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Mechanistic modelling of micropollutant co-metabolism in WWTPs

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Preserving & Enhancing the Global Water Environment

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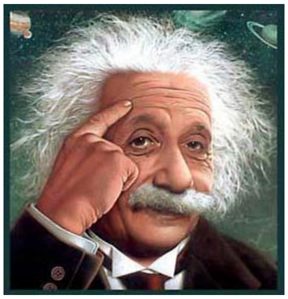
Introduction

Co-metabolism

- A process in which microorganisms, while growing at the expense of one substrate, have the capacity to transform other compounds without deriving any direct benefit from the metabolism (Venkataramani and Ahlert, 1985).

Introduction

Theory of co-metabolism

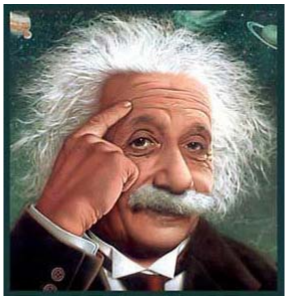


- Biodegradability less likely structure ≠ natural products;
- Microorganisms: metabolic potential to break down various SOCs;

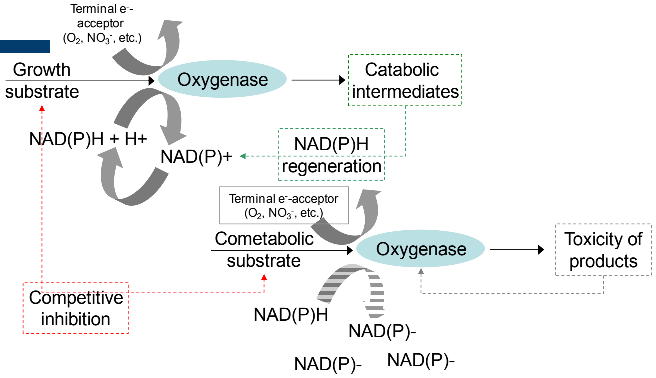
Introduction

Theory of co-metabolism

- Enzymes don’t have perfect substrate specificity;
- Xenobiotics w/ structural similarities = analogous biotransformation pathways.



Introduction



Co-metabolism depends on:

- Energy generation and regeneration of reductive forces (NAD(P)H);
- Type of electron acceptor (e.g., oxygen, nitrate)
- Growth substrate (competitive inhibition, preference → energy balance)

Evolution of co-metabolism models

Criddle (1993)

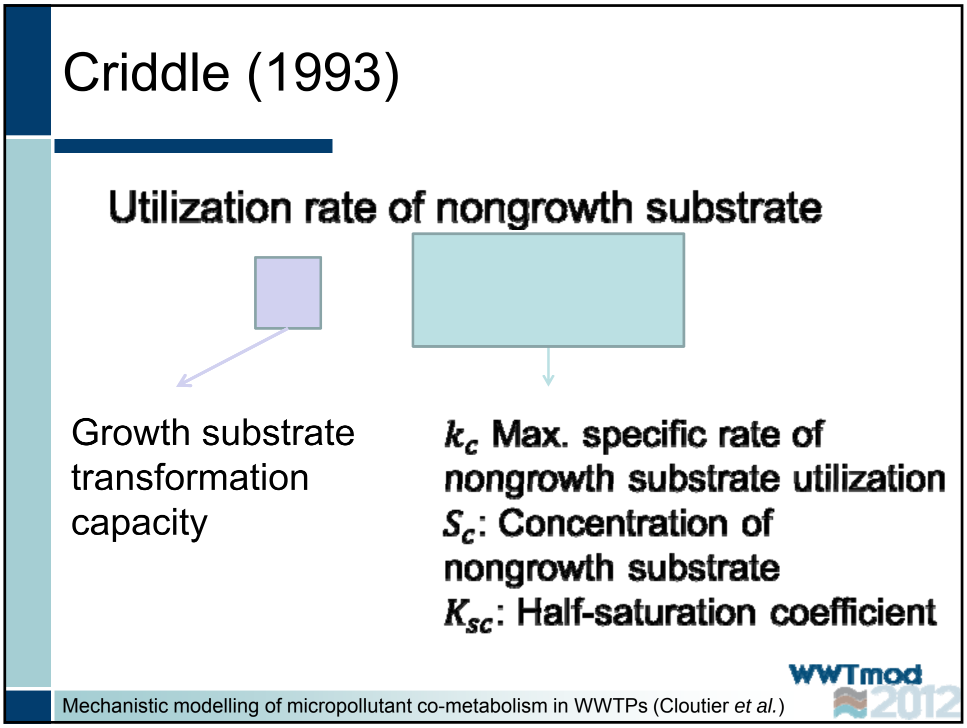
- Older models = Resting cells only
- Includes the effects:
  - On growing and non-growing cells
  - Of endogenous cell decay
  - Of product toxicity
  - Of competitive inhibition

Criddle (1993)

Utilization rate of growth substrate

Maximum specific rate of utilization of growth substrate

S_g: Concentration of growth substrate
K_{sg}: Half-saturation coefficient



Criddle (1993)

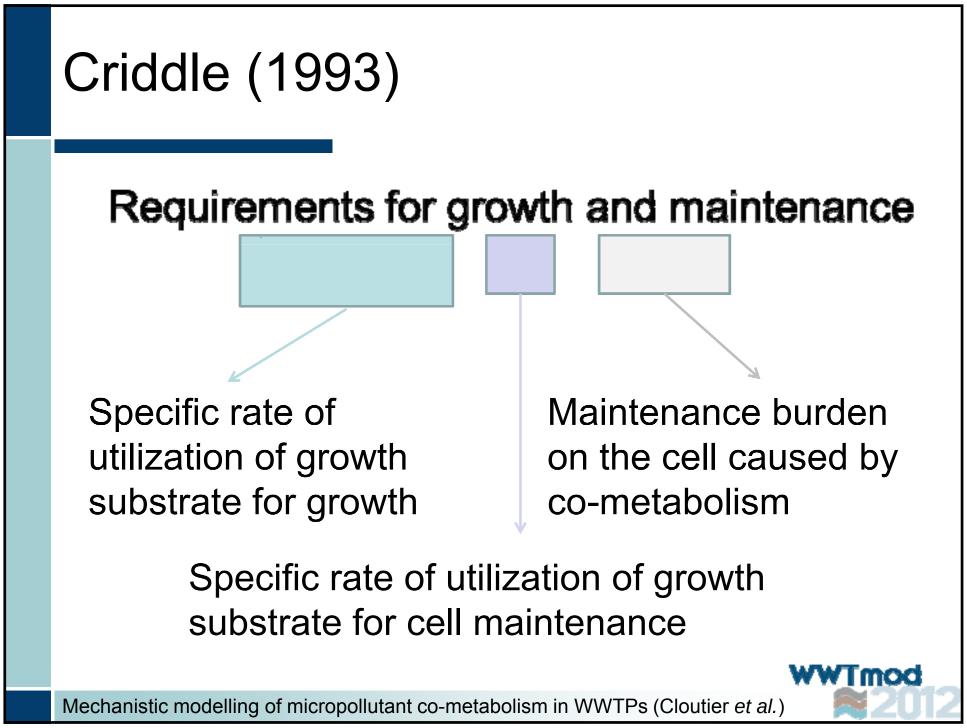
Utilization rate of nongrowth substrate

Growth substrate transformation capacity

k_c Max. specific rate of nongrowth substrate utilization

S_c: Concentration of nongrowth substrate

K_{sc}: Half-saturation coefficient



Criddle (1993)

Requirements for growth and maintenance

Specific rate of utilization of growth substrate for growth

Maintenance burden on the cell caused by co-metabolism

Specific rate of utilization of growth substrate for cell maintenance

Criddle (1993)

Requirements for growth and maintenance

Mass of nongrowth substrate transformed by a unit of mass of cells (absence of endogenous decay)

Maximum growth yield

Criddle (1993)

Requirements for growth and maintenance

μ: specific growth rate

b: endogenous decay constant

Criddle (1993)

Co-metabolism model

Evolution of co-metabolism models

Chang and Alvarez-Cohen (1995)

- Extension of the Criddle (1993) model
- Reducing energy limitation:
  - Cell growth and decay
  - Product toxicity
  - Competitive inhibition

Chang and Alvarez-Cohen (1995)

Co-metabolic substrate degradation rate

$$\frac{\partial S_c}{\partial t} = -k_c\left(\frac{R}{K_R + R}\right)\left(\frac{S_c}{K_{Sc}\left(1 + {}^{S_g}/_{K_{Sg}}\right) + S_c}\right)X$$

R: reducing energy (NAD(P)H)
K_R: half-saturation constant of reducing energy

Competitive inhibition term

Evolution of co-metabolism models

Plósz et al. (2010)

- Dynamic model for xenobiotics
- Co-metabolic processes
  - Co-metabolic biodegradation
  - Competitive inhibition
- Model also describes
  - Sorption / desorption
  - Parent compound formation

Plósz et al. (2010)

Co-metabolic substrate degradation rate

$$\frac{\partial C_{LI}}{\partial t} = -\overbrace{k_{Bio} \cdot C_{LI} \cdot X_{SS}}^{\text{Pseudo-first order term}} \cdot \boxed{f(S_S)} \cdot \boxed{f(C_{O\_2})}$$

Impacts of growth substrate

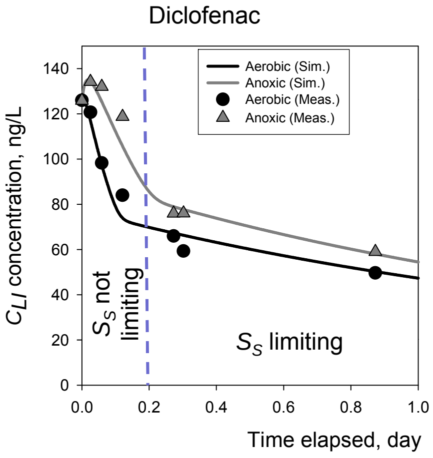
e.g., for antibiotics $\frac{K_S \cdot \eta}{K_S \cdot \eta + S_S}$

Aerobic and anoxic biotransformation rates

$\frac{S_O}{K_O + S_O}$ or $\frac{K_O}{K_O + S_O}$

Plósz et al. (2010)

Growth substrate can enhance the biotransformation of nongrowth substrate



Evolution of co-metabolism models

Delgadillo-Mirquez et al. (2011)

- Dynamic model for the PAHs fate
- Anaerobic condition
- Four compartment system
  - Availability of each compartment for biodegradation
- Does not include competitive inhibition and product toxicity

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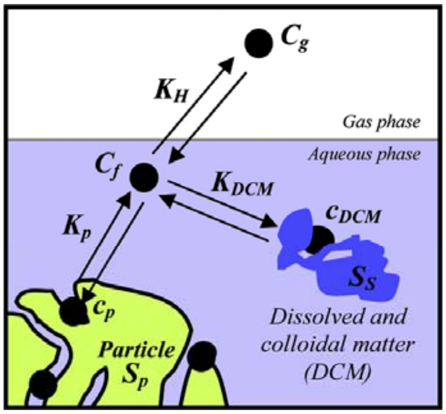
Delgadillo-Mirquez et al. (2011)

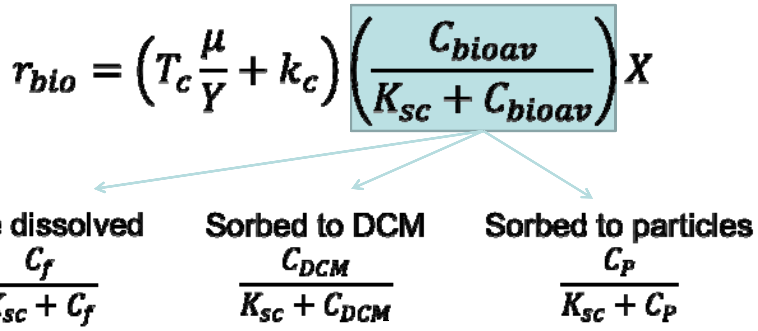
Four compartment system



Delgadillo-Mirquez et al. (2011)

Process rate for co-metabolic degradation

- Analogous equation to Criddle (1993)



$$r_{bio} = \left(T_c \frac{\mu}{Y} + k_c\right) \boxed{\left(\frac{C_{bioav}}{K_{sc} + C_{bioav}}\right)} X$$

Free dissolved

$$\frac{C_f}{K_{sc} + C_f}$$

Sorbed to DCM

$$\frac{C_{DCM}}{K_{sc} + C_{DCM}}$$

Sorbed to particles

$$\frac{C_P}{K_{sc} + C_P}$$

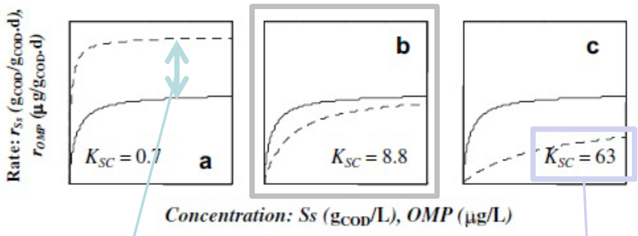
Delgadillo-Mirquez et al. (2011)

Three hypothesis for bioavailability

a) Only the free dissolved compartment
b) Free dissolved + sorbed to DCM
c) All three compartments

Calibration performed with exper. data

Delgadillo-Mirquez et al. (2011)



Degradation rate faster for PAH than for S_S

$K_{SC} >> C_f$, implies that free compartment degradation < particle compartment degradation

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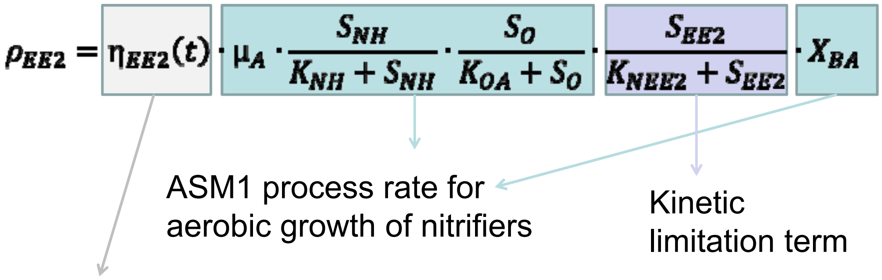
Evolution of co-metabolism models

Clouzot et al. (2011)

- Dynamic model for the fate of EE2
- Batch experiment – unadapted biomass
- Considers co-metabolism by growing nitrifiers (+ sorption/desorption)
- Does not include competitive inhibition and product toxicity

Clouzot et al. (2011)

Process rate for co-metabolic degradation



$$\rho_{EE2} = \boxed{\eta_{EE2}(t)}\cdot\boxed{\mu_A\cdot\frac{S_{NH}}{K_{NH}+S_{NH}}\cdot\frac{S_O}{K_{OA}+S_O}}\cdot\boxed{\frac{S_{EE2}}{K_{NEE2}+S_{EE2}}}\cdot\boxed{X_{BA}}$$

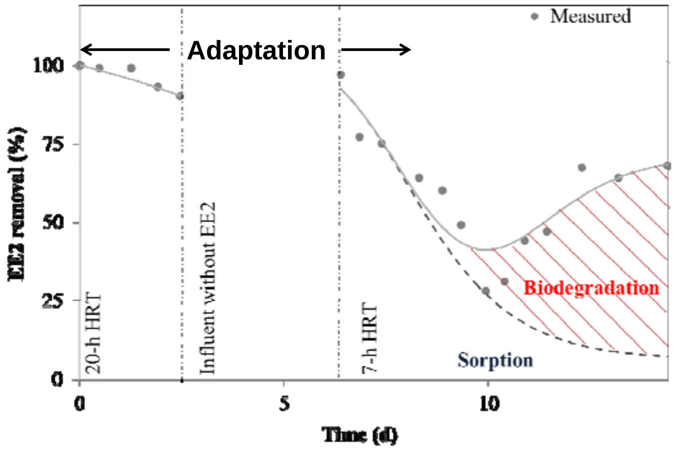
ASM1 process rate for
aerobic growth of nitrifiers

Kinetic
limitation term

Verhulst-type
logistic function
(adaptation)

$$\frac{d\eta_{EE2}}{dt} = k_{ACC}\cdot\eta_{EE2}\cdot\left(1-\frac{\eta_{EE2}}{\eta_{EE2,max}}\right)$$

Clouzot et al. (2011)



Conclusion

- Several kinetic models for co-metabolism
  - Developed in the 80’s and 90’s
  - Most of them didn’t consider growing cells
  - Criddle model (and extensions) is a reference
- Application to wastewater treatment
  - Competitive inhibition often neglected
  - Some compounds are only degraded by nitrifiers
  - Effects of growth substrate concentration?
  - What MPs are degraded by co-metabolism?
  - Standardization of co-metabolism models?