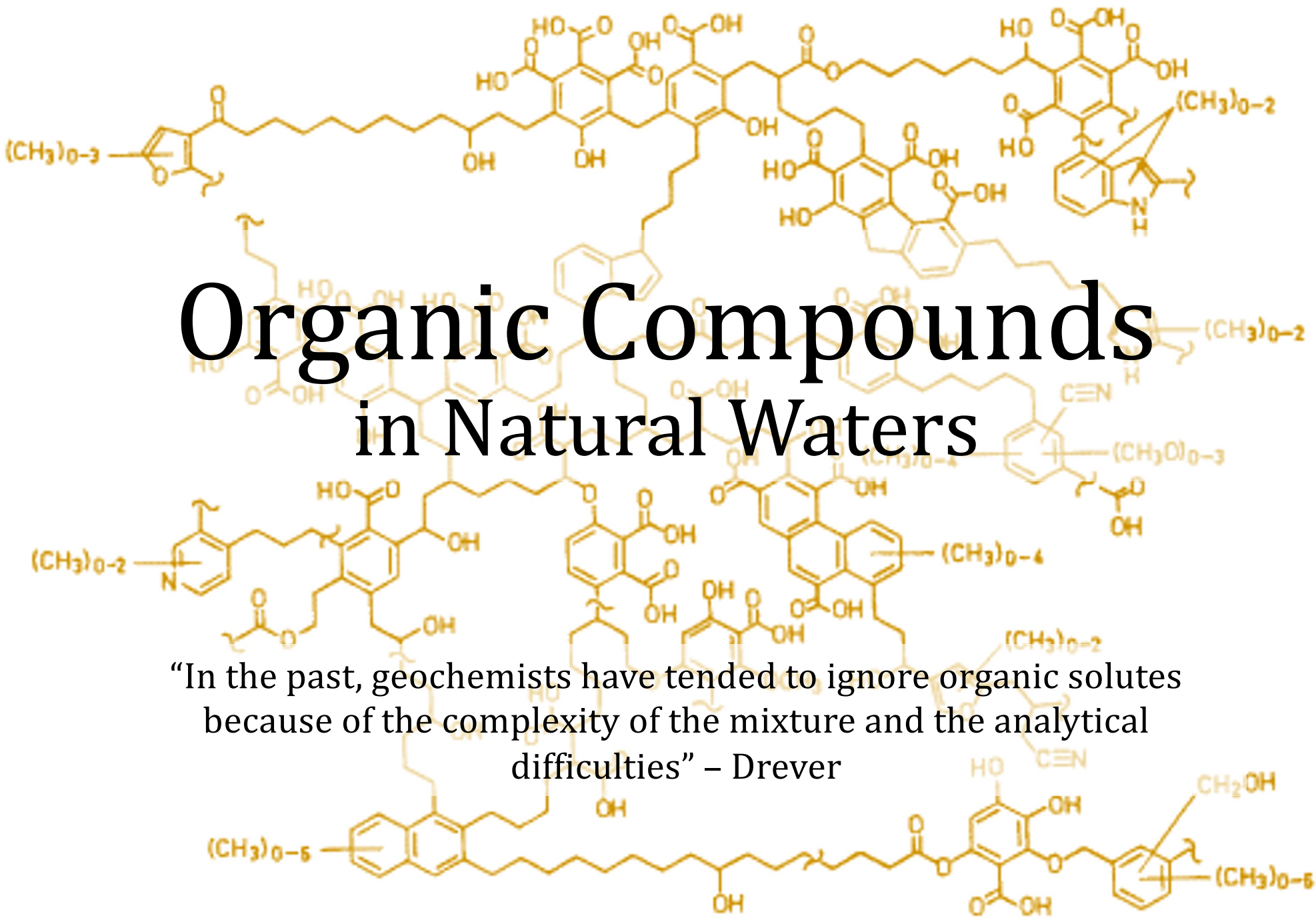


Organic Compounds
in Natural Waters

"In the past, geochemists have tended to ignore organic solutes because of the complexity of the mixture and the analytical difficulties" – Drever

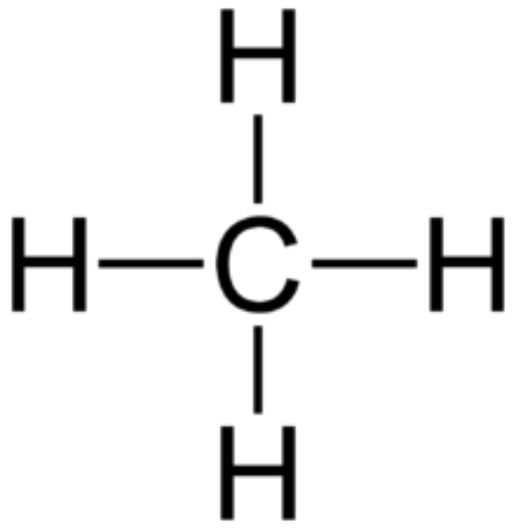
Topic outline:

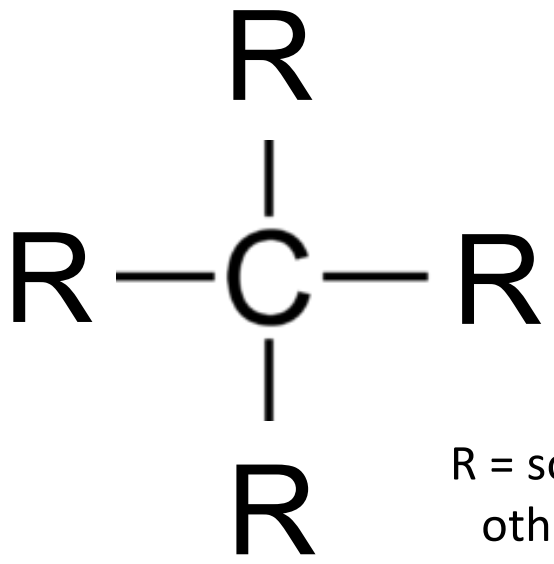
1. What is an organic compound?
2. Chemical bonds and chemical structures
3. Major categories of organic compounds
4. Important organic functional groups
5. Chemistry of organic matter in the environment
6. Techniques used to analyze organic matter

Structure of Organic Compounds

Organic compound: A compound containing the element C bonded to the element H (excluding carbonate compounds such as CO_2, HCO_3^-, $CaCO_3$, $FeCO_3$…)

Carbon forms four bonds with other elements





R = something other than H

The *approximate* composition of natural organic matter is CH_2O

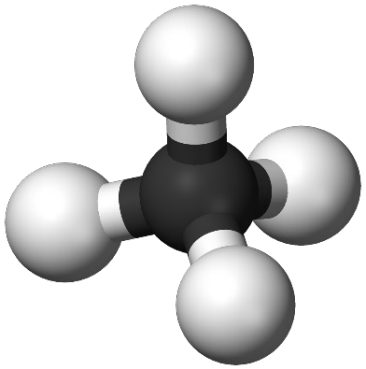
Carbon: The building block of organic matter

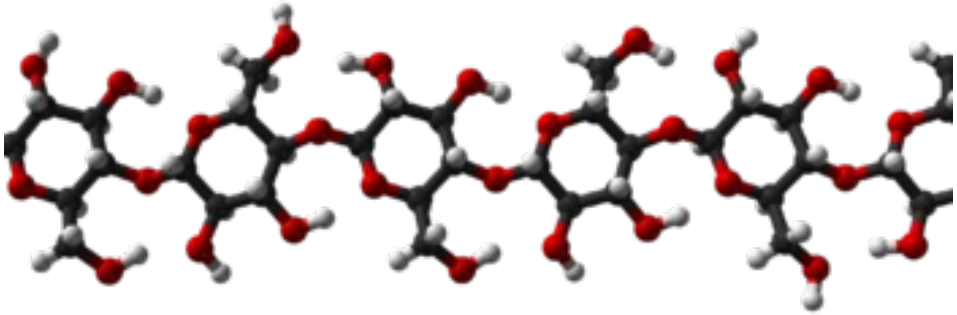
- Carbon forms up to 4 covalent bonds and is typically bonded to O or H in organic matter
- Carbon compounds decompose to CO_2 (aerobic respiration) or $CO_2 + CH_4$ (anaerobic respiration)

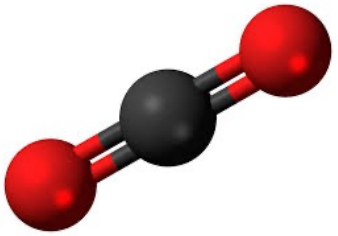
Reduced form
C(-4)

Organic Matter
C(0)

Oxidized form
C(+4)







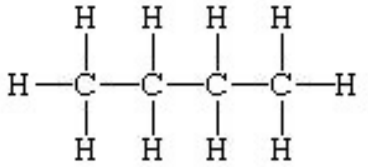
CH_4 ⟵ Anaerobic respiration | Aerobic respiration ⟶ CO_2

Structure of Organic Compounds

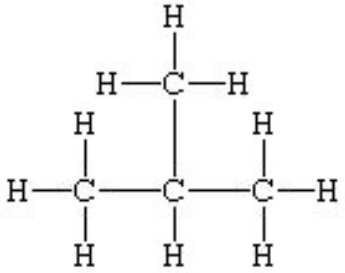
Aliphatic compounds

- Straight, branched, or cyclic chains of hydrocarbons

Alkanes (saturated): single bonds

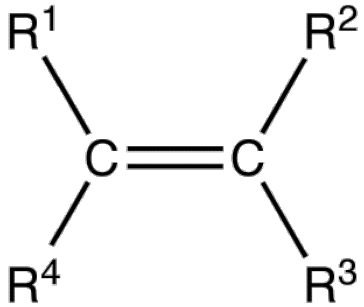


n-butane, $CH_3CH_2CH_2CH_3$



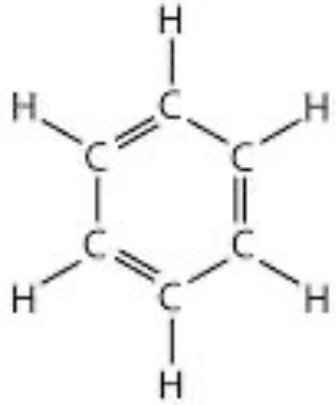
isobutane, $(CH_3)_3CH$

Alkenes (unsaturated): contain at least one double bond



Aromatic compounds

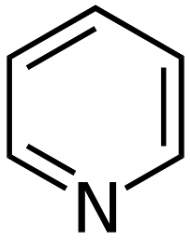
- Contain at least one cyclic ring with alternating double bonds (benzene); delocalized electrons

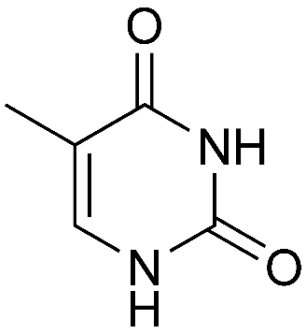


or

Heterocyclic compounds

- A ring that contains a heteroatom (typically N or O) that is not C





What happens when we burn organic molecules?

$$\text{“}CH_2O\text{”} + O_2 \rightarrow CO_2 + H_2O$$

1) C-H bonds are broken
   → Energy is released

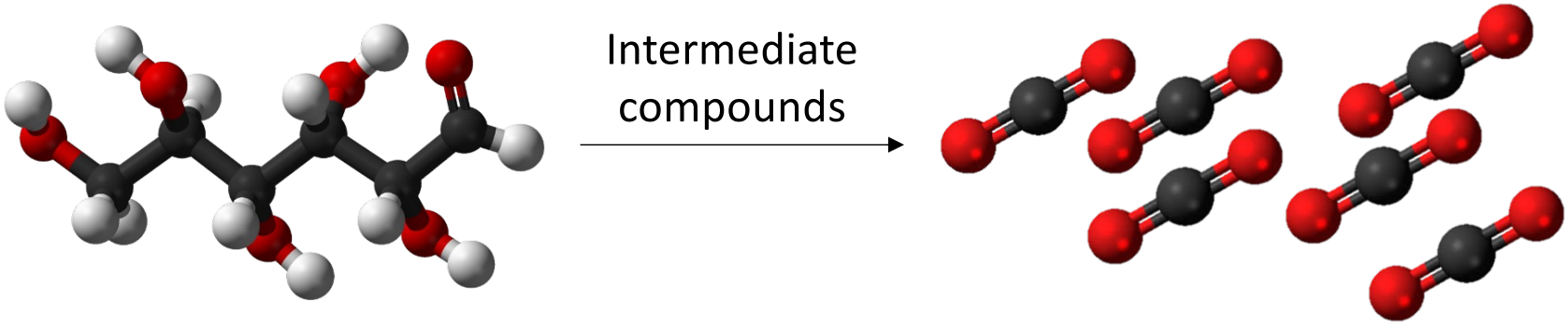
2) Oxygen from the air forms chemical bonds with C

3) Eventually, organic molecule is completely converted to CO_2 gas

Aerobic Respiration

Glucose oxidation:

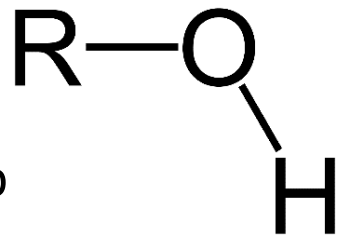
$$C_6H_{12}O_6 + 6\ O_2 \rightarrow 6\ CO_2 + 6\ H_2O + \text{energy}$$



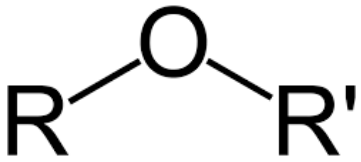
C(+0) in organic matter is oxidized to CO_2

Major Functional Groups

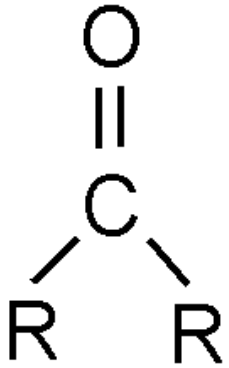
Alcohol
Hydroxyl (OH) group



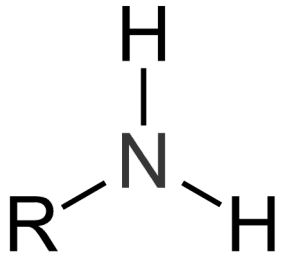
Ether
O bonded to two C atoms



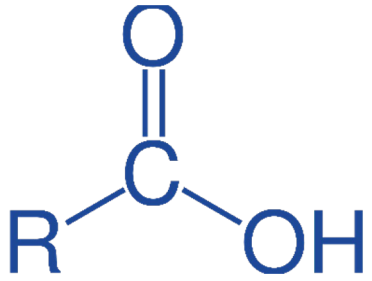
Carbonyl
C double bonded to the O atom



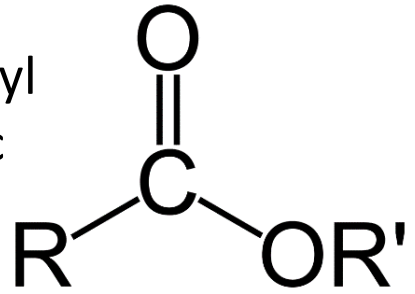
Amines
N atom bonded to one or more C-H groups



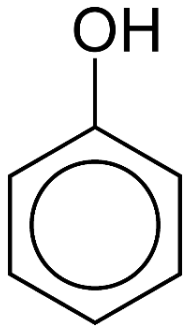
Carboxyl
C doubled bonded to O and single bonded to a hydroxyl group



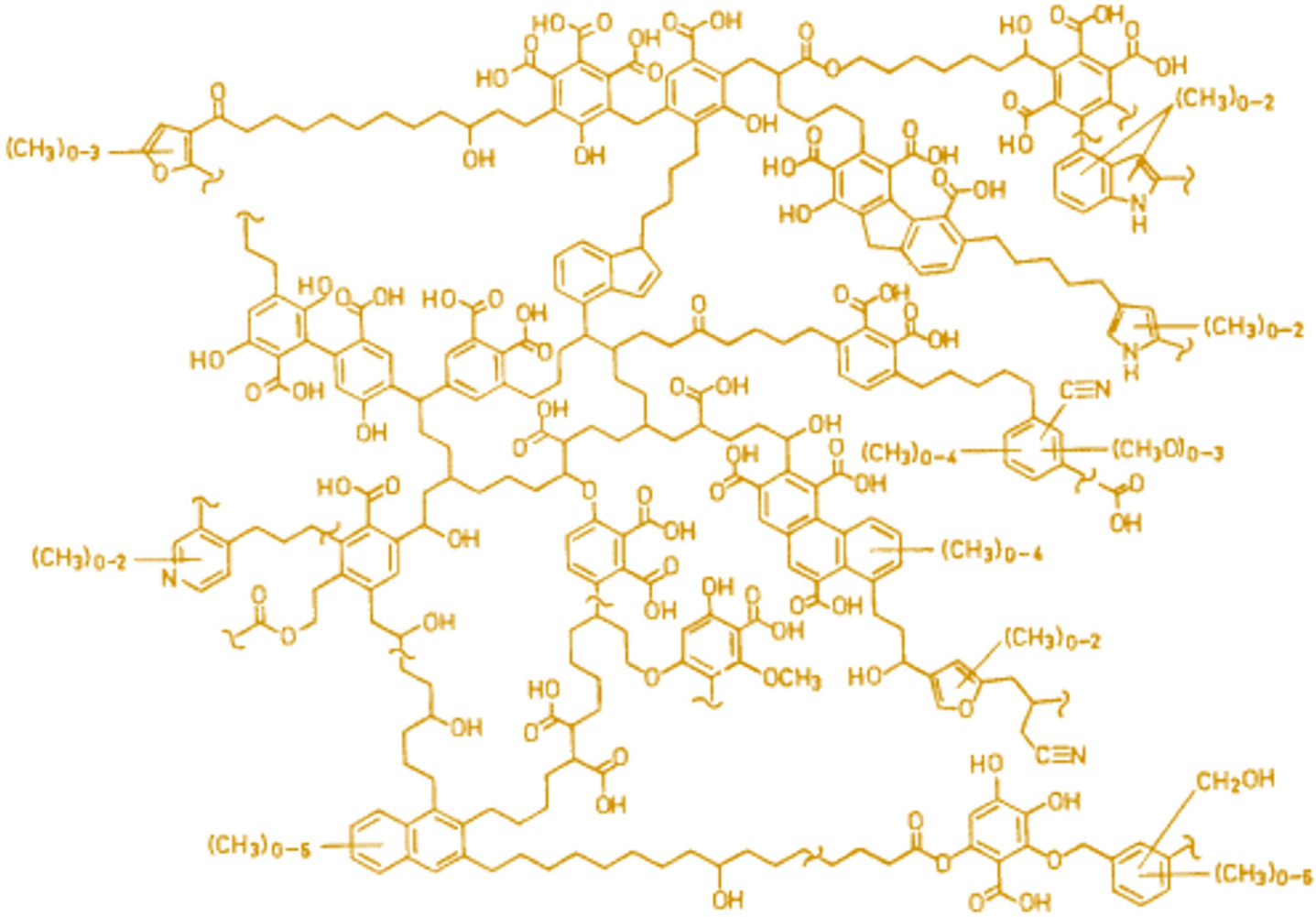
Ester
Replaces H in carboxyl with another organic group



Phenols
Hydroxyl group bonded to a benzene ring



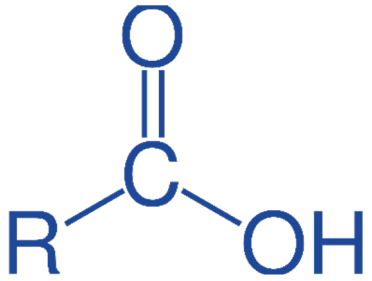
What are functional groups?



Functional groups are specific **groups** (moieties) of atoms or bonds within molecules that are responsible for the chemical reactions of those molecules.

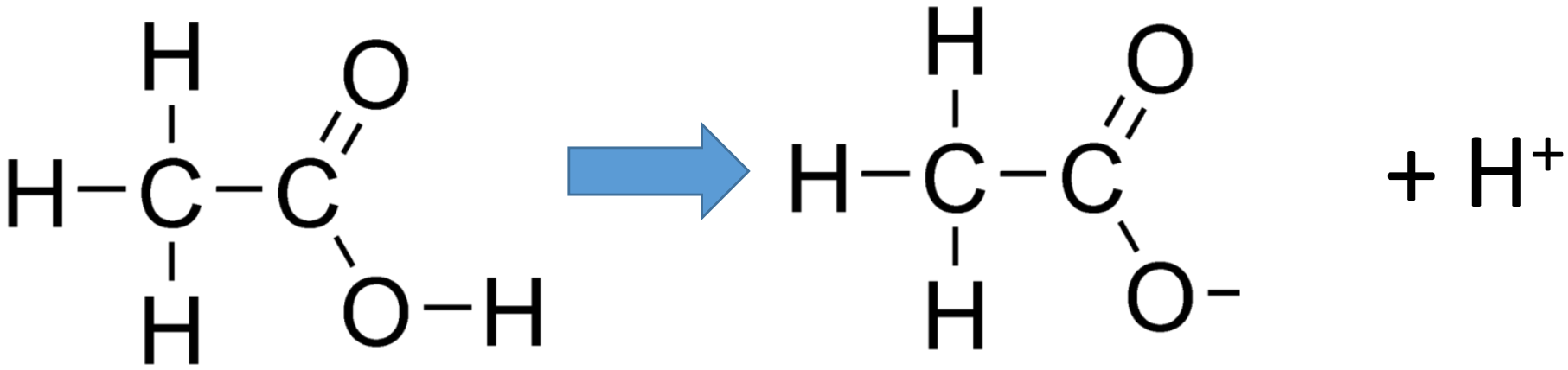
Carboxylic acids contain carboxyl groups

Carboxyl
C doubled bonded to O and single bonded to a hydroxyl group



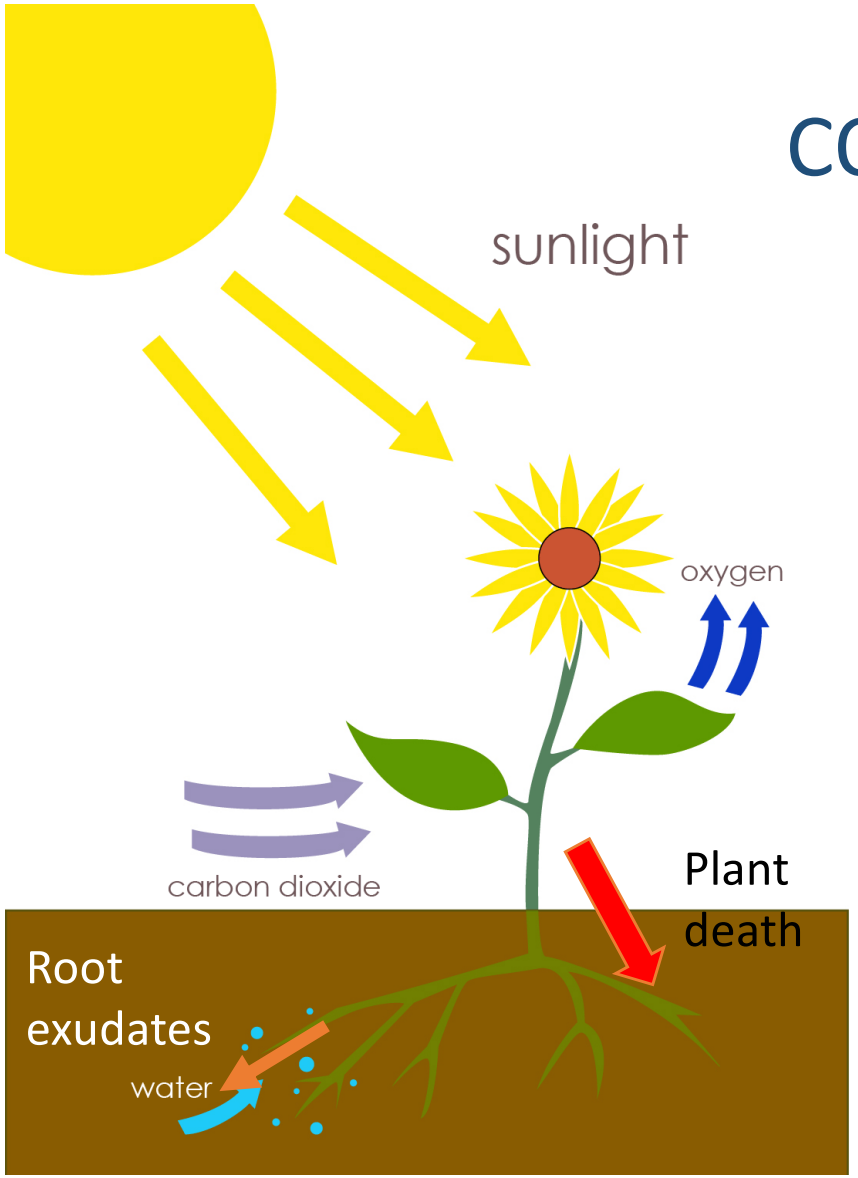
The "R" can represent any type of organic group, from CH_3 to something highly complex

Example: acetic acid (CH_3COOH)



Organic Matter in the Environment

Where does organic matter come from?



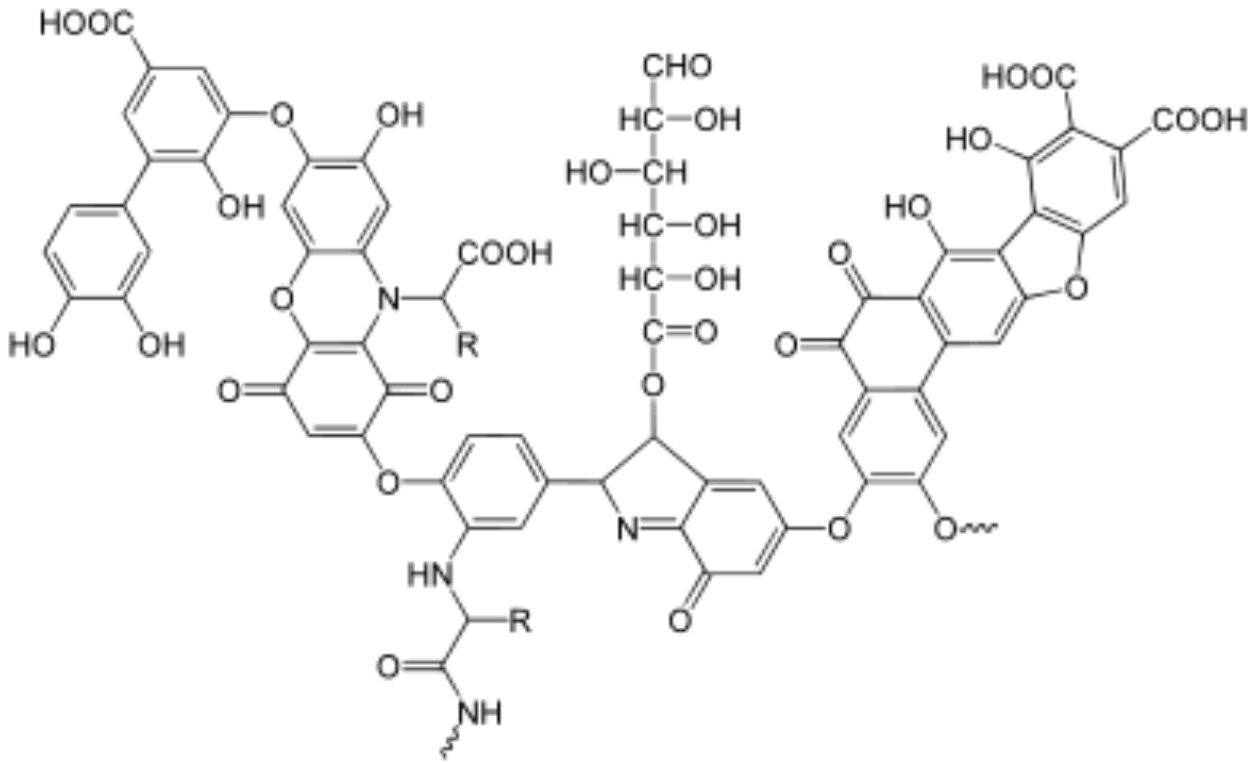
$$CO_2 + H_2O + h\nu \rightarrow \text{“}CH_2O\text{”} + O_2$$

- Plants harvest energy from sun to form organic molecules
- Organic molecules form plant tissue or root exudates
- Other organisms burn the organic molecules for fuel

Refer to the note

Natural organic matter is often classified by coarse properties

Humic substances – “A general category of naturally occurring, biogenic, heterogeneous organic substances that can generally be characterized as being yellow to black in color, of high molecular weight, and refractory” – products of microbial decomposition of organic matter



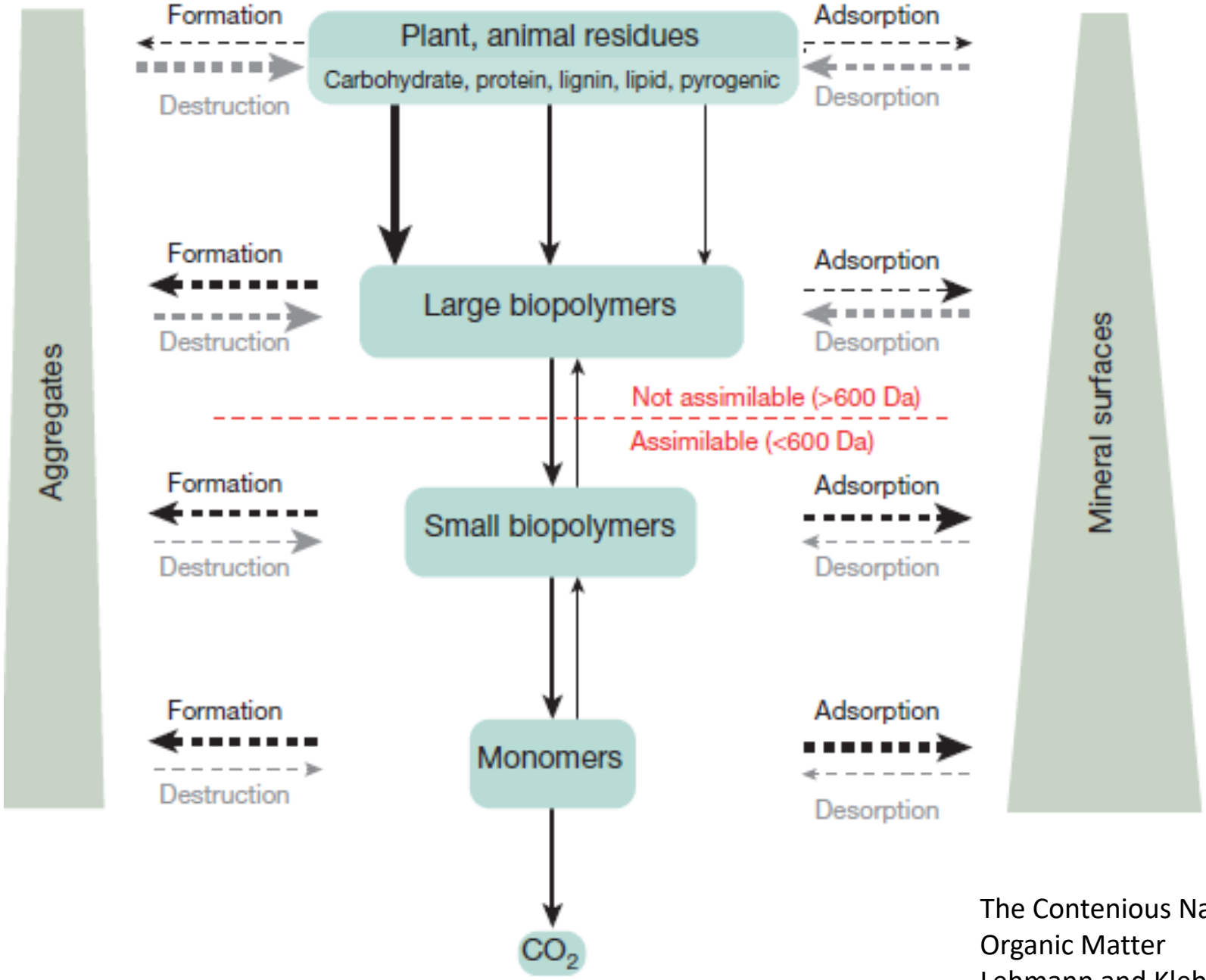
Three operational definitions for humic substances:

Humin – insoluble in water under all pH conditions

Humic acids – insoluble in water at pH < 2 but soluble at higher pH; low O/C ratio

Fulvic acids – soluble in water under all pH conditions; high O/C ratio

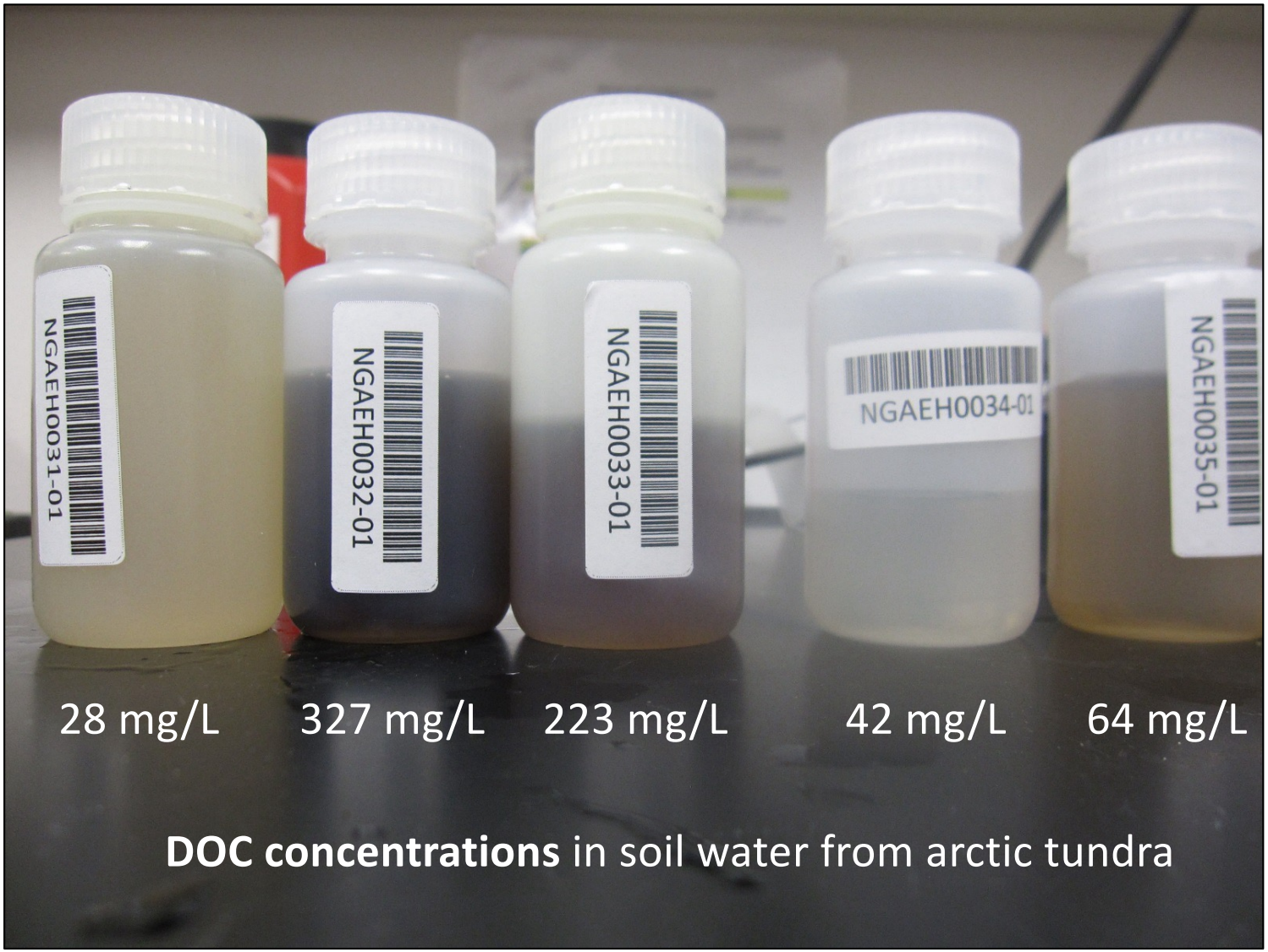
Breakdown of organic matter is controlled by biological and mineralogical factors



The Contenious Nature of Soil Organic Matter
Lehmann and Kleber (2015)
Nature

Dissolved organic matter (usually measured as DOC) forms via:

1) Breakdown of larger, insoluble molecules (before CO_2)
2) Biosynthesis

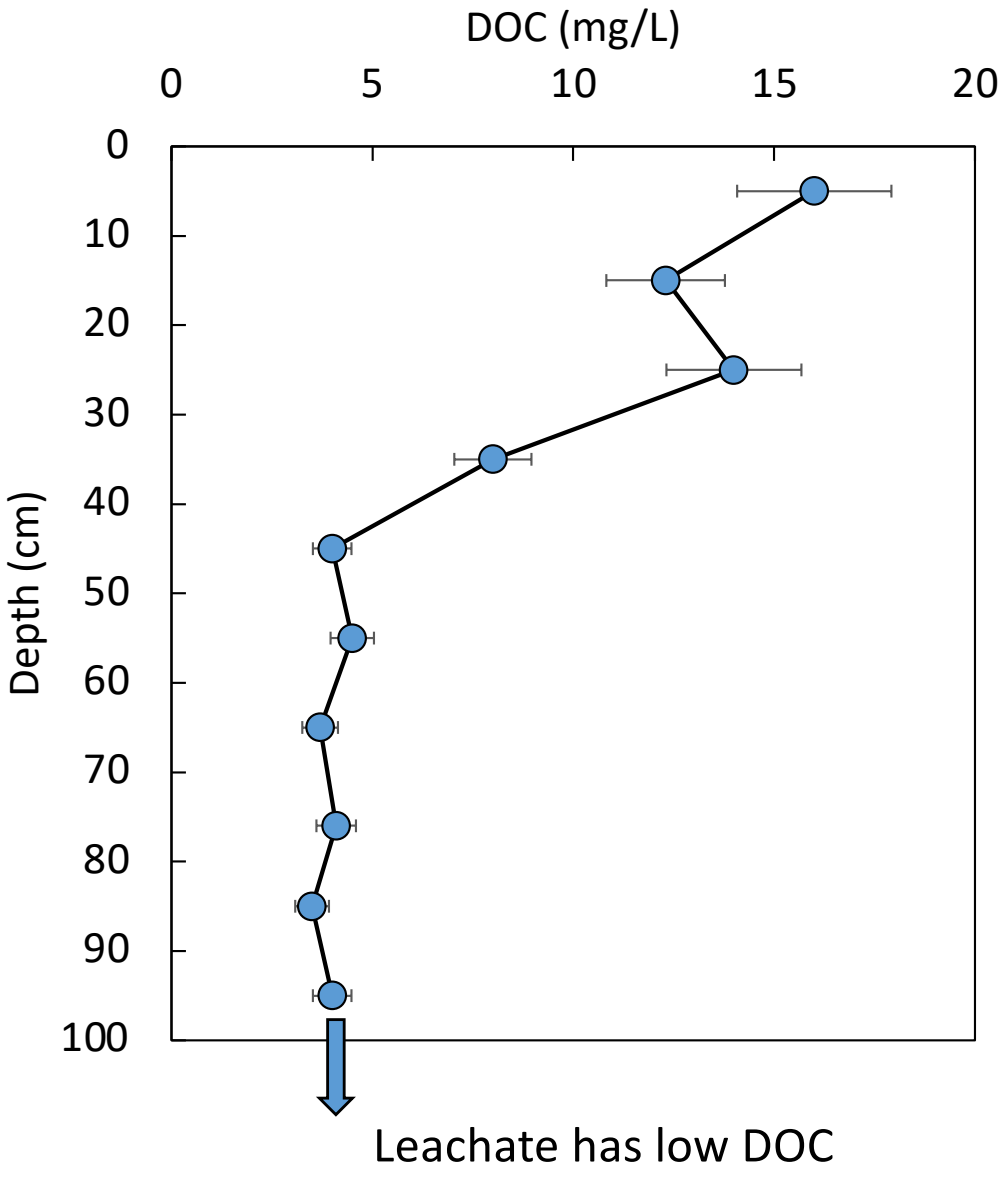


DOC concentrations in soil water from arctic tundra

DOC in soil solution

- Variable concentrations (5 to > 50 mg/L) that depend on the soil organic content
- formed from breakdown of leaf litter and organic matter near the surface
- percolate down through a soil profile and either bound to soil particles or are degraded by microorganisms

Example plot of DOC in soil water



DOC in Groundwater

- DOC concentrations: low (< 2 mg/L) due to removal of organic compounds during infiltration of water through soil

Rivers and Lakes: DOC concentrations: highly variable (5 – 20 mg/L) and dependent on inputs

- DOC can be low at low stream discharge (fed by groundwater) but increase with increasing discharge due to inputs from organic-rich soil water (runoff)

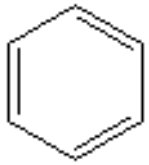
Oceans: DOC concentrations: low (~ 1 mg/L)

- Derived from continental runoff and photosynthesis near the surface which fixes CO_2 as organic matter

Unnatural Organic Matter in the Environment: Organic Pollutants

Nonaqueous phase liquids (NAPL) – nonpolar organic liquids with poor solubility in water that form separate phases in the subsurface

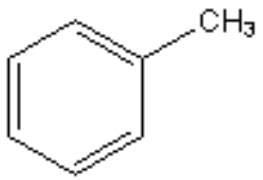
- LNAPL – light (density < water); e.g., gasoline
- DNAPL – dense (density > water); e.g., chlorinated hydrocarbons



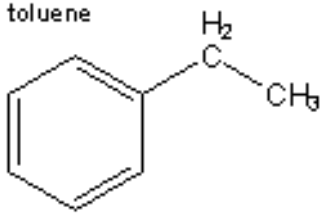
benzene

Aromatic hydrocarbons: BTEX (benzene, toluene, ethylbenzene, xylene)

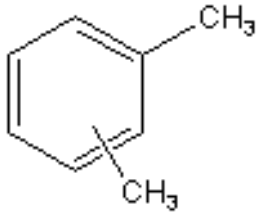
- carcinogenic, harmful to central nervous system



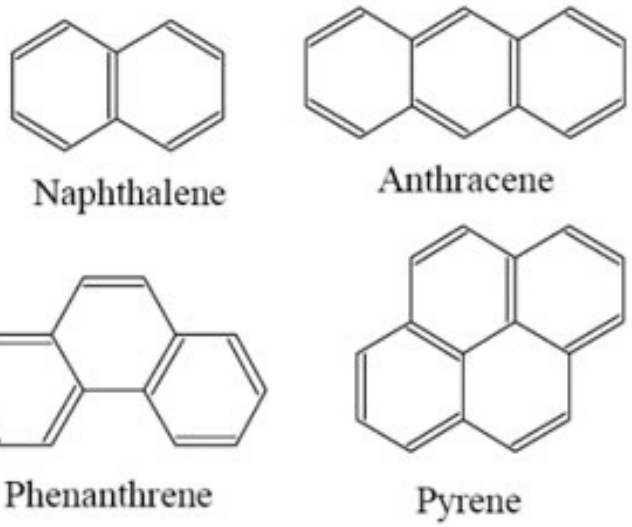
toluene



ethylbenzene

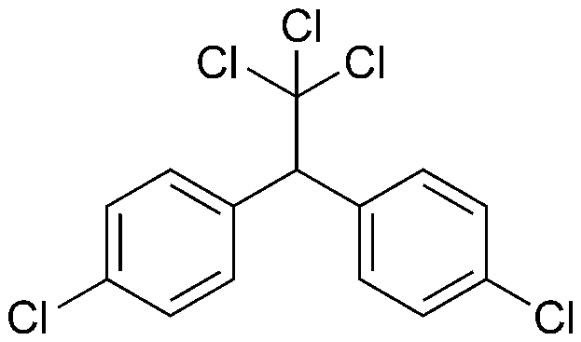


xylenes



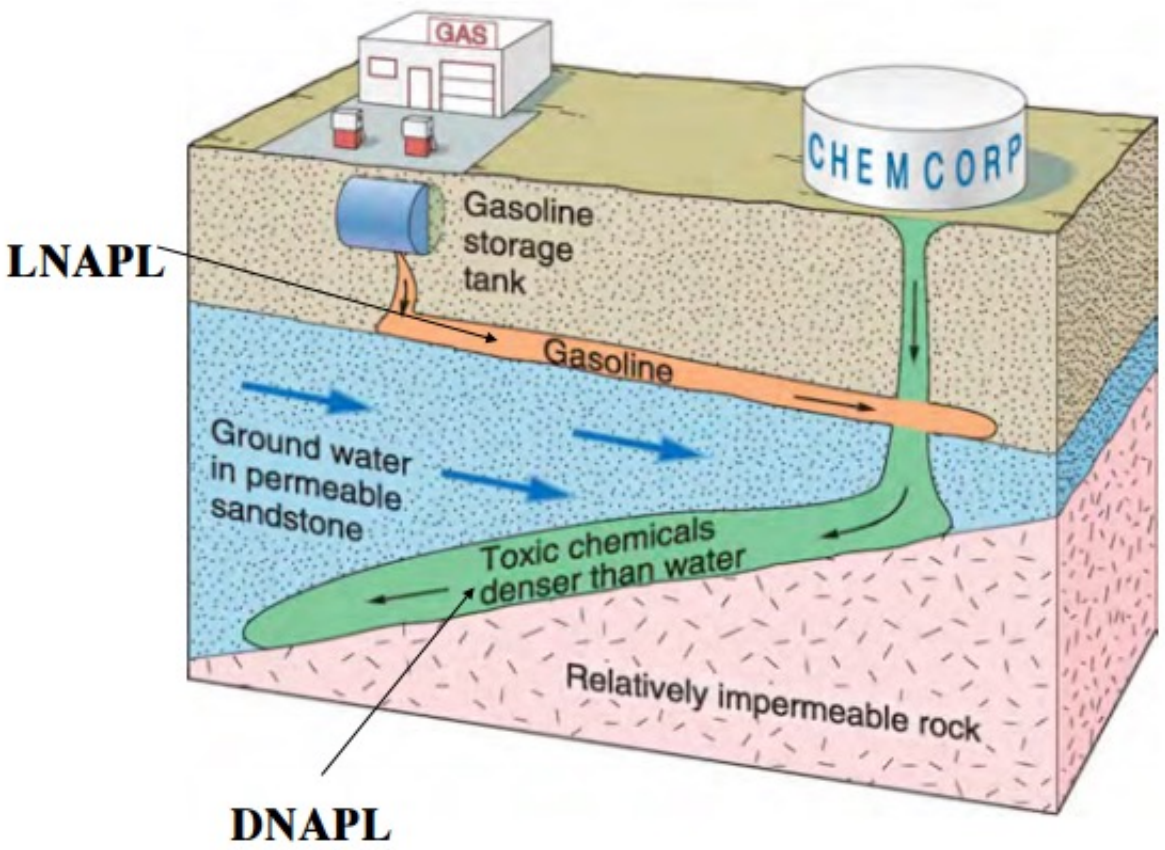
Polynuclear aromatic hydrocarbons (PAH)

Chlorinated hydrocarbons



LNAPLs

Less dense than water; Spread across surface of groundwater

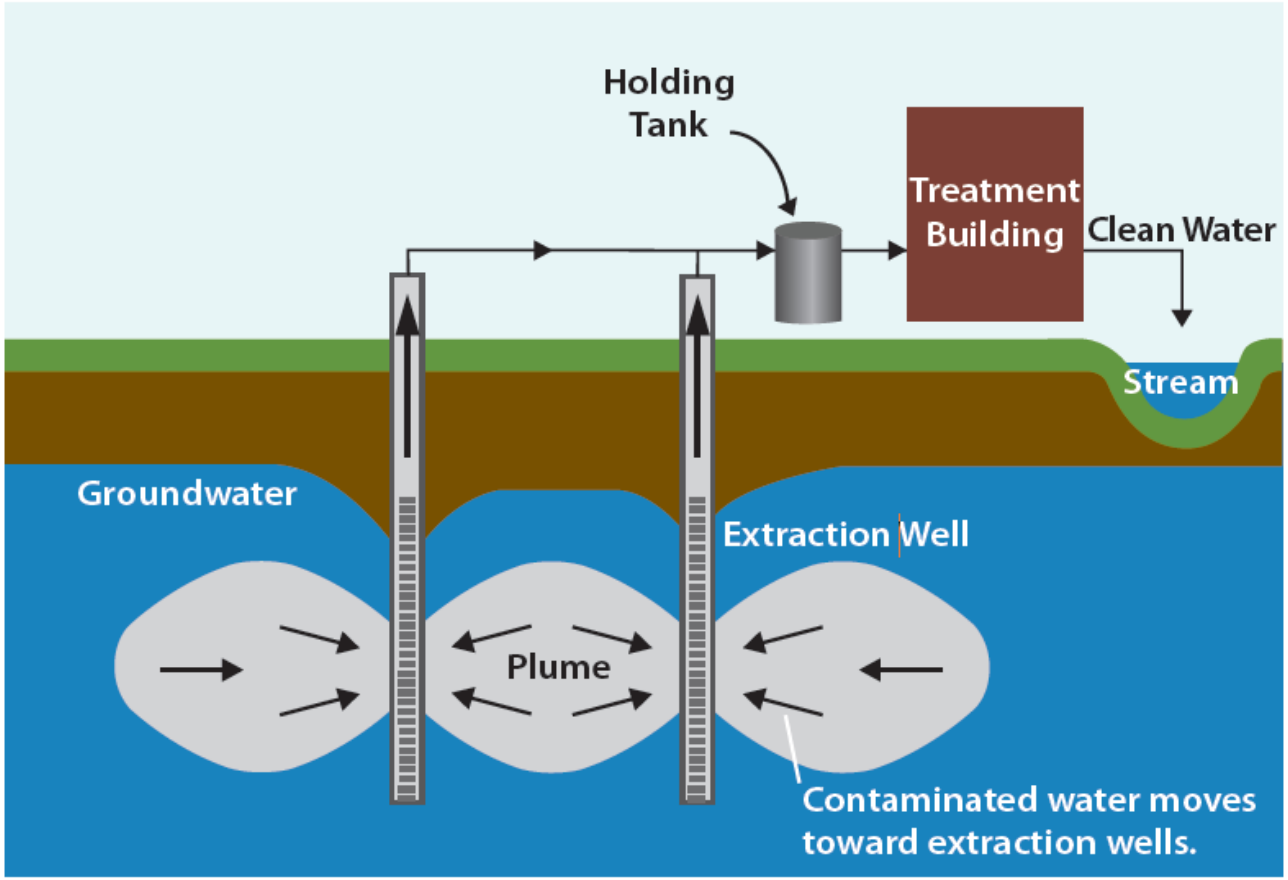


DNAPLs

More dense than water; Spread across surface of impermeable layers at depth (e.g., aquitards)

Pump and treat

- contaminated groundwater is pumped out of an aquifer and treated at the surface to remove contaminants; can be used to mitigate spread of a contaminant plume;
- Problems: difficult to remove all of the contaminants from the water and to treat it



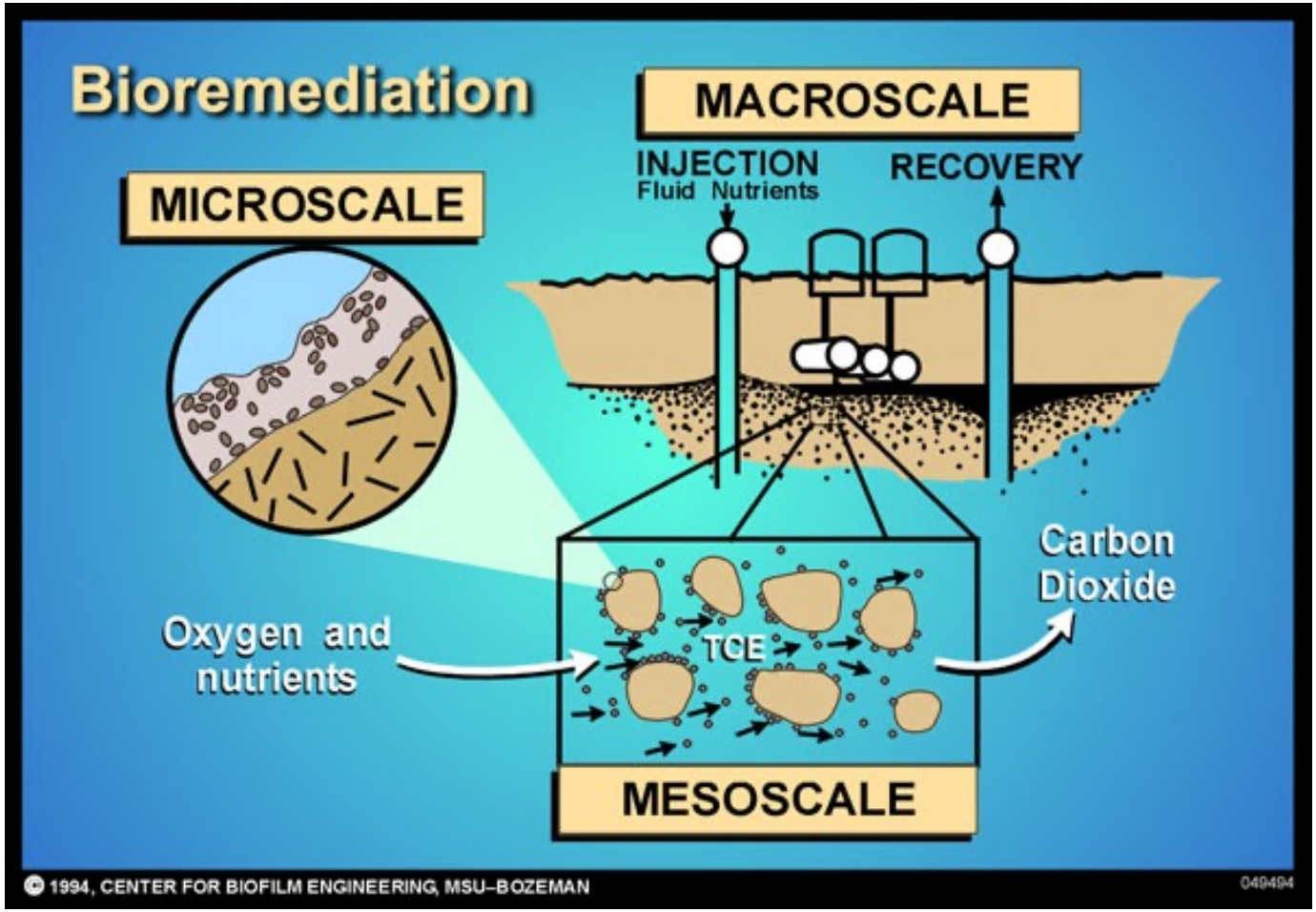
Example of a Pump and Treat System with Two Extraction Wells.

EPA Pump and Treat Diagram

Remediation methods

Bioremediation

- Stimulating microbial activity to enhance decomposition of organic contaminants into CO_2
- Problems: the contaminants are usually difficult for microbes to degrade; can form harmful byproducts



Remediation methods

Challenges for remediating organic pollutants:

a. Dispersion – movement of pollutants through the subsurface
b. Adsorption – binding of pollutants to organic and mineral surfaces

Polar compounds

- adsorb to surface charges on clay minerals and oxides

Nonpolar compounds

- Partition out of water; strongly adsorb to nonpolar phases in the subsurface; e.g., solid organic matter coatings on minerals

- ***Adsorption*** of nonpolar compounds follows distribution coefficient (K_d):

$$K_d = C_{ads}/C_{soln}$$

- The distribution coefficient for an organic molecule depends on its hydrophobicity, affinity for natural organic matter, and abundance of natural organic matter

Techniques to analyze natural organic matter

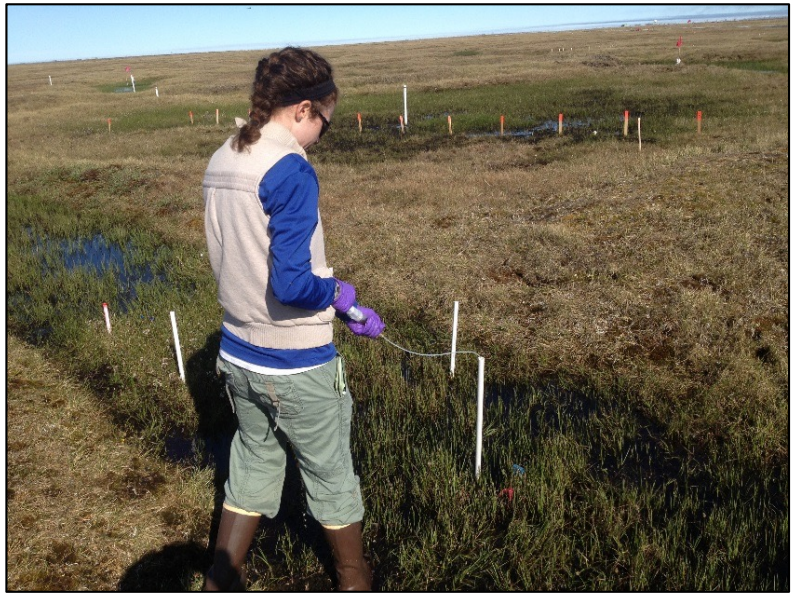
How to collect water samples for analysis of DOC:

Collection:

Soil water: collect water from PVC pipes installed in the ground at various depths

Lysimeters: pull water from unsaturated soils

Piezometers: collect water from saturated soils



Storage:

a) **Store** in amber glass vials (not plastic!) that have been combusted at 550°C to remove organic contamination; amber prevents light degradation

b) **Filtration**: filter water through 0.2 or 0.45 µm filter to remove microbes

c) **Chemical treatment**: acidify water with hydrochloric acid to prevent microbial activity

d) **Chilling**: Store in fridge at 4°C until analysis

Organic matter in the environment

Dissolved Organic Carbon (DOC) – defined as all organic carbon that passes through a 0.45 µm filter

Total Organic Carbon (TOC) – all organic carbon in an unfiltered sample
(includes particulates larger than 0.45 µm diameter)

Techniques to analyze natural organic matter

Quantifying the concentration of organic C

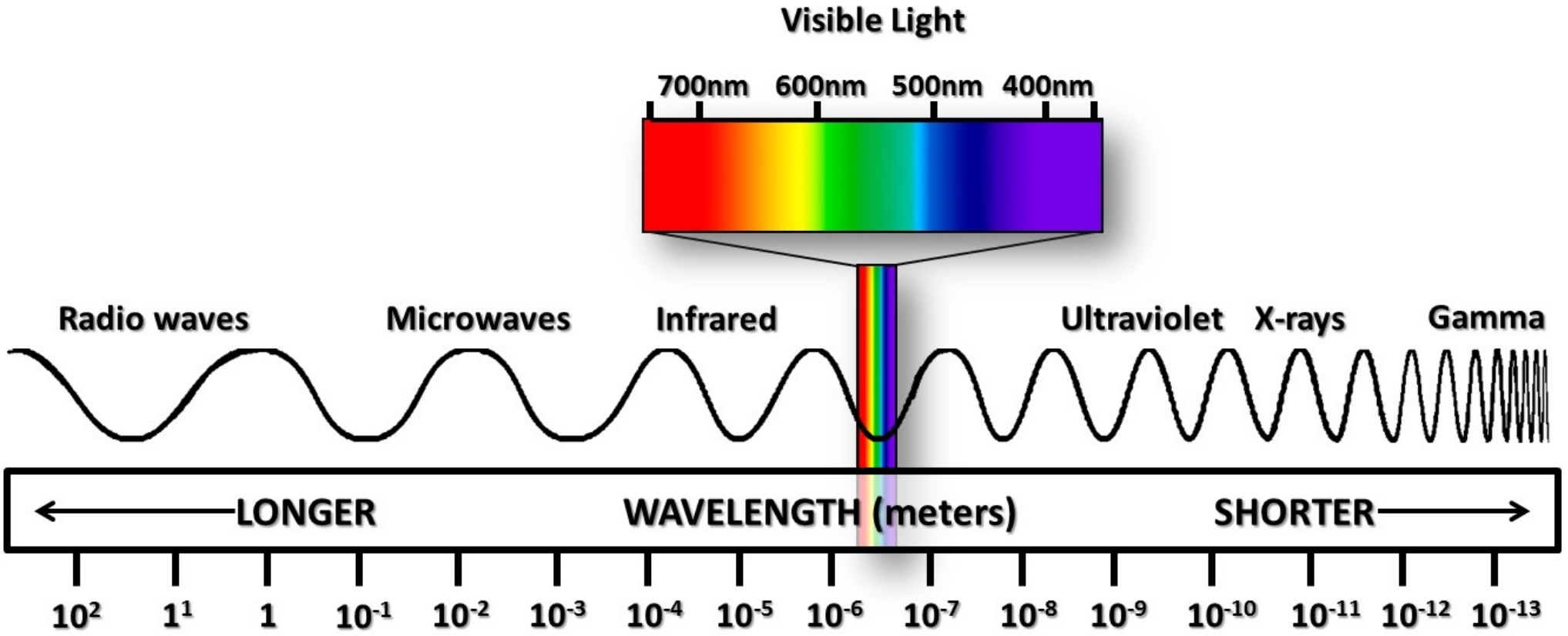
1. **TOC analyzers** – quantification of CO_2 released from combustion of organic matter; can be done on aqueous or solid samples depending on instrument
2. **"Loss on ignition"** – burns off all organic matter (CH_2O) in an oven, and the weight difference is used to approximate C content

$$\text{“}CH_2O\text{”} + O_2 \rightarrow CO_2 + H_2O$$

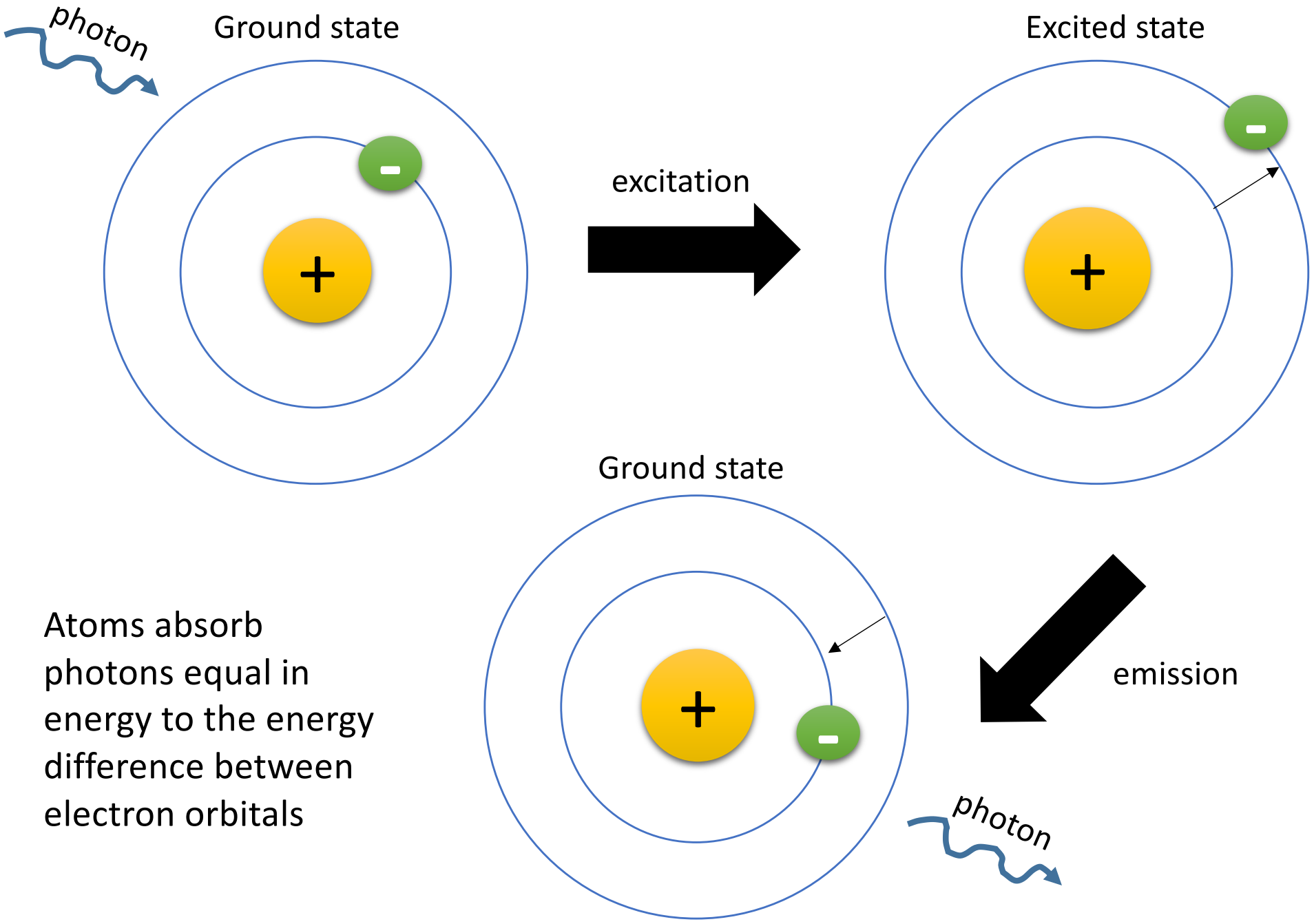
Techniques to analyze natural organic matter

Characterizing the chemical composition of organic C:

Spectroscopy – study of interaction between light and matter



Techniques to analyze natural organic matter



Atoms absorb photons equal in energy to the energy difference between electron orbitals

Techniques to analyze natural organic matter

Ultraviolet-visible spectroscopy (UV-Vis)

- measures absorbance of ultraviolet and visible light by organic compounds