Tema 8a – Remocion Biologica de Nutrientes
Biological Nutrient Removal (BNR)

CI7115 – Biotecnología Ambiental

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El N se debe ir

Reasons for ammonia-N control:

1. Oxygen demand (4.57 g O_2/g N for NH_4^+-N). Medium-strength sewage has 40 mg TKN/L, giving an NOD of (40)(4.57) =183 mg O_2 demand/L. Wow!
2. Toxicity to fish and other aquatic life. The toxic species is free ammonia. Since pK_a for ammonium/ammonia is 9.1, the problem is greatest at high pH. State standards depend on temperature and pH.
3. Nutrient for algal growth, eutrophication (N>0.3 mg/L can cause a bloom).
4. Ammonia increases chlorine demand for disinfection due to the formation of chloramines. (Note: chloramines are disinfectants, so this could be a reason to add(!) ammonium to the effluent).

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Reasons for nitrite-N control:

1. Oxygen demand (1.14 g O_2/g N for NO_2^--N).
2. Methemoglobinemia ("Blue Baby" syndrome). U.S. drinking water standard is 1 mg NO_2^--N/L.
3. Nutrient for algal growth, eutrophication.
4. Disinfection chlorine demand.

Reasons for nitrate-N control:

1. Methemoglobinemia ("Blue Baby" syndrome). U.S. drinking water standard is 10 mg NO_3^--N/L. European standard is 50 mg NO_3^--N /L.
2. Nutrient for algal growth, eutrophication.

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Control de N

Total Kjeldahl Nitrogen (TKN) = organic N + NH_3-N

Organic N includes amino acids, chitin, proteins, nucleotide bases, etc.

Forms of nitrogen in wastewater:

Forms of nitrogen	Abreviation	Definition	Conc in medium strength municpal wastewater (mg N/L)
Ammonia	NH_3	NH_3	0
Ammonium ion	NH_4^+	NH_4^+	25
Total ammonium nitrogen	TAN	NH_4^++ NH_3	25
Nitrite	NO_2^-	NO_2^-	0
Nitrate	NO_3^-	NO_3^-	0
Total inorganic nitrogen	TIN	NH_4^++ NH_3+ NO_2^- + NO_3^-	25
Total Kjeldahl Nitrogen	TKN	Organic N ("bound N") + NH_4^++ NH_3 ("free N")	40
Organic Nitrogen	Organic N	TKN – (NH_4^++ NH_3)	15
Total Nitrogen	TN	Organic N + Inorganic N	40

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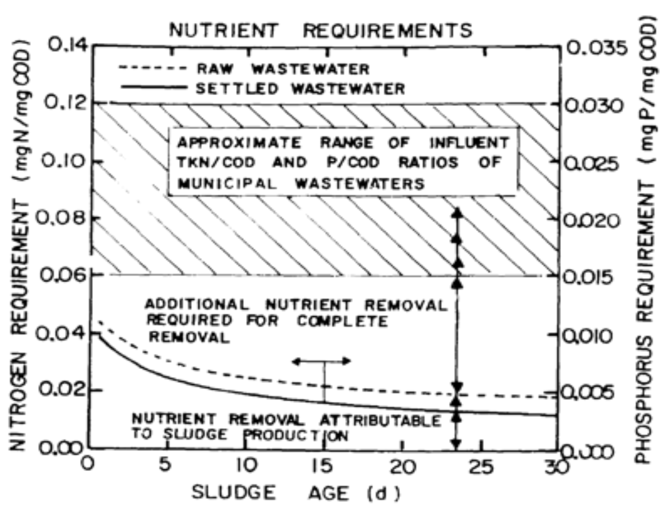
Estándares típicos de N

	mg N/L
USA Ammonia – depends on pH, fish species, temperature Nitrate, drinking water	See: http://www.epa.gov/waterscience/standards/ammonia/factsheet.html http://www.epa.gov/waterscience/standards/ammonia/ 10
SINGAPORE Ammonia Nitrate - watercourse - controlled watercourse	No standard? No standard? 4.5

Not enough nutrients are removed by cell synthesis in a conventional treatment plant



Cómo controlar el N?

Process	NH_4^+	NO_2^- & NO_3^-
Air stripping	X	
Ion exchange	X	X
Nitrification	X	
Denitrification		X
Chlorination	X	
Plant uptake	X	X
Reverse osmosis	X	X
Electrodialysis	X	X

Treatment objective	Lowest cost system
BOD removal only	Biological
Ammonia removal only	?
BOD + ammonia removal	Biological
Organic + total N removal	Biological?

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Nitrificación

A Two-Step Aerobic Process

Nitrosomonas

$$NH_4^+ \xrightarrow[O_2]{} NO_2^-$$

Nitrobacter

$$NO_2^- \xrightarrow[O_2]{} NO_3^-$$

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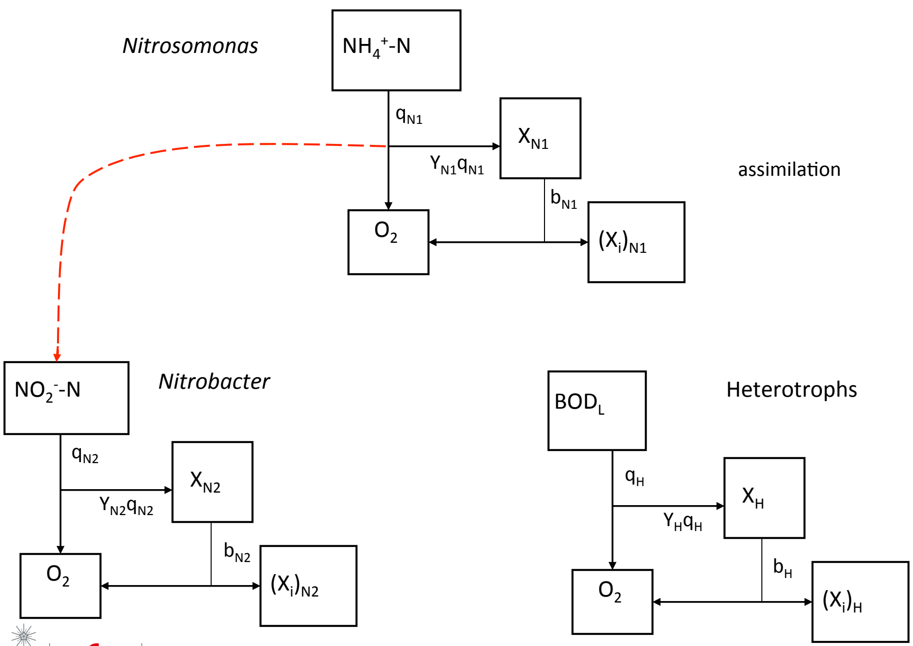

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Design Example 2: Single Tank Nitrification and BOD_L removal

1. Determine waste characteristics and effluent requirements:

$Q° = 1000\ m^3/d$
$N° = 50$ mg/L NH_4^+-N
$X_d° = 40$ mg/L
$X_i° = 45$ mg/L
$S° = 10$ mg/L
$\gamma = 1.2$ mg COD/mg vss
$S_p° = 48$ mg/L
$N^e_{max} = 2.5$ mg/L NH_4^+-N
$X_v^e = 20$ mg/L

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2. Select coefficients and design factors.

Aerobic heterotrophs

Y_H = 0.45 g vss/g BOD_L

$\hat{q}_H$ = 20 g vss/g BOD_L –d

b = 0.1 d^{-1}

K_H = 100 mg/L BOD_L

k_{hyd} = 0.1 d^{-1}

Nitrosomonas

Y_{N1} = 0.33 g vss/g NH_4^+-N

b_{N1} = 0.11 d^{-1}

$\hat{q}_{N1}$ = 2.3 g NH_4^+-N /g vss-d

K_{N1} = 1.0 mg/L NH_4^+-N

Nitrobacter

Y_{N2} = 0.083 g vss/g NO_2^--N

b_{N2} = 0.11 d^{-1}

$\hat{q}_{N2}$ = 9.8 g NO_2^--N /g vss-d

K_{N2} = 1.0 mg/L NO_2^--N

f_d = 0.8

SF = 10

Design value for X_v = 2500 mg/L

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3. Calculate $\left[\theta_x^{min}\right]_{lim}$ for each organism type

For heterotrophs: $\left[\theta_x^{min}\right]_{lim}$ **=** [(0.45)(20)-0.1]$^{-1}$ = **0.1 d**

For *Nitrosomonas*: $\left[\theta_x^{min}\right]_{lim}$ **=** [(0.33)(2.3)-0.11]$^{-1}$ = **1.5 d**

For *Nitrobacter*: $\left[\theta_x^{min}\right]_{lim}$ **=** [(0.083)(9.8)-0.11]$^{-1}$ = **1.4 d**

4. Select $\theta_x^d = S.F. \bullet \left[\theta_x^{min}\right]_{lim}$ **=** (10)(1.5) = **15 days**

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5. Solve

$$S = S^e = \frac{K_H\left(1 + b_H\theta_x^d\right)}{\theta_x^d\left(Y_H\hat{q}_H - b_H\right) - 1} = \frac{100[1+(0.1)(15)]}{15[(0.45)(20)-0.1]-1} = 1.9 \text{ mg BOD}_L/\text{L}$$

$$N_1^e = \frac{K_{N1}\left(1 + b_{N1}\theta_x^d\right)}{\theta_x^d\left(Y_{N1}\hat{q}_{N1} - b_{N1}\right) - 1} = \frac{1[1+(0.11)(15)]}{15[(0.33)(2.3)-0.1]-1} = 0.3 \text{ mg/L } NH_4^+\text{-N} << 2.5 \text{ mg/L, so OK}$$

$$N_2^e = \frac{K_{N2}\left(1 + b_{N2}\theta_x^d\right)}{\theta_x^d\left(Y_{N2}\hat{q}_{N2} - b_{N2}\right) - 1} = \frac{1.3[1+(0.11)(15)]}{15[(0.083)(9.8)-0.11]-1} = 0.4 \text{ mg/L}^\circ NO_2^- - \text{N remaining}$$

6. Determine volume requirement using the expression:

$$X_v = \frac{\theta_x}{\theta}\left[X_i^o + \frac{X_d^o}{1 + k_{hyd}\theta_x} + \frac{Y_H\left(1+0.2b_H\theta_x\right)\left(S_{eff}^o - S\right)}{1+0.2b_H\theta_x} + \frac{Y_{N1}\left(1+0.2b_{N1}\theta_x\right)\left(N_1^{o'} - N_1\right)}{1+0.2b_{N1}\theta_x} + \frac{Y_{N2}\left(1+0.2b_{N2}\theta_x\right)\left(N_2^{o'} - N_2\right)}{1+0.2b_{N2}\theta_x}\right]$$

<u>Problem</u>: N is both **assimilated** and **oxidized**. How can we account for assimilation of N?

<u>Strategy</u>: Determine cell production rates, then calculate the N removed inside these cells. To get the cell production rate for the heterotrophs, we need $S°_{eff}$:

$S^o_{eff} = S° + k_{hyd}\theta_x S_p°/(1+k_{hyd}\theta_x)$
$\quad = 20 + (0.1)(15)(48)/(1+(0.1)(15)) = 48$ mg/L

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$$\text{Heterotroph production rate} = Q^o\left[\frac{Y_H\left(S^o_{eff} - S\right)\left(1 + 0.2b_H\theta_x\right)}{1 + b_H\theta_x}\right]$$

$$= \left[\frac{1000\ m^3}{d}\right]\left[\frac{0.45\ g\ vss/g\ BOD_L\left(48 - 1.9\right)g\ BOD_L/m^3\left[1 + 0.2\left(0.1\ d^{-1}\right)\left(15\ d\right)\right]}{1 + \left(0.1\ d^{-1}\right)\left(15\ d\right)}\right]\left[\frac{kg}{1000\ g}\right]$$

$$= Q^o\left(\overline{X_H} + \overline{X_i}\right) = \left[\frac{1000\ m^3}{d}\right]\left[\frac{\left(8.3 + 2.5\right)g}{m^3}\right]\left[\frac{kg}{1000\ g}\right] = 10.8\ kg\ vss/d$$

N uptake in heterotrophs = (14 g N/113 g VSS)(10.8 kg vss/d) = 1.3 kg N/d

mg N/L assimilated = [mass flow rate (kg/d) ÷ flow rate (m^3/d)]g/L x (10^3 mg/g)
= (1.3 ÷1000)(10^3) = 1.3 mg N/L

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Conc of N remaining after heterotrophs get their share = 50 –1.3 = 48.7 mg/L

This is the concentration of N left over for *Nitrosomonas* (=N_1°').

$$\text{Nitrifier production rate} = Q^o\left[\frac{Y_{N1}\left(N^{o'}_{eff} - N\right)\left(1 + 0.2b_{N1}\theta_x\right)}{1 + b_{N1}\theta_x}\right]$$

$$= \left[\frac{1000\ m^3}{d}\right]\left[\frac{0.333\ g\ vss/g\ N\left(48.7 - 0.3\right)g\ N/m^3\left[1 + 0.2\left(0.11\ d^{-1}\right)\left(15\ d\right)\right]}{1 + \left(0.11\ d^{-1}\right)\left(15\ d\right)}\right]\left[\frac{kg}{1000\ g}\right]$$

$$= Q^o\left(\overline{X_{N1}} + \overline{\left(X_i\right)_{N1}}\right) = \left[\frac{1000\ m^3}{d}\right]\left[\frac{\left(6.0 + 2.0\right)g\ vss}{m^3}\right]\left[\frac{kg}{1000\ g}\right] = 8\ kg\ vss/d$$

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N uptake rate in *Nitrosomonas* = (14 g N/113 g VSS)(8 kg vss/d) = 1.0 kg/d

mg N/L assimilated = [mass flow rate (kg/d) ÷ flow rate (m^3/d)]g/L x (10^3 mg/g)
= (1.0 ÷1000)(10^3) = 1.0 mg N/L

Conc N available to Nitrobacter = 50 – 1.3 –1.0 – 0.3 = 47.4 mg N/L = $N_2^{o'}$

(0.3 mg N/L is NH_4^+-N left undegraded in the effluent, so it is not available to *Nitrobacter*)

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Finally, we can compute θ:

$$\theta = \frac{\theta_x}{X_v}\left[X_i^o + \frac{X_d^o}{1+k_{hyd}\theta_x} + \frac{Y_H(1+0.2b_H\theta_x)(S_{eff}^o - S)}{1+0.2b_H\theta_x} + \frac{Y_{N1}(1+0.2b_{N1}\theta_x)(N_1^{o'} - N_1)}{1+0.2b_{N1}\theta_x} + \frac{Y_{N2}(1+0.2b_{N2}\theta_x)(N_2^{o'} - N_2)}{1+0.2b_{N2}\theta_x}\right]$$

$$\theta = \frac{15}{2500}\left[45 + \frac{40}{1+(0.1)(15)} + 8.3 + 2.5 + 6.0 + 2.0 + \frac{0.083(1+0.2(0.11)(15))(47.4-0.4)}{1+0.2(0.11)(15)}\right]$$

= 15/2500(45.0 + 16.0 + 8.3 + 2.5 + 6.0 + 2.0 + 1.5 + 0.5) = 15/2500(81.8) = 0.49 d

Say that θ = 0.5 day.

V=Qθ = (1000 m^3/d)(0.5 d) = 500 m^3

7. Determine O_2 requirements using a balance on oxygen equivalents

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O_2 eq para las células

COD of cells

$C_5H_7O_2N + 5O_2 = 5CO_2 + NH_3 + 2H_2O$ $\qquad \frac{COD}{WT} = \frac{5(32)}{113} = 1.416$

NOD of cells

Each mole of $C_5H_7O_2N$ yields 1 mole NH_3 upon oxidation so:

$NH_3 + 2O_2 = HNO_3 + H_2O$ $\qquad \frac{NOD}{WT} = \frac{2(32)}{113} = 0.566$

ThOD of cells

$C_5H_7O_2N + 7O_2 = 5CO_2 + HNO_3 + 3H_2O$ $\qquad \frac{ThOD}{WT} = \frac{7(32)}{113} = 1.98$

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O_2 eq para el ammonio y el nitrito

$NH_3 + 2O_2 = HNO_3 + H_2O$ $\qquad \frac{NOD}{N} = \frac{2(32)}{14} = 4.57$

$HNO_2 + 0.5O_2 = HNO_3$ $\qquad \frac{NOD}{N} = \frac{0.5(32)}{14} = 1.14$

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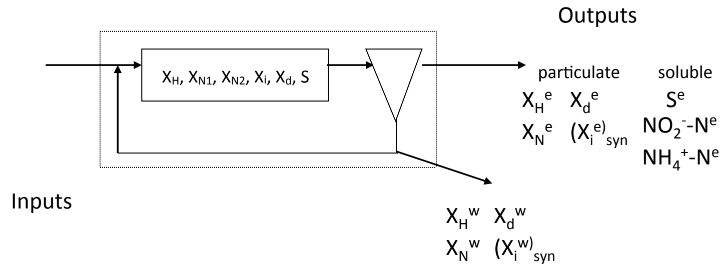
Demanda de O_2 – Nitrificación en un sólo tanque



1000(10+48)/1000=58 kg/d COD

1000(50)(4.57)/1000=229 kg/d NOD

Total input = 287 kg/d ThOD

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Output O_2 eqs

O2 demand	Mass flow rate Expression	(kg/d)	COD WT	COD flow (kg/d)	NOD WT	NOD flow (kg/d)	ThOD WT	ThOD flow (kg/d)
$X_H + (Xi)_H$	1000 (8.3+2.5)/1000=	10.8	1.42	15.3	0.57	6.1	1.98	21.4
$X_{N1} + (Xi)_{N1}$	1000 (6.0+2.0)/1000=	8.0	1.42	11.3	0.57	4.5	1.98	15.9
$X_{N2} + (Xi)_{N2}$	1000 (1.5+0.5)/1000=	2.0	1.42	2.8	0.57	1.1	1.98	4.0
X_d	1000 (16)/1000=	16.0	1.2	19.2				19.2
NH_4^+-N	1000 (0.2)/1000=	0.2			4.57	0.9		0.9
NO_2^--N	1000 (0.4)/1000=	0.4			1.14	0.5		0.5
S^e	1000 (1.9)/1000=	1.9	1.0	1.9				1.9
TOTAL OUTPUT OXYGEN EQUIVALENTS				50.6		13.2		63.7

O_2 requirement = input - output = 287 - 64 = 223 kg/d

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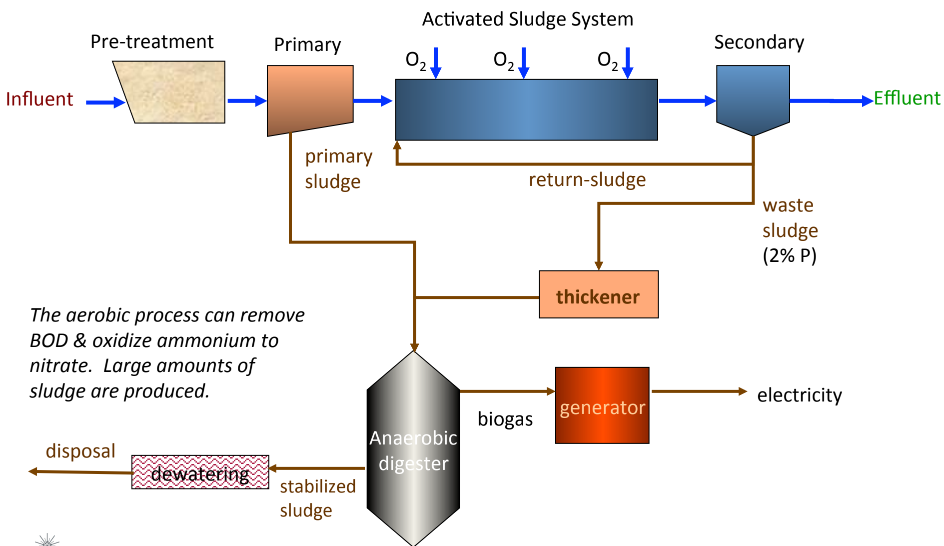
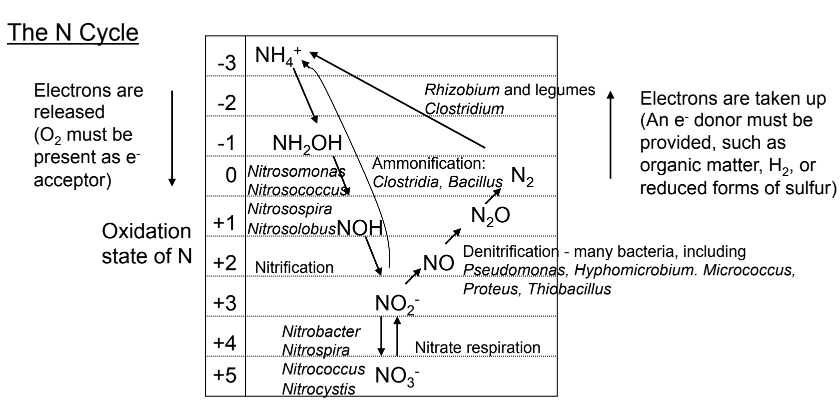
Single-Stage Nitrification in Conventional Muncipal Wastewater Treatment



The aerobic process can remove BOD & oxidize ammonium to nitrate. Large amounts of sludge are produced.

Nitrificación y Denitrificación



Cinética de la Nitrificación

Factors affecting nitrification:

- Temperature - cold temperatures greatly reduce rate.
- Dissolved oxygen - nitrifiers are sensitive to DO, K_o =0.5 mg/L
- Low pH (<6) inhibits nitrification.

Modified expression for the specific growth rate:

$$\mu = \hat{\mu}(T)\left[\frac{O}{K_o + O}\right]\left[\frac{N}{K_N + N}\right] - b(T) \qquad \theta_x^{min} = \frac{1}{\mu}$$

$$\theta_x^d = SF\left[\theta_x^{min}\right] \qquad SF \geq 2$$

Kinetic parameters are given as a function of temperature in Tables 9.1 and 9.2 (text).

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Requisitos de bufer para nitrificación

The energy reaction for nitrification is:

$NH_4^+ + 2O_2 = 2H^+ + NO_3^- + H_2O$ [Note that strong acid is formed]

Nitrification requires a pH>6, so nitrification is self-limiting unless enough alkaline buffer is present to neutralize the acid.

If we express alkalinity as $CaCO_3$, where:

$CaCO_3 + 2H^+ = Ca^{2+} + H_2CO_3$

One mole of $CaCO_3$ neutralizes all of the protons produced by oxidation of one mole of NH_4^+. The formula weight of one mole of $CaCO_3$ is 100, so 100 g of $CaCO_3$ neutralizes the acid from oxidation of 14 g NH_4^+-N. The ratio is 100/14 = 7.14 g $CaCO_3$/g N.

Medium strength wastewater contains 40 mg TKN/L, so we need 40(7.14) = 286 mg $CaCO_3$/L of alkalinity. This exceeds the available buffer in many wastewaters (often only around 100 mg $CaCO_3$/L).

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Untreated sewage in Bangladesh

Sewage → Algal blooms

↓

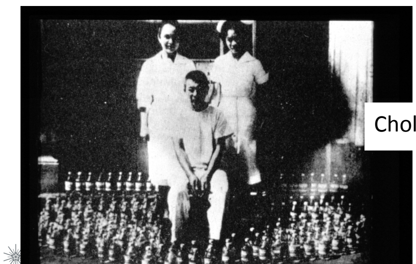
Zooplankton blooms

↓

V. cholerae blooms

↓

Human host



Cholera

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