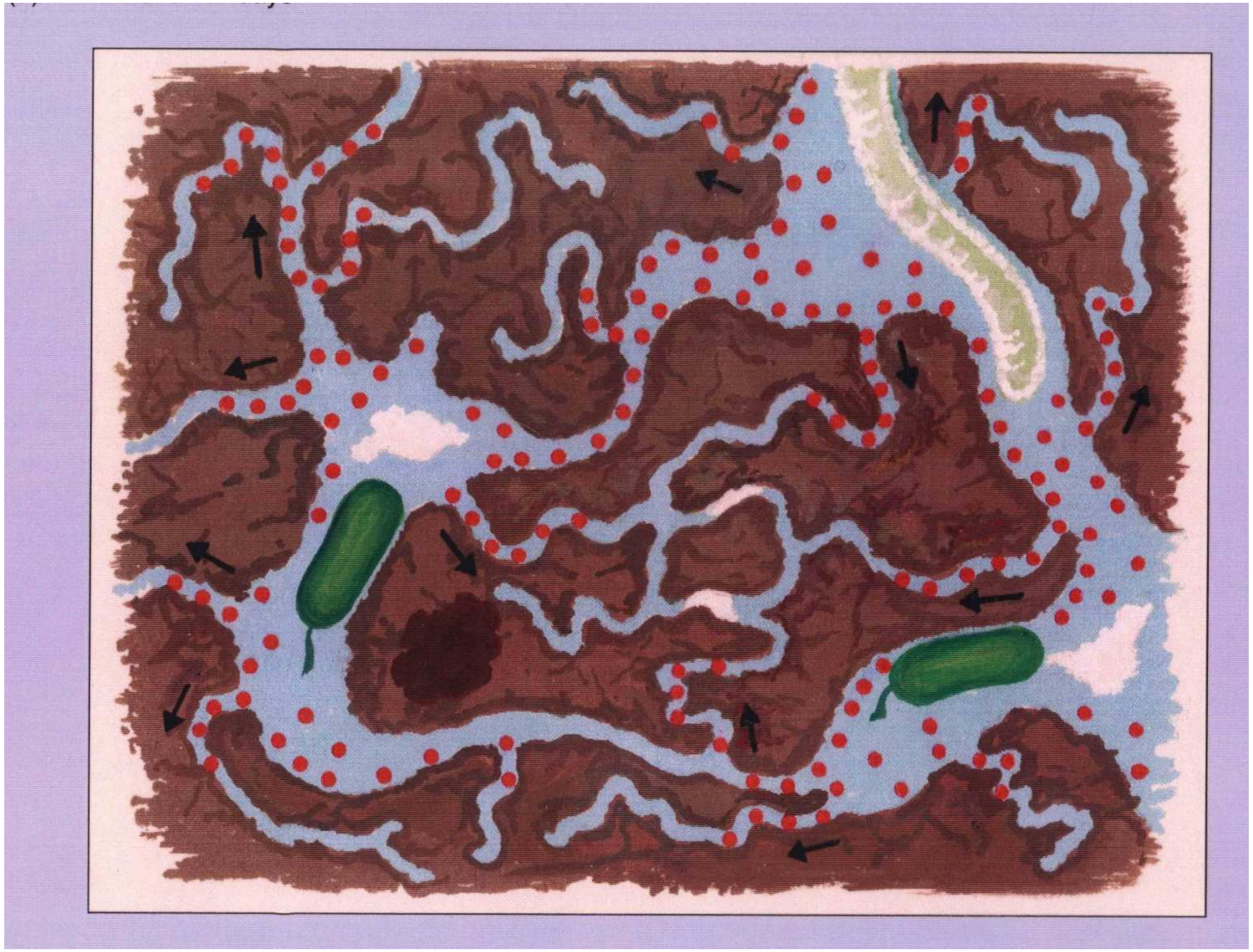
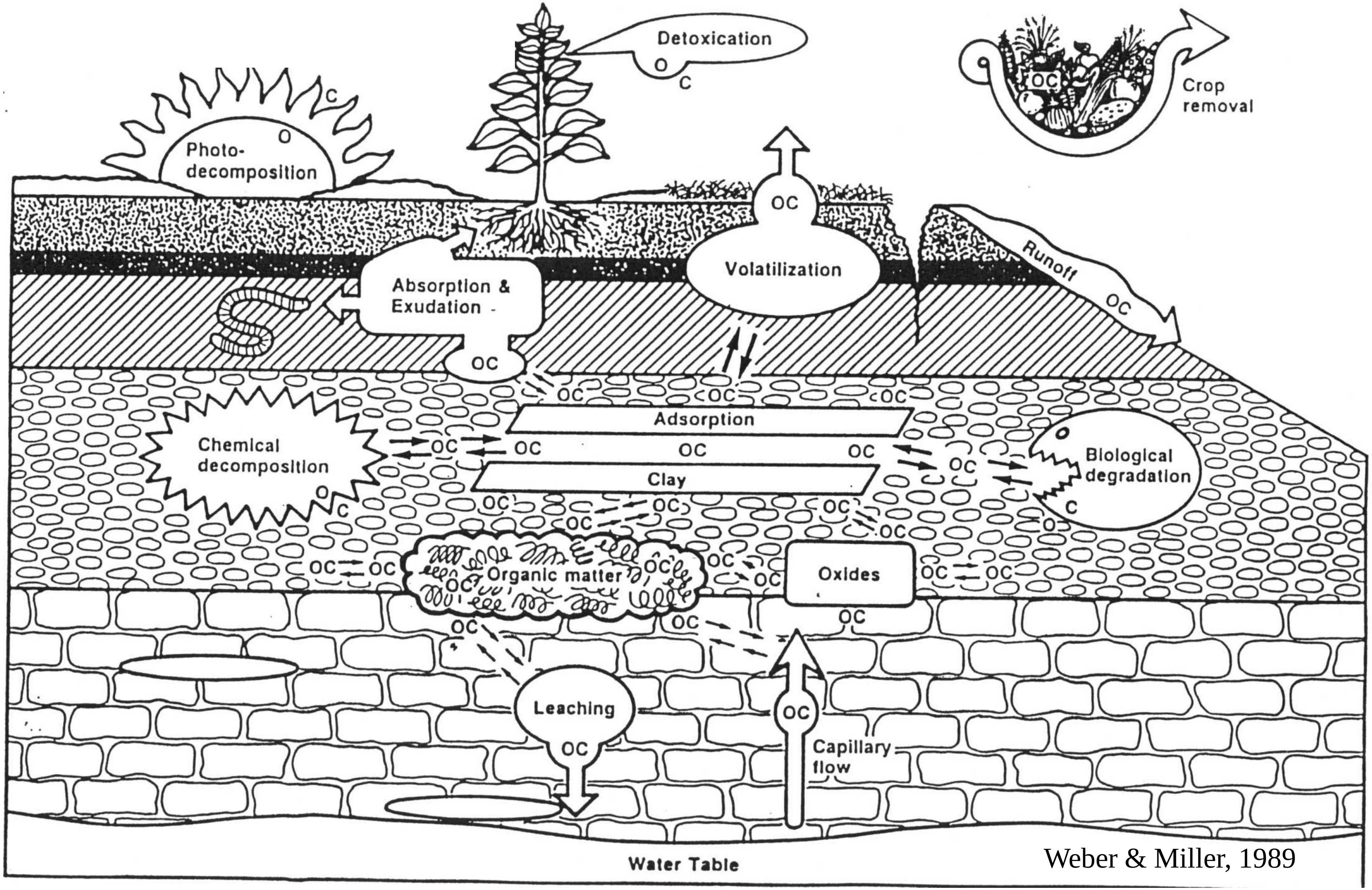
Pesticide Sorption And Bioavailability In Soil



Fate Of Organic Chemicals In Soil



Weber & Miller, 1989

Why Is Sorption Important?

The fate and effects of organic compounds in the environment are largely determined by their sorption to solid phases. For example:

- Transport to surface and ground waters from contaminated soils and sediments
- Accumulation by organisms
- Biodegradation by microorganisms

all depend on sorption

Sorption - Definitions

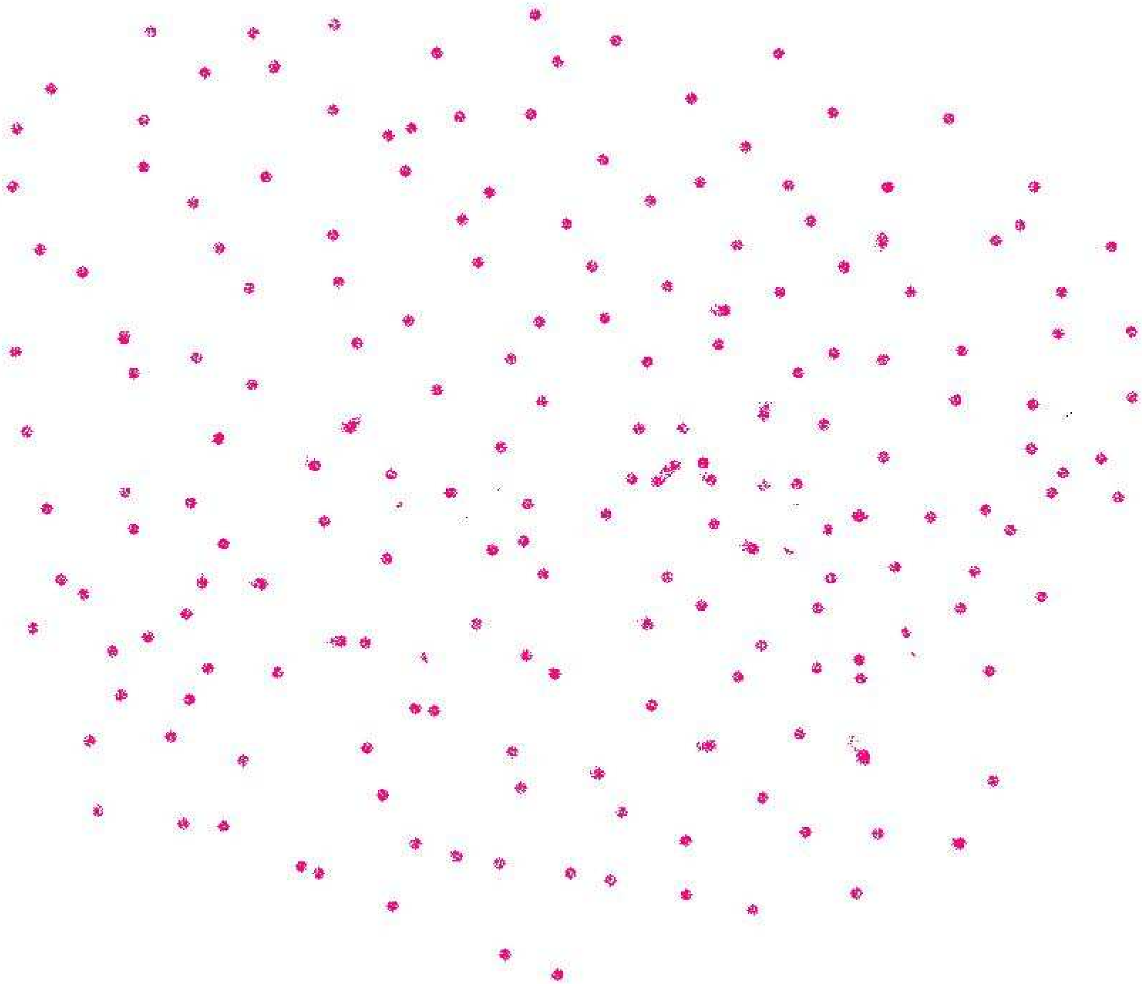
- *Sorption* is a phase distribution process that accumulates solutes at surfaces and interphases (i.e., adsorption) or from one phase to another (i.e., partitioning or absorption)

- *Adsorption* – condensation of vapors or solutes (*adsorbates*) on surfaces or interior pores of a solid (*adsorbent*)

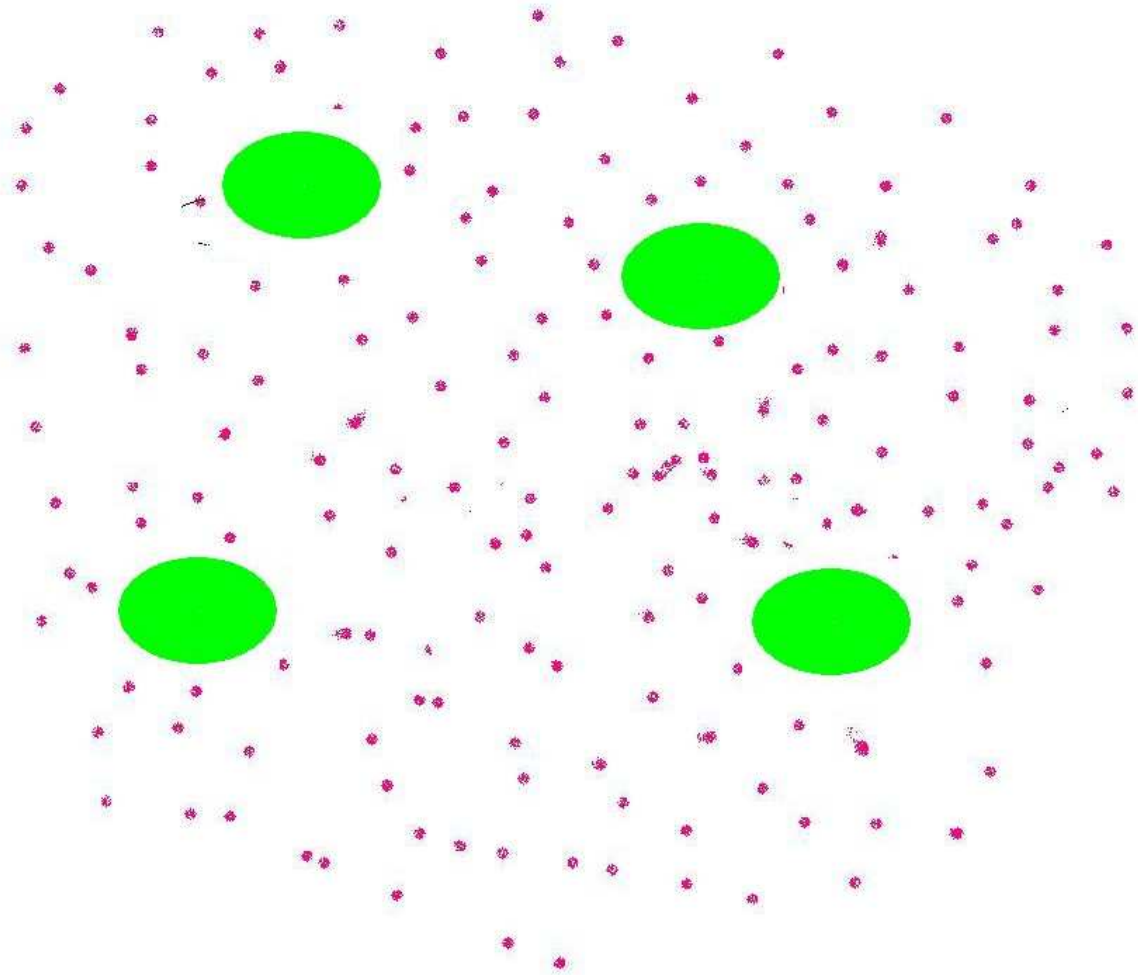
- *Absorption or partitioning* (solubilization) – uptake in which the sorbed adsorbate permeates into the network of an organic medium by forces common to solution. Analogous to the extraction of an organic compound from water into an organic phase. Homogeneous distribution of the sorbed material through the entire volume of the solid phase

- *Desorption* – release of sorbed compound (often rate-limiting for degradation)

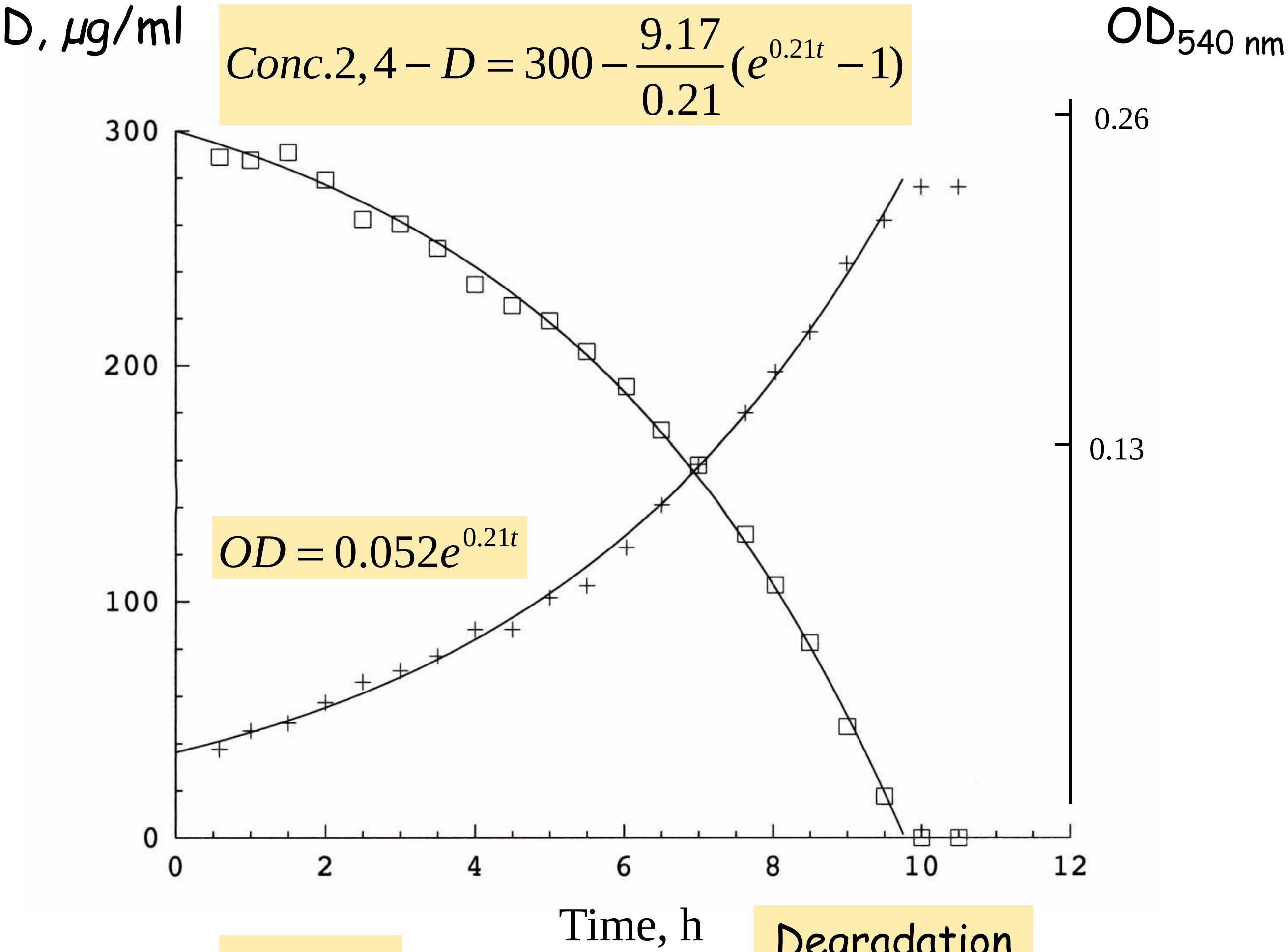
Chemical Freely Available



Degraded Within Hours Or Days



Degradation Of 2,4-D In Solution



$$Conc. 2,4-D = 300 - \frac{9.17}{0.21}(e^{0.21t} - 1)$$

$$OD = 0.052e^{0.21t}$$

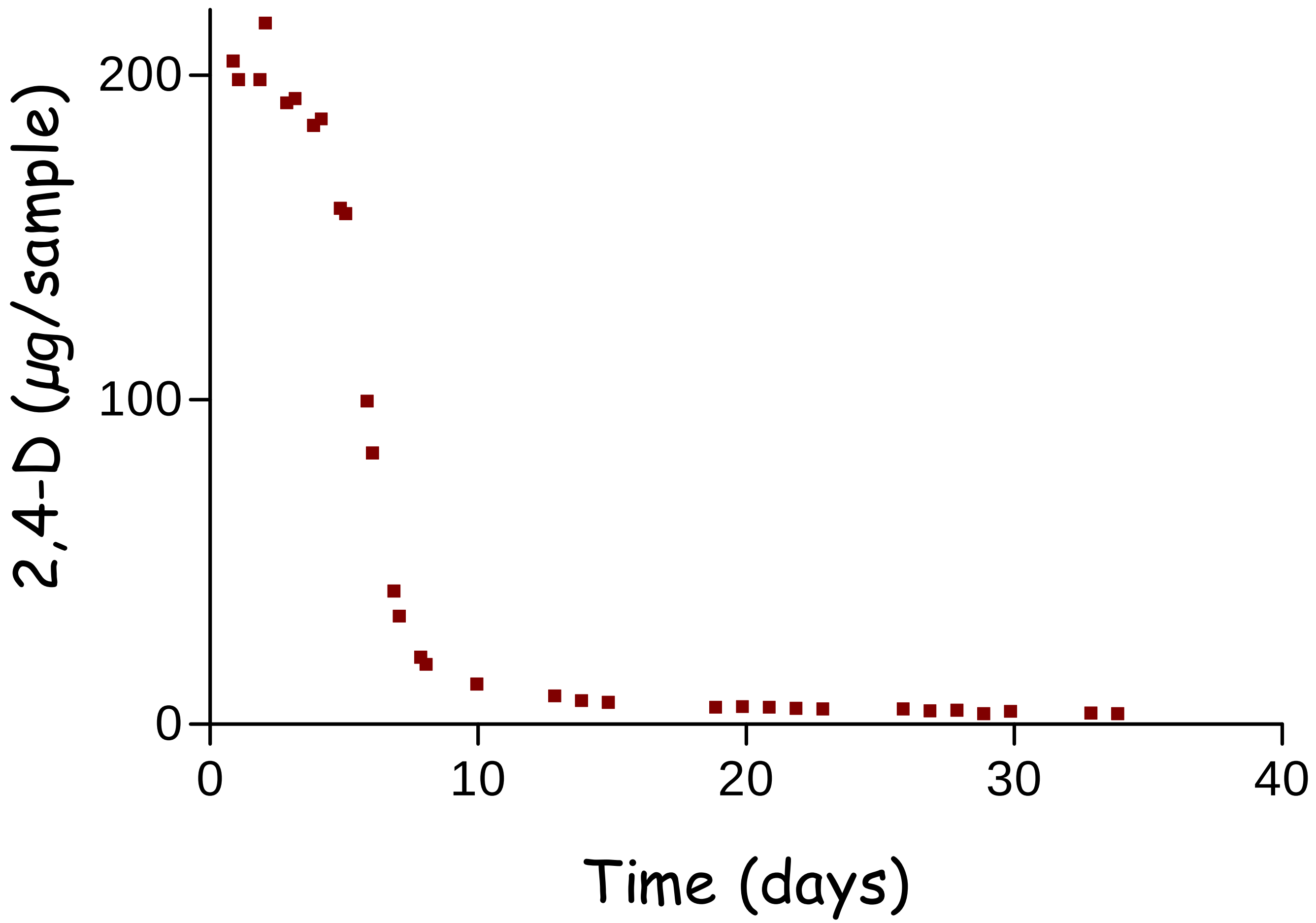
Growth

$$N = N_0 e^{\mu t}$$

Degradation

$$c = c_0 - \frac{qN_0}{\mu}(e^{\mu t} - 1)$$

Degradation Of 2,4-D In Soil



Trophic Interactions At Different Scales

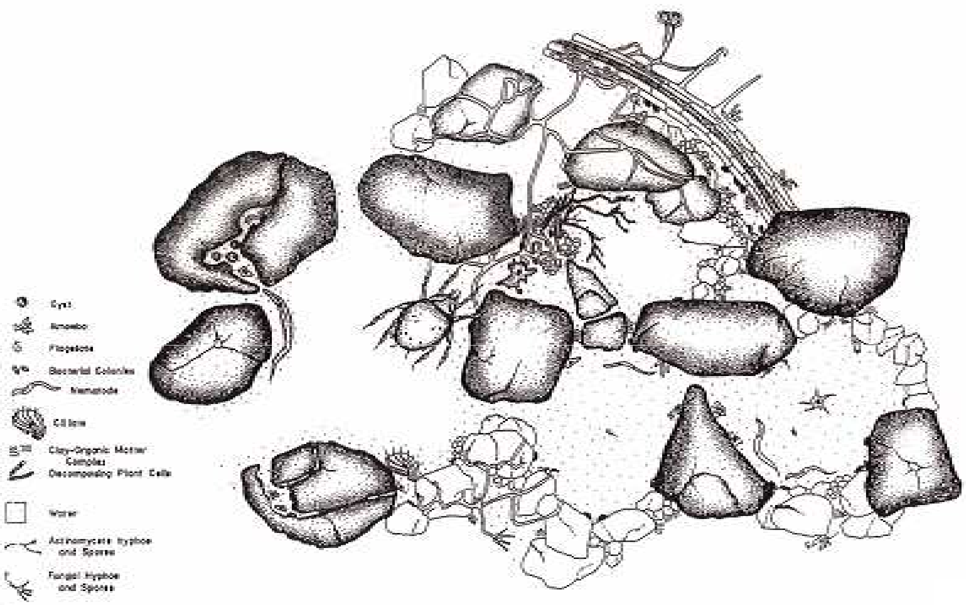
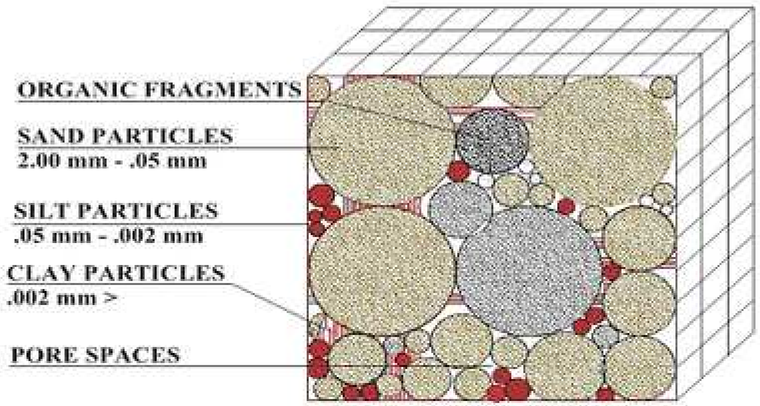


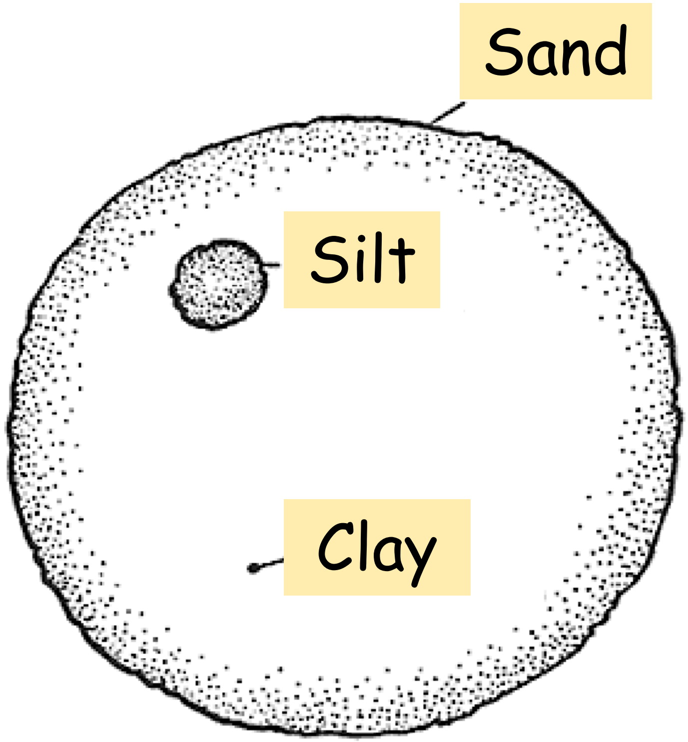
Figure 5.2. Trophic relationships among different groups of soil organisms are controlled by accessibility to their resources. Ti illustration represents approximately 1 cm^3 of a highly structured microzone in the surface horizon of a grassland soil. Courtesy S. Rose and T. Elliott, personal communication.)

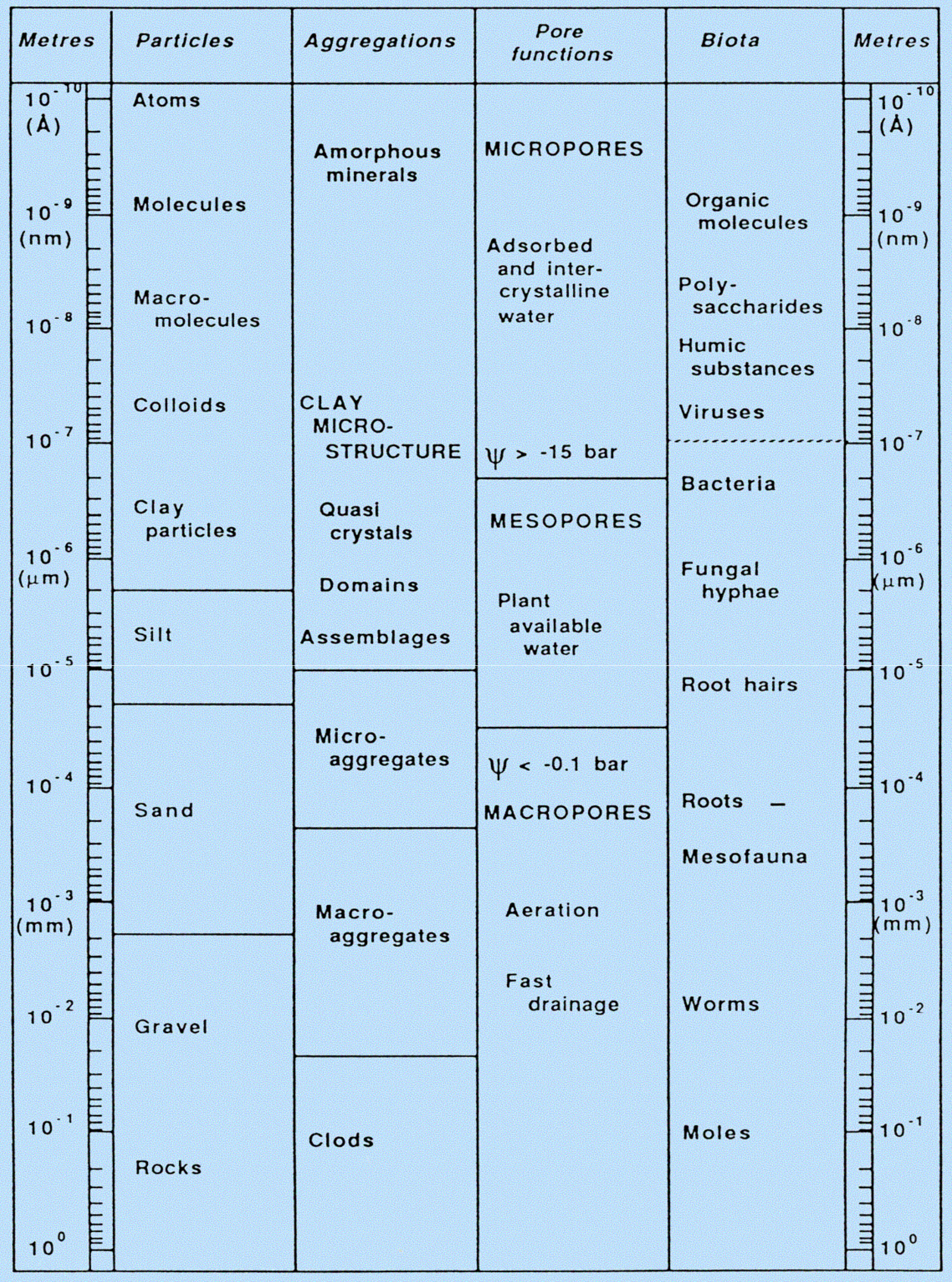


Amount Of Microorganisms And Organic Matter In Arable Soil

Microorganism	Amount per g of soil	Dry weight (kg/ha)
Bacteria	3×10^9	700
Protozoa	3×10^4	35
Fungi	100 m living	875
Σ		1610
Organic matter ton/ha		65-70 (0-15 cm)
% (w/w) microorganisms of the organic matter		2

Scale In Soil Structure





Scale in soil structure (Waters & Oades, 1991)

Specific Surface Area

A cube with side length 1 cm

Side length	Area/cube	Number of cubes	Total surface area
1 cm	6 cm^2	1	1 x 6 cm^2 = 6 cm^2
1 mm	6 mm^2	10^3	10^3 x 6 mm^2 = 6000 mm^2 = 60 cm^2
0.1 mm	0.06 mm^2	10^6	10^6 x 0.06 mm^2 = 60 000 mm^2 = 6 dm^2
10 μm	600 μm^2	10^9	10^9 x 600 μm^2 = 6000 cm^2 = 60 dm^2
1 μm	6 μm^2	10^{12}	10^{12} x 6 μm^2 = 600 dm^2 = 6 m^2
0.1 μm	0.06 μm^2	10^{15}	10^{15} x 0.06 μm^2 = 60 m^2

CEC And Specific Surface Area Of Some Clay Minerals

Clay mineral	CEC meq/100 g	Surface area m^2/g
Vermiculite	100-150	600-800
Montmorillonite	80-150	600-800
Illite	10-40	65-100
Chlorite	10-40	25-40
Kaolinite	3-15	7-30
Fe- and Al-hydroxides	2-6	100-800

CEC = Cation-Exchange Capacity

The Soil Is A Desert

Specific surface area: 100 m^2/g

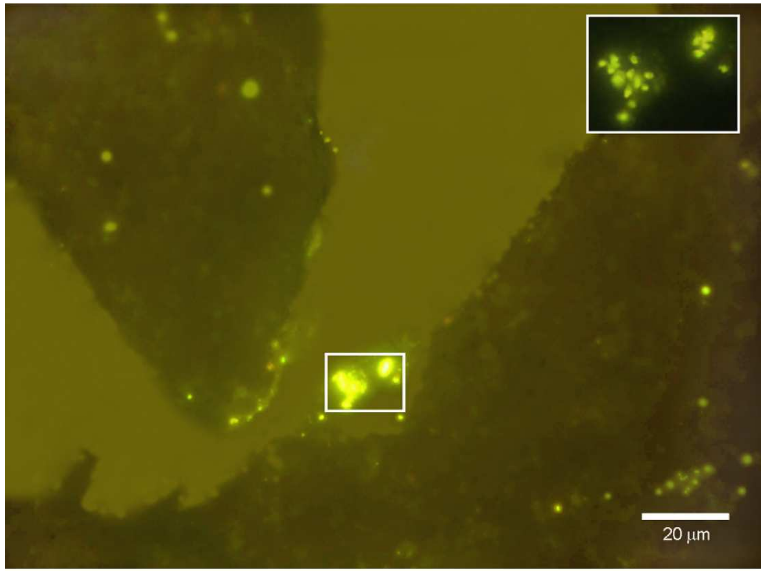
Amount bacteria: $10^8/g$

Cover only 0.01 % of the surfaces

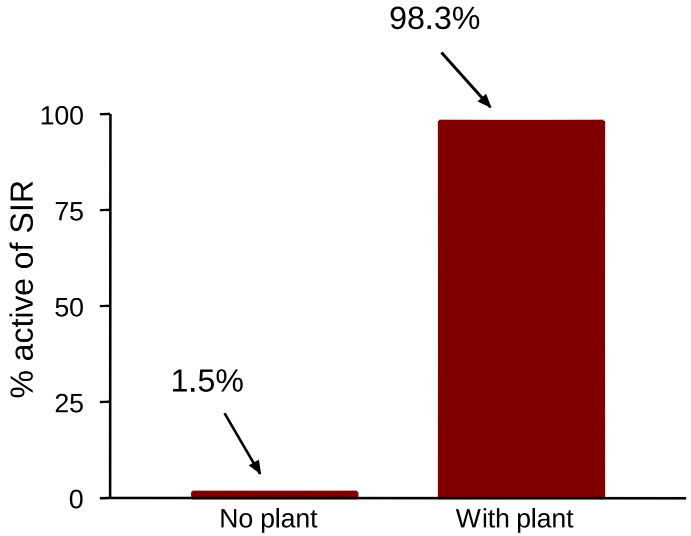
In addition

- At least 90 % of the surfaces are not accessible for microorganisms or enzymes

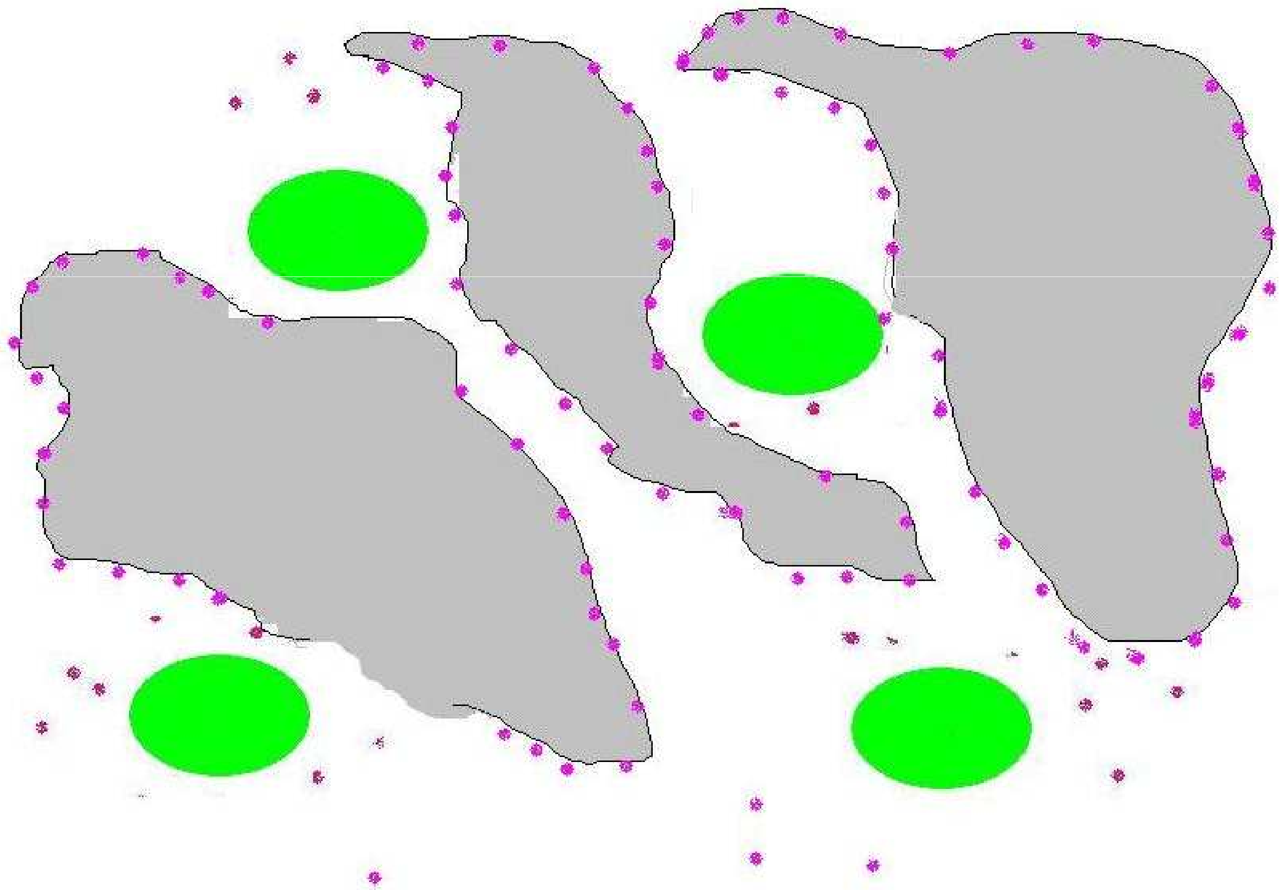
- Only 1-10 % of the microorganisms are active in the absence of plants - starvation



Relative amount of active microorganisms

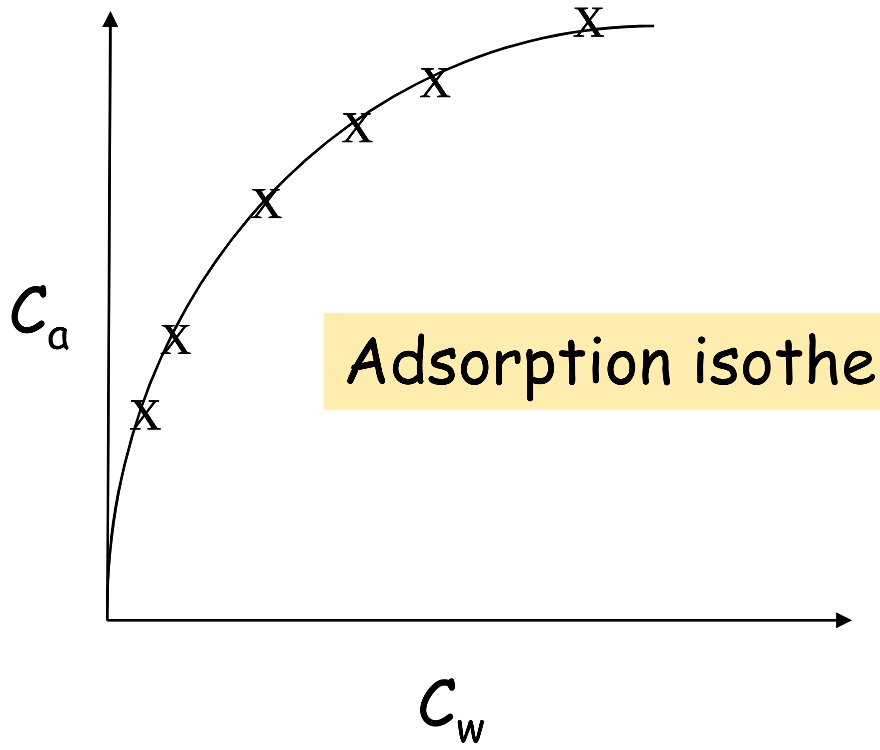


Adsorption Decreases Concentration In Solution



Measurement Of Adsorption

- Mix 0.01 M $CaCl_2$ with sieved (< 2 mm) soil
- Add pesticide
- Mix (often 24 h)
- Measure concentration in solution, C_w
- Calculate concentration on soil (mass balance), C_a



Adsorption isotherm

At equilibrium

C_a = amount adsorbed per mass of sorbent

C_w = concentration in solution

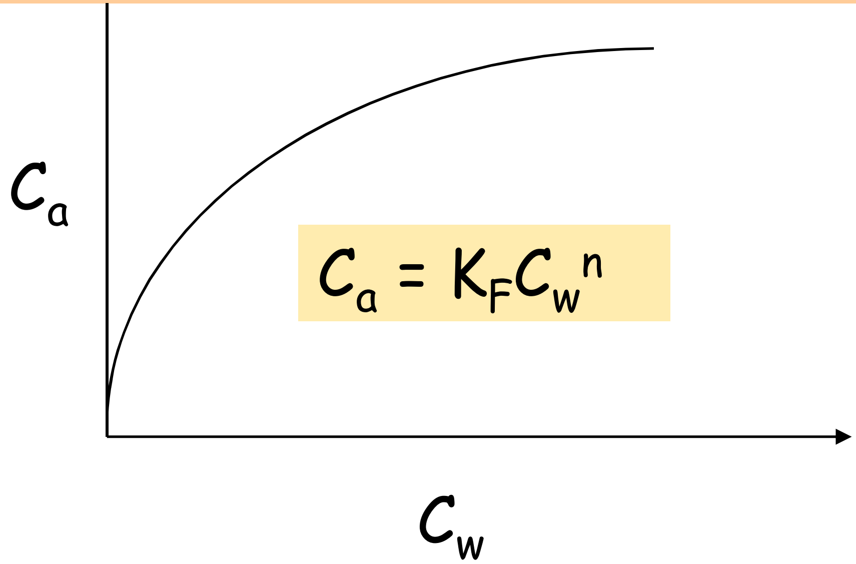
Adsorption

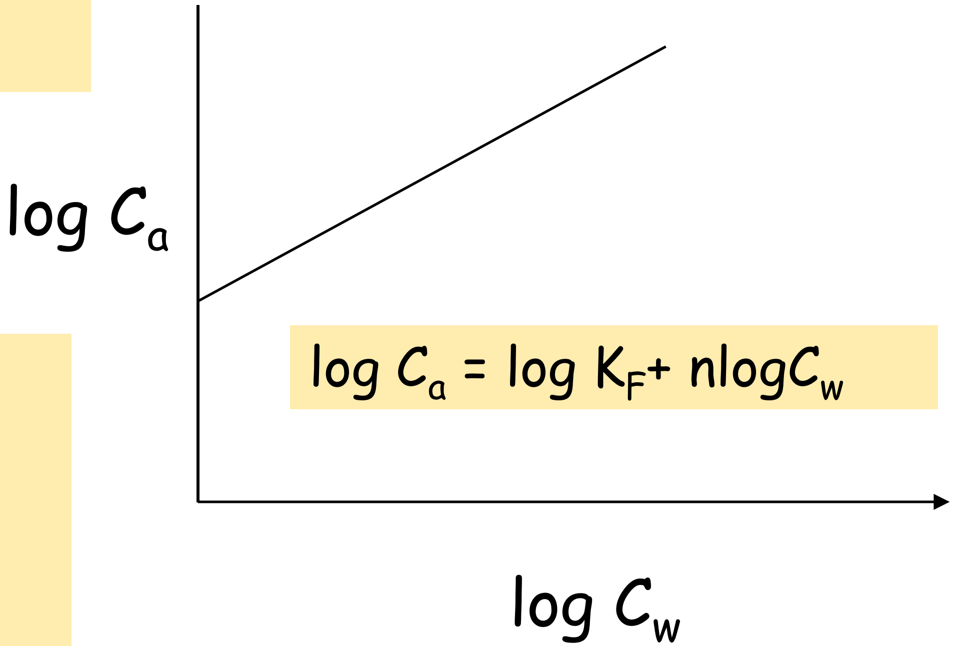
The Freundlich model

$$C_a = K_F C_w^n$$

where K_F and n are respectively the Freundlich adsorption constant and the isotherm linearity parameter

($K_F = K_d$ when n = 1)





- On Surfaces
- Temperature dependent
- Saturation
- Competition between solutes

Partition Ratios

partition coefficient, distribution coefficient, distribution ratio, partition constant

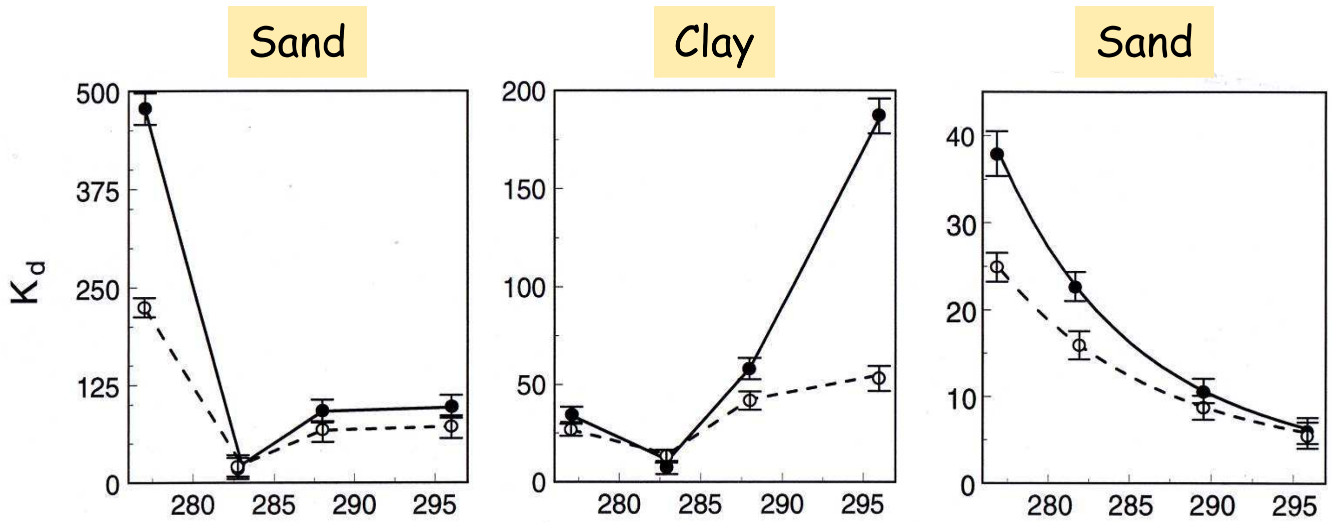
The ratio of the concentration of a substance A in one phase to its concentration in the other phase at equilibrium, e.g. for an soil/aqueous system: K_d = [A]soil/[A]aq

K_d	soil – water (distribution coefficient)
K_{oc}	organic carbon – water (= K_d/f_{OC})
K_{om}	organic matter - water (= K_d/f_{om})
K_{ow}	n-octanol - water
K_{aw}	air – water

Adsorption

- Often non-linear adsorption isotherms
- Temperature dependent
- Competition between solutes

According to the OECD Guideline 106, adsorption is measured at 20-25 °C. In Uppsala, Sweden the monthly mean temperature at 2-4 dm never exceeds 10-15 °C and the mean annual air temperature is 5.6 °C



Temperature dependence of Kd for linuron in three soils at 0.2 (solid line) and 0.5 mg/kg soil

Effect Of Adsorption On The First-Order Degradation Rate Constant

Adsorbed pesticide, C_a

↕ K_d

Pesticide in solution, C_w

↓ k

Degradation products

$$K_d = \frac{c_a}{c_w}$$

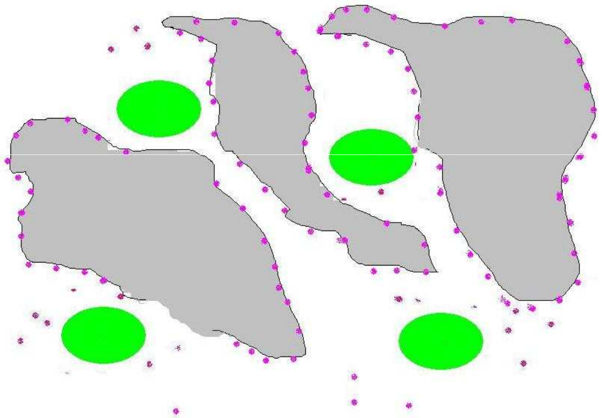
$$c_{tot} = c_a W_{soil} + c_w V_{water}$$

$$-\frac{dc_{tot}}{dt} = kc_w V_{water} = \frac{kc_{tot}}{1 + \frac{W_{soil}}{V_{water}} K_d}$$

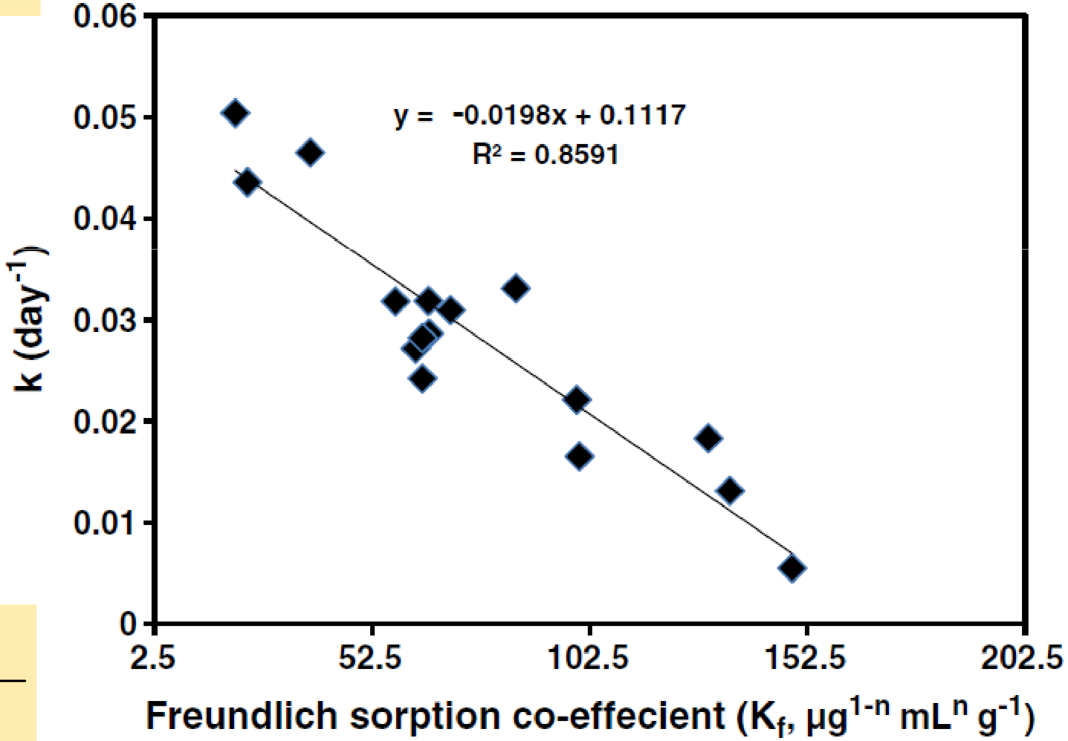
Adapted from Andersson, 1976

Relationship Between The First-Order Degradation Rate Constant k For Glyphosate And The Freundlich Coefficient

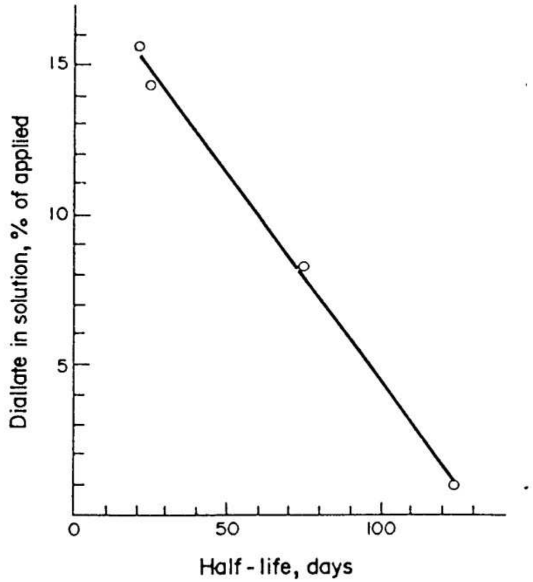
Adsorption decreases concentration in solution



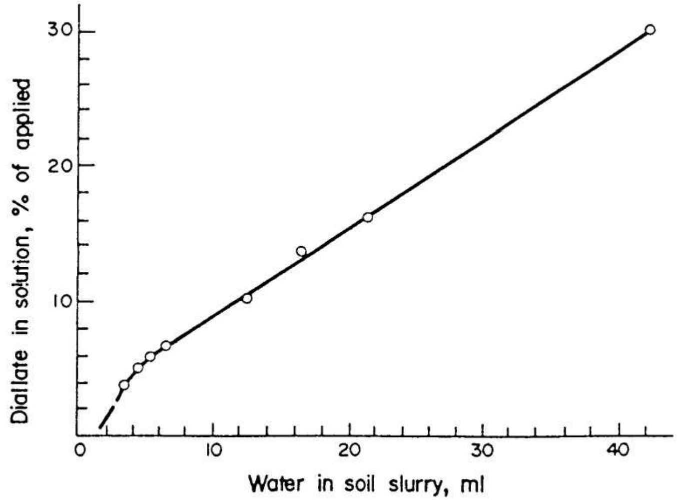
$$-\frac{dc_{tot}}{dt} = kc_w V_{water} = \frac{kc_{tot}}{1+\frac{w_{soil}}{V_{water}} K_d}$$



The Available Fraction Determines The Degradation Rate And Can Be Decreased By Adsorption And Increased By Dilution



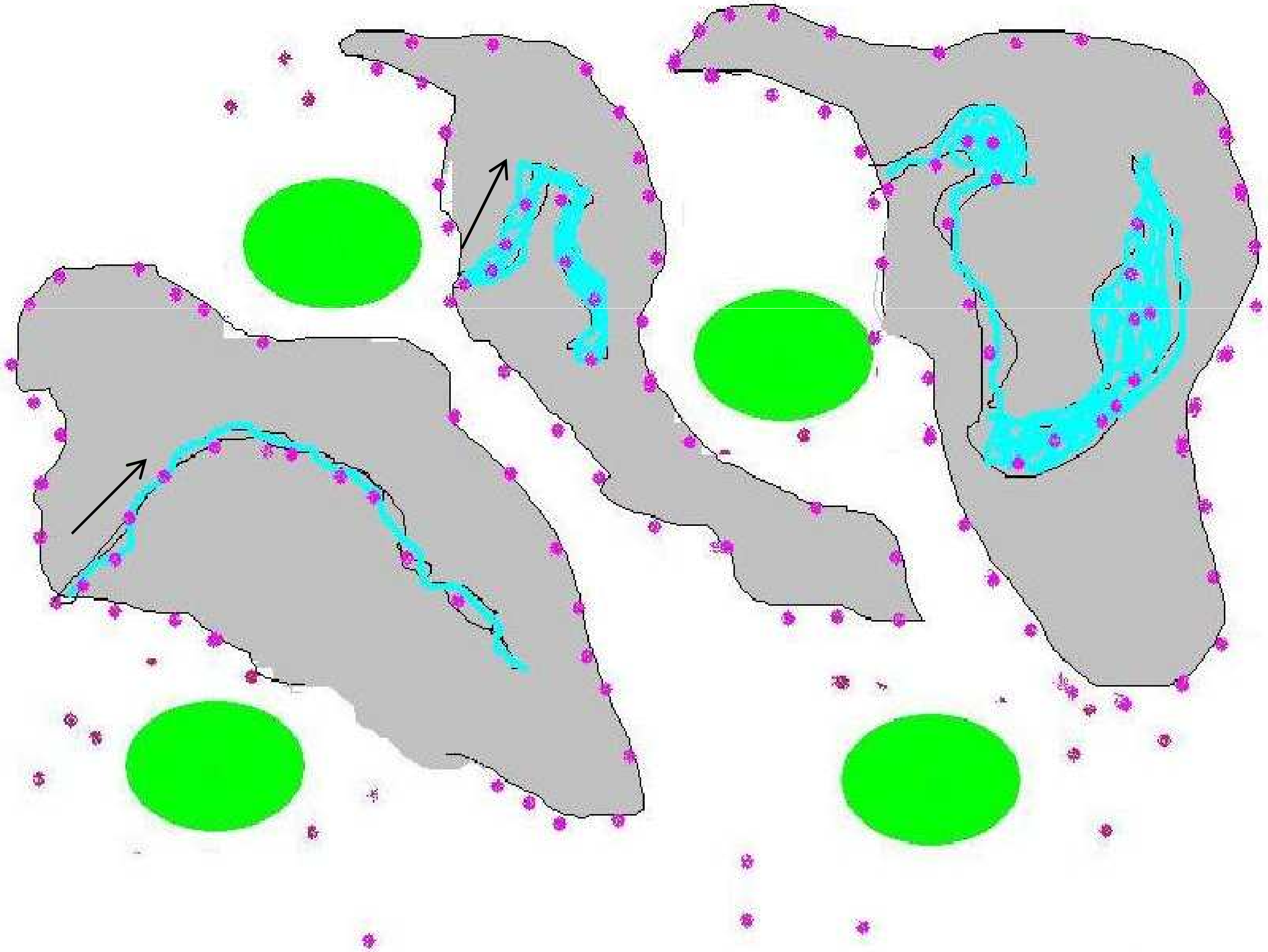
Increasing amounts of active carbon



Dilution

Andersson, 1981

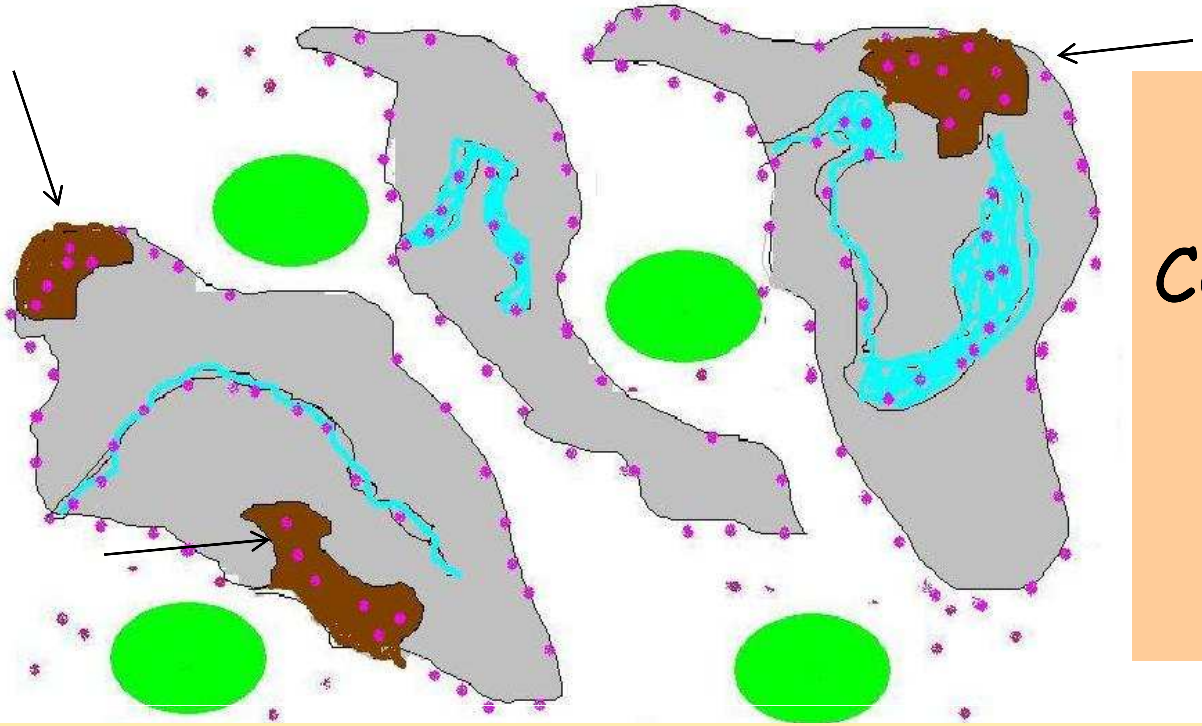
Interior Of Particles Loaded By Time-Dependent Intra-Particle Diffusion



Rates Of Time-Limited Sorption And Desorption

- The diffusion of sorbate molecules within soil organic matter and micro- and mesopores can be extremely slow and often limits the overall sorption and desorption processes

- Times required for sorption by soils and sediments to attain apparent equilibrium may vary from days to years



Lipophilic Compunds Dissolve In Humic Substances (Partitioning)

- Linear equilibrium sorption isotherms
- Strong dipole interaction of minerals with water excludes nonionic compound
- The compound partitions or is forced into the organic matter
- The extent of uptake closely related to the organic matter content
- No competition between solutes
- Not strongly temperature dependent

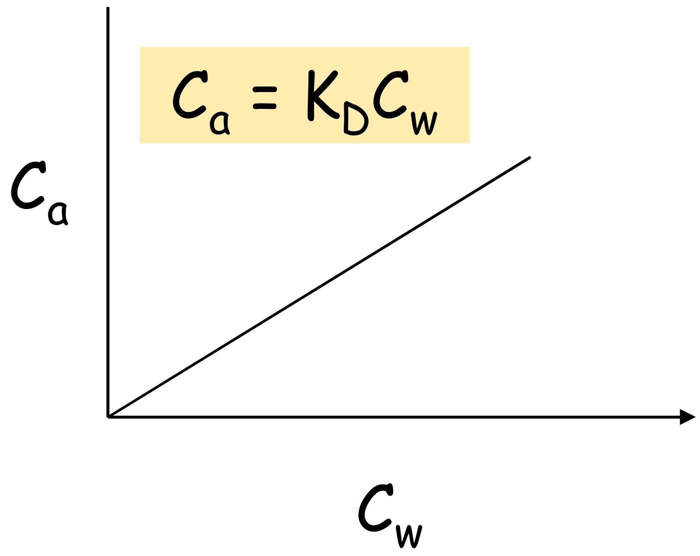
Linear Equilibrium Sorption Isotherms (partitioning)

The linear partitioning model

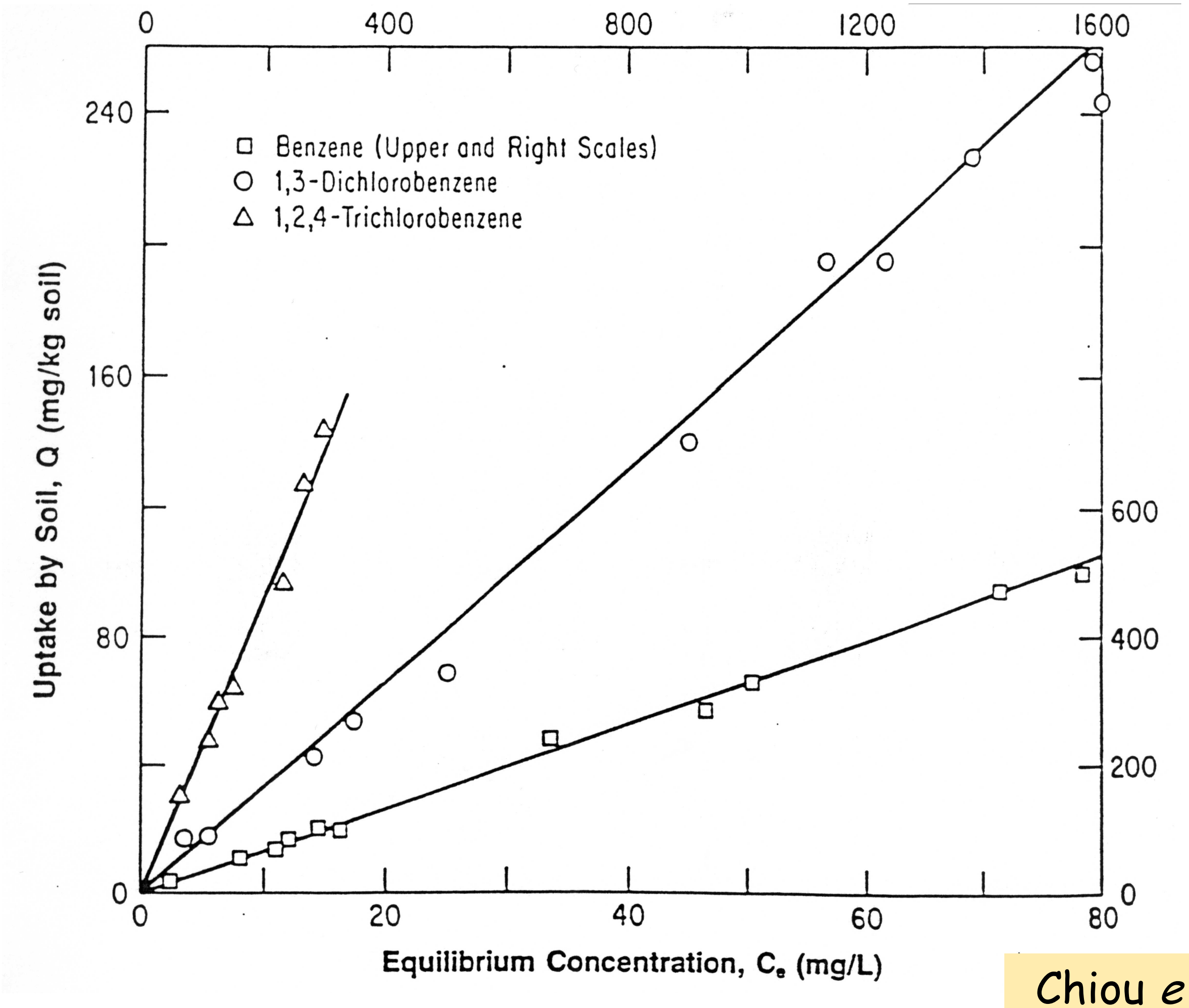
$$C_a = K_D C_w$$

where C_a and C_w are the equilibrium solid-phase and aqueous-phase solute concentrations, respectively

Based on the hypothesis that soil humus is an amorphous gel- or liquid-like phase that has no limitation of "sites" or spaces to accommodate lipophilic comounds as the solute concentration increases

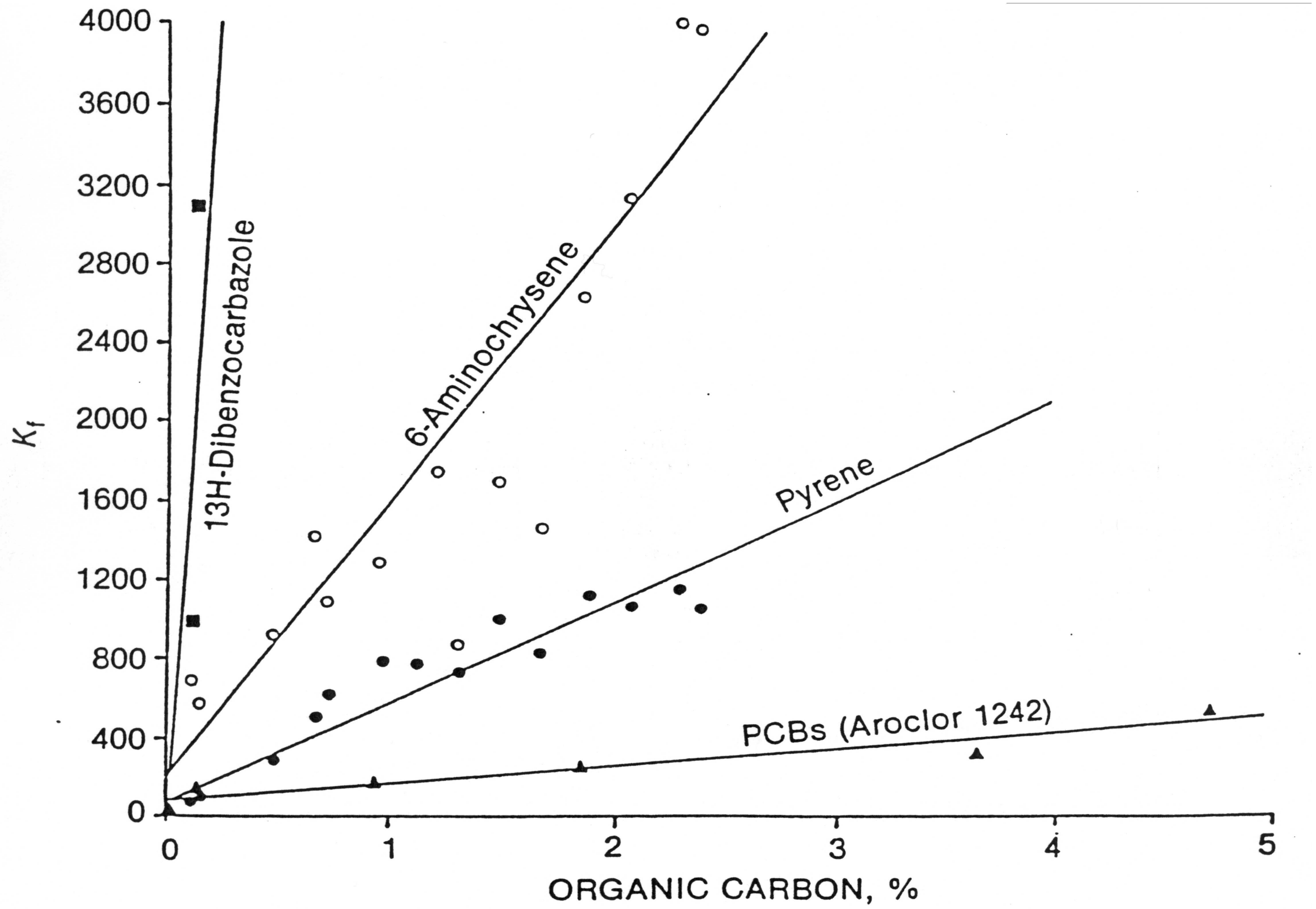


Linear Equilibrium Sorption Isotherms For Most Nonionic Organic Compounds On Humic Substances



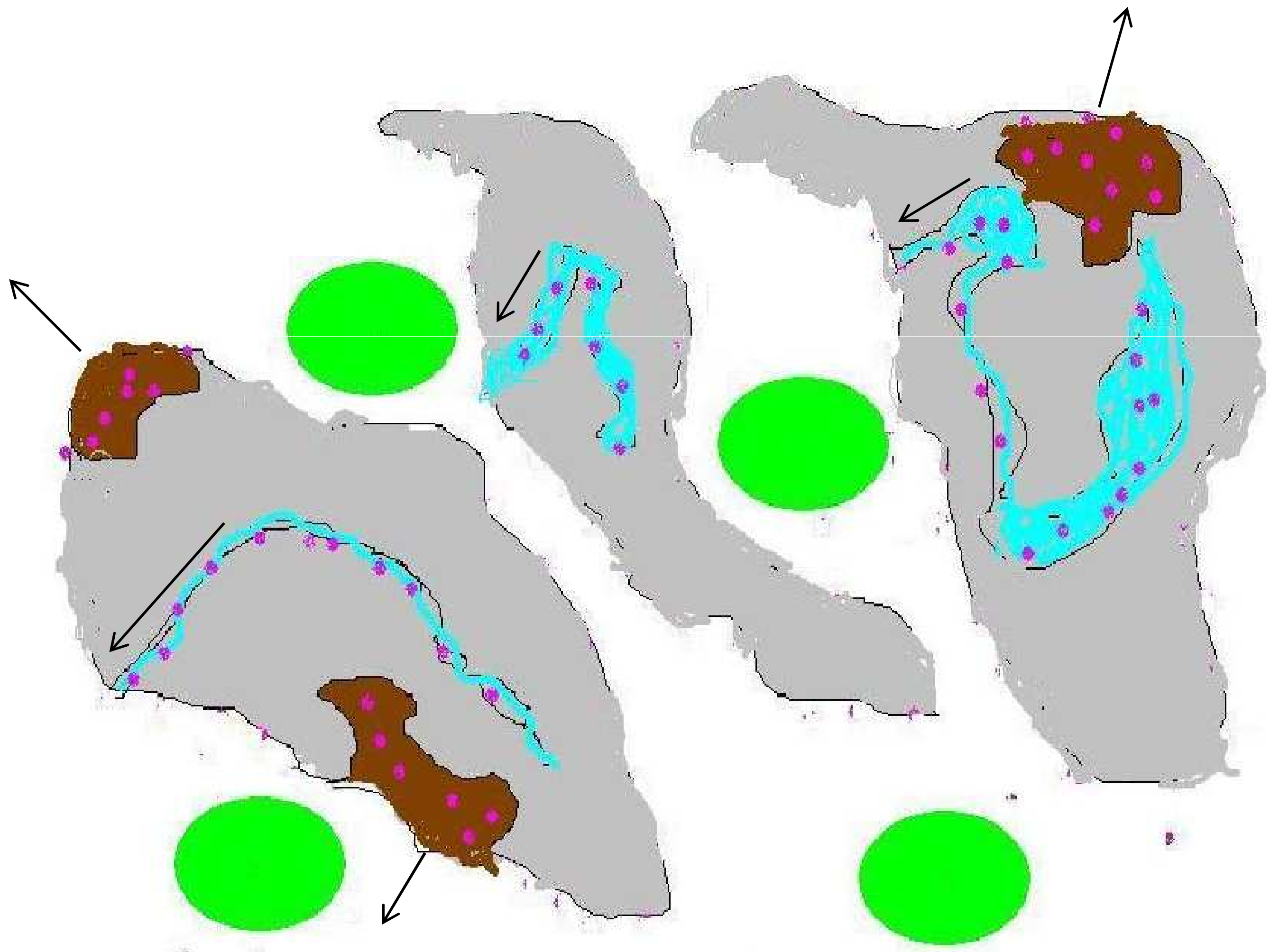
Chiou *et al.*, 1983

The Extent Of Uptake Closely Related To The Organic Matter Content



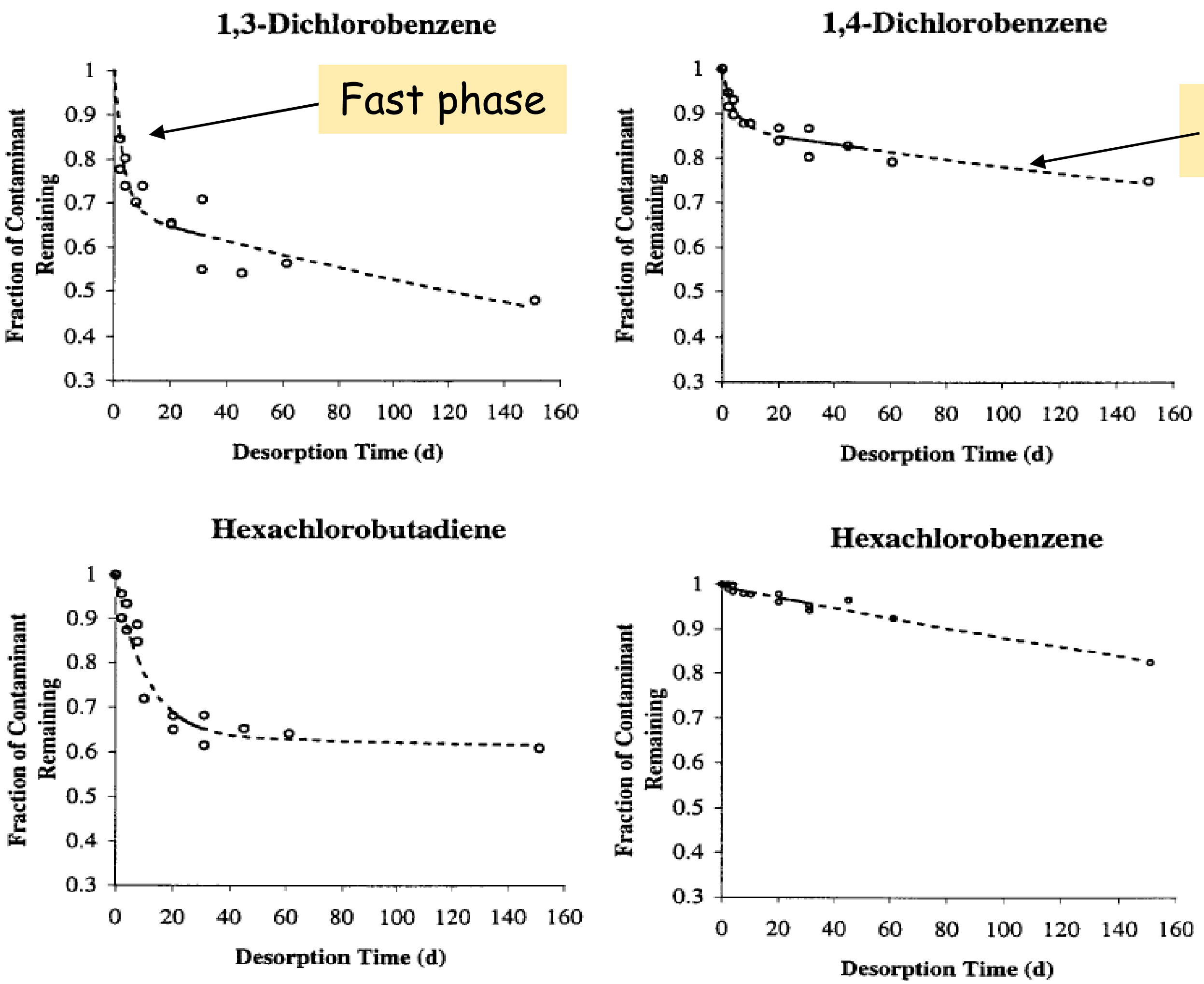
Hassett et al., 1983

Time-Limited Desorption Often Rate-Limiting For Degradation (Takes Months To Years)



Desorption Of Four Contaminants From Sediment

A.T. Kan et al. / Environmental Pollution 108 (2000) 81–89



Desorption half-lives

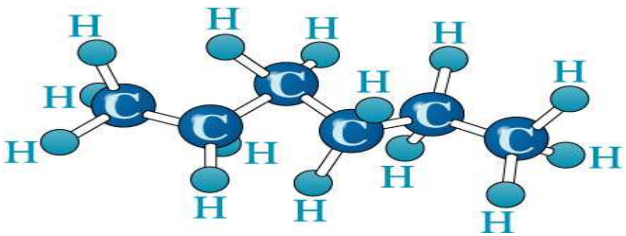
Fast phase: 3-6 days

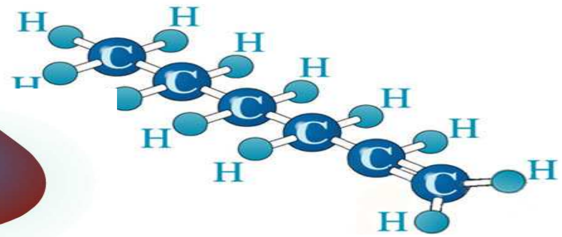
Slow phase 0.8-8.6 years

$$\frac{q(t)}{q_0} = \phi_{\mathrm{Fast}} \cdot \exp(-k_{\mathrm{Fast}} \cdot t) + (1 - \phi_{\mathrm{Fast}}) \cdot \exp(-k_{\mathrm{Slow}} \cdot t)$$

Some Successful Bioremediations

Petroleum

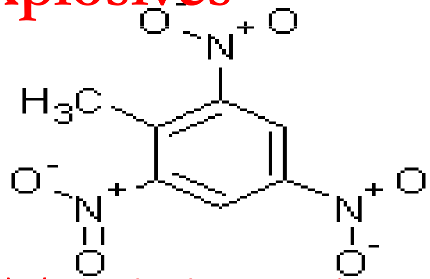




Paraffins

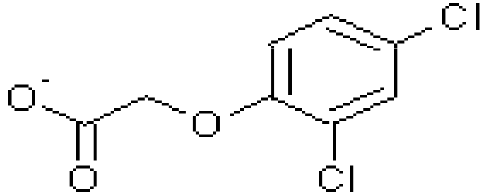
Olefins

Explosives

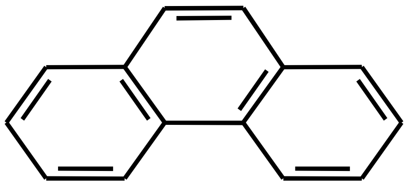


TNT (trinitrotoluene)

Pesticides



Low-molecular weight PAH



Phenanthrene

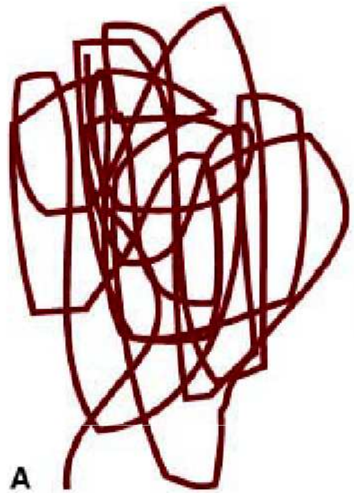
All these compounds are relatively water soluble (not very lipophilic)

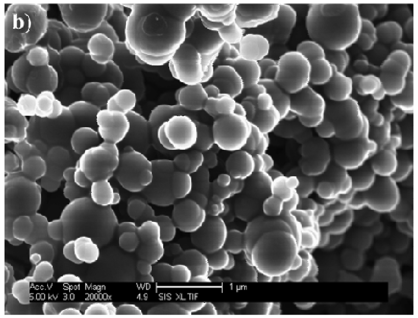
Soil Organic Matter (SOM) Most Important For Sorption Of Organic Compounds

- Humic substances

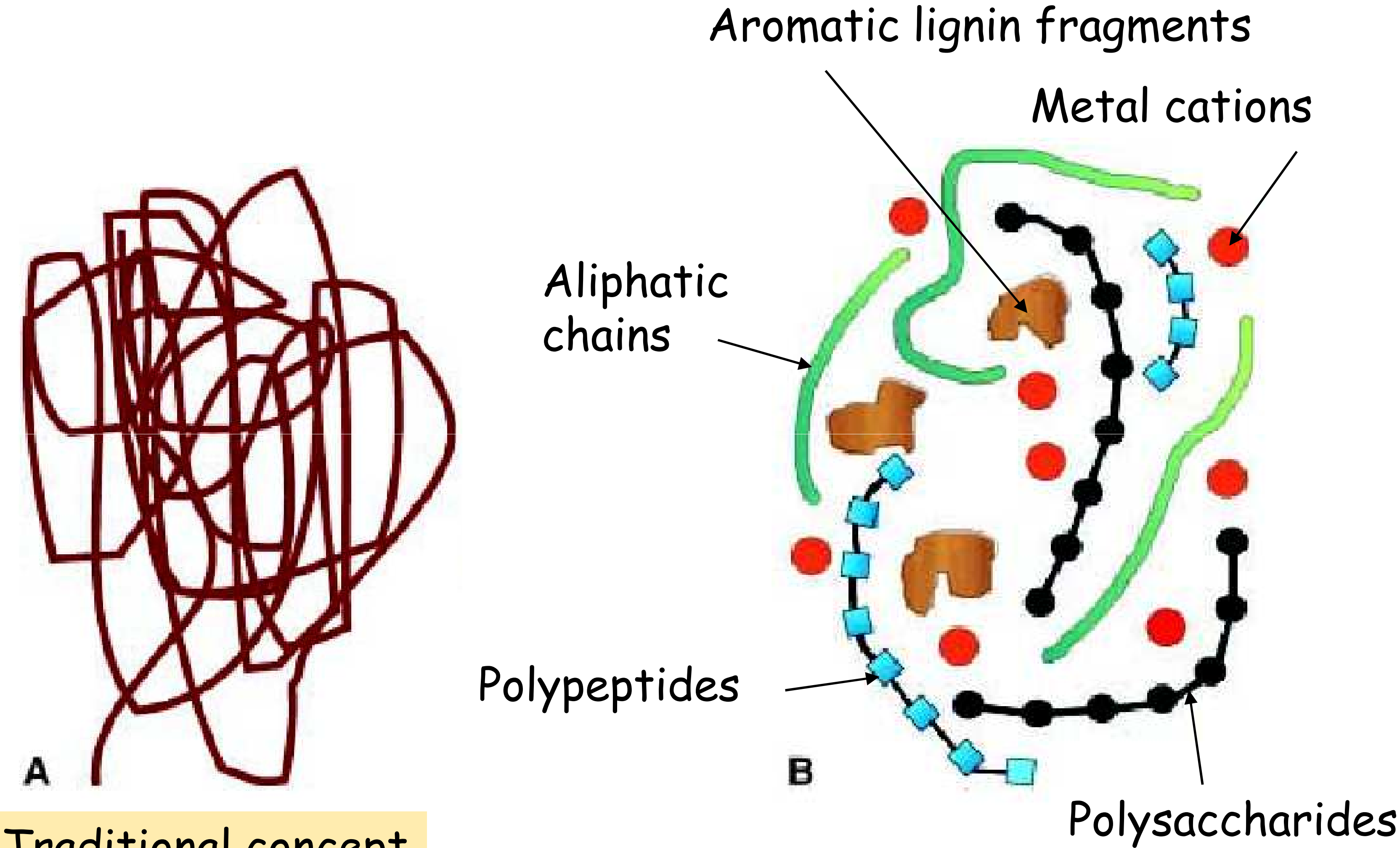
- Black carbon (from fires, combustion)

- Kerogen (solid organic matter in sedimentary rock)





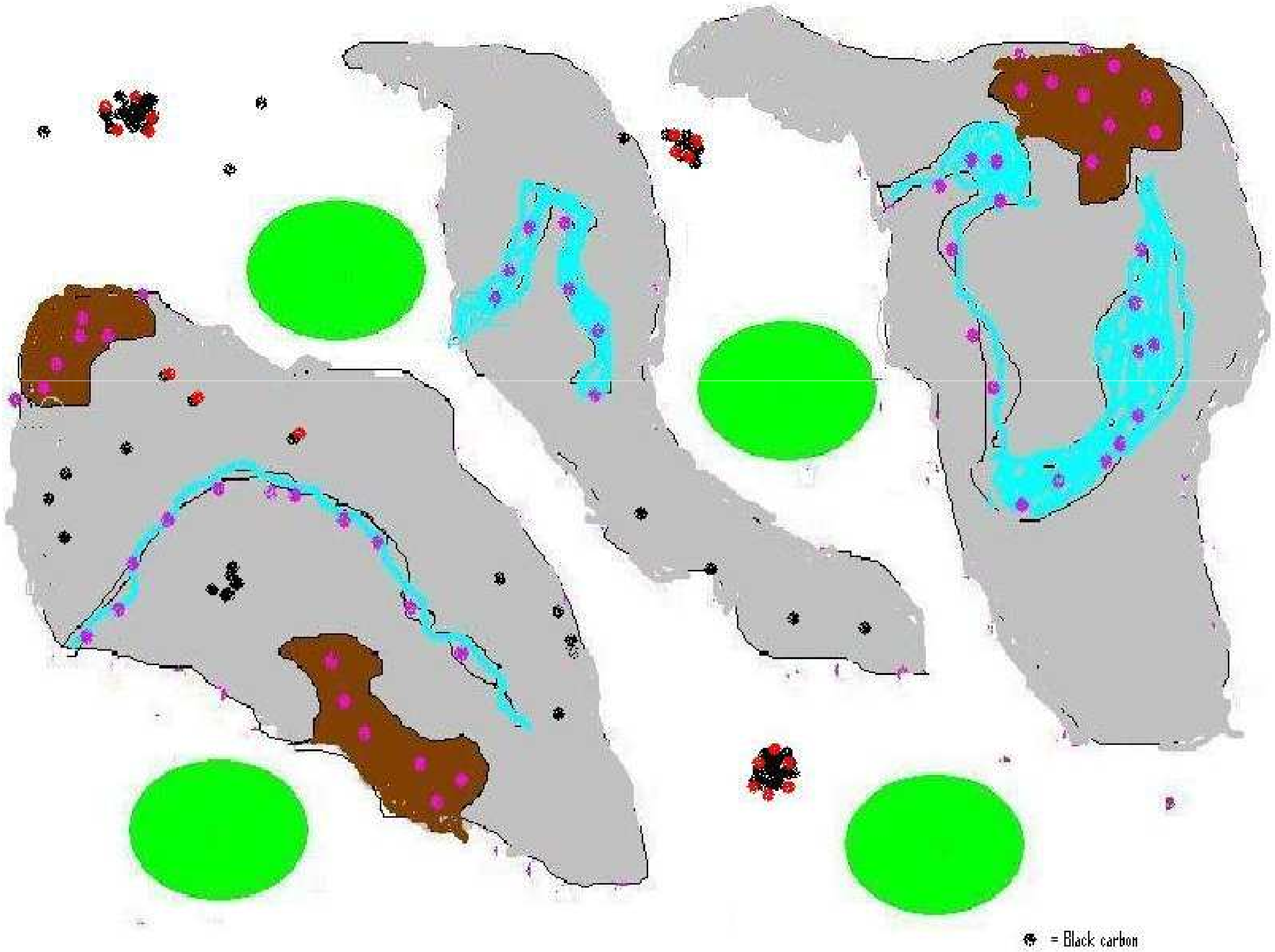
The Structure Of Humic Substances



Traditional concept
Macromolecules
M_w > 1,000,000 Da

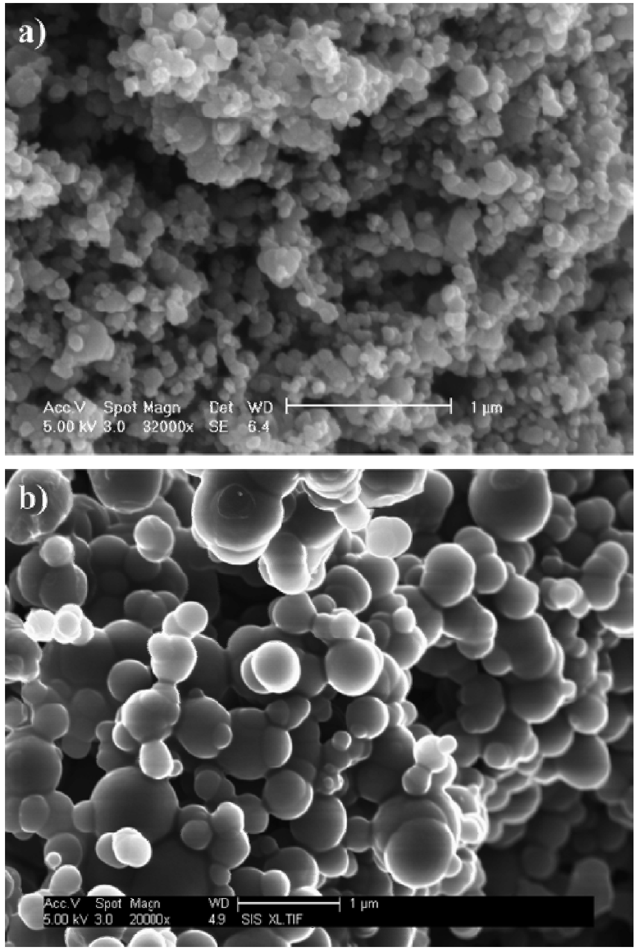
New concept, Gel, M_w <2,000 Da
Simpson *et al.*, 2002

Black Carbon Can Substantially Contribute To Adsorption



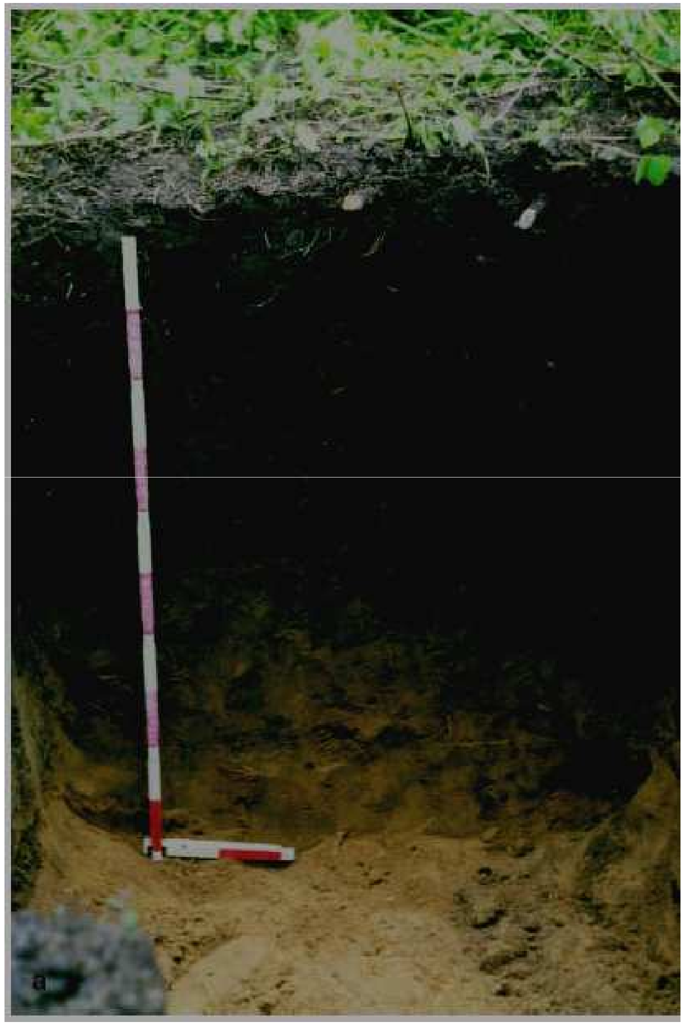
Black Carbon

- Pyrogenic carbon particles (*e.g.* soot, charcoal)
- Resists decomposition
- Highly porous, nanopores <10 Å width
- Large surface area (2 to 776 m^2/g)
- Sorption 10-10000 times stronger than on other organic carbon
- Supersorbent (like active carbon)



Hong *et al.*, 2003

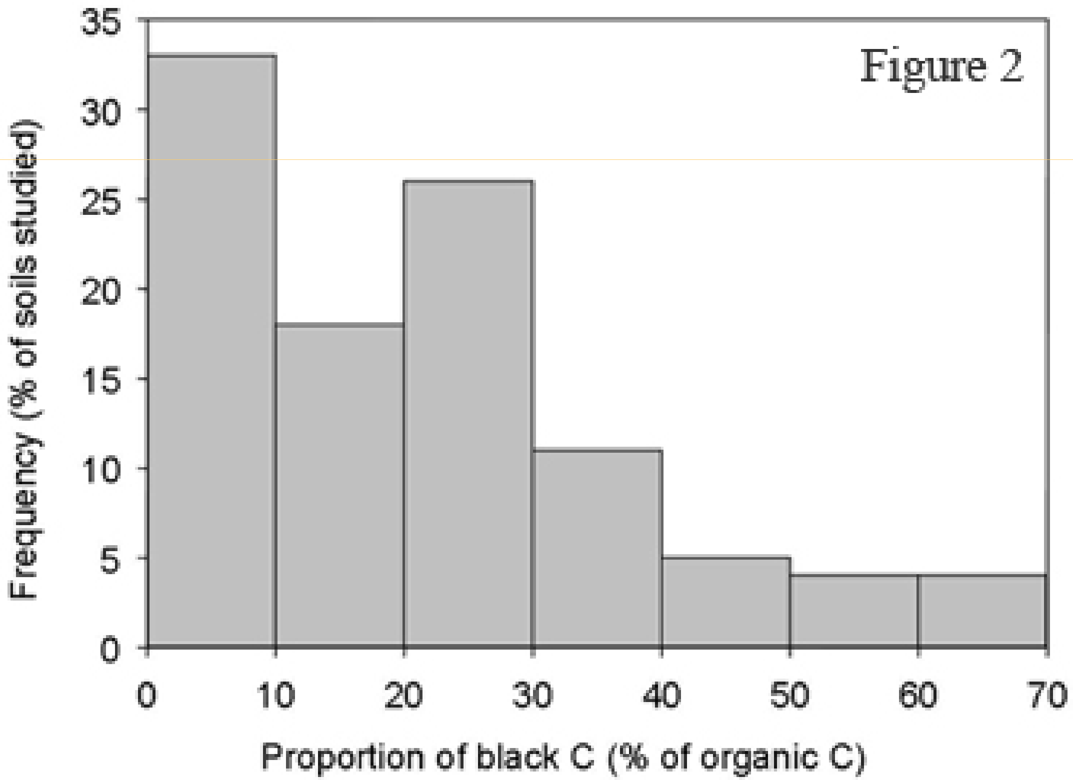
Typical Profiles Of 'Terra Preta' And Oxisol Sites



Glaser *et al.,* The 'Terra Preta' phenomenon: a model for sustainable agriculture in the humid tropics. Naturwissenschaften (2001) 88:37–41

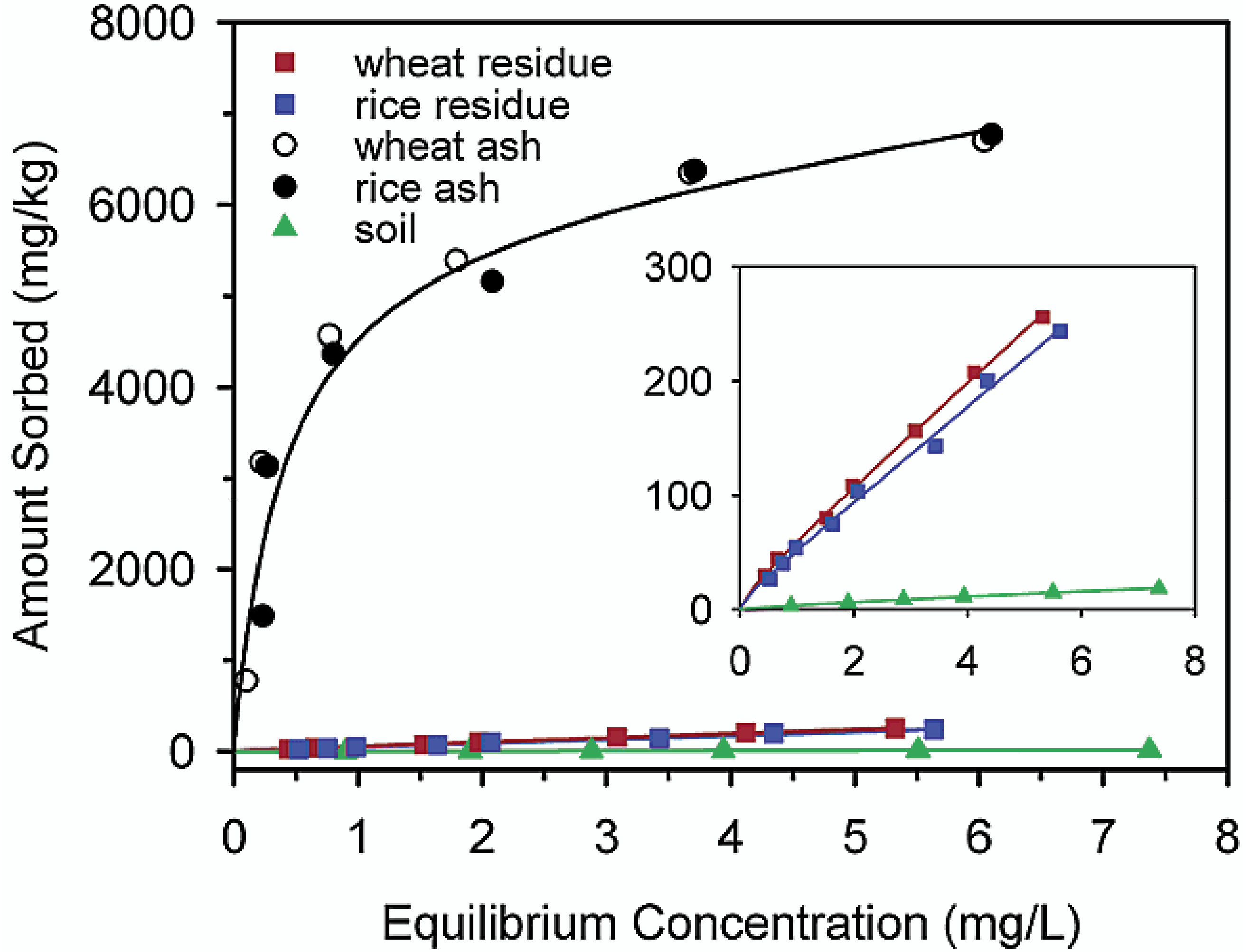
Amounts Of Black Carbon In Different Soils

- Levels surprisingly high
- Long times of accumulation (fires)
- Soot in industrialised regions
- Recalcitrant (resistant to degradation)



Source: Cheng et al, 2005 (unpublished)

Influence Of Black Carbon On Diuron Adsorption



Above the wheat ash content of 0.05%, the sorption was largely controlled by the ash (residues from 1-3 harvests mixed into 0-15 cm)

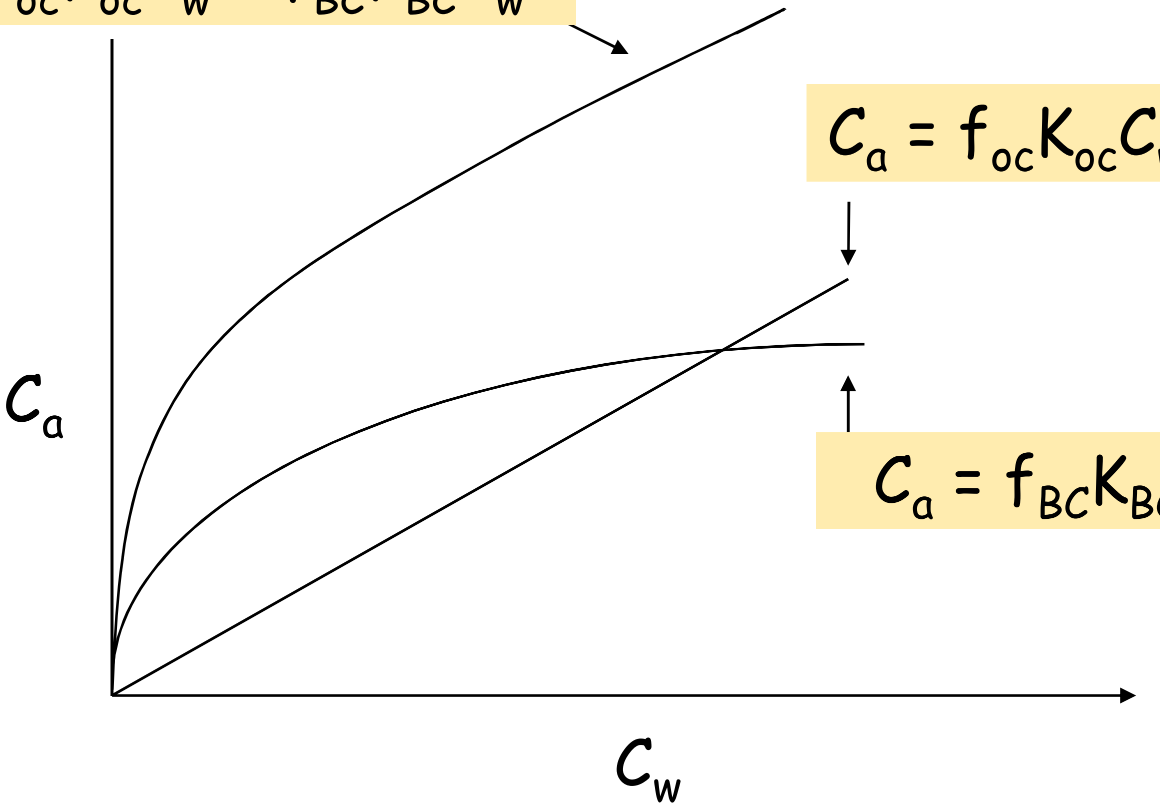
Yang & Sheng, 2003

The Composite Model (for lipophilic compounds)
Absorption In Organic Carbon (OC)
And Adsorption On Black Carbon (BC)

$$C_a = f_{oc}K_{oc}C_w + f_{BC}K_{BC}C_w^n$$

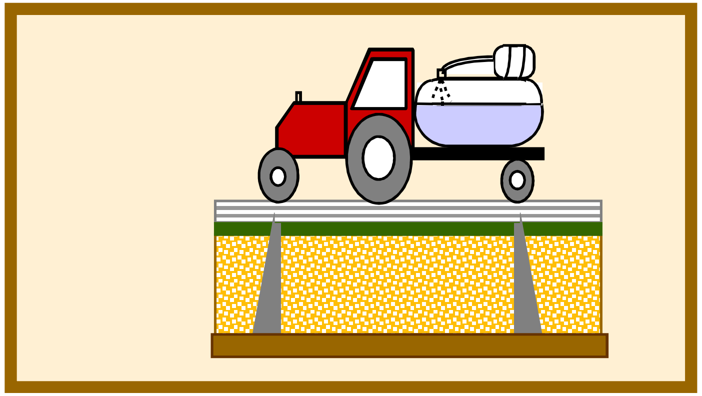
$$C_a = f_{oc}K_{oc}C_w$$

$$C_a = f_{BC}K_{BC}C_w^n$$



Equation from Accardi-Dey & Gschwend, 2002

Potential Use Of Black Carbon

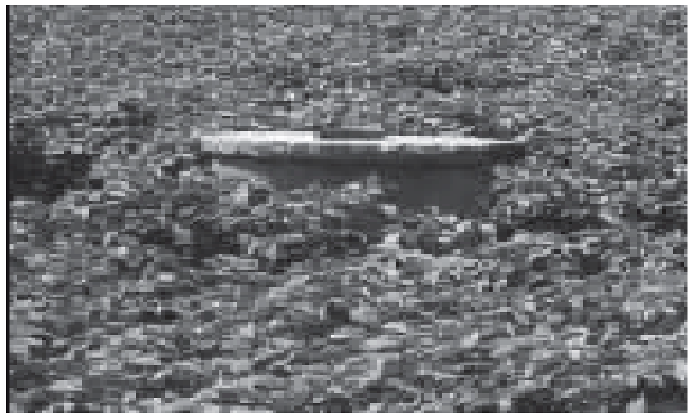


The bottom of the biobed

Railway embankments

Parking places

Yards



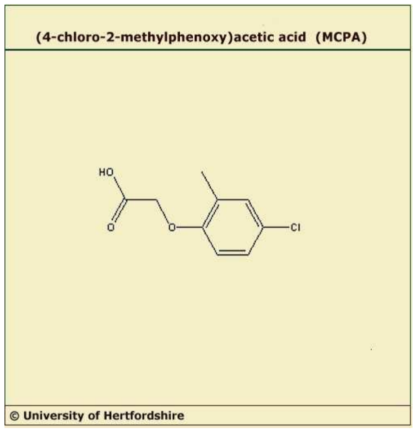
Inspection wells
for drainage systems

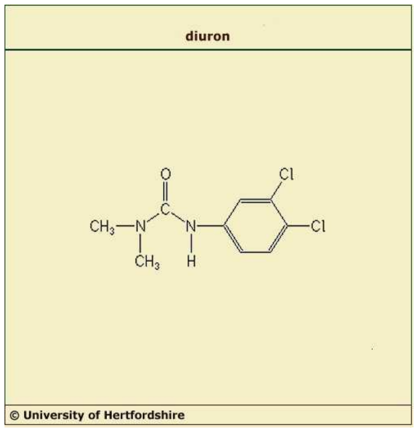
Effect Of Black Carbon On Adsorption Of Pesticides

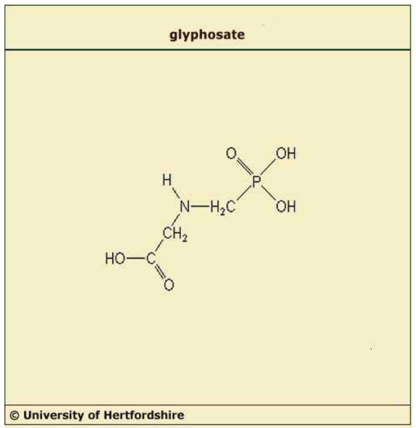
Test substances

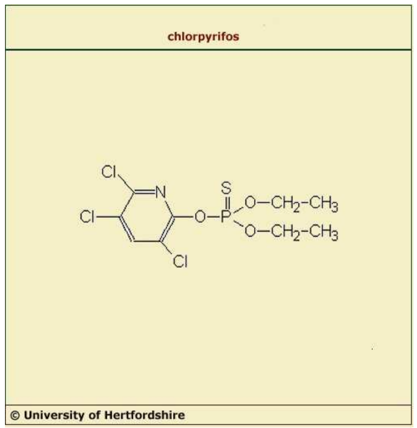
Pesticide	Typ	Grupp	Water Isolubility mg/L	Log K_{ow}	pK_a	DT_{50} typical	K_{oc}
MCPA	H	Aryloxy-alkanoic acid	29390	-0.81	3.73	15	74
Diuron	H	Phenylurea	35.6	2.87	-	75.5	1067
Glyphosate	H	Phosphono-glycine	10500	-3.2	2.3, 5.7, 10.2	12	28700
Chlor-pyrifos	I	Organo-phosphate	1.05	4.7	-	50	8151

Källa: The PPDB, Pesticide Properties Database, http://sitem.herts.ac.uk/aeru/footprint/en/index.htm



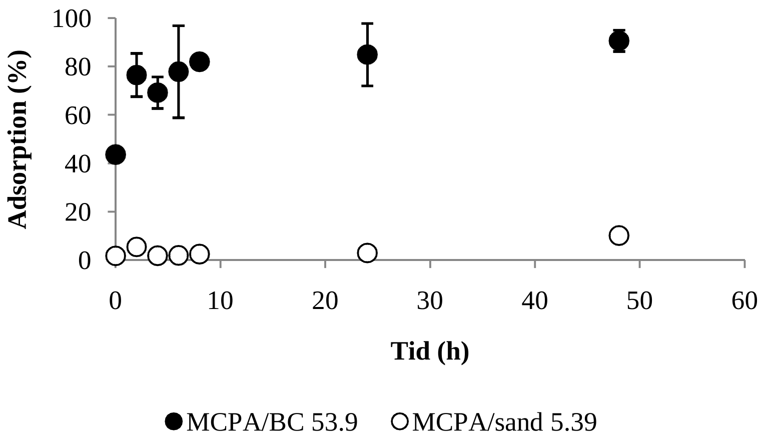


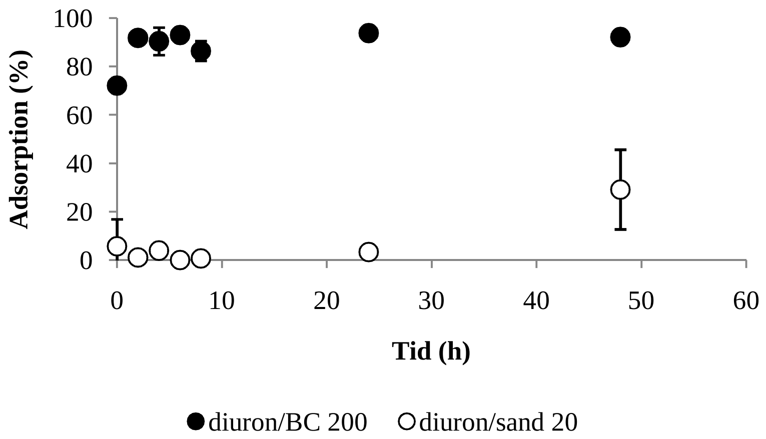


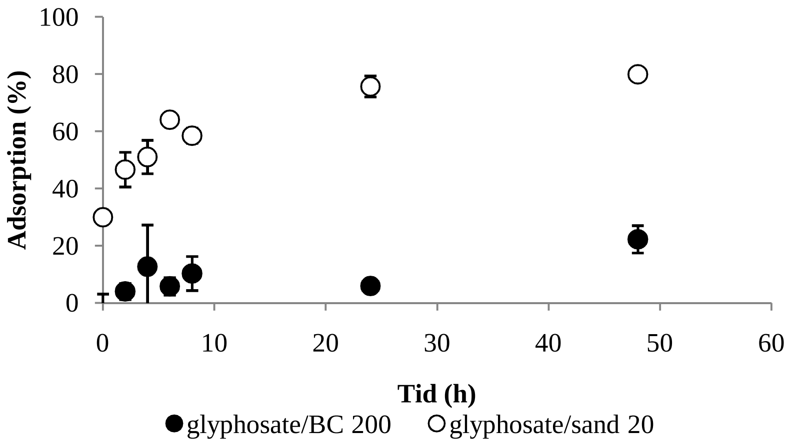


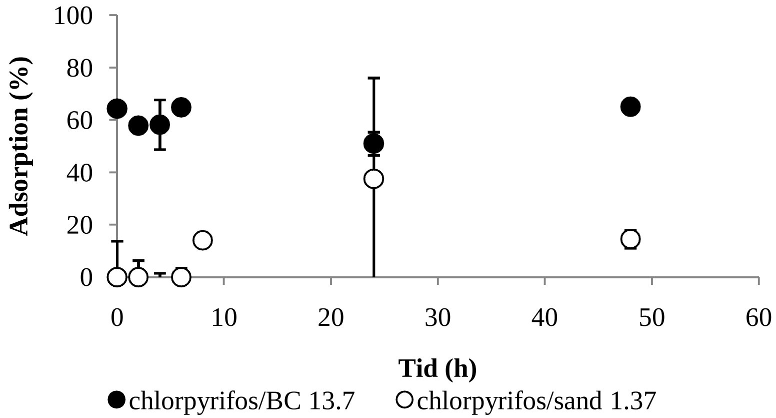
Adsorption On Black Carbon

Different times





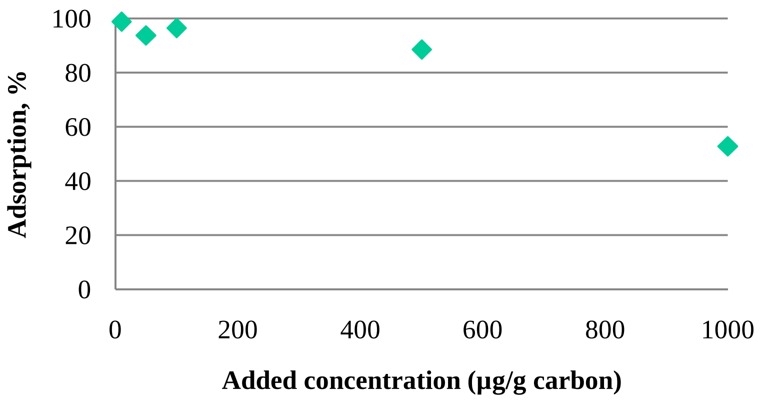




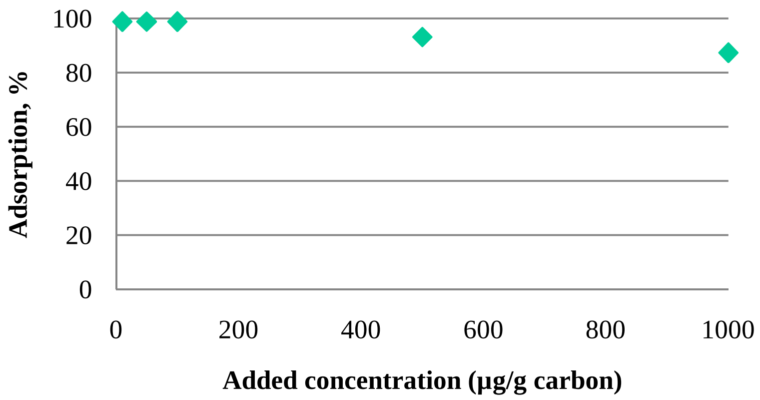
Adsorption On Balck Carbon

Different concentrations

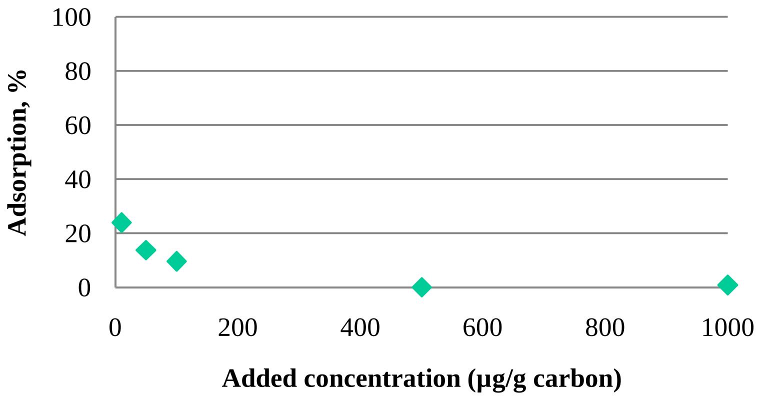
MCPA



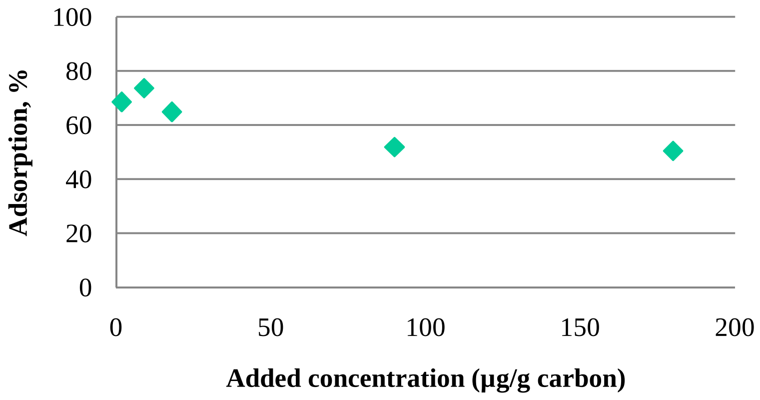
Diuron



Glyphosate

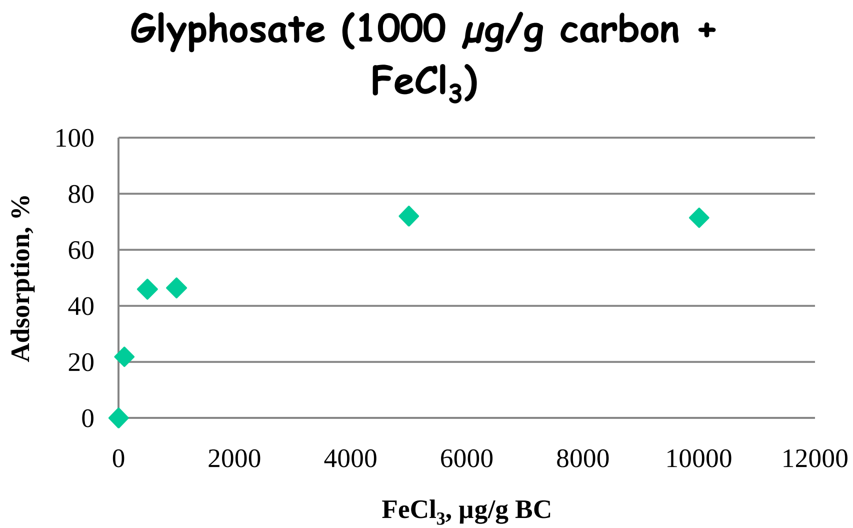


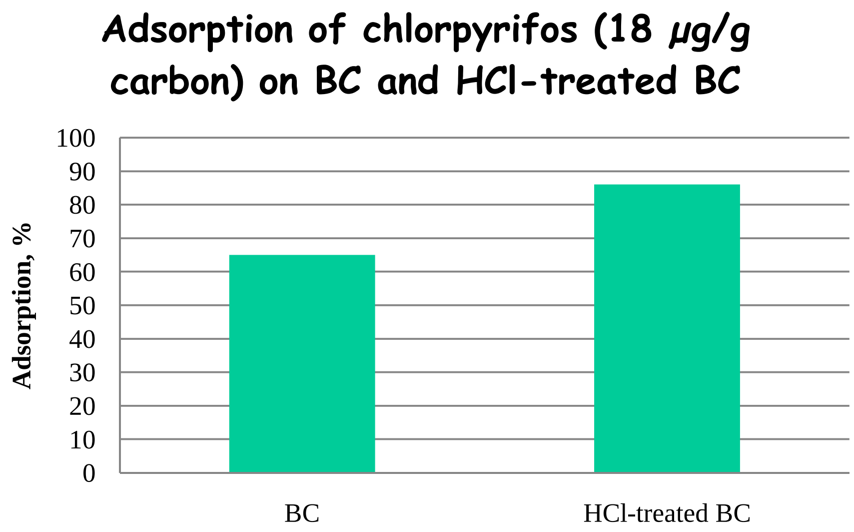
Chlorpyrifos



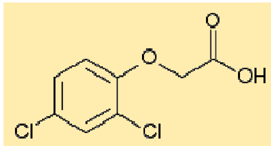
Adsorption On Black Carbon

Modification of the carbon

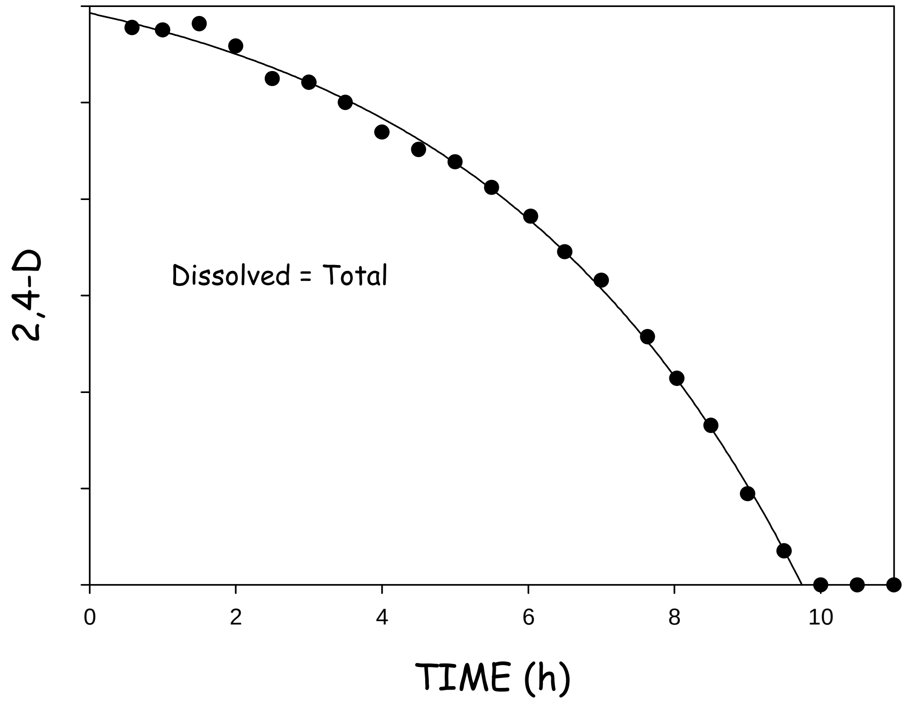


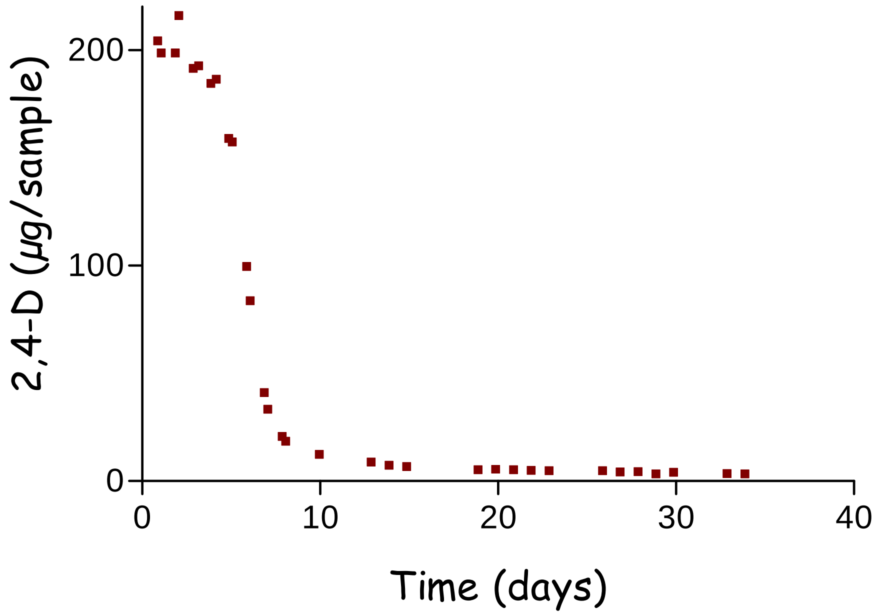


Degradation Of 2,4-D In Solution And In Soil

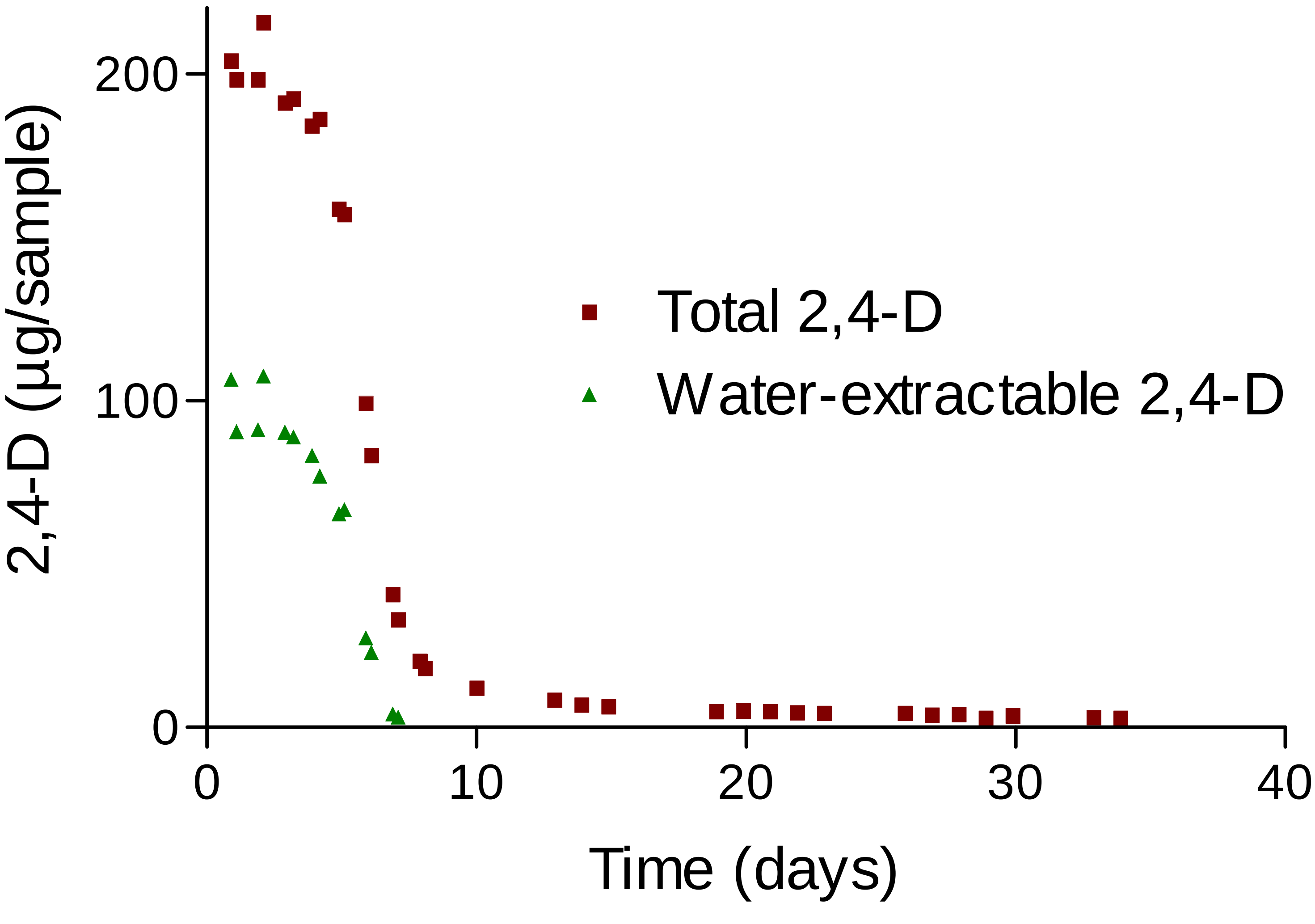


2,4-D

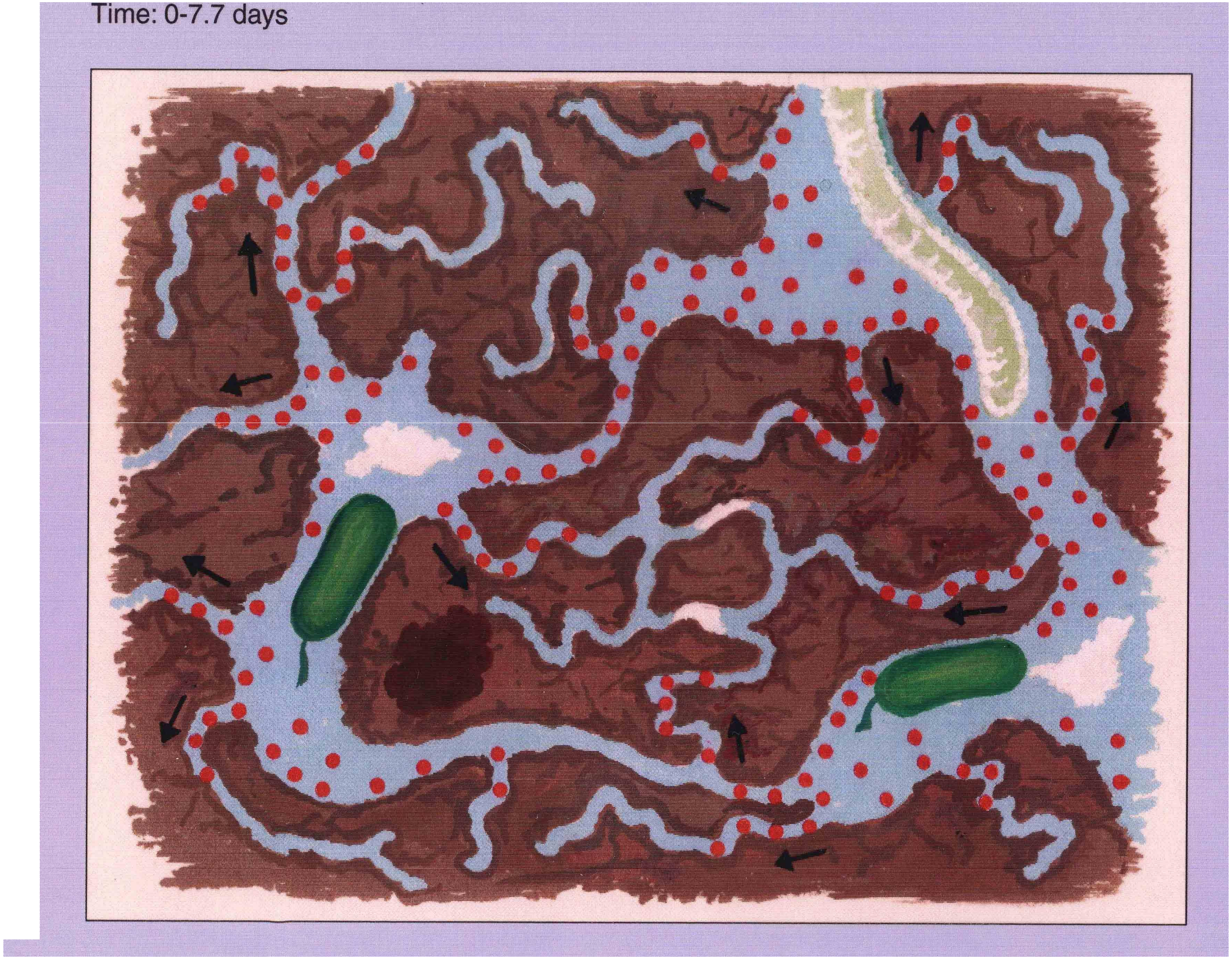




Degradation of 2,4-D in Soil



Equilibrium Sorption And Time-Limited Absorption



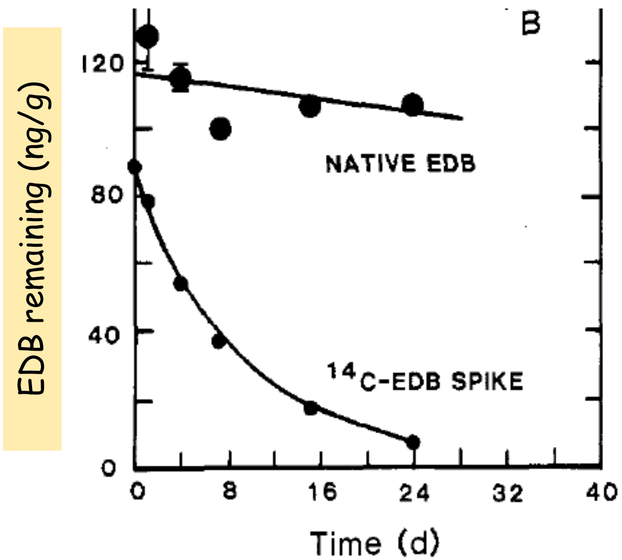
Time-Limited Desorption

Time-Dependent Availability Important For:

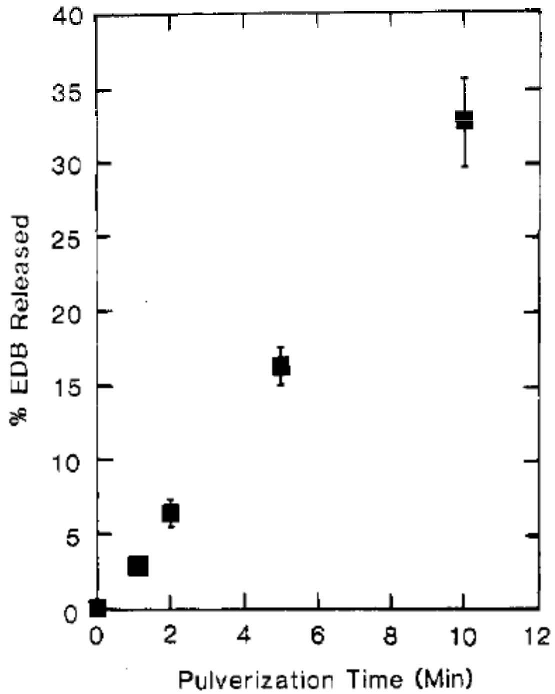
- Extractability
- Degradation kinetics
- Desorption
- Efficacy of pesticides
- Leaching
- Microbial activity
- Volatilisation
- Bioaccumulation
- Toxicity
- Risk assessment
- Remediation of soils and sediments

“Young” And “Old” 1,2-dibromoethane (EDB)

EDB degradation in soil suspensions by indigenous microbes showing the persistence of native EDB compared to a freshly added ^{14}C-EDB spike

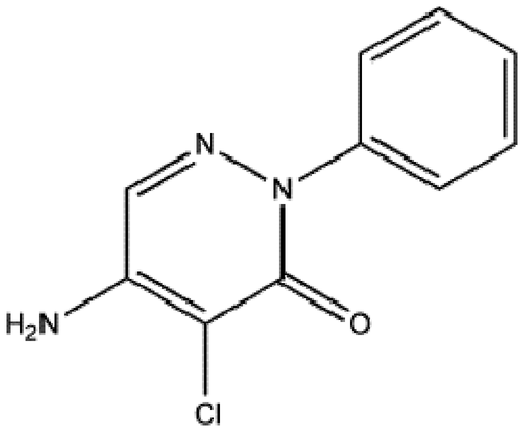


Percent of EDB released from the soil into water as a function of pulverization time in a ball mill

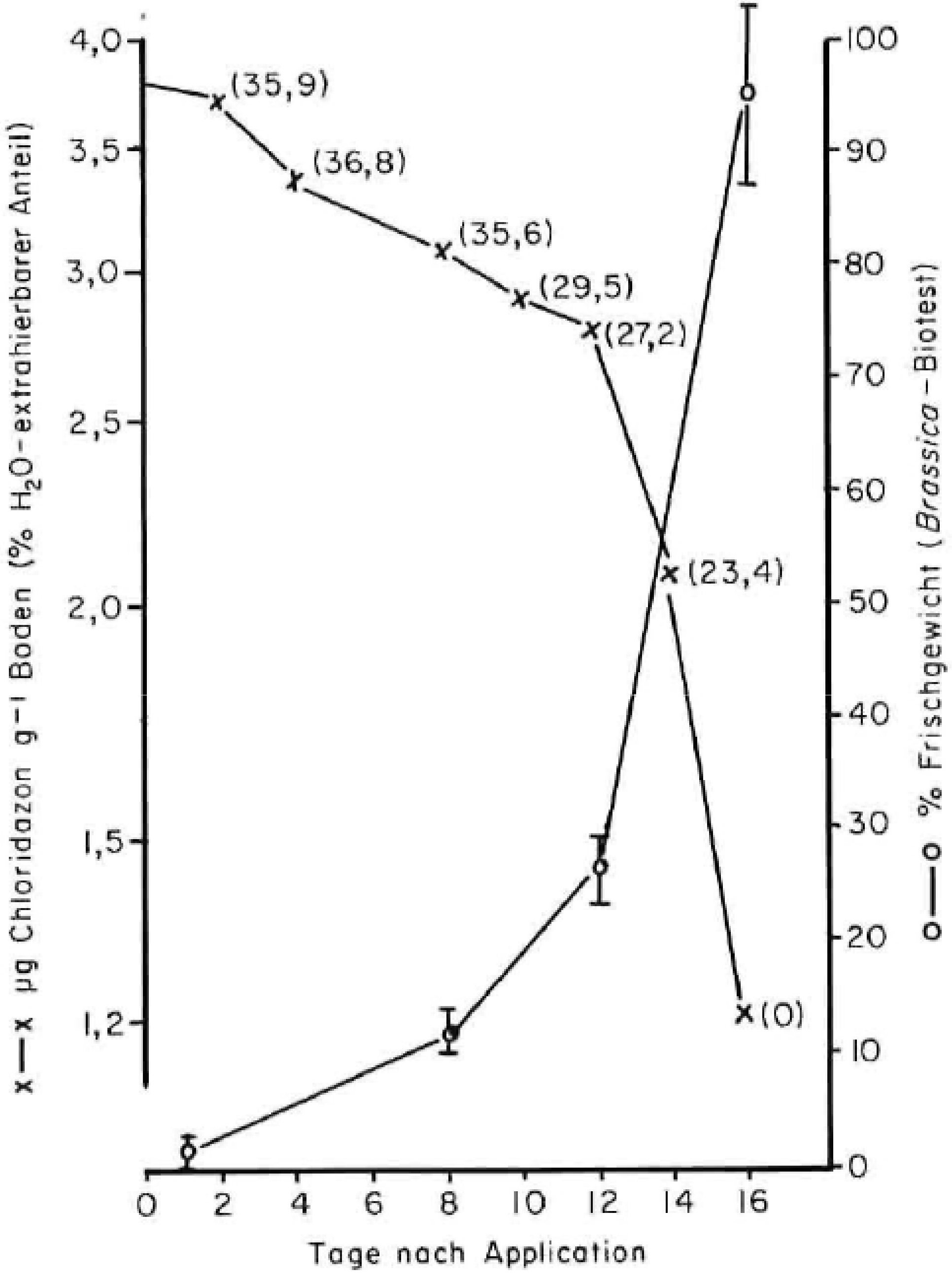


Steinberg et al., 1987

Herbicidal Activity Dependent On H_2O-Extractable Fraction

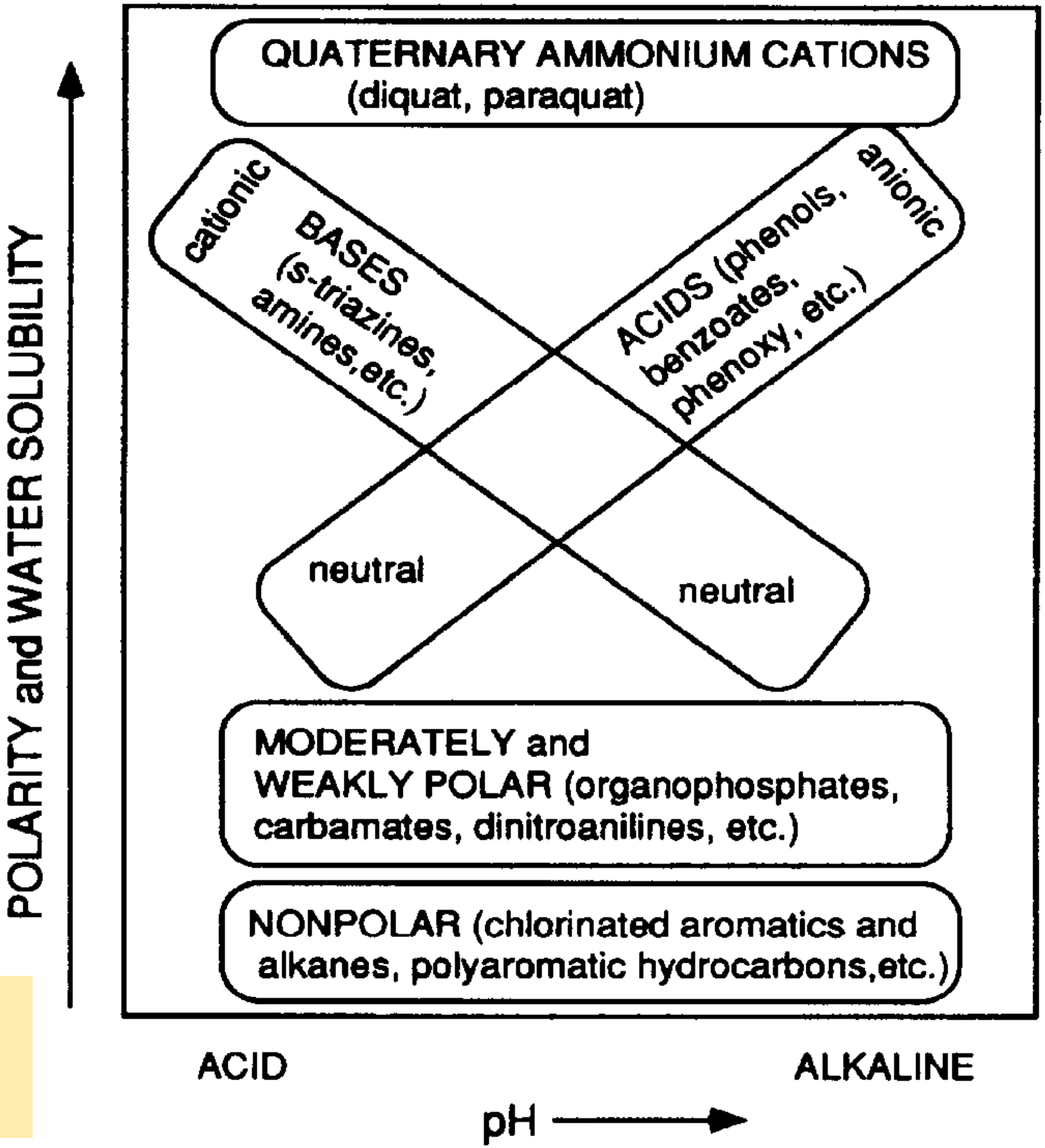


Chloridazon



Fan De Fang *et al.*, 1983

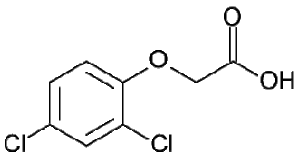
Effect Of pH On Polarity And Water Solubility



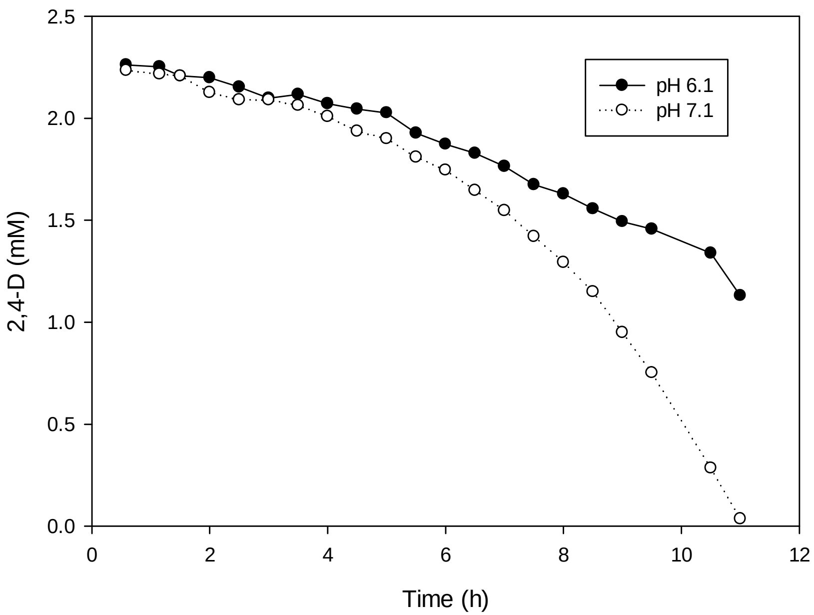
McBride, M.B. 1994. Environmental chemistry in soils. Oxford Univ. Press, Oxford.

Phenol Suicide

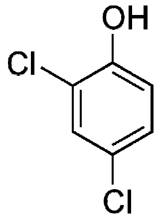
2,4-D



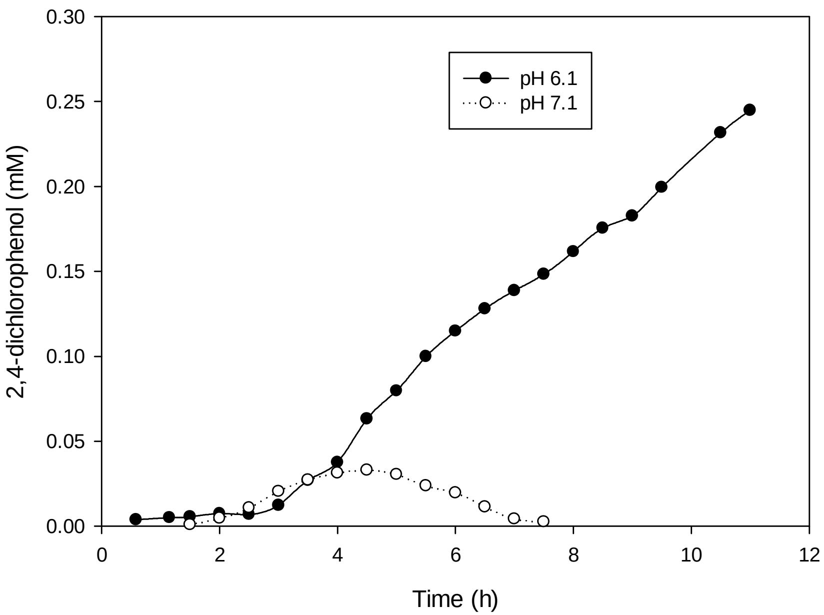
$pK_a = 2.6$



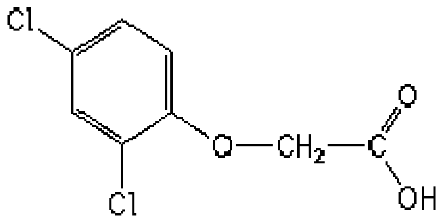
2,4-dichlorophenol



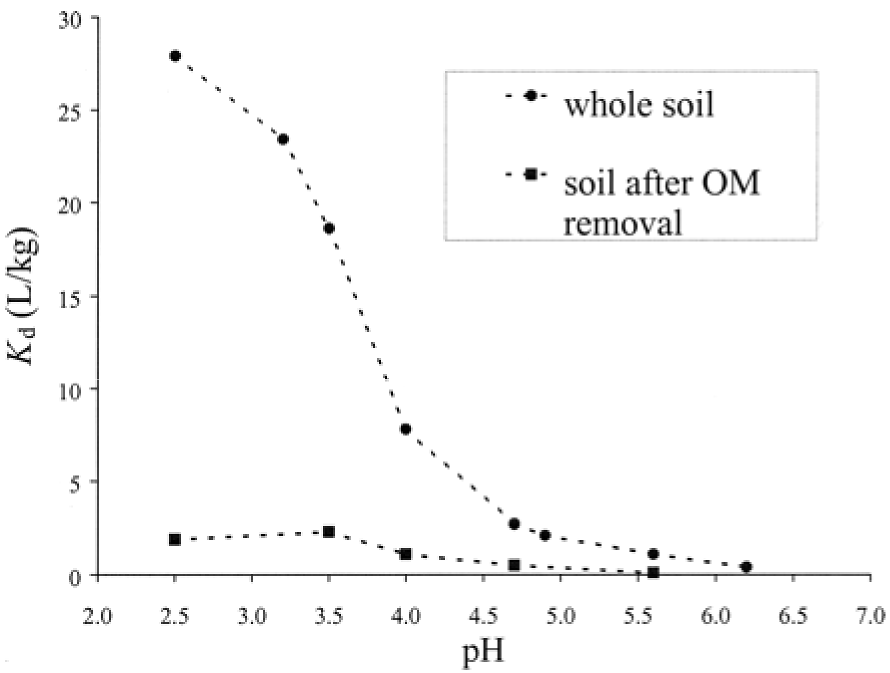
$pK_a = 7.8$



Effect Of pH On Sorption Of 2,4-D On Soil With And Without Organic Matter



pK_a = 2.6



Log K_{ow}

pH 5: 2.14
pH 7: 0.18
pH 9: 0.10

Sorption coefficients of 2,4-D measured for whole soil with 16 g/kg organic C, and when organic matter was largely reduced (1 g/kg organic C), as a function of pH

Spadotto and Hornsby, 2003