Course Water and Wastewater Treatment – Part I

Wastewater treatment

Nutrient removal - 1

Biological removal: Basics and implementation
Chemical removal

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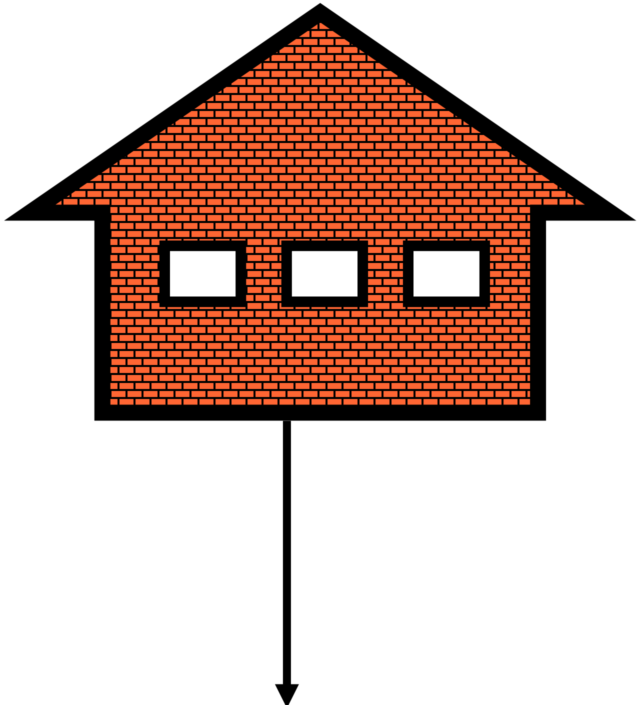
Nitrogen and phosphorous concentrations in wastewater treatment plant (WWTP) influent

Nitrogen that arrives at WWTP



$$O{=}C(NH_3)_2 \longrightarrow 2\ NH_4^+ + CO_2 \longrightarrow \text{WWTP}$$

urea

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

Concentrations of different forms of phosphorous in wastewater after utilisation of phosphate-free detergents

Form of phosphorous	Concentration in wastewater (mg P/L)			Proportion (%)
	normal	concentrated	diluted	
Total phosphorous	10	14	6	100
Ortho-phosphate	7	10	4	~70
Poly-phosphate	0	0	0	0
Organic Phosphorous	3	4	2	~30

Daily phosphorous release per capita according source

Source	Phosphorous release (g P/cap./day)		Proportion (%)	
	1980	1994	1980	1994
Urine	1.1	1.1	24	45
Feces	0.5	0.5	11	21
Food waste	0.3	0.3	7	13
Laundry	2.1	0.1	45	4
Other detergents	0.5	0.3	11	13
Constructed surfaces	0.1	0.1	2	4
Total	4.6	2.4	100	100

Daily phosphorous release per capita according form

Form of phosphorous		Phosphorous release (g P/cap./day)		Proportion (%)	
		1980	1994	1980	1994
Particulate phosphorous	*Total*	0.9	0.9	20	37
Dissolved phosphorous	*Total*	3.7	1.5	80	63
	Polyphosphate	***2.5***	***0.3***	***54***	***13***
	Orthophosphate	*1.0*	*1.0*	*22*	*42*
	Organic phosphorous	*0.2*	*0.2*	*4*	*8*
Total phosphorous		**4.6**	**2.4**	100	100

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

Wastewater standards in OEaux 1998 (état 1er juillet 2008)

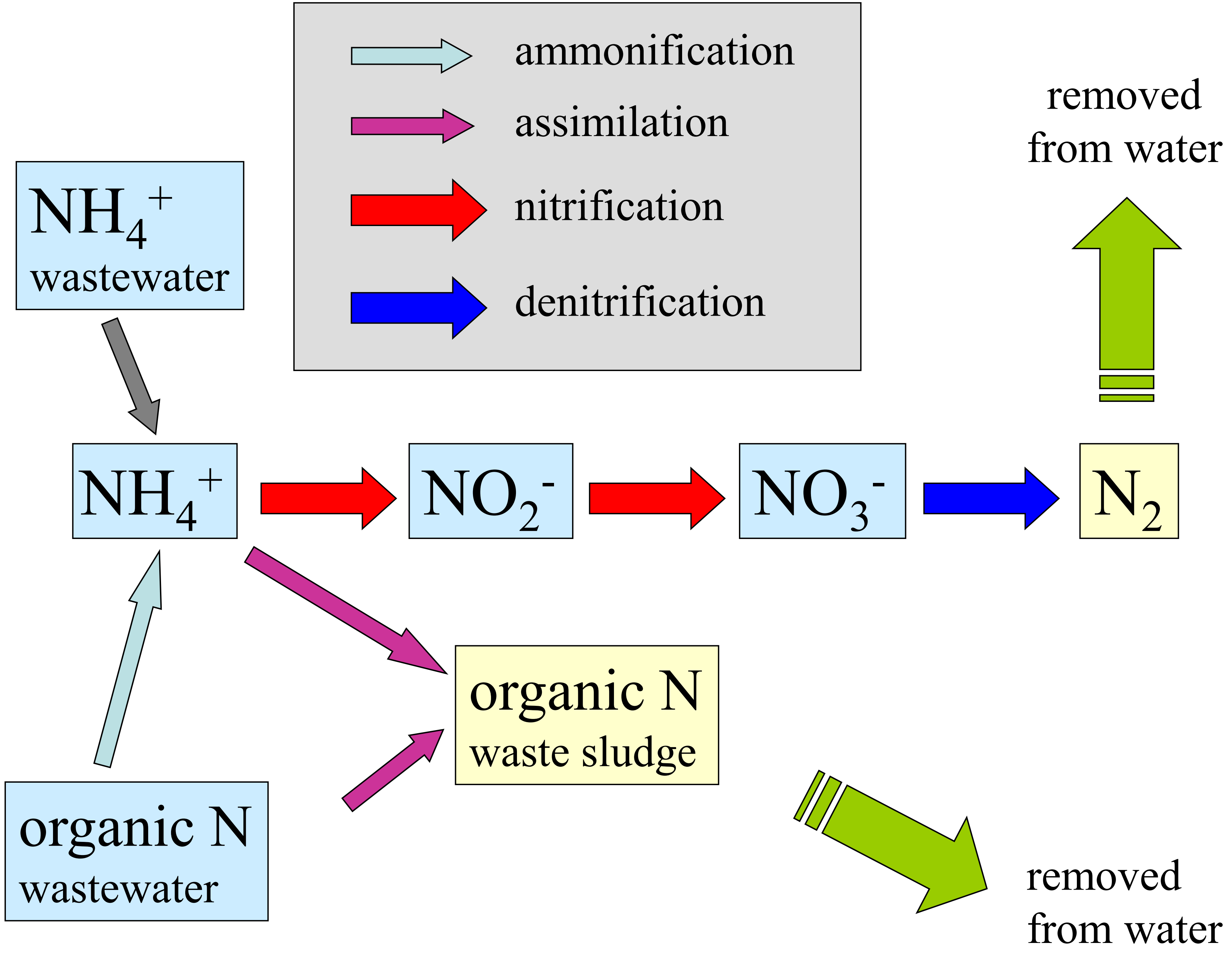
Parameter	Size WWTP (capita)	Concentration (mg/L)	Treatment efficiency (%)
SS	< 10'000 > 10'000	20 15	-- --
BOD_5	< 10'000 > 10'000	20 15	90 90
$N\text{-}NH_4$	--	2 (if possibility of negative impact on receiving surface water)	90 ($N\text{-}NH_{4,eff}$ / TKN_{inf})
$N\text{-}NO_2$	--	0.3 (indicative 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

Phosphorous – a valuable resource in waste sludge

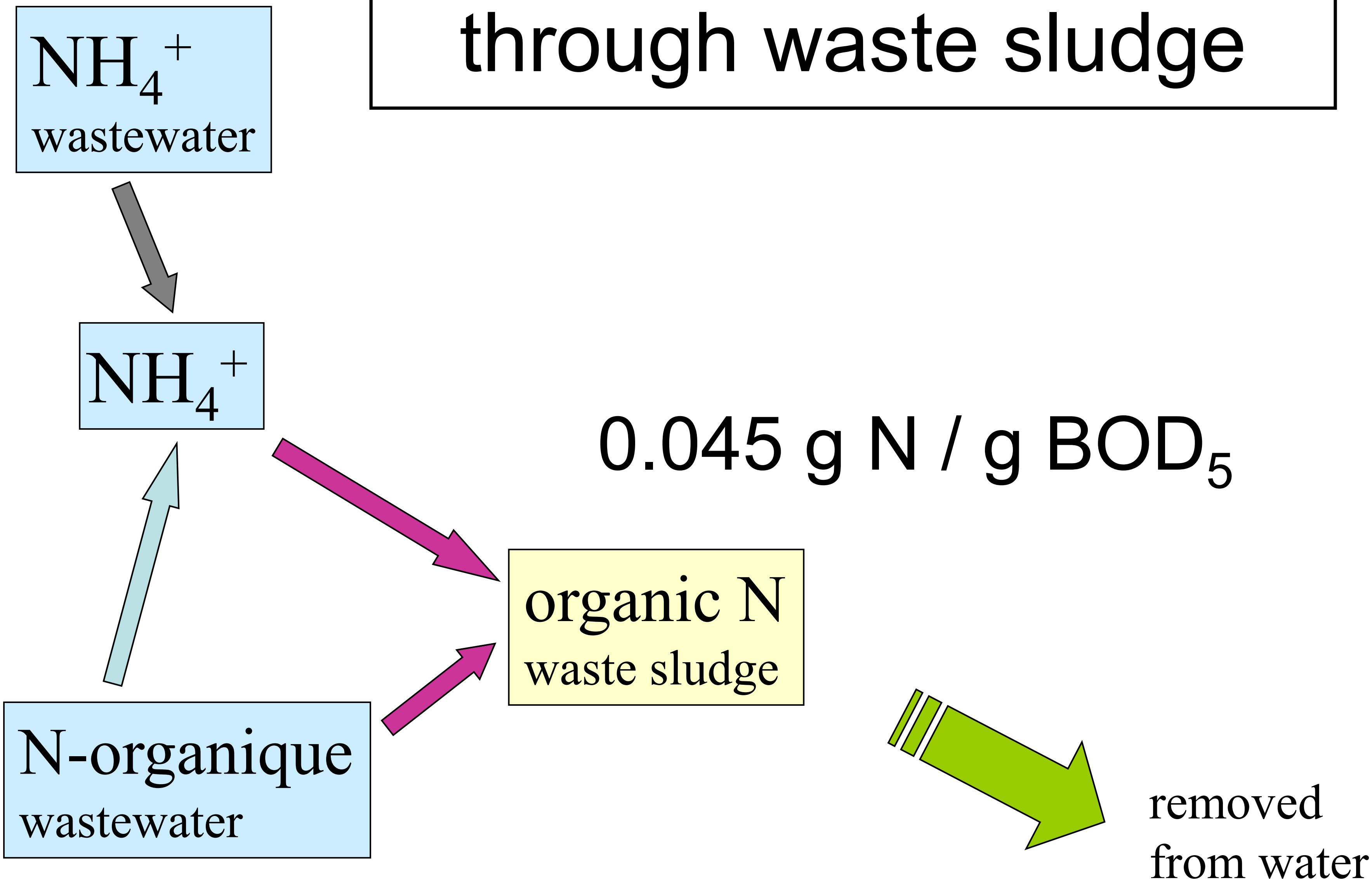
From 2026, the phosphorus from wastewater, sewage sludge or their ash must be recovered and upgraded

- The environmental authorities have decided to phase out waste sludge spreading in 2003 - and since 2006 all waste sludge has been incinerated.
- 64% is disposed of in sludge incineration plants, 14% in household waste incineration plants and the remaining 22% in cement factories.
- The 783 **Swiss wastewater treatment plants produce nearly 5,700 tonnes of phosphorus each year**, which could be recovered and thus **meet the needs of agriculture with a native source**.
- Switzerland imports nearly 15,000 net tonnes of phosphorus each year, of which 4,200 in the form of mineral fertilizers, 6,200 as fodder and 2,600 as food.

Biological nitrogen removal


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

Nitrogen removal through waste sludge



$0.045\ g\ N\ /\ g\ BOD_5$

Removal of nitrogen by waste sludge

	Concentration in wastewater (mg/L) ou (g/m^3)		
	normal	**concentrated**	**diluted**
BOD_5	250	350	150
Total nitrogen	50	80	30
Eliminated by waste sludge (mg/L)	12.5	17.5	7.5
Eliminated by waste sludge (%)	25	22	25

Nitrification (1)

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + H_2O + 2\ H^+$$

$$\Delta G° = -270\ (kJ/mol\ NH_4^+\text{-}N)$$

Nitrosomonas
Nitrosospira
Nitrosococcus

$$NH_3 + O_2 + 2\ H^+ \rightarrow NH_2OH + H_2O$$

ammonium mono-oxygenase
(amoA)
(inhibited by thiourea and hydrazine)

Nitrification (2)

$$NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$$

$$\Delta G° = -80\ (kJ/mol\ NH_4^+\text{-}N)$$

Nitrobacter
Nitrospira

Nitrification reactions including biomass formation

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

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

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

Influence of temperature on growth rate

$$\mu_{max}(T) = \mu_{max}(T_{20}) \cdot e^{\theta_T \cdot (T-20)}$$

$\mu_{max(T)} =$ Growth rate at temperature T (°C)

$\mu_{max}(T_{20}) =$ Growth rate at 20°C

$\theta_T =$ Temperature coefficient (change of μ_{max} per °C)

θ_T of *Nitrosomonas*	= 0.106
θ_T of *Nitrobacter*	= 0.062

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**

Saturation constants of different organisms

Bacteria	**K_N [mg N/l]**		**K_{O2} [mg O_2/l]**
	10°C	**20°C**	**20°C**
Nitrosomonas	0.3	1.5	0.5-1.0
Nitrobacter	0.8	1.5	0.5-1.5
Heterotrophic bactéria	--	5	0.5-1.0

Influence of different environmental parameters on growth rates

$$\mu = \mu_{\max} \frac{\left[NH_4^+\right]}{10^{0.051T-1.158} + \left[NH_4^+\right]} \cdot e^{0.098(T-15)} \cdot \frac{[DO]}{K_{O_2} + [DO]} \cdot \left[1 - 0.833 \cdot \left|pH_{opt} - pH\right|\right]$$

with:	T	=	temperature in °C
	[DO]	=	dissolved oxygen concentration (mg/L)
	pH_{opt}	=	pH optimum equal to 7.2
	μ_{max}	=	maximal growth rate

Denitrification

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

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

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

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

Values of μ_{max} and K_s of denitrifying bacteria

μ_{max} (organic matter)	3-6	d^{-1}
μ_{max} (methanol)	5-10	d^{-1}
K_{s,NO_3}	0.2-0.5	$gNO_3^- - Nm^{-3}$
$K_{s,COD}$	10-20	$gCODm^{-3}$
$K_{s,MeOH}$	5-10	$gCODm^{-3}$
$K_{i,O_2(NO_3)}$	0.1-0.5	gO_2m^{-3}

Denitrification rate

$$r_d = \frac{\mu_d}{Y_d}$$

r_d = denitrification rate in mg NO_3^--N reduced mg^{-1} VSS d^{-1}

Y_d = yield in biomasse in mg VSS mg^{-1} NO_3^--N reduced

$$0.65\ \mathbf{C_{18}H_{19}O_9N} + 4.89\ NO_3^- + 4.89\ H^+ \rightarrow$$

$$C_5H_7NO_2 + 2.27\ N_2 + 6.7\ CO_2 + 5.12\ H_2O$$

Influence of temperature

$$r_T = r_{20} \cdot e^{\theta_T \cdot (T - 20)}$$

θ_T of denitrifyers = 0.11

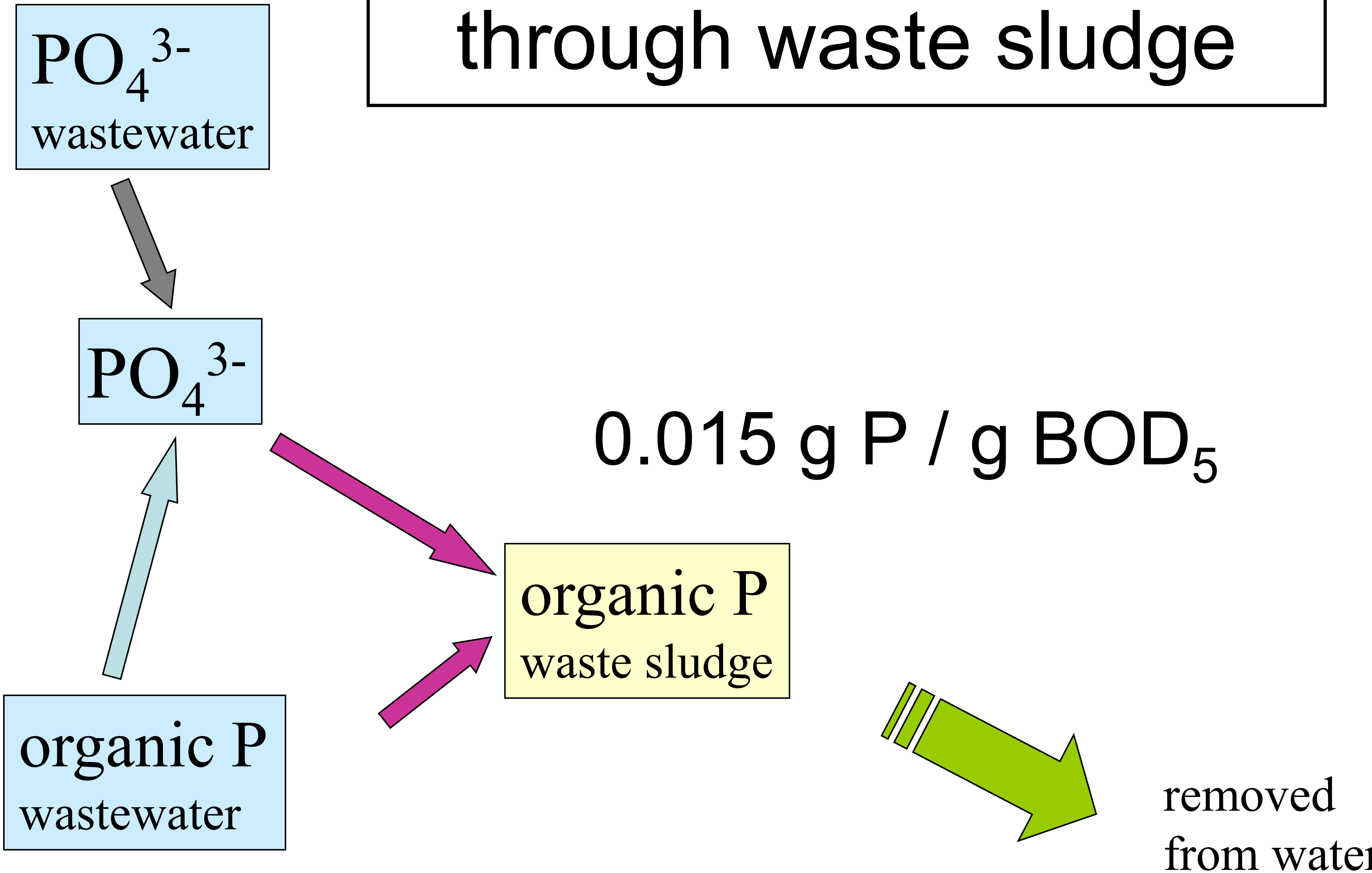
for temperatures between 5 and 27°C

Influence of different environmental factors

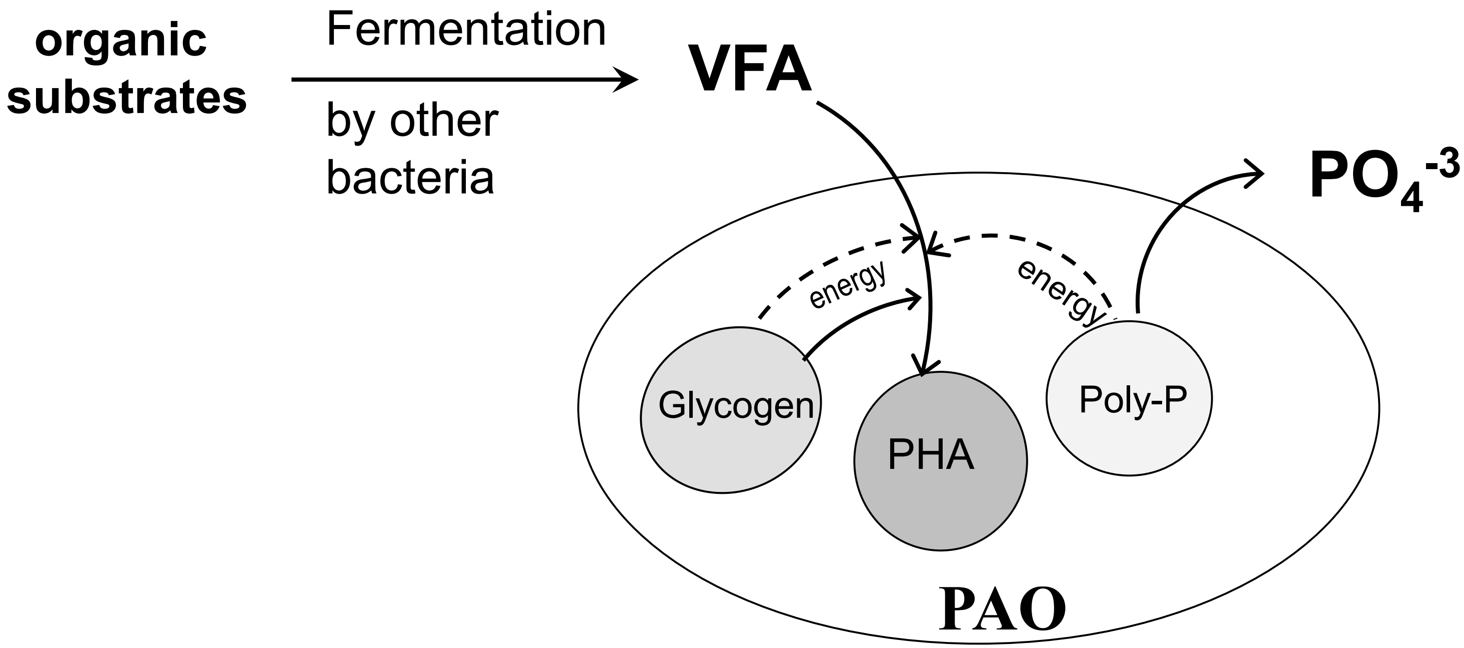
$$\mu = \mu_{\max} \frac{NO_3}{K_{S,NO_3} + NO_3} \cdot \frac{S}{K_S + S} \cdot \frac{K_{I,O_2(NO_3)}}{K_{I,O_2(NO_3)} + S_{O_2}}$$

Biological phosphorous removal

Phosphorous removal through waste sludge



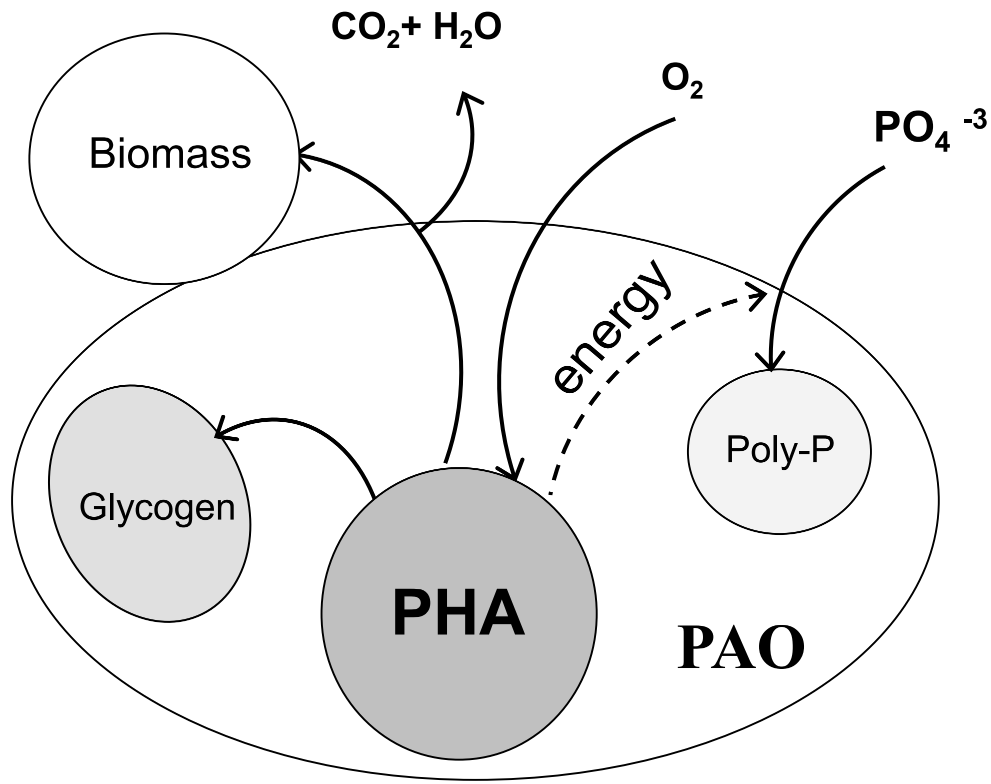
Metabolism of PAO: Anaerobic phase



$$2C_2H_4O_2 + (HPO_3) + H_2O \longrightarrow (C_2H_4O_2)_2 + PO_4^{3-} + 3H^+$$

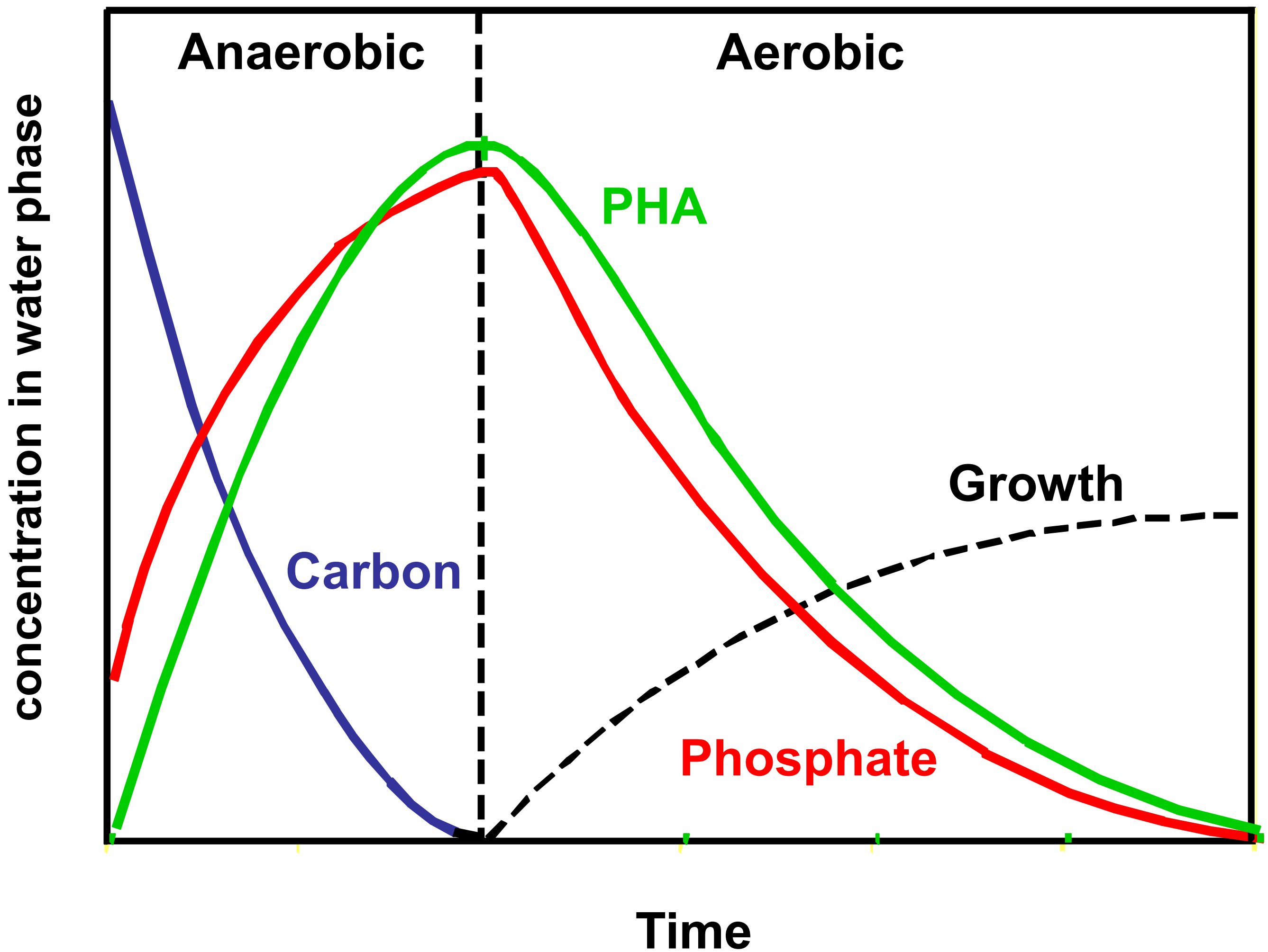
PAO = Phosphate accumulating organisms

Metabolism of PAO: Aerobic phase



$$C_2H_4O_2 + 0.16\ NH_4^+ + 1.2\ O_2 + 0.2\ PO_4^{3-} \longrightarrow 0.16\ C_5H_7NO_2 + 1.2\ CO_2 + 0.2\ (HPO_3) + 0.44\ OH^- + 1.44\ H_2O$$

Concentration profiles during different phases



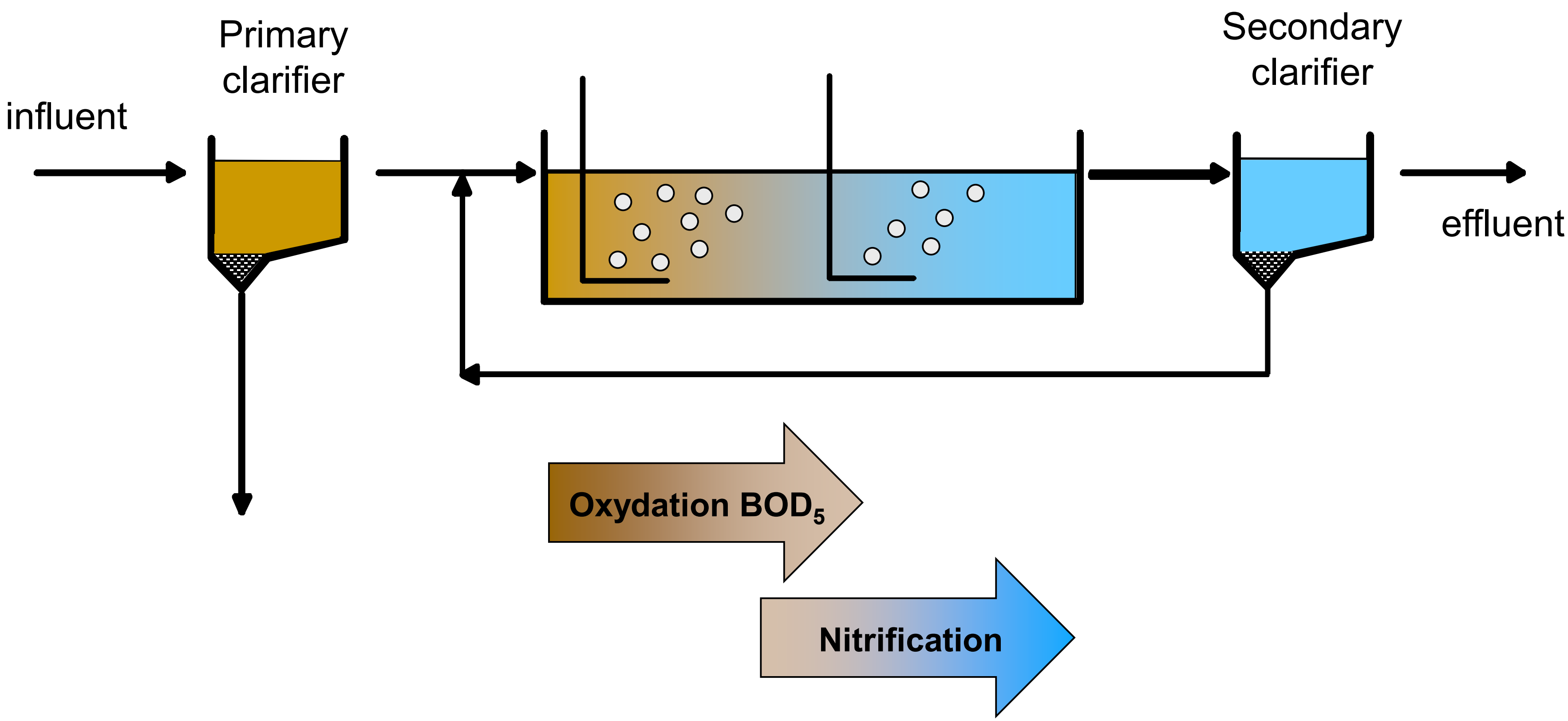
Reaction constants	Symbol	Values	Units
Maximal acetate consumption rate	k_{HAc}	0.5-2	**g COD(Hac) g^{-1}COD(X)d^{-1}**
Saturation constant for acetate	$K_{S,\ HAc}$	2-6	**g HAc m^{-3}**
Temperature coefficient	θ_T	0.01-0.02	**$°C^{-1}$**
Saturation constant for phosphate	$K_{S,\ PO4}$	0.1-0.5	**g P m^{-3}**
Maximal growth rate	$\mu_{max,\ P}$	2-4	**d^{-1}**
Growth yield	$Y_{max,\ P}$	0.5-0.6	**g COD(B) g^{-1}COD(HAc)**
Growth yield	$Y_{max,\ P}$	0.6-0.8	**g VSS g^{-1}COD(HAc)**
Growth yield	$Y_{max,\ P}$	0.07-0.10	**g P g^{-1}COD(HAc)**

Implementation of biological nutrient removal

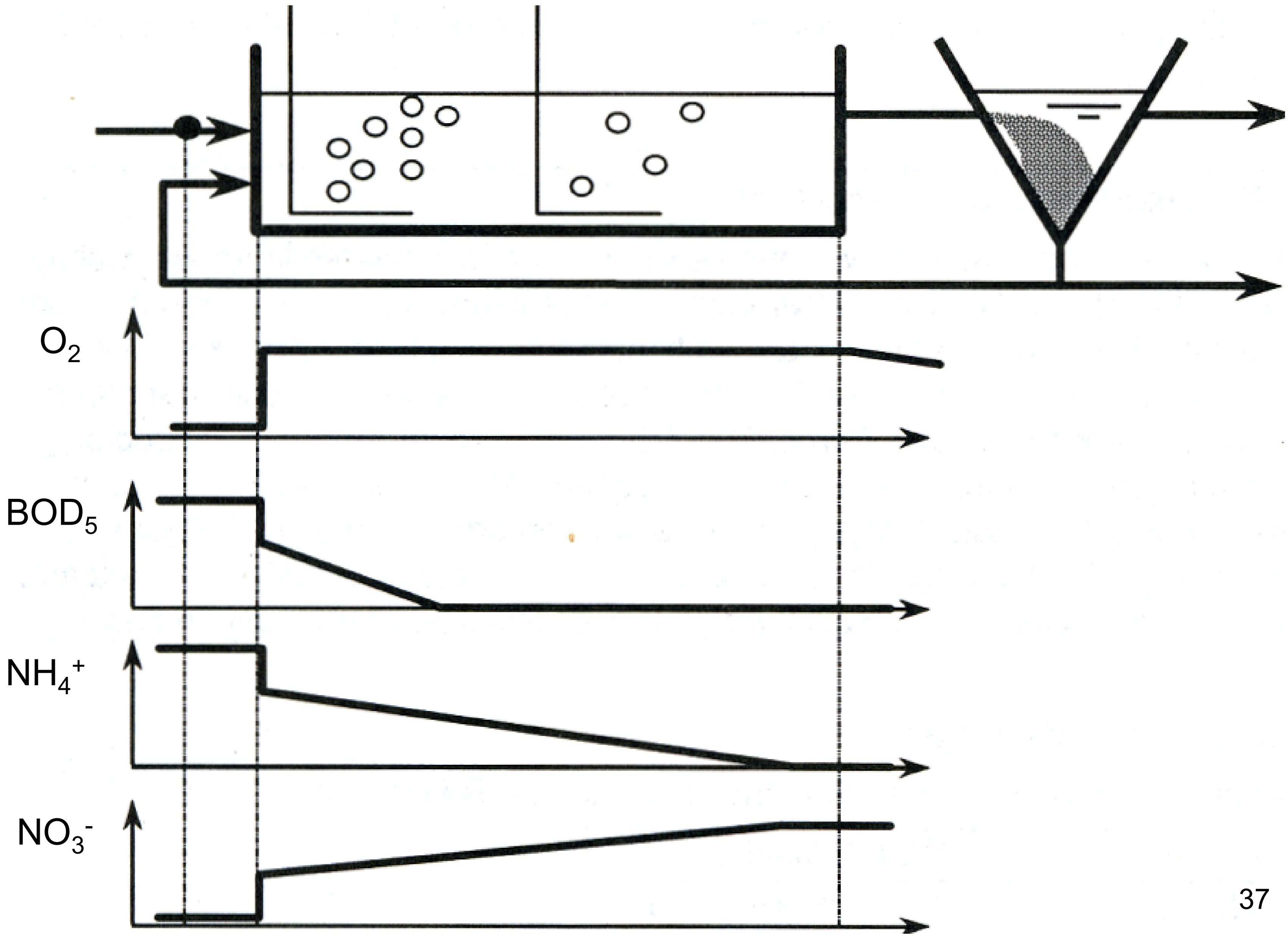
Implementation of nitrification

- Nitrifyers are specialized bacteria needing oxygen as electron acceptor and having a slow growth rate
- Nitrifyers normally loose competition with heterotrophs for oxygen asking for separation of the two processes nitrification and aerobic organic matter degradation

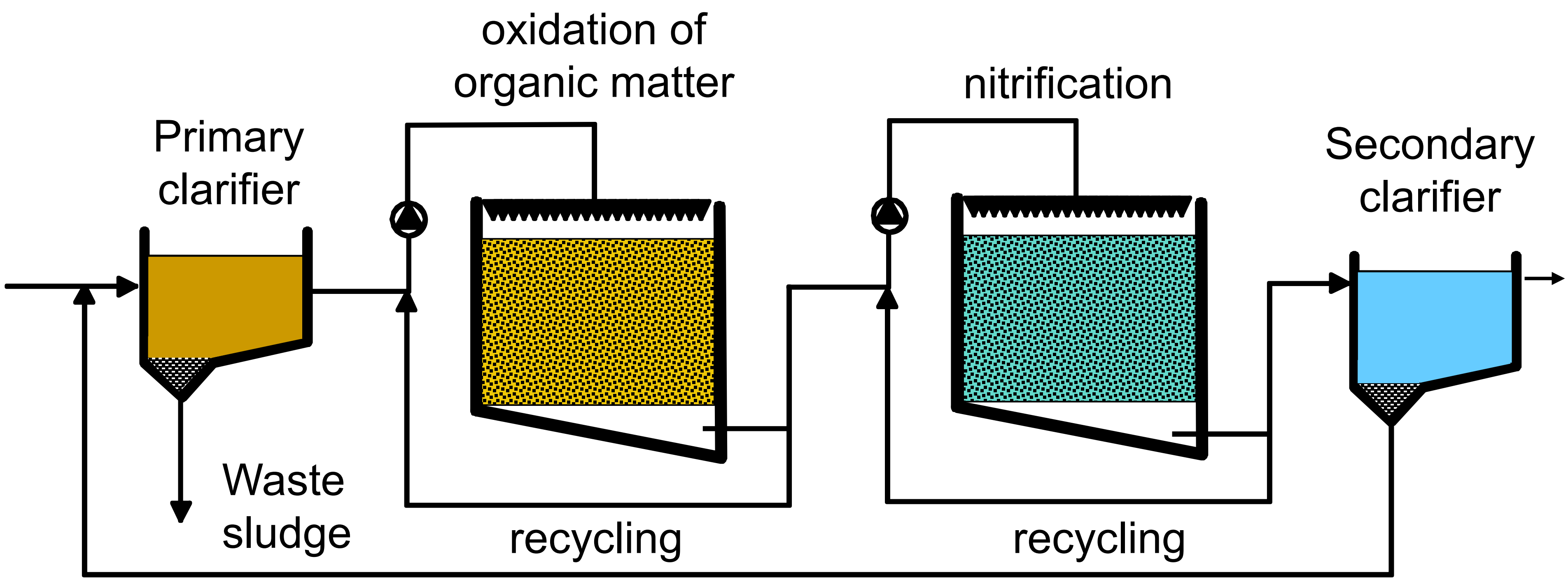
Aeration tank in activated sludge treatment systems



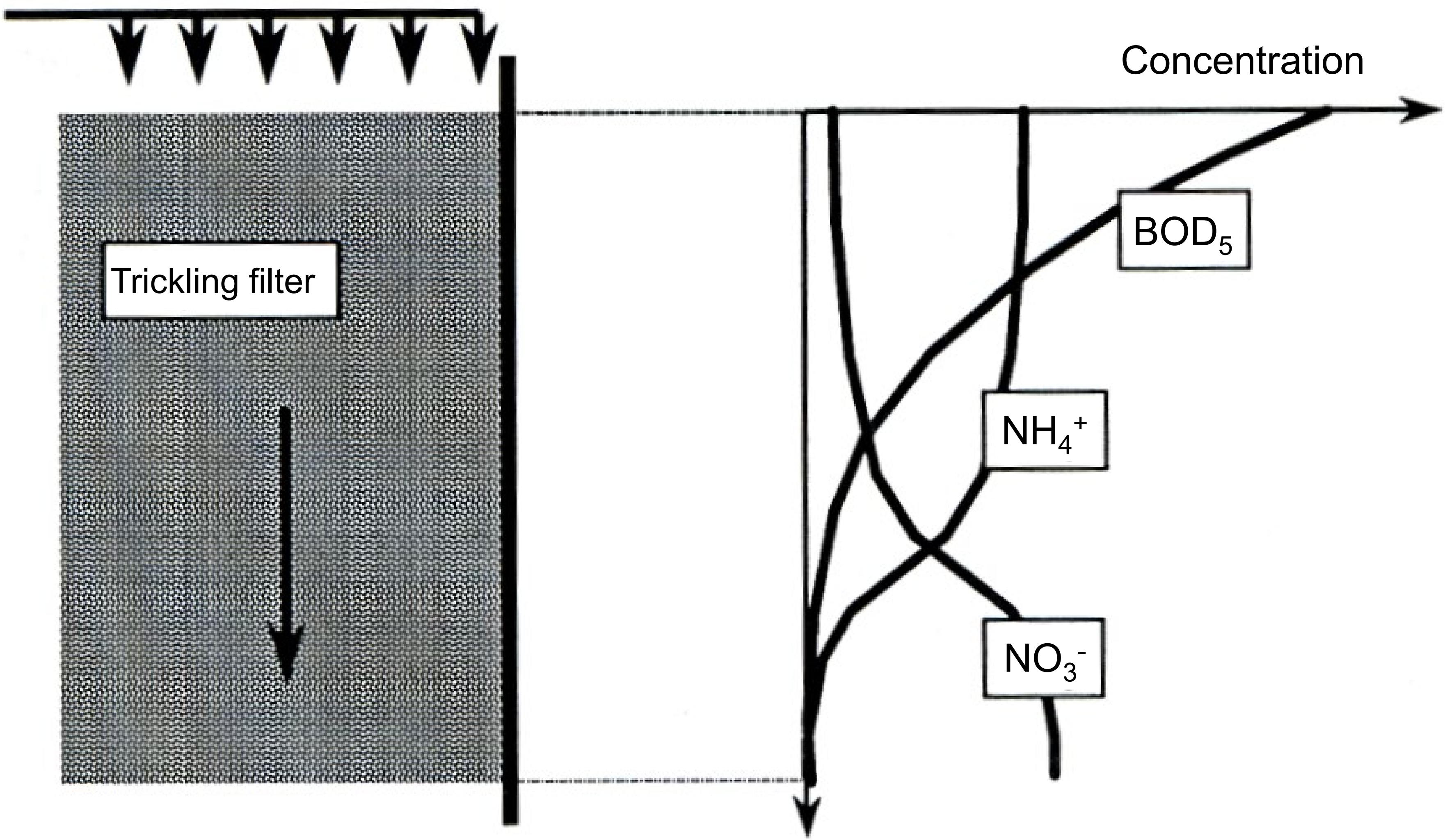
Concentration profiles in aeration tank with plug-flow mode



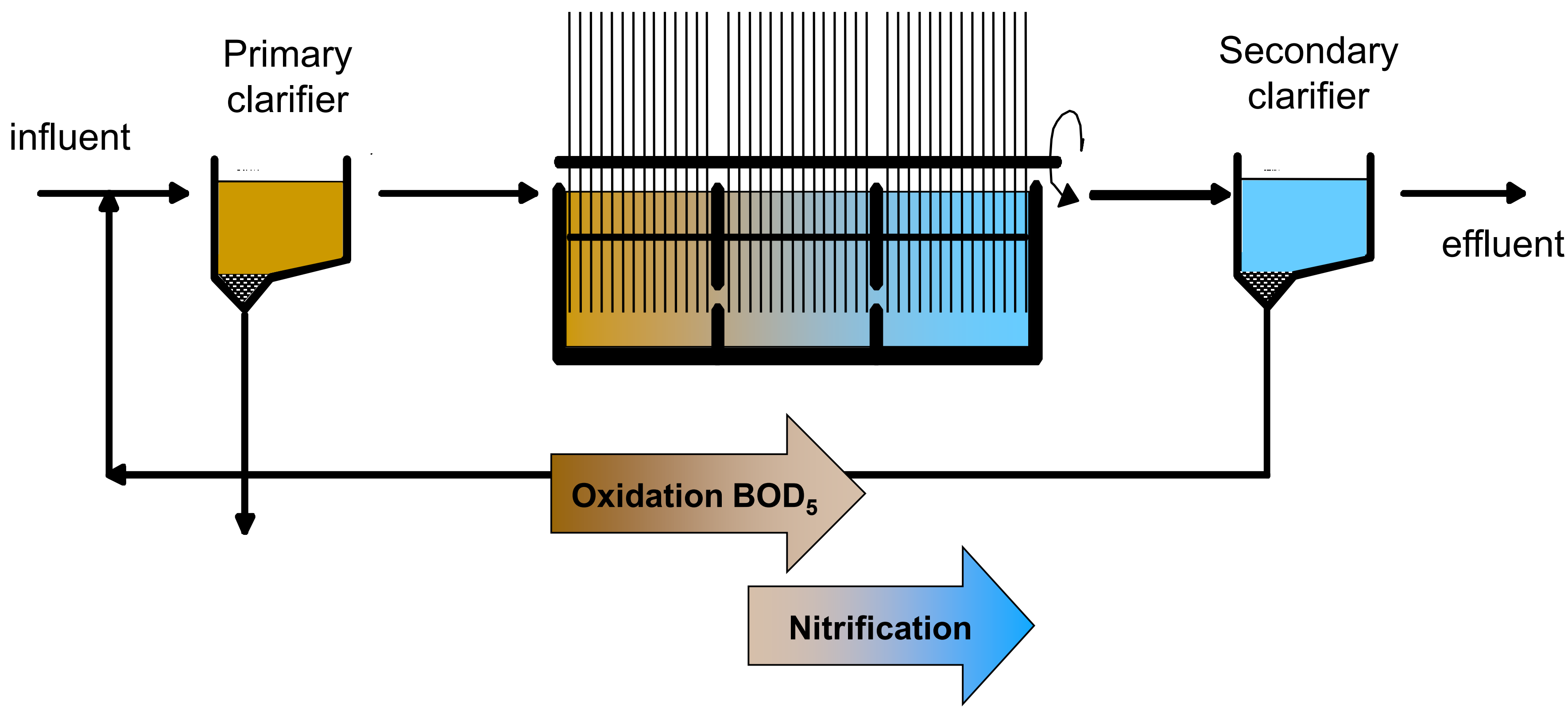
Biotrickling filters



Concentration profiles in nitrifying biotrickling filter



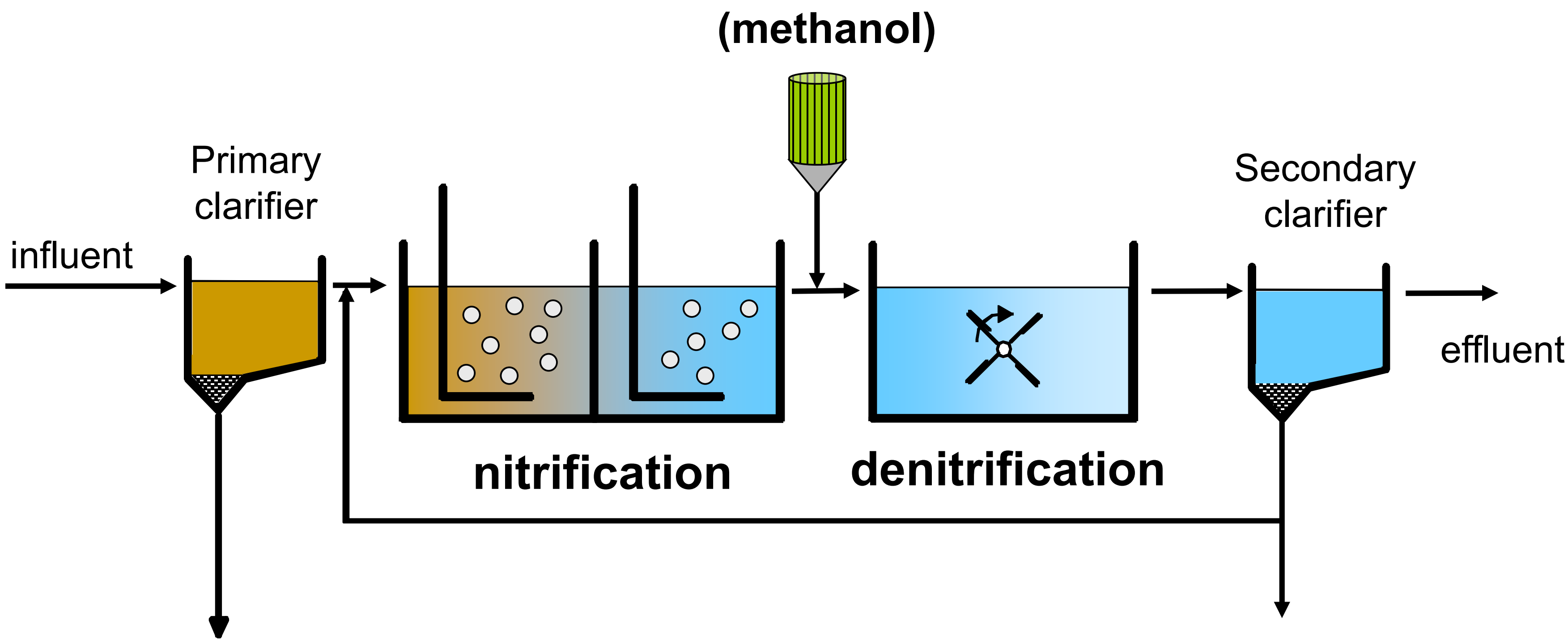
Biological contactors



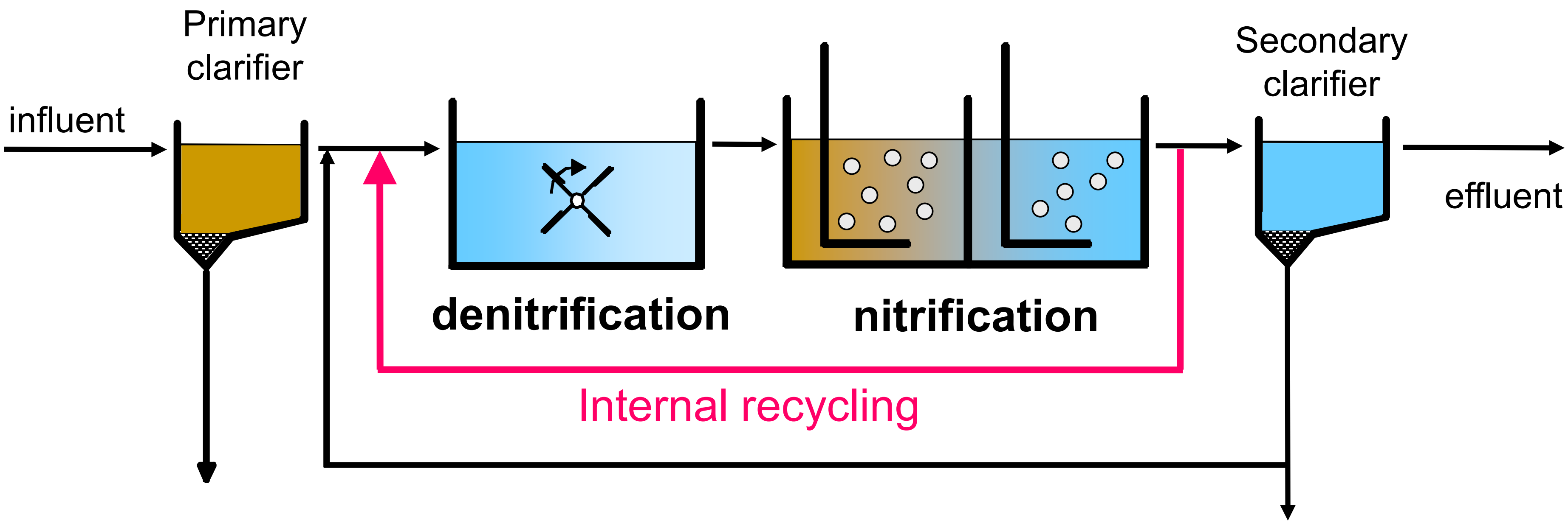
Implementation of denitrification

- Denitrifyers are heterotrophic bacteria using nitrate as electron acceptor if no oxygen is present
- Denitrifyers need organic matter as energy and carbon source

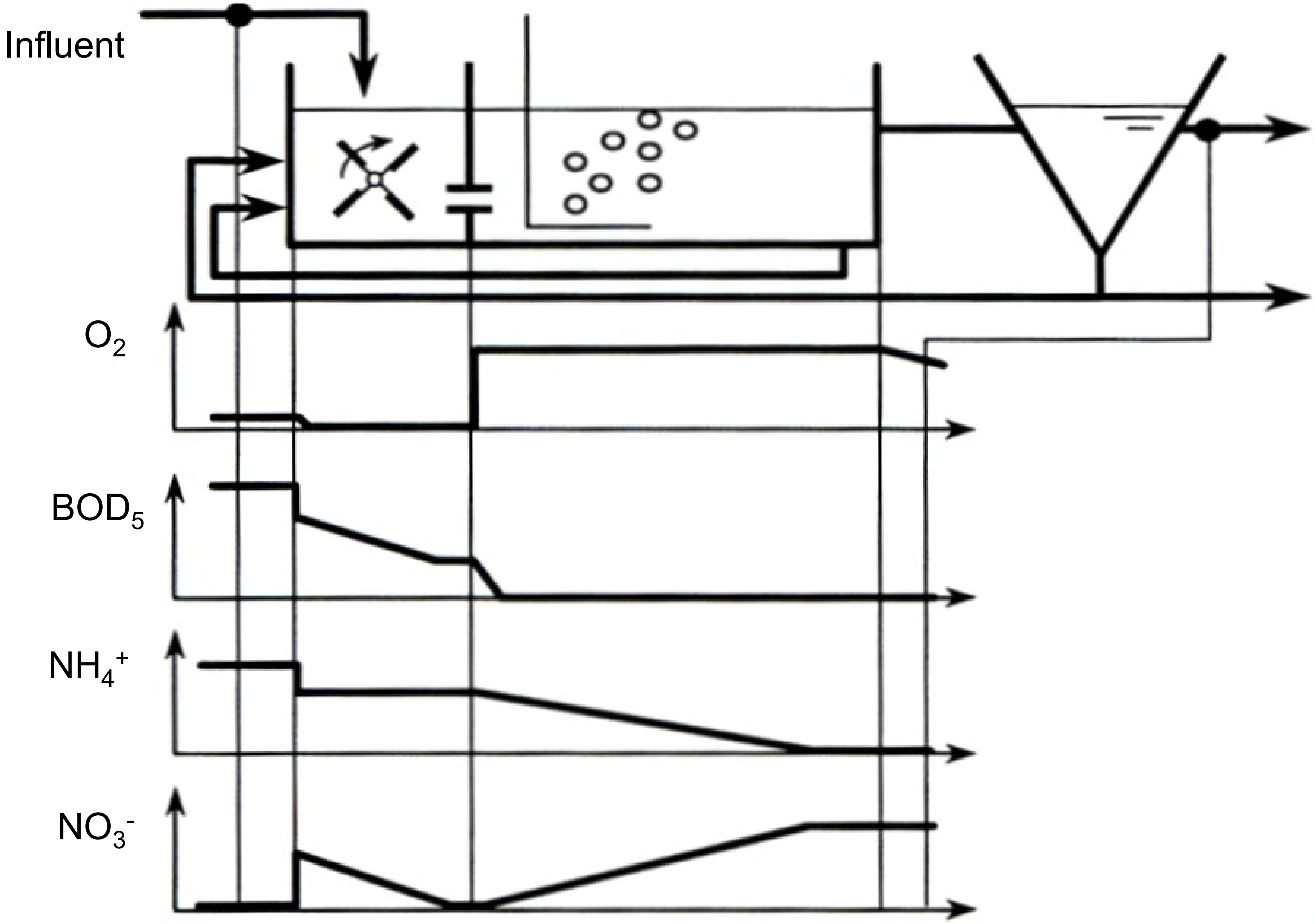
Post-denitrification in activated sludge systems



Pre-denitrification in activated sludge systems



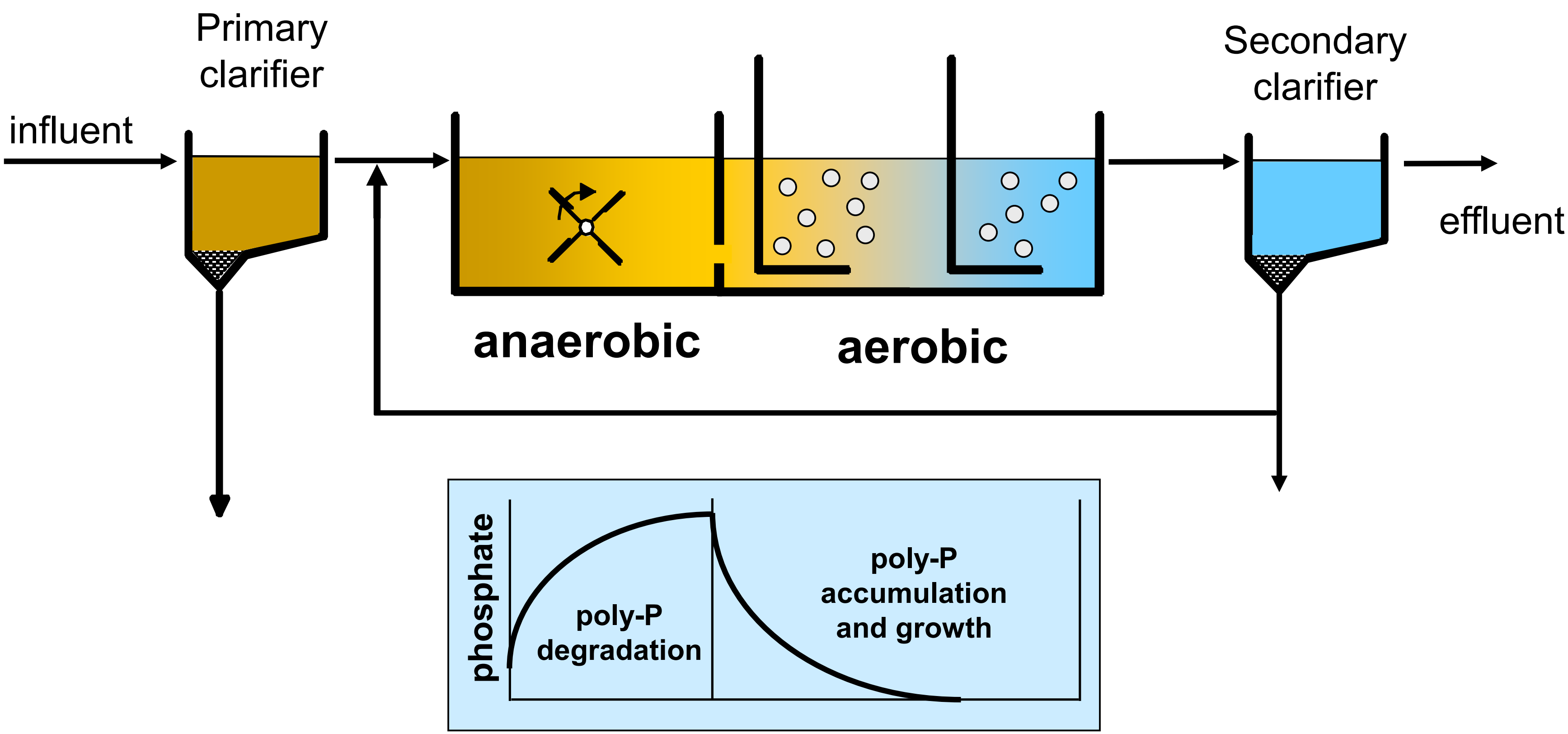
Concentration profiles in « aeration » tank with plug-flow mode



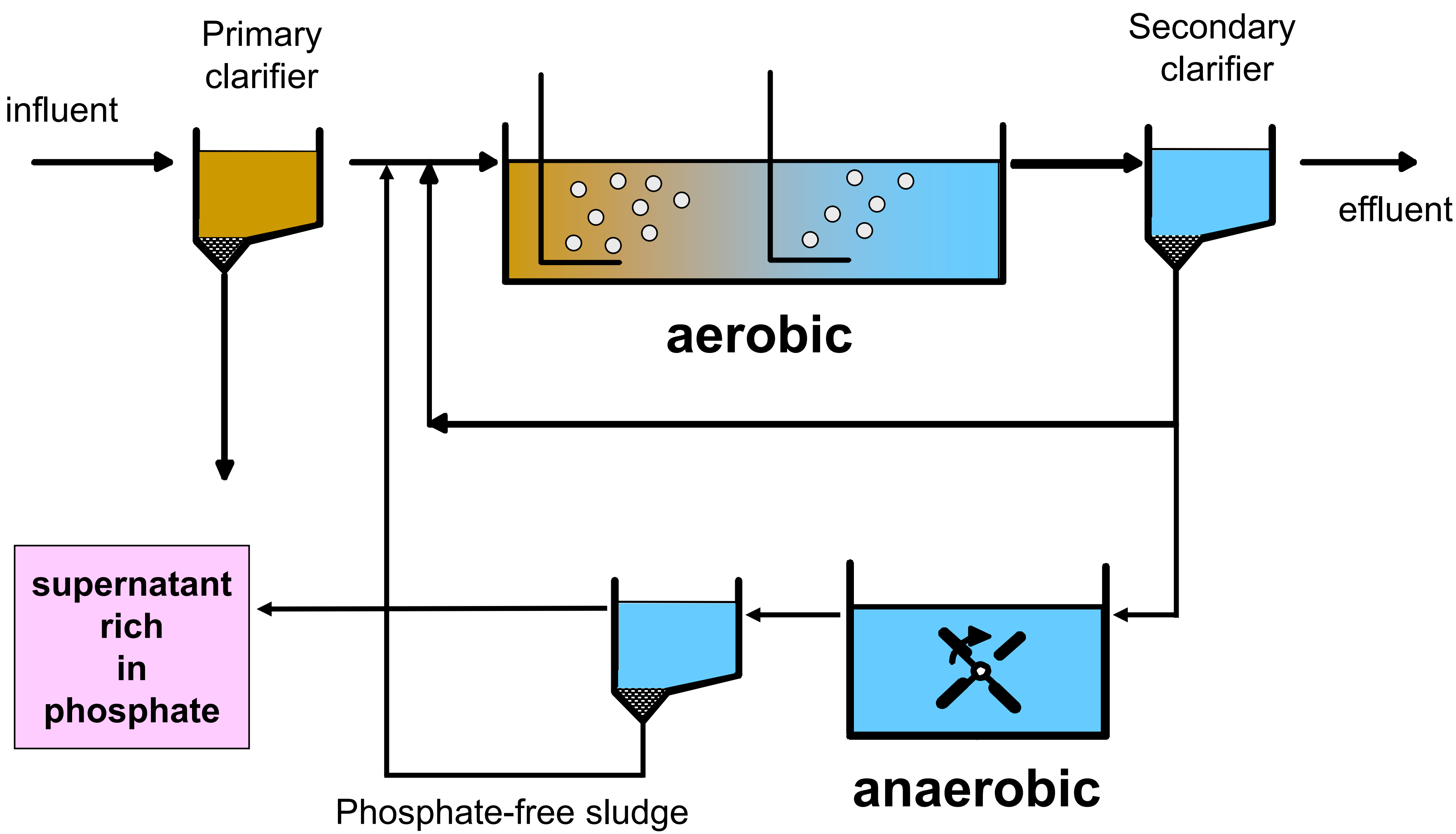
Implementation of biological phosphate removal

- PAOs need alternation of anaerobic and aerobic phases
- Some PAOs can also denitrify, hence there should be absence of nitrate during anaerobic phase
- PAOs need VFAs for PHA formation, hence there should be presence of easily biodegradable organic compounds in anaerobic zone

The A/O process
for biological dephosphatation

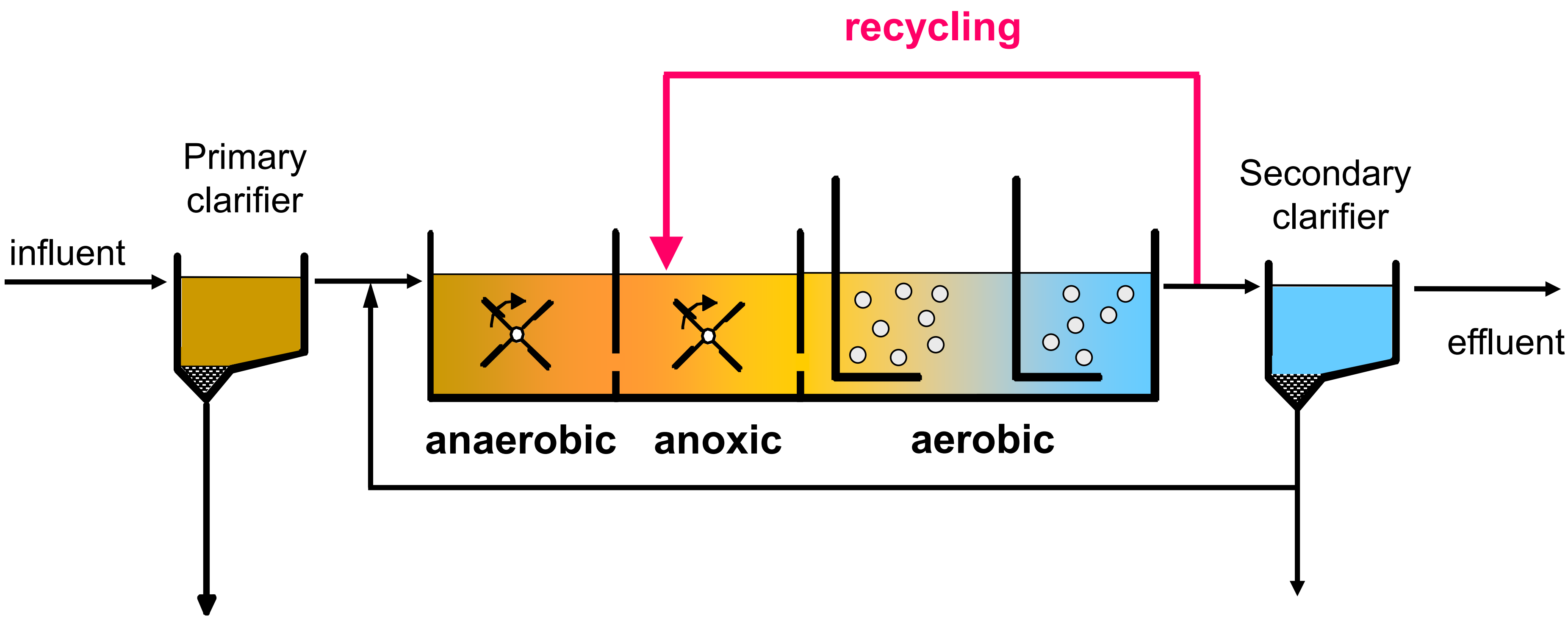


The PhoStrip process
for biological dephosphatation



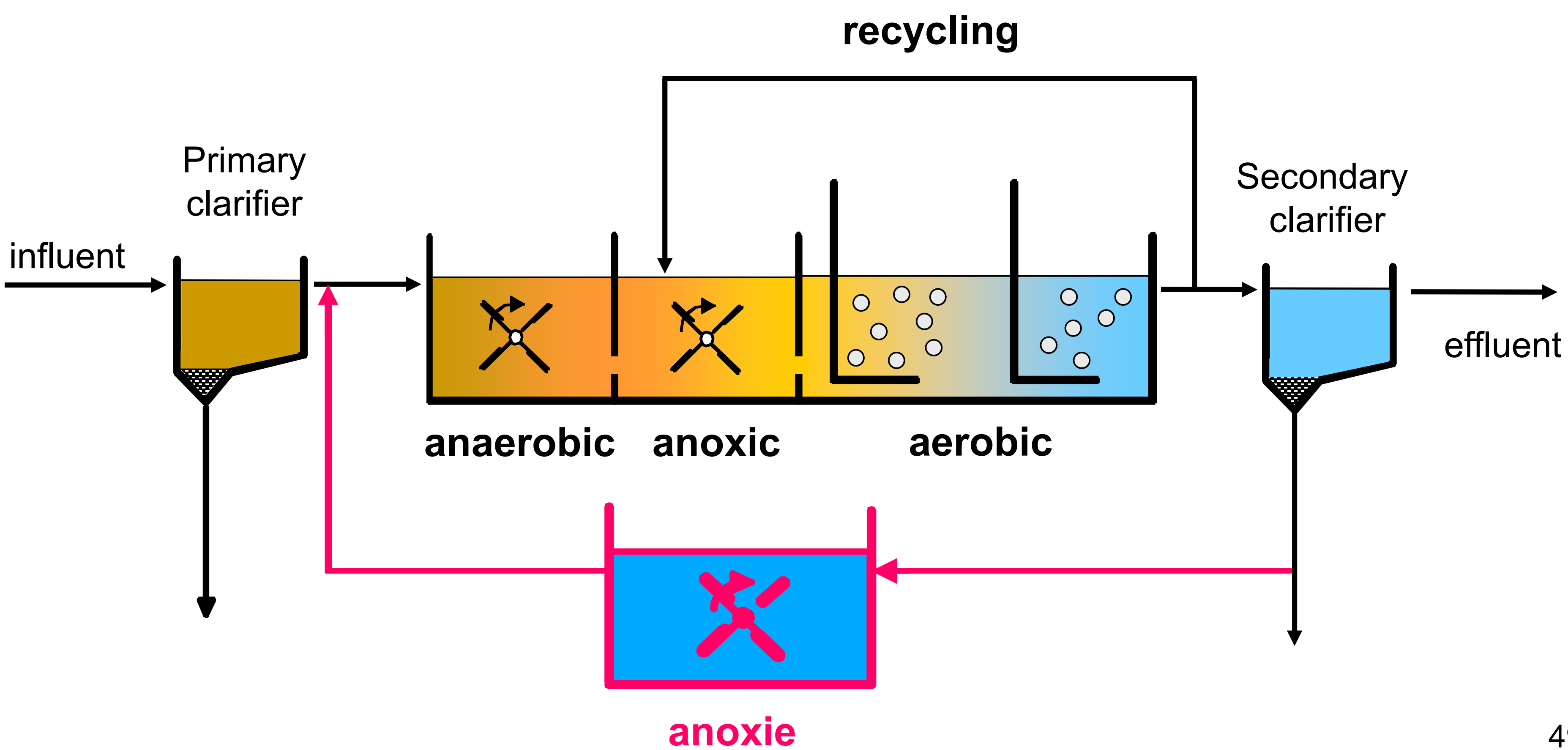
The A^2/O process

for biological dephosphatation



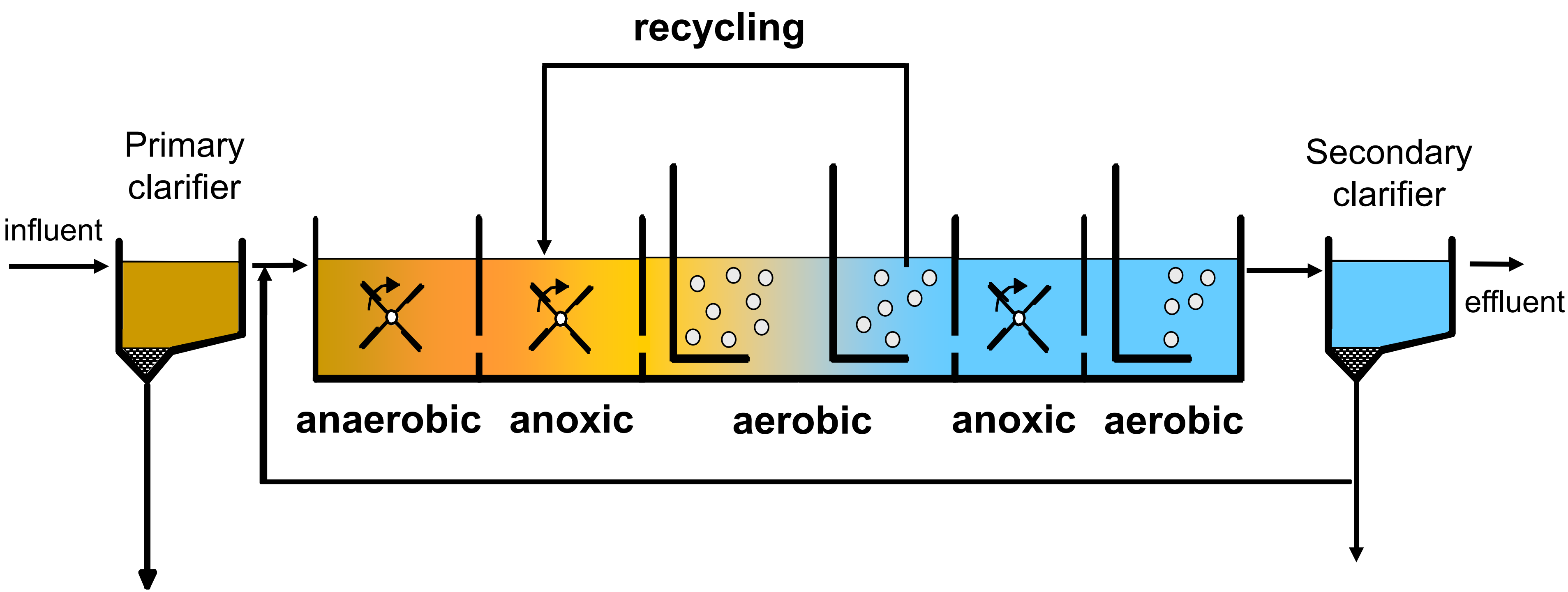
The JHB process

for biological dephosphatation

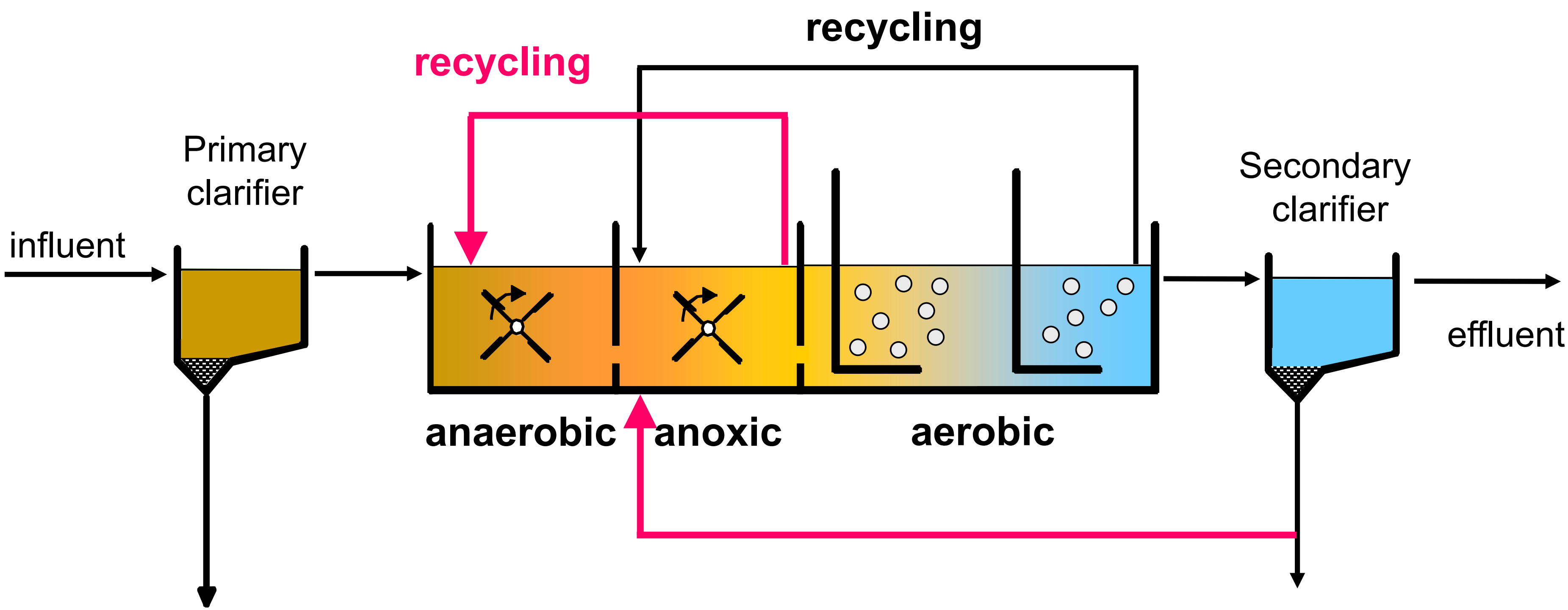


The Bardenpho process

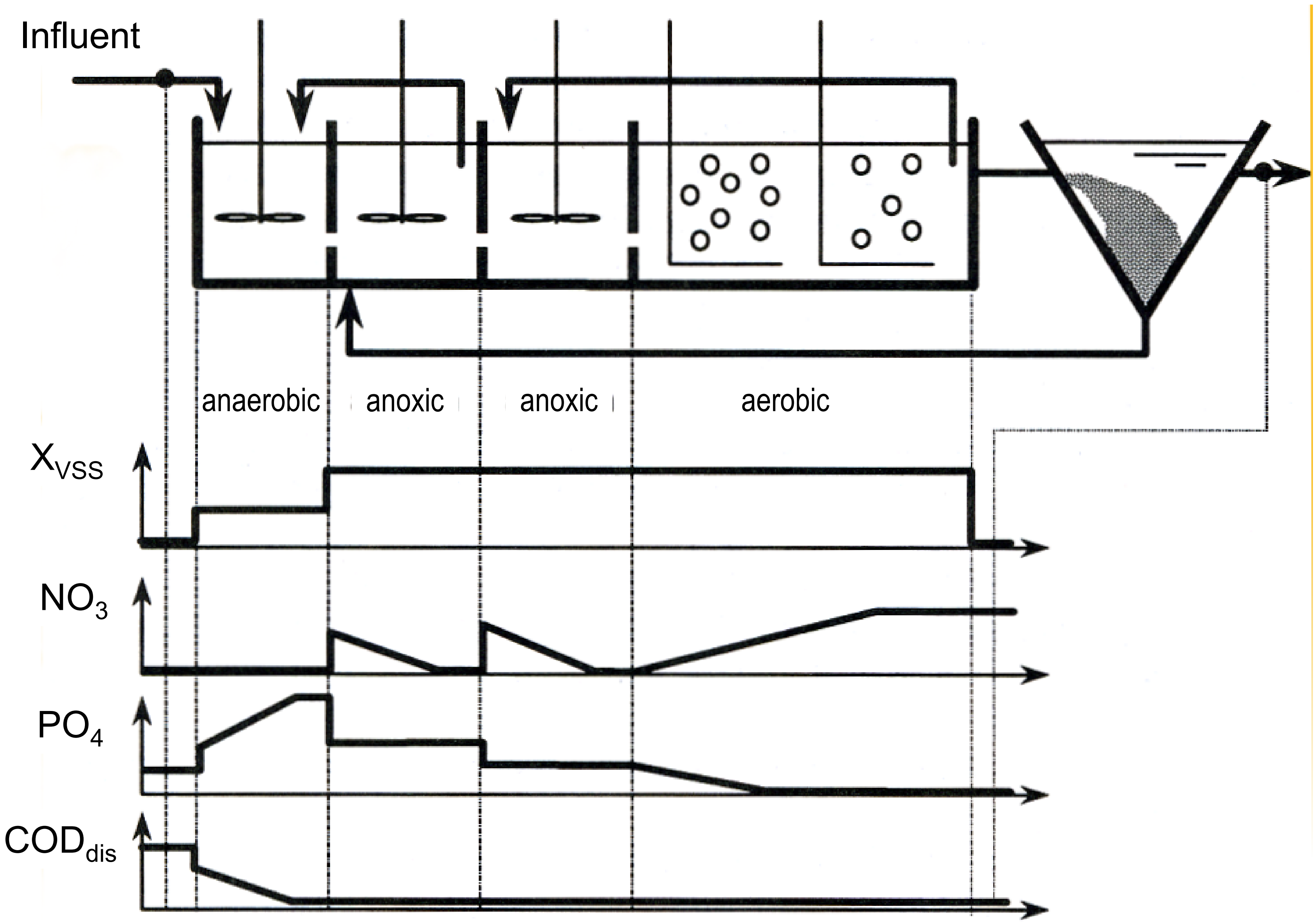
for biological dephosphatation



The UCT process
for biological dephosphatation



Concentration profiles in treatment tanks with plug-flow mode



Chemical phosphorous removal

since about 30 years in Switzerland

<u>In 1993:</u>

60% equiped with chemical dephosphatation and about 75% of wastewater treated

Different steps involved in chemical dephosphatation

- precipitation
- coagulation
- flocculation
- la separation

Precipitation (1)

- iron chloride ($FeCl_3$)
  iron sulfate ($FeSO_4$)
- aluminium sulfate ($Al_2(SO_4)_3$)

Main reaction

$Me^{3+} + H_nPO_4^{(3-n)-} \leftrightarrow MePO_4 + nH^+$

Side reaction

$Me^{3+} + 3HCO_3^- \leftrightarrow Me(OH)_3 + 3CO_2$

Precipitation (2)

- lime ($Ca(OH)_2$)

<u>Main reaction</u>

$5\ Ca^{2+} + 7\ OH^{-} + 3\ H_2PO_4^{-} \leftrightarrow Ca_5OH(PO_4)_3 + 6\ H_2O$

<u>Side reaction</u>

$Ca^{2+} + CO_3^{2-} \leftrightarrow CaCO_3$

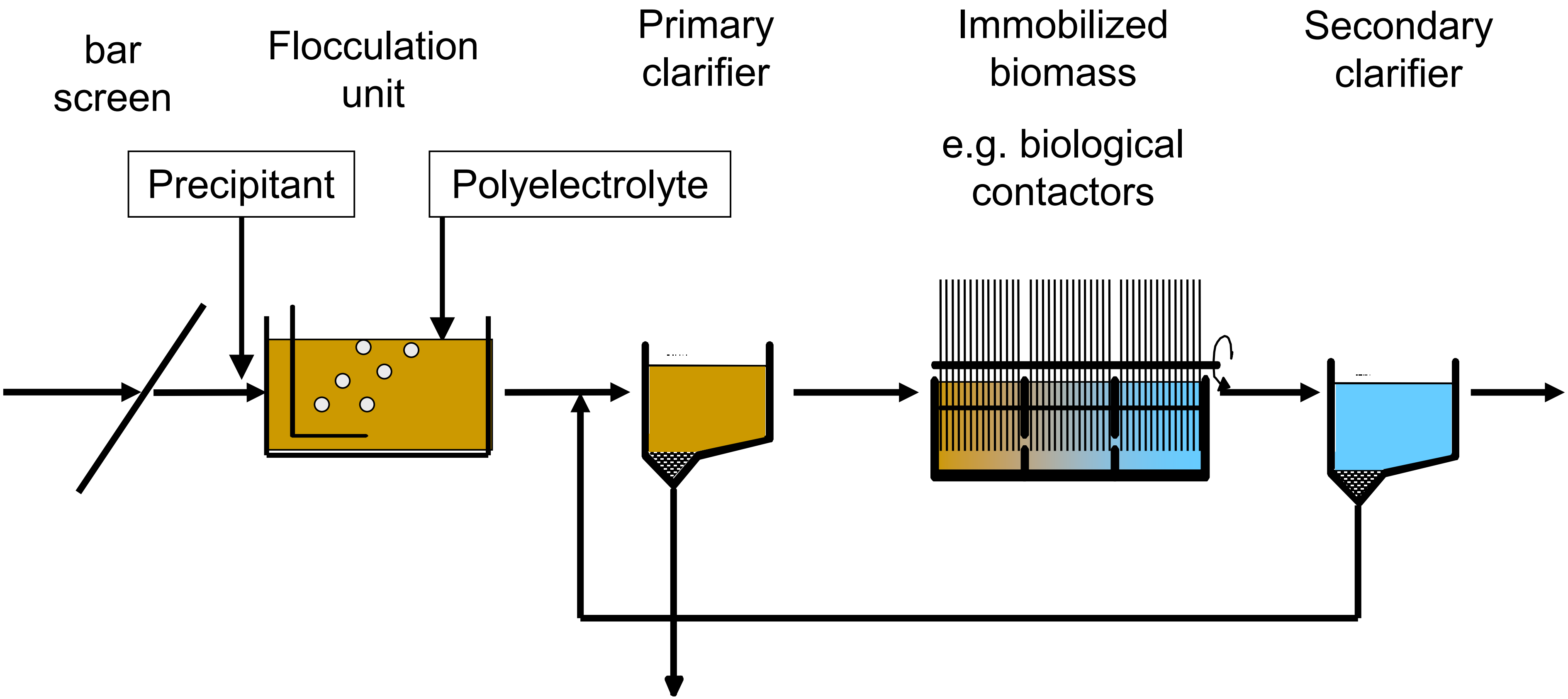
Coagulation

- formation of primary particles (∅: 10-50 µm) from colloids (∅: <1 µm) formed by precipitation
- formation of these primary particles due to destabilisation induced by chemical coagulants
- destabilisation can be produced by three ways:
  - bridges between colloids
  - trapping by adsorption on big particles
  - decrease of electrostatic repulsion due to cations

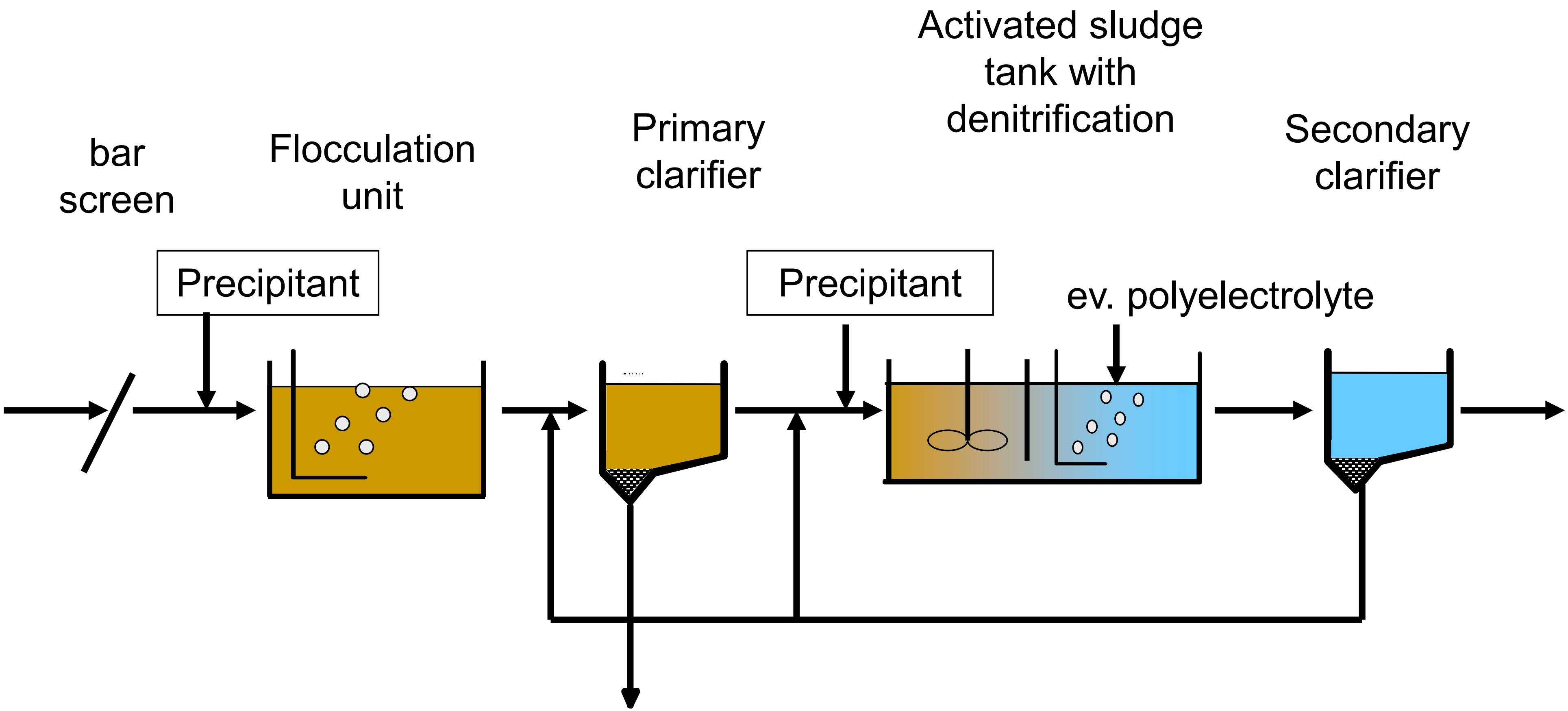
Flocculation

- formation of flocs (∅: >100 µm) due to collisions between primary particles in the tank with agitation
- a reversible process
- degree of flocculation depends on :
  - hydraulic retention time
  - number of flocculation tanks
  - type of precipitant used

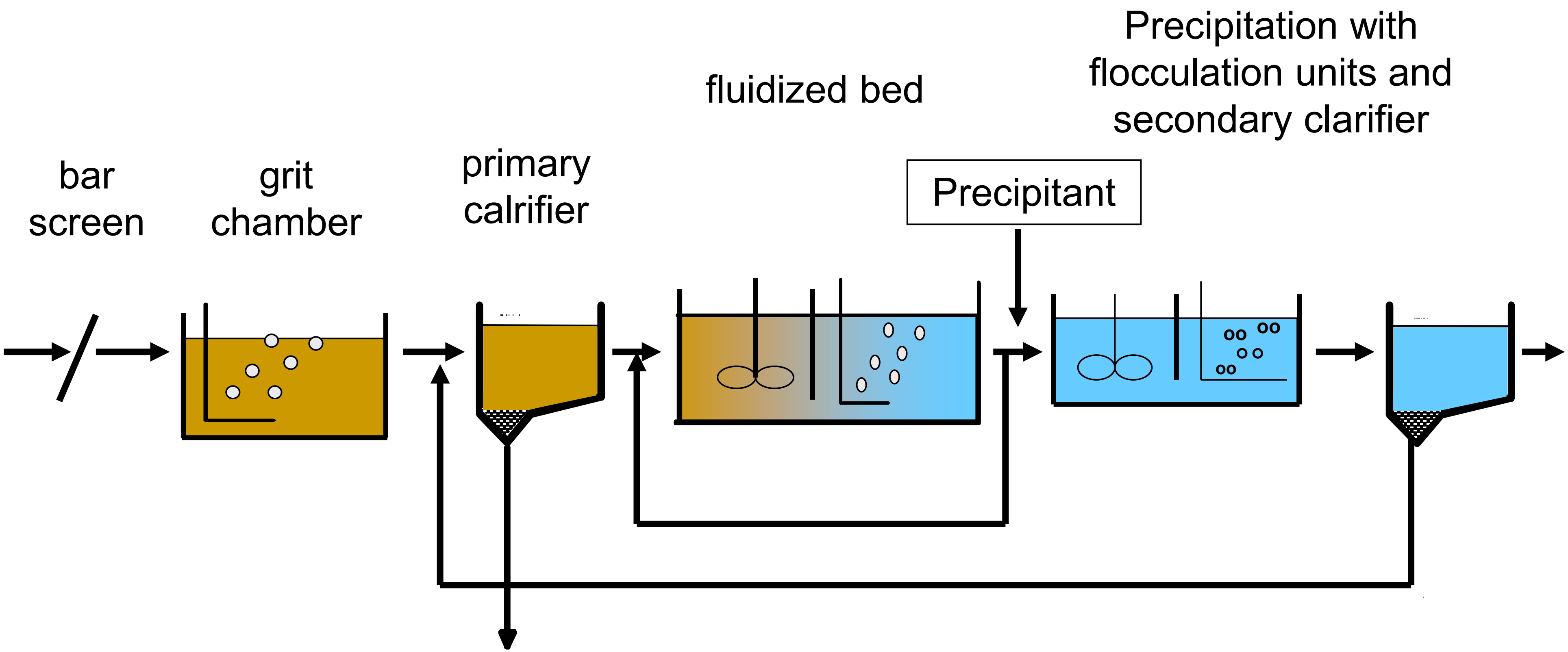
Pre-precipitation



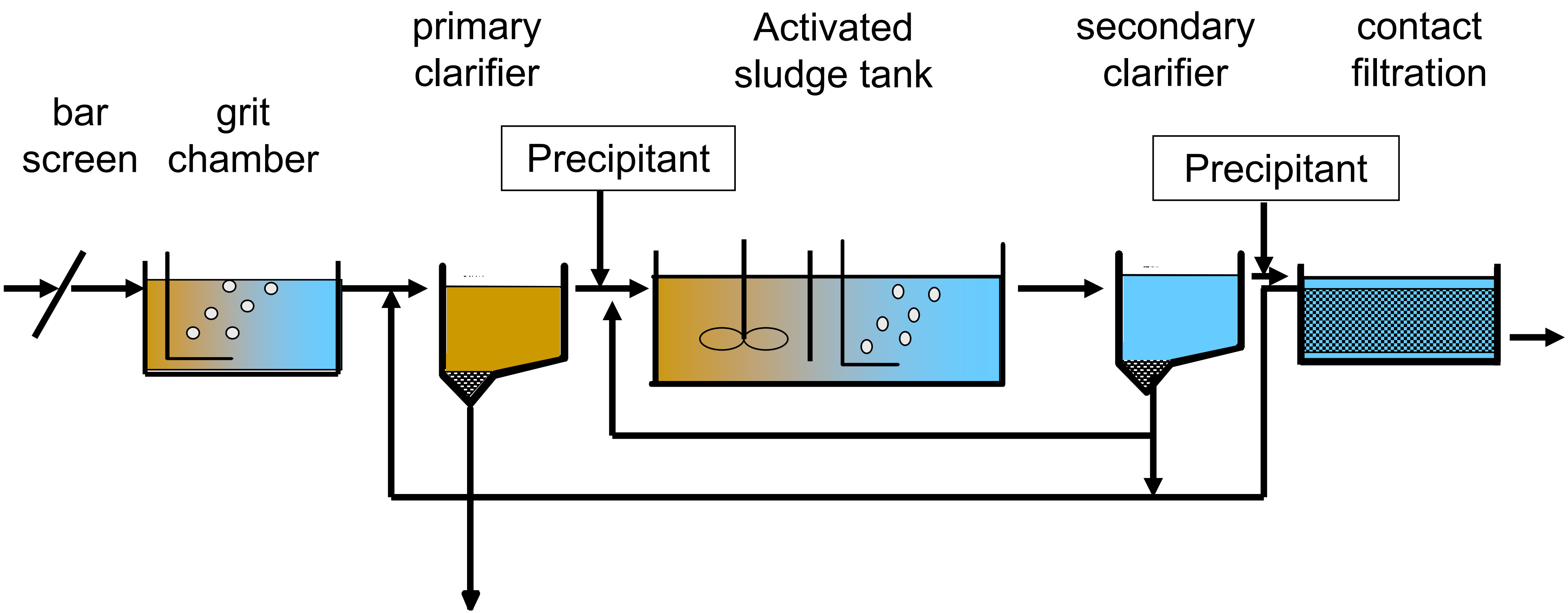
Simultaneous precipitation



Post-precipitation



Contact filtration



Annual costs of three types of precipitants*

Precipitant	Quantity (t / y)	Unit costs (CHF / t)	Annual costs (CHF)
$FeCl_3$	91,8	250.-	22'950.-
$FeSO_4$	129,6	90.-	11'700.-
$Al_2(SO_4)_3$	146,0	210.-	30'700.-

* Hypothesis: WWTP treating wastewater of 10’000 cap with a load of 4 g/cap/d

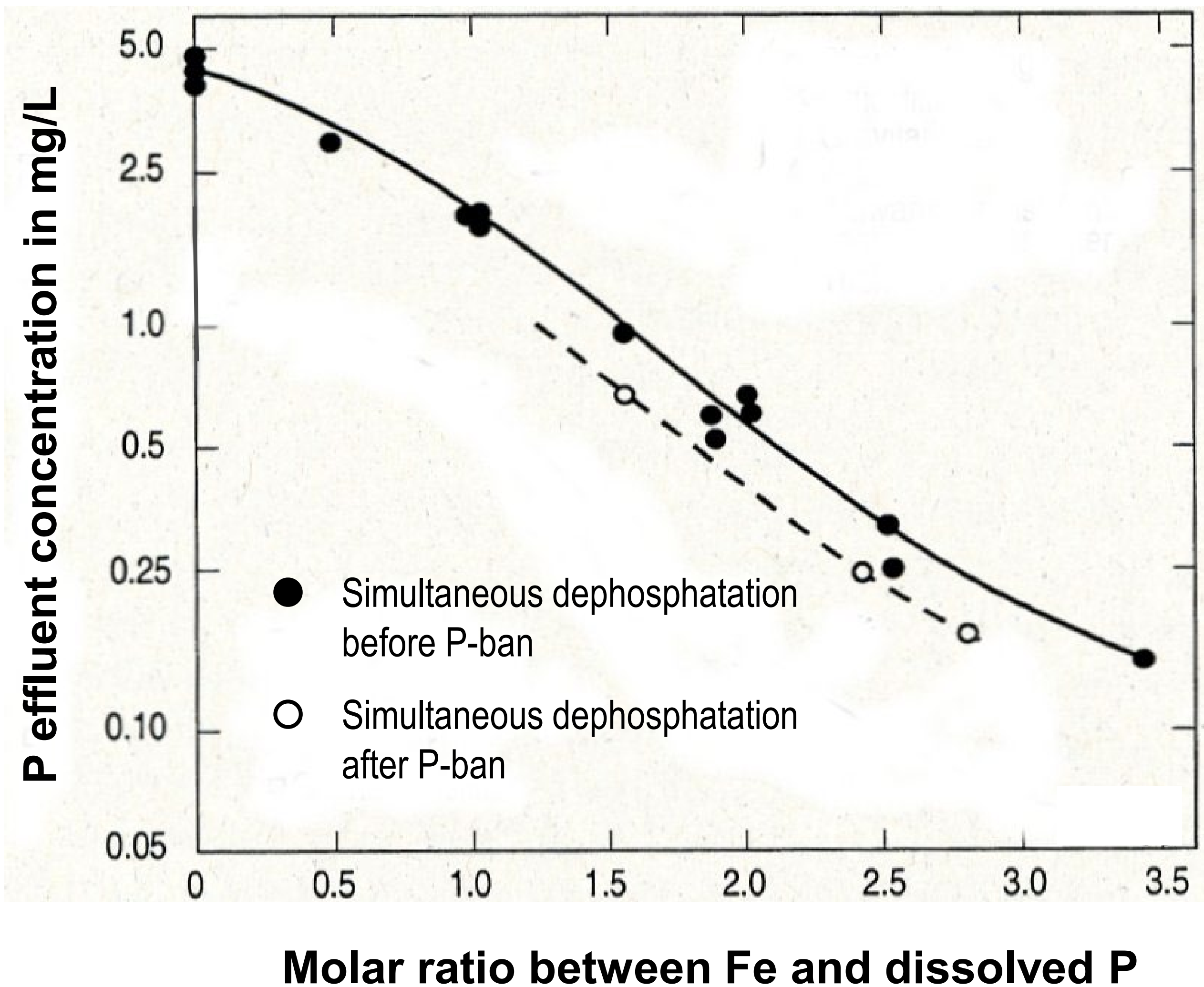
Dosage example (1)

- The daily wastewater volume to treat is 12'000 m^3.
- The wastewater contains P_{total} = 6 mg/L
- Phosphate is removed by simultaneous precipitation with ferric iron chloride

The question to answer is :

- ***What hourly dosage of a 40% ferric iron chloride solution has to applied in order to reach a P_{total} concentration = 0,8 mg/L ?***

Relationship between molar Fe-P ratio and P concentration reached in WWTP effluent



Dosage Example (2)

1) P_{total} = 6 mg/l = 6 g/m^3

2) Molar mass of P = 31 g/mol → P = 6/31 = 0.19 mol/m^3

3) Fe/P = 1,5 → moles of Fe to add = 1.5 × 0.19 = 0.29 mol/m^3

4) The ferric iron chloride solution is added to the aeration tanks with a pump that can be regulated at hourly flow rates.

5) $Q_h = Q_d$ / 24 = 12’000 / 24 = 500 m^3/h

6) The pump has to add 0.29 × 500 = 145 mol Fe / h

7) Fe/$FeCl_3$ = 1 → 145 mol $FeCl_3$/h

Dosage Example (3)

8) Molar mass of $FeCl_3$ = 162.2 g/mol

9) Mass of $FeCl_3$ per hour = 145 × 162.2 = 23’519 g/h = 23.5 kg/h

10) A solution of 40% $FeCl_3$ (w/v) is used → 23.5/0.4 = 58.75 kg solution/h

11) The density of the solution is 1.42 kg/L → 58.75/1.42 = 41,37 L/h

12) That represents a volume of 993 L/d or ~ 1 m^3/day