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

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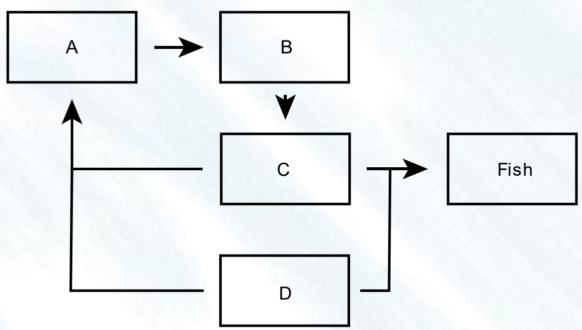
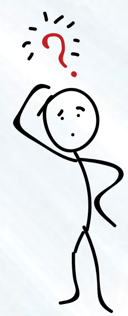
Model formulation

From a conceptual diagram to equations





$$\frac{dA}{dt} = F_{CA} + F_{DA} - F_{AB}$$

$$\frac{dB}{dt} = F_{AB} - F_{BC}$$

$$\frac{dC}{dt} = F_{BC} - F_{C\text{-}Fish} - F_{CA}$$

…

mass/energy balance + consistent regarding units

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Mathematical formulation

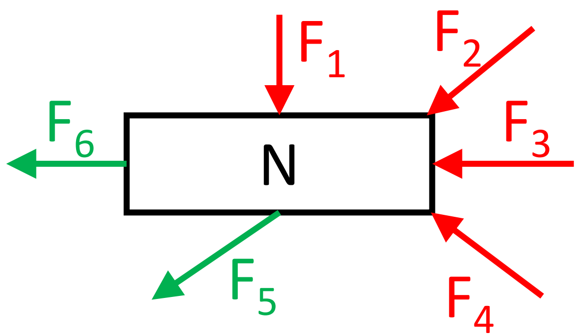
Conservation laws: mass/energy balance equation

One equation for **each state variable!**

$$\frac{d\mathrm{StateVariable}}{dt} = Flux_{in} - Flux_{out}$$

Rate of change

Example:

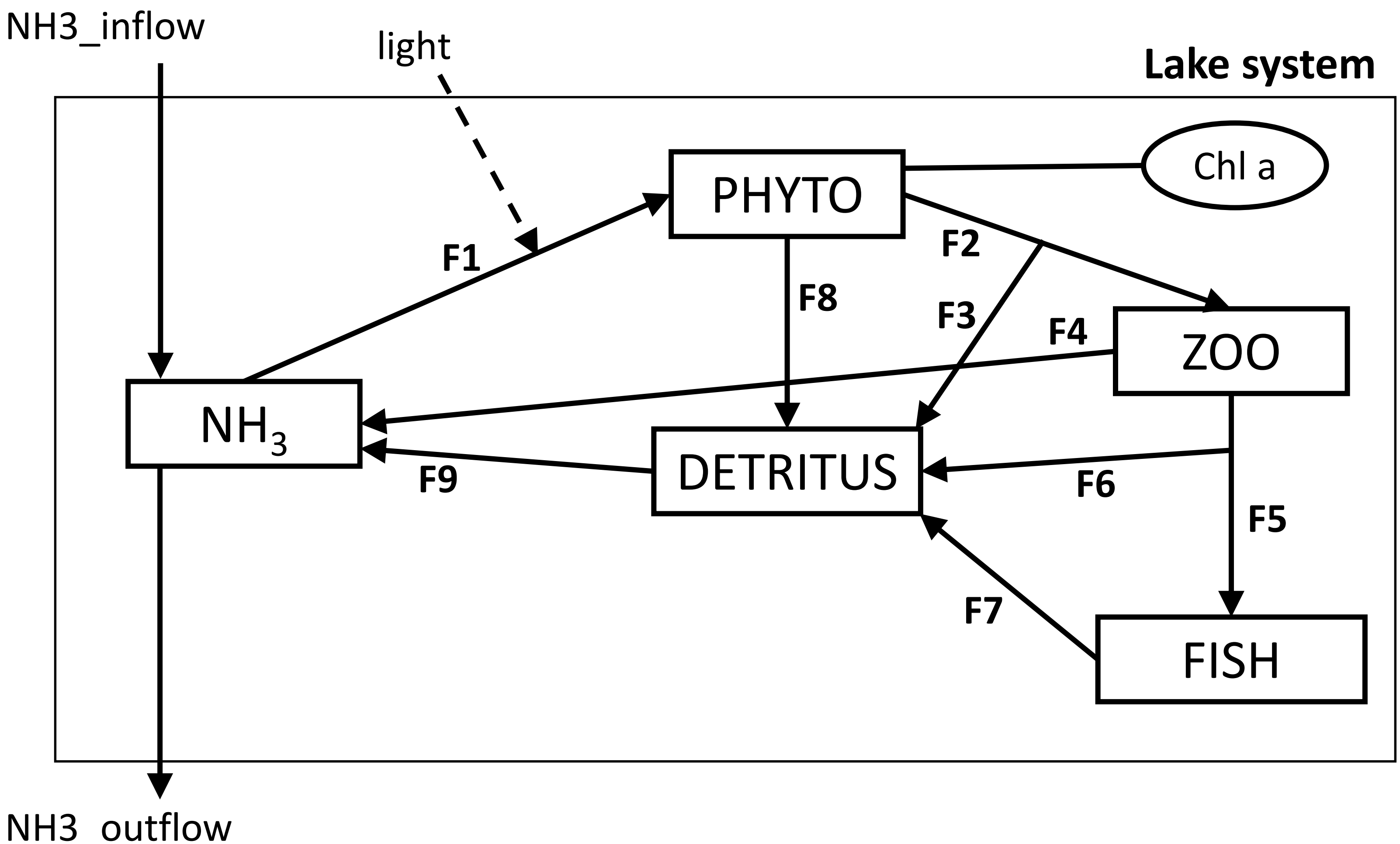


Concentration of N (**mol N m**$^{-3}$)

$$\underbrace{\frac{d[\mathrm{N}]}{dt}}_{} = F_1 + F_2 + F_3 + F_4 - F_5 - F_6$$

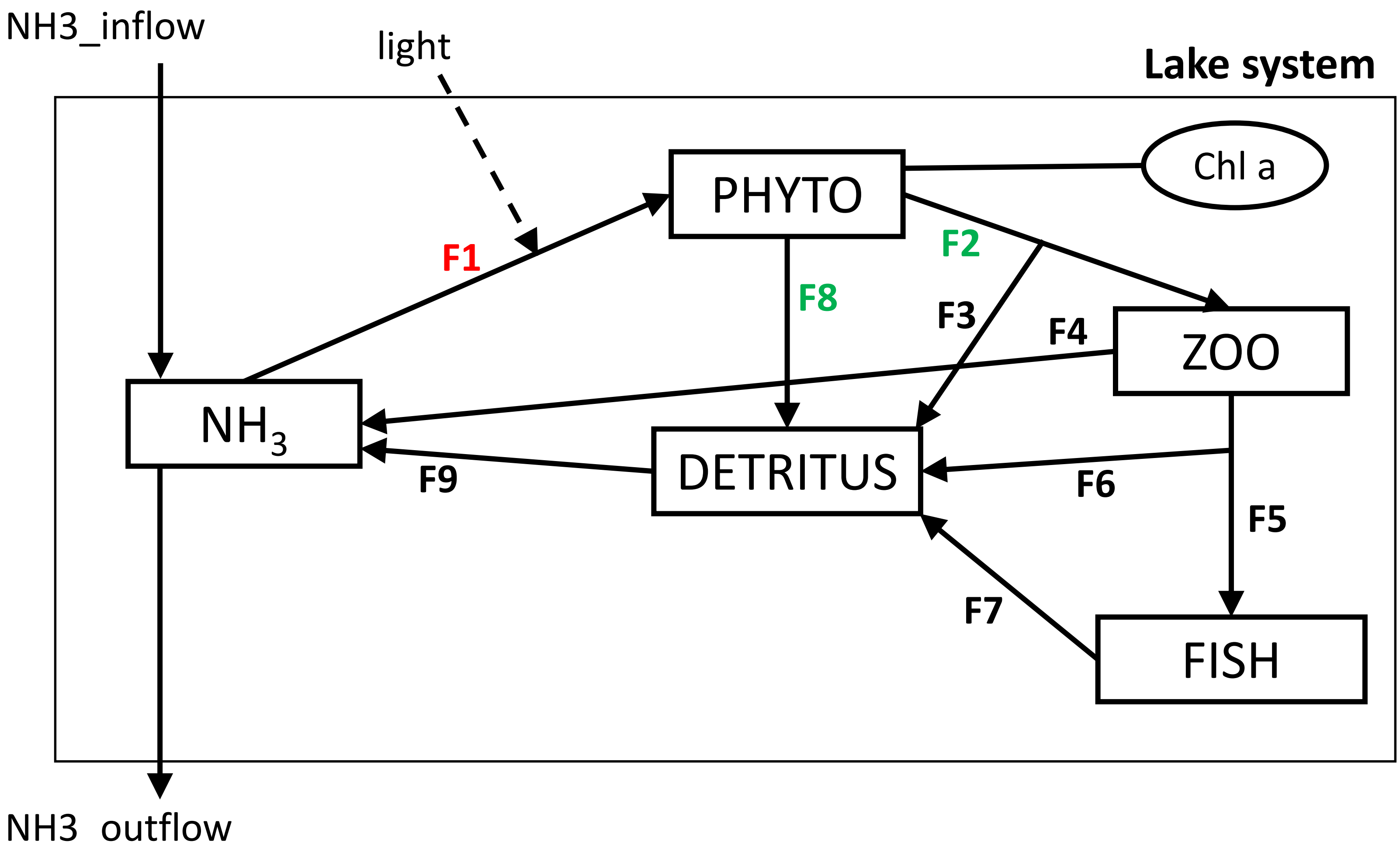
Rate of change of [N] (**mol N m**$^{-3}$ **s**$^{-1}$)

Lake system example



Unit of **each** state variable: **mol N m^{-3}** (mole of N per m^3 of water-column)

Lake system example



$$\frac{d[\mathrm{PHYTO}]}{dt} = {\color{red}F_1} {\color{green}- F_2 - F_8}$$

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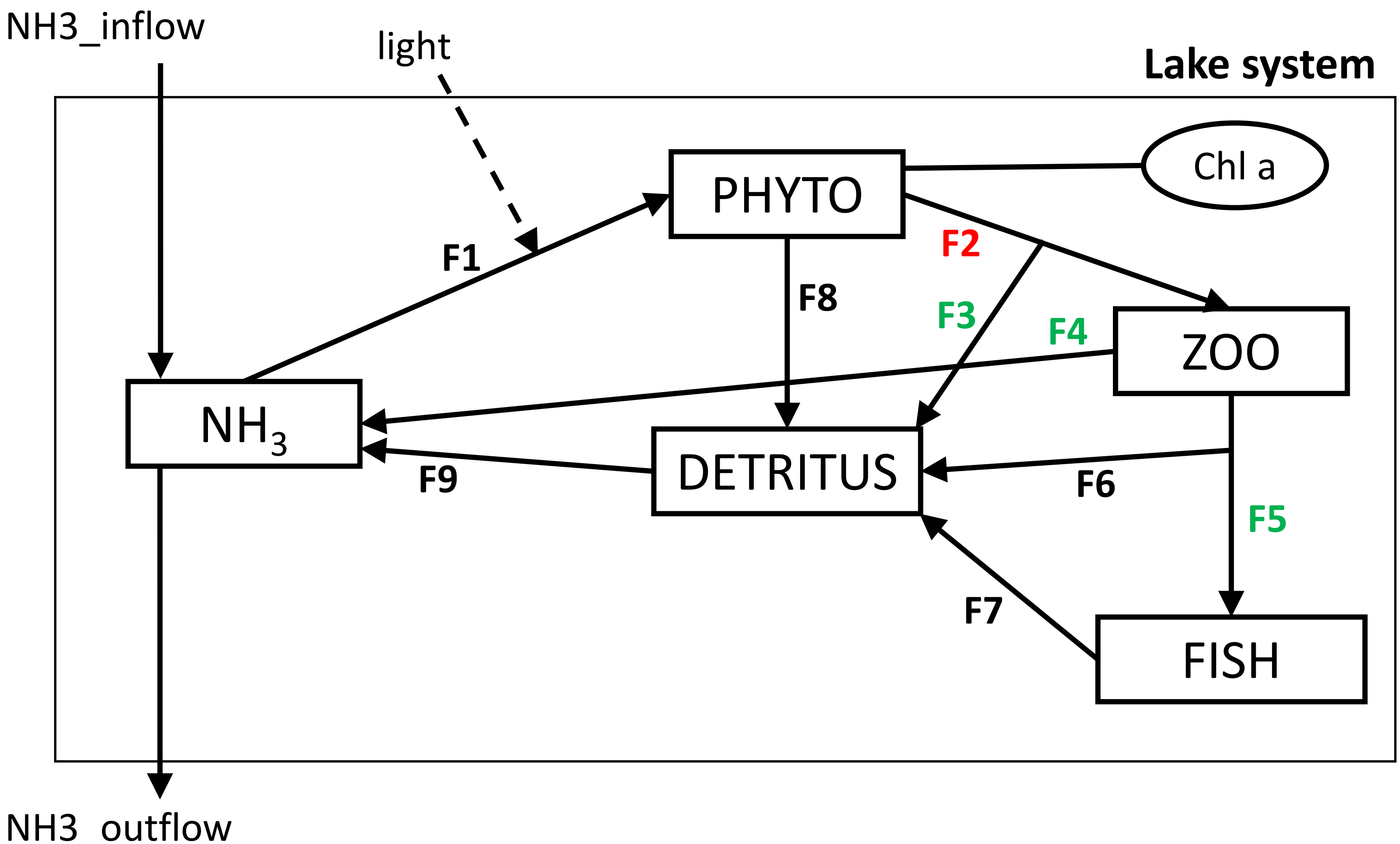
Lake system example



$$\frac{d[\mathrm{ZOO}]}{dt} = F_2 - F_3 - F_4 - F_5$$

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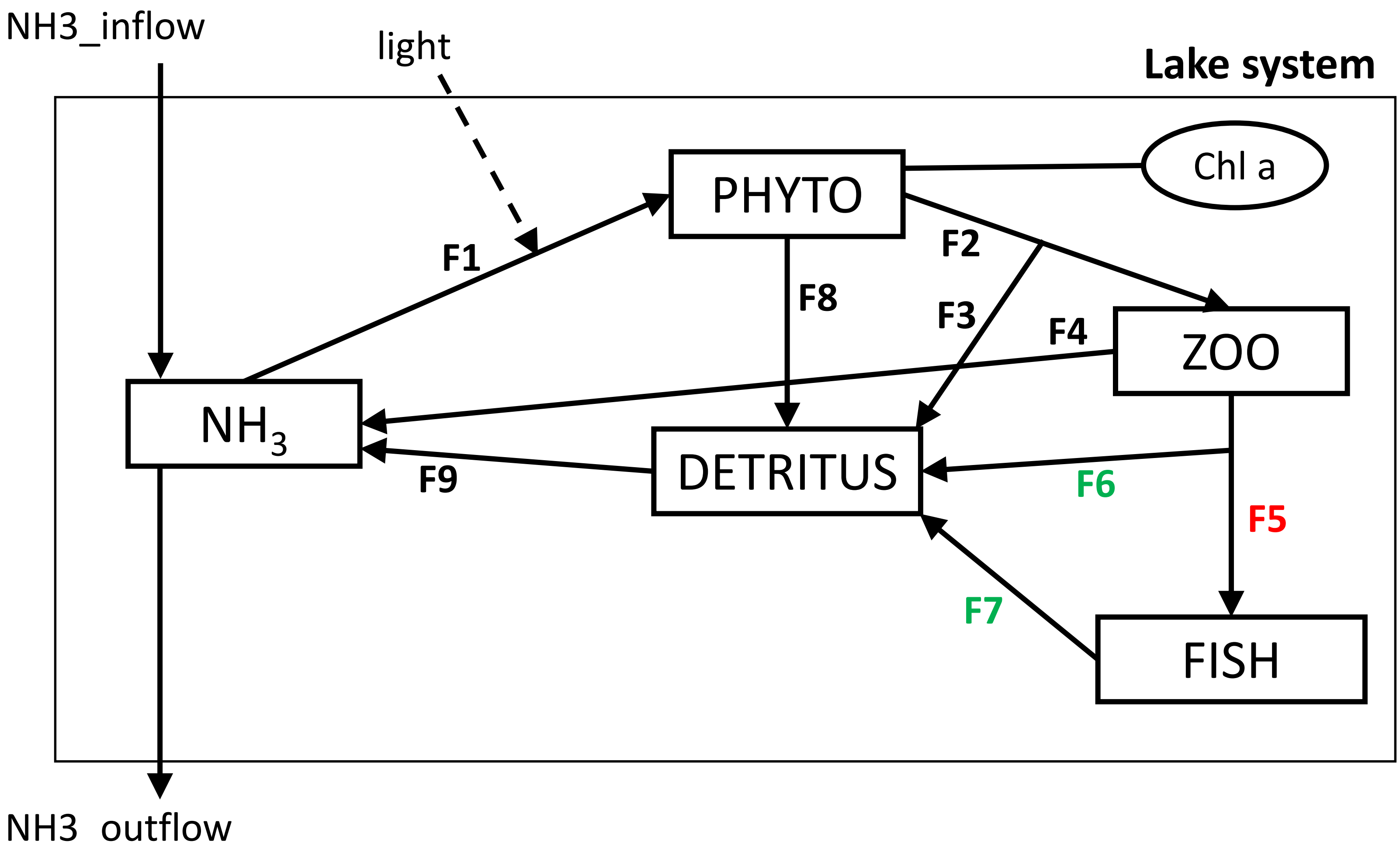
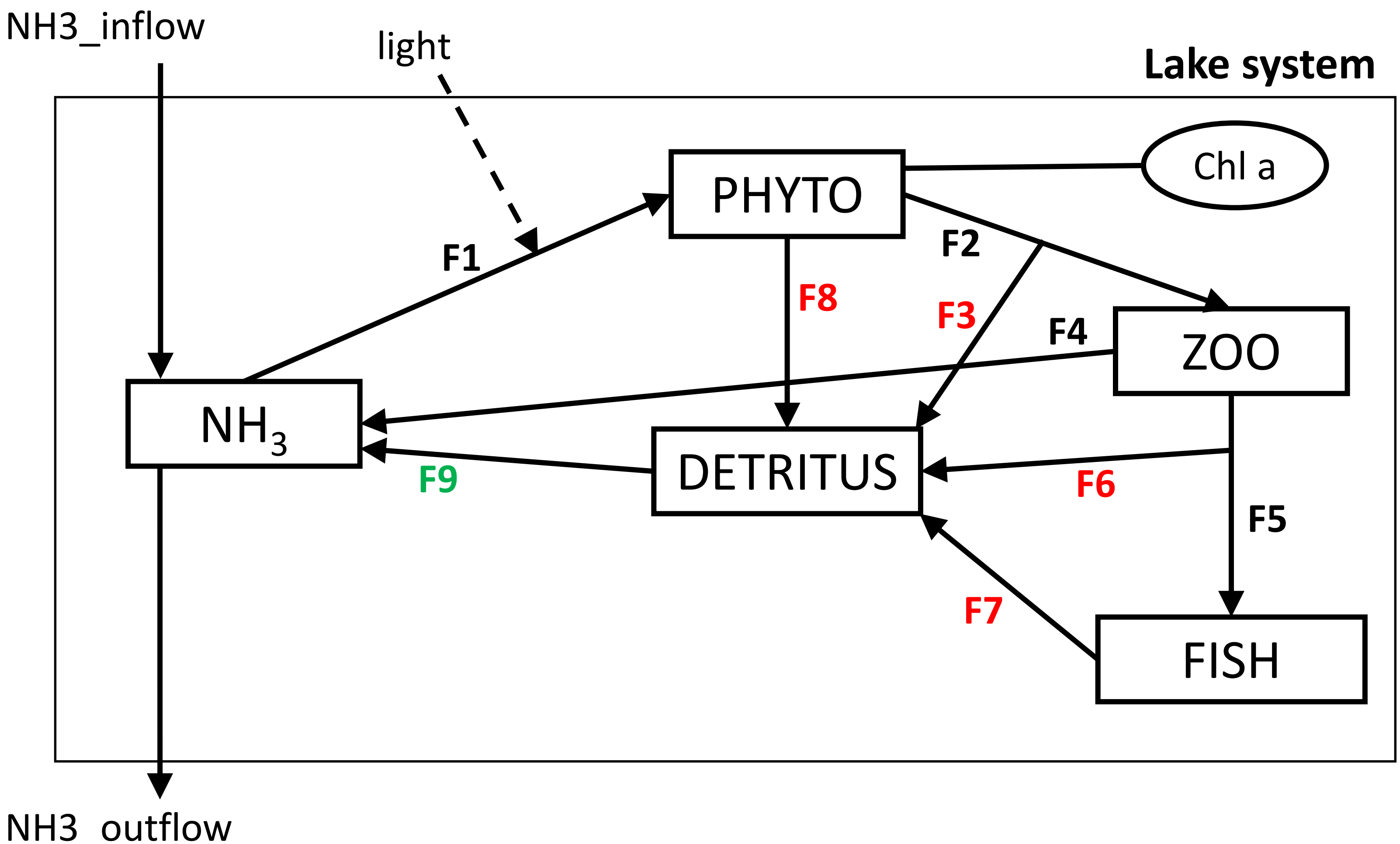
Lake system example



$$\frac{d[\mathrm{FISH}]}{dt} = F_5 - F_6 - F_7$$

Lake system example



$$\frac{d[\mathrm{DETRITUS}]}{dt} = F_3 + F_6 + F_7 + F_8 - F_9$$

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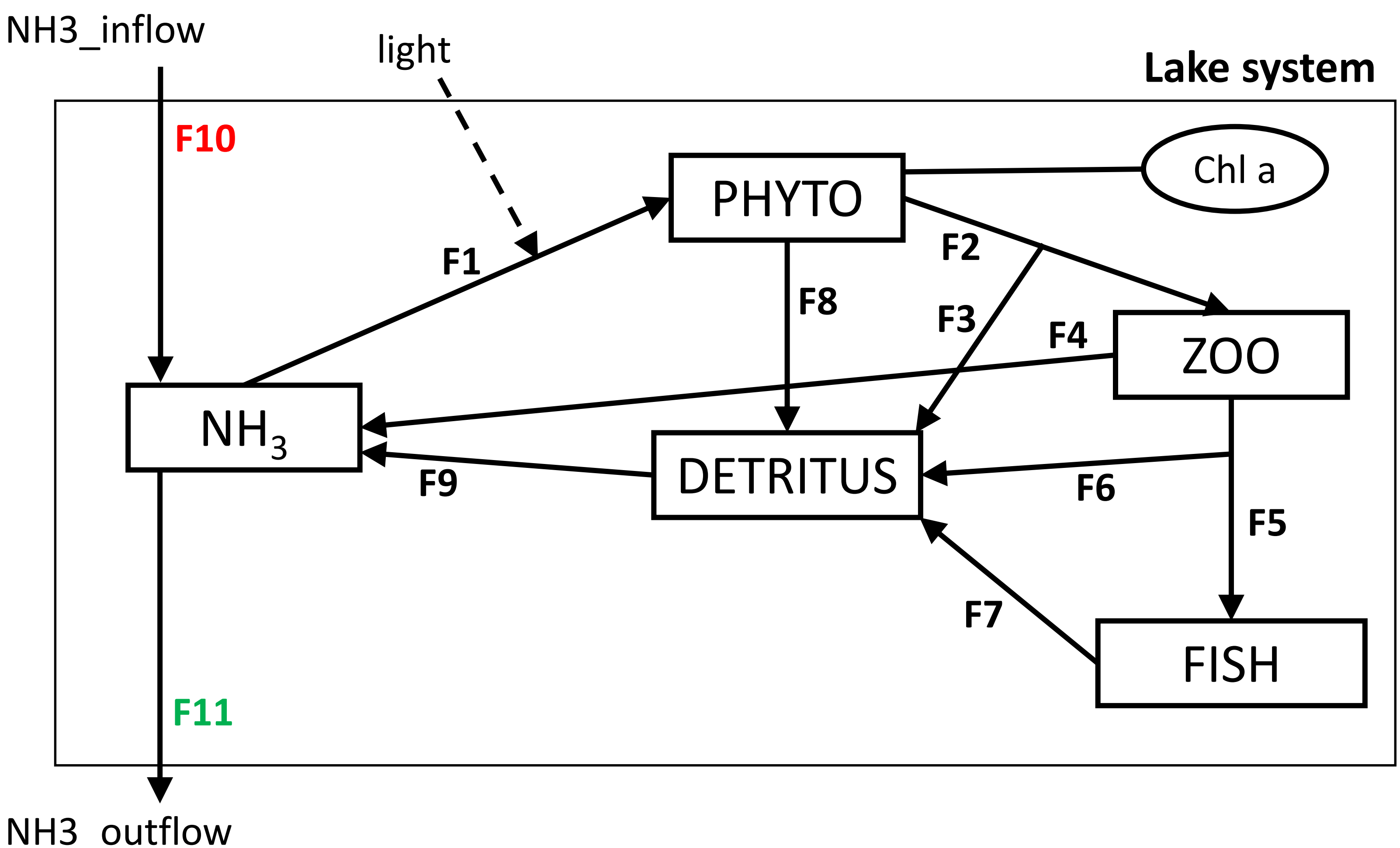
Lake system example



$$\frac{d[\mathrm{NH3}]}{dt} = F_4 + F_9 - F_1 + F_{10} - F_{11}$$

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Lake system example

5 state variables -> 5 equations

$$\frac{d[\mathrm{PHYTO}]}{dt} = F_1 - F_2 - F_8$$

$$\frac{d[\mathrm{ZOO}]}{dt} = F_2 - F_3 - F_4 - F_5$$

$$\frac{d[\mathrm{FISH}]}{dt} = F_5 - F_6 - F_7$$

$$\frac{d[\mathrm{DETRITUS}]}{dt} = F_3 + F_6 + F_7 + F_8 - F_9$$

$$\frac{d[\mathrm{NH3}]}{dt} = F_4 + F_9 - F_1 + F_{10} - F_{11}$$

Consistency check!

$$\frac{d[\mathrm{PHYTO}]}{dt} = F_1 - F_2 - F_8$$

$$\frac{d[\mathrm{DETRITUS}]}{dt} = F_3 + F_6 + F_7 + F_8 - F_9$$

$$\frac{d[\mathrm{ZOO}]}{dt} = F_2 - F_3 - F_4 - F_5$$

$$\frac{d[\mathrm{NH3}]}{dt} = F_4 + F_9 - F_1 + F_{10} - F_{11}$$

$$\frac{d[\mathrm{FISH}]}{dt} = F_5 - F_6 - F_7$$

Total sum

$$\frac{d[\mathrm{N}_{tot}]}{dt} = \frac{d([\mathrm{PHYTO}]+[\mathrm{ZOO}]+[\mathrm{FISH}]+[\mathrm{DETRITUS}]+[\mathrm{NH3}])}{dt} =$$

$$= F_1 - F_2 - F_8 + F_2 - F_3 - F_4 - F_5 + F_5 - F_6 - F_7 + F_3 + F_6$$
$$+ F_7 + F_8 - F_9 + F_4 + F_9 - F_1 + F_{10} - F_{11}$$

$$\frac{d[\mathrm{N}_{tot}]}{dt} = F_{10} - F_{11}$$

Net rate of increase in the concentration of **total** Nitrogen in the lake water is given by the **difference** between the external **import** and **export**.

Consistency check!

$$\frac{d[\mathrm{PHYTO}]}{dt} = F_1 - F_2 - F_8$$

$$\frac{d[\mathrm{ZOO}]}{dt} = F_2 - F_3 - F_4 - F_5$$

$$\frac{d[\mathrm{FISH}]}{dt} = F_5 - F_6 - F_7$$

$$\frac{d[\mathrm{DETRITUS}]}{dt} = F_3 + F_6 + F_7 + F_8 - F_9$$

$$\frac{d[\mathrm{NH3}]}{dt} = F_4 + F_9 - F_1 + F_{10} - F_{11}$$

Total sum

$$\frac{d[\mathrm{N}_{tot}]}{dt} = \frac{d([\mathrm{PHYTO}]+[\mathrm{ZOO}]+[\mathrm{FISH}]+[\mathrm{DETRITUS}]+[\mathrm{NH3}])}{dt} =$$

$$= F_1 - F_2 - F_8 + F_2 - F_3 - F_4 - F_5 + F_5 - F_6 - F_7 + F_3 + F_6 + F_7 + F_8 - F_9 + F_4 + F_9 - F_1 + F_{10} - F_{11}$$

In a **closed** system (i.e., **no external import/export** $F_{10} = F_{11} = 0$)

$$\frac{d[\mathrm{N}_{tot}]}{dt} = 0$$ as expected.

Check of units!

$$\frac{d[\mathrm{PHYTO}]}{dt} = F_1 - F_2 - F_8$$

$$\frac{d[\mathrm{ZOO}]}{dt} = F_2 - F_3 - F_4 - F_5$$

$$\frac{d[\mathrm{FISH}]}{dt} = F_5 - F_6 - F_7$$

$$\frac{d[\mathrm{DETRITUS}]}{dt} = F_3 + F_6 + F_7 + F_8 - F_9$$

$$\frac{d[\mathrm{NH3}]}{dt} = F_4 + F_9 - F_1 + F_{10} - F_{11}$$

Unit of **each state variable**:	mol N m^{-3}
Unit of the **time-derivative**:	mol N m^{-3} s^{-1}
Unit of the **fluxes**:	mol N m^{-3} s^{-1}

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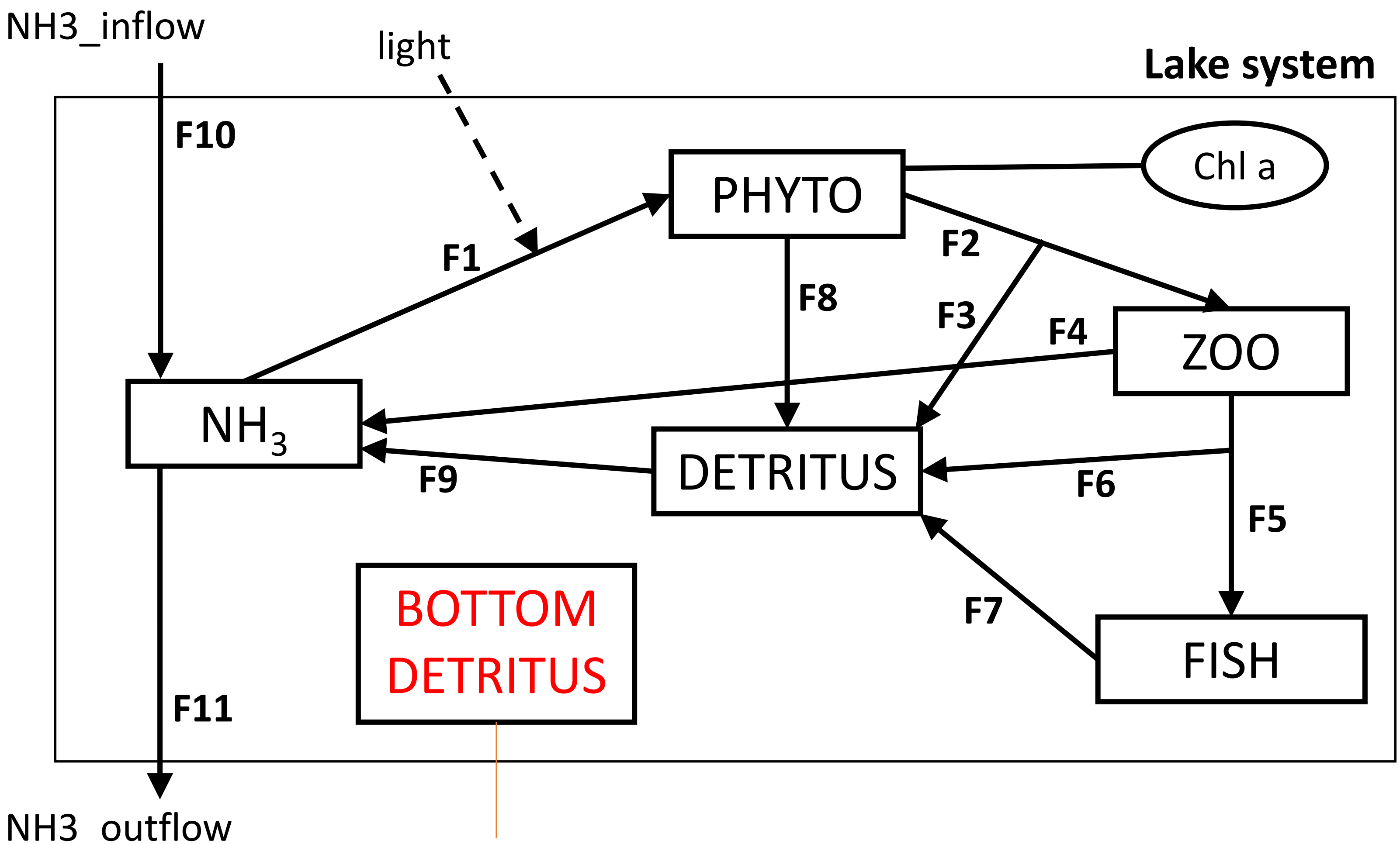
But . . .

Different state variables **can** have different units

Different fluxes **can** have different units

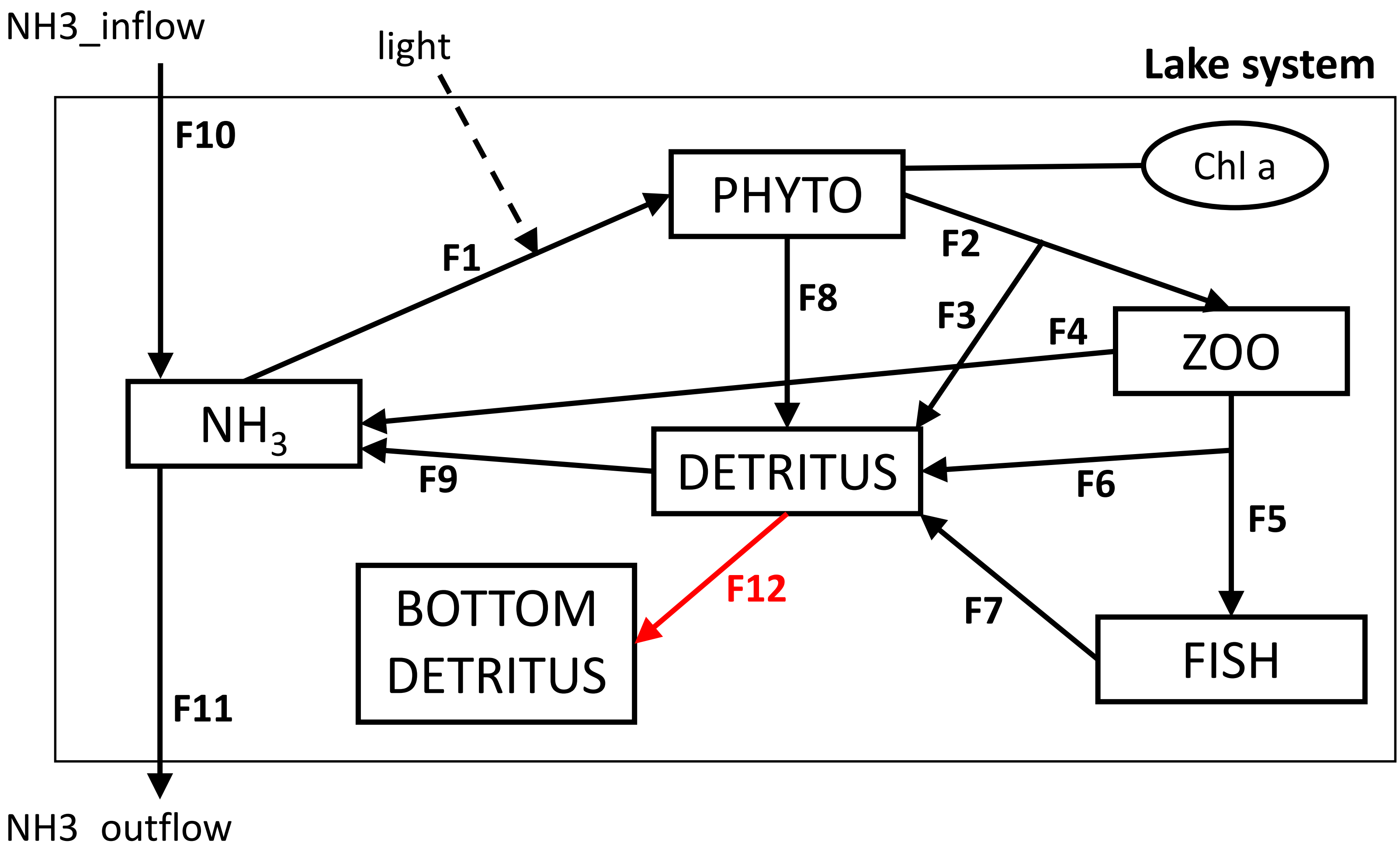
Check of units is **essential** to verify model consistency!

Enhanced lake model



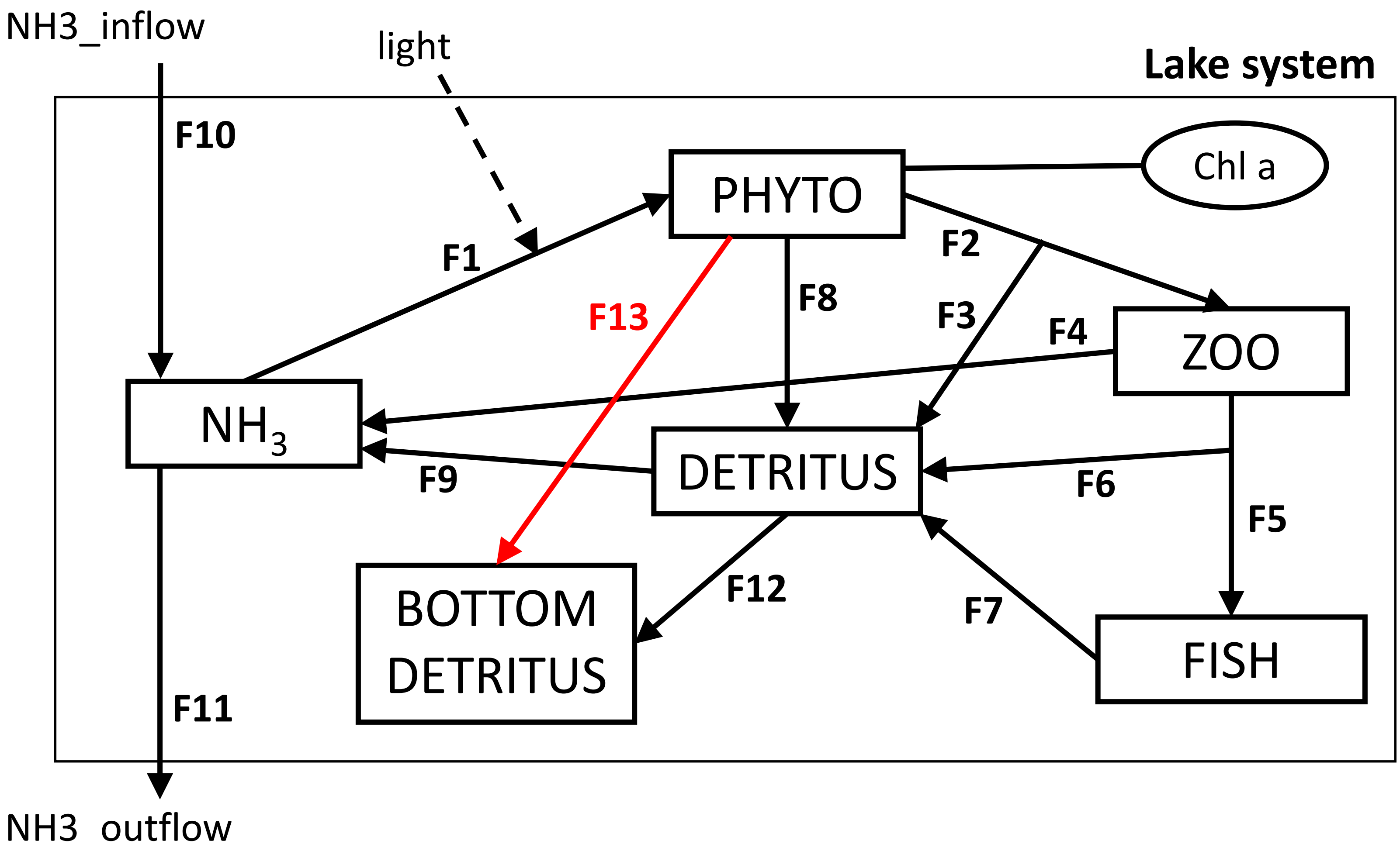
mol N **m^{-2}** amount of Nitrogen in the **sediment column below** the sediment-water interface

Enhanced lake model



F12 = sedimentation of the free-floating detritus onto the lake bottom

Enhanced lake model



F13 = sedimentation of the phytoplankton onto the lake bottom followed by death

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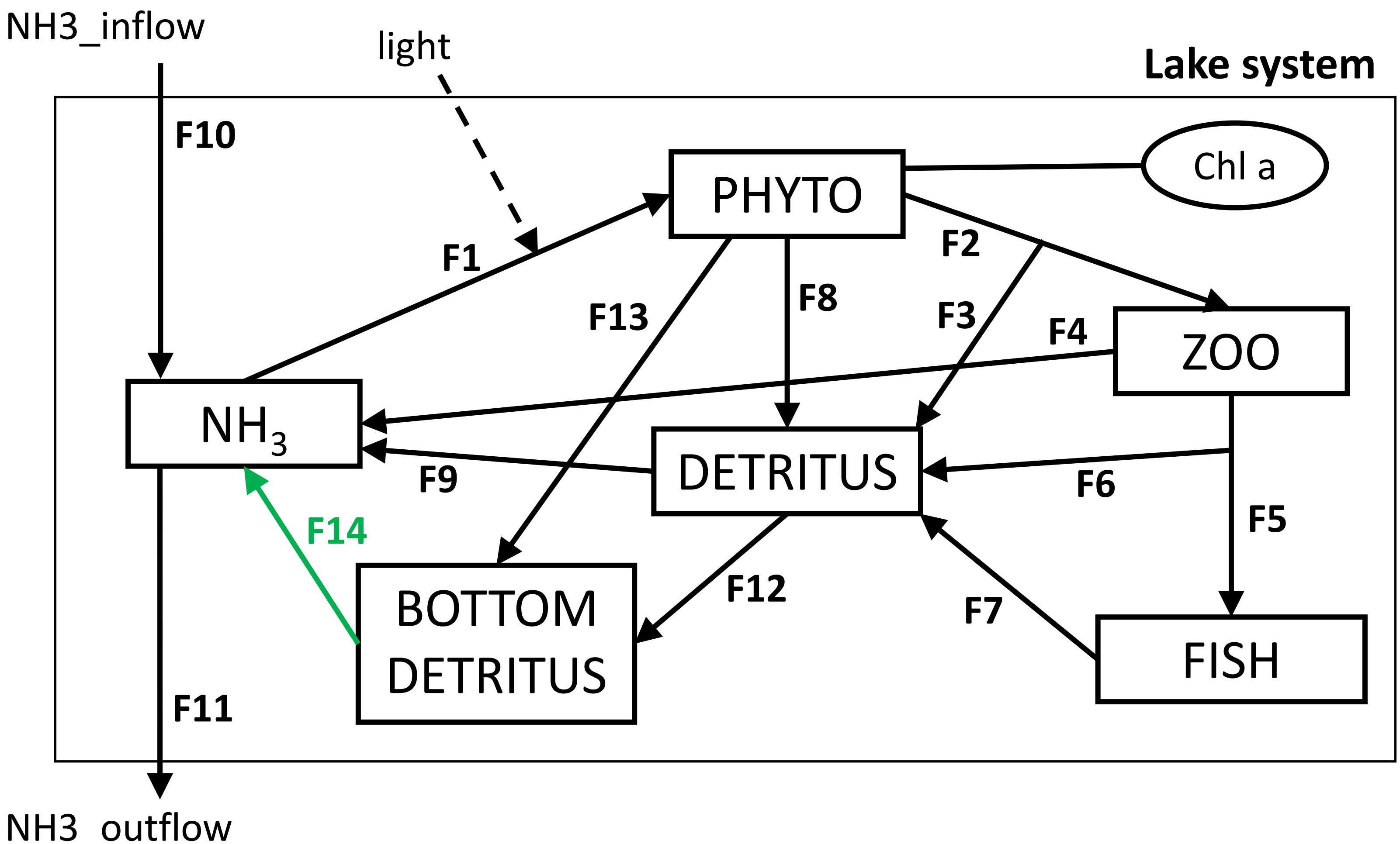
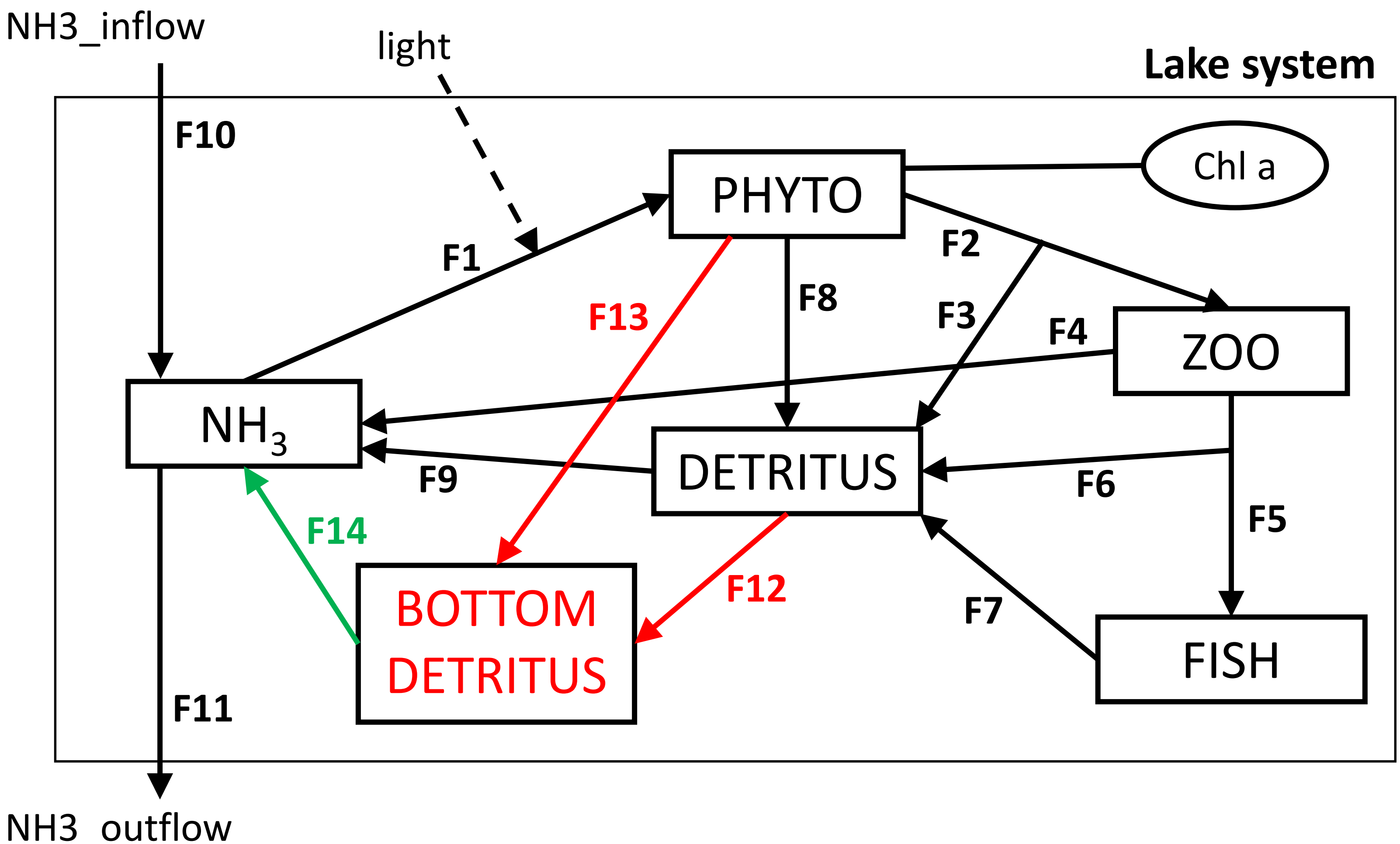
Enhanced lake model



F14 = transport of ammonia produced in the sediment via detritus mineralization

Enhanced lake model



$$\frac{d[\mathbf{BOT\_DET}]}{dt} = \underbrace{F_{12} + F_{13} - F_{14}}_{\textbf{benthic-pelagic coupling}}$$

mol N m^{-2} s^{-1}

mol N m^{-2} s^{-1}

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How do we implement benthic-pelagic coupling?

Incorrect approach:

$$\frac{d[\mathrm{NH3}]}{dt} = F_4 + F_9 - F_1 + F_{10} - F_{11} + \cancel{F_{14}}$$

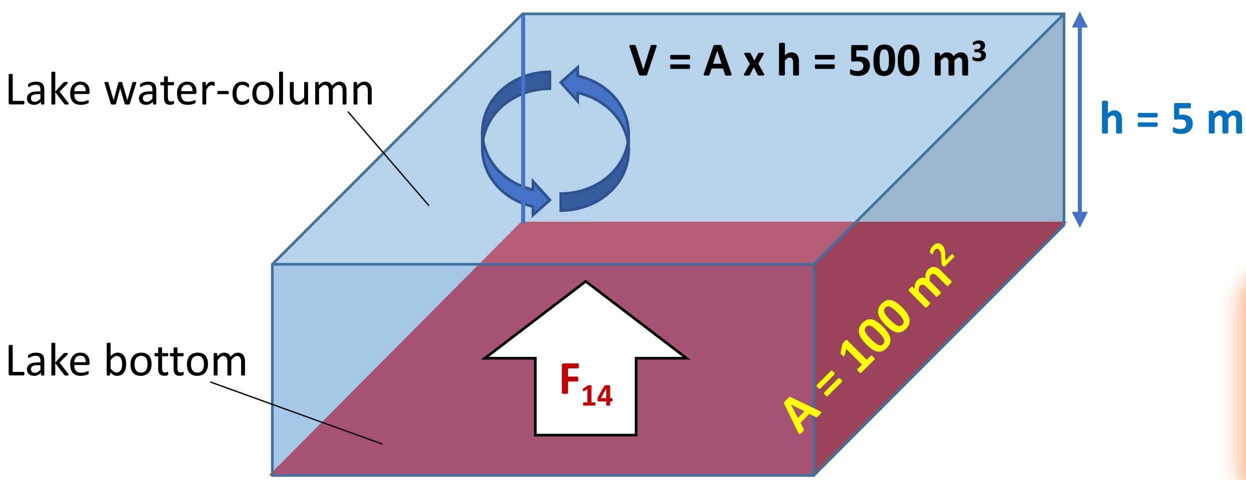
mol N m^{-3} s^{-1} ??? **mol N m^{-2} s^{-1}**

How do we implement benthic-pelagic coupling?

Incorrect approach:

$$\frac{d[\mathrm{NH3}]}{dt} = F_4 + F_9 - F_1 + F_{10} - F_{11} + \cancel{F_{14}}$$

mol N m^{-3} s^{-1} ← ??? ← **mol N m^{-2} s^{-1}**



mol N m^{-3} s^{-1}

$$\boxed{\frac{d[N_{pelagic}]}{dt} = \frac{F_{benthic}}{h}}$$

Total amount of NH_3 leaving the sediment = F_{14} x 100 (mol N s^{-1})

This amount is diluted in the volume V = 500 m^3

Concentration change in the water-column = F_{14} x 100 / 500 = F_{14} / 5

Correct mass balance equations

$$\frac{d\mathrm{PHYTO}}{dt} = F_1 - F_2 - F_8 \boxed{- \frac{F_{13}}{h}}$$

$$\frac{d\mathrm{DETRITUS}}{dt} = F_3 + F_6 + F_7 + F_8 - F_9 \boxed{- \frac{F_{12}}{h}}$$

$$\frac{d\mathrm{ZOO}}{dt} = F_2 - F_3 - F_4 - F_5$$

$$\frac{d\mathrm{NH3}}{dt} = F_4 + F_9 - F_1 + F_{10} - F_{11} \boxed{+ \frac{F_{14}}{h}}$$

$$\frac{d\mathrm{FISH}}{dt} = F_5 - F_6 - F_7$$

$$\boxed{\frac{d\mathrm{BOT\_DET}}{dt} = F_{12} + F_{13} - F_{14}}$$

Consistency check:

$$\frac{d\mathrm{N}_{tot}}{dt} = \frac{d[\mathrm{PHYTO} + \mathrm{ZOO} + \mathrm{FISH} + \mathrm{DETRITUS} + \mathrm{NH3} + \mathrm{BOT\_DET/h}]}{dt} = F_{10} - F_{11}$$ ✓

Units check:

$\frac{d\mathrm{PHYTO}}{dt}$ = … = mol N **m^{-3}** s^{-1} F_1 … F_{11} = mol N **m^{-3}** s^{-1} F_{12}/h … F_{14}/h = mol N **m^{-3}** s^{-1} ✓

BOT_DET/h = mol N **m^{-3}** $\frac{d\mathrm{BOT\_DET}}{dt}$ = mol N **m^{-2}** s^{-1} F_{12} … F_{14} = mol N **m^{-2}** s^{-1} ✓

Mass balances in chemical equations

$$\alpha A + \beta B \rightarrow \gamma C + \delta D$$

Our choice: $\boxed{R = \frac{dD}{dt}}$ **reaction rate**: mole D per time.

$$\frac{\alpha}{\delta} A + \frac{\beta}{\delta} B \rightarrow \frac{\gamma}{\delta} C + D$$

Change in the reactants: $\frac{dA}{dt} = -\frac{\alpha}{\delta} R$ $\frac{dB}{dt} = -\frac{\beta}{\delta} R$

Change in the products: $\frac{dC}{dt} = +\frac{\gamma}{\delta} R$ $\frac{dD}{dt} = +R$

Example: organic matter degradation

Redfield ratio: the average C:N:P ratio in the organic matter = 106:16:1

1 mole of "Redfield" organic matter: $(CH_2O)(NH_3)_x(H_3PO_4)_y$ x=16/106, y=1/106

$$(CH_2O)(NH_3)_x(H_3PO_4)_y + O_2 \rightarrow CO_2 + x\,NH_3 + y\,H_3PO_4 + H_2O$$

Our choice: **R** = oxidation rate **in moles of organic matter per time**.

$$\frac{d\mathrm{OrganicMatter}}{dt} = -R + \ldots \qquad \frac{d\mathrm{O_2}}{dt} = -R + \ldots$$

$$\frac{d\mathrm{NH_3}}{dt} = +xR + \ldots \qquad \frac{d\mathrm{H_3PO_4}}{dt} = +yR + \ldots$$

$$\frac{d\mathrm{CO_2}}{dt} = R + \ldots$$

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Mathematical formulation

Conservation laws: mass/energy balance equation

$$\frac{d\text{StateVariable}}{dt} = Flux_{in} - Flux_{out}$$

Each flux has **two components**:

ecological/chemical **process** & **transport**

- Chemical reactions
- Nutrient assimilation
- Grazing
- Mineralization
- Etc.

- Diffusion
- Advection

One mass-balance equation for **each state variable!**

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