



Presentation to



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## **Determining Labile and Recalcitrant Organic Nitrogen for TMDL Projections**

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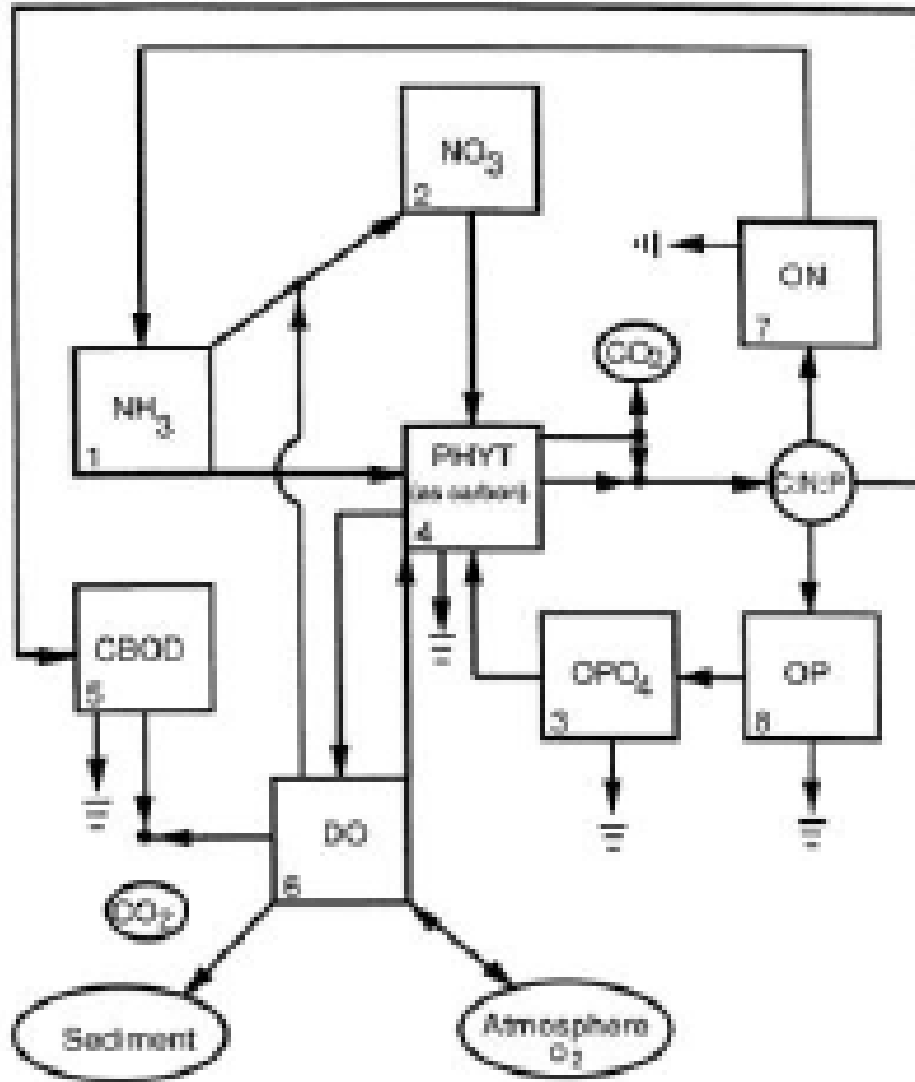
# ORGANIC NITROGEN

- o **Total Nitrogen limits are included in some NPDES Permits**
- o **The amount of organic nitrogen that is converted to ammonia may be over predicted for modeling purposes**
  - QUAL2E
  - WASP
  - RIV1Q

# WHY IS THIS IMPORTANT?

- **Emphasis has been placed on nutrient limitations for some dischargers.**
  - Total Nitrogen
    - $\text{TKN} + \text{NO}_2 + \text{NO}_3$
    - $\text{TKN} = \text{NH}_3 + \text{Organic Nitrogen}$
- **Ammonia can contribute to deoxygenation**
  - 4.57 mg/L oxygen removed during conversion of ammonia to nitrite and then to nitrate
- **Recalcitrant organic nitrogen**
  - Does not contribute to dissolved oxygen consumption since it is not hydrolyzed to ammonia
  - Does not contribute to nuisance algal blooms

# NITROGEN CYCLE



- o **NH<sub>3</sub> = Ammonia**
- o **NO<sub>3</sub> = Nitrate**
- o **ON = Organic Nitrogen**

Figure from WASP User's Manual (USEPA)

# TOTAL NITROGEN

- o **Total Nitrogen**
  - Total Kjeldahl Nitrogen (TKN)
    - Ammonia
    - Organic Nitrogen
  - Nitrite + Nitrate
- o **For receiving streams where nutrients are a concern, many NPDES permits have limits on total nitrogen.**

# AMMONIA IN THE ENVIRONMENT

- **Ammonia (NH<sub>3</sub>) affects water quality**
  - Can be converted to nitrite, which is then converted to nitrate
    - Full conversion of 1 mg/L NH<sub>3</sub> to NO<sub>3</sub> utilizes 4.57 mg/L of dissolved oxygen
  - Can be utilized by algae as a nutrient
    - Converted to organic nitrogen
  - Too much ammonia can contribute to nuisance algal blooms

# NITRATE IN THE ENVIRONMENT

- **Nitrate can be utilized by algae as a nutrient**
  - Nitrate is converted to organic nitrogen
  - Too much nitrate can cause nuisance algal blooms
- **During anoxic conditions, nitrate can be utilized as an oxygen source.**
  - Anoxic conditions are not expected when streams are meeting water quality standards

# ORGANIC NITROGEN

- o **Determination of Organic Nitrogen**
- o **Hydrolysis**
- o **Partitioning Organic Nitrogen**
  - Recalcitrant – unable to break down in a reasonable period of time
  - Labile – able to break down (will hydrolyze to ammonia)



# DETERMINATION OF ORGANIC NITROGEN

- o **Organic nitrogen can be partitioned into recalcitrant and labile portions through the use of a time series biochemical oxygen demand (BOD) analysis.**
- o **Following the completion of the time series BOD analysis, the organic nitrogen remaining can be considered to be recalcitrant.**
- o **Calculations based on the chemical analyses for the nitrogen series can also provide an estimate for the partitioning of labile and recalcitrant organic nitrogen.**

# THREE METHODS FOR ANALYSIS OF RECALCITRANT ORGANIC NITROGEN

- **Utilizing Ultimate BOD and Georgia EPD program, LTBOD**
  - Calculate Nitrogenous BOD (NBOD)
  - Calculate the amount of ammonia required
    - $\text{NBOD} / 4.57 = \text{Ammonia converted}$
  - Initial TKN and Ammonia
  - Assume that all ammonia is converted completely to nitrate (no build-up of nitrite)
- **Analyze the change in nitrate concentration over the course of the time series BOD test**
  - Assume that no nitrate is utilized by biology during study
- **Analyze the change in TKN concentration and the ammonia concentration**

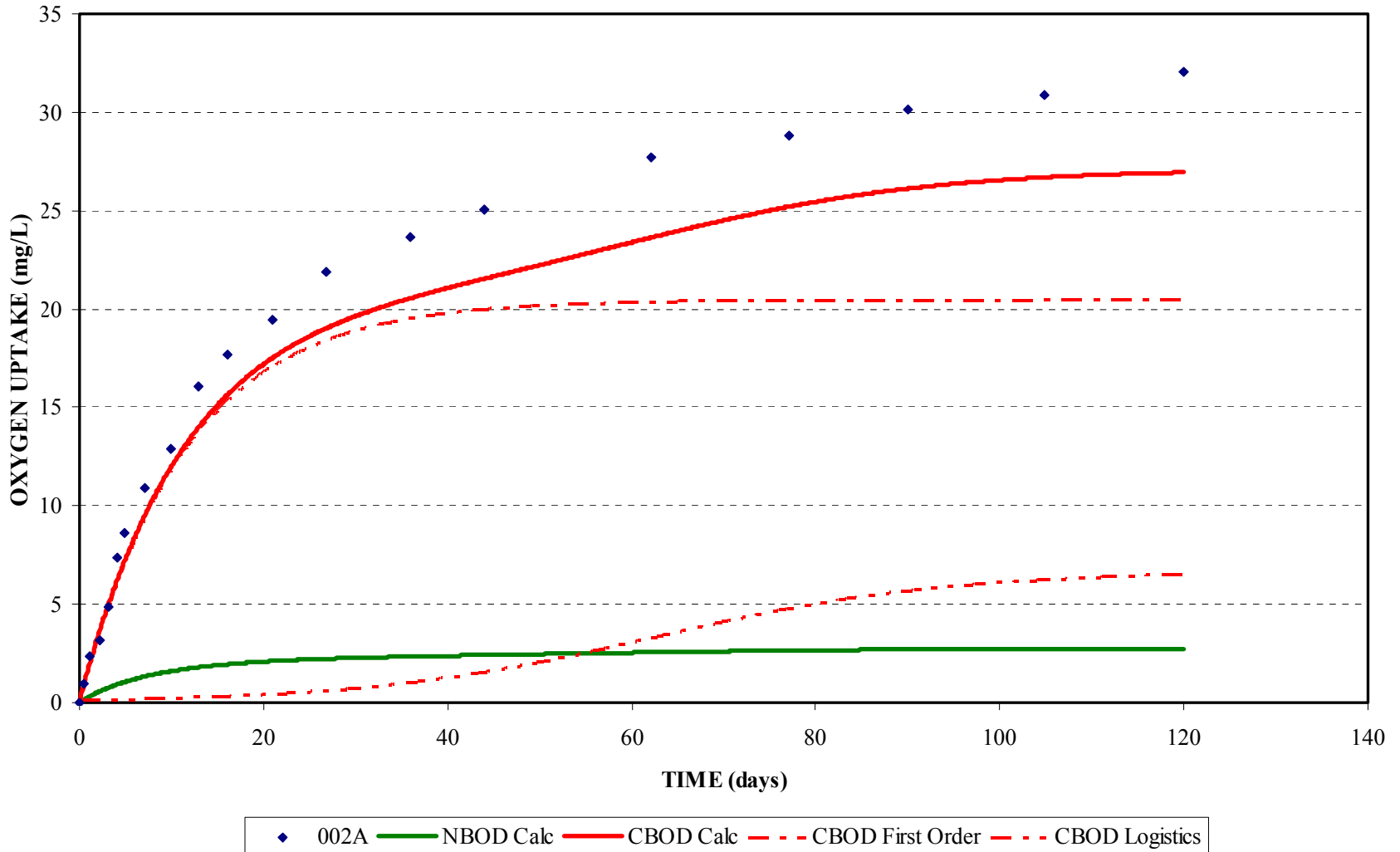
# TIME SERIES BIOCHEMICAL OXYGEN DEMAND

- **For pulp and paper mill effluents, the USEPA has recommended conducting time series BOD for a period of 90 to 110 days.**
- **Samples are collected at time 0, 20, 45, 60, 75, and 90 days for the analysis of the following:**
  - **Total Kjeldahl Nitrogen (TKN)**
  - **Ammonia (NH<sub>3</sub>)**
  - **Nitrite+Nitrate (NO<sub>2</sub>+NO<sub>3</sub>)**
- **Organic Nitrogen is determined by subtracting the ammonia result from the TKN result.**

# TIME SERIES BOD SETUP



# TIME SERIES BOD ANALYSIS



# CHEMICAL DATA

- o **Time = 0 days**
  - $\text{NH}_3 = 0.24 \text{ mg/L}$
  - $\text{TKN} = 1.9 \text{ mg/L}$
  - $\text{NO}_2 + \text{NO}_3 = 0.46 \text{ mg/L}$
- o **Organic Nitrogen**
  - $\text{TKN} - \text{NH}_3$ 
    - $1.66 \text{ mg/L}$
- o **Time = 120 days**
  - $\text{NH}_3 = 0.055 \text{ mg/L}$
  - $\text{TKN} = 0.85 \text{ mg/L}$
  - $\text{NO}_2 + \text{NO}_3 = 1.4 \text{ mg/L}$
- o **Organic Nitrogen**
  - $\text{TKN} - \text{NH}_3$ 
    - $0.795 \text{ mg/L}$
- o **Recalcitrant may be determined by the following:**
- o **Organic Nitrogen – 0.795 mg/L remaining**
  - 48% Recalcitrant
- o **Nitrate production = 0.94 mg/L  $\text{NH}_3$  converted to nitrate**
  - $0.94 \text{ mg/L} - 0.24 \text{ mg/L} = 0.7 \text{ mg/L}$  of organic nitrogen converted.
  - 58% Recalcitrant

# SOURCES OF ERROR

- **Time series BOD Analysis**
  - Reaeration
- **Chemical samples taken during time series BOD**
- **Low nitrogen concentrations in samples**
  - Reporting limits used for this study
    - $\text{NH}_3$                     0.05 mg/L
    - TKN                         0.5 mg/L
    - $\text{NO}_2 + \text{NO}_3$          0.25 mg/L

# CONCLUSIONS

- o **A mill that has a total nitrogen permit limit based upon a TMDL may have a larger margin of safety than given by the model results.**
  - Recalcitrant organic nitrogen may have been included as labile organic nitrogen.





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optimizing environmental resources – water, air, earth

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