Process Optimization of a Petroleum Refinery Wastewater Treatment Facility Using Process Modeling and Site Specific Biokinetic Constants

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Outline

- Dynamic Modeling of WWTP's
- Process Model Applications to Support Operational Decision-Making
  - Optimal Number of Batch Runs to Treat High Strength COD Wastewater
  - Optimal Incubation Period for Microbes to Treat a Large Quantity of Free Oil Released to the WWTP
- Determination Of Site-Specific Kinetic Constants of the Existing WWTP
- Conclusions

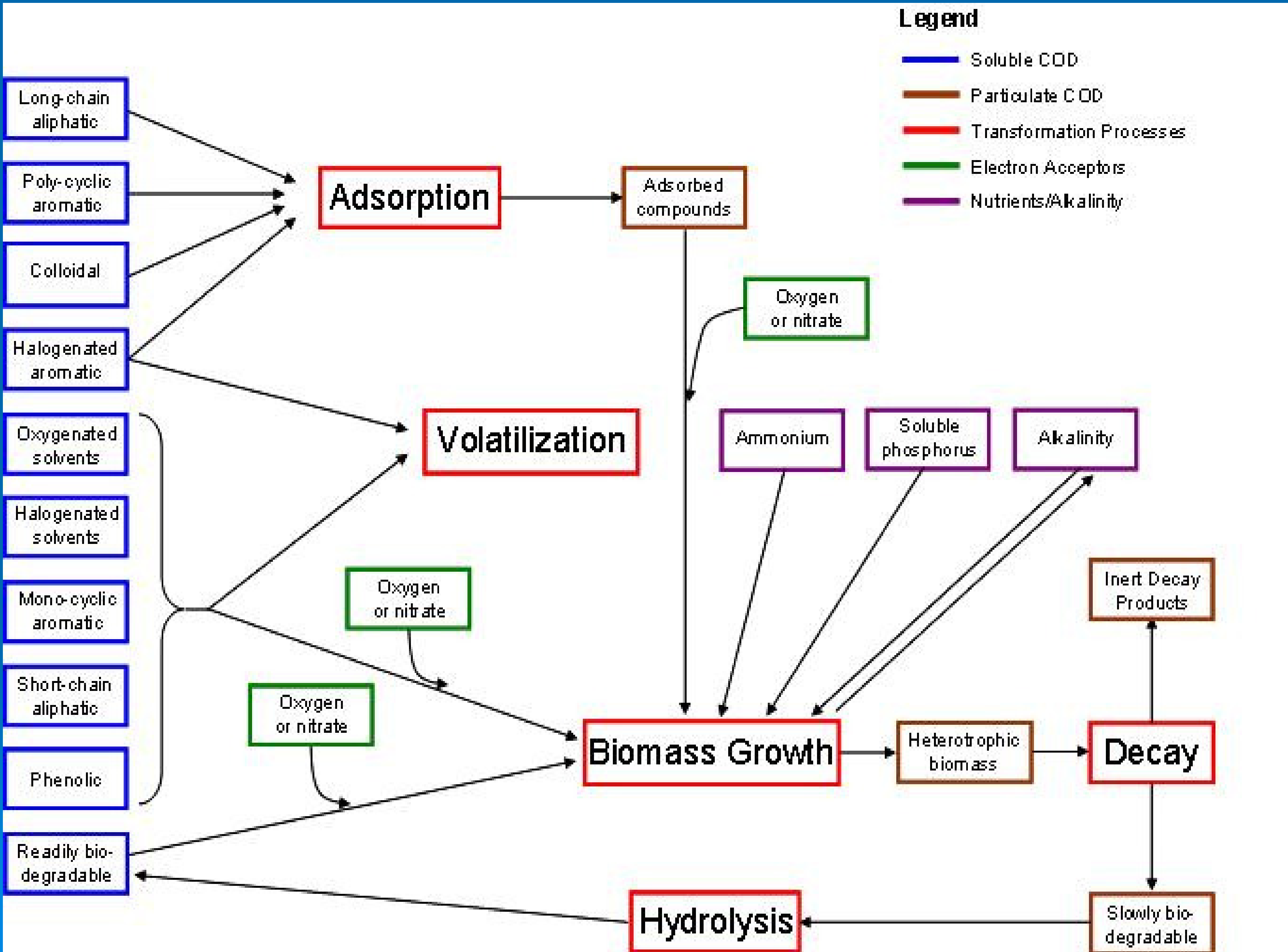
Dynamic Modeling of WWTP's

- **What does a model do?**
  - Calculates mass & volumetric balances
  - Includes reaction rates, settling rates, process constraints, …
  - Tracks component concentrations as time progresses
  - Predicts system behavior

- Understanding your system
  - What are the most sensitive parameters?
    - Am I adjusting the correct process controls?
    - How can I minimize costs?
    - Identify process bottlenecks

Motivation for MantisIW Model

- Existing activated sludge models used primarily for municipal wastewater
- Challenges for existing models
  - Pollutants/processes tailored to municipal wastewater
  - Customization of variables/equations may be required
  - May need additional substrate variables
    - Additional COD fractions, sulfur compounds
  - May need new processes
    - Surface volatilization, air stripping, adsorption, sulfur oxidation, and toxic inhibition
  - Suggests need for general-purpose industrial model



Legend
Soluble COD
Particulate COD
Transformation Processes
Electron Acceptors
Nutrients/Alkalinity
Long-chain aliphatic
Poly-cyclic aromatic
Colloidal
Halogenated aromatic
Oxygenated solvents
Halogenated solvents
Mono-cyclic aromatic
Short-chain aliphatic
Phenolic
Readily bio-degradable
Adsorption
Adsorbed compounds
Oxygen or nitrate
Volatilization
Ammonium
Soluble phosphorus
Alkalinity
Oxygen or nitrate
Oxygen or nitrate
Inert Decay Products
Biomass Growth
Heterotrophic biomass
Decay
Hydrolysis
Slowly bio-degradable

Process Optimization Case Study

Petroleum Refinery Wastewater Treatment Facility

Why Is Refinery Wastewater Bio-Treatment So Difficult to Control ??

1. **Multiple Waste Sources from Individual Oil Processing Units, each with considerable Variation in their contributions to the Central Collection System (Source Control \ Equalization)**
2. **Biologically Inhibitory and Recalcitrant Substances Present in the Influent**
3. **Frequent excursions into Biological Unsteady State Conditions.**
4. **Frequent periods of time running with Non-Optimized Process Control Variables in the Bioreactor**
5. **Generation of Toxic Intermediates in the Bioreactor from Incomplete Oxidation of Recalcitrant Molecules in Influent.**
6. **Process Control Strategy based on Trial & Error instead of on a Mathematical Basis**
7. **Lack of Sufficient Analytical and Operator Process Control Tools**
8. **Inadequate System Design Basis (Empirical vs. Theoretical \ Assumed Biokinetic Constants)**

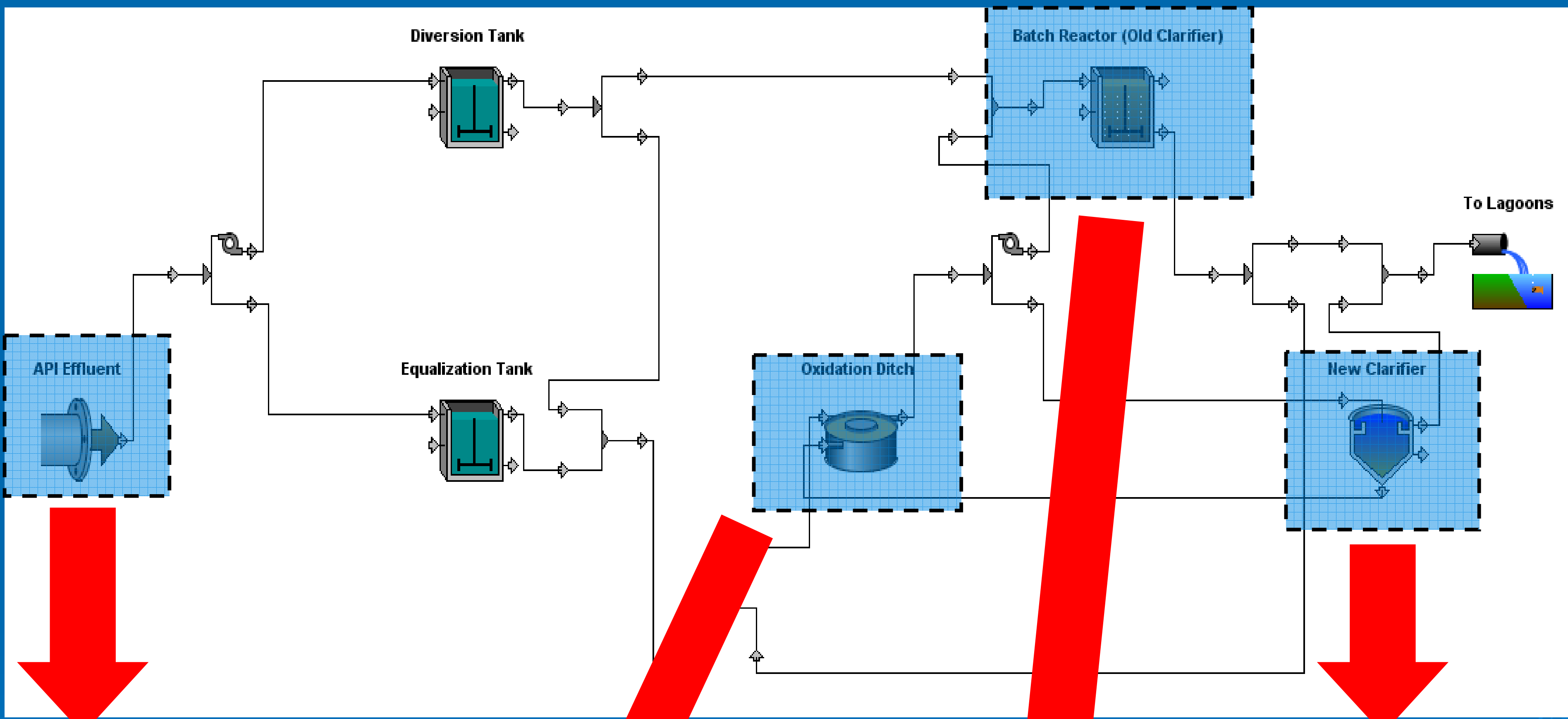
Petroleum Refinery WWTP Optimization

- WWTP treats average of 0.8 MGD of wastewater from a refinery which produces 85,000 BPD of sour crude oil
  - Typical challenges of profitable operations while meeting permit requirements for wastewater discharges and sludge disposal
- MantisIW model as implemented in GPS-X™ was used to evaluate WWTP operations
  - Overall mandate to improve compliance reliability by using innovative process control strategies

Scope of Petroleum Refinery WWTP Optimization

- Maximize the capacity of the existing wastewater treatment facility and infrastructure
- Determine the maximum plant loading capacity and establish site-specific biokinetic constants for the existing wastewater treatment facility
- Implement operational changes and process control strategies to improve oxygen transfer efficiency and oxygen utilization rates

Petroleum Refinery GPS-X^{TM} Model



API Effluent

- Q = 0.8 MGD
- COD = 1050 mg/L (mostly soluble, O&G)
- TKN = 40 to 90 mg/L
- Phenols = 50 mg/L

Secondary Clarifier

Sidestream Batch Reactor Retrofit

Can be operated in series, parallel or isolation

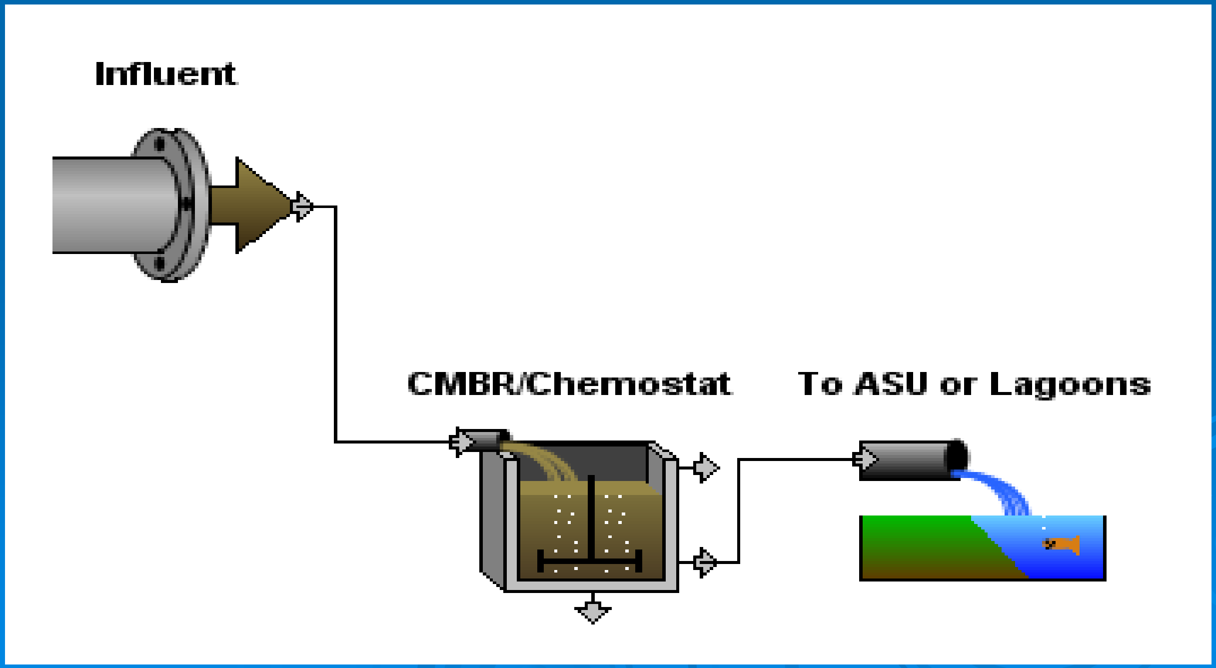
Oxidation Ditch Activated Sludge Unit w/ Brush Aerators

Complete Mix Batch Reactor (CMBR) Implementation

- In May 2010, an old out-of-service secondary clarifier was converted into a CMBR and retrofitted with a new fine bubble diffused air system to increase treatment capacity

Complete Mix Batch Reactor (CMBR) GPS-X™ Model

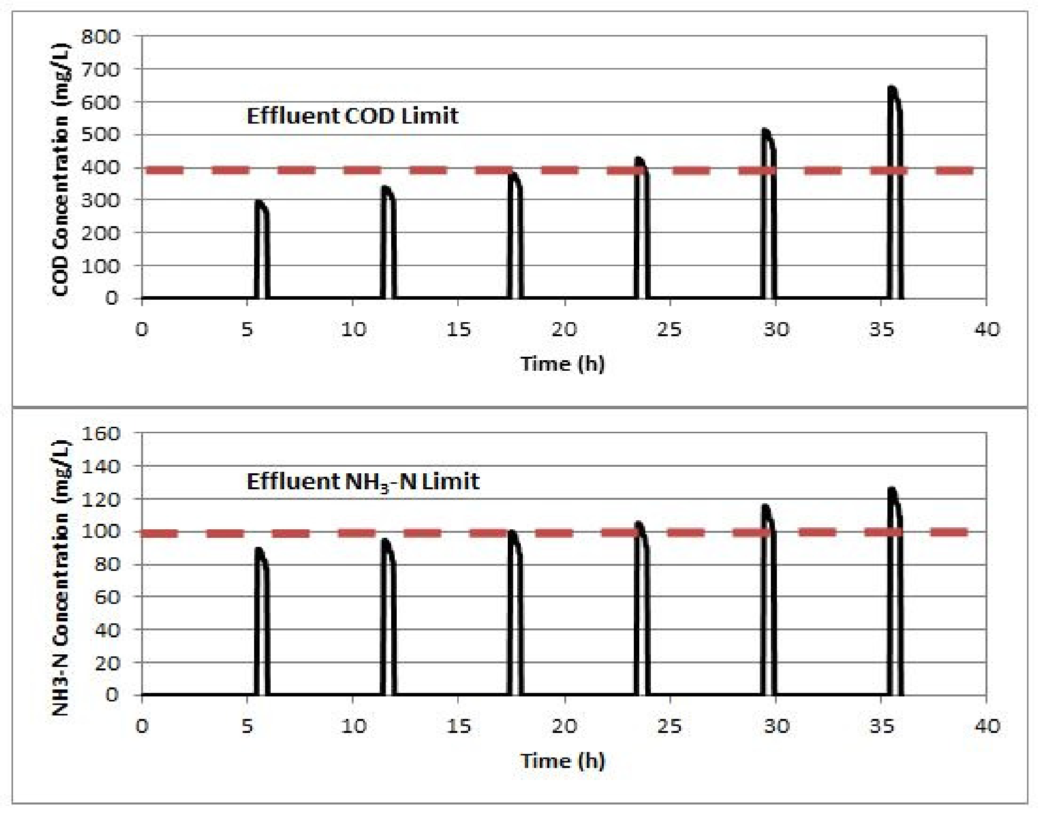
- A GPS-X™ model of the CMBR was created to evaluate the performance of different CMBR operating modes under different influent loading



Complete Mix Batch Reactor (CMBR) GPS-X™ Model

- Model used to evaluate operating the CMBR as a sidestream chemostat reactor for the treatment of intermittently generated high-strength COD and inhibitory waste streams
  - contains significant amounts of amine solutions, phenolic caustics, sulfidic caustics, undesirable slop oils, hydrogen sulfide, and spent catalysts
- Influent concentrations ranged from:
  - COD: 2,500 mg/L to 4,000 mg/L
  - NH_3-N: 275 mg/L to 350 mg/L
  - Phenols: 250 mg/L to 400 mg/L

CMBR Chemostat Effluent



- Simulation analysis indicated that after 4 six-hour batch runs, reactor would need to be dumped and reseeded to meet predefined effluent criteria
- Without this valuable insight from model, a “trial and error” approach would have been used in the field and the CMBR effluent concentration would have been significantly higher

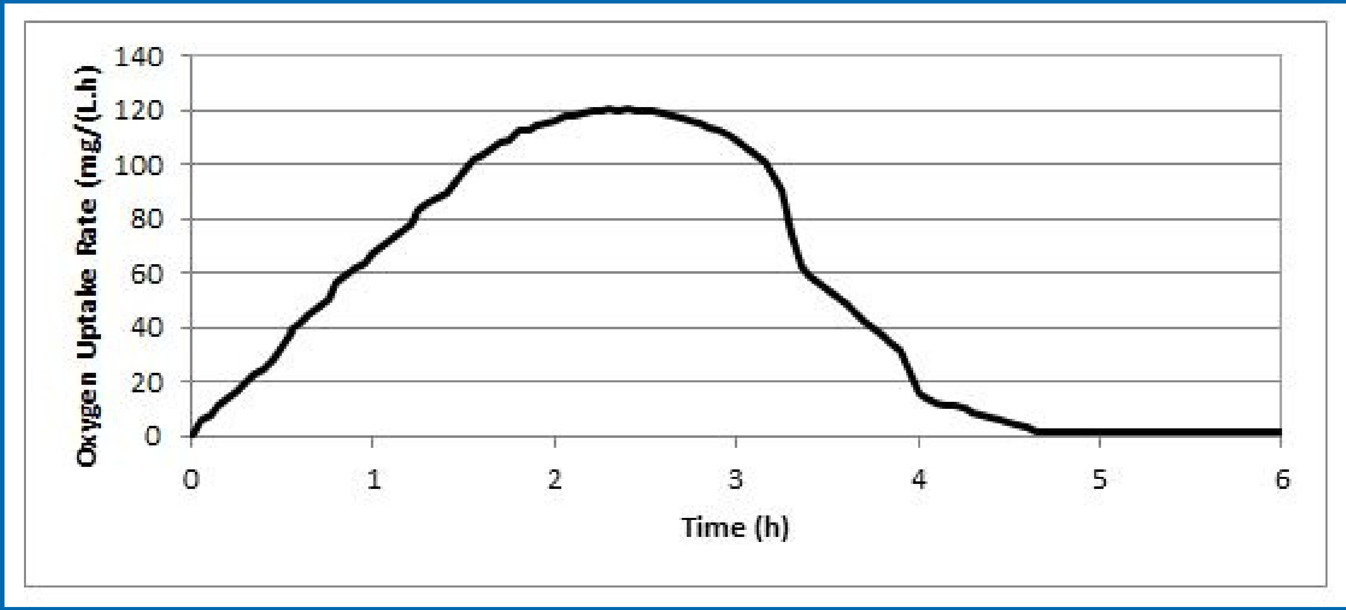
Complete Mix Batch Reactor (CMBR) GPS-X™ Model

- A second model application was initiated during a wastewater plant upset in July 2010
  - Combination of inadvertent sewer dumps, malfunctioning WWTP equipment, and rain resulted in greatly reduced diversion tank availability
- The oxidation ditch, secondary clarifier and the first lagoon became coated with 1.5 inches of floating free oil
  - NPDES permit compliance became threatened for a number of contaminants
  - OUR decreased below 15 mg/(L·h) during the upset

Complete Mix Batch Reactor (CMBR) GPS-X™ Model

- CMBR was deployed as a sidestream chemostat reactor to treat the floating free oil
  - Floating free oil was collected by vacuum truck from wastewater surface for input to the chemostat reactor
- Model used to determine the optimal batch run length for the microbes to consume the free oil under aerobic conditions
  - OUR was plotted to track the microbial activity in the CMBR

CMBR Chemostat Batch Length Determination



- Simulation analysis indicated that after a 4-hour period, the microbial activity under aerobic conditions was minimal; a 4-hour CMBR batch length was implemented
- After this time, 50% of the CMBR batch was blended with the oxidation ditch influent and the CMBR was refilled with vacuum truck discharge
- This batching was repeated a total of 4 times

CMBR Chemostat Free Oil Treatment

- Main benefits to batch procedure:
- Microbes were able to consume the free oil
- ASU was augmented with CMBR "oil consuming" conditioned biomass
- During peak periods free oil upset:
- Bulk water O&G levels: 1,000 mg/L to 5,000 mg/L
- Float O&G levels: 10,000 mg/L to 100,000 mg/L
- After 4 hours, no free oil observed in CMBR
- After 14 hours, no free oil remains on ASU surface
- After 24 hours, the clarifier effluent O&G levels were consistently below 15 mg/L

Implementation of an MCRT Process Control Strategy and Development Site-Specific Biokinetic Constants

F:M vs. MCRT Strategy

In some wastewater applications, the use of the F:M strategy for control of the Activated Sludge process works well. However, in many types of industrial settings, perhaps none more notable than Oil Refining, this strategy falls way short of adequate. This is due to:

1. Wide ranges of relative biodegradability of the substrate (Food) in the influent.
2. Wide ranges of variability in the influent.
3. The intermittent presence of biologically toxic and inhibitory compounds in the influent.

Inherently, the actual calculation of F:M has several pitfalls:

1. In Oil Refinery Wastewater, there is no representative quick test for the substrate. BOD5 would be representative, but does not meet quick adjustment turnaround times. COD, TOC, and TPH do not have a consistent linear relationship to BOD5 in refinery wastewater. As such, considerable error in process control enters right in the mere calculation itself. Conversely, the use of the MCRT strategy does not depend on measuring the substrate.
2. Unlike the use of the Mean Cell Retention Time (MCRT) strategy, F:M cannot be directly related mathematically to the microbial growth rates. As such, most of the operational and process control benefits of Biokinetic Modeling cannot be effectively achieved with F:M. Only MCRT can capture the entire spectrum of benefits which translate in operational cost savings.
3. Unlike the MCRT strategy, the process for determination of the optimum target control ranges for F:M is not practical under the conditions that oil refinery AS processes operate. As such, the optimum target F:M ranges are usually based on some other plant’s design and characteristics, which usually do not match the specific plant’s process considerations.
4. Adjustment of Sludge Wasting Rates to control the F:M Ratio is a Trial and Error process. With the use of the MCRT strategy, Sludge Wasting is calculated precisely and administered mathematically to hit the target control range.

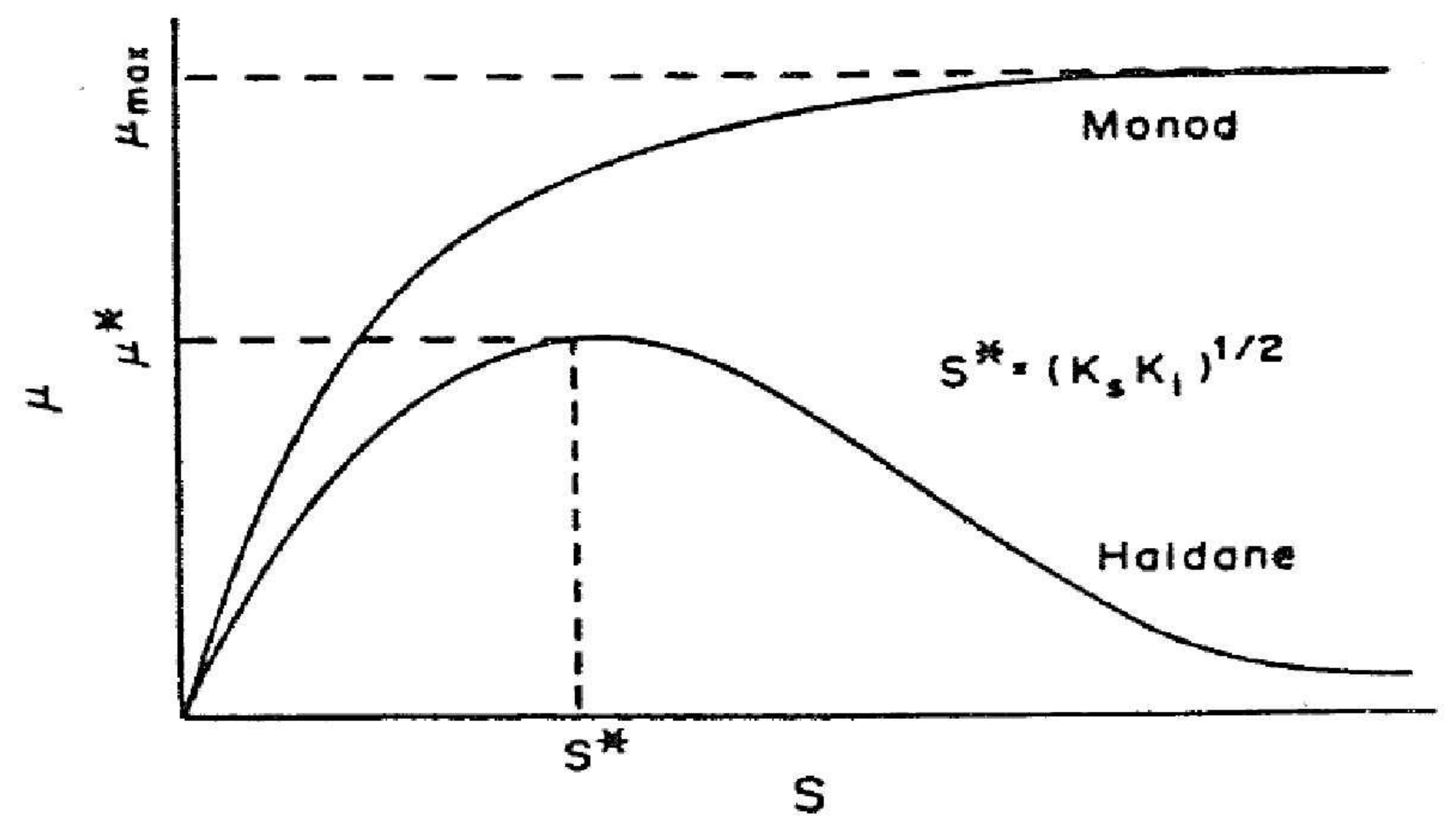
Wesley Eckenfelder: The Father of Biokinetic Modeling

1. **First Eckenfelder Model: 1st Order Kinetics for Substrate Removal.**
2. **McKinney Model: 1st Order Kinetics for Substrate Removal.**
3. **Lawrence-McCarty Model: Empirical Monod Kinetics for Substrate Removal.**
4. **Gaudy Model: Empirical Monod Kinetics for Substrate Removal.**
5. **Second Eckenfelder Model: 2nd Order Kinetics for Substrate Removal as a function of the change in Substrate.**
6. **Many Hybrids and Derivations; All based on relating Growth Rate to Substrate Utilization, using either:**
   1. **Batch Growth Technique.** (https://safestorage.rr.com/download.asp?NAME=\kincannon%2Dstover%2Epdf)
   2. **Substrate Utilization Technique.** (http://refinerywater.zoomshare.com/files/Caribbean_Gulf.pdf)
7. **Gaudy Respirometric Model: Oxygen Uptake Rate correlated to Growth Rate and Substrate Utilization.** (https://safestorage.rr.com/download.asp?NAME=\Gaudy+Procedure%2Epdf)

Monod & Haldane

- Monod Equation (Relatively Non-Inhibitory)
  - $$\mu = \frac{\mu_{max} S}{K_s + S}$$
- Haldane Equation (Severely Inhibitory)
  - $$\mu = \frac{\mu_{max} S}{K_s + S + S^2 / K_i}$$

Monod vs. Haldane



Key Biokinetic Modeling Expressions

(Lawrence & McCarty Model)

- θ = MCRT = Mean Cell Retention Time
- μ = 1 / MCRT = Growth Rate of Microbial Population
- Y = Cell Yield (Biomass \ Sludge Production)
- U = Specific Substrate Utilization Rate
- K_d = Decay Rate Coefficient
- K = Specific Substrate Utilization Coefficient
- k = Maximum Substrate Utilization Rate (True Plant Capacity)
- K_s = Half Saturation Constant (Effluent ---> ½ k)
- S_e = Effluent Substrate (WWTP Discharge Levels)

Key Biokinetic Evaluations

- $1 / MCRT = (Y)(U) - K_d$
  - [Growth Rate vs. Substrate Utilization]
- $S_e = (1 / MCRT + K_d) / (Y)(K)$
  - [Effluent Substrate vs. MCRT]
- $Y = (1 / MCRT + K_d) / (K)(S_e)$
  - [Biomass Generation vs. CO_2]

CASE HISTORY: REFINERY FULL SCALE PLANT BIOKINETIC CONSTANTS DETERMINED & INPUT INTO SOFTWARE PLATFORM

Biokinetic Constant	Value
k – Maximum Substrate Utilization Rate	0.274 mg COD mg VSS^{-1} d^{-1}
K_s – Half Saturation Constant	165.8 mg COD L^{-1}
K – Specific Substrate Utilization Coefficient	0.0017 L mg COD^{-1} d^{-1}
Y – Cell Yield	0.424 mg VSS mg COD^{-1}
K_d – Decay Rate Coefficient	0.01 d^{-1}

CASE HISTORY: REFINERY FULL SCALE PLANT MEASURED vs. PUBLISHED (ASSUMED) BIOKINETIC CONSTANTS

Biokinetic Constant	Measured	Published
k – Maximum Substrate Utilization Rate	0.274 mg COD mg VSS-1 d-1	3.0 mg COD mg VSS-1 d-1
Ks – Half Saturation Constant	165.8 mg COD L-1	40 mg COD L-1
K – Specific Substrate Utilization Coefficient	0.0017 L mg COD-1 d-1	0.75 L mg COD-1 d-1
Y – Cell Yield	0.424 mg VSS mg COD-1	0.3 mg VSS mg COD-1
Kd – Decay Rate Coefficient	0.01 d-1	0.06 d-1

WHY BIOKINETIC MODELING HAS FAILED IN THE PAST IN OIL REFINERY BIOREACTORS

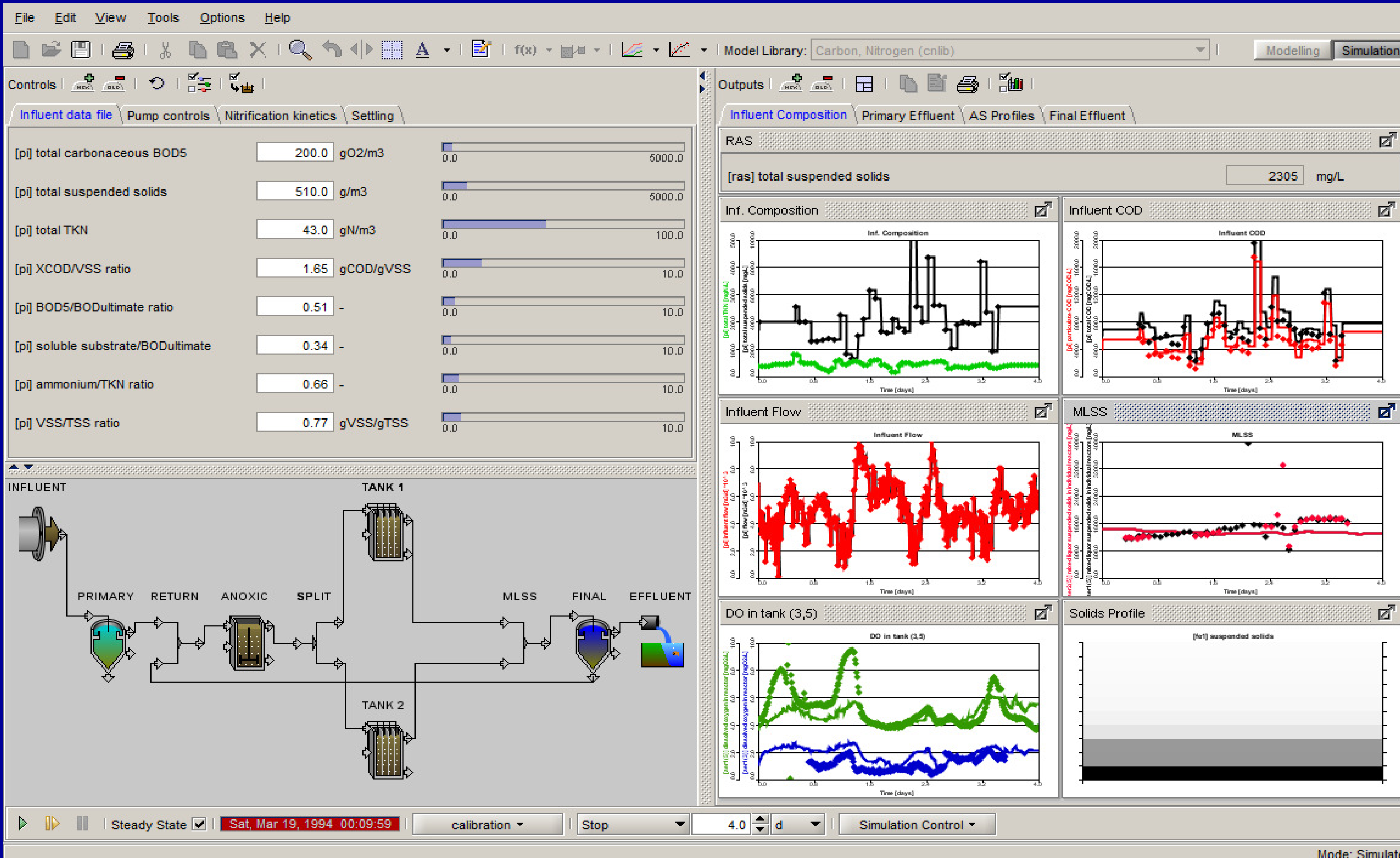
1. The facilities never determined the full scale plant biokinetic constants, and used either Published constants (Assumed) or Lab-Determined constants (Ignores many design considerations), both of which are not representative
2. The facilities did not deploy Steady State MCRT Process Control Targeting in the Bioreactor
3. Failure to measure or compensate for K_i

Benefits of Biokinetics to Operational Process Control

1. **Calibration of the Engineering Design Equations for construction and operation of the WWTP.**
2. **Quantitative Determination of the Optimum Targets \ Adjustments for the Process Control Variables under any set of Environmental & Operational conditions.**
3. **Accurate Prediction of Effluent Quality at Hypothetical Operating conditions.**
4. **Deployment of Operational Cost Simulation Models which Predict Effluent Quality vs. $$.**

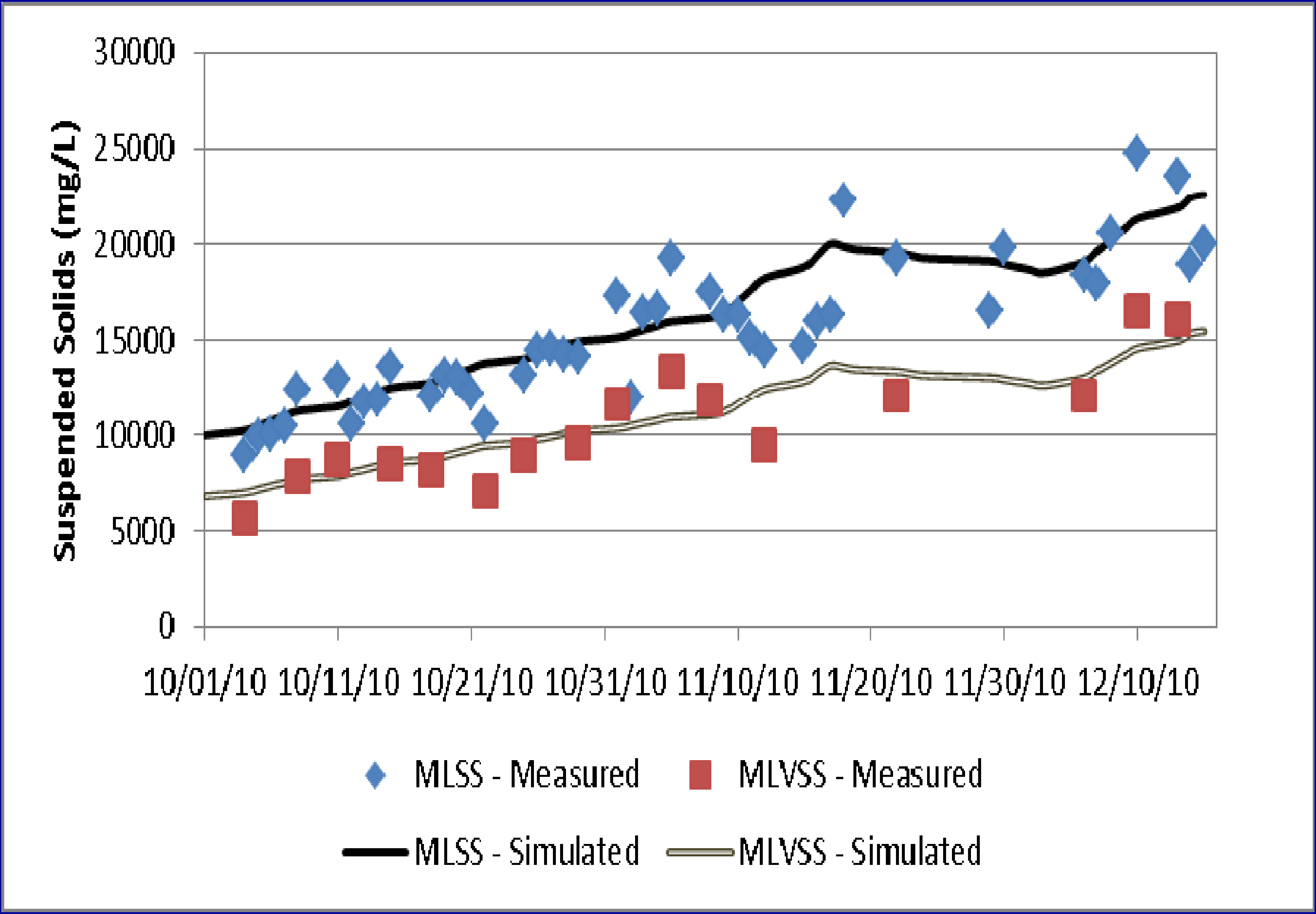
Let Software Do The "What-If" Predictions

(Accurate Prediction Results requires Plant Specific Biokinetic Constants)



SOFTWARE DEMO: http://refinerywater.zoomshare.com/3.html

SOFTWARE MODEL SIMLATION vs. ACTUAL PLANT MEASUREMENTS



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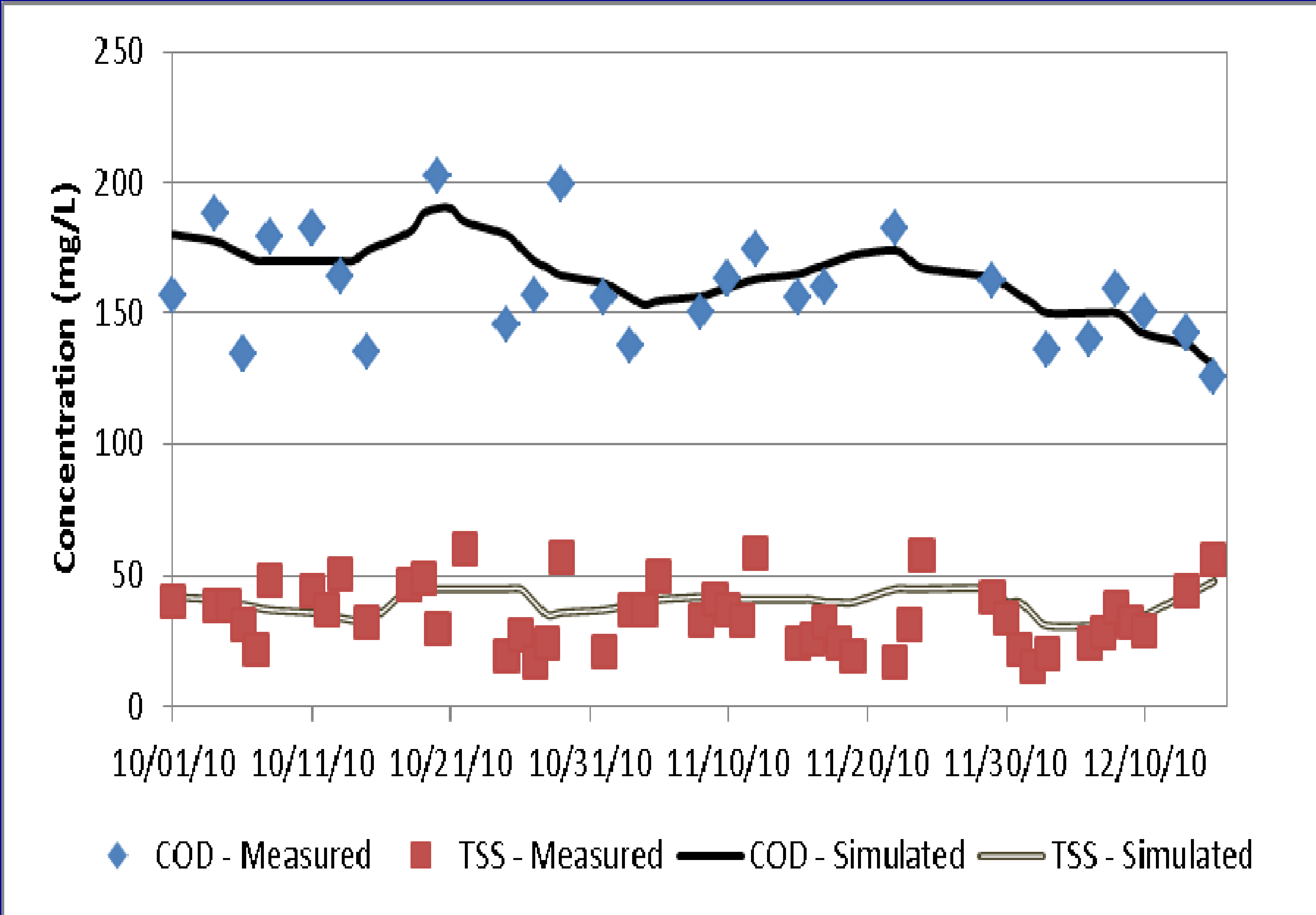

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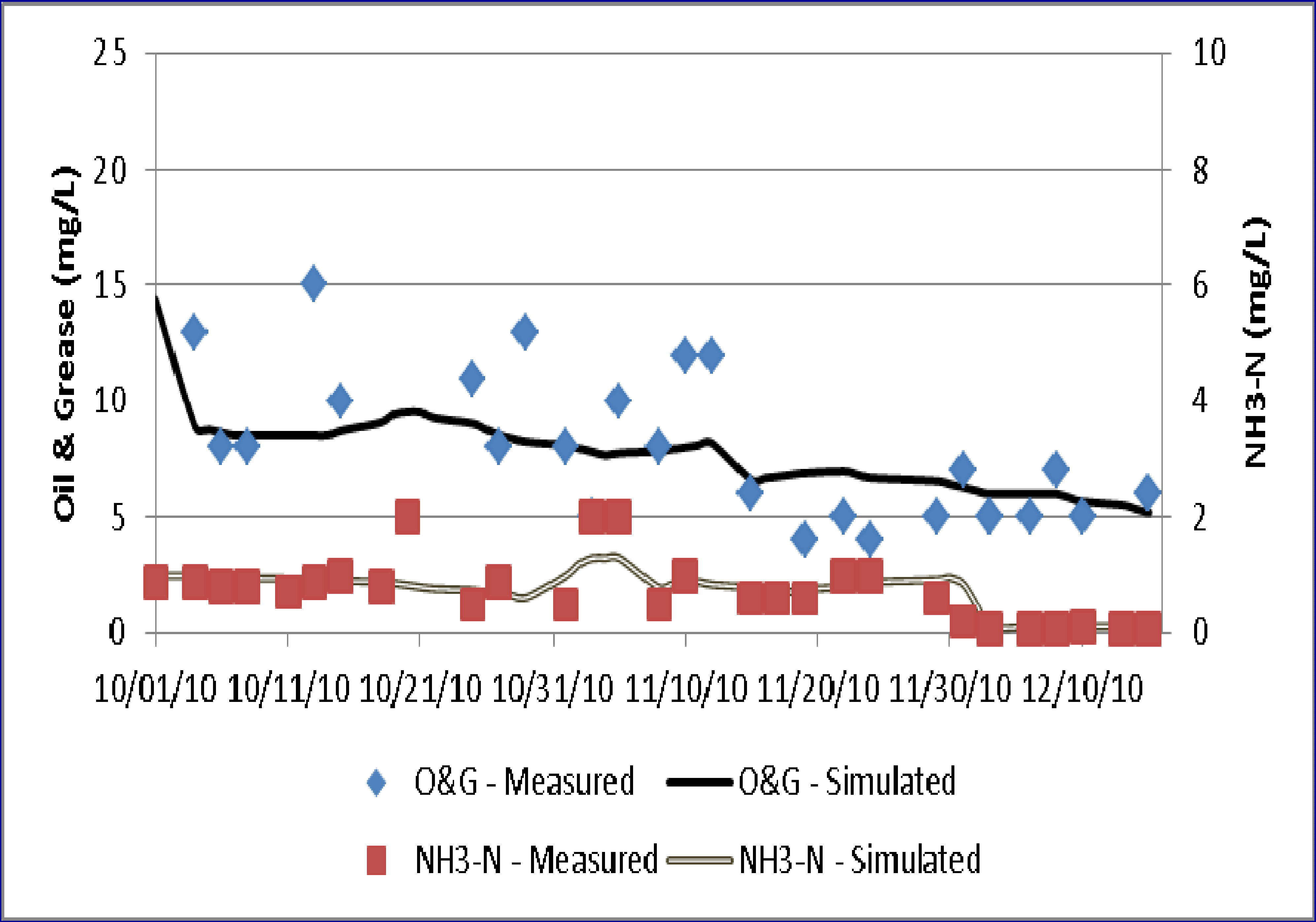


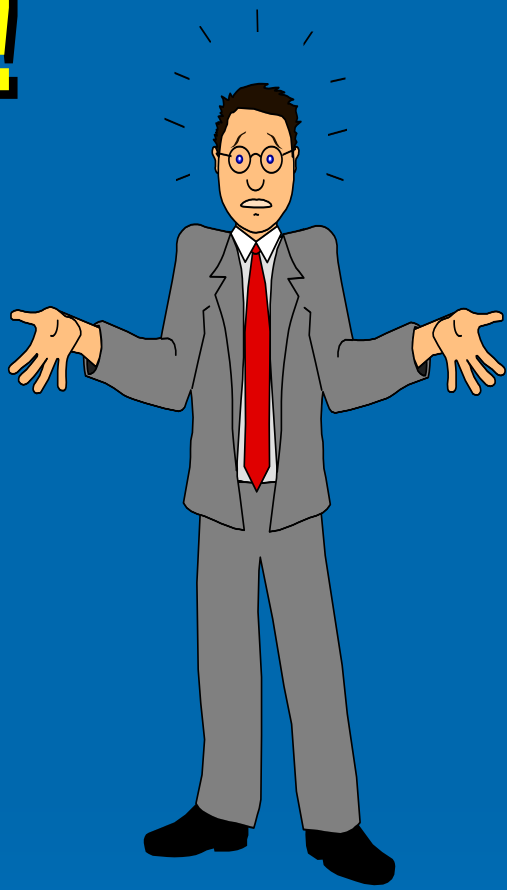
Conclusions

- MantisIW model provides general framework and allows for flexibility in modeling a wide variety of industrial activated sludge processes
- Calibrated models utilizing the site-specific biokinetic constants can be used to analyze WWTP operations and accurately predict the plant performance under hypothetical operating conditions

Conclusions

- Operational strategies can be complex and models can provide insights and quantify alternatives to support decision-making
- Once the maximum plant loading capacity has been established, models can be used to determine if an existing facility is adequate to treat the anticipated wastewater load or if capital improvements are required to meet effluent standards

Thank-You!



Any Questions?

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