Covid Impact on Nitrification in Wastewater

By: Tracy Finnegan

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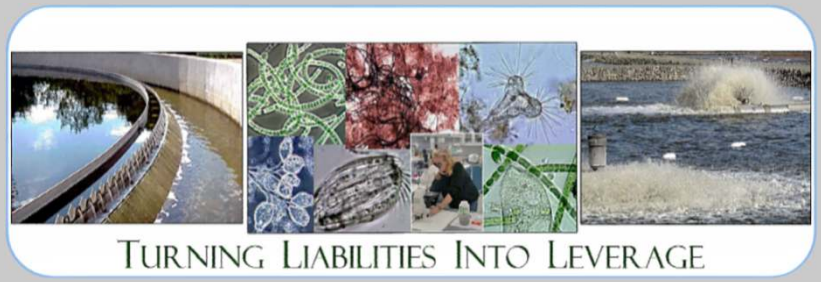

Agenda

- Overview of Nitrification
- Amines
- Covid Impact
- Total Math Balance
- Troubleshooting

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Nitrification- Why remove Nitrogen?

Nitrogenous Compounds discharged from wastewater treatment plants can have many harmful effects

- *toxicity to fish life*
- *reduction of chlorine disinfection efficiency*
- *dissolved oxygen depletion*
- *adverse public health effects*
- *reduction in the suitability of water for reuse*

The degree of Nitrification or Denitrification required is dictated by the maximum allowable limit in the effluent as governed by NPDES permits

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Forms of Nitrogen typically found in Wastewater

- N2 - Nitrogen Gas
- NH3 - Ammonia
- NH4 - Ammonium
- NO2 - Nitrite
- NO3 - Nitrate
- TKN - Ammonia + Organic Nitrogen
- Total Nitrogen - TKN + NOx

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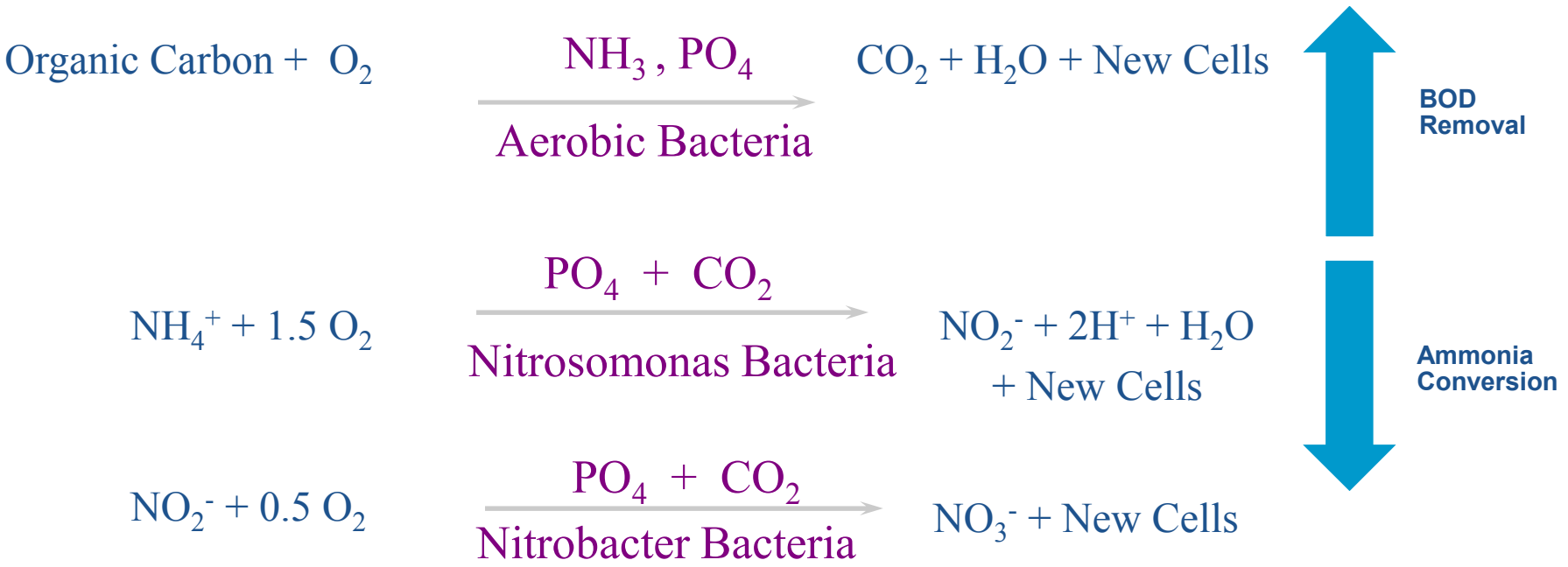
Carbon and Nitrogen Processes



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Biological Nitrification

As Ammonia is removed it is transformed

- *For each 1 gram of NH3-N oxidized to NO3, 0.15 grams of new bacteria cells are formed*

Most of the NH3-N is used as an energy source

- *It is used in a non-assimilative way so only a small amount of biomass (sludge) is produced*

Nitrification occurs 3-4 times slower than Carbonaceous oxidation

Carbon dioxide (CO_2) or carbonate is used as the carbon source in Nitrification

4.5 parts of O_2 is needed for every part of NH3 to be degraded

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The Nitrification Process

First Conversion (Ammonium to Nitrite)

Nitrosomonas bacteria oxidize ammonium to nitrite via hydroxylamine

$$2NH_4^+ + O_2 \rightarrow 2NH_2OH + 2H^+$$

$$NH_4^+ + 1.5\ O_2 \rightarrow NO_2^- + 2H^+ + H_2O$$

Second Conversion (Nitrite to Nitrate)

Nitrobacter bacteria convert nitrite to nitrate

$$NO_2^- + 0.5\ O_2 \rightarrow NO_3^-$$

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Controlling Factors in Nitrification

- **Alkalinity (pH)**
  - Nitrification rates are rapidly depressed as the pH is reduced below 7.0
  - 7.5 to 8.5 is considered optimal
  - 7.14 lbs. of M-alkalinity are destroyed per lb. of ammonia-nitrogen oxidized
  - ***pH does not mean alkalinity is ok!!!*
- **Wastewater Temperature**
  - Nitrification is inhibited at low wastewater temperature
  - Up to five times as much detention time may be needed in the winter vs. the summer months
  - During winter, increasing MLVSS, MCRT will help
  - Desired range is 60° to 95°F

30% of the troubleshooting we find-- Temperature is below 55°F

Many times insufficient Alkalinity

Most often, Amines are not broken down

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Alkalinity

- **Common Sources of Alkalinity include:**
  - **Lime Ca(OH)2**
  - **Caustic Soda NaOH**
  - **Soda Ash Na2HCO3**

Chemicals Added For Phosphorus Removal Also Destroy Alkalinity

- ***5.3 - 13.5 lbs. Alkalinity per lb. Fe added***
- ***6.0 - 9.0 lbs. Alkalinity per lb. Al added***

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More Controlling Factors in Nitrification

- **Dissolved Oxygen**
  - Nitrification has a substantial Oxygen requirement
  - 4.5 lb. O2 /lb. $NH4^{+}$-N
  - Aeration tank O2 usually maintained 1.0 to 4.0 mg/L
- **Nitrogenous Food**
  - BOD5 / TKN Ratio
    - The fraction of nitrifying organisms decreases as this ratio increases
    - Ortho-phosphate nutrient may also have to be added if deficient
- **Detention Time**
- **MCRT, F/M, or Sludge Age**
- **Toxic Materials**

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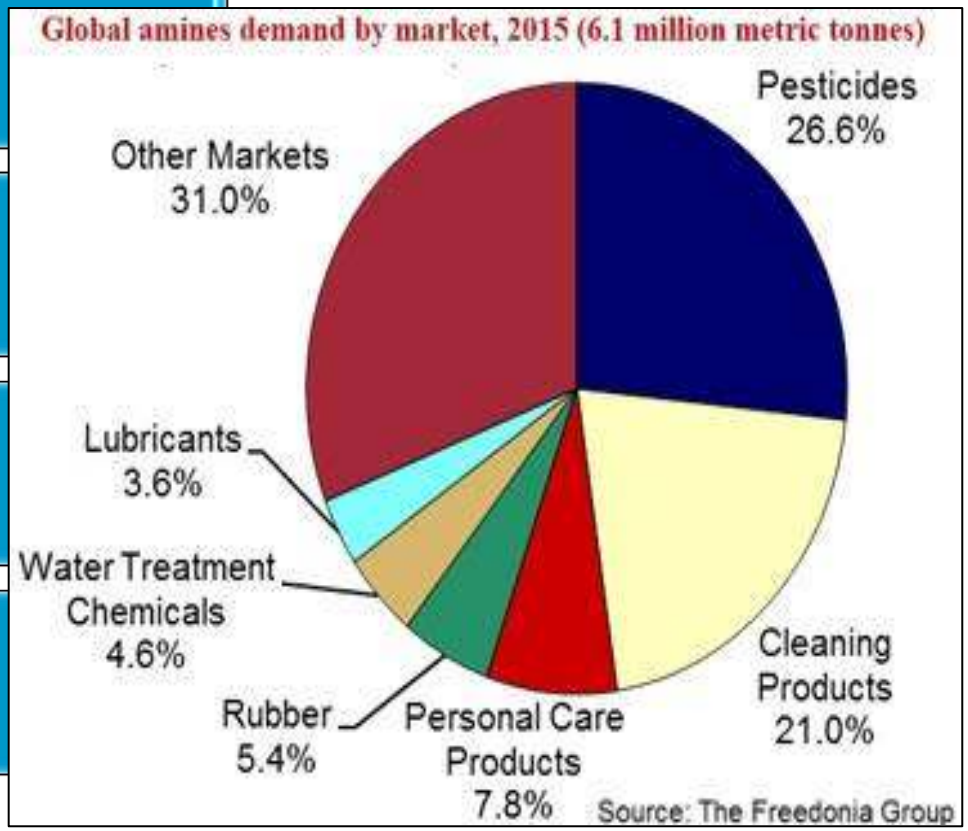
Amines

- *Municipalities are not used to testing the influent for Amines*
- *In the past cleaning compounds had bleaches or caustic*
- *Tons of additional restaurants*
- *New in home cleaning solutions*
- *Covid impact*



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Covid Impact

- Tons of municipalities reporting Nitrification inhibition in 2020
- In reality, “Amines” levels have increased due to added sanitation and Covid changes
- More binge eating or house cleaning as people stay at home
- Wipes and hand sanitizers, floor cleaners
- Drugs- Opiate analgesics such as morphine, codeine, and heroin are tertiary Amines. Ephedrine and phenylephrine, as Amine hydrochlorides, are used as decongestants.

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Customer Data

- Significant increases in TKN-Amines from 2019-2020-- double and triple levels
- One plant influent Amine levels were usually 40-50 in 2019/ spikes up to 125 after Covid in 2020!
- Check your historical data and compare

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Seasonal and Holidays

- Seasonal fluctuations
- Port-a-potties during festivals
- Holidays

12/11/2019	3.49	39.30	27.41
12/12/2019	3.54		
12/13/2019	3.42		
12/14/2019	3.51		
12/15/2019	3.53		28.89
12/16/2019	3.47		
12/17/2019	3.43		
12/18/2019	3.38	40.70	30.45
12/19/2019	3.43		
12/20/2019	3.45		
12/21/2019	3.52		
12/22/2019	3.43		30.08
12/23/2019	3.46		
12/24/2019	3.57		
12/25/2019	3.20	54.55	37.62

(Actual plant data from a municipality)

7/8/2020	3.74	79.40	44.72
7/9/2020	3.85		
7/10/2020	4.05		
7/11/2020	3.73		
7/12/2020	3.64		28.61
7/13/2020	3.77		
7/14/2020	3.72		
7/15/2020	4.29	72.60	39.00

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Where would these Amines or Nitrogen compounds come from?

Personal care products or household cleaning products may contain amine compounds. Restaurants, hospitals and hotels using cleaning and sanitizing agents. The food industry requires the use of disinfectants to sanitize food preparation areas, and serve preservative functions.

Many institutional and fast food restaurants as well as many industrial plants, especially food plants need to use biocides in order to keep the working areas clean or sterile. This can be accomplished by addition of biocides; chemical compounds that are toxic to the present microorganisms. Biocides are used in an environment or a system to bring about rapid effective population reductions from which the microorganisms cannot easily recover. There are various different biocides, some of which have a wide range of effect on many different kinds of bacteria. They can be divided up into oxidizing agents and non-oxidizing agents.

Oxidizing agents:
Chlorine, Chlorine dioxide, Chloroisocyanurates, Hypochlorite, Ozone

Non-oxidizing agents include:
Acrolein, Amines, Chlorinated phenolics, Copper salts, Organo-sulphur compounds, Quaternary ammonium salts, Tertiary amines, amine oxides, Fatty Amines & Other Nitrogen Compounds

Quaternary ammonium salts are surface-active chemicals that consist generally of one nitrogen atom, surrounded by substitutes containing eight to twenty-five carbon atoms on four sides of the nitrogen atom. Quaternary amines are soluble in both water and organic liquids and can greatly accelerate certain chemical reactions when added to a heterogeneous system. These amines are highly toxic and are as equally effective as chlorine dioxide disinfectants. This antibacterial activity is considered desirable for maintaining a sterile living environment.

These compounds are generally most effective against bacteria in alkaline pH ranges. They are positively charged and will bond to the negatively charged sites on the bacterial cell wall. These electrostatic bonds will cause the bacteria to die due to stresses in the cell wall. They also cause the normal flow of life-sustaining compounds through the cell wall to stop, by declining its permeability. Use of quaternary ammonium salts is limited, due to their interaction with oil when present and the fact that they can cause foaming.

Amines
Amines are effective surfactants that can act as biocides due to their ability to kill microorganisms. They can enhance the biocidal effect of chlorinated phenolics when they are applied in water.

Personal Care Products: Quaternary ammonium compounds are often used in contact lens solutions for cleaning and preservative purposes among other uses. Recently detergent manufacturers began to employ quaternary amines in order

Below is a list of some of the compounds that your customers might be using that can impact your wastewater treatment plant- Amines are in more compounds than you might think

Surfactant and Cleaning Chemicals and Their Functions
ADMA® alkyldimethylamines and DAMA® dialkylmethylamines for amine oxides, quaternary ammonium compounds and betaines used in cleaning systems, biocides, fabric softeners and conditioners

Fabric softeners, conditioners	ADMA® tertiary amines	
	Ampholak	Amphoterics
	Armeen	Fatty amines
	Armosoft	Quaternary Ammonium salts and esterquats
Detergents	Aromox	Amine oxides
	Arquad	Quaternary Ammonium salts and esterquats
	Ethomeen	Ethoxylated amines
	Kortacid	Fatty acids
	Nouracid	Fatty acids
Hard Surface Cleaning (Industrial Cleaning and Institutional Cleaning)	Berol	Nonionics
	Ethomeen	Ethoxylated amines
	Aromox	Amine Oxides
	Elfan	Anionic
	Arquad	Quat. Ammonium salts
	Nouracid	Fatty acids
	Kortacid	Fatty acids
	Arquad	Quaternary ammonium compounds and esterquats
	Armocare	Quaternary ammonium compounds and esterquats
Personal Care	Ethomeen	Ethoxylated amines
	Ethoduomeen	Ethoxylated diamines
	Elfacos	Specialty polymers
		Cocoyl isethionate

Sanitizers

Amines are a carbon compound with a nitrogen component and are present in many cleaning and sanitation products.
---Here are some examples of their SDS sheets:

Disinfecting wipes

3. Composition/information on ingredients

Substance/mixture : Mixture

Ingredient name	%	CAS number
ethanol	1 - 5	64-17-5
D-Glucopyranose, oligomeric, C9-11-alkyl glycosides	0.5 - 1.5	132778-08-6
Quaternary ammonium compounds, benzyl-C12-16-alkyldimethyl, chlorides	0.1 - 1	68424-85-1

Antibacterial hand soap

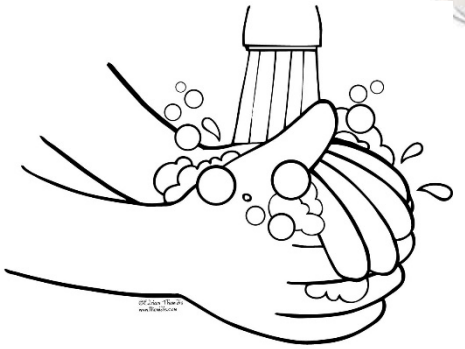
3. COMPOSITION/INFORMATION ON INGREDIENTS

Substance

Not applicable.

Mixture

Chemical name	CAS No.	Weight-%	Hazardous Material Information Review Act registry number (HMIRA registry #)	Date HMIRA filed and date exemption granted (if applicable)
Benzalkonium Chloride 0.13% w/w	68391-01-5	0.13	-	-
Water	7732-18-5	50 - 100	-	-
Lauramine Oxide	1643-20-5	0 - 10	-	-
Cocamidopropyl Betaine	61789-40-0	0 - 10	-	-
Lauramidopropylamine Oxide	61792-31-2	0 - 10	-	-
Sodium Chloride	7647-14-5	0 - 10	-	-
Myristamidopropylamine Oxide	67806-10-4	0 - 10	-	-
Glycerin	56-81-5	0 - 10	-	-
Fragrance	FRAGRANCE	0 - 10	-	-
Distearetth-75 IPDI	53533-75-8	0 - 10	-	-
PEG-150 Distearate	9005-08-7	0 - 10	-	-
Citric Acid	77-92-9	0 - 10	-	-
Tetrasodium EDTA	64-02-8	0 - 10	-	-
Benzophenone-4	4065-45-6	0 - 10	-	-
Sodium Benzoate	532-32-1	0 - 10	-	-
Red 33	3567-66-6	0 - 10	-	-
Red 40	25956-17-6	0 - 10	-	-
Yellow 5	1934-21-0	0 - 10	-	-



Composition of Typical General Purpose Cleaning Agent

Disinfectant spray

3. Composition / Information on Ingredients

Ingredient(s)	CAS #	Percent
Ethanol	64-17-5	40 - 60
Butane	106-97-8	2.5 - 10
Propane	74-98-6	1 - 2.5
Alkyl (40% C12, 50% C14, 10% C16) dimethyl benzyl ammonium saccharinate	Not Applicable	0 - 0.1

Cleaning agents containing quaternary ammonium compounds such as alkylbenzyldimethyl ammonium chloride can be found in most grocery stores and supermarkets under a variety of brands. Some typical cleaning agents are listed below. (It should be noted that many detergents do not reveal their complete composition on the label.)

Typical Enzyme Detergents

Cleaning Agent	pH	Comments
Pearl Plus (Flexo)	10	Active ingredient alkyl dimethyl benzylammonium chloride
Pine Scented	9	Corrosive to skin and eyes Household Cleaner Use rubber gloves Contains quaternary ammonium chlorides
Lysol	8	Corrosive Contains alkyl dimethylbenzyl ammonium chloride Use rubber gloves

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More Amines or Nitrogen compounds

Sanitizer

SECTION 3. COMPOSITION/INFORMATION ON INGREDIENTS

Product AS SOLD
Pure substance/mixture : Mixture

Chemical name	CAS-No.	Concentration (%)
n-alkyl (C14 50%; C12 40%; C16 10%) dimethyl benzyl ammonium chloride	68424-85-1	8.68
Octyl decyl dimethyl ammonium chloride	32426-11-2	6.51
Didecyl Dimethyl Ammonium Chloride	7173-51-5	3.906
Dioctyl dimethyl ammonium chloride	5538-94-3	2.604
ethanol	64-17-5	4.34
Alcohols, C9-11, ethoxylated	68439-46-3	5 - 10
ethylenediamine tetraacetate	64-02-8	1 - 5
disodium metasilicate	6834-92-0	1 - 5

Antibacterial wipes

3. Composition / Information on Ingredients

Ingredient(s)	CAS #	Percent
Ethanol	64-17-5	2.5 - 10
Alkyl (50%C14, 40%C12, 10%C16) dimethyl benzyl ammonium chlorides	Not Applicable	0.1 - 1

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And More Nitrogen!

Floor cleaner

SECTION 3. COMPOSITION/INFORMATION ON INGREDIENTS

Product AS SOLD
Pure substance/mixture : Mixture

Chemical name	CAS-No.	Concentration (%)
Dodecyldimethylamine oxide	1643-20-5	1 - 5
C10-16 Polyglycoside	110615-47-9	1 - 5
Monoethanolamine	141-43-5	1 - 5

Bathroom cleaner

Ingredient	C.A.S. No.	% by Wt
1-OCTYL-2-PYRROLIDINONE	2687-94-7	10 - 30 Trade Secret *
WATER	7732-18-5	10 - 30 Trade Secret *
HYDROXYACETIC ACID	79-14-1	10 - 30 Trade Secret *
MALIC ACID	6915-15-7	10 - 30 Trade Secret *
AMINES, COCO ALKYLDIMETHYL, N-OXIDES	61788-90-7	1 - 5 Trade Secret *
ETHOXYLATED C9-11 ALCOHOLS	68439-46-3	1 - 5 Trade Secret *
Fragrance Added	Mixture	0.1 - 1.5 Trade Secret *

Sanitizer

SECTION II – COMPOSITION AND INGREDIENTS

Ingredients/Chemical Name: (Actives) Mixture of N-Alkyl (C_{12-18})-N,N-dimethyl –N-benzylammonium chloride and N-Alkyl (C_{12-14})-N,N-dimethyl-N-ethylbenzylammonium chloride

Hazardous Ingredients as defined by OSHA, 29 CFR 1910.1200.

Chemical Name	CAS No.	TWA/TLV	Composition Range (%)
N-Alkyl (C_{12-18})-N,N-dimethyl –N-benzylammonium chloride	68391-01-5	None established	7.0
N-Dodecyl-N,N-dimethyl-N- ethyl benzylammonium chloride	27479-28-3	None established	4.7
N-Tetradecyl-N,N-dimethyl-N- ethyl benzylammonium chloride	27479-29-4	None established	2.3
Ethanol	64-17-5	ACGIH TLV: 1000 mg/m^3	1.0 - 4.0
Water	7732-18-5		Balance

Not just homes…..

- Industrial users, Food production, hotels, hospitals, schools, restaurants

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Digesters and Dewatering

Don't forget that some of the chemicals used onsite at the treatment plant may also contain Amines. Not all Safety Data Sheets show the COD or BOD or nitrogen in the chemical formulation. Test all products in your own lab. Polymers, alum, ferric, salts and metals can also cause issues with toxicity, especially to nitrifiers. Test for TOC and TKN. The TOC test will give better results than the COD test. High nitrates interfere with COD testing. Notice the Acrylamide copolymer in the sample MSDS table below, a Nitrogen compound. Most cationic or anionic polymers are ADAM, MADAM or EPI/DMA which contain amine compounds.

Polymers can not only have high organic loading, but may also have high levels of amines

Section 3. Composition/Hazardous Ingredients

Component	CAS Registry #	Wt.%
Petroleum distillate hydrotreated light	64742-47-8	15 - 40
Adipic acid	124-04-9	1 - 5
POE 6 Tridecyl alcohol	78330-21-9	1 - 5
Acrylamide copolymer	Proprietary	< 50

Dewatering Decant

Digester Decant

Testing For Nitrogen and Amines In The Influent

Total Kjeldahl Nitrogen (TKN)

TKN = ORG- N + NH3-N

Digest sample in sulfuric acid and catalyst

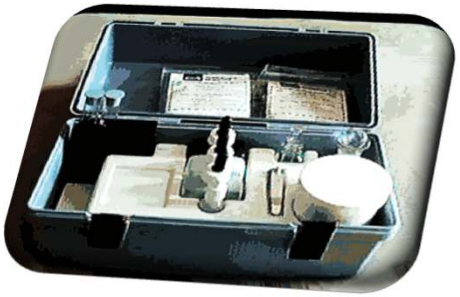
Org-N - ------ > NH4-N

Steam distillation to determine Ammonia content

Organic Nitrogen (by difference)

ORG-N = TKN - NH3-N

TKN = ORG-N + NH3-N



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Testing

- Total Nitrogen - For practical purposes in wastewater analysis
- **TN = ORG TN = ORG-N + NH_3-N + NO_2-N + NO_3-N**
- **TKN = OR TKN = ORG- N + NH_3-N**
- **TON = NO_2 TON = NO_2-N + NO_3-N**

Hach Test N Tube reagents-
Test 'N Tube™ Analysis Products
FAST, EFFICIENT ANALYSIS FOR 8 KEY WASTEWATER PARAMETERS
Nitrogen, Total Reagent Set, Test 'N Tube, 50/tests Product #: 2672245

- Nitrogen, Total Reagent Set, (Test 'N Tube)
- Method: Persulfate Digestion
- Range: up to 25.0 mg/L
- 50/test

Phosphorus
1. Total Phosphorus
2. Reactive Phosphorus
3. Acid Hydrolysable Phosphorus

Nitrogen
1. Total Nitrogen
2. Total Inorganic Nitrogen
3. Ammonia
4. Nitrate
5. Nitrite Wastewater analysts all over

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How to do the Total Math for N in a Biological System

Influent ---- Aeration Basin ---- Effluent

TKN (Amines and NH3)
Nitrates
Nitrites

BOD removal will remove 5 ppm NH3 per each 100 ppm- remainder has to be consumed by nitrification

TKN, NH3 plus Nitrates and Nitrates should equal total influent number minus BOD correlation

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Influent Example
BOD- 300
TKN-75
NH3-35
Nitrates-0
Nitrites-0

Since the BOD degraders consume 15 ppm N as a nutrient source-
300 ppm BOD/100 *5=15
60 ppm would be left for nitrification

Final Effluent Example
BOD- 3
TKN-0
NH3-.005
Nitrates-56
Nitrites-4

**Therefore, that means there are 35 parts in the TKN as NH3 and the rest are amines- 40 PPM

** Always make sure you measure Solids dewatering supernatant as well as digestor supernatant. They are often overlooked in the total math analyses.

Ammonia (NH3) values are approximately 60% of the Total kjeldahl nitrogen (TKN) values

Total Kjeldahl Nitrogen (TKN) generally equals 15-20 % of the Biochemical Oxygen Demand (BOD) of the raw sewage.

Additional Means of Controlling Nitrogen in WWTP's

Increase MLSS

Bioaugmentation-
Use of carbonaceous bacteria to break down Amines

- in the aeration basin
- upstream in lift stations

Use of Nitrosomonas and Nitrobacter to seed or recover from an upset

MicroClear 207 for high FOG MicroBlock Solid for FOG

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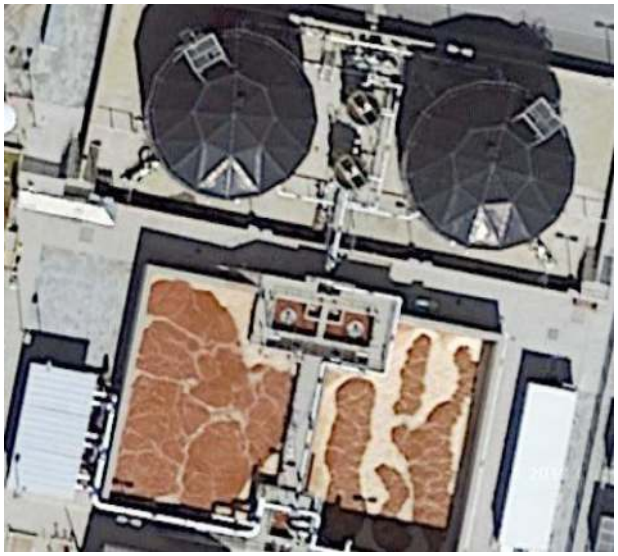
Another Example-- Pharmaceutical Plant

**Pharmaceutical plant-- high Amines and Nitrogen in anoxic and aeration basin



1. Started on a program with the addition of Bioaugmentation MicroSolv 200 and MicroClear M100 micronutrients and adjusted N and P values

2. Use of MicroSolv 600L required to break down high levels of ammonia after toxic shock events

3. Amine spikes of 155-185 occur 1-2 times per week, sent to EQ tank for slow bleed into system

4. Recommended addition of a small amount of MicroSolv 200 into EQ tank to pretreat amines and break them down, prior to the aeration basin and lessen the effect of toxicity

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Questions

&

Answers

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Check out our ELearning Website at WASTEWATERELEARNING.COM!

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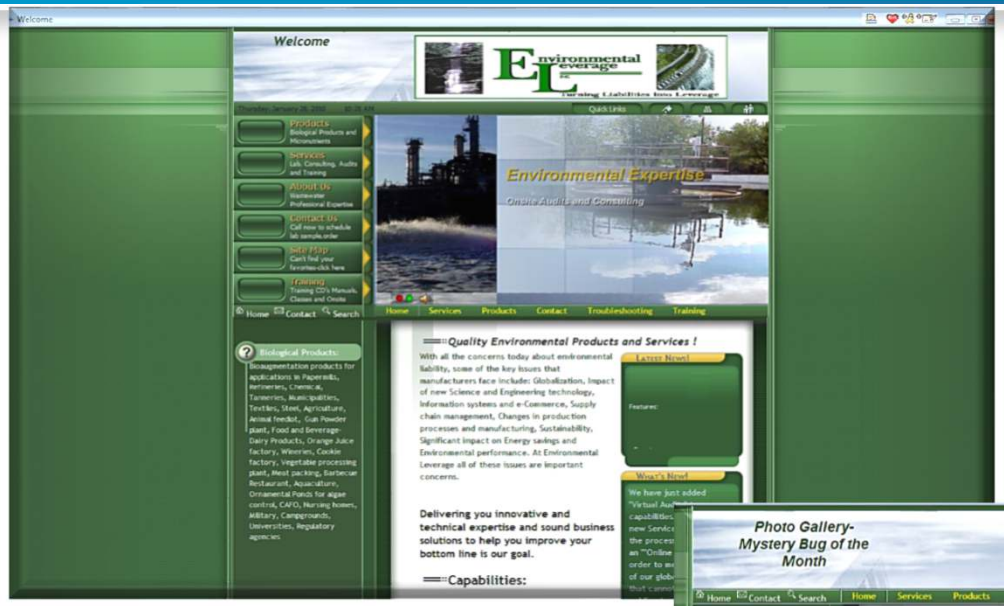

- Training
- Troubleshooting
- Filamentous
- Higher Life Forms
- Products
- Bug of the Month
- Microscopic

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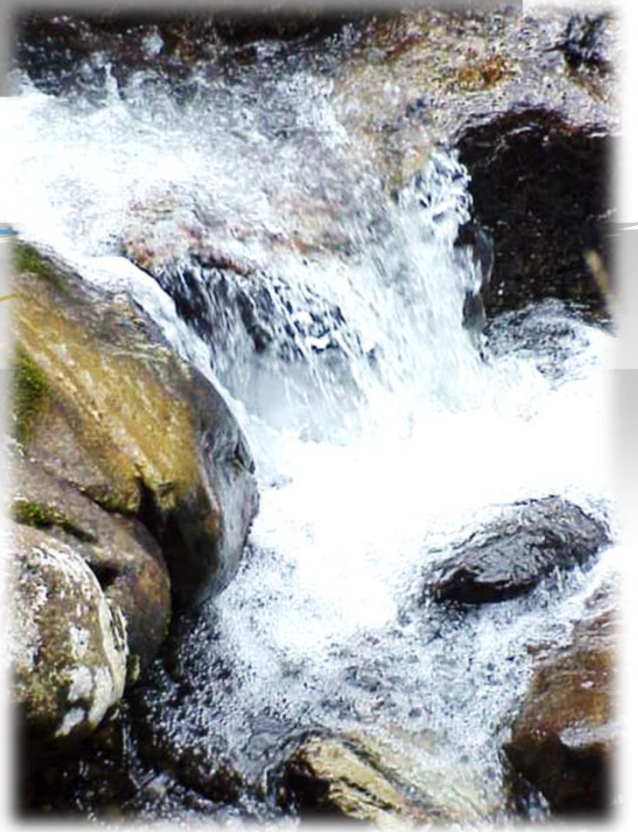

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BIOLOGICAL WASTEWATER TREATMENT PRODUCTS: Environmental Leverage® Inc. carries a full line of biological products that come in various forms - Water Soluble Pouches, Powder, Liquid or Solids in various different containers and numerous sizes specifically designed to fit your needs. Each productis specifically formulated for each task. Ask for individual product bulletins for the product that meets your needs. Environmental Leverage can help you with product dosing and program requirements all the way through your application of our products. Below is a short list of products that may be applicable.

MicroClear® 201…Wastewater Treatment - Biological product specifically formulated to be effective in enhancing municipal wastewater biology in Activated Sludge, Lagoons, Aeration basins, Fixed film systems RBC's, oxidation ditch & trickling filters. Reduces BOD & TSS.

MicroClear® 207…Waste Water Treatment & Sewer formulation FOG control…Improved biological product, specifically formulated and packaged for use in treatment plants, lift stations & sewers to help degrade grease build-up and stop blockage.

MicroClear® 101…Ponds, Lakes or Rivers…Formulated for Lagoons, Wastewater treatment, Ornamental ponds that often have run-off water with pollutants that cause excess algae growth. For use in Lakes, Rivers and Canals. Reduces BOD / TSS.

MicroSolv™ 200 Industrial - Formulation for use in degrading many types of organics in Industrial Wastewater Applications. Specially formulated blend of microorganisms, micro/macronutrients, and surface tension suppressants/penetrants. These safe, naturally occurring bacteria are designed to handle difficult organics and hard to degrade chemicals found in industrial wastewater facilities.

MicroBlock™ Solid Slow Release bio block products that are specifically formulated and packaged for use in lift stations, large restaurant grease traps, portable outhouse, collection tanks and upstream areas from wastewater systems.

MicroClear® BioNite™ - Odor & FOG Control - is a proprietary formulation of ingredients containing a nitrate-based Electron Acceptor for Control of Odors. Contains a specially formulated, proprietary blend of microorganisms, micro/macronutrients, alternate oxygen source and surface tension suppressants/penetrants. Because of the diversity of the microorganism systems incorporated into this product it is specifically developed for use in situations where there is a particular high impact from odors as well as fats, oils and grease. This product can be used in the treatment of liquid & solid organic waste.

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Key Capabilities of Environmental Leverage Inc.

Environmental Consulting
- Implementing process changes can help avoid major problems.
- Environmental compliance is a must.
- Locating key issues that management must continually track and improve.

On-Site Audit & Troubleshooting Wastewater Systems
- Monitor and control techniques are explored.
- To search & identify areas to implement process changes can help avoid major problems.
- System optimization, equipment efficiency and operational excellence.
- Beneficial Re-Use.
- Surcharge Reduction

Wastewater Training On-Site
- To properly train operators & lab personnel to control / monitor your system in order to predict upsets.
- Train to use the microscope as a monitoring tool to better understand the bacteria in your system.
- Teaching personal how to be proactive and reduce Total Costs of Operation while also achieving compliance.

Training CD's, Manuals & Material for Wastewater
- Learn the clues that the Microbiology give.
- Learn the power to enable you to optimize your system.
- Learn the Microbiology and use it to troubleshoot your system.

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Wastewater Microscopic Biomass Analysis
- Microscopic analyses of any biological system should be a critical component of any ongoing daily monitor and control programs.
- Lab sheets to correlate health of the system, any changes in floc structures, higher life forms, filamentous identification, polysaccharide coating of the bacteria and suspended solids can be determined by using a microscope and examining the biomass.
- This is a tool that can help not only show exactly what the health of the system is at a given time, but can also help predict which direction the plant is headed. Ask for brochure for cost and send us your biomass sample.

www.EnvironmentalLeverage.com or Phone: 630-906-9791