Does oil toxicity increase as it weathers??

Answer: It depends!!

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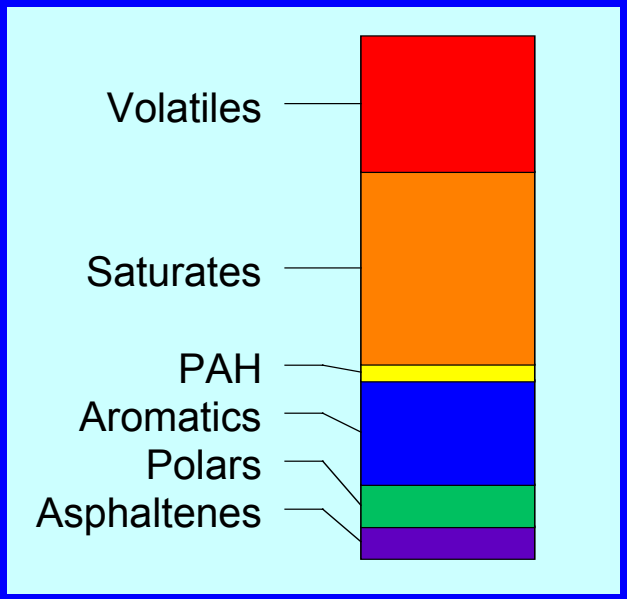
It depends on the composition of the oil and the conditions under which it weathers in the environment



Compositional Variability

- May consist of hundreds (gasoline) to thousands (middle distillate, residual fuels, crude oils) of hydrocarbons
- Natural or remediation-enhanced weathering of hydrocarbons in sediment substantially alters its composition, physical/chemical properties, toxicity

Measurement Considerations

- Measurement methods for TPH are by definition ***operational***
- Select the method(s) most appropriate to project goals

It depends on how you measure the exposure concentration of oil (the dose)

MAH contribute most to the toxicity of WAFs of fresh crude oil
Measured as a hazard index (HI)

Oil WAF	MAH	PAH	Phenols	Total HI
Fresh Wonnich	2.57	0.29	0.14	3.00
Wonnich 150°C+	NA	0.58	0.08	0.66
Wonnich 200°C+	0.53	0.93	0.12	1.58
Fresh Campbell	2.23	0.07	0.05	2.35
Campbell 150°C+	1.60	0.18	0.08	1.86
Campbell 200°C+	0.26	0.42	0.05	0.73
Fresh Agincourt	NA	0.03	<0.001	0.03
Agincourt 150°C+	0.03	0.04	<0.001	0.07
Agincourt 200°C+	0.03	0.14	0.002	0.17
Agincourt 250°C+	NA	0.06	<0.001	0.06
Fresh Diesel	0.12	0.30	0.07	0.49
Diesel 200°C+	0.11	0.24	0.05	0.40
Diesle 250°C+	0.02	0.77	0.03	0.82

It depends on how you measure the exposure concentration of oil (the dose) - Continued

PAHs become more important as oil weathers, but still don't account for all the oil toxicity: degradation products contribute.

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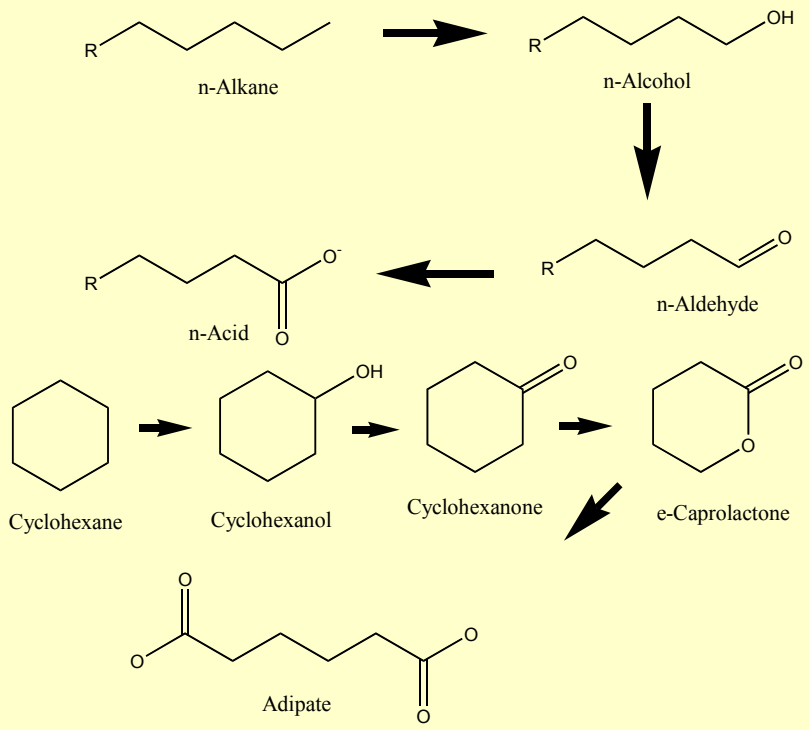
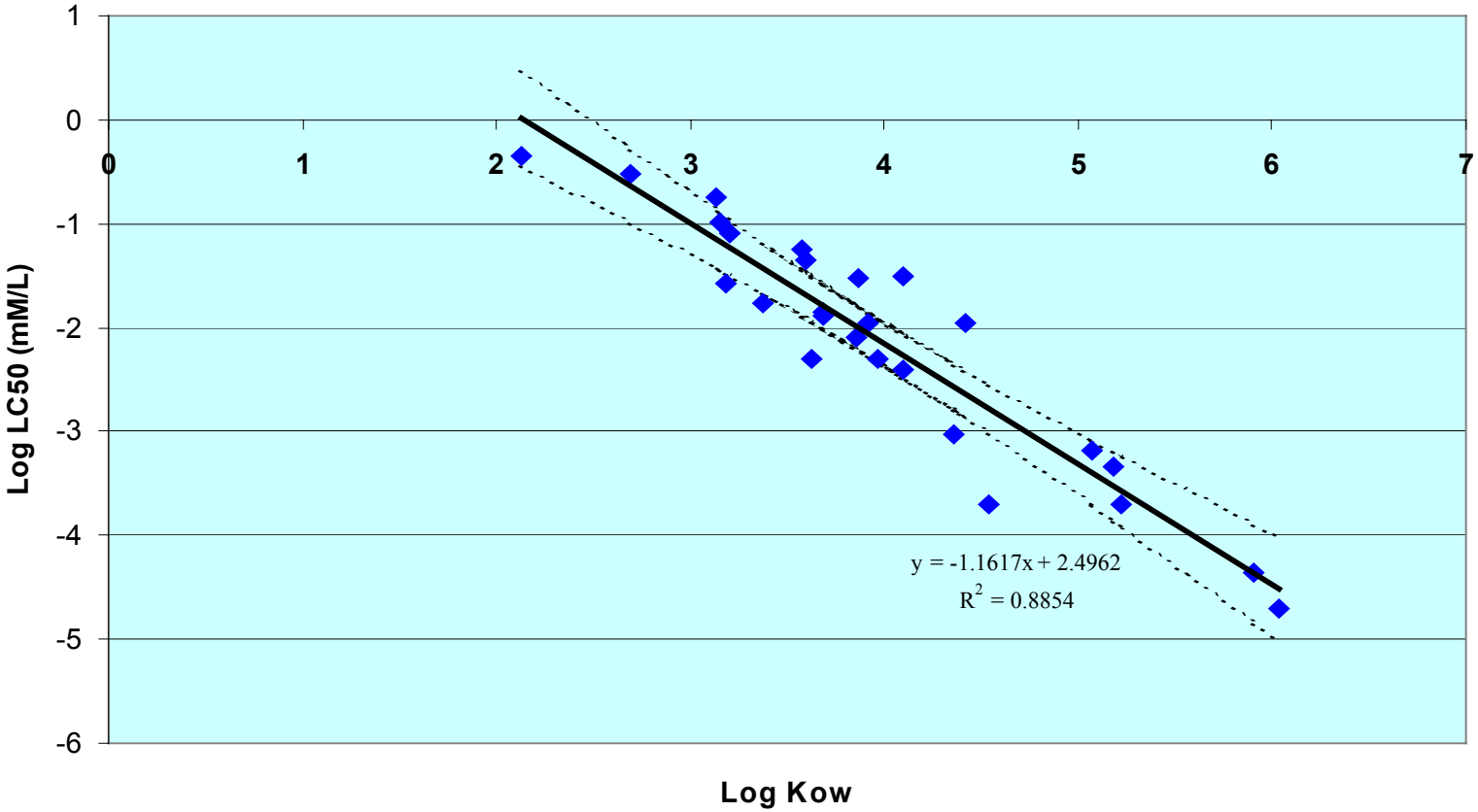
PAH concentration can not be used as a measure of toxic dose

- Chemical composition changes as oil weathers.
- Oxidation products (see right) and degradation products (e.g. ammonia and sulfide) may form and contribute to toxicity.
- Degradation processes different in lab and field – lab results can't be extrapolated to field



Toxicity of PAHs and other oil ingredients increases (LC50 decreases) as MW increases



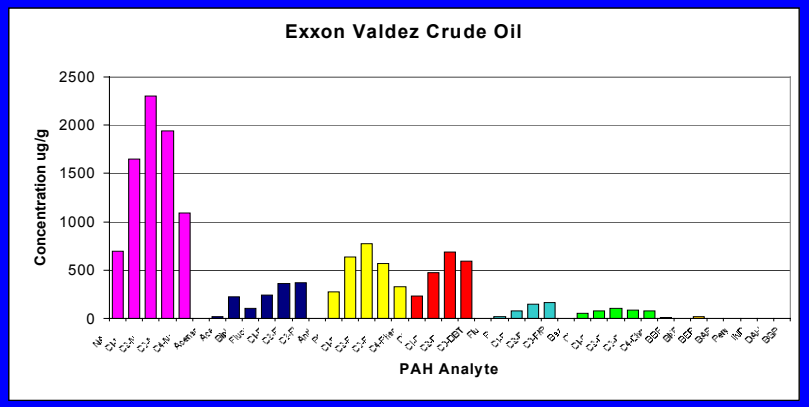
PAH Solubility and LC_{50} decrease with Increasing Molecular Weight. Saturated Solutions of High MW PAHs are not Toxic (S).

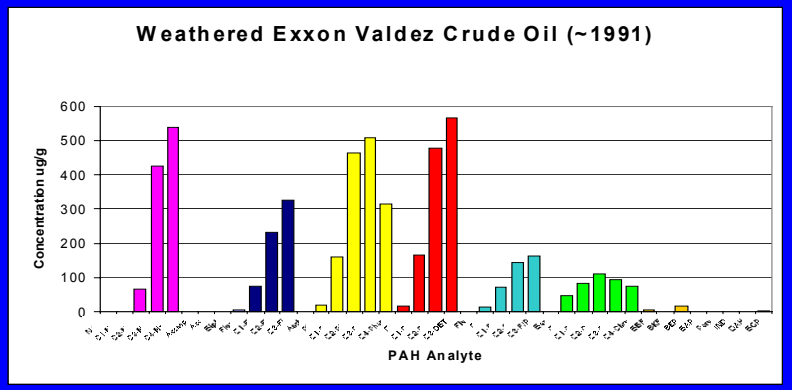
Compound	Solubility (mg/L	LC_{50} (mg/L)
Naphthalene	31	4.88
2-Methylnaphthalene	25	1.46
1-Methylnaphthalene	28	1.42
2-Ethylnaphthalene	8.0	0.38
Biphenyl	7.2	1.42
2,6-Dimethylnaphthalene	1.7	0.48
2,3-Dimethylnaphthalene	2.5	0.38
Acenaphthene	3.8	1.35
Fluorene	1.9	0.72
Phenanthrene	1.1	0.27
Anthracene	$4.6x10^{-3}$	0.29^{S}
1-Methylphenanthrene	0.27	0.064
Pyrene	0.13	0.061
Fluoranthene	0.24	0.054
Benzo(a)fluorene	0.045	0.036
Benz(a)anthracene	0.011	0.01
Chrysene	$1.9x10^{-3}$	0.013^{S}
Benzo(a)pyrene	$1x10^{-3}$	0.008^{S}
Coronene	$1.4x10^{-4}$	0.001^{S}
Benzo(ghi)perylene	$1.4x10^{-4}$	0.002^{S}
Dibenz(a,h)anthracene	$5.8x10^{-4}$	0.001^{S}

S LC_{50} greater than aqueous solubility.

Weathering changes the chemical/physical/biological properties of crude oil

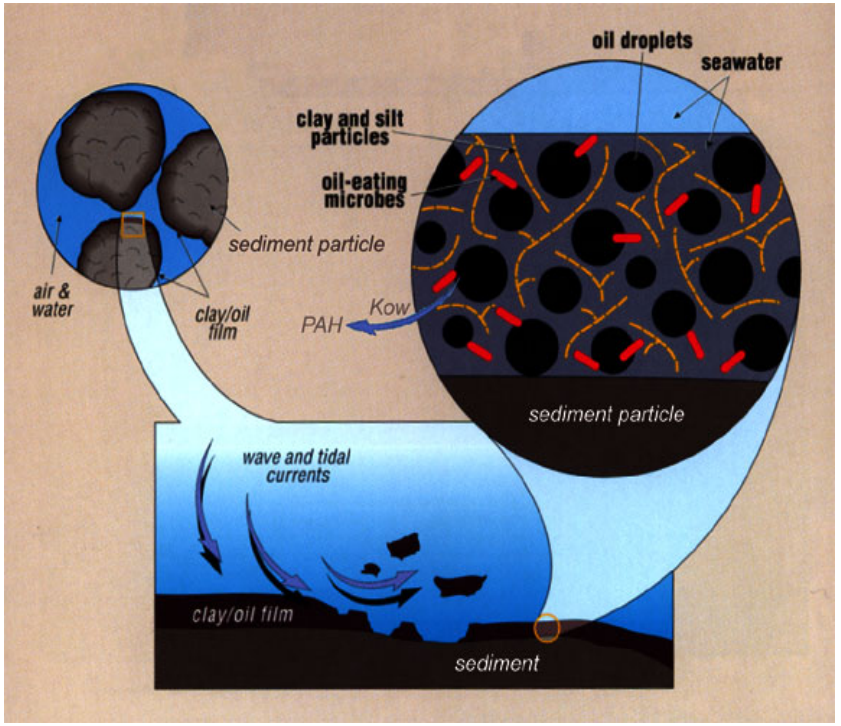
- Low MW PAHs are lost.
- High MW PAHs may be enriched relative to low MW PAHs.
- Oil viscosity and asphaltene concentrations may increase.
- Bioavailability of PAHs from the oil decreases due to decrease in accessibility.



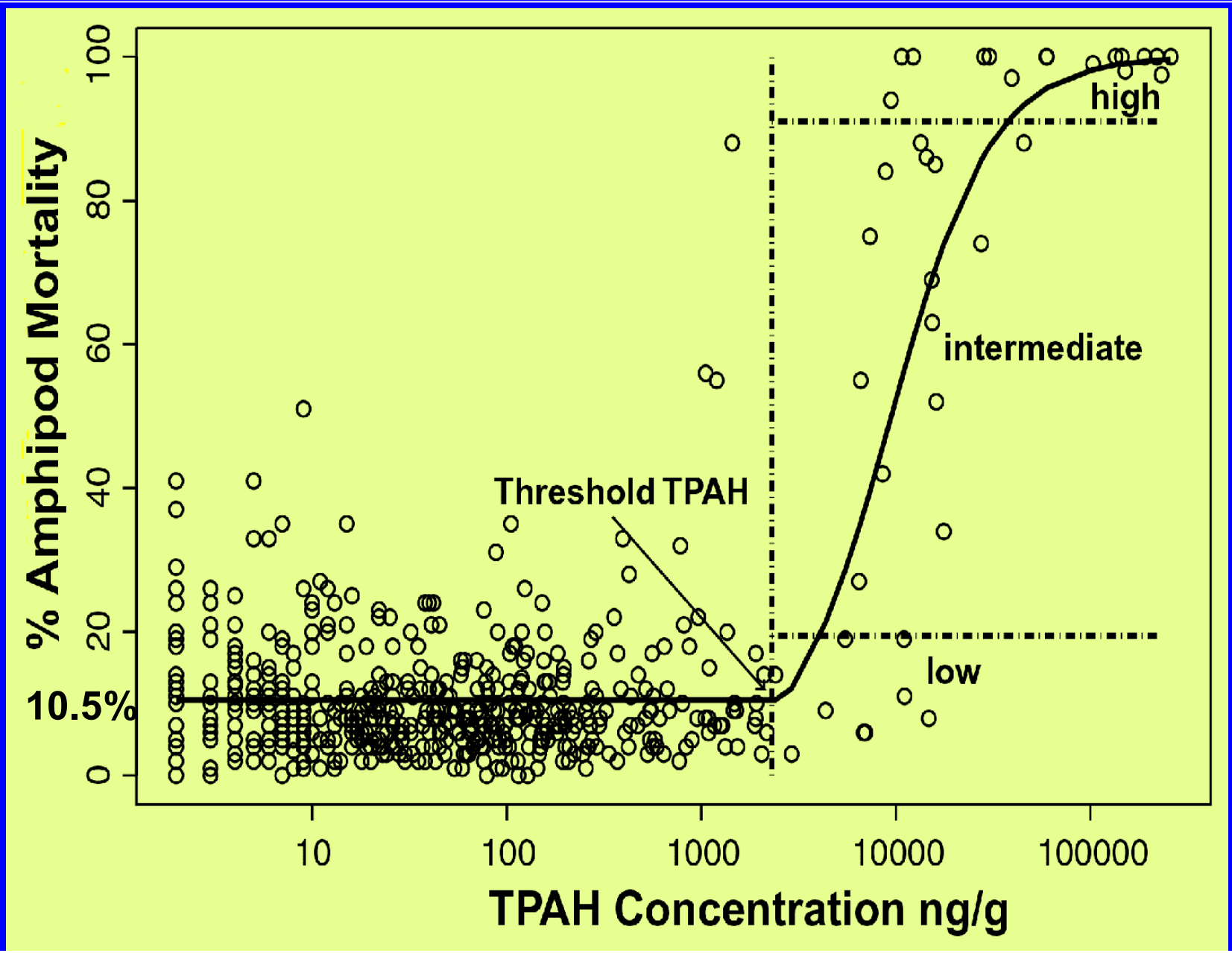


Toxicity of oil buried in shoreline sediments is limited by low accessibility and bioavailability

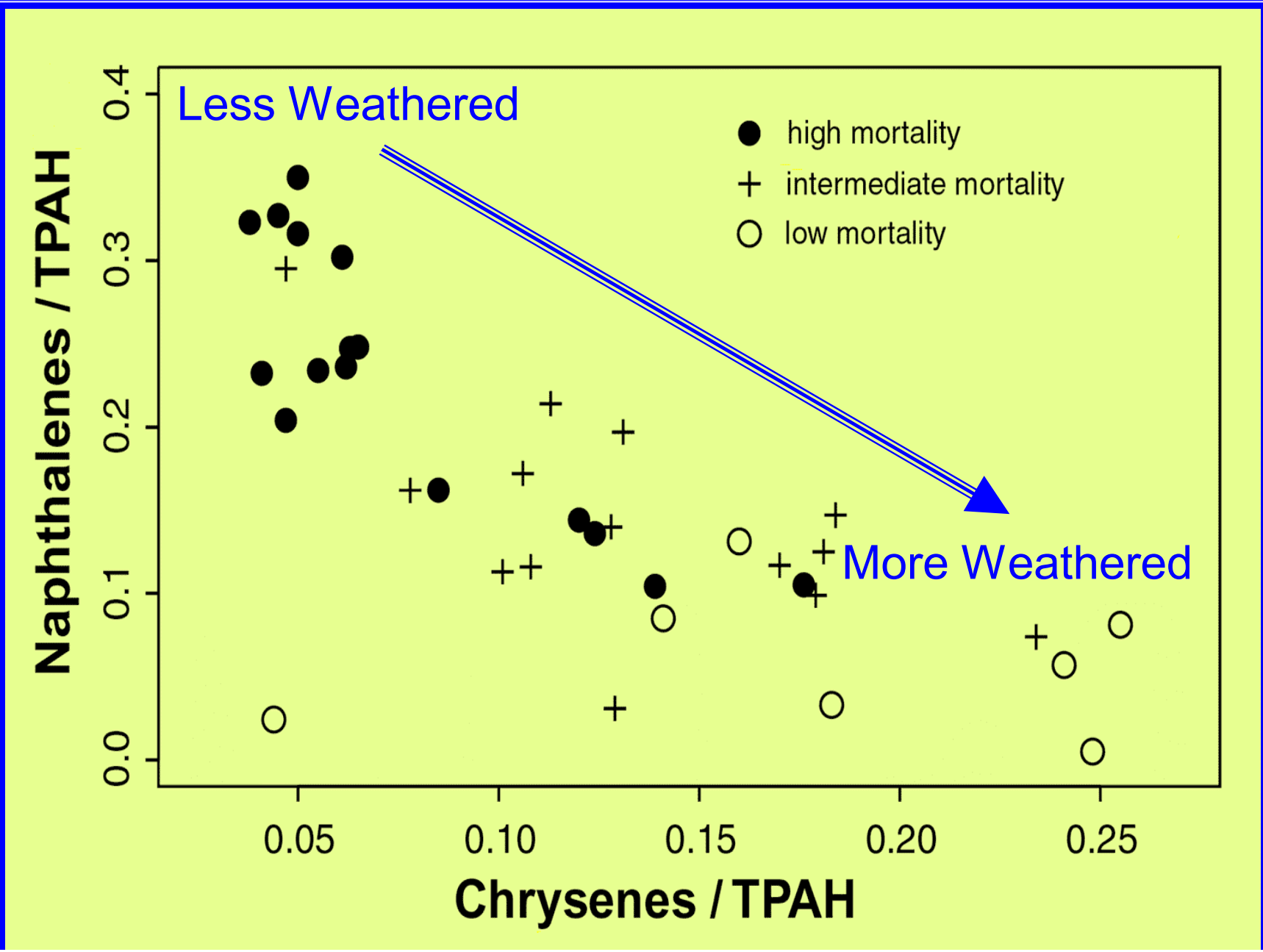
- PAHs partition from oiled sediment into solution in pore water and overlying water (limited by oil/water interface).
- Oily particles may be washed from sediments into pore water and overlying water.
- Partitioning declines with weathering as viscosity increases and oil develops a skin.
- Oil deposit is remote from receptors, limiting contact.



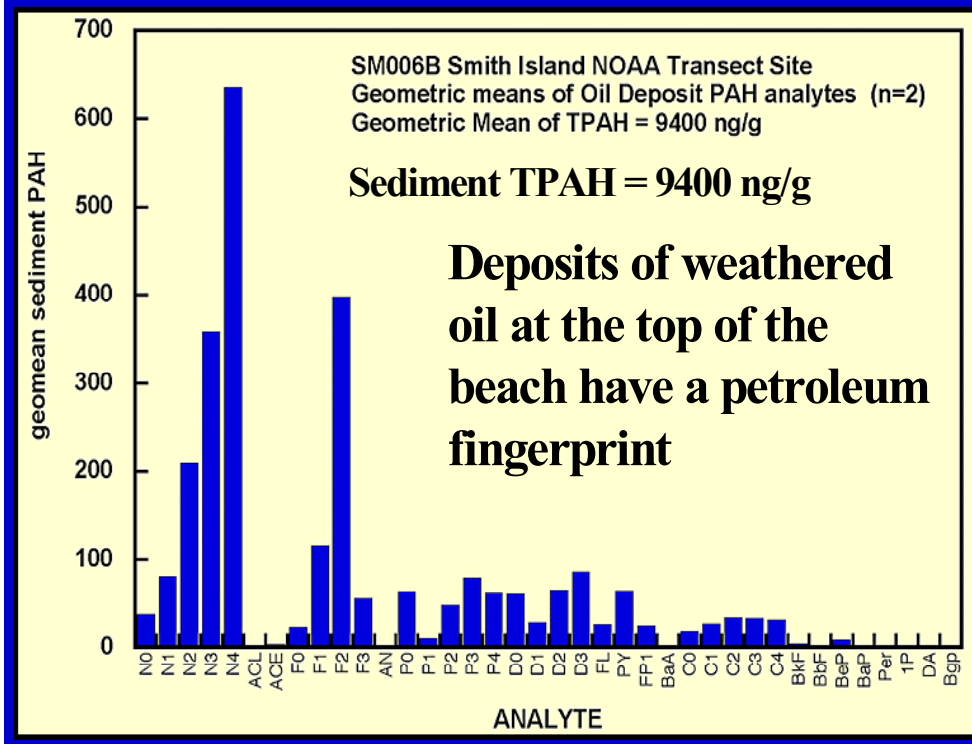
Toxicity of weathered intertidal oil, measured as TPAH, variable due to variable contribution of other oil ingredients and degradation products to toxicity.

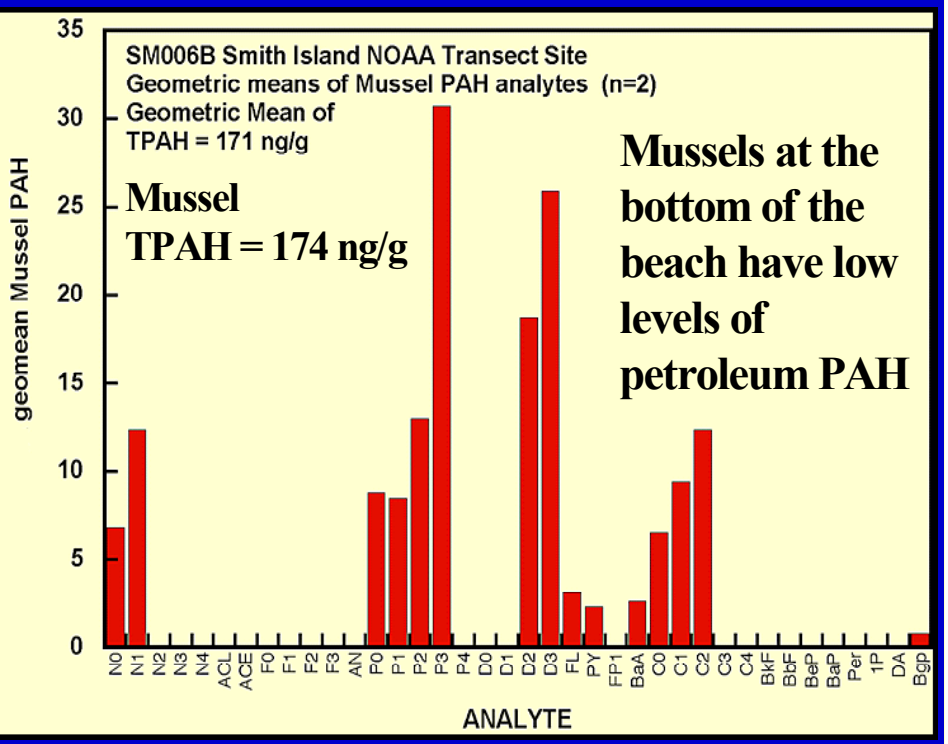


Naphthalene is depleted and chrysene is enriched during oil weathering, yet toxicity decreases. High MW PAHs have low bioavailability.



Smith Island SM006, buried oil has low bioavailability and toxicity



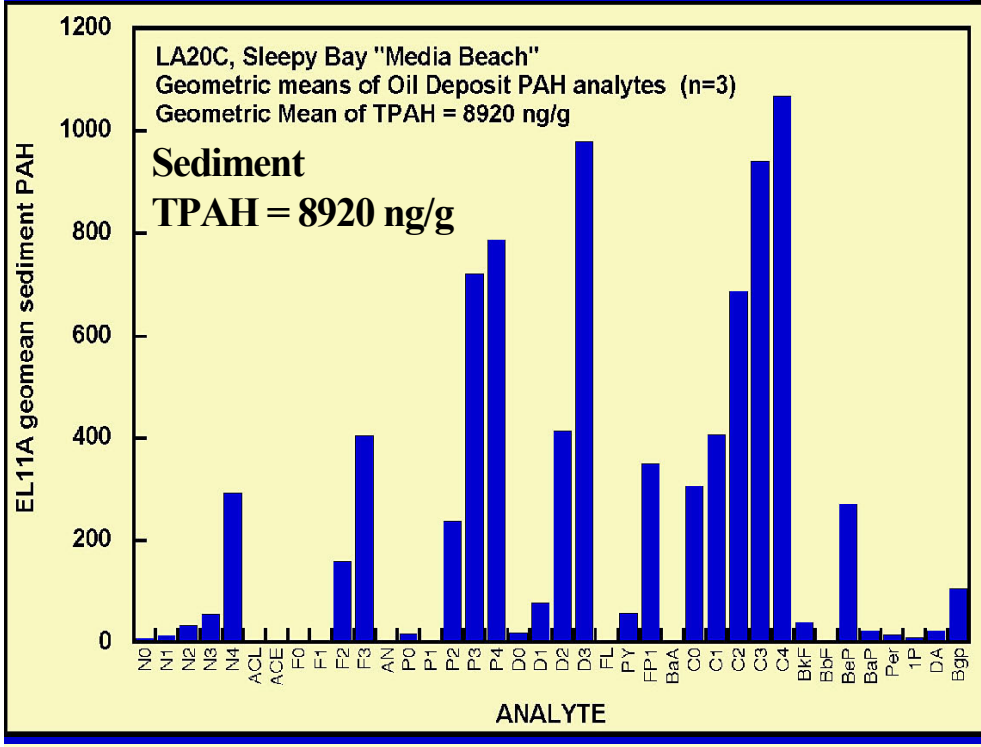


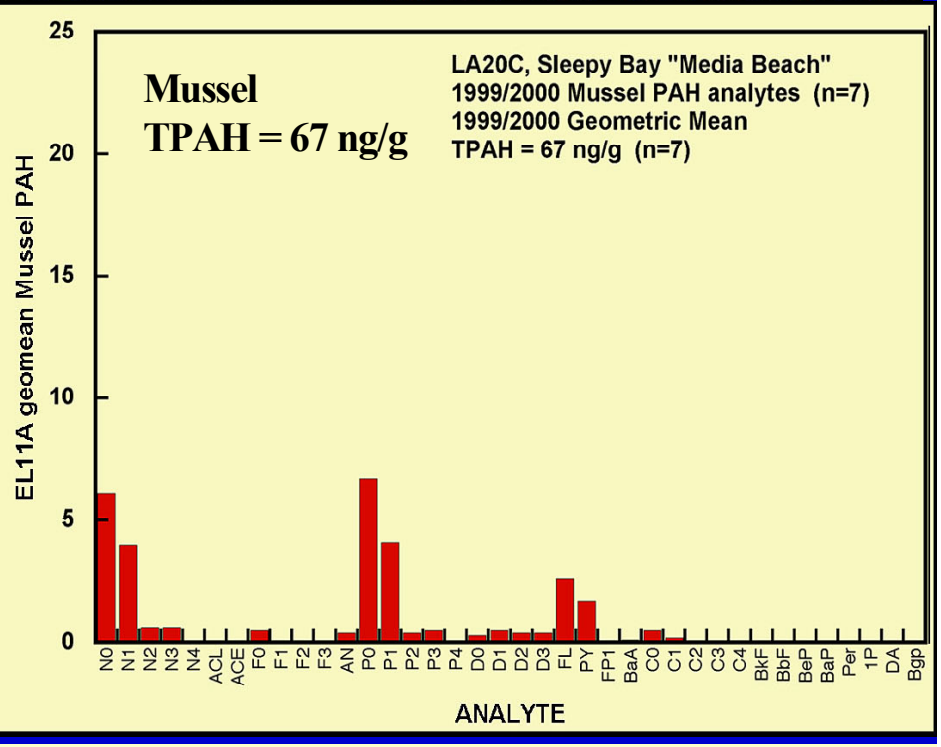
LA20C, Sleepy Bay 2000

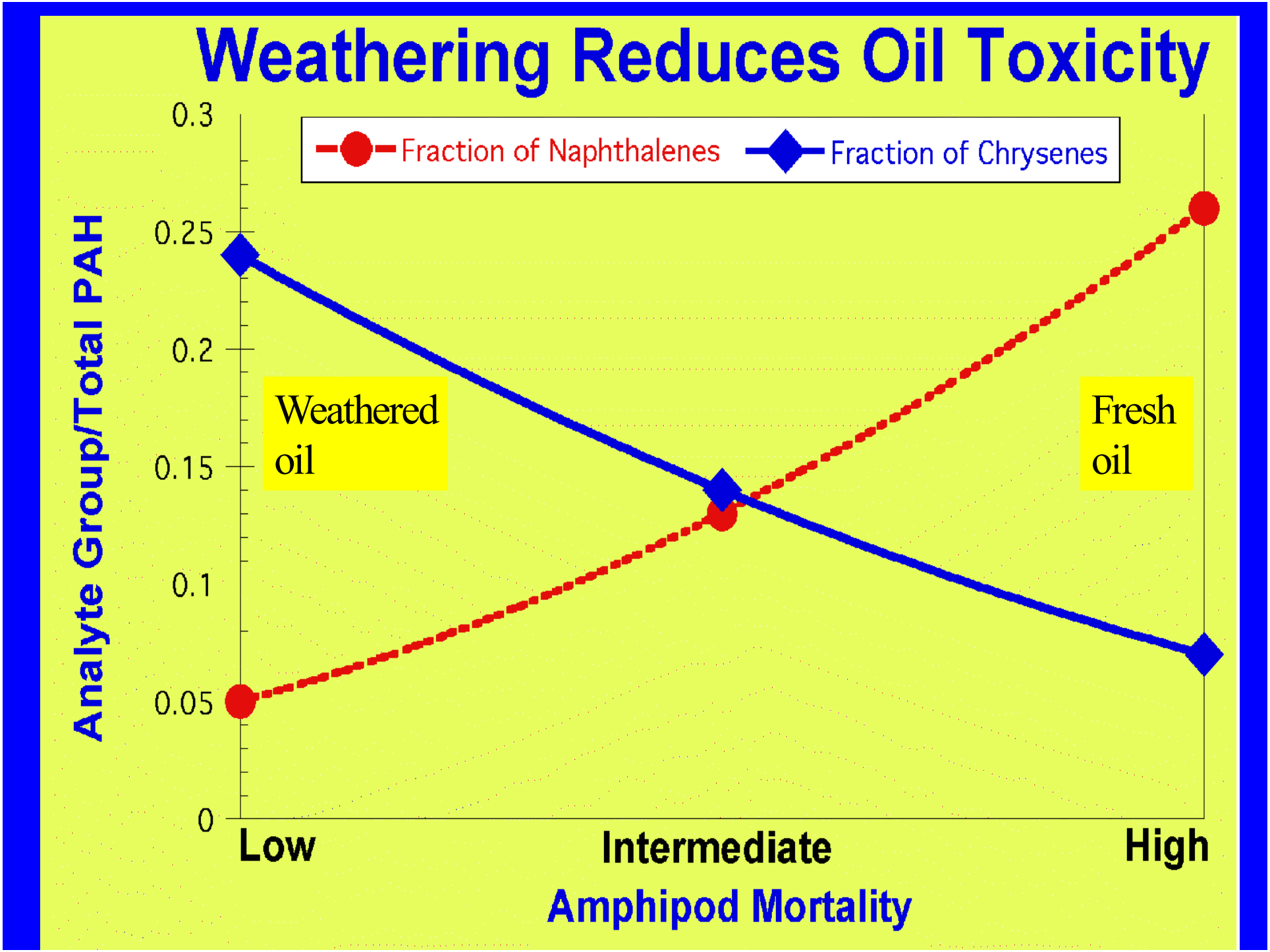
Isolated deposits of very weathered oil at the top of the beach show a petroleum fingerprint.

PAH in mussels at bottom of beach have mostly a pyrogenic fingerprint.

Bioaccessibility and bioavailability decrease as oil weathers.






Weathering Reduces Oil Toxicity
Fraction of Naphthalenes
Fraction of Chrysenes
Analyte Group/Total PAH
0.3
0.25
0.2
0.15
0.1
0.05
0
Weathered oil
Fresh oil
Low
Intermediate
High
Amphipod Mortality

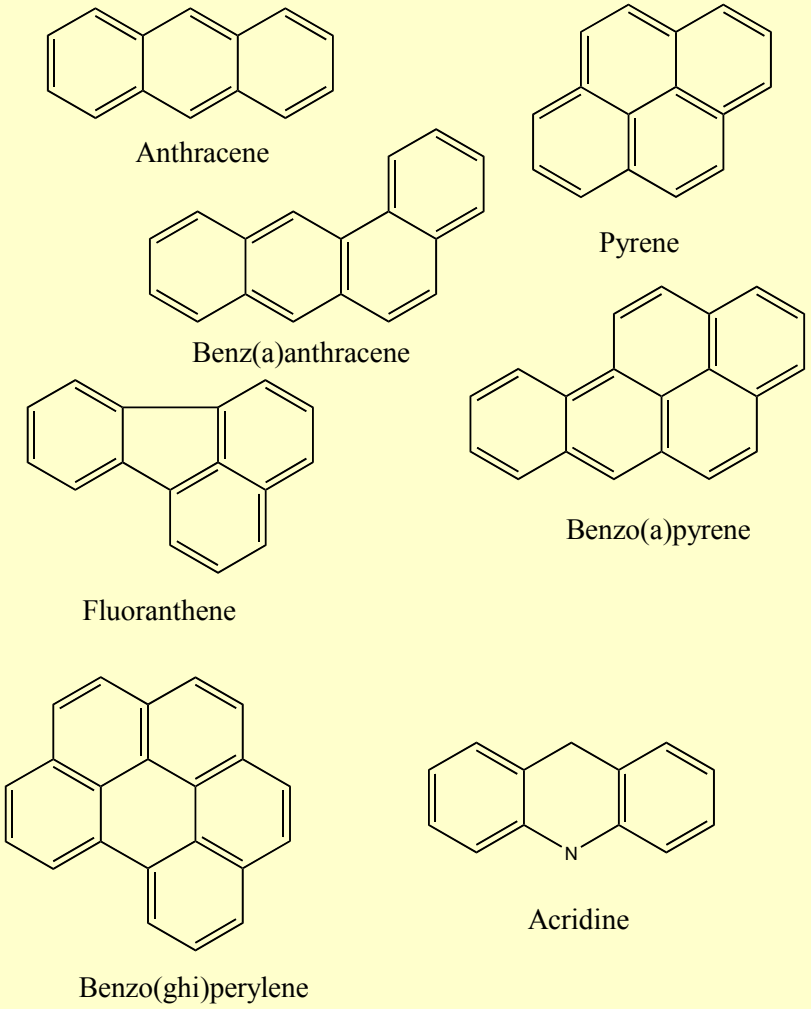
Does Oil Toxicity Increase as it Weathers?

- Answer – No!
  - ✓ If oil on the shore is accessible, it weathers and washes away rapidly.
  - ✓ If oil has low accessiblity, it is persistent but not harmful because:
    - ➢ Hydrocarbon partitioning into water is slow
    - ➢ Oil is isolated from receptors preventing direct exposure.
- Toxicity of oil on the shore decreases as it weathers.

The toxicity of some PAHs is increased by exposure to UV radiation from sunlight

Most of the phototoxic PAHs are more abundant in pyrogenic than petrogenic PAH assemblages.

The influence of phototoxicity on the toxicity of oil spilled in the ocean is poorly understood.



There are two mechanisms of phototoxicity, photosensitization and photomodification

- In photosensitization, the PAH is bioaccumulated and activated by UV to produce oxygen radicals that damage tissues (bottom)
- In photomodification, the PAH is oxidized to a quinone that is more toxic than the parent PAH (top).