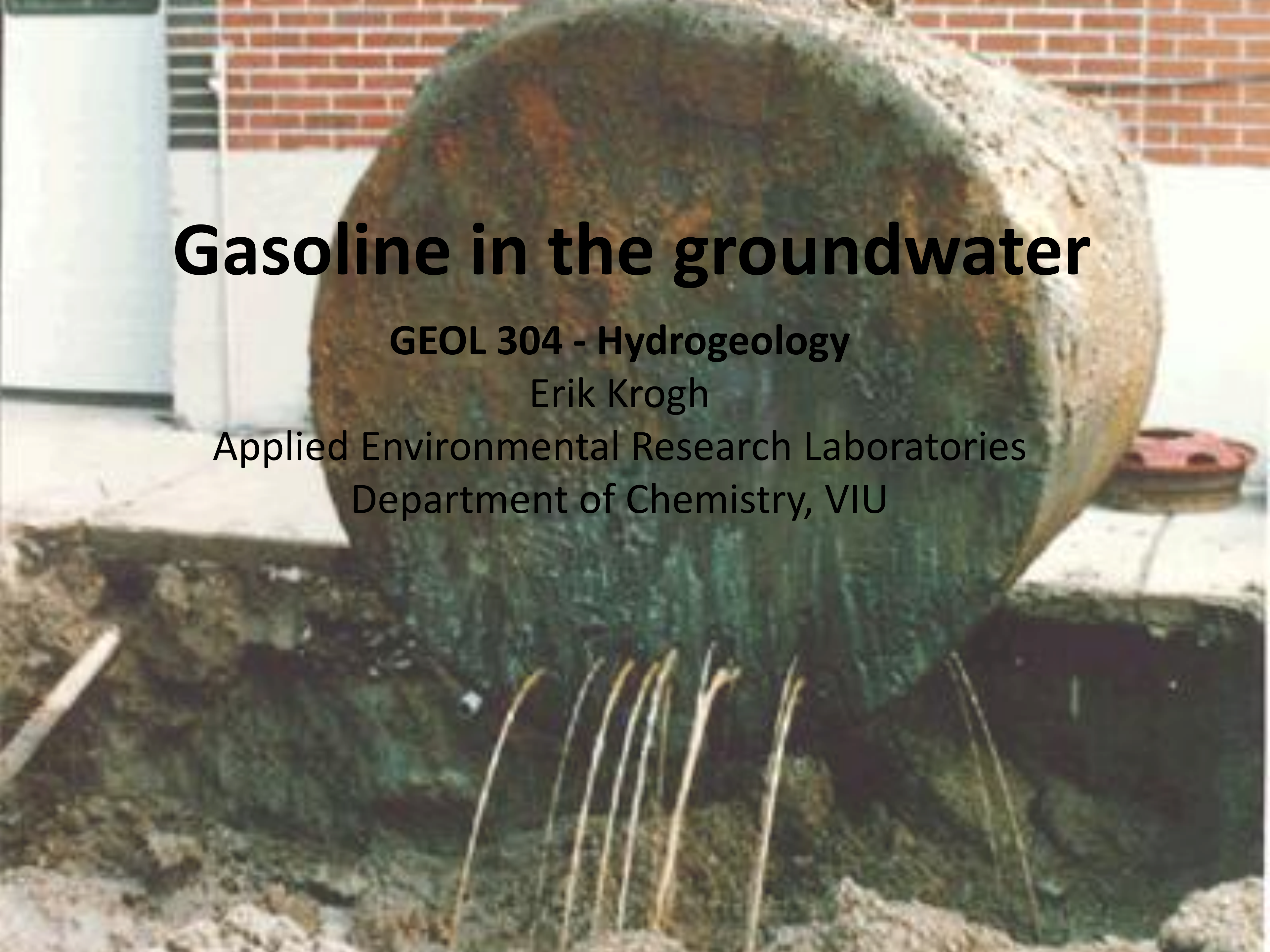


Gasoline in the groundwater

GEOL 304 - Hydrogeology

Erik Krogh
Applied Environmental Research Laboratories
Department of Chemistry, VIU

Outline

Chemical Composition

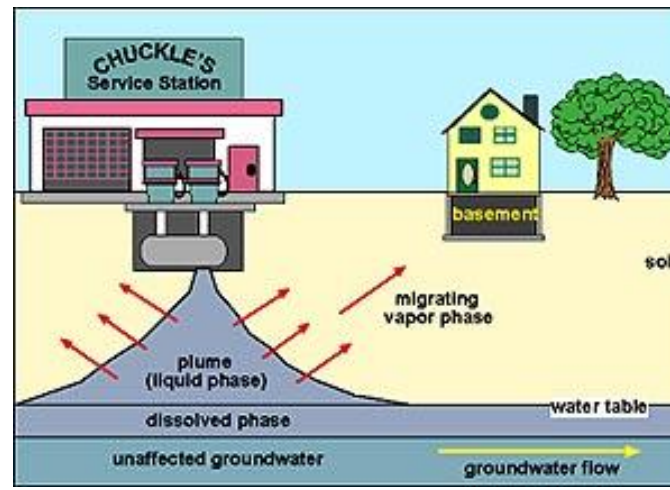
complexity

Refining and Reforming

additives

Physical Properties

vapour pressure, water solubility



Environmental Fate and Distribution

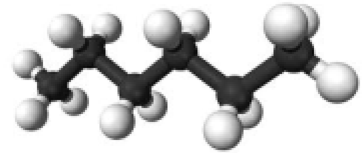
mobility, degradation, sorption

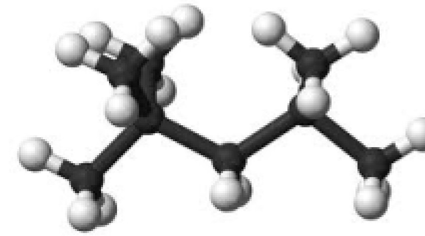
Chemical Composition

Major Hydrocarbon Components ($C_5 – C_{20}$)

Alkanes (C_nH_{2n+2})

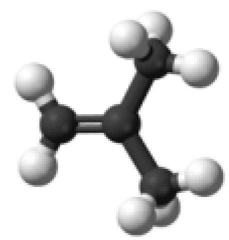
e.g., hexane, isooctane

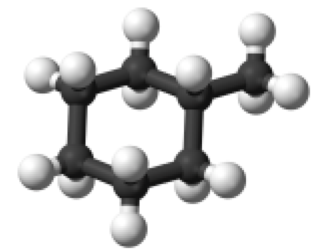




Alkenes & Cycloalkanes (C_nH_{2n})

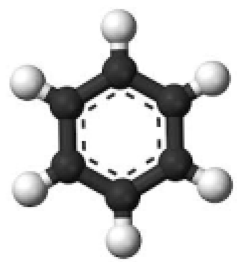
e.g., isobutene, methylcyclohexane

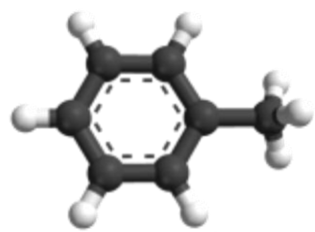


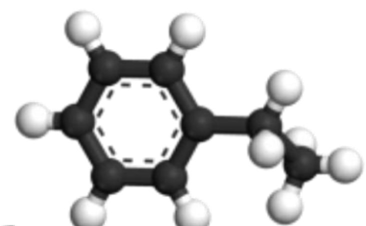


Aromatics

e.g., BTEX

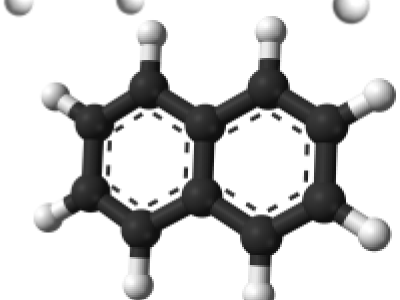




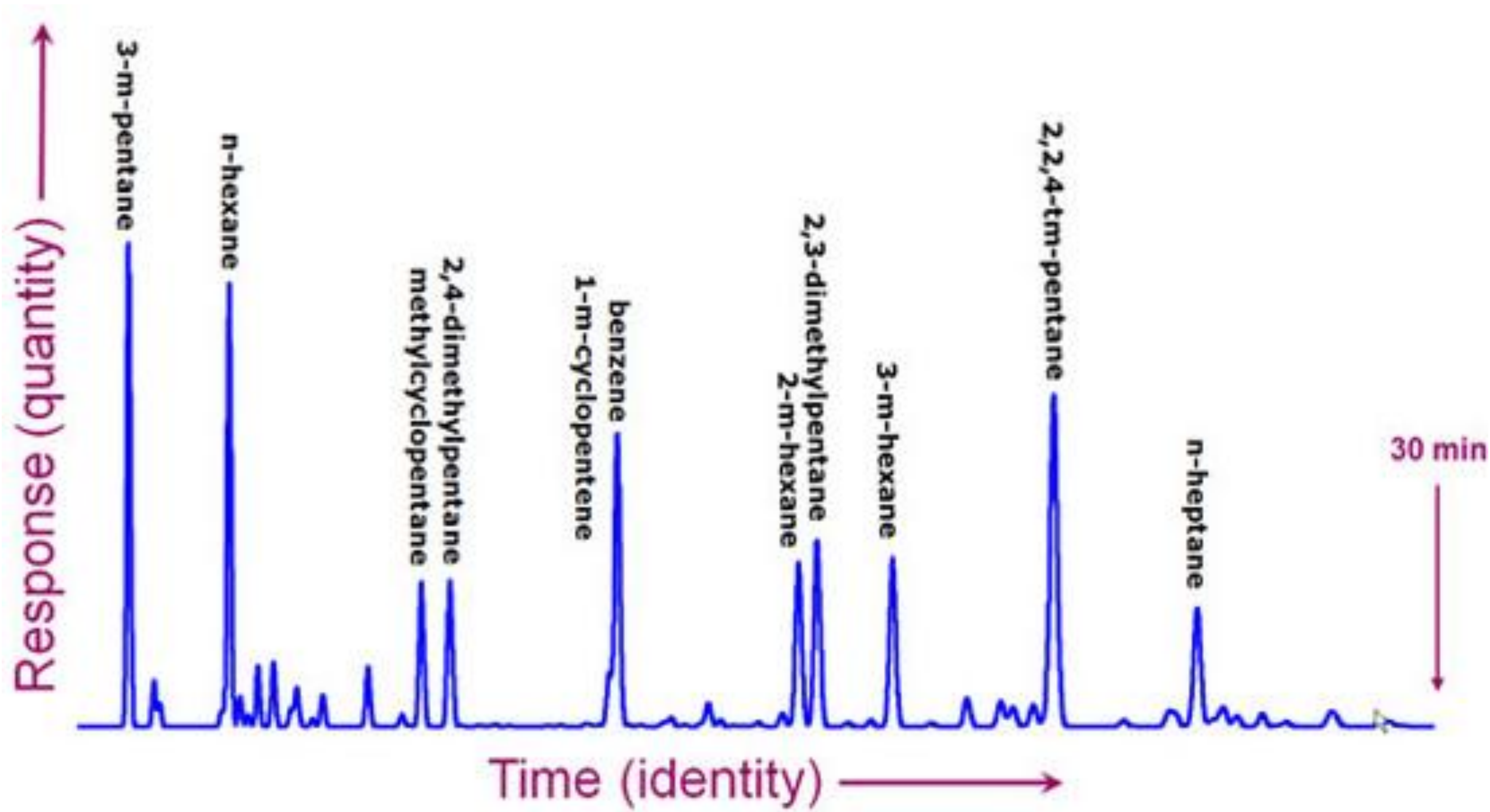


PAHs

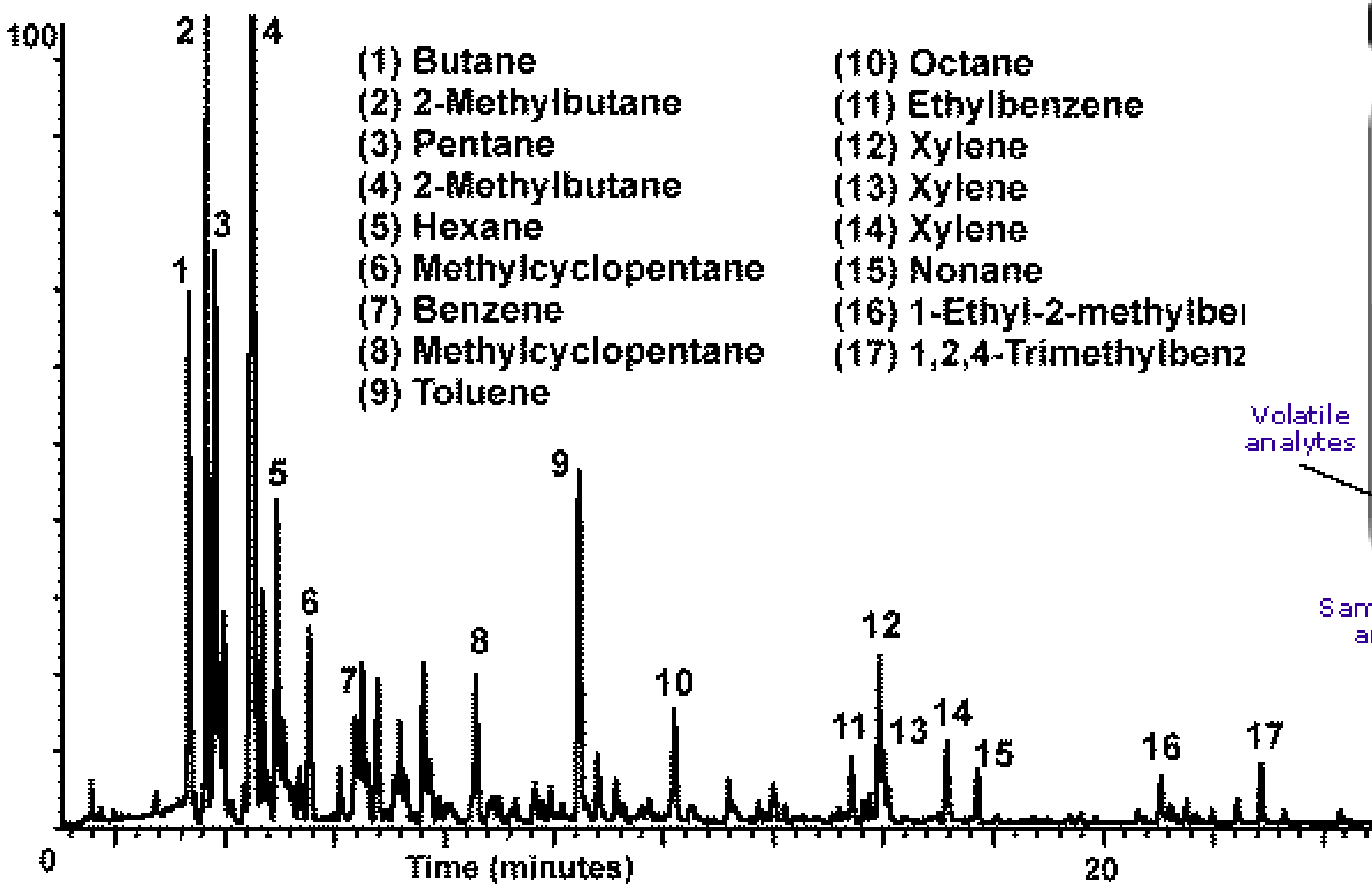
e.g., naphthalene

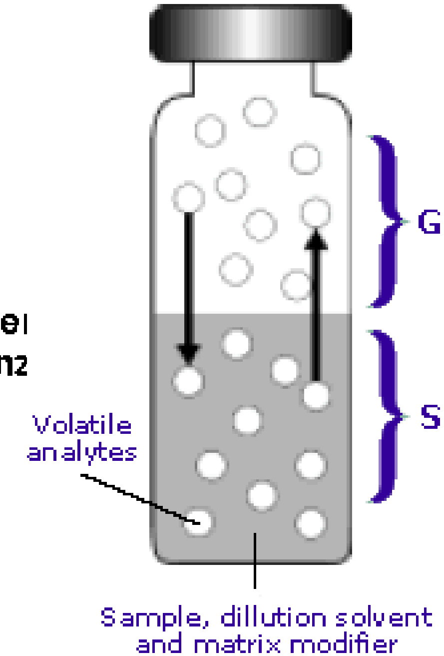


Gas Chromatographic (GC) Separation

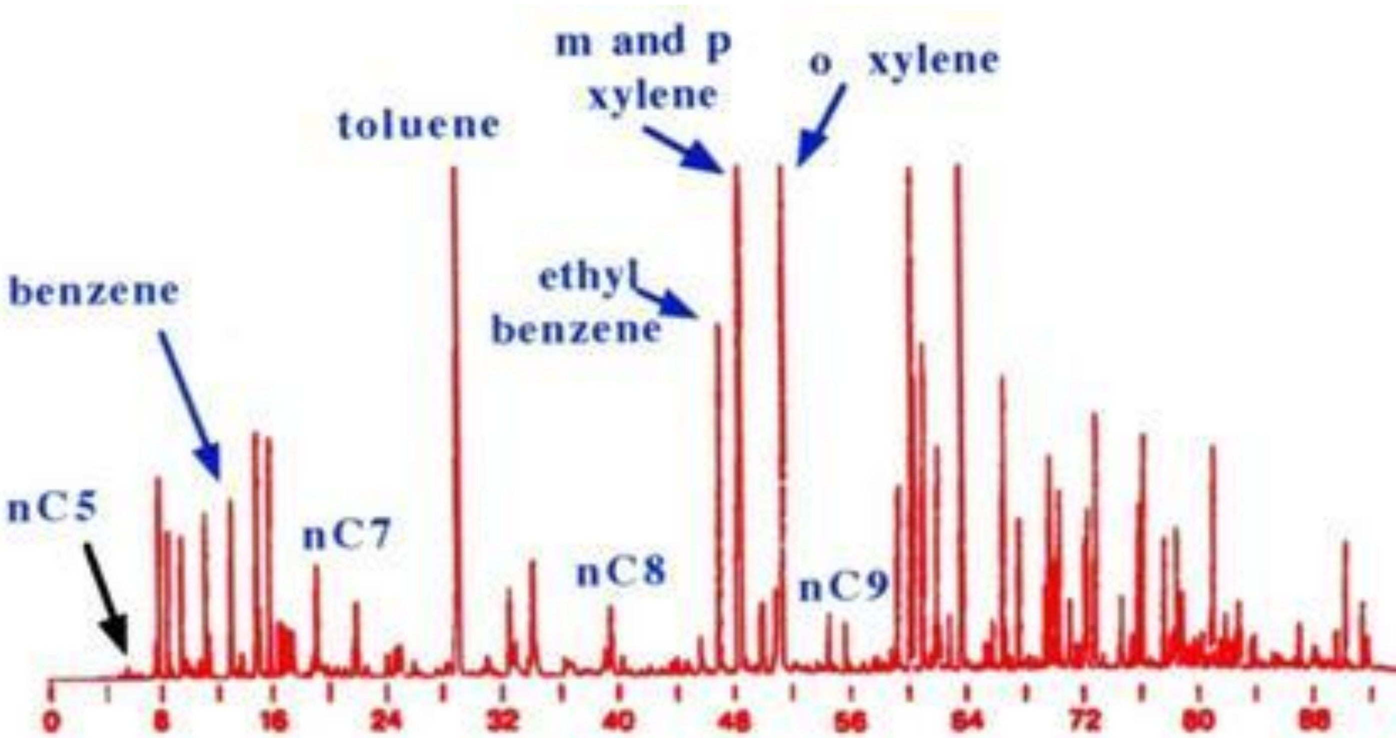


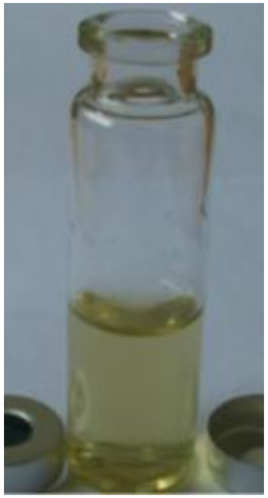
GC Analysis of Gasoline Vapours



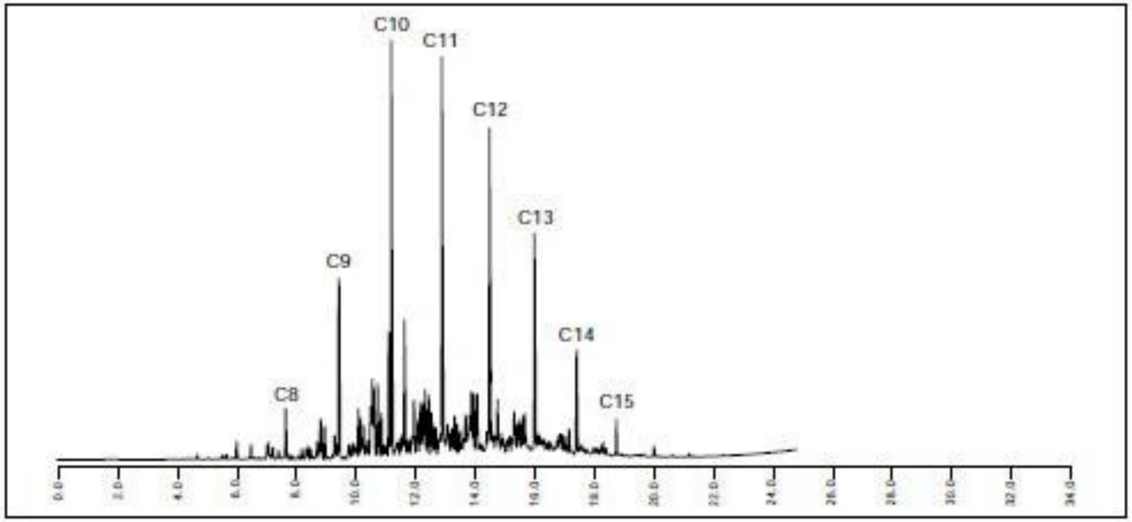


GC Analysis of Gasoline (refined)

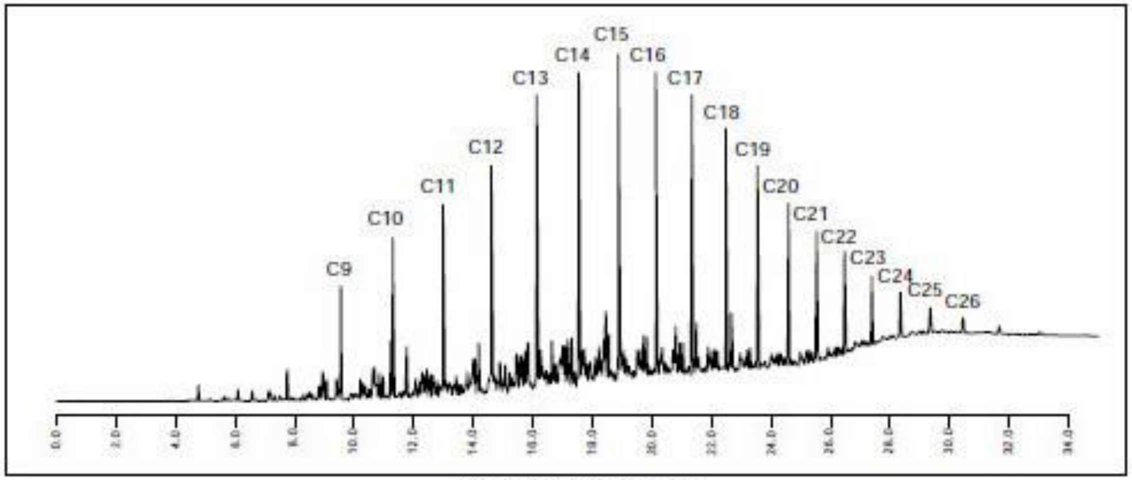




GC Analysis of Kerosene and Light Crude Oil



Analysis of Kerosene

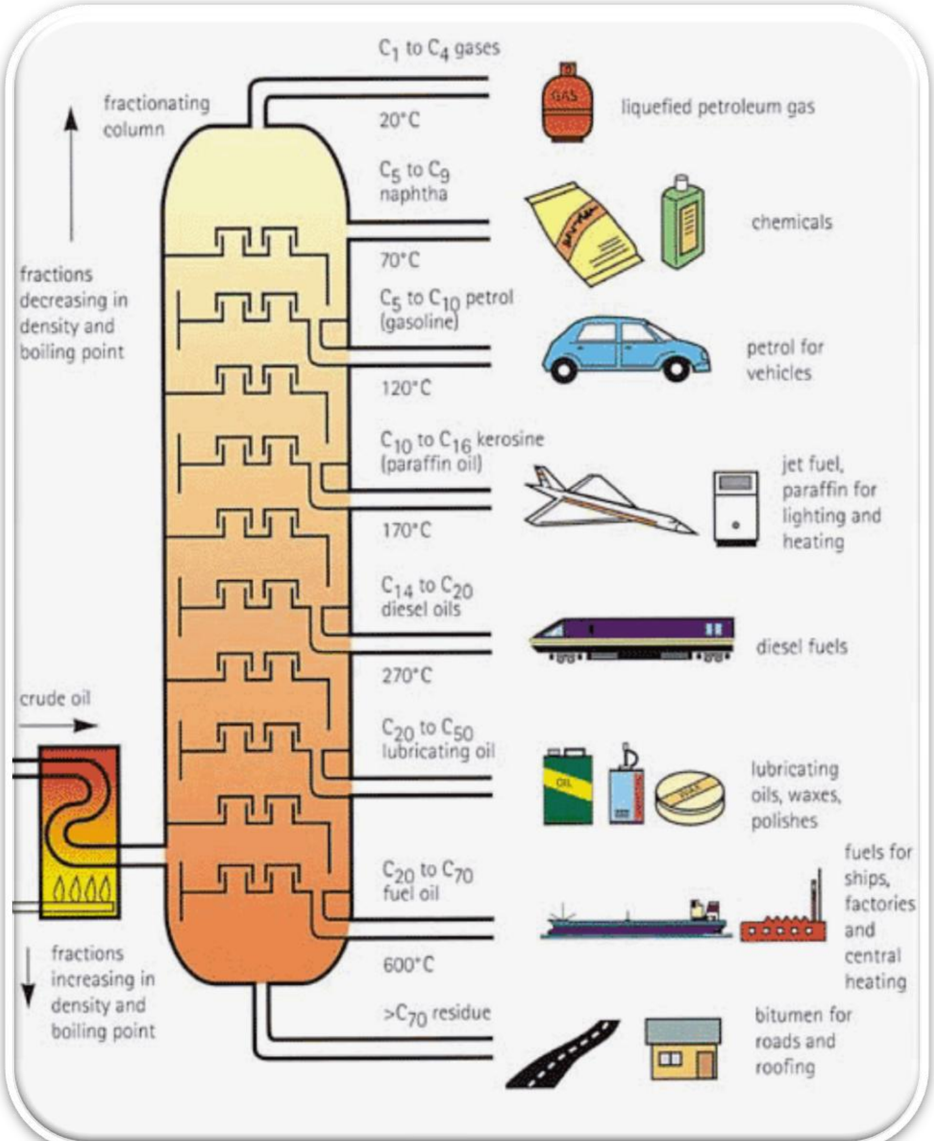


Analysis of Light Oil

Fuel Types

Fuel Grade	**#Carbons**	**BP Range**
Gasoline	$C_4 - C_{12}$	0 – 225 ºC
Jet Fuel	$C_{12} - C_{18}$	150 – 320 ºC
Diesel Fuel	$C_{12} - C_{20}$	150 – 400 ºC
Lube Oil	$C_{20} - C_{40}$	350 – 500+ ºC
Crude Oil	$C_2 - C_{100+}$	0 – 700+ ºC

Fractional Distillation into Fuel Types



Refining & Reforming
Cracking, Isomerization
Fuel Additives

Crude Oils

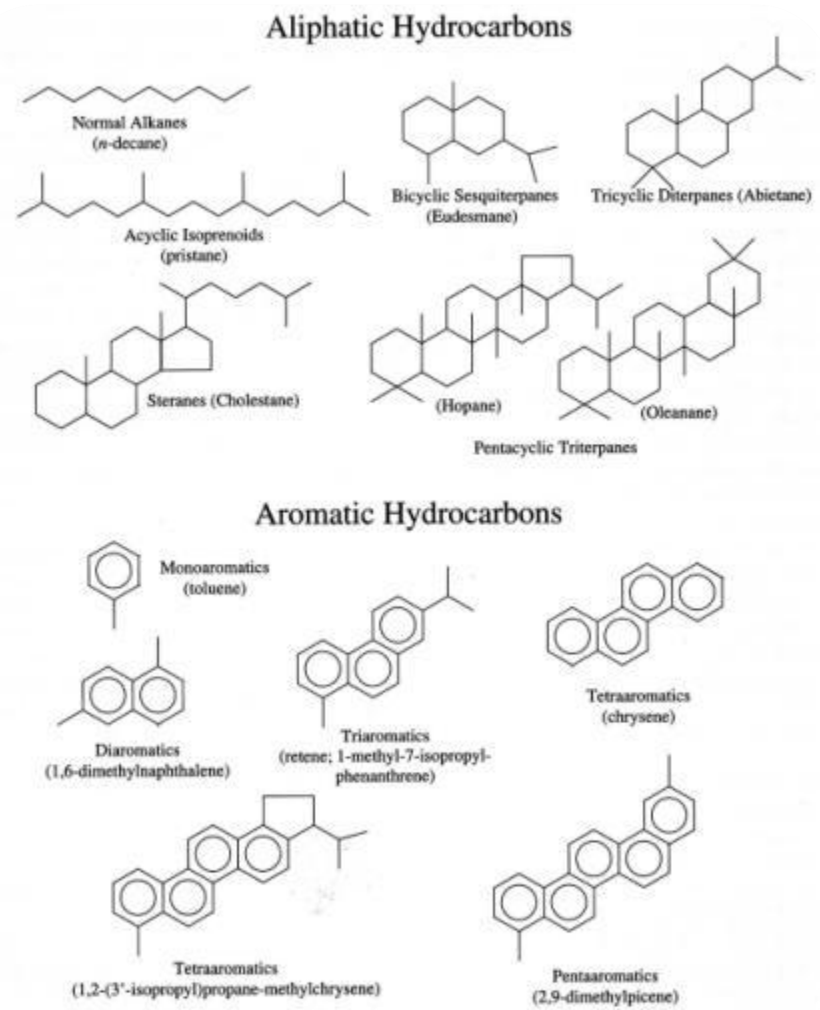


Figure 1-3 Examples of aliphatic and aromatic hydrocarbons in crude oils.

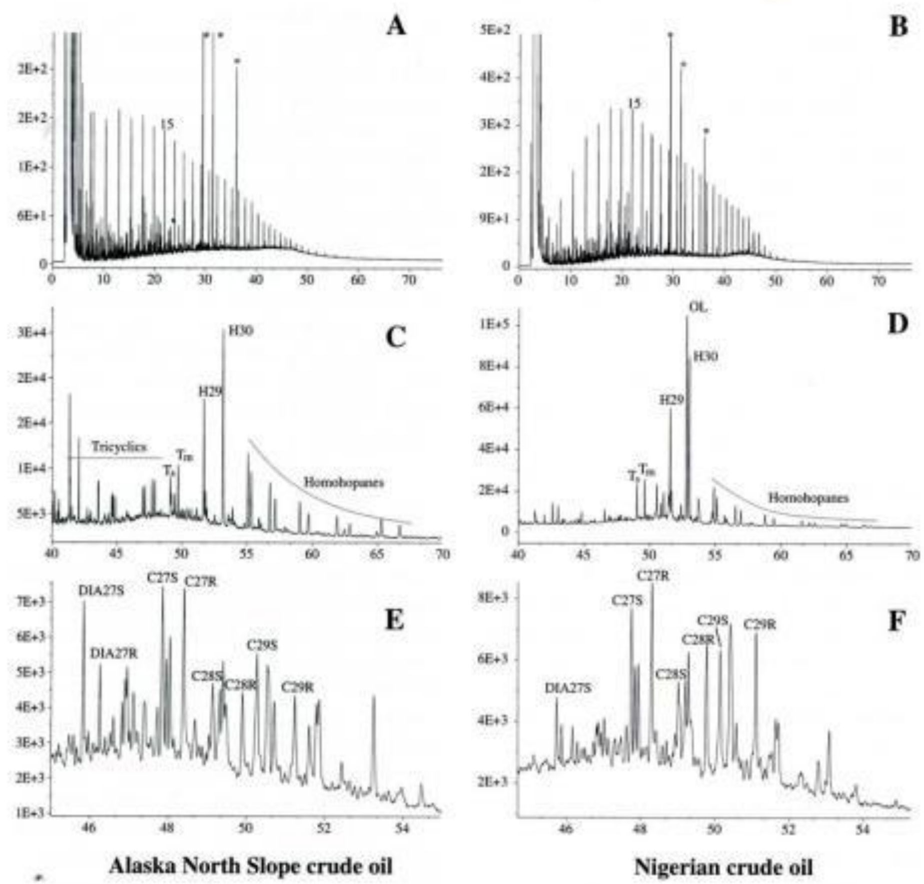
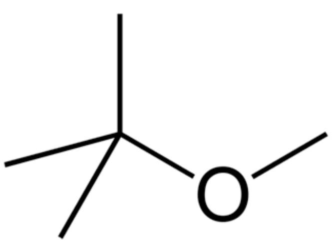


Figure 1-4 Example of the disparate primary chemical fingerprinting features in crude oils from the North Slope of Alaska and the Niger Delta, Nigeria. (a–b) GC/FID chromatograms, (c–d) partial m/z 191 mass chromatograms, and (e–f) partial m/z 217 mass chromatograms. * = internal standards, left to right: o-terphenyl, 5α-androstane and tetracosane-d_{50}.

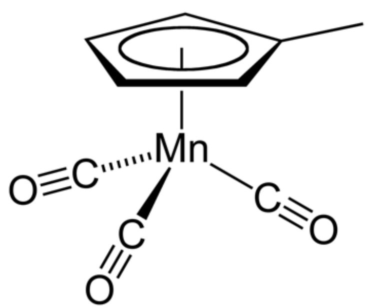
Gasoline Additives

Structures of some gasoline additives

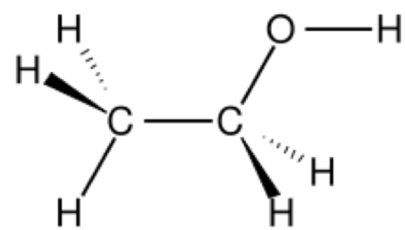
MTBE
(oxygenate)



MMT
(organometallic)



Ethanol
(oxygenate)



Fuel Type Markers

Pb / TEL: pre 1990 leaded gasoline and current Aviation Gasoline

Mn / MMT: 1970's – 2004 gasoline

MTBE: late 1990's gasoline

Sulphur content in gasoline vs diesel

Benzene content in gasoline

Ca, Ba, Mg, Zn, P, etc. in lube oils

Alternate Fuels

Ethanol

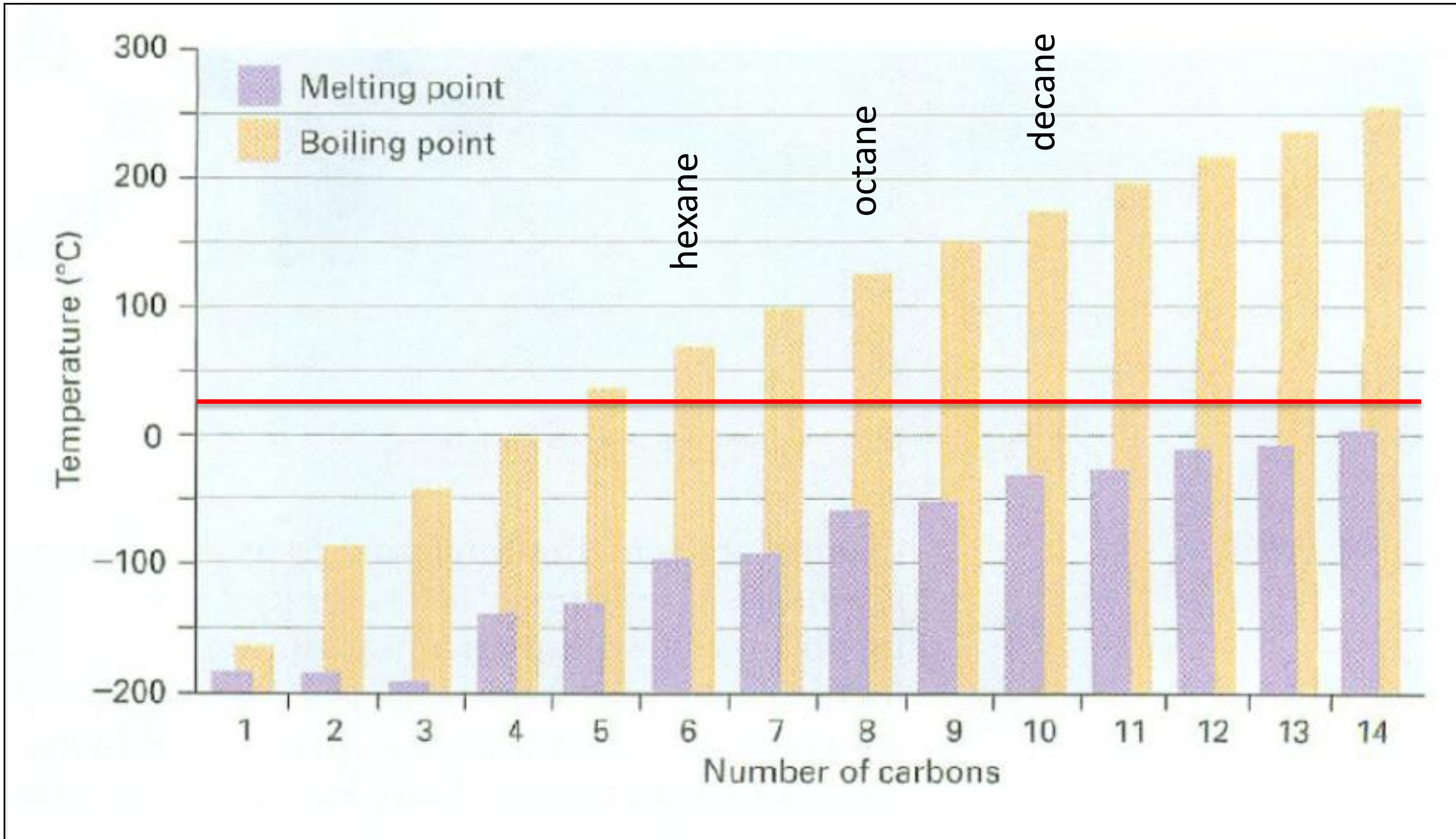
e.g., typically E10

Fatty Acid Methyl Esters (FAMEs)

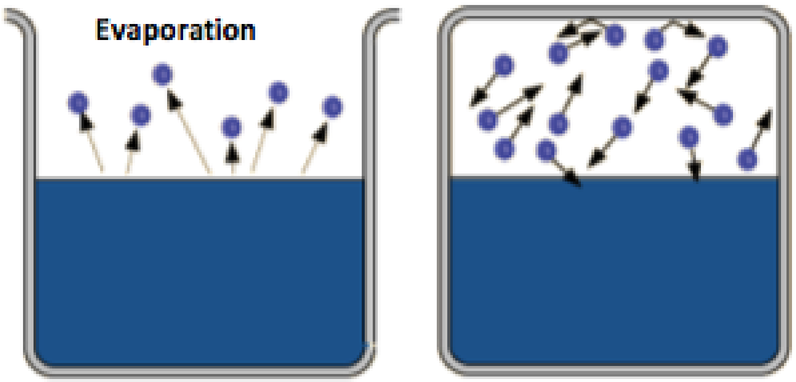
e.g., biodiesel esters

GTL / Paraffinic diesel fuel (from CH_4)

Physical Properties – MPs & BPs



Physical Properties – Vapour Pressure (P^o) & Water Solubility (C_w)



Size matters – small hydrocarbons are more volatile (i.e., higher P^o)

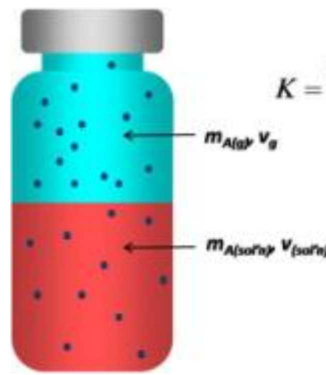
Size matters – small hydrocarbons are more water soluble (i.e., higher C_w)

π's matter – alkenes and aromatics are more water soluble (c.f. BTEX)

Environmental Fate & Distribution

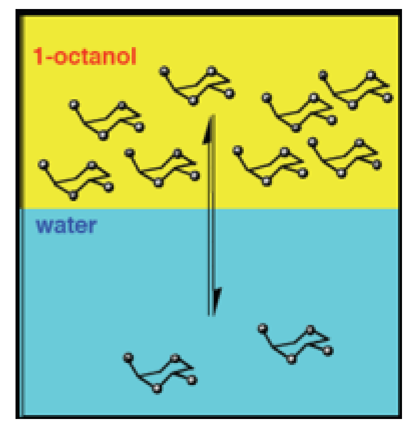
Partition Constants

Air-Water (K_{aw})



$$K = \frac{[A_{sol'n}]}{[A_g]} = \frac{m_{A(sol'n)}/v_{(sol'n)}}{m_{A(g)}/v_g}$$

Octanol-Water (K_{ow})

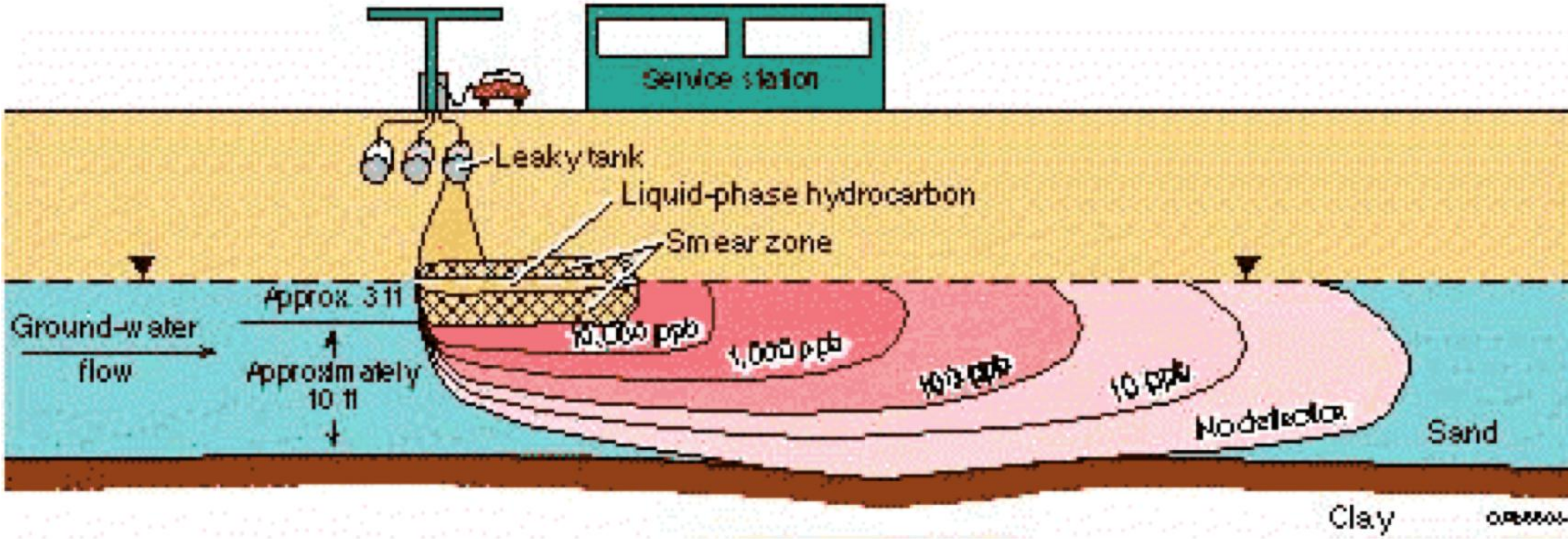


Sediment-Water (K_{oc} or K_d)

Physical Properties

Compound	P^o	C_w	K_{aw}	K_{ow}	K_{oc}
Methylcyclo-hexane					
Isooctane					
Benzene					
Toluene					
Naphthalene					

Groundwater contamination by MTBE



[MTBE] < 20 ppb (taste/odour) health ? potential carcinogen not regulated (AWWA)

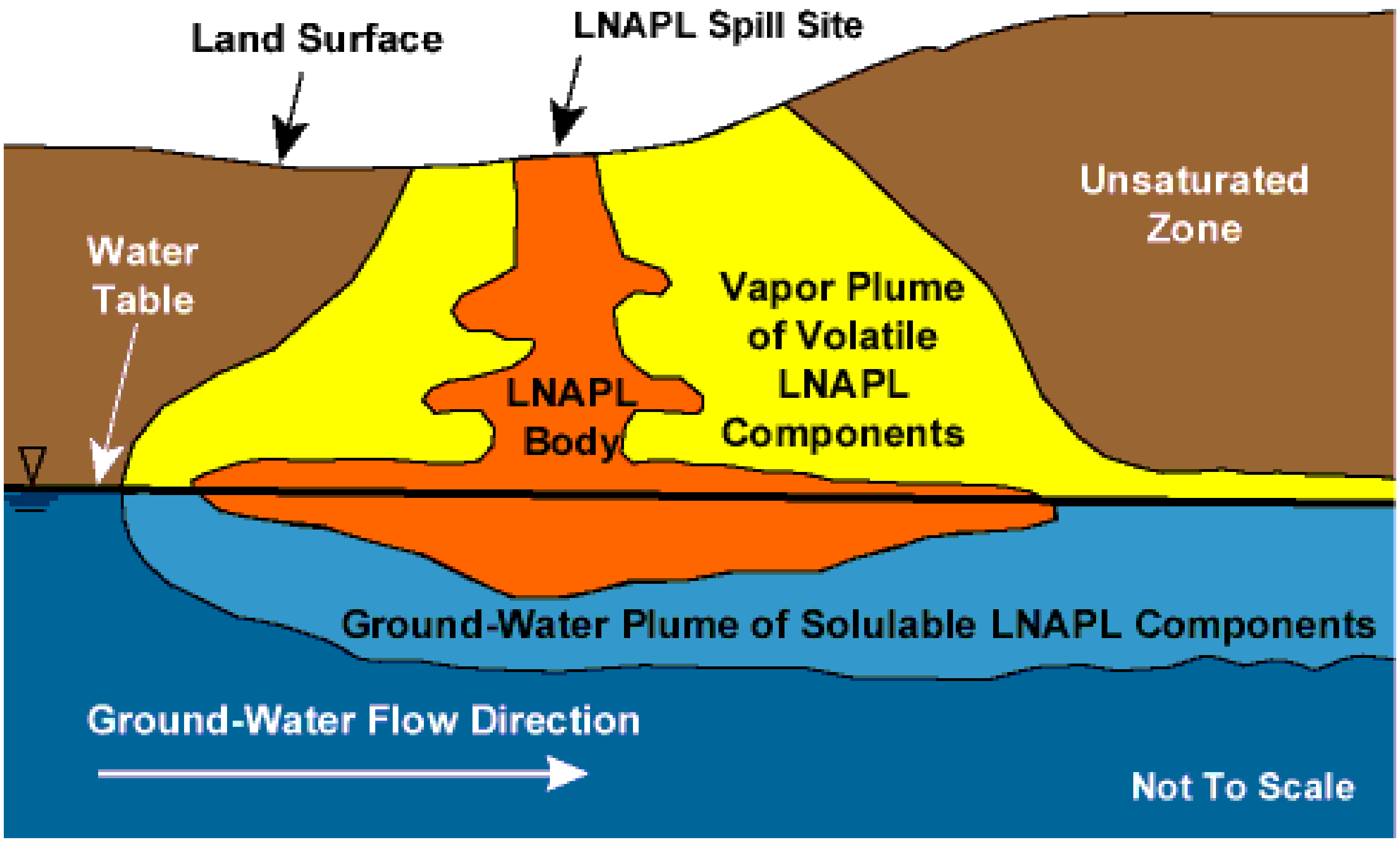
20% of the groundwater in areas where MTBE is used contaminated (USGS)

MTBE is highly water soluble low Kow, low sorbtivity to sediments

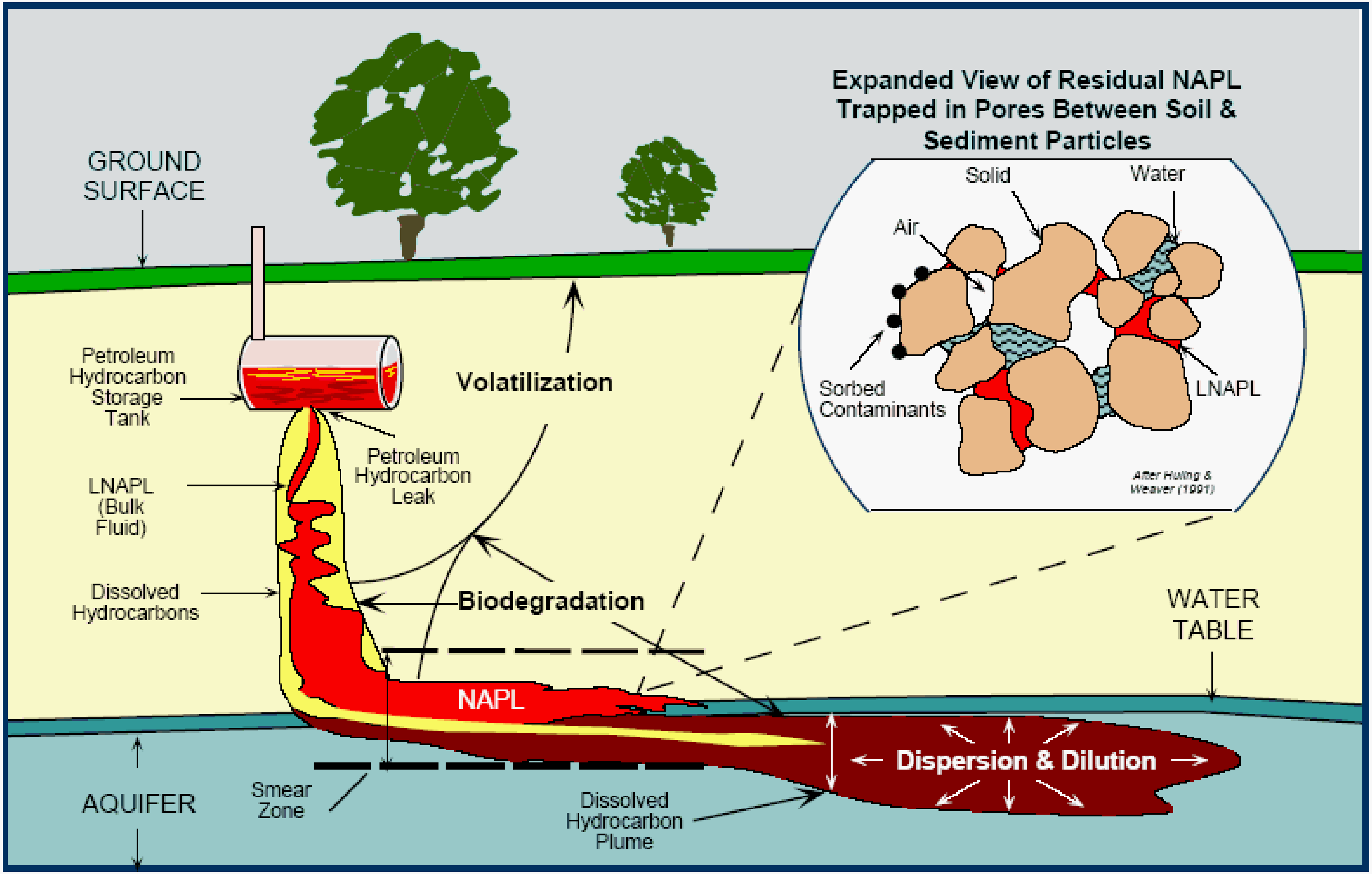
Non-Aqueous Phase Liquids (NAPL)

Light **NAPL**s – hydrocarbons, petroleum products

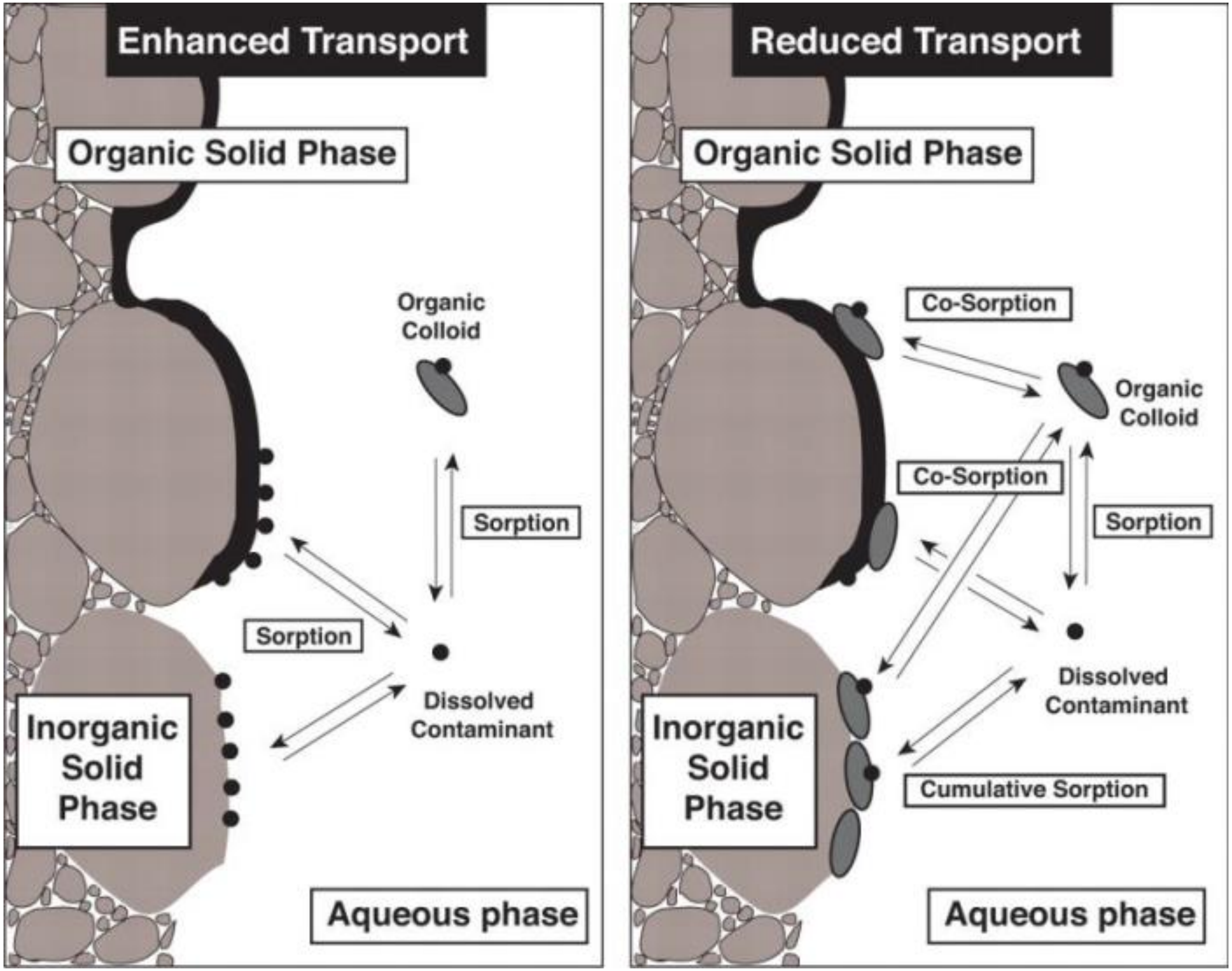
Dense **NAPL**s – chlorinated solvents



http://toxics.usgs.gov/definitions/lnapls.html

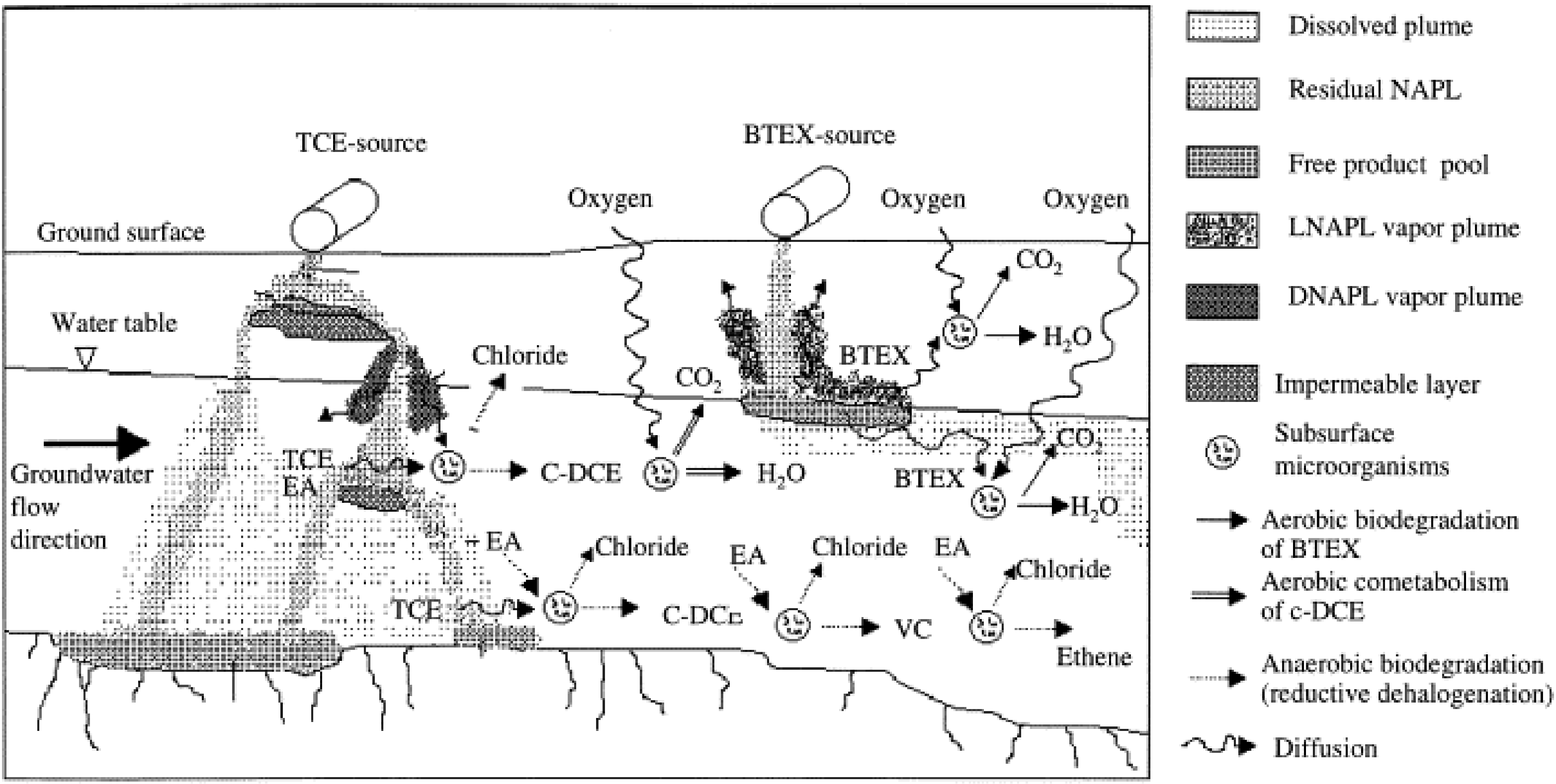


Expanded View of Residual NAPL Trapped in Pores Between Soil & Sediment Particles
Solid
Water
Air
Sorbed Contaminants
LNAPL
After Huling & Weaver (1991)
GROUND SURFACE
Petroleum Hydrocarbon Storage Tank
Volatilization
LNAPL (Bulk Fluid)
Petroleum Hydrocarbon Leak
Dissolved Hydrocarbons
Biodegradation
WATER TABLE
NAPL
Dispersion & Dilution
AQUIFER
Smear Zone
Dissolved Hydrocarbon Plume



Enhanced Transport
Organic Solid Phase
Organic
Colloid
Sorption
Sorption
Dissolved
Contaminant
Inorganic
Solid
Phase
Aqueous phase
Reduced Transport
Organic Solid Phase
Co-Sorption
Organic
Colloid
Co-Sorption
Sorption
Dissolved
Contaminant
Inorganic
Solid
Phase
Cumulative Sorption
Aqueous phase

Attenuation and Transformations



Aerobic Microbial Degradation

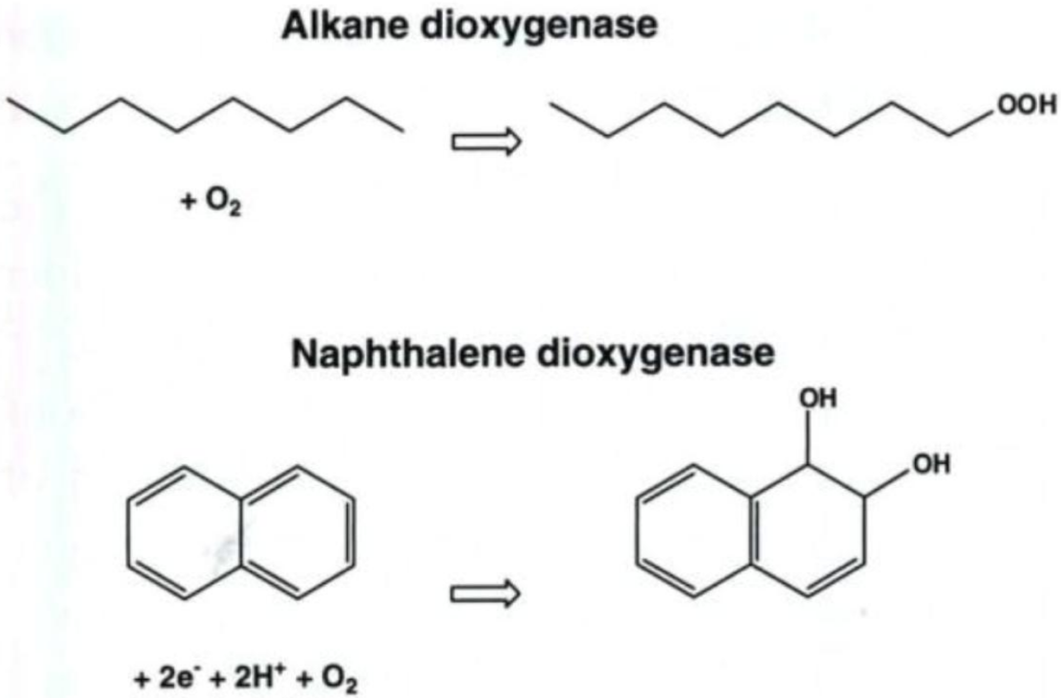
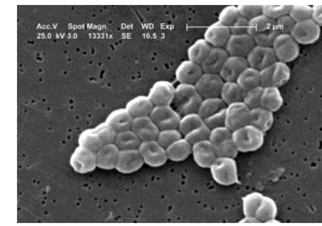


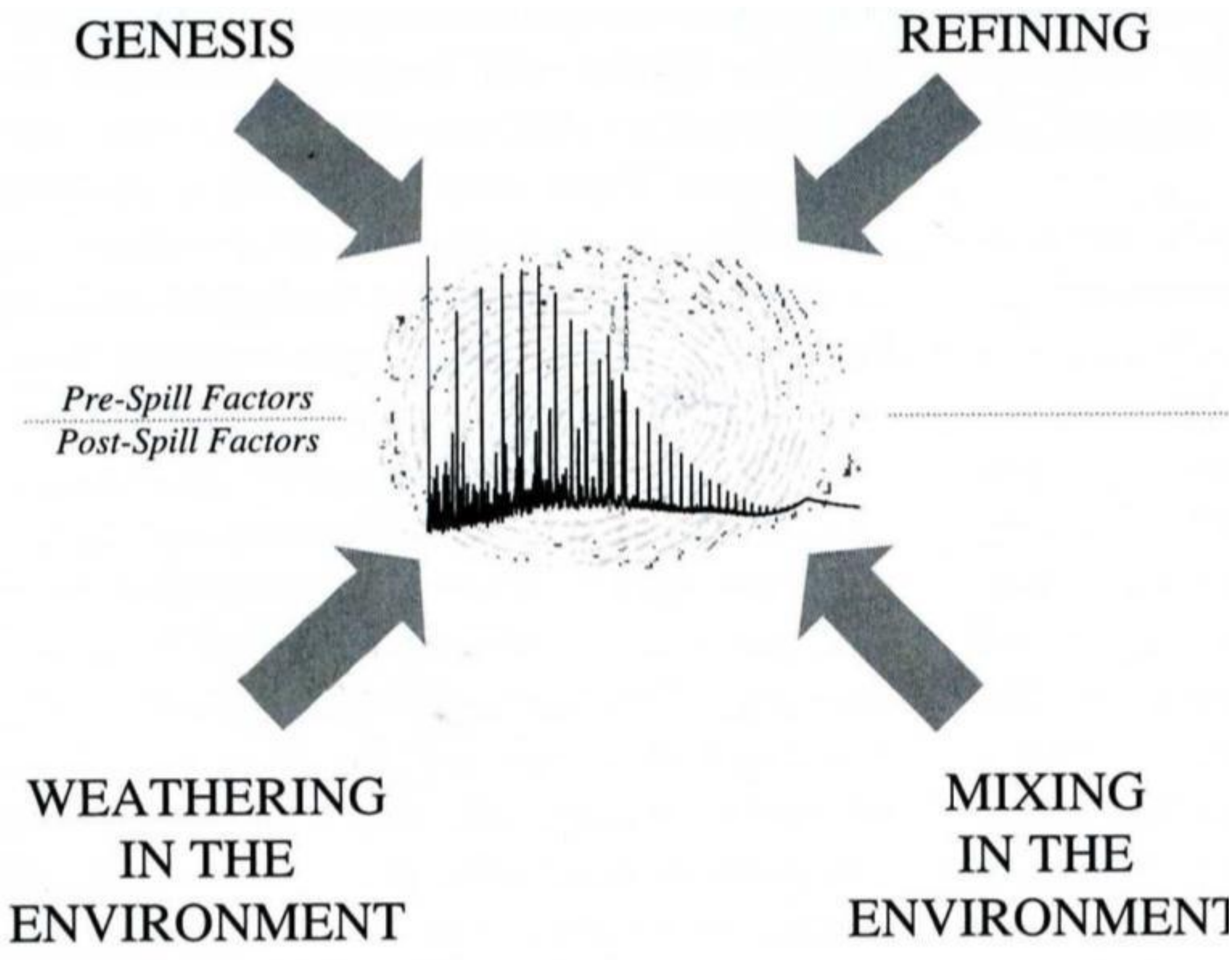
Figure 11-2 Typical reactions catalyzed by hydrocarbon dioxygenases. The alkane dioxygenase of an *Acinetobacter* apparently converts alkanes to alkanehydroperoxides (Maeng et al., 1996). Naphthalene dioxygenase of *Pseudomonas putida* oxidizes naphthalene to *cis*-naphthalene-1,2-dihydrodiol (Karlsson et al., 2003).



Attenuation Reactions for Toluene

Table 11-1 Comparison of Aerobic and Anaerobic Respiration Reactions

e-*Acceptor*	*Reaction (Toluene)*	*ΔG°, kJ/mol Toluene*	*Molar Ratio*	*Mass Ratio*
	Aerobic respiration			
O_2	$C_7H_8 + 9O_2 \rightarrow 7CO_2 + 4H_2O$	–3913	9	3.1
	Denitrification			
NO_3^-	$C_7H_8 + 7.2NO_3^- + 0.2H^+ \rightarrow 3.6N_2 + 7HCO_3^- + 0.6H_2O$	–3554	7.2	4.8
	Manganese reduction			
Mn(IV)	$C_7H_8 + 21MnO_2 + 14H^+ \rightarrow 7MnCO_3 + 14MnO + 7H_2O$	–3502	21	27
	Iron reduction			
Fe(III)	$C_7H_8 + 94Fe(OH)_3 \rightarrow 7FeCO_3 + 29Fe_3O_4 + 145H_2O$	–3398	94	109
	Sulfate reduction			
$SO_4^=$	$C_7H_8 + 4.5SO_4^{2-} + 3H_2O \rightarrow 7HCO_3^- + 2.5H^+ + 4.5HS^-$	–205	4.3	4.5
H_2O (CO_2)	*Methanogenesis*			
	$C_7H + 7.5H_2O \rightarrow 2.5HCO_3^- + 2.5H^+ + 4.5CH_4$	–131	7.5	1.5


GENESIS
REFINING
Pre-Spill Factors
Post-Spill Factors
WEATHERING IN THE ENVIRONMENT
MIXING IN THE ENVIRONMENT

Summary

Complex Hydrocarbon Mixtures

Composition depends on source, refining (additives), ‘weathering’, degradation & mixing

Range of Physical-Chemical Properties

Migration & Attenuation depends on vapour pressure, water solubility, partitioning (i.e., K_{aw}, K_{ow} and K_d)