Matrix notation to describe complex biochemical systems

The Petersen matrix

In environmental systems as well as in reactors for pollution control, several biochemical reactions occur simultaneously.

For their comprehensive description a matrix notation is widely employed, namely:

Petersen matrix

It has got:

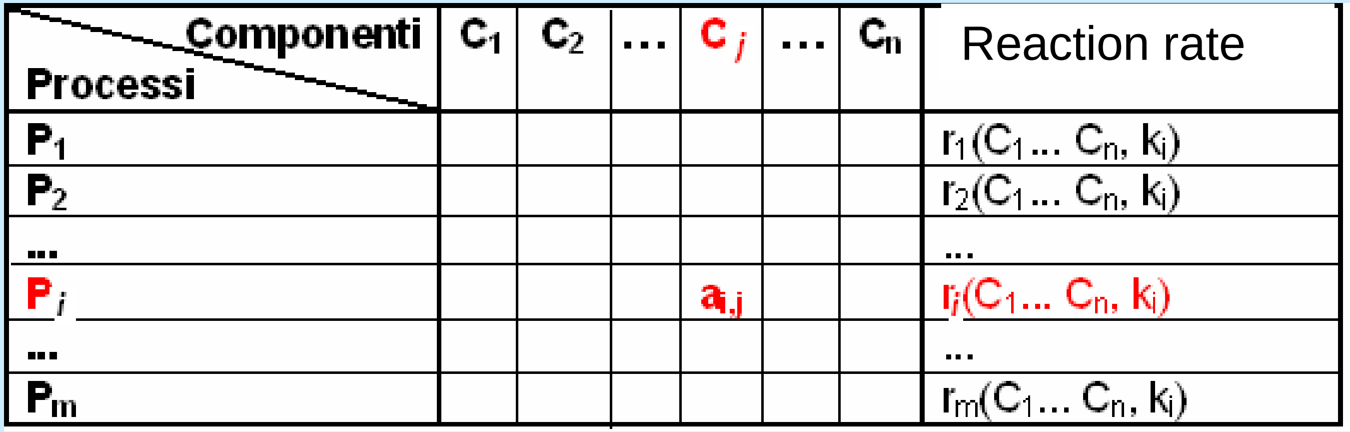
- as many columns as the number of relevant components that are involved (chemicals, pollutants, biomasses, gases)

-As many rows as the number of processes (biochemical reactions) that act on components

→ reaction **stoichiometry**

-One further column is added to host the description of the **kinetics** of each transformation (kinetic equation).

The Petersen matrix



Componenti / Processi	C_1	C_2	…	C_j	…	C_n	Reaction rate
P_1							$r_1(C_1 \dots C_n, k_i)$
P_2							$r_2(C_1 \dots C_n, k_i)$
…							…
P_i				$a_{i,j}$			$r_i(C_1 \dots C_n, k_i)$
…							…
P_m							$r_m(C_1 \dots C_n, k_i)$

According to the Petersen notation:

- $a_{i,j}$ = 0 if component C_j is not affected by process P_i
- $a_{i,j}$ < 0 if component C_j is a substrate of process P_i
- $a_{i,j}$ > 0 if component C_j is a product of process P_i

$a_{i,j}$ may be adimensional if all components are expressed according to the same measuring unit, or they may be dimensional if hybrid units are used

The Petersen matrix

Properties

If all components are expressed in mass and according to the same M.U. ($\boldsymbol{a_{i,j}}$ adimentional) & if all components are included (none omitted) then the mass conservation principle states that, for each process:

$$\forall i : \sum_{j=1}^{n} a_{i,j} = 0$$

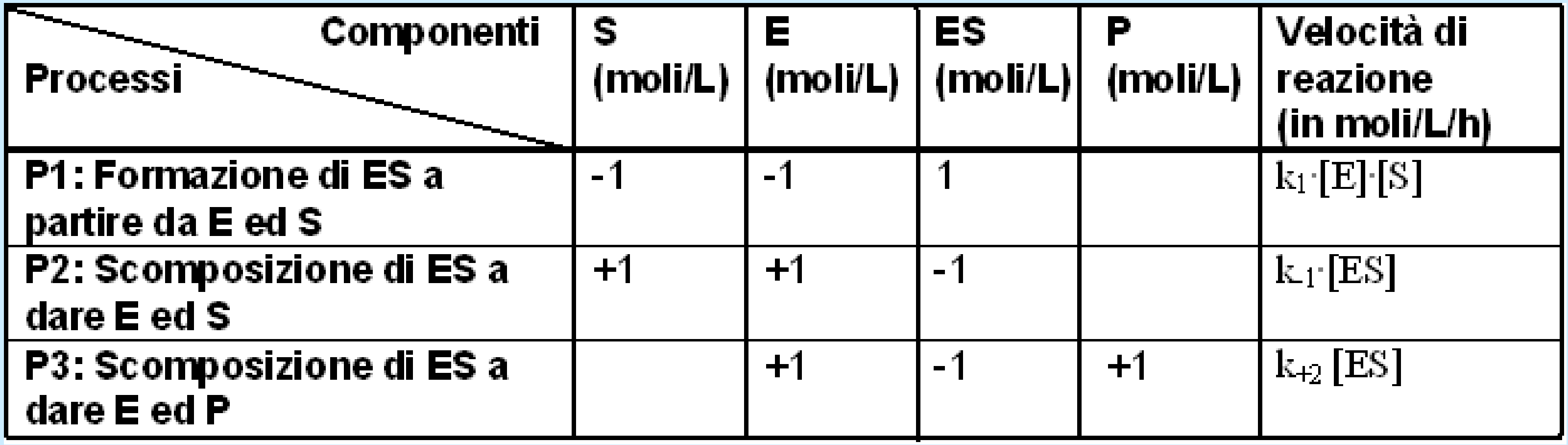
Moreover, the rate of variation of each component for the simultaneous effect of all processes, can be easily assessed:

$$\forall j : r_{Cj} = \frac{d[C_j]}{dt} = \sum_{i=1}^{m} a_{i,j} \cdot r_i$$

The Petersen matrix

Example: Micaelis-Menten enzimatic reaction

$$S + E \underset{k_{-1}}{\overset{k_{+1}}{\rightleftarrows}} ES \xrightarrow{k_{+2}} P + E$$



Componenti Processi	S (moli/L)	E (moli/L)	ES (moli/L)	P (moli/L)	Velocità di reazione (in moli/L/h)
P1: Formazione di ES a partire da E ed S	-1	-1	1		$k_1 \cdot [E] \cdot [S]$
P2: Scomposizione di ES a dare E ed S	+1	+1	-1		$k_{-1} \cdot [ES]$
P3: Scomposizione di ES a dare E ed P		+1	-1	+1	$k_{+2}\,[ES]$

$$r_{Cj} = \frac{d[Cj]}{dt} = \sum_{i=1}^{m} a_{i,j} \cdot r_i$$

$$\Longrightarrow$$

$$\begin{cases} \dfrac{d[S]}{dt} = -k_1[E][S] + k_{-1}[ES] \\ \dfrac{d[E]}{dt} = -k_1[E][S] + (k_{-1} + k_2)[ES] \\ \dfrac{d[ES]}{dt} = k_1[E][S] - (k_{-1} + k_2)[ES] \\ \dfrac{d[P]}{dt} = k_2[ES] \end{cases}$$

The Petersen matrix

Example:

Processes:
P1: Hydrolysis of particulate organic matter (X) to form soluble products (S):

Stoichiometry: $X_s \rightarrow S$

reaction kinetics = Contois (*) with respect to X_s/X_b

P2: Aerobic Growth of biomass (Xh) with consumption of soluble organics

Stoichiometry: $S + (1-Y)O_2 \rightarrow Y\ X_b$

reaction kinetics = first order with respect to biomass concentration and monod-type with respect to oxygen and soluble organics concentration.

The Petersen matrix

Example:

(*) **Contois kinetic model**:

I

$$r_{contois} = \frac{k \cdot X_S / X_b}{k_x + X_S / X_b} = k \cdot \frac{X_S}{k_x \cdot X_b + X_S}$$

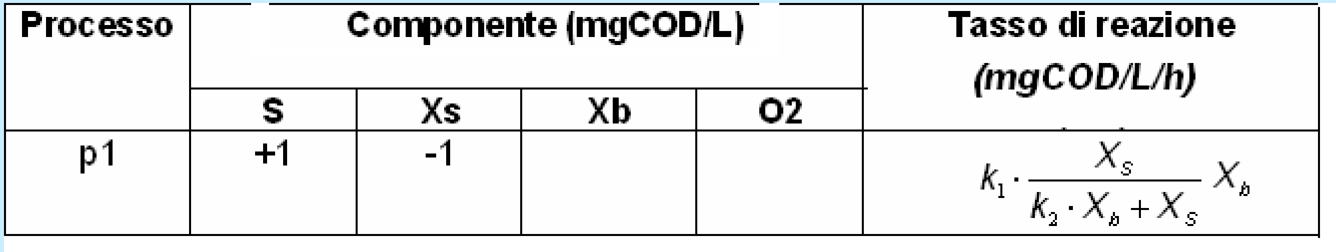
For $X_s >> X_b$ the fractionary term tends to 1

The Petersen matrix will be made of:

4 columns: S, X_s, X_b, O_2 + kinetics columns

2 rows p_1,p_2,

For p_1 we can write:



Processo	**Componente (mgCOD/L)**				**Tasso di reazione (mgCOD/L/h)**
	S	**Xs**	**Xb**	**O2**	
p1	+1	-1			$k_1 \cdot \frac{X_S}{k_2 \cdot X_b + X_S} X_b$

with: k_1: in $gCOD_{Xs}$/L/h

k_2: -

The Petersen matrix

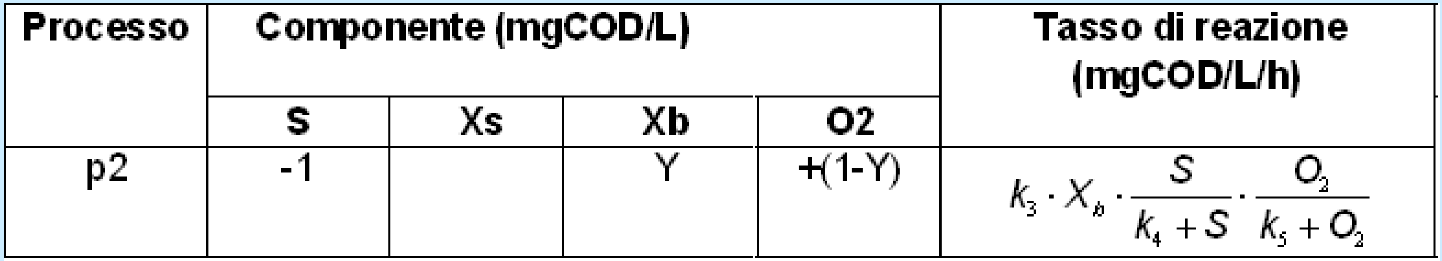
(followed)

When considering p2, it has to be understood that when expressing O2 in COD terms, the following conversion applies:

1 gO_2 = - 1 gCOD

This comes from the fact that O2 receives and does not release electrons, that is why it corresponds to a negative ‘COD’.

Then:



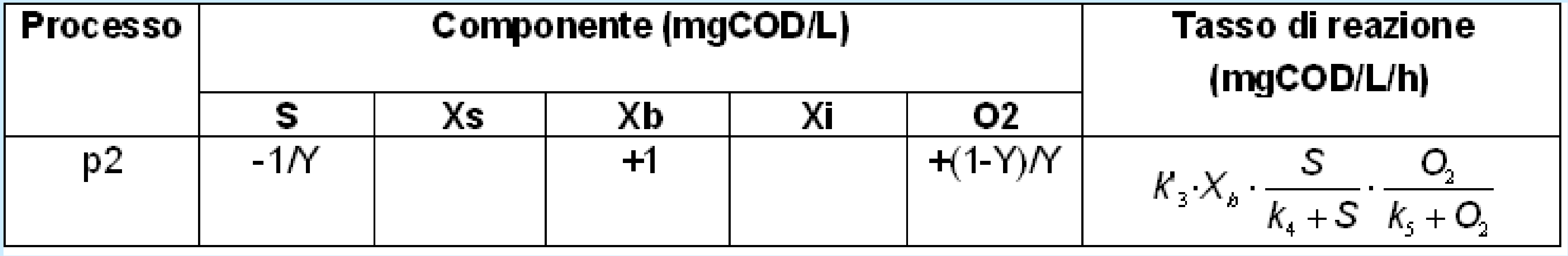
Processo	Componente (mgCOD/L)				Tasso di reazione (mgCOD/L/h)
	S	Xs	Xb	O2	
p2	-1		Y	+(1-Y)	$k_3 \cdot X_b \cdot \frac{S}{k_4 + S} \cdot \frac{O_2}{k_5 + O_2}$

With k_3: 1/h, k_4 mg/L, k_5 (mg/L)

The Petersen matrix

(followed)

Process p2:
It can be also expressed with reference to biomass formation instead of substrate uptake.
By dividing all stoichiometric coefficient by Y:



Processo	**Componente (mgCOD/L)**					**Tasso di reazione (mgCOD/L/h)**
	S	**Xs**	**Xb**	**Xi**	**O2**	
p2	-1/Y		+1		+(1-Y)/Y	$K'_3 \cdot X_b \cdot \frac{S}{k_4 + S} \cdot \frac{O_2}{k_5 + O_2}$

With k'_3: 1/h, k_4 mg/L, k_5 (mg/L)

And: $k'_3 = k_3 \cdot Y$

The Activated Sludge Model
International Water Association (IWA)

The ASM 1

The Activated Sludge Model was proposed by the International Water Association (IWA) in 1987 as the state of the art model for activated sludge description.
The first release (ASM1) considers biological processes involved in the removal of the organic matter and nitrogen.

It comprises:

- *13 components* (organics, nitrogen substances, biomasses, oxygen, alkalinity)

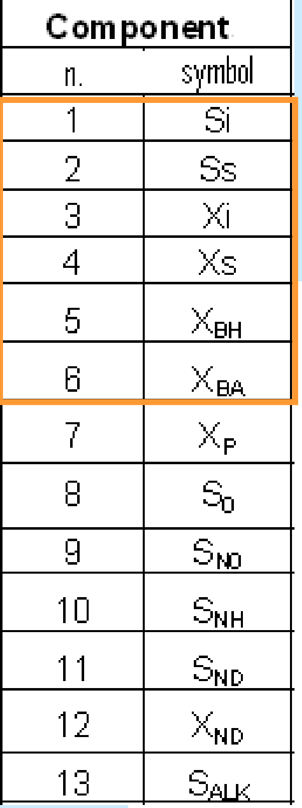
- *8 processes:* (biomass growth/decay, hydrolysis and ammonification)

- *4 stoichiometric parameters*

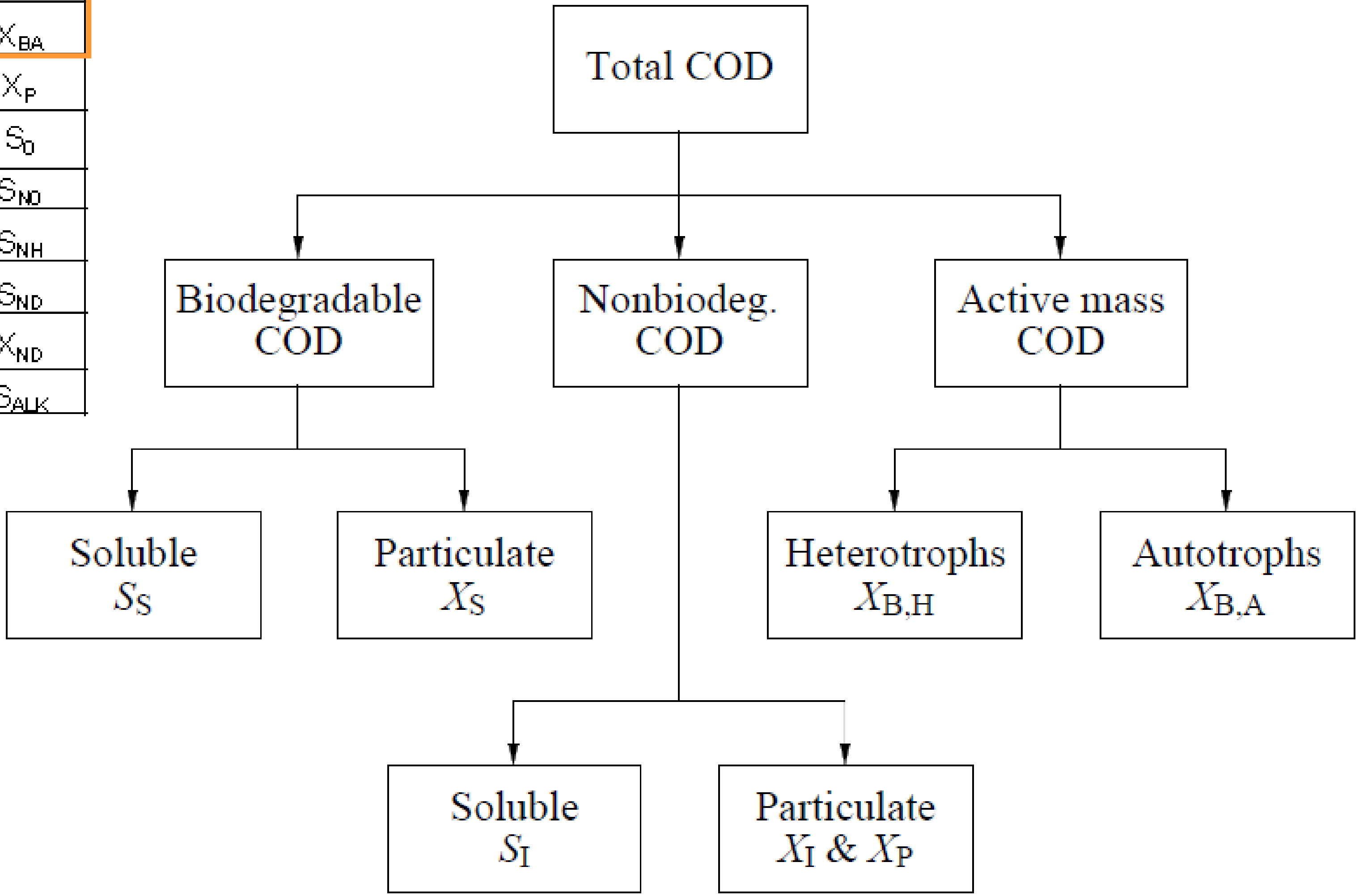
- *13 kinetic constants*

The ASM 1: components

Organic compounds (mgCOD/L)



Component	
n.	symbol
1	S_i
2	S_S
3	X_i
4	X_S
5	X_{BH}
6	X_{BA}
7	X_P
8	S_O
9	S_{NO}
10	S_{NH}
11	S_{ND}
12	X_{ND}
13	S_{ALK}



Total COD

Biodegradable COD

Nonbiodeg. COD

Active mass COD

Soluble S_S

Particulate X_S

Heterotrophs $X_{B,H}$

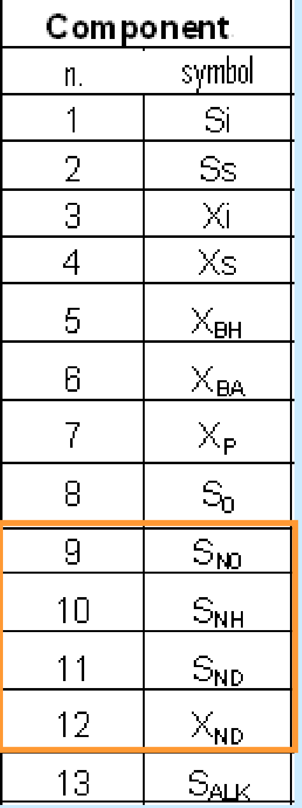
Autotrophs $X_{B,A}$

Soluble S_I

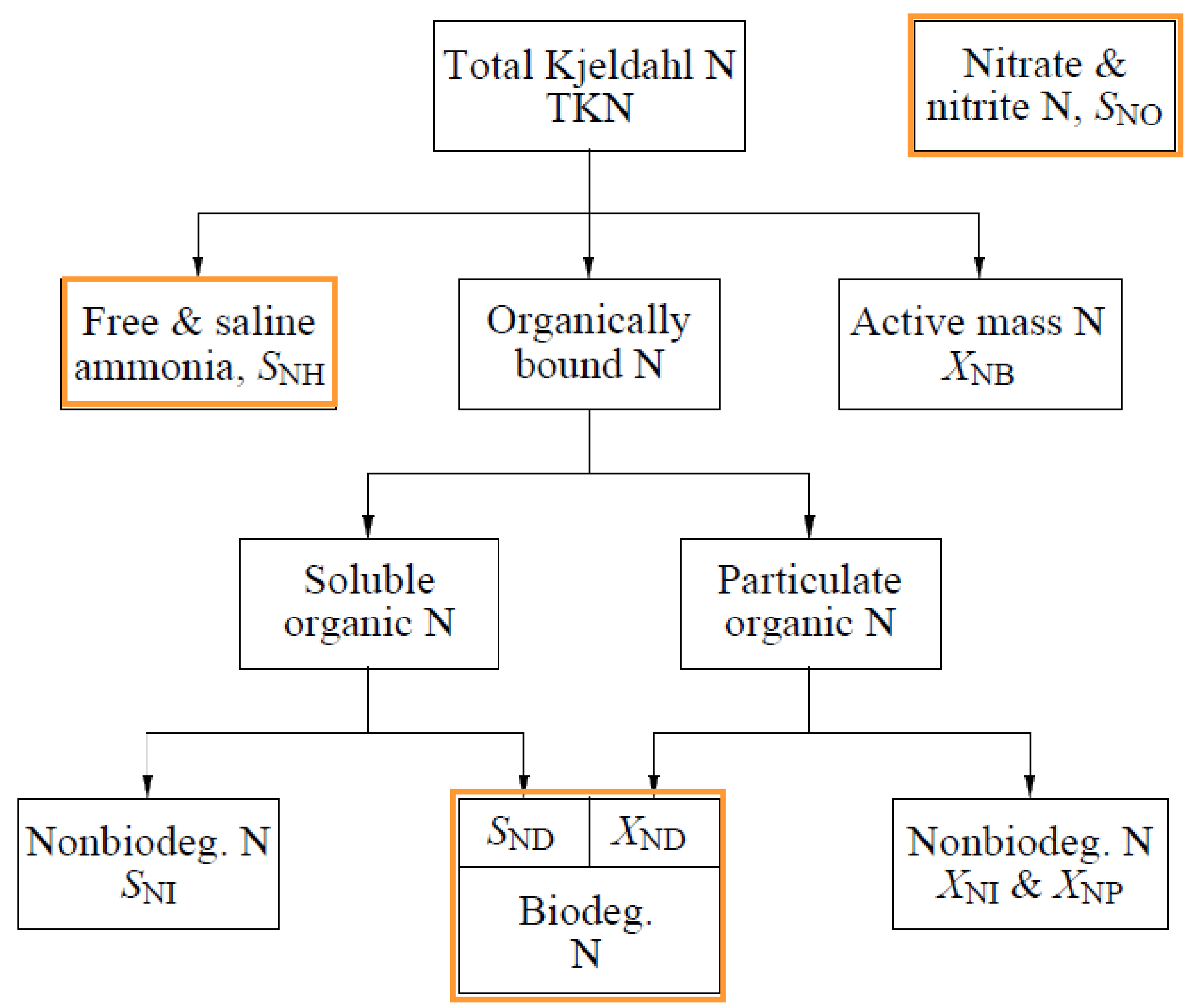
Particulate X_I & X_P

The ASM 1 : components

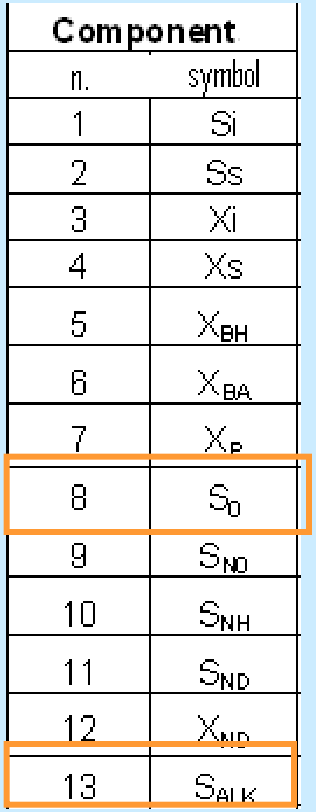
Nitrogen compounds (mgN/L)



Component	
n.	symbol
1	S_I
2	S_S
3	X_I
4	X_S
5	X_{BH}
6	X_{BA}
7	X_P
8	S_O
9	S_{NO}
10	S_{NH}
11	S_{ND}
12	X_{ND}
13	S_{ALK}



The ASM 1 : components



Component	
n.	symbol
1	S_I
2	S_S
3	X_I
4	X_S
5	X_{BH}
6	X_{BA}
7	X_P
8	S_O
9	S_{NO}
10	S_{NH}
11	S_{ND}
12	X_{ND}
13	S_{ALK}

Dissolved oxygen (mgO2/L)

Alkalinity (mM)

The ASM 1 : processes

- Biomass growth processes
  - – Aerobic growth of heterotrophs: (process 1)
  - – Anoxic growth of heterotrophs: (process 2)
  - –Aerobic growth of autotrophs (process 3)
- Biomass decay processes:
  - – decay of heterotrophs (process 4)
  - – decay of autotrophs (process 5)

Processes that convert substrates into more biomass utilisable forms

- Ammonification of the soluble organic nitrogen (process 6)
- Hydrolysis of X_S (process 7)
- Hydrolysis of X_{ND} (process 8)

The ASM 1 : processes

Process 1: Aerobic growth of heterotrophs

Stoichiometry $$\frac{1}{Y_H}S_S + \left(\frac{1-Y_H}{Y_H}\right)S_O + i_{XB}S_{NH} + \frac{i_{XB}}{14}S_{ALK} \rightarrow X_{BH}$$

A fraction of the readily biodegradable substrate is used for growth of heterotrophic biomass and the balance is oxidized for energy, giving rise to an associated oxygen demand.

•Ammonium is uptaken as N-source

•There is an alkalinity change due to ammonia uptake from a solution where it is present as ammonium-ion: ($NH_4^+ \leftrightarrow NH_3 + H^+$).

→ 1 mole of H^+ is released, and consumes 1 mole of alkalinity, per mole of NH_3 (equal to 14 g of N).

The ASM 1 : processes

Process 1: Aerobic growth of heterotrophs:

kinetic equation: $$r_{Xbh} = \hat{\mu}_H \cdot \left(\frac{S_S}{S_S + k_S} \right) \cdot \left(\frac{S_O}{S_O + k_{OH}} \right) \cdot X_{BH}$$

The growth is modeled as first order for concentration of biomass and by using Michaelis-Menten terms for both the concentration of S_S and S_O that may be rate limiting

The ASM 1 : processes

Process 2: Anoxic growth of heterotrophs

Stoichiometry: $\frac{1}{Y_H}S_S + \frac{1-Y_H}{2{,}86 \cdot Y_H}S_{NO} + i_{XB}S_{NH} + (\frac{i_{XB}}{14} - \frac{1}{14} \cdot \frac{1-Y_H}{2{,}86 \cdot Y_H})S_{ALK} \rightarrow X_{BH}$

A fraction of the readily biodegradable substrate is used for growth of heterotrophic biomass and the balance is oxidized for energy giving rise to an associated nitrate demand (reduced to nitrates).

$$NO_3^- + 6H^+ + 5e^- \rightarrow 1/2N_2 + 3H_2O$$

1 mole N = 14 g N = 5 e- = 5·8 g COD
→ 1 gN = -2,86 gCOD

- There is an alkalinity change due to ammonia and nitrate uptake

The ASM 1 : processes

Process 2: Anoxic growth of heterotrophs:

kinetic equation: $\hat{\mu}_H \cdot \left(\frac{S_S}{S_S + k_S} \right) \cdot \left(\frac{S_{NO}}{S_{NO} + k_{NO}} \right) \cdot \left(\frac{K_{OH}}{K_{OH} + S_O} \right) \cdot \eta_g \cdot X_{BH}$

The growth is modeled as first order for concentration of biomass and by using Michaelis-Menten terms for both the concentration of S_S and S_O that may be rate limiting

A switching function is used so that anoxic growth does not take place when oxygen is present (oxygen is a non-competitive inhibitor)

$\eta g<1$: This reduced rate could either be caused by a lower maximum growth rate under anoxic conditions or because only a fraction of the heterotrophic biomass is able to use nitrate as electron acceptor

The ASM 1 : processes

Process 3: Aerobic growth of autotrophs

Stoichiometry: $$\left(\frac{1}{Y_A}+i_{XB}\right)S_{NH}+\frac{4{,}57-Y_A}{Y_A}O_2+\left(\frac{i_{XB}}{14}+\frac{2}{14\cdot Y_A}\right)S_{ALK}\rightarrow X_{BA}+\frac{1}{Y_A}S_{NO}$$

As commented before.

Ammonium is used both as N-source and e-donor. It is oxidized to nitrate. Alkalinity consumption is associated with ammonium uptake and nitrate production

Remember that: $NH_3 + 2\ O_2 \rightarrow NO_3^- + H^+ + H_2O$;

So: 1 mole NH_3 = 14 g N = 2 mole O2 = 64 g COD
→ 1 gN = 4,57 g COD

The ASM 1 : processes

Process 3: Aerobic growth of autotrophs:

kinetic equation: $\hat{\mu}_A \cdot \left(\frac{S_{NH}}{S_{NH} + k_{NH}} \right) \cdot \left(\frac{S_O}{S_O + k_{OA}} \right) \cdot X_{BA}$

The growth is modeled as first order for the concentration of biomass and by using Michaelis-Menten terms for both the concentration of S_{NH} and S_O that may be rate limiting.

The ASM 1 : processes

Process 4: Decay of heterotrophs

Stoichiometry: $X_{BH} \rightarrow (1 - f_P) \cdot X_S + f_P \cdot X_P + i_{XB} \cdot (1 - f_P) \cdot X_{ND}$

The process is modeled according to the death-regeneration hypothesis:

dead organisms produce particulate organics:
- a portion is considered to be non-biodegradable (cell debris X_P).
- the remaining fraction adds to the pool of slowly biodegradable substrate.
- the organic nitrogen associated with the X_{BH} becomes available as particulate organic nitrogen.

No loss of COD is involved and no electron acceptor is utilized.

The ASM 1 : processes

Process 4: Decay of heterotrophs :

kinetic equation: $b_H \cdot X_{BH}$

The decay process is modeled as first order for the concentration

Its rate is independent from the available electron acceptor.

The ASM 1 : processes

Process 5: Decay of autotrophs

Stoichiometry: $X_{BA} \rightarrow (1 - f_P) \cdot X_S + f_P \cdot X_P + i_{XB} \cdot (1 - f_P) \cdot X_{ND}$

Kinetic equation: $b_A \cdot X_{BA}$

The ASM 1 : processes

Process 6: Ammonification

Stoichiometry: $S_{ND} \rightarrow S_{NH} + \frac{1}{14} \cdot S_{Alk}$

Biodegradable soluble organic nitrogen is converted via extracellular enzymes to ammoniacal nitrogen.
Alkalinity is formed from the formation of the ammonium ion.

Kinetic equation: $k_A \cdot X_{BH} \cdot S_{ND}$

first-order process for both soluble organic nitrogen and heterotrophs

The ASM 1 : processes

Process 7: Hydrolysis of particulated organics

Stoichiometry: $X_S \rightarrow S_S$

Slowly biodegradable substrate enmeshed in the sludge mass is broken down extracellularly, producing readily biodegradable substrate available to the organisms for growth.

Kinetic equation: $k_H \cdot \left(\frac{X_S / X_{BH}}{X_S / X_{BH} + k_X} \right) \cdot \left[\left(\frac{S_O}{S_O + k_{OH}} \right) + \eta_h \left(\frac{S_{NO}}{S_{NO} + k_{NO}} \right) \left(\frac{K_{OH}}{K_{OH} + S_O} \right) \right] \cdot X_{BH}$

The kinetics is that one of a *surface reaction* and occurs only under aerobic and anoxic conditions. The rate of hydrolysis is reduced under anoxic conditions compared with aerobic conditions by a factor ηh (<1). The rate is also first-order with respect to the heterotrophic biomass present but saturates as the amount of entrapped substrate becomes large in proportion to the biomass.

The ASM 1 : processes

Process 8: Hydrolysis of particulate nitrogen

Stoichiometry: $X_{ND} \rightarrow S_{ND}$

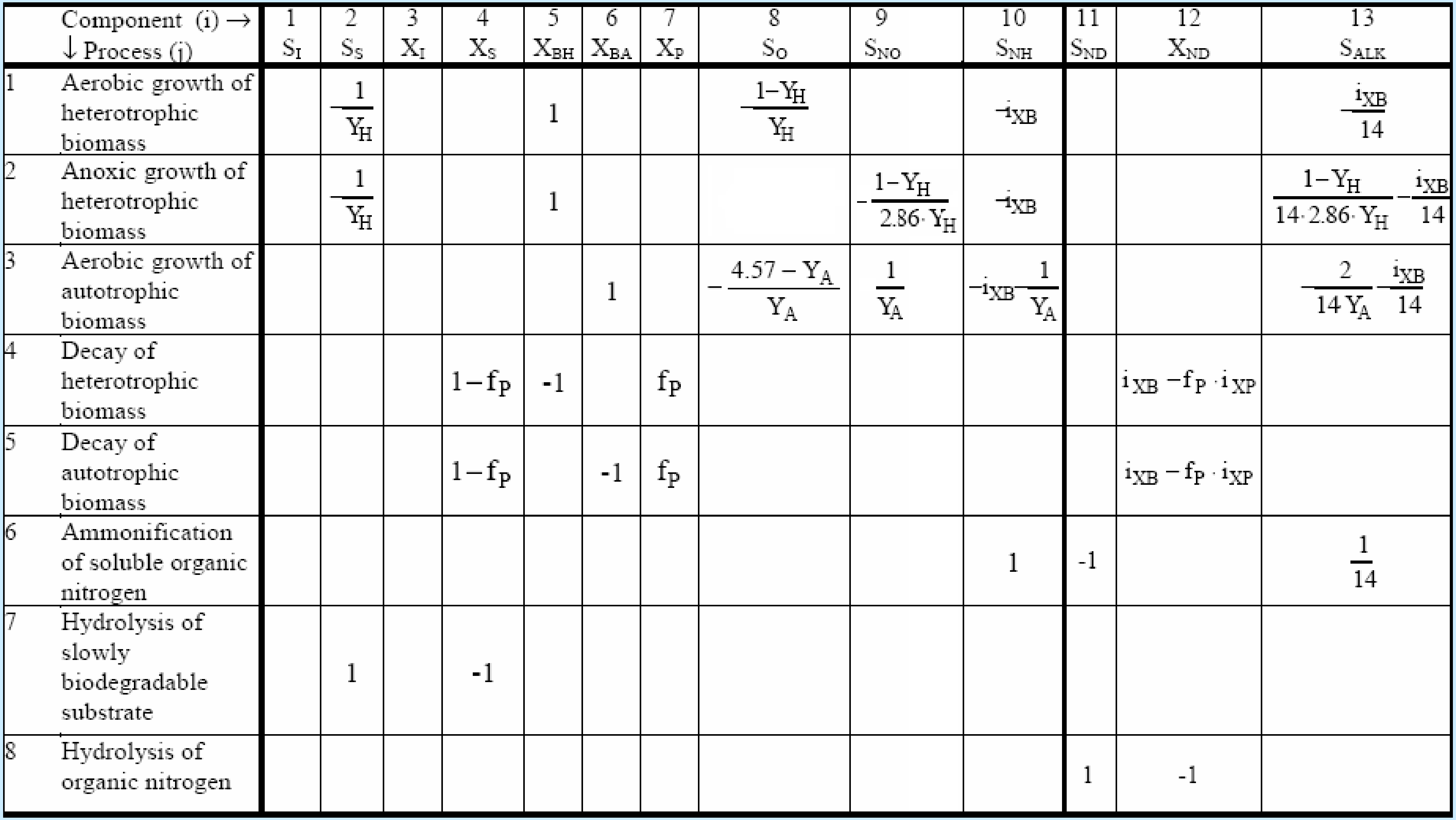
Biodegradable particulate organic nitrogen is broken down to soluble organic nitrogen

Kinetic equation: $k_H \cdot \left(\frac{X_{ND}/X_{BH}}{X_{ND}/X_{BH} + k_X} \right) \cdot \left[\left(\frac{S_O}{S_O + k_{OH}} \right) + \eta_h \left(\frac{S_{NO}}{S_{NO} + k_{NO}} \right) \left(\frac{K_{OH}}{K_{OH} + S_O} \right) \right] \cdot X_{BH}$

The rate is proportional to the hydrolysis reaction for entrapped organics described above

The ASM 1 : processes

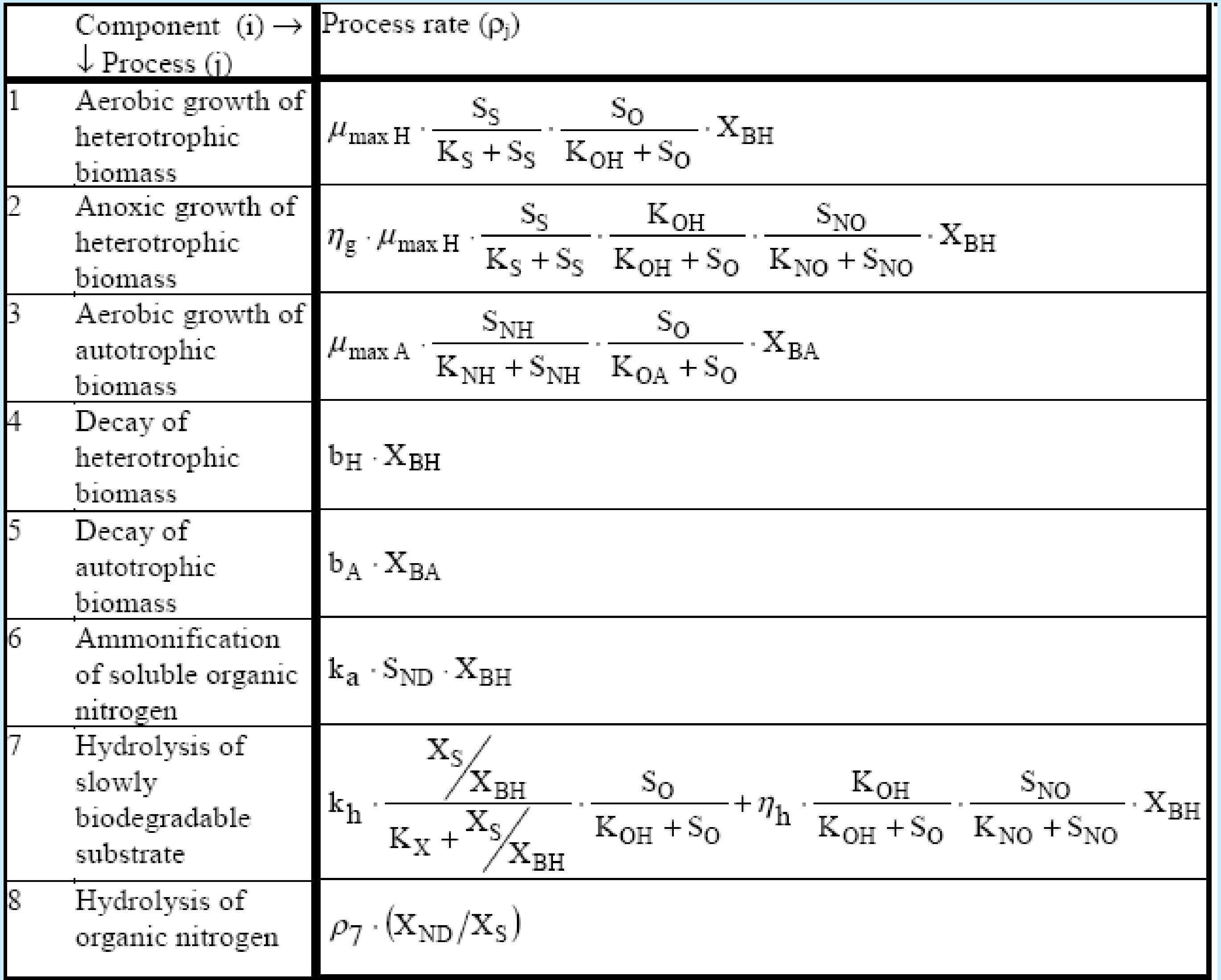
Overall Petersen Matrix



Component (i) → ↓ Process (j)	1 S_I	2 S_S	3 X_I	4 X_S	5 X_{BH}	6 X_{BA}	7 X_P	8 S_O	9 S_{NO}	10 S_{NH}	11 S_{ND}	12 X_{ND}	13 S_{ALK}
1 Aerobic growth of heterotrophic biomass		$-\frac{1}{Y_H}$			1			$-\frac{1-Y_H}{Y_H}$		$-i_{XB}$			$-\frac{i_{XB}}{14}$
2 Anoxic growth of heterotrophic biomass		$-\frac{1}{Y_H}$			1				$-\frac{1-Y_H}{2.86\cdot Y_H}$	$-i_{XB}$			$\frac{1-Y_H}{14\cdot 2.86\cdot Y_H}-\frac{i_{XB}}{14}$
3 Aerobic growth of autotrophic biomass						1		$-\frac{4.57-Y_A}{Y_A}$	$\frac{1}{Y_A}$	$-i_{XB}-\frac{1}{Y_A}$			$-\frac{2}{14\,Y_A}-\frac{i_{XB}}{14}$
4 Decay of heterotrophic biomass				$1-f_P$	-1		f_P					$i_{XB}-f_P\cdot i_{XP}$	
5 Decay of autotrophic biomass				$1-f_P$		-1	f_P					$i_{XB}-f_P\cdot i_{XP}$	
6 Ammonification of soluble organic nitrogen										1	-1		$\frac{1}{14}$
7 Hydrolysis of slowly biodegradable substrate		1		-1									
8 Hydrolysis of organic nitrogen											1	-1	

The ASM 1 : processes

Overall Petersen Matrix



	Component (i) → ↓ Process (j)	Process rate (ρ_j)
1	Aerobic growth of heterotrophic biomass	$\mu_{\max H} \cdot \frac{S_S}{K_S + S_S} \cdot \frac{S_O}{K_{OH} + S_O} \cdot X_{BH}$
2	Anoxic growth of heterotrophic biomass	$\eta_g \cdot \mu_{\max H} \cdot \frac{S_S}{K_S + S_S} \cdot \frac{K_{OH}}{K_{OH} + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot X_{BH}$
3	Aerobic growth of autotrophic biomass	$\mu_{\max A} \cdot \frac{S_{NH}}{K_{NH} + S_{NH}} \cdot \frac{S_O}{K_{OA} + S_O} \cdot X_{BA}$
4	Decay of heterotrophic biomass	$b_H \cdot X_{BH}$
5	Decay of autotrophic biomass	$b_A \cdot X_{BA}$
6	Ammonification of soluble organic nitrogen	$k_a \cdot S_{ND} \cdot X_{BH}$
7	Hydrolysis of slowly biodegradable substrate	$k_h \cdot \frac{X_S / X_{BH}}{K_X + X_S / X_{BH}} \cdot \frac{S_O}{K_{OH} + S_O} + \eta_h \cdot \frac{K_{OH}}{K_{OH} + S_O} \cdot \frac{S_{NO}}{K_{NO} + S_{NO}} \cdot X_{BH}$
8	Hydrolysis of organic nitrogen	$\rho_7 \cdot (X_{ND}/X_S)$

The ASM 1

Remember that the *Petersen matrix* helps in identifying the overall rate of reaction of each component

E.g.: For heterotrophic biomass:

$$\frac{dX_{BH}}{dt} = \hat{\mu}_H \cdot \left(\frac{S_S}{S_S + k_S} \right) \cdot X_{BH} \cdot \left[\left(\frac{S_O}{S_O + k_{OH}} \right) + \eta_g \cdot \left(\frac{S_{NO}}{S_{NO} + k_{NO}} \right) \cdot \left(\frac{K_{OH}}{K_{OH} + S_O} \right) \right] - b_H \cdot X_{BH}$$

For dissolved oxygen:

$$-\frac{dS_O}{dt} = \hat{\mu}_H \cdot \left(\frac{S_S}{S_S + k_S} \right) \cdot \left(\frac{S_O}{S_O + k_{OH}} \right) \cdot X_{BH} \cdot \frac{1 - Y_H}{Y_H} + \hat{\mu}_A \cdot \left(\frac{S_{NH}}{S_{NH} + k_{NH}} \right) \cdot \left(\frac{S_O}{S_O + k_{OA}} \right) \cdot X_{BA} \cdot \frac{4{,}57 - Y_A}{Y_A}$$

The ASM 1

Applications:

Simulation of the behavior of activated sludge processes as a support in operation, diagnosis, scenario analysis

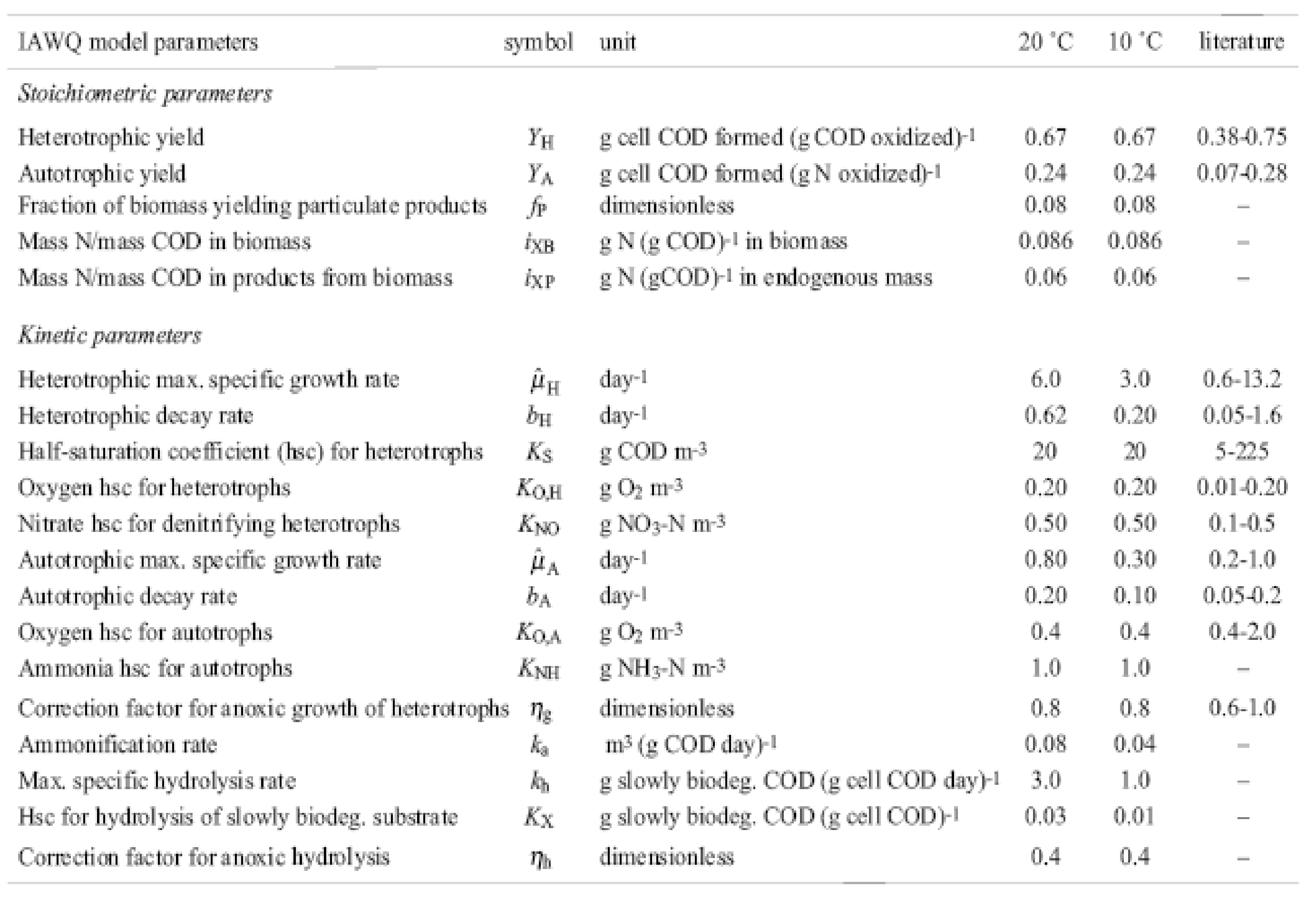
It is however necessary the:

- the influent flow is characterized according to the ASM components
- Stoichiometric parameters and kinetic constants are appropriately tuned

- For urban/domestic wastewaters, reliable reference values are available
- For industrial wastewaters, a calibration phase is needed.

The ASM 1

Default parameters values



IAWQ model parameters	symbol	unit	20 °C	10 °C	literature
Stoichiometric parameters					
Heterotrophic yield	Y_H	g cell COD formed (g COD oxidized)$^{-1}$	0.67	0.67	0.38-0.75
Autotrophic yield	Y_A	g cell COD formed (g N oxidized)$^{-1}$	0.24	0.24	0.07-0.28
Fraction of biomass yielding particulate products	f_P	dimensionless	0.08	0.08	–
Mass N/mass COD in biomass	i_{XB}	g N (g COD)$^{-1}$ in biomass	0.086	0.086	–
Mass N/mass COD in products from biomass	i_{XP}	g N (gCOD)$^{-1}$ in endogenous mass	0.06	0.06	–
Kinetic parameters					
Heterotrophic max. specific growth rate	$\hat{\mu}_H$	day^{-1}	6.0	3.0	0.6-13.2
Heterotrophic decay rate	b_H	day^{-1}	0.62	0.20	0.05-1.6
Half-saturation coefficient (hsc) for heterotrophs	K_S	g COD m^{-3}	20	20	5-225
Oxygen hsc for heterotrophs	$K_{O,H}$	g O_2 m^{-3}	0.20	0.20	0.01-0.20
Nitrate hsc for denitrifying heterotrophs	K_{NO}	g NO_3-N m^{-3}	0.50	0.50	0.1-0.5
Autotrophic max. specific growth rate	$\hat{\mu}_A$	day^{-1}	0.80	0.30	0.2-1.0
Autotrophic decay rate	b_A	day^{-1}	0.20	0.10	0.05-0.2
Oxygen hsc for autotrophs	$K_{O,A}$	g O_2 m^{-3}	0.4	0.4	0.4-2.0
Ammonia hsc for autotrophs	K_{NH}	g NH_3-N m^{-3}	1.0	1.0	–
Correction factor for anoxic growth of heterotrophs	η_g	dimensionless	0.8	0.8	0.6-1.0
Ammonification rate	k_a	m^3 (g COD day)$^{-1}$	0.08	0.04	–
Max. specific hydrolysis rate	k_h	g slowly biodeg. COD (g cell COD day)$^{-1}$	3.0	1.0	–
Hsc for hydrolysis of slowly biodeg. substrate	K_X	g slowly biodeg. COD (g cell COD)$^{-1}$	0.03	0.01	–
Correction factor for anoxic hydrolysis	η_h	dimensionless	0.4	0.4	–

The ASM 1

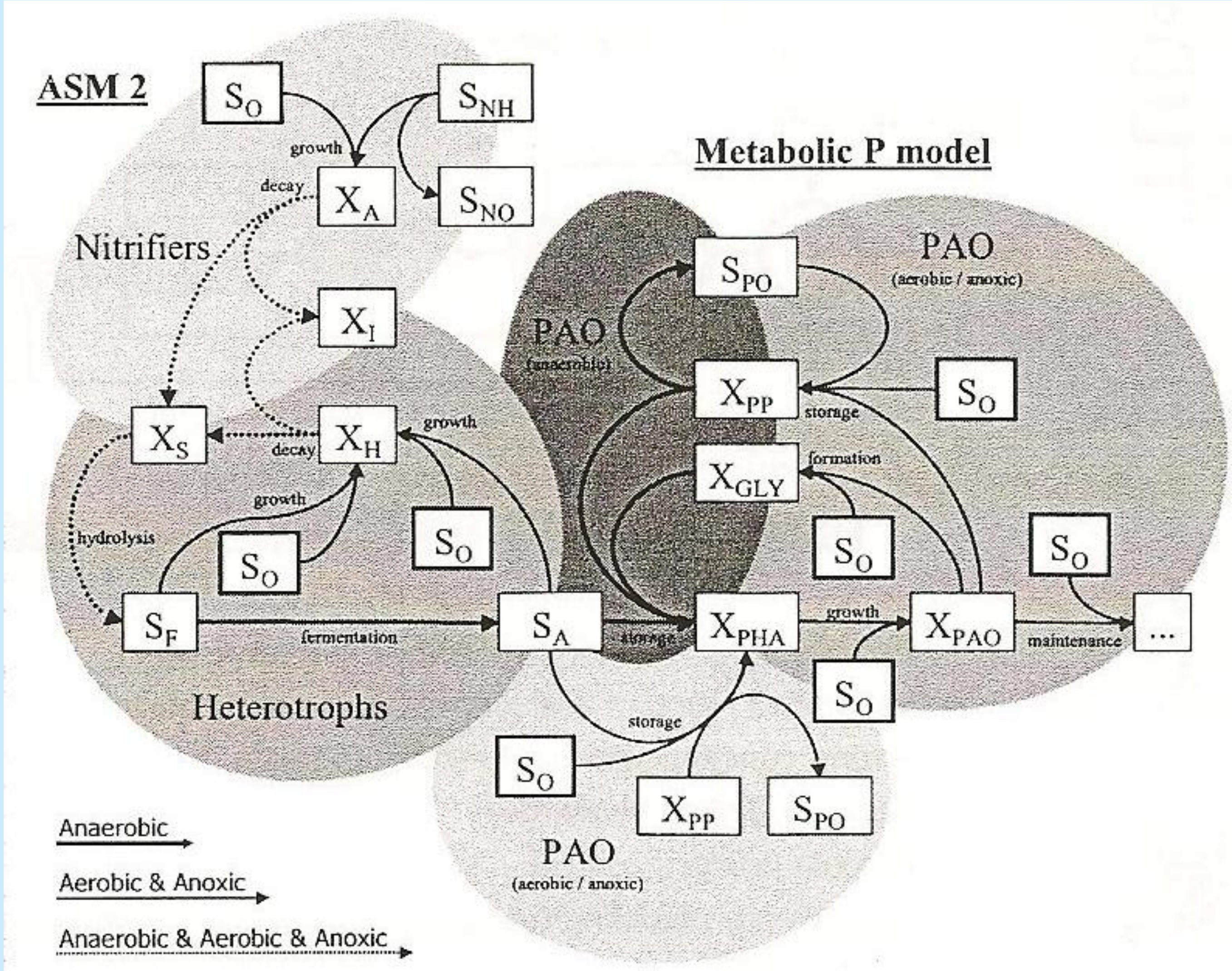
Relevant Model Restrictions

- Arrhenius equations need to be added to account for seasonal temperature variations.
- The pH is constant and near neutrality. The inclusion of alkalinity in the model allows the user to detect potential problems with pH control, but not to model them.
- Changes in the wastewater character cannot be properly handled by the model.
- The effects of limitations of nitrogen, phosphorus and other inorganic nutrients on the removal of organic substrate and on cell growth have not been considered.
- The correction factors for denitrification are fixed and constant for a given wastewater.
- The coefficients for nitrification are assumed to be constant and to incorporate any inhibitory effects that other waste constituents are likely to have on them.
- The heterotrophic biomass is homogeneous and does not undergo changes in species diversity with time.
- The entrapment of particulate organic matter in the biomass is assumed to be instantaneous.
- Hydrolysis of organic matter and organic nitrogen are coupled and occur simultaneously with equal rates.
- The type of electron acceptor present does not affect the loss of active biomass by decay.

From ASM1 to ASM2

Relevant modifications

- It includes the biological P-removal



From ASM1 to ASM3

Relevant modifications :

- It includes intracellular *storage* compounds
- The decay process is substituted by the endogenous respiration process