Pesticide degradation in soil
Pesticide sorption and bioavailability in soil
Modelling variation of pesticide degradation and sorption in soil

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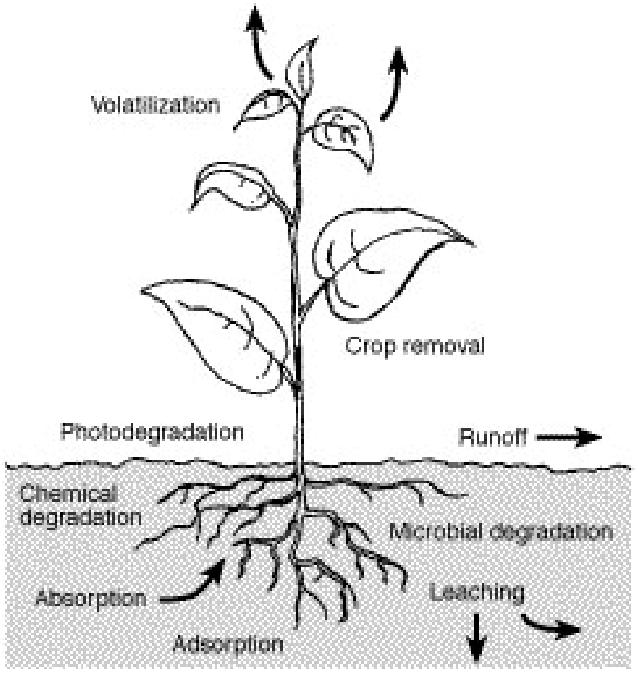
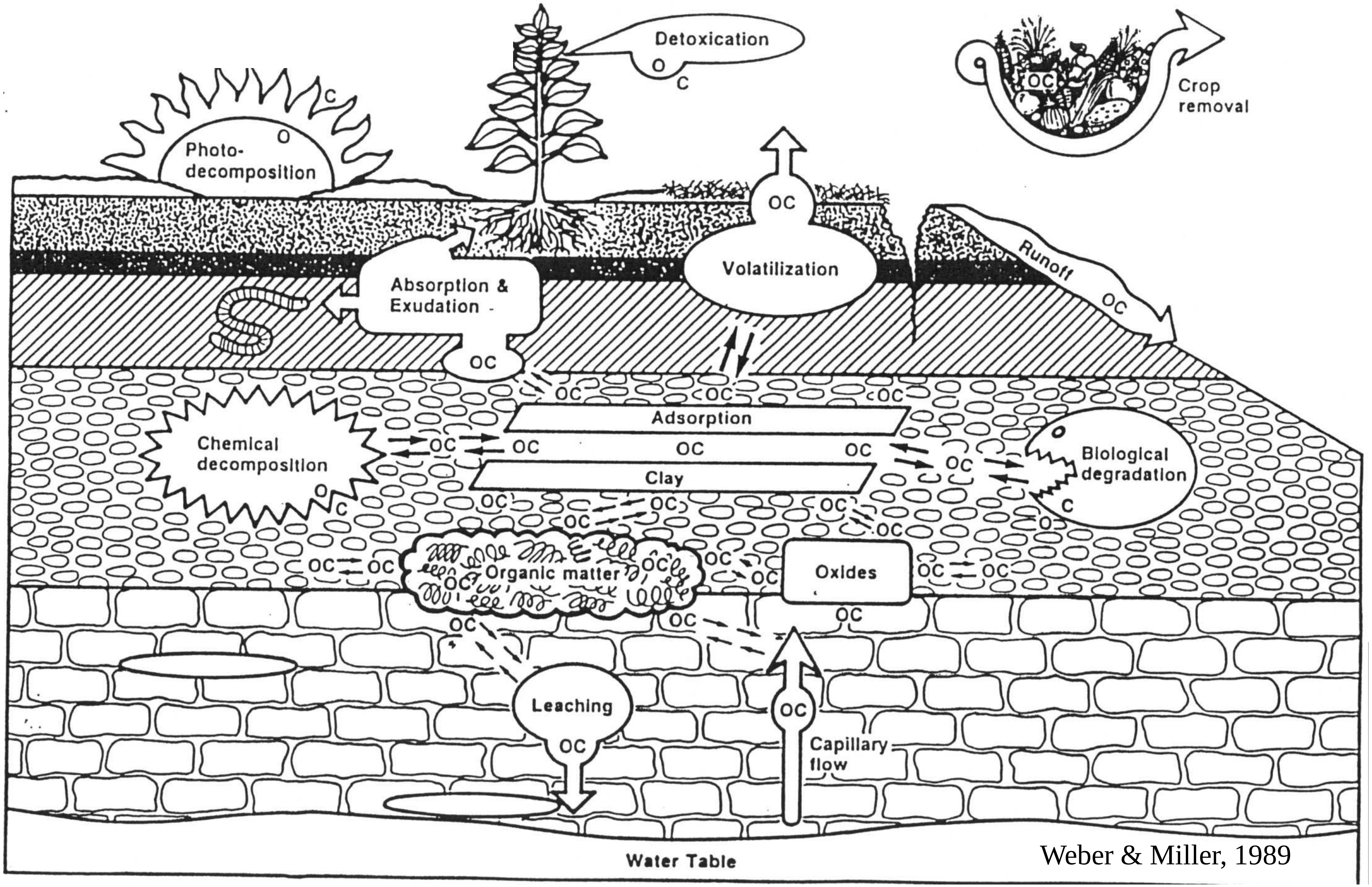
SLU

Pesticide Degradation In Soil

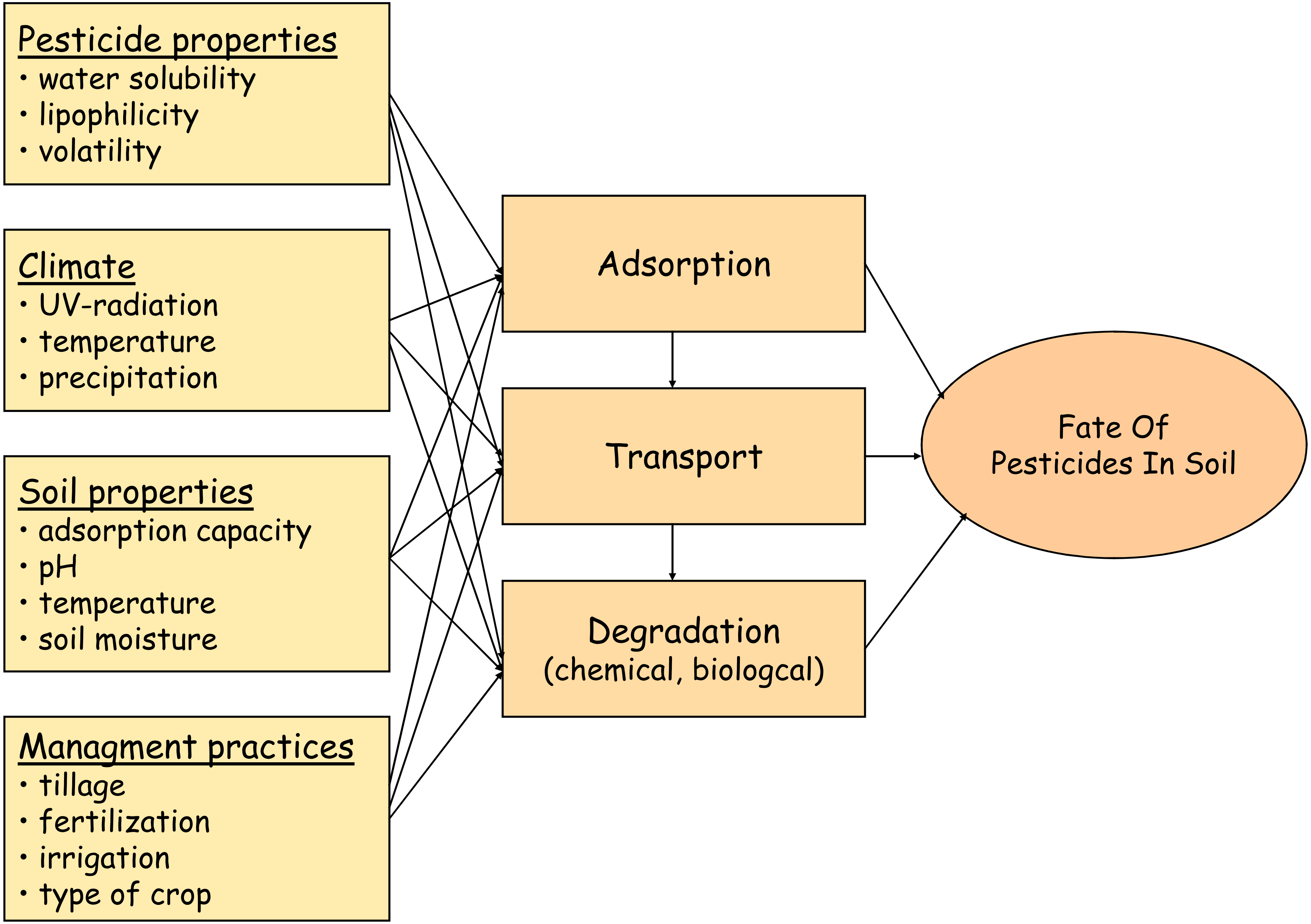
1. Fate of pesticides
2. Kinetics
3. Variables Determining Degradation
   - Structure
   - Availability
   - Quantity of microorganisms
   - Activity of microorganisms
4. Metabolites – formation and degradation



Fate Of Pesticides In Soil



Weber & Miller, 1989



Pesticide properties
- water solubility
- lipophilicity
- volatility

Climate
- UV-radiation
- temperature
- precipitation

Soil properties
- adsorption capacity
- pH
- temperature
- soil moisture

Managment practices
- tillage
- fertilization
- irrigation
- type of crop

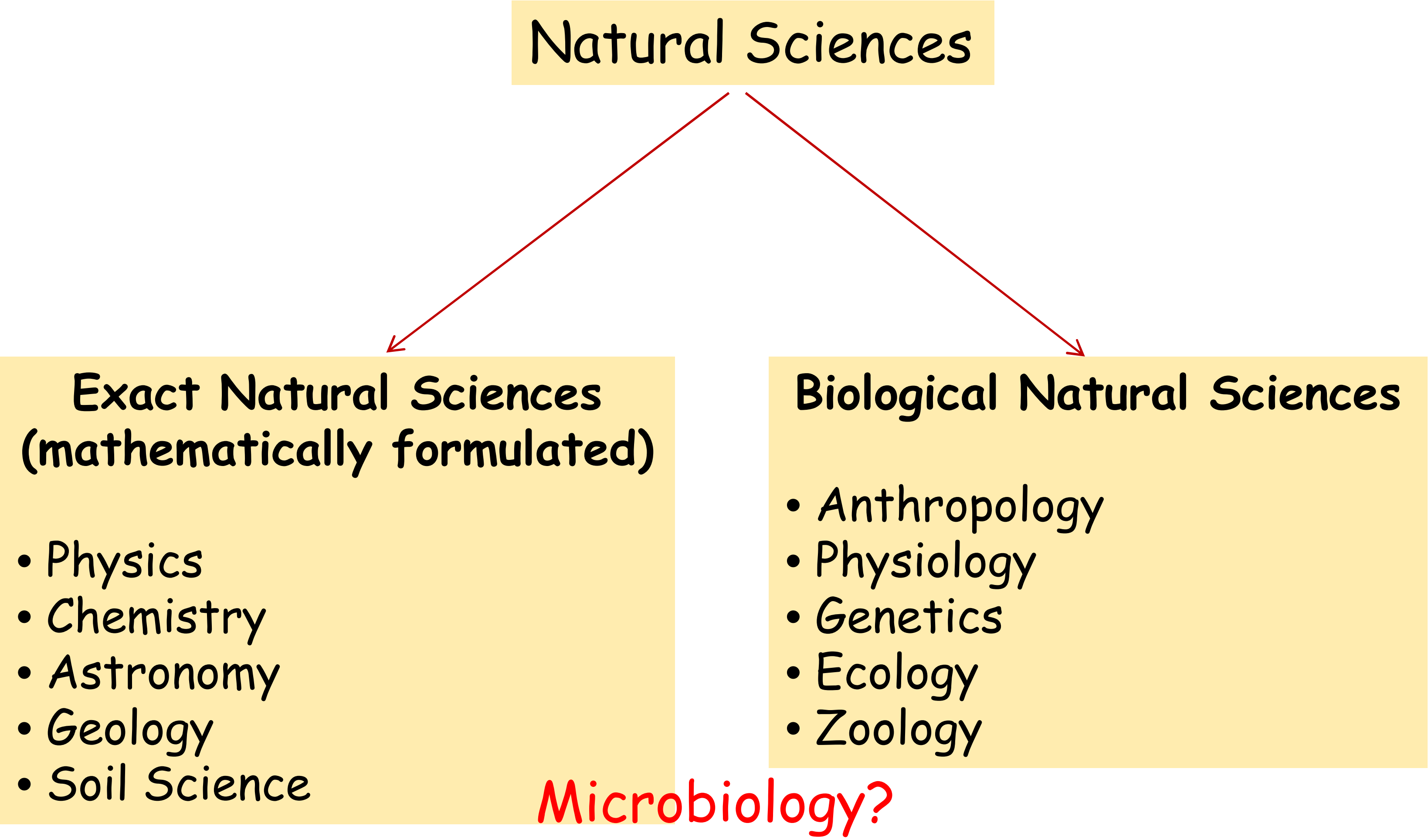
Adsorption

Transport

Degradation
(chemical, biologcal)

Fate Of
Pesticides In Soil

Where Does Microbiology Belong?



Natural Sciences

Exact Natural Sciences (mathematically formulated)

- Physics
- Chemistry
- Astronomy
- Geology
- Soil Science

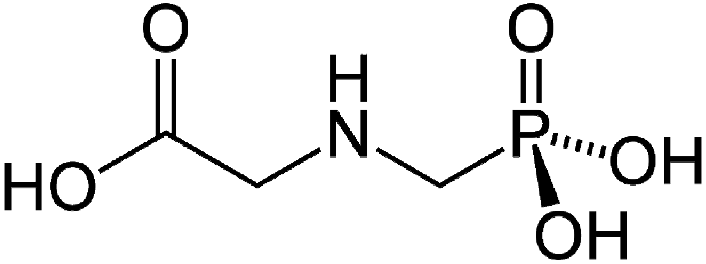
Biological Natural Sciences

- Anthropology
- Physiology
- Genetics
- Ecology
- Zoology

Microbiology?

Statistics And Natural Sciences

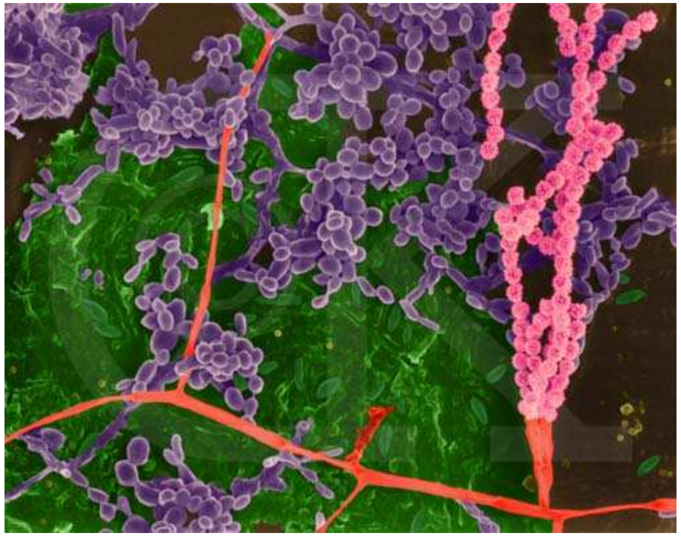
Chemistry, n = 10^{17}/Kg



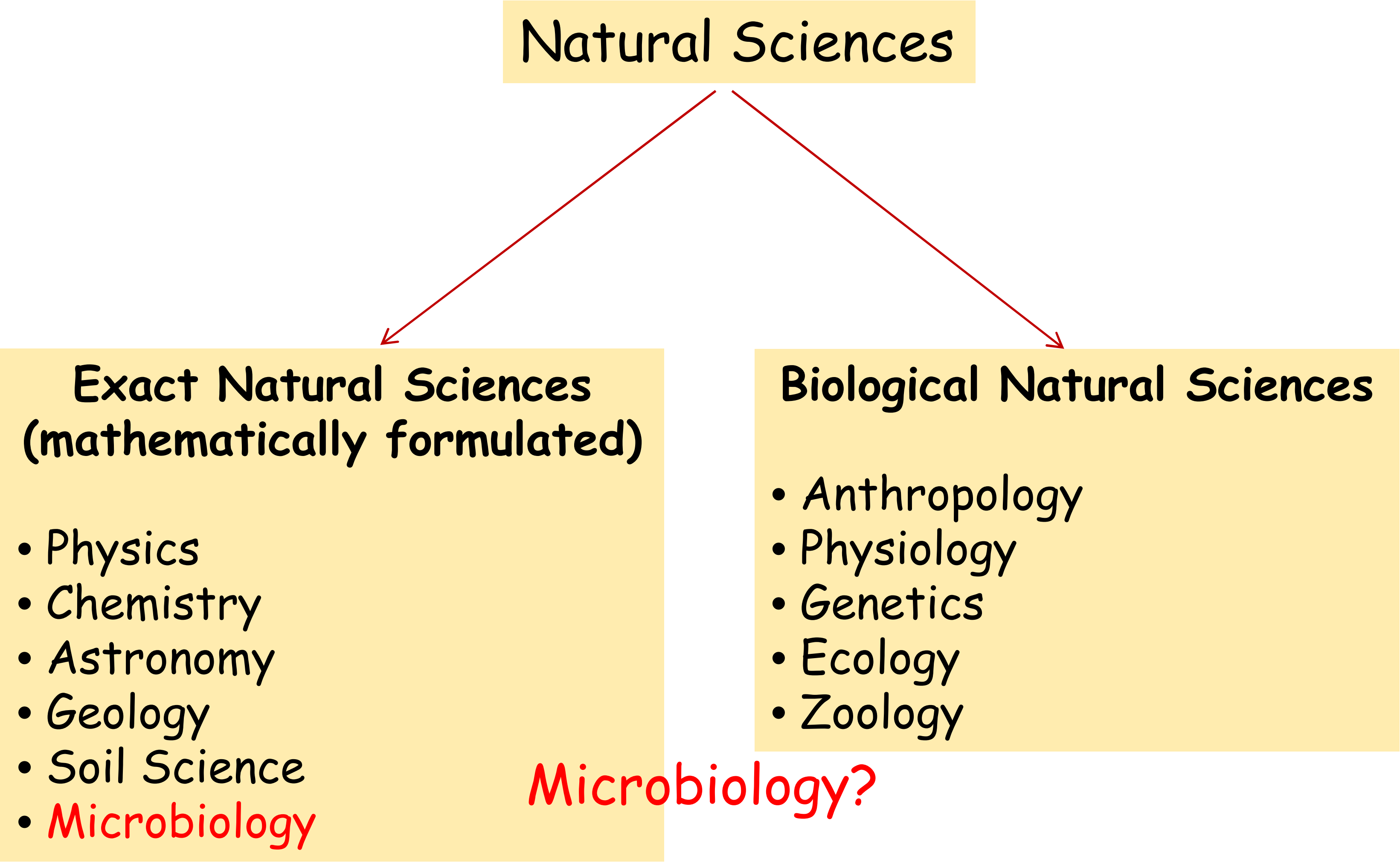
Soil Science
Surface area = 10 ha/Kg

Zoology, n = 5

Microbiology, n = 10^{11}/Kg



Where Does Microbiology Belong?



Natural Sciences

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Microbiology?

Microbial Kinetics

Kinetics refer to time-dependent phenomena

Why study kinetics?

- Elucidate reaction mechanisms and rate-limiting steps (*e.g.* bioremediation often desorption-limited)
- Powerful tool

Applications

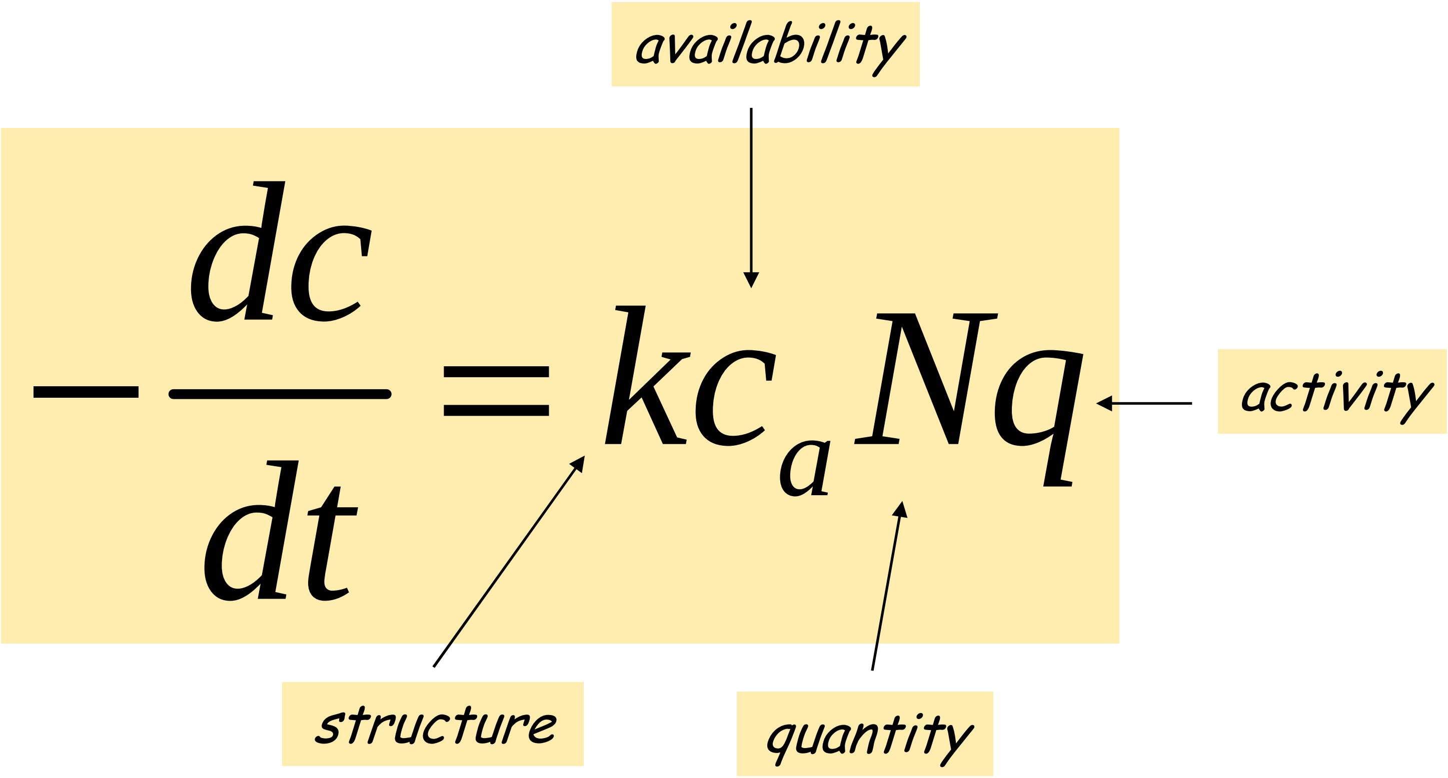
- To understand the fate of applied fertilizers, pesticides, sludges, wastes and organic pollutants in soil with time, and thus improve nutrient availability and the quality of our surface- and groundwaters

Major Variables Determining Microbial Metabolism of Pesticides in Soils

- The *structure* of the pesticide (water solubility, lipophilicity, volatility, metabolic/cometabolic)
- The *availability* of the chemical to the organisms or enzyme systems responsible for metabolism
- The *quantity* of microorganisms or enzyme systems which have the capacity to degrade the chemical
- The *activity* level or physiological state of the organisms

Andersson, 1994

The Same In Mathematics



$$-\frac{dc}{dt} = \underbrace{k}_{\text{structure}}\overset{\text{availability}}{c_a}\underbrace{N}_{\text{quantity}}\overset{\text{activity}}{q}$$

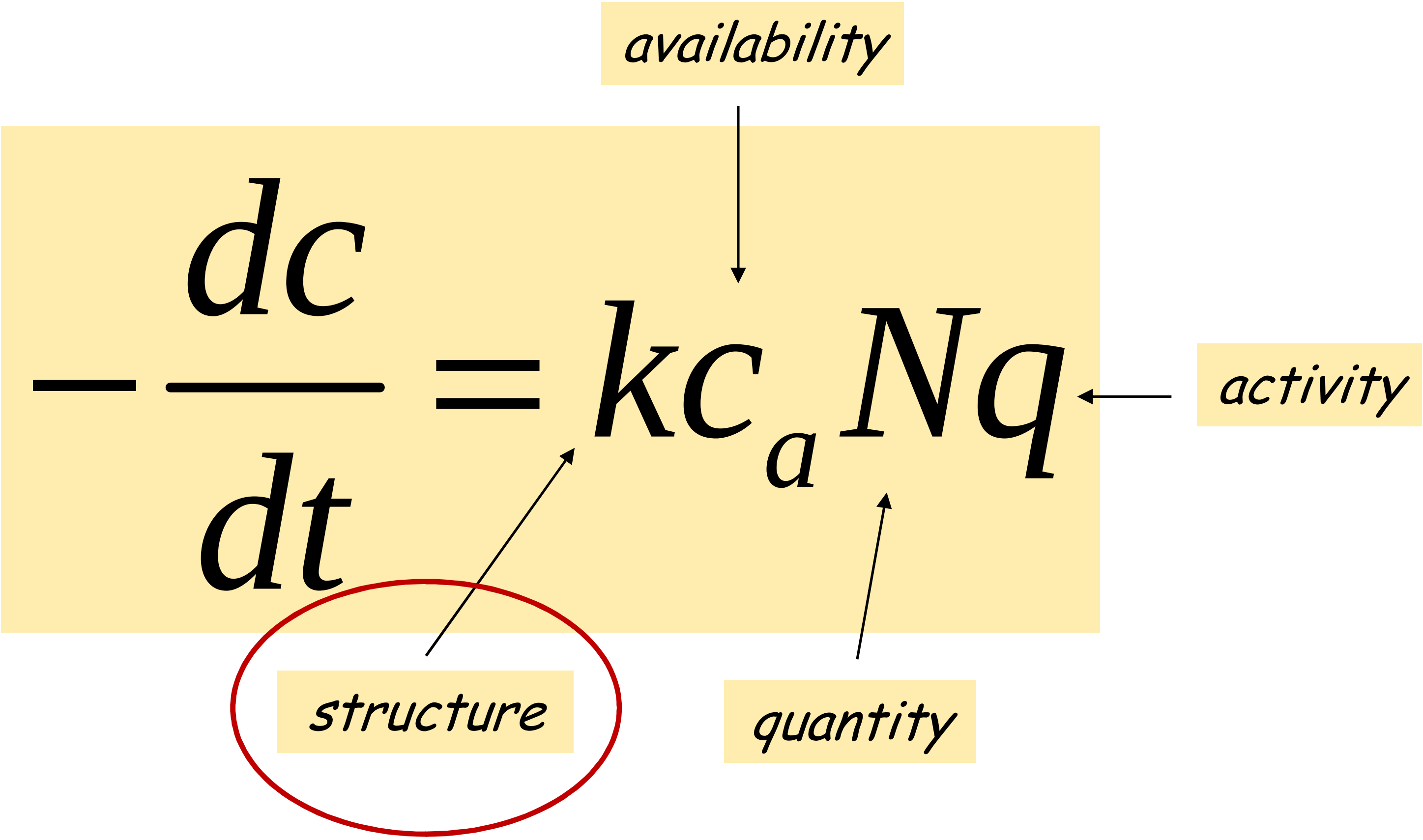
availability

activity

structure

quantity

Major Variables Determining Microbial Metabolism of Pesticides in Soils



availability

$$-\frac{dc}{dt} = kc_a Nq$$

activity

structure

quantity

Many Pollutants Are Degraded Cometabolically

Cometabolism
The simultaneous degradation of two compounds, in which the degradation of the second compound (the secondary substrate) depends on the presence of the first compound (the primary substrate)

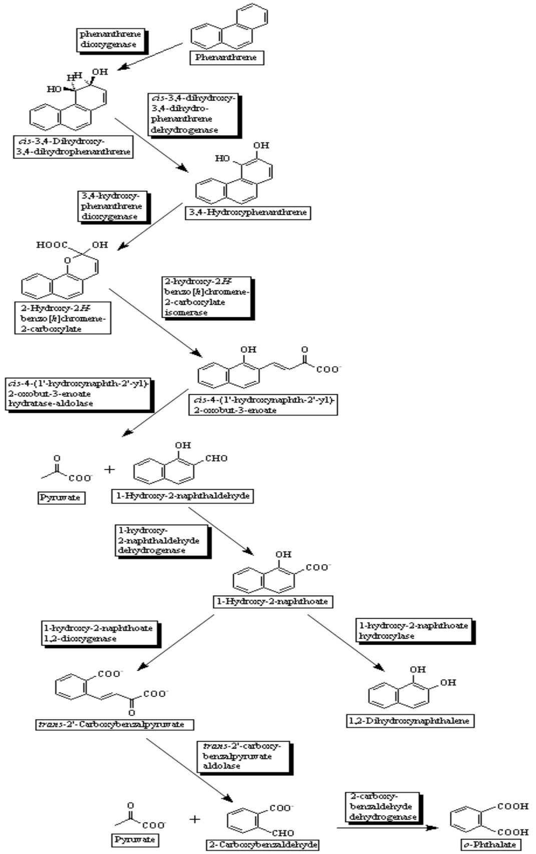
Examples of compounds degraded comeatbolically by the white-rot fungus *Chanerochaete chrysosporium*

Type of compound	**Example**
Aromatic hydrocarbons	Benzo(a)pyrene Phenanthrene Pyrene
Chlorinated organics	Atrazine Chloroanilines DDT Pentachlorophenol Trichlorophenol Polychlorinated biphenyls, Arochlor Polychlorinated dibenzo-*p*-dioxins Dichlorophenoxyacetic acid
Nitrogen aromatics	2,4-Dinitrotoluene (DNT) 2,4,6-Trinitrotoluene (TNT) Hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX)
Pesticides	Isoproturon Bentazone

Pollutant Structure Determines If The Compound Can Support Metabolic Degradation

Metabolic degradation
Pollutant serves as carbon and energy source for growth

In Soil Many Compounds Are Degraded Both Metabolically And Cometabolically By Many Different Microorganisms



Degradation of phenanthrene

Biodegradation Pathways

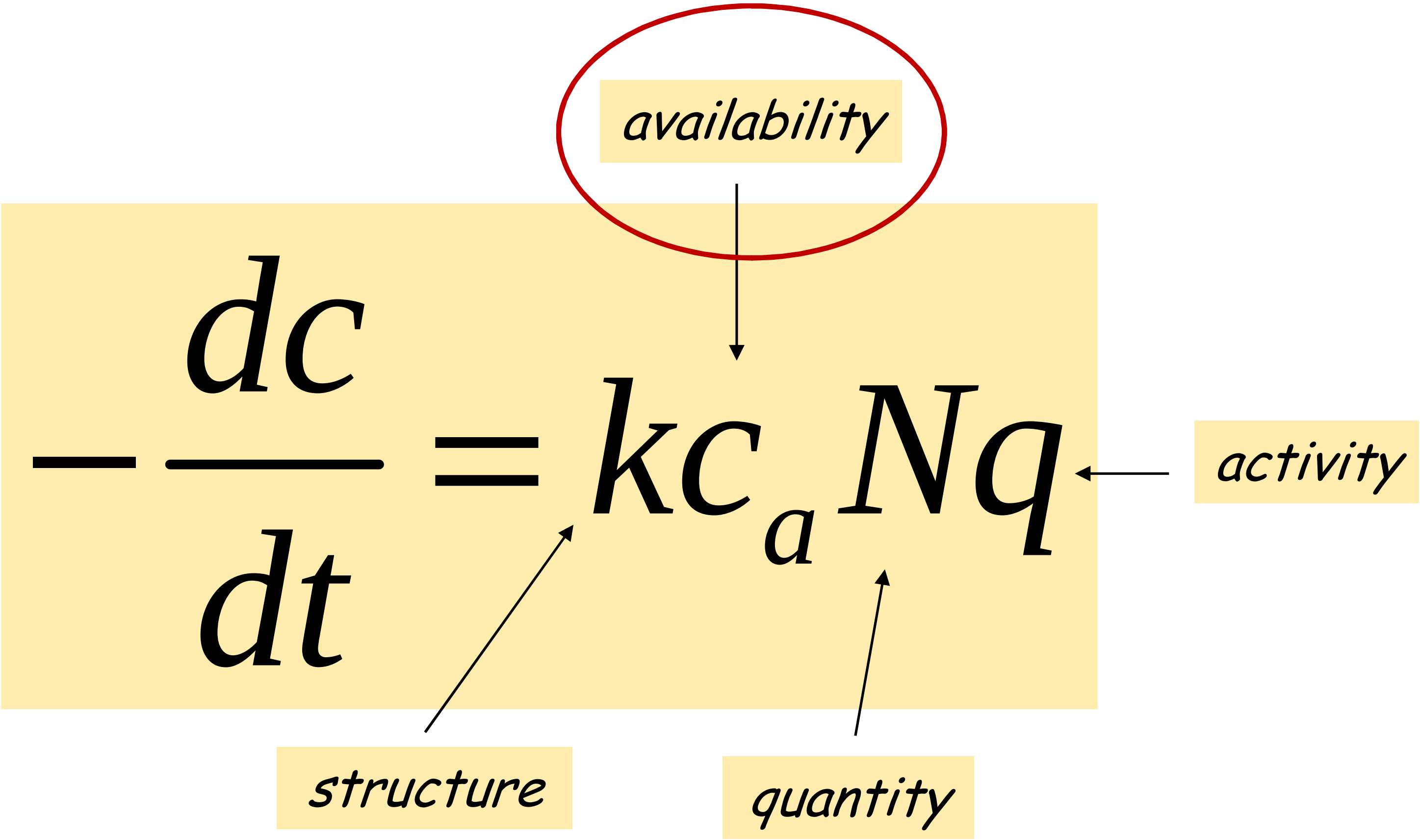
UM-BBD

UNIVERSITY OF MINNESOTA
BIOCATALYSIS / BIODEGRADATION DATABASE

The University of Minnesota Biocatalysis/Biodegradation Database
Microbial biocatalytic reactions and biodegradation pathways primarily for xenobiotic, chemical compounds

http://umbbd.msi.umn.edu/

Major Variables Determining Microbial Metabolism of Pesticides in Soils



$$-\frac{dc}{dt} = k c_a N q$$

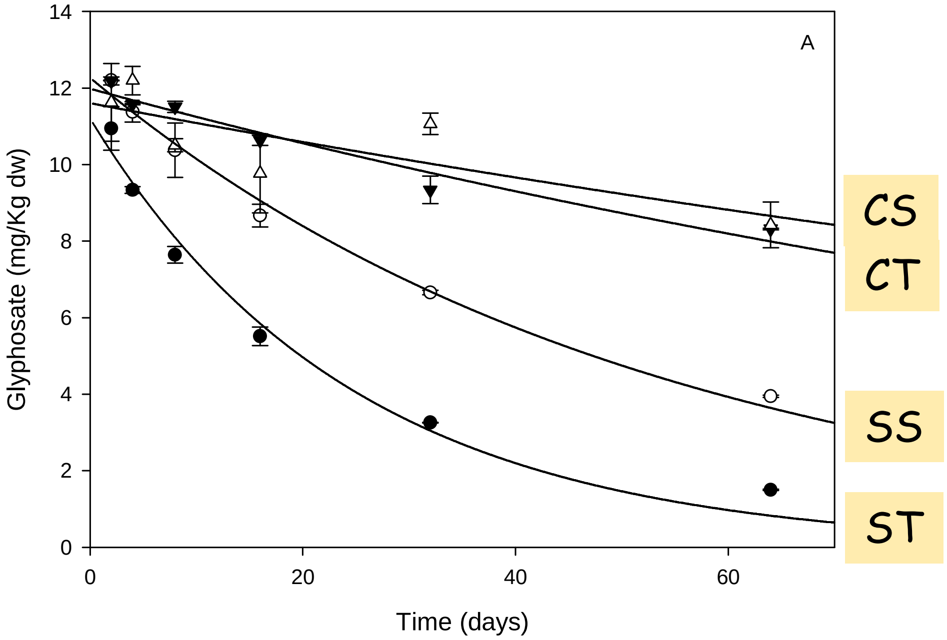
availability

activity

structure

quantity

Degradation Of Glyphosate In Top- and Subsoils Of Clay and Sand



Soil	Half-life days
Clay subsoil	151
Clay topsoil	110
Sand subsoil	37
Sand topsoil	17

First-order degradation

$$-\frac{dc}{dt}=kc$$

$$c=c_0e^{-kt}$$

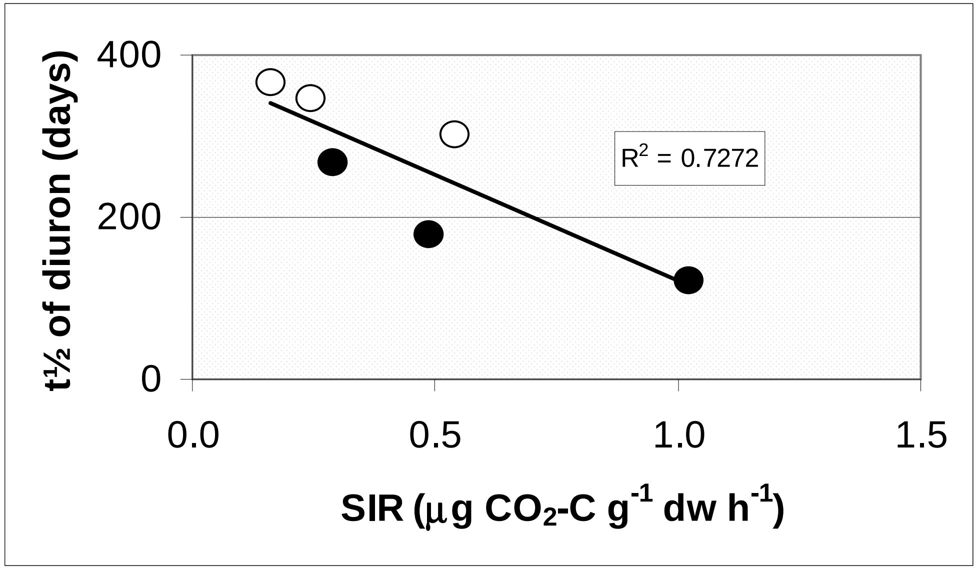
Half-life = ln(2)/k

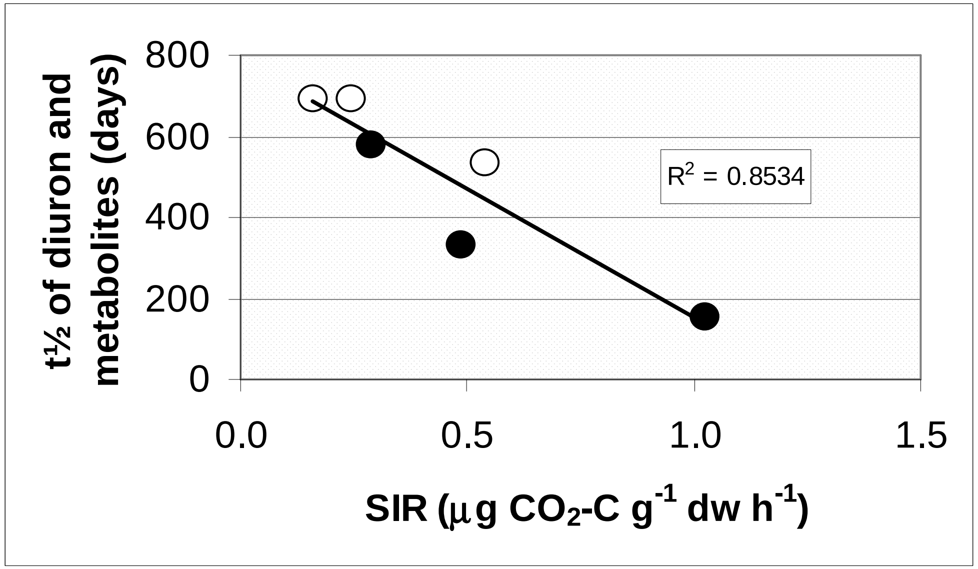
Degradaton rate determined by c_a

Major Variables Determining Microbial Metabolism of Pesticides in Soils

$$-\frac{dc}{dt} = \underbrace{k}_{\text{structure}\nearrow}\,\overset{\text{availability}}{\overset{\downarrow}{c_a}}\,\underbrace{N}_{\text{quantity}\uparrow}\,q \leftarrow \text{activity}$$

Effect Of The Size Of The Microbial Biomass On Diuron Degradation In Soil Mixtures From Railway Embankments

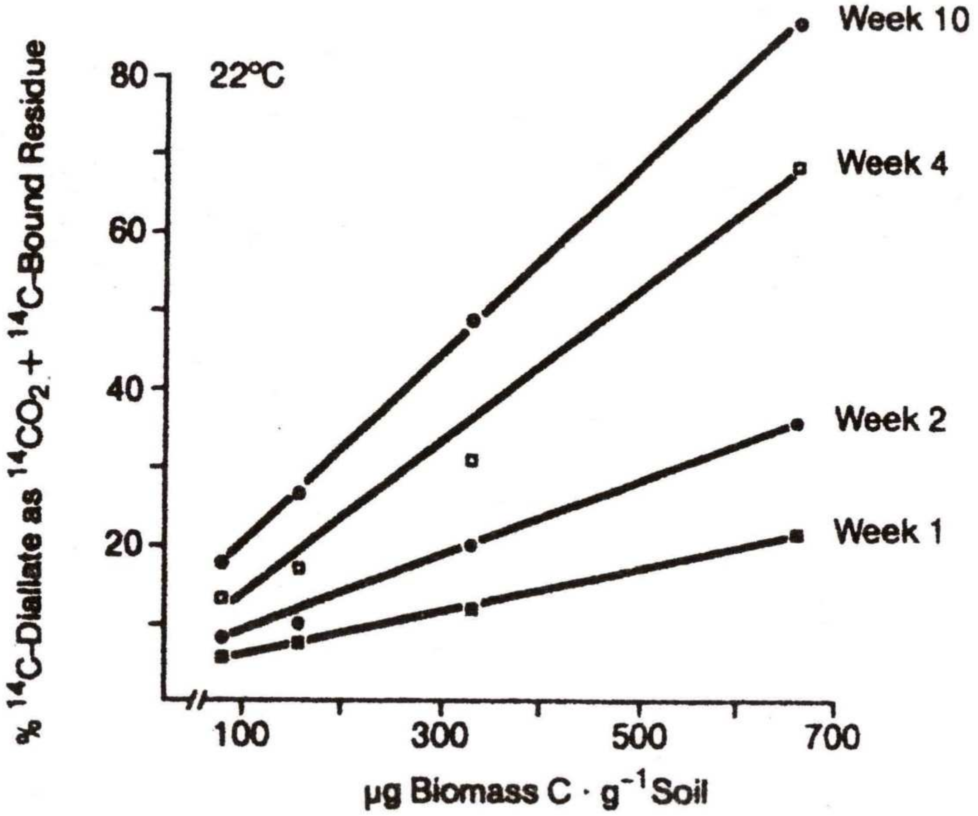




Cederlund, 2004

SIR = Substrate Induced Respiration = microbial biomass

Relationship Between Quantity of Microbial Biomass and Diallate Degradation



Frehse & Andersson, 1983

Metabolic Degradation

Exponential growth

$$\frac{dN}{dt} = \mu N$$

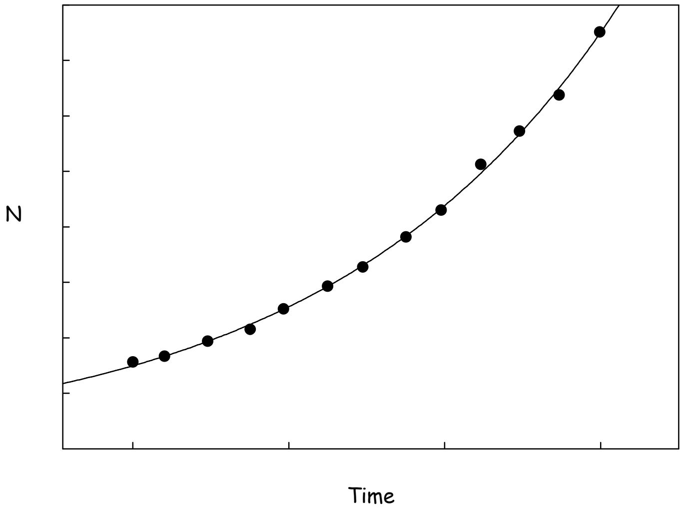
$$N = N_0 e^{\mu t}$$

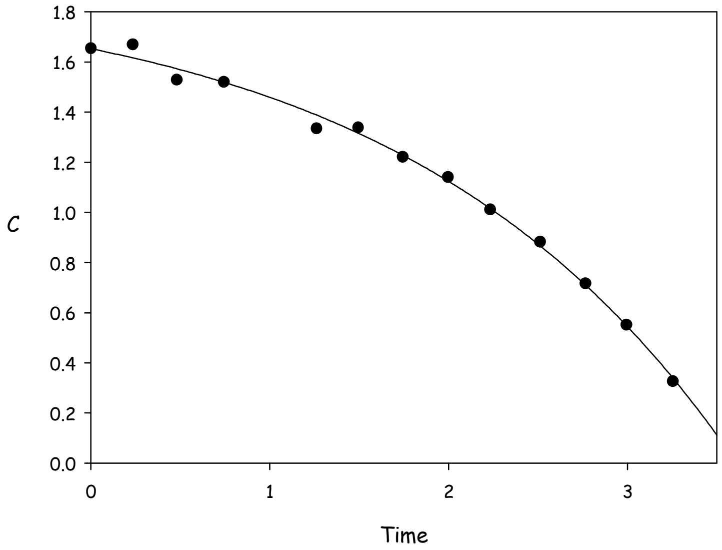
Growth-linked degradation

$$-\frac{dc}{dt} = qN$$

$$-\frac{dc}{dt} = qN_0 e^{\mu t}$$

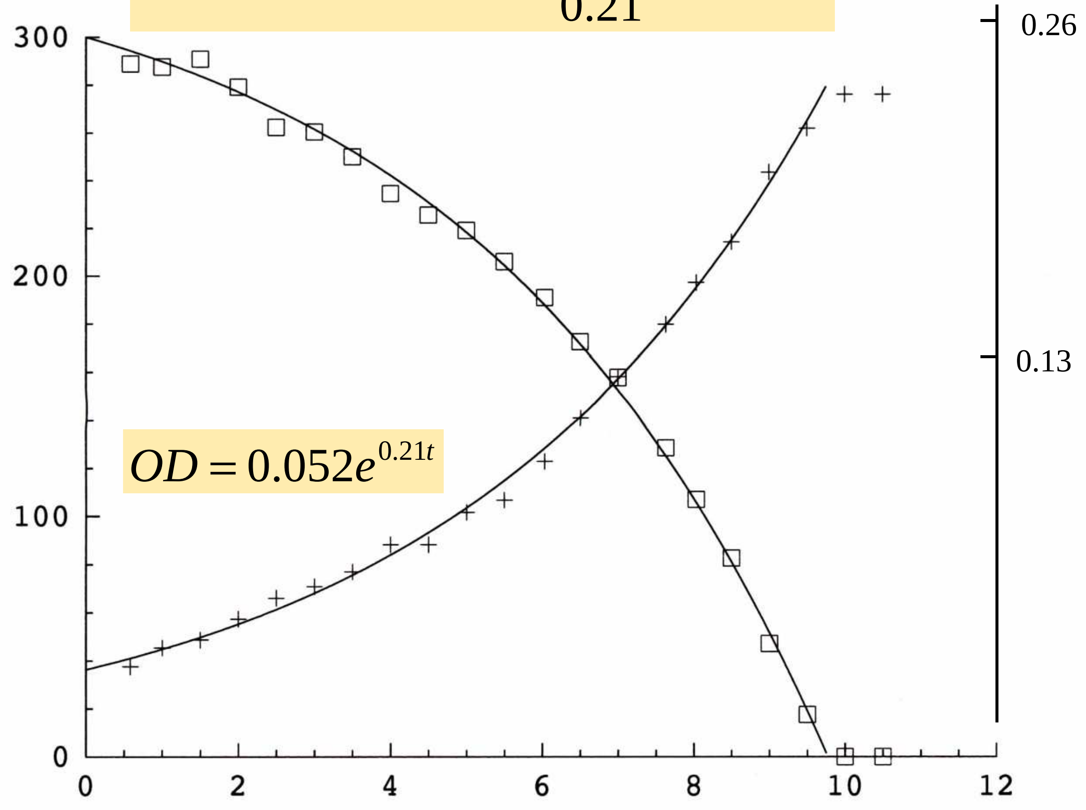
$$c = c_0 - (\frac{qN_0}{\mu})(e^{\mu t} - 1)$$





Degradation Of 2,4-D In Solution

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



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

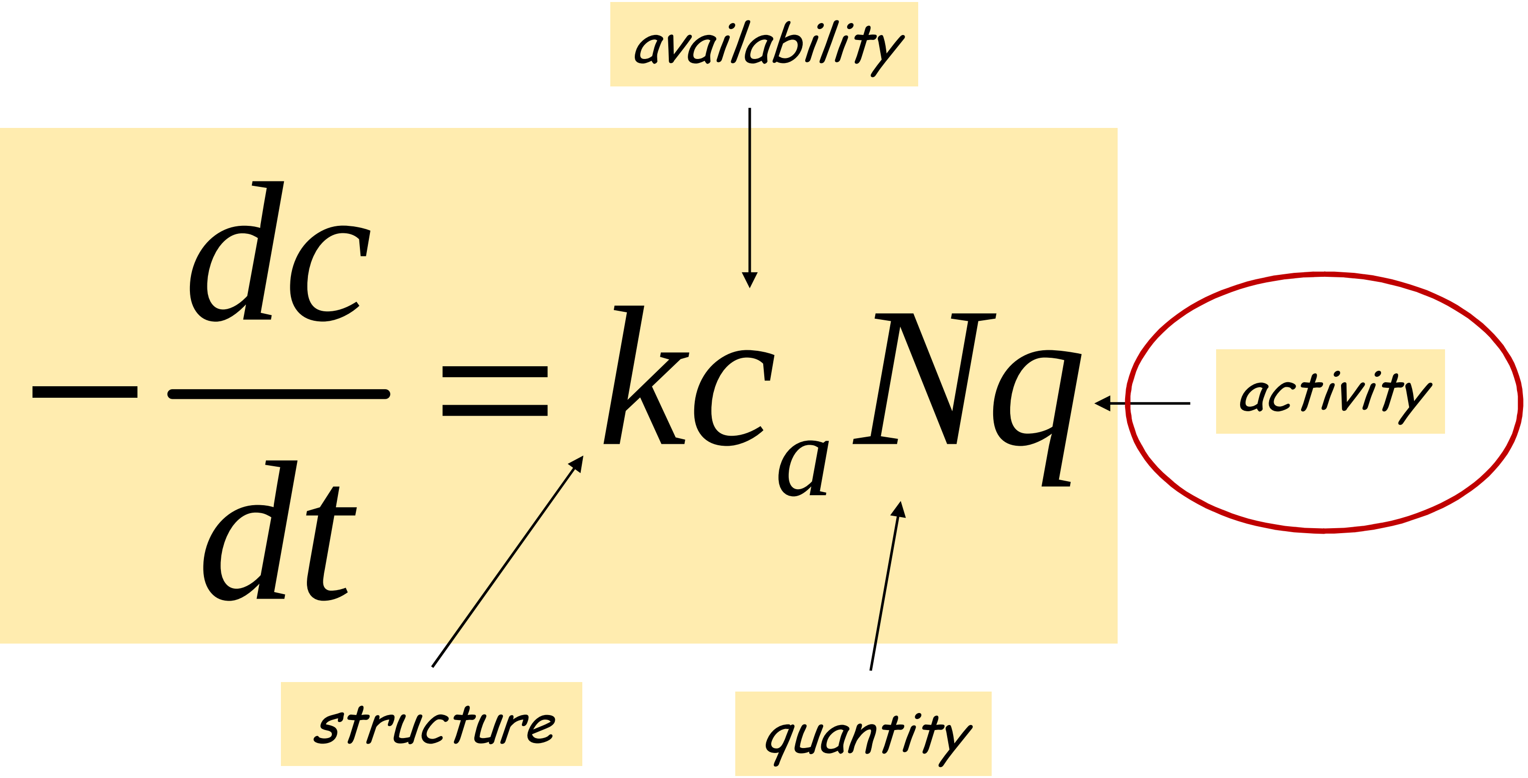
Growth

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

Degradation

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

Major Variables Determining Microbial Metabolism of Pesticides in Soils



availability

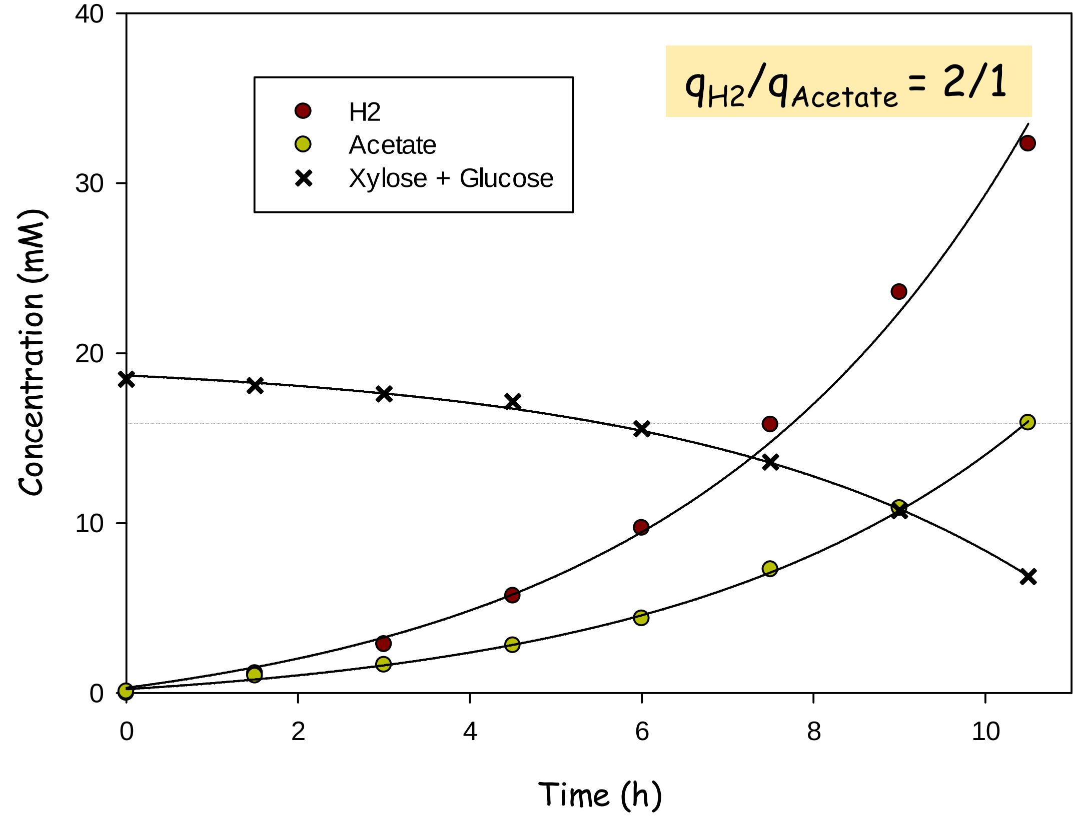
$$-\frac{dc}{dt} = k c_a N q$$

activity

structure

quantity

Growth-linked Product Formation



$q_{H2}/q_{Acetate} = 2/1$

Growth-linked product formation

$$\frac{dp}{dt} = qN$$

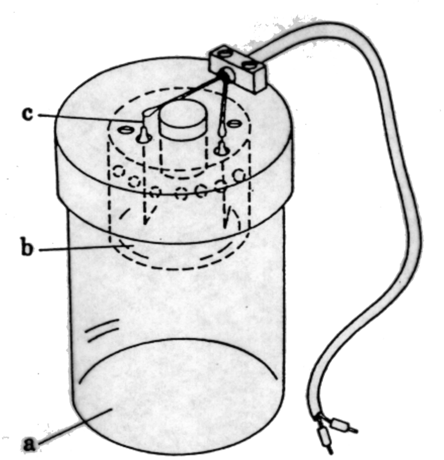
$$\frac{dp}{dt} = qN_0 e^{\mu t}$$

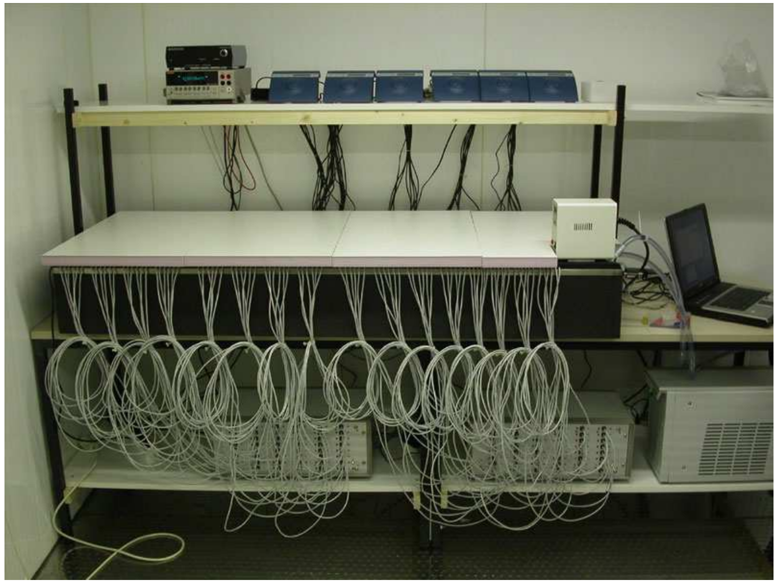
$$p = p_0 + \left(\frac{qN_0}{\mu}\right)(e^{\mu t} - 1)$$

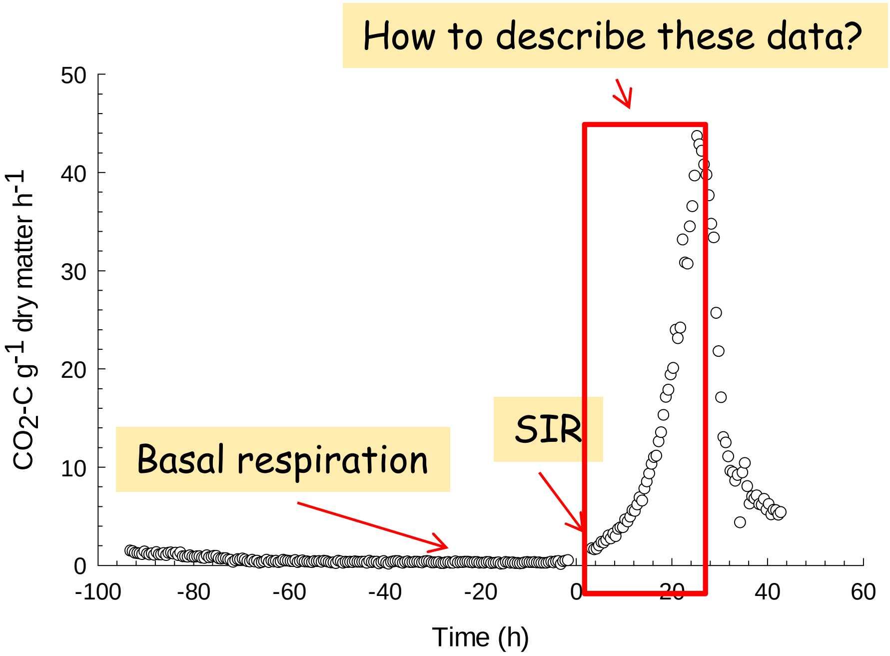
Acetate and H_2-formation from growth of *Caldicellulosiruptor saccharolyticus* on a xylose-glucose mixture

van de Werken *et al.*, 2008

Substrate Induced Respiration





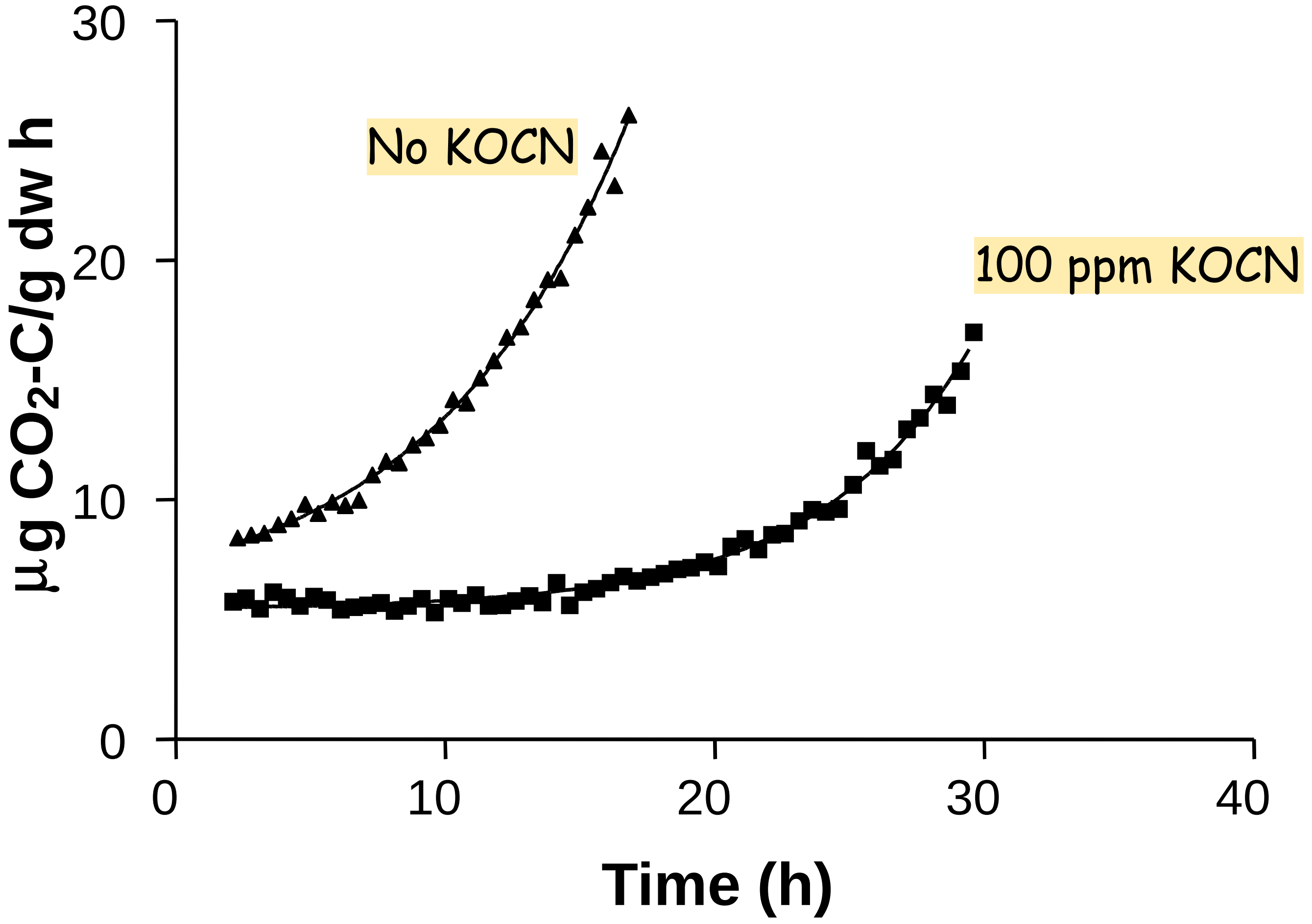


How to describe these data?

SIR

Basal respiration

Effect Of Cyanate On SIR



Kinetics of Substrate Induced Respiration (SIR)

When glucose is mixed into soil, the active microorganisms start to grow exponentially, while the dormant ones only increase their respiration rate

$$\frac{dp}{dt} = qN$$

Active

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

$$\frac{dp}{dt} = qN_0 e^{\mu t} = r e^{\mu t}$$

$$p = p_0 + \frac{r}{\mu}(e^{\mu t} - 1)$$

Dormant

$$N = N_0$$

$$\frac{dp}{dt} = qN_0 = K$$

$$p = p_0 + Kt$$

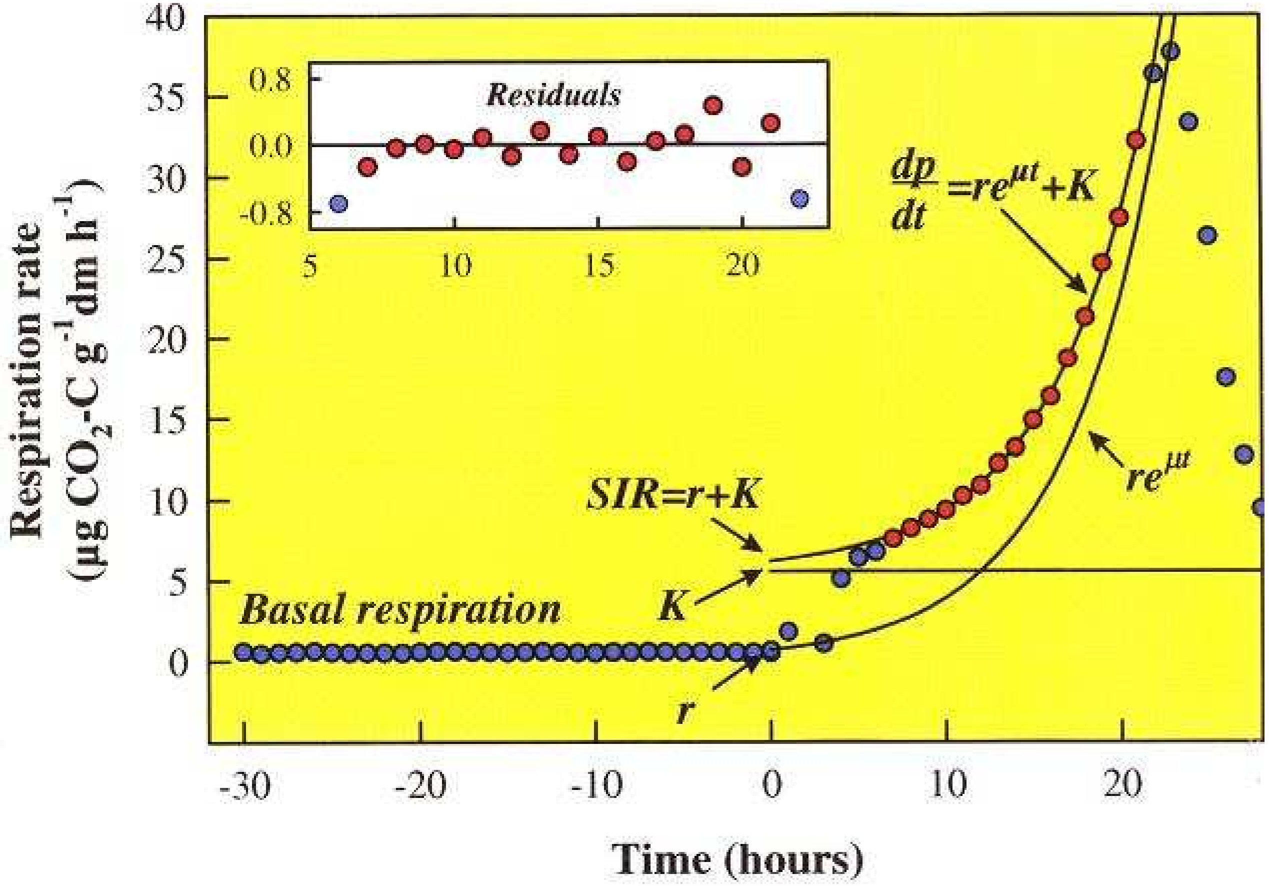
Active + Dormant

$$\frac{dp}{dt} = r e^{\mu t} + K$$

$$p = p_0 + \frac{r}{\mu}(e^{\mu t} - 1) + Kt$$

SIR = dp/dt when t = 0 → SIR = r + K

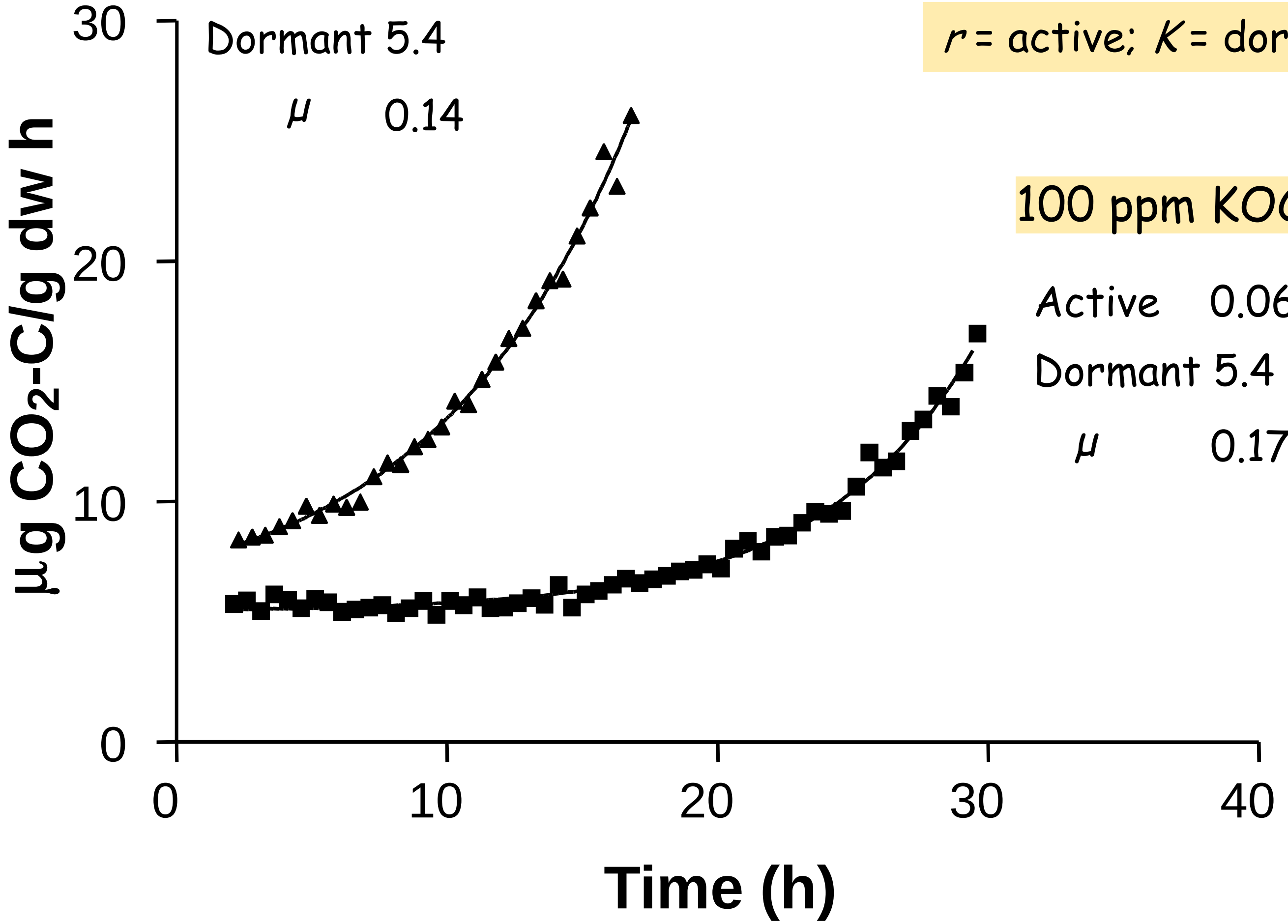
Kinetics of Substrate Induced Respiration (SIR)



Effect of Cyanate On The Active/Dormant-Distribution

$$p = p_0 + \frac{r}{\mu}(e^{\mu t} - 1) + Kt$$

r = active; K = dormant



No KOCN

Active 2.0

Dormant 5.4

μ 0.14

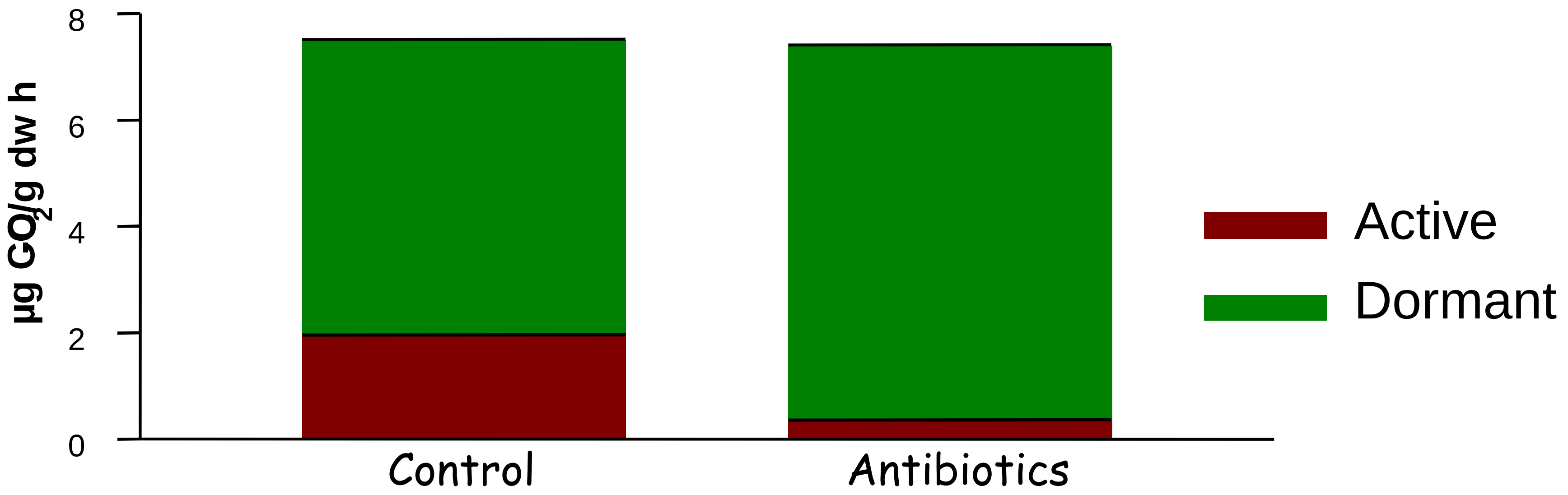
100 ppm KOCN

Active 0.06

Dormant 5.4

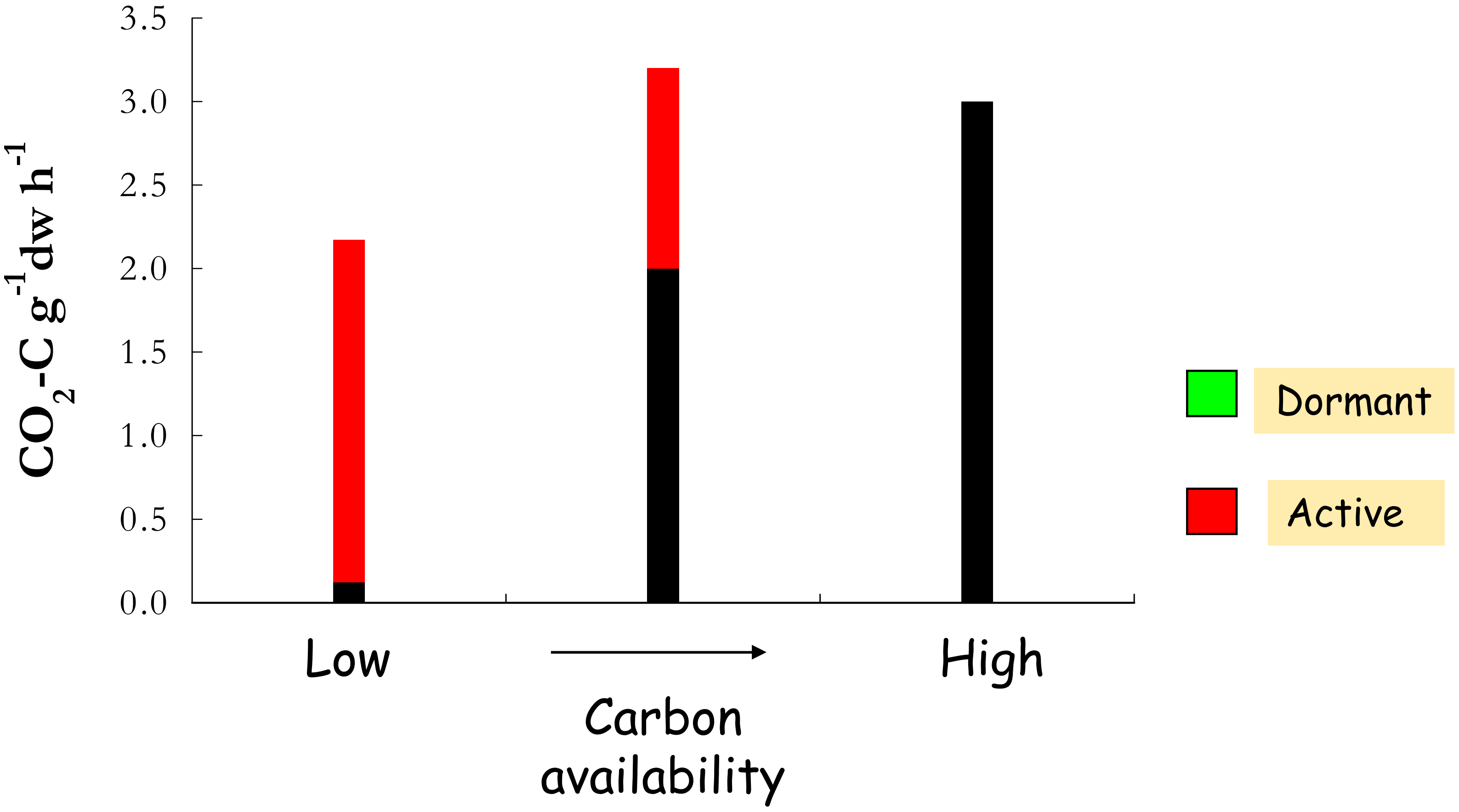
μ 0.17

Effect Of Cycloheximide And Streptomycin On The Active/Dormant-Distribution



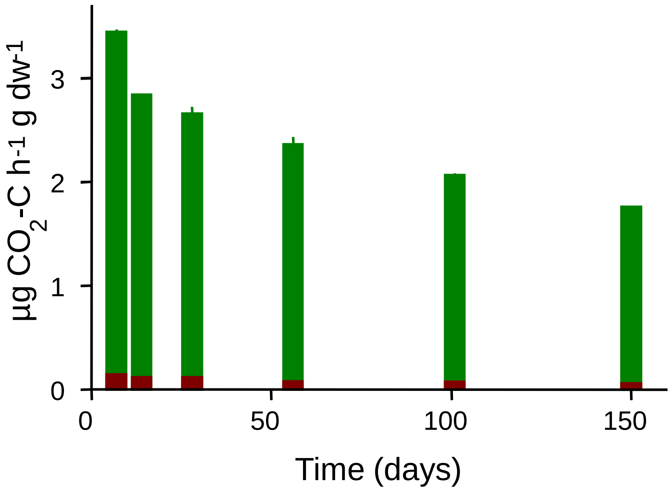
The antibiotics force the microorganisms into a non-growing state without affecting the size of the biomass

Is The Distribution Between Active And Dormant Microorganisms Determined By Carbon Availability?



Effect Of Lucerne And Straw Additions On The Distribution Between Active And Dormant Microorganisms

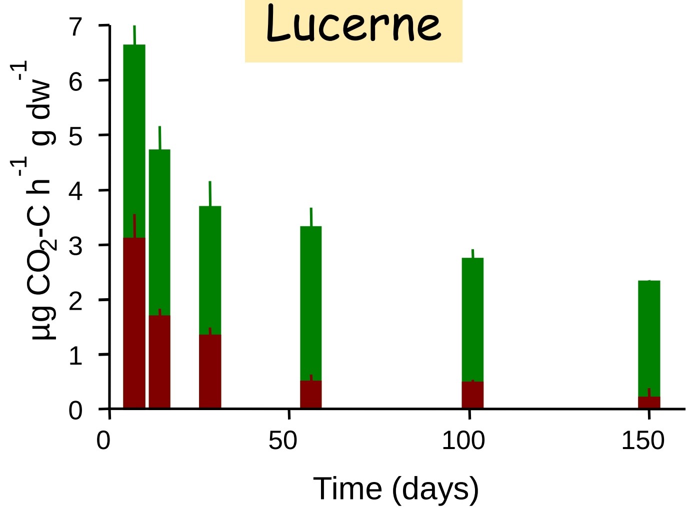
Control



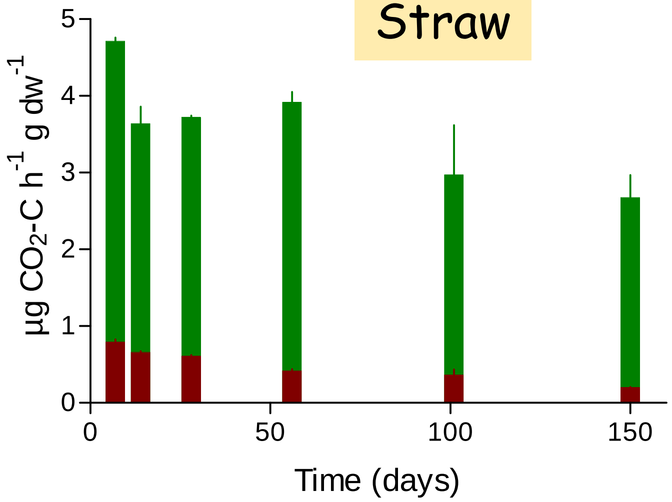
🟥 Active

🟩 Dormant

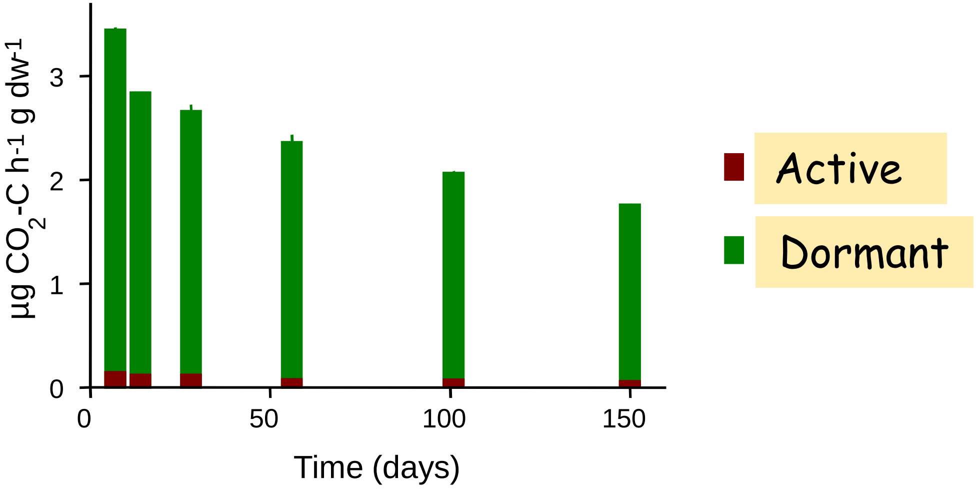
Lucerne



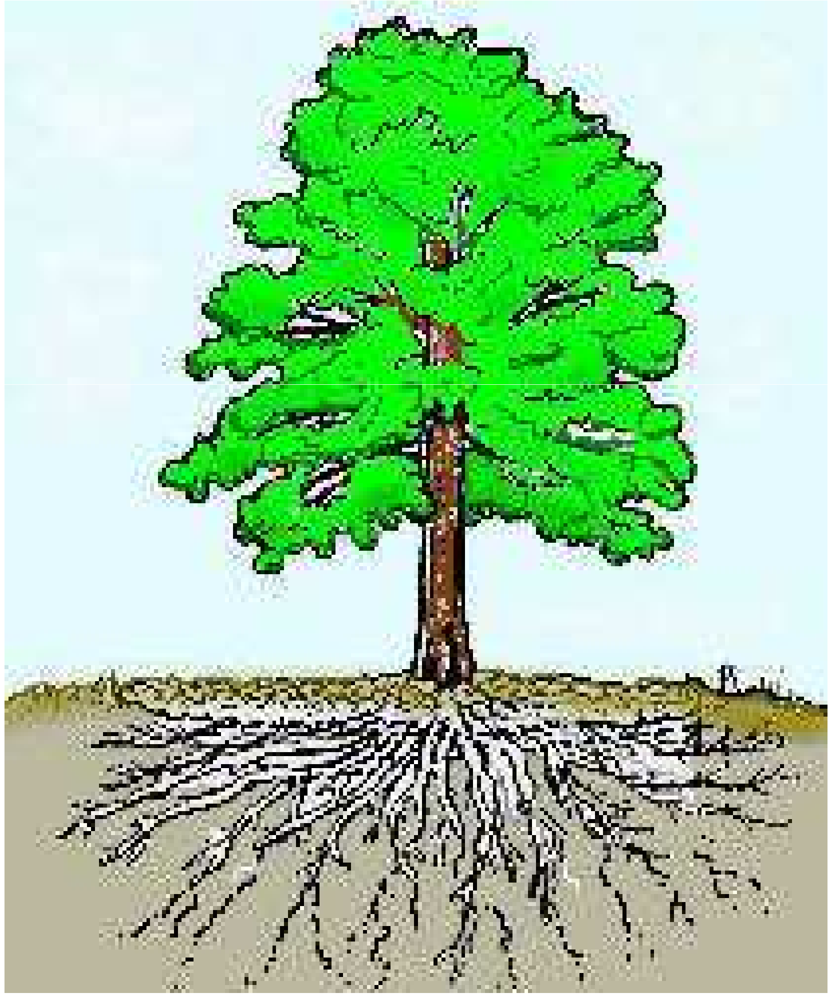
Straw



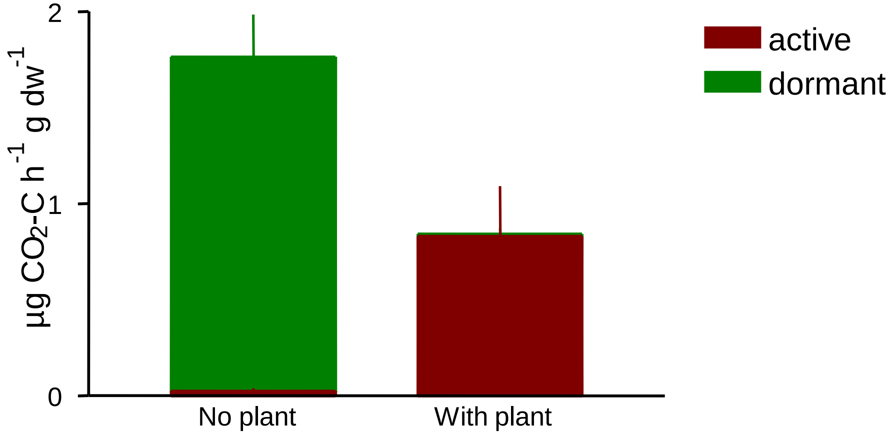
Incubations Without Addition Of Carbon Source Give Dying Soils



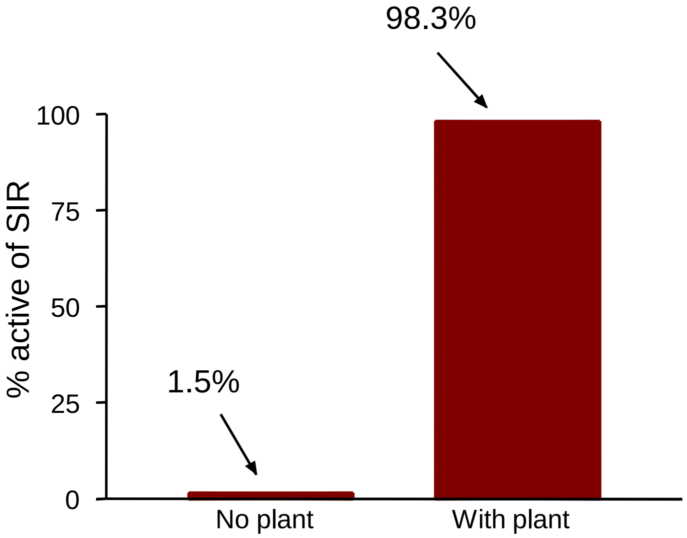
The Rhizosphere Activates Microorganisms



Distribution between active and dormant microorganisms



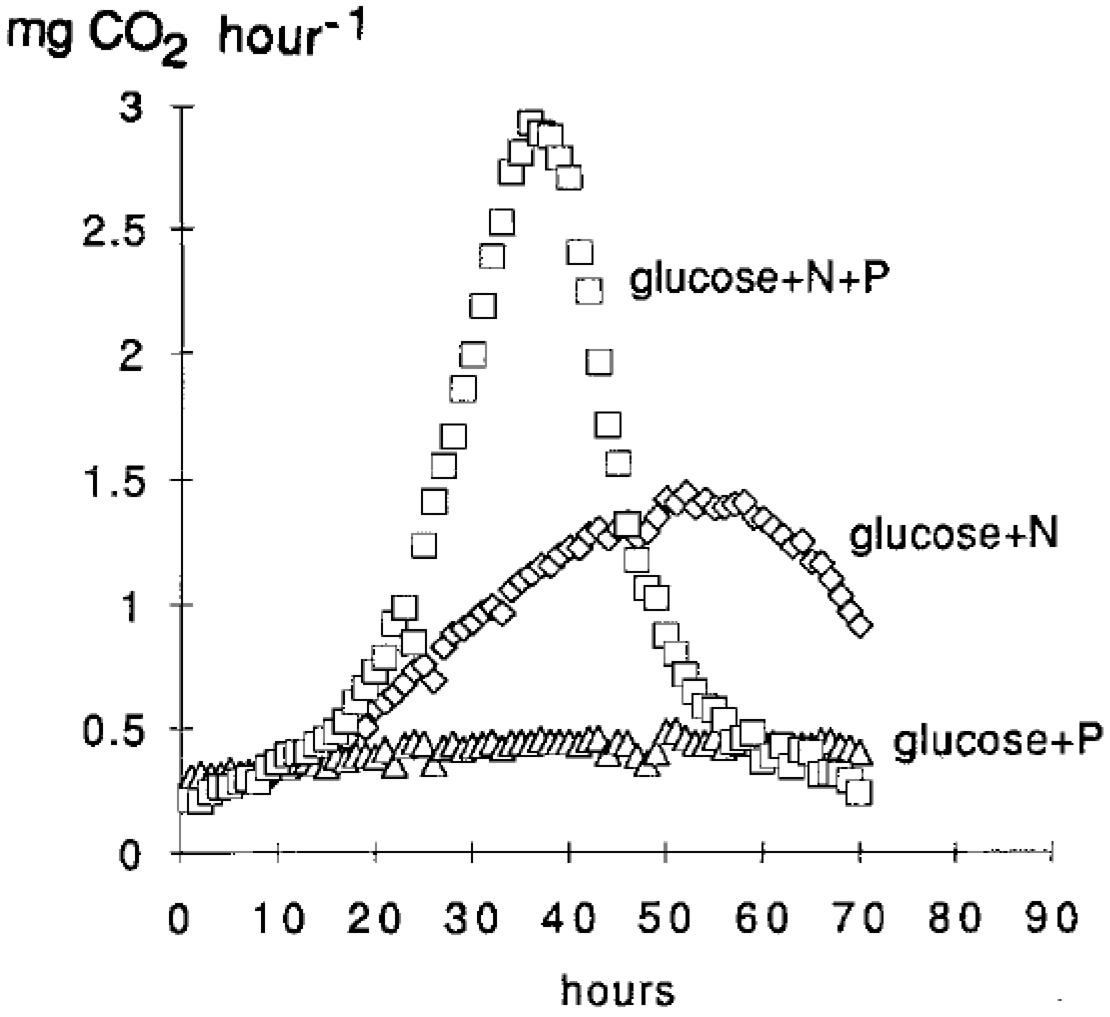
Relative amount of active microorganisms



Several studies show enhanced pesticide degradation in the rhizosphere

Limiting Nutrients For Growth

Respiration measurements can also be used to find which nutrients are growth-limiting



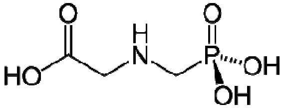
Nordgren, 1992

Summary OF Some Useful Equations

First-order degradation	Exponential growth	Growth-linked degradation	Growth-linked product formation	Zero-order product formation	SIR
$-\frac{dc}{dt}=kc$	$\frac{dN}{dt}=\mu N$	$-\frac{dc}{dt}=qN$	$\frac{dp}{dt}=qN$	$\frac{dp}{dt}=K$	$\frac{dp}{dt}=qN+K$
		$-\frac{dc}{dt}=qN_0e^{\mu t}$	$\frac{dp}{dt}=qN_0e^{\mu t}$		$\frac{dp}{dt}=qN_0e^{\mu t}+K$
$c=c_0e^{-kt}$	$N=N_0e^{\mu t}$	$c=c_0-(\frac{qN_0}{\mu})(e^{\mu t}-1)$	$p=p_0+(\frac{qN_0}{\mu})(e^{\mu t}-1)$	$p=p_0+Kt$	$p=p_0+(\frac{qN_0}{\mu})(e^{\mu t}-1)+Kt$

Just One More Equation …

Glyphosate

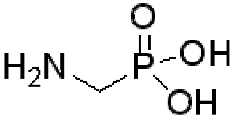


- Cometabolic degradation

(not used as substrate but as P-source)

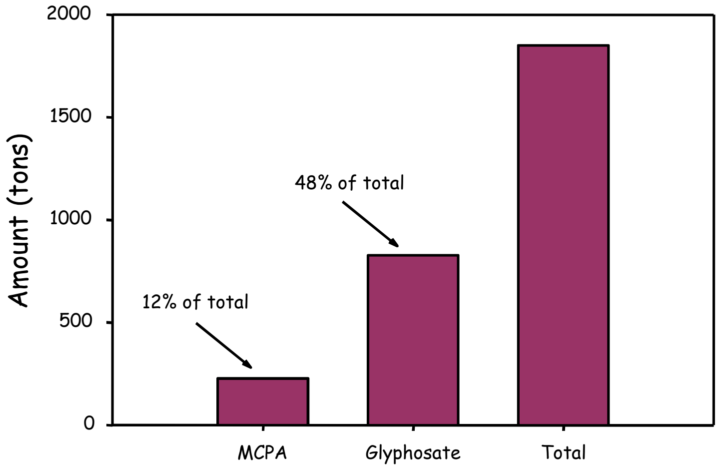
- 50% degraded in 4-180 days

AMPA



- Generally considered to be more persistent than glyphosate
- Footprint database: AMPA classified as persistent with a typical $t_{1/2}$ of 151 days, compared to 12 days for glyphosate

Used Amounts of Pesticides in Sweden 2008



Formation And Degradation Of A Metabolite

Glyphosate degradation

$$\frac{dc_G}{dt} = -kc_G$$

$$c_G = c_{G0}e^{-kt}$$

$$k = k_1 + k_3$$

AMPA formation and degradation

$$\frac{dc_A}{dt} = 0.66k_1c_G - k_2c_A$$

$$\frac{\text{Mw AMPA}}{\text{Mw Glyphosate}} = 0.66$$

Fraction AMPA formed

$$\frac{k_1}{k_1 + k_3} = \frac{k_1}{k}$$

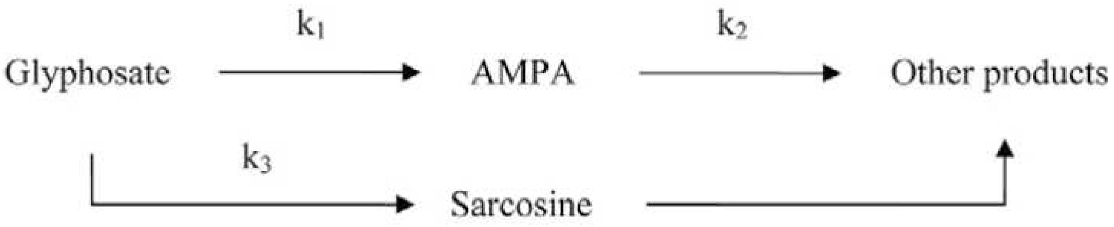
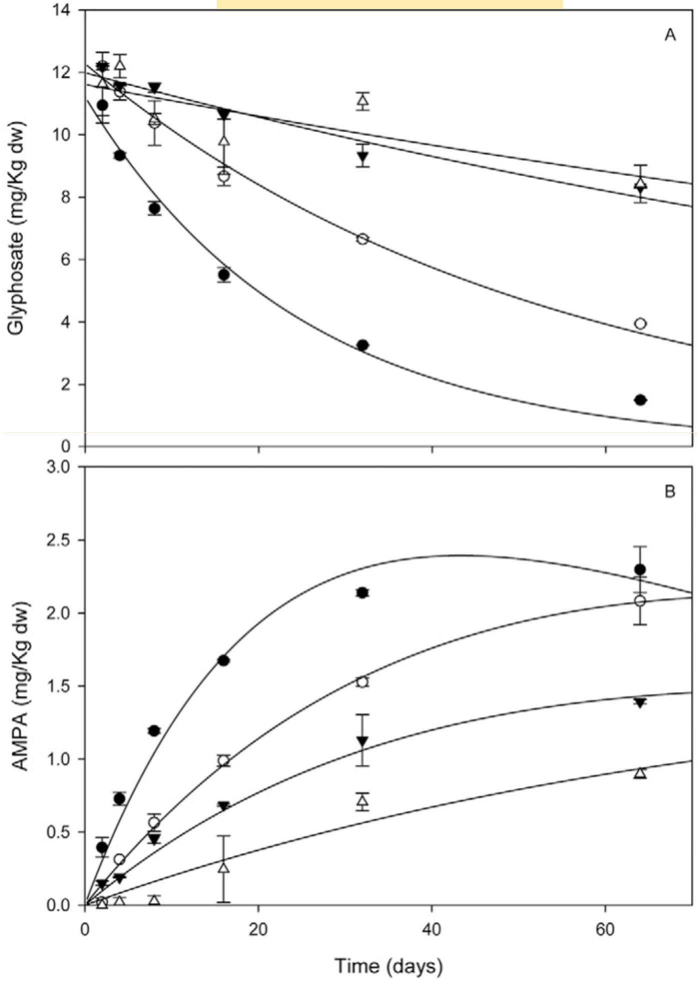


Fig. 1. Branched reaction scheme with the first-order rate coefficients k_1 and k_3 for the degradation of glyphosate to aminomethylphosphonic acid (AMPA) and sarcosine, respectively, and k_2 for the degradation of AMPA

$$c_A = \frac{0.66k_1c_{G0}}{k_2 - k}(e^{-kt} - e^{-k_2t})$$

Quantifying Glyphosate And AMPA Concentration Data In Soil

$$c_G(t) = c_{G0} e^{-k t}$$



$$c_A = \frac{0.66 k_1 c_{G0}}{k_2 - k}\left(e^{-kt} - e^{-k_2 t}\right)$$

Soil	Glyphosate	AMPA	Fraction AMPA formed
	$t_{1/2}$ (days)		k_1/k
Sand topsoil	17	60	0.53
Sand subsoil	37	91	0.48
Clay topsoil	110	35	1
Clay subsoil	151	98	0.61

Correlation Between $t_{1/2}$ For Glyphosate And K_f, And $t_{1/2}$ For AMPA And % Organic Matter