Presentation to

TAPPI
people resources solutions

November 7, 2006
Atlanta, Georgia

Determining Labile and Recalcitrant Organic Nitrogen for TMDL Projections

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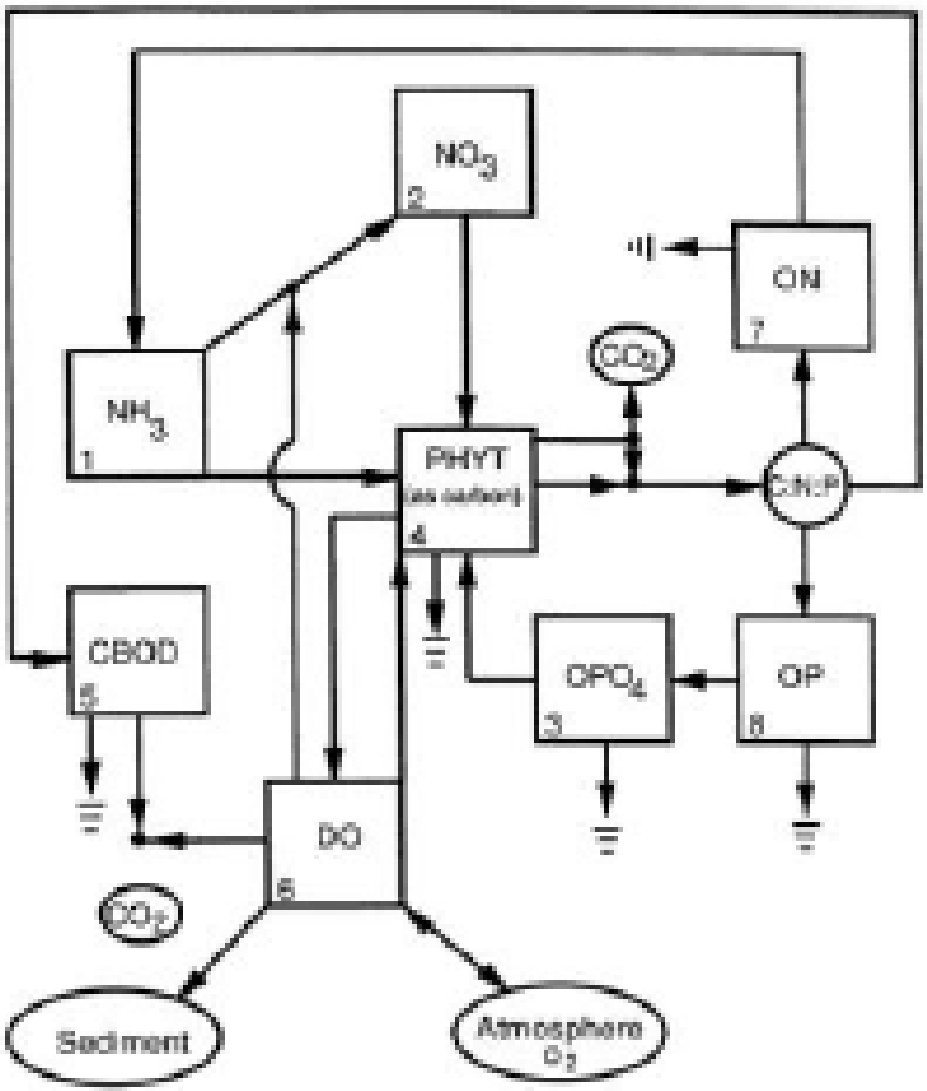
ORGANIC NITROGEN

- **Total Nitrogen limits are included in some NPDES Permits**
- **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
    - TKN + NO_2 + NO_3
    - TKN = NH_3 + 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



- NH_3 = Ammonia
- NO_3 = Nitrate
- ON = Organic Nitrogen

Figure from WASP User's Manual (USEPA)

TOTAL NITROGEN

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

AMMONIA IN THE ENVIRONMENT

- **Ammonia (NH_3) affects water quality**
  - Can be converted to nitrite, which is then converted to nitrate
    - Full conversion of 1 mg/L NH_3 to NO_3 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

- **Determination of Organic Nitrogen**
- **Hydrolysis**
- **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

- Organic nitrogen can be partitioned into recalcitrant and labile portions through the use of a time series biochemical oxygen demand (BOD) analysis.
- Following the completion of the time series BOD analysis, the organic nitrogen remaining can be considered to be recalcitrant.
- 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

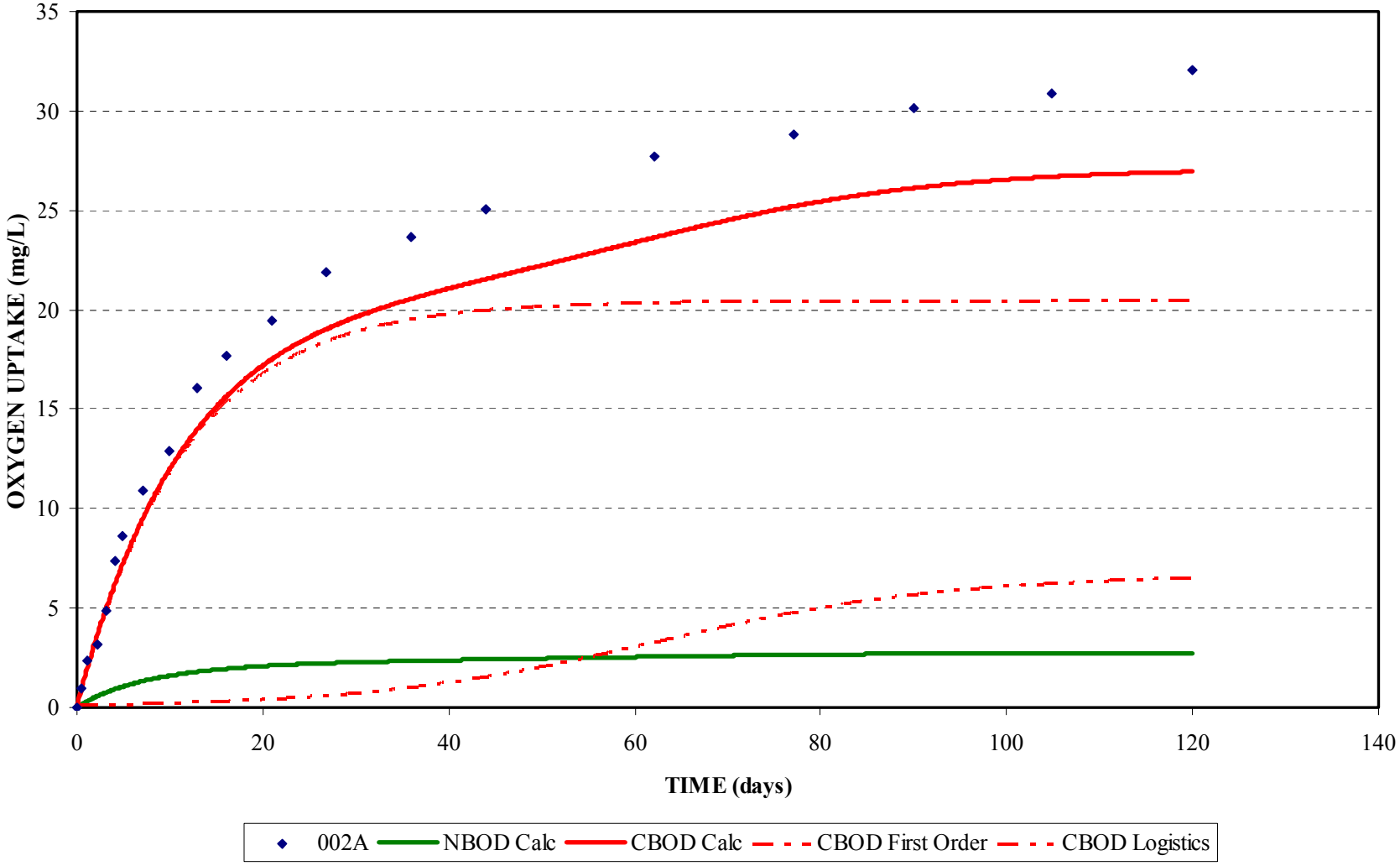
- **Utilizing Ultimate BOD and Georgia EPD program, LTBOD**
  - Calculate Nitrogenous BOD (NBOD)
  - Calculate the amount of ammonia required
    - NBOD / 4.57 = Ammonia converted
  - Initial TKN and Ammonia
  - Assume that all ammonia is converted completely to nitrate (no build-up of nitrite)
- **Analyze 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_3)
  - Nitrite+Nitrate (NO_2+NO_3)
- **Organic Nitrogen is determined by subtracting the ammonia result from the TKN result.**

TIME SERIES BOD SETUP

TIME SERIES BOD ANALYSIS



CHEMICAL DATA

- **Time = 0 days**
  - NH_3 = 0.24 mg/L
  - TKN = 1.9 mg/L
  - NO_2+NO_3 = 0.46 mg/L
- **Organic Nitrogen**
  - TKN – NH_3
    - 1.66 mg/L

- **Time = 120 days**
  - NH_3 = 0.055 mg/L
  - TKN = 0.85 mg/L
  - NO_2+NO_3 = 1.4 mg/L
- **Organic Nitrogen**
  - TKN – NH_3
    - 0.795 mg/L

- **Recalcitrant may be determined by the following:**
- **Organic Nitrogen – 0.795 mg/L remaining**
  - 48% Recalcitrant
- **Nitrate production = 0.94 mg/L NH_3 converted to nitrate**
  - 0.94 mg/L – 0.24 mg/L = 0.7 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
    - NH_3 0.05 mg/L
    - TKN 0.5 mg/L
    - NO_2+NO_3 0.25 mg/L

CONCLUSIONS

- **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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