Nitrogen Removal Training Program

Module 1
Nitrogen in the Aquatic Environment

- **Forms of Nitrogen and Nitrogen Transformations**
- **Nitrogen in Surface Waters**
- **Water Quality Impacts of Nitrogen Discharges**
- **Nitrogen in Wastewater**

Forms of Nitrogen and Nitrogen Transformations

Forms of Nitrogen in the Environment

Unoxidized Forms of Nitrogen

- Nitrogen Gas (N_2)
- Ammonia (NH_4^+, NH_3)
- Organic Nitrogen (urea, amino acids, peptides, proteins, etc...)

Oxidized Forms of Nitrogen

- Nitrite (NO_2^-)
- Nitrate (NO_3^-)
- Nitrous Oxide (N_2O)
- Nitric Oxide (NO)
- Nitrogen Dioxide (NO_2)

Nitrogen Fixation

- **Biological Fixation - Use of atmospheric nitrogen by certain photosynthetic blue-green algae and bacteria for growth.**

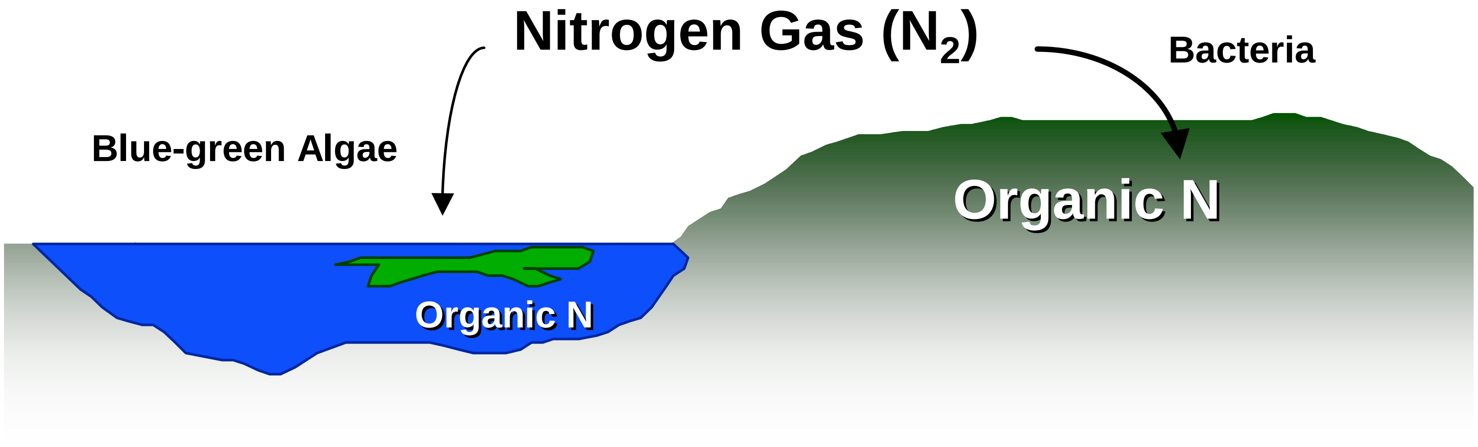
  Nitrogen Gas (N_2) → Organic Nitrogen

- **Lightning Fixation - Conversion of atmospheric nitrogen to nitrate by lightning.**

  Nitrogen Gas (N_2) + Ozone (O_3) —***lightning***→ Nitrate (NO_3^-)

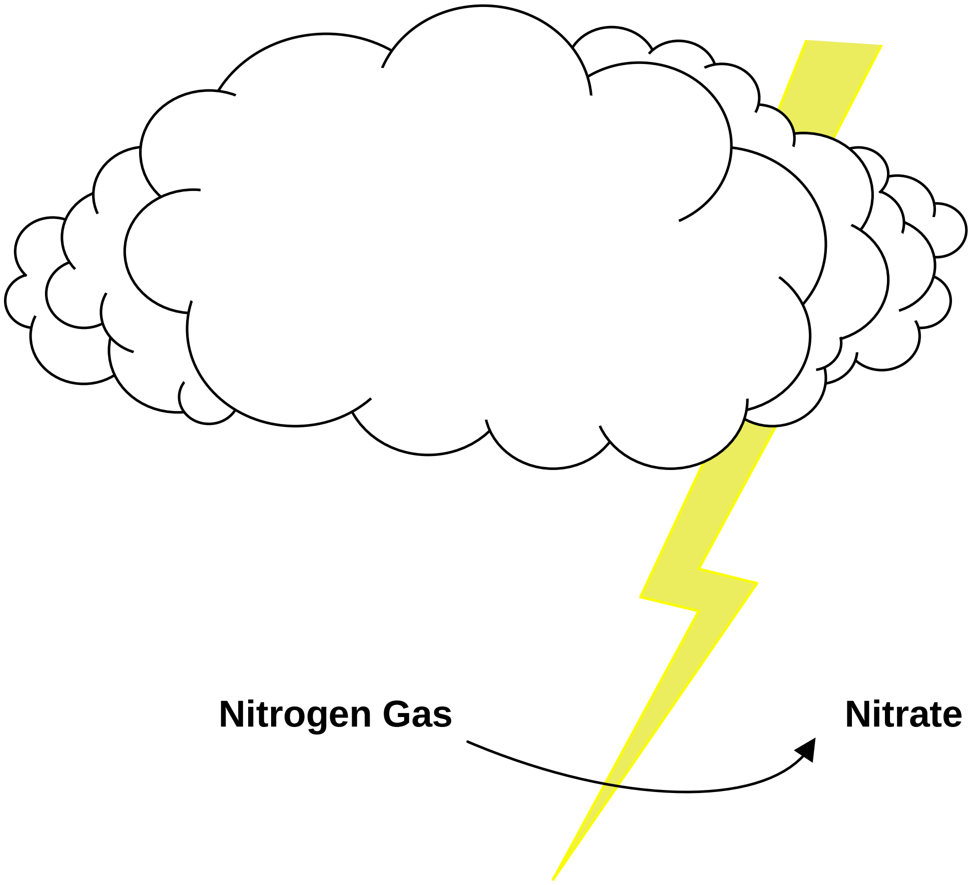
- **Industrial Fixation - Conversion of nitrogen gas to ammonia and nitrate-nitrogen (used in the manufacture of fertilizers and explosives).**

Biological Nitrogen Fixation



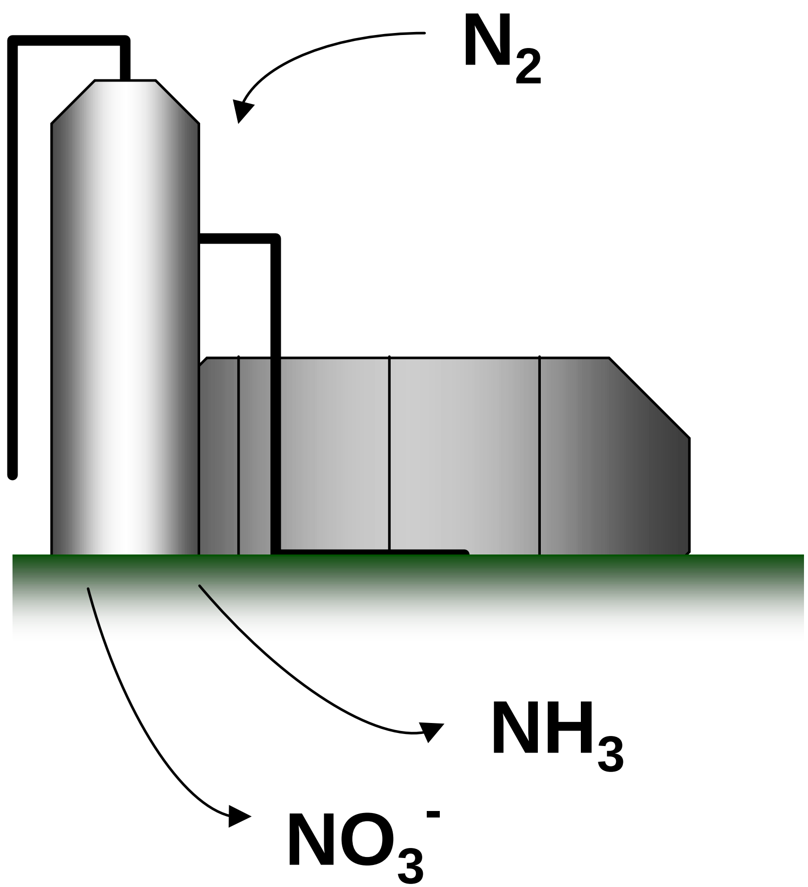
Certain blue-green algae and bacteria use atmospheric nitrogen to produce organic nitrogen compounds.

Atmospheric Fixation



Lightning converts Nitrogen Gas and Ozone to Nitrate.

Industrial Fixation



Nitrogen gas is converted to ammonia and nitrate in the production of fertilizer and explosives.

Ammonification and Assimilation

Ammonification - Conversion of organic nitrogen to ammonia-nitrogen resulting from the biological decomposition of dead plant and animal tissue and animal fecal matter.

Organic N + microorganisms $\longrightarrow$ ammonia (NH_4^+/NH_3)

Assimilation - Use of ammonia and nitrate-nitrogen by plants for growth

Ammonia (NH_4^+/NH_3) + Carbon Dioxide (CO_2) + Sunlight + Plants $\longrightarrow$ Plant Tissue (Organic N)

Nitrate (NO_3^-) + Carbon Dioxide (CO_2) + Sunlight + Plants $\longrightarrow$ Plant Tissue (Organic N)

Hydrolysis and Amination

Hydrolysis - Conversion of organic nitrogen to ammonia nitrogen by enzymes secreted by bacteria, plants and animals in a reaction which adds water.

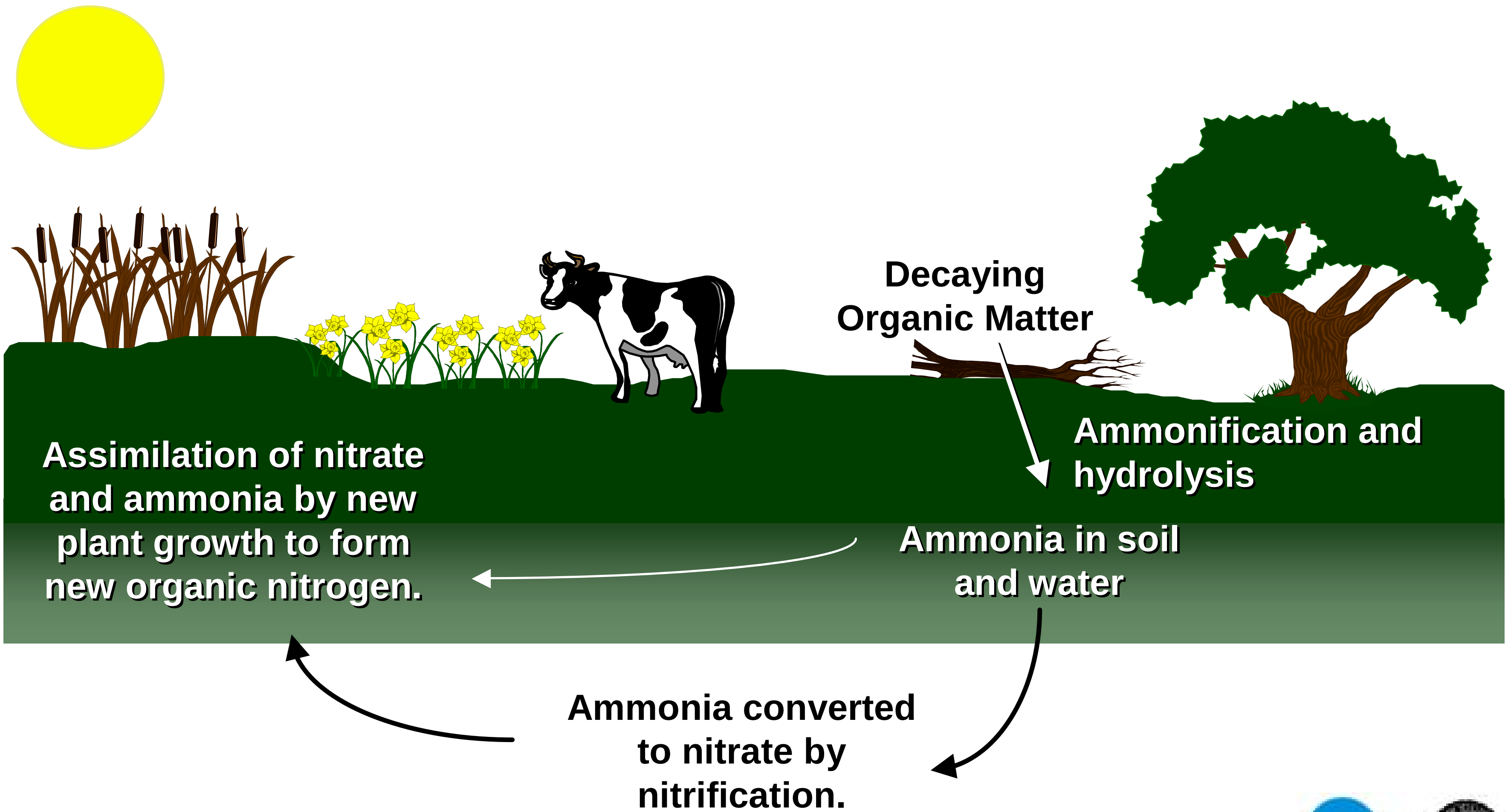
$$\underset{\text{(Protein)}}{C\text{-}NH_2} + H_2O \xrightarrow{\text{Protease}} \underset{\text{(Organic C)}}{C\text{-}OH} + \underset{\text{(Ammonia)}}{NH_3}$$

$$\underset{\text{(Urea)}}{H_2NCONH_2} + H_2O \xrightarrow{\text{Urease}} \underset{\text{(Bicarbonate)}}{HCO_3^-} + \underset{\text{(Ammonia)}}{NH_3}$$

Amination - Use of ammonia-N by bacteria to form new bacteria

$$\text{Ammonia} + \text{Organic C} + \text{Oxygen} + \text{Phosphorus} \longrightarrow \text{New Bacteria}$$

Ammonification & Hydrolysis Followed by Nitrification and Assimilation



Combustion (Incineration)

Incineration

Biomass + Oxygen ⟶ Carbon Dioxide + Oxidized - N + Water Vapor

(contains C,H,N,P) { N_2O, NO, NO_2}

Automobile Combustion of Fossil Fuels Containing Nitrogen

Incomplete Oxidation Generates N_2O (Nitrous Oxide)

Additional Oxygen Converts it to Nitric Oxide

$$2N_2O + O_2 \longrightarrow 4NO$$

Substantial Excess Oxygen Can Convert it to Nitrogen Dioxide

$$2NO + O_2 \longrightarrow 2NO_2$$

Dissolution of Combustion Products

Acid Rain From Stack Emissions

Nitric Oxide + Oxygen + Water → Nitrous Acid → Nitric Acid

$$4NO + O_2 + 2H_2O \rightarrow 4HNO_2$$

Nitrous Acid

$$2HNO_2 + O_2 \rightarrow 2HNO_3$$

Nitric Acid

Nitrogen Dioxide + Water → Nitrous Acid → Nitric Acid

$2NO_2$ H_2O $2HNO_2$

Acid Enters Soil As Acid Rain

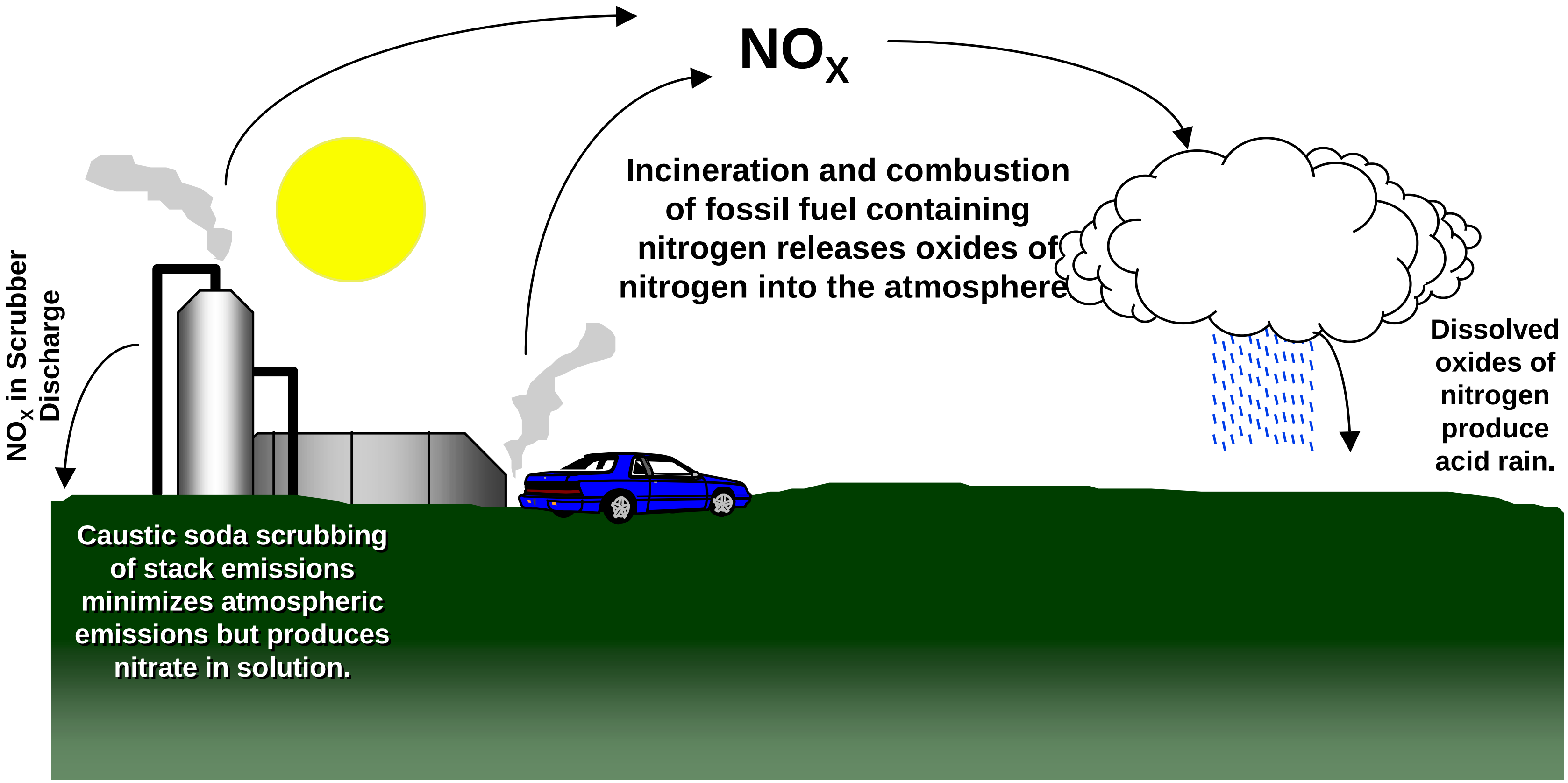
Scrubbing of Stack Emissions to Reduce Acid Rain

Caustic Soda Scrubbing Neutralizes Acid (H^+) to Water

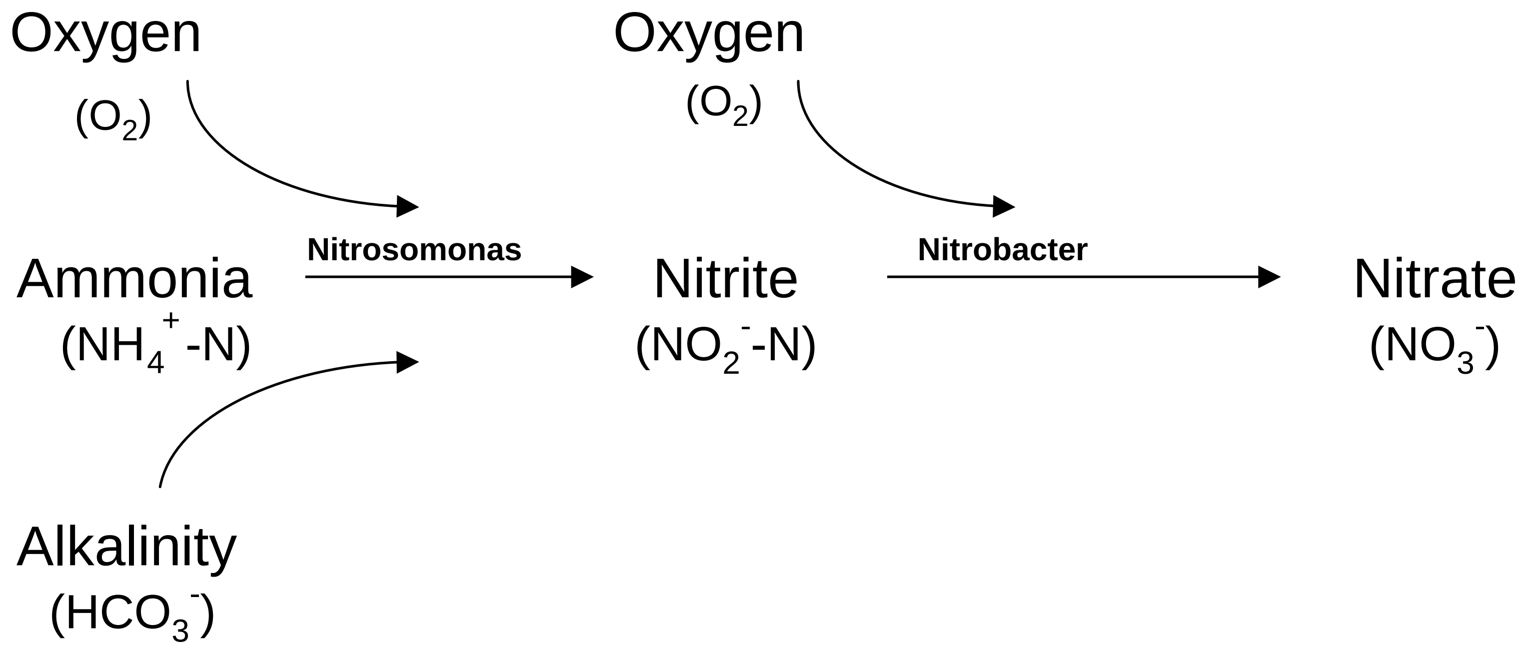
$$HNO_3 \rightarrow H^+ + NO_3^-$$

$$H^+ + NO_3^- + NaOH \rightarrow NO_3^- + H_2O + Na^+$$

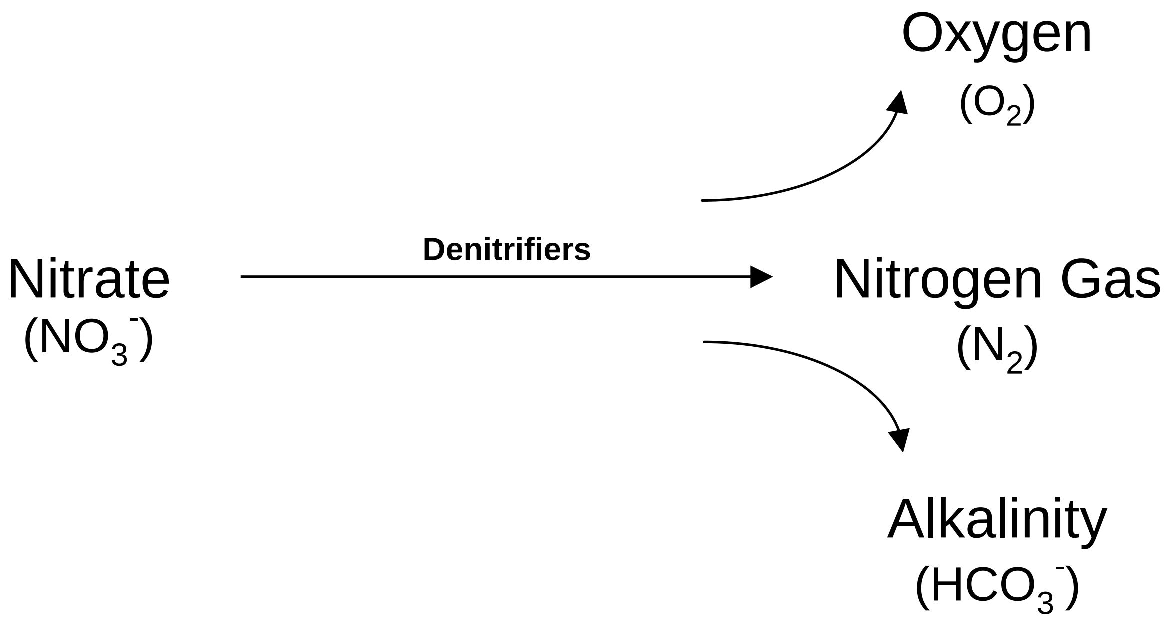
Combustion & Scrubbing



Biological Oxidation (Nitrification)



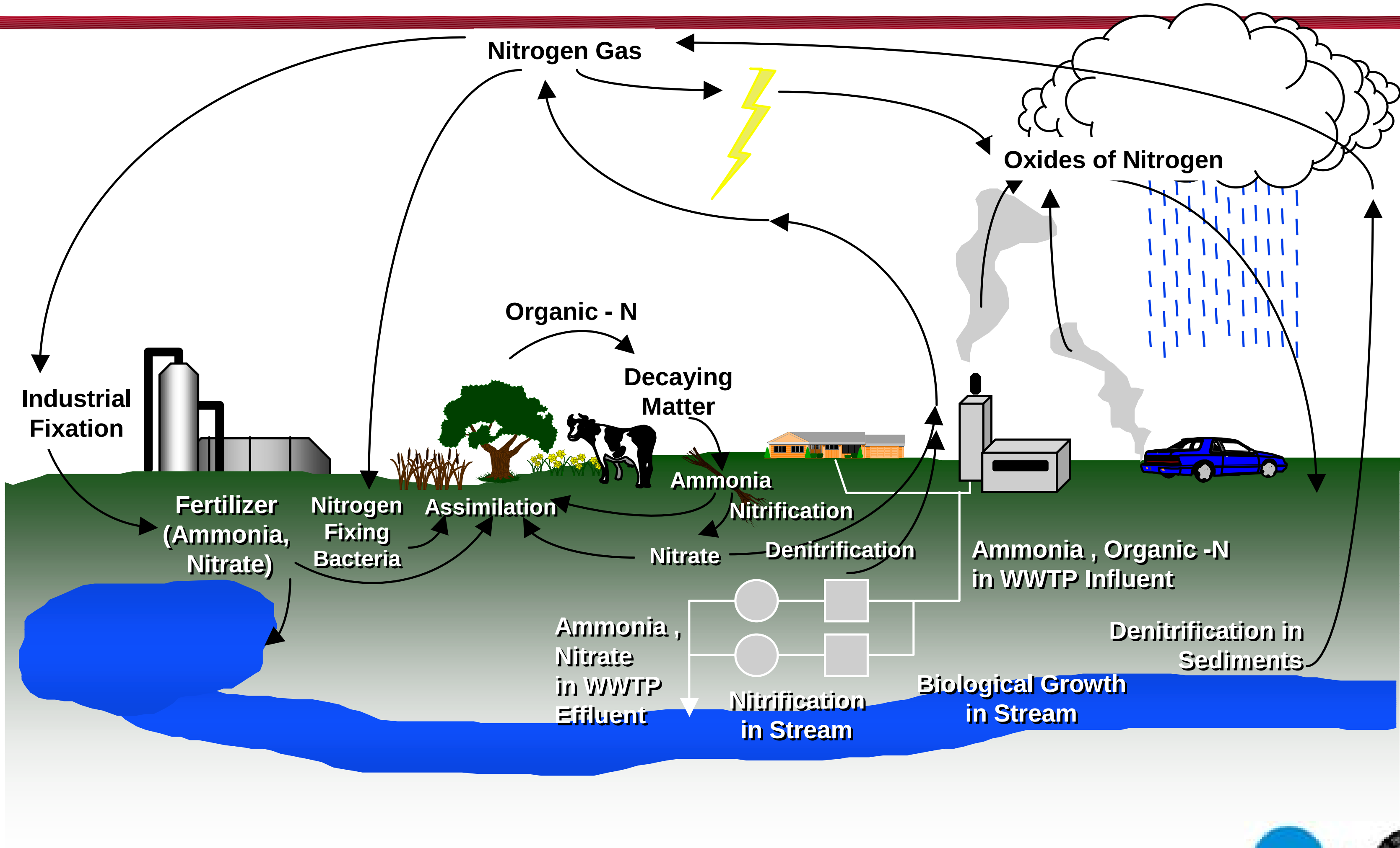
Denitrification in Anoxic Environment



Definition: Aerobic Environment Contains Dissolved Oxygen (D.O.) and Oxidized - N (Nitrate - N and Nitrite - N)

Anoxic Environment Contains Oxidized - N, but has no Dissolved Oxygen.

The Nitrogen Cycle



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Nitrogen in Surface Waters

Nitrogen Concentrations in Natural Waters

Type	N Forms	N Concentrations	Source
Spring Water	Ammonium-N Nitrate-N	Typically Low (near zero)	Contaminated Groundwater
Mountain Stream	Nitrate-N	Typically Low (near zero)	Atmosphere
Large River	Ammonium-N Nitrate-N Organic-N	Low-Moderate 0 - 0.5 mg/l 0 - 0.1 mg/l	Municipal Wastewater, Runoff from Agriculture
Clean Lake	Ammonium-N Nitrate-N Organic-N	0 - 0.1 mg/l Constant w/Depth 0 - 0.3 mg/l Constant w/Depth 0 - 0.1 mg/l	Atmosphere Runoff
Eutrophic Lake	Ammonium-N Nitrate-N Organic-N	0 - 4.5 mg/l Increases w/Depth 0.1 mg/l 0 - 0.2 mg/l Decreases w/Depth	Municipal Wastewater, Runoff from Agriculture

Nitrogen Concentrations in Runoff

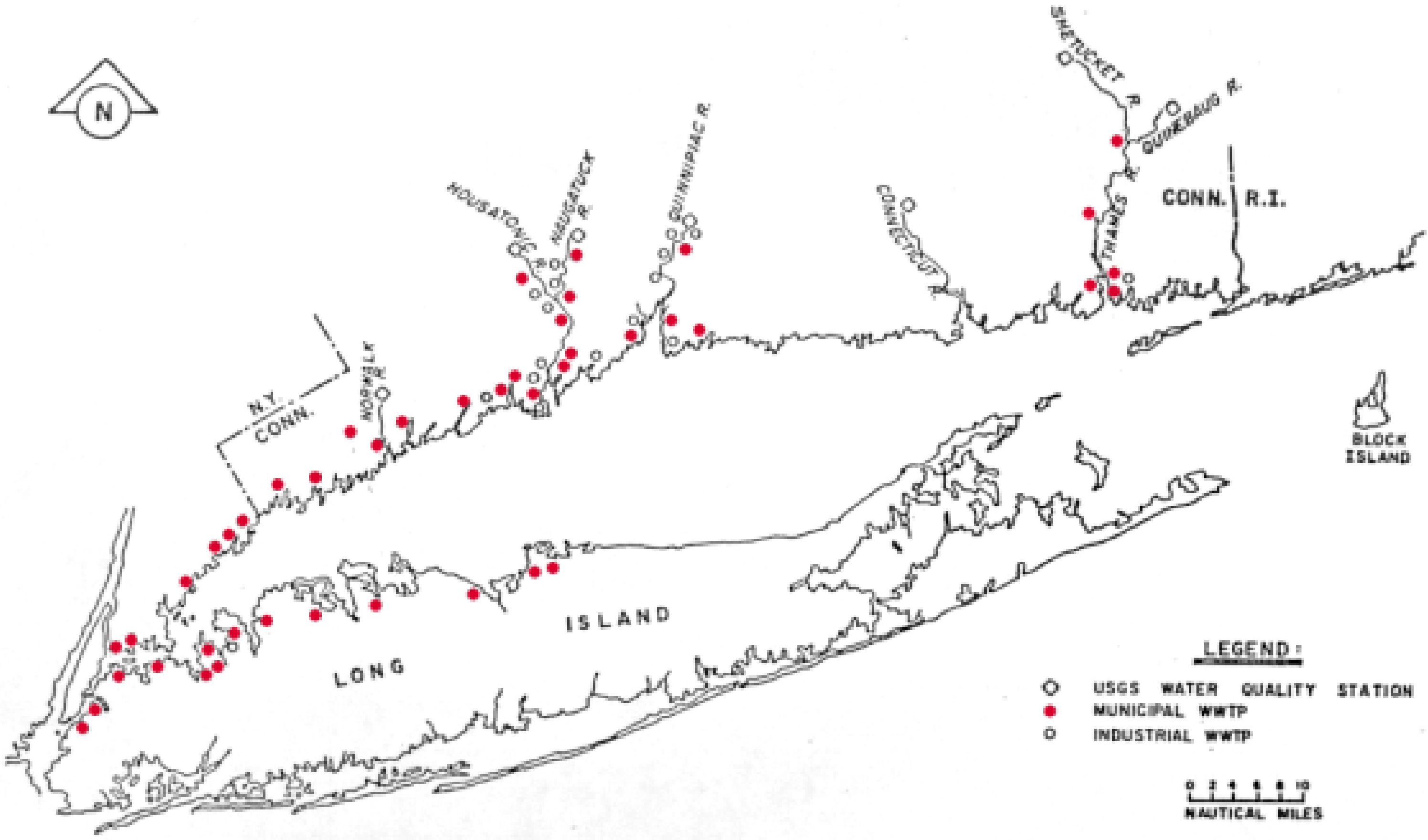
Type	N Forms	N Concentrations
Natural Runoff	Ammonium-N	< 0.1 mg/l
	Nitrate-N	< 0.5 mg/l
Agriculture Runoff	Ammonium-N	0.1 - 1 mg/l
	Nitrate-N	0 - 10+ mg/l (typ. 0 - 1.0 mg/l)
Urban Runoff	Organic-N	0.1 - 1+ mg/l
	Ammonium-N	0.1 - 2+ mg/l
	Nitrate-N	0.1 - 0.5+ mg/l

Atmospheric Nitrogen: Representative Concentrations & Unit Areal Loadings

Location	Nitrogen Form	Sampling	Measurement
Representative Concentrations, mg N/L			
Long Island Sound	Ammonia	Precipitation	0.13
	Nitrate and Nitrite	Precipitation	0.32
Geneva, NY	Ammonia Plus Nitrate-Nitrogen	Precipitation	1.1
Ottawa, ON	Inorganic Nitrogen	Snow	0.85
	Ammonia	Rain	1.8
	Nitrate	Rain	0.35
Cincinnati, OH	Total Nitrogen	Precipitation	1.27
	Inorganic Nitrogen	Precipitation	0.69
Representative Areal Loadings, kg/ha/yr			
Potomac River	Total Nitrogen	Precipitation and Dust	18.6
Lake Huron (Northwest)	Total Nitrogen	Precipitation and Dust	11
Central Europe	Total Nitrogen	Precipitation and Dust	20.0 - 30.0
Hamilton, ON	Total Nitrogen	Precipitation and Dust	6.5
	Total Nitrogen	Dust	2.6
Seattle, WA	Nitrate	Dust	0.71

Source: USEPA Nitrogen Control Manual, EPA/625/R-93/010, September 1993

Sources of Nitrogen in Long Island Sound



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Source: National Estuary Program Long Island Sound Study Presentation on LIS Hydrodynamic and Water Quality Model LIS 3.0, Hydroqual, Inc. April 11, 1996

Distribution of Sources of Nitrogen to Long Island Sound
Tons / Year (Percent)

Sources	Point	Nonpoint (Natural)	Nonpoint (Enriched)	Total
STPs & Industry	25,700(28)	--	--	25,700(28)
Tributaries	3,900(4)	11,600(13)	4,900(5)	20,400(22)
Coastal Runoff & CSOs	--	800(1)	3,500(4)	4,300(5)
Atmosphere	--	4,600(5)	2,200(2)	6,800(7)
Boundaries	--	22,900(25)	10,700(12)	33,600(37)
TOTAL	29,600(33)	39,900(44)	21,300(23)	90,800(100)

Source: Long Island Sound Study, Comprehensive Conservation & Management Plan, 1993

Water Quality Impacts of Nitrogen Discharges

Biostimulation of Surface Waters (Eutrophication)

- **Excessive Plant Growth and/or Algae Blooms**
- **Impacts on Water Quality Include:**
  - **Deterioration of aesthetic quality**
  - **Odors from decomposing algae**
  - **DO depletion which can adversely affect fish life**
- **Factors Required for Algae Growth:**
  - **Nitrogen**
  - **Phosphorus**
  - **Carbon Dioxide**
  - **Light**
  - **Micronutrients**
- **Phosphorus Is Typically the Limiting Factor for Algae Growth in Rivers and Lakes.**
- **Nitrogen Can Be a Limiting Factor for Algae Growth in Estuaries.**

Ammonia Toxicity

- **Molecular ammonia (NH_3) can have toxic effects on aquatic life**

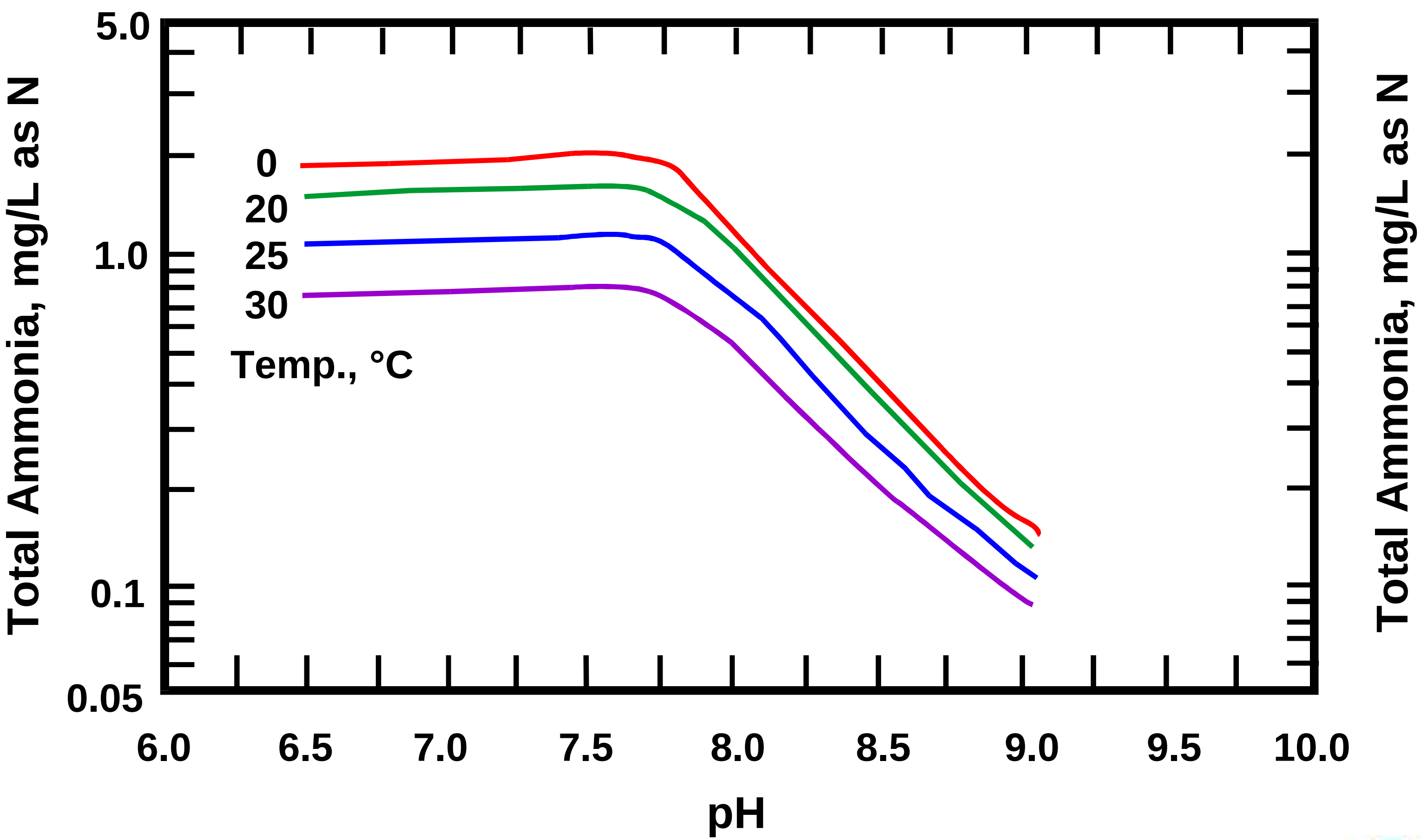
- **Effects may be either acute (i.e. fish mortality) or chronic (impacts on reproduction, tumors, etc.)**

- **Ammonia toxicity is impacted by water temperature and pH conditions**

    - As pH increases, toxic effects are observed at lower total ammonia (NH_3 + NH_4^+) concentrations

    - As temperature increases, toxic effects are observed at lower total ammonia concentrations

EPA Chronic Criteria for Ammonia (Salmonids Absent)



Source: USEPA Nitrogen Control Manual, EPA/625/R-93/010, September 1993

Nitrite and Nitrate in Drinking Water

- Nitrite and Nitrate in drinking water have been medically linked to methemoglobinemia, a sometimes fatal blood disorder affecting infants (“blue babies”).
- Nitrate can be reduced to nitrite under certain conditions in the stomach and saliva.
- Nitrite can bind to iron on hemoglobin reducing transfer of oxygen to cell tissues.
- Result is suffocation accompanied by bluish tinge to skin.

Effect of Nitrification in Receiving Waters

- Naturally occurring microorganisms can oxidize ammonia to nitrite then nitrate
- Biological nitrification reduces dissolved oxygen concentrations in receiving waters and may impact aquatic life
- Magnitude of DO depletion is impacted by receiving water characteristics, wastewater discharge loadings, and environmental conditions
- Nitrification rates increase significantly with increasing water temperature. As a result, impacts are most severe during summer when low flow conditions generally coincide with high temperatures.

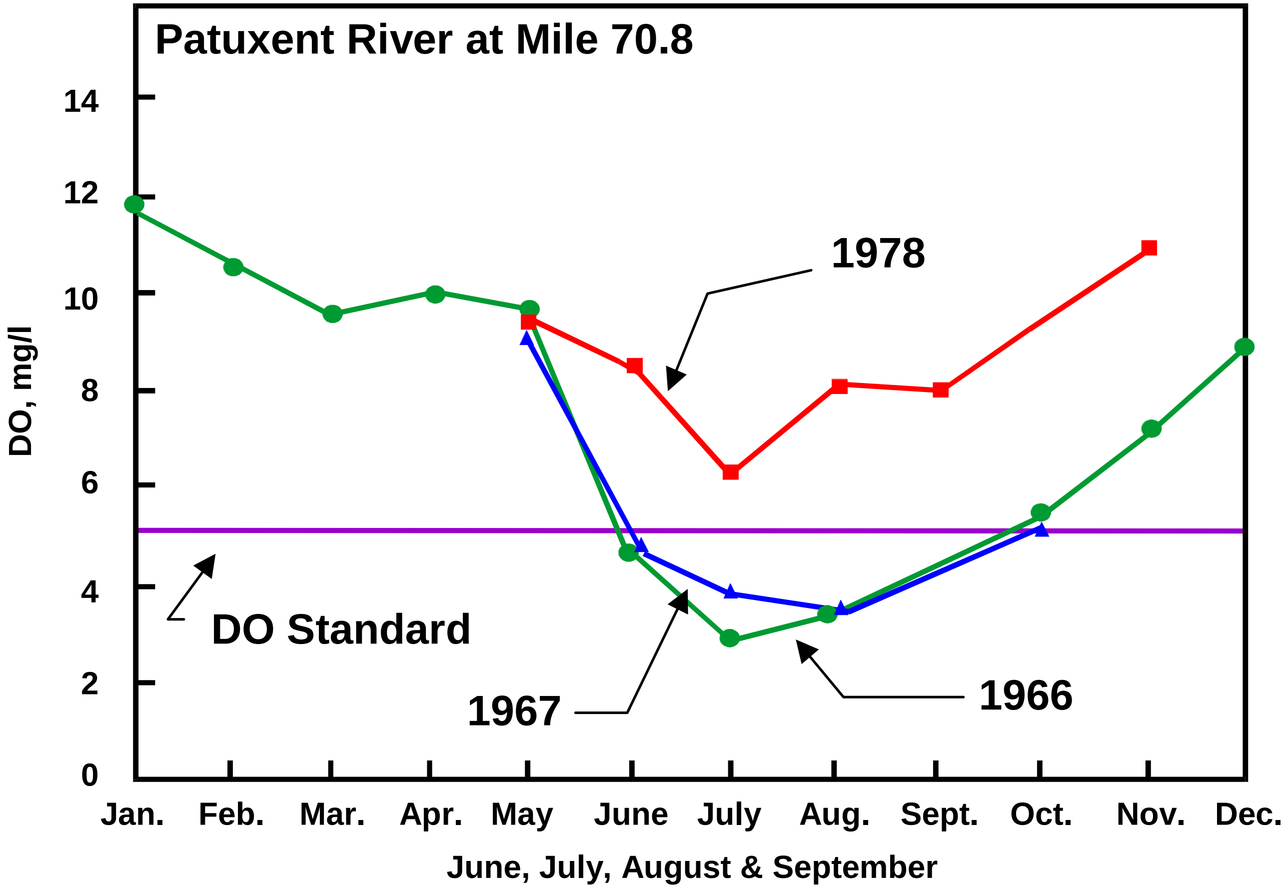
Example of DO Improvement to River Segments after Treatment Plant Upgrade for Nitrification

Laurel Parkway Plant, Patuxent River, MD.

		Before	After
POTW Effluent	$CBOD_5$, (kg/d)/(mg/L)	159/9.5	17.3/0.45
	NH_3-N, (kg/d)/(mg/L)	128/9.5	5/0.14
Total of all Sources	$CBOD_5$, (kg/d)	176	35.5
	NH_3-N, (kg/d)	135	32.3
Stream	Average DO, mg/L	5.5	7.9
	Minimum DO, mg/L	3.8	7.6
	Maximum $CBOD_5$	18	<1.0
	Maximum NH_3 -N, mg/L	2.2	0.1

Source: USEPA Nitrogen Control Manual, EPA/625/R-93/010, September 1993

Improved Dissolved Oxygen Levels in Patuxent River Due to Treatment Plant Upgrade for Nitrification



	Mean, mg/L		
	1966-67	1978	% Change
DO	3.7	7.6	+108%

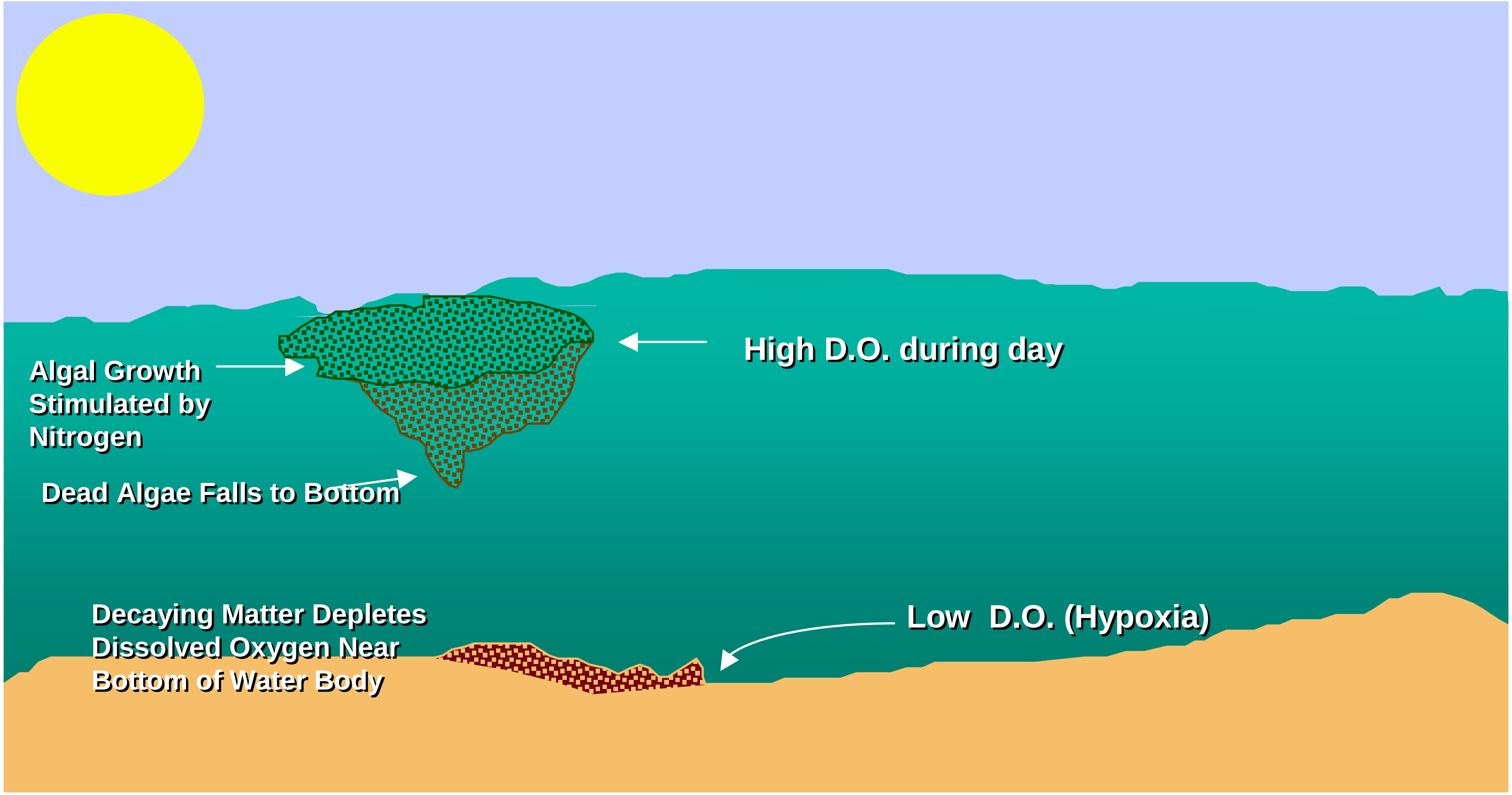
Source: USEPA Nitrogen Control Manual, EPA/625/R-93/010, September 1993

Effect of Ammonium Oxidation on Total Oxygen Demand of Treated Wastewater Discharge

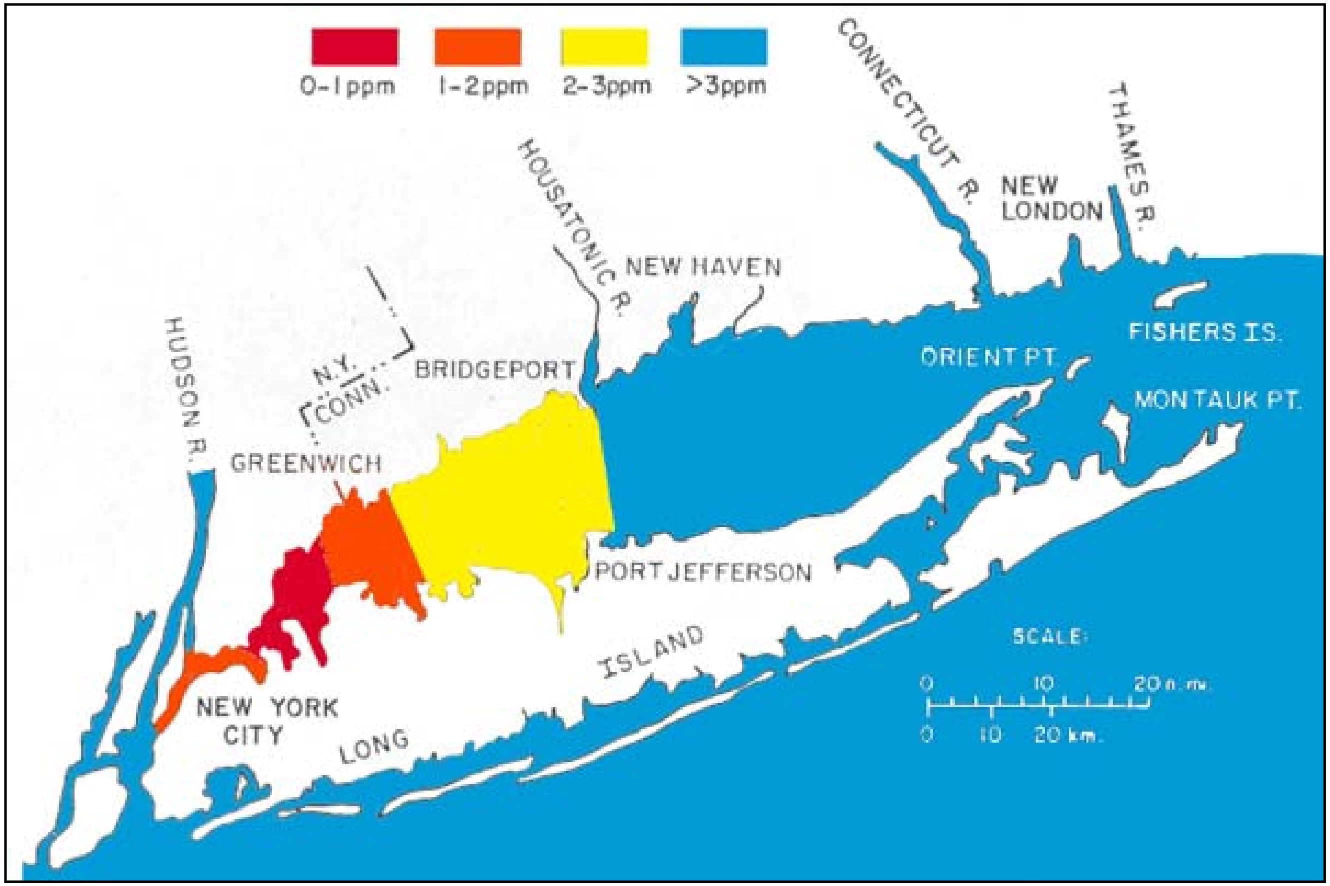
Parameter	Raw Wastewater Concentration (mg/l)	Secondary Effluent Concentration (mg/l)	Secondary Effluent Concentration with Nitrification (mg/l)
Organic Matter, mg BOD_5/L	250	25	20
Organic Oxygen Demand, mg BOD/L	375 (1.5 x organic matter conc)	37	30
Organic and Ammonia Nitrogen, mg TKN/L	25	18	1.5
Nitrogenous Oxygen Demand, mg NOD/L	115 (4.6 x TKN conc)	92	7
Total Oxygen Demand, mg TOD/L	490	129	37
Percent TOD Due to Nitrogen	23.5	71.3	18.9
Percent Organic BOD Removed	_	90	92
Percent TOD Removed	_	73.7	92.5

Source: USEPA Nitrogen Control Manual, EPA/625/R-93/010, Sept. 1993

Impacts of Decaying Plant & Algal Matter on Dissolved Oxygen



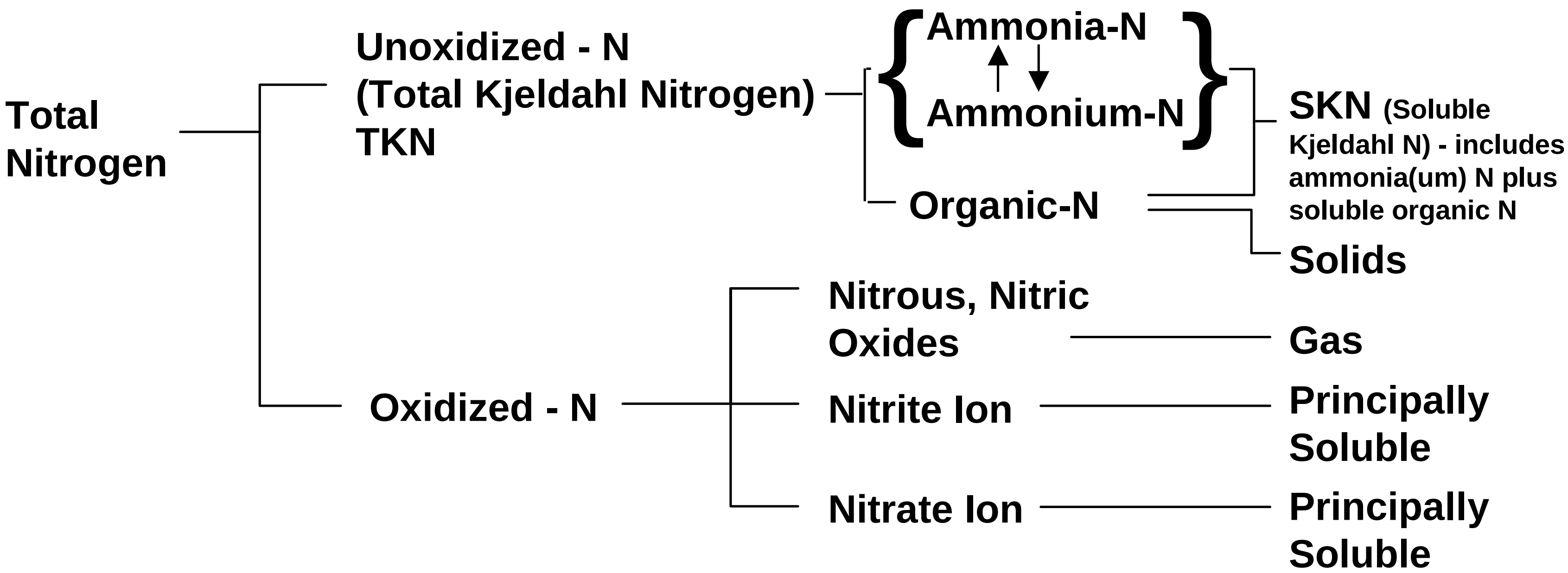
Long Island Sound Bottom Water Dissolved Oxygen



Source: National Estuary Program Long Island Sound Study Presentation on LIS Hydrodynamic and Water Quality Model LIS 3.0, Hydroqual Inc., April 11,1996

Nitrogen in Wastewater

Forms of Nitrogen



Forms of Ammonia

$$NH_3 \quad + \quad H^+ \longrightarrow NH_4^+$$

Ammonia (toxic to fish)

Ammonium (not toxic to fish)

Near neutral pH, most dissolved ammonia will be in the ionic (NH_4^+) form

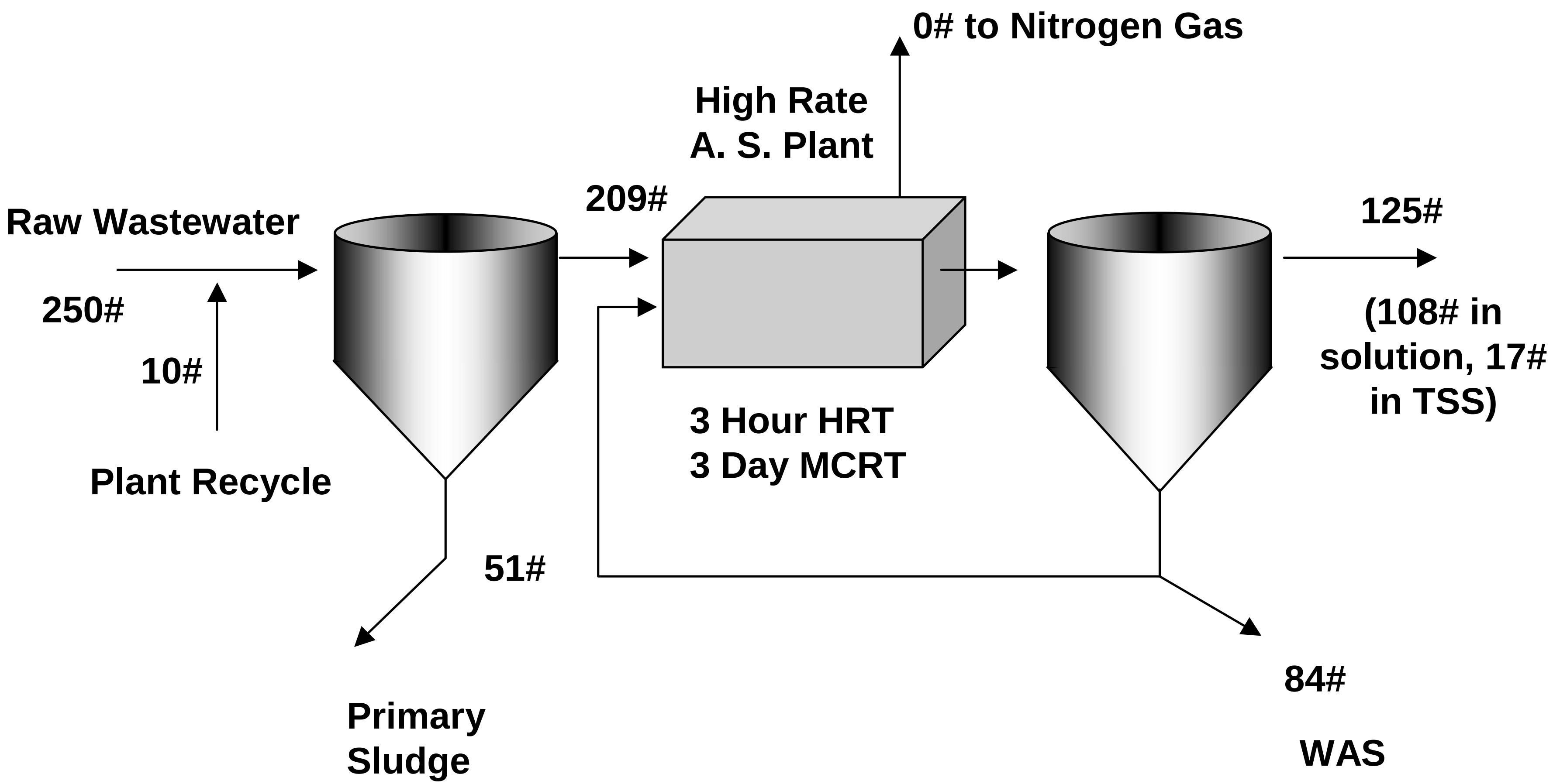
Typical Nitrogen Concentrations in Municipal & Industrial Wastewaters

	Municipal Wastewater			Industrial Wastewater		
	High I/I	**Low I/I**	**Septage**	**Vegetable Based Industry**	**Animal Based Industry**	**Landfill Leachate**
NH_4^+-N	10	25	150	<5	10-1000	—
SKN	12	35	200	—	—	100-300
TKN	15	45	300	<5	100-1000	150-500
NO_2^--N/ NO_3^--N	0	0	0	0	0 - 500	0
BOD_5	80	200	1000	1000	—	500-2000
COD	160	450	2000	2500	—	1500-5000

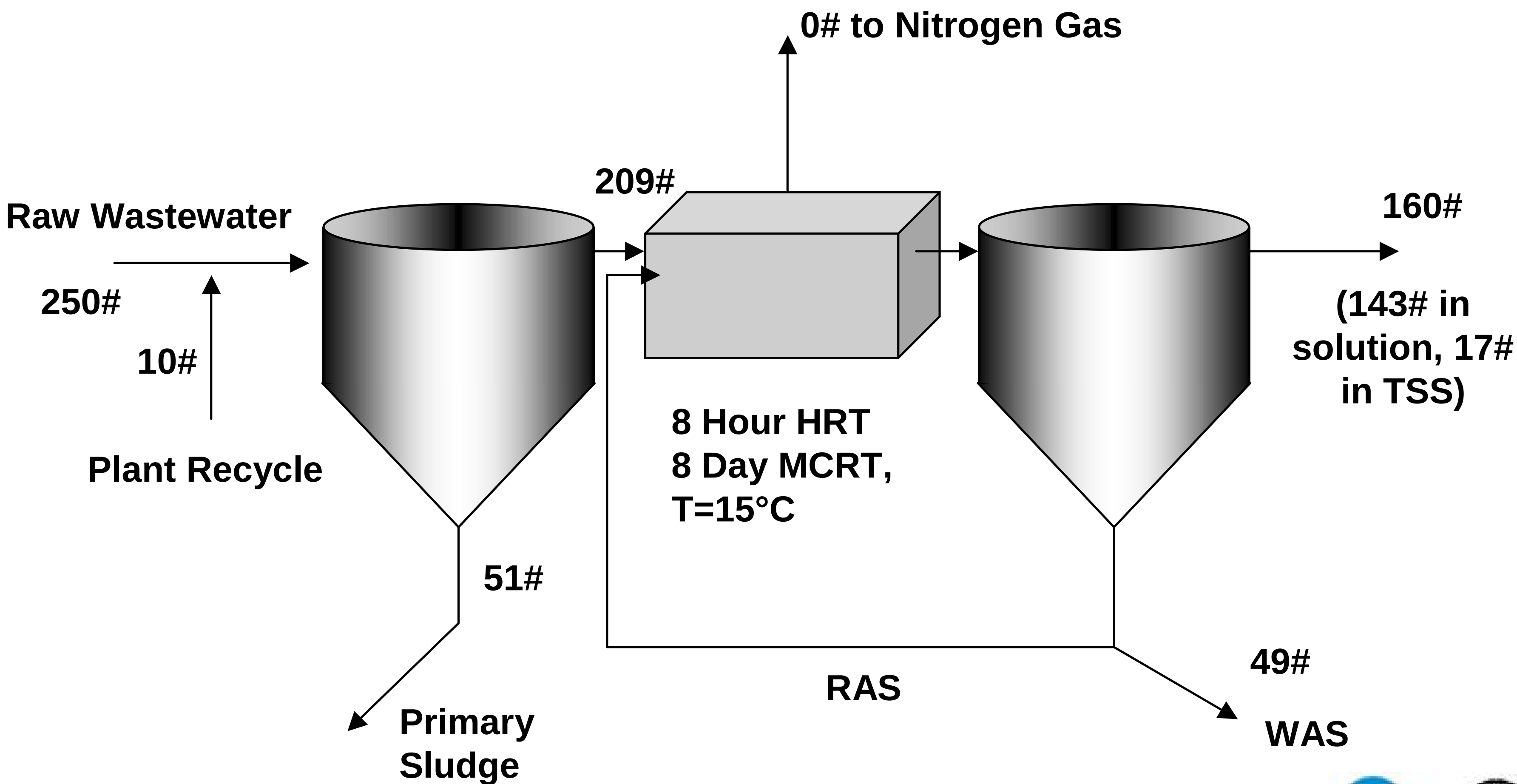
Typical Concentrations of Nitrogen in Influent & Effluent

	Raw Municipal Influent	Primary Effluent	Secondary Effluent (No Nitrification)	Secondary Effluent (Nitrified)
NH_4^+-N	15	16	12	1.0
SKN	18	18	13	1.2
TKN	30	25	15	2.2
NO_2^--N	0	0	0	0.1
NO_3^--N	0	0	0	17
Total N				
Soluble Organic - N				
Organic - N				

Nitrogen Balance in an Activated Sludge Plant Flow = 1 MGD, High Rate



Nitrogen Balance in a Nitrifying Activated Sludge Plant, Flow = 1 MGD



Nitrogen Balance in a Nitrogen Removal Activated Sludge Plant Flow = 1 MGD