Wastewater Nutrient Optimization & Nitrogen Removal 2018

By

Brett Ward
Municipal Technical Advisory Service

Nutrient Removal

- More Complex: Advanced Treatment, Tertiary Treatment
  - Chemical/Physical Treatment
  - Biological Treatment
    - Traditional Treatment-Oxidation Process
    - Nitrogen Removal-Oxidation then Reduction
    - Phosphorus- Reduction then Oxidation
- Complex and often a delicate processes

AS Review- Plant Configurations

- Plug Flow
  - DO may vary
  - DO demand changes
  - Rate of metabolism changes
  - BOD drops
- Multi Ring Ditch
- ~Intermittent fed SBR

AS Review- Plant Configuration

- Complete Mix
  - DO ~ equal
  - DO demand ~equal
  - BOD ~ equal
  - Rate of metabolism ~equal
- Single ring ditch
- ~Continuous fed SBR

Oxidation / Reduction

- Oxidation- add oxygen, releases energy
  - We oxidize BOD, NH_3 to treat sewage, removing the high energy oxygen demanding pollutants.
- Reduction- removes oxygen from NO_2 and NO_3 , reactions that occur when DO is at or near zero.
- PAO's must have both conditions

Bacterial Habitat

Three Different Habitats

- Different by design
- Different by operations and controls
- Operators must control the bacteria!

What are Nutrients? Think Fertilizer

- Nutrients
  - Nitrogen and Phosphorus
  - Two main fertilizer elements needed for growing green plants.
  - They contribute to aquatic plant growth,
  - Excess plant growth clogs streams and,
  - When they die add a organic matter/BOD and nutrient load back onto the stream

How do you remove nutrients?

- Nitrogen
  - Biologically- nitrification followed by denitrification
  - Chemically- ammonia stripping, breakpoint Cl_2
- Phosphorus
  - Biologically-to ~ 0.5-1.0 mg/L
  - Chemically-with or without biological removal

NITROGEN REMOVAL

Forms of Nitrogen in the Environment

Unoxidized Forms of Nitrogen

- Nitrogen Gas (N_2)

  Air is 78 % N_2

- Ammonia (NH_4^+, NH_3)
  - pH 9.0 50%/50%

- Organic Nitrogen (urea, amino acids, peptides, proteins, etc...)

Oxidized Forms of Nitrogen

- Nitrite (NO_2^-)
- Nitrate (NO_3^-)

- Nitrous Oxide (N_2O)

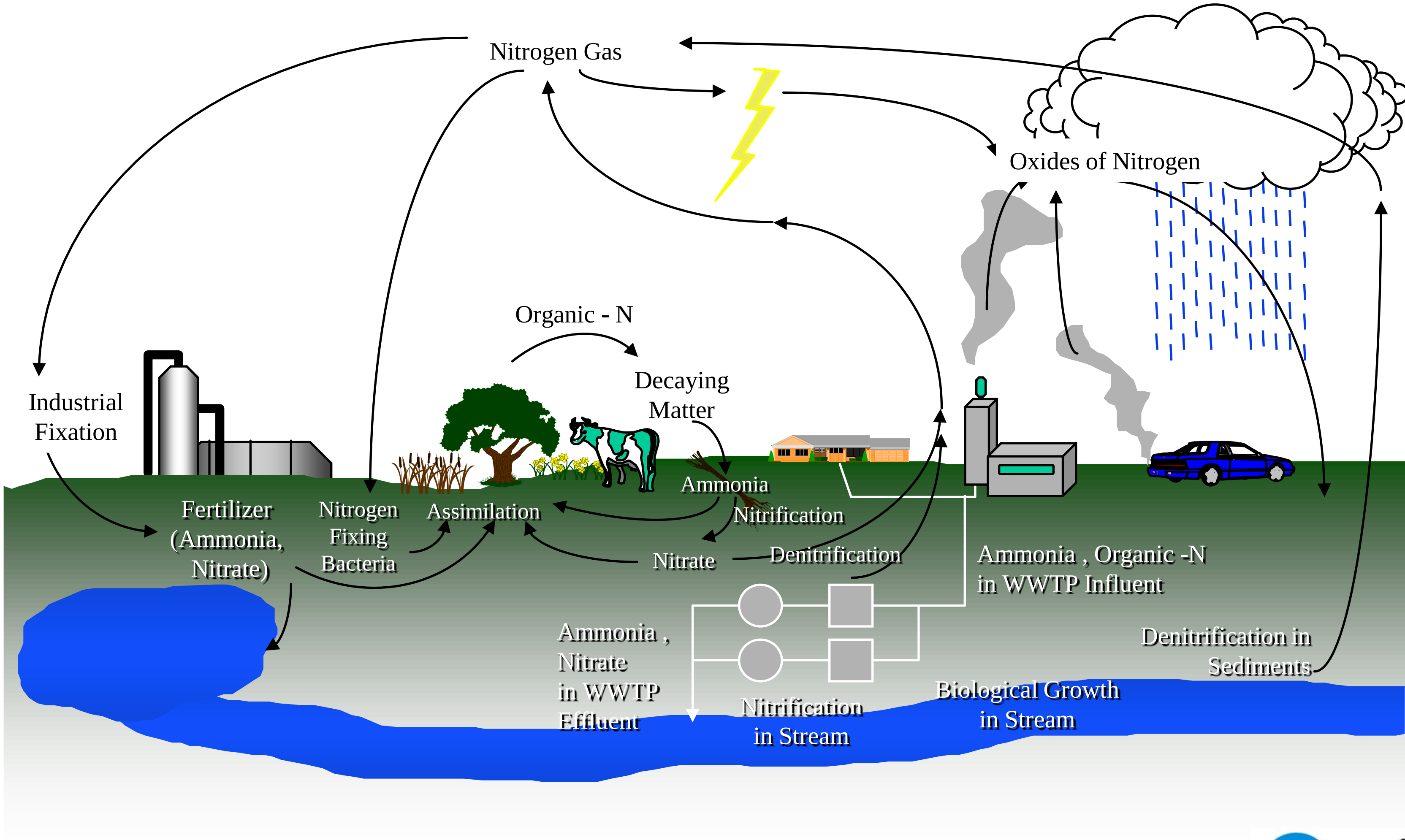
  NOS, O_2 fm 21% to 33% anesthetic

- Nitric Oxide (NO)

  Impt. in cell communication, precursor of NO_2

- Nitrogen Dioxide (NO_2)
  - Brown toxic gas & pollutant

The Nitrogen Cycle



Fate of N: effluent, land, landfill, atmosphere

4 Tests & 4 Types of Nitrogen

- Total Nitrogen
  - Unoxidized - N (Total Kjeldahl Nitrogen) TKN
    - Ammonia-N ↑↓ Ammonium-N
    - Organic-N
    - SKN (Soluble Kjeldahl N) - includes ammonia(um) N plus soluble organic N
    - Solids
  - Oxidized - N
    - Nitrous, Nitric Oxides — Gas
    - Nitrite Ion — Principally Soluble
    - Nitrate Ion — Principally Soluble

Processes to Meet Limits

Limits	Process	Products
– BOD	Organic Oxidation	CO_2, H_2O, NH_3
– Ammonia	Nitrification	Nitrite/Nitrate

- Total Nitrogen

• Organic Rem.	Ammonification	Ammonia
• Ammonia Rem.	Nitrification	Nitrite/Nitrate
• Nitrite/Nitrate Rem.	Denitrification	Nitrogen Gas

Nitrogen & Ammonia Sources

- Sewage
- Meat/milk processing
- Hauled in Waste
- Interstate Rest Area
  - 100mg/L
- Schools, Factories
- Ammonia Refrigeration
- Anaerobic Digester
  - 500-1000 mg/L
  - Leacheate
- STEP or Grinder CS

1st, Organic Nitrogen Removal,

BOD Bugs Convert Organic Nitrogen (amino acids, proteins in BOD & TSS)(ammonification) to NH_3

$$BOD + BOD_{Bugs} + O_2 = More\ BOD_{Bugs} + CO_2 + H_2O + NH_3$$

2nd, Ammonia(NH_3) Removal

- Nitrification- Biological oxidation of NH_3 to NO_2 then NO_3

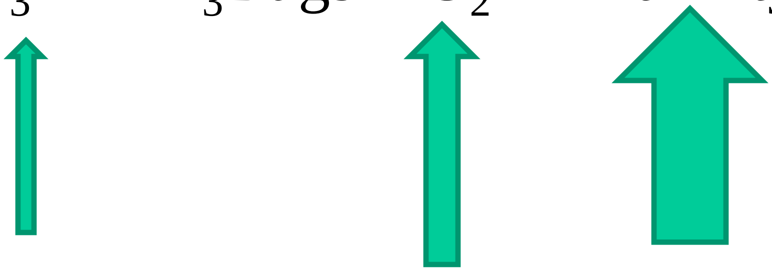
- Removal Factors
  - Plant Design
  - Dissolved Oxygen
  - Microorganisms
  - Alkalinity
  - Temperature
  - No Toxics

Designs to Remove Ammonia

- Activated Sludge- Extended Aeration, Conventional, Step Feed (marginal), Contact Stabilization (poor)
- Fixed Film-Trickling Filter, Biotower, RBC, IFAS, MBBR
- Natural/Biological- lagoons, wetlands, often marginal

Ammonia Conversion Chemistry

NH_3 + NH_3Bugs + O_2 + Alkalinity = More NH_3Bugs + NO_3



1 mg/L 4 mg/L 7mg/L

NH_3 + AOB’s → NO_2 + NOB’s → NO_3

Dissolved Oxygen

- For each mg/L NH_3 four times as much oxygen is needed as for BOD removal
  - D.O. 1.5-4.0 mg/L, max growth rate at 3.0
  - The most common reason for poor nitrification is low D.O.
  - But, plants will fully nitrify at lower D.O. levels, even as low as 0.5 mg/L
  - If DO< 1.5 additional DO may be helpful
  - Hydraulic Detention Time affects

Nitrification (ammonia removal)

- Two key groups of bacteria
  - AOB's-Ammonia Oxidizing Bacteria, Nitrosomonas, and others
  - NOB's- Nitrite Oxidizing Bacteria, Nitrobacter, and others
  - Autotrophic- energy and carbon from inorganic sources
  - Obligate Aerobes- must have free oxygen

Nitrification-Microorganisms

- Are there sufficient microorganisms?
  - What is MLSS, or Mean Cell Residence Time (MCRT)
    - $MCRT = \frac{\text{Total solids in system}}{\text{Solids Wasted}}$
  - Generally want MCRT > 2 days, >8 in winter

Alkalinity

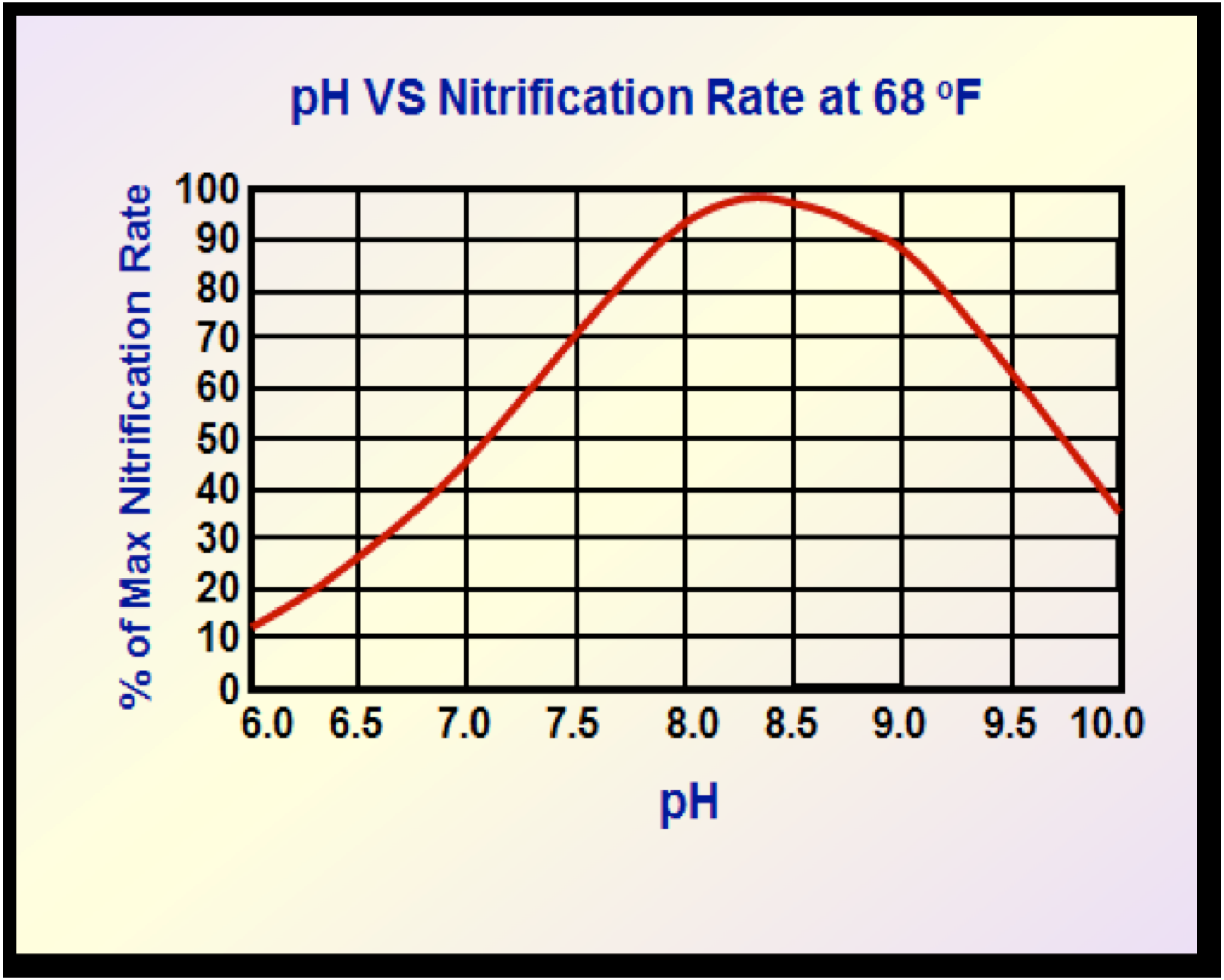
- Alkalinity- capacity of the water to neutralize acid
- Standard Method is a titration test, but for process control "swimming pool" strips are okay

Alkalinity

- If Alkalinity is low, pH drop also
- Check influent and effluent alkalinity
  - If effluent Alk. < 50mg/L, add alkalinity
  - Influent Alk. < (Influent NH_4 * 7.14) + 50, add alkalinity
  - If there is a pH drop across the aerator or digester, add alkalinity.
  - Optimum pH is 8.3 s.u.

Tennessee Alkalinity

- Three areas of the state with low alkalinity
  - Deep West TN, Cumberland Plateau/Mountains and extreme eastern mountains


pH VS Nitrification Rate at 68 °F
% of Max Nitrification Rate
100
90
80
70
60
50
40
30
20
10
0
6.0
6.5
7.0
7.5
8.0
8.5
9.0
9.5
10.0
pH

Supplemental Alkalinity

- Add high pH materials
  - Caustic, NaOH, Sodium Hydroxide
    - Liquid, very caustic, need feed equipment, cheap
  - Hydrated Lime, $Ca(OH)_2$, Calcium Hydroxide
    - Dry powder, very dusty, 50lbs bags, or truckloads
    - Does not dissolve well
  - $Mg(OH)_2$, Magnesium Hydroxide, Max $pH<9$
  - Soda Ash, Na_2CO_3, Sodium Carbonate
  - $NaHCO_3$, Sodium Bicarbonate, very good but $

Adjust aerator or digester alkalinity

- Use same products used to raise pH
  - Alkalinity needed and lbs or product

  - Lbs of alk needed *0.76 = lbs of lime
  - Lbs of alk needed * 0.8 = lbs of NaOH
  - Lbs of alk needed * 1.08= lbs of soda ash
  - Lbs of alk needed * 1.72= lbs of Sodium Bicarbonate

Temperature impacts Nitrification

- Temperature impacts the rate of oxidation
  - 100% at 29º
  - 55% at 25º
  - 38 % at 20º
  - 25% at 15º
  - 17% at 10º
- Need more bugs and longer MCRT in Winter
- Starting Nitrification at 4º C is ~ impossible

Toxicity

- Toxics
  - The nitrifying bacteria are wimps!
  - They often are the first to die with a toxic dump
    - Especially the NOB’s
  - Quaternary Ammonia compounds
    - ….. “ammonium chloride”….

Compounds that Inhibit Nitrification

- **Organic Compounds:**
- **Acetone** | **Phenol**
- **Carbon Disulfide** | **Ethylenediamine**
- **Chloroform** | **Hexamethylene Diamine**
- **Ethanol** | **Aniline**
- **Monoethanolamine**

- **Metals and Inorganic Compounds:**
- **Zinc** | **Sodium Cyanide**
- **Free Cyanide** | **Sodium Azide**
- **Perchlorate** | **Hydrazine**
- **Copper** | **Sodium Cyanate**
- **Mercury** | **Potassium Chromate**
- **Chromium** | **Cadmium**
- **Nickel** | **Arsenic (trivalent)**
- **Silver** | **Fluoride**
- **Cobalt** | **Lead**
- **Thiocyanate** | **Quaternary Ammonia Compounds**

High Effluent Ammonia NH_3

- Oxidative Pressure
  - More Bugs, longer solids detention time in the aerator, more Air- oxidation rate highest at 3.0 mg/L D.O.
- Longer Hydraulic Detention in Aerator
- Alkalinity additions if needed
- Absence of Toxic impacts
- Temperature

Biological Ammonia Oxidation

- Highest rate of oxidation (removal) is at DO of 3.0 mg/L, Temp of 29º, pH of 8.3, and high reactor ammonia concentrations.

- Treatment is always a compromise,
- Longer HDT and MCRT makes for the various non-optimum conditions.

Chemical Removal of NH_3

- Ammonia Stripping
  - At pH 11 and 25º C, 98% of ammonia is in the gas form and will evaporate to the air.
- Breakpoint chlorination
  - $Cl_2:NH_3$ ration of 10:1
- Ion Exchange

Denitrification, conversion of NO_3 to Nitrogen Gas

- 1st organic N removed
- 2nd ammonia removed
- 3rd nitrite/nitrate removed
- This should give low Total Nitrogen
- TSS ~ 12% N

Denitrification Benefits

- Meet the Permit
- Recycle Oxygen
- Recover Alkalinity/pH
- Improve Effluent
- Select against Filaments
- Improved Solids Proc.
- Save Dollars

Total Nitrogen Limits

- Total Nitrogen

  $TN = TKN + NO_2 + NO_3$

  TKN = Organic Nitrogen (BOD & TSS) + Ammonia

  NO_2: generally low

- Nitrate, NO_3 parameter of concern

Removing Nitrate Through Biological Denitrification

- Create the needed environment
  - Nitrate must be present
  - Anoxic Zone, Dissolved Oxygen < 0.3 mg/L
  - BOD or food must be available
  - BOD organisms must be present
  - ORP to – 100mV

Biological Denitrification

- Anoxic Process- no free dissolved oxygen
- Heterotrophic bacteria- BOD bugs
  - Facultative- use oxygen or nitrite/nitrate
  - Forced, by design or operations into anoxic respiration for nitrate / nitrogen removal

Denitrification

- BOD + BOD $_{Bugs}$ + O_2 = More BOD $_{Bugs}$ + CO_2 + H_2O + NH_3
- NH_3 + NH_3Bugs + O_2 + Alkalinity = More NH_3Bugs + NO_3

NO_3 Nitrogen gas

- BOD + BOD $_{Bugs}$ + ~~O_2~~ = more BOD $_{Bugs}$ + CO_2 + H_2O + N_2 + Alk.

Denitrification, Examples

Clarifier Denitrification-NO!

Settleometer Denitrification

Denitrification Efficiency

- BOD + BOD $_{Bugs}$ + O_2 = More BOD $_{Bugs}$ + CO_2+ H_2O + NH_3

  1mg/L 1-1.5 mg/L

- NH_3 + NH_3Bugs + O_2+ Alkalinity = More NH_3Bugs + NO_3
- 1 mg/L 4mg/L 7mg/L

NO_3 Nitrogen gas

- BOD + BOD $_{Bugs}$ + ~~O_2~~ = more BOD $_{Bugs}$ + CO_2+ H_2O + N_2 + Alk.

  1mg/L .35 mg/L 80% 50%

Speed of Denitrification

Fast

- DO = 0.0 mg/L
- Soluble BOD available

Slow

- DO > 0.3 mg/L
- Little Food
  - Endogenous Respiration
    - Extended Aeration
    - Digester

Speed of Denitrification

- Dissolved Oxygen vs Denitrification Rate
- 0.0 mg/L--100%
- 0.1 mg/L--40%
- 0.2 mg/L--20%
- 0.3 mg/L--10%

- BOD bacteria
  - Soluble BOD vs Particulate BOD
  - pH 6.5-8.5
  - Temperature
    - Slower when cold
    - Faster when warm
      - 2x/10º C increase

Removing Nitrate Through Biological Denitrification

- Create the needed environment
  - Nitrate must be present
  - Anoxic Zone, Dissolved Oxygen < 0.3 mg/L
  - BOD or food must be available
  - BOD organisms must be present
  - ORP to – 100mV

Denitrification & ORP

ORP & Metabolic Processes

ORP Condition	ORP mV	Process Ranges	Process
Mildly Negative	+50 0 -50 -100	Classic Anoxic Zone Extended Anoxic Zone	Anoxic Zone
Moderately Negative	-150 -200 -250 -300	Classic Ferm Zone Extended Ferm Zone	Fermentaion Zone
Strongly Negative	-350 -400 -450 -500	Fully Anaerobic	Anaerobic (Methane) Zone

Denitrification Options

- Post Denitrification with Carbon(CBOD) feed (methanol, glycerin) and filters
- Modified Anoxic/Oxic Activated Sludge
  - Modifed Ludzack-Ettinger
- Full Biological Nutrient Removal Design
  - Bardenpho
- Anoxic Selector- RAS and Influent
- Off/On Aeration

Making Your Plant Denitrify

- Locate the basin which best meets the denitrification requirements.
  - Primary clarifier, depends of piping
  - Aeration basin, perhaps
  - Final clarifier, no way!
  - Other basins, what do you have?

Aerator is Common Choice

- Turn the air "OFF",
- Denitrify
- Turn the air back "ON"

Nitrogen Sources & Fate

Sources

- Sewage
  - Organic
  - Inorganic- Ammonia
- Industrial
  - Process wastewater
  - Refrigeration
- Other
  - Trucked in waste
  - Leachate

Fate of Nitrogen

- Leaves the plant in one of three ways.
  - Effluent
    - Organic, NH_3, NO_3
  - Biosolids or sludge
    - Organic, Ammonia, NO_3
  - Atmosphere
    - Nitrogen gas

The End !