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A Simple Approach for Identifying Contaminants of Most Concern to Underground Drinking Water Supplies from Hydraulic Fracturing Operations

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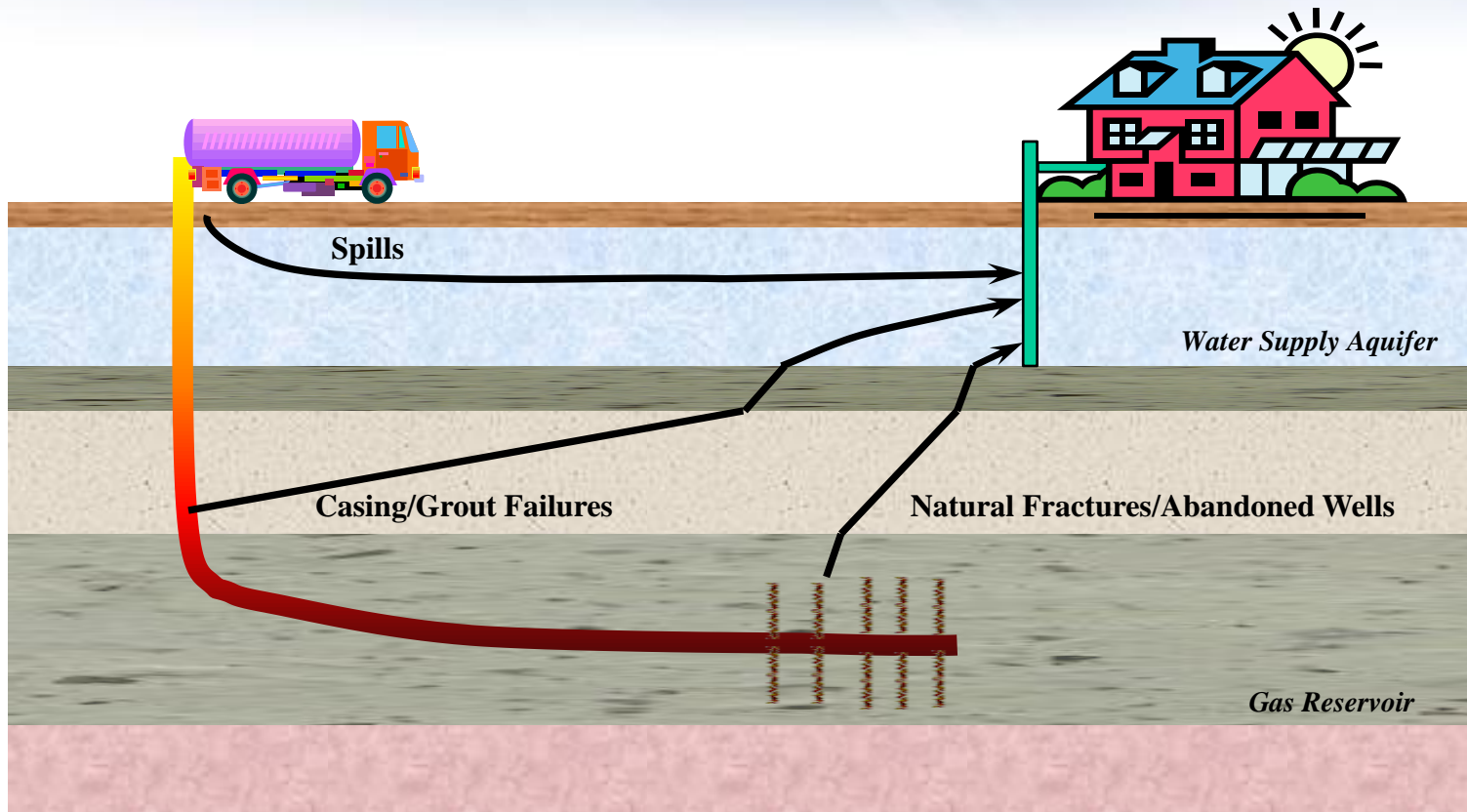
EPA Hydraulic Fracturing Workshop

(Fate and Transport)

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392 Chemicals in hydraulic fracturing fluids
207 Chemicals in flow back and produced waters

(USEPA, 2011)

Objective:

To determine which contaminants are likely to be of most concern with regard to hydraulic fracturing.

Approach:

- Identify contaminants reported from laboratory tests, injection water compositions and from groundwater sampling at field hydraulic fracturing tests,
- Estimate the relative toxicity of the contaminants,
- Estimate the mobility of those contaminants.

Estimate “Toxicity”

- obtain maximum reported aqueous concentration (C_{\max}),
- determine some “safe” contaminant concentration (C_{MCL})
 - drinking water standards (EPA)
 - secondary drinking water standards (EPA)
 - state drinking water standards/guidelines
 - foreign drinking water standards/guidelines (Canada, UK, EU)
 - Identify (e.g., from ATSDR, EPA databases) an oral Maximum Risk Level (MRL) or similar criterion to estimate C_{MCL}
- divide C_{\max} by C_{MCL}

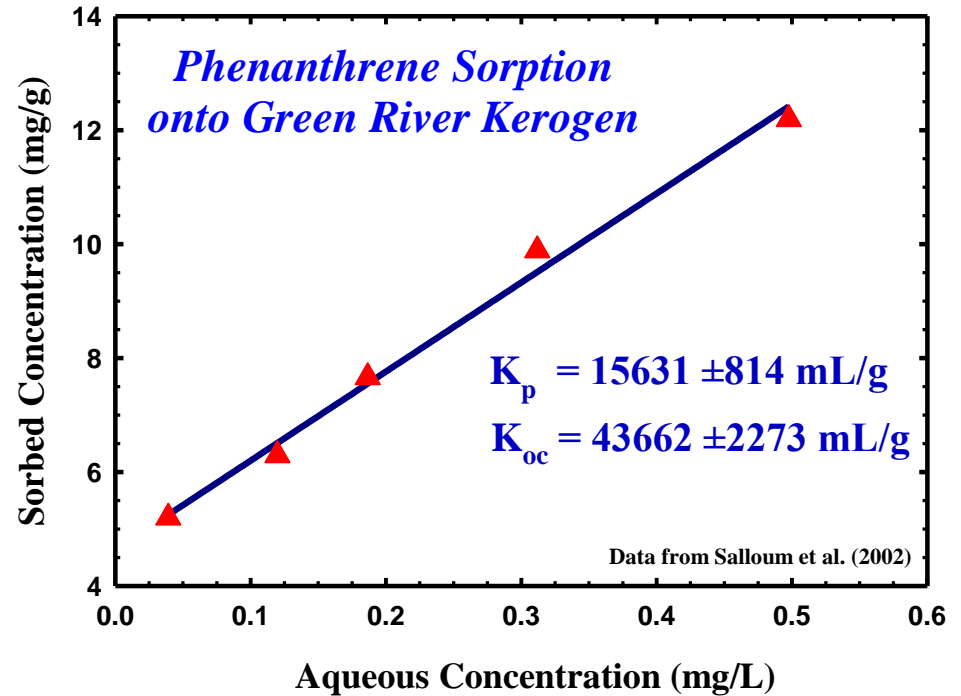
Estimating “Mobility”

- **Estimate retardation factor**
- **Mobility = $1/R$**

Neutral, hydrophobic Organics:

$$R = 1 + \frac{\rho_b}{\theta_w} K_p$$

$$C_s = K_p C_{aq}$$



R = retardation factor

K_p = soil partition coefficient

Neutral, hydrophobic Organics:

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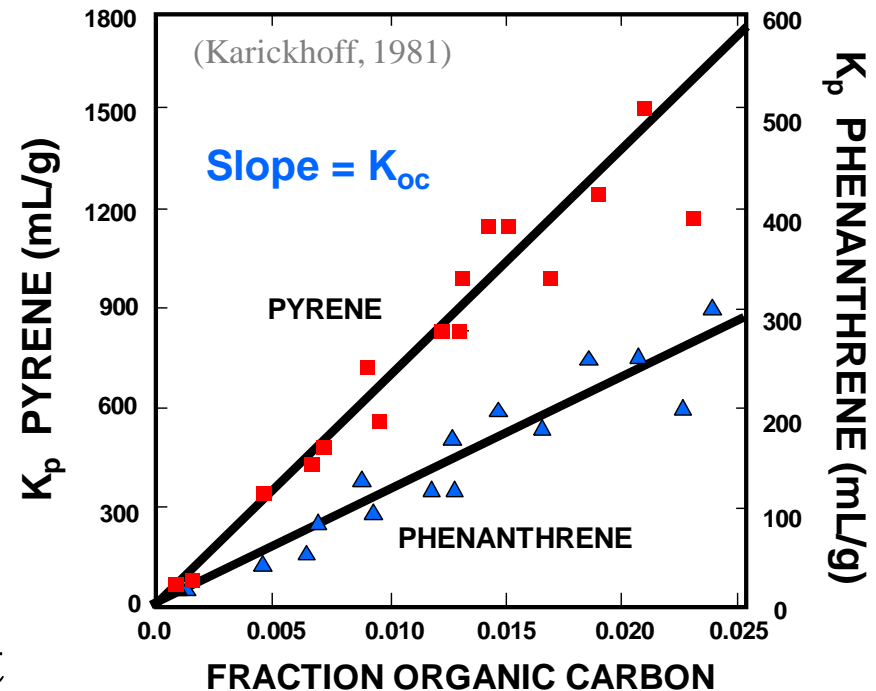
$$K_p = f_{oc} K_{oc}$$

R = retardation factor

K_p = soil partition coefficient

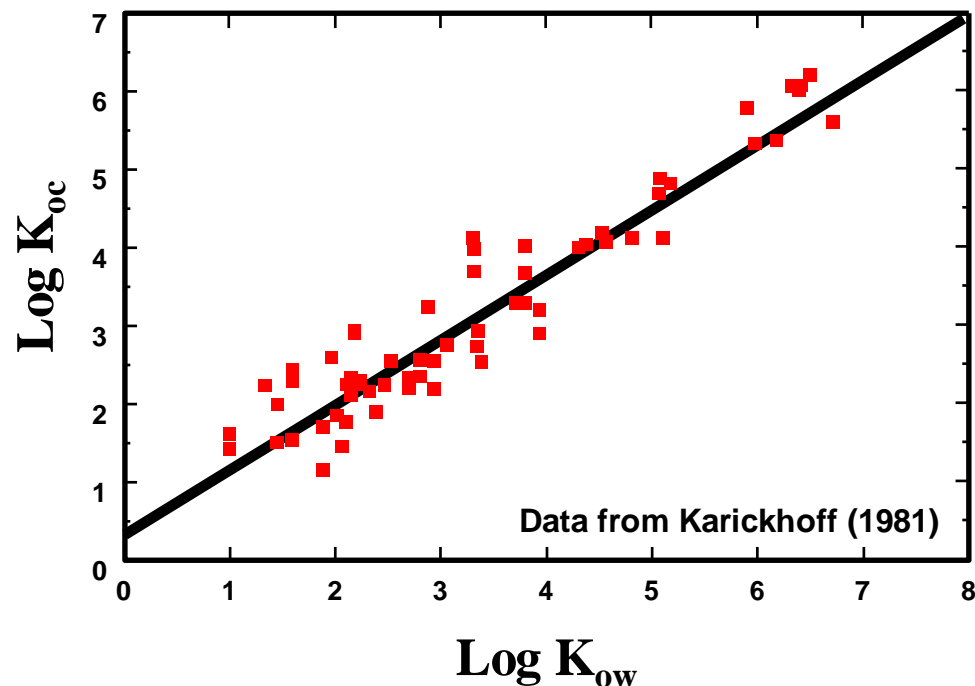
f_{oc} = fraction of organic carbon in soil

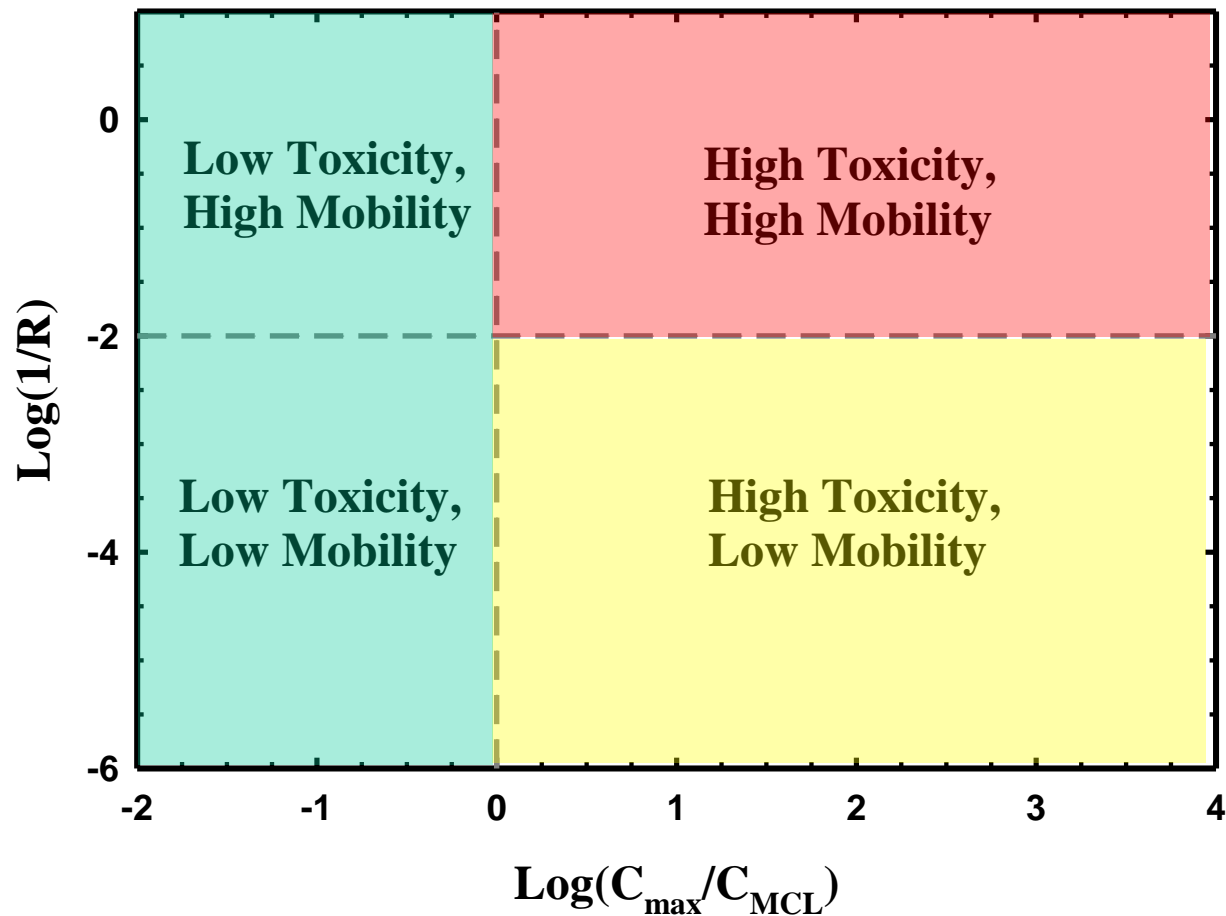
K_{oc} = partition coefficient between aqueous phase
and soil carbon phase



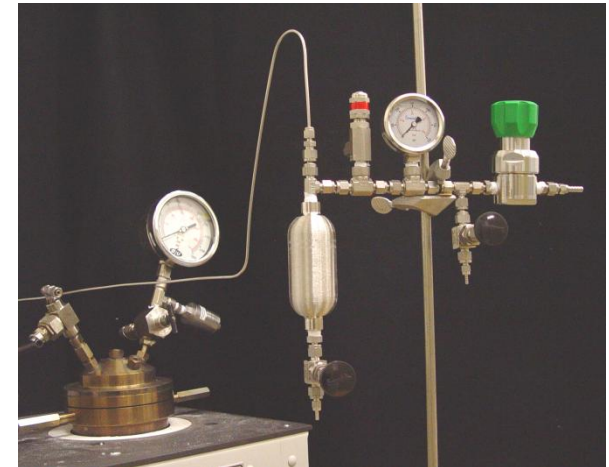
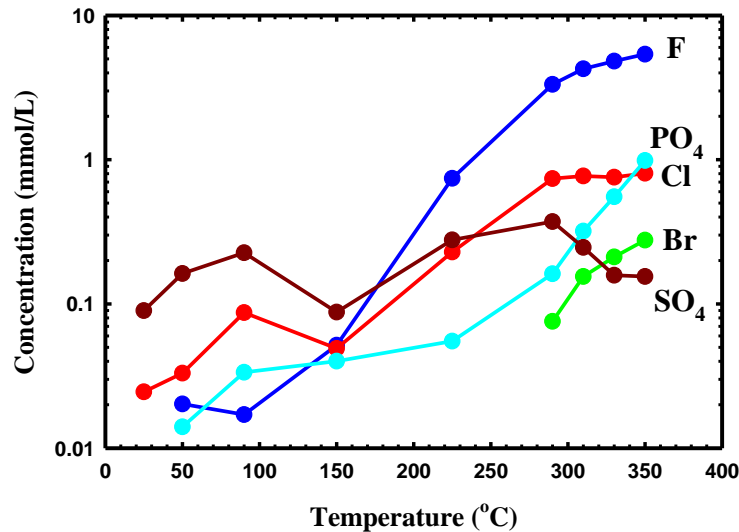
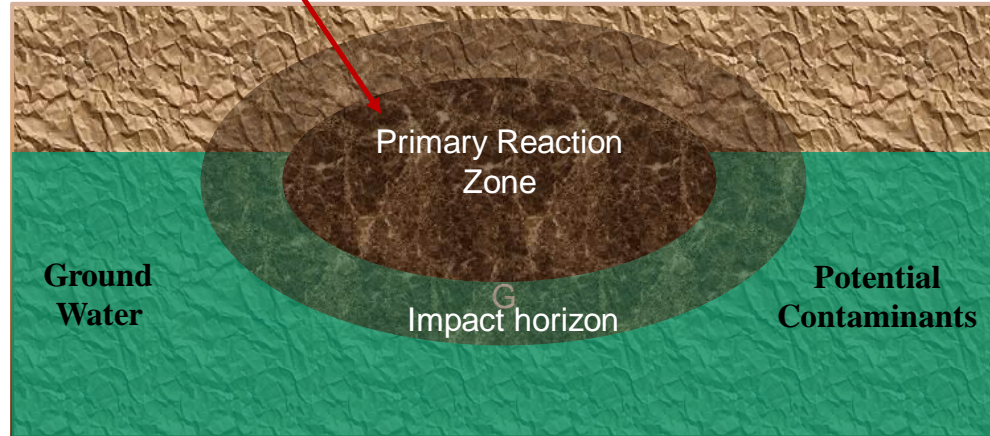
Neutral, hydrophobic Organics:

Empirical and Structure-based relationships between K_{oc} and the octanol-water partition coefficient (K_{ow})





Example: Application to Oil Shale Retorting

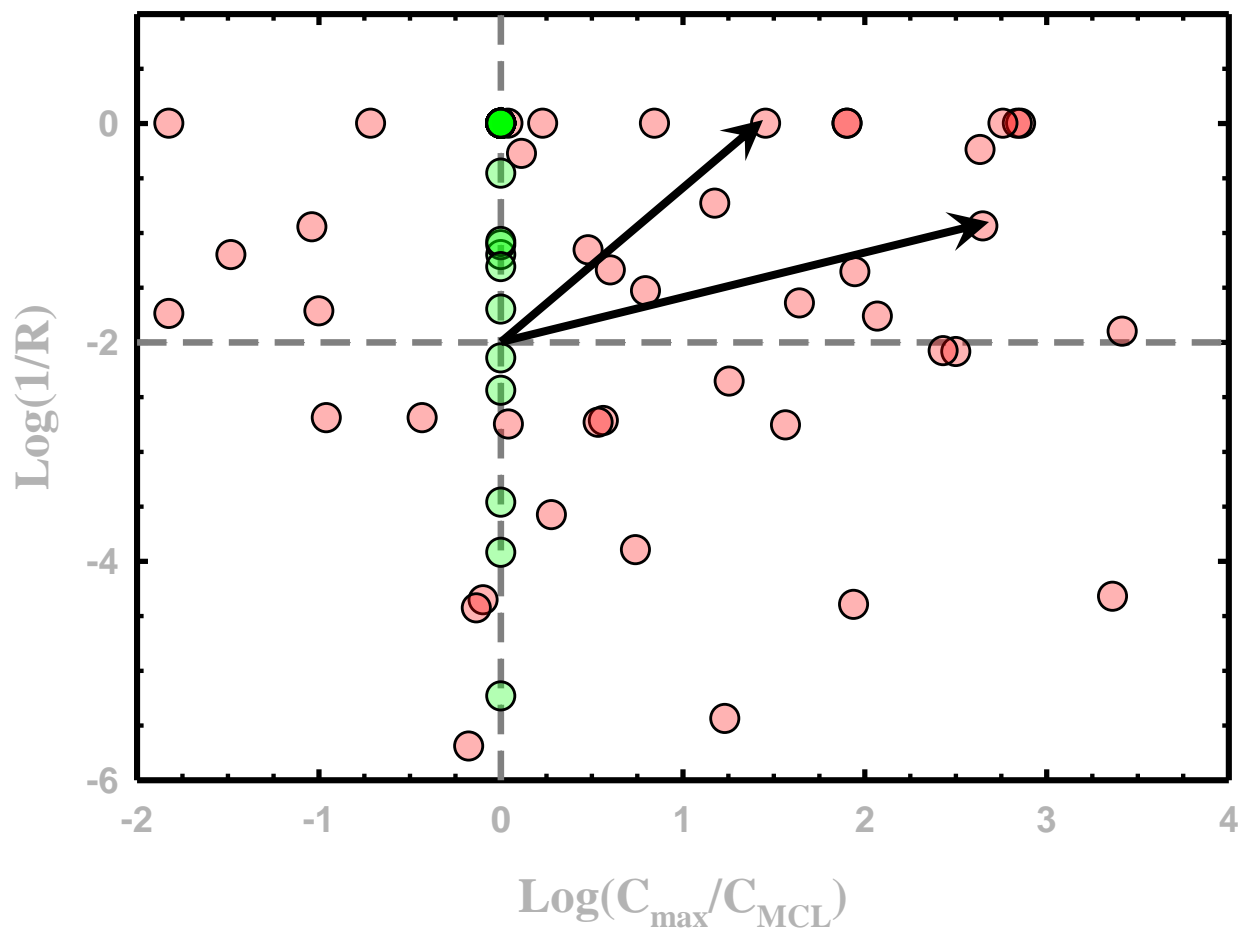


Organic Contaminants

79 Reported Compounds

- **phenols (2,4-dimethylphenol)**
- **ketones (2-butanone)**
- **alcohols (2-ethyl-2-hexanol)**
- **organic acids (benzoic acid)**
- **aromatics (benzene)**
- **nitrogen compounds (pyridine)**
- **alkanes (trimethylcyclohexane)**
- **PAHs (phenanthrene)**
- **halogenated compounds (tribromophenol)**

Organic Contaminants



Organics of Most Concern

Benzene

1-Methylnaphthalene

2-Butanone

Aniline

2-methylphenol

3- and 4- Methylphenol

acetonitrile

Phenol

Thiophene

Pyrrole

2-Methylnaphthalene

Benzidine

Isophorone

Chloroethane

2-pyrrolidone

vinyl chloride

Bromomethane

4-methylphenol

Acetone

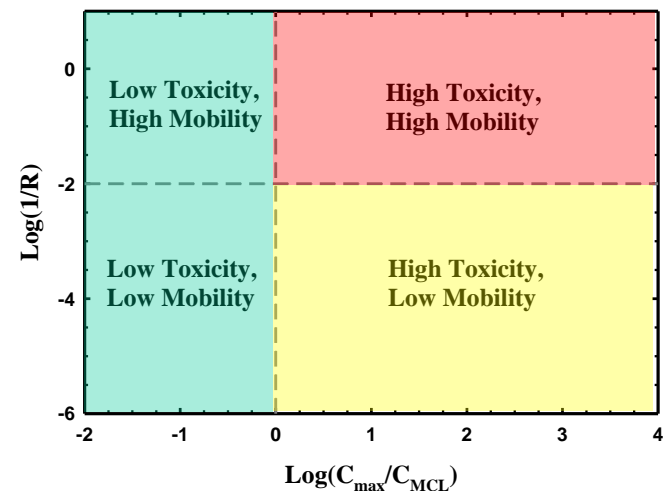
2-Hexanone

Limitations with the Approach

- **Use of maximum observed concentrations,**
- **How to include frequency of occurrence,**
- **Insufficient guidelines or MCLs,**
- **Lack of octanol/water partition data for some compounds,**
- **Partition coefficients are a function of temperature,**
- **Have not included potential biodegradation,**
- **Potential mineral precipitation,**
- **Potential for colloidal transport,**
- **Additional difficulties with fracture flow.**

Summary

- Obtain data (field and laboratory) on concentrations associated with hydraulic fracturing,
- Consider the risk of these contaminants based on their relative mobility and toxicity,
- Create an initial prioritized list of contaminants that should be considered,
- Identify potential contaminants that require additional information.



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The statements made during the workshop do not represent the views or opinions of EPA. The claims made by participants have not been verified or endorsed by EPA.

There is concern that hydraulic fracturing operations for natural gas extraction could potentially contaminate groundwater supplies. We illustrate an approach we have employed for *in-situ* oil shale development to help identify contaminants that are likely to pose the greatest risk based on the contaminants' mobility, concentration, and toxicity. Mobility, addressed from the sorption characteristics of the compounds, is estimated under the expected subsurface geochemical conditions (pH, Eh, total organic carbon) using published experimental data and linear free energy relationships. We use the ratio of the concentration to some guideline concentration (e.g., an MCL) as a measure of the "toxicity" of that contaminant. A plot of mobility versus toxicity provides a simple graphical view of the relative risk for the transport of various contaminants from the near field to the far field. A Euclidean norm centered on a point of unit toxicity and low mobility can be used to order potential contaminants of concern. We illustrate the application of this approach using an oil shale retorting example and discuss limitations in the assumptions and available data. Applying an approach such as this to chemicals used in hydraulic fracturing fluids could help set research and development priorities for additional research.