North Central/Eastern Kentucky Water and Wastewater Operators Association Annual Fall Conference

October 23, 2013

The Basics of Nitrogen Removal
Session 3

Dan Miklos, Senior Associate, Midwest Region

HAZEN AND SAWYER
Environmental Engineers & Scientists

Nitrogen Basics
Agenda

- Nitrogen Basics
  - Nitrogen inputs to the plant
  - Nitrogen Compounds
  - Calculate total nitrogen removal rates in the effluent discharge
- Nitrogen Removal through Sludge Yield
  - Nitrogen removal with sludge yield
- Nitrification
  - 3D Floc explanation for varying nitrification rates
- Denitrification
- Questions

KWWOA

Nitrogen Inputs to the POTW

- Nitrogen input to a POTW
  - Influent TKN (Total Kjeldahl Nitrogen): Testing terminology.
    - Ammonia plus Organic Nitrogen
    - Increase in ammonia concentration in the summer reflects a “faster” conversion of organic nitrogen to ammonia in the summer versus winter. The total nitrogen loading remains consistent.
    - Nitrogen loading appears to remains consistent with flow changes unlike BOD_5.

KWWOA

Nitrogen Inputs to the POTW

- Nitrogen input to a POTW
  - Average daily per capita generation of nitrogen is approximately 16 grams.
  - Approximately 60% is in organic form while 40% is ammonium form.
  - Bacterial decomposition of protein results and hydrolysis of urea moves organic nitrogen to ammonium.
  - Typical concentrations at a POTW are dependent on sewer geographic capacity, inflow/infiltration and ambient climate conditions. At a minimum, typical concentrations in Kentucky reverse to at least 40% organic and 60% ammonium.

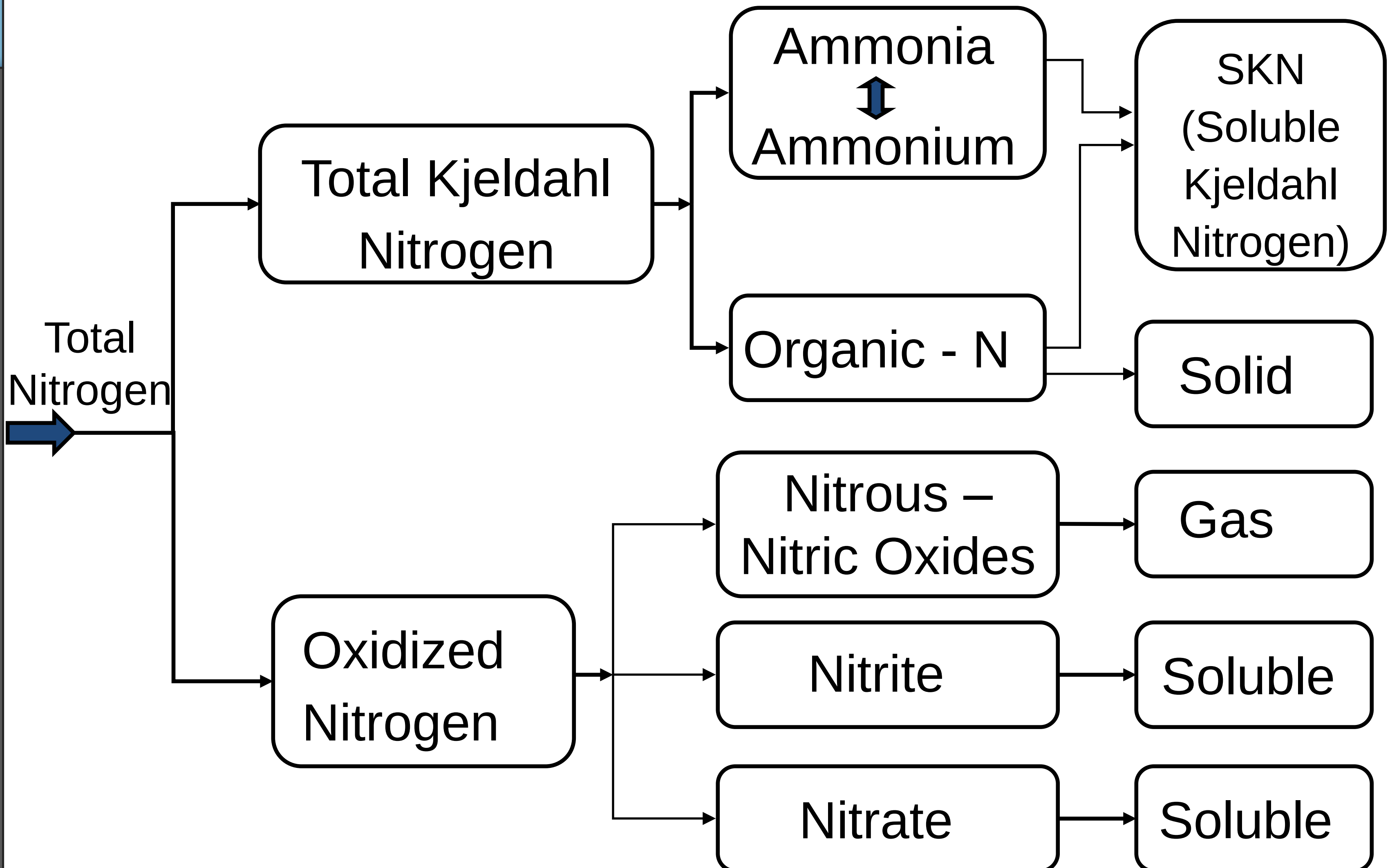
Nitrogen Compounds in the Environment

Nitrogen Compound	Formula	Oxidation State
Ammonia	NH_3	-3
Ammonium Ion	NH_4^+	-3
Nitrogen Gas	N_2	0
Nitrite Ion	NO_2	+3
Nitrate Ion	NO_3	+5

- Un-ionized molecular ammonia exists in equilibrium with the ammonium ion depending on pH and temperature. Little ammonia exists at pH levels less than neutral.

KWWOA

Forms of Nitrogen



Forms of Nitrogen

- Total Kjeldahl Nitrogen

  TKN = Organic - N + Ammonia

- Soluble Kjeldahl Nitrogen

  SKN = Soluble Organic – N + ammonia

- Total Nitrogen

  Total N = TKN (organic + ammonia) + nitrate + nitrite

KWWOA

Wastewater Characterization of Nitrogen in Influent & Effluent

	Raw Influent	Primary Effluent	Secondary Effluent (No Nitrification)	Secondary Effluent (Nitrified)
NH_4^+ - N	14	17	12	1.0
SKN	18	18	13	1.2
TKN	28	24	15	2.2
NO_2^- - N	0	0	0	0.1
NO_3^- - N	0	0	0	16.0
Total N	28	24	15	18.3
Sol. Organic - N	4	1	1	0.2
Organic - N	14	7	3	1.2

Why regulate nitrogen in the effluent?

- Biological Nutrient Removal typically includes both Nitrogen and Phosphorus limits.
- Typically, the only nitrogen based NPDES effluent limitation in Kentucky is ammonia nitrogen.
- Ammonium as nitrogen contributes to the oxygen demand and is regulated through Qual2 Modeling. Ammonia is also regulated in Kentucky through aquatic toxicity (as a function of stream pH & temperature).

Nitrogen in the Effluent

- Ammonia gas is very soluble in water, reacting to form ammonium hydroxide (NH_4OH). It exists in equilibrium with ammonium (NH_4^+) based on pH and temperature
- In the presence of higher pH, free ammonia gas is formed. This un-ionized form of ammonia is toxic to most aquatic organisms.
- The distribution of ammonia versus ammonium is the basis of summer and winter NPDES limits.

Nitrogen

- All forms of nitrogen are available as a “nutrient” to aquatic plants. Eutrophication contributes both directly to oxygen sags in the stream (photosynthetic plants) during no light and indirectly through aquatic decomposition and subsequent oxidation.
- The TMDL process will eventually implement total nitrogen limits based on the nutrient impact of nitrogen. Ammonia oxidation to nitrate eliminates toxicity but still results in nutrient impact to the stream. Eventually we will have to control the nitrate discharge from ammonia oxidation.

The Fate of Nitrogen in the Plant

Formation of Nitrogen Compounds

- Fixation
  - Inert nitrogen gas to compounds that can be used by plants and animals.
    - Biological: organic nitrogen compounds
    - Atmospheric (lightning): nitrate
    - Industrial: ammonium and nitrate
- Ammonification
  - Decomposition of animal, plant tissue & fecal matter
    - Synthesis with green plants and sunlight (Nitrate and Ammonia/Ammonium) creates proteins through Fixation. Proteins (organic nitrogen) are decomposed to ammonia/ammonium.

Formation of Nitrogen Compounds

- Synthesis or Assimilation
  - Plant protein formation with ammonia/nitrate compounds – green plants. Animals using protein from plants and other animals.
  - Protein formation by chemosynthetic plants (our bugs) – formation of cellular material through building of proteins and the cell wall.
- Nitrification
  - Biological oxidation of ammonium in two (2) steps: Ammonia to nitrite (AOB) and nitrite to nitrate (NOB).
- Denitrification
  - Biological scavenging of oxygen from nitrite/nitrate generates nitrogen gas to the atmosphere.

How do we control a total Nitrogen discharge?

Start with the Biology…..

Typical composition of bacterial cells on a dry basis

Carbon	50%
Oxygen	20%
Nitrogen	12.5%
Hydrogen	8%
Phosphorus	3%
Sulfur	1%
Potassium	1%
Sodium	1%
Calcium	0.5%
Magnesium	0.5%
Other	2.5%

Typical bacterial cell:

$C_{60}H_{87}O_{23}N_{12}P$

If P is not used, the typical cell formula is:

$C_5H_7NO_2$

KWWOA

Nutrient Removal – Biological MLSS Component

- Biological assimilation of N and P
  - Assume cells are 12.5% nitrogen and 3% phosphorus (not optimized for Phosphorus control).
  - Assume a cell yield (net growth following decay) is 0.65 (0.65 lbs/lb BOD_5 removed)
  - Net cell yield is multiplied by the % cell content
    - N is (0.125)*(0.65)=8.15 lbs per 100 lbs biomass.
    - P is (.03)*(0.65)=1.95 lbs per 100 lbs biomass.
  - Assume a flow of 1.0 MGD @ 160 mg/L of $CBOD_5$

KWWOA

Nutrient Removal – Biological MLSS Component

- Biological assimilation of nitrogen:
  - Assume the WWTP flow of 1.0 MGD @ 160 mg/L of $CBOD_5$ resulted in a growth of 867 lbs of biomass (at the yield of 0.65).
  - If 12.5% of the biomass is nitrogen, 108 lbs of nitrogen are removed in the biosolids.
  - If the influent concentration is 24 mg/L TKN, 200 lbs of N were received in the influent.
  - The remaining pounds (200 – 108) = 92 lbs must be nitrified to meet NPDES effluent ammonia limitations (11 mg/L of the total nitrogen input of 24 mg/L).

Nitrogen Removal - Nitrification

- The WWPT nitrogen removal must count on additional microbiology other than assimilation ($CBOD_5$) if an effluent ammonia limit is to be met.
    - Some POTWs that operate with significant paper mill and dairy discharge (nitrogen deficient) can meet near 0 mg/L ammonia discharge values through just assimilation (with no nitrification required). Nitrogen in this case is hauled out as biosolids.
- A separate culture of nitrifying bacteria must be optimized for ammonia removal (to remove ammonia that is left after assimilation and growth).

KWWOA

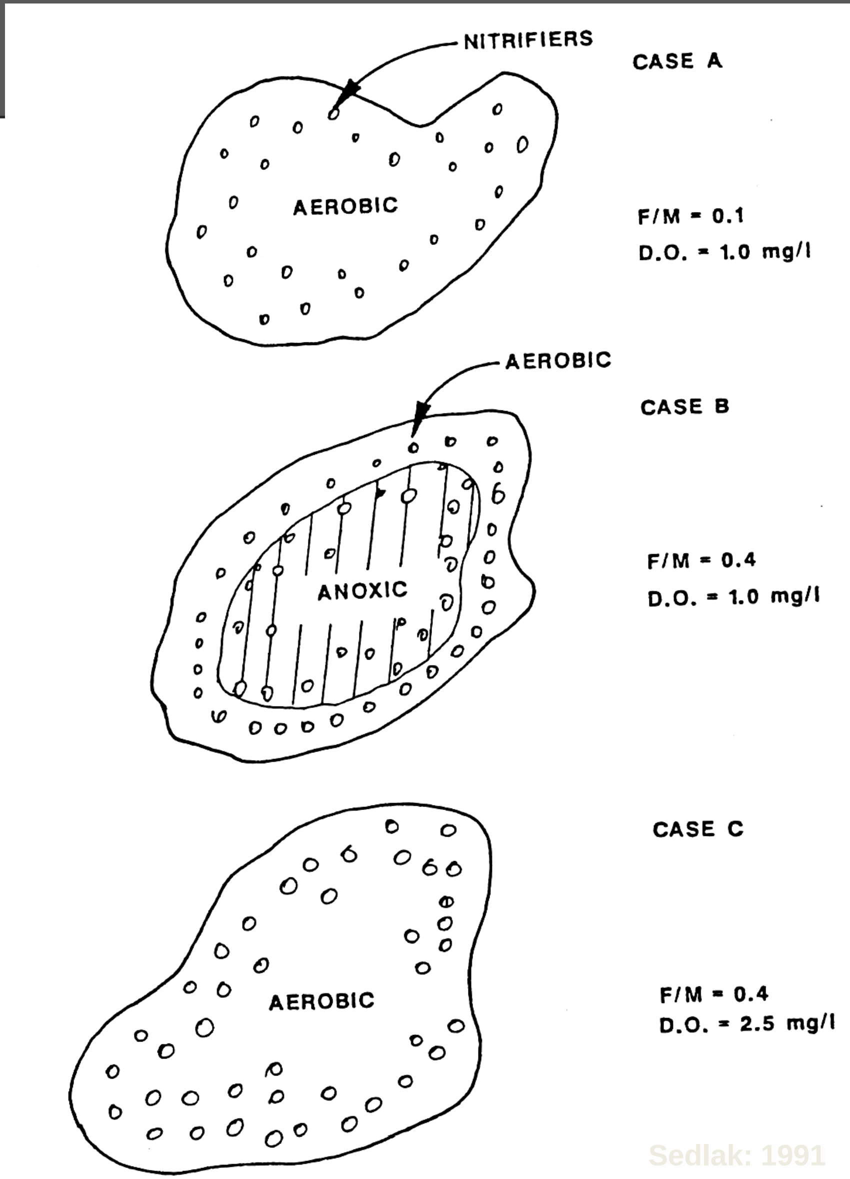
Activated Sludge Microbiology - Nitrifiers

- Nitrifiers are thought to typically range from 1-4% of the population.
- AOB (Nitrosomonas) is responsible for the loss in alkalinity with the production of nitrous acid (destroying approximately 7.14 mg/L of alkalinity for mg/L of ammonia oxidized).
- Nitrification can be stopped with a loss in available alkalinity. Total alkalinity results below pH operating range of the microbiology are not available for nitrification.
- Nitrification inhibition due to loss of alkalinity is most often seen in aerobic digestion where water chemistry results in high nitrates, high nitrites and high ammonia results. Dissolved oxygen is typically considered the limitation.

Activated Sludge Microbiology - Nitrifiers

- Nitrification is expected to use 4.57 mg/L of dissolved oxygen for each mg/L of ammonia.
- Nitrification rates vary significantly based on the residual oxygen levels. If high ORP levels are present, lower dissolved oxygen levels are required. If low ORP values are present, high residual oxygen levels are required to maintain the same nitrification rate.
- Nitrification has included the 3 dimensional concepts for dissolved oxygen control of the process.
- Nitrification rates have been shown to double from a dissolved oxygen of 1.0 mg/L to 3.0 mg/L.

Activated Sludge Microbiology - Nitrifiers



The 3-D Floc concept allows for changes in ORP demand due to load or floc condition. Nitirification rates with the same dissolved oxygen vary due to floc.

Estimating Oxygen Supply in your Reactor

- Oxygen supply approximations:
  - Mechanical aeration – USEPA rule of thumb (combined horsepower):
    - Surface mechanical aerators 3.0 lbs O_2 / hp – hr
    - Submerged turbine aerators 2.0 lbs O_2 / hp – hr
    - Jet Aerators 2.8 lbs O_2 / hp – hr
  - Diffused aeration transfer efficiency (rule of thumb)

    Coarse bubble = 0.5% per foot submergence

    Medium bubble = 0.8% per foot submergence

    Fine bubble = 1.2% per foot submergence
- Calculate oxygen per SCFM
  - Specific weight of air = 0.075 lb/cf
  - Oxygen in air = 20% by weight

lbs O_2/day = SCFM * 1,440 mins/day * 0.075 lb/cf * 0.20 O_2 * transfer

Oxygen Mass Balance with Nitrification

- Oxygen Mass Balance in Reactors
  - Calculate oxygen demand: Traditional versus oxygen uptake rate / respiration.
    - BOD_5 loading times 1.0 mg/L / lb BOD_5 treated added to Ammonia loading times 4.6 mg/L / lb ammonia oxidized.
  - Ammonia that is being used in assimilation (growth of cells) is not used in the oxygen demand calculation. This is an engineering approach used during design.
  - OUR in mg/L/hr times MG times 24 hours in a day. OUR can be measured in different parts of the aeration process and used to determine oxygen demand through your treatment process.

Oxygen Requirements in Pounds/Day

- Oxygen requirements in pounds per day:
  - BOD_5 Removal Only:

    $(1)*(BOD_5 \text{ mg/L})*(8.34)$

  - With Nitrification:

    $(1)*(BOD_5 \text{ mg/L})*(8.34) + (4.6)*(NH_4^+\text{-N mg/L})*(8.34)$

  - With Denitrification Credit =

    $(1)*(BOD_5 \text{ mg/L})*(8.34) + (4.6)*(NH_4^+\text{-N mg/L})*(8.34)$

    $- \ (2.86)*(NO_2^- \ NO_3^- \text{- N mg/L})*(8.34)$

Nitrogen Removal – Denitrification

- Then a separate culture of dentrifiers must also be optimized for removal of the oxidized ammonia byproducts (nitrite/nitrate) for total N compliance
- The separate culture of "dentrifiers" must also be optimized in the BNR process to utilize carbon ($CBOD_5$) to denitrify the oxidized ammonia byproducts (nitrite/nitrate).
- Excess Nitrogen (nitrogen not contained in the biomass) must be oxidized and then denitrified and discharged into the atmosphere to maintain total nitrogen compliance.

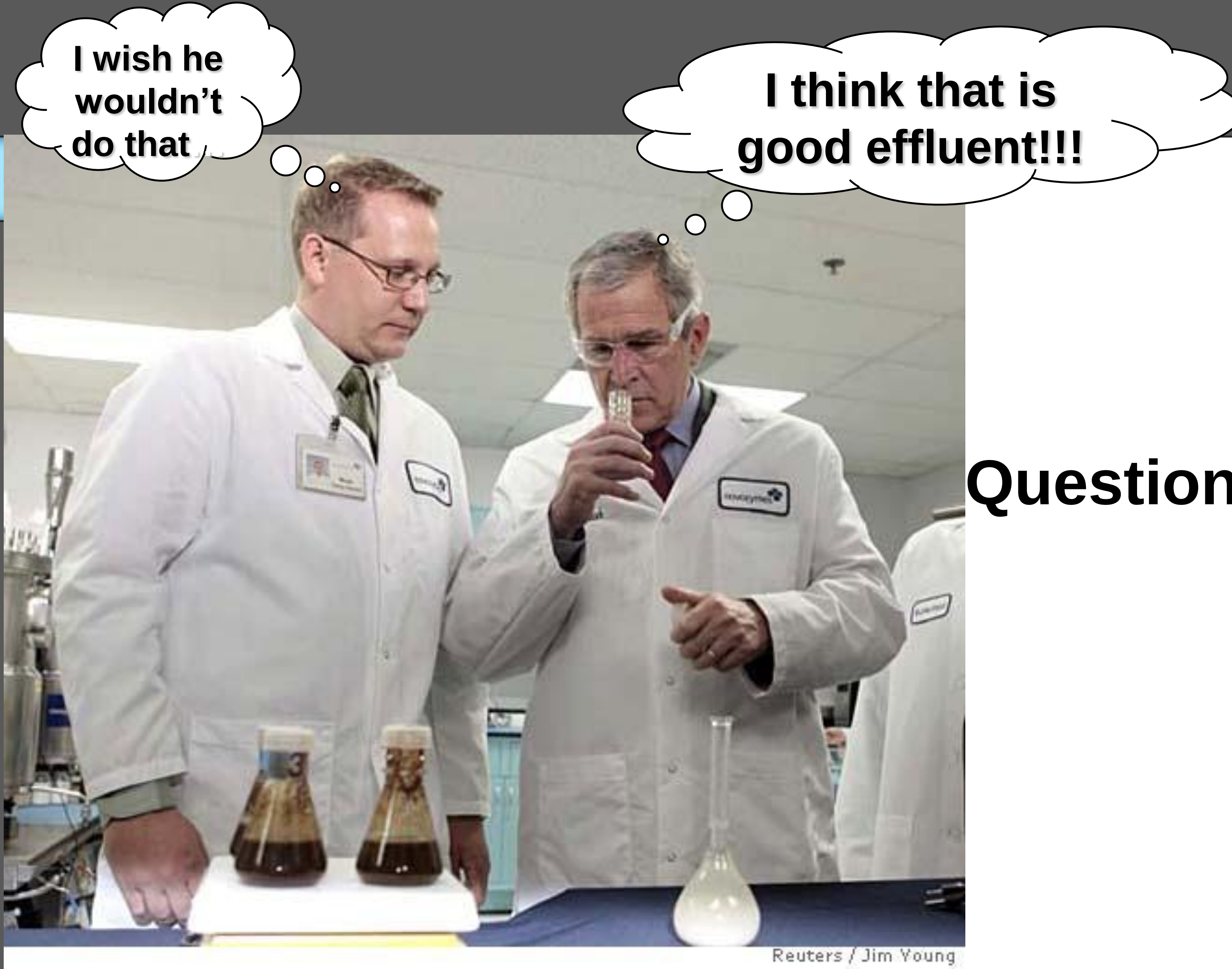
KWWOA

AOB/NOB Change with Aerated Anoxic

- Dan Noguera first published in Water Science Technology in 2002.
- Adding small amounts of oxygen induces simultaneous nitrification and denitrification with dissolved oxygen less than detection.
- This process feature allows Nitrosospira bacteria to dominate as the AOB and NOB.
- Dan Noguera's Bacteria in the genus *Nitrosospira* are significant AOBs while bacteria in the genus *Nitrospira* have been shown to be the dominant organisms in nitrite to nitrate (NOB) in oxidation ditch facilities.
  - That means that nitrification can proceed with carbonaceous removal and Nitrification can proceed without measurable dissolved oxygen.

The Aerated Anoxic Process

Dan Noguera at the University of Wisconsin and Chuck Applegate (while Envirex). Envirex promoted aerated anoxic operation for simultaneous nitrification and denitrification & funded Dan's research.


I wish he wouldn't do that
I think that is good effluent!!!
Reuters / Jim Young

Questions?