyclic Aromatic Hydrocarbons (PAHs) (Environmental and Human Health Effects). Scientific Criteria Document (revised).*

Bioavailability

- Bioavailability refers to the amount of a substance available to an organism at any given time for assimilation and possible toxicity.
- The sorption and desorption mechanisms, which include K_{OC}, have a direct correlation to the bioavailability of PAHs from coal.
- The assumption that 100% of PAHs detected using standard laboratory extraction processes are bioavailable likely overestimates exposure.
  - Laboratory methods use organic solvents to extract PAHs from soils and the aim of the methods is to quantify the total amount of PAHs present in the sample.
  - In choosing strong organic solvents, the resulting extract is not representative of biological processes that will determine bioavailability and will overestimate the potential toxicity of PAHs.
  - When PAHs are present in soil, bioavailability declines to less than 20% (CCME 2008).

Bioavailability – Case Study

- Bioavailability of PAHs from Gulf of Alaska Coals vs Exxon Valdez crude oil
- Coal samples with high PAH content (~4,000 mg/kg) had nondetectable bioavailability when tested using a bacterial biosensor.
- Conversely, the biosensor exposure to PAHs from the Exxon Valdez crude oil exhibited a dose-dependent response.



Deepthike, H.U., et al. (2009). *Unlike PAHs from Exxon Valdez Crude Oil, PAHs from Gulf of Alaska Coals are not Readily Bioavailable.* Environmental Science and Technology, 43, 5864-5870.

Risk Paradigm: Source → Pathway → Receptor

- Source
    - Contaminants of concern
- Receptor
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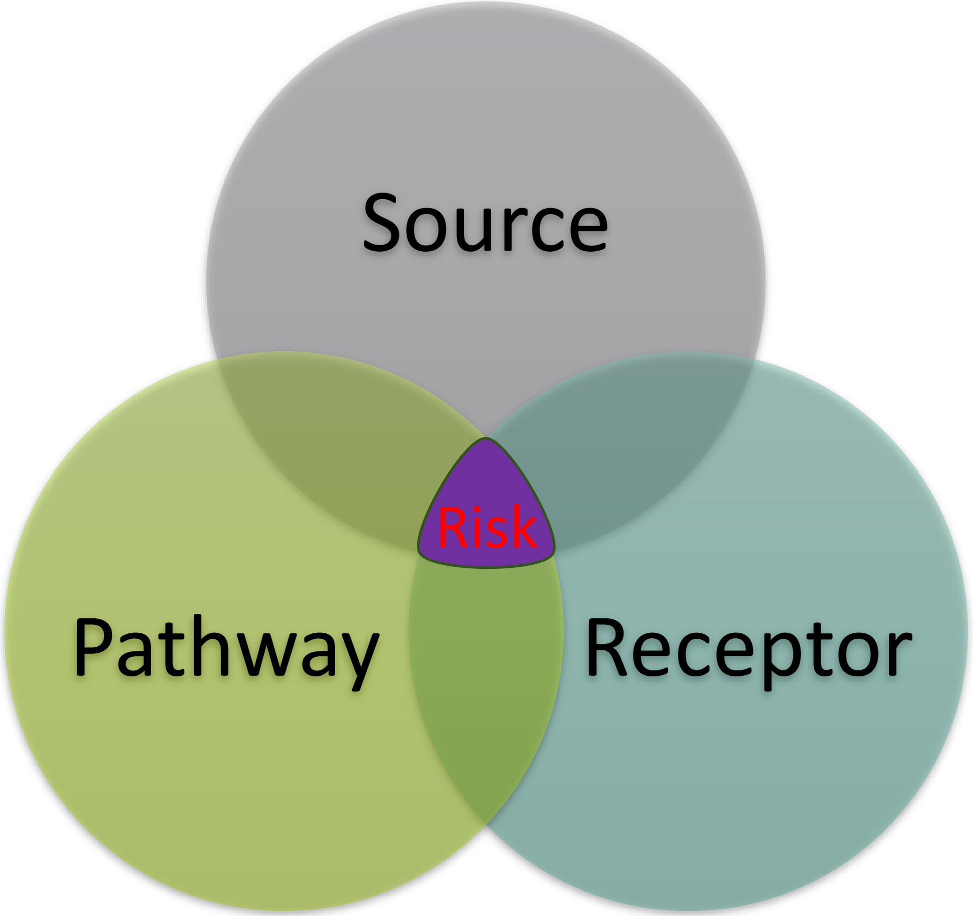
    - Describes how the contaminants get to the receptor
- For risk to exist, all three need to be present



Risk Paradigm: Source → Pathway → Receptor

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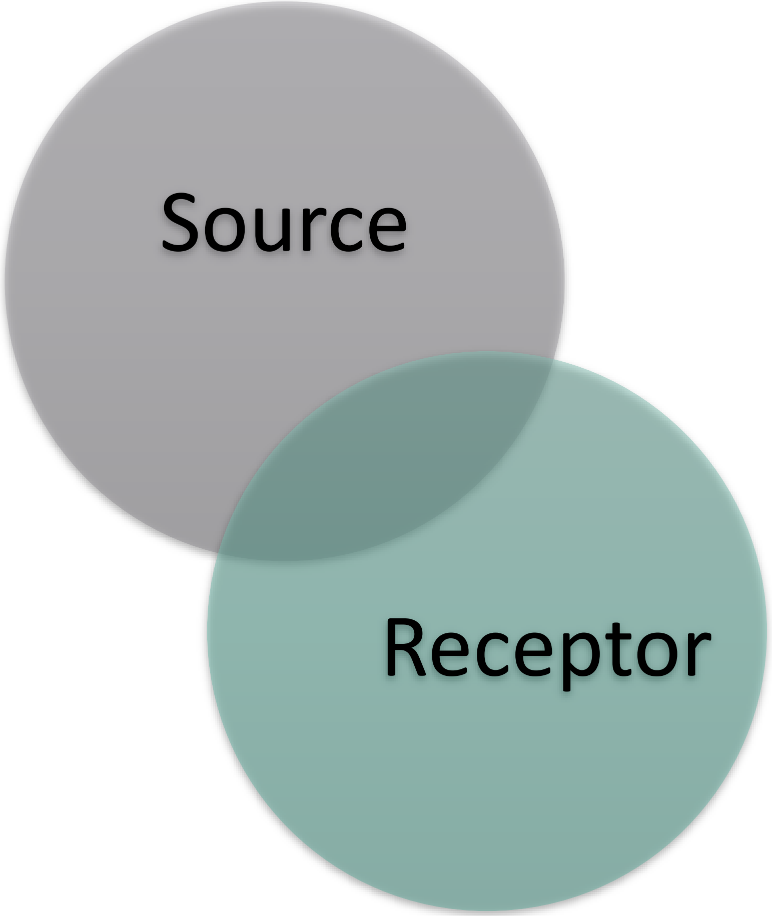
- ~~Pathway~~
    - ~~Describes how the contaminants get to the receptor~~
- ~~For risk to exist, all three need to be present~~

If there is no mechanism for the source to reach the receptor, does Risk exist?



Key Takeaways

- Guidelines are built on assumptions that are generic
- Source identification is important
  - Investigate source origin rather than assuming human-caused impacts
- Natural PAHs behave differently in the environment
  - May not fit with a simple conceptual site model for a contaminated site
  - As the K_{OC} increases, so does the guideline
- Opportunity to do better if we know the source of PAHs

Thank you!

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