Nitrogen

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Bend, OR
Nitrogen in the Environment
## Where Nitrogen is Found

<table>
<thead>
<tr>
<th></th>
<th>ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Universe</td>
<td>1,000</td>
</tr>
<tr>
<td>Earth’s Crust</td>
<td>20</td>
</tr>
<tr>
<td>Fresh water</td>
<td>0.24</td>
</tr>
<tr>
<td>Sea water</td>
<td>0.5</td>
</tr>
<tr>
<td>Human*</td>
<td>26,000</td>
</tr>
</tbody>
</table>

*80 kg (176 lb) person has 2,080 grams (4.6 lb) of N
Nitrogen is Neither Lost nor Created

- **Ammonia Nitrogen, NH₃**
- **Atmospheric Nitrogen, N₂**
- **Nitrate Nitrogen, NO₃**
- **Nitrite Nitrogen, NO₂**

- **Fixation of Nitrogen**
- **Electrical Discharge**
- **Degradation**
- **Nitrification (Aerobic)**
- **Denitrification (Anoxic)**
Reason for Concern: **Nitrogen Has Doubled in Ecosystems in Past 100 yr.**

This increase coincides with increases in population and industrialization.
Impacts of Nitrogen Pollution

- Ammonia and nitrite toxicity
- Blue baby syndrome
- Oxygen sag
  - Eutrophication
  - Hypoxia – dead zones
Hypoxia - Dead Zones

Even before the oil spill the Gulf has had large areas of DO < 2 mg/L

6,200 square miles
Natural Sources of Nitrogen in Water

- Urea
- Decomposition
- Fixation
- Electrical Discharge
Manmade Nitrogen in Water

- Combustion of Fossil Fuels returns as precip.

- Agriculture –
  - Farming – N fertilizers, N fixers (soybeans, peas)
  - Livestock

- Point Sources (WWTPs) - minor, but significant
Nitrogen in Wastewater

- Human waste – 12 g N per person/day
  - 150 gal/person/d (567 L) = 21 mg/L N
- Food waste
- Fertilizer manufacture
- Contribution from detergents
Classification of Nitrogen Compounds

Total Kjeldahl Nitrogen (TKN)

Nitrite, Nitrate

Organic N

Ammonia

Total Nitrogen (TN)

TIN
## Concentrations of Nitrogen in Wastewater Influent

<table>
<thead>
<tr>
<th>Nitrogen</th>
<th>mg/L</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total</td>
<td>20 to 85</td>
</tr>
<tr>
<td>Organic</td>
<td>8 to 35</td>
</tr>
<tr>
<td>Ammonia</td>
<td>12 to 50</td>
</tr>
<tr>
<td>Nitrite</td>
<td>&lt; 1</td>
</tr>
<tr>
<td>Nitrate</td>
<td>&lt; 1</td>
</tr>
</tbody>
</table>
Septage and Side Streams

- Anaerobically Digested Sludge Dewatering Filtrate
  800 mg/L TKN - typical
- Septage 100-800, average 400 mg/L TKN

As we will discuss later these side streams can be a problem for nitrifying systems.
Regulatory Agencies Moving Toward Nutrient Limitations

- Ammonia < 1.0 to < 3.0 mg/L
- Total Nitrogen < 10 mg/L

<table>
<thead>
<tr>
<th>Metric</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Average Daily Total Suspended Solids (TSS)</td>
<td>2.4 mg/L</td>
</tr>
<tr>
<td>Maximum Daily TSS</td>
<td>10.2 mg/L</td>
</tr>
<tr>
<td>Average Daily Ammonia (as N)</td>
<td>0.72 mg/L</td>
</tr>
<tr>
<td>Average Daily Nitrate + Nitrite (as N)</td>
<td>7.33 mg/L</td>
</tr>
<tr>
<td>Average Daily Total Dissolved Solids</td>
<td>242 mg/L</td>
</tr>
<tr>
<td>Average Daily Electrical Conductivity</td>
<td>392 μmhos/cm</td>
</tr>
</tbody>
</table>

1 5-day, 20°C biochemical oxygen demand
3 ways N leaves WWTP

- Effluent
- Sludge
- Atmosphere
Nitrogen Removal
Treatment Methods

- **Biological - Nitrification/Denitrification**

- **Physical/Chemical**
  - Air Stripping
    - Raise pH to 11 - 12
    - Aerate
    - Occurs with sludge lime stabilization
Breakpoint Chlorination Curve

At breakpoint 7-10 Cl₂ to 1 NH₃

- Initial Chlorine Demand
- Inorganic Compounds Replacing Agents
  - Formation of chloro-organic compounds and chloramines
- Combined residual
  - Oxidation of Combined Residual
  - Formation of free chlorine and presence of chloro-organic compounds not oxidized
- Combined residual
  - Free and combined residual
  - Breakpoint

Chlorine residual, mg/L

Chlorine dosage, mg/L
Nitrification: Results of Removing One Pound of Ammonia Nitrogen

4.2 LB of oxygen are consumed
  – Doubles Carbon Removal Oxygen Demand

7.1 LB of alkalinity are consumed
  – Lowers pH

0.08 LB of inorganic carbon are consumed

0.17 LB of new cells are formed
Nitrification Step 1

- **Nitrosomonas**

  \[
  2\text{NH}_4^+ + 3\text{O}_2 + \text{inorganic-C} > 2\text{NO}_2^- + 2\text{H}_2\text{O} + 4\text{H}^+ + \text{new cells}
  \]

  **Forms Nitrite**

  **Forms Acid**

  **Consumes Oxygen**

  **Nitrosomonas growth rate controls the nitrification rate**
Nitrification Step 2

- **Nitrobacter**
  
  $2\text{NO}_2^- + \text{O}_2 + \text{inorganic-C} \rightarrow 2\text{NO}_3^- + \text{new cells}$

The growth rate of nitrifiers is 10 – 20 slower than heterotrophs.
Nitrifiers' Growth Rate Depends on …

- Total Kjeldahl Nitrogen (TKN) concentration
- Dissolved oxygen (DO)
- pH
- Temperature
- Alkalinity
Nitrifiers' Growth Rate Depends on TKN Concentration

In a nitrifying system the nitrifier population will increase to match the average TKN concentration.
Dissolved Oxygen (DO) Requirement

- Nitrifiers are obligate aerobes.
- AB target range DO should be 2.0 – 4.0 mg/L.
- Nitrification can occur at DOs as low as 0.3 mg/L

At 17°C and pH 7
pH and Nitrification

- Optimal - 7.2 to 8.0.
- The growth at 6.5 rate is half the rate at pH 7.2
Temperature

Decrease from 20°C (68°F) to 15°C (59°F) = 38% decrease in nitrifier growth rate
Alkalinity

- Less than 50-60 mg/L inhibits nitrification
- Typical raw wastewater = 120 – 250 mg/L alkalinity
- For Example:
  - Influent TKN = 21 mg/L, then 7.1 x 21 = 149 mg/L + 50 = ~199 mg/L needed for nitrification
  (Assumes no denitrification)
Denitrification

- Heterotrophic bacteria
  - Grow 10-20 times faster than nitrifiers
- Switch from oxygen to nitrates in anoxic conditions
- COD/TKN ratio of 8+
- Restores alkalinity
Denitrification

$\text{NO}_3^- + \text{CH}_3\text{OH} + \text{H}_2\text{CO}_3 \ (\text{Carbonic Acid})$

Satisfies O$_2$ Requirement

$\text{NO}^\wedge, \text{N}_2\text{O}^\wedge, \text{N}_2^\wedge + \text{H}_2\text{O} + \text{HCO}_3^- \ (\text{Bicarbonate})$

Increases Alkalinity

Gaseous forms of N
Results of Removing One Pound of Nitrate Nitrogen

- 2.86 LB of oxygen demand are satisfied
- 3.6 LB of alkalinity are produced
- 2.47 LB of organic-C are consumed
- 0.45 LB of new cells are produced
Factors Affecting Denitrification

- $\text{NO}_3^-$ concentration
- $\text{O}_2$ concentration
  - $\text{O}_2 > 0.5$ suppresses activity
- Source of organic-C
  - Rate limiting
- pH between 7 and 8
  - Optimal
Benefits of Denitrification

- Reduces nitrate and nitrite
- Reduces BOD
- Produces alkalinity (raises pH)
- Reduces aeration requirement
- Improves phosphorus removal
Nit/Denit Can Occur at the Same Time if O$_2$ Cannot Penetrate to the Floc Completely

Simultaneous nitrification / denitrification can occur in the reactor and/or the clarifier
WWT Processes for Biological Nitrogen Removal
Oxidation Ditch Used for N Removal

Aerator
(Aerobic zone)
(Aerobic zone)
DO probe

H3 > NO

DO 2-4 mg/L

NO3 Source

DO < 0.5 mg/L

NO3 > N2^*
SBR Operating Sequence to Remove N

1. **Fill**
   - **Influent**
   - **Carbon Source**
     - **NO3 Source**
   - **NO3 > N2^**
   - **Anoxic (air off, mixer on)**

2. **React**
   - **DO < 0.5 mg/L**
   - **NH3 > NO3**
   - **Aerobic (air on)**

3. **Settle**
   - **Air off, mixer off**

4. **Decant**
   - **Effluent**
   - **Denitrification may start during idle stage**

5. **Idle**
   - **WAS**
     - **Air and/or Mixer on and/or off**
Activated Sludge Nitrification/Denitrification Process Schematic

Variations:
- A2/O Process
- Bardenpho Process
- Membrane Bioreactor (MBR)

Diagram:
- Carbon Source
- NO₃ Source
- DO < 0.5 mg/L
- NH₃ > NO₃
- DO 2-4 mg/L
- ML Pump
- RAS, 0.5 Q
- RAS pump
- WAS
Non-Nitrification Process Control Strategy

- Anticipate wastewater temperature
  - As WW temperature increases lower SRT
- Match biomass to BOD
- Monitor lead indicators
  - Alkalinity (Influent – Effluent)
  - Effluent Nitrites (NO₂)
Non-Nitrification Process Control Strategy

- Maintain AB DO of 2 – 4 mg/L, especially at the front end of the aeration basin
  - Lower DO short term only if needed
- If nitrification can not be avoided:
  - Create anoxic zone to recapture energy, alkalinity
  - Recycle mixed liquor
Nitrification without Denitrification Control Strategy

- Avoid clarifier denitrification
  - Increase RAS Flow
- Monitor pH for permit and process
- Maintain Nitrifying SRT based on temperature, pH, and DO.
  - Use nitrification model to determine SRT
  - Possibly run nitrification profile
Nitrification Profile

Nitrification complete in first 2/3 of aeration basin leaving 1/3 for safety factor

NH$_3$ / NO$_3$ Samples

NH$_3$ Conc.

Detention Time
Nitrification with Denitrification Control Strategy

- SRT based on temp, pH, DO + safety factor
- Maintain enough biomass for BOD
- Mixed liquor return 1-4 x Influent Flow
- Return rates 30-100% Influent Flow
- Monitor anoxic zone DO and Oxygen Reduction Potential (ORP)
- Monitor aerobic zone DO
Nitrification with Denitrification

Maintain DO at front end of aerobic zone > 2 mg/L to reduce filamentous bacteria

Carbon Source

NO₃ Source

DO 2-4

Aerobic

NH₃ > NO₃

RAS, 0.5 Q

Q

Anoxic

NO₃ > N₂

ORP 0 - -300 mv

DO < 0.5

RAS pump

ML Pump

WAS

Q
Sources of DO in Anoxic Zones

- Mixed liquor recycle
- Cascading influent and/or RAS
- Back mixing from aerobic zone
Seasonal Nitrification

- Surface water discharge, required to nitrify in summer and not in winter.
- Reversed when water is used for reuse in summer and discharged in winter.
Moving from Non-Nitrifying to Nitrifying

- Target nitrifying SRT for conditions
- Start 3-4 sludge ages before target
  - Remember nitrifiers are slow growing
- Change rapidly to minimize nitrite lock
- Use nitrifying seed for < 13C (55F)
The Reverse - Nitrifying to Non-Nitrifying

- Target non-nitrifying SRT
- Begin at end of nitrifying period
- Decrease SRT rapidly
Move Rapidly In and Out of Nitrification to Avoid Partial Nitrification

For 20 degrees C

Denitrification in Clarifier
NO₂ > N₂

As the temperature decreases
the MCRT required increases

Partial Nitrification

NO₂ and NH₃
Interference with Cl₂
Disinfection
Seasonal Nitrification Oxygen Requirement for cBOD and nBOD

O₂ required changes moving in and out of nitrification

O₂ Consumed (relative)

nBOD

cBOD

MCRT, Days

0 5 10 15 20 25 30

0 20 40 60 80 100

CH2M HILL
Nitrification/Denitrification with Biological Phosphorus Removal

- Biological P removal works best at low SRT
- Same Strategy as Nitrification/Denitrification:
  + Minimum SRT based temp, pH, DO
  + Nitrates in RAS upsets P removal

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**Diagram:**

- **Anaerobic**
  - P Release
  - DO = 0
  - ORP < -300 mv

- **Anoxic**
  - DO < 0.5
  - ORP 0 - -300 mv

- **Aerobic**
  - DO = 2-4

- **RAS, 0.5 Q**
  - NO3 ~ 0

- **WAS**

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**Flowchart**

- 1-2Q
- ML Pump
- RAS pump
- Q
- Q

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**Legend:**

- Carbon Source
- Q
- ML Pump
- ORP < -300 mv
- P Uptake
Nitrogen Treatment Problems
Toxics that inhibit the nitrification process

- Herbicides > 0.0 mg/L
  - Collection system root control
- Thiourea > 0.0 mg/L
- Halogenated solvents > 0.0 mg/L
- Heavy metals > 10 to 20 mg/L
- Cyanide > 1 to 2 mg/L
- Wood preservatives > 20 mg/L
Ammonia Bleed Through

Nitrifiers match avg. loading

High NH₃ loading caused by side streams
Ammonia Bleed Through Mitigation

WWTP Diurnal TKN

- **Belt Press**
- **Septage**
- **Influent**

**Avg. N removal increases**
**Fewer spikes exceed capacity**

**Move dewatering to earlier in the day**
Chlorination

- Erratic nitrite demand
- Breakpoint chlorination
Excess Filamentous Bacteria Causing Foaming and/or Bulking

Quick Fix
Cl2 to RAS, Mixed Liquor

Reduce Solids Loading to Clarifier

For the long term ...
Control of Filamentous Bacteria

- Maintain a minimum SRT for process goals
  - Filaments grow more slowly than floc formers
- Use clarifier model to predict loading
Control of Filamentous Bacteria Foaming

- Do not let foam accumulate
  - Keep foam moving toward skimmers.

- Do not return foam to the head of the plant.
  - Ideally get foam completely out of the system.

- Spray concentrated (0.1 to 0.35 percent) chlorine directly on foam accumulations
  - Not very effective
Control of Foam in Anaerobic Digesters

- Foam gas separator for fixed cover
- Spray bars for floating cover
- Treat the foam at it’s source – the activated sludge
Discussion