

# NITROGEN AND PHOSPHORUS: TREATMENT CONCEPTS

**CDM**

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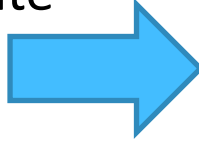


# Nitrogen Topics

- **Problems:** why remove?
- **Forms:** what is found in wastewater?
- **Conversions:** what reactions change one form to another?
- **Removal concepts:** how is N removed from wastewater?
- **Process considerations:** what design and operational factors influence removal?

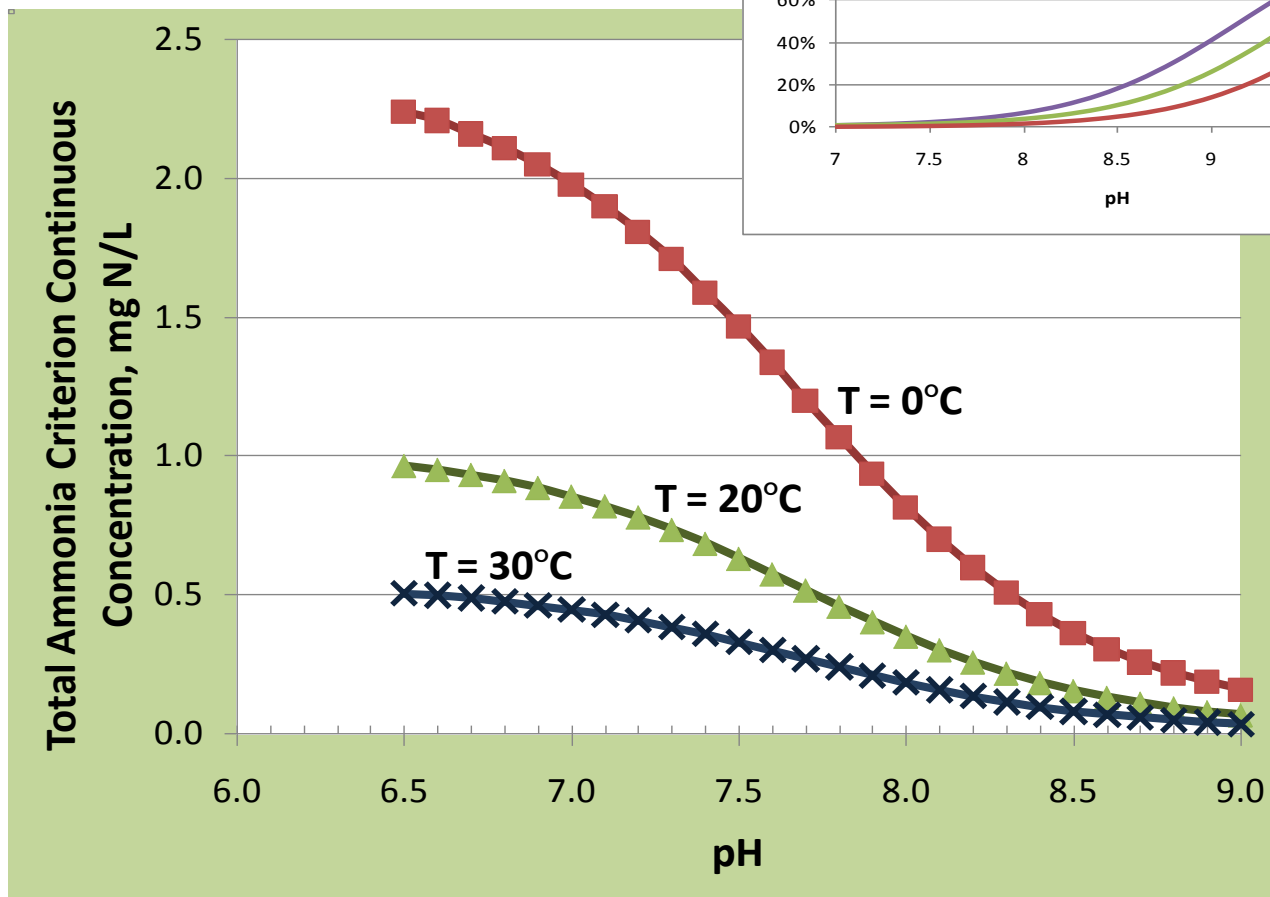
# Problems: Why Remove Nitrogen?

- Ecological consequences:
  - Greenhouse gases
  - Nitrogen may stimulate excess algae growth (eutrophication)
  - Oxidation of ammonia exerts high oxygen demand
  - Ammonia is toxic to aquatic organisms (< 1 mg/L total ammonia as N)



# Problems: Ammonia Toxicity

From 2009 Draft EPA document: data shown are for CCC with mussels present

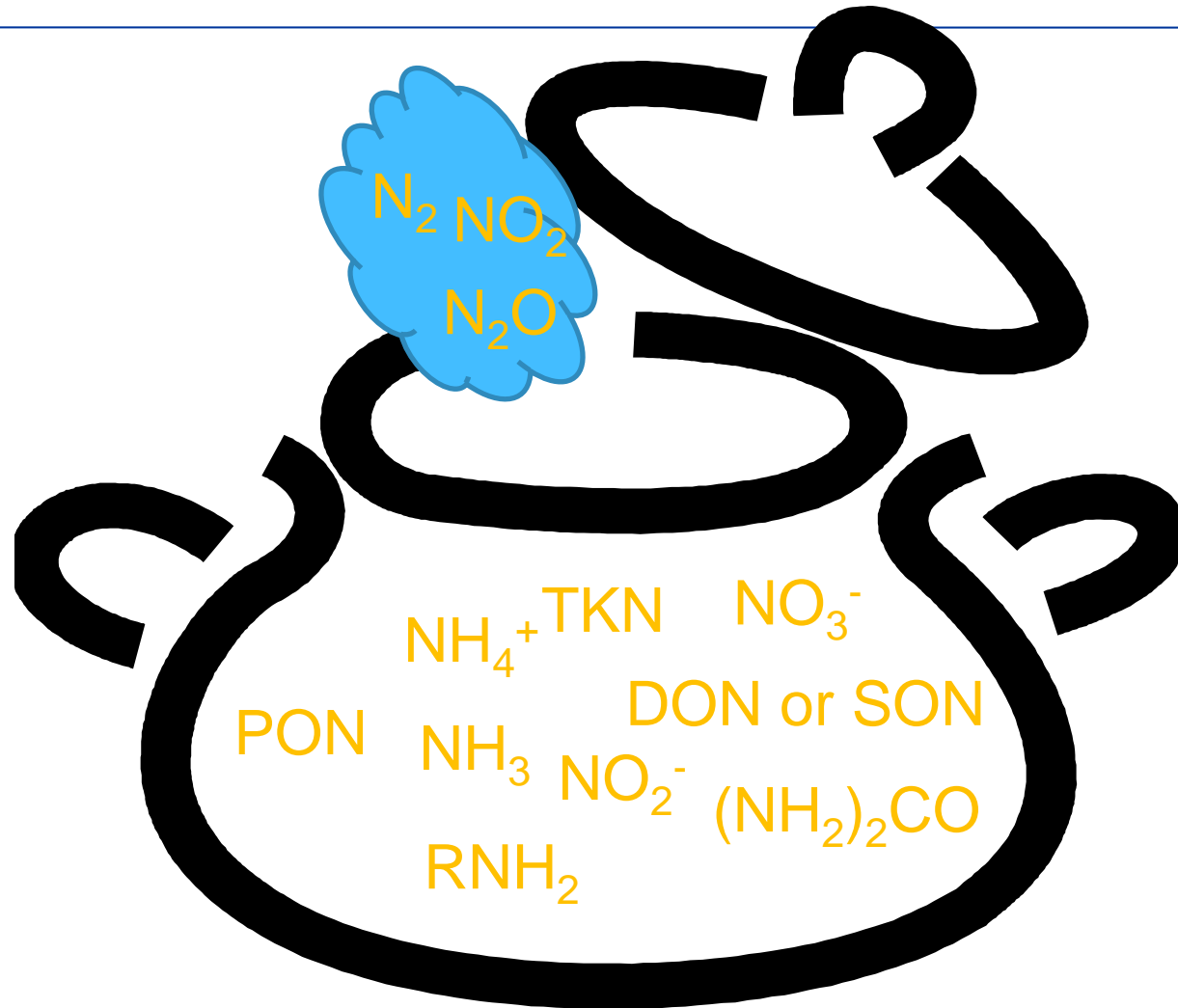


# Problems: Why Remove Nitrogen?

- Human/health consequences:
  - Nitrate: need  $< 10$  mg/L for potable water
  - Ammonia in drinking water supplies increases chlorine demand to achieve a free residual



# Forms: What N is Found in Wastewater?



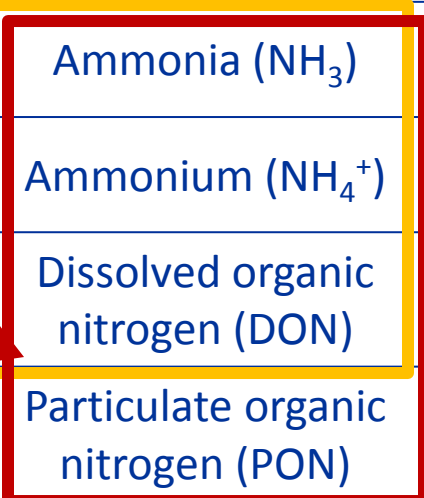
# Forms: Basic Categories

- (Gas vs.) dissolved vs. particulate
- Organic vs. inorganic

# Forms: N Compounds

Compound	Dissolved or Particulate?	Organic vs. Inorganic?
Nitrite ( $\text{NO}_2^-$ )	Dissolved	Inorganic
Nitrate ( $\text{NO}_3^-$ )	Dissolved	Inorganic
Ammonia ( $\text{NH}_3$ )	Dissolved	Inorganic
Ammonium ( $\text{NH}_4^+$ )	Dissolved	Inorganic
Dissolved organic nitrogen (DON)	Dissolved	Organic
Particulate organic nitrogen (PON)	Particulate	Organic

Filtered  
TKN



Unfiltered  
(total) TKN



## Forms: TIN? TKN? TN???

- TIN = nitrate + nitrite = NO<sub>x</sub>
- TKN = ammonia + organic nitrogen
- TN = NO<sub>x</sub> + TKN  
= NO<sub>x</sub> + ammonia + SON + PON

# Forms: Typical Concentrations in Raw Domestic Wastewater

		Wastewater Strength		
Form		Strong	Medium	Weak
TKN	Total	85	40	20
	Organic	35	15	8
	Ammonia	50	25	12
	Nitrite/Nitrate	0	0	0

Ammonia ~ 60% of TKN

(Metcalf & Eddy)

# Forms: A Note on DON/SON and PON

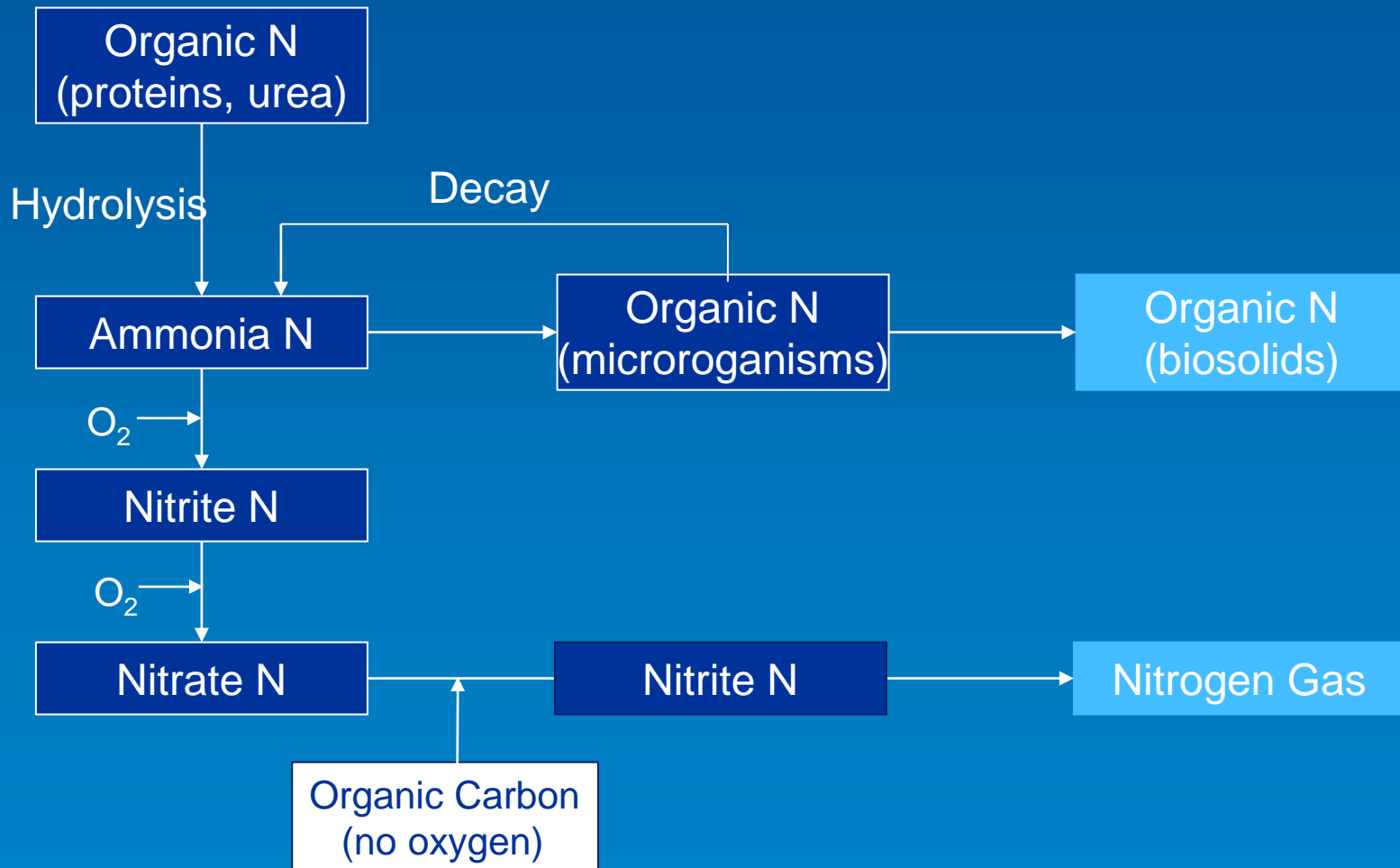
- DON or SON:
  - Urea, amino acids
  - Refractory component (rDON) is not removed with biological treatment: some rDON in raw (~1-2% of raw TKN) and some rDON produced in process
- PON
  - Algae, organic particles
  - Biomass



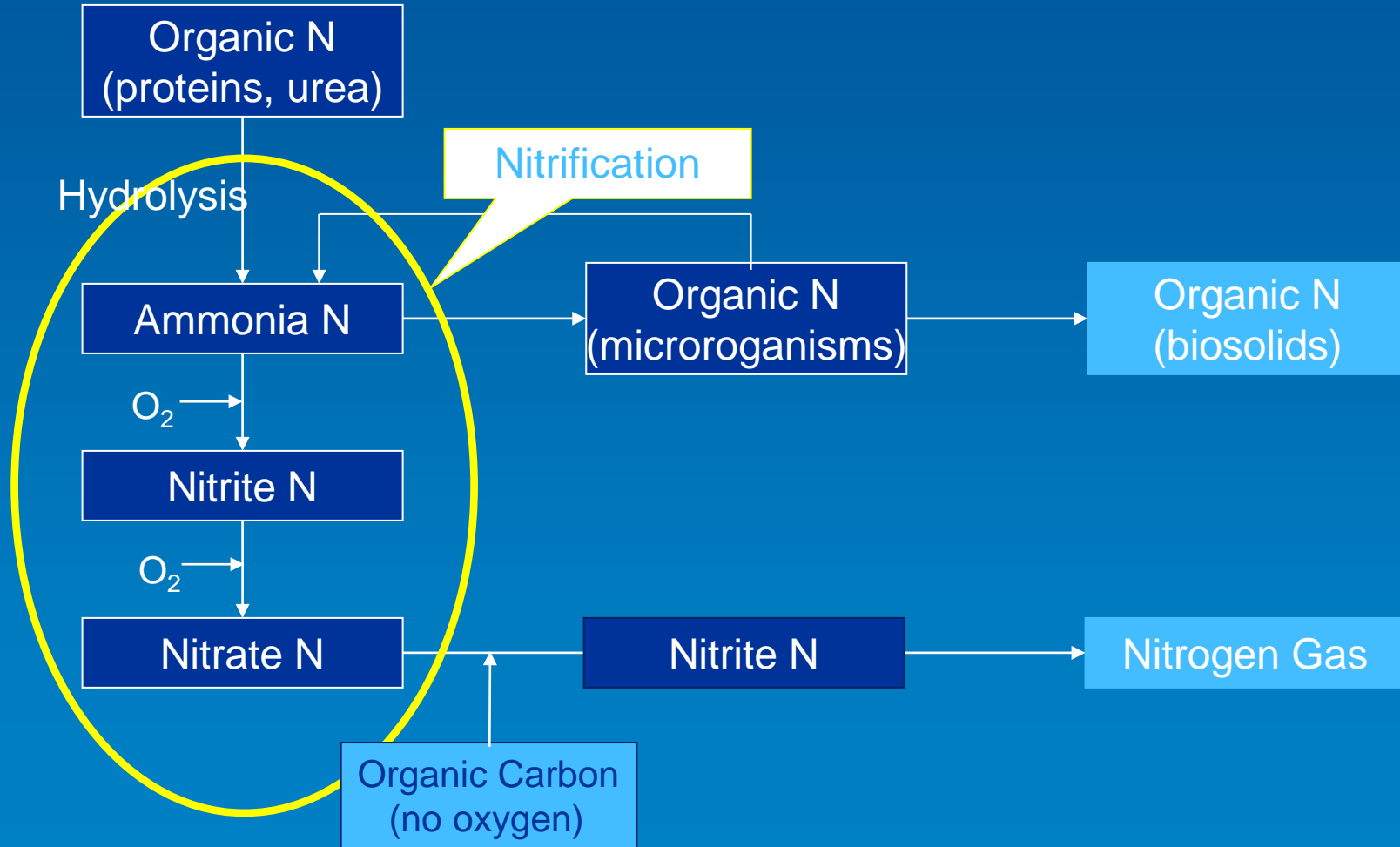
# Conversions: Overview

- Organic nitrogen converted to inorganic: **hydrolysis**
- Inorganic nitrogen used for growth
  - Incorporate into biomass: **assimilation**
  - Convert from ammonia to nitrate: **nitrification**
  - Convert from nitrate to nitrogen gas: **denitrification**

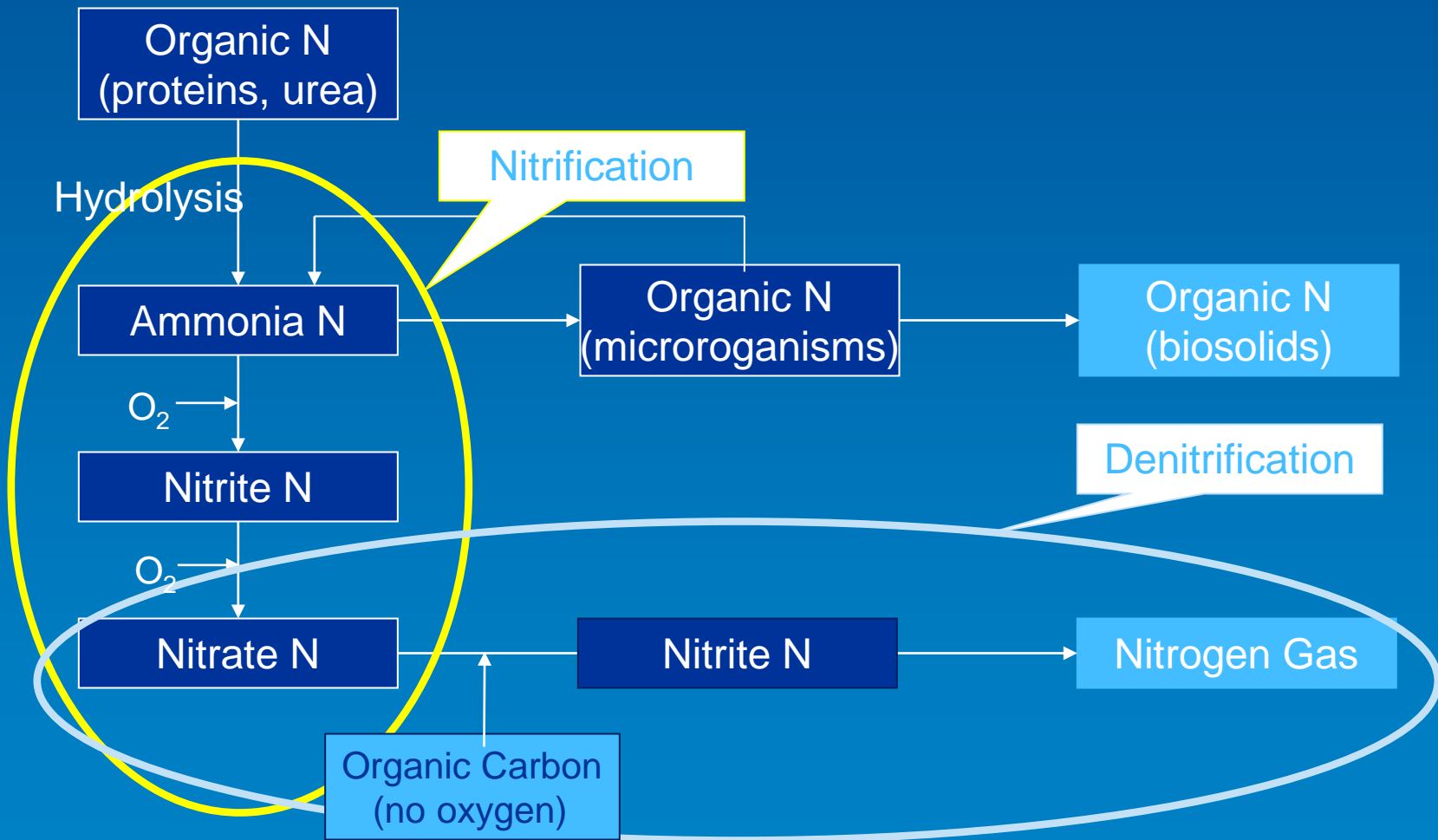
# Conversions: N Cycle in WWTP



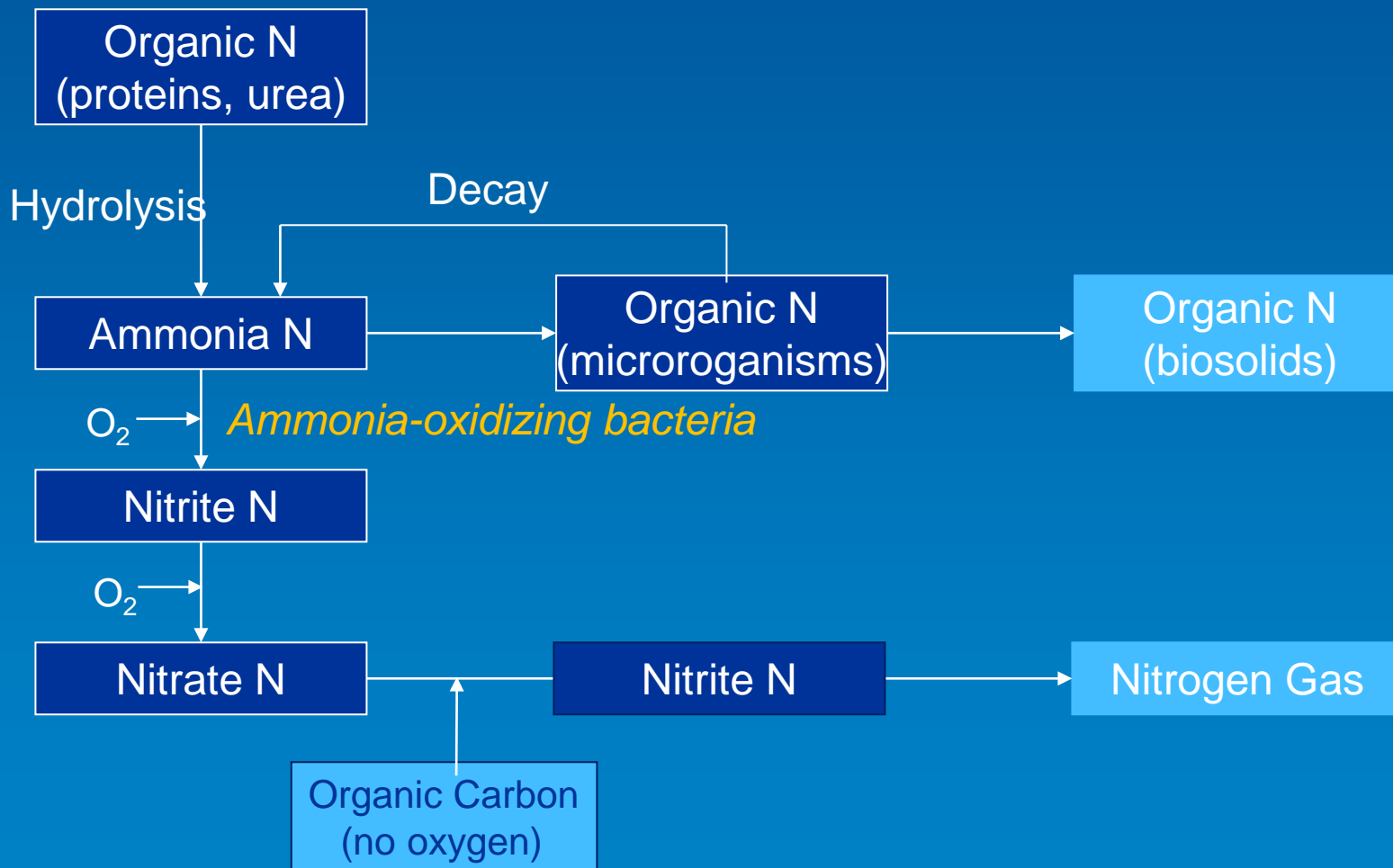
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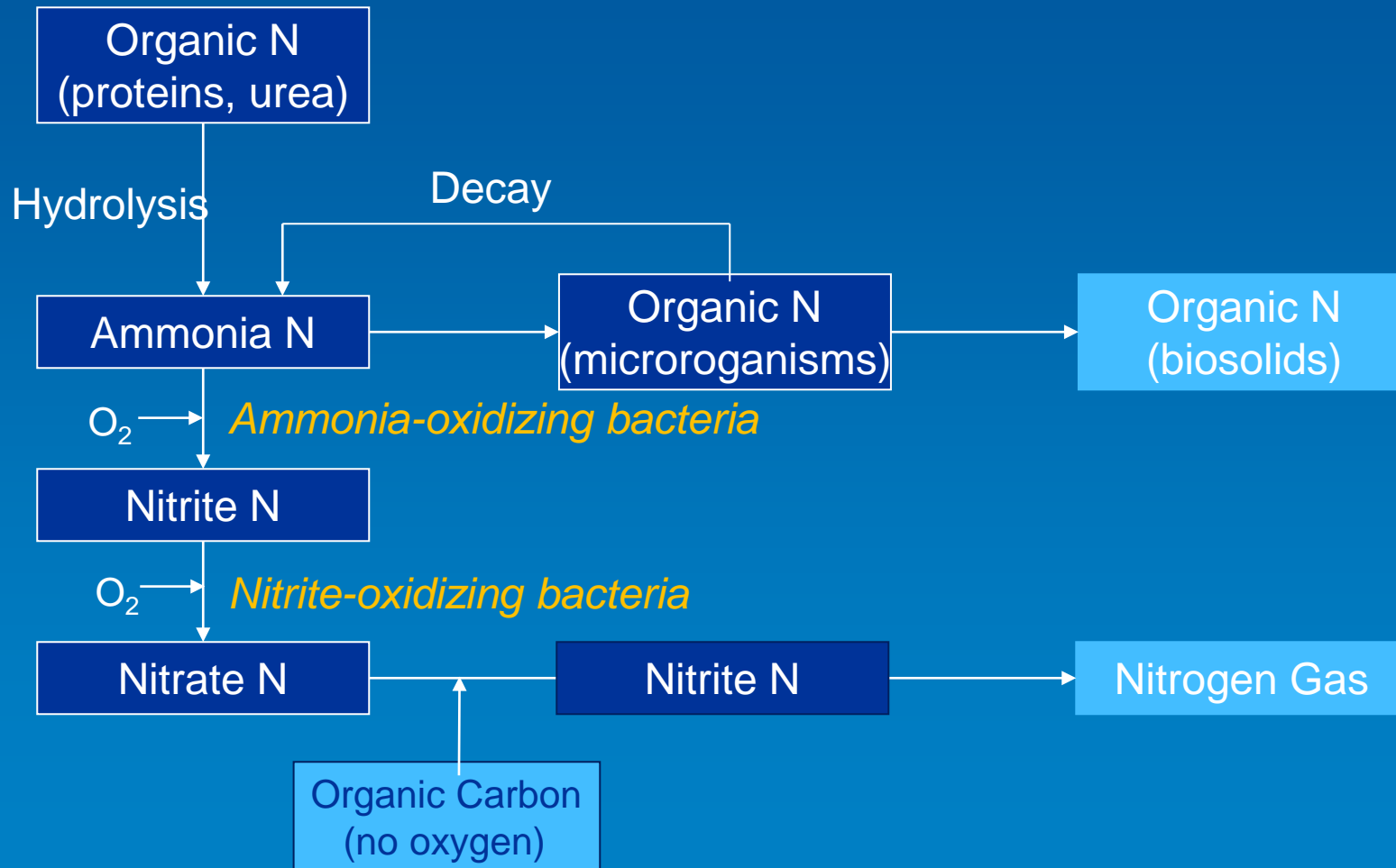
# Conversions: N Cycle in WWTP



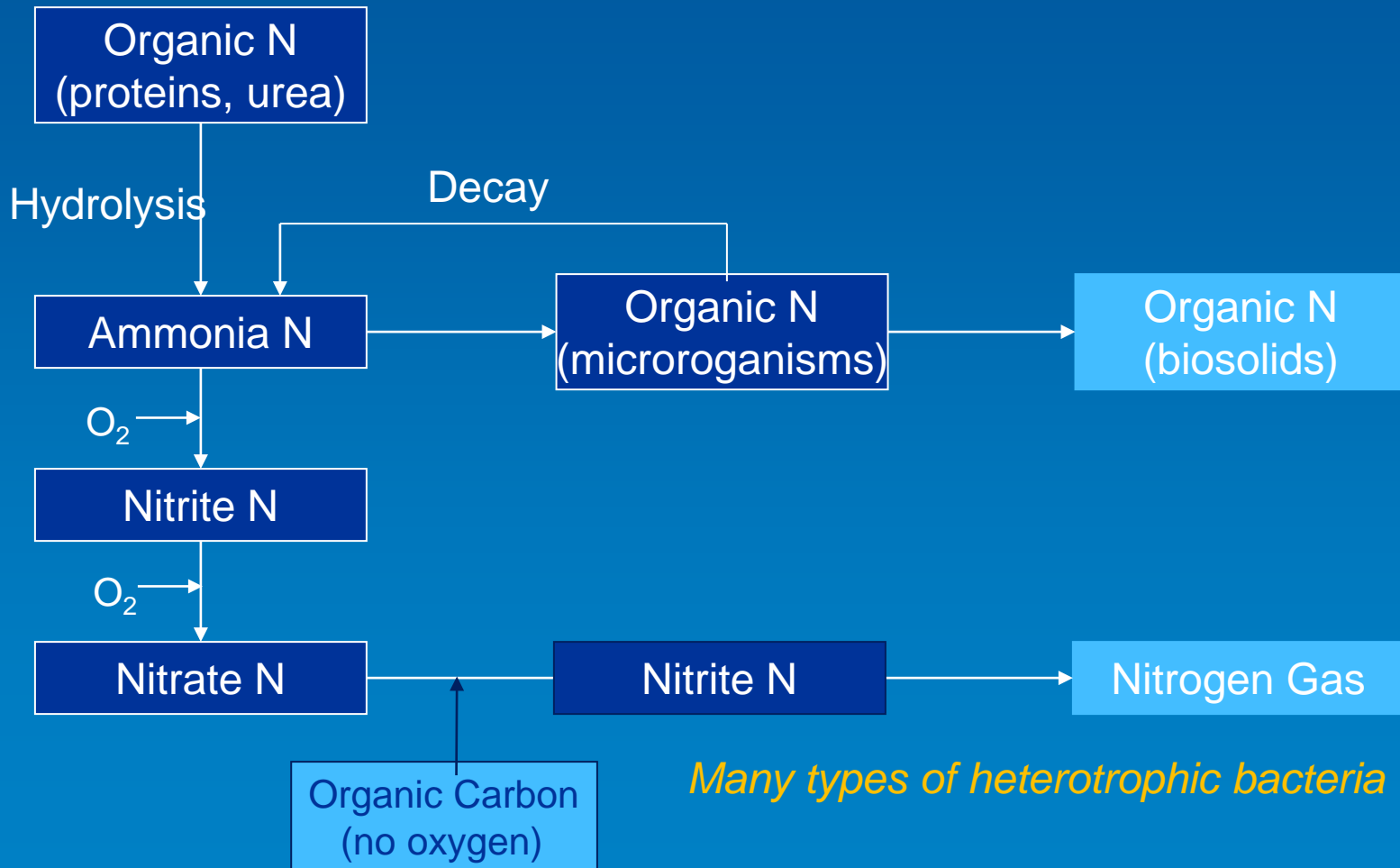
# Conversions: N Cycle in WWTP



# Conversions: N Cycle in WWTP



# Conversions: N Cycle in WWTP



# Removal Concepts: Basic Ideas

- What comes in must go out
  - Air
  - Water
  - Solids
- Transform to an acceptable or removable form
  - Air (N<sub>2</sub> gas)
  - Water (effluent, e.g. nitrate)
  - Solid (biosolids)
- Remove solids
  - Sedimentation
  - Filtration
  - Membrane separation



# Removal Concepts: Incorporation into Biomass

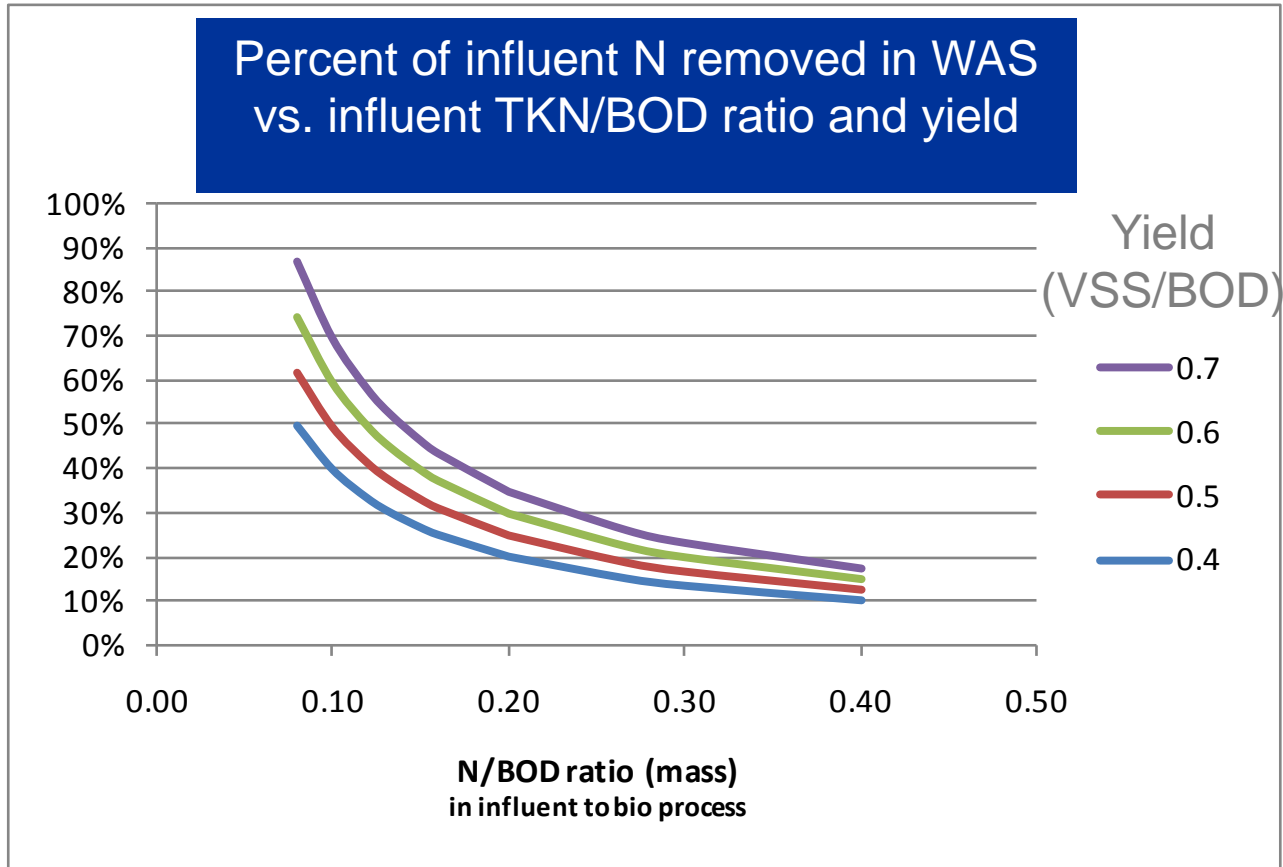
- All biological processes
- Incorporation of ammonia (or nitrate) into biomass during growth:  $C_{12}H_{87}O_{23}N_{12}P$
- Waste biomass  $\sim 10\%$  N
- Removes TN

# Removal Concepts:

## Incorporation into Biomass (cont.)

- Effect of influent BOD and TKN
  - Higher BOD → more WAS → higher percent N removed as WAS
  - Lower influent TKN:BOD ratio → higher percent N removed as WAS
- Effect of yield
  - Higher yield → more WAS → higher percent N removed as WAS

# Removal Concepts: Incorporation into Biomass

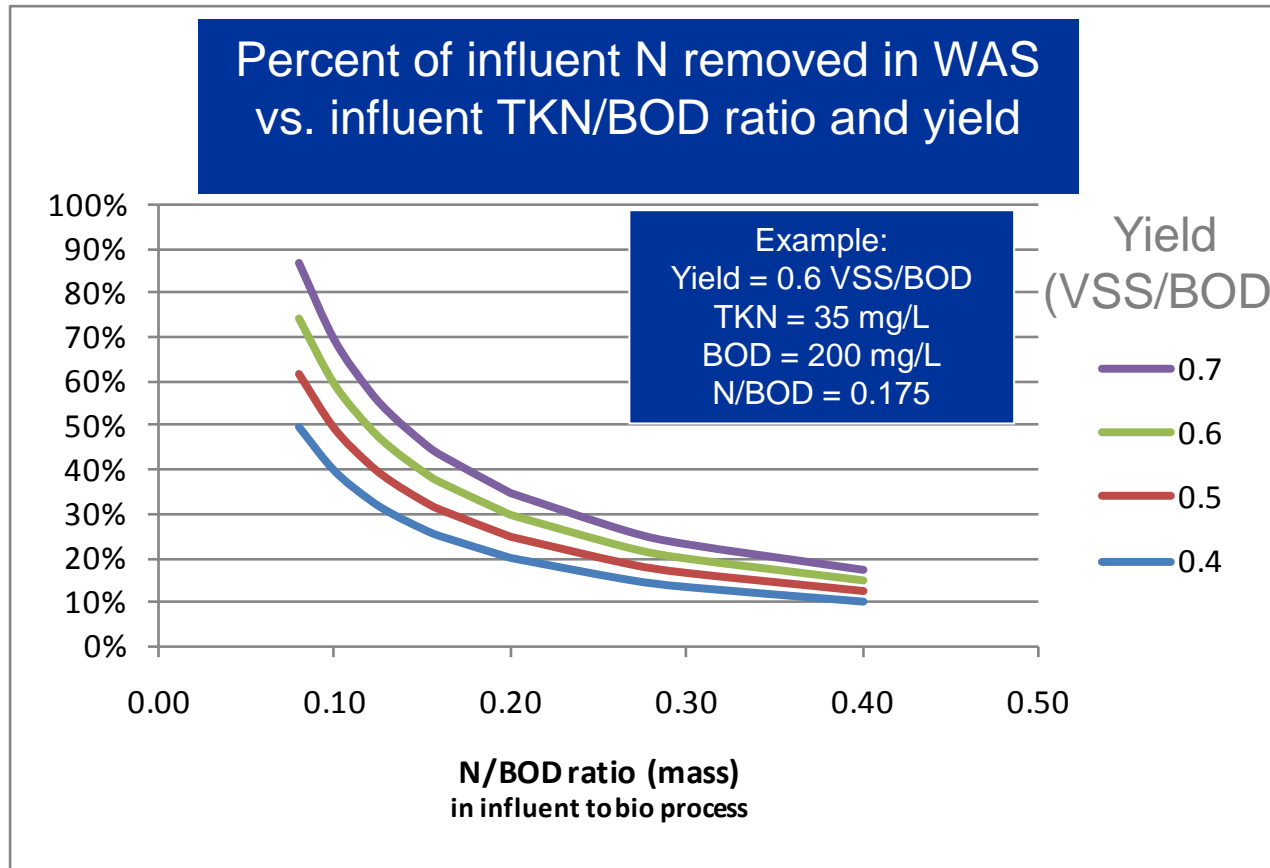


Shorter SRT  
Colder Temp

↕

Longer SRT  
Warmer Temp

# Removal Concepts: Incorporation into Biomass

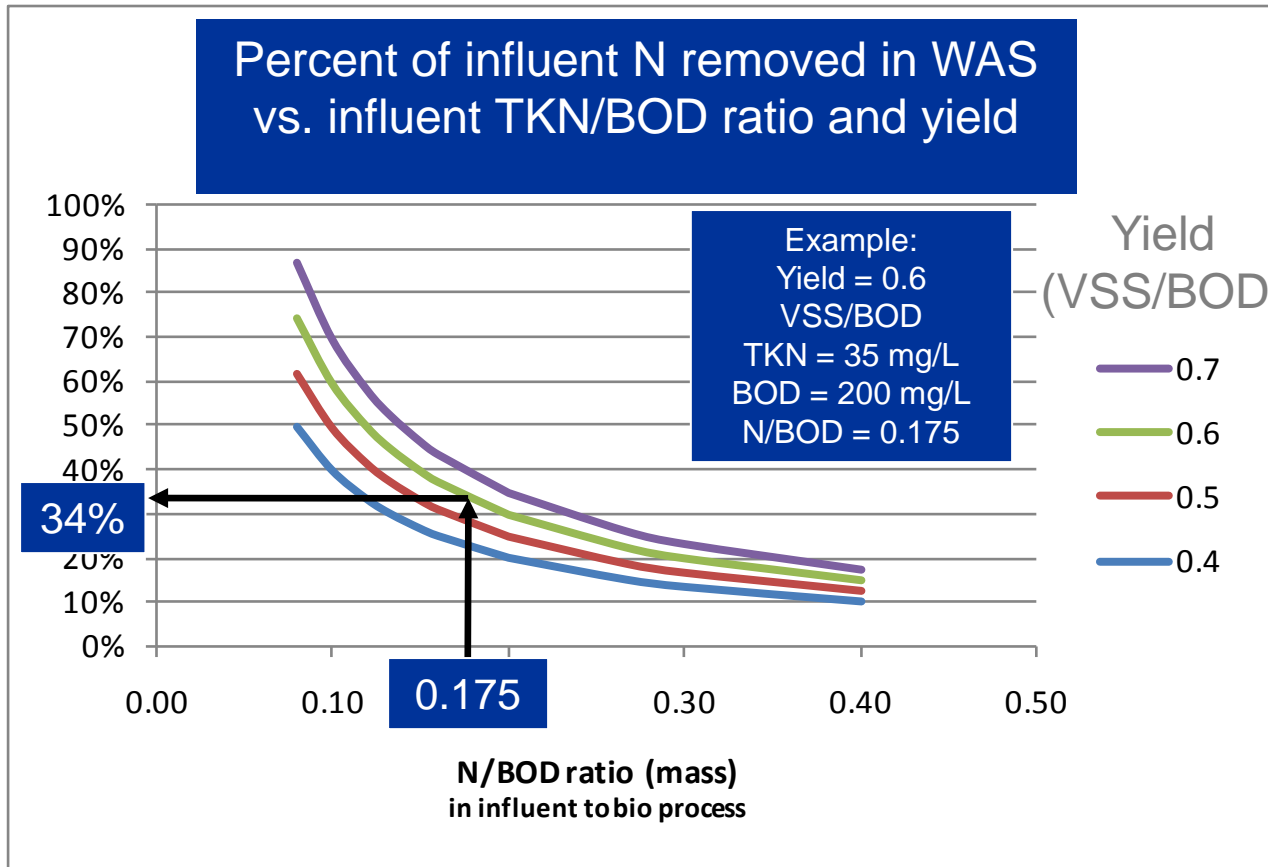


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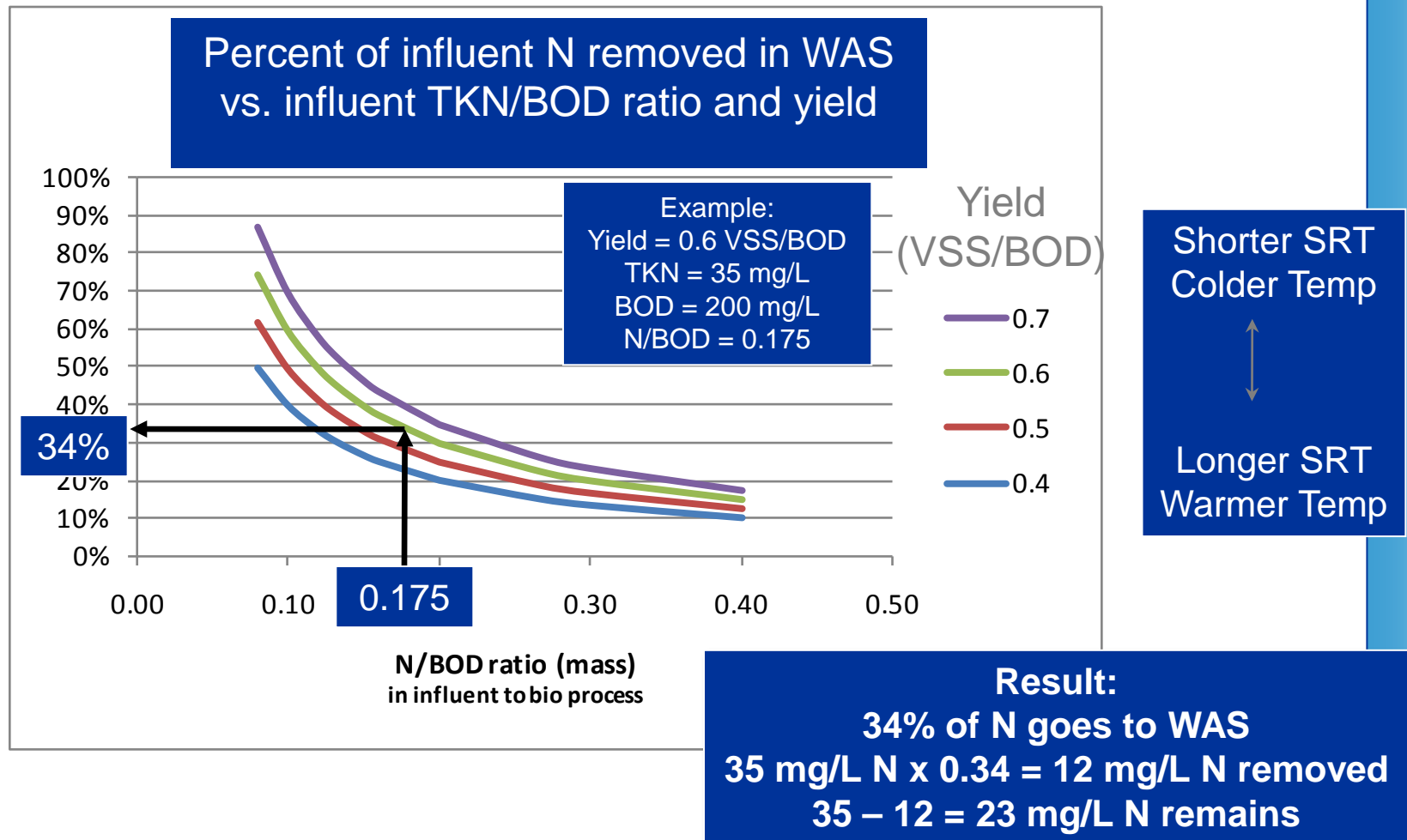


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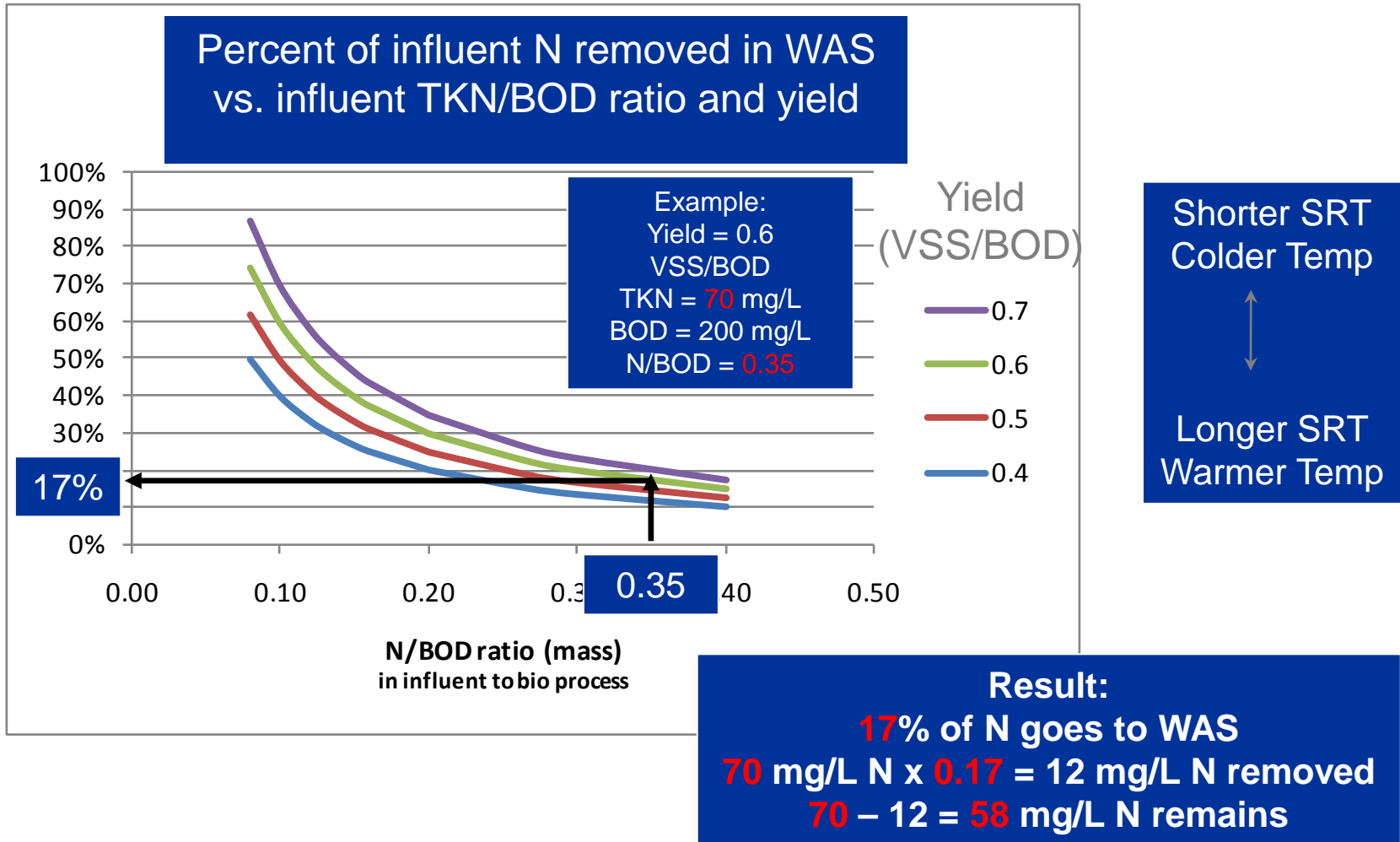
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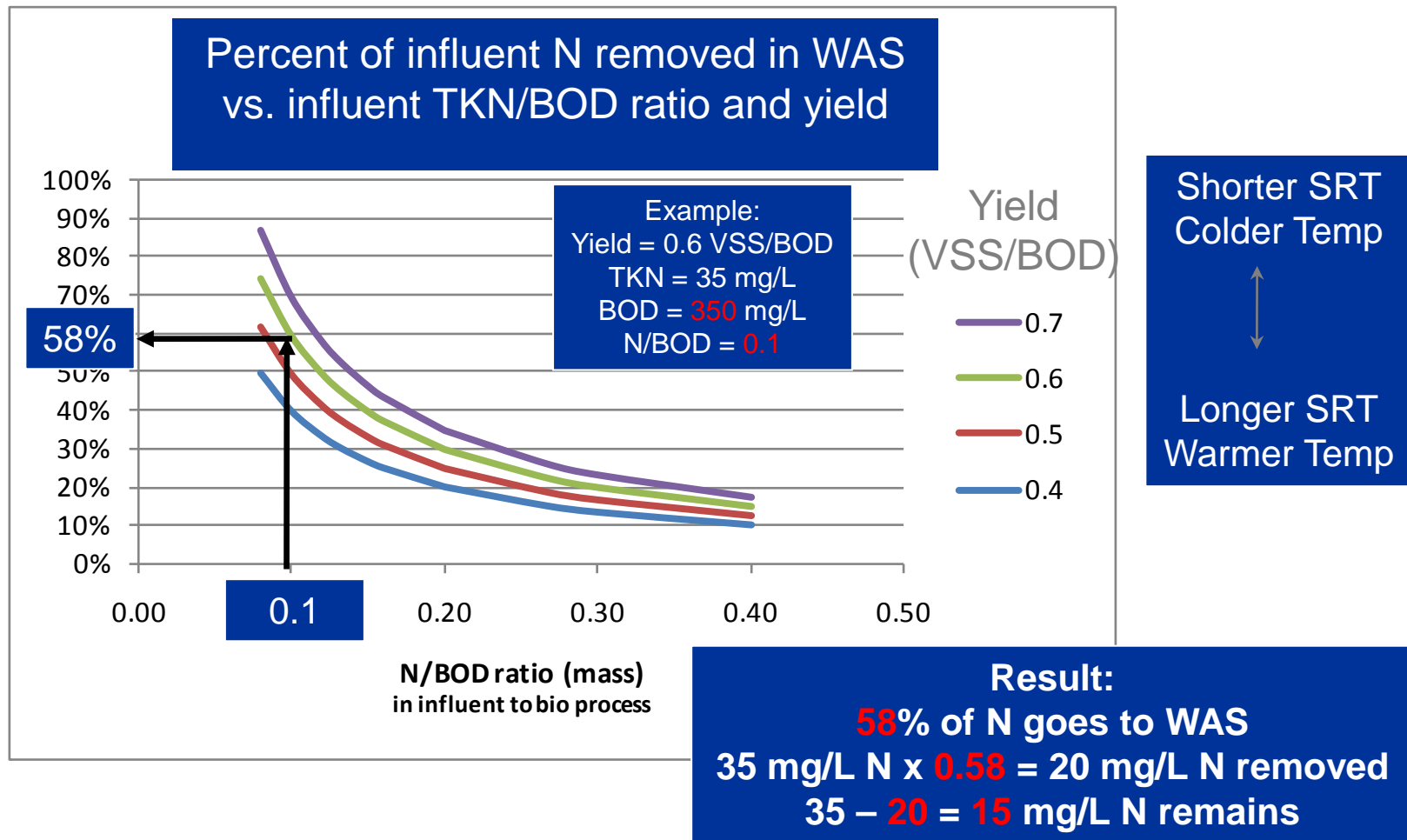
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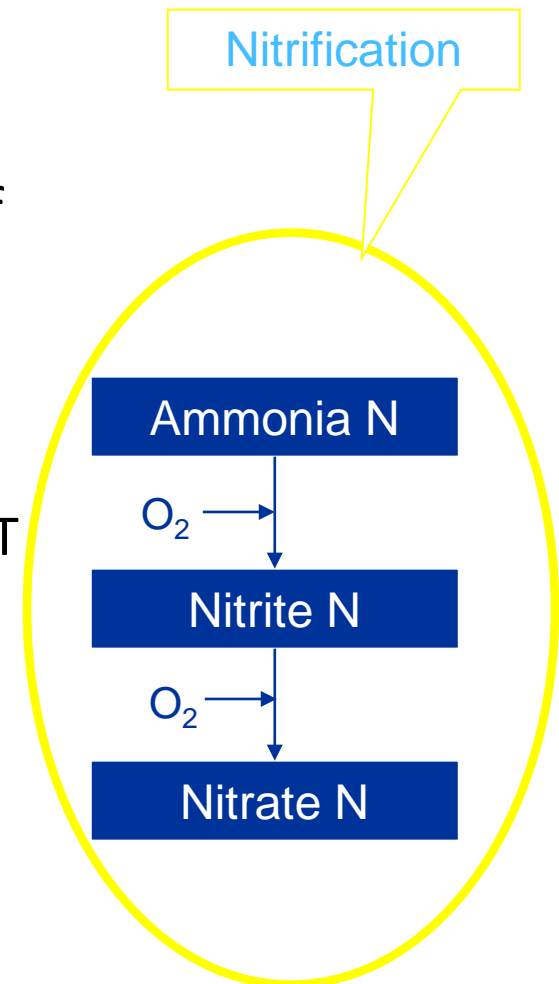


# Removal Concepts: Incorporation into Biomass



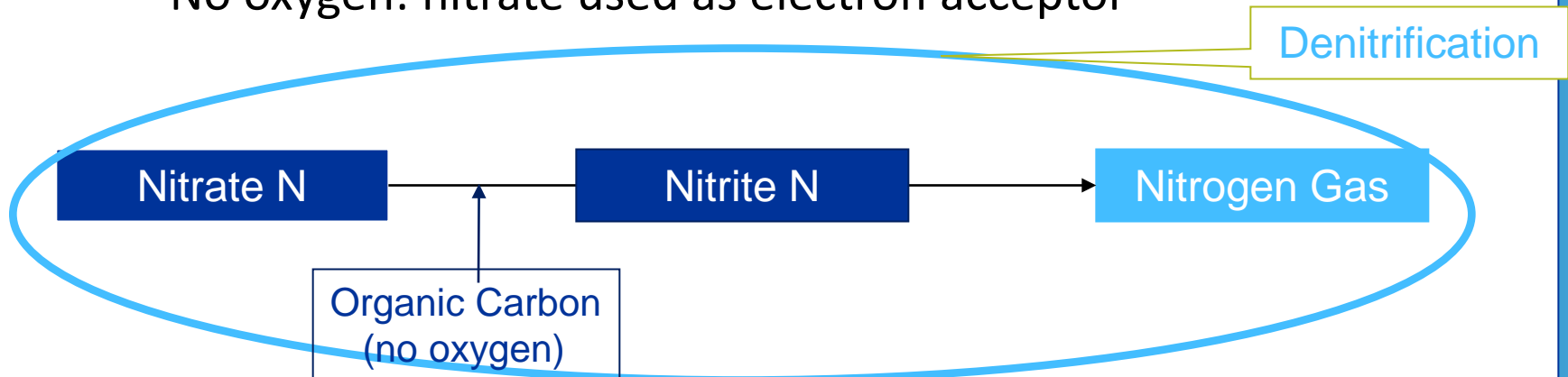
# Removal Concepts: Nitrification

- Conversion of ammonia to nitrate
- Does not remove TN
- Mitigates toxicity and oxygen demand of effluent ammonia
- Conditions for nitrification:
  - Ammonia-oxidizing and nitrite-oxidizing biomass (“nitrifiers”): need adequate SRT at given temperature
  - Oxygen: 4.6 mg O<sub>2</sub> / mg N nitrified
  - Adequate pH: 7.1 mg CaCO<sub>3</sub> alkalinity / mg N nitrified



# Removal Concepts: Denitrification

- Conversion of nitrate to nitrogen gas
- $N_2$  goes to atmosphere (atmosphere is 78%  $N_2$ )
- Removes TN
- Conditions for denitrification:
  - Denitrifying bugs (“facultative heterotrophs” or methylotrophs)
  - Carbon!
  - No oxygen: nitrate used as electron acceptor



# Removal Concepts:

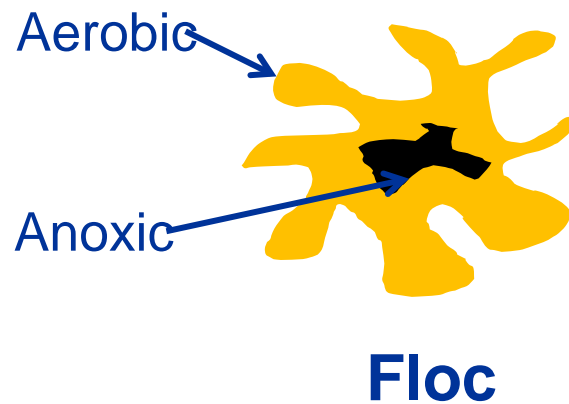
## Denitrification – Carbon Sources

- Wastewater (free!)
  - Domestic wastewater:  $C_{10}H_{19}O_3NP_{0.1}$
- Bugs endogenous decay (slow...)
  - Bugs:  $C_{12}H_{87}O_{23}N_{12}P$
- External source (\$\$\$)
  - Want carbon, don't want more N (or P)
  - Typical carbon sources:
    - Methanol:  $CH_3OH$
    - Glycerol:  $C_3H_5(OH)_3$

# Removal Concepts:

## Denitrification - Anoxia

- Anoxic (no oxygen) conditions may be unintentional:
  - Middle of floc
  - Dead zones in aerobic basin



# Removal Concepts:

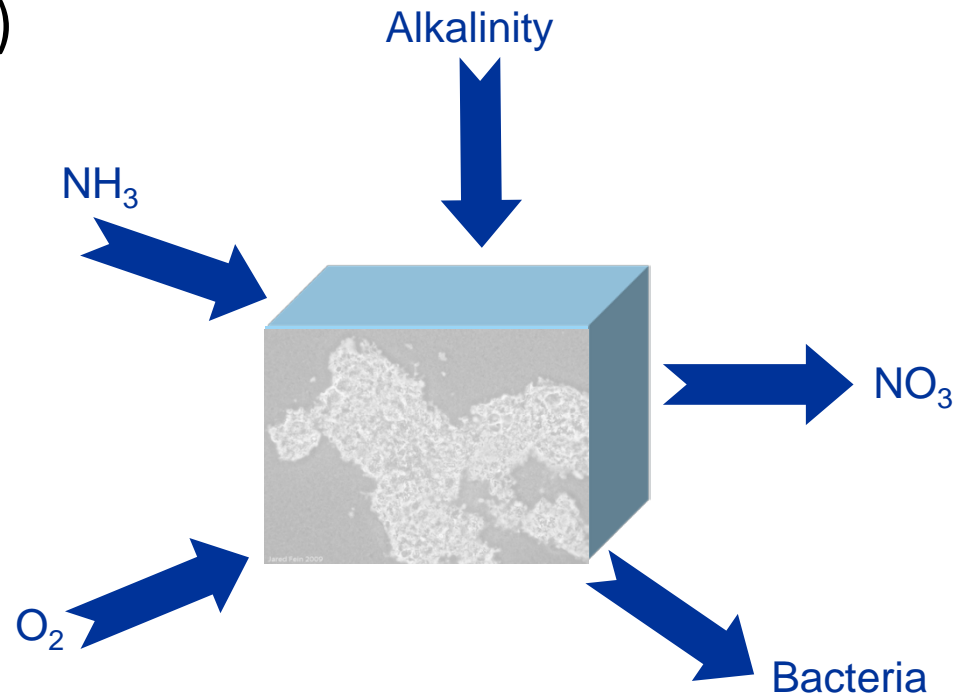
## Denitrification - Benefits

- Recover alkalinity
  - Nitrification consumes alkalinity:  $-7.1 \text{ mg CaCO}_3/\text{mg N nitrified}$
  - Denitrification generates alkalinity:  $+3.6 \text{ mg CaCO}_3/\text{mg N denitrified}$
  - Save chemical \$
- Reduce oxygen supply required for oxidation of organics
  - Denitrification “credit” =  $2.8 \text{ mg O}_2/\text{mg NO}_3^-$  reduced
  - Save energy \$
- To reap these benefits, denitrification must occur upstream of nitrification

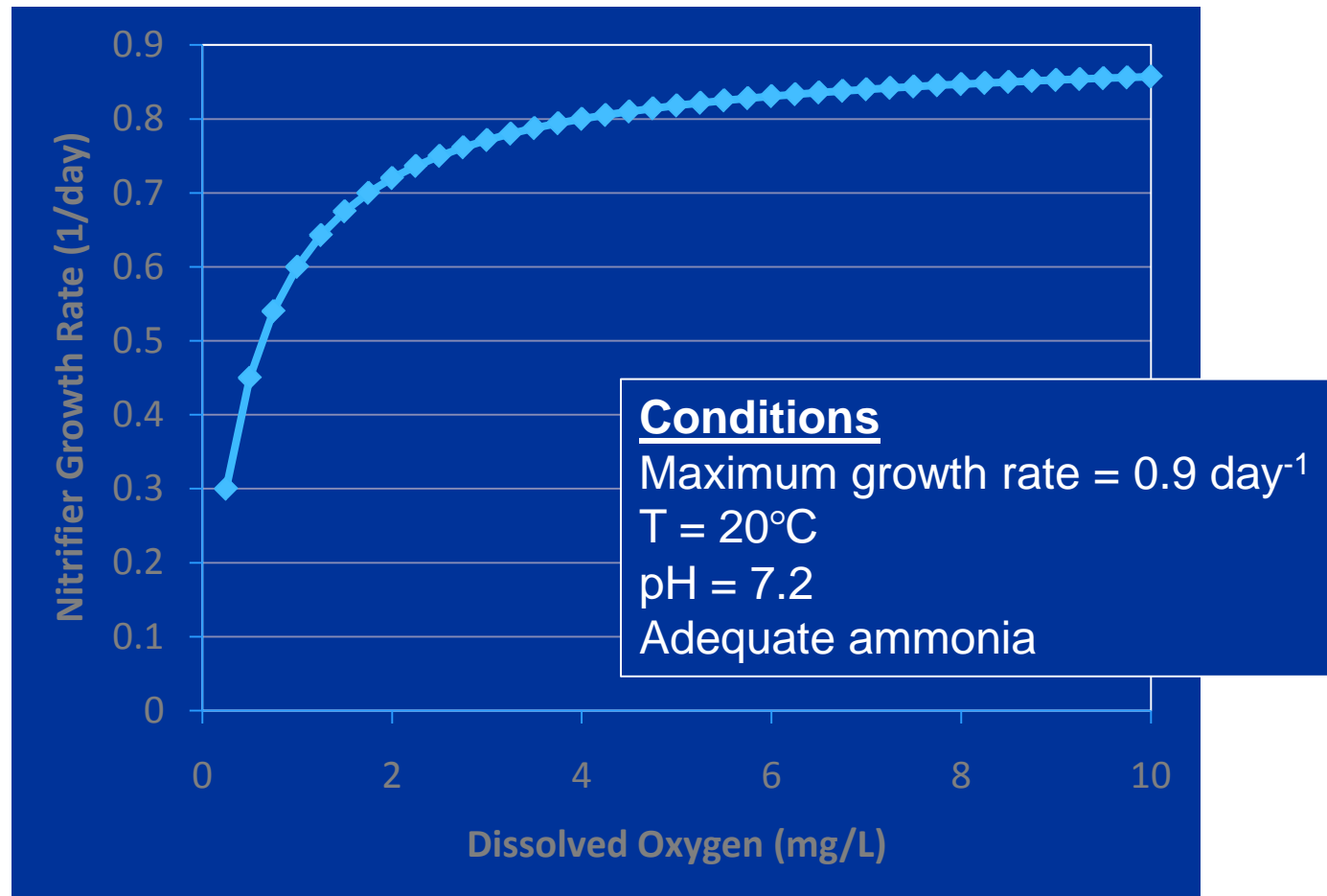


# Process Considerations: Conditions for Nitrification

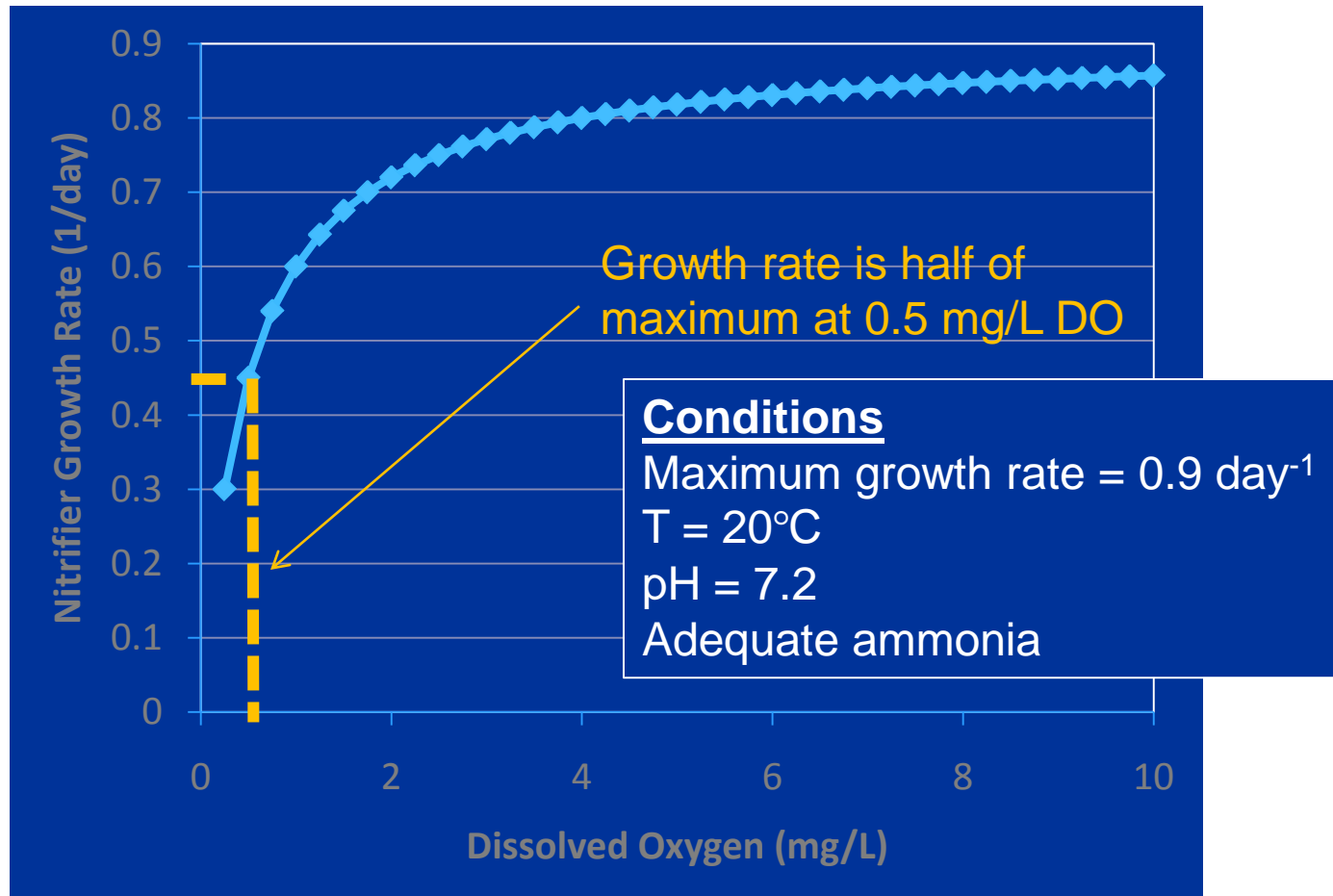
- Ammonia-oxidizing and nitrite-oxidizing bacteria (“nitrifiers”)
- Oxygen (electron acceptor)
- Alkalinity (pH sensitivity)
- No toxics
- Adequate temperature



# Process Considerations: Nitrification & Oxygen



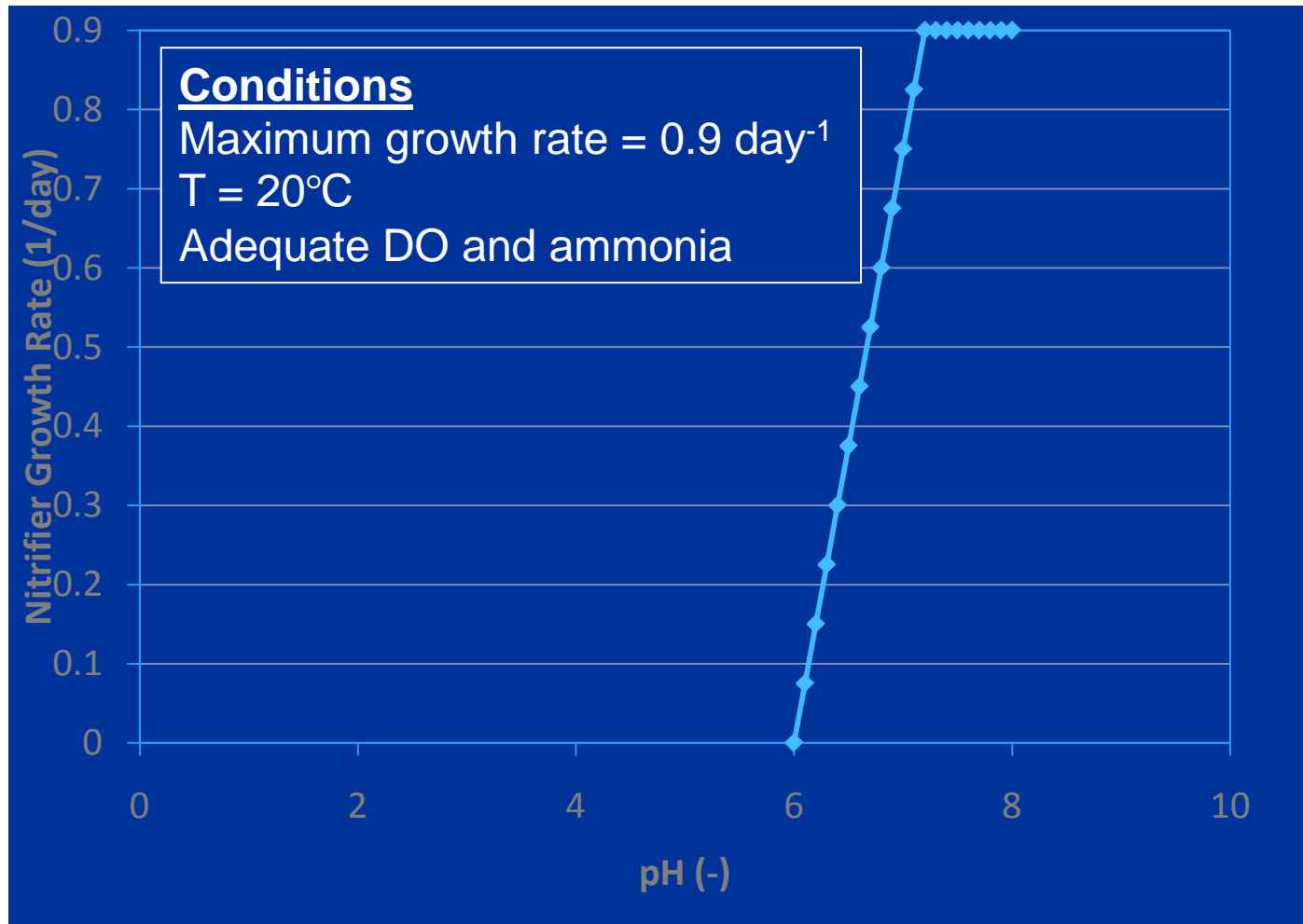
# Process Considerations: Nitrification & Oxygen



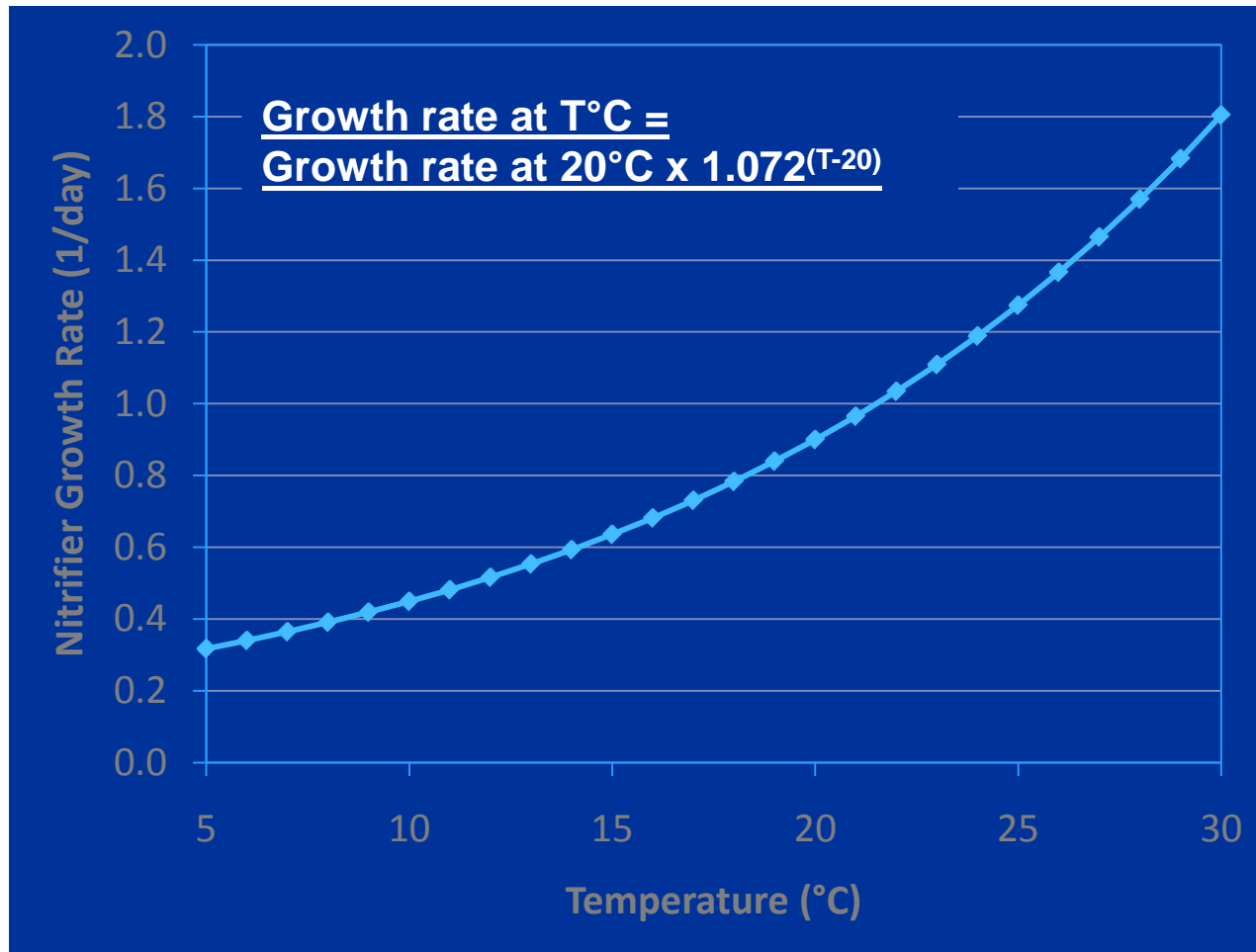
# Process Considerations: Nitrification and pH

- Optimal nitrification occurs at pH ~ 7.2
- Rates decline significantly below pH ~ 6.8
- Rates at pH ~ 6 are < 10% of maximum

# Process Considerations: Nitrification & pH



# Process Considerations: Nitrification & Temperature



# Process Considerations:

## Nitrification – Washout SRT

- Washout of nitrifiers occurs when SRT is too short to allow microorganisms to accumulate
- Nitrifier growth rate is temperature-dependent
- Therefore, minimum SRT to avoid washout is also temperature-dependent

# Process Considerations:

## Nitrification – Washout SRT

Temperature	Washout SRT	Washout SRT Times 2.5 Safety Factor
(°C)	(days)	(days)
9	4.7	11.8
10	4.3	10.8
11	3.9	9.9
12	3.6	9.0
13	3.3	8.2
14	3.0	7.5
15	2.8	6.9
16	2.5	6.4
17	2.3	5.8
18	2.1	5.4
19	2.0	4.9
20	1.8	4.5
21	1.7	4.2
22	1.5	3.9
23	1.4	3.6
24	1.3	3.3
25	1.2	3.0

# Process Considerations:

## Process Flow for Short SRT

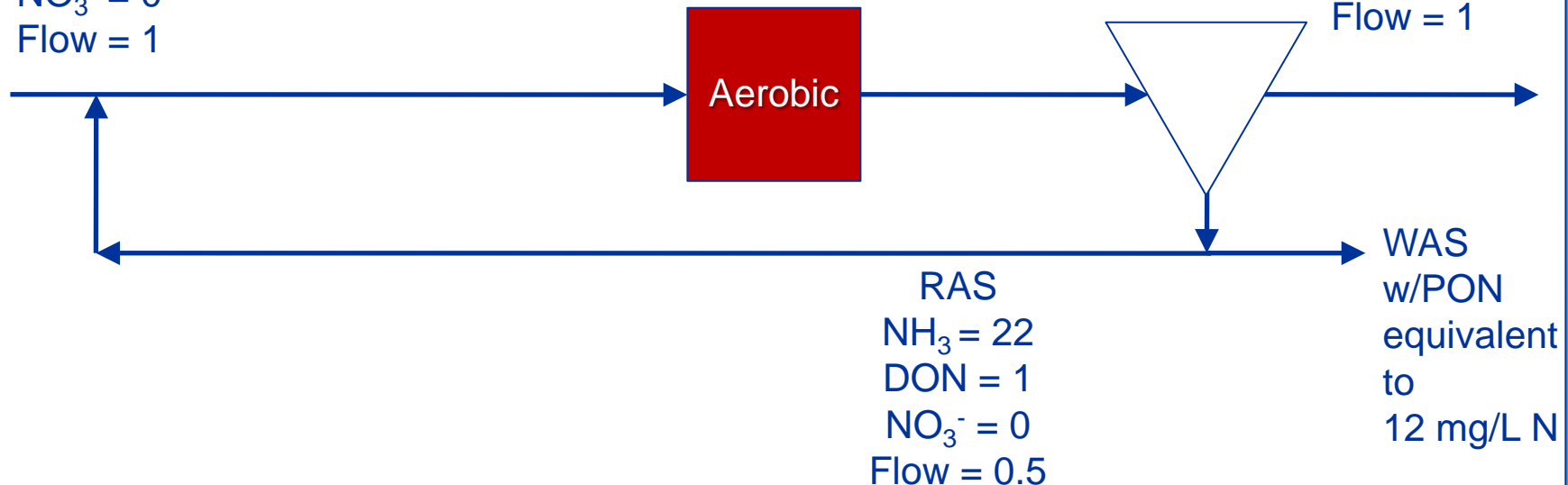
### Not nitrifying

35 mg/L N in, 34% to WAS = 12 mg/L to WAS

35 - 12 = 23 mg/L N remains

22 mg/L ammonia N + 1 mg/L DON = 23 mg/L TKN

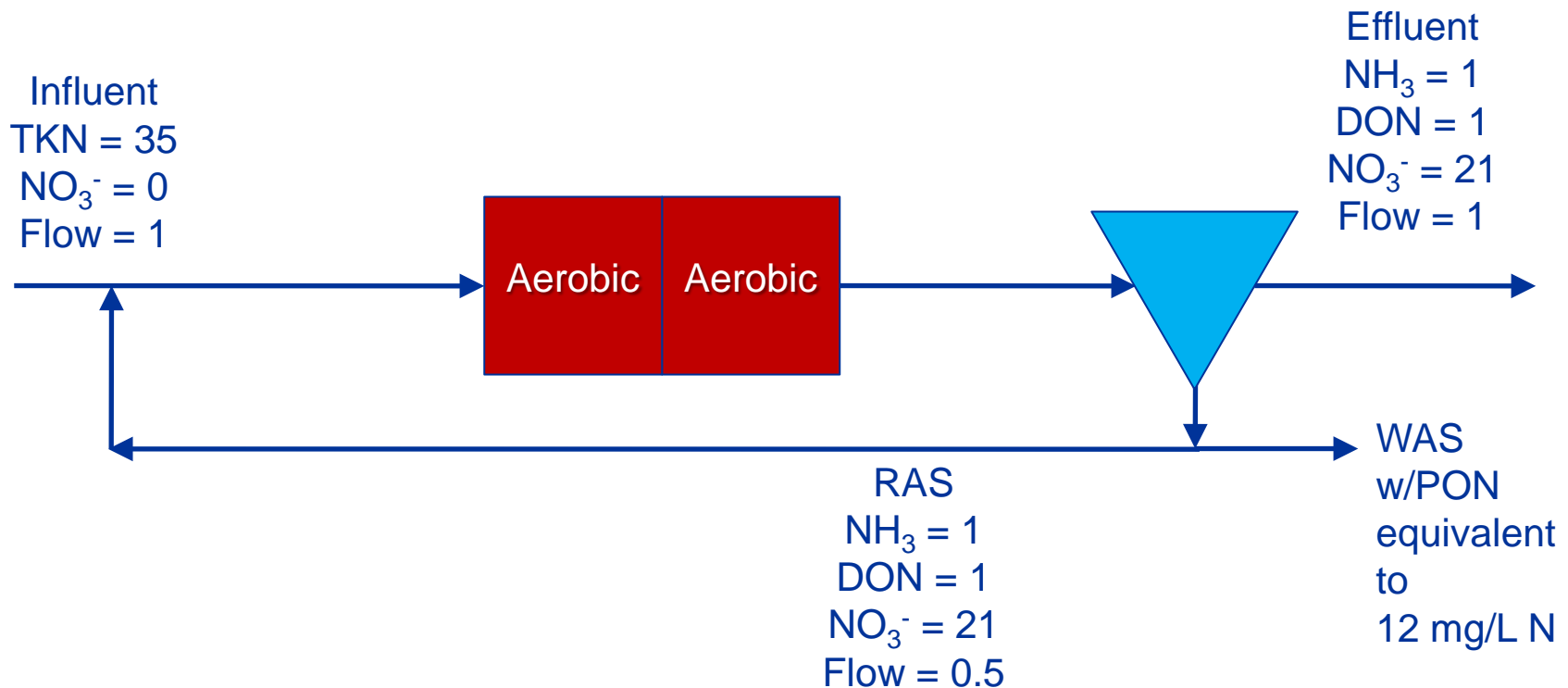
Influent  
TKN = 35  
 $\text{NO}_3^- = 0$   
Flow = 1



# Process Considerations: Process Flow for Long SRT

## Nitrifying

21 mg/L ammonia N converted to nitrate  
 $21 \times 7.1 = 149$  mg/L  $\text{CaCO}_3$  alkalinity consumed  
1 mg/L DON remains; TKN = 2 mg N/L

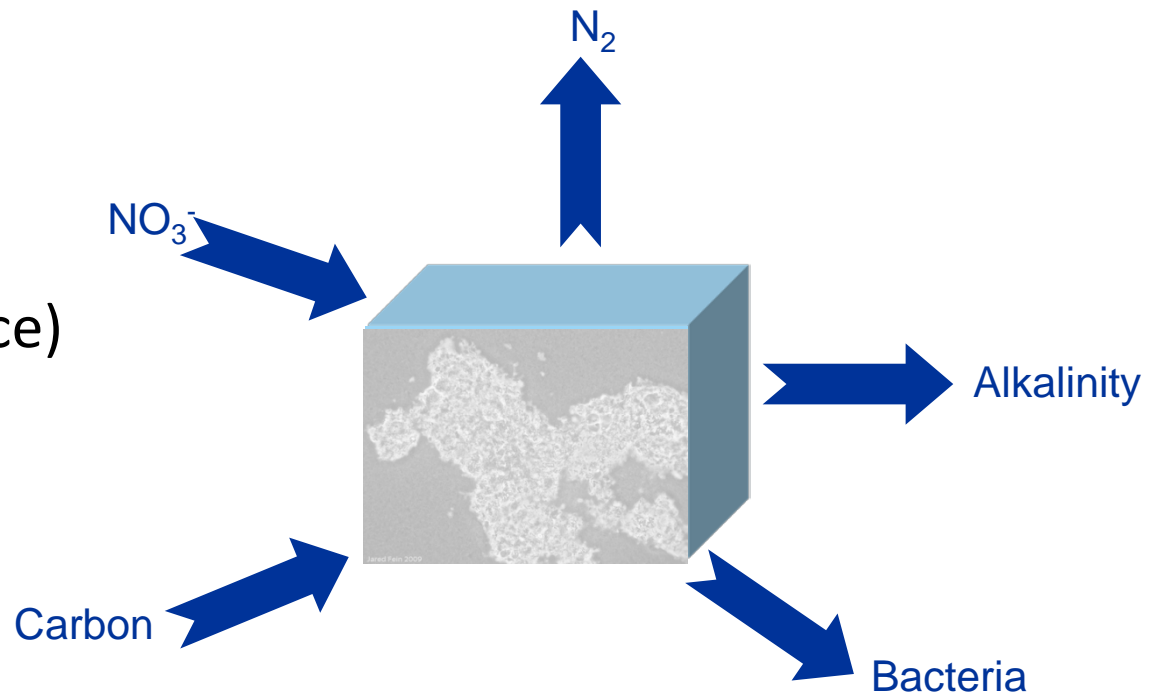


# Process Considerations: Nitrification and Toxics

- Sensitive to many compounds: metals, phenolic compounds, cyanates, amines, tannins etc.
- Unionized ammonia ( $\text{NH}_3$ ) is also toxic
  - 100 mg N/L ammonia at pH 7 and  $T = 20^\circ\text{C}$  inhibits ammonia oxidation
  - 20 mg N/L ammonia at pH 7 and  $T = 20^\circ\text{C}$  inhibits nitrite oxidation
- Unionized nitrous acid ( $\text{HNO}_2$ )

# Process Considerations: Conditions for Denitrification

- Denitrifying bacteria (“facultative heterotrophs” or methanol utilizers)
- No oxygen
- Nitrate
- Carbon (BOD or external source)



# Process Considerations: Denitrification – Anoxia with SNDN

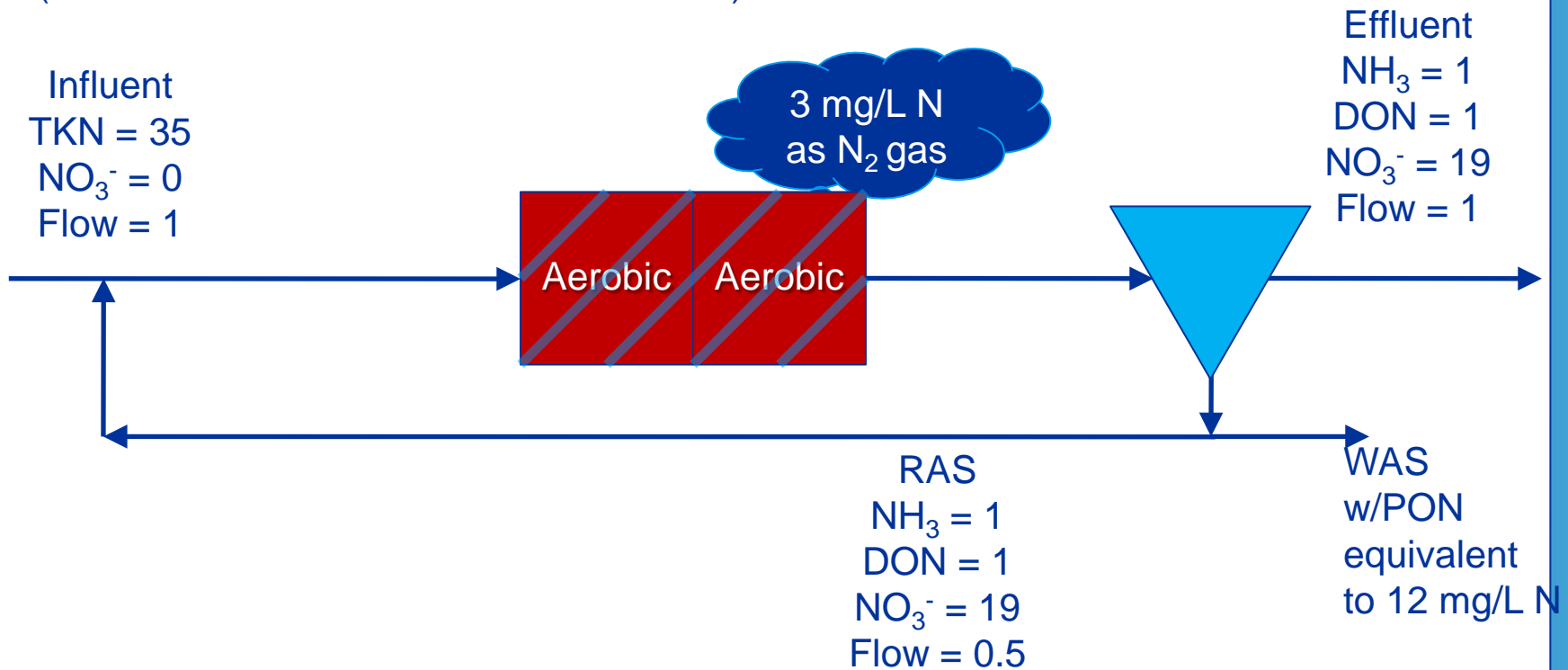
## Some Anoxic Time or Space

Some denitrification due to anoxic zones within aeration basin

Estimate by monitoring effluent nitrate, example 19 mg/L effluent nitrate N

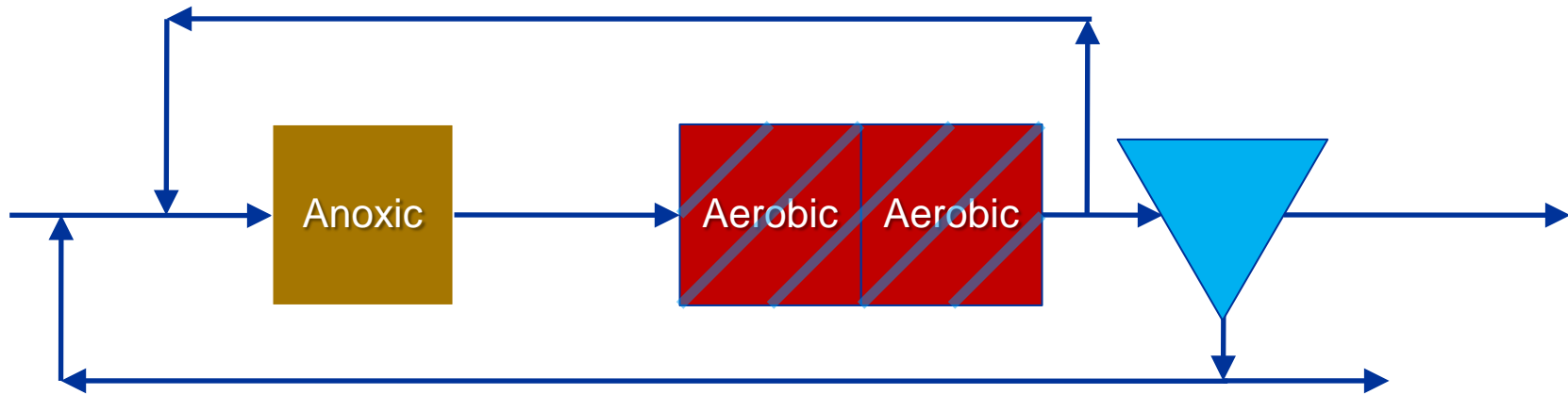
$21 - 19 = 2$  mg/L nitrate N removed by unintentional SNDN

(Simultaneous Nitrification/DeNitrification)



# Process Considerations: Denitrification – Anoxic Zones

## Anoxic Space

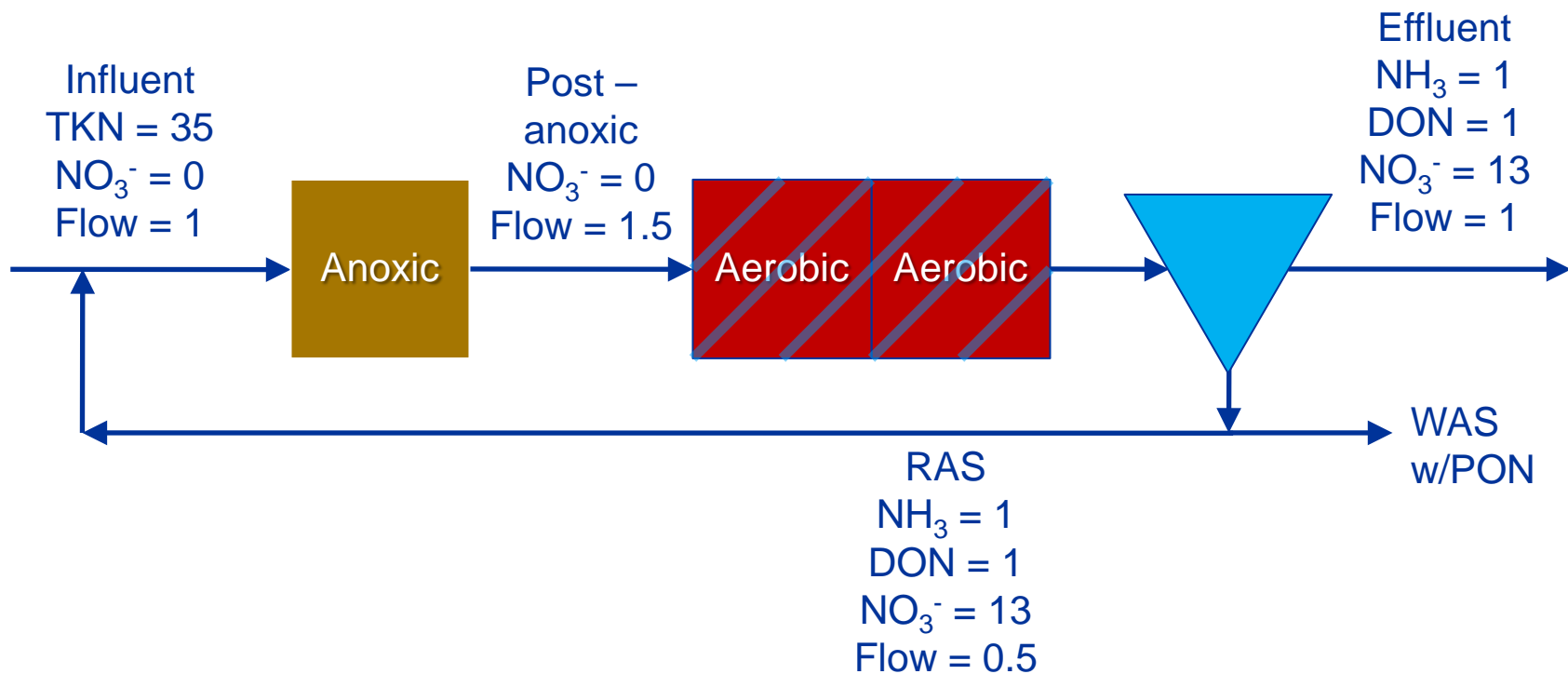


# Process Considerations: Denitrification – Nitrate

- Nitrification must occur first
- Nitrate typically delivered to anoxic zone via internal nitrified mixed liquor recycle and RAS

# Process Considerations: Denitrification – LE Recycle

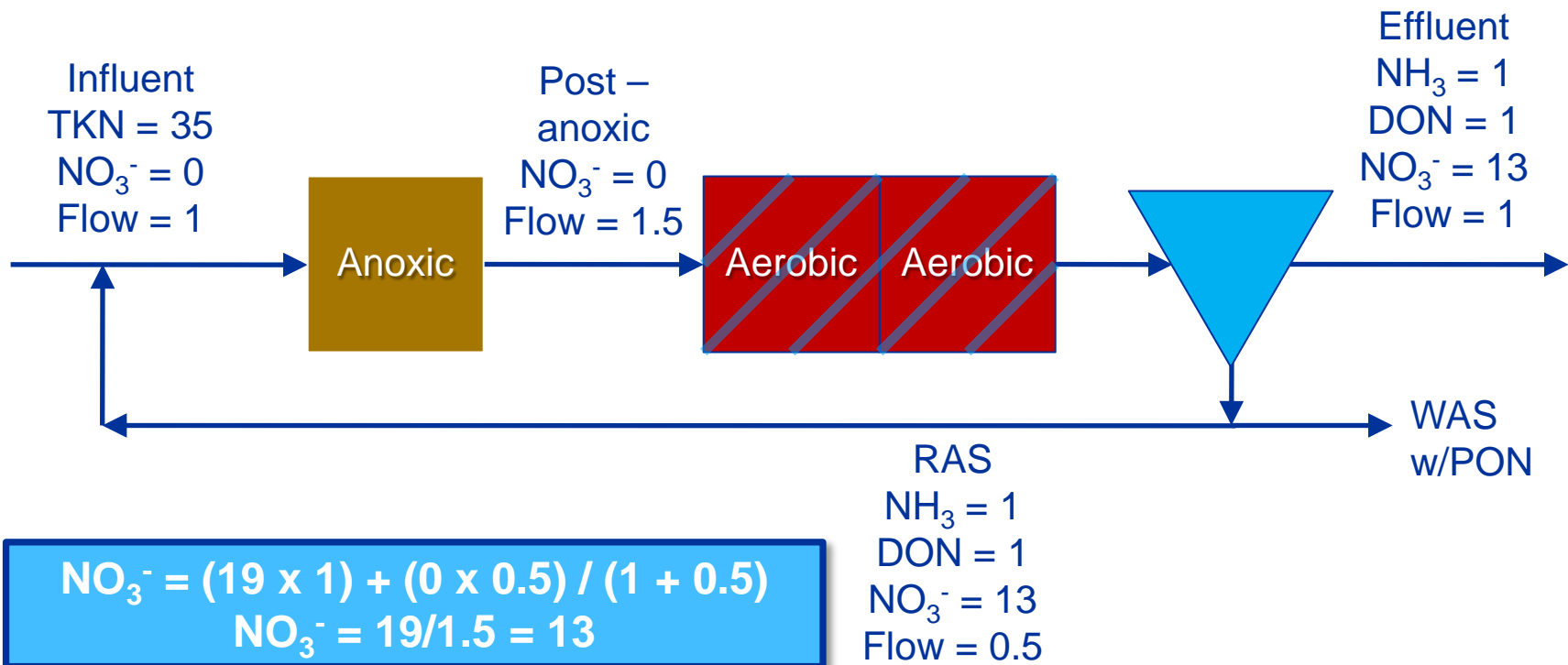
0.5 Q nitrate recycle: 1Q infl = 0.5Q denite/1.5Q total = 33% denite  
33% of 19 mg/L N recycled for denite = 6 mg/L N denitrified  
19 – 6 = 13 mg/L nitrate N remains in effl



# Process Considerations:

## Denitrification – LE Recycle

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# Process Considerations:

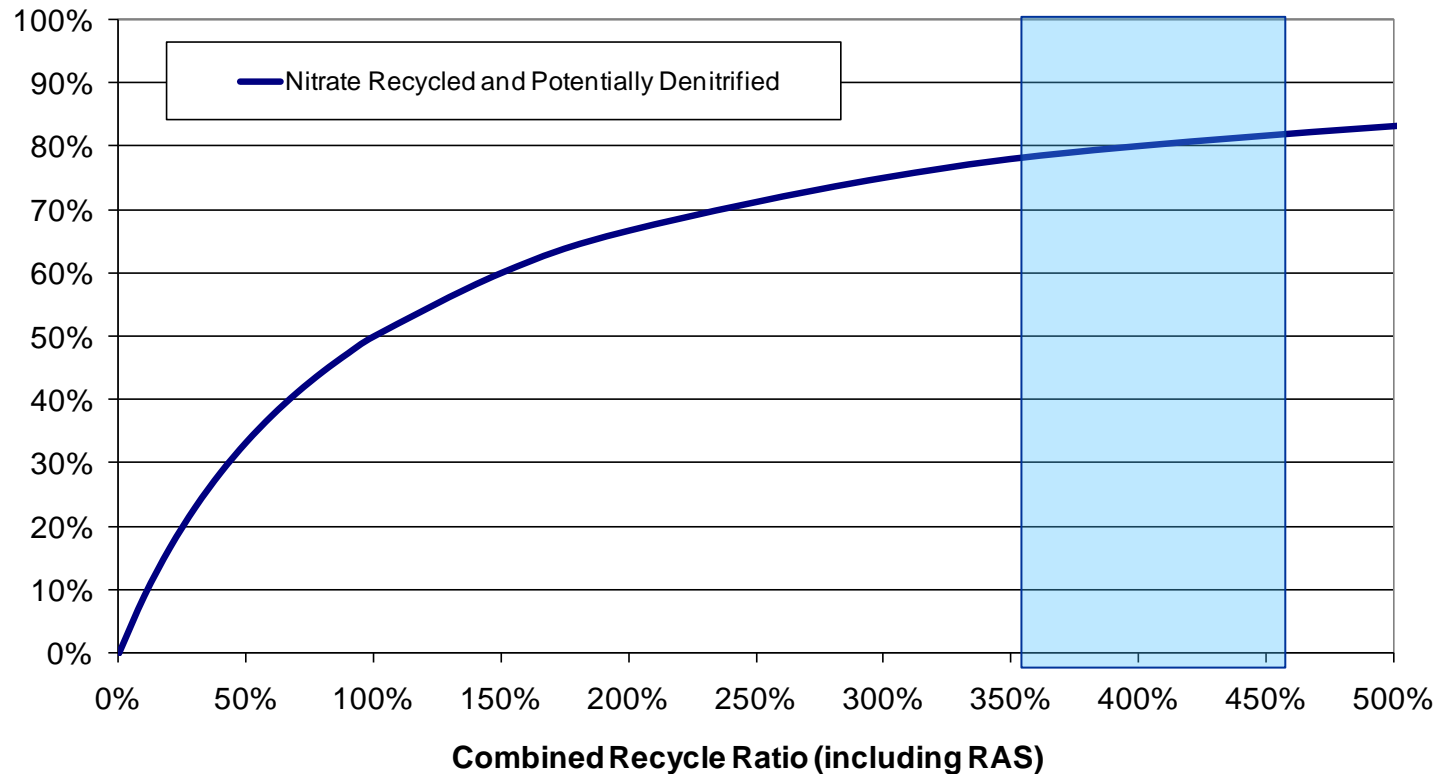
## Denitrification – Recycle Efficacy

Influent Flow, parts	Recycle Flow, parts	Total Anoxic Flow	Potential Denitrification = % Recycle
1	0.5	1.5	$0.5/1.5 = 33\%$
1	1	2	$1/2 = 50\%$
1	2	3	$2/3 = 67\%$
1	3	4	$3/4 = 75\%$
<b>1</b>	<b>4</b>	<b>5</b>	<b><math>4/5 = 80\%</math></b>
<b>1</b>	<b>5</b>	<b>6</b>	<b><math>5/6 = 83\%</math></b>
1	8	9	$8/9 = 89\%$
1	10	11	$10/11 = 91\%$
1	20	21	$20/21 = 95\%$

Benefit of increasing recycle declines, typically use 350% - 450%

# Process Considerations: Denitrification – Recycle Efficacy

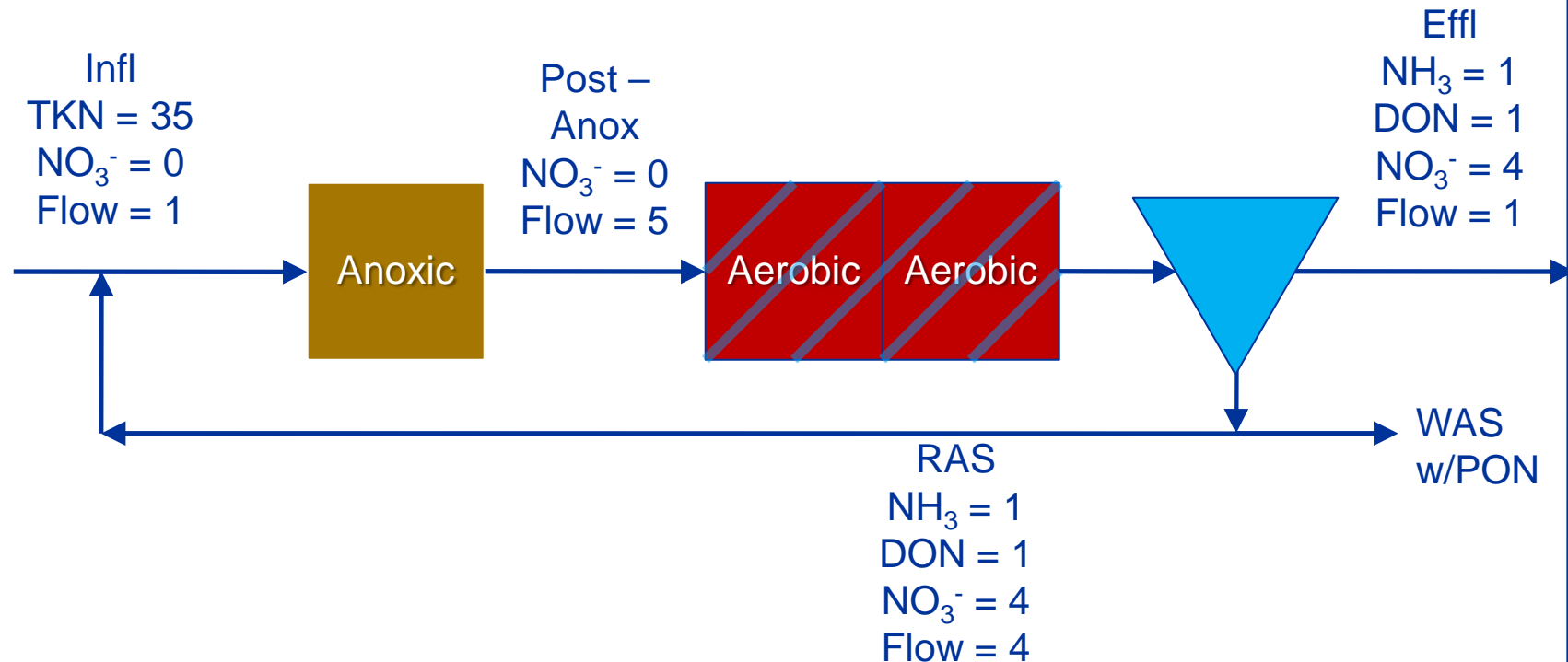
**Denitrification based on Recycle to initial anoxic zone  
(ex. MLE process)**



# Process Considerations:

## Denitrification – Increase LE Recycle

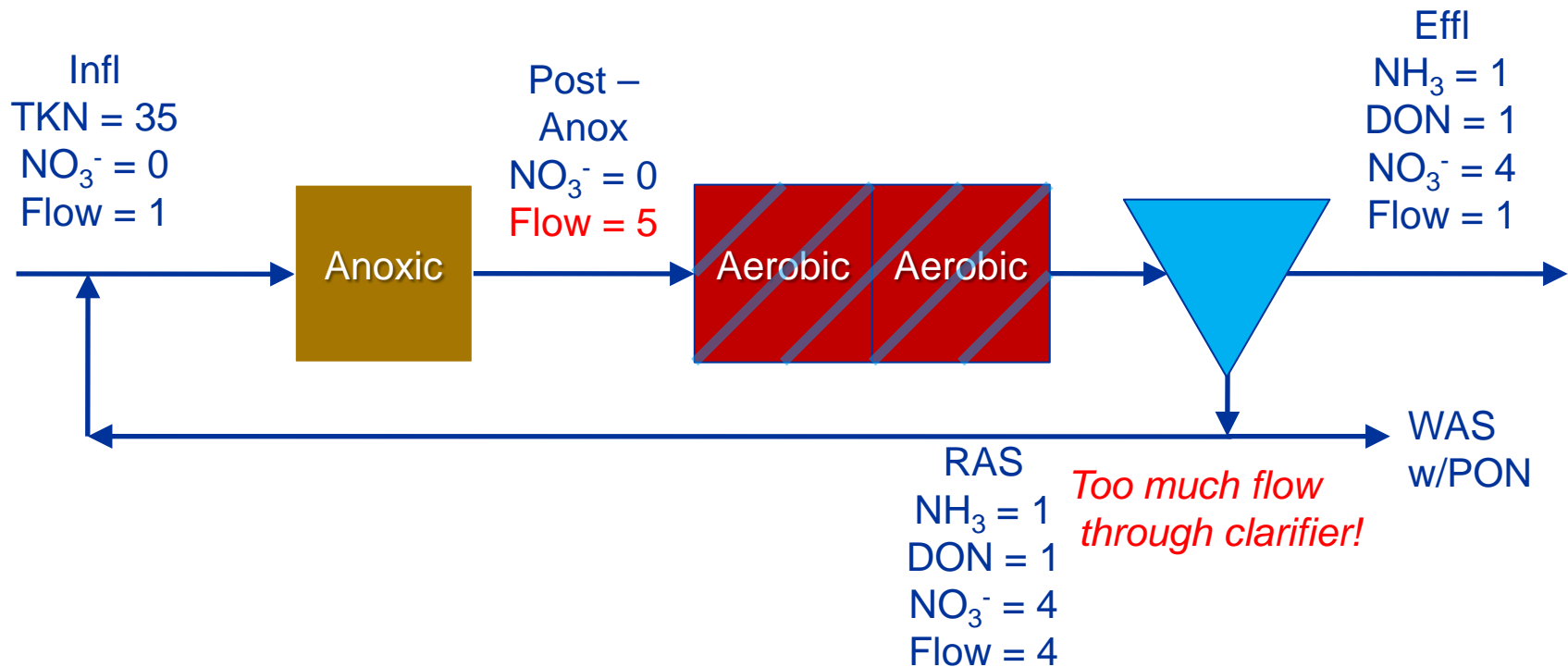
4 Q nitrate recycle: 1Q infl = 4Q denite/5Q total = 80% denite  
80% of 19 mg/L recycled for denite = 15 mg/L N denitrified  
19 – 15 = 4 mg/L nitrate N remains



# Process Considerations:

## Denitrification – Increase LE Recycle

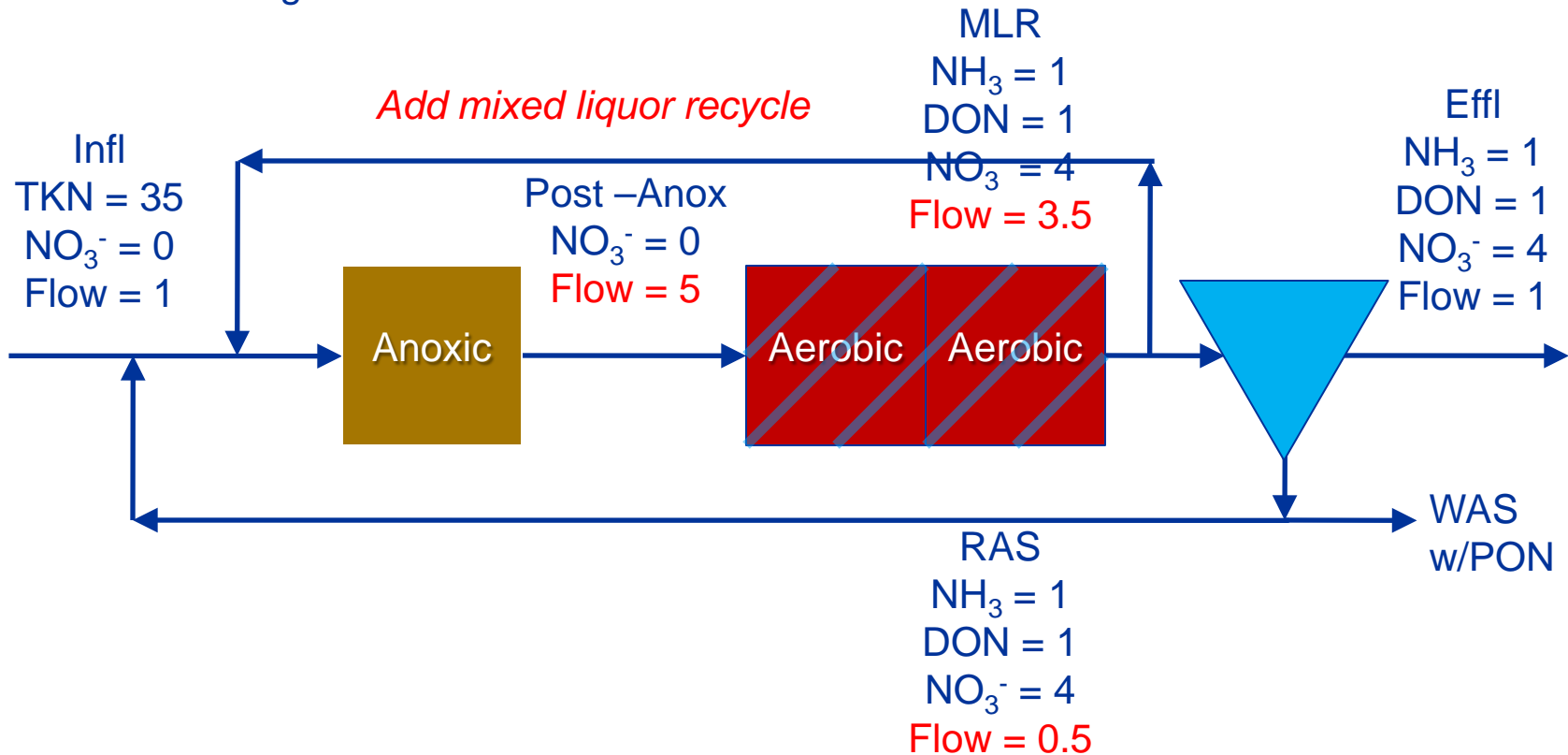
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# Process Considerations:

## Denitrification - MLE

4 Q nitrate recycle: 1Q infl = 4Q denite/5Q total = 80% denite  
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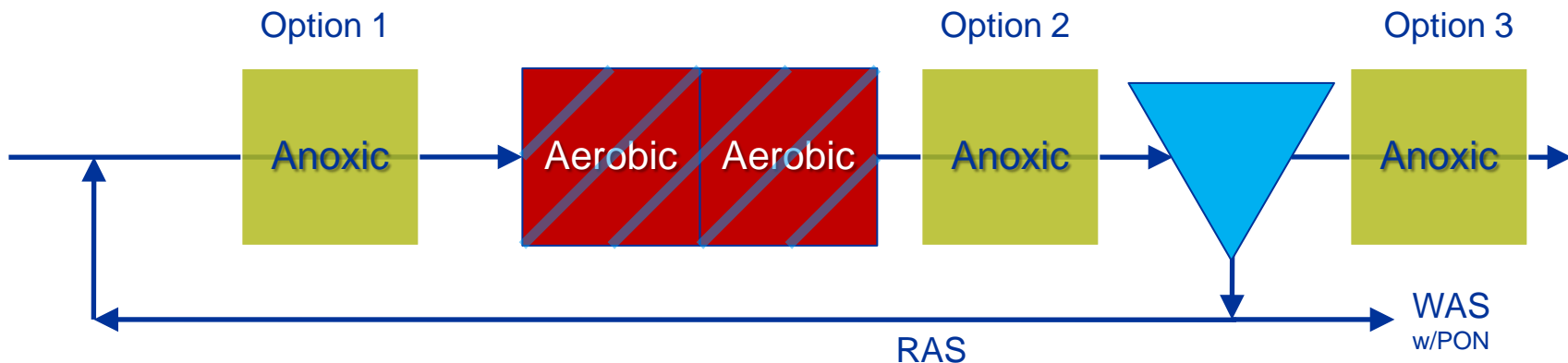


# Process Considerations: Denitrification – Carbon

**Option 1:** BOD from WW, recycle to deliver nitrate  
ex. Modified Ludzak Ettinger Process (MLE)

**Option 2:** BOD from endogenous decay(may add carbon), nitrate present  
ex. Four Stage Bardenpho process (Option 1 & 2) (endogenous C adds ammonia N and P)

**Option 3:** BOD from external carbon source, nitrate present  
ex. Denite filter



No alkalinity recovery or decrease in oxygen demand for options 2 & 3

# Process Considerations: Carbon Options

Product	Strength	NFPA Rating			Freezing Point, C	SG	COD Content, g/L	COD:N Ratio Required
		Health	Fire	Reactivity				
Methanol	100%	1	3	0	-97	0.79	1200	4.6
Ethanol	100%	1	3	0	-114	0.79	1650	4.7
Acetic Acid	100%	3	2	2	17	1.05	1100	3.6
Corn Syrup	50% glucose	0	0	0	12	1.22	700	5.6
MicroC-G	100%	0	0	0	-8	1.20	650	6.5
Glycerin	80% (20% water)	1	1	0	18	1.19	1800	7.0

# Process Considerations: Effluent Nitrogen

- Effluent DON (eDON) = TKN not converted to ammonia in biological WW treatment process
- Some may be slowly biodegradable “recalcitrant” or “refractory” (rDON)
- Some produced in process
- WERF indicates > 60% of biological WWTPs in VA & MD have eDON  $\geq 1$  mg/L

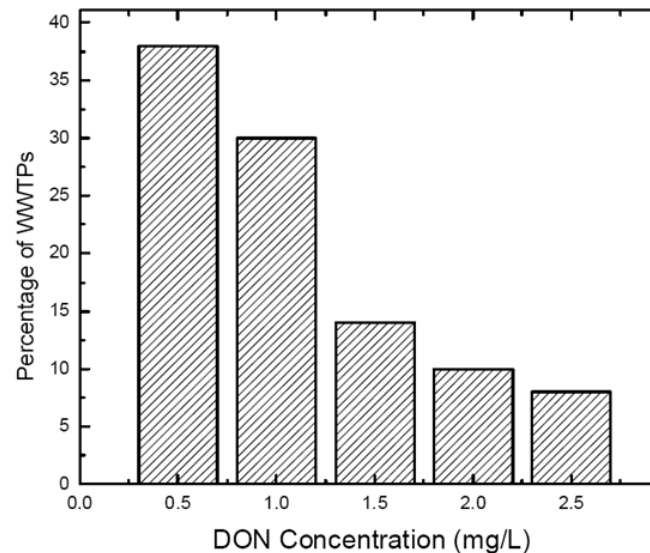


Figure 2. Summary of effluent dissolved organic nitrogen (DON) concentration (0.45  $\mu$ m filtration) from 188 Maryland and Virginia wastewater treatment plants (Pagilla, 2007)

# Process Considerations: Range of N in ENR Effluents

COMPONENT	NITROGEN (mg/L as N)	
Soluble	HIGH LOW	
Organic	2.5	0.5
Ammonia	0.75	0.25
Nitrate + Nitrite	2.0	1.0
<b>Subtotal</b>	<b>5.25</b>	<b>1.75</b>
Particulate	0.50	0.25
Organic		
<b>Total</b>	<b>5.75</b>	<b>2.0</b>

# Process Considerations:

## Effluent TN Components for TN = 4

- Assume 4 mg/L TN limit
  - 1 mg N/L DON
  - 0.25 mg N/L PON
  - 0.25 mg N/L ammonia
  - Allows ~ 1.5 mg N/L NO<sub>x</sub>
- Nitrification and denitrification processes must be very effective