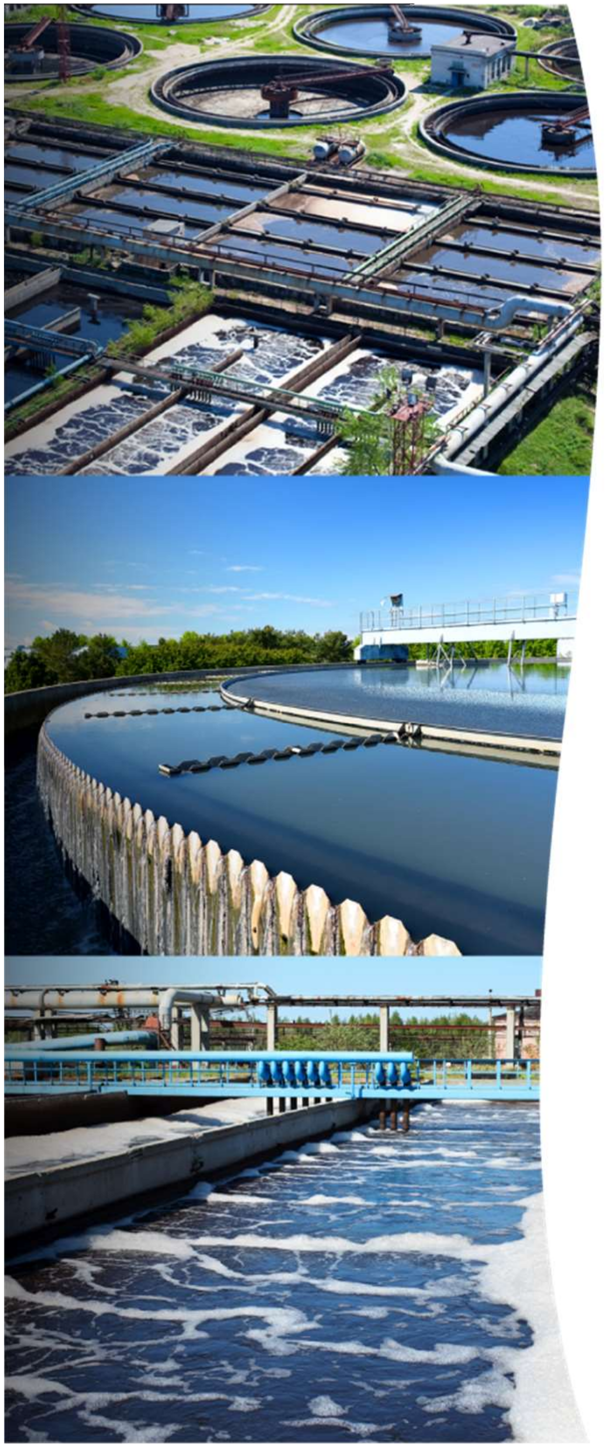


Probiotic® SOLUTIONS™

Nitrification-Denitrification
By Heather Jennings

http://mandynolan.com.au/blog/living-on-the-edge

Know Your Influent

- After debris removal, influent contains:
  - 99.9% Water
  - 0.1% Solids
    - 30% of solids are suspended
    - 70% of solids are dissolved
- Chemically, influent is a 50/50 mix of inorganics and organics
- For treatment, 100:5:1, BOD:N:P is required

Know Your Influent

- Influent fluctuates
  - Quantity Changes
    - Seasonal, I/I
    - Tourist Seasons (Rodeos, Football Games)
    - Schools/University Schedules
- Typical wastewater is 0.3 to 0.8 BOD/COD
  - BOD/COD > 0.5 easily treated by biological treatment
  - BOD/COD < 0.3 indicates toxic environment, low food, or needs biological augmentation

Nitrogen

- Nitrogen Gas (N_2)
- Nitrate (NO_3)
- Nitrite (NO_2)
- Ammonia (NH_3)
- Organic Nitrogen

TIN= Total Inorganic Nitrogen

TKN= Total Kjeldahl Nitrogen

- Total Nitrogen includes all sources of nitrogen but gaseous form

Nitrogen

- TKN of influent wastewater
  - 25%–40% organic nitrogen
  - 60%–75% ammonia/ammonium
  - Percentages are dependent on pH, temperature, and detention time in the collection system
- Small fraction of influent nitrogen is nitrate and nitrite

Nitrogen

- Ratio of TKN/BOD_5 for domestic wastewater is 0.1 to 0.2
  - Higher ratios may indicate
    - Recycle Streams
    - Septic, and/or
    - Industrial Waste
- Example
  - If BOD_5 is 250 mg/L, then TKN should be
    - (250) x (0.1) = 25 mg/L
    - (250) x (0.2) = 50 mg/L

Ammonia

- Why do we care about ammonia and nitrates?
  - Ammonia, nitrate, and nitrite can be toxic
  - Ammonia exerts an oxygen demand
  - Ammonia and nitrate stimulate the growth of algae and aquatic plants
  - Ammonia, nitrate, and nitrite can cause facility operational problems

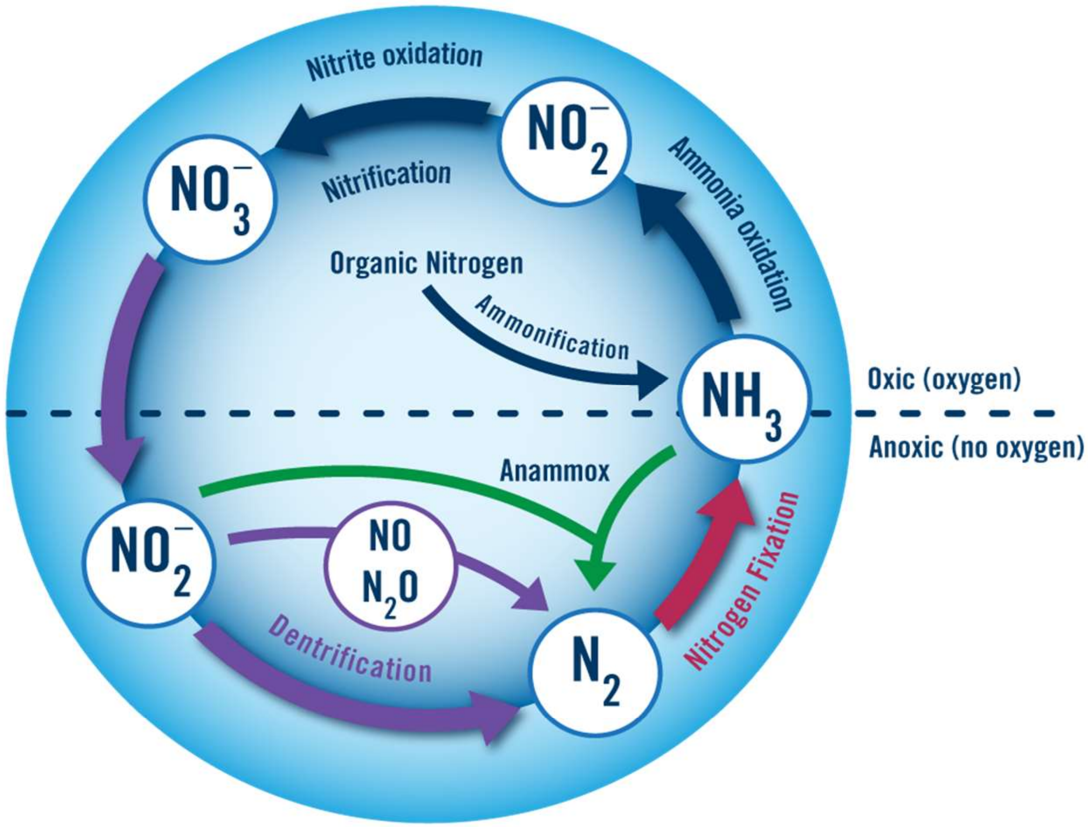
Nitrogen Removal

- Three biological treatment steps are required for nitrogen removal:
  - In a **bio-oxidation step**, organic nitrogen is anaerobically broken down to ammonia nitrogen;
  - In a subsequent **nitrification step**, ammonia nitrogen in the wastewater is aerobically converted to nitrate nitrogen; and
  - In a final **denitrification step**, nitrate nitrogen is anaerobically or anoxically converted to nitrogen gas.

Nitrogen Cycle

- Elements
  - **Fixation**: nitrogen (N_2) in the atmosphere is converted into ammonium (NH_4^+)
  - **Ammonification**: bacteria or fungi convert the organic nitrogen within the solids back into ammonium (NH_4^+)
  - **Nitrification**: oxidation of ammonium (NH_4^+) is performed by bacteria, into nitrates (NO_3^-)
  - **Denitrification**: reduction of nitrates back into the largely inert nitrogen gas (N_2)

Nitrogen Cycle *(Cont'd)*



Bacteria

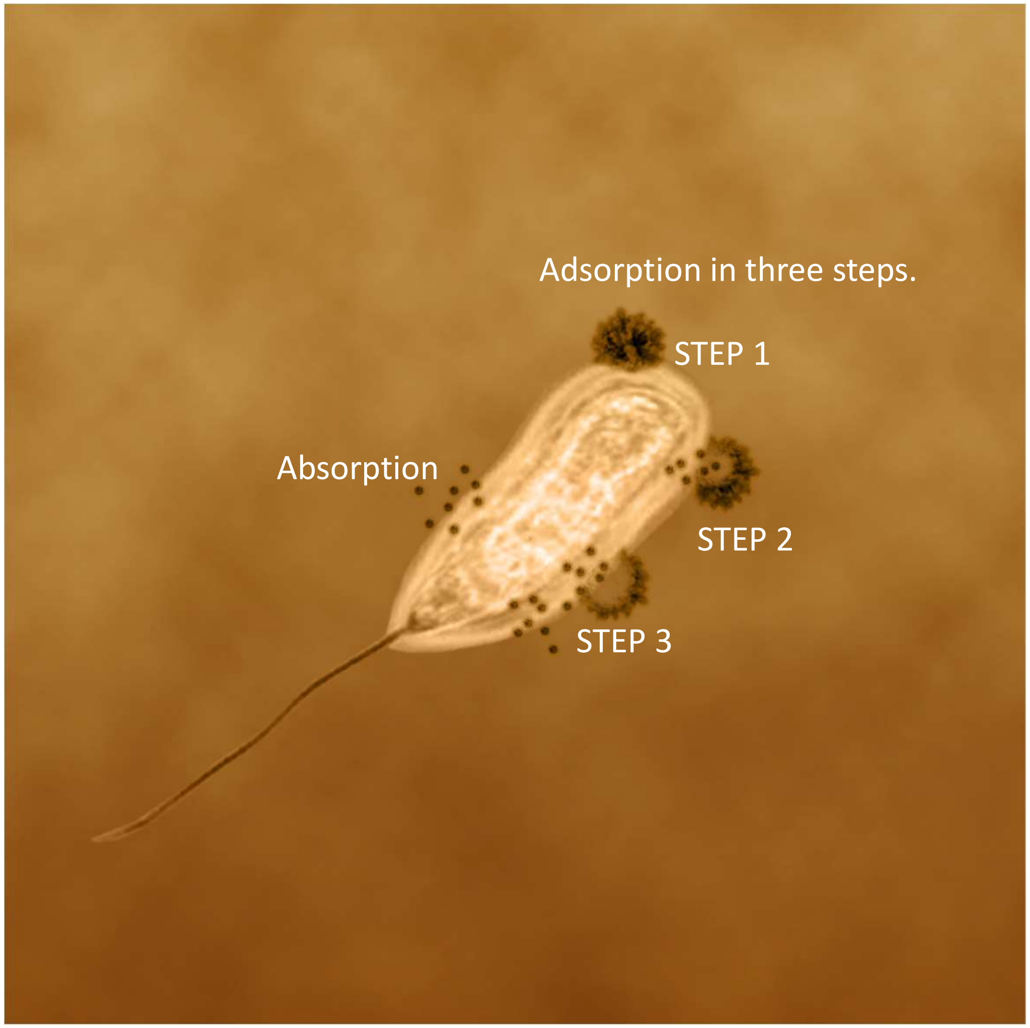
- Solid particles of “food” can be eaten by two methods.
  - Absorption
    - Small soluble units of food pass through the bacteria’s cell walls.
    - Solids are then broken down by endoenzymes in the cytoplasm for use

Bacteria *(Cont'd)*

– Adsorption

- Food particles and bacteria that are too big to pass through the cell membrane stick to the cell
- The bacteria then secrete exoenzymes, which dissolve food particles into very small units, making food available for **absorption**
- Solids are then broken down by endoenzymes in the cytoplasm for use

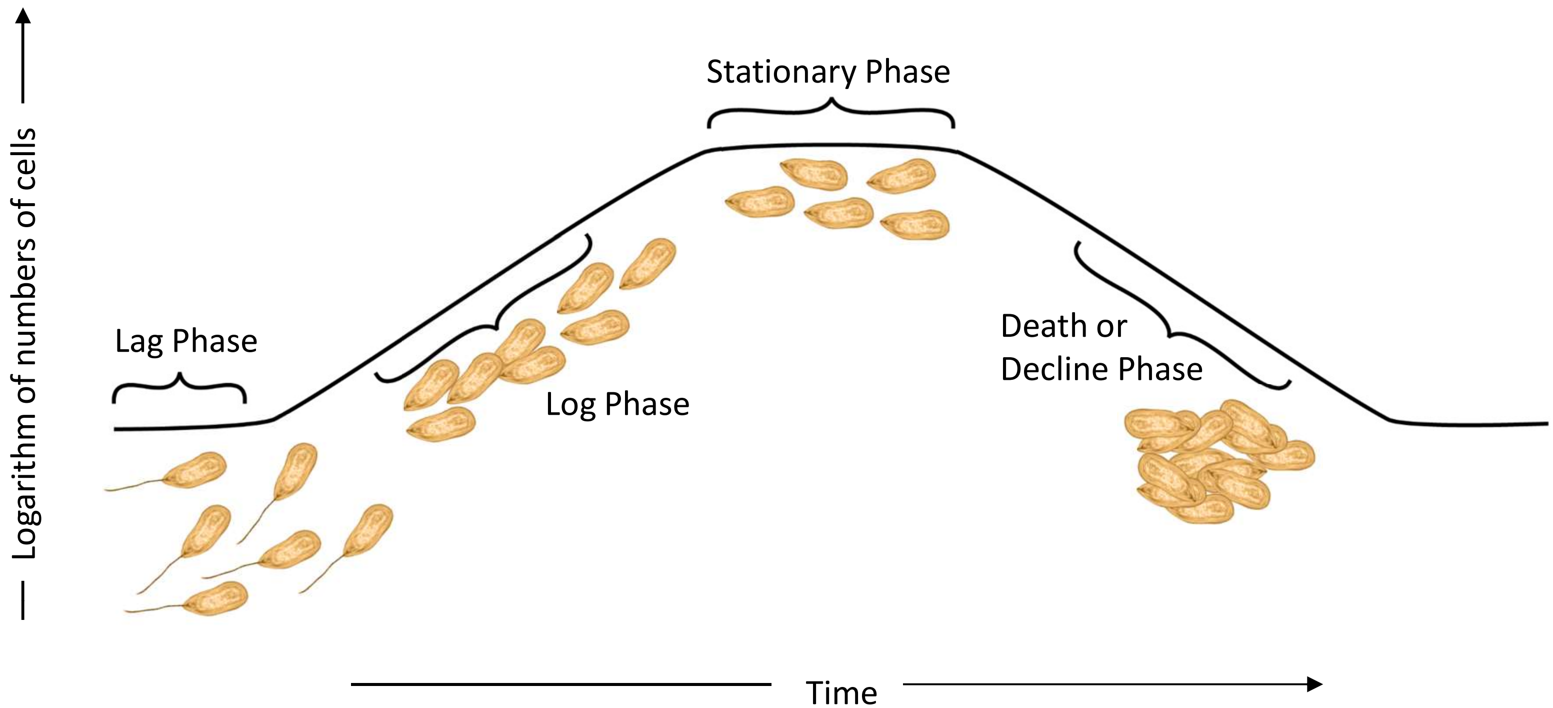
Bacteria: Adsorption & Absorption



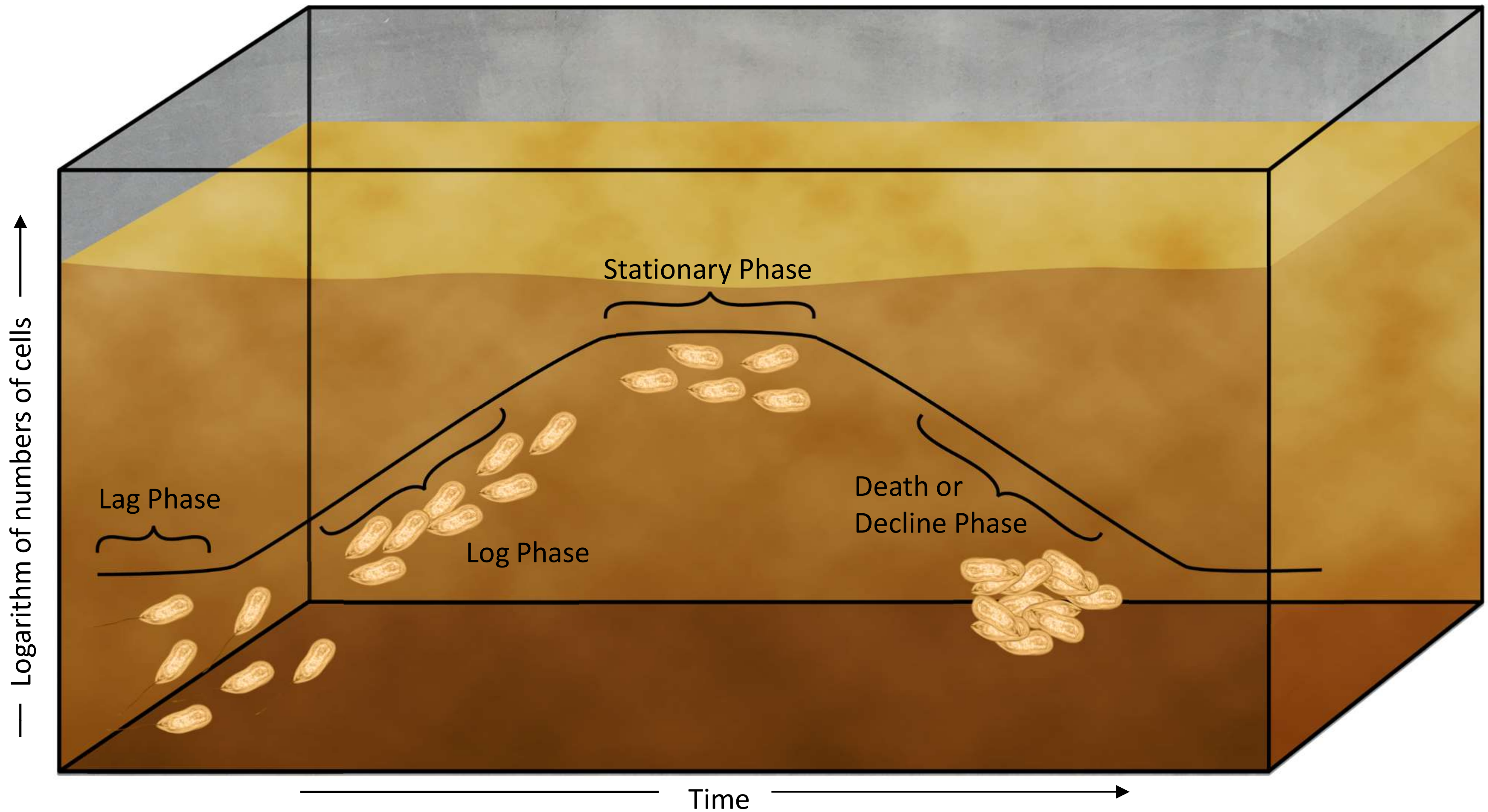
Bacteria *(Cont'd)*

"We are the **Borg**. Your biological and technological distinctiveness will be added to our own. Resistance is futile."
—TNG

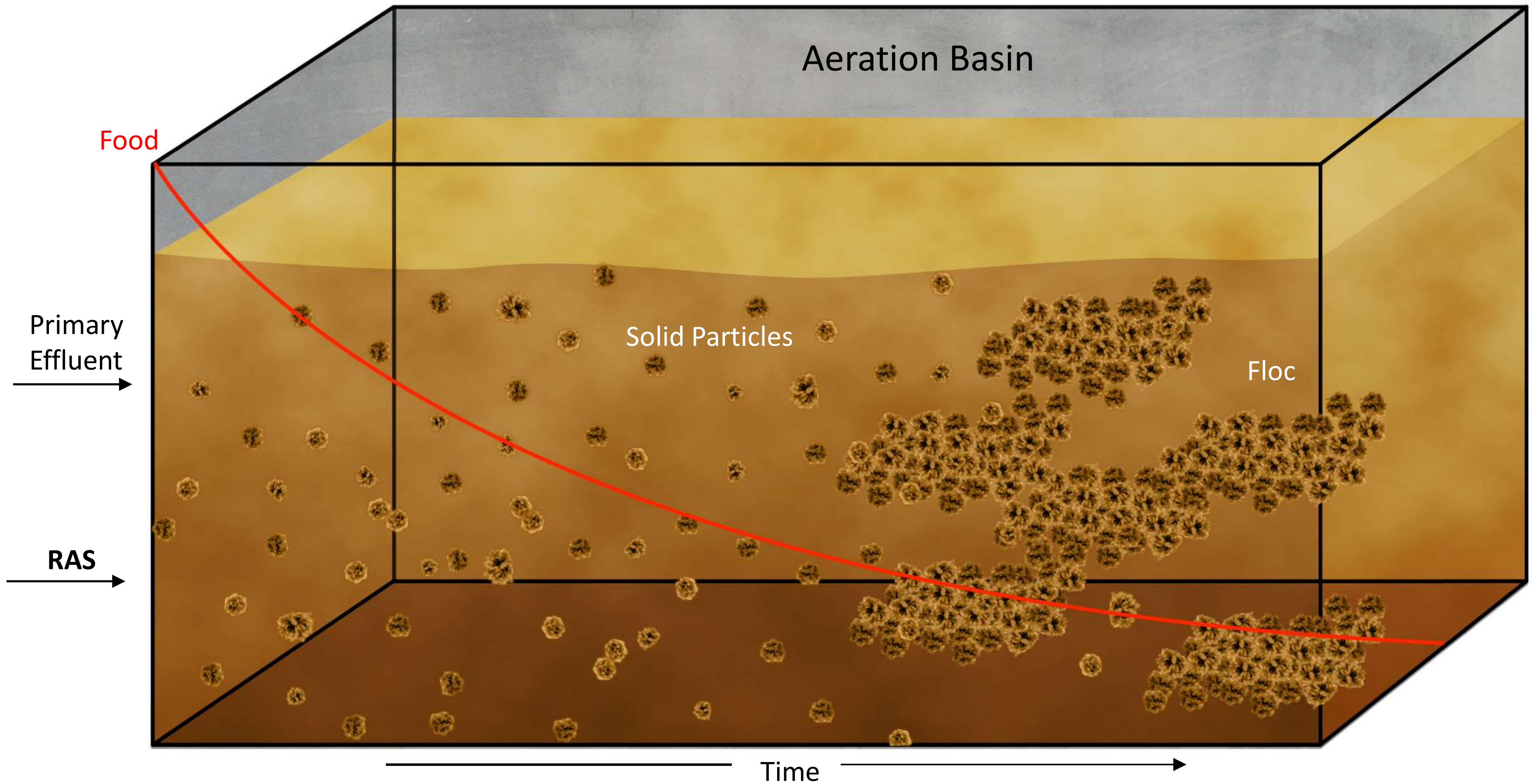
Bacteria *(Cont'd)*



Bacteria *(Cont'd)*



Bacteria (Cont'd)



Bacteria *(Cont'd)*

- Nitrifiers have a significant lag phase
  - Cell Residence Time (CRT) must be long enough
  - > 5 Days (minimum)
  - Best > 8 Days
- Denitrifiers
  - Nitrosomonas may double every 7 hours and Nitrobacter every 13 hours.
  - More realistically, they will double every 15–20 hours.

POP QUIZ

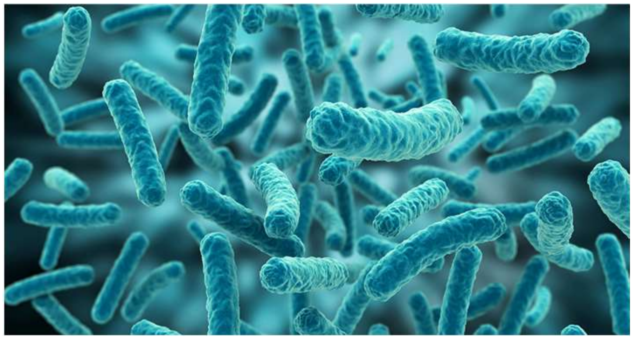
What Impacts Nitrification/Denitrification

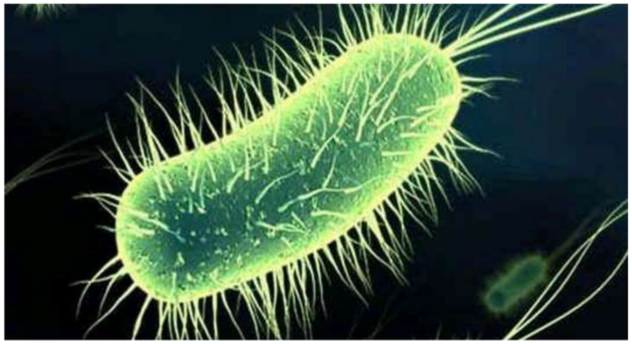
- Temperature
- NH_3-N concentration
- D.O.
- pH, influent and during the process
- Alkalinity, influent and during the process
- Sludge retention time
- Toxicity

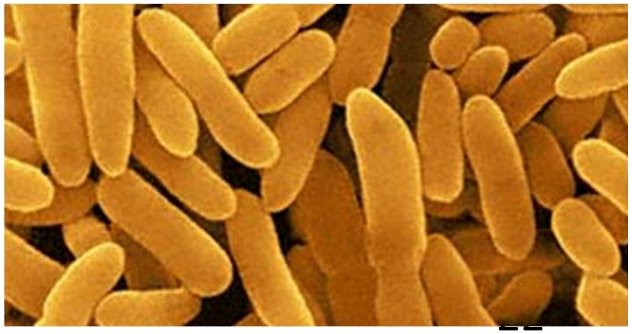
Nitrification

Nitrification is the first step to reducing Total N in a Wastewater Treatment Facility

- Reduce Ammonia to Nitrate, does not remove Nitrogen
- Requires high levels of Oxygen and BOD
- Oxygen serves as electron acceptor
- The process is accomplished by microorganisms known as nitrifiers . . . *Nitrosomonas, Nitrospira, Nitrospina gracilis, Nitrobacter*



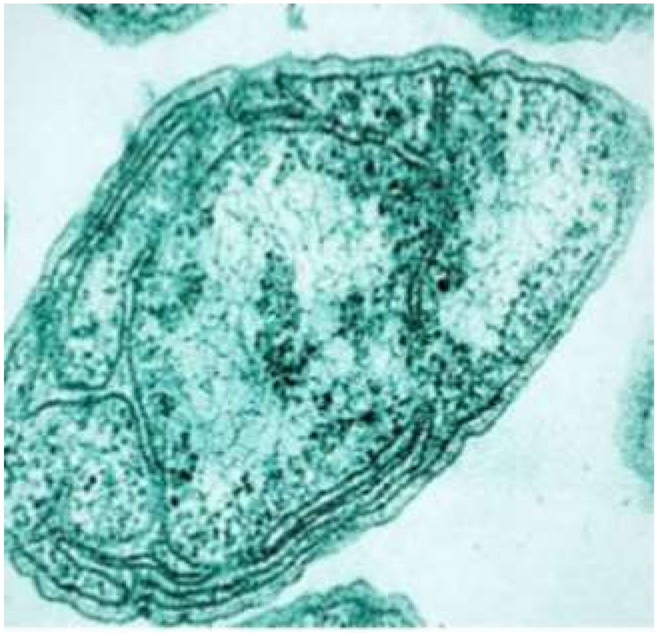




Nitrification (Cont'd)

- Chemically, what nitrification looks like
  - By *Nitrosomonas*
    - $NH_4^+ + 1.5O_2 \rightarrow NO_2^- + H_2O + 2H^+$
  - By *Nitrobacter*
    - $NH_4^+ + 2O_2 \rightarrow NO_3^- + 2H^+ + H_2O$
  - By Nitrifiers
    - $NO_2^- + 0.5O_2 \rightarrow NO_3^-$
- This is accomplished by bacteria!

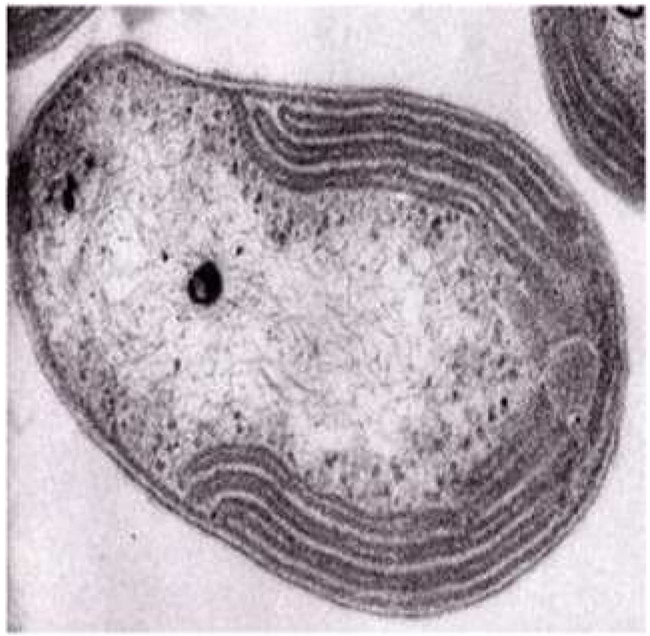
Nitrification *(Cont'd)*



Nitrosomonas

$$\text{Ammonia} + \text{Oxygen} \Rightarrow NO_2^- + \text{Acid} + \text{More } \textit{Nitrosomonas}$$

Nitrification *(Cont'd)*



$$\textit{Nitrobacter}$$

$$\text{Nitrite} + \text{More Oxygen} \Rightarrow NO_3^- + \text{More } \textit{Nitrobacter}$$

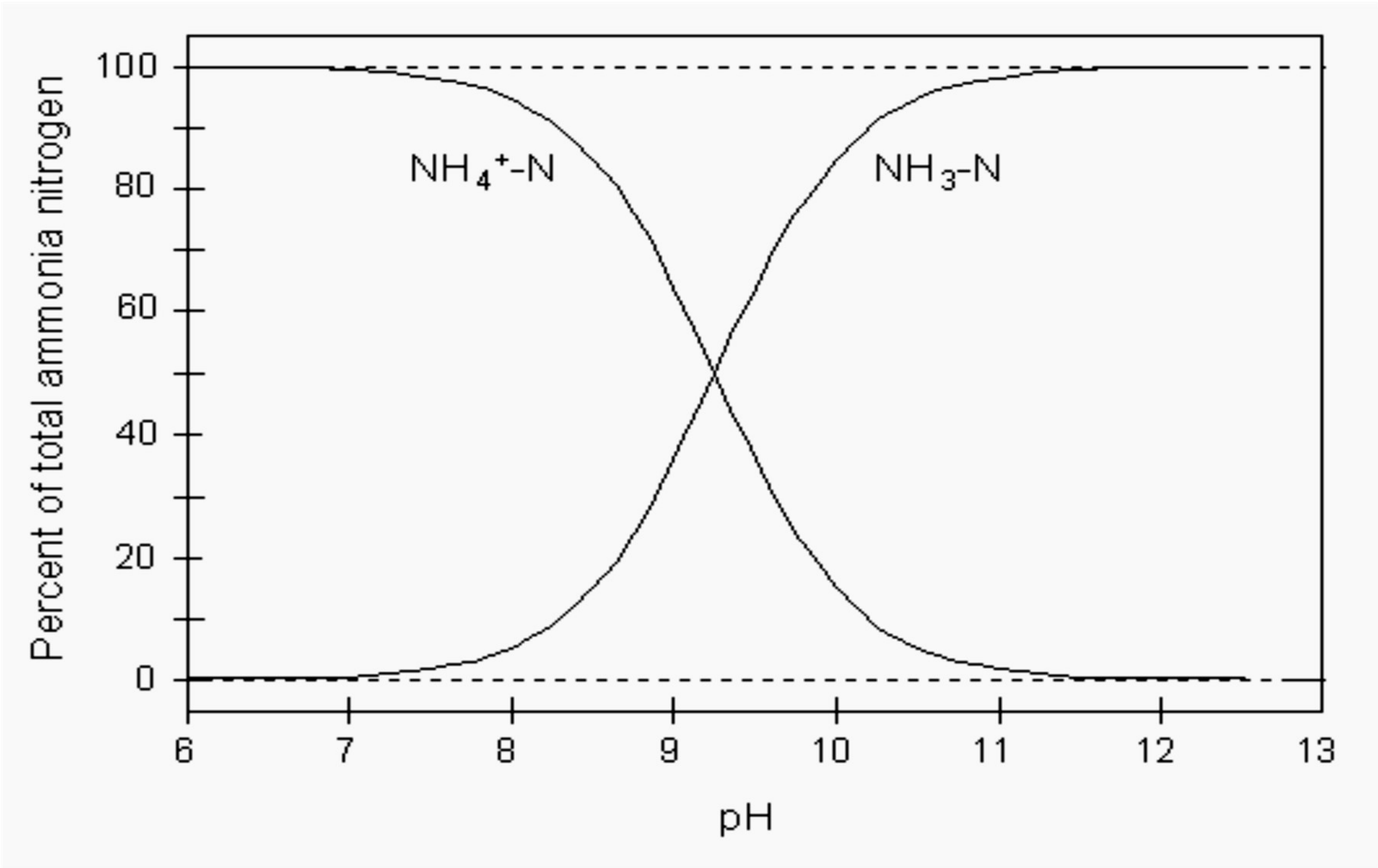
Nitrification (Cont'd)

- Temperature, 77°F (25°C) for optimal
  - Below 50°F (10°C)
  - Expect Maximum of 50% Nitrification
- Not all the ammonia will be removed
  - Last 0.5 mg/L is hardest to remove
- Dissolved Oxygen nitrification > 2.0 mg/L for optimal nitrification
  - Higher D.O.s are required at lower F/M and high SRTs
  - 4.6 lb O_2 required to oxidize 1 lb NH_3

Nitrification *(Cont'd)*

- Aerobic Mean Cell Residence Time (MCRT)
  - 4 to 15 days
- pH – 6.5 to 8 optimal
  - Nitrifiers need NH_3-N, not NH_4^+-N
  - As pH decreases, ionization increases and less NH_3-N is available.
  - At low pH, nitrifiers are starving.

Nitrification *(Cont'd)*



Nitrification *(Cont'd)*

- Alkalinity
  - Nitrification produces acid
  - 7.1 lb of alkalinity for every 1.0 lb of ammonia-N oxidized
- Influent alkalinity can be process limiting
  - test the clarifier effluent for alkalinity, ammonia, nitrite, and nitrate.
- Low influent alkalinity may require chemical addition
  - Sodium hydroxide, soda ash, lime

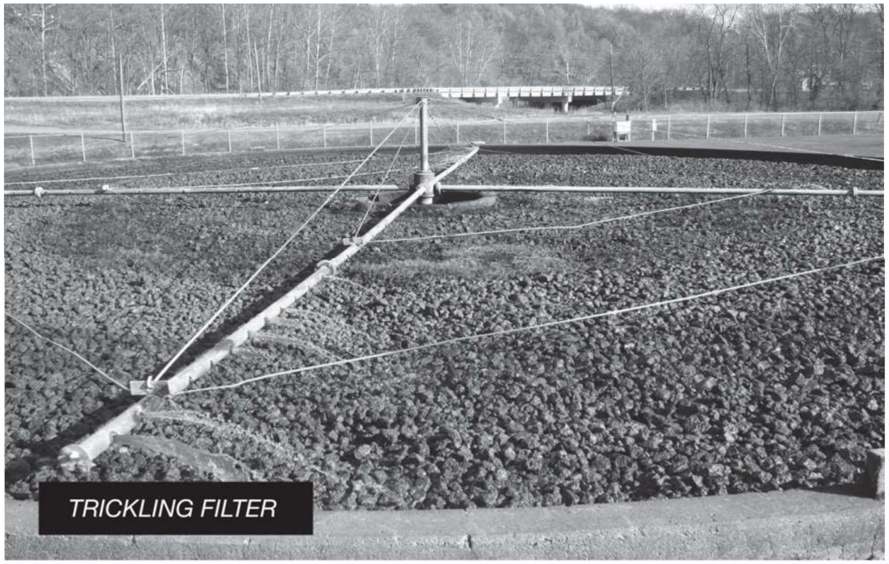
Nitrification (Cont'd)

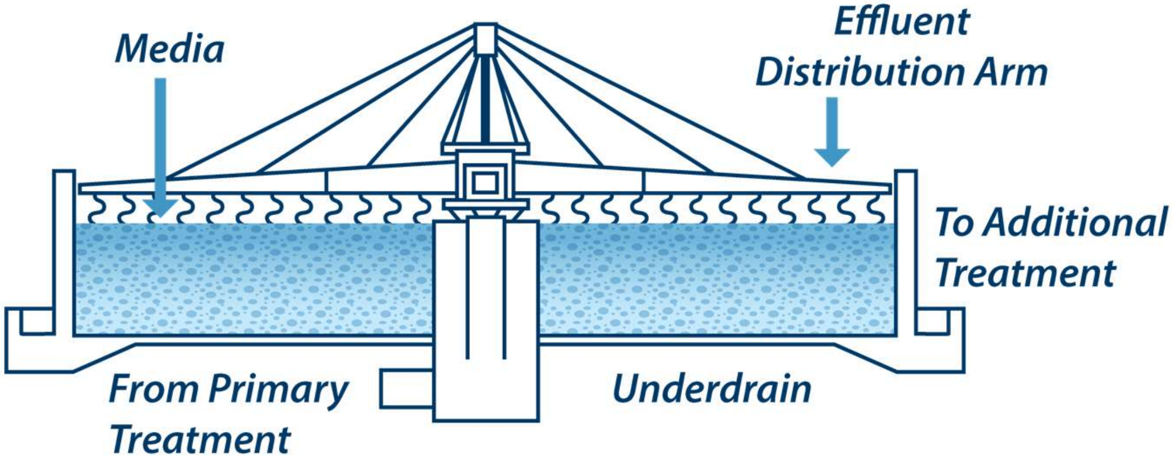
- Retention time
  - React time must be long enough (> 5 hrs.)
  - F:M Ratio must be low enough (< 0.25)
  - RAS returned slowly, in low quantities at low loading times
  - Dependent on D.O., pH, temperature, and target removal rate
- Toxicity
  - Heavy metals, organic chemicals
  - Overloading of ammonia, heavy FOG

Nitrification *(Cont'd)*

- In nitrification, BOD must be removed first!
  - Nitrifiers cannot outcompete heterotrophic bacteria that form when a large BOD source is available
  - Example: BOD removal and nitrification can occur in the same trickling filter.
    - BOD conversion occurring in the upper portion
    - Nitrification occurring in the lower portion of the filter media
    - Sacrifice efficiency

Nitrification *(Cont'd)*

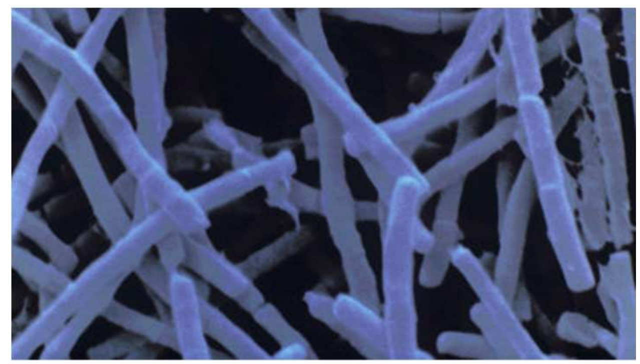




POP QUIZ

Denitrification

- Denitrification is accomplished by microorganisms known as denitrifiers . . . *Achromobacter, Aerobacter, Bacillus, Brevibacterium, Flavobacterium, Lactobacillus, Micrococcus, Proteus, Spirillum, Pseudomonas . . .*
- Heterotrophic, can use low DO or NOx
- Carbon source is BOD (3g BOD: 1g N), Volatile Fatty Acids (VFAs) simplest BOD carbon source



Denitrification *(Cont'd)*

- Chemically, what denitrification looks like with methanol

$$6NO_3^- + 5CH_3OH \rightarrow N_2 + 5CO_2 + 7H_2O + 6OH^-$$

- This is accomplished by bacteria!

Denitrification *(Cont'd)*

- The denitrification process consists of
  - Excluding dissolved oxygen,
  - Maintaining the proper detention time, and
  - Ensuring an adequate carbon source to drive the organisms to denitrify.
    - Highest rates are achieved with addition of an easily assimilated carbon source, such as methanol.
    - Lower denitrification rate is achieved with raw wastewater or primary effluent as the carbon source.
    - Lowest denitrification rate is observed with endogenous decay as the source of carbon.

Denitrification *(Cont'd)*

- Temperature
  - Process Temperature, Optimum 86°-95°F (30°–35°C)
  - Temperature changes of -Δ 10°C reduces to 75% of maximum
- Denitrification requires about BOD:NO_3 to be 3:1
  - Carbon is the electron donor and nitrated N is an electron acceptor
  - Denitrification requires good mixing

Denitrification (Cont'd)

- D.O.
  - D.O. (> 0.1 mg/L) is allowed to exist in the anoxic zone, denitrification will be reduced
  - D.O. (> 0.5 mg/L) can create a toxic environment for the denitrifiers
  - Accurately calibrated D.O. meter is a basic and essential process control check.

Denitrification *(Cont'd)*

- Anoxic retention time
  - Time in the anoxic zone should be around 1–2 hours
  - Less than 1 hour not enough time for the complete utilization of any residual D.O. and for complete denitrification.
  - Excessive detention will overstress or even kill the strict aerobes (nitrifiers) in the system and the entire nitrogen removal process will stop.
  - Mixed liquor recycling is used to maintain the desired detention times.

Denitrification *(Cont'd)*

- Anoxic zones located at the beginning of an aeration basin
  - Stress caused by the anoxic conditions facultative organisms take up BOD
  - This depletes BOD that is the main food source for many filamentous-type bacteria
  - This actually naturally selects against many filamentous bacteria, and anoxic zone used like this are typically called bioselectors or anoxic selectors
  - This does not select against microthrix parvicella and a few other filamentous bacteria, may still have issues.

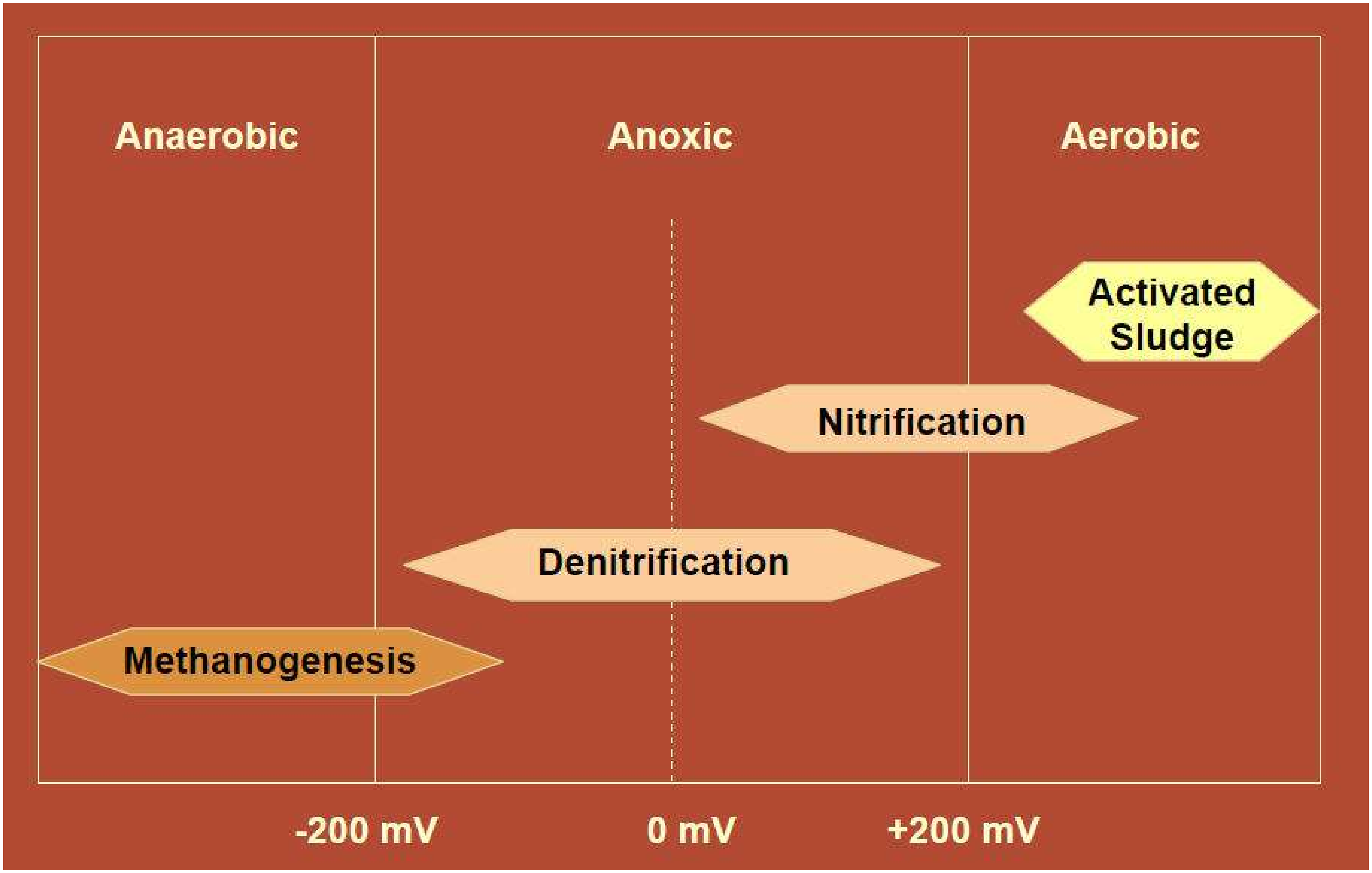
Denitrification *(Cont'd)*

- Half of alkalinity consumed during Nitrification can be recovered during Denitrification
  - Alkalinity is produced at ratio of 3.57 alk:1 nitrate-N reduced
- Alkalinity deficiency in influent
  - Test the clarifier effluent for alkalinity, ammonia, nitrite and nitrate.
    - Verify alkalinity is very low (< 40 mg/L as $CaCO_3$), the ammonia/ammonium levels have increased, nitrite is present, and nitrate nitrogen has decreased.
  - Just 1 to 2 mg/L of nitrite is all it takes to lose 5 to 10 mg/L of chlorine residual.

Denitrification *(Cont'd)*

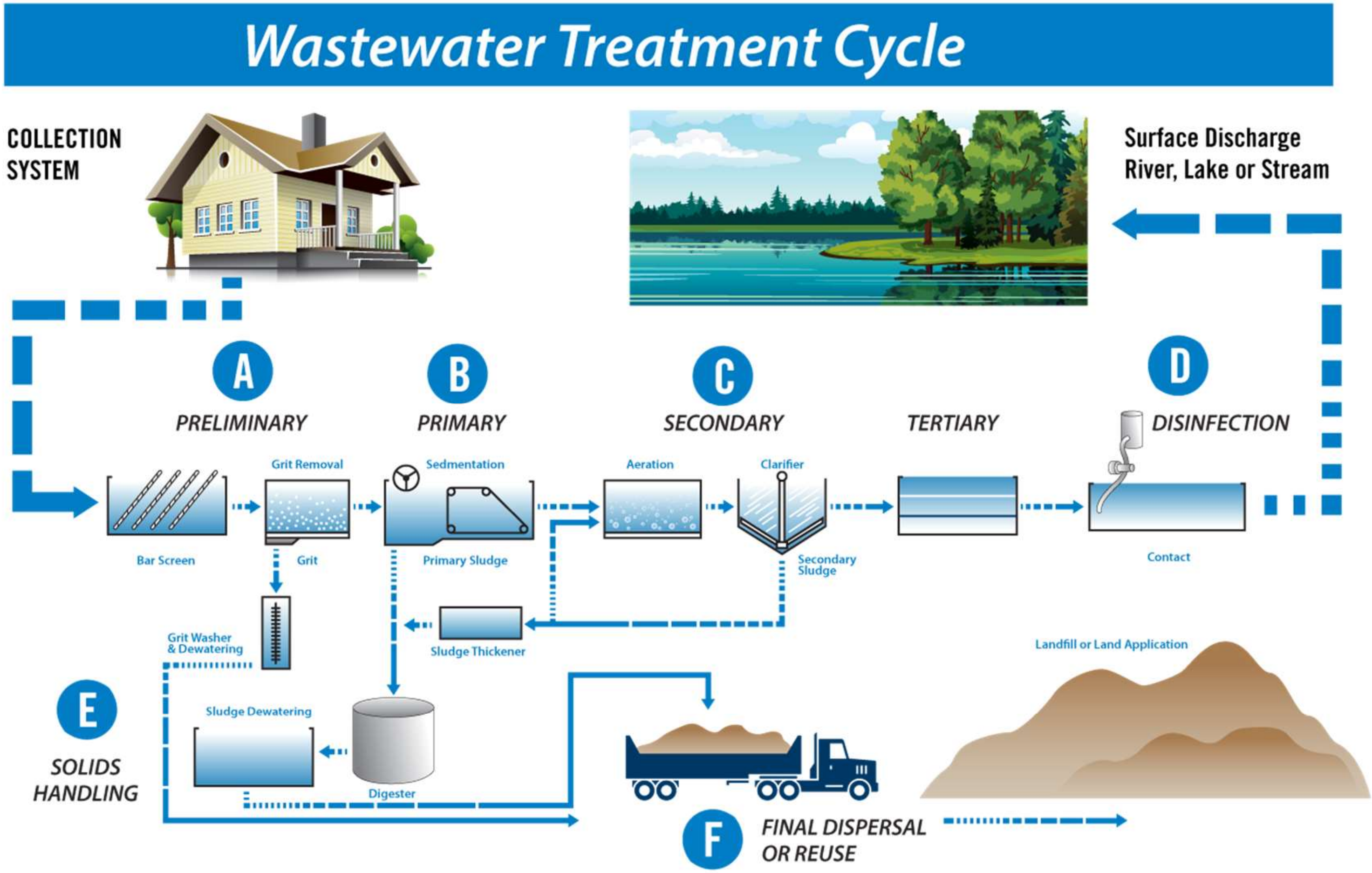
- ORP
  - The electrical potential (mv) required to transfer electrons from one compound to another.
    - Capacity of a solution to either release or accept electrons from chemical reactions
    - **OILRIG** -**O**xidation **I**s **L**oss, **R**eduction **I**s **G**ain *(of electrons)*
  - Used as a qualitative measure of the state of oxidation.
    - It does not tell you how fast or even if it will happen

Denitrification (Cont'd)

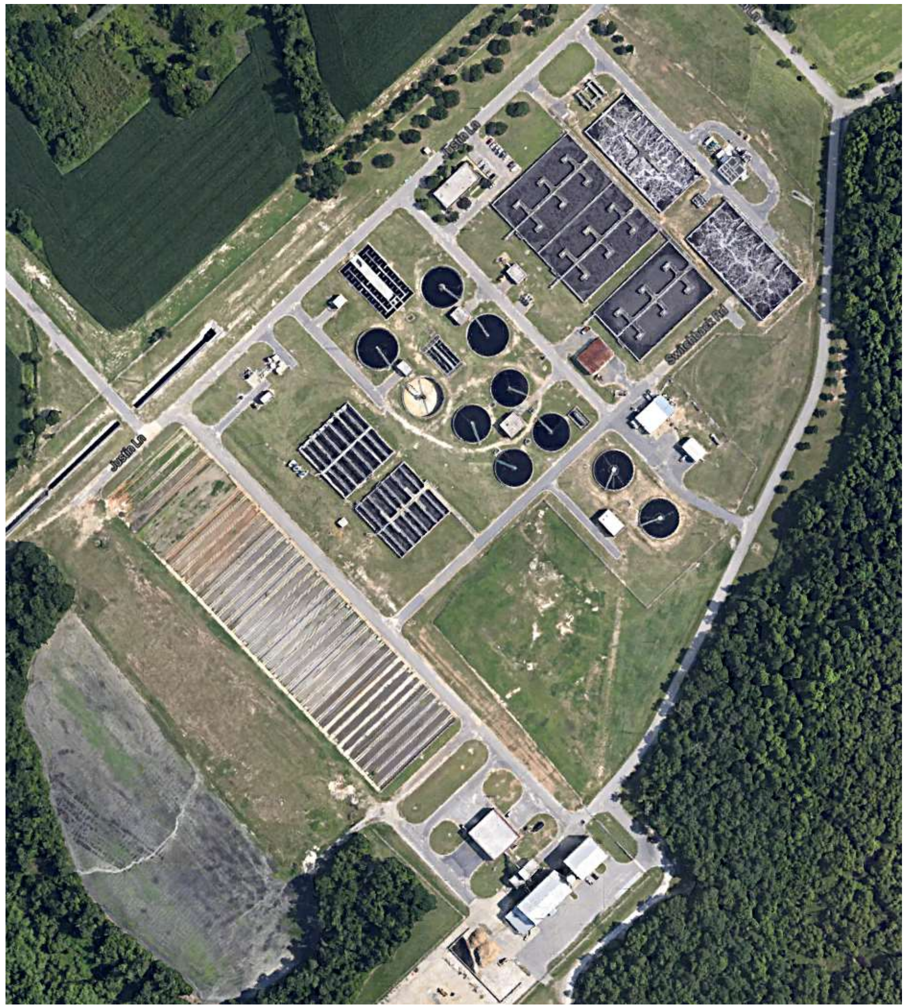


POP QUIZ

Suspended Treatment

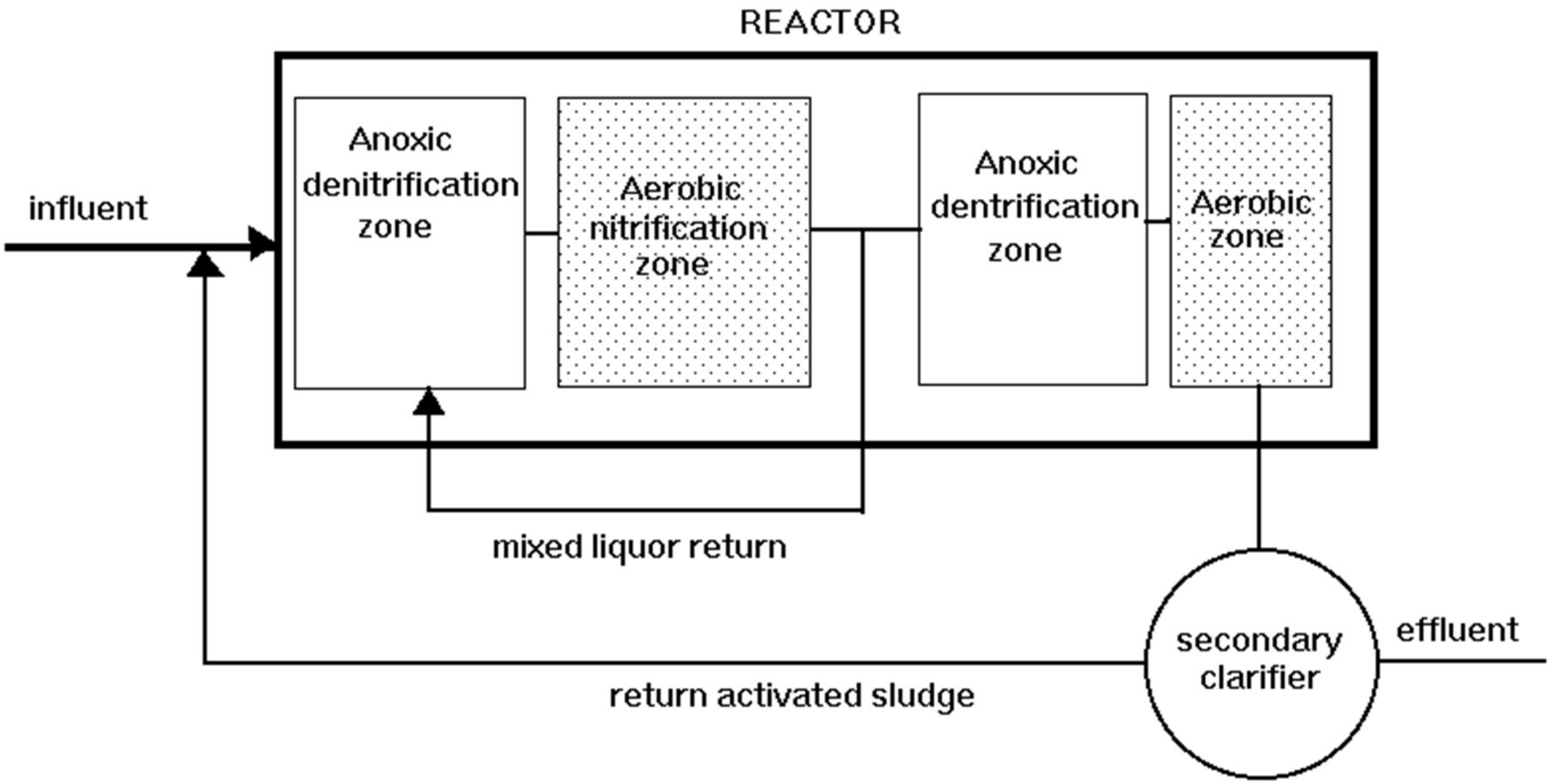


Suspended Treatment *(Cont'd)*



Suspended Treatment (Cont'd)

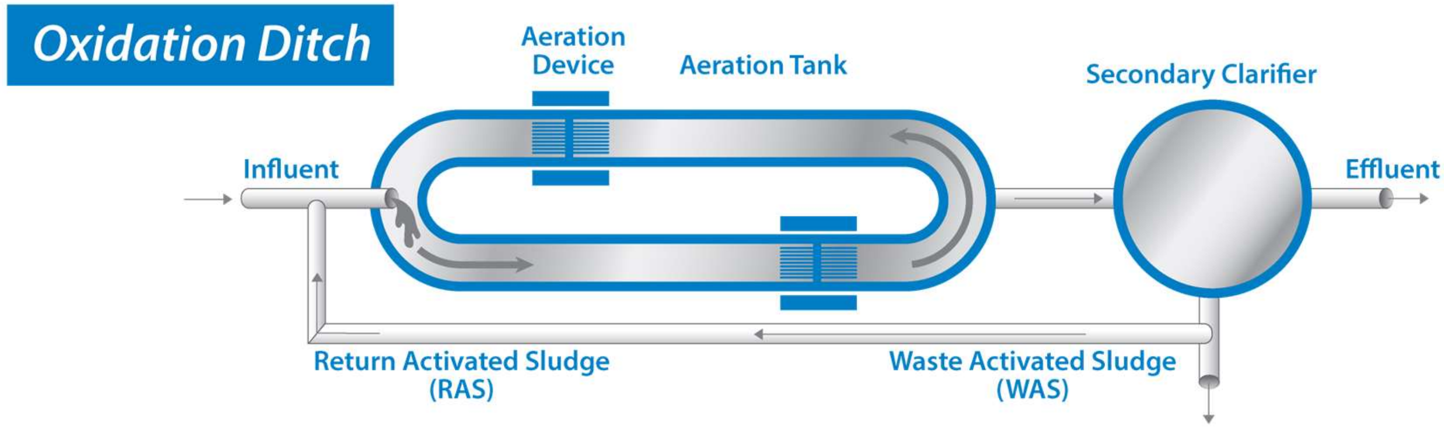
Bardenpho – 4 Stage



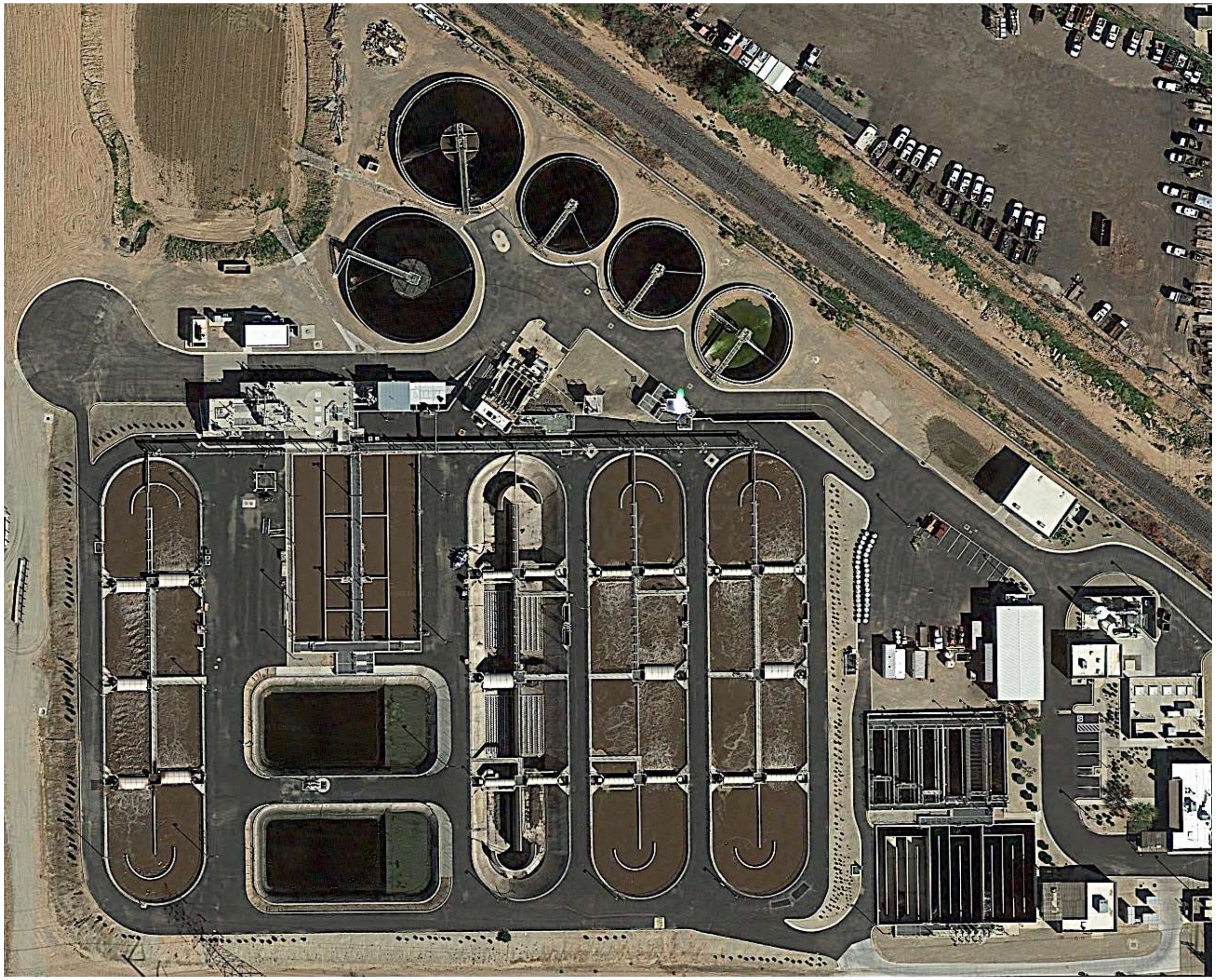
Suspended Treatment (Cont'd)

Suspended Technologies *(Cont'd)*

- The oxidation ditch is a variation of the activated sludge process.
  - Ring or oval-shaped channel equipped with mechanical aeration devices, such as brush rotors or disc aerators.

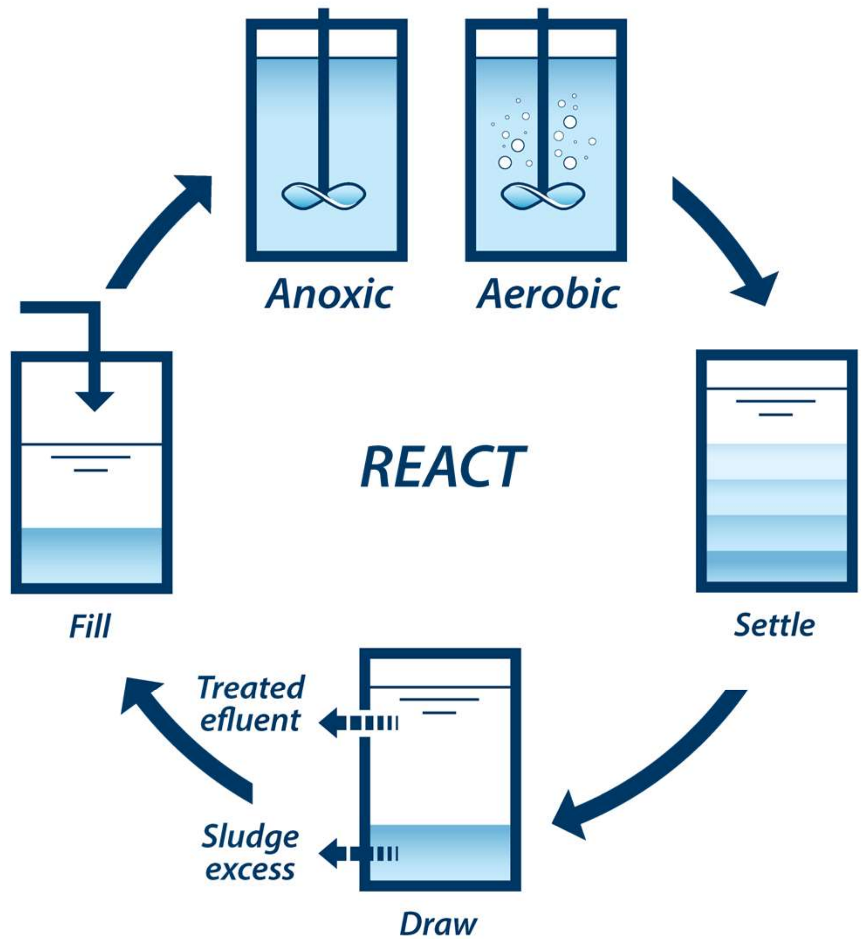


Suspended Technologies (Cont'd)



Suspended Technologies *(Cont'd)*

- A sequencing batch reactor (SBR) uses one tank for the entire treatment process



Suspended Technologies *(Cont'd)*

Comparison of Denitrification Alternatives

System Type	Advantages	Disadvantages
Combined carbon oxidation nite/denite suspended growth with endogenous carbon source	No methanol required, lesser number of units required, better control of filamentous bacteria, adaptable to P removal	Denite occurs at **very** slow rate, longer detention time and larger structures without methanol
Combined carbon oxidation nite/denite suspended growth with wastewater carbon source	No methanol required, lesser number of units required, better control of filamentous bacteria, adaptable to P removal	Denite occurs at slow rate, longer detention time and larger structures without methanol
Suspended-growth using methanol following a nite stage	Denite is rapid with high N removal, small structures required, easily optimized	Methanol required, greater number of unit processes than combined systems
Attached growth using methanol following a nite stage	Denite is rapid and high N removal, stability not linked to clarifier but on media, easily optimized	Methanol required, greater number of unit processes than combined systems

Breakpoint Chlorination

- Breakpoint Chlorination is the process in which ammonia/ammonium can be oxidized to nitrogen gas with chlorine.
- Chlorine also oxidizes all other pollutants as well.
- Breakpoint is when with chlorine addition everything is oxidized and there is a free residual of chlorine.

$$NH_4^+ + HOCl \leftrightarrow NH_2Cl + H_2O + H^+$$

$$2NH_2Cl + HOCl \leftrightarrow N_2 + 3HCl + H_2O$$

Breakpoint Chlorination (Cont'd)

- Remember, it takes 10 pounds of chlorine to oxidize 1 pound of ammonia into nitrogen gas!
  - Impractical for any use other than for polishing an effluent following another nitrogen removal process
  - Amount of Cl_2 Consumed, 5 mg Cl / mg NO_2
- Free chlorine residuals like chlorine and hypoclorous acid and hypochlorite ions, create trihalomethanes (THM).
  - Most of which are carcinogenic or mutagenic

POP QUIZ

New Perspectives

- Simultaneous Nite/Denite
- Looking at VFA’s impact on Nite/Denite
- Nutrients

Simultaneous Nitrification/Denitrification

Operations:

- Maintain mixing and regulate by Oxidation-Reduction Potential (ORP)
- As Nitrate is depleted ORP drops, ORP drops slowly at first then substantially the more nitrates are reduced
- Nitrate reduction occurs: ORP range of +50 to -50 mV
- ORP below -50 mV indicates that nitrate is depleted and that anaerobic conditions exist.
- May be time consuming for manual operation

Simultaneous Nitrification/Denitrification *(Cont'd)*

Considerations:

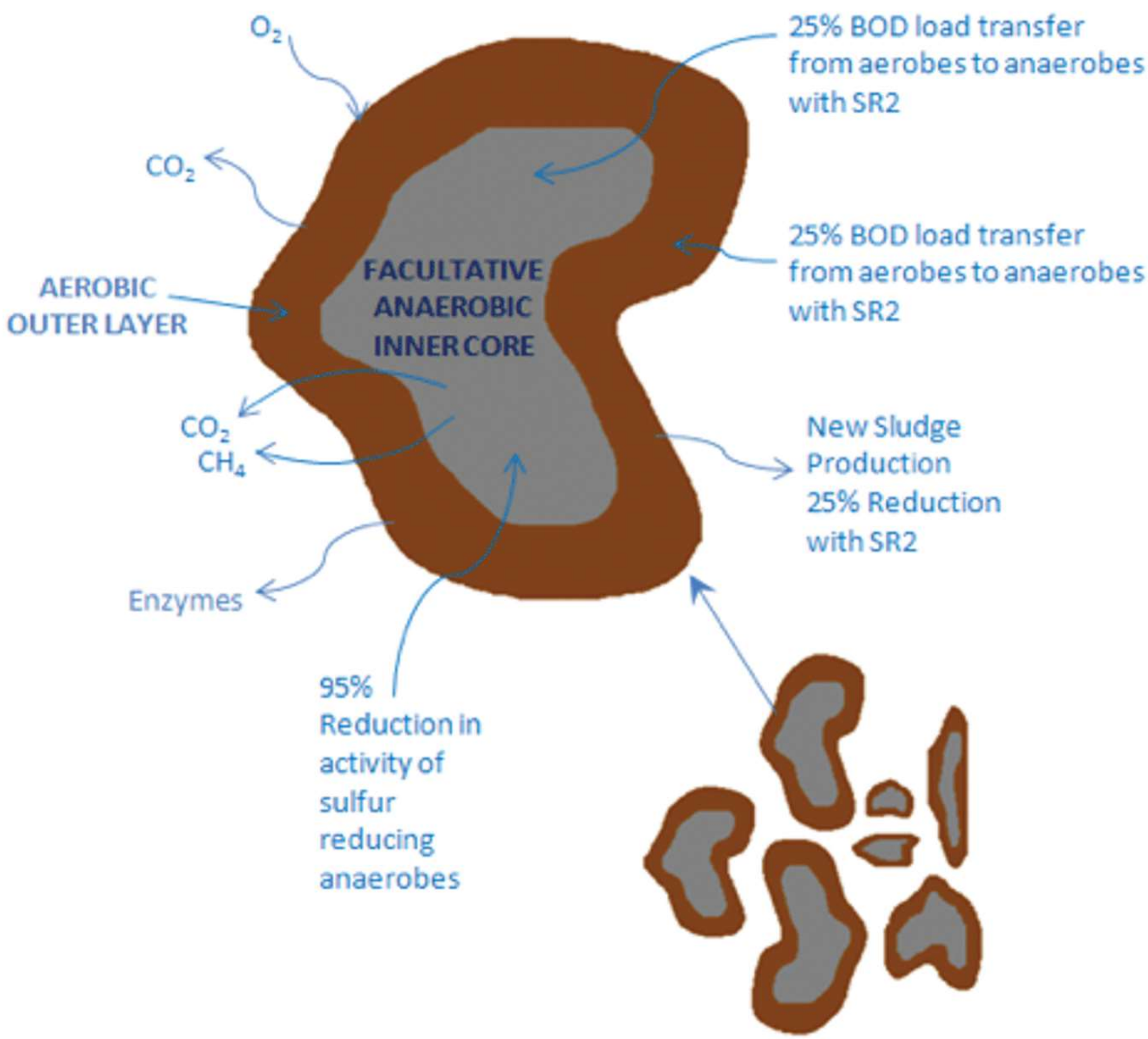
- High DO concentration required for complete Nitrification.
- Nitrification is dependent on the Oxygen Uptake Rate (OUR) of mixed liquor
- Quasi-anoxic zones develop as distance from DO injection increases
  - In these low DO locations, the heterotrophic bacteria begin the nitrogen removal process.

Simultaneous Nitrification/Denitrification *(Cont'd)*

Considerations:

- Ditch Configuration: MLSS enters anoxic zone first
  - This can consume raw organics up front and denitrification rate will be higher than if the only carbon source occurs by endogenous respiration.
  - Denitrification rate occurring by endogenous respiration is a much slower process.

Simultaneous Nitrification/Denitrification *(Cont'd)*

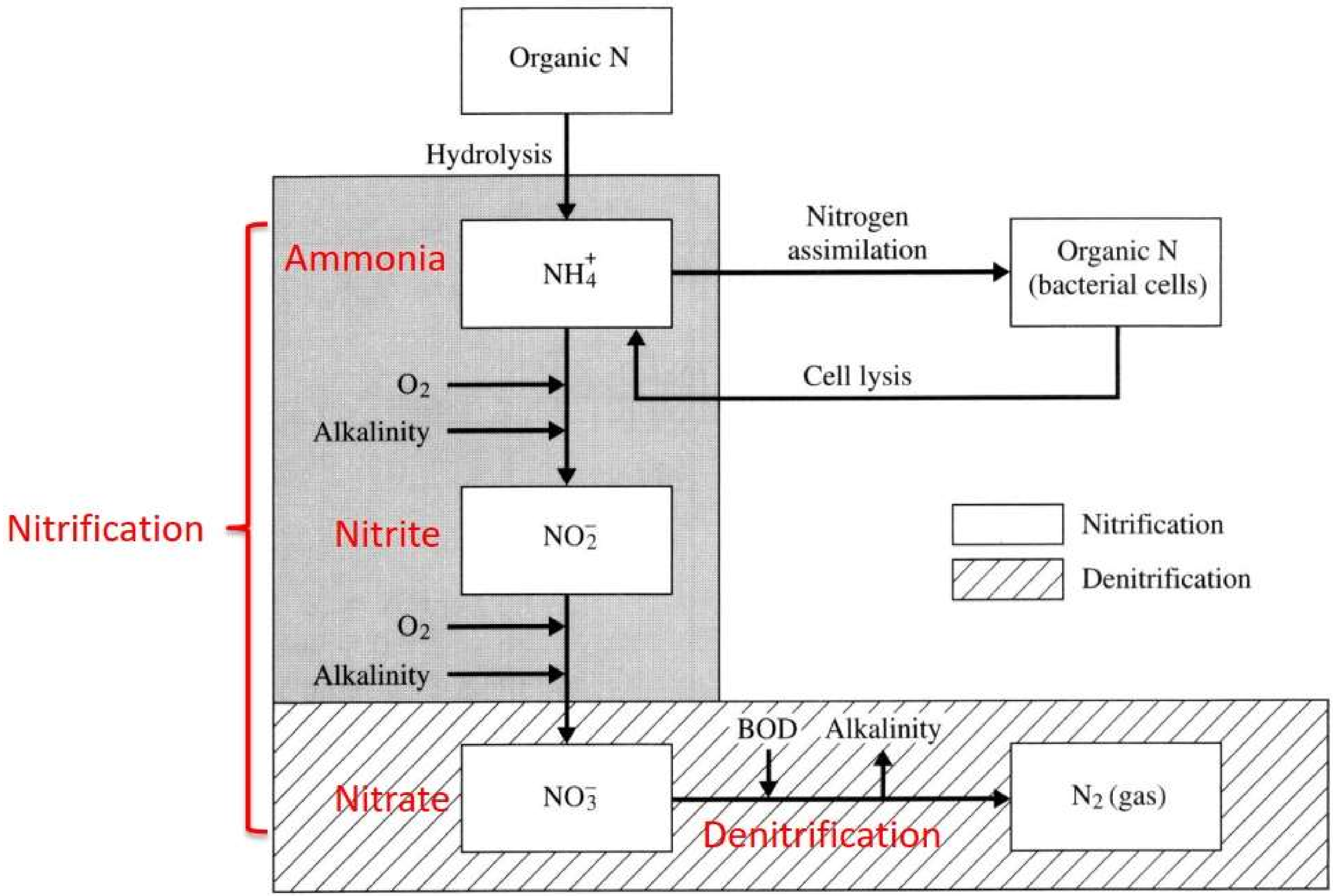


- The loading on the plant affects the oxygen uptake and may require a higher DO to drive the oxygen into the inner layers of the floc to avoid complete anaerobic conditions which can cause disintegration of the floc.

BOD/Carbon Addition

- BOD/Carbon Addition
  - Humates, Fulvic and Humic Acids
  - Dog Food/Rabbit Feed
  - Carbohydrates
    - Molasses
  - Food Production Wastes
    - Brewery
    - Milk Productions
  - Glycerin
    - Carbon X
    - Micro C

BOD/Carbon Addition



Volatile Fatty Acids

- Volatile Fatty Acids (VFA's) impact on Nite/Denite
  - VFA's acetic, propionic, butyric, isobutyric, valeric, isovaleric and caproic acids
  - Volatile fatty acids (VFAs), produced during anaerobic treatment processes, can affect both nitrite oxidation and aerobic denitrification

Volatile Fatty Acids *(Cont'd)*

- VFAs were shown to reduce nitrate formation via nitrite oxidation in activated sludge systems and to stimulate aerobic denitrification in pure cultures.
- Nitrite removal inhibition by VFAs observed in activated sludge systems may be due to the level of aerobic denitrification that occurs.

Troubleshooting

– Example clarifier, solids have "popped" to the surface
  - It is possible for bacteria that have settled in the clarifier to become buoyant and float to the surface if they are retained in the clarifier too long.
  - This is due to denitrification and, if severe, will bring the entire settled sludge blanket to the surface

TABLE 13.3 NITRIFICATION TROUBLESHOOTING GUIDE

(Adapted from *PERFORMANCE EVALUATION AND TROUBLESHOOTING AT MUNICIPAL WASTEWATER TREATMENT FACILITIES*, Office of Water Program Operations, U.S. EPA, Washington, DC.)

INDICATOR/OBSERVATION	PROBABLE CAUSE	CHECK OR MONITOR	SOLUTION
1. Decrease in nitrification unit pH with loss of nitrification.	1a. Need more alkalinity to offset nitrification acidic effects.	1a. Alkalinity in effluent from nitrification unit.	1a. If alkalinity is less than 10 mg/*L*, start addition of lime or sodium hydroxide to nitrification unit.
	1b. Addition of acidic wastes to sewer system.	1b. Raw waste pH and alkalinity.	1b. Initiate source control.
2. Inability to completely nitrify.	2a. Oxygen concentrations are limiting nitrification.	2a. Minimum DO in nitrification unit should be 1 mg/*L* or more.	2a. Increase aeration supply or decrease organic (BOD) loading on nitrification unit.
	2b. Cold temperatures are limiting nitrification.	2b. Temperatures.	2b. Decrease organic loading on nitrification unit or increase biological population in nitrification unit. (Increase MCRT.)
	2c. Increases in total daily influent nitrogen loads have occurred.	2c. Current influent nitrogen concentrations.	2c. Place added nitrification units in service or modify pretreatment to remove more nitrogen.
	2d. Biological solids too low in nitrification unit.	2d. MCRT should be greater than 10 days; in cold temperatures it may need to be greater than 15 days.	2d. (1) Decrease organic loading on nitrification unit and decrease wasting or loss of sludge from nitrification unit. (2) Add settled raw wastewater (primary effluent) to nitrification unit to generate biological solids.
	2e. Peak hourly ammonium concentrations exceed available oxygen supply.	2e. Ammonium concentrations.	2e. Install flow equalization system to minimize peak concentrations or increase oxygen supply.
3. In two-stage activated sludge system, SVI (see Chapter 7, Section 7.3) of nitrification sludge is very high (greater than 250).	3. Nitrification is occurring in first stage.	3. Nitrate in first stage effluent.	3. Transfer sludge from first stage to second and maintain lower MCRT in first stage.
4. Loss of solids from final clarifier.	4. (See activated sludge and sedimentation/flotation chapters, *OPERATION OF WASTEWATER TREATMENT PLANTS*, Volumes I and II.)		
5. Loss of solids from trickling filter or RBC.	5. (See trickling filter and RBC chapters, *OPERATION OF WASTEWATER TREATMENT PLANTS*, Volume I.)		

TABLE 13.4 DENITRIFICATION TROUBLESHOOTING GUIDE

(Adapted from *PERFORMANCE EVALUATION AND TROUBLESHOOTING AT MUNICIPAL WASTEWATER TREATMENT FACILITIES*, Office of Water Program Operations, U.S. EPA, Washington, DC.)

INDICATOR/OBSERVATION	PROBABLE CAUSE	CHECK OR MONITOR	SOLUTION
1. Effluent COD shows sudden increase.	1. Excessive addition of methanol (or other oxygen-demanding material used).	1. Methanol dose.	1a. Reduce methanol addition.
			1b. Install automated methanol feed system.
			1c. Install aerated stabilization unit for removal of excess methanol.
2. Effluent nitrate shows sudden increase.	2a. Inadequate methanol addition.	2a. Methanol feed system malfunction.	2a. Correct malfunction.
	2b. pH has drifted outside 7-7.5 range due to low pH in nitrification stage.	2b. Alkalinity.	2b. Correct pH with addition of lime or soda ash to raise pH to 7-7.5 range.
	2c. Loss of solids from denitrifier due to failure of sludge return.	2c. Denitrifier unit solids and clarifier unit.	2c. Increase sludge return; decrease sludge wasting; transfer sludge from carbonaceous unit to denitrifier.
	2d. Excessive DO.	2d. Denitrifier DO should be as near zero as possible (less than 0.5 mg/L).	2d. Reduce DO level. Turn some mixers off or reduce speed of blowers.
3. High head loss across packed bed or fluidized bed denitrification units.	3a. Excessive solids accumulation in filter.	3a. Length of filter run—if 12 hours or more, this is the probable cause.	3a. Initiate full backwash cycle.
	3b. Nitrogen gas accumulating in filter.	3b. Run times of less than 12 hours indicate this may be the cause.	3b. Backwash bed for 1-2 minutes and return to service.
4. Packed bed or fluidized bed denitrifier that has been out of service blinds immediately upon start-up.	4. Solids have floated to top of bed and blind filter surface.	4. Solids on filter surface.	4. Backwash beds before removing them from service and immediately before starting them.

Nutrients

Arizona – Facility Flow – 8 MGD WWTP intended to do the following:

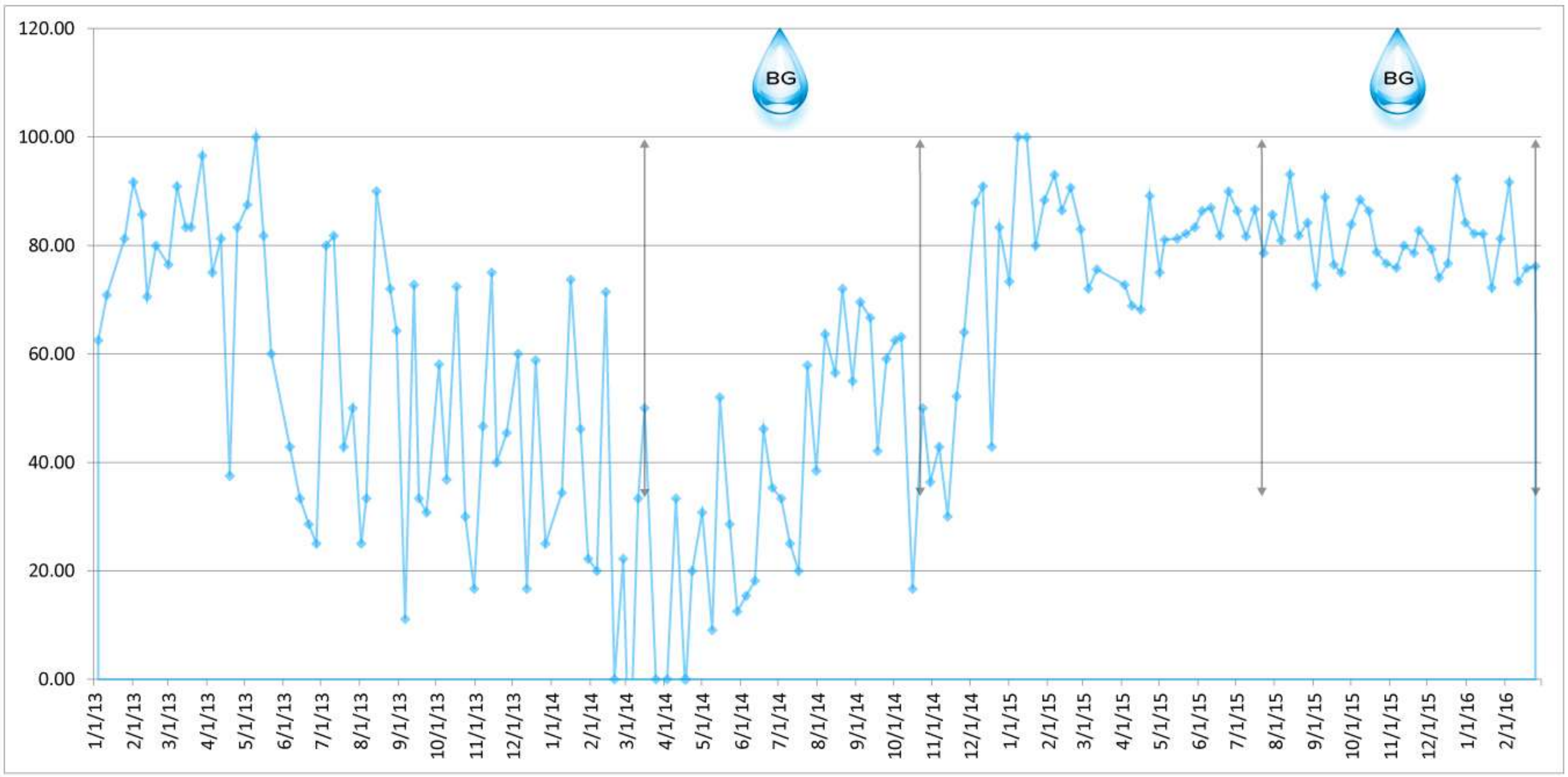
- Reduce sludge wasting
- Reduce foaming
- Improve SVI

Results:

- Eliminated foam
- Lowered disinfection chemical usage and power
- Improved SVI
- Concentrated treatment (3 units)
- Lowered BOD
- Stabilized Nitrogen Removal

Nutrients (Cont'd)

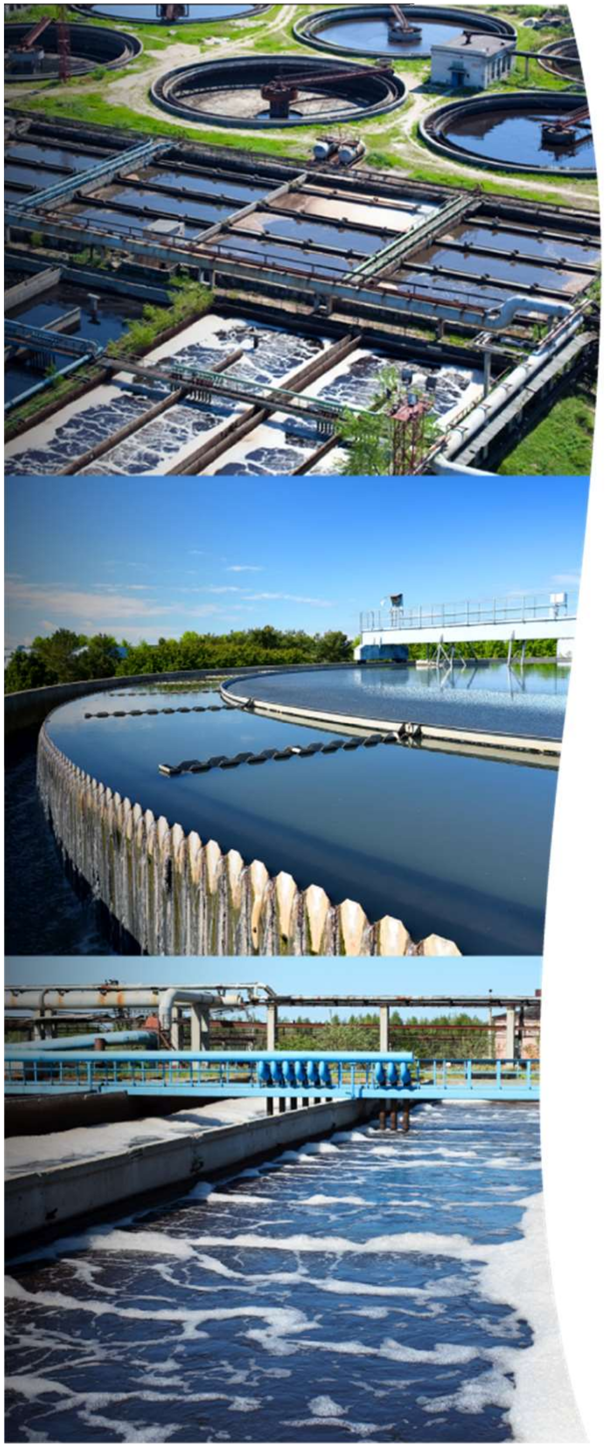
Effluent Nitrates/Nitrites % Removal



Stable operation is achieved when essentially complete nitrification (greater than 90%) occurs.

References

- Michigan Department of Environmental Quality Operator Training and Certification Unit, Activated Sludge Process Control Training Manual for Wastewater Treatment Plant Operators, http://www.michigan.gov/documents/deq/wrd-ot-activated-sludge-manual_460007_7.pdf
- New Mexico Wastewater Systems Operator Certification Study Manual, http://www.nmrwa.org/sites/nmrwa.org/files/WastewaterOperatorStudyManual.pdf
- *Treatment Plant Operator* (magazine) Eye on Alkalinity**,** Ron Trygar http://www.tpomag.com/editorial/2011/05/eye_on_alkalinity
- Long Island Sound Nitrogen Removal Training Program, Module 2 Activated Sludge Operational Strategies for Nitrogen Removal, http://www.dec.ny.gov/docs/water_pdf/module2.pdf
- Wastewater Engineering, Treatment Disposal Reuse, McGraw-Hill, Metcalf and Eddy, 1991
- *Microbiological Examination of Water and Wastewater*, Lewis Publishers, Maria Csuros, Csaba Csurus, 1999
- Minnesota Pollution Control Agency, Phosphorus Treatment and Removal Technologies https://www.pca.state.mn.us/sites/default/files/wq-wwtp9-02.pdf
- Activated Sludge: What Can an Operator Control? **Dennis Plzak,** Presentation at BHN 2016 World Conference
- Volatile Fatty Acids: Effects on Nitrite Removal and Nitrate Formation during Activated Sludge Treatment, Merve Oguz University of Tennessee, Knoxville



Probiotic® SOLUTIONS™

Thank You