ENV-405 Session 2
Wastewater treatment
Lecture 2 Nov 11

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Slides acknowledgment: Christof Holiger, Shilva Shrestha

Today's content:

1. Review energetics for microbiological systems.

2. Overview carbon (COD) removal

3. Nitrogen removal

Biological systems gain energy from redox reactions.

- A quote by Nobel Prize-winning biochemist Albert Szent-Györgyi: "Life is nothing but an electron looking for a place to rest"
- Review (watch by yourself) what is Redox Reaction? https://www.youtube.com/watch?v=lQ6FBA1HM3s

A **redox reaction** (short for *reduction–oxidation reaction*) is a chemical reaction in which electrons are transferred between two chemical species.

It always involves **two processes happening at the same time**:

Oxidation → loss of electrons

- The species that loses electrons is the **reducing agent** (it gets oxidized).

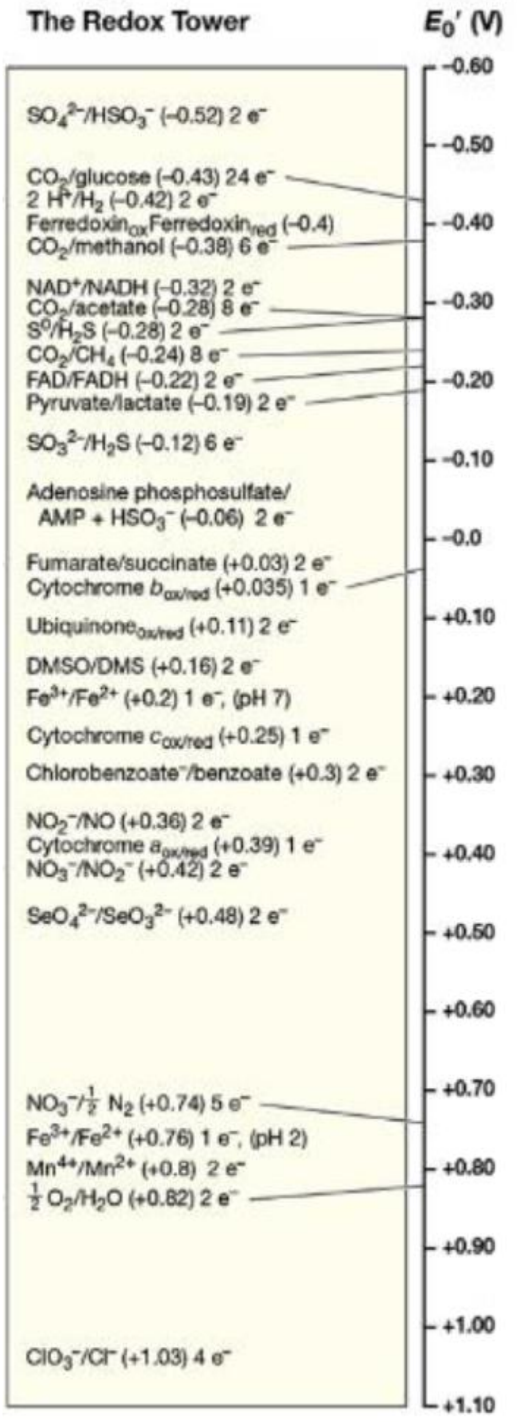
Reduction → gain of electrons

- The species that gains electrons is the **oxidizing agent** (it gets reduced).

Always need an electron donor and an electron acceptor!

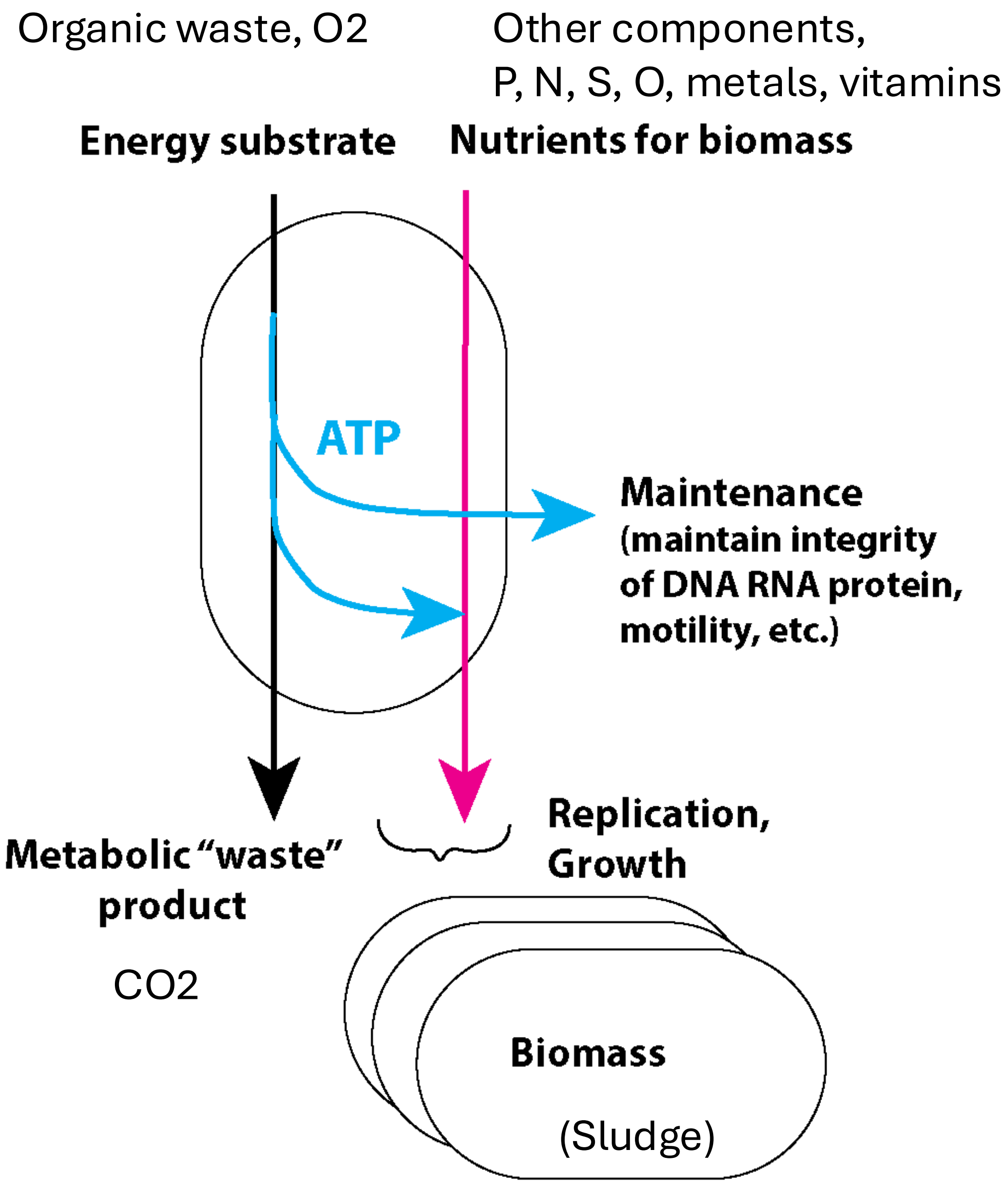
The redox tower illustrates how microbes gain energy by moving electrons *downhill* from higher-energy donors to lower-energy acceptors.

Again, there always need an electron donor **and** an electron acceptor!



The energy production reaction or metabolic pathway supports biomass synthesis.

In WWT, biomass is the main component of sludge.



For example, we could write combined equation of energy production and biomass synthesis:

Stoichiometric equation for wastewater oxidation

$$4\ C_8H_{12}O_3N + 25\ O_2 \rightarrow 2\ C_5H_7O_2N + 2\ NH_4^+ + 2\ HCO_3^- + 20\ CO_2 + 12\ H_2O$$

Observed growth yield (measured by biomass) is lower than Theoretical growth yield (calculated by substrate consumption), due to maintenance and decay.

$$\mathbf{Y} = \frac{\text{Mass of New Biomass Produced}}{\text{Mass of Substrate Consumed}}$$

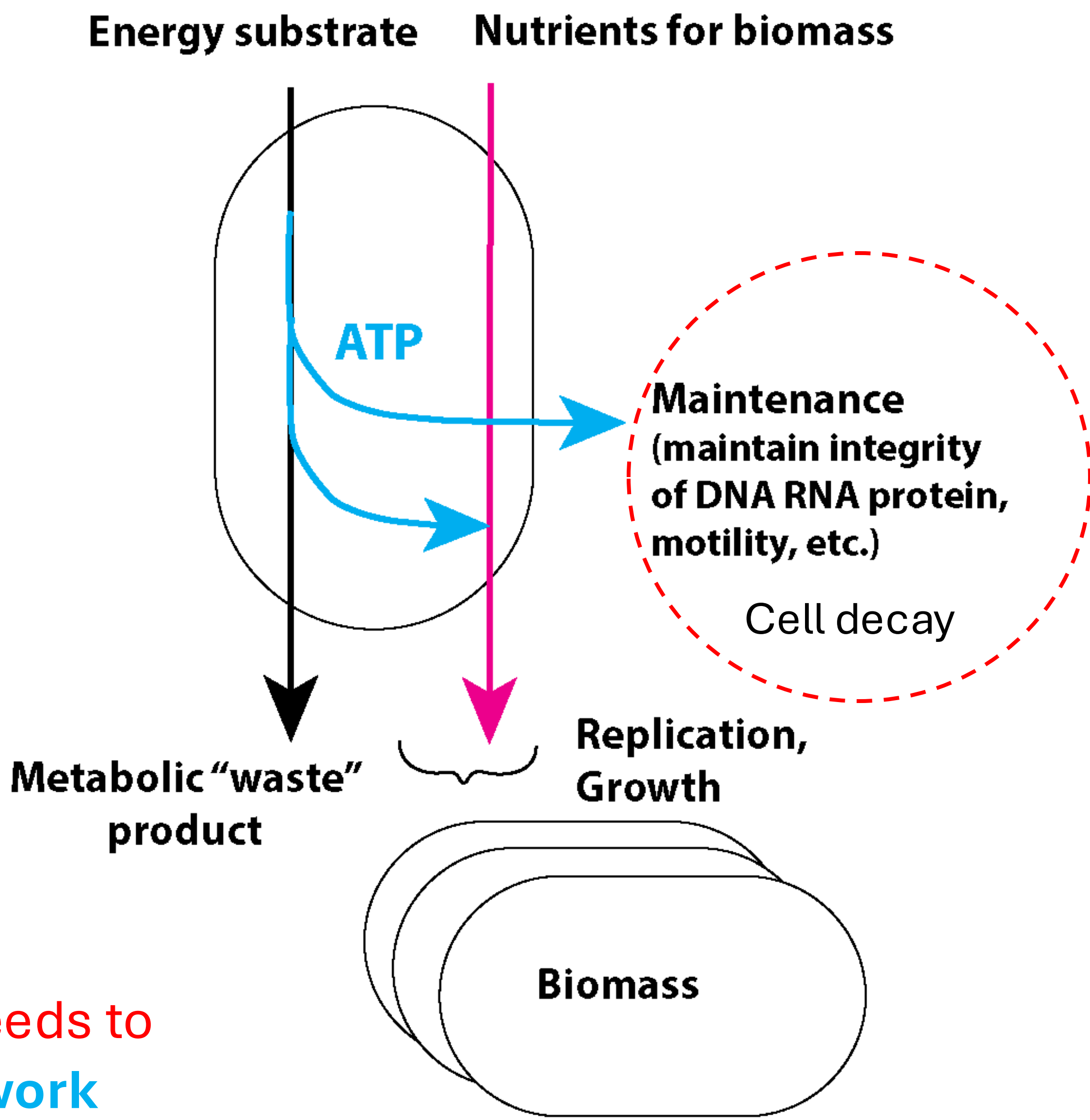
Y = True growth yield

Y_{obs} = Observed growth yield

$$Y(Y_{obs}) = \frac{\text{(Net) Amount of biomass formed}}{\text{(Net) Amount of substrate consumed}}$$

Yield influenced by:

- Substrate
- Organisms
- Growth environment (Terminal electron acceptor, pH, Temperature)



The same goes for growth rate; the real growth rate needs to be corrected by environmental conditions. → **Homework**

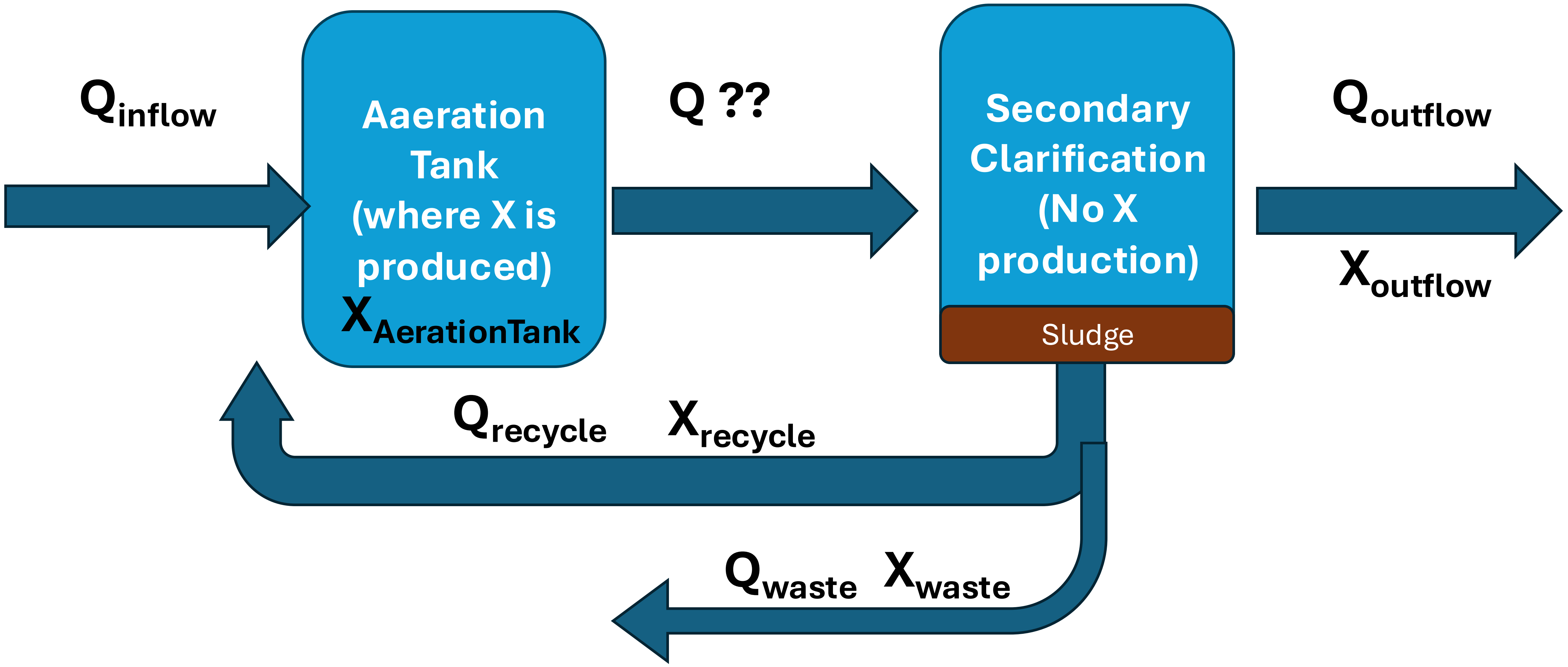
Carbon (COD) removal: (Chapter 4 in the book)

- Overall, for the removal of each contaminant or nutrient or element, we either try to turn them into gas or heavy material (heavier than water) for sedimentation, such as CO_2 and biomass.

- We discussed mass balance last week. In the example problem, we assumed a constant concentration in the aeration tank, which is based on the assumption that this is a steady-state reactor (like CSTR).

Mass balance: the production and recycling of sludge X

HOMEWORK 1



Mass balance for the whole system?

Mass balance for the Secondary clarification?

- Some parameters that are important:

Sludge retention time (SRT): the average time sludge remain in the system before being removed.

Hydraulic retention time (HRT): the average time wastewater spends in a treatment reactor before exiting.

$$SRT = \frac{\text{Mass of sludge in reactor}}{\text{Mass of sludge wasted per day}}$$

$$SRT = \frac{X_{TSS} \cdot V_R}{X_{TSS} \cdot Q_w} = \frac{V_R}{Q_w}$$

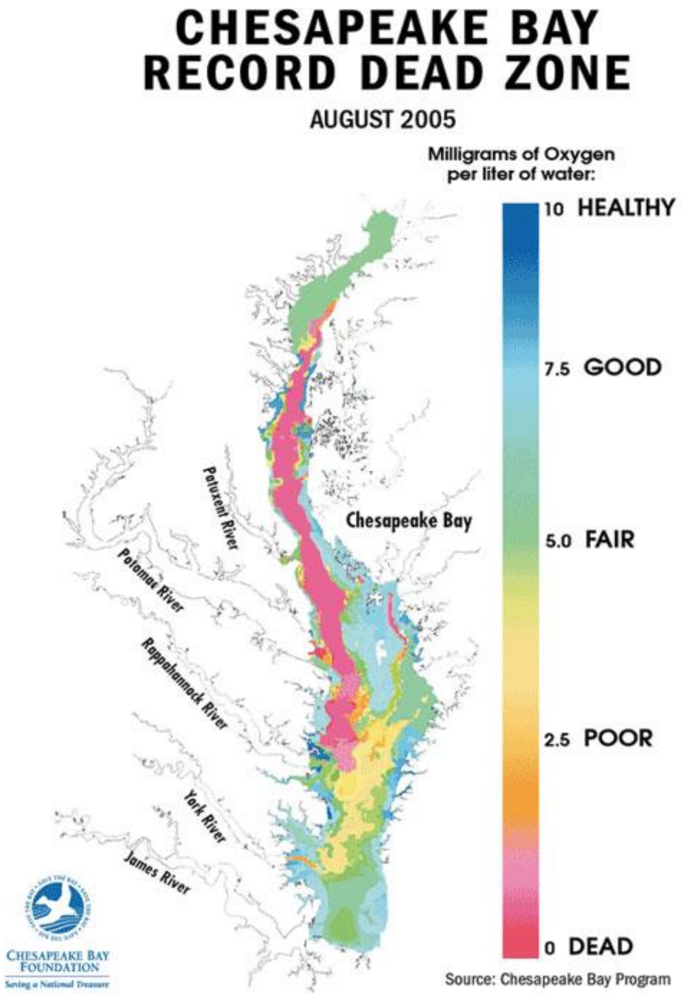
$$HRT_n = \frac{V_R}{Q_i}$$

SRT and **HRT** are separated in WWT because **biomass is retained. SRT** is controlled by **sludge wasting** → microbes can be recycled back into the reactor with return activated sludge, so they stay much longer than the water. WHY?

- **Maintains high biomass concentration** → more microbes available to degrade organic matter and nutrients.
- **Decouples SRT from HRT** → microbes can be kept longer than the water, allowing growth of slow-growing organisms (e.g., nitrifiers).
- **Improves process stability** → system can handle variable loads without washing out microbes.
- **Enhances treatment efficiency** → higher removal of BOD, nitrogen, and phosphorus.

Need for nutrient removal

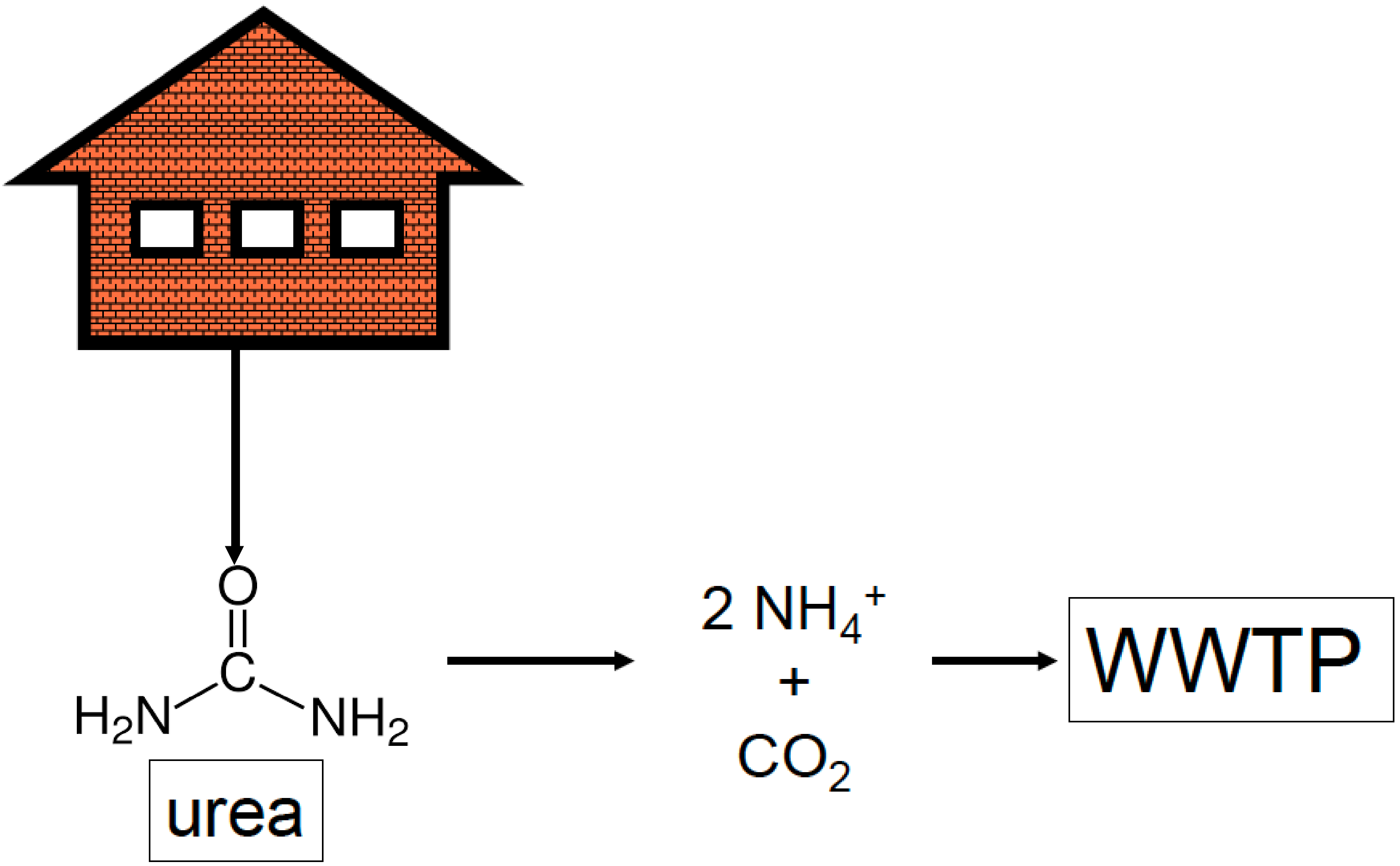
- Why do we need nitrogen oxidation/removal?
- NH_3 is toxic to fish,
  - exerts O_2 demand
  - N stimulates algae growth, contributes to accelerated eutrophication



Relevance

- Wastewater contains: Org-N and NH_3 (= TKN, Total Kjeldahl Nitrogen)
- Org-N is broken down to NH_3 (ammonification)
- NH_3 supports microbial growth (N assimilation)
- If BOD:TKN < 25, indicates excess NH_3

Nitrogen that arrives at WWTP



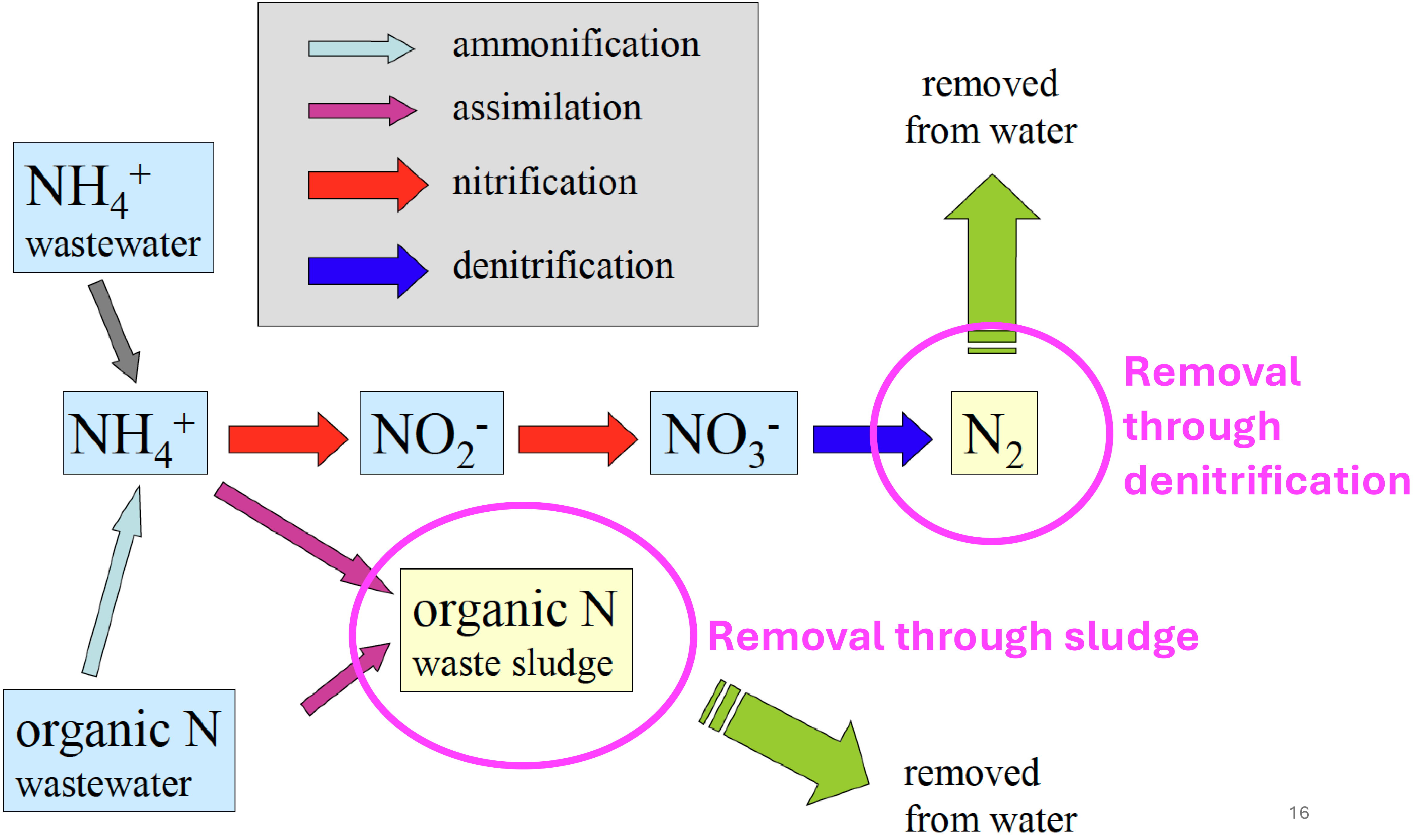
Concentrations of different forms of nitrogen in Swiss urban wastewater

Form of nitrogen	Concentration in wastewater (mg N/L) or (g N/m^3)			Proportion (%)
	normal	concentrated	diluted	
total nitrogen*	50	80	30	100
ammonium	30	50	18	~60
nitrate	0.5	0.5	0.5	0.5-3
organic nitrogen	20	30	12	~40

* total nitrogen = Kjeldahl nitrogen

Effluent quality standards as requested by Swiss legislation (OEaux 1998)

Parameter	Size WWTP (capita)	Concentration (mg/L)	Treatment efficiency (%)
SS	< 10'000 > 10'000	20 15	-- --
BOD_5	< 10'000 > 10'000	20 15	90 90
$N\text{-}NH_4$	--	2 (if possibility of negative impact on receiving surface water)	90 ($N\text{-}NH_{4,eff}$ / TKN_{inf})
$N\text{-}NO_2$	--	0.3 (indicative value)	--
Total N	--	If WWTP effluent discharged in sensitive surface waters, one has to try to remove as much N as possible at reasonable costs.	--
Total P	--	0.8 (if WWTP effluent discharged in lakes and river Rhine)	80


ammonification
assimilation
nitrification
denitrification
removed from water
NH_4^+ wastewater
NH_4^+
NO_2^-
NO_3^-
N_2
Removal through denitrification
organic N waste sludge
Removal through sludge
organic N wastewater
removed from water

Oxidation states of nitrogen

Oxidation States of Key Nitrogen Compounds

Compound	Oxidation state of N atom
Organic	−3
Ammonia (NH_3)	−3
Nitrogen gas (N_2)	0
Nitrous oxide (N_2O)	+1 (average per N)
Nitric oxide (NO)	+2
Nitrite (NO_2^-)	+3
Nitrogen dioxide (NO_2)	+4
Nitrate (NO_3^-)	+5

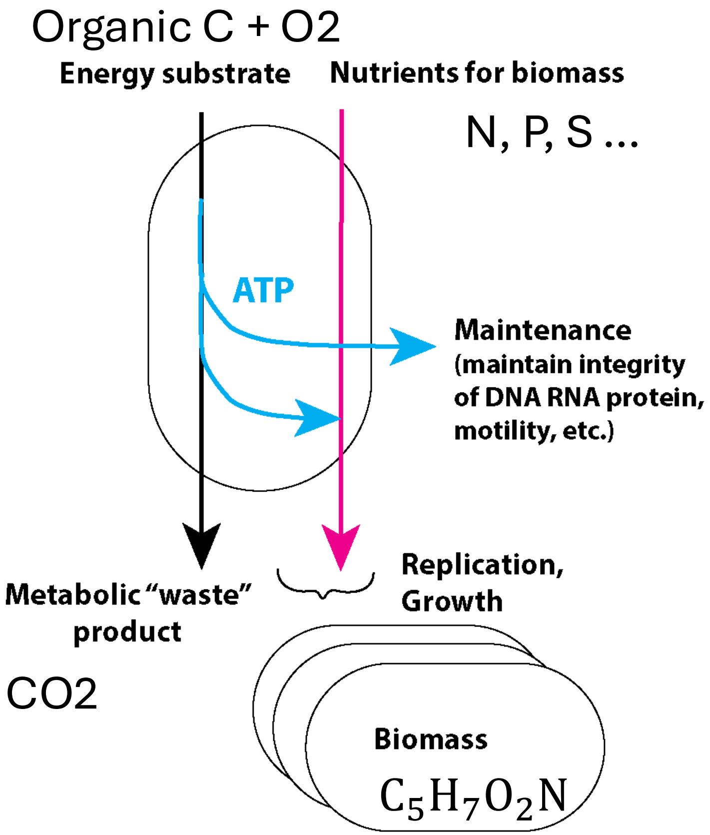
Inorganic nitrogen compounds are some of the most common electron acceptors in anaerobic respiration

Nitrogen is first removed through sludge produced by aerobic heterotrophs as part of their biomass.

- Microbes eat certain ratio of N and C for growth:
- **0.045 g N / g BOD5**

Since **nitrogen assimilation is directly proportional to *biodegradable* substrate utilization (growth)**, we relate it to **BOD_5, not COD**.

- In this way, removal of C and N is always coupled by a certain ratio. If N is high, we need other bacteria to degrade it more independently and directly.

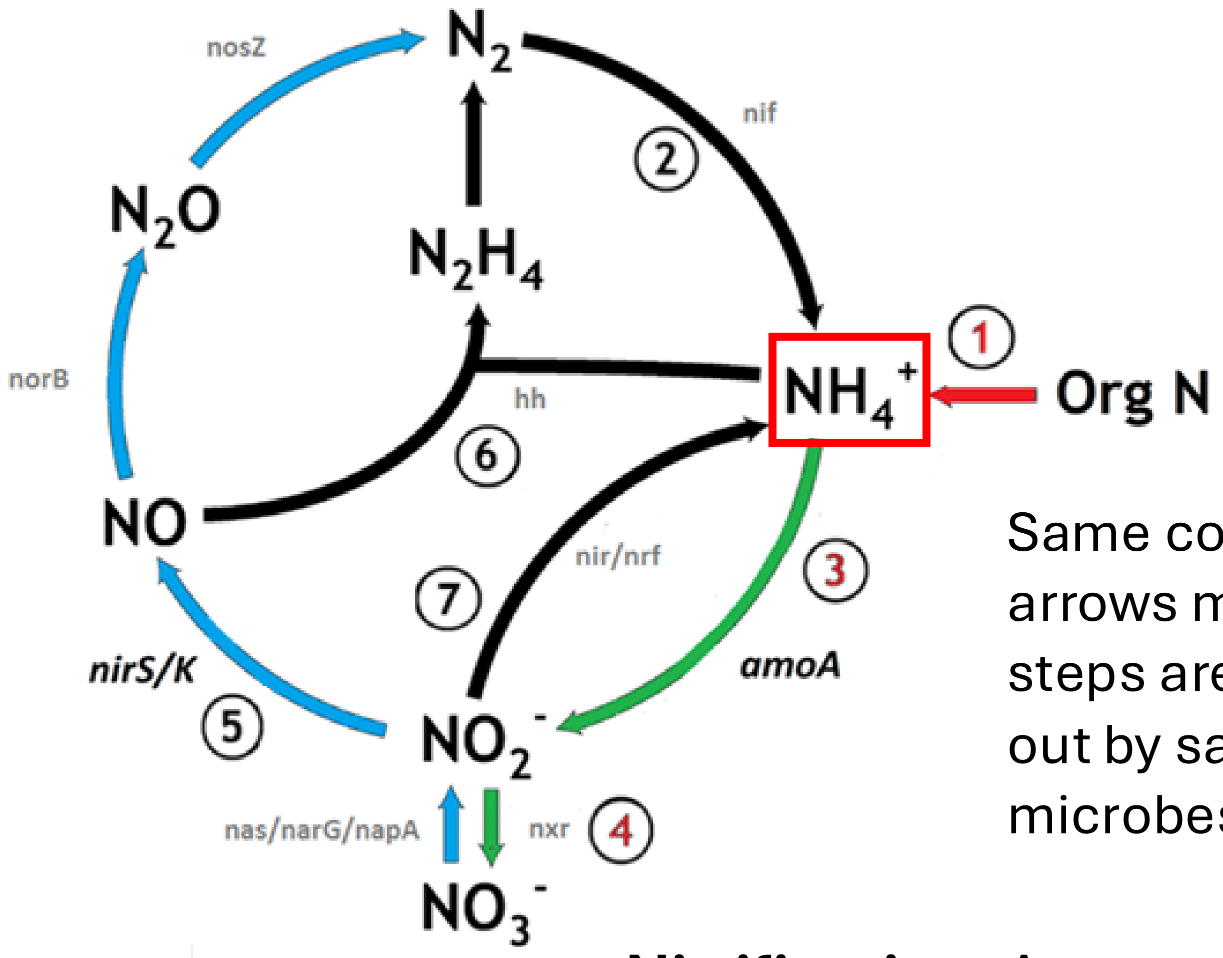


Additional (majority) of N is removed by nitrification+denitrification

Nitrification: Ammonia (NH_4^+) → nitrite (NO_2^-) → nitrate (NO_3^-)

Denitrification: NO_3^- → N_2 gas

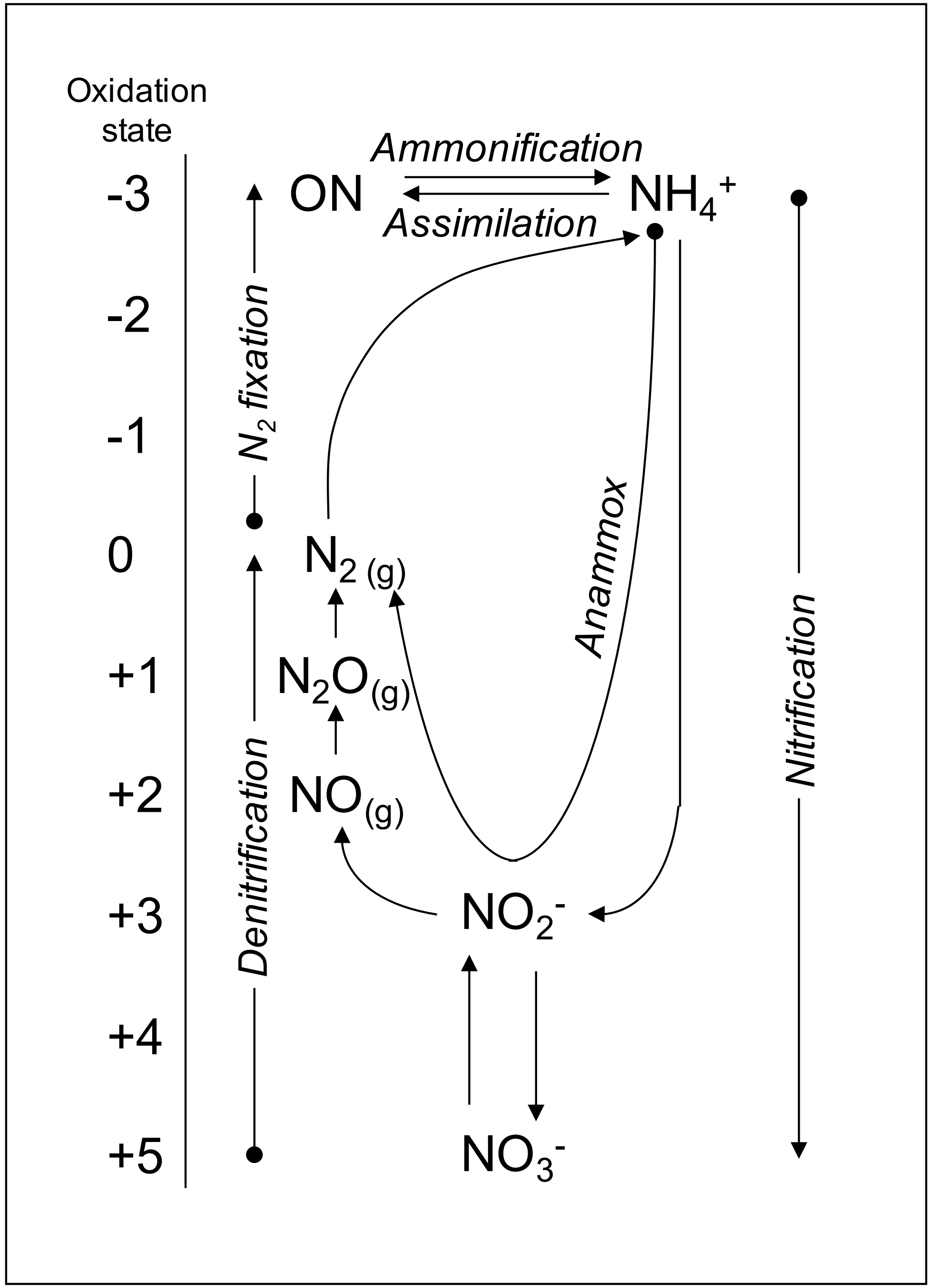
Redox Cycle for Nitrogen



Same color of arrows means the steps are carried out by same kind of microbes.

Nitrification: Ammonia (NH_4^+) → nitrite (NO_2^-) → nitrate (NO_3^-)

Denitrification: NO_3^- → N_2 gas



Nitrification

- Nitrification is carried out by two groups of aerobic bacteria and archaea: (autotrophic, chemolithotrophic, aerobic)
- AOBs (Nitrosomonas, *Nitrosococcus, Nitrosopira*) and AOAs
- NOBs (*Nitrobacter, Nitropira, Nitrococcus*)
- Note: comammox can do both steps, oxidizing ammonia to nitrate, but is not competitive against AOB and NOB.

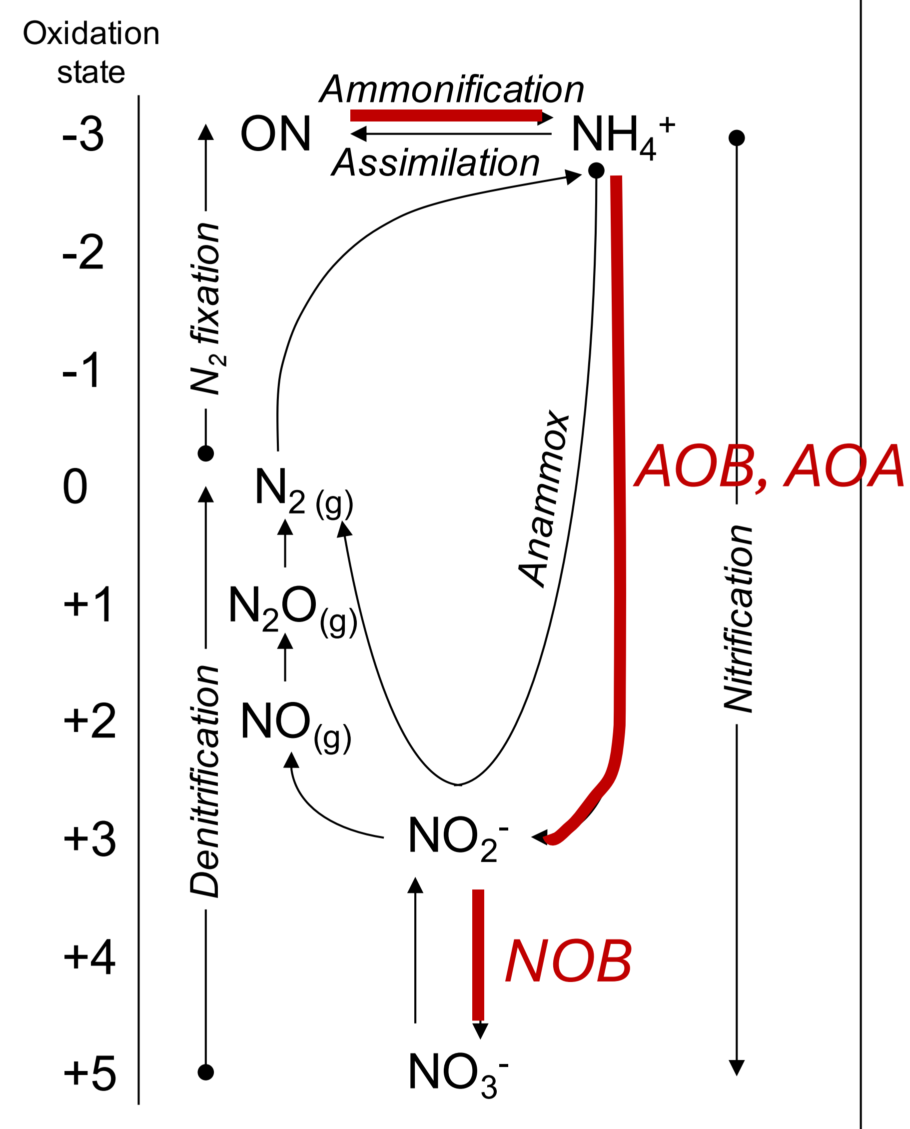


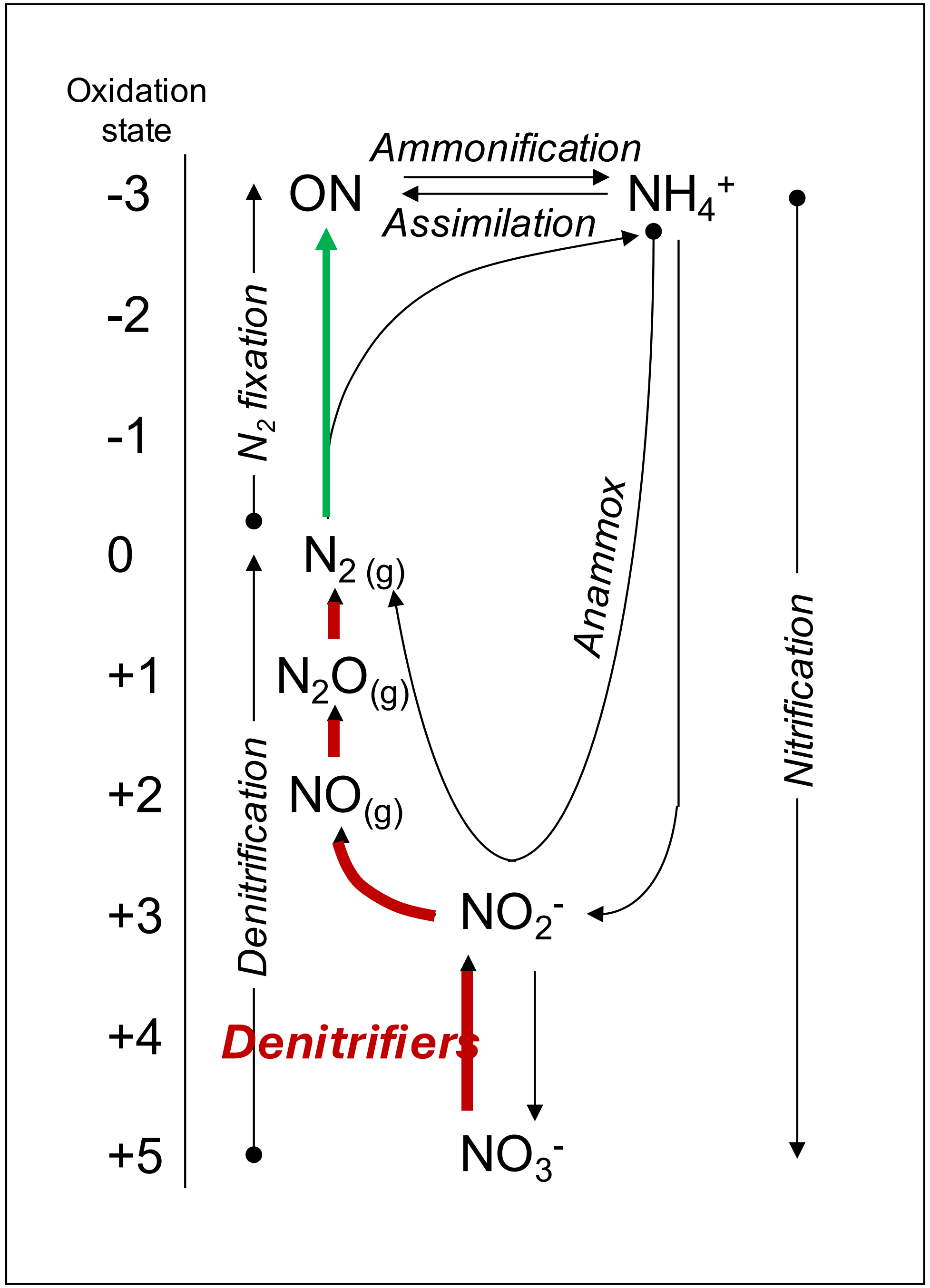
Figure 2.1, GDLF

$$NH_4^+ + 1.816O_2 + 0.1316CO_2 \rightarrow 0.0263\,C_5H_7O_2N + 0.974NO_3^- + 1.974H^+ + 0.92H_2O$$

Denitrification

- Anoxic
- Can be reduced with two electrons to nitrite or further to nitric oxide, nitrous oxide, or dinitrogen
- N_2O is a very very potent greenhouse gas

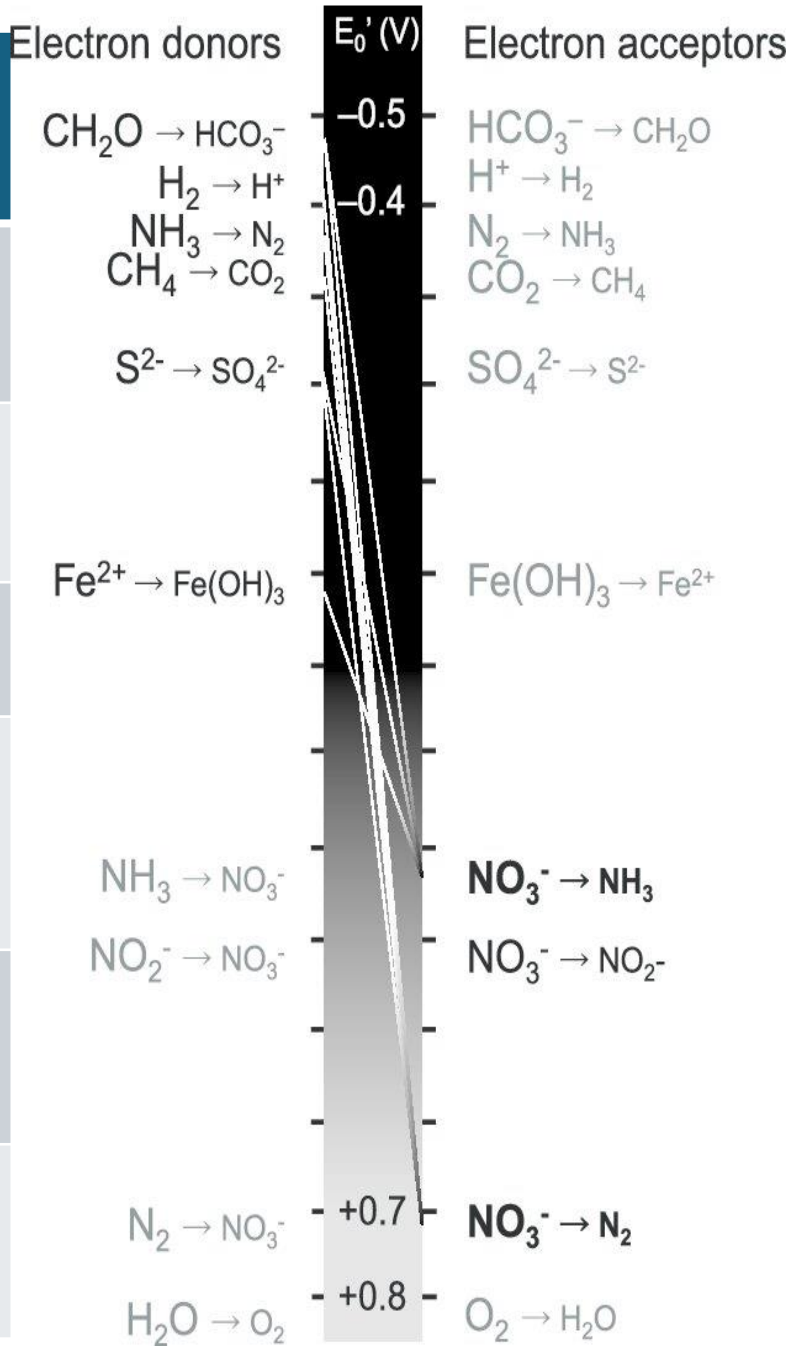
Nitrous oxide is considered to be 265 to 273 times worse than CO_2 over a 100-year timescale.



Compare!!

HOMEWORK

Name	Aerobic heterotrophs	Nitrifiers (autotroph)	Denitrifiers (heterotrophs)
Need O2 as electron acceptor?	Yes	Yes	No
What is the electron donor for energy?	Organic C	Ammonia	Organic C
Energy production reaction	Organic C + O2 → CO2 + H2O + NH3	NH_3 + O2 → NO_2^- NO_2^- + O2 → NO_3^-	Organic C + NO_3^- + → N2 + CO2
What is the carbon source for biomass synthesis??	Organic C	CO2!!!	Organic C
Where does the energy couple sit on redox tower?	Very far away	Closer	Quite far away
Growth rate and yield	Faster, more biomass/substrate	Slower, less biomass/substrate	Kind of fast, much biomass/substrate



Nitrification

- Low growth rate (µm) and yield (Y), needs larger SRT (Θ_c)
- Low Ks, ~ 1 mg N/L, can get very low effluent NH_3 concentration, zero order
- Sensitive to temperature changes – low T needs larger SRT
- Sensitive to pH. Need to keep pH > 6.5
- Generate H^+, consume alkalinity, needs 7 g CaCO3/g NH4+-N
- Conventional wisdom… need high D.O. > 0.5 mg/L,

Nitrifiers are specialized bacteria needing oxygen as electron acceptor and having a slow growth rate

HOMEWORK 2

Nitrification (1)	Nitrification (2)
$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + H_2O + 2\ H^+$	$NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$
$\Delta G^\circ = -270$ (kJ/mol NH_4^+-N)	$\Delta G^\circ = -80$ (kJ/mol NH_4^+-N)
Nitrosomonas *Nitrosospira* *Nitrosococcus*	*Nitrobacter* *Nitrospira*

Growth difference: *Nitrosomonas* grows faster than *Nitrobacter*. This is related to the difference in energy-producing metabolic reaction.

AOBs (ammonia oxidizing bacteria) vs NOBs (nitrite oxidizing bacteria)

- NOBs have a higher substrate utilization rate than AOBs (exhibit a higher specific substrate utilization rate)

- Adjust growth conditions that differentially affect AOB and NOB
  - An alkaline pH (7.5–8.5) favors the growth of AOB over NOB
  - At 35^{o}C, AOB grows faster than NOB

Nitrification reactions including biomass formation

HOMEWORK 2

$$80.7NH_4^+ + 114.55\ O_2 + 160.4\ HCO_3^- \longrightarrow$$
$$C_5H_7NO_2 + 79.7\ NO_2^- + 82.7\ H_2O + 155.4\ H_2CO_3$$

$$134.5NO_2^- + NH_4^+ + 62.25\ O_2 + HCO_3^- + 4\ H_2CO_3 \longrightarrow$$
$$C_5H_7NO_2 + 134.5\ NO_3^- + 3\ H_2O$$

$$NH_4^+ + 1.86\ O_2 + 1.98\ HCO_3^- \longrightarrow$$
$$0.020\ C_5H_7NO_2 + 0.98\ NO_3^- + 1.88\ H_2CO_3 + 1.04\ H_2O$$

Nitrifiers grow slower than heterotrophs (the ones that eat organic carbon for energy), this needs to be taken care of.

Growth rates of differents organisms

Bacteria	μ_{max} [d^{-1}]			t_d [h]	
	10°C	20°C	30°C	10°C	20°C
Nitrosomonas	0.30	0.85	2.47	55	20
Nitrobacter	0.55	1.11	2.06	31	18
Heterotrophic bacteria	3	6	--	5.5	2.8
E. coli	--	--	30*	--	33 min

* at 37°C

Note: here u_{max} is the maximum growth rate they can reach under specificied temperature and optimized conditions. Real growth rate need to be corrected for the reactor environment.

Nitrification and Its Impacts

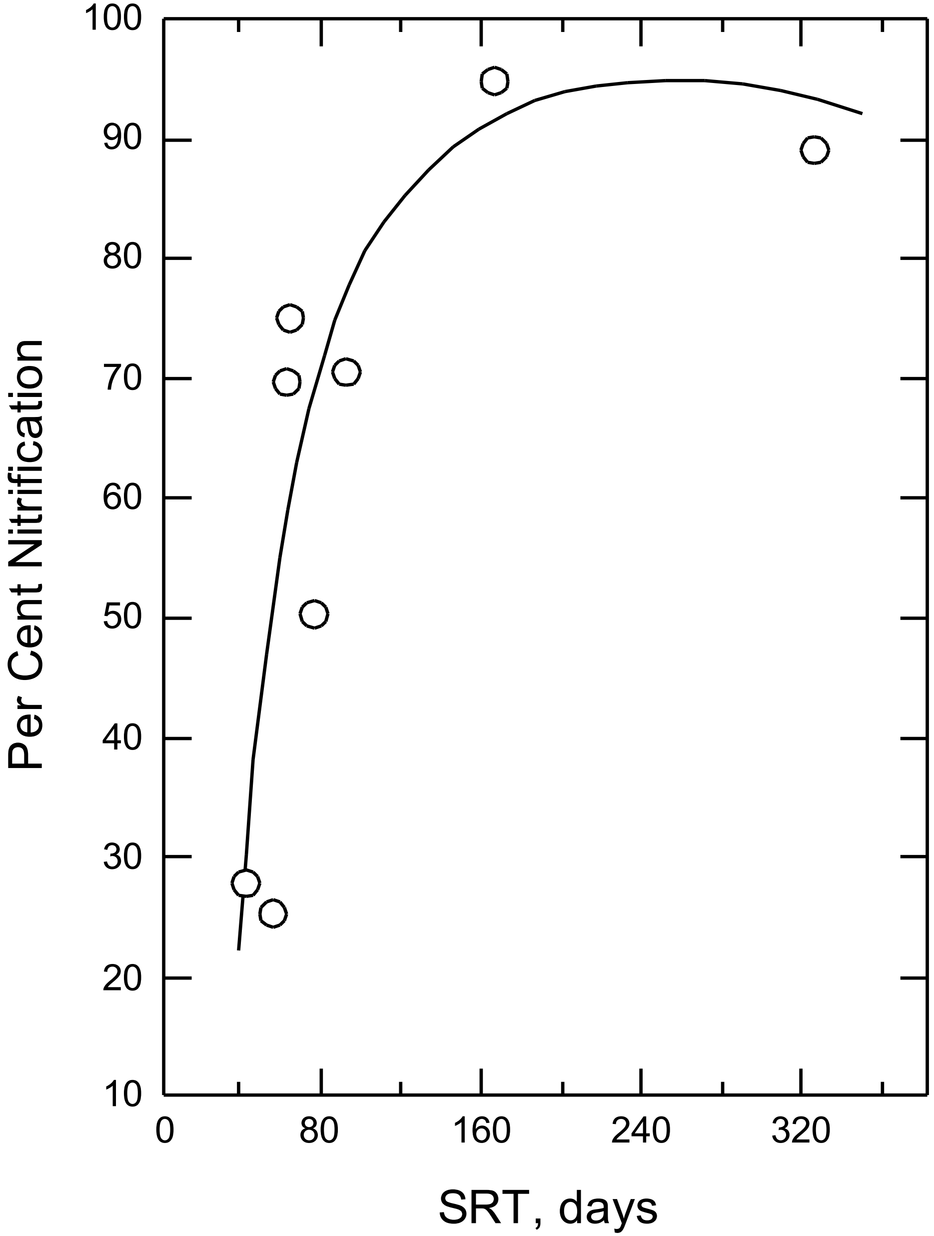


Figure 6.6 Effect of SRT on the performance of nitrification in a CSTR receiving a wastewater containing inhibitory compounds. (Adapted from Bridle et al.[8])

Nitrification and Its Impacts

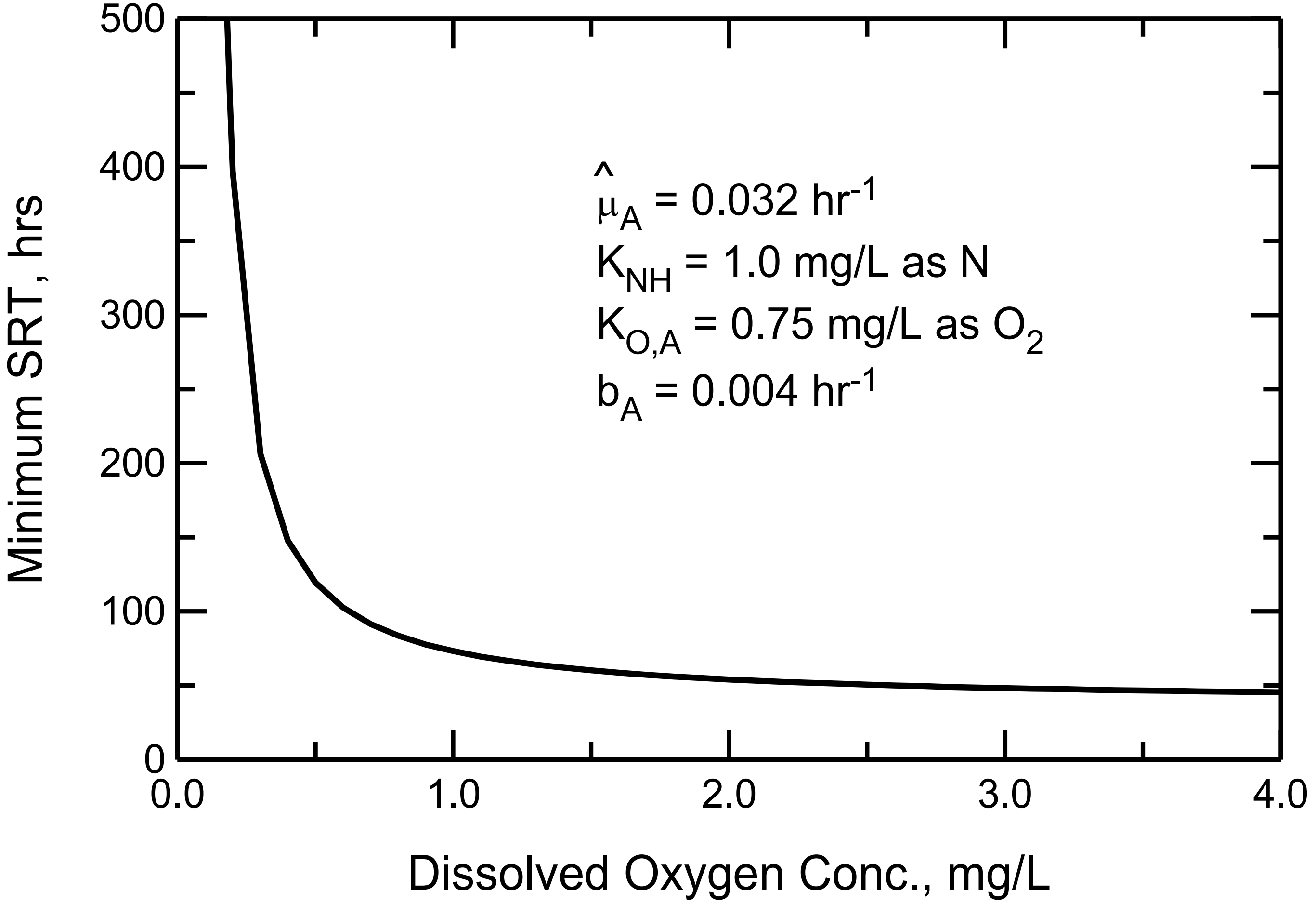


Figure 6.7 Effect of dissolved oxygen concentration on the minimum SRT required for nitrification in a CSTR receiving an ammonia-N concentration of 30 mg/L. Parameter values are for a temperature of 20°C.

Nitrification and Its Impacts

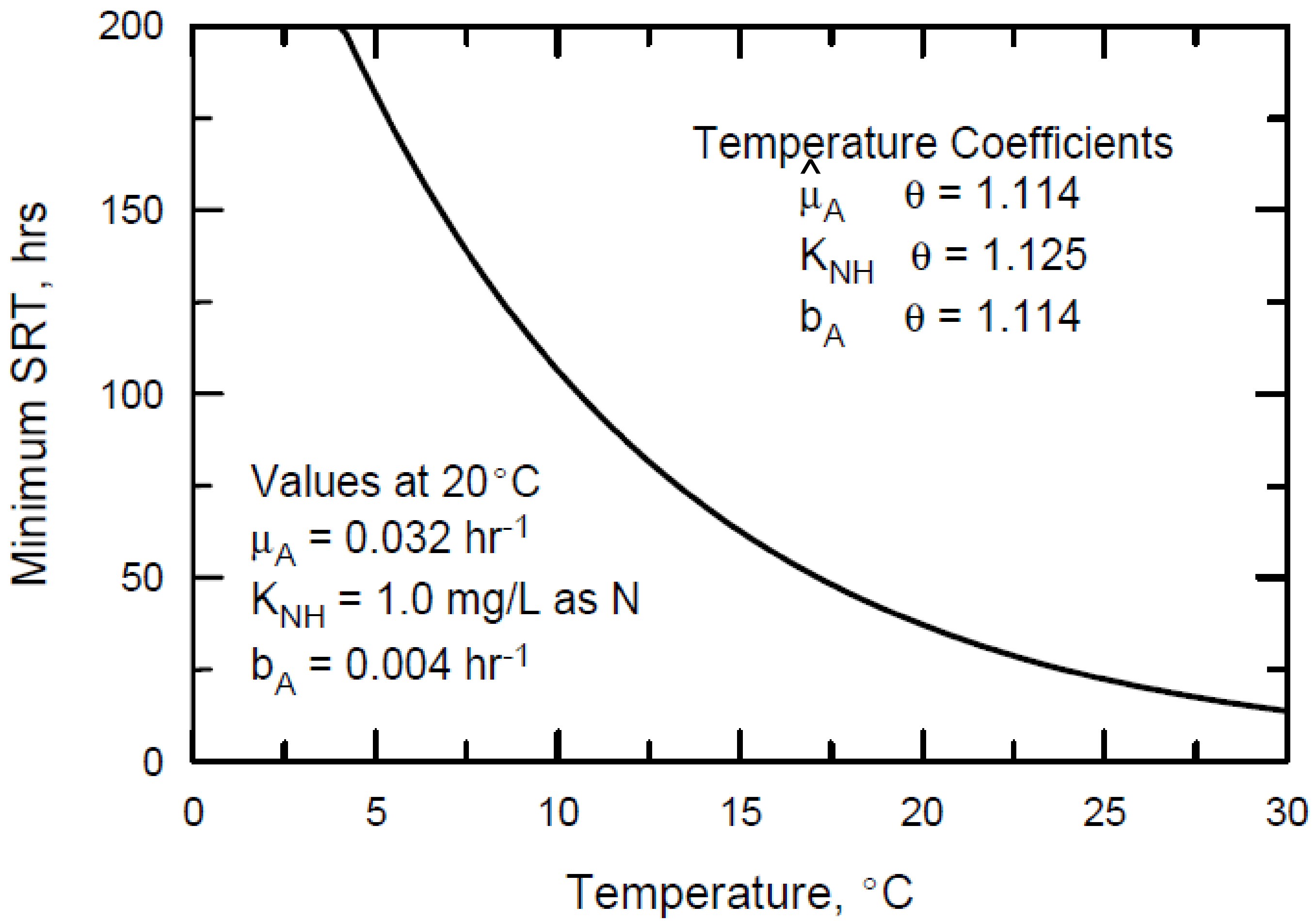


Figure 6.8 Effect of temperature on the minimum SRT required for nitrification in a CSTR receiving an ammonia-N concentration of 30 mg/L. The dissolved oxygen concentration is not limiting.

Nitrification and Its Impacts

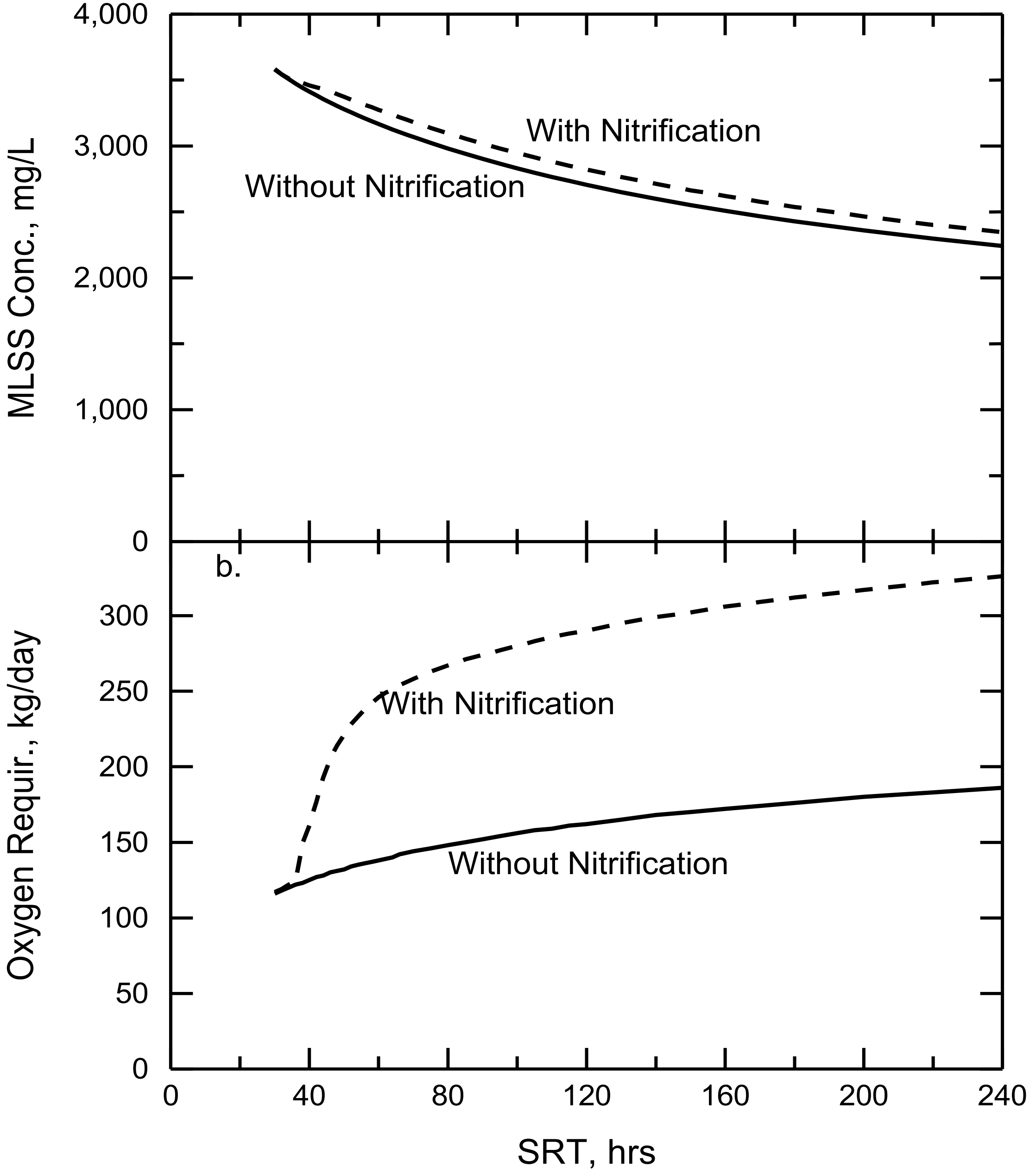
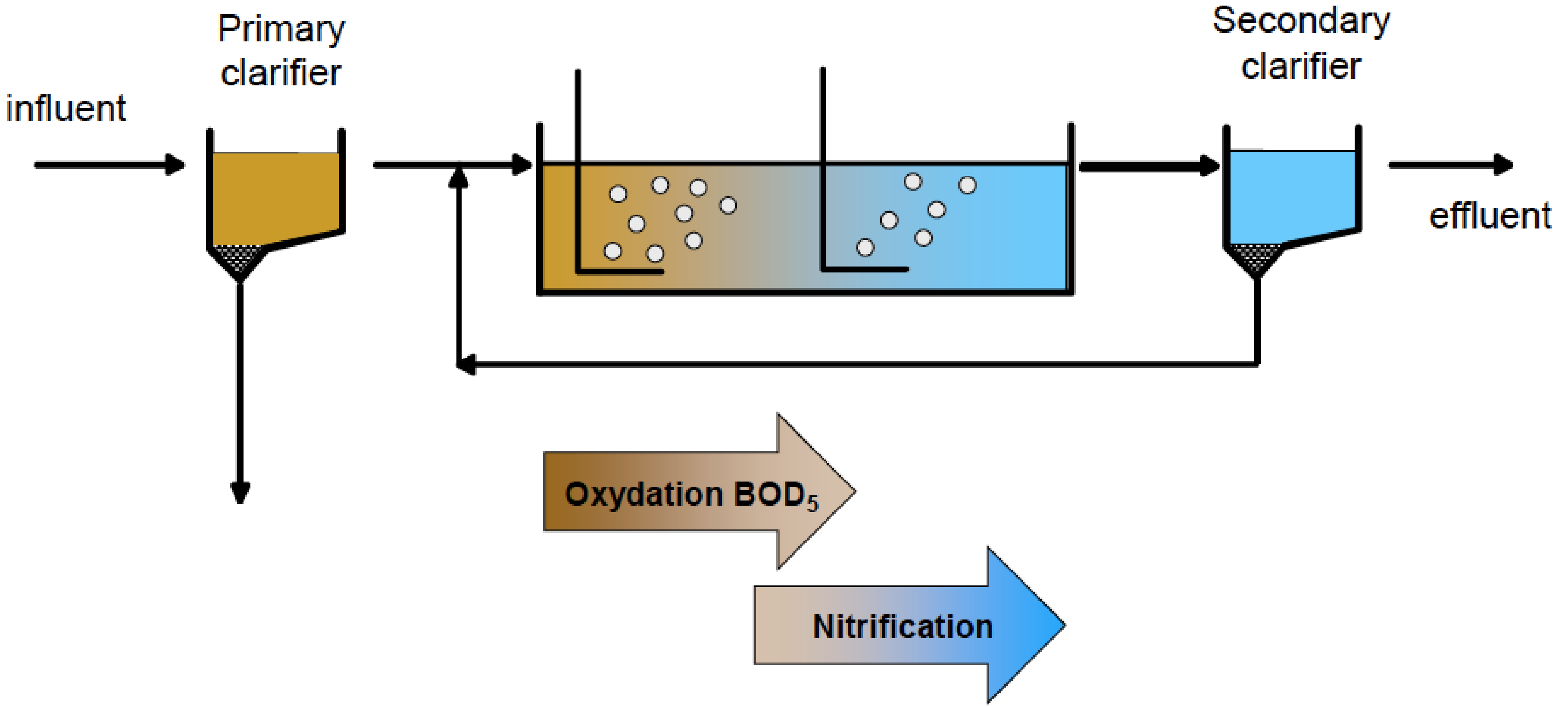


Figure 6.9 Effects of SRT and nitrification on the MLSS concentration and oxygen requirement in a CSTR with $\Theta_c/\tau = 20$. Parameter values are given in Table 6.3 and the influent conditions are given in Table 6.6. The value of was set equal to zero to eliminate nitrification in one case. The dissolved oxygen concentration was fixed at 4.0 mg/L. The MLSS concentration is expressed in COD units; to convert to TSS units, divide by $i_{O/XB,T}$ = 1.2 mg COD/mg TSS.

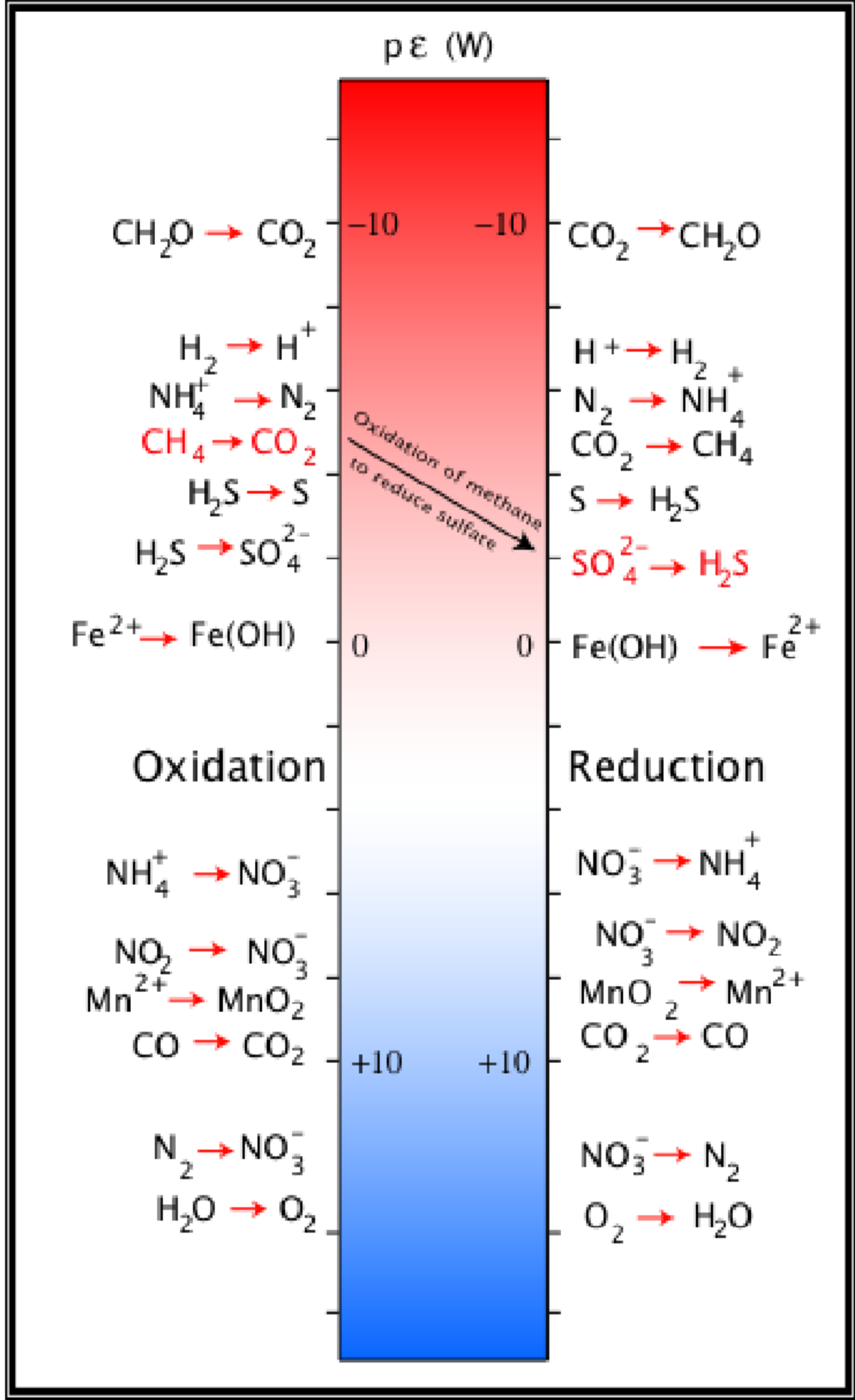
Nitrifiers normally lose competition with heterotrophs for O_2 asking for separation of the two processes nitrification and aerobic organic matter degradation



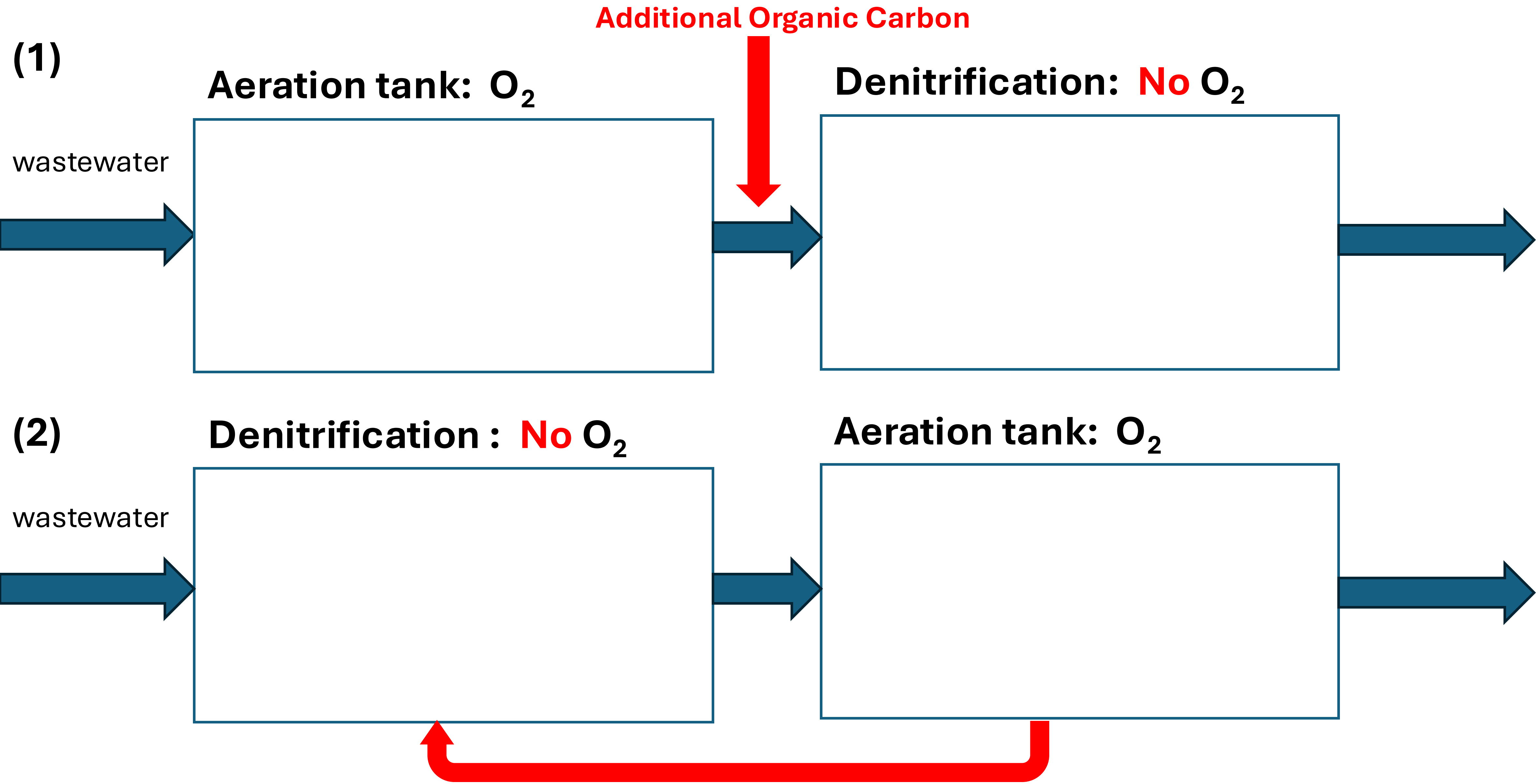
Implementation of denitrification

Denitrifyers are heterotrophic bacteria using nitrate as electron acceptor if no oxygen is present.

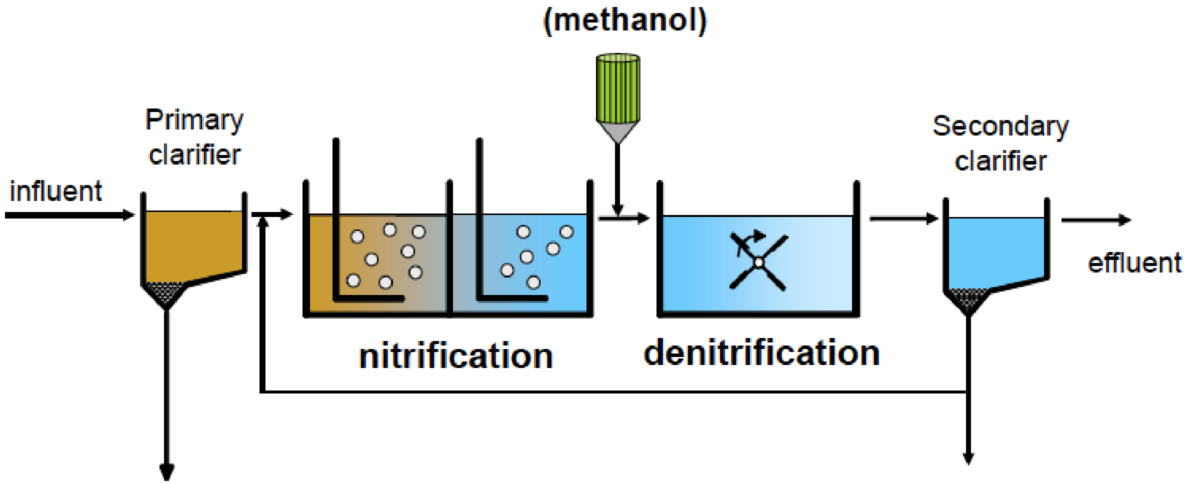
Denitrifyers **need organic matter as energy and carbon source** as the other half of the redox reaction.



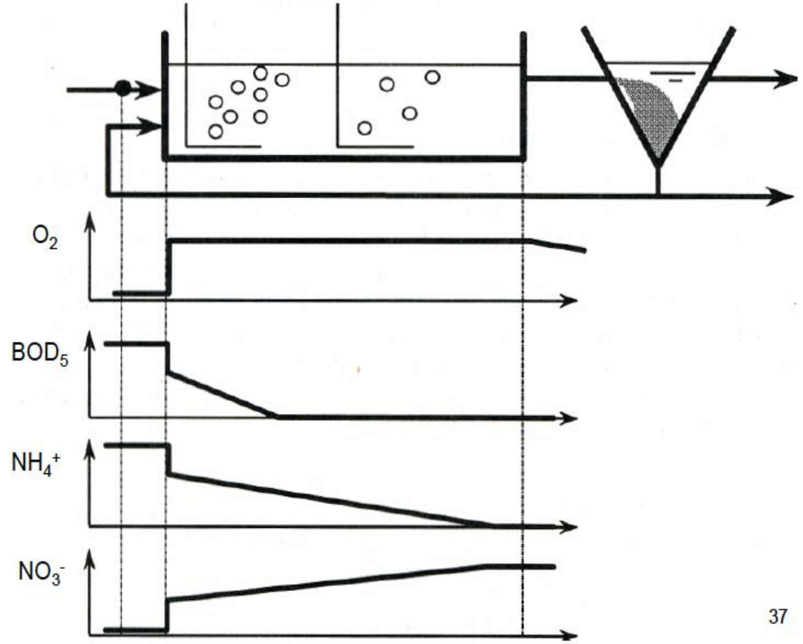
We have two options here, what are the consequences?



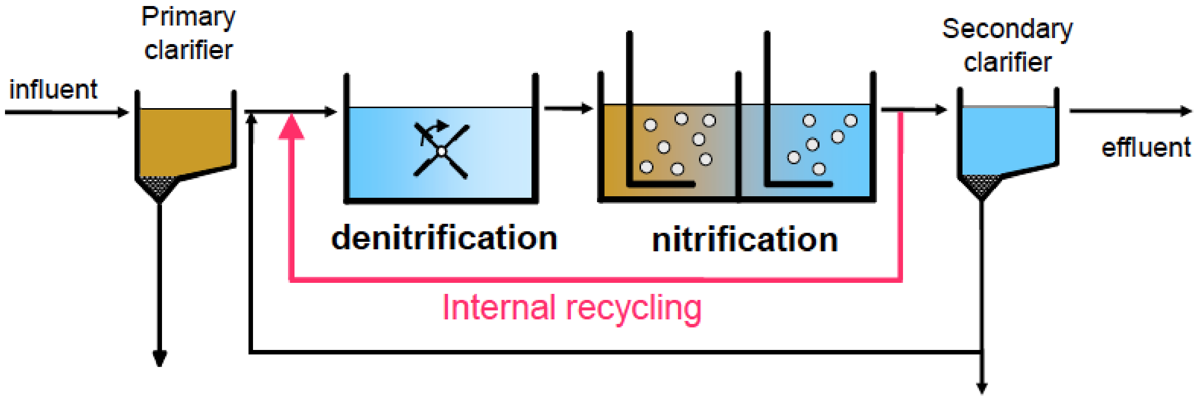
Post-denitrification in activated sludge systems

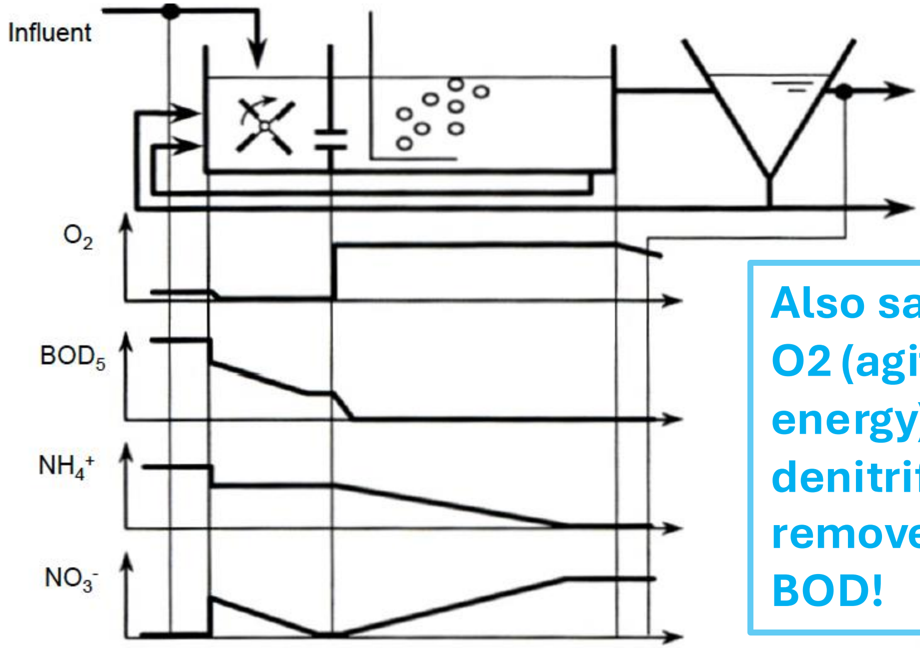


Concentration profiles in aeration tank with plug-flow mode



Pre-denitrification in activated sludge systems





Also save some O2 (agitation energy) if we use denitrification to remove some BOD!

Denitrification

Depends on where the denitrication reaction sits in the treatment train, ammonia may or may not be available as nitrogen source direct for biomass synthesis:

$$NO_3^- + 6\,H^+ + 5\,e^- \rightarrow 0.5\,N_2 + 3\,H_2O$$

Pseudomonas, Bacillus, Spirillum, Hyphomicrobium, Agrobacterium, Acinetobacter, Propionobacterium, Rhizobium, Coryne-bacterium, Cytophage, Thiobacillus, Alcaligenes, ……

$$0.65\,C_{18}H_{19}O_9N + 4.89\,NO_3^- + 4.89\,H^+ \rightarrow C_5H_7NO_2 + 2.27\,N_2 + 6.7\,CO_2 + 5.12\,H_2O$$

Denitrification reactions including organic matter oxidation, nitrogen assimilation, and biomass formation

$$0.61\,C_{18}H_{19}O_9N + 4.54\,NO_3^- + 0.39\,NH_4^+ + 4.15\,H^+ \longrightarrow C_5H_7NO_2 + 2.27\,N_2 + 5.98\,CO_2 + 5.15\,H_2O$$

$$0.65\,C_{18}H_{19}O_9N + 4.89\,NO_3^- + 4.89\,H^+ \longrightarrow C_5H_7NO_2 + 2.27\,N_2 + 6.7\,CO_2 + 5.12\,H_2O$$

What also changes during the nitrication/denitrification processes?

HOMEWORK

Nitrification releases H^+
Denitrification consumes H^+

Alkalinity
Alkalinity is a measure of **the capacity of water to neutralize acids** (i.e., to resist a decrease in pH).

Most treatment processes generate acids, not bases. For example, biological oxidation of organics → CO_2 → carbonic acid. So we use Alkalinity as a critical parameter instead of acidity!

- Alkalinity measures the "buffering capacity" of water.
- In natural and engineered waters, alkalinity comes mainly from bicarbonate (HCO_3^-), carbonate (CO_3^{2-}), and hydroxide (OH^-) ions.

Denitrification and Its Impact

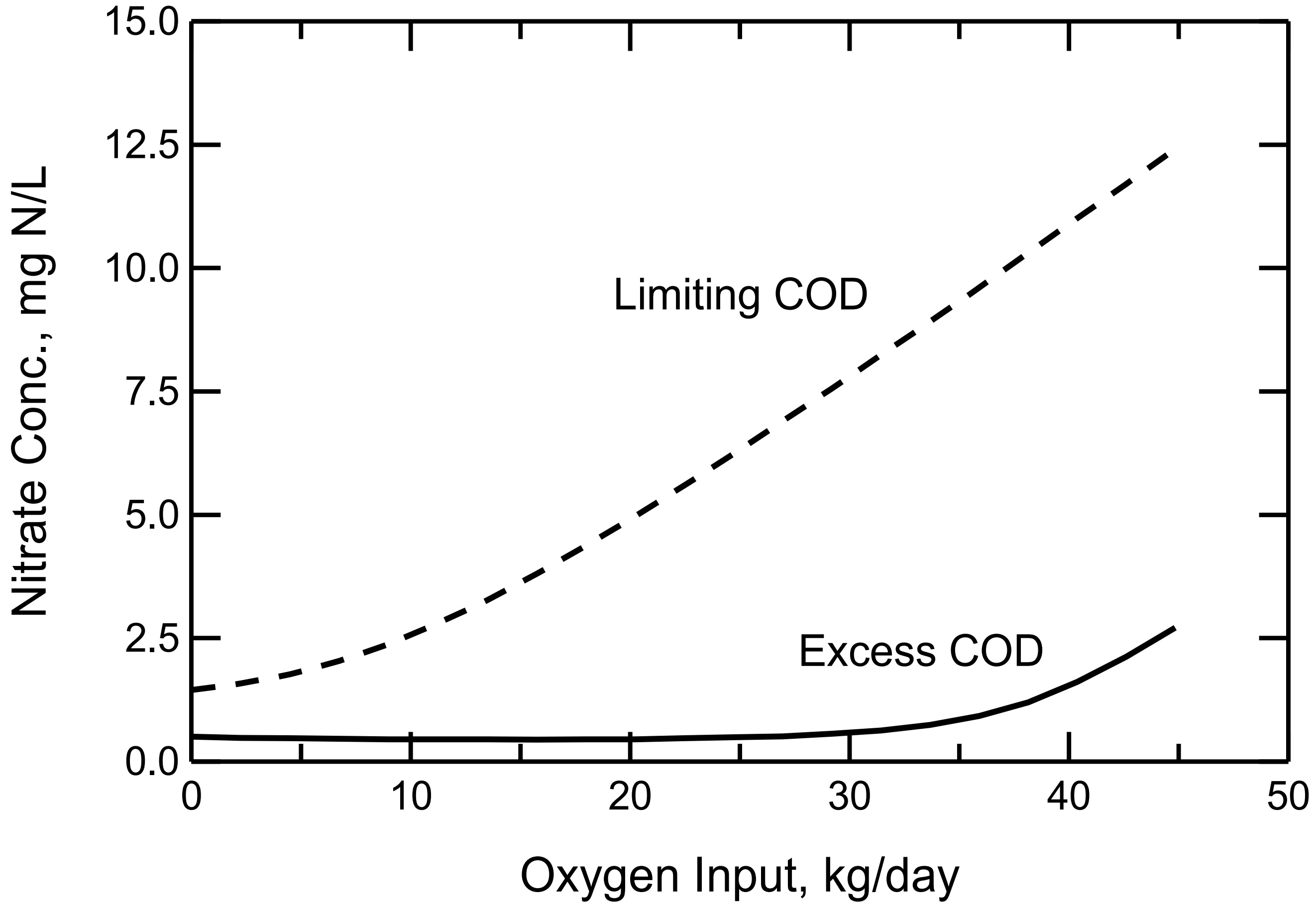


Figure 6.11 Effect of oxygen input rate on denitrification in a CSTR operated at an SRT of 240 hrs. Parameter values are given in Table 6.3 and the influent conditions are given in Table 6.6. For the limiting COD case the influent nitrate-N concentration was 60 mg/L whereas in the excess COD case it was 50 mg/L. The influent flow was 1000 m^3/day.

Denitrification and Its Impact

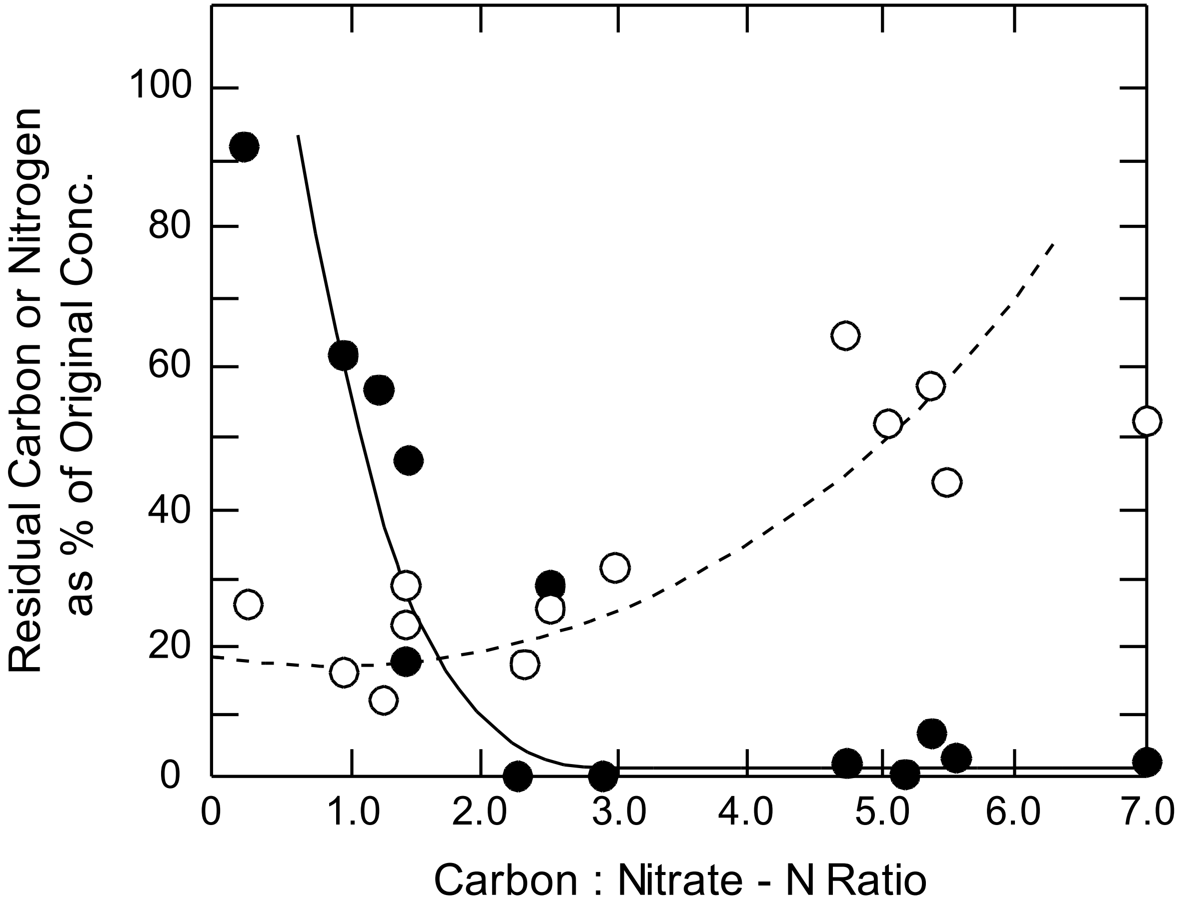


Figure 6.12 Effect of S_{SO}/S_{NOO} (expressed as C/N ratio) on the removal of carbon (○) and nitrogen (●) in a CSTR operated under anoxic conditions. (From K. Wuhrmann, Discussion of 'Factors affecting biological denitrification of wastewater' by R. N. Dawson and K. L. Murphy. *Advances in Water Pollution Research, Jerusalem, 1972*, 681-682, 1973. Reproduced by permission of Dr. K. L. Mechsner.)