FACTORS INFLUENCING THE BIOLOGICAL AND PHYSICAL AVAILABILITY OF CHEMICALS IN CONTACT WITH SOIL PARTICLES

Joe Pignatello

The Connecticut Agricultural Experiment Station, New Haven

2021 virtual Annual Meeting of the
Connecticut Association of Wetland Scientists

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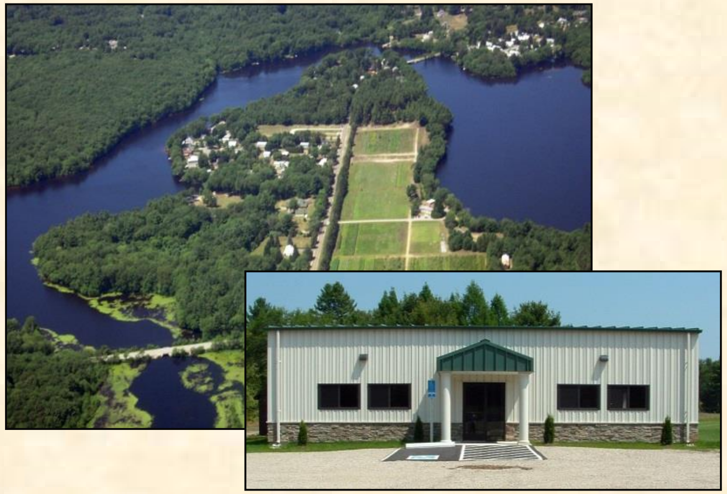
Main Laboratories, New Haven

Valley Laboratory Windsor

Lockwood Farm Hamden



Griswold Research Center

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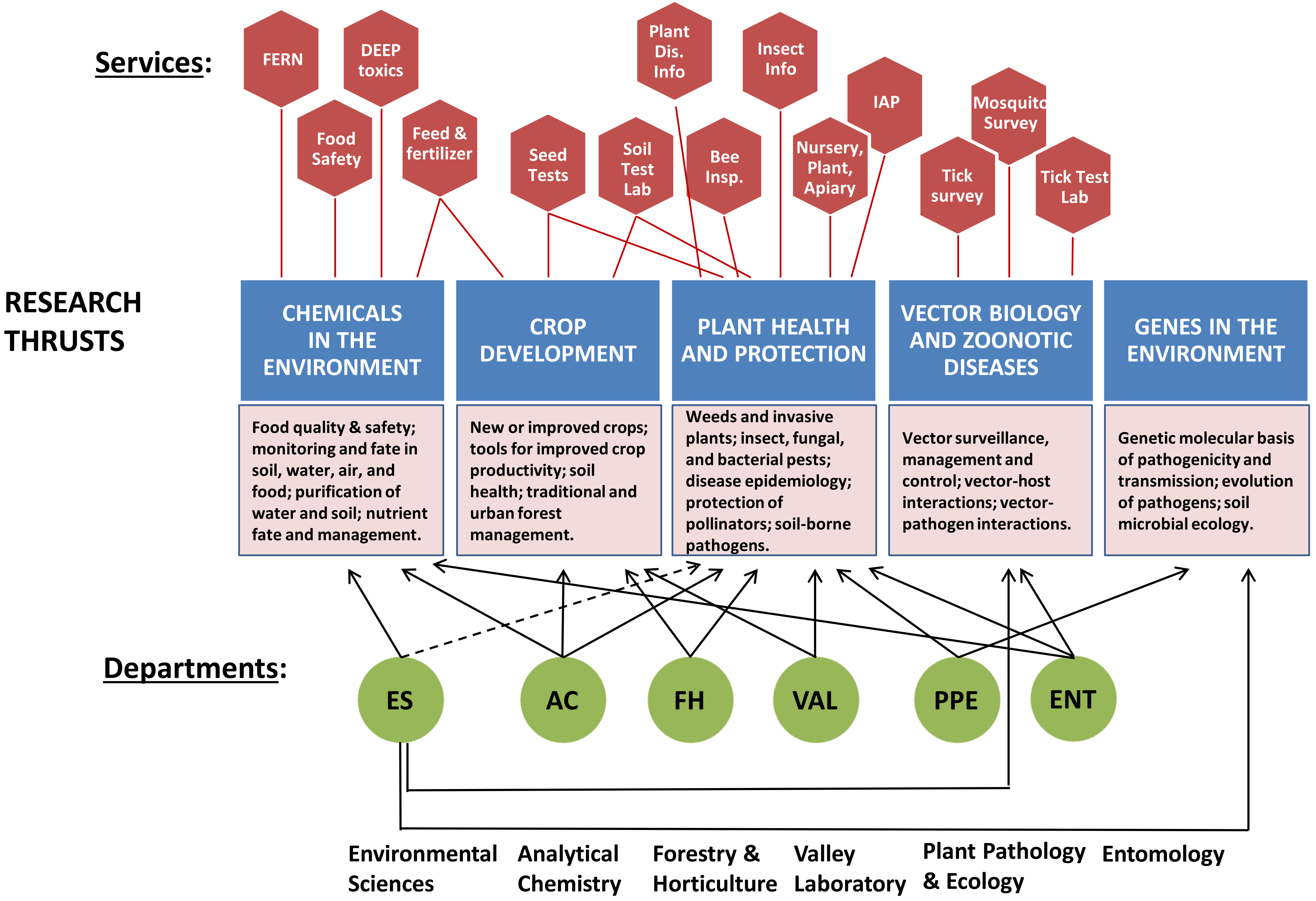
CAES Mission Statement:

"…to develop, advance, and disseminate scientific knowledge, improve agricultural productivity and environmental quality, protect plants, and enhance human health and well-being through research for the benefit of Connecticut residents and the nation."



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Soil and Water Quality

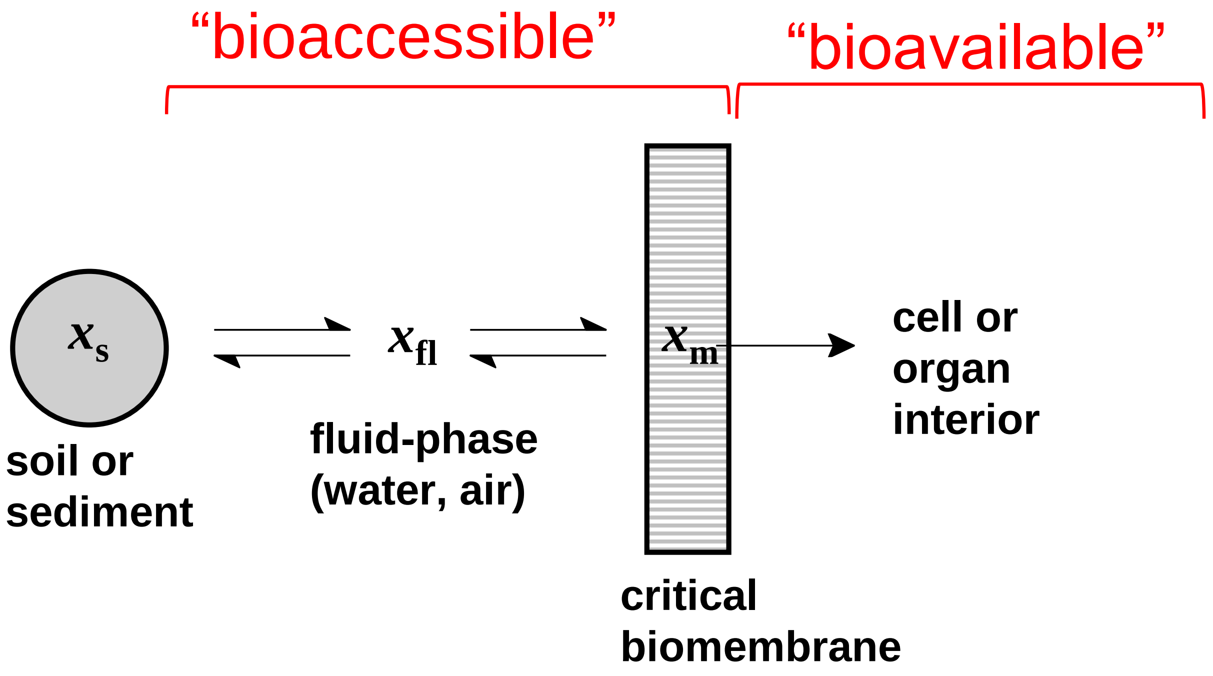
- Behavior and bio-availability of pollutants in the soil environment.
- Research on physical-chemical methods to remove and/or destroy pollutants in soil, water, and air.
  - **insecticides and herbicides**
  - **combustion byproducts**
  - **pharmaceuticals and personal care products**
  - **dyes**
  - **chlorinated solvent compounds**
  - **per- and polyfluorinated compounds (PFAS)**
  - **nutrient pollution**
- Natural chemical and photochemical processes in the environment.

Bioavailability

- “Importance of soil properties and processes on bioavailability of organic compounds,” J. J. Pignatello* and S. L. Nason. In: J-J. Ortega-Calvo and J. R. Parsons (eds), *The Handbook of Environmental Chemistry: Bioavailability of Organic Chemicals in Soil and Sediment*. Springer. 2020.

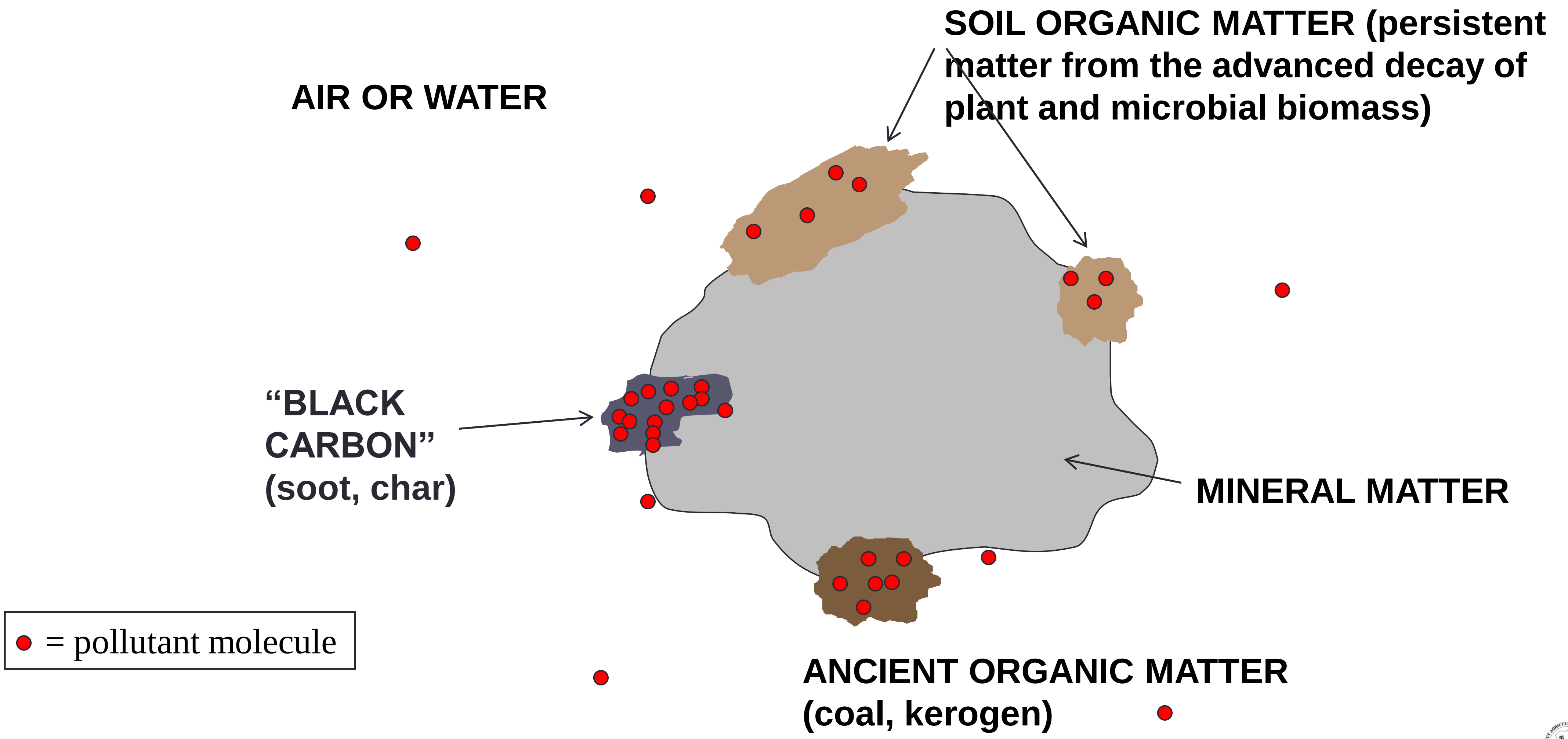
- ‘Bioavailability of contaminants in soil,” J.J. Pignatello. In: A.J. Singh, et al. (eds.), *Advances in Applied Bioremediation in Soil Biology 17*, Springer-Verlag, Heidelberg, Germany, 2009; pp 35-71.

bioavailability model



- distribution between soil fluids and soil particles **(sorption/desorption)**
- transport through the fluid to the organism interface
- diffusion across a critical biomembrane (CBM) to enter cell or organ
- transport through the organism to site of toxic action

Dynamic partitioning between soil particles and soil fluids:



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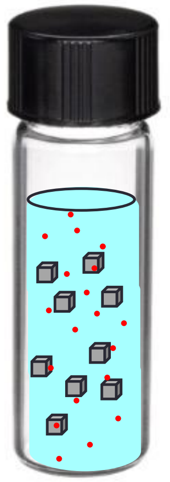
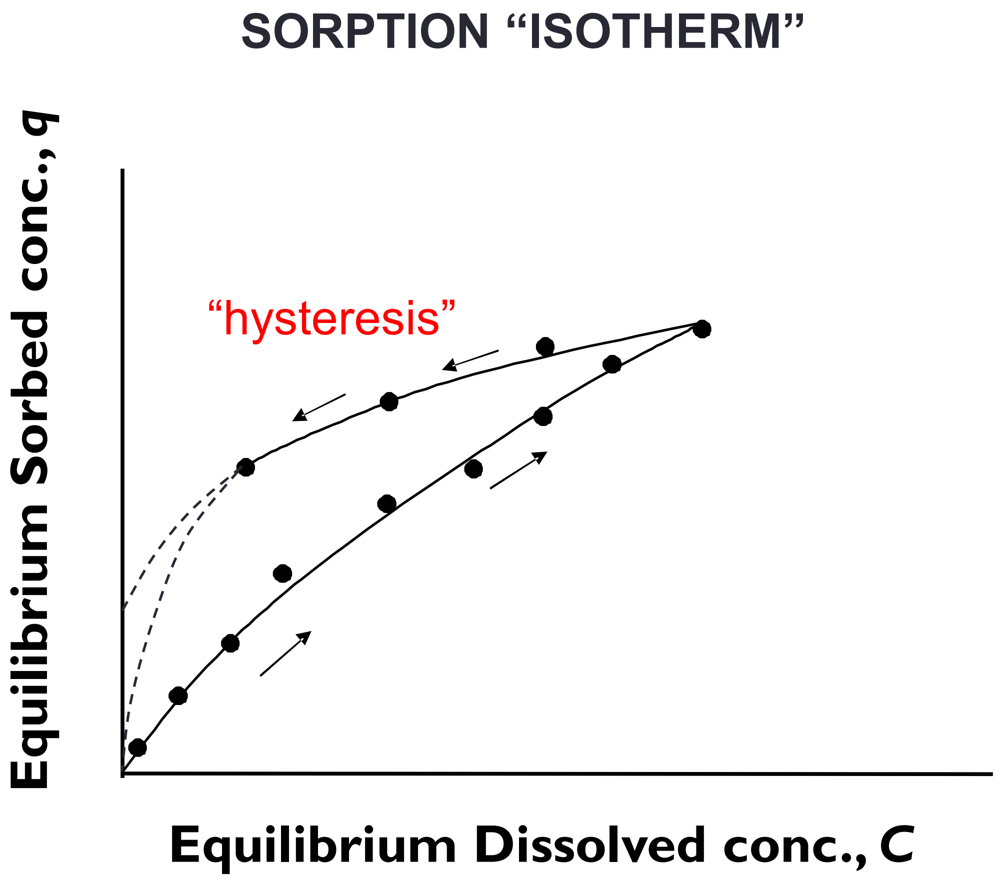
How do we measure sorption?

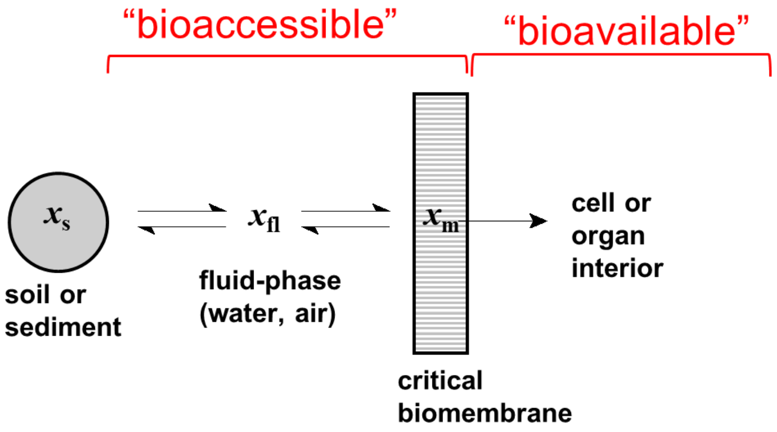


1. adsorption: water + particles + chemical mixed gently until apparent equilibrium is reached.
2. desorption: chemical concentration in water is lowered by stepwise removal or dilution.



Dynamic partitioning between soil particles and soil fluids and its relationship to bioaccessibility:

- Organisms cannot directly access adsorbed molecules.
- Thus, **sorption** imparts **resistance** to bioaccessibility by limiting the solid-to-liquid exchange of molecules.
- Sorption is often not completely reversible; release is typically slower than uptake.
- **Facilitated bioaccessibility** is an ability of the organism itself to actively or passively promote their assimilation of a pollutant.
- A major issue in risk analysis is how to reliably predict the percentage that is ultimately not bio-accessible, and therefore protective of the organism(s).
  How clean is clean?

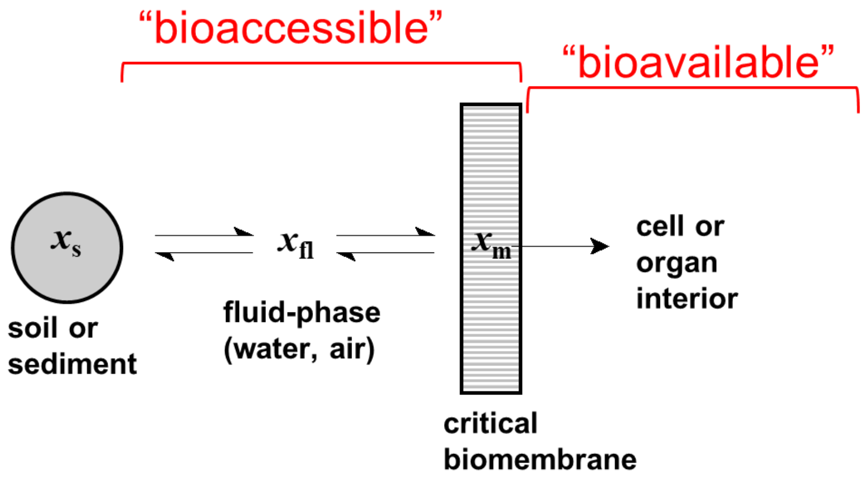


Potential causes of facilitated bioaccessibility:

- The "surface depletion" effect
  (removal from the fluids surrounding the soil particle promotes further desorption)

- Alteration of the soil matrix properties
  - chemistry of or around particles (e.g., pH)
  - physical structure of particles

- Release of "bio-surfactant" molecules
  - microbes: lipids, phospholipids, glycolipids
  - plants: root exudates
  - animals:
    - bile acids in digestive juices
    - dermal oils
    - lung fluids (phospholipids)



Residues of the soil fumigant, ethylene dibromide (EDB) in two field soils

Biodegradation by soil bacteria of historic (native) residues of EDB *vs* freshly-added EDB

Br-CH_2CH_2-Br

EDB

Br-$^{14}CH_2CH_2$-Br

^{14}C-EDB

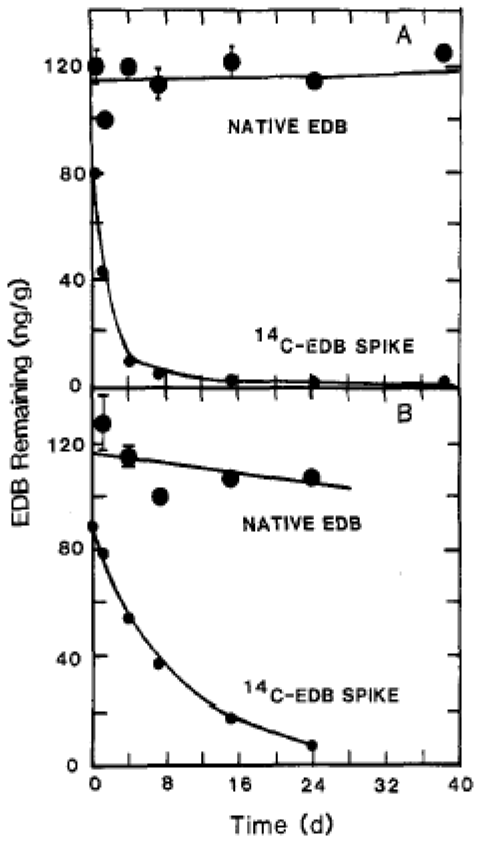


Figure 6. EDB degradation in soil suspensions by indigenous microbes showing the persistence of native EDB compared to a freshly added [^{14}C]EDB spike: (A) Lockwood soil and (B) Warehouse Point soil. The range of duplicates, when larger than the size of the symbol, is indicated by error bars.

Lockwood soil,
0.9 years since last application

Warehouse Point soil,
3 years since last application

Bioaccessibility is subject to aging effects

Steinberg , Pignatello et al., *Environ. Sci. Technol.* 21: 1201 (1987).

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Residues of the soil fumigant, ethylene dibromide (EDB) in two field soils

Desorption rate of native EDB into water at different temperatures

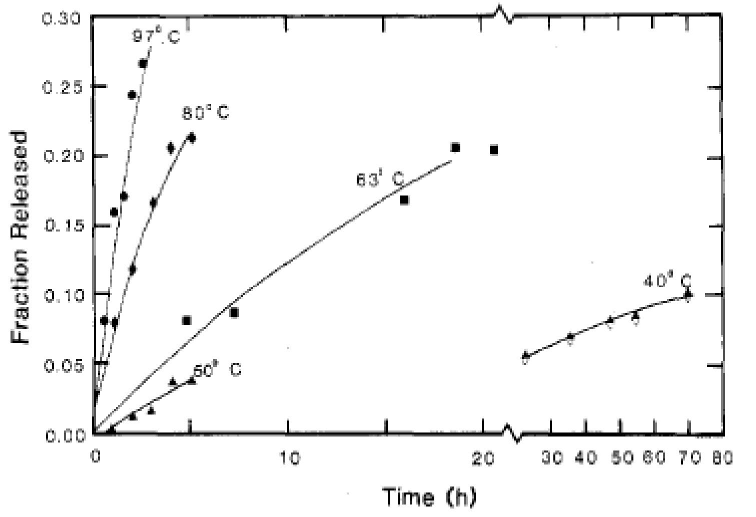


Figure 2. Effect of temperature on native EDB release from Lockwood soil. Fraction released = [C]/([S] + [C]) (see text).

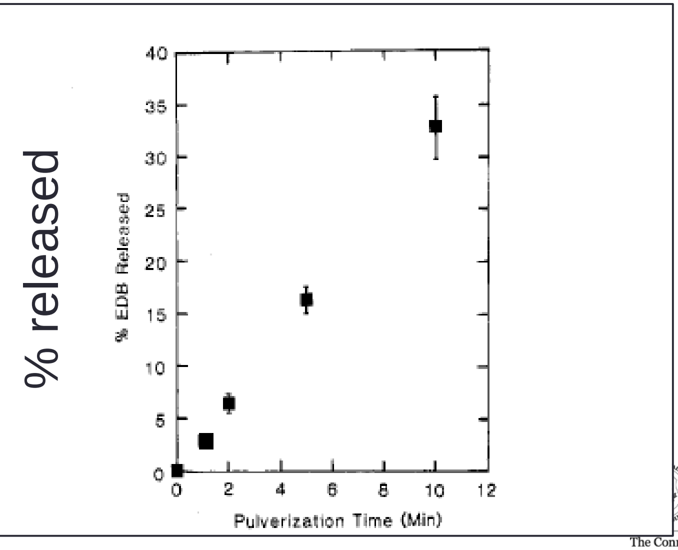
Diffusion coefficients and calculated time for 50% equilibrium at 20 °C (5 g soil in 10 mL water)

Table II. Best Fit Values of Effective Diffusivity D_{eff} and Time Required To Reach 50% of Equilibrium According to a Radial Diffusion Equation

soil	mean particle radius, μm	D_{eff} for best fit to data, cm^2/s[a]	time for 50% of equilibrium, years
Lockwood	13.8	8×10^{-17}	23
Warehouse Point	13.8	2×10^{-17}	31

[a] By visual inspection of plots.

Effect of soil pulverization time in a ball mill on EDB release into water at 20 °C

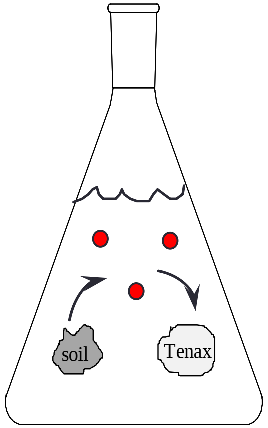


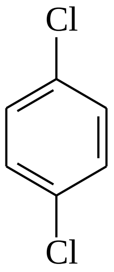
Pulverization time (min)

Release is highly sensitive to temperature and particle size

Steinberg , Pignatello et al., *Environ. Sci. Technol.* 21: 1201 (1987).

Fraction remaining after exhaustive extraction of ^{14}C-1,4-dichlorobenene sorbed to a high-organic matter soil and a low-rank coal





1,4-dichlorobenzene

Sorption for 0.5-1 year, followed by 3-times exhaustive desorption to Tenax for 21 days each

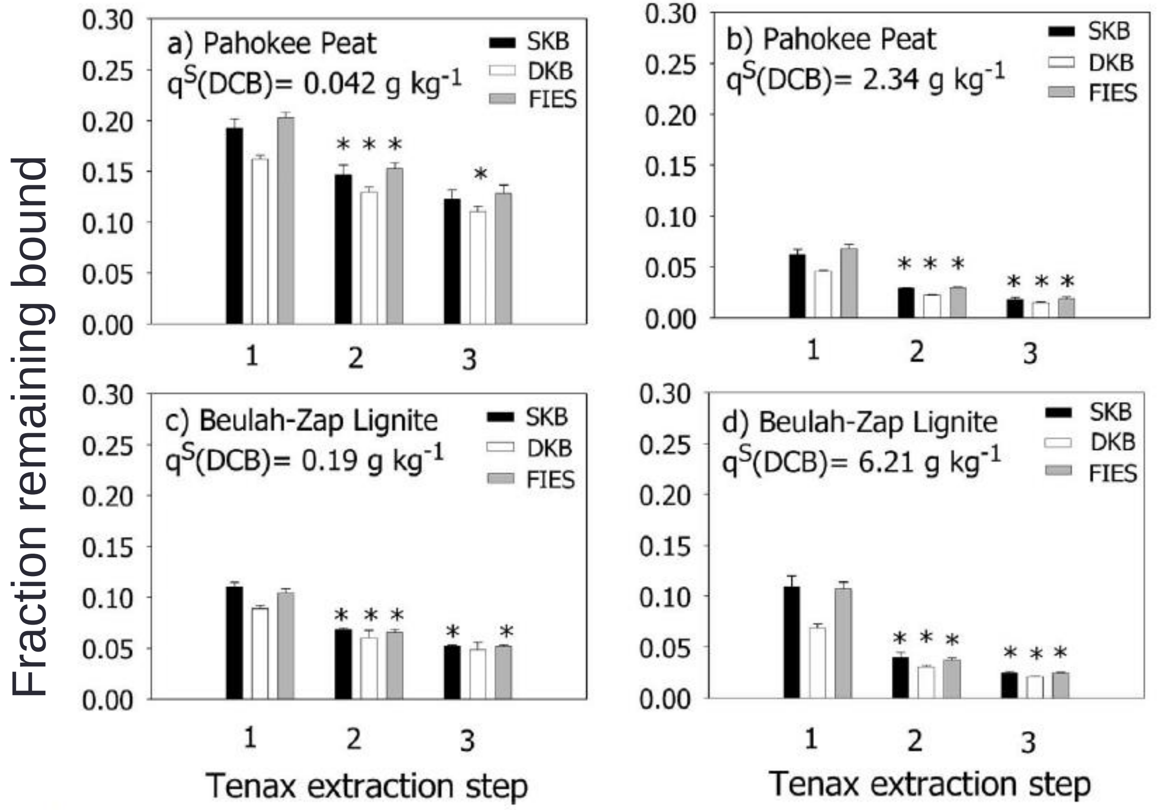


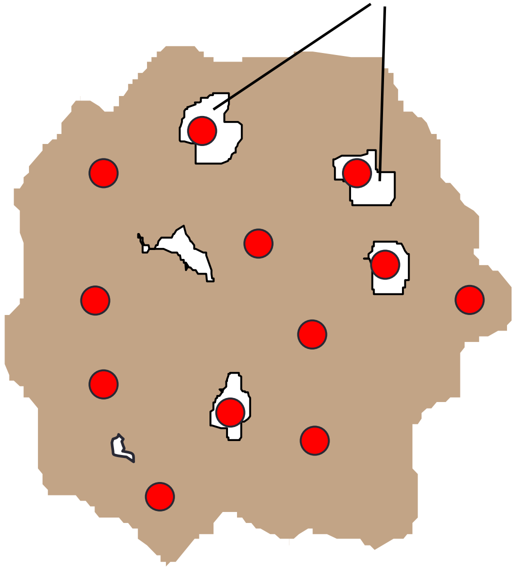
Fig. 6. Fraction (F^X_{Tenax}) of total initial 1,4-dichlorobenzene sorbed at the sorption point (q^S) remaining in Pahokee peat (**a**, **b**) and Beulah-Zap lignite (**c**, **d**) after consecutive Tenax extraction steps (X = 1 to 3). Error bars represent standard deviations of triplicates except for bulk sorption kinetics (SKB) in panel a and bulk desorption kinetics (DKB) in panel b (both duplicates). Asterisk indicates that the decrease in F^X_{Tenax} is statistically significant from the previous extraction step at $p = 0.01$ (comparison of the means of two samples using pooled estimates of standard deviations). There was no significant difference in F^3_{Tenax} among the SKB, DKB, and forward isotope exchange (FIES) at the sorption point experiments ($p \leq 0.01$) in all cases except panel d.

A small fraction of chemical diffuses into "tight" adsorption sites within particles

Sander and Pignatello, *Environ. Toxicol. Chem.* 28: 447-457, (2009).

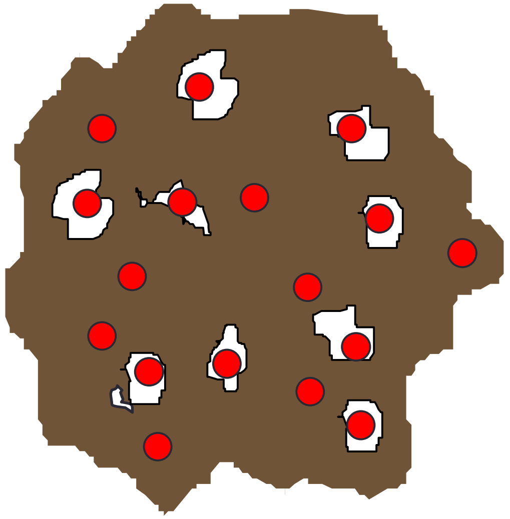
Ordinary soil organic matter

closed pores (“holes”) of molecular dimensions



low surface area and porosity

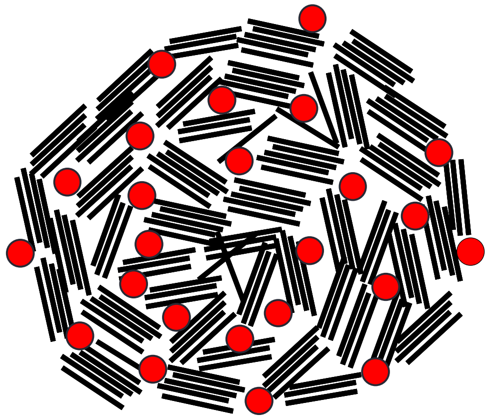
Ancient organic matter (coal, kerogen)



intermediate surface area and porosity

Black carbon

extensive micropore networks

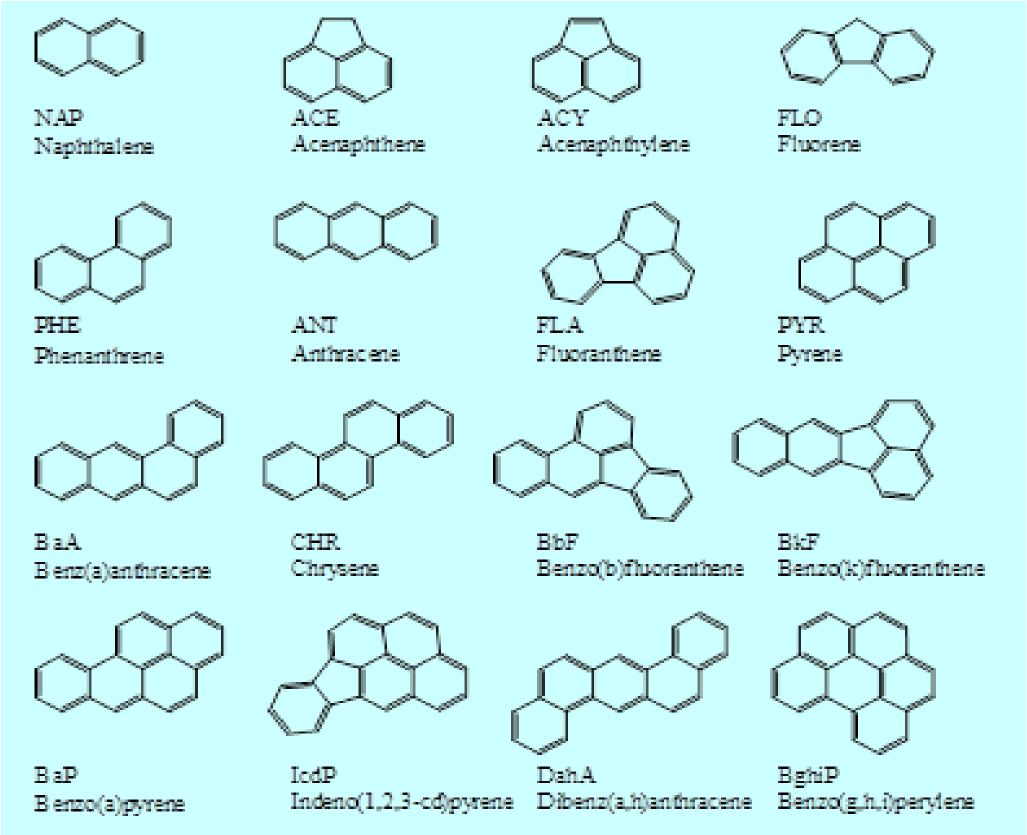


high surface area and porosity

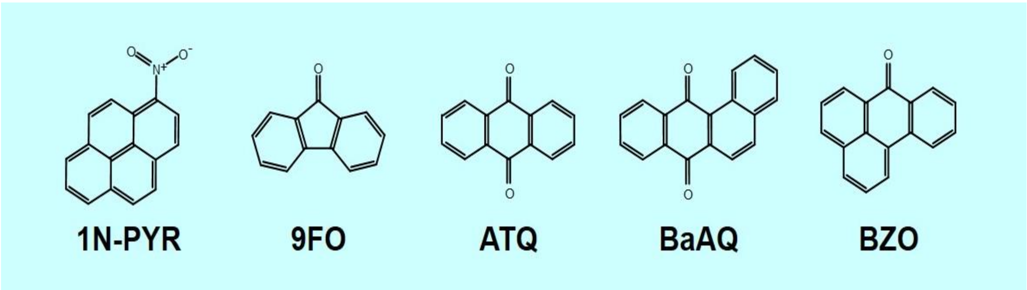
Resistant desorption is due to physical entrapment in molecular-size pores mainly in organic matter components of the soil.

Polycyclic Aromatic Hydrocarbons (combustion byproducts)

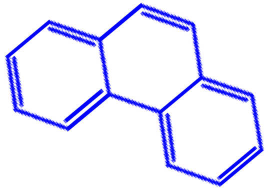
PAHs
(EPA stds.)



oxo- and nitro-
PAH
derivatives



Phenanthrene sorption and biodegradation in soil-water mixtures

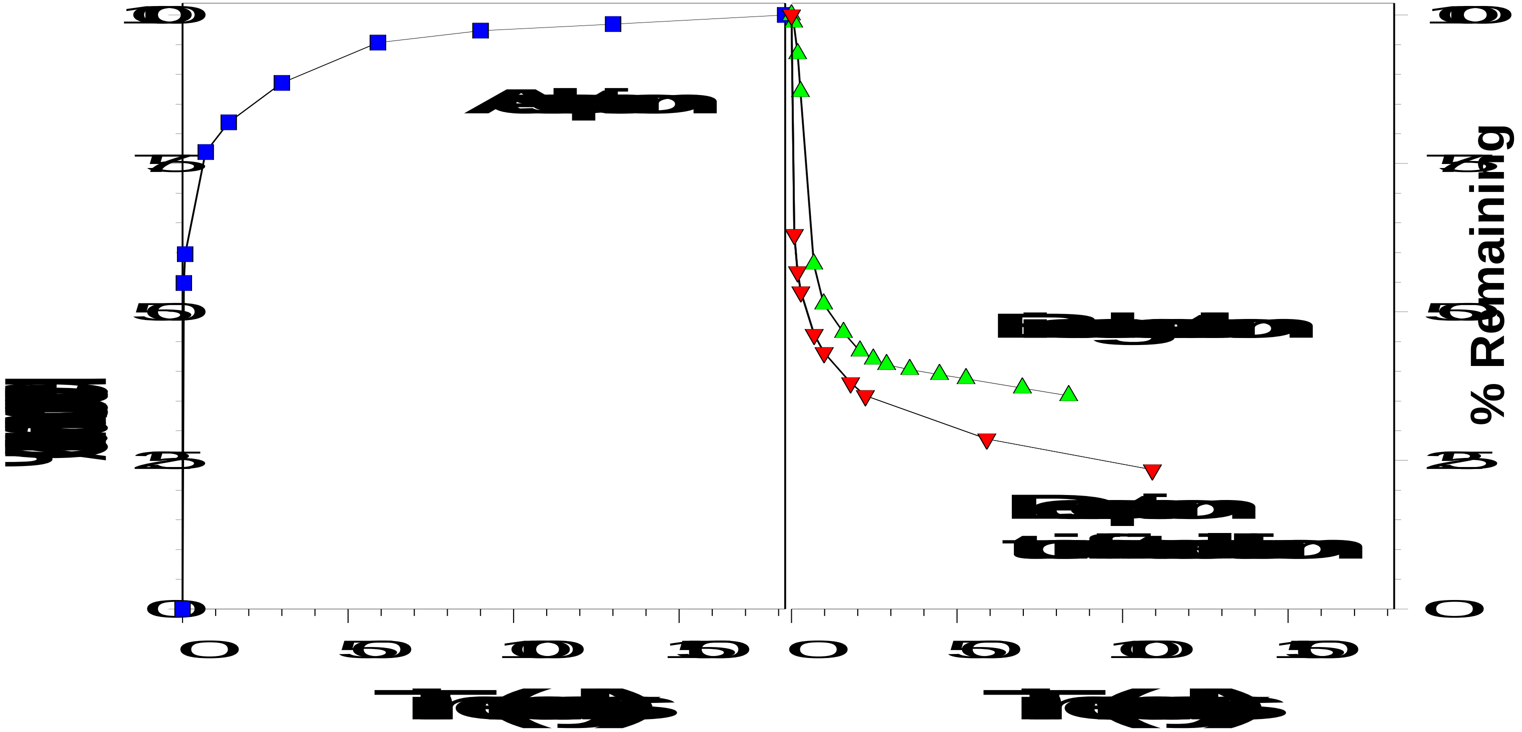


Phenanthrene

Port Hueneme soil, one of 15

Rate of uptake from water by sterile soil

In separate experiments:
- Desorption to infinite sink, Tenax or
- Biodegradation by *Pseudomonas sp.*



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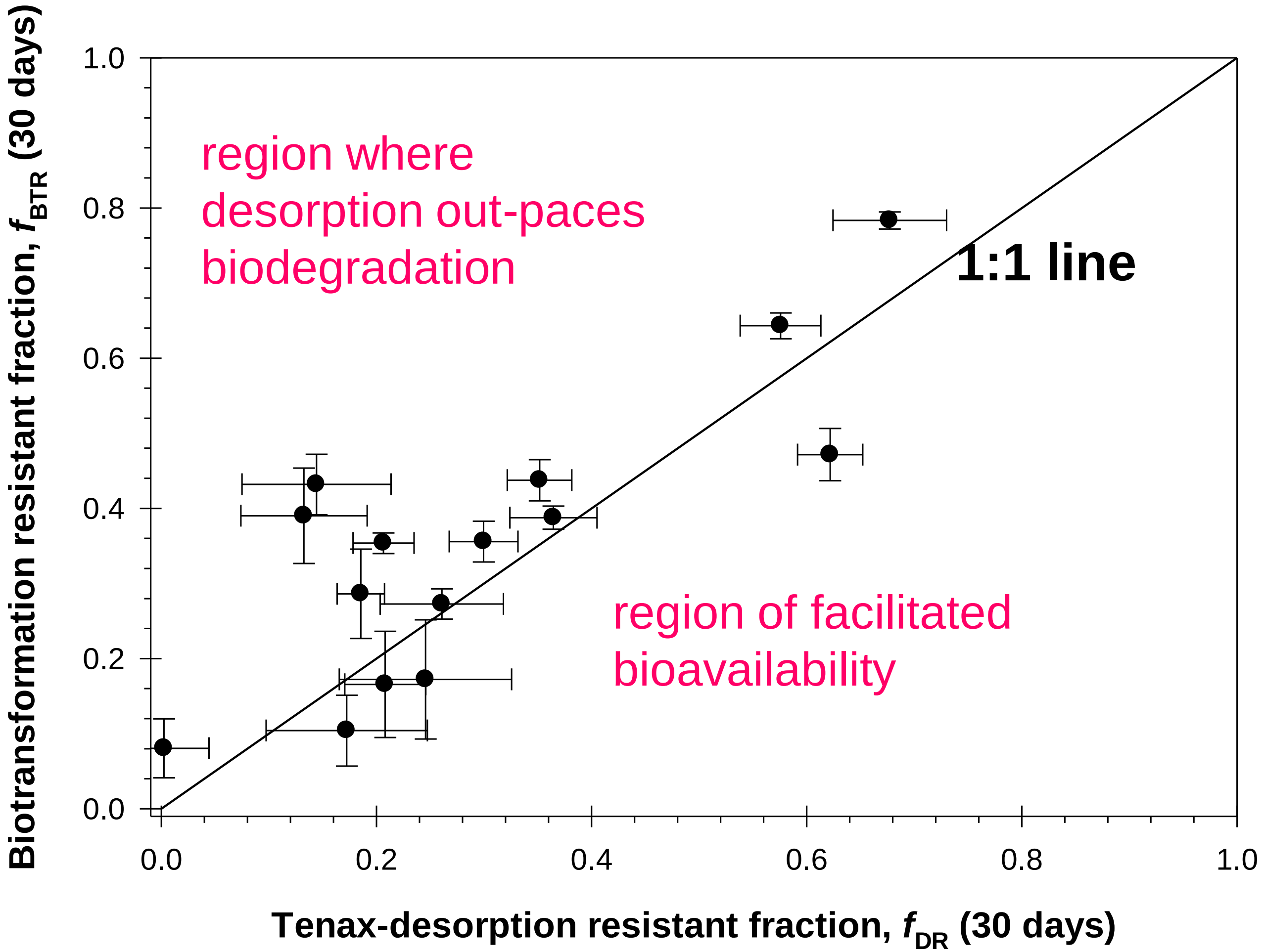
Braida, Pignatello et al., *Environ. Toxicol. Chem.*, 23: 1585 (2004).

Correlation between biodegradation resistance and desorption resistance of phenanthrene in 15 different soils



Braida et al., *Environ. Toxicol. Chem.*, 23: 1585 (2004).

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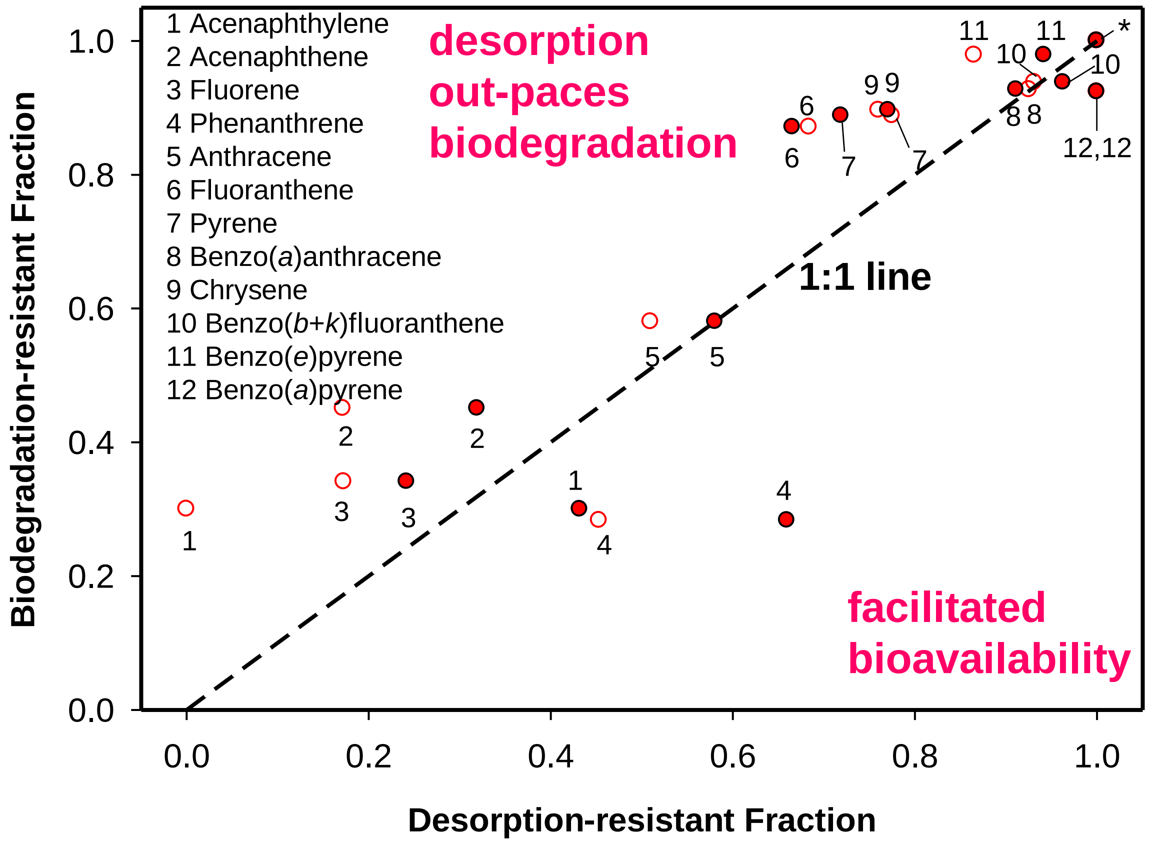
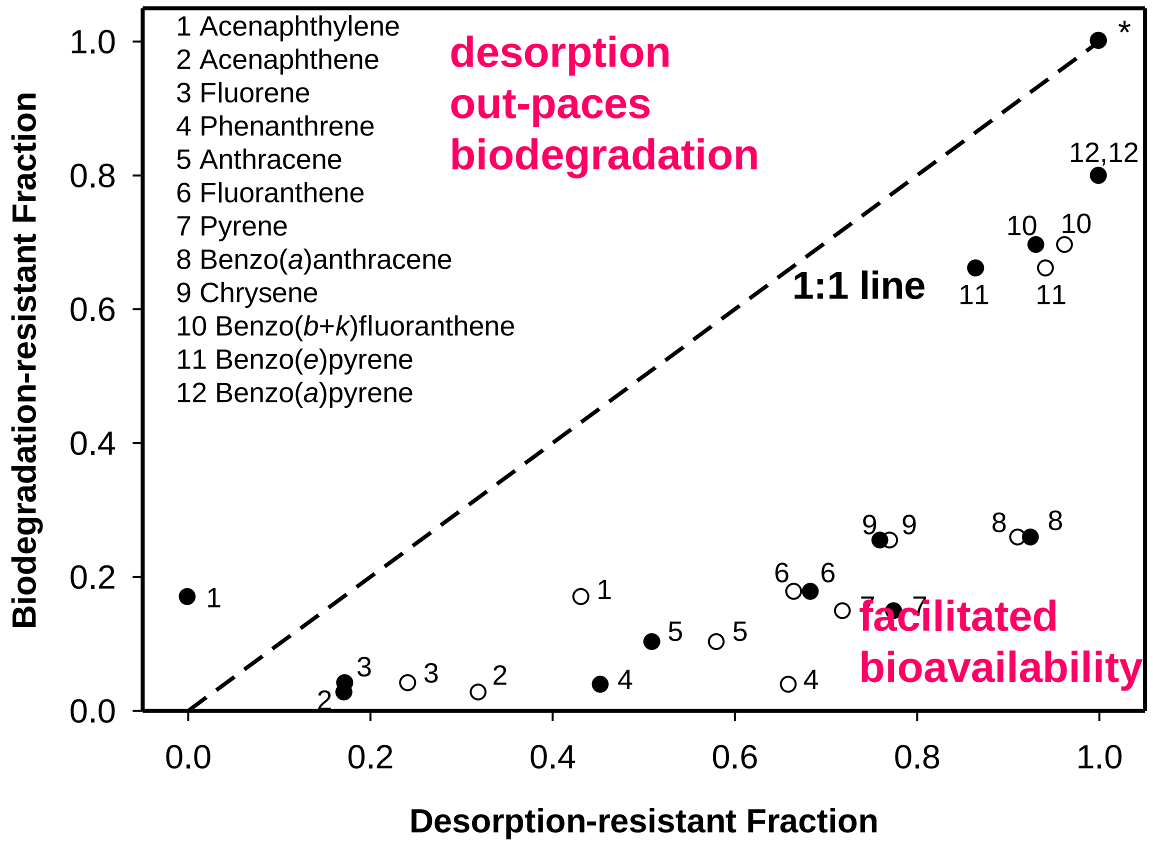
PAHs in coal-tar contaminated soil at a former manufactured gas plant site in Winsted, CT

Biodegradation by native bacteria (93 d) *vs.* desorption to Tenax, 103 d

in plain water



in water with N, P, K and trace nutrient metals



Li et al., *ET&C* 24: 741 (2005)

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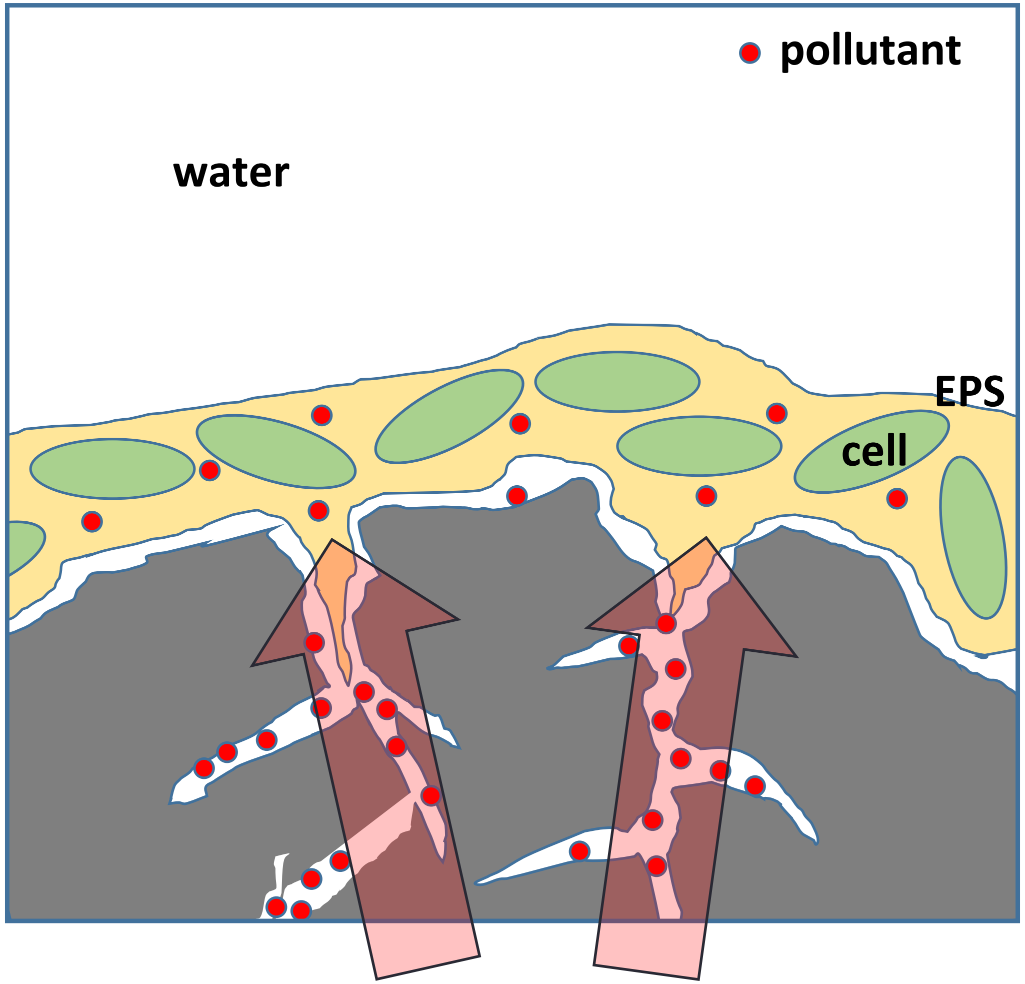
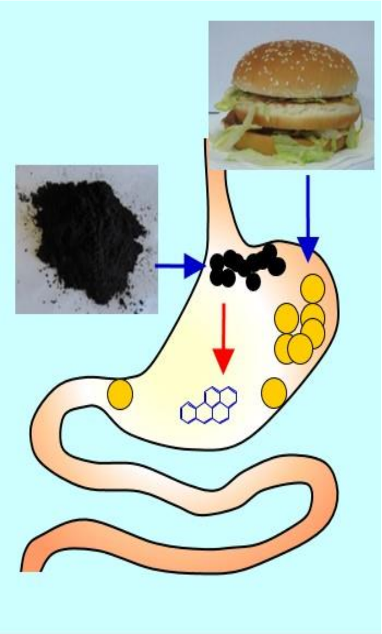
A possible cause of facilitated bioavailability

- “surface depletion” hypothesis: cells deplete chemical in stagnant layer very close to the particle surface. This drives molecular diffusion from interior of the particle.



Bioaccessibility of PAH residues in a fuel soot using an *in vitro* gastro-intestinal model (composite soot sample from local fuel oil boilers)

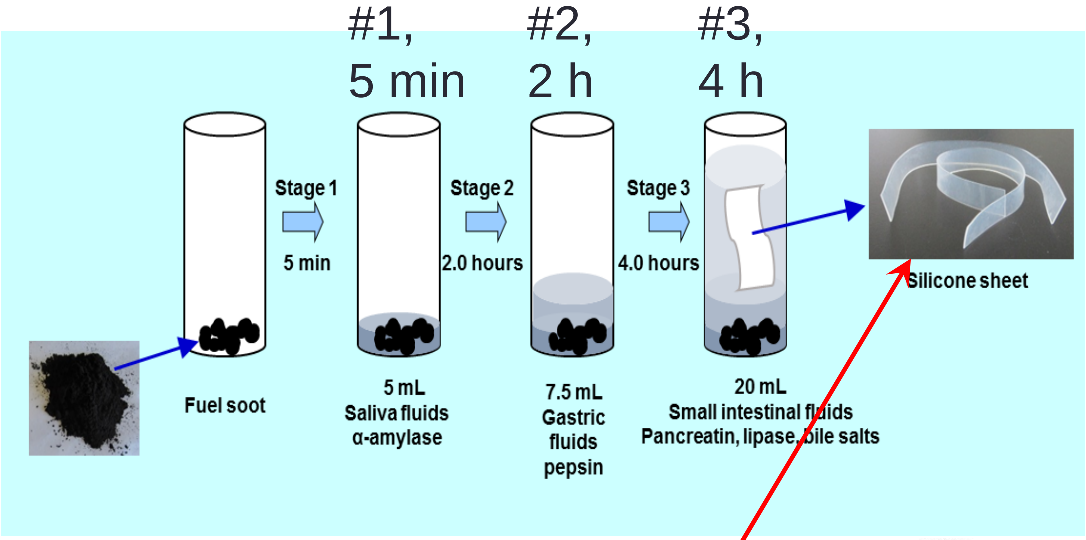
most uptake occurs in SI



#1(salivary)

#2 (gastric)

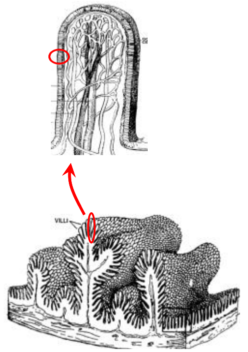
#3 (small intestine)



- ❑ fasting conditions
- ❑ fed conditions (carbohydrate, protein, or vegetable fat added at step #1)

SILICONE SHEET:

- hydrophobic
- fast diffusion
- mimics uptake by intestinal epithilium



villi in lining of small intestine

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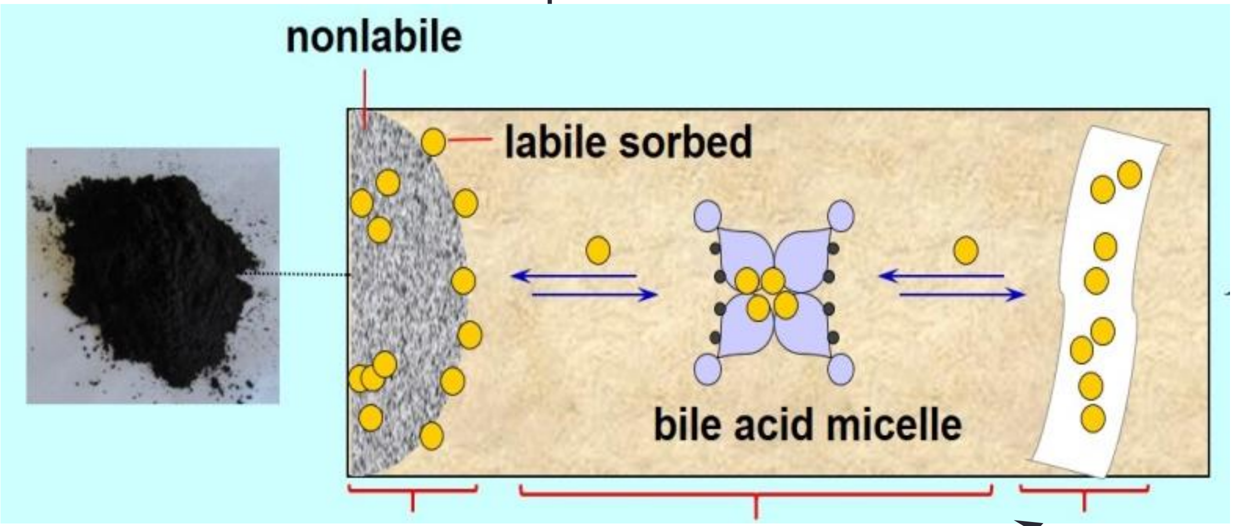
Zhang et al. *ES&T*, 49, 14641 (2015); ibid 49, 3905 (2015); ibid *Env. Pollut.* 218, 901 (2016).

Bioaccessibility of PAH residues in a fuel soot using an *in vitro* gastro-intestinal model

adsorbed but
resists desorption



adsorbed yet easy to come off, $B_{r,labile}$

Bioaccessible fraction, B_{app}

Limiting bioaccessibility,
$B_{lim} = B_{app} + B_{r,\ labile}$

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Zhang et al. *ES&T*, 49, 14641 (2015); ibid 49, 3905 (2015); ibid *Env. Pollut.* 218, 901 (2016).

Bioaccessibility of PAH residues in a fuel soot using an *in vitro* gastro-intestinal model

- the silicone sheet increases bioaccessibility of PAHs in soot
- B_{lim} ranges ~30 to ~65% of total analytical concentration of PAHs. Implications for risk assessment?
- Bioaccessibility increases with co-consumption of food, **especially food high in fat**.
  - food stimulates bile acids release (surfactant effect)
  - fat helps extract PAH residues from soot

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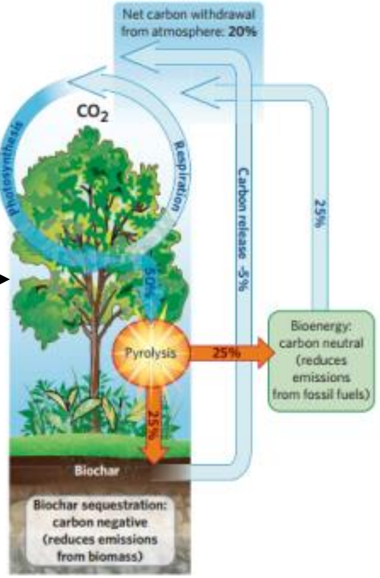
Zhang et al. *ES&T*, 49, 14641 (2015); ibid 49, 3905 (2015); ibid *Env. Pollut.* 218, 901 (2016).

APPLICATIONS OF BIOCHAR IN AGRICULURAL AND ENVIRONMENTAL MANAGEMENT

Biomass waste material

heat (400-800 °C) no air

carbon sequestration

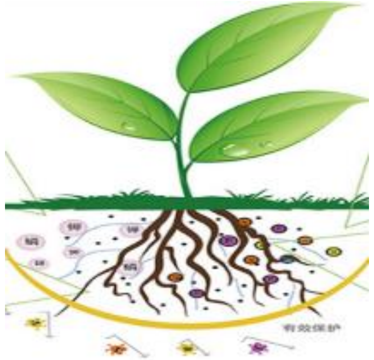


soil fertility

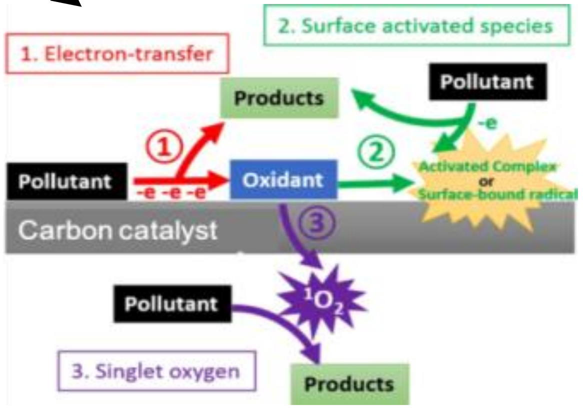
nutrient regulation

sorbents

catalysts



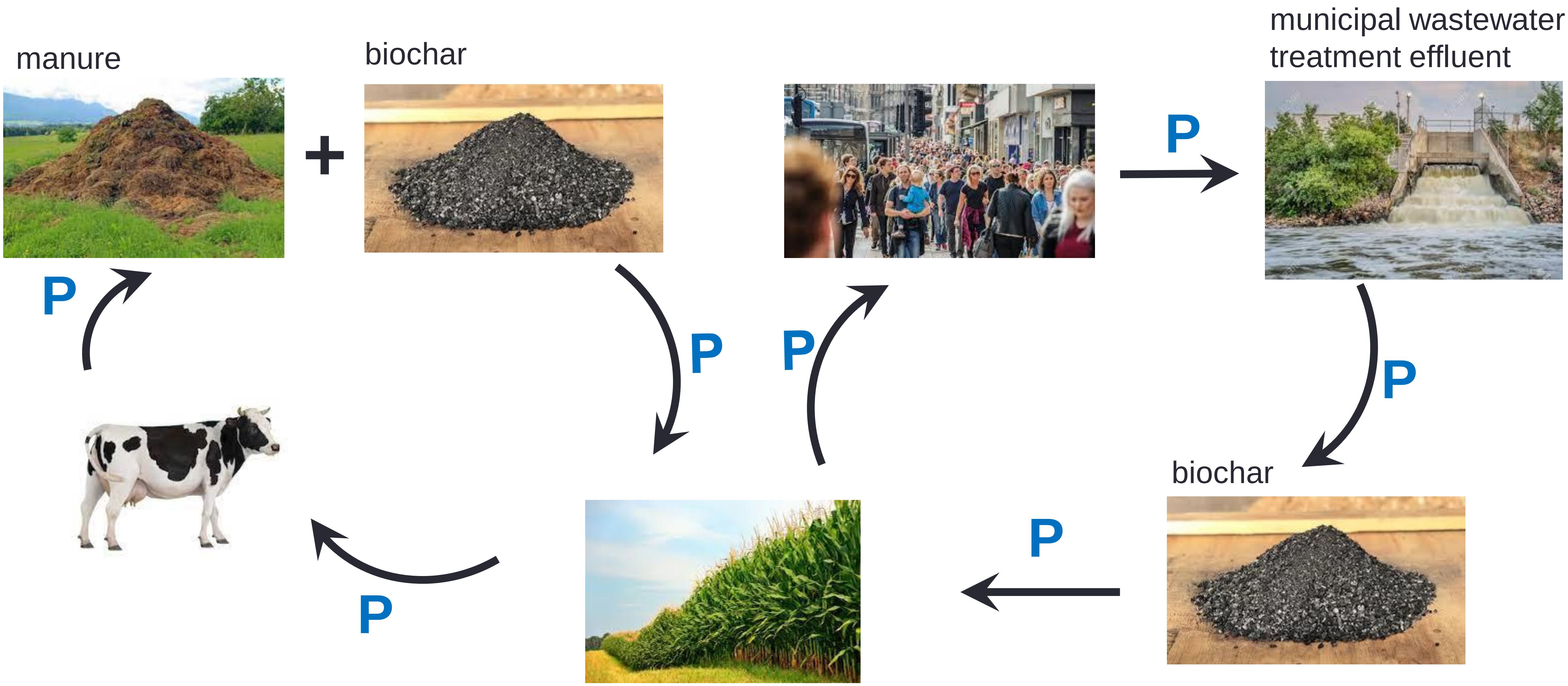
Improve soil aggregate structure
Improve acidity soil
Conserve moisture and fertilizer



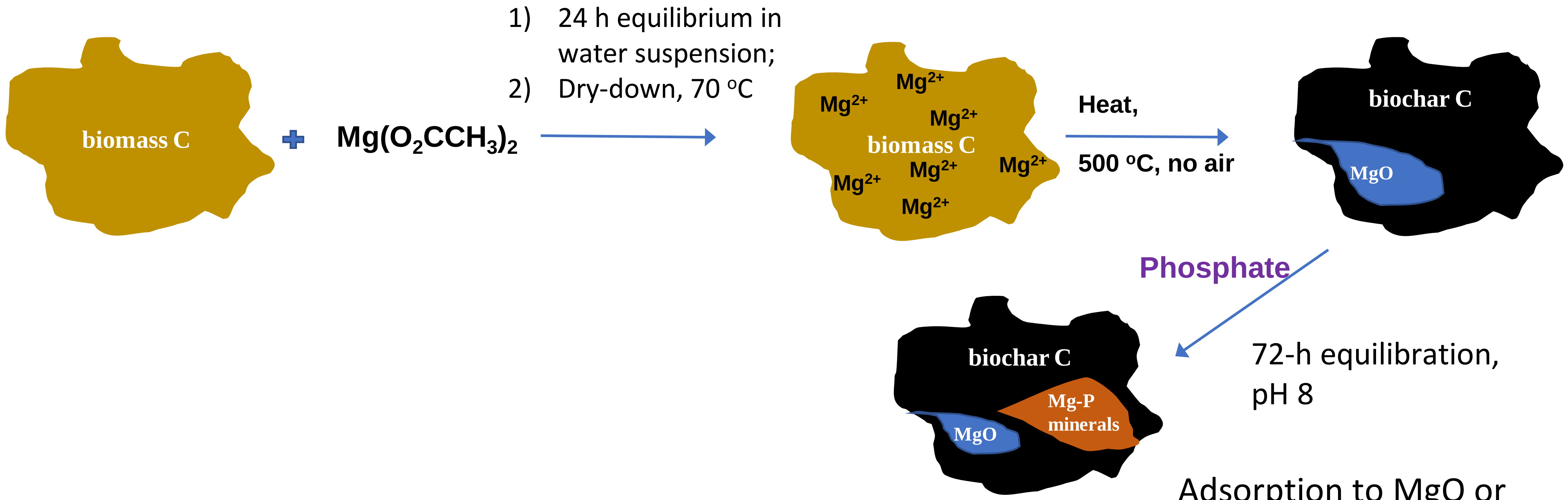
Lehmann J. et al. *Nature* 2007, 447, 143
Lehmann J. et al. *Front Ecol Environ*. 2007, 5, 381
Marris, E. *Nature* 2006, 442, 624

Liu, W. et al. *Chem. Rev*. 2015, 115, 12251
Woolf D. et al. *Nature Commun*. 2010, 1, 1
Duan et al., *Appl. Catal. B-Environ*. 2018, 224, 973

Design of biochars for capturing and recycling of nutrients (phosphorous) to achieve sustainable food production while protecting the environment.

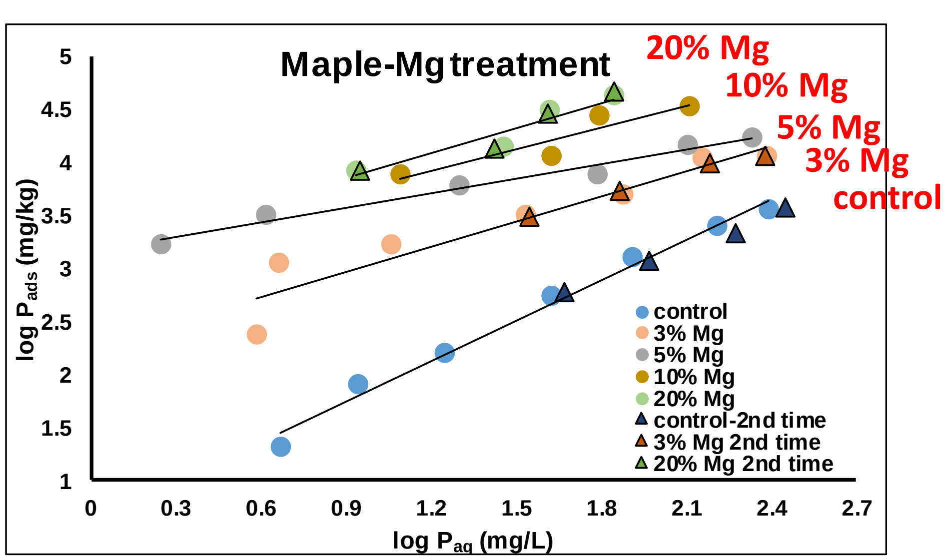


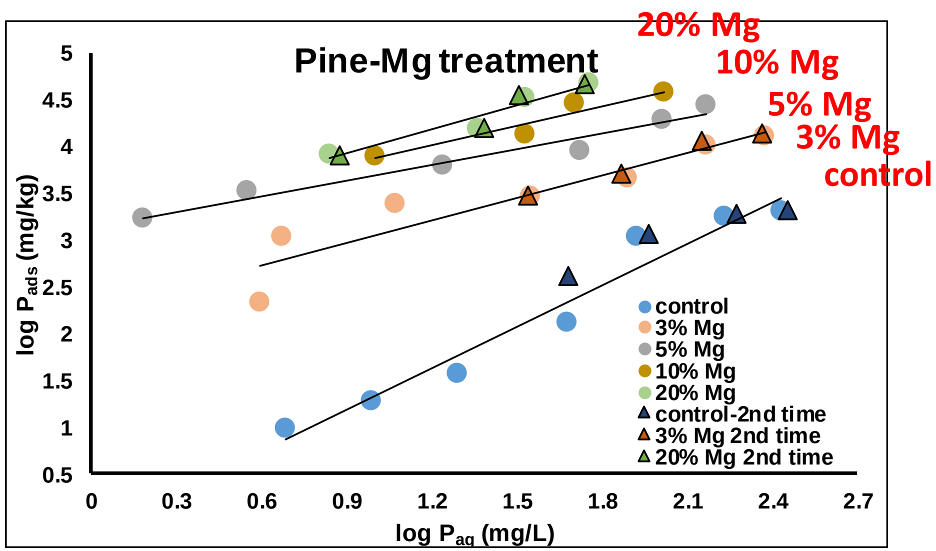
Tailoring of biochars for phosphorus adsorption: Magnesium oxide-doped chars



Adsorption to MgO or formation of sparingly-soluble P minerals, e.g., $MgHPO_4$ and $Mg(H_2PO_4)_2$

Phosphate isotherms on Mg-treated maple and pine biochars





72 h, pH 8

As much as 300-fold enhancement in P binding over the control

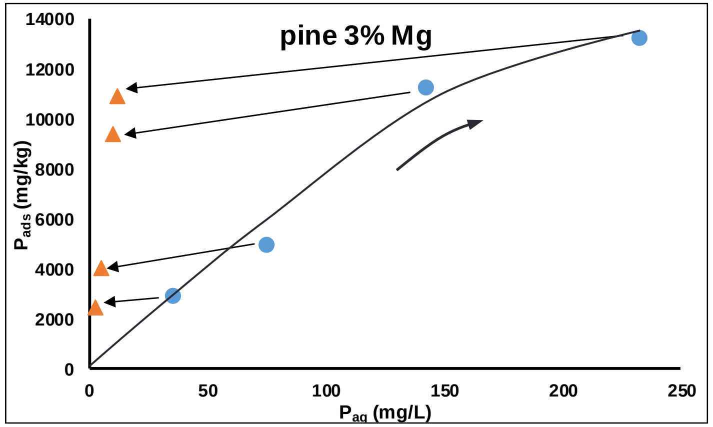
Wang et al. *J.Colloid Interf. Sci.* 579, 258 (2020)

Reversibility of P binding to Mg-treated pine biochar

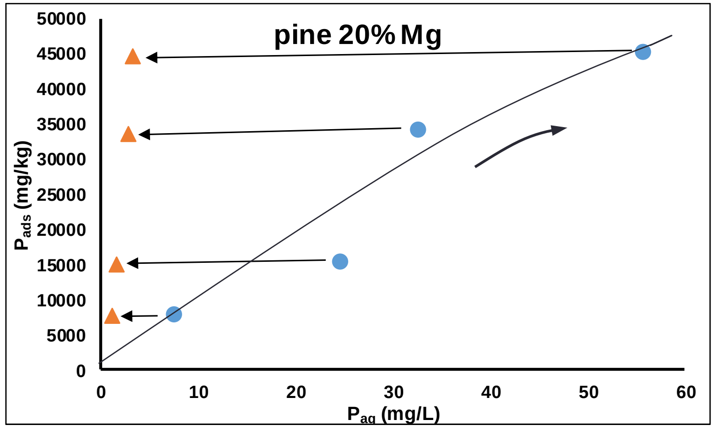
Desorption at selected points on adsorption branch. Diluent: ultrapure water.

72 h;
pH 8

3% Mg



20 % Mg

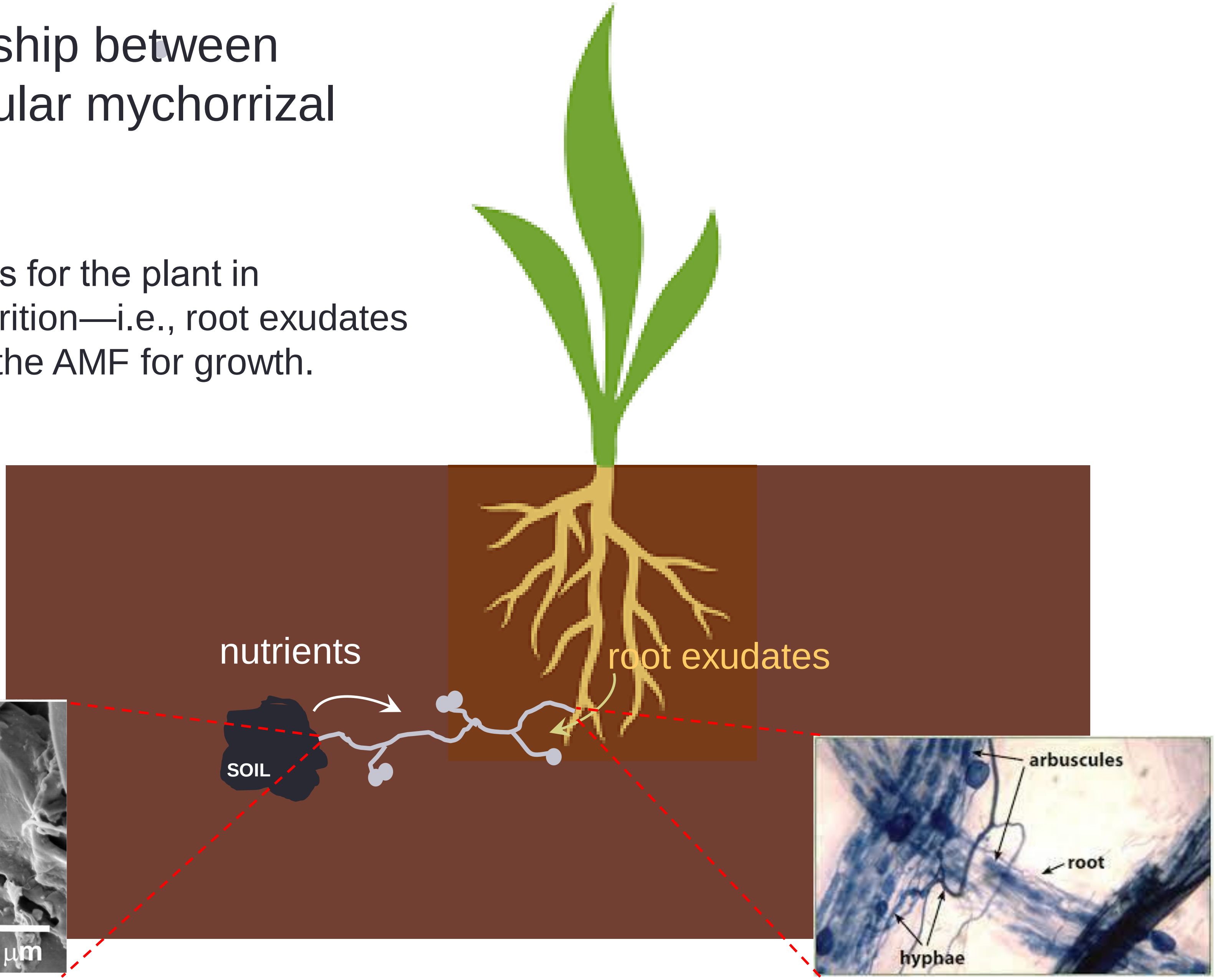


However, P binding is essentially irreversible. Bio-unavailable?

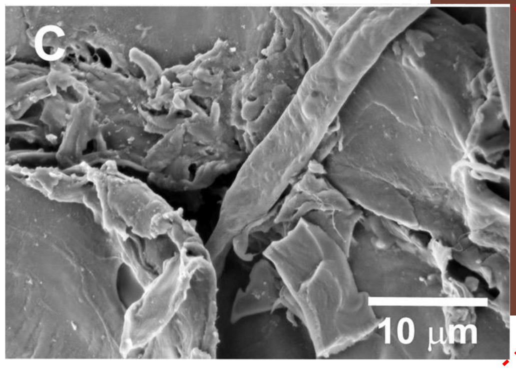
Wang et al. *J.Colloid Interf. Sci.* 579, 258 (2020)

Symbiotic relationship between plants and arbuscular mychorrizal fungi (AMF)

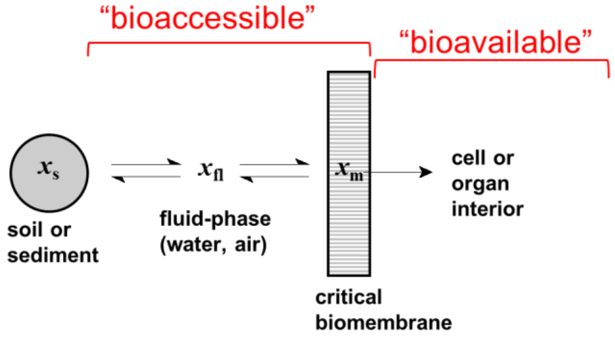
The AMF “mine” nutrients for the plant in exchange for carbon nutrition—i.e., root exudates (sugars, etc.)—used by the AMF for growth.



Hammer et al. *Soil Biol. Biochem.* 252 (2014)



Summary



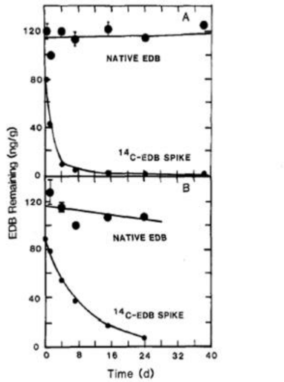
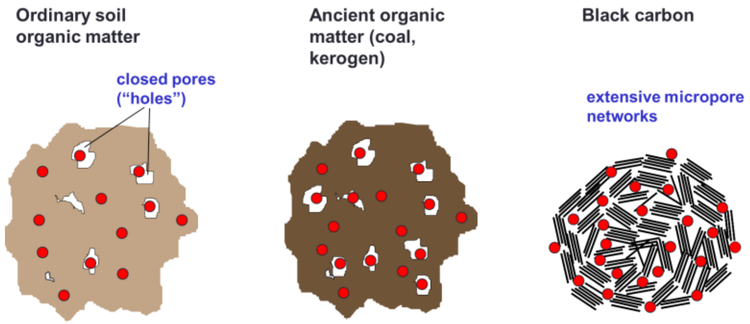
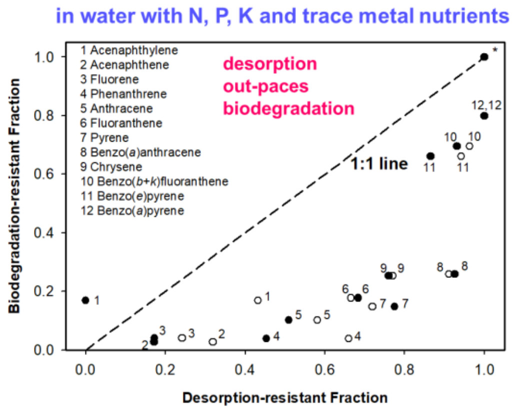
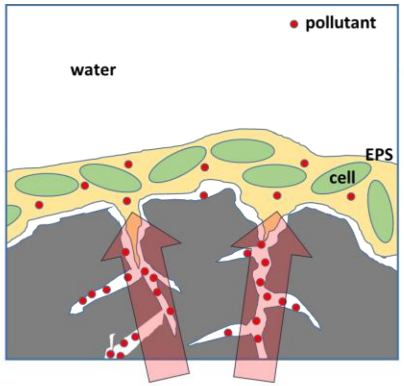
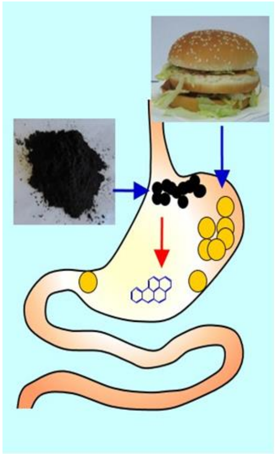


Figure 6. EDB degradation in soil suspensions by indigenous microbes showing the persistence of native EDB compared to a freshly added [^{14}C]EDB spike: (A) Lockwood soil and (B) Warehouse Point soil. The range of duplicates, when larger than the size of the symbol, is indicated by error bars.





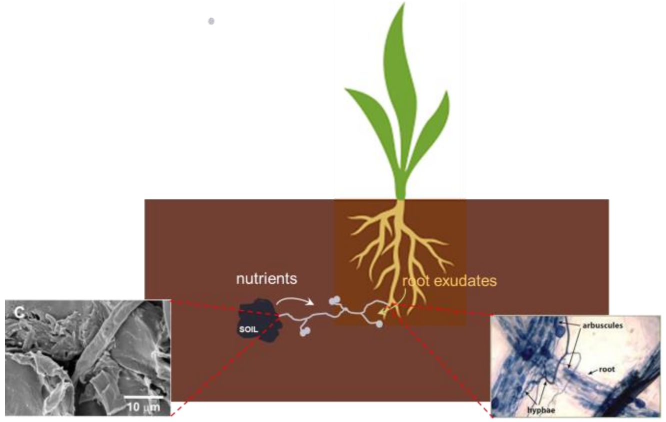




#1(salivary)

#2 (gastric)

#3 (small intestine)



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