NITROGEN AND PHOSPHORUS: TREATMENT CONCEPTS

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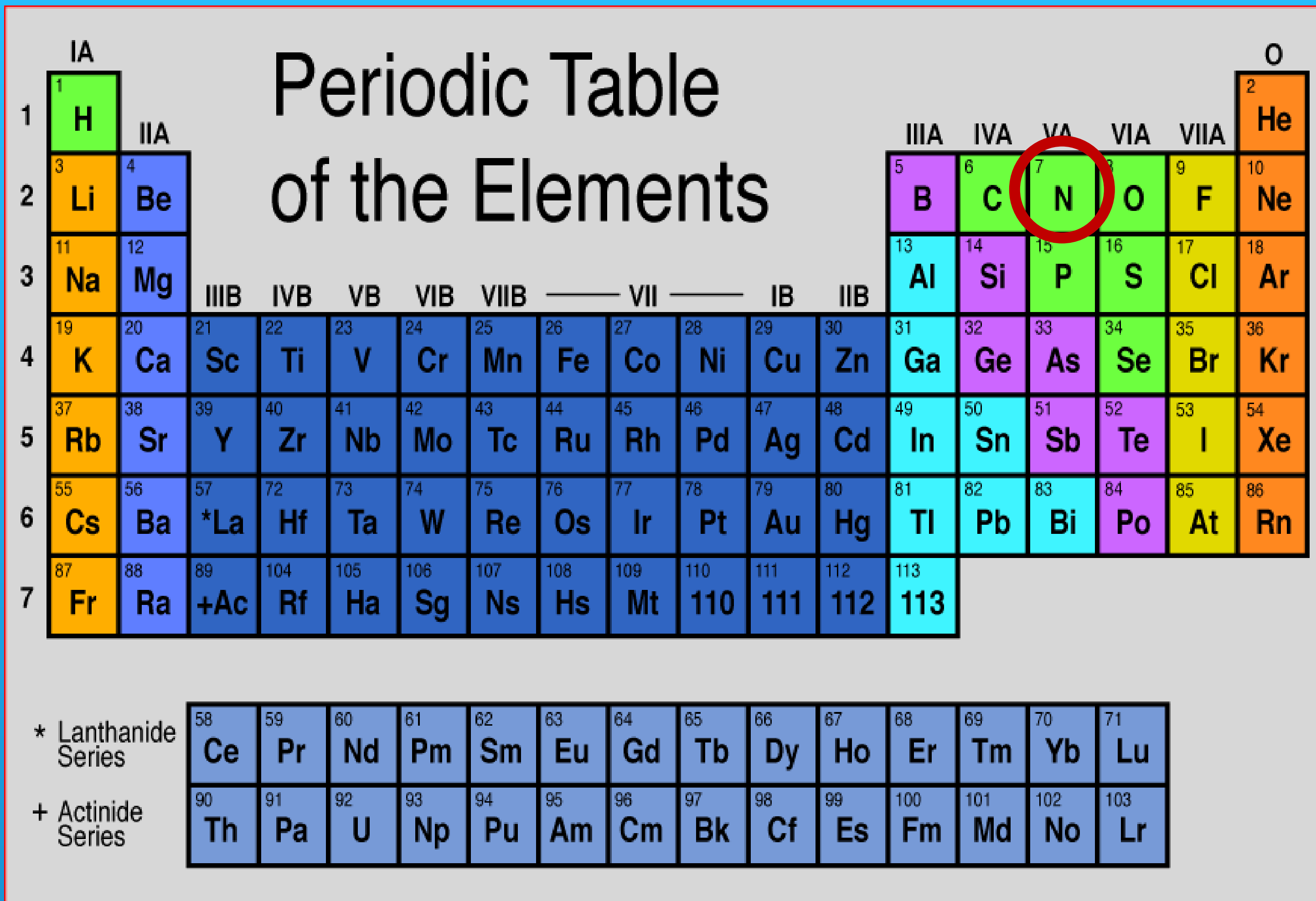
Part I: Nitrogen



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)

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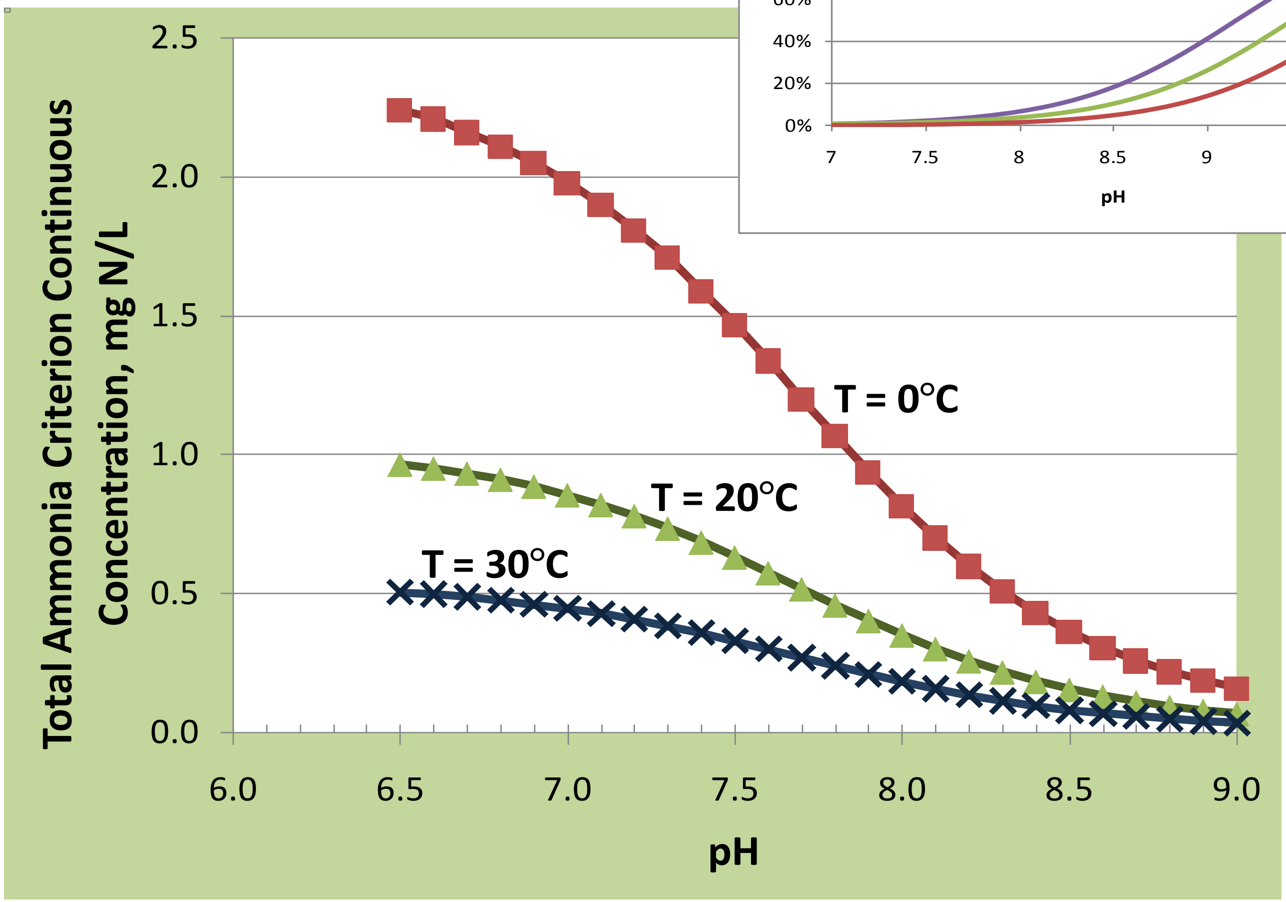
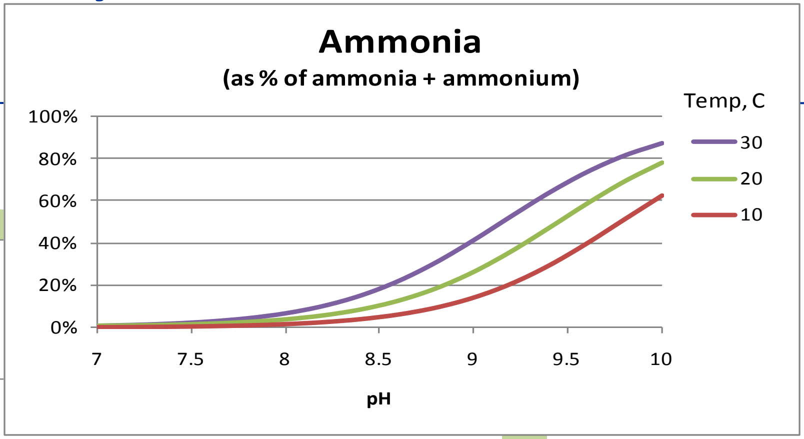
Problems: Ammonia Toxicity

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

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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 (NO_2^-)	Dissolved	Inorganic
Nitrate (NO_3^-)	Dissolved	Inorganic
Ammonia (NH_3)	Dissolved	Inorganic
Ammonium (NH_4^+)	Dissolved	Inorganic
Dissolved organic nitrogen (DON)	Dissolved	Organic
Particulate organic nitrogen (PON)	Particulate	Organic

Filtered TKN (Ammonia, Ammonium, DON)

Unfiltered (total) TKN (Ammonia, Ammonium, DON, PON)

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Forms: TIN? TKN? TN???

- TIN = nitrate + nitrite = NOx
- TKN = ammonia + organic nitrogen
- TN = NOx + TKN

  = NOx + ammonia + SON + PON

Forms: Typical Concentrations in Raw Domestic Wastewater

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

TKN (Organic + Ammonia)

Ammonia ~ 60% of TKN

(Metcalf & Eddy)

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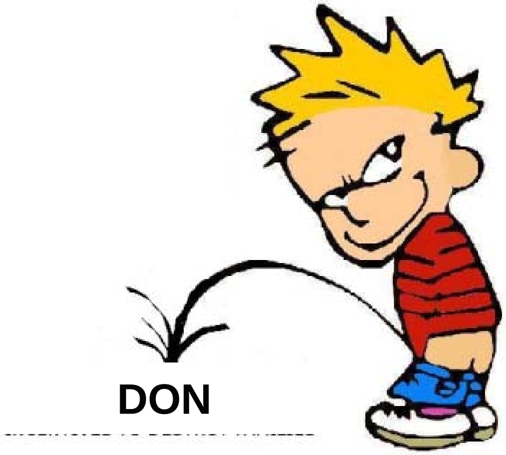
Forms: A Note on DON/SON and PON

- 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



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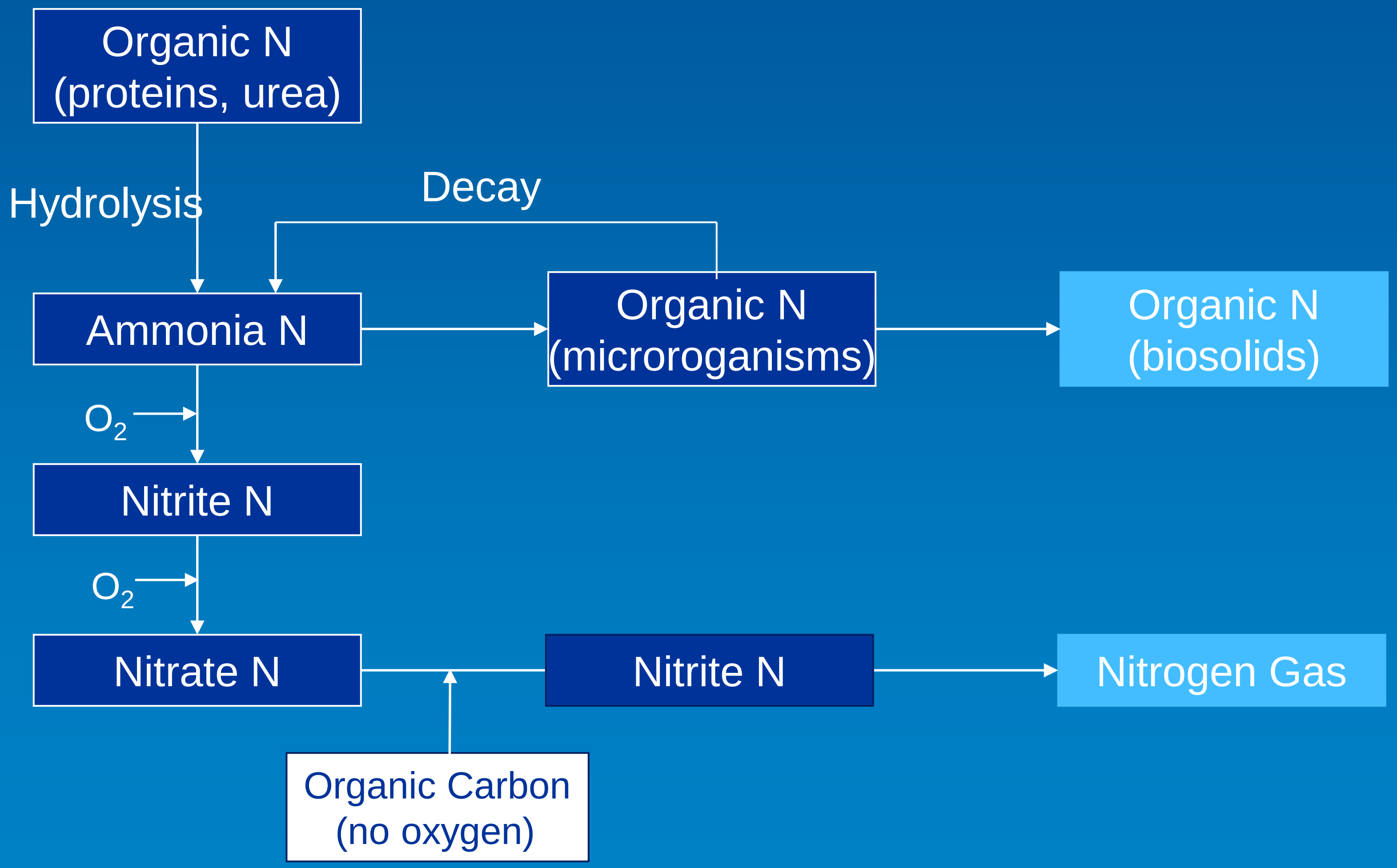
Conversions: Overview

- 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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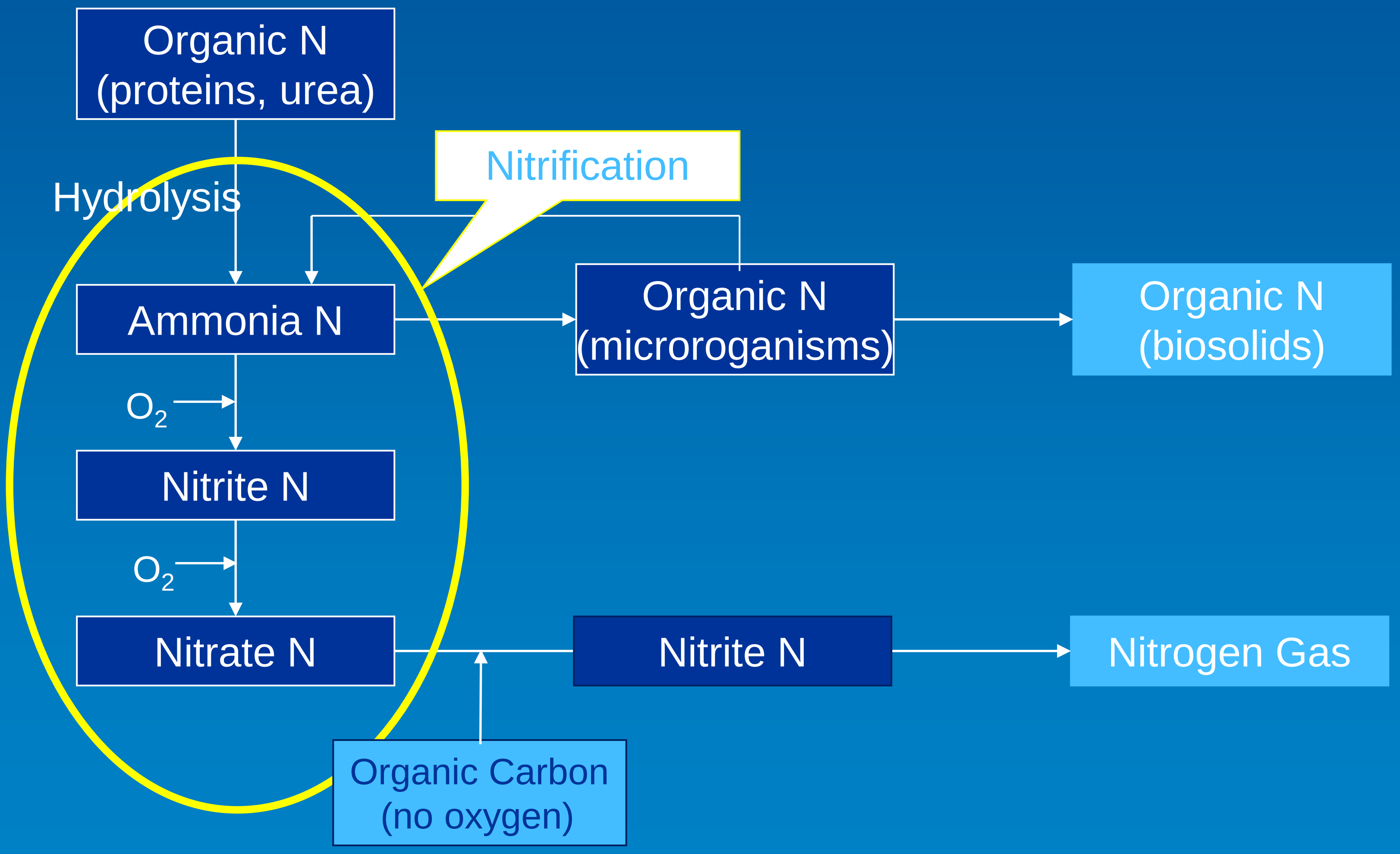

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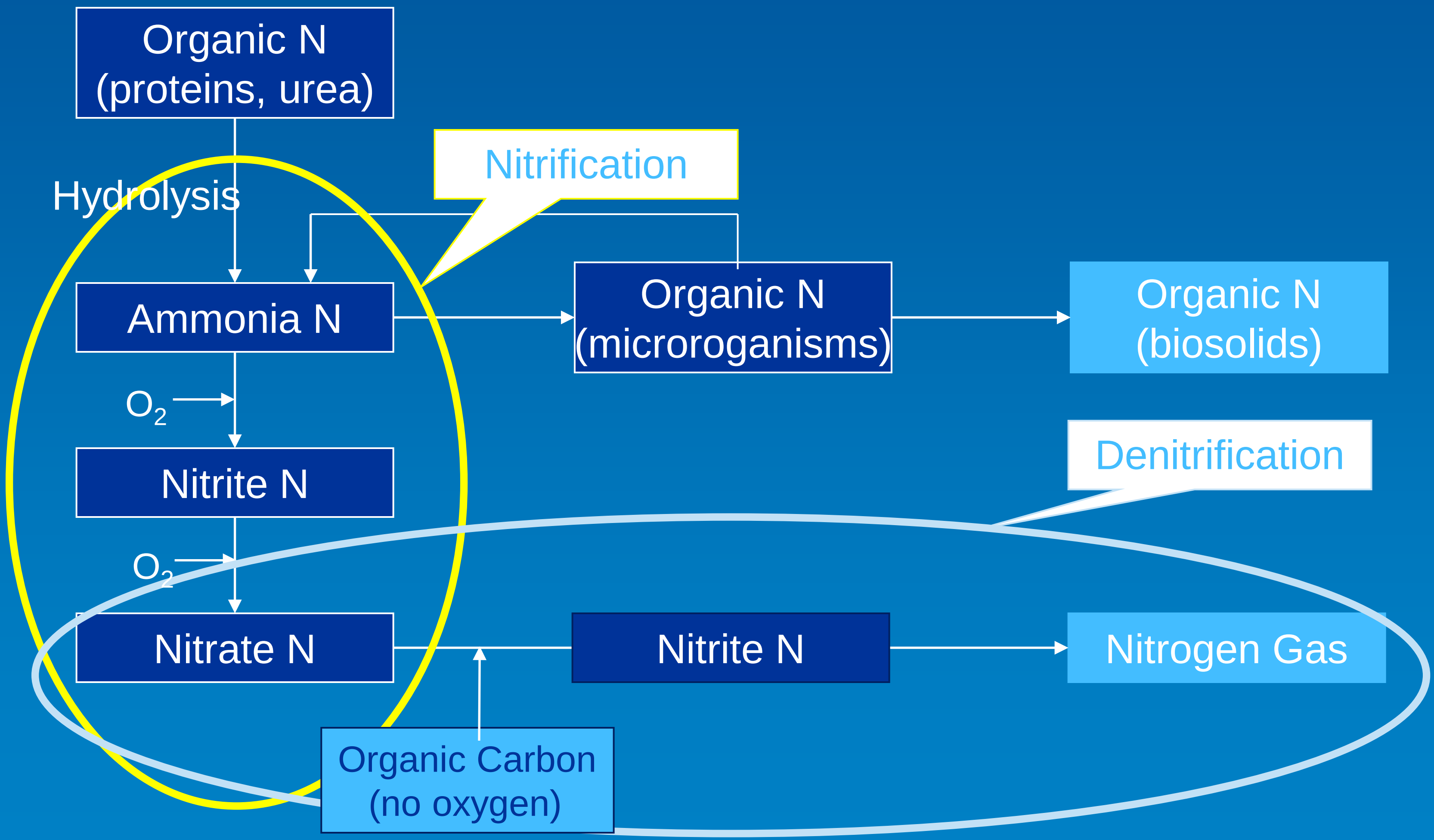

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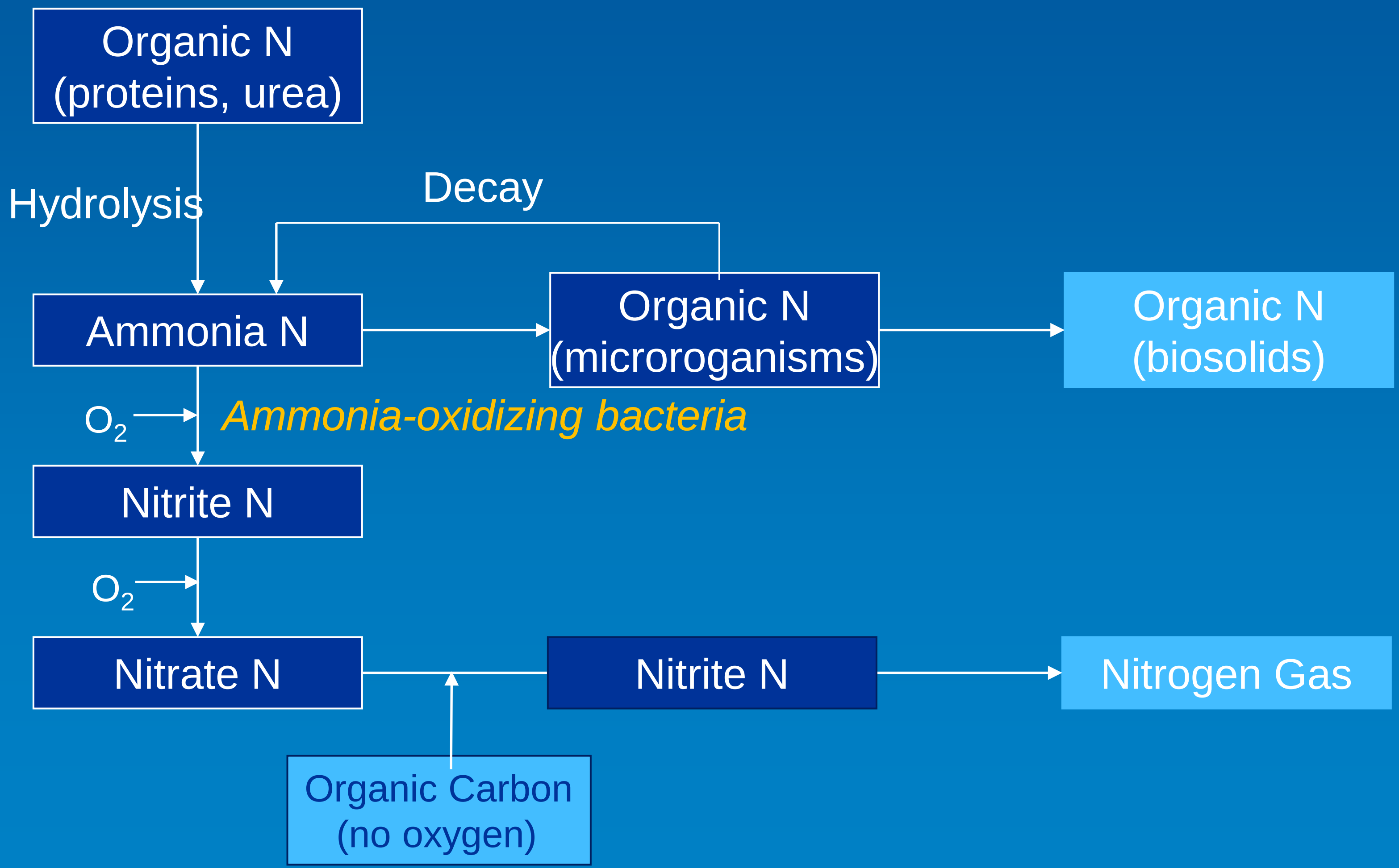

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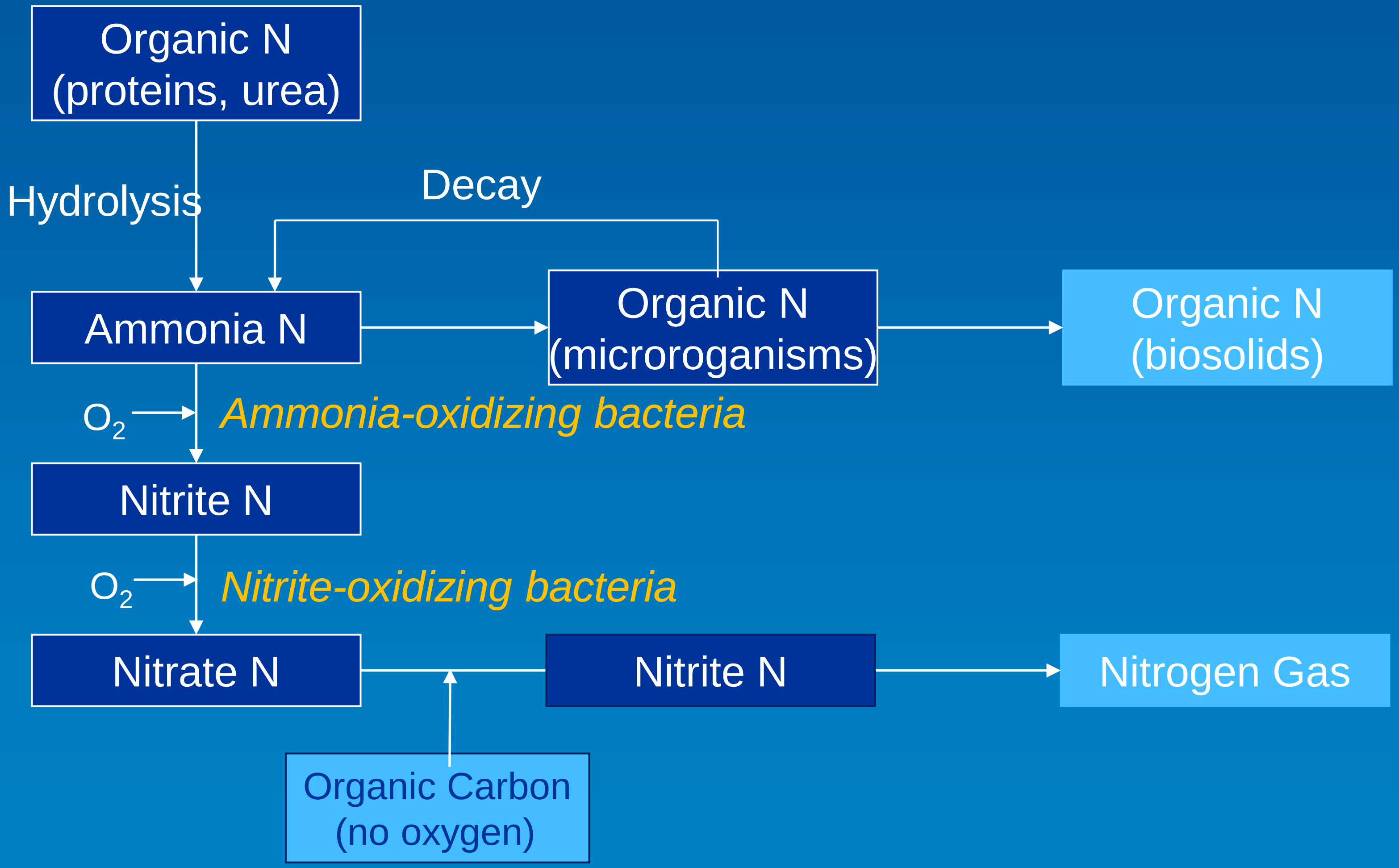

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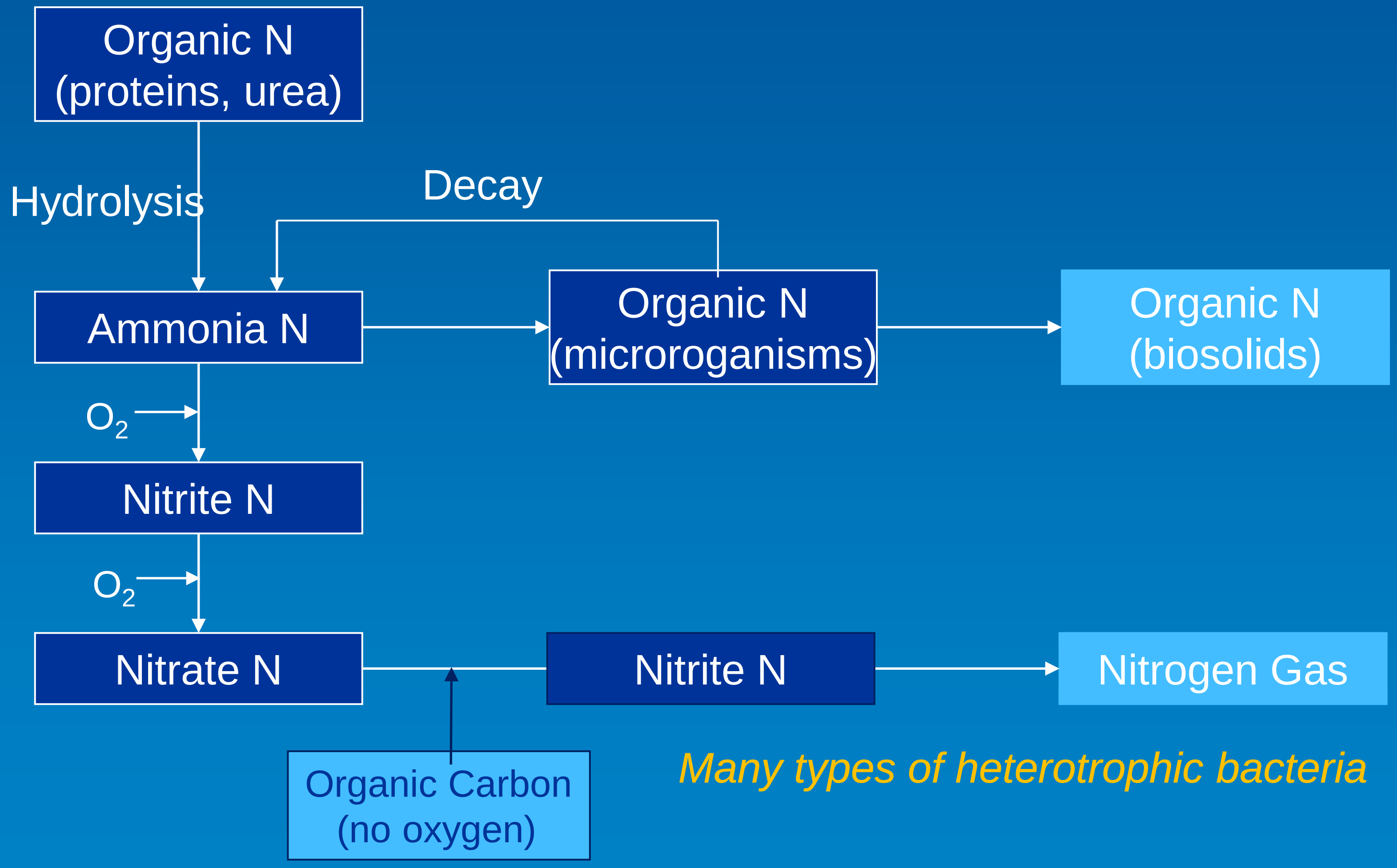

Removal Concepts: Basic Ideas

- What comes in must go out
  - Air
  - Water
  - Solids
- Transform to an acceptable or removable form
  - Air (N2 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 ~ 10% N
- Removes TN

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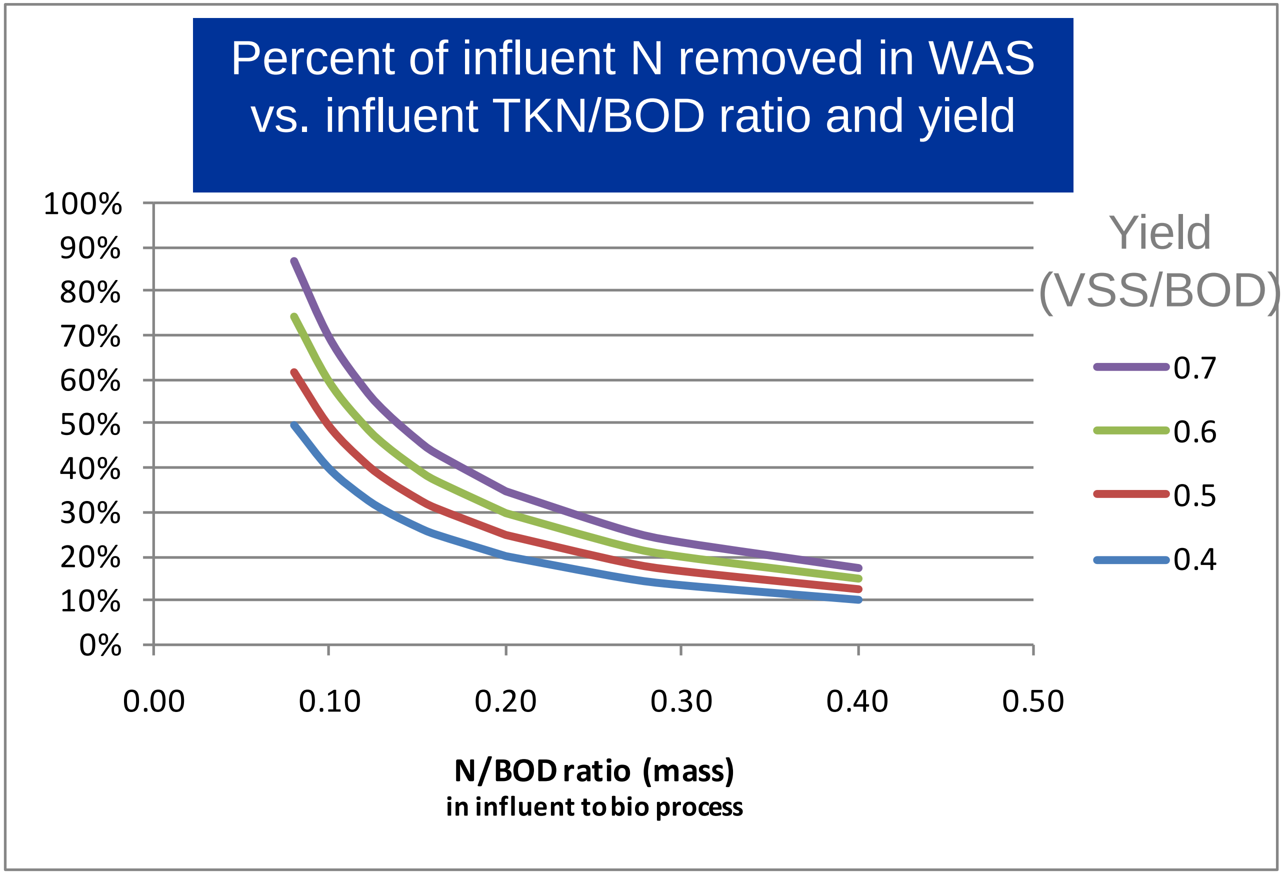
Removal Concepts:
Incorporation into Biomass (cont.)

- 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

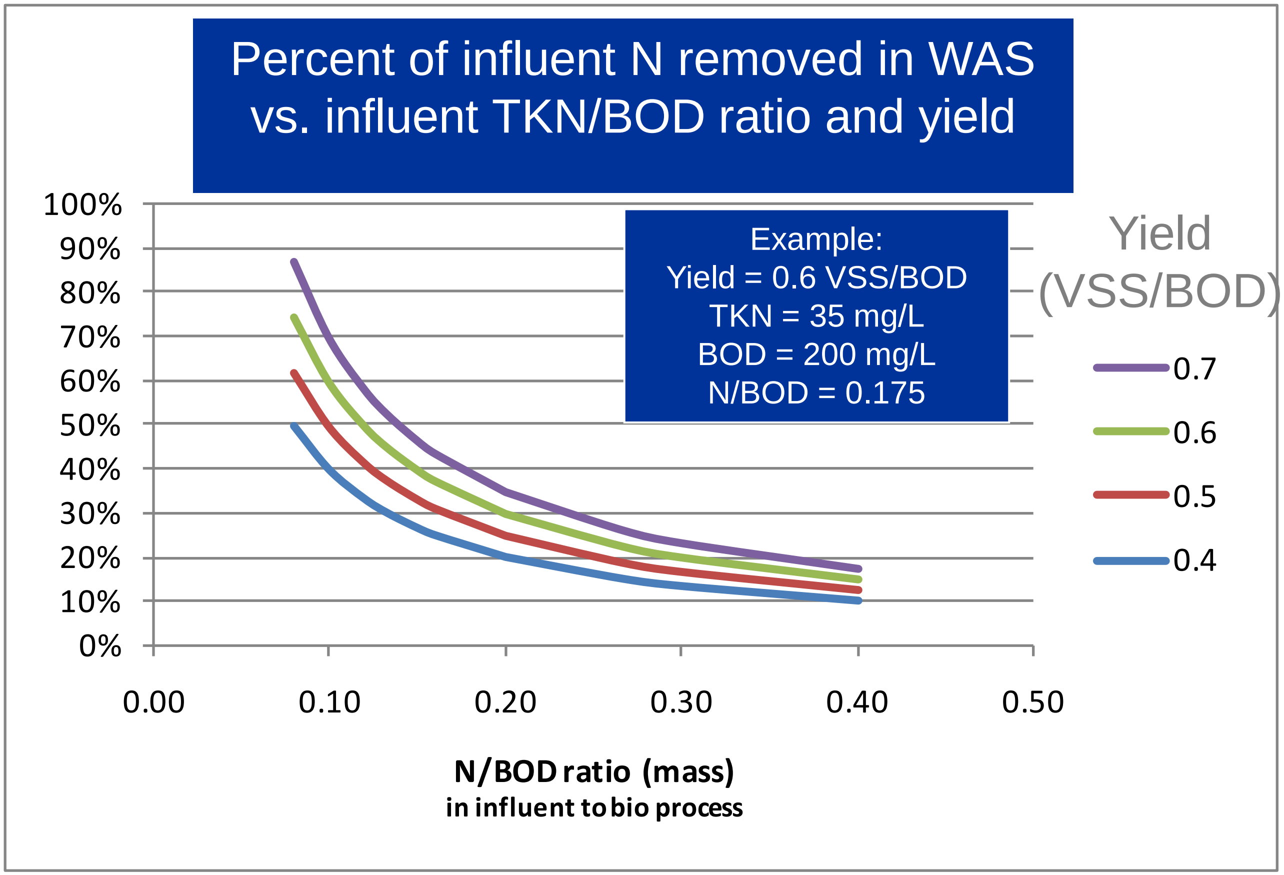
Removal Concepts: Incorporation into Biomass



Shorter SRT
Colder Temp

Longer SRT
Warmer Temp

Removal Concepts: Incorporation into Biomass



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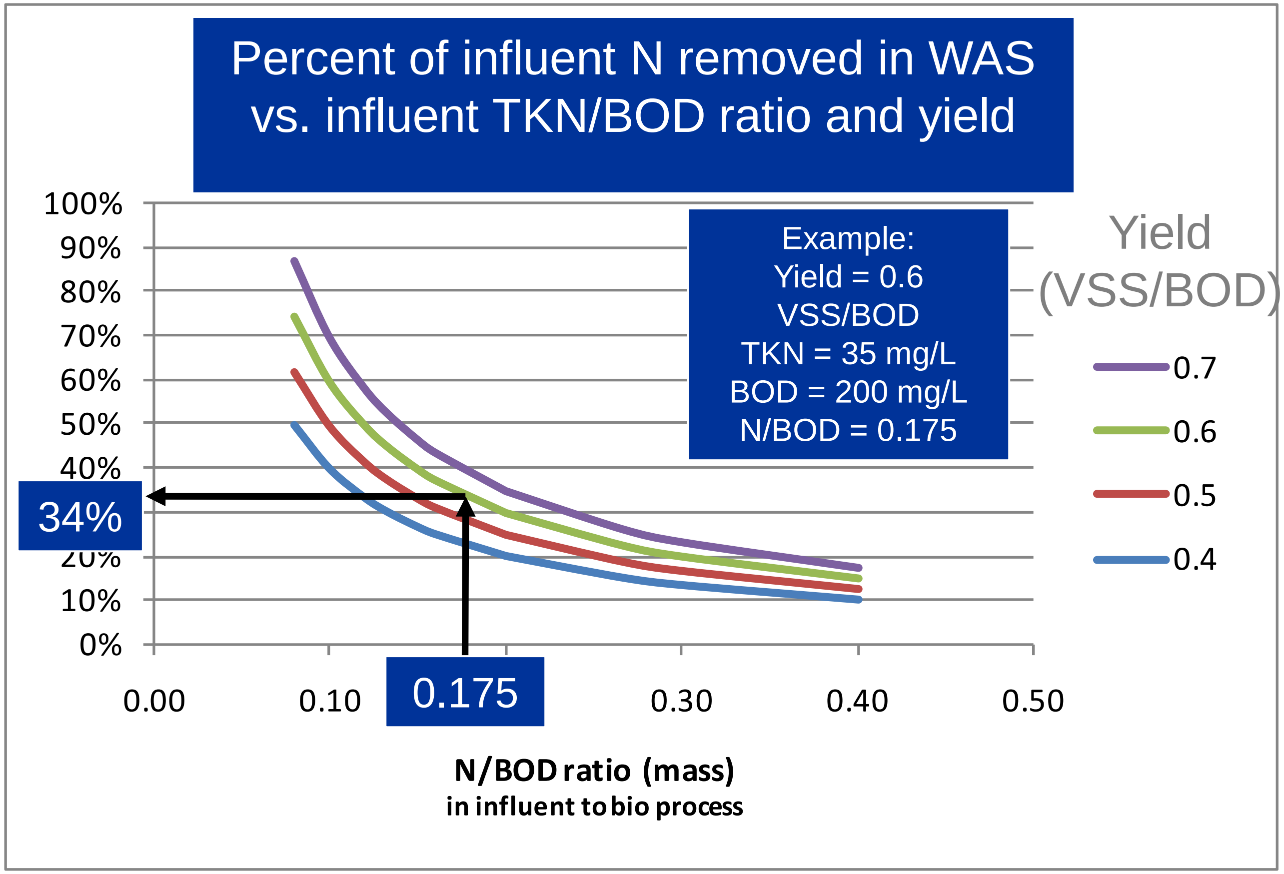
Removal Concepts: Incorporation into Biomass



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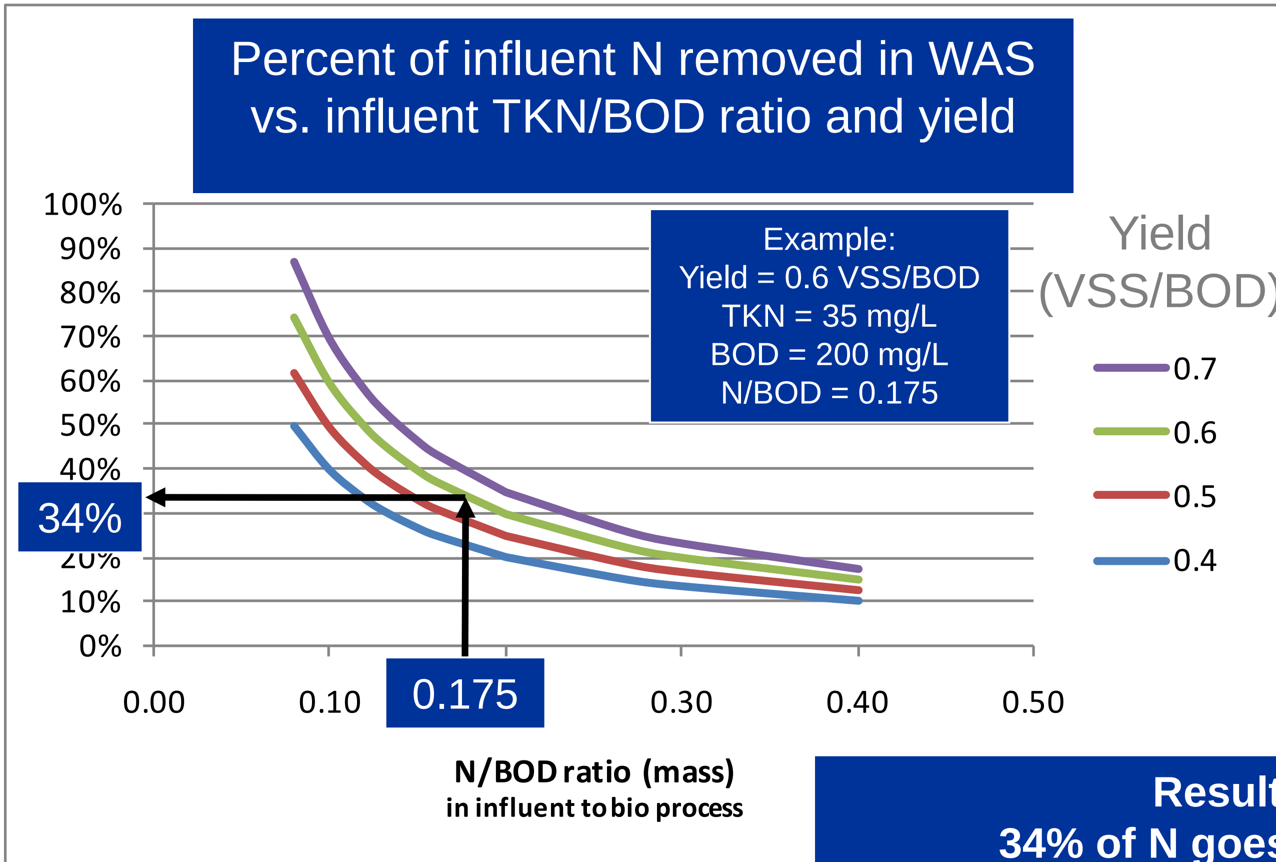
Removal Concepts: Incorporation into Biomass

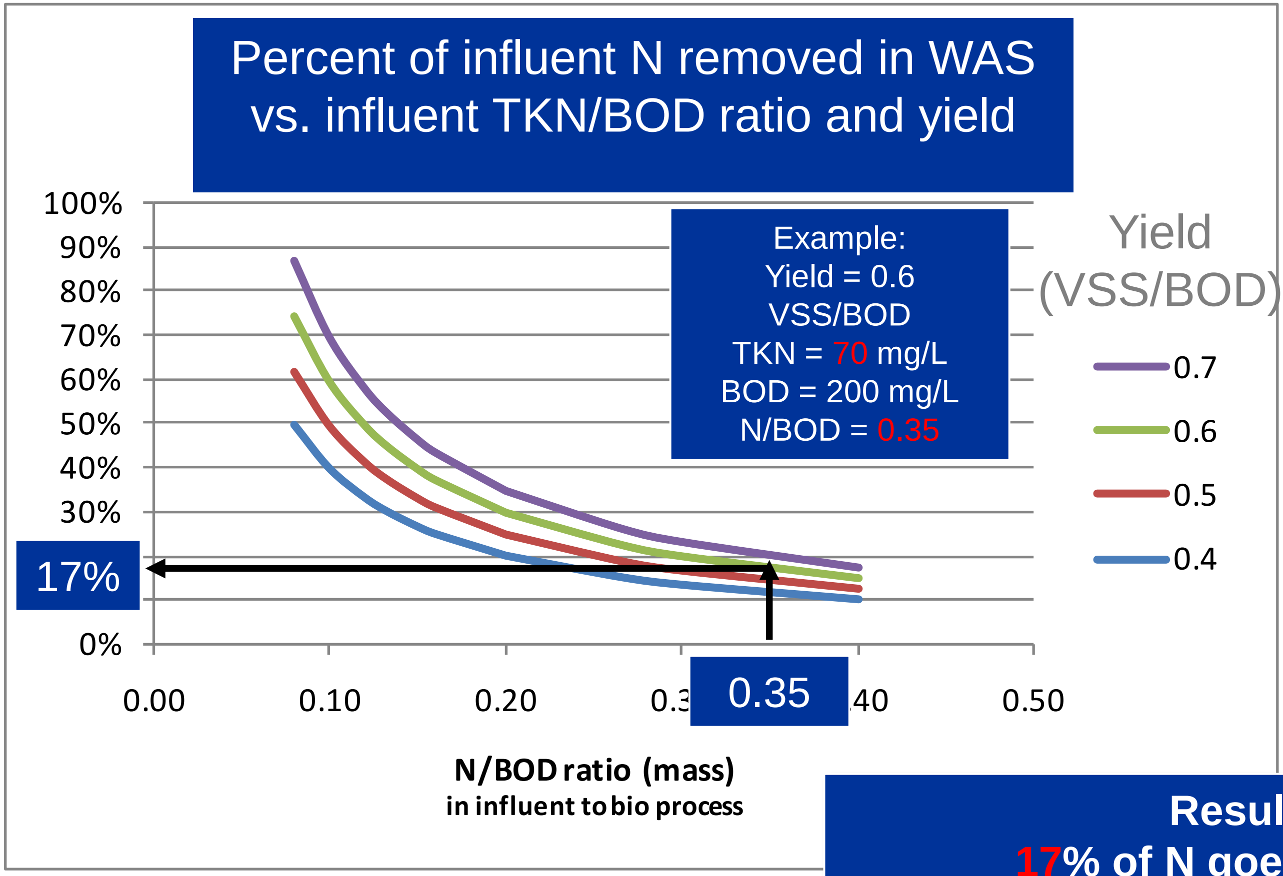


Shorter SRT
Colder Temp

Longer SRT
Warmer Temp

Result:
34% of N goes to WAS
35 mg/L N x 0.34 = 12 mg/L N removed
35 – 12 = 23 mg/L N remains

Removal Concepts: Incorporation into Biomass

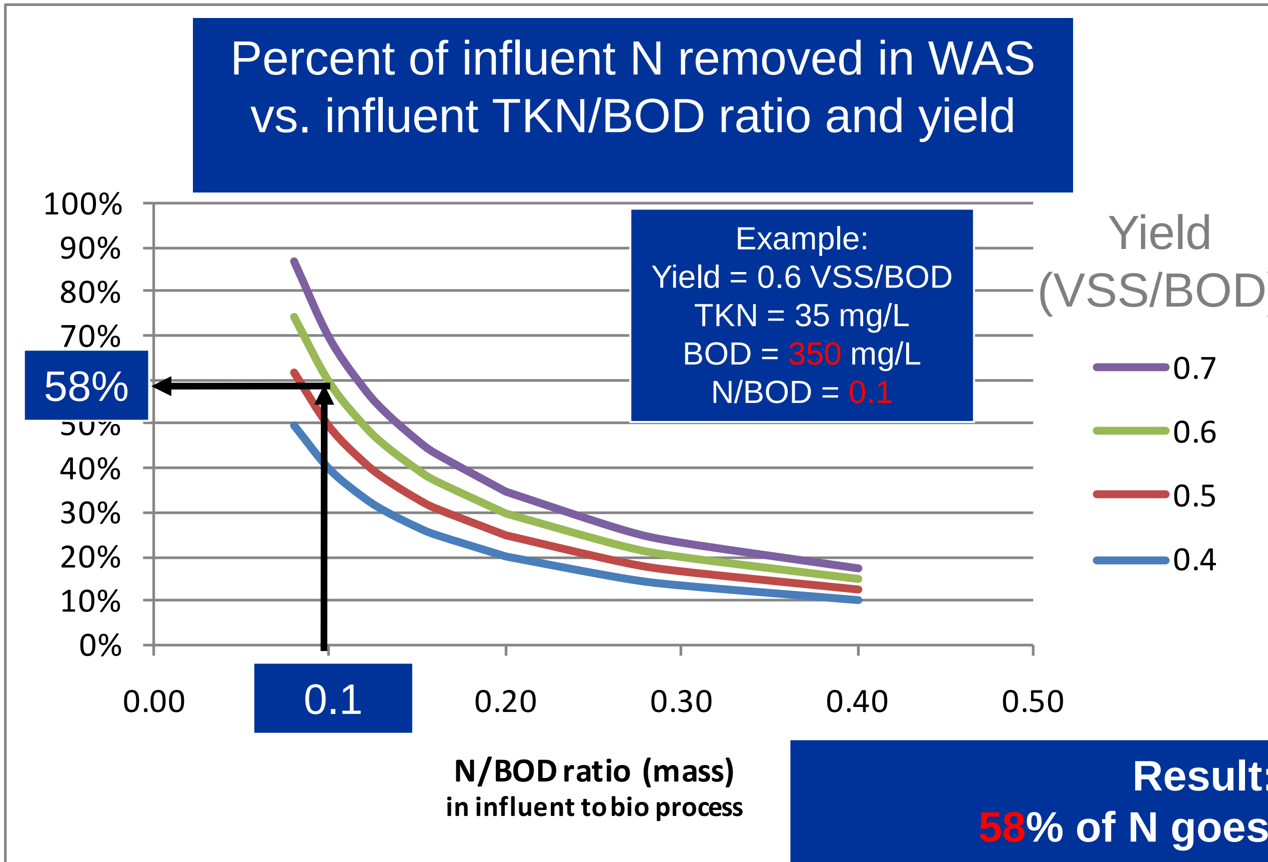


Shorter SRT
Colder Temp

Longer SRT
Warmer Temp

Result:
17% of N goes to WAS
70 mg/L N x 0.17 = 12 mg/L N removed
70 – 12 = 58 mg/L N remains

Removal Concepts: Incorporation into Biomass



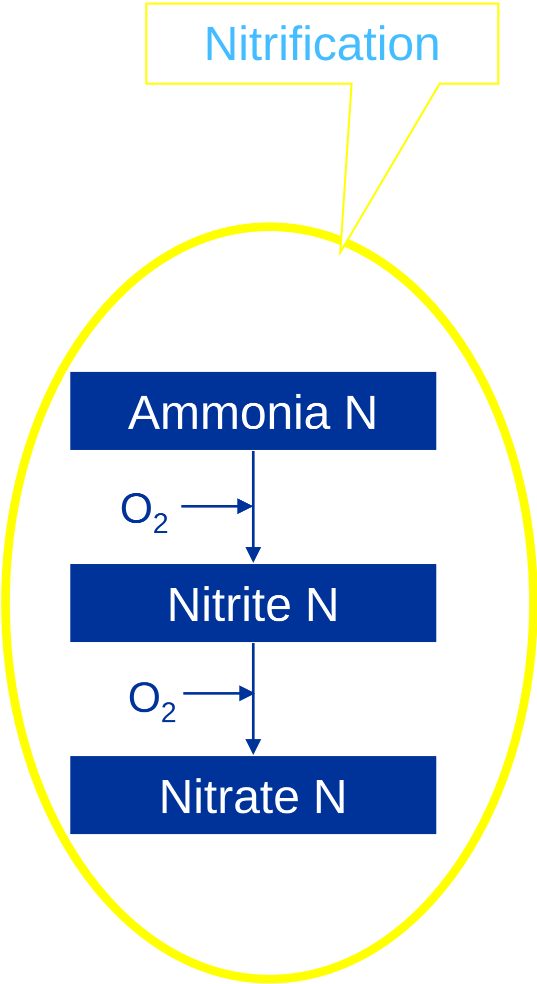
Shorter SRT
Colder Temp

Longer SRT
Warmer Temp

Result:
58% of N goes to WAS
35 mg/L N x 0.58 = 20 mg/L N removed
35 – 20 = 15 mg/L N remains

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_2 / mg N nitrified
  - Adequate pH: 7.1 mg $CaCO_3$ alkalinity / mg N nitrified



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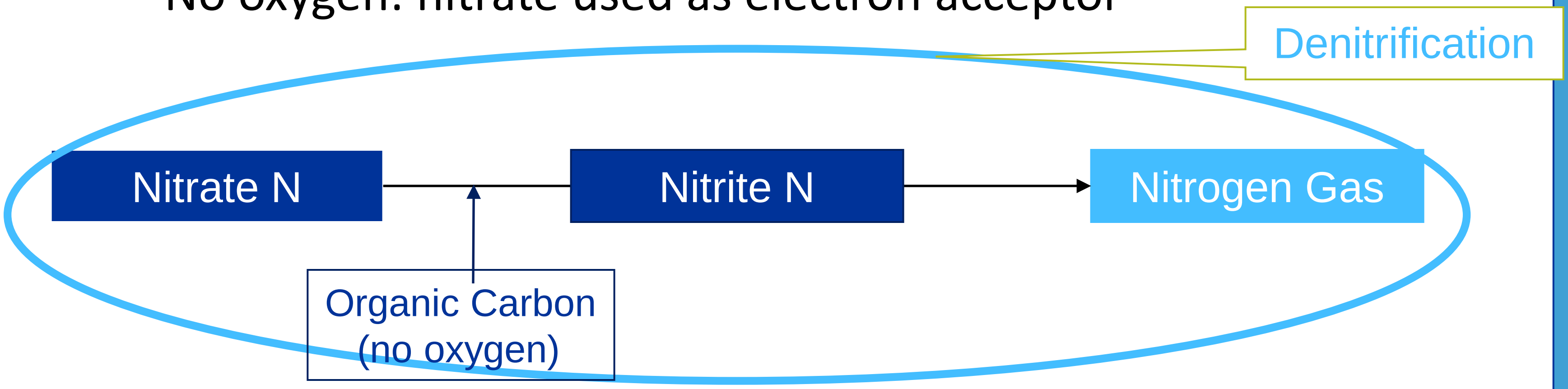
Removal Concepts: Denitrification

- 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

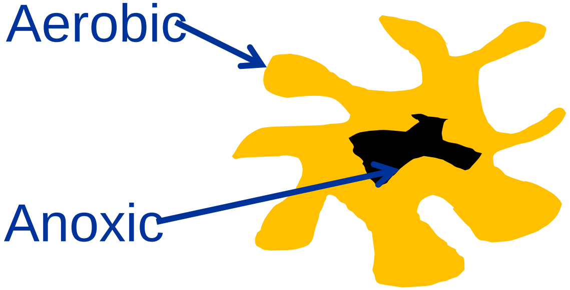


Removal Concepts:
Denitrification – Carbon Sources

- 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 courses:
    - 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



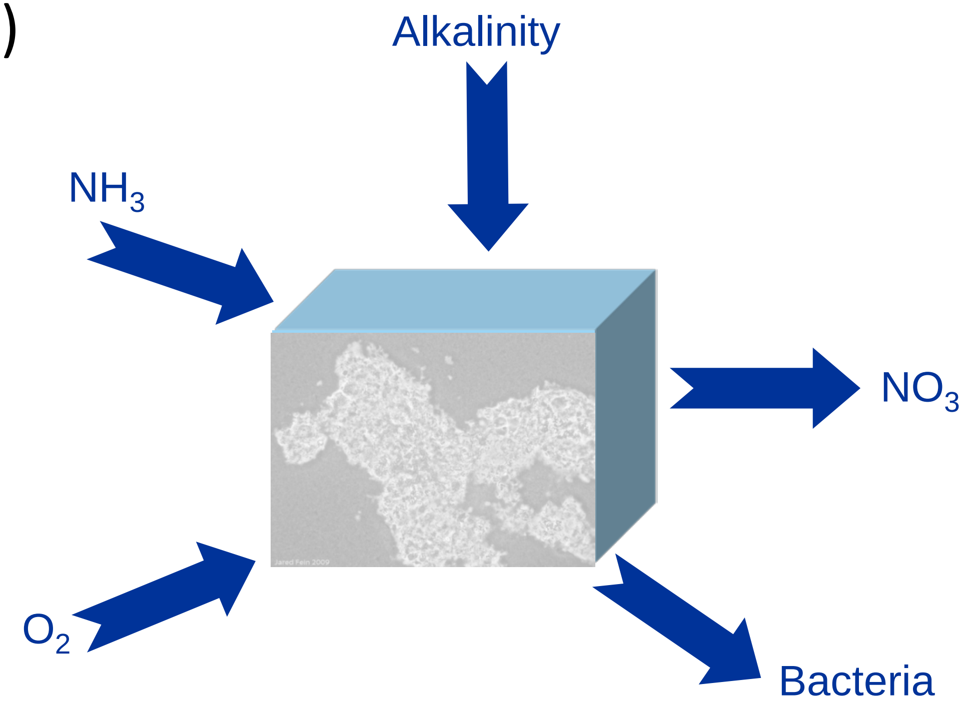
Floc

Removal Concepts:
Denitrification - Benefits

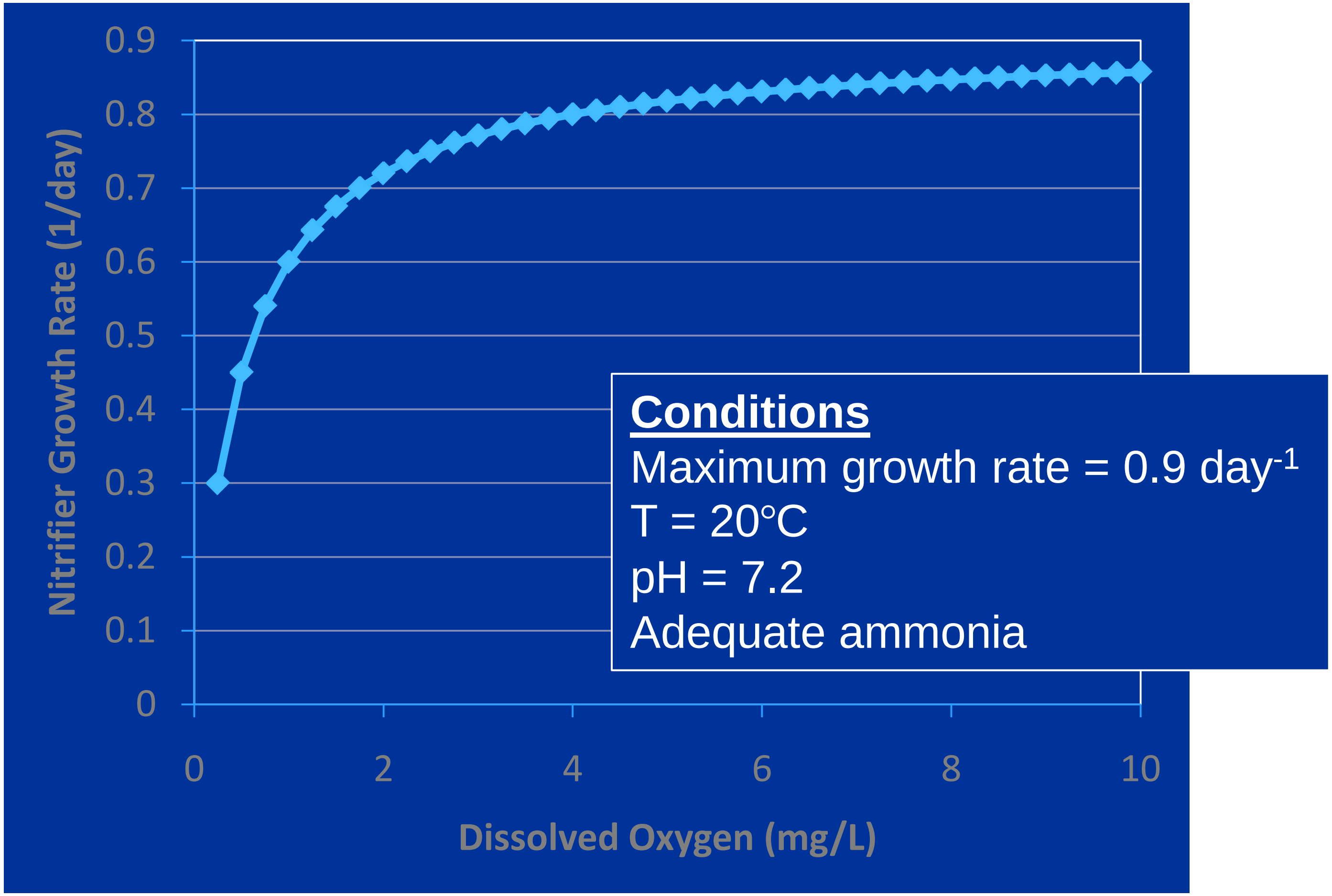
- Recover alkalinity
  - Nitrification consumes alkalinity: -7.1 mg $CaCO_3$/mg N nitrified
  - Denitrification generates alkalinity: +3.6 mg $CaCO_3$/mg N denitrified
  - Save chemical $
- Reduce oxygen supply required for oxidation of organics
  - Denitrification "credit" = 2.8 mg O_2/mg NO_3- reduced
  - 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



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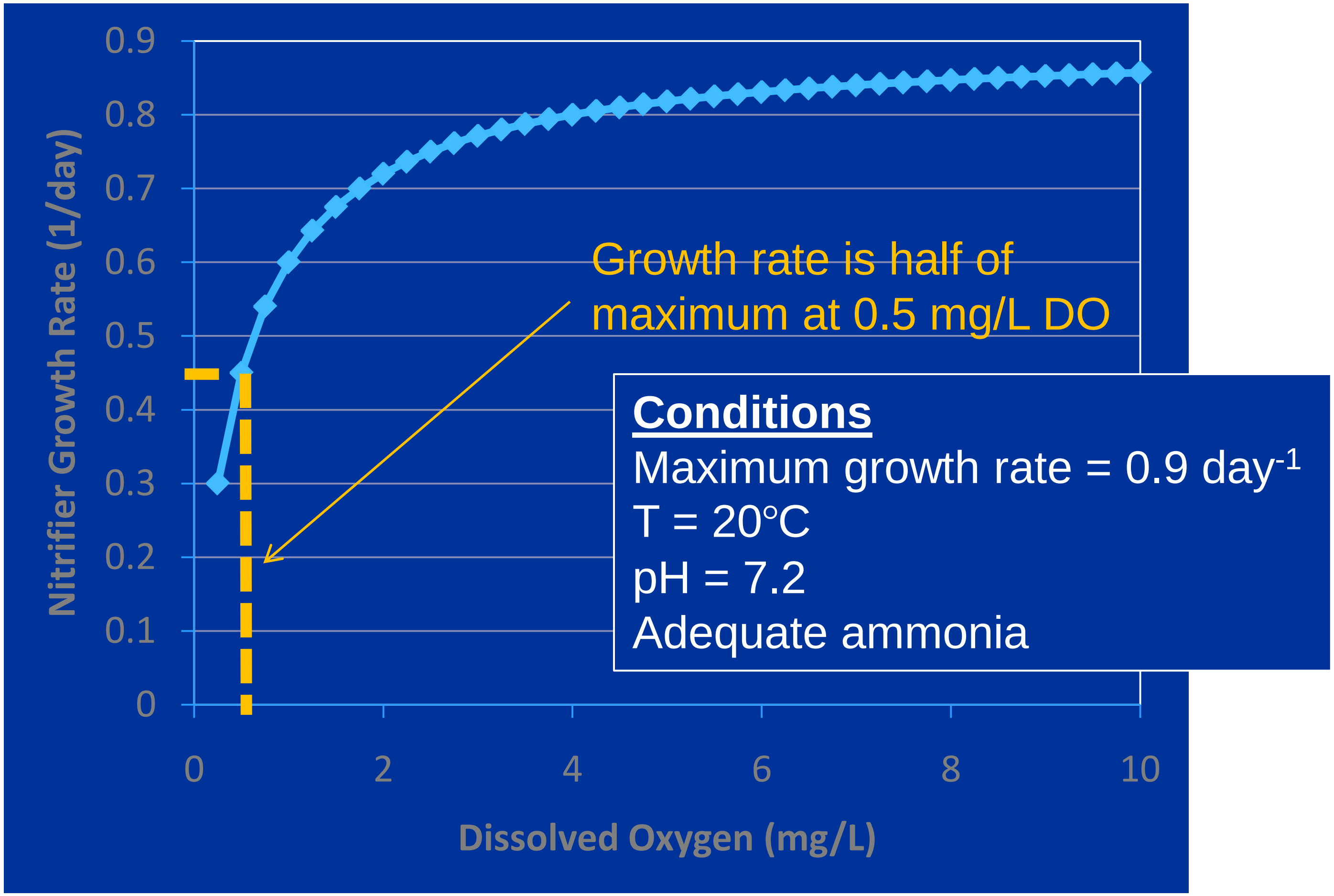
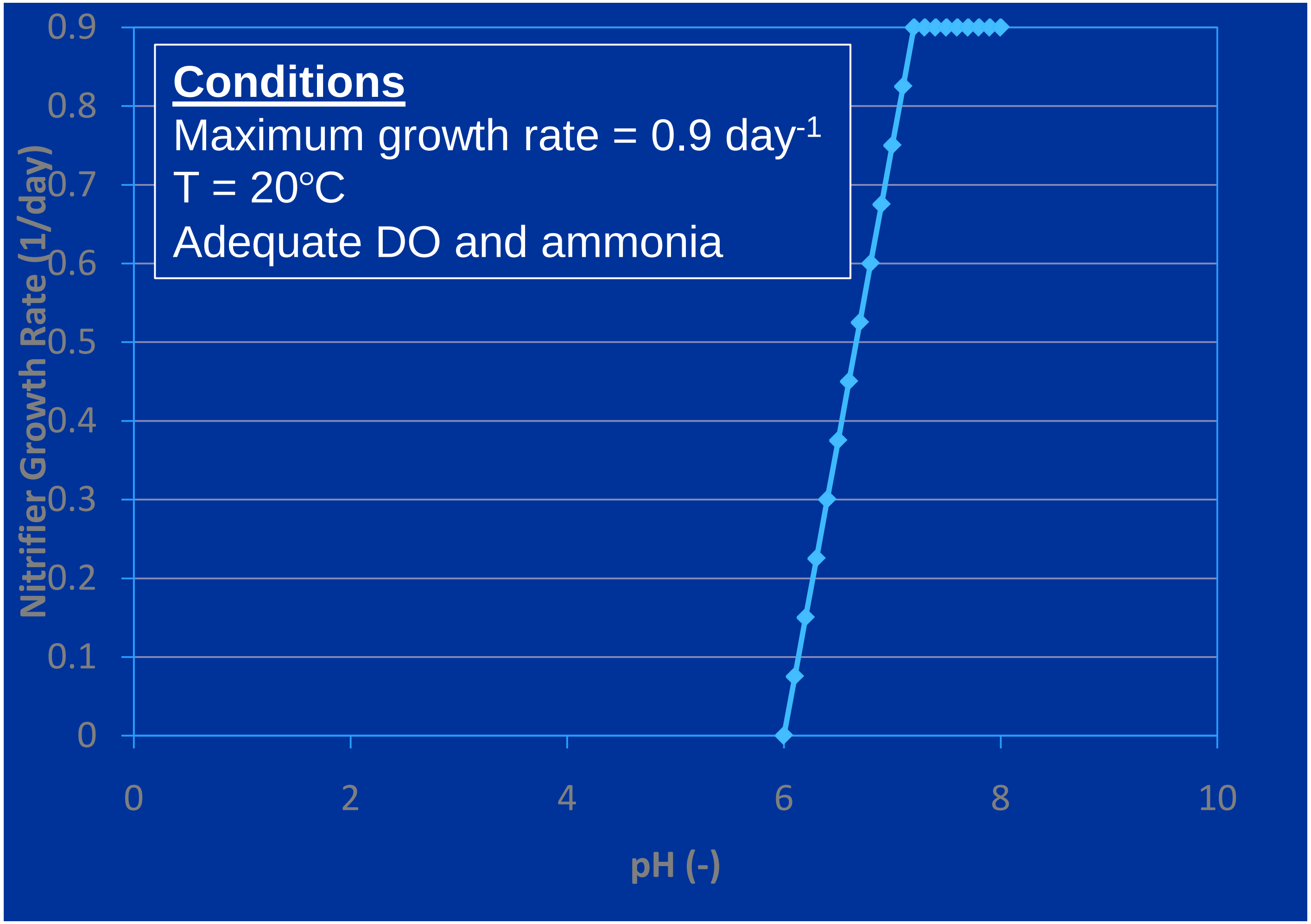
Process Considerations: Nitrification & Oxygen



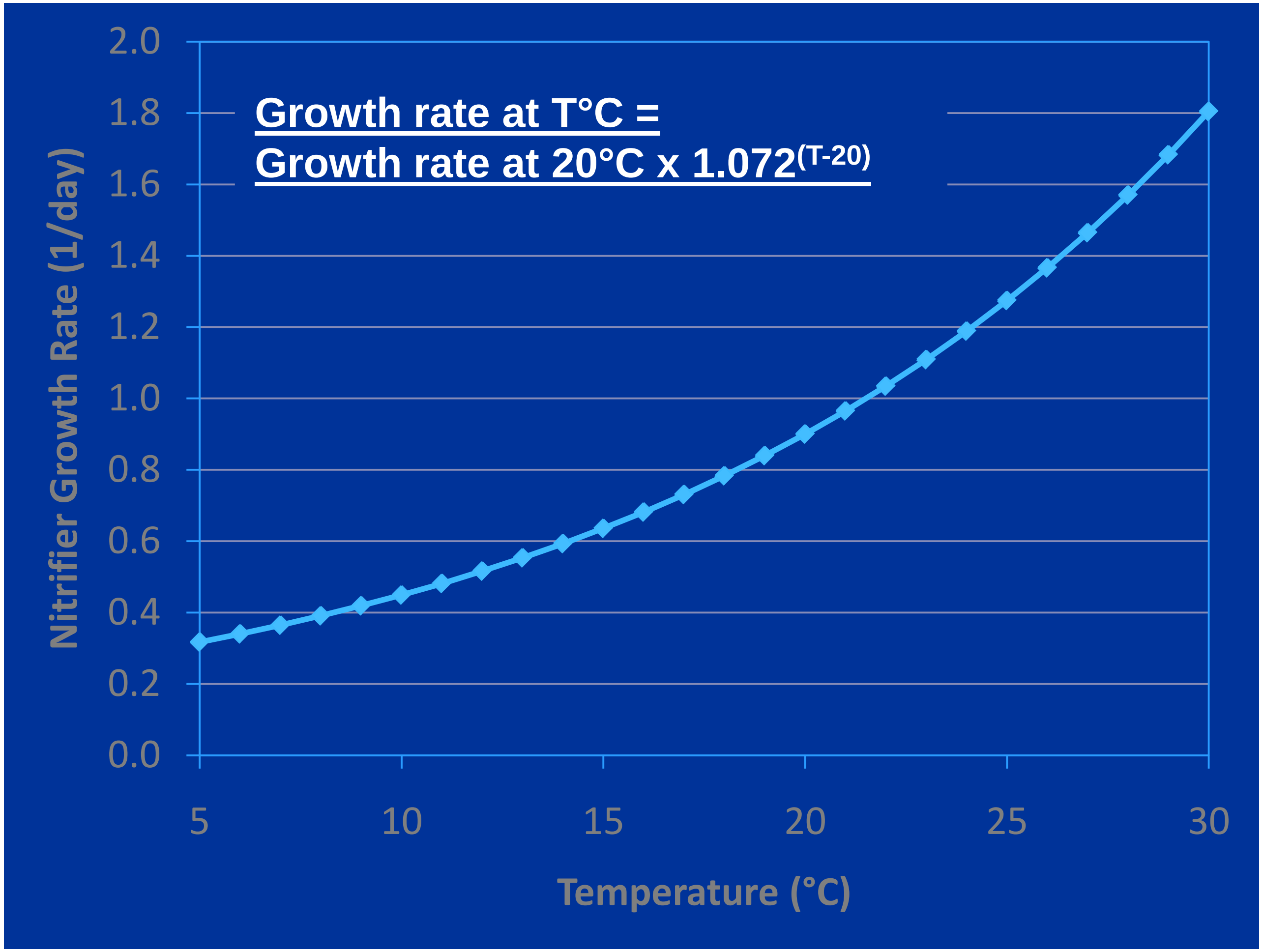
Process Considerations:
Nitrification and pH

- 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

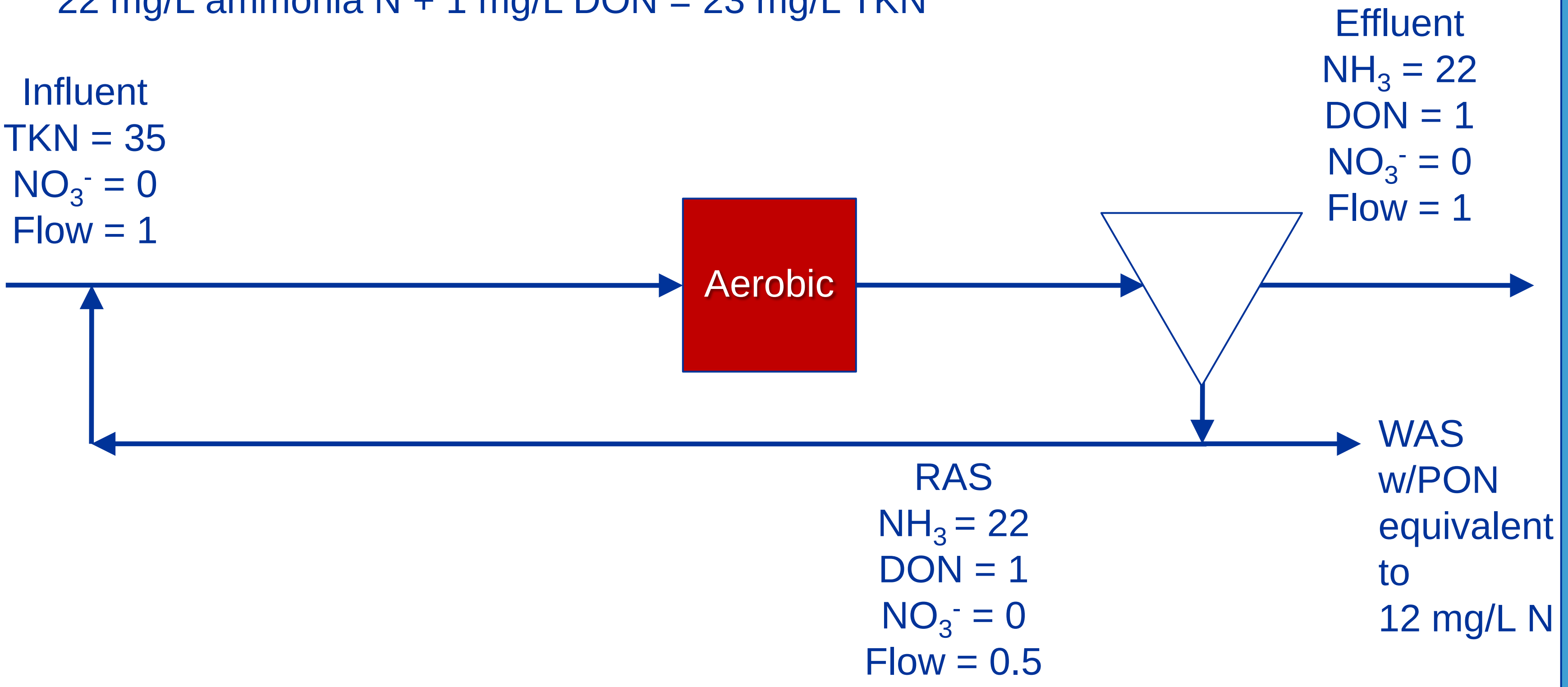
Temperature	Washout SRT	Washout SRT Times 2.5 Safety Factor
(ºC)	(days)	(days)
9	4.7	11.8
10	4.3	10.8
11	3.9	9.9
12	3.6	9.0
13	3.3	8.2
14	3.0	7.5
15	2.8	6.9
16	2.5	6.4
17	2.3	5.8
18	2.1	5.4
19	2.0	4.9
20	1.8	4.5
21	1.7	4.2
22	1.5	3.9
23	1.4	3.6
24	1.3	3.3
25	1.2	3.0

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



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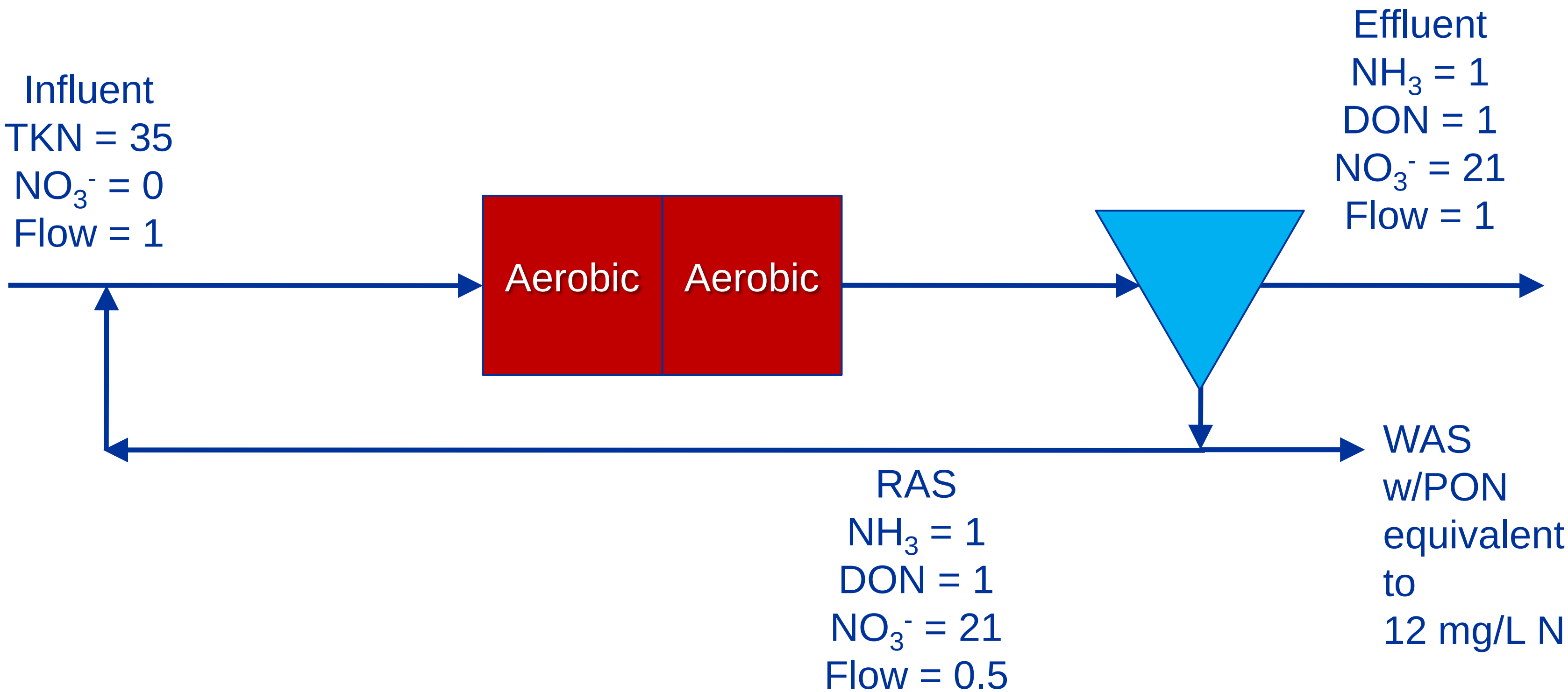
Process Considerations:
Process Flow for Long SRT

Nitrifying

21 mg/L ammonia N converted to nitrate
21 x 7.1 = 149 mg/L $CaCO_3$ alkalinity consumed
1 mg/L DON remains; TKN = 2 mg N/L



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Process Considerations: Nitrification and Toxics

- Sensitive to many compounds: metals, phenolic compounds, cyanates, amines, tannins etc.
- Unionized ammonia (NH_3) is also toxic
  - 100 mg N/L ammonia at pH 7 and T = 20°C inhibits ammonia oxidation
  - 20 mg N/L ammonia at pH 7 and T = 20°C inhibits nitrite oxidation
- Unionized nitrous acid (HNO_2)

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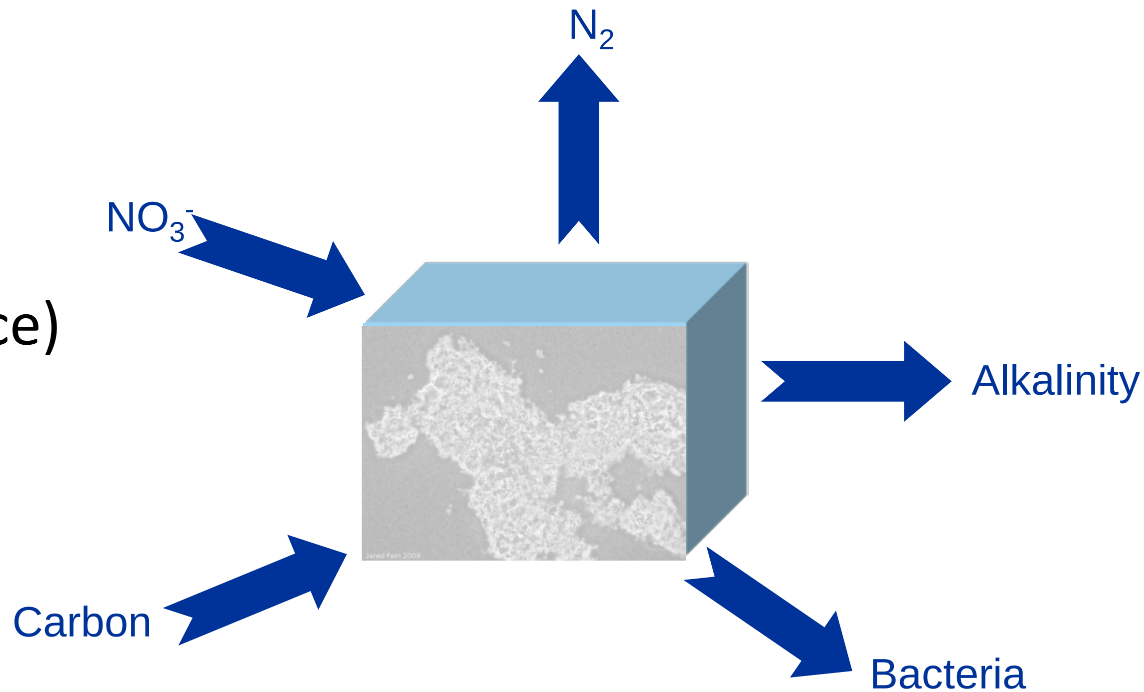
Process Considerations:
Conditions for Denitrification

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

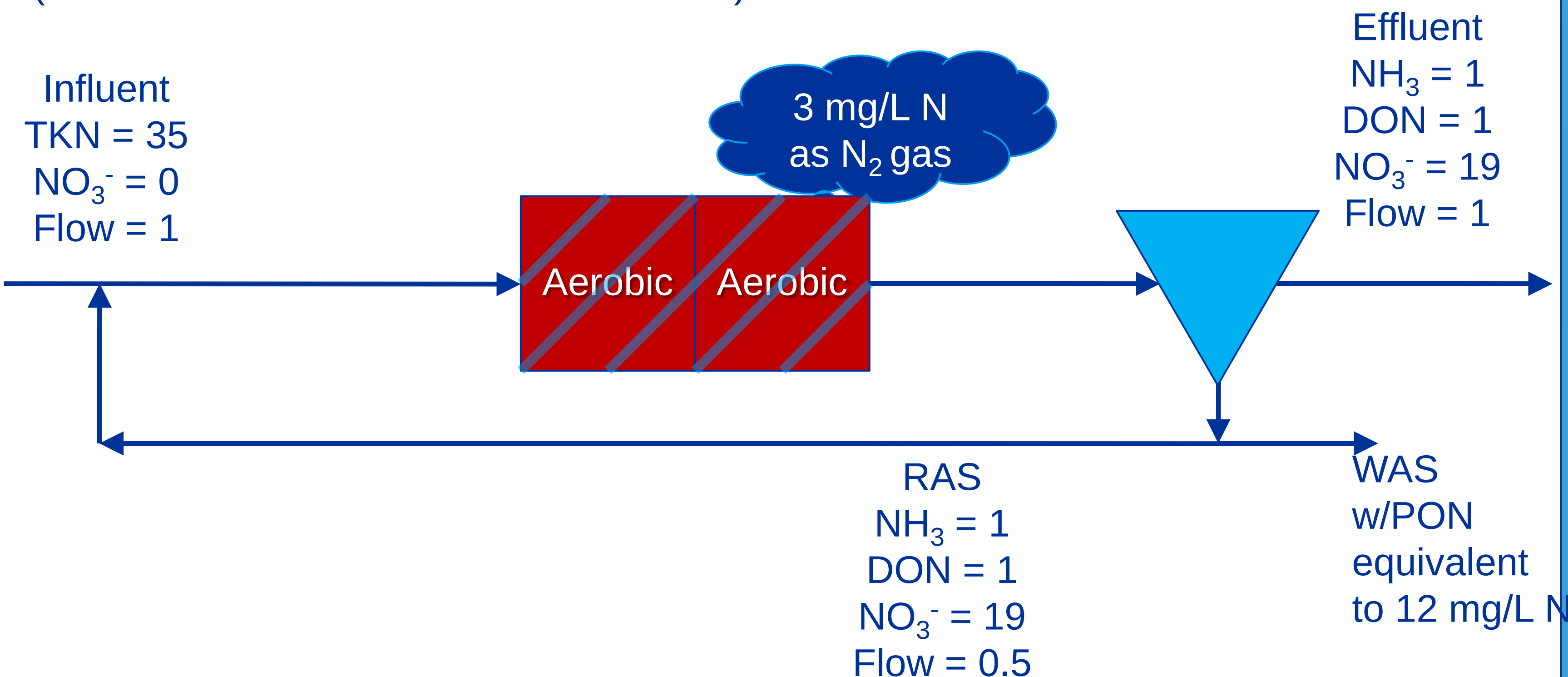


Process Considerations:

Denitrification – Anoxia with SNDN

<u>Some Anoxic Time or Space</u>

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)



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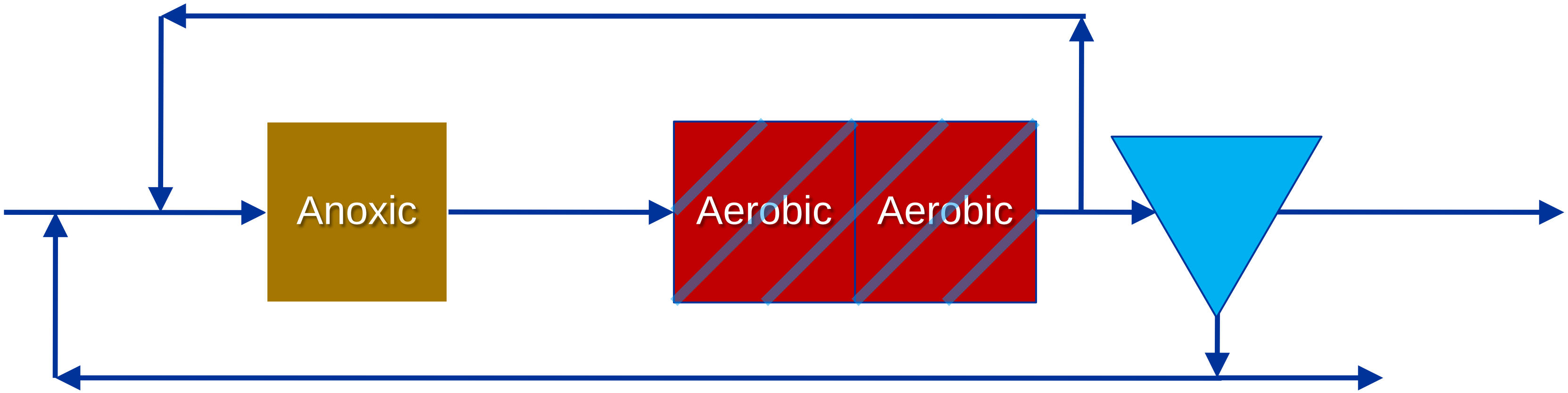
Process Considerations:

Denitrification – Anoxic Zones

Anoxic Space

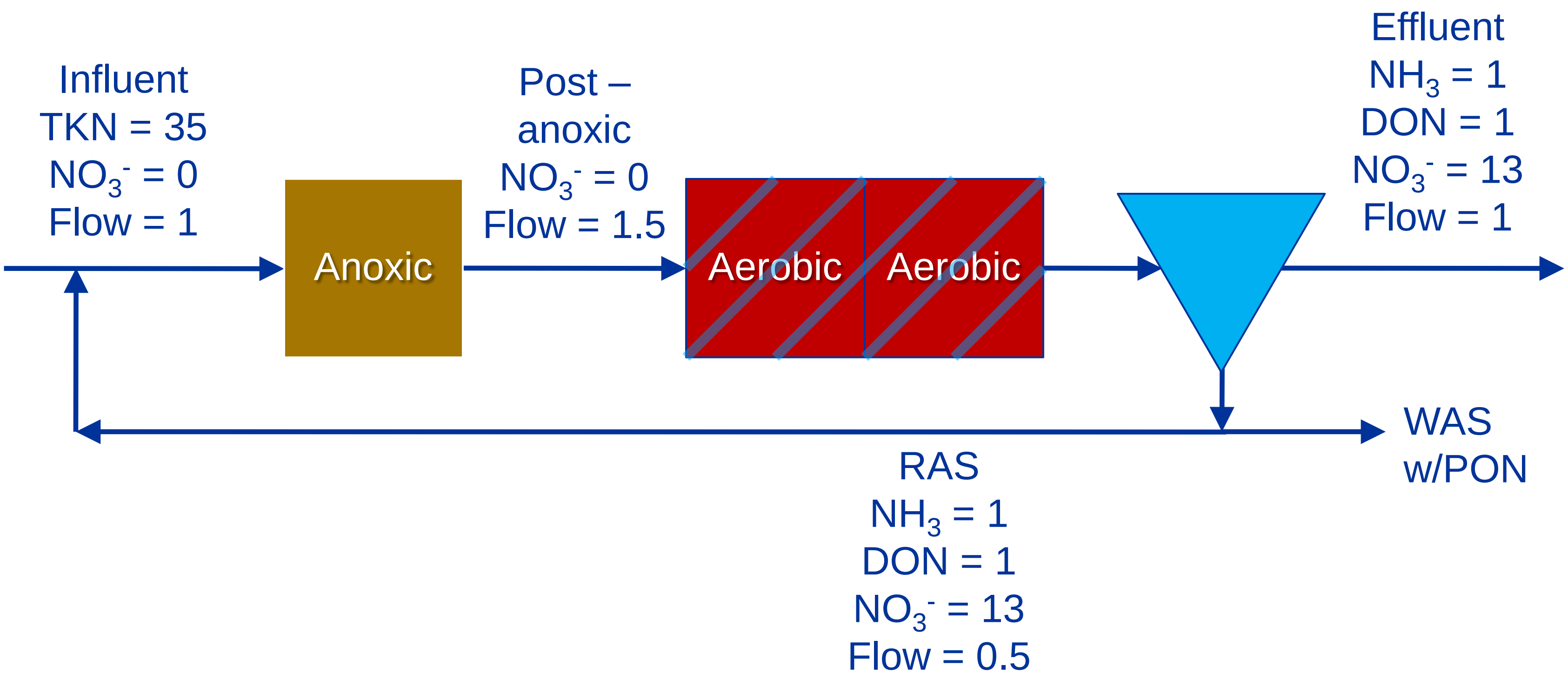


Process Considerations: Denitrification – Nitrate

- 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



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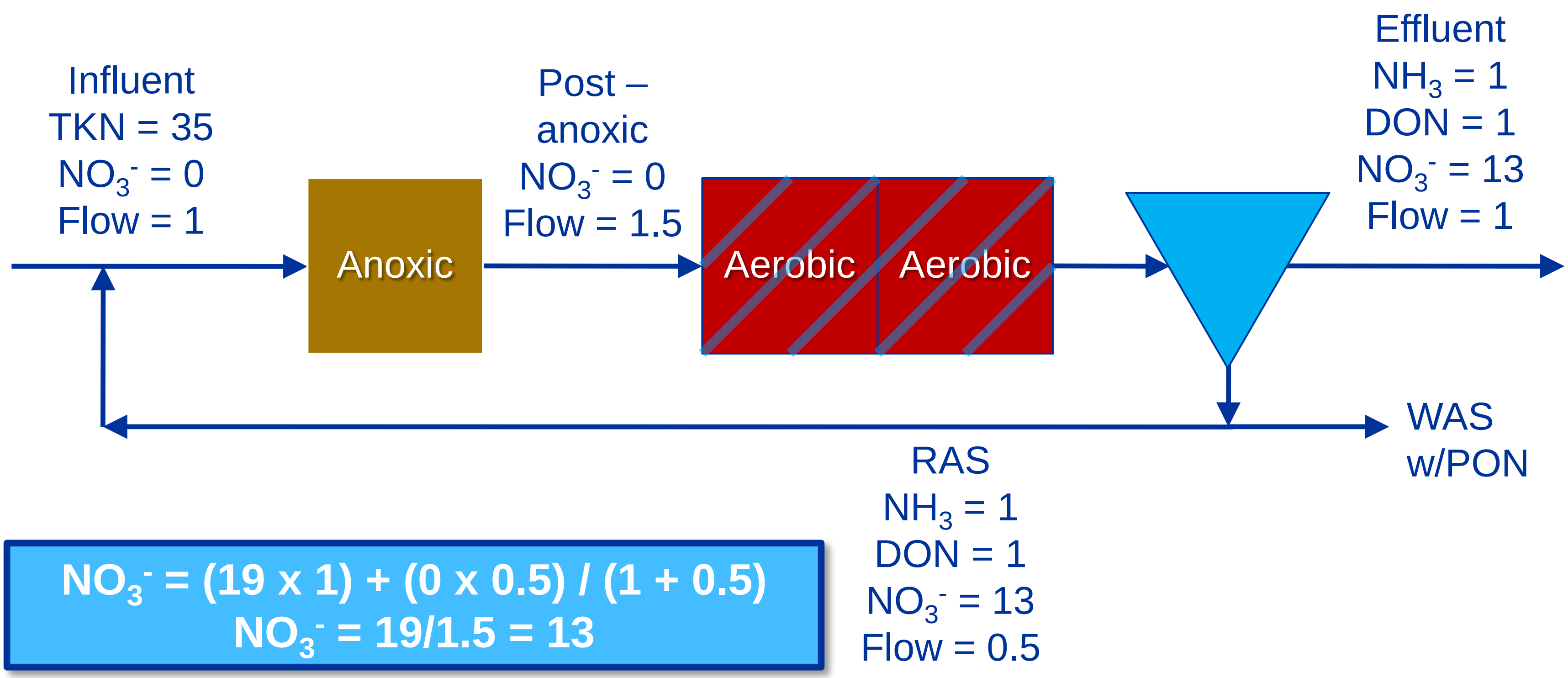


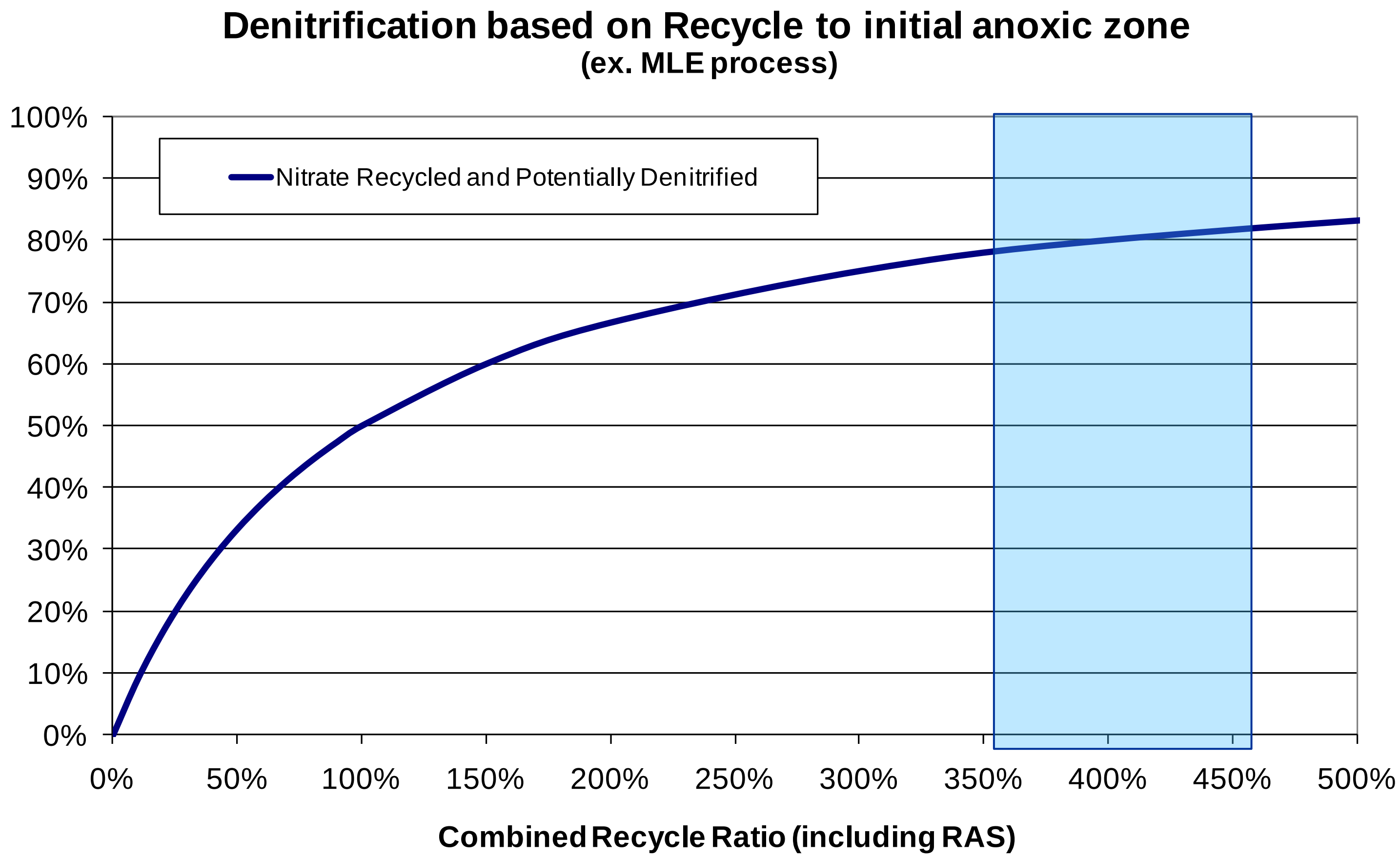
Process Considerations:
Denitrification – Recycle Efficacy

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%
1	**4**	**5**	**4/5 = 80%**
1	**5**	**6**	**5/6 = 83%**
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:

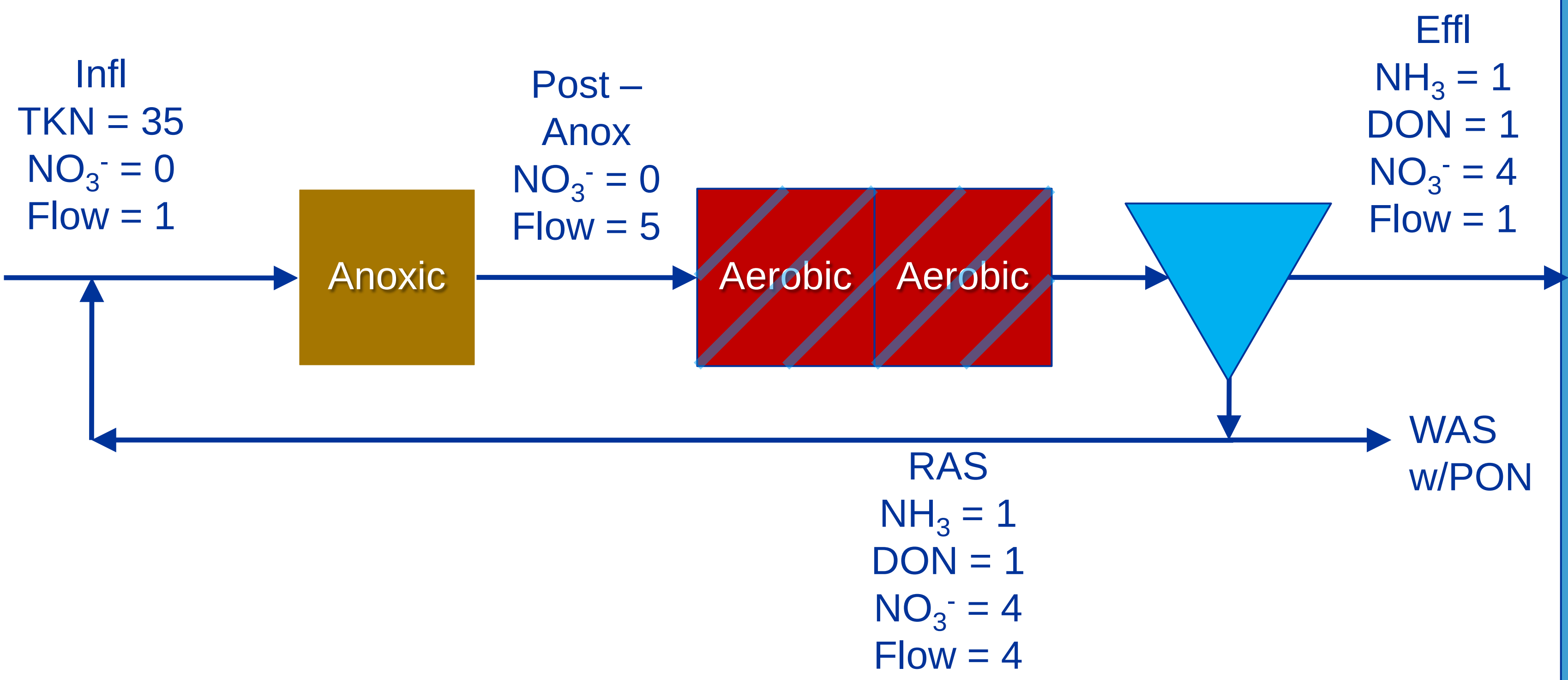
Denitrification – Recycle Efficacy



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



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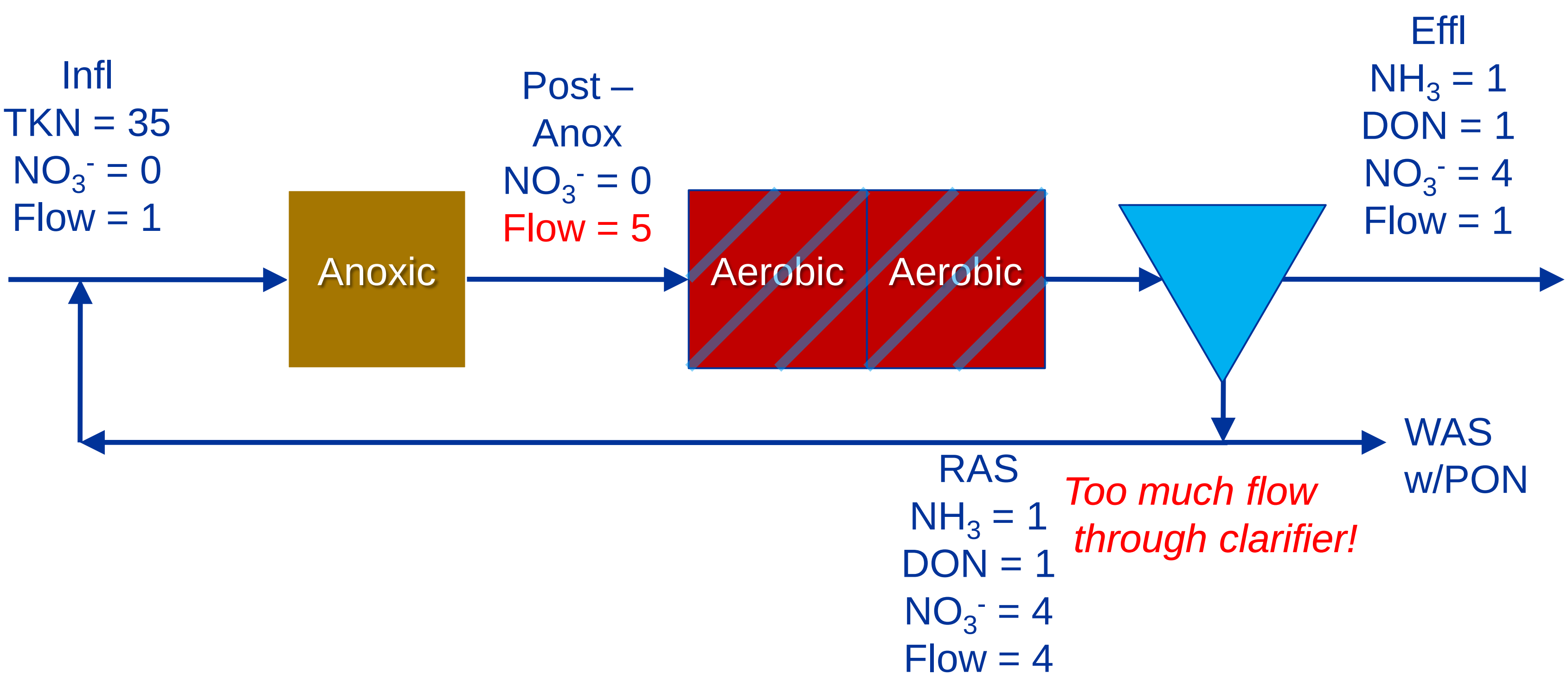

Process Considerations:

Denitrification - MLE

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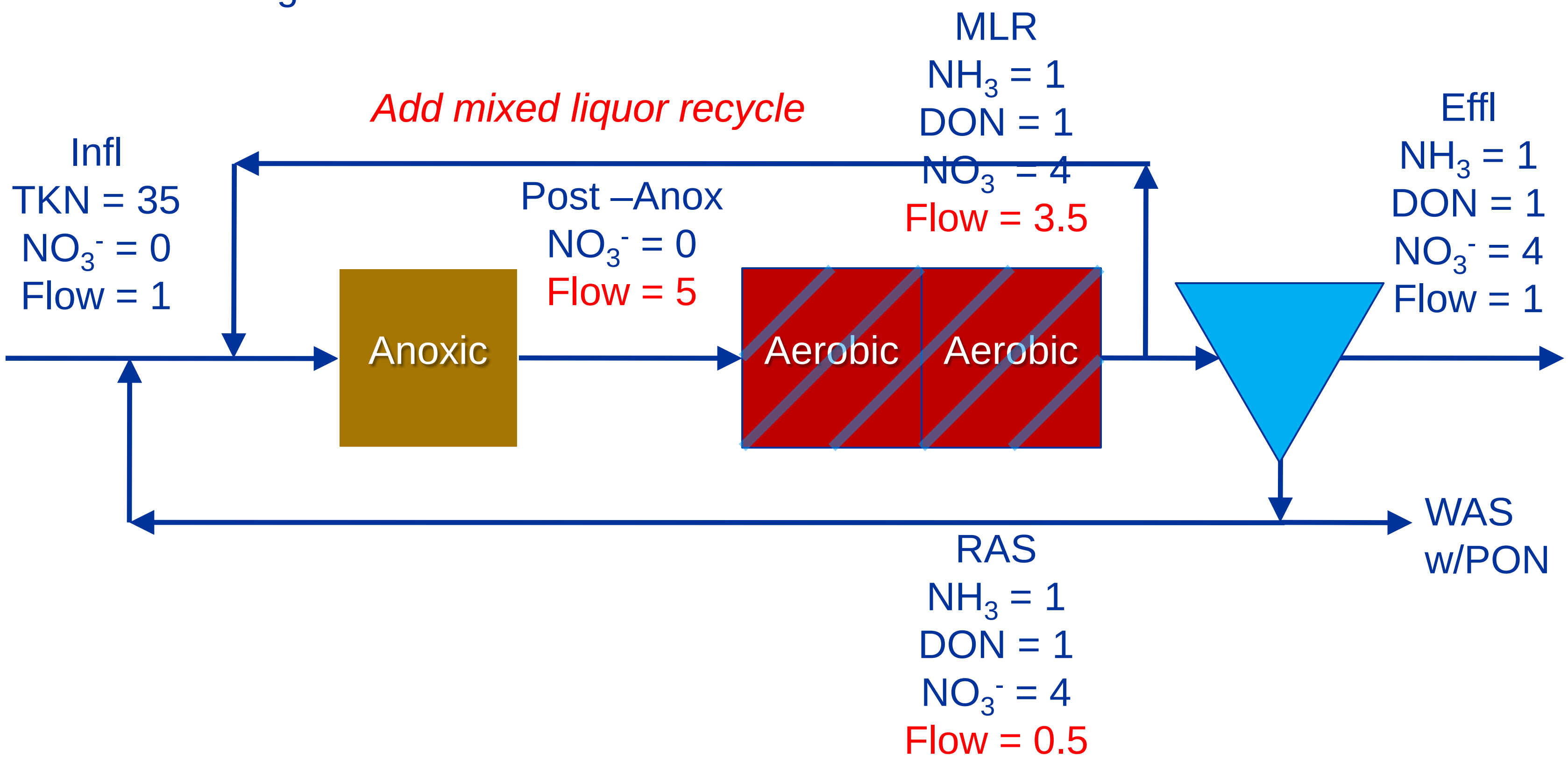

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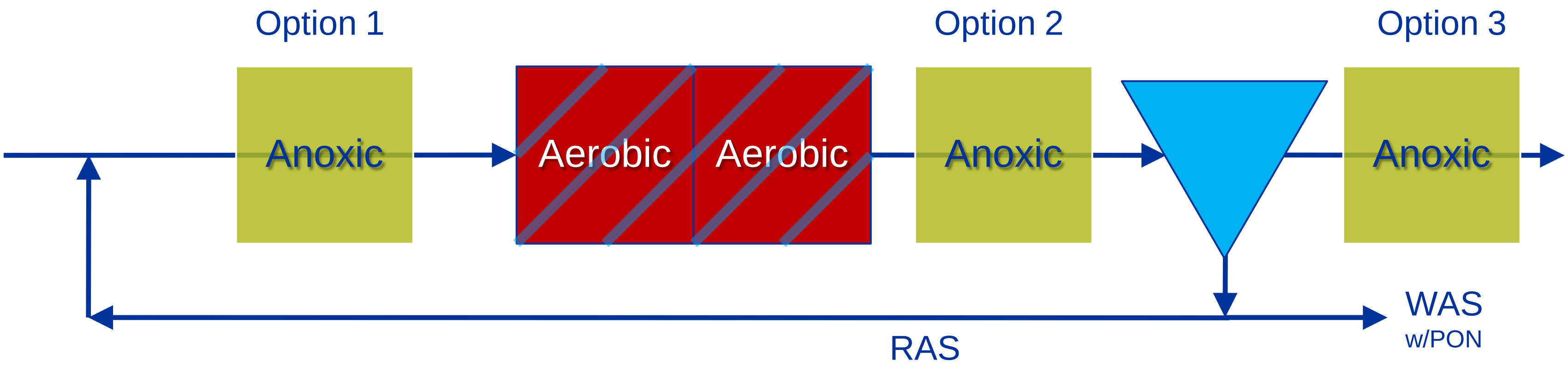
Process Considerations: Denitrification – Carbon

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 ≥ 1 mg/L

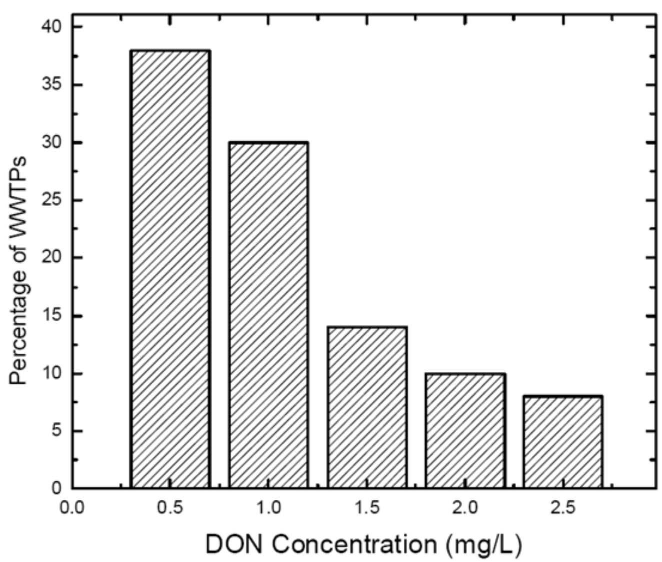


Figure 2. Summary of effluent dissolved organic nitrogen (DON) concentration (0.45 µm filtration) from 188 Maryland and Virginia wastewater treatment plants (Pagilla, 2007)

Process Considerations:
Range of N in ENR Effluents

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

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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 NOx
- Nitrification and denitrification processes must be very effective

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