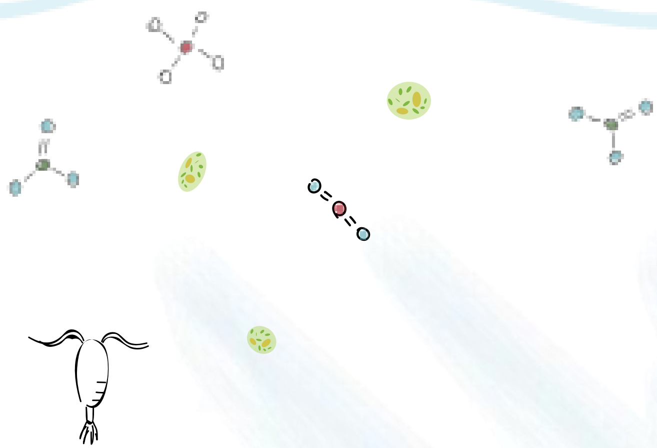


Reactive Transport in the Hydrosphere

Department of Earth Sciences, Faculty of Geosciences, Utrecht University

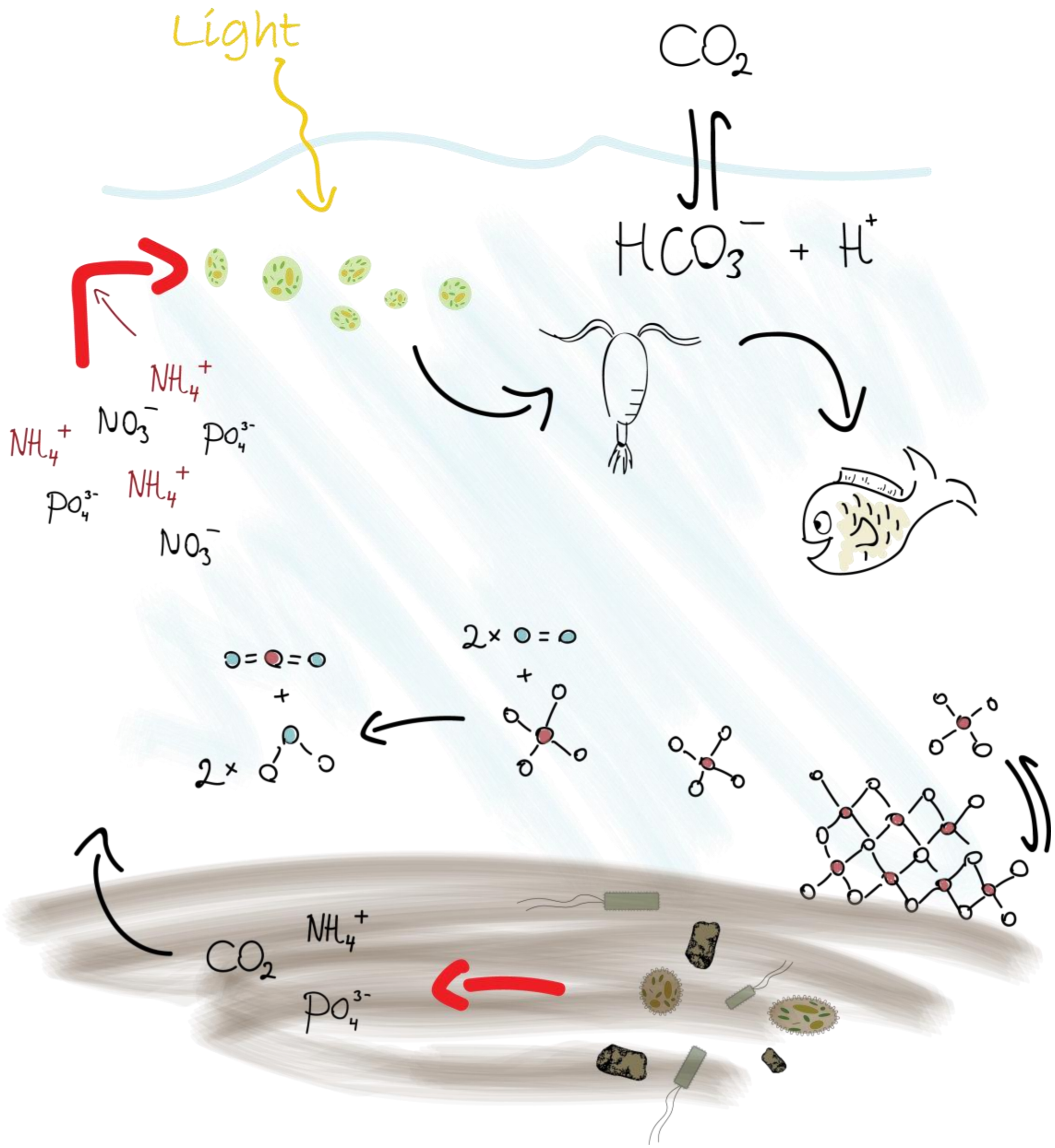
Lecturers: Lubos Polerecky and Karline Soetaert

Illustrations, narration and video editing: Renee Hageman
Additional contributions: Dries Bonte, University Ghent
Audio effects: mixkit.co

Universiteit Utrecht

GHENT UNIVERSITY

Rate laws for . . .



Chemical reactions

- Irreversible
- Reversible
- Enzyme-catalyzed (**metabolic**)
    - Substrate limitation
    - Substrate inhibition
    - Rate saturation

Large-scale models

Partitioning between phases

- Mineral dissolution / precipitation
- Gas exchange

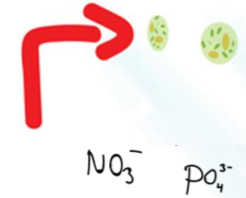
Ecological interactions

- Grazing, predator-prey type

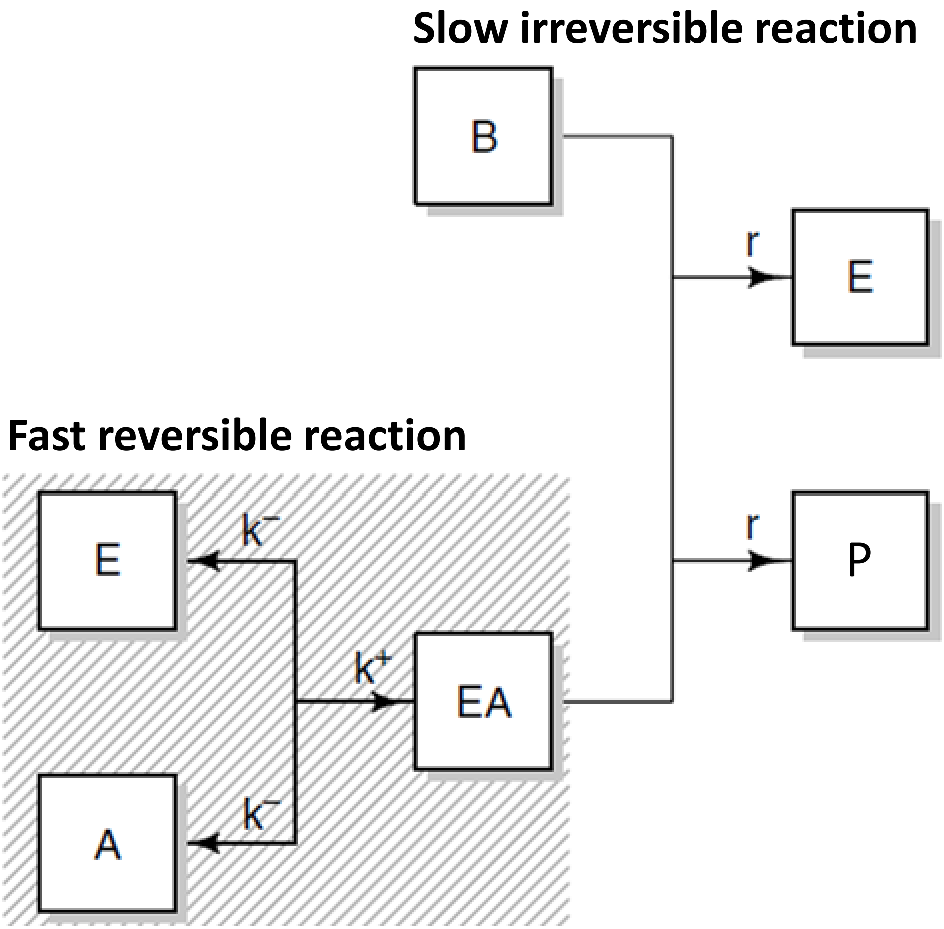
Transport

- processes **mediated** by **living creatures, catalyzed by enzymes**

Application to **metabolic reactions**



Reaction scheme for an **enzyme-catalyzed reaction:**



Fast reversible reaction

$$A + E \underset{k^-}{\overset{k^+}{\rightleftharpoons}} EA$$

Slow irreversible reaction

$$EA + B \xrightarrow{r} P + E$$

Overall reaction

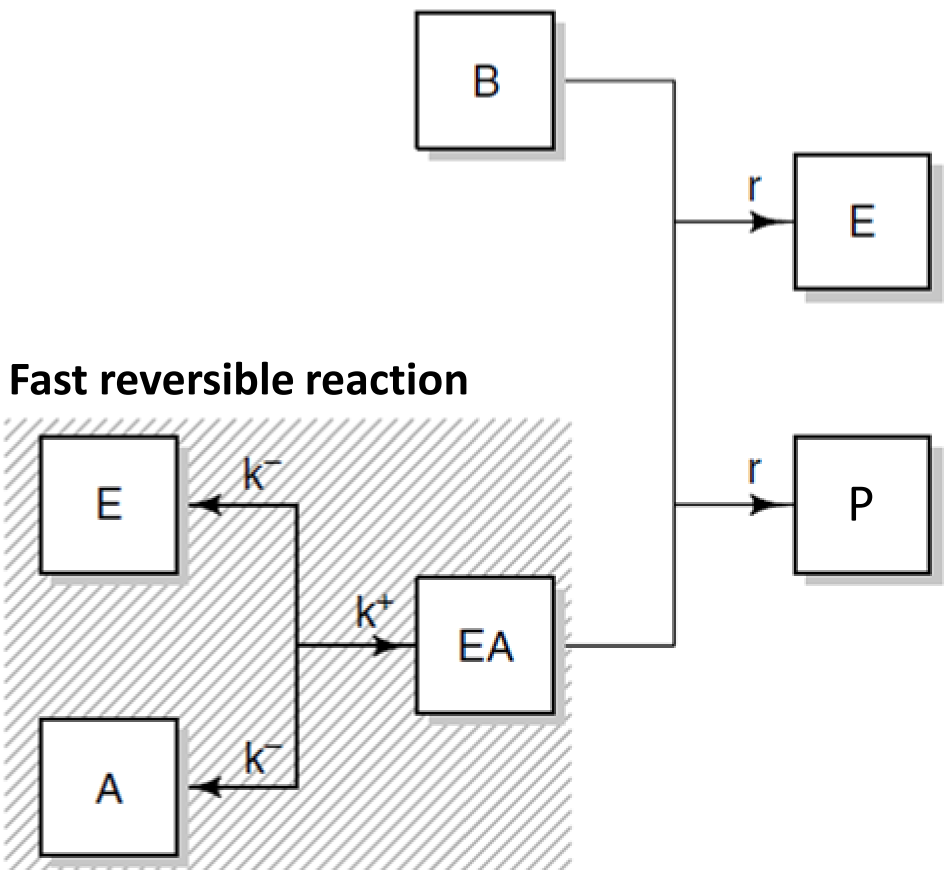
$$A + B \xrightarrow{r_f} P$$

$$\boxed{r_f = ???}$$

Application to **metabolic reactions**

Reaction scheme for an **enzyme-catalyzed reaction:**

Slow irreversible reaction



Fast reversible reaction

$$A + E \underset{k^-}{\overset{k^+}{\rightleftharpoons}} EA$$

Slow irreversible reaction

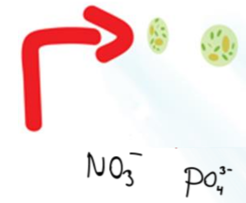
$$EA + B \xrightarrow{r} P + E$$

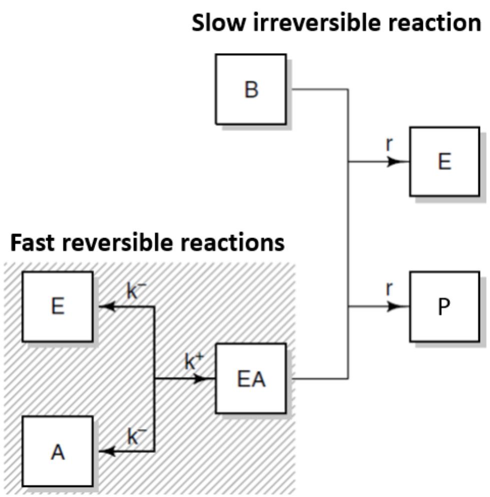
Overall reaction

$$A + B \xrightarrow{r_f} P$$

$$\boxed{r_f = ???}$$

Application to **metabolic reactions**





$$\frac{d[\mathrm{A}]}{dt} = -k^+ \cdot [\mathrm{A}] \cdot [\mathrm{E}] + k^- \cdot [\mathrm{EA}]$$
$$\frac{d[\mathrm{B}]}{dt} = -r \cdot [\mathrm{B}] \cdot [\mathrm{EA}]$$
$$\frac{d[\mathrm{P}]}{dt} = r \cdot [\mathrm{B}] \cdot [\mathrm{EA}]$$
$$\frac{d[\mathrm{E}]}{dt} = r \cdot [\mathrm{B}] \cdot [\mathrm{EA}] - k^+ \cdot [\mathrm{A}] \cdot [\mathrm{E}] + k^- \cdot [\mathrm{EA}]$$
$$\frac{d[\mathrm{EA}]}{dt} = -r \cdot [\mathrm{EA}] \cdot [\mathrm{B}] + k^+ \cdot [\mathrm{A}] \cdot [\mathrm{E}] - k^- \cdot [\mathrm{EA}]$$

Details in the Textbook, p. 261

$$A + B \xrightarrow{\mathrm{r_f}} P$$

Michaelis-Menten (Monod) kinetics

Mass balance equations:

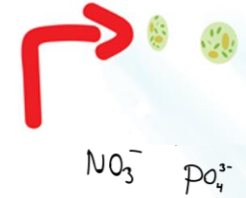
$$\frac{dP}{dt} = -\frac{dA}{dt} = -\frac{dB}{dt} = r_f \boxed{\frac{[A]}{[A] + K_A}} [\mathrm{B}]$$

(unit: s^{-1})

$$r_f = r[E_{tot}] = r\boxed{([E] + [EA])}$$ Total enzyme concentration

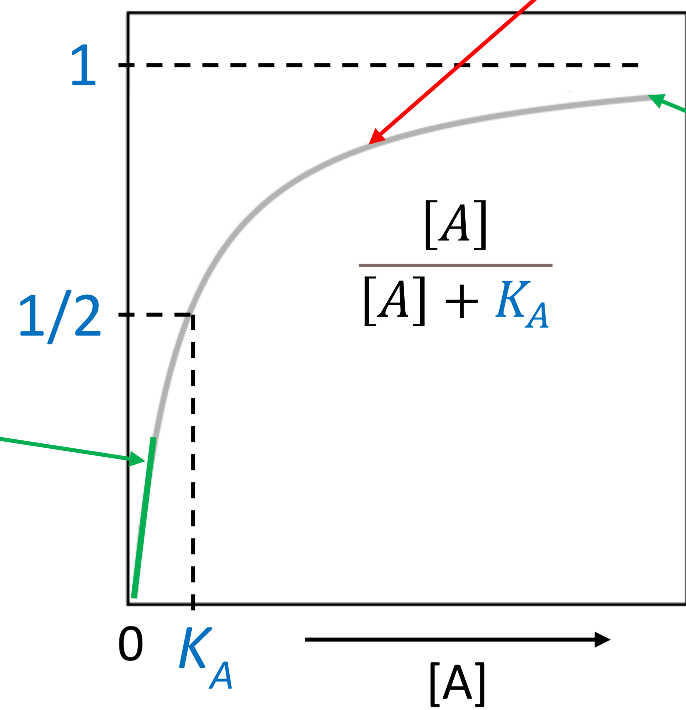
$K_A = k^- / k^+$ Enzyme **affinity** to **(rate-limiting) substrate A** (unit: mol m^{-3})

Michaelis-Menten kinetics



$$A + B \xrightarrow{r_f} P$$

$$\frac{dP}{dt} = -\frac{dA}{dt} = -\frac{dB}{dt} = r_f \boxed{\frac{[A]}{[A] + K_A}} [B]$$



$[A] \ll K_A$

$$\frac{[A]}{[A]+K_A} \approx \frac{[A]}{K_A}$$

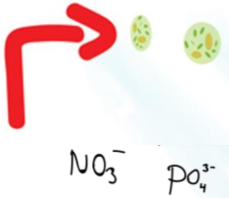
First-order kinetics with respect to A.

$[A] \gg K_A$

$$\frac{[A]}{[A]+K_A} \approx 1$$

Rate is **saturated** with respect to A.

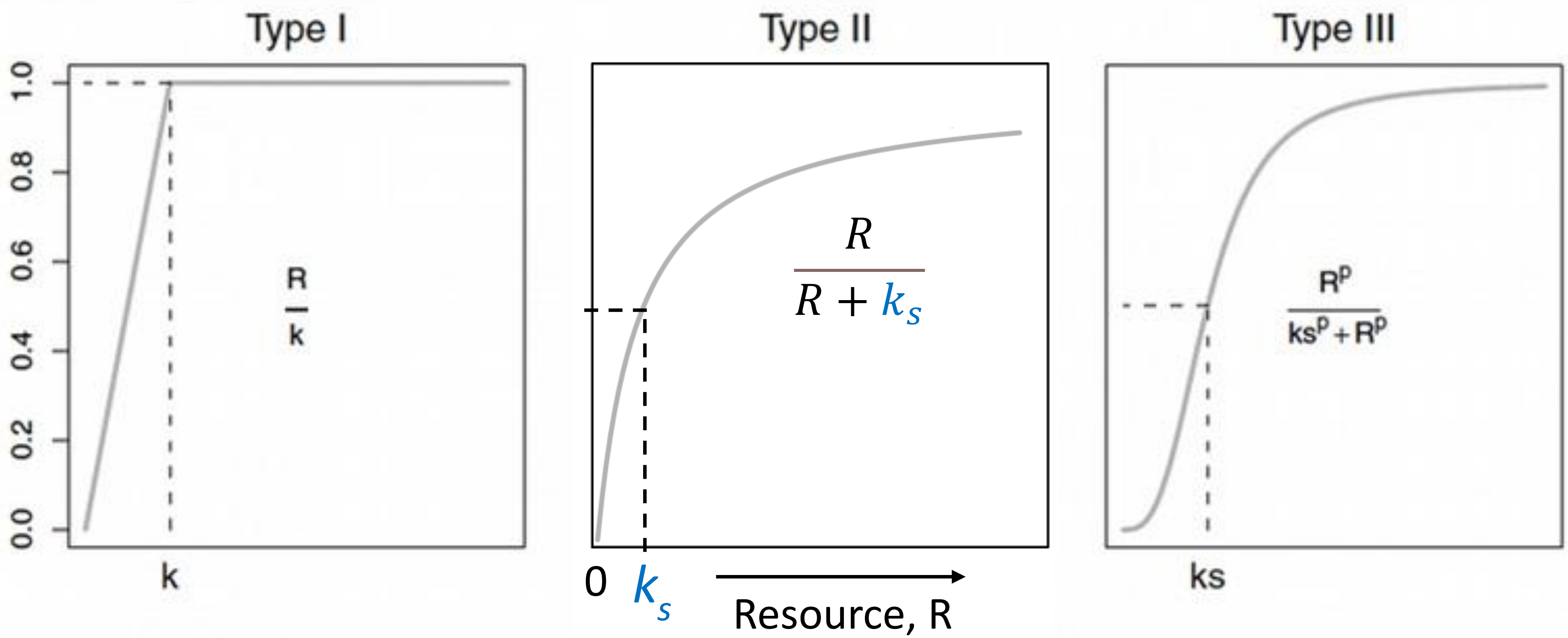
Other forms of metabolic reaction kinetics



Linear up until A=k

Michaelis-Menten

Sigmoidal



Application to organic matter mineralization

Aerobic

$$(CH_2O)(NH_3)_x(H_3PO_4)_y + O_2 \xrightarrow{r_a} CO_2 + x\,NH_3 + y\,H_3PO_4 + H_2O$$

$$\frac{d[C_{org}]}{dt} = -r_a \cdot \boxed{\frac{[O_2]}{[O_2] + K_{O2}}} \cdot [C_{org}]$$

Michaelis-Menten kinetics (O_2)

Application to organic matter mineralization

Aerobic

$$(CH_2O)(NH_3)_x(H_3PO_4)_y + O_2 \xrightarrow{r_a} CO_2 + x\,NH_3 + y\,H_3PO_4 + H_2O$$

$$\frac{d[C_{org}]}{dt} = -r_a \cdot \frac{[O_2]}{[O_2] + K_{O2}} \cdot [C_{org}]$$

via Denitrification

$$(CH_2O)(NH_3)_x(H_3PO_4)_y + 4/5\,HNO_3 \xrightarrow{r_n} CO_2 + 2/5\,N_2 + x\,NH_3 + y\,H_3PO_4 + 7/5\,H_2O$$

$$\frac{d[C_{org}]}{dt} = -r_n \boxed{\cdot \frac{[HNO_3]}{[HNO_3] + K_{HNO3}}} \cdot [C_{org}]$$

Michaelis-Menten kinetics (HNO_3)

Application to organic matter mineralization

Aerobic

$$(CH_2O)(NH_3)_x(H_3PO_4)_y + O_2 \xrightarrow{r_a} CO_2 + x\,NH_3 + y\,H_3PO_4 + H_2O$$

$$\frac{d[C_{org}]}{dt} = -r_a \cdot \frac{[O_2]}{[O_2] + K_{O2}} \cdot [C_{org}]$$

via Denitrification

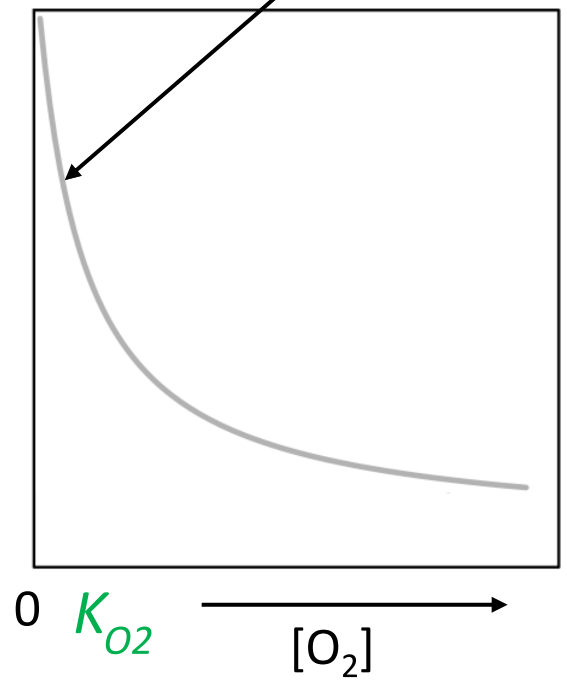
$$(CH_2O)(NH_3)_x(H_3PO_4)_y + 4/5\ HNO_3 \xrightarrow{r_n} CO_2 + 2/5\ N_2 + x\,NH_3 + y\,H_3PO_4 + 7/5\ H_2O$$

$$\frac{d[C_{org}]}{dt} = -r_n \cdot \frac{[HNO_3]}{[HNO_3] + K_{HNO3}} \cdot [C_{org}]$$

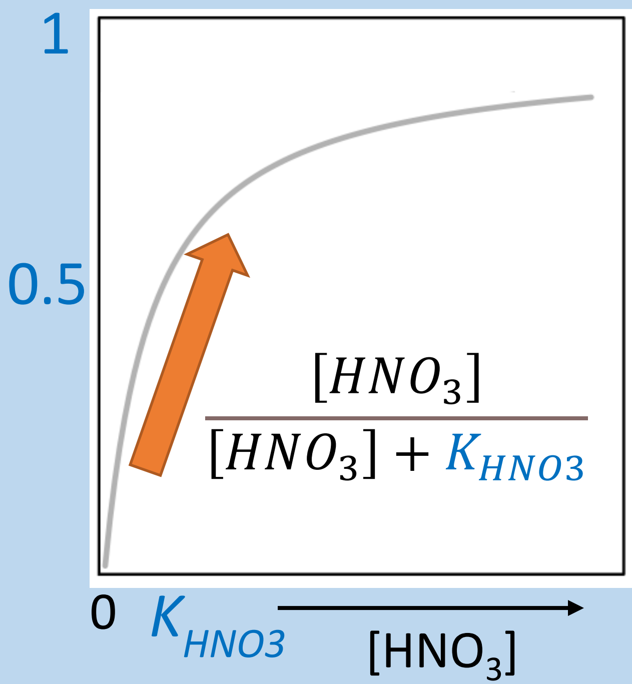
BUT: Aerobic mineralization is **preferred** over denitrification when O_2 is available. How can we **model** this?

Rate inhibition

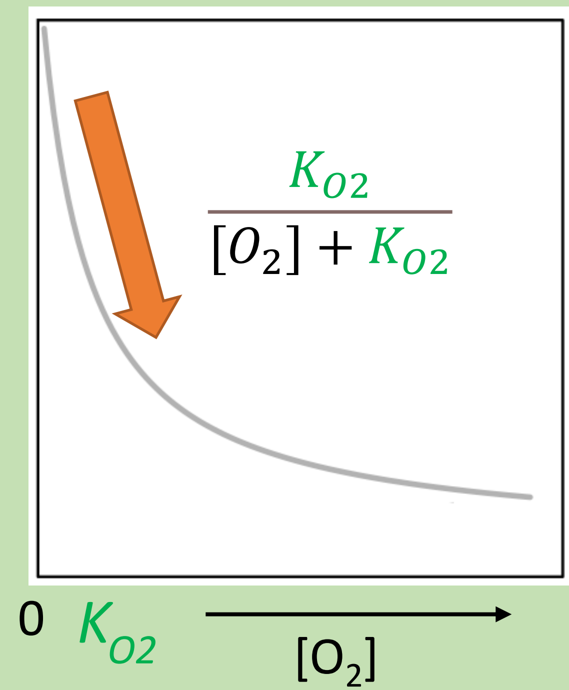
$$1 - \frac{[O_2]}{[O_2] + K_{O2}} = \frac{K_{O2}}{[O_2] + K_{O2}}$$



Rate inhibition



Rate limitation

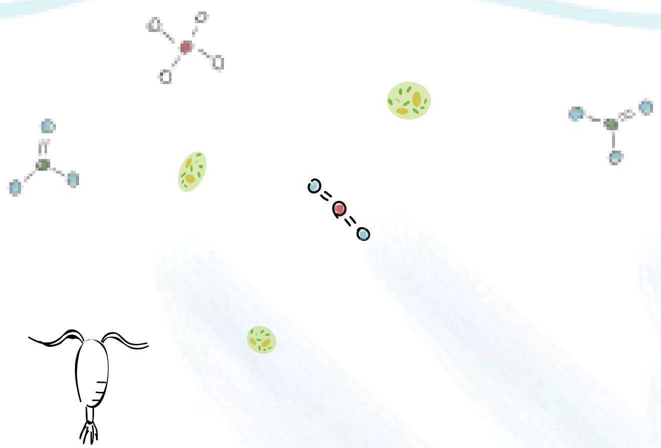


Rate inhibition

$$Denitrification = r_m \cdot \boxed{\frac{[HNO_3]}{[HNO_3] + K_{HNO3}}} \cdot \boxed{\frac{K_{O2}}{[O_2] + K_{O2}}} \cdot [C_{org}]$$

Universiteit Utrecht

GHENT UNIVERSITY



Reactive Transport in the Hydrosphere

Department of Earth Sciences, Faculty of Geosciences, Utrecht University

Lecturers: Lubos Polerecky and Karline Soetaert

Illustrations, narration and video editing: Renee Hageman
Additional contributions: Dries Bonte, University Ghent
Audio effects: mixkit.co

Universiteit Utrecht

GHENT UNIVERSITY