Nitrification and Denitrification

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Agenda

- Sources and Types of Nitrogen
- Need for Nitrogen Removal
- Physical/Chemical Nitrogen Removal
- Define Biological Nitrification
  - ✓ Chemical equations (stoichiometry)
  - ✓ Organisms involved

Agenda

- Unit Processes for Nitrification
- Define Biological Denitrification
  - ✓Chemical equations (stoichiometry)
  - ✓Organisms involved
- Unit Processes for Denitification

Sources and Types of Nitrogen

Quantities

- ✓ 16 grams/cap/day.
- ✓ 20 to 85 mg/L influent concentrations typical.

Recycle Streams

- ✓ Digester supernatant
- ✓ Belt press filtrate

Typical Forms

- ✓ 40% organic
- ✓ 60% ammonia
- ✓ <1% nitrate

Ammonification

Rule of Thumb

- 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
- TKN / NH3-N is about 0.65

TKN = Total Kjedahl Nitrogen

If BOD_5 is 250 mg/L, then TKN should be

(250)•(0.1) = 25 mg/L

(250)•(0.2) = 50 mg/L

Ammonia = 16 – 33 mg/L

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

TIN

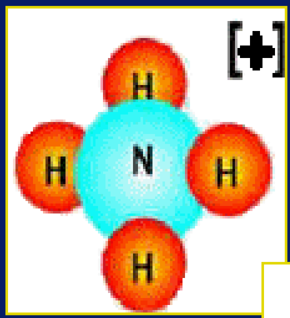
TKN

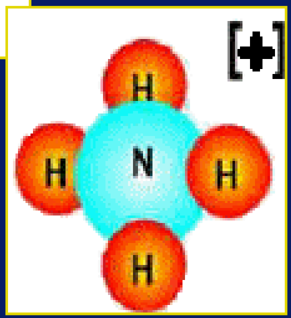
Analysis Methods

Need for Nitrogen Removal

Types of Ammonia Transfer, Removal, and Conversion

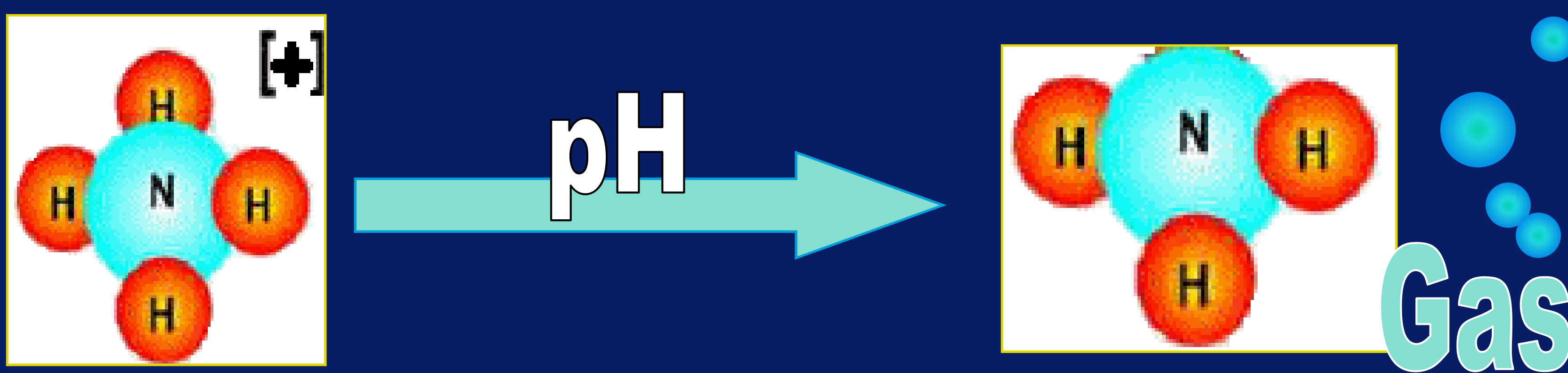
- NH_3-N Stripping
- Ion Exchange
- Breakpoint Chlorination
- Natural Wetlands
- Biological Nitrification





NH_3-N Stripping

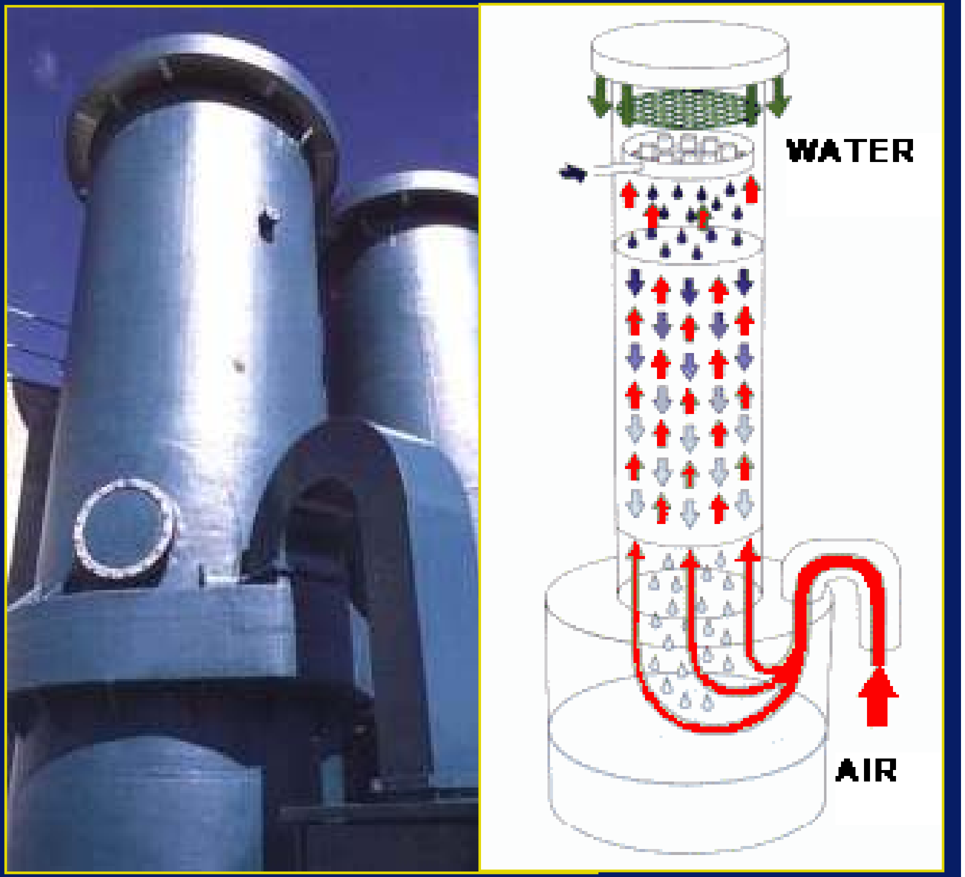
- Really only used in industrial applications.
- Ammonium ion predominant in Wastewater
- Convert to gaseous NH_3-N by raising pH up to 10.5 – 11.5 S.U.



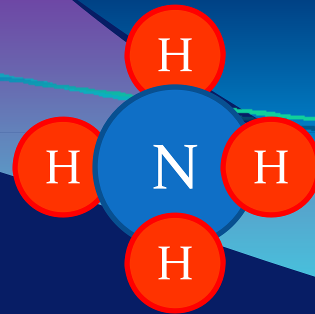
NH_3-N Stripping

- At pH 11 and 25ºC, gaseous form is ~98%
- Stripping tower with high air flow to "strip"

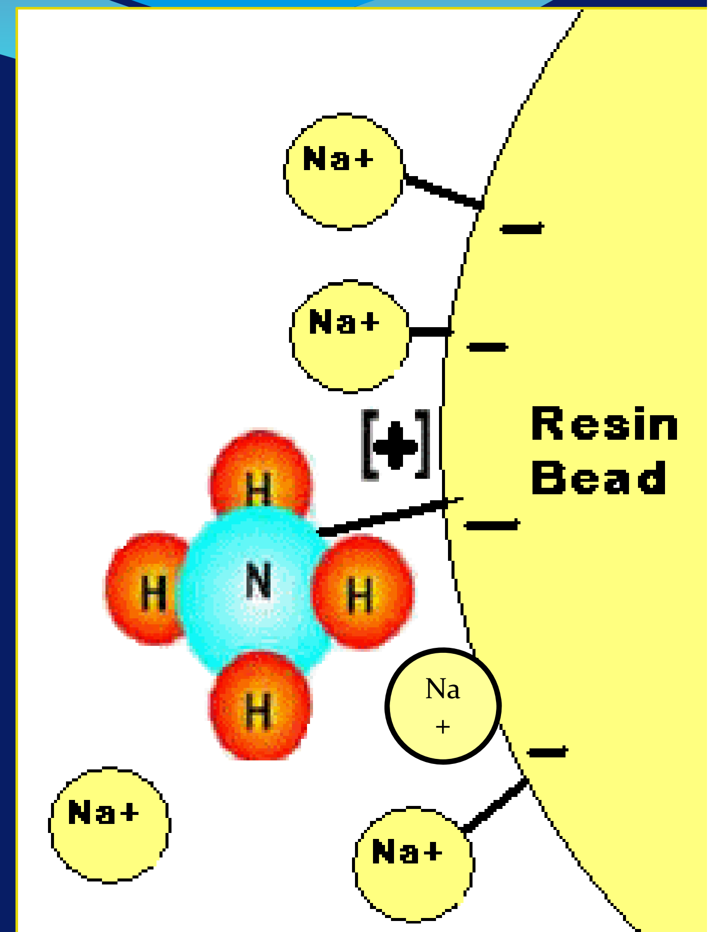
Same principal behind ion selective electrode test.



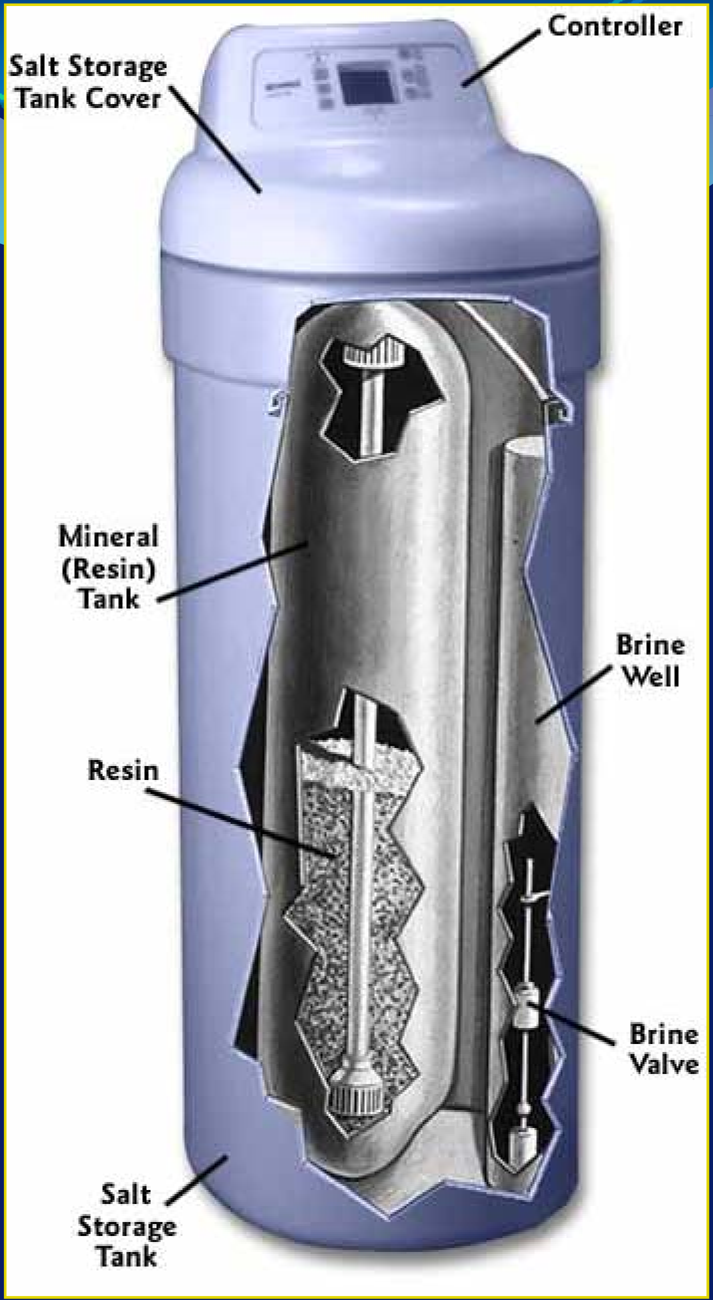
Ion Exchange



- Typically used for small flows.
- Wastewater passes over resin bed containing ions of same charge.
- Ammonia ions are “exchanged” for ions on resin, typically sodium.
- Resin beds must be regenerated.

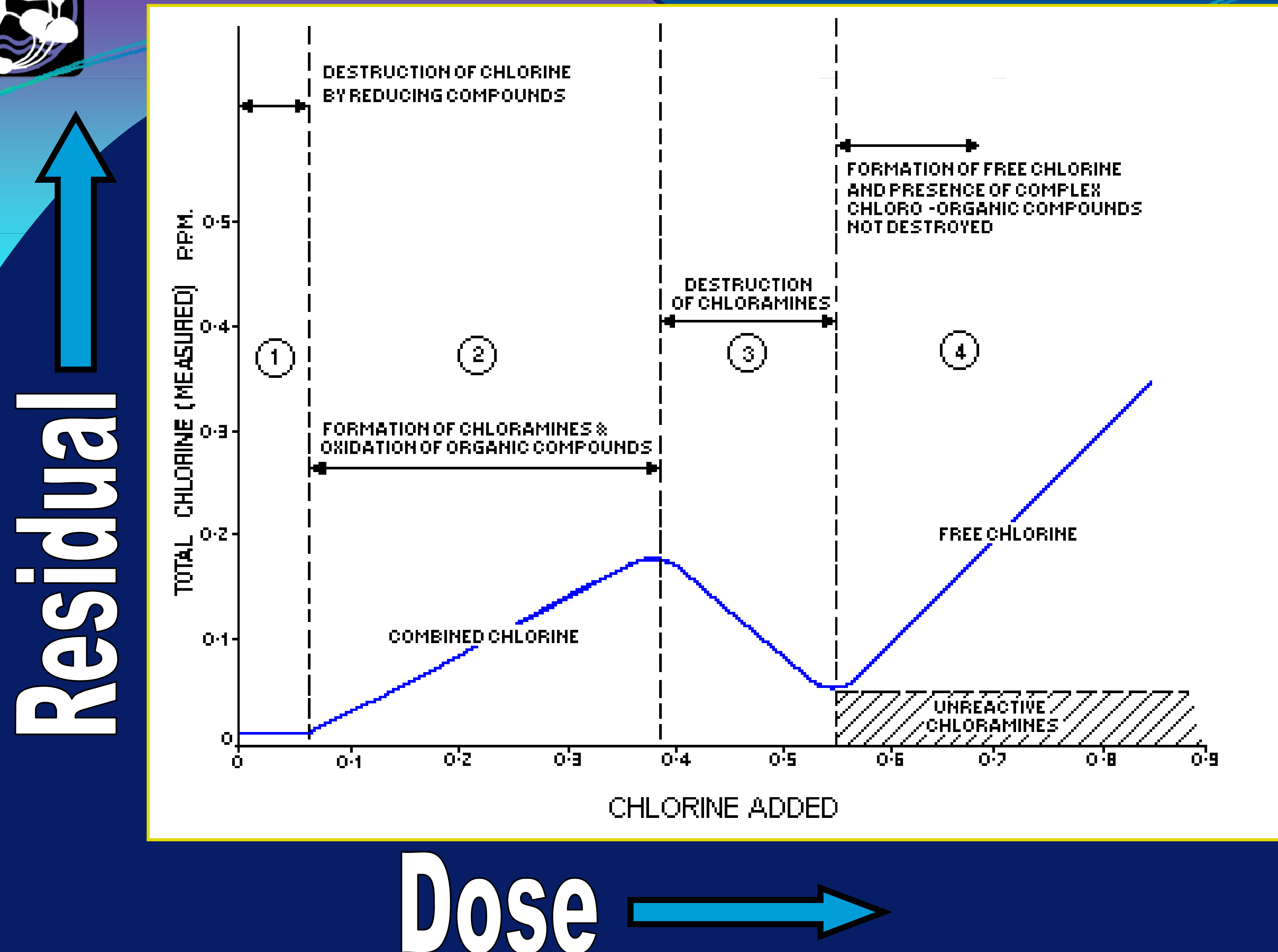


Ion Exchange



Breakpoint Chlorination

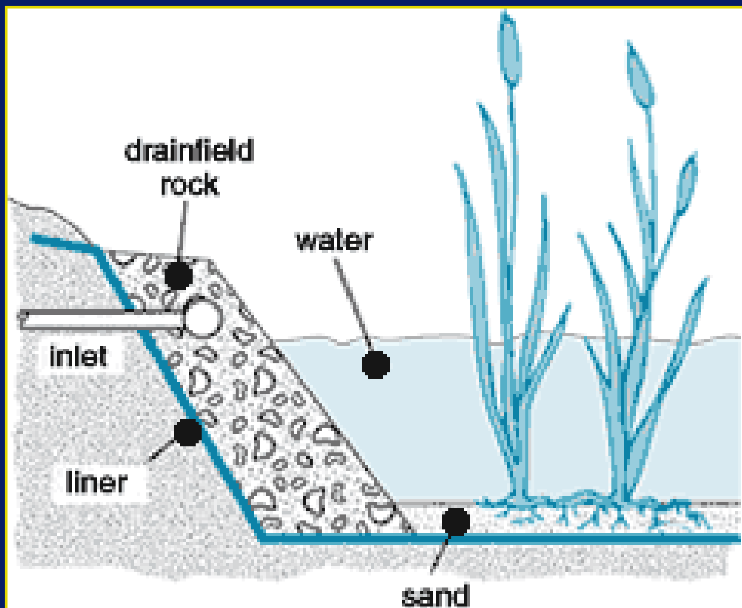
- NH_3-N can be converted to N_2 with Cl_2
- Cl_2/NH_3-N ratio of 10:1 needed
- **EXPENSIVE** – use a polishing step


Residual
DESTRUCTION OF CHLORINE BY REDUCING COMPOUNDS
FORMATION OF FREE CHLORINE AND PRESENCE OF COMPLEX CHLORO -ORGANIC COMPOUNDS NOT DESTROYED
DESTRUCTION OF CHLORAMINES
FORMATION OF CHLORAMINES & OXIDATION OF ORGANIC COMPOUNDS
1
2
3
4
TOTAL CHLORINE (MEASURED) P.P.M.
0·5
0·4
0·3
0·2
0·1
0
FREE CHLORINE
COMBINED CHLORINE
UNREACTIVE CHLORAMINES
0
0·1
0·2
0·3
0·4
0·5
0·6
0·7
0·8
0·9
CHLORINE ADDED
Dose

Natural Wetlands

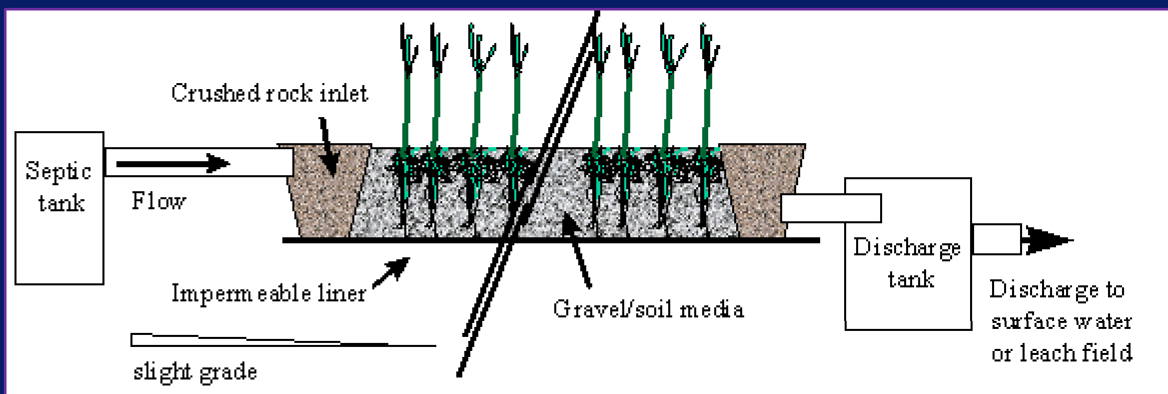
- Plants such as hyacinth or duckweed grown in lagoon systems.
- Plants use ammonia as a nitrogen source (fertilizer).
- Nitrogen is incorporated into biomass.
- Periodic harvesting of plants removes nitrogen from the system.

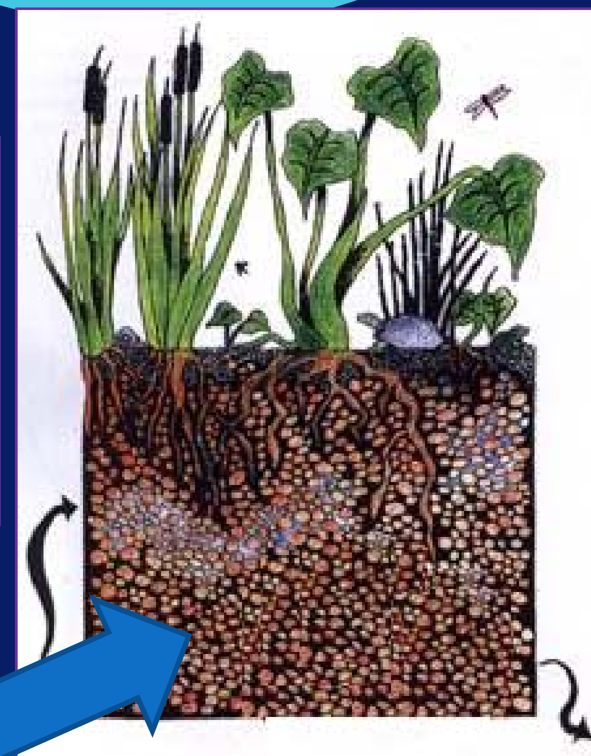
Natural Wetlands – Free Surface



- Assimilative nutrient removal only
- Removes very little ammonia

Natural Wetlands: Subsurface Flow





- Nitrifying bacteria grow here
- Removes ammonia well when warm

Duckweed

Define Biological Nitrification

- Two-step conversion of NH_3-N to NO_3-N.
- Nitrification is carried out by two unrelated groups of organisms.
  - Ammonia-oxidizing bacteria, *Nitrosomonas*
  - Nitrite-oxidizing bacteria, *Nitrobacter*

Define Biological Nitrification

- *Nitrosomonas* convert ammonia to nitrite.
- *Nitrobacter* covert nitrite to nitrate.
- Overall Stoichiometric Equation: $1.0NH_4^+ + 1.8O_2 + 0.8CO_2 \rightarrow 0.02C_4H_7O_2N + 1.0H_2O + 1.0NO_3^- +$ **$2.0H^+$**

Biological Nitrification

- Consumes 4.33 grams of O_2 and 7.14 grams of alkalinity per gram of NH_3-N oxidized
- Forms 0.15 grams of new cells per gram of NH_3-N oxidized
- Consumes 0.08 grams of inorganic Carbon per gram of NH_3-N oxidized
- Organic loading to process also a factor. Nitrifiers can’t compete with heterotrophs.

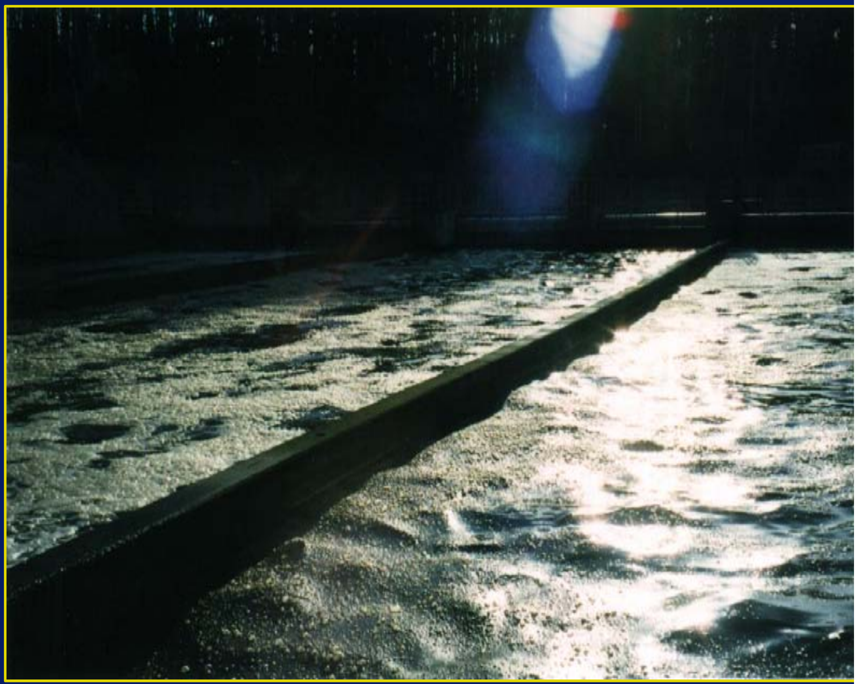
Biological Nitrification Processes

- Suspended Growth
  - Activated Sludge
- Fixed Film or Attached Growth
  - Trickling Filters (tertiary)
  - Rotating Biological Contactors (RBCs)
  - Biological Aerated Filters (BAFs)
- Hybrid Processes
  - Kaldnes, Ringlace, etc.

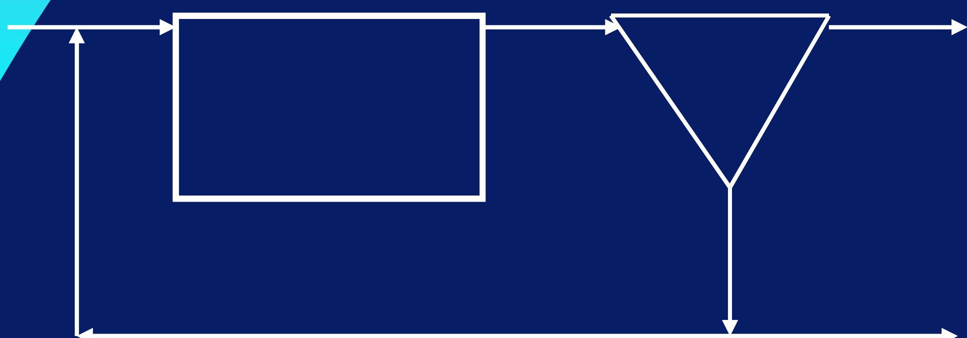
"Now then, Simpkins. What makes you think you could become a circus clown?"

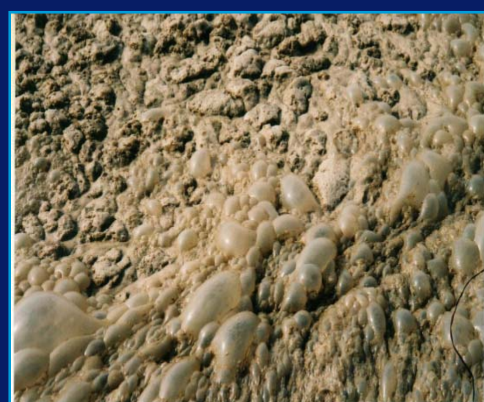
Conventional Activated Sludge

- Nitrification rates relatively low.
- Air (and electrical demand) high.
- Operator intensive.
- Flexible. Easy to expand for later denitrification.



Activated Sludge Nitrification





MCRT > 5 days

MLSS increases with MCRT

When MLSS is too high, clarifier is overloaded.

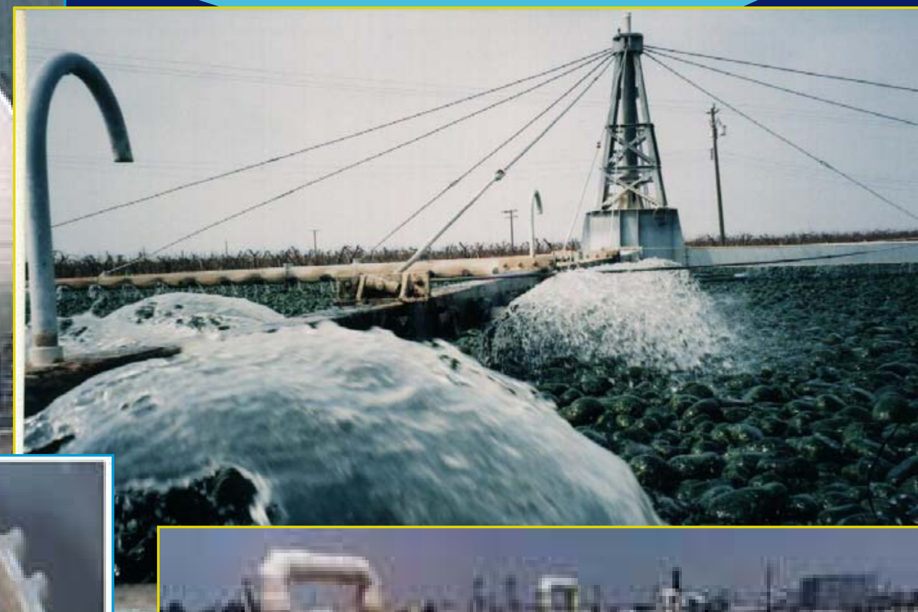
Really old sludge can have other problems!

Activated Sludge Nitrification

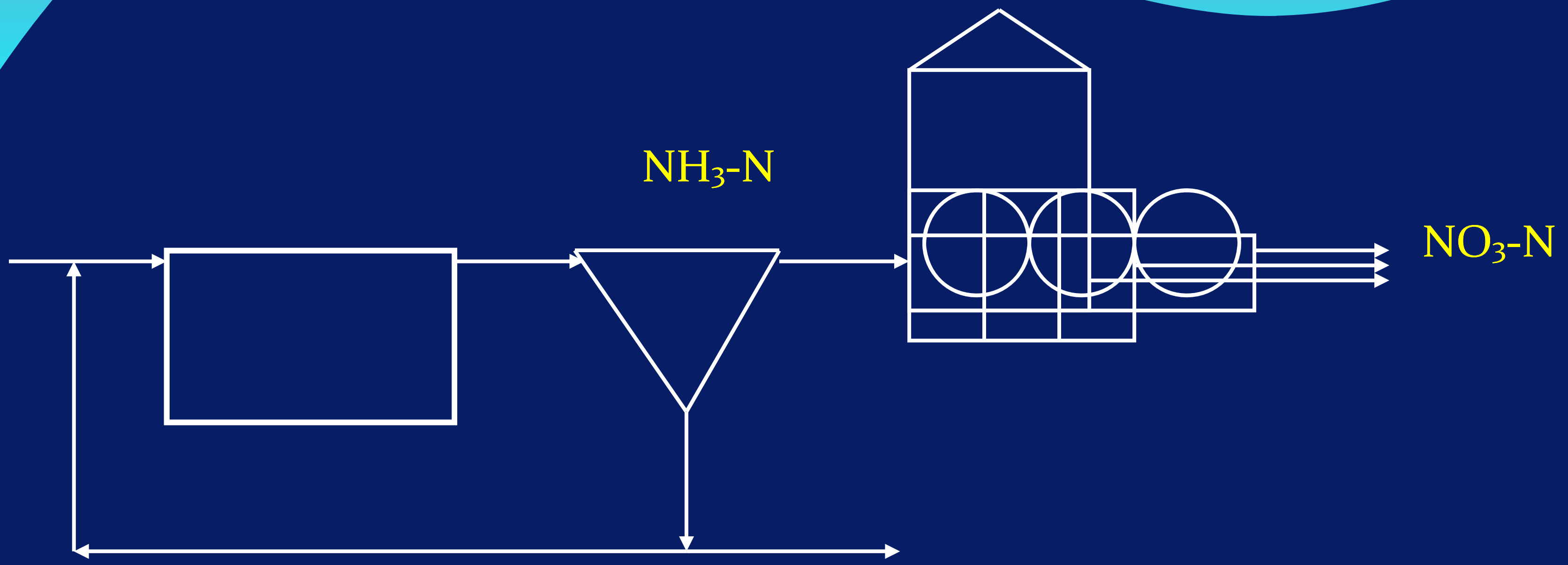
- Requires higher MCRT, >5 days
- Colder temps mean longer MCRTs
- Maintain DO near 2 mg/L
- Danger of denitrification in clarifier
  - “ashing” or “popping blanket”
- Most activated sludge configurations are capable of supporting nitrification

Ashing and Floating Sludge

Fixed Film Processes



Tertiary Nitrification



Secondary Clarifier Effluent

<20 mg/L TSS

<20 mg/L sBOD

Final Effluent

Low TSS, BOD, NH_3-N

High DO, NO_3-N

Wastewater Characteristics That Can Impact Nitrification

Mean Cell Residence Time

- How long have the cells been in the system?
- Calculate by
  - Take the total amount of solids in the system (aeration basin + clarifier).
  - Divide by the amount of solids wasted per day.

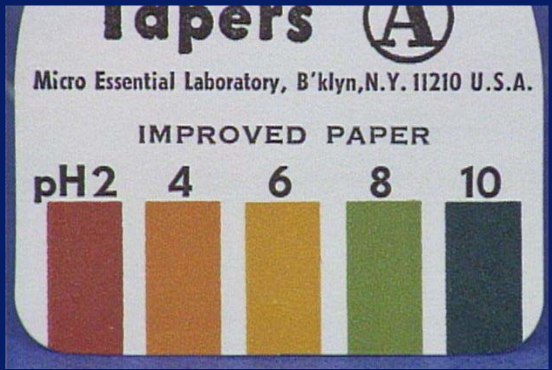
Mean Cell Residence Time

- Generally an MCRT > 5 days is needed for stable nitrification.
- Nitrifying bacteria grow very, very slooowly.
- Nitrification in fixed film processes follows a different set of rules.

Temperature

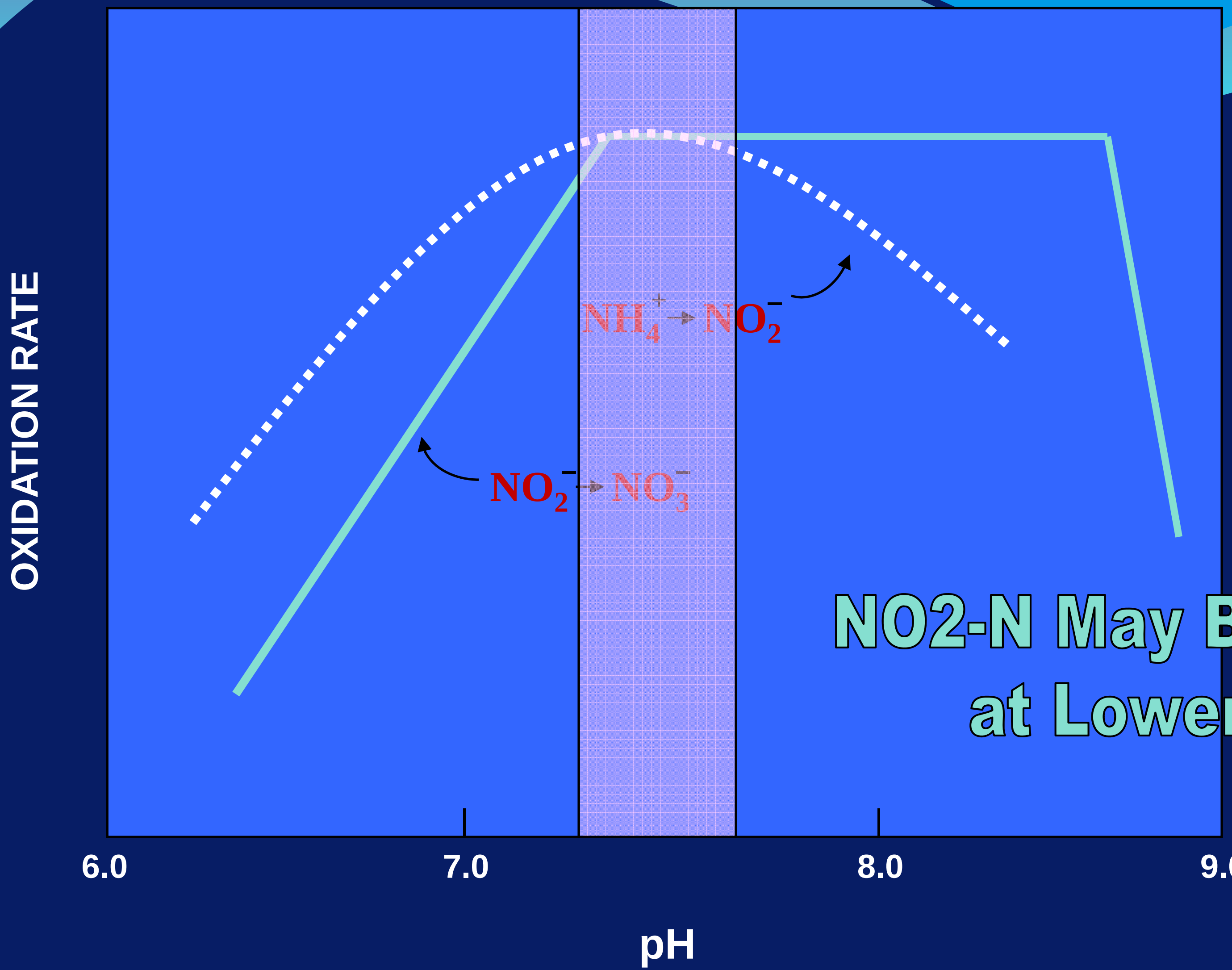
- Nitrification can take place between 10 and 35 degrees C.
- Rates increase as temperature increases.
- Below 5 degrees C, nitrification essentially stops.
- Activated sludge processes are more susceptible to temperature effects than fixed film systems.

pH



- Nitrifiers are sensitive to changes in pH
- Reported "optimum" pHs vary between 5.8 and 8.5 S.U. – ***A wide range!***
- USEPA - Nitrification rates decrease outside pH range 7.0 – 9.0

EFFECT OF pH ON AMMONIA OXIDATION



NO2-N May Build-Up at Lower pH

Why Low pH Affects Nitrifiers

- Nitrifiers need NH^{3-}N, not NH^{4+}-N
- As pH decreases, ionization increases and less NH3-N is available.

$$NH_4^+ \xleftrightarrow{pH} NH_3$$

- At low pH, nitrifiers are starving.

Why Low pH Affects Nitrifiers

- May account for some of the variation in pH optimums reported in the literature.
- Hydrogen ion toxicity at $pH < 5.7$
- Keep in mind that bacteria adapt.
- Less than perfect conditions are better than changing conditions.

pH versus Alkalinity

- pH is a measure of hydrogen ion concentration.
- Alkalinity is a measure of a water's ability to neutralize acid.
- Water with high alkalinity will always have a high pH, but water with high pH does not always have high alkalinity.
- Both measurements are needed!

Why Low Alkalinity Affects Nitrifiers

- Alkalinity neutralizes acid.
- Inadequate alkalinity results in low pH.
- Nitrifiers can't use organic compounds for synthesis and growth. Autotrophs
- Carbonate alkalinity may satisfy their need for an inorganic carbon source.

Alkalinity Calculations

- 7.14 mg of Alkalinity are consumed for every mg of NH_3-N converted to NO_3-N.
- If the influent contains 25 mg/L of NH_3-N, you need (25)*(7.14) = 178 mg/L of alkalinity.

Nitrification

- Residual or excess alkalinity may be needed to maintain a suitable pH range for nitrification. About 60 to 70 mg/L as $CaCO_3$.
- Literature states that alkalinity becomes rate limiting below ~100 mg/L as $CaCO_3$.
- To maintain a residual alkalinity of 100 mg/L in previous example, 278 mg/L of influent alkalinity is needed.

Sources of Alkalinity

- For every mg of _____ added, ____ mg of alkalinity as $CaCO_3$ is gained.

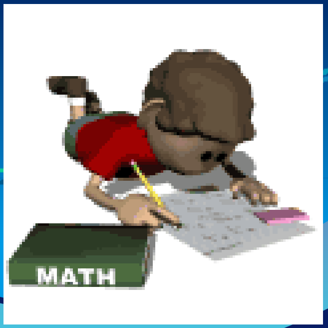
CaO	Quick Lime	1.8
$Ca(OH)_2$	Slaked Lime	1.4
$NaOH$	Caustic	1.2
Na_2CO_3	Soda	0.9

Dissolved Oxygen

- Nitrification is an aerobic process.
- Nitrifiers are OBLIGATE AEROBES
- For optimum nitrification rates, D.O. should be maintained near 2.0 mg/L.
  - Throughout the aeration basin.
  - Check D.O. levels in multiple places.
- Nitrifiers can't compete as well for oxygen as heterotrophic bacteria.
- If not enough oxygen is present, the heterotrophs will get it first.

Dissolved Oxygen

- Calculate difference in oxygen demand between no, partial, and complete nitrification.
- By definition, BOD oxidation requires 1.0 lb of oxygen for every lb of BOD
- Design engineers use 1.2 – 1.5 lbs of oxygen for every lb of BOD for calculations
- Ammonia oxidation requires 4.33 lbs of oxygen for every lb of ammonia-N.



PLANT DATA

Influent Flow = 10 MGD

Influent BOD = 250 mg/L

Influent NH3-N = 30 mg/L

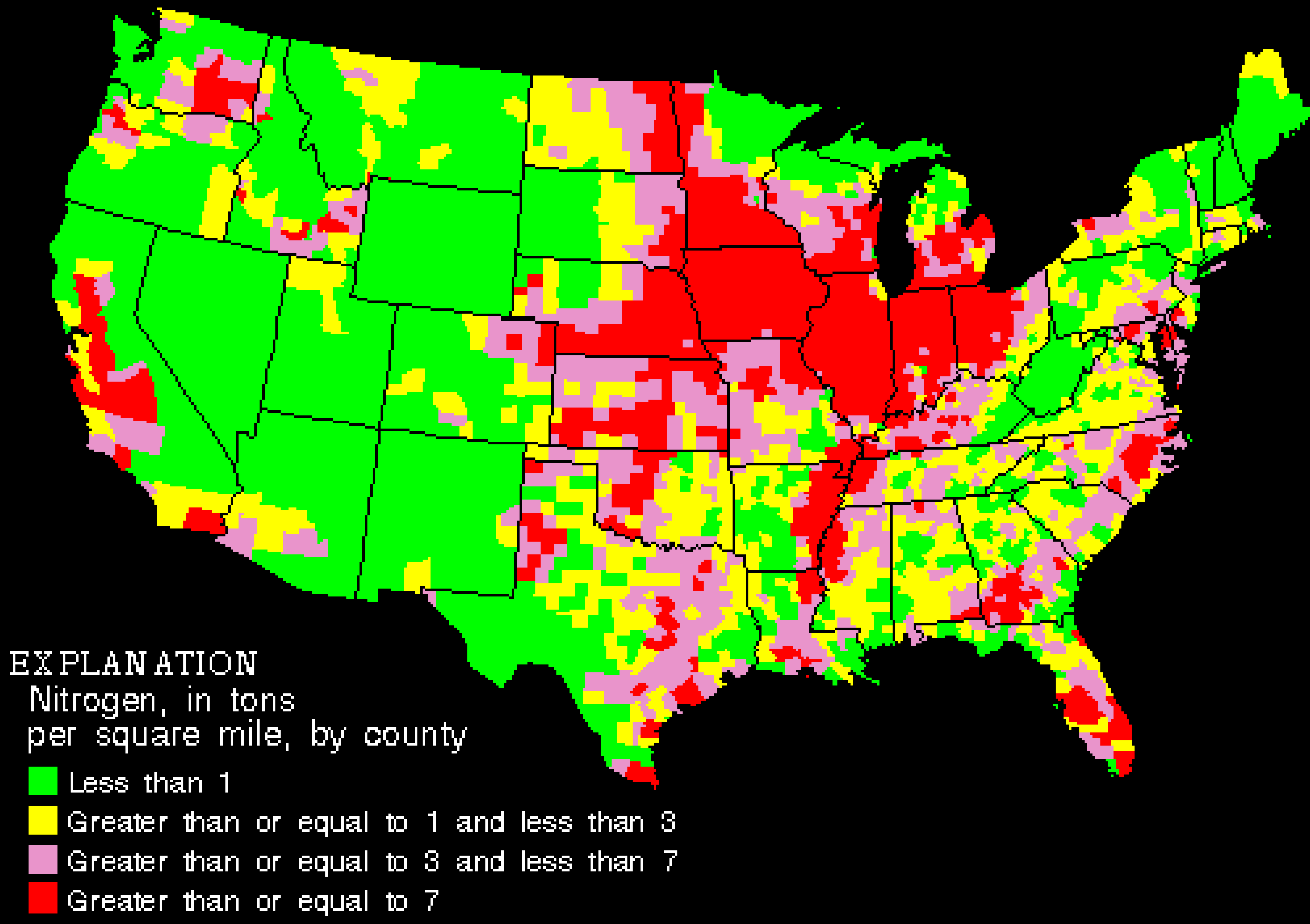
20,850 lbs/day

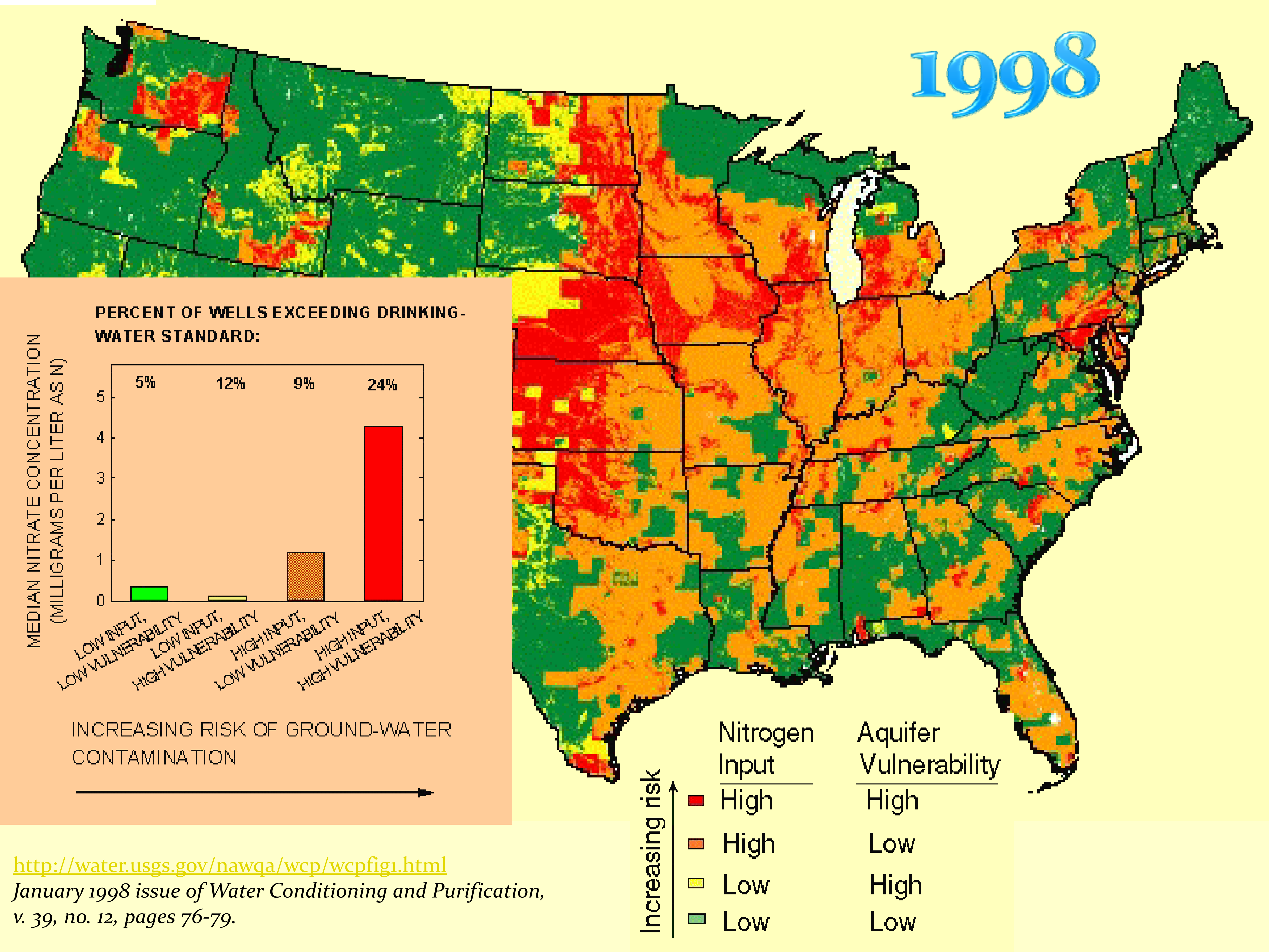
2,502 lbs/day

If there is no nitrification, ~26,000 lbs/day of oxygen.

If half of NH_3-N is nitrified, need another 5,600 lbs/day of oxygen. Double this amount for complete nitrification.

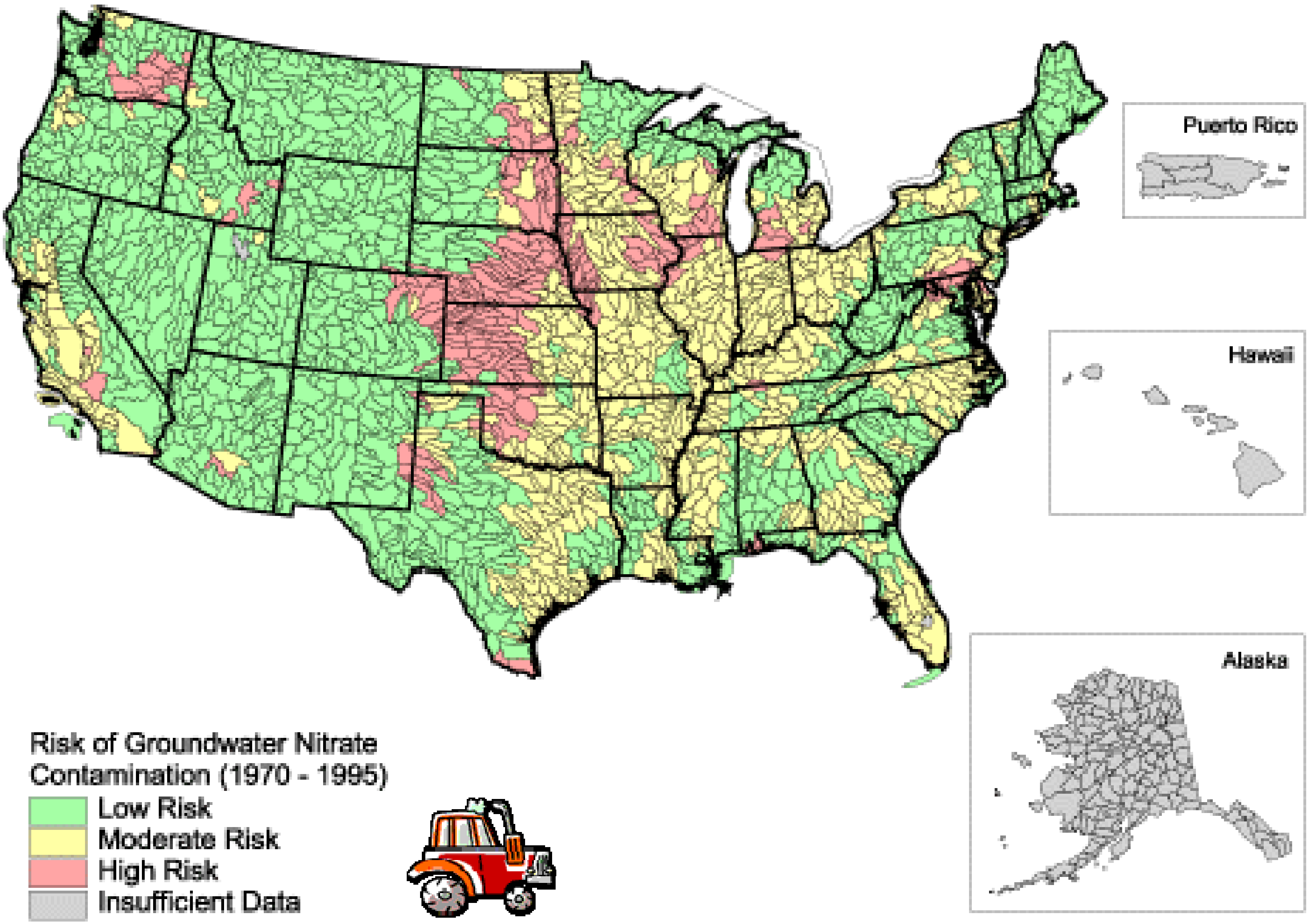
Estimated nonpoint-source inputs of nitrogen applied in commercial fertilizer, 1987





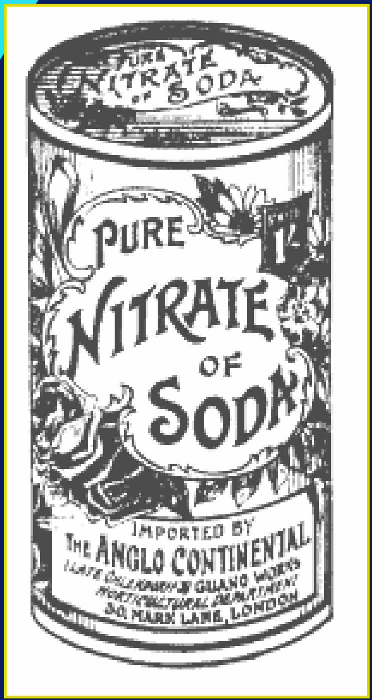
http://water.usgs.gov/nawqa/wcp/wcpfig1.html

January 1998 issue of Water Conditioning and Purification, v. 39, no. 12, pages 76-79.



Puerto Rico
Hawaii
Alaska
Risk of Groundwater Nitrate Contamination (1970 - 1995)
Low Risk
Moderate Risk
High Risk
Insufficient Data

Denitrification



- Nitrification is Only Half of the Nitrogen Removal Process.
- Nitrate also Contributes to:
  - Eutrophication of Receiving Waters
  - Aquatic Toxicity (High Concentrations)
  - "Blue Baby Syndrome"
  - Accidental Death of Cattle.
- Safe Drinking Water Limit = 10 mg/L

Denitrification

- Accomplished by Many Different Kinds of Facultative Bacteria.
- Facultative Bacteria can “breathe” Oxygen or Nitrate or Sulfate.
- Given a Choice – DO, then NO_3, then SO_4
- Denitrifiers are heterotrophs and **MUST** Have an Organic Carbon Food Source.

BOD / COD

Denitrification

Organic Carbon

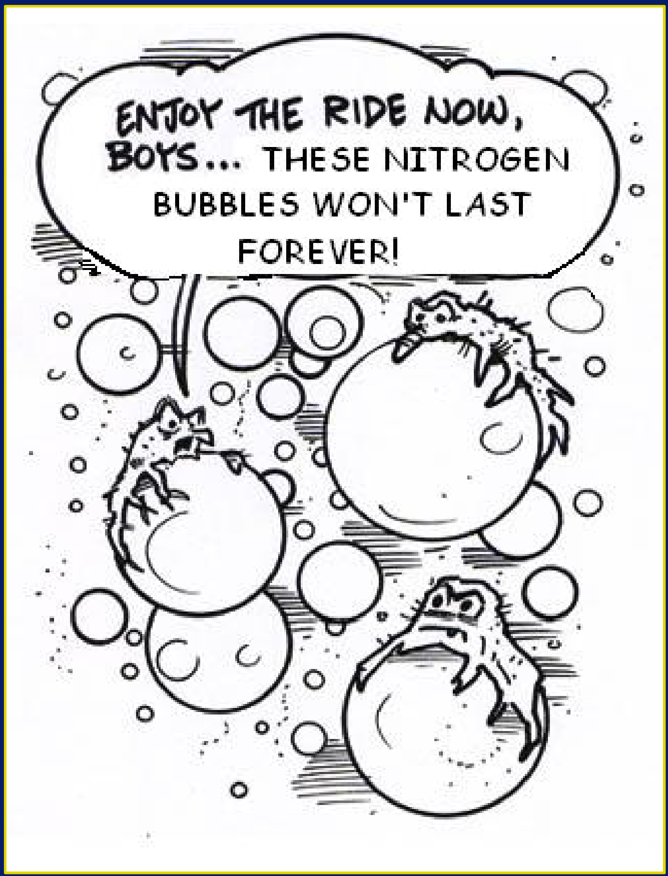
$$NO_3^- + {}^5/_6\, CH_3OH \rightarrow {}^5/_6 CO_2 + {}^1/_2 N_2 + {}^7/_6 H_2O + OH^-$$

Alkalinity

Denitrification

- Produces 3.57 grams of alkalinity per gram of NO_3-N reduced.
- Forms ~0.5 grams of new cells per gram of NO_3-N reduced.
- Consumes 1.9 grams of Organic Carbon as Methanol per gram of NO_3-N reduced. *(equivalent to 2.86 grams of COD)*

Denitrification



Conditions to Denitrify

- DO < 0.6 mg/L
- Excess nitrate
- Carbon source
  - Influent BOD
  - Methanol
  - Molasses
  - Waste Beer

Preventing Denitrification

Preventing Denitrification

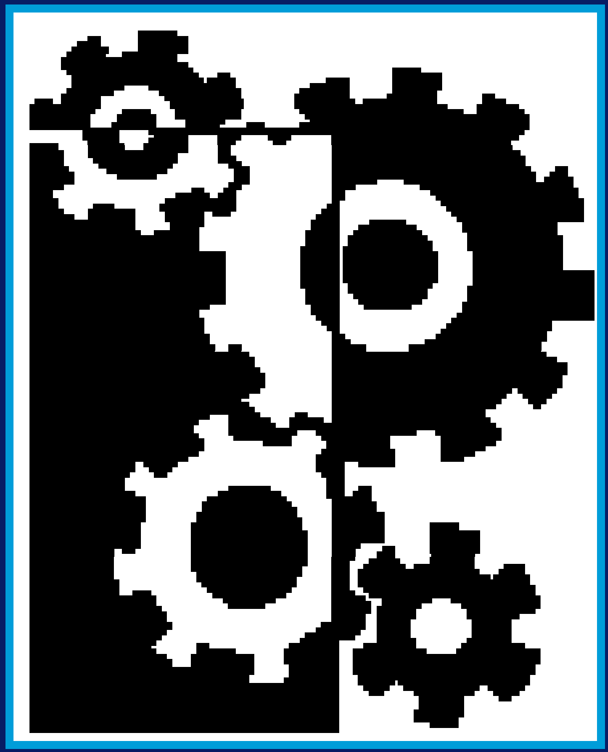
Configurations for Total Nitrogen Removal

When you need to nitrify and denitrify.

Factors to Remember

- BOD Removal
  - ✓ Uses 1.2 grams O_2
- Nitrification
  - ✓ Uses 4.33 grams O_2 per gram NH_3-N.
  - ✓ DO at 2 mg/L
  - ✓ Uses 7.14 grams alkalinity.
  - ✓ Does not use BOD.
  - ✓ Produces Acid.
- Denitrification
  - ✓ Uses nitrate instead of oxygen.
  - ✓ DO < 0.6 mg/L
  - ✓ Uses 1.90 grams methanol or 2.86 grams COD per gram of NO_3-N.
  - ✓ Produces 3.57 grams alkalinity.

How does this work?



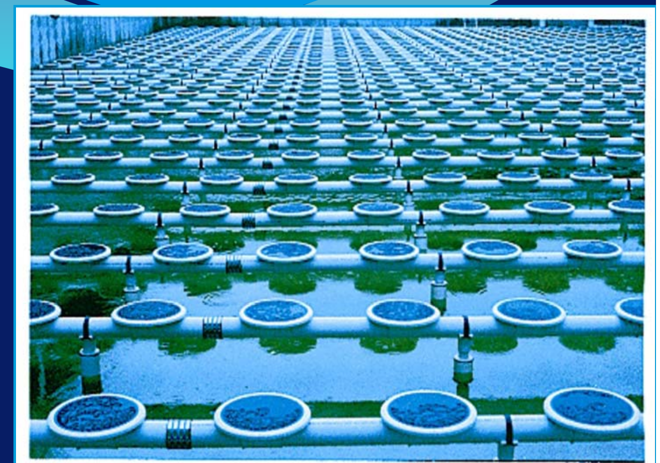
- Nitrifiers and denitrifiers do NOT have compatible needs.
  - Dissolved Oxygen
  - Organic Matter
- Nitrification must happen first.
- Denitrifiers need a carbon source.

Types of Nitrate Removal

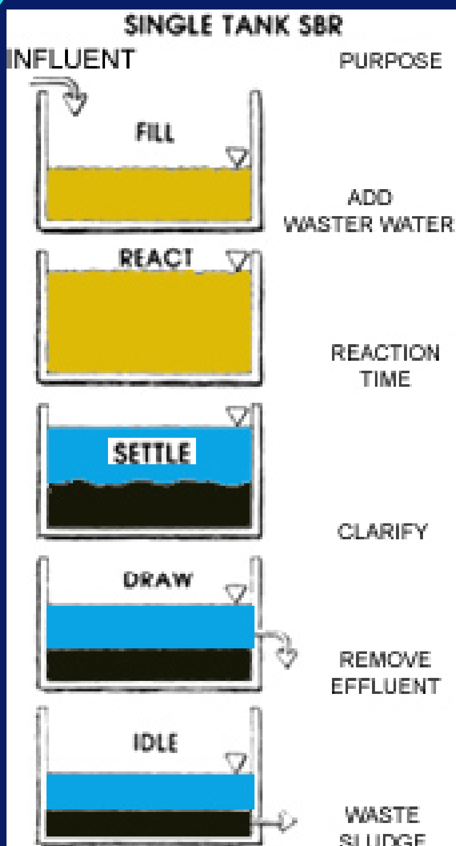
- Chemical reduction
- On/Off Aeration in Activated Sludge
- Anoxic Zones in Activated Sludge
- Tertiary Denitrification
  - BAF
- Recycle to Upstream Rock Filters

On/Off Aeration

- Nitrification and Denitrification take place in the same basin.
  - Sequencing Batch Reactor
- Control with Oxidation Reduction Potential or simply timing.
- Air on about 2/3 of total time.
- Simplest method of nitrate removal.



On/Off Aeration



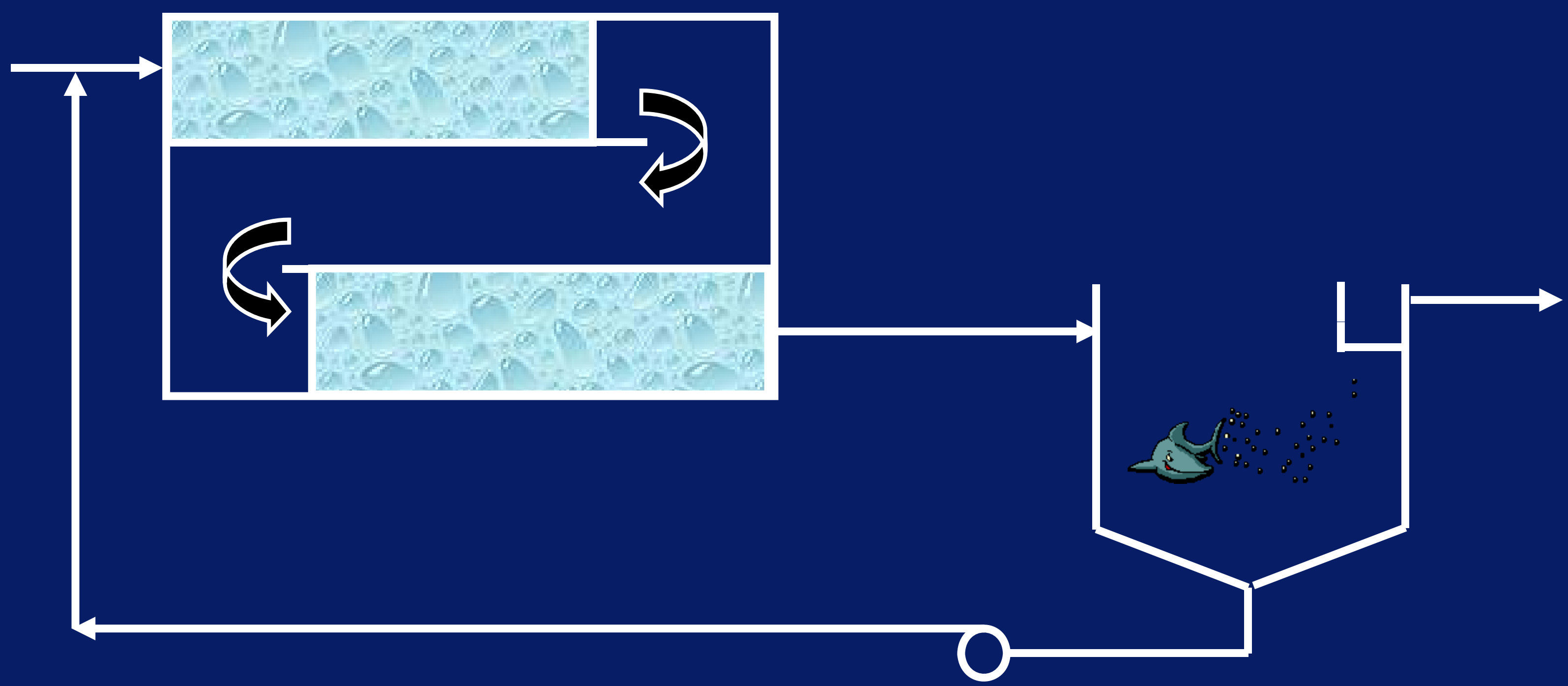
- Uses less air for BOD removal.
- Very efficient, TIN<8 mg/L.
- Prevents floating blankets in the secondary clarifiers.

- Regains alkalinity
- Moderates pH
- SBR shown, works in most systems

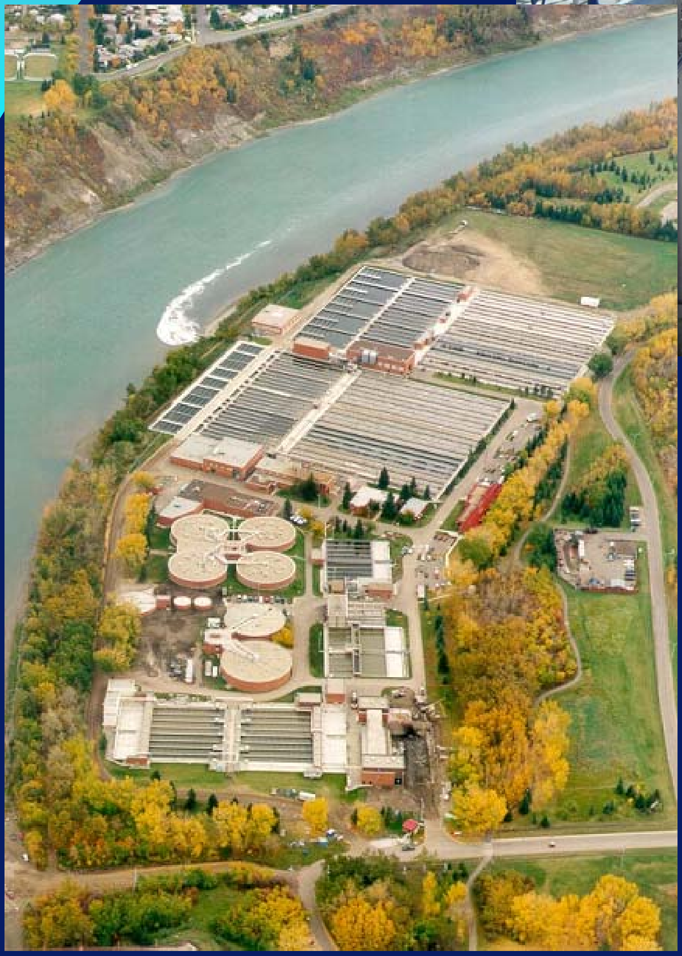
Anoxic Zones

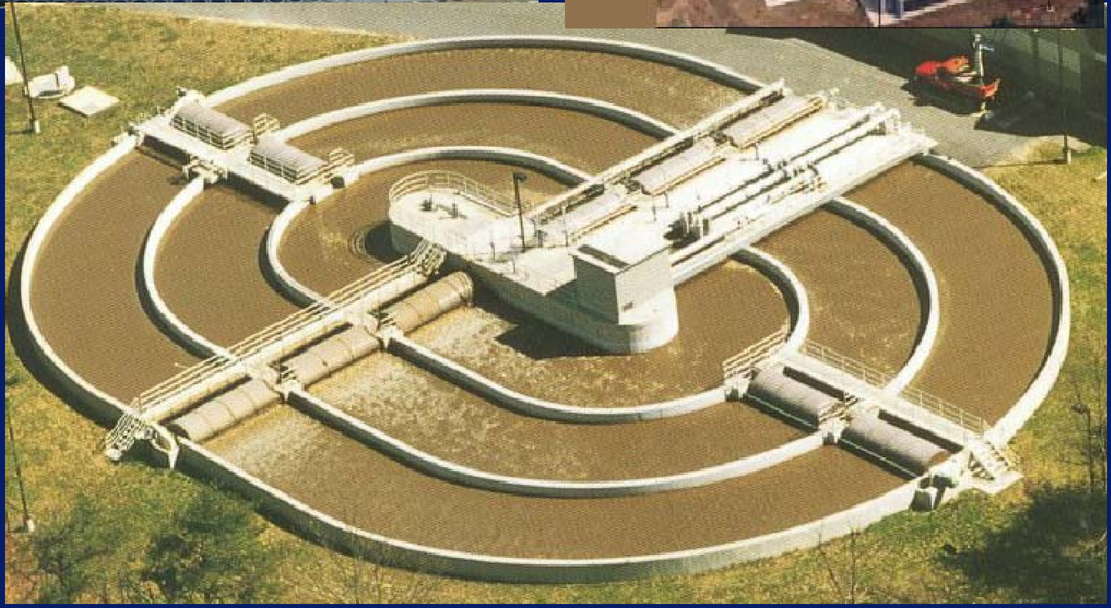
- On/Off aeration in Space instead of Time
- Aeration basin is divided in aerated and unaerated (anoxic) zones.
- Pumps MAY recirculate flow between the anoxic oxic zones.
- Total N removed depends on recycle ratio.
  - At 100% Q_{INF}, Maximum 50% removed.
  - At 200% Q_{INF}, Maximum 67% removed.
  - At 400% Q_{INF}, Maximum 83% removed.

Anoxic Zones – Plug Flow

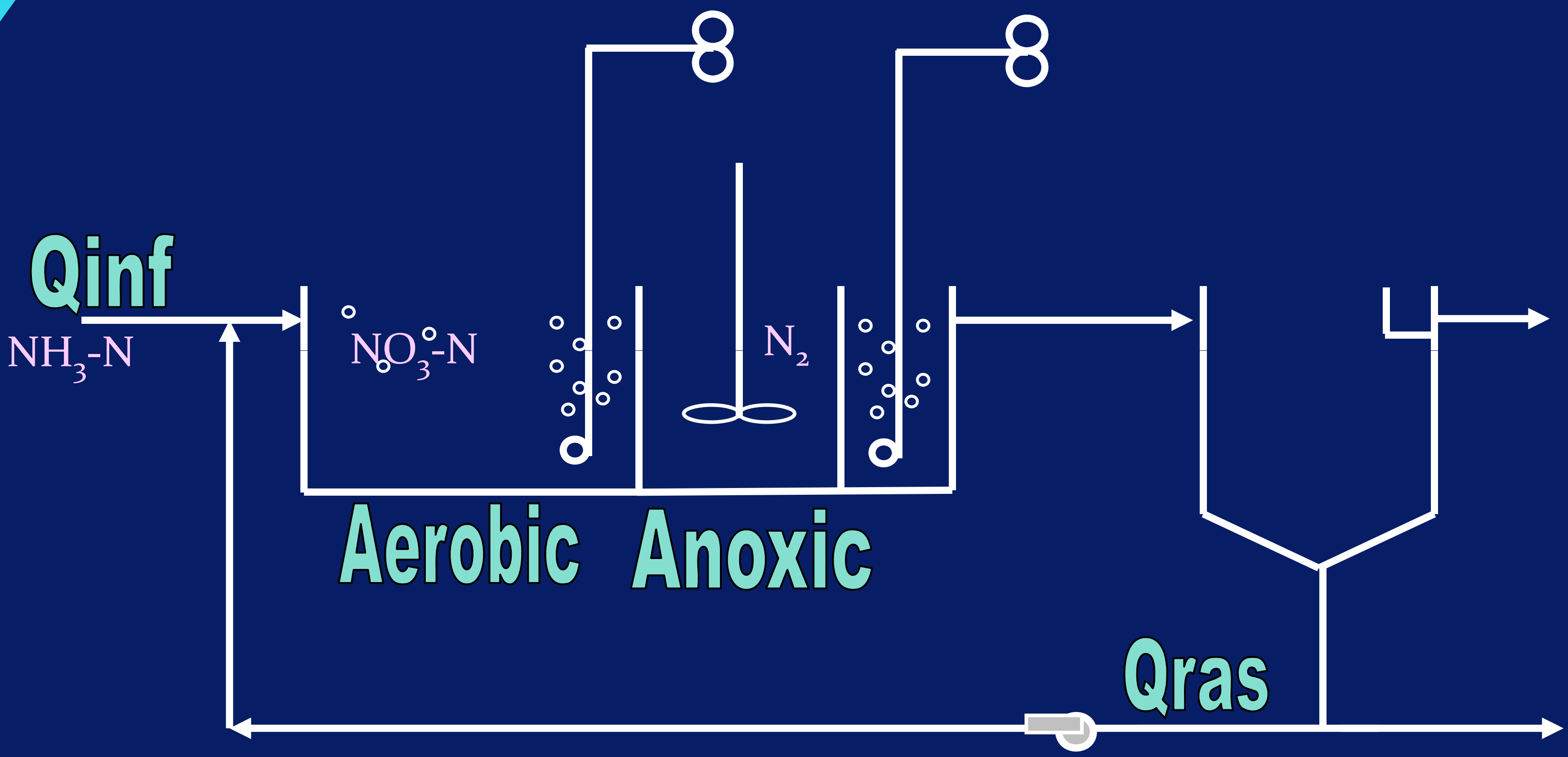


Plug Flow Activated Sludge



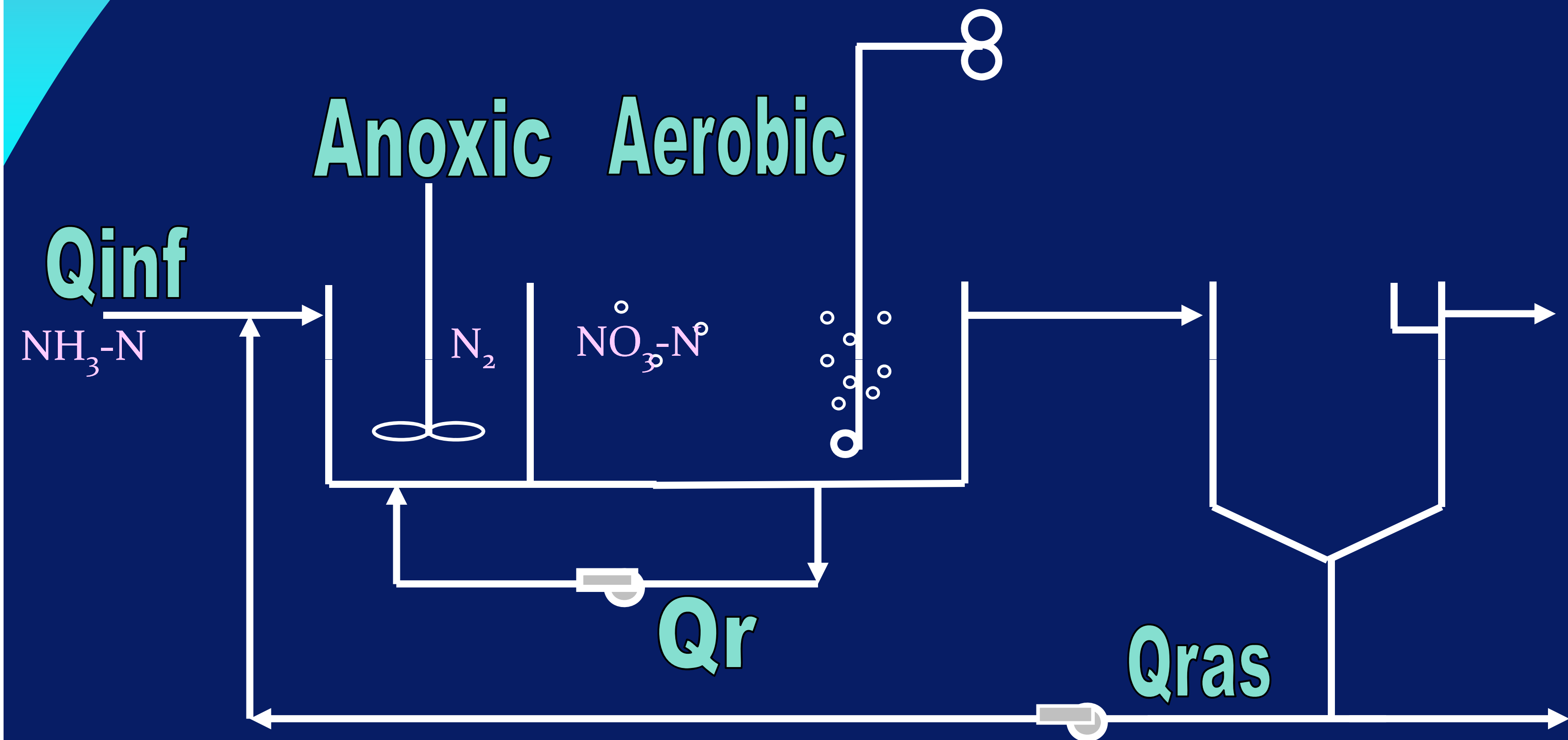


Anoxic Zones



Anoxic Zones

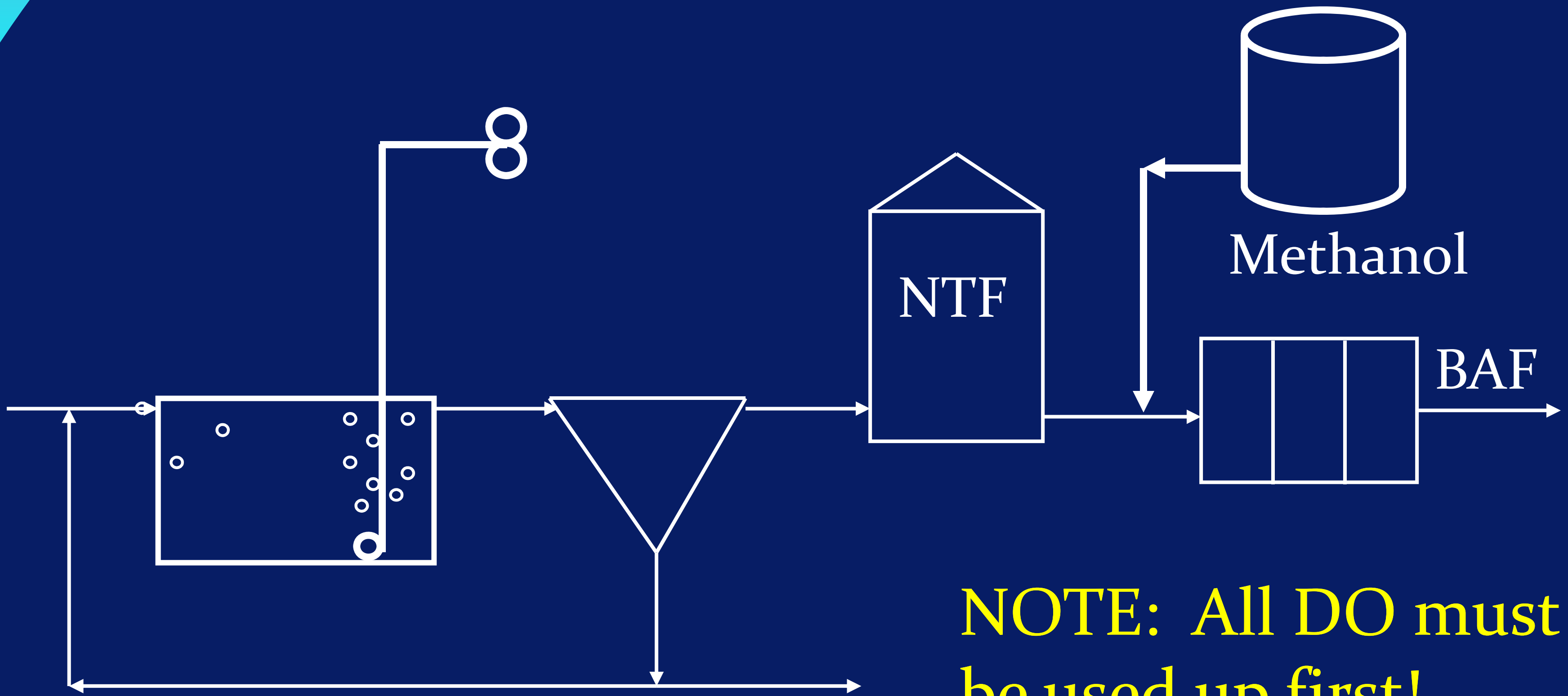
$$\frac{Qr}{Qinf} = \%\ Recycle$$



Tertiary Denitrification

- Necessary when:
  - Tertiary nitrification already in place.
  - Aeration basins not large enough to nitrify and denitrify.
  - Site constraints on process footprint.
  - Very low nitrate limits must be met.
- REQUIRES external carbon source.

Tertiary Denitrification

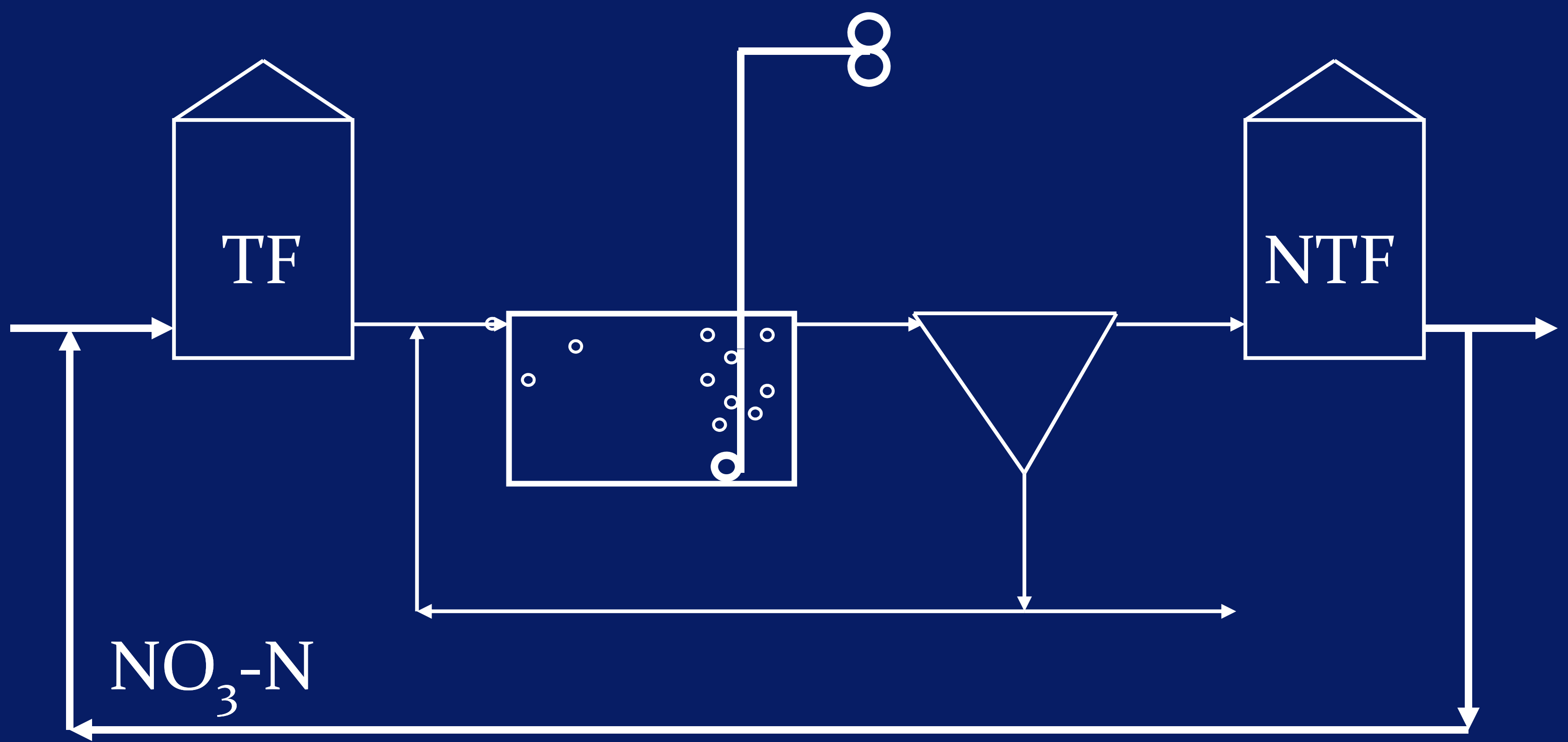


NOTE: All DO must be used up first!

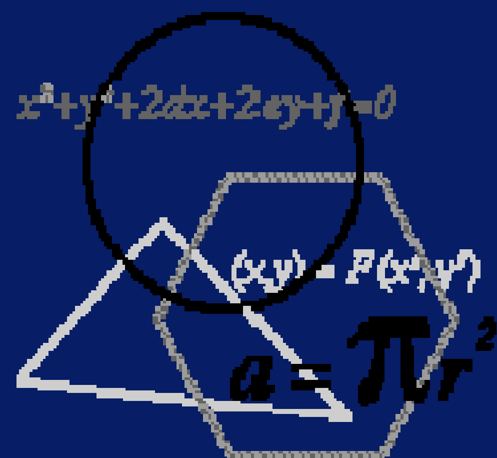
Tertiary Denitrification

- Very effective. NO_3-N < 2 mg/L
- Expensive!!!
- Does not regain alkalinity.
- Overdose of methanol may cause a permit violation.
- Safety issues surrounding methanol

Recycle to Roughing Filter



Review, Review, Review



1. This much COD is needed for every mg/L of nitrate that must be denitrified to nitrogen gas. The COD source could be primary effluent or methanol.
   A. 1.90 mg/L
   B. 2.86 mg/L
   C. 3.57 mg/L

2. This much alkalinity is regained for every mg/L of nitrate denitrified to nitrogen gas.
   A. Alkalinity is not regained in this reaction.
   B. 7.14 mg/L
   C. 3.57 mg/L
   D. 2.00 mg/L

3. With respect to natural systems, this element is most often the one that limits the growth of algae and other organisms.

A. Nitrogen
B. Iron
C. Potassium
D. Magnesium
E. Phosphorus

4. This much methanol is needed for every mg/L of nitrate that must be denitrified to nitrogen gas. Assume no other carbon source is present.
   A. 1.90 mg/L
   B. 2.86 mg/L
   C. 3.57 mg/L
   D. 4.33 mg/L

5. Within wastewater, nitrogen does not occur in which basic forms.

   A. Organic Nitrogen
   B. Nitrate
   C. Ammonia
   D. Nitrite
   E. Nitrogen gas

6. What is the correct order of nitrification?
   A. Ammonium > Nitrite > Nitrate
   B. Nitrite > Ammonium > Nitrate
   C. Ammonium > Nitrate > Nitrite
   D. Ammonium > Nitrite > Nitrate > Nitrogen gas

7. Denitrification occurs in what zone?
   A. Aerobic
   B. Fermentation
   C. Anoxic
   D. Reaeration

8. Nitrobacter bacteria obtain their energy by oxidizing nitrite nitrogen to _______ nitrogen.
   A. Nitrate
   B. Nitrite
   C. Ammonia
   D. Nitrogen gas

9. An anoxic zone is primarily used to __________.
   A. Nitrify
   B. Denitrify
   C. Remove BOD
   D. Remove phosphorus

10. Nitrosomonas bacteria obtain their energy by oxidizing ammonia nitrogen to _______ nitrogen.

A. Nitrate
B. Ammonia
C. Nitrite
D. Nitrogen gas

11. Nitrification consumes this many pounds of alkalinity for every pound of ammonia oxidized to nitrate.

12. Denitrification can be inhibited when the DO concentration is higher than this.

   A. 0.5 mg/L
   B. 1.0 mg/L
   C. 2.0 mg/L
   D. 4.0 mg/L

13. Recycle ratios of up to _______ % are necessary to achieve total inorganic nitrogen concentrations below 10 mg/L.

- 200%
- 400%
- 100%
- 800%

14. For tertiary denitrification, this supplemental carbon source is often added.
    A. Dog food
    B. Corn syrup
    C. Methanol
    D. Beer

15. This is the primary reason for limiting nitrate concentrations in receiving waters.
    A. Drinking water standard of 10 mg/L NO3-N.
    B. Excess nitrate stimulates algae blooms
    C. Excess nitrate causes odor problems downstream
    D. Nitrate is toxic to aquatic life and exerts a large oxygen demand.

16. What happens when denitrification takes place in the clarifier blanket?

17. How low does the influent sBOD to a trickling filter need to be for maximum nitrification rates?

    A. <10 mg/L
    B. <20 mg/L
    C. <50 mg/L
    D. <80 mg/L
    E. <5 mg/L

18. Since nitrification is an acid generating process, it consumes __________.

A. Chlorine

B. pH units

C. Alkalinity

D. Biochemical oxygen demand

19. While BOD removal requires 1.5 lbs of oxygen per lb of BOD, nitrification requires this many lbs per lb of ammonia nitrogen.

20. Name the two nitrifying bacteria.

A. Pfisteria and nitrobacter
B. Nitrosomonas and nitrobacter
C. Nitrosomonas and pfisteria
D. Methanogens and acid formers

21. Nitrosomonas & Nitrobacter are ______ ______, needing oxygen to survive.

   A. Aerobic bacteria
   B. Facultative aerobes
   C. Obligate aerobes
   D. Finicky aerobes

22. Theoretically, ____lbs. of alkalinity is consumed per lb. of ammonia

A. 8.34

B. 3.12

C. 6.55

D. 7.14

23. The consumption of bicarbonate alkalinity by nitrifiers has the effect of raising the pH.

A. False

B. True

24. The reduction of nitrate ion to nitrogen gas by heterotrophic bacteria is called ______________?

A. Respiration
B. Nitrification
C. Denitrification
D. Anoxic zone

25. This concentration of nitrite is typical for a wastewater treatment plant effluent.

A. <0.5 mg/L NO2-N

B. 1-3 mg/L NO2-N

C. 5-10 mg/L NO2-N

D. >10 mg/L NO2-N

26. All of these requirements must be met before denitrification can take place. Check all that apply.

a) Presence of nitrate.
b) Absence of oxygen.
c) Presence of food (BOD)
d) Absence of a carbon source.
e) Methanol addition.

27. While nitrification is carried out by specialized autotrophic bacteria, denitrification can be done by a variety of these.

A. Coliforms
B. Heterotrophs
C. Anaerobes
D. Obligate aerobes
E. Ciliates

28. It is advantageous to denitrify following nitrification as nearly half of this may be recovered.

A. Dissolved Oxygen
B. Alkalinity
C. Nitrogen
D. Suspended solids
E. Phosphorus

29. This common atmospheric gas is the end product of denitrification.

A. Carbon Dioxide
B. Oxygen
C. Water vapor
D. Nitrogen Gas

30. Nitrogen sources in a wastewater treatment plant include all of these except

A. Digester supernatant return
B. Septic receiving
C. Industrial discharges
D. Urine and feces
E. Return activated sludge

31. Nitrogen ammonia is typically this percentage of the TKN entering a wastewater treatment plant

A. 30%
B. 60%
C. 90%
D. None of these is correct.

32. The process of chemically burning nitrogen away with sodium hypochlorite is referred to as

A. Chlorooxidation
B. Breakpoint chlorination
C. Ion exchange
D. Chemo-vaporization

33. As water temperatures drop, the MCRT should be ___________ to maintain stable nitrification.

A. Set to 10 days
B. Increased
C. Decreased
D. Set above 5 days

Answers

1. B
2. B
3. E
4. A
5. E
6. A
7. C
8. A
9. B
10. C
11. 7.14
12. A
13. B
14. C
15. A
16. Blanket pops or Ashing
17. B
18. C
19. 4.33
20. B
21. C
22. D
23. A
24. C
25. A
26. A. B, and C are correct
27. B
28. B
29. D
30. E
31. B
32. B
33. B

Fun With Math

INFLUENT DATA

- Q = 3 MGD
- NH_3-N = 25 mg/L
- NO_3-N = 5 mg/L
- Alk = 260 mg/L
- BOD = 225 mg/L

CALCULATE

- Effluent Alkalinity
  - Nitrification
  - Denitrification
- Pounds Methanol to Add
- Oxygen Demand

Questions?

Thank You for Coming!