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"Management of Carbon and Nutrient Loads: The Case of the Ria de Aveiro, Portugal"

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MANAGEMENT OF CARBON AND NUTRIENT LOADS: THE CASE OF THE RIA DE AVEIRO, PORTUGAL

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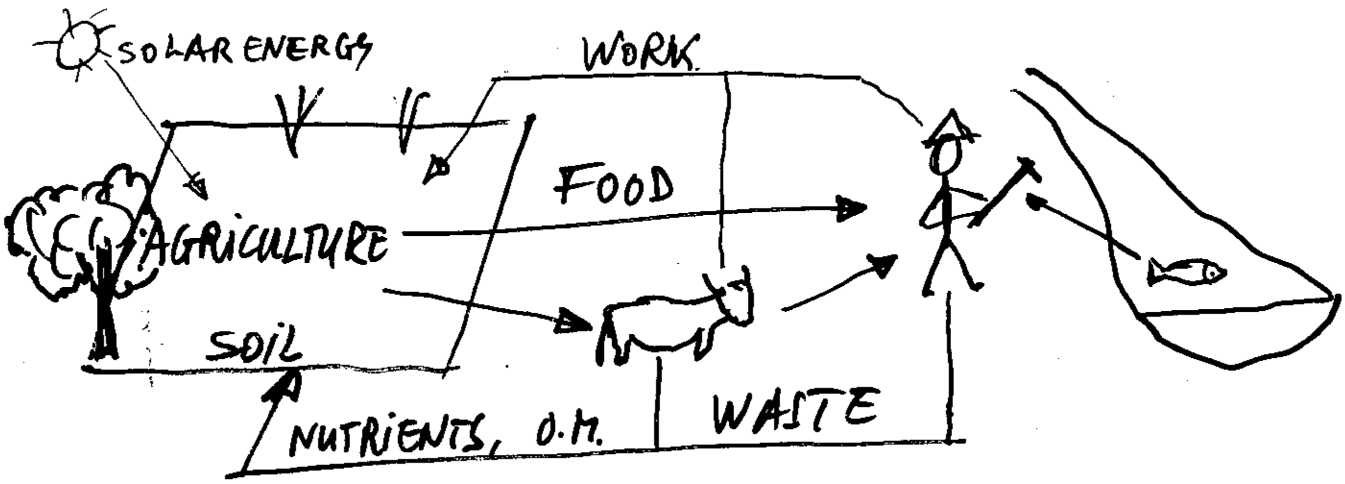
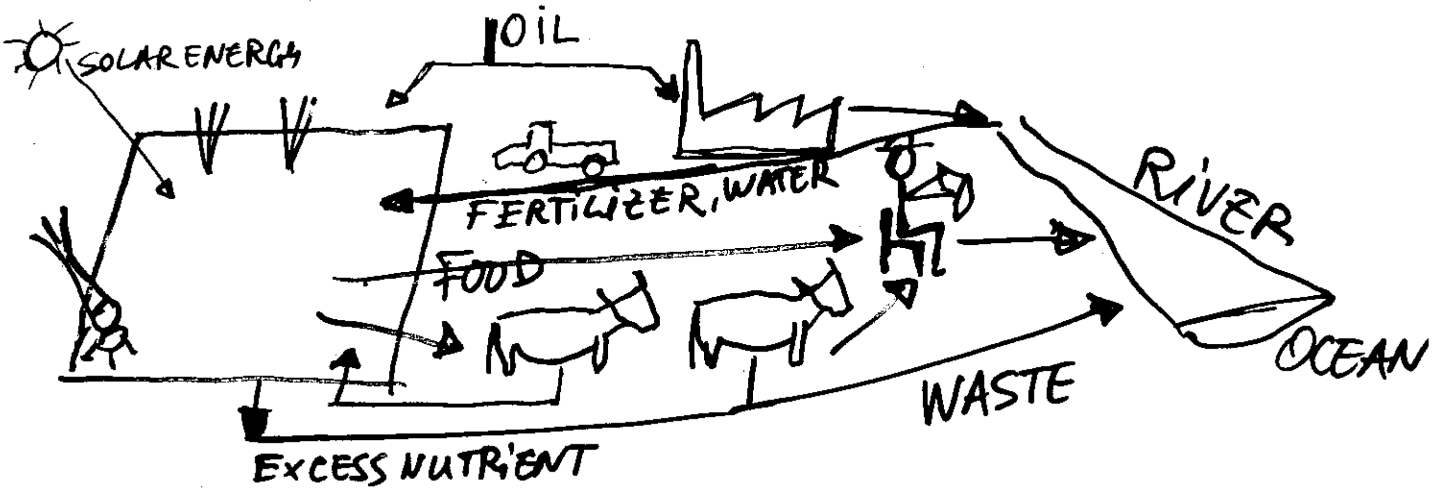
BASIC CONCEPTS:

* CAUSES OF CARBON AND NUTRIENT POLLUTION

TRADITIONAL ECONOMY → CLOSED SYSTEM



TECHNOLOGICAL ECONOMY → OPEN SYSTEM



* INTER-RELATION BETWEEN TERRESTRIAL AND AQUATIC ECOSYS.

HUMAN ACTIVITIES:

INTENSIVE AGRICULTURE / DEFORESTATION / URBAN GROWTH

⇓ DEACREASE OF MINIMUM FLOW ⇓

⇓ INCREASE OF MAXIMUM FLOW ⇓ EROSION OF SOIL

ENRICHEMENT OF NUTRIENTS IN THE AQUATIC ENVIRONMENT ; OTHER FORMS OF POLLUTION

* PARAMETERS FOR TOTAL PERTURBATION OF INLAND AND COASTAL WATERS

$$J = f\left[\frac{\text{FLOW}}{\text{AREA}} ; \frac{\text{INHABITANTS}}{\text{AREA}} ; \frac{\text{GROSS PRODUCTION}}{\text{HABITANT}} \right]$$

EXAMPLES:

WATER QUALITY CHANGE FOR DENSITIES OVER:

	INHAB. / Km^2	INHAB. / $(m^3 s^{-1})$
⟶	100	2000
RIVER RHINE	140	15 000
ALL WORLD	27	3 000

SO: WATER IS SCARCE; EVEN WITH LOW DENSITIES WATER QUALITY IS AT RISC.

WATER QUALITY SYSTEM

* FACTORS OF WATER QUALITY (INPUT VARIABLES)
  - METEOROLOGY – PRECIPITATION; EVAPORATION
  - HIDROLOGY – INFILTRATION; RUNOFF
  - GEOLOGY – PERMEABILITY; METEORIZATION OF ROCK
  - BIOLOGY – TRANSFORMATION; ACCUMULATION
  - HUMAN ACTIVITIES – CHANGES IN LOADS

$$LOAD = A + k \cdot Q$$

A – POINT SOURCE
k – NON-POINT

* WATER QUALITY PARAMETERS (STATE VARIABLES)

CONCENTRATIONS OF:
- DISSOLVED OXYGEN
- ORGANIC CARBON
- FORMS OF NITROGEN: NO_3, NO_2, NH_3, $N_{ORG.}$
- FORMS OF PHOSPHORUS: TOTAL, ORGANIC, DISSOLVED
- TOTAL SOLIDS, SUSPENDED SOLIDS, TURBIDITY
- METALS; SPECIFIC ORGANIC COMPOUNDS

MICROBIOLOGICAL INDICATORS (COLIF. BACTERIA)

BIOLOGICAL INDICATORS (INVERTEBRAT; ALGAE)

BIO-TESTS: ECOTOXICITY

* WATER QUALITY CRITERIA (OUTPUT; OBJECTIVS)
  - DIRECT USE OF WATER: PUBLIC SUPPLY; INDUSTRY; RECREATION; IRRIGATION; PROD. OF SEA FOOD
  - PRESERVATION OF LIFE: (DIFFICULT, BUT ... IN THE UE WATER POLICY DIRECTIVE)

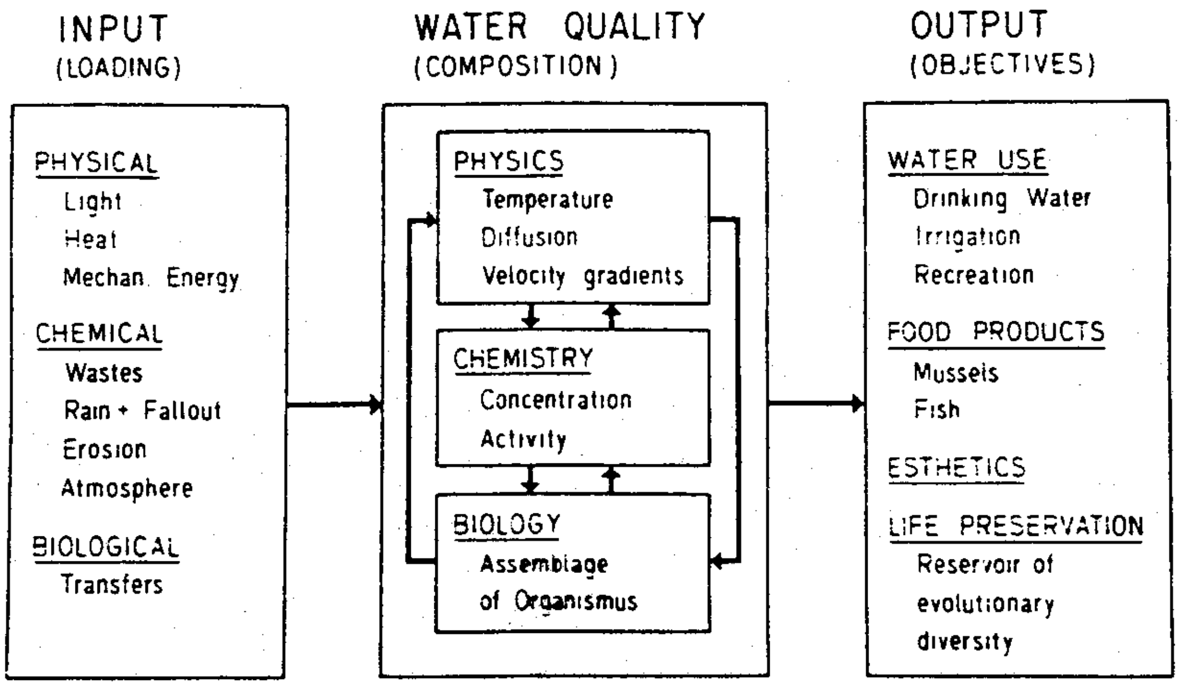


Figure 11.4 Transfer functions between loading, water quality, and water use.

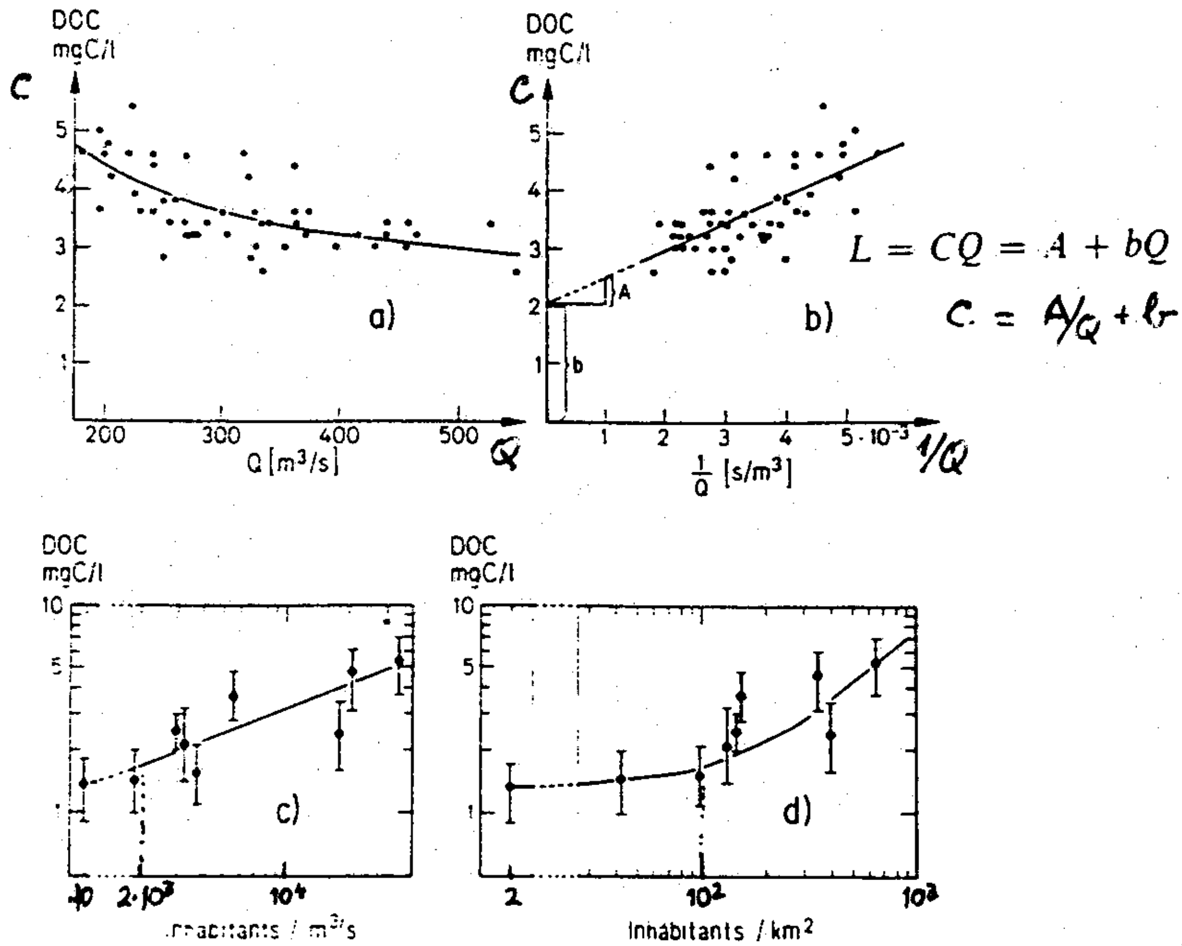


Figure 11.5 Dependence of dissolved organic Carbon (DOC) on rate of flow, Q (*a* and *b*) and on population density (*c* and *d*) (Example 11.1). In (*a*) and (*b*) data from the river Aare (Switzerland) are plotted. In (*c*) and (*d*) DOC data with a mean range between 5 and 95% values (i.e., values observed in more than 5% and less than 95% of all samples) of various rivers are given (cf. J. Zobrist, J. Davis, and Hugi, Gas Wasser Abwasser 57, 402 (1977) and J. Davis and Zobrist, Progr. Water Technol.

* PERTURBATION OF AQUATIC ECOSYSTEM

- CHANGE IN THE RELATION BETWEEN RESPIRATION AND PHOTOSYNTHESIS IS A COMMON PROBLEM
- CAUSED BY INCREASE IN THE LOADS OF ORGANIC MATTER OR NUTRIENTS FOR ALGAE
- THIS PROBLEM ARRISES BECAUSE IN AQUATIC ECOSYSTEMS PRODUCTION AND CONSUMPTION MUST BE IN BALANCE TO MANTAIN:
    - LOW PRIMARY BIOMASS
    - MANY TROPHIC LEVELS
    - COMPLEX FOOD WEB
    - LARGE CONSUMER BIOMASS
    - REDUCED ACTIVITY OF DECOMPOSERS

OBS: SOIL BASED ECOSYSTEMS HAVE OPPOSITE PROPERTIES

* LIMITING NUTRIENTS FOR ALGAE

- MAJOR MACRO-NUTRIENTS ARE: C, N, P, Ca, K, S
- IN AQUATIC ECOSYSTEMS C IS CONTROLED BY CALCO-CARBONIC EQUILIBRIUM:

$$CO_{2(g)} \leftrightarrow HCO_3^- \leftrightarrow CaCO_{3(s)}$$

- N IN FORMS NH_3, NO_2, NO_3 IS BIOAVAILABL[E]
  CAN BE LIMITING IN FRESH WATER (ENRICHE[D])
  USUALY LIMITING IN SEA WATER
- P IN FORM PO_4 IS BIOAVAILABLE;
  [illegible] IN FRESH WATER

* POLUTION BY N COMPOUNDS

SPECIES		EFFECTS
$HNO_{3\,(g)}$	(+5)	POLUTION OF AIR ACIDIFICATION
$NO_{2\,(g)}$	(+4)	TOXIC TO PLANTS
$NO_{(g)}$	(+2)	OZONE LAYER DISTRUCTION
$N_2O_{(g)}$	(+1)	
$N_{2\,(g)}$	(0)	MAJOR GAS IN ATMOSPHERE (78%)
$NH_{3\,(g)}$	(-3)	TOXIC
$NO_3^-{}_{(aq)}$	(+5)	POLUTION OF WATER EUTROPHICATION ; HEALTH EFFECTS
$NO_2^-{}_{(aq)}$	(+3)	
$NH_4^+{}_{(aq)}$	(-3)	ACIDIFICATION; TOXIC TO FISH
$N_{ORG.}$	(-3)	

* POLUTION BY P COMPOUNDS

$PO_4^{3-}{}_{(aq)}$	(+5)	POLUTION OF WATER EUTROPHICATION
P_2O_5	(+5)	
$P_{ORG.}$	(+5)	
PO_4^{3-} (ADSORBED)		

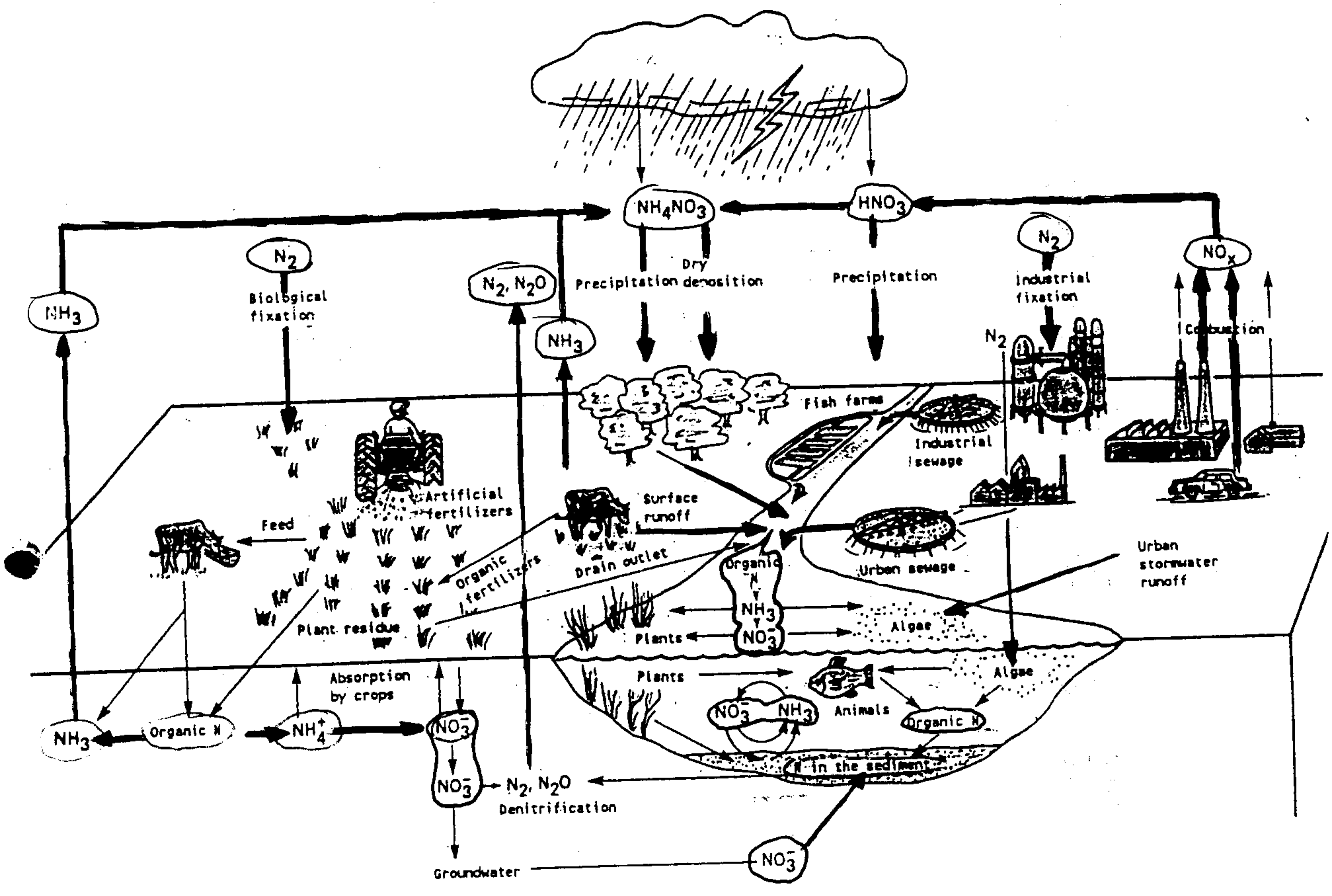


Fig. 4.1
The nitrogen cycle (Nat. Agency of Environmental Protection 1984).

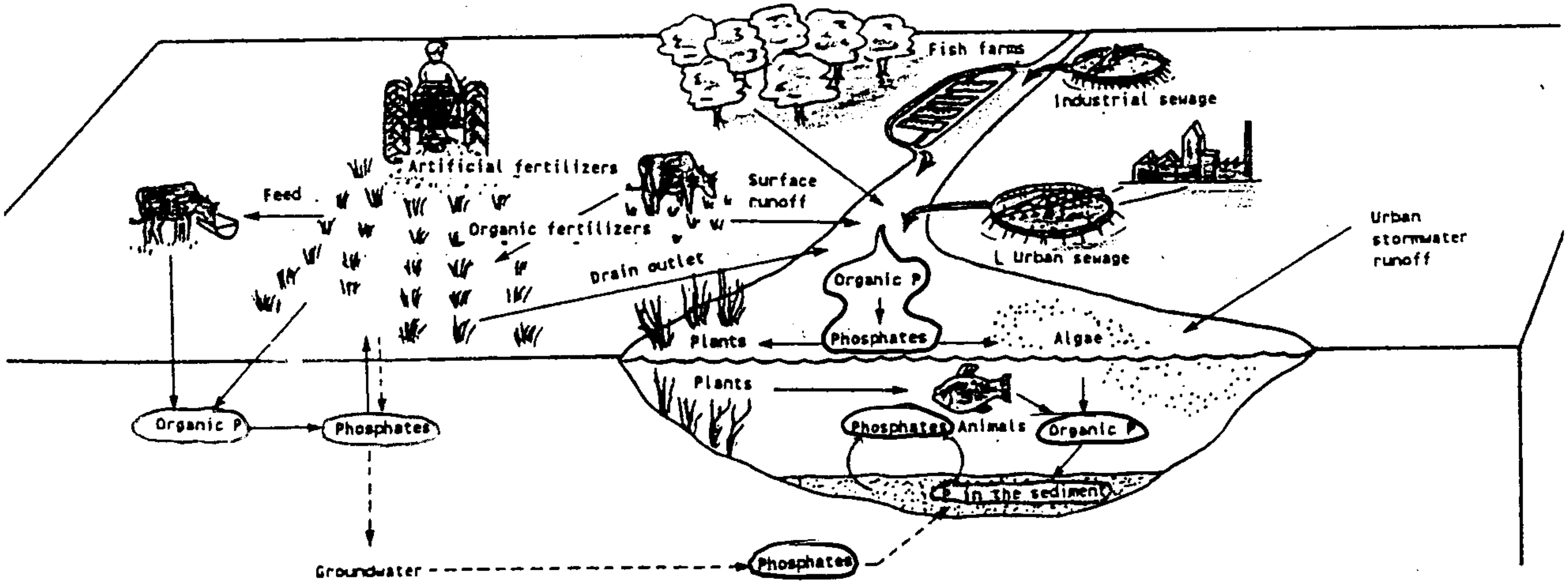


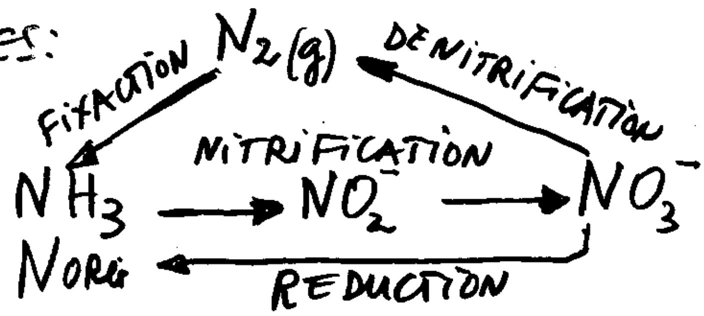
Fig. 4.2
The phosphorus cycle (Nat. Agency of Environmental Protection 1984a)

* TRANSFORMATION OF N COMPOUNDS

		ΔG^0 KJ mol^{-1}
CHEMICAL PROCESSES:	$0.5 N_2 + 0.5 O_2 \rightarrow NO$	+87
	$NO + 0.5 O_2 \rightarrow NO_2$	−35
	$0.5 N_2 + 1.25 O_2 + 0.5 H_2O \rightarrow HNO_3$	−26

BIOLOGICAL PROCESSES:

OBS: NO MECHANISM FOR OXIDATION OF N_2 TO NO_3^-



NITRIFICATION:	$NH_4^+ + 1.5 O_2 \rightarrow NO_2^- + H_2O + 2H^+$	−290
	$NO_2^- + 0.5 O_2 \rightarrow NO_3^-$	−72
DENITRIFICATION:	$NO_3^- + 1.25 CH_2O + H^+ \rightarrow 0.5 N_2 + 1.75 H_2O + 1.25 CO_2$	−595
	$NO_3^- + CH_2O + H^+ \rightarrow 0.5 N_2O + 1.5 H_2O + CO_2$	−417
FIXATION:	$0.5 N_2 + 1.5 H_2 + H^+ \rightarrow NH_4^+$	

REDUCTION (PHOTOSYNTHESIS)

$$106\, CO_2 + 16\, NO_3^- + HPO_4^{2-} + 122\, H_2O + 18 H^+ \rightarrow C_{106}H_{263}O_{110}N_{16}P + 138\,C$$

* SOURCES OF N COMPOUNDS (GLOBAL)

- NATURAL (LIGHTNING; BIOLOGICAL) 100 − 150 MTON/y
- MAN (INDUSTRY; COMBUSTION) 140 MTON/y
- BURNING BIOMASS 50 "

* URBAN EMISSION TO WATER

- CARBON (TOC) 45 g C/INHAB/DAY
- NITROGEN (N_{TOTAL}) 14 g N/INHAB/DAY
- PHOSPHORUS (P_{TOTAL}) 2,5 g P/INHAB/DAY

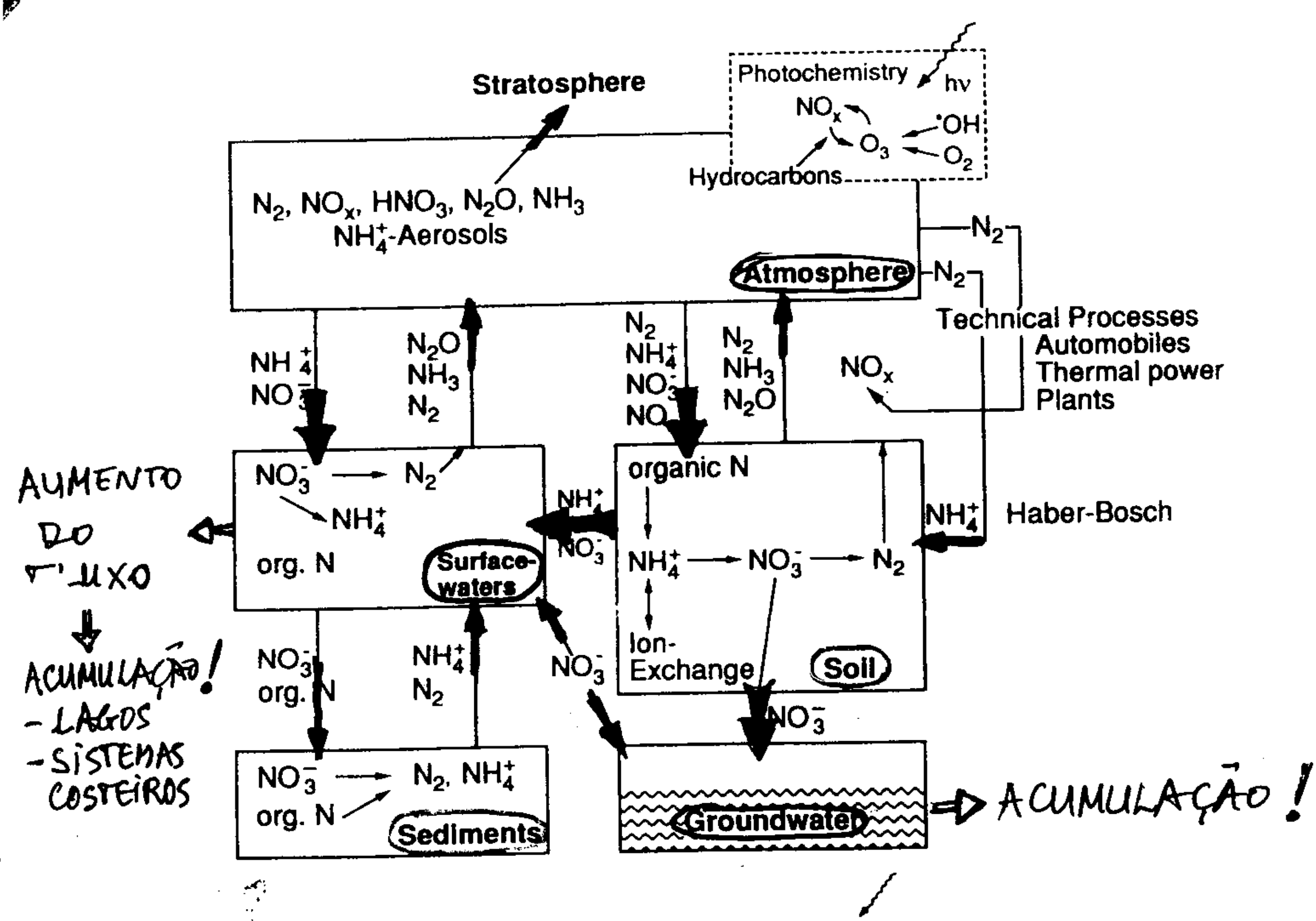


Figure 15.22. A schematic survey on the transformation and distribution of N compounds in various reservoirs of the environment. $N_2 \rightarrow$ Org N $\rightarrow NH_4^+$. As shown by reactions (4) and (5) in Table 15.9, H_2 or organic material (for our calculations we use "$\{CH_2O\}$") can—from a thermodynamic point of view—reduce nitrogen to N(-III) (organic N and NH_4^+). The free energy released in these processes are very small. As is evident from Table 8.6 and Figure 8.14, the reduction of N_2 to NH_4^+ (pH = 7) can occur only under very reducing conditions ($\widetilde{p\epsilon} < -4$) whereas the reduction of $CO_2(g)$ to $\{CH_2O\}$ is possible under slightly less reducing ($p\epsilon < 1$) conditions. The biological fixation of $N_2(g)$ needs additional energy which is obtained from photosynthesis (blue-green algae and bacteria in symbiosis with plants). The nitrogen fixed is initially present as organic nitrogen which upon decomposition yields NH_4^+ (and NH_3). The industrial N_2 fixation produces also NH_3.

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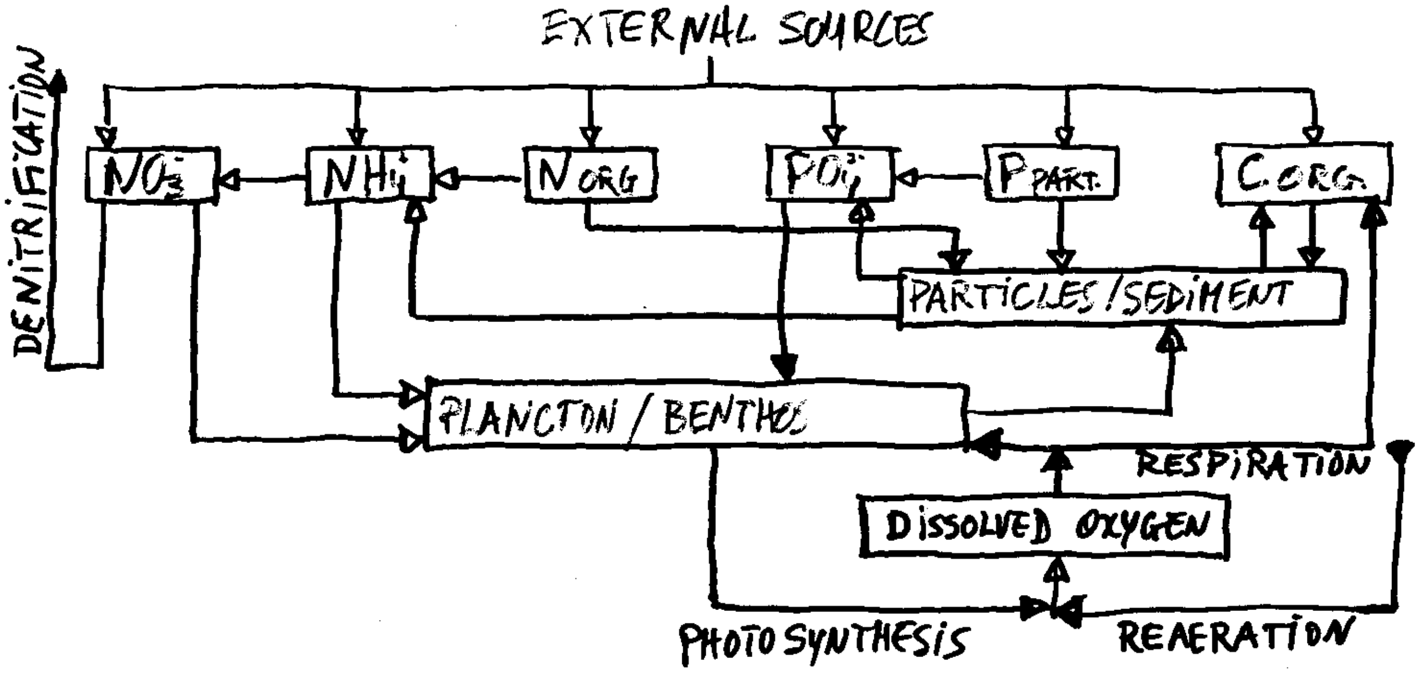
* MODELS FOR TRANSFORMATION PROCESSES



* TRANSFORMATION RATES (FIRST ORDER)

- DECOMPOSER RESPIRATION: $BOD_t = L_0 \left(1 - e^{-K_1 t}\right)$
- RESPIRATION & REAERATION (STREETER - PHELPS)

$$DO_t = C_S - \frac{K_1 L_0}{K_2 - K_1}\left[e^{-K_1 t} - e^{-K_2 t}\right] - (C_S - C_0)\, e^{-K_2 t}$$

- PHYTOPLANCTON GROWTH (CHLOROPHYLL):

$$Ch_t = CL_0\, e^{[K_{PC} - K_{SED} - K_{PR} - K_{ZR}]\,t}$$

K_{PC} ↓ GROWTH, K_{SED} ↓ SEDIMEN., K_{PR} ↓ RESPIR., K_{ZR} ↓ ZOOPLANCTON GRAZING

- NITRATE CONCENTRATION

$$NO_{3t} = NO_{3_0} \cdot e^{-K_{ND} t} + NH_3\left[1 - e^{-K_{Ni} t}\right] - \frac{N}{CL}\left[e^{K_{PC} t} - 1\right] \cdot CL$$

↓ DENITRIFICATION ↓ NITRIFICATION ↓ PLANCTON GROWTH

- AMONIA CONCENTRATION

$$NH_{3t} = NH_{3_0} \cdot e^{-K_{Ni} t} + N_{ORG}\left[1 - e^{-K_{NR} t}\right] - \frac{N}{CL}\left[e^{K_{PC} t} - 1\right] \cdot CL$$

↓ NITRIFICATION ↓ HIDROLYSIS ↓ PLANCTON GROWTH