Water Environment Research Foundation (WERF) Bioavailable Phosphorus (BAP) Reports

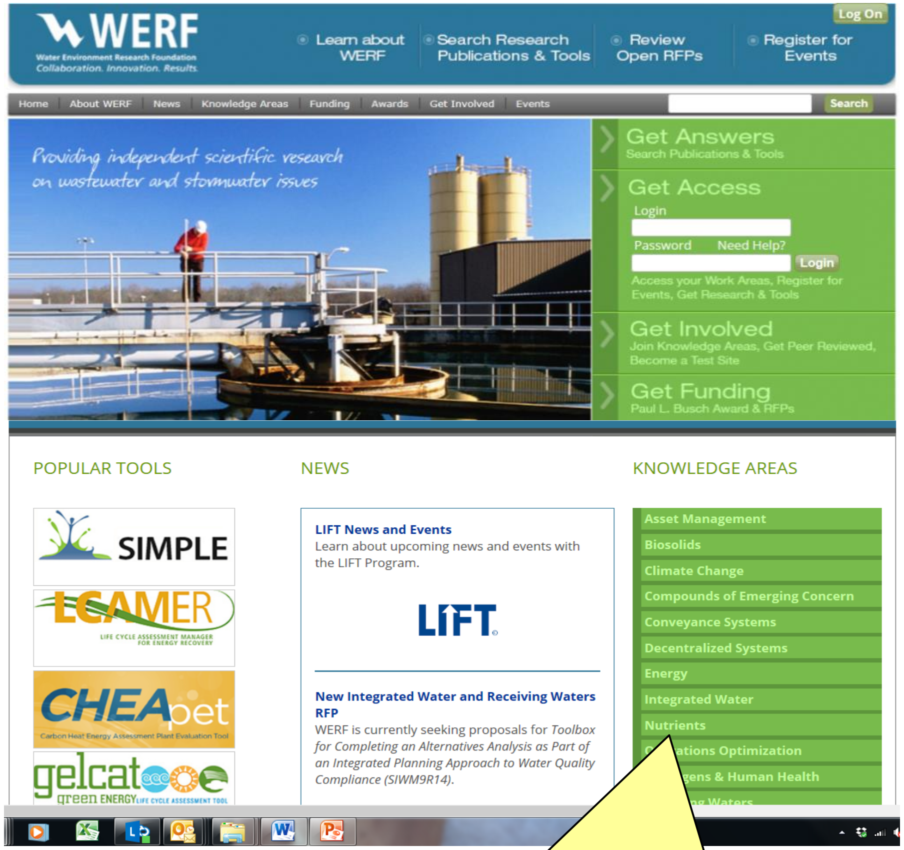
David L. Clark, HDR Engineering, Inc.
dclark@hdrinc.com
May 21, 2015

Water Environment Research Foundation (WERF) Bioavailable Phosphorus (BAP) Reports

- WERF Nutrient Challenge
- Overview of Phosphorus Speciation and Bioavailability
- New WERF BAP Reports
  - "The Bioavailable Phosphorus (BAP) Fraction in Effluent from Advanced Secondary and Tertiary Treatment" (NUTR1R06m)
  - "Mineralization Kinetics of Soluble Phosphorus and Soluble Organic Nitrogen in Advanced Nutrient Removal Effluents" (NUTR1R06p)
- Applications

Water Environment Research Foundation (WERF) Nutrient Challenge

www.werf.org



Go to ***KNOWLEDGE AREAS: Nutrients***
>50 completed and ongoing projects

Original Objectives

- Provide science-based solutions and recommendations that:

  (1) support utility decisions to use sustainable wastewater nutrient removal technologies to meet various receiving water body requirements and other wastewater treatment goals (e.g., climate change, sustainability, cost-effectiveness, reliability), and

  (2) inform regulatory decision making that is moving toward increasingly higher levels of nitrogen and phosphorus removal.

WERF's Nutrient Challenge includes work completed or done in partnership with many utilities, consultants, universities, organizations, etc., including:

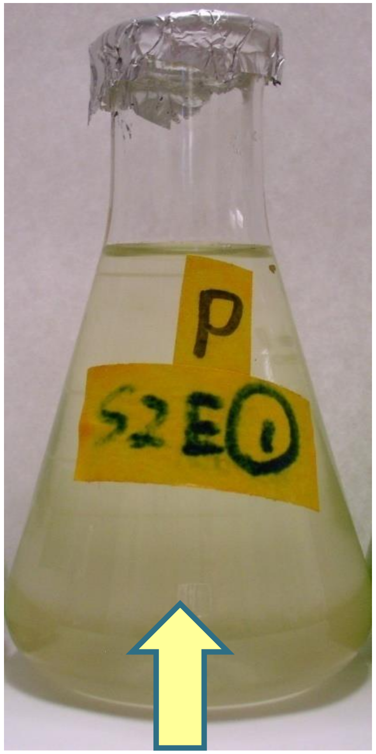
Consulting Firms	Utilities	Other Agencies	Universities
• **HDR, Inc.** *,+ • CH2H-Hill + • AECOM + • Passaro Engineering • Black & Veatch • Hazen and Sawyer • Envirosim, Canada • Brown and Caldwell ** Lead Contractor* *+ Core team member*	• DC Water, DC • Hampton Roads Sanitation District, VA • Coeur d'Alene, ID • City of Las Vegas, NV • Spokane County, WA • City of Spokane, WA • City of Hayden, ID • Inland Empire Paper Co • New York City DEP, NY • Clean Water Services, OR • Spokane City, ID • Spokane County, ID • Coeur d'Alene, ID • City of Las Vegas, NV • City of Stamford, CT • Alexandria Renew, VA • Truckee Meadows, NV • Edmonton, Canada • Sydney Water Corp.	• USEPA Region III, Chesapeake Bay Program Scientific Technical Advisory Committee (STAC) • Metropolitan Washington Council of Govts (MWCOG) • MEGA (Modeling Experts Group of the Americas) • Connecticut DEEP / Nitrogen Credit Advisory Board • USEPA • WEF • IWA	• University of Washington + • University of California – Berkeley • Columbia University, NY • Howard University, DC • Gdansk University, Poland • Northeastern University • Wilfrid Laurier University, Canada • University of Waterloo, Canada • University of Utah • Illinois Institute of Technology

Overview of Phosphorus Speciation and Bioavailability

Advanced Treatment and Effluent Nutrient Speciation and Bioavailability

Reduced Concentration	*Altered Speciation*	*Reduced Bioavailability*

Secondary Effluent BAP



Alum/settled Effluent BAP

Alum/Filtered Effluent BAP

Michael T. Brett & Bo Li Phosphorus Bioavailability Studies, University of Washington

Some Dissolved Organic Nitrogen (DON) and Nonreactive Dissolved Phosphorus (nRDP) is Readily Available to Algae and Some is Not

Coconuts and Bananas Postulate **-- Bo Li, University of Washington**

Bioavailable

- Reactive P (PO_4^{-3})
- Amino acids

Recalcitrants

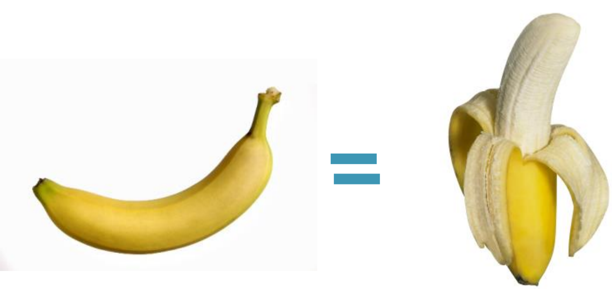
Inorganic P

- Apatite
- ($Ca_3(PO_4)_2$)
- $AlPO_4$
- $FePO_4$
- ....

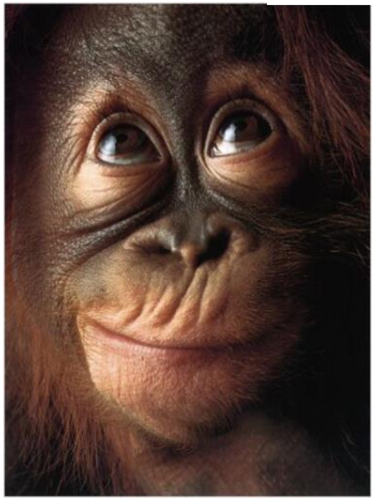
N and P in humic substances

Organic P

- Polyphosphate
- Inositol hexakisphophate
- L-α-phosphatidyl choline
- phosphoenol pyruvate
- Glycerophosphate



Readily Bioavailable



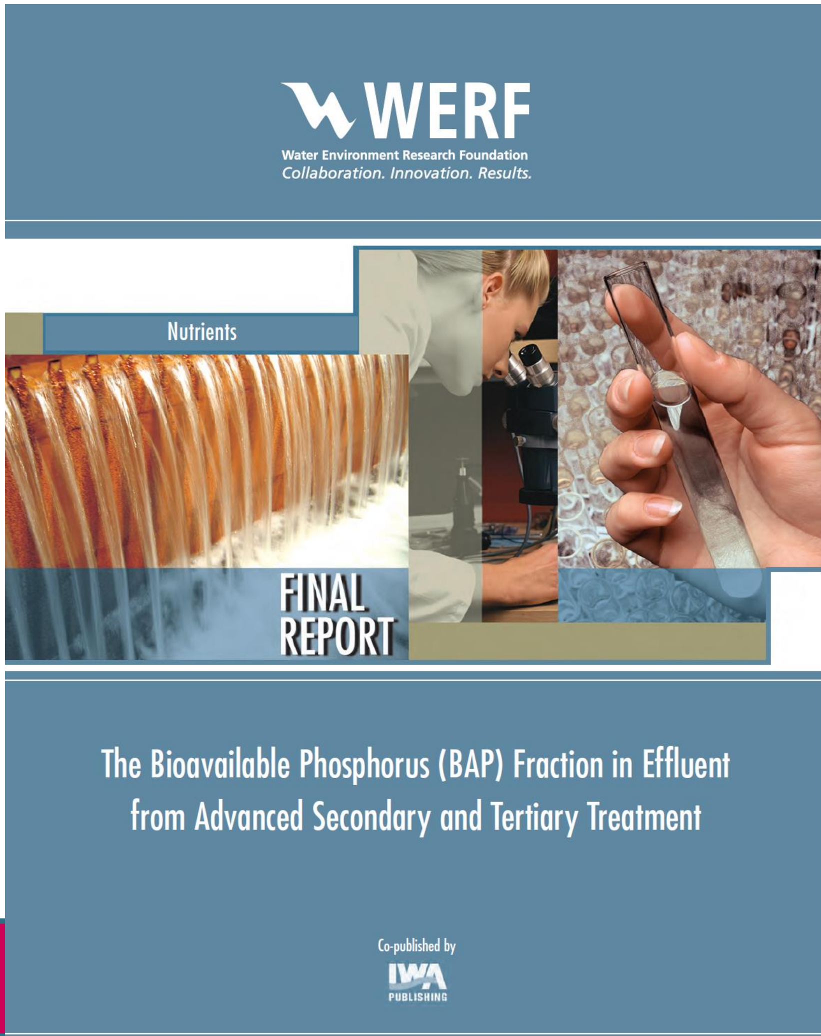
Michael T. Brett & Bo Li, University of Washington libo@u.washington.edu

New WERF Bioavailable Phosphorus (BAP) Reports

“The Bioavailable Phosphorus (BAP) Fraction in Effluent from Advanced Secondary and Tertiary Treatment” (NUTR1R06m)

Michael T. Brett & Bo Li, University of Washington

- Algal Bioassays
- Bioavailable P Determined for 17 Facilities
  - Wide Range of Treatment Processes
    - Chemical and Biological P Removal
    - Single and Two-Stage Tertiary
    - Membranes



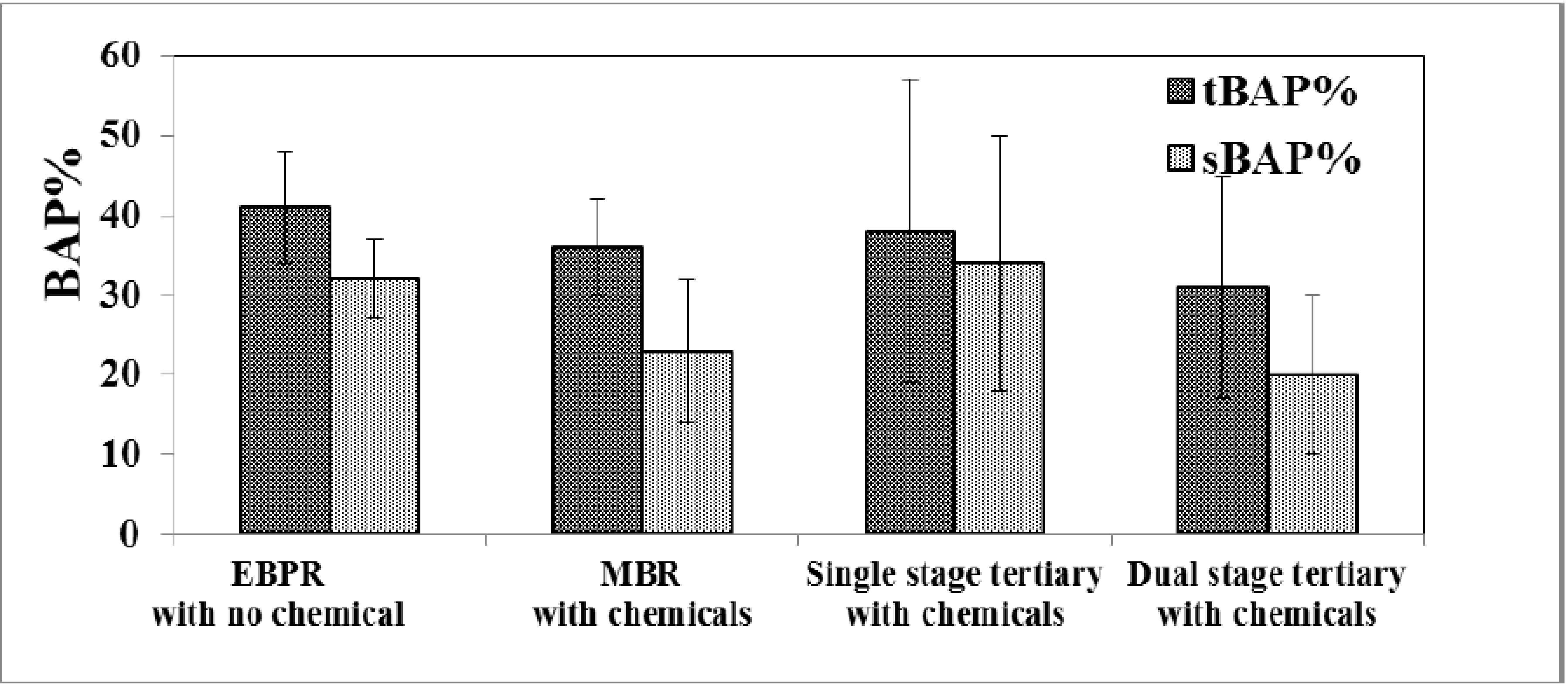
Effluent Sampled

- Bio-P (No Chem)
  - Coeur d'Alene MBR
  - Snoqualimie
  - North Durham
- MBR w/Chem
  - Broad Run
  - Ruidoso
- Single Stage Filter w/Chem
  - Coeur d'Alene TMF
  - Syracuse Actiflo (Onondaga County)
  - DC Water Blue Plains
  - Hayden 1st Sage BluePro
  - Las Vegas
  - South Durham
- Dual Stage Tertiary w/Chem
  - Iowa Hill
  - Coeur d'Alene 2 Stage BluePro
  - Hayden BluePro 2nd Stage
  - Farmers Korner
  - CWS Rock Creek & Durham

Findings

- Effluent P Speciation and Bioavailability Varies with Treatment Process
  - >50% Effluent P Recalcitrant in Most Cases
  - Higher Chemical Doses Decreased BAP
- Bioavailability of P Species
  - Classic SRP Characterization Poor Predictor of BAP
- Recalcitrant P Compounds
  - Humic-Metal-P Complexes (HMEP)
    - Humic Substances are Natural Organic Matter in Soil and Water Formed by Microbial Degradation of Plant Matter and Resistant to Further Degradation
  - Phytic Acid (Storage Form of P in Plant Tissue)
  - Apatite (Phosphate Minerals)

Figure 8-2. BAP% Comparison for Different Types of Advanced Nutrient Removal Processes



- >50% Effluent P Recalcitrant in Most Cases

Comparison of Biological P Removal v. Chemical P Removal

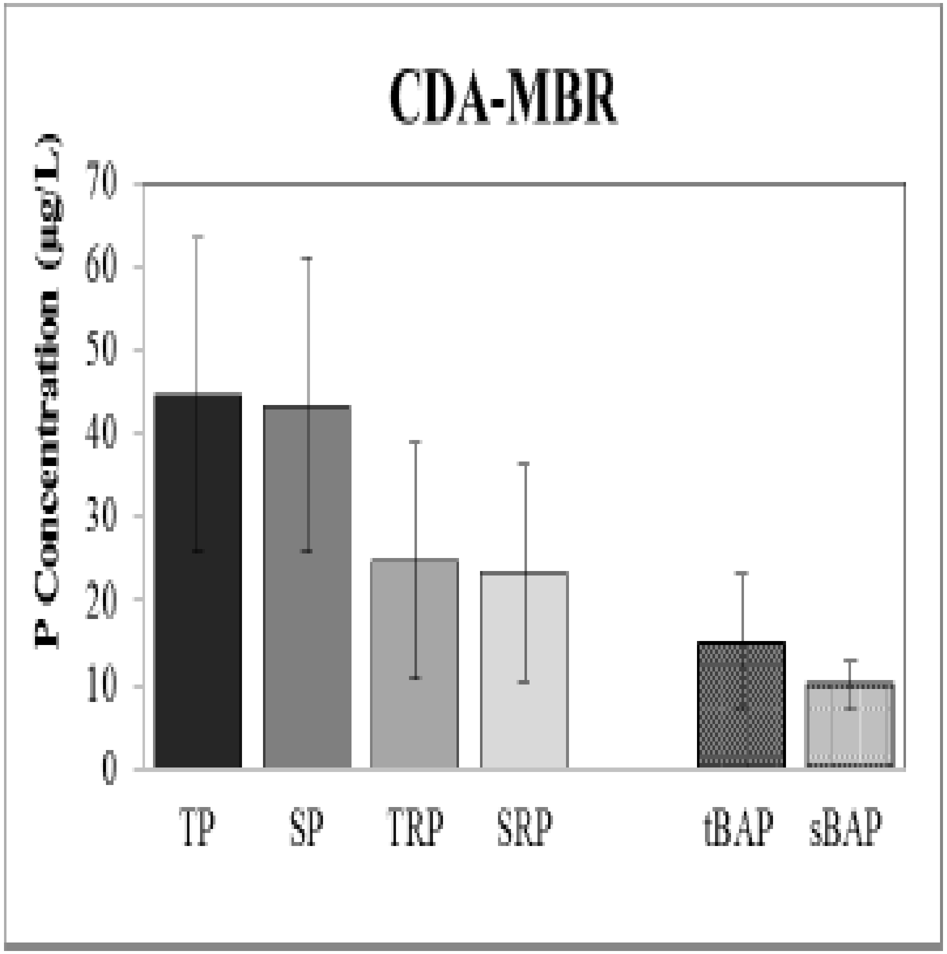


Figure 4-1. P Concentrations Result for MBR System in Coeur d'Alene.

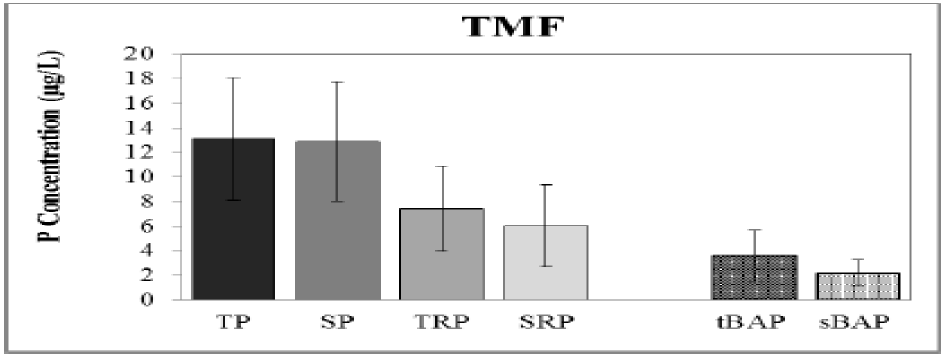


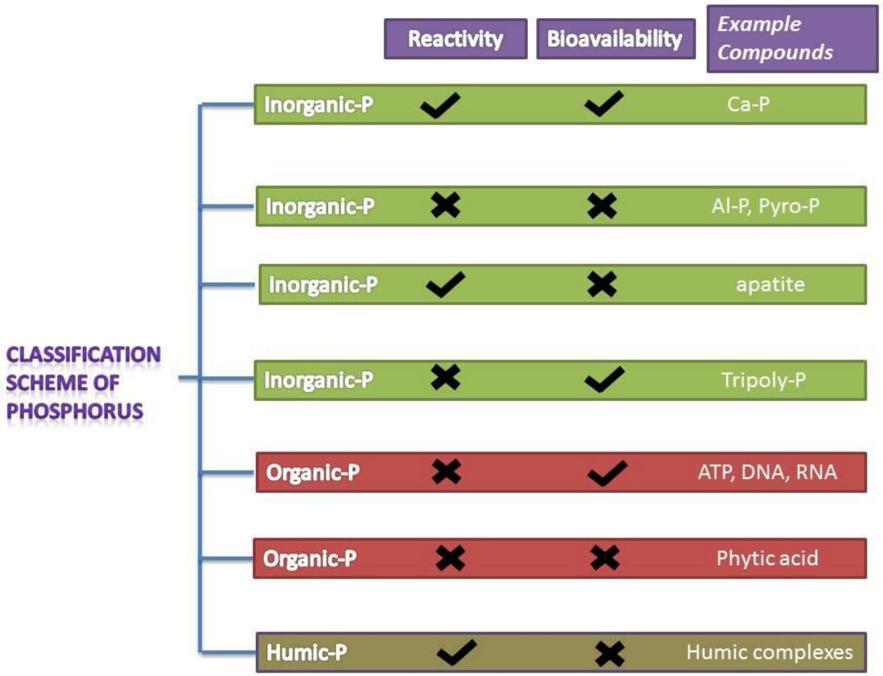
Figure 6-2. P Concentrations Result for CDA-TMF.

tBAP<20 ug/L

tBAP<5 ug/L

Bioassays of 21 P Compounds

- Findings
  - 17 Cases Did Not Fit Classic Assumption That SRP = Bioavailable
  - Humic- (Al/Fe)-P Complexes
    - Alias as SRP. Not Bioavailable
  - Phytic Acid Low BAP in Effluent
  - Apatite Low BAP in Natural Waters
- Implications
  - “Classic” Measurements Generally are SRP, TP, etc
    - WQ Model Setup Uses “Classic” Measurements as Input
  - Simulation of BAP
    - Adapt WQ Model Setup to New Measurements/Classifications of P



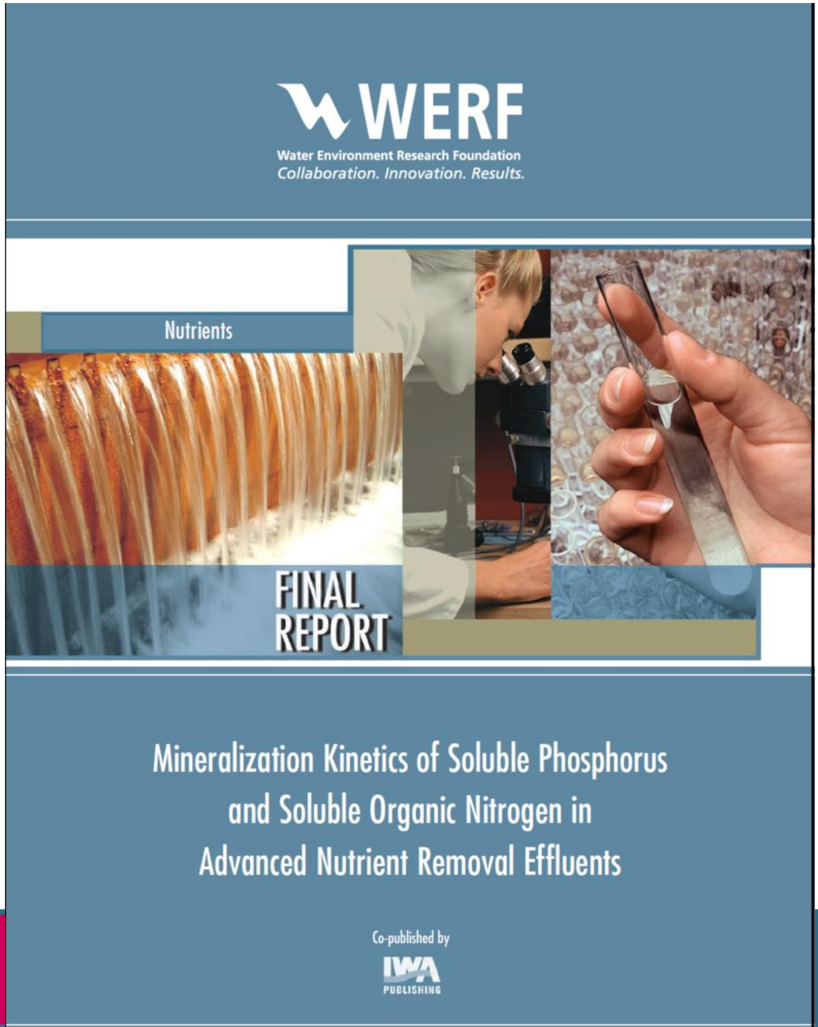
Conclusions

- Water Quality Modelers and Permit Writers Should Consider Importance of BAP
  - For Ultra Low Effluent P (<100 ug/L) Circumstances
- Total Reactive Phosphorus (TRP) Strongly Associated with Bioavailable Phosphorus (BAP)
  - TRP Provides Fast, Simple and Conservative Estimate of BAP
  - TRP Gives Good Estimate of BAP without Bioassay Work

"Mineralization Kinetics of Soluble Phosphorus and Soluble Organic Nitrogen in Advanced Nutrient Removal Effluents" (NUTR1R06p)

Bo Li, Lu Fan, Michael T. Brett, University of Washington

- Mineralization Kinetics for Phosphorus
  - Organic P Turned Into Inorganic
- Algal Bioassays
- Effluent Sampled
  - Spokane County
  - Post Falls
  - Hayden
  - Coeur d'Alene
  - Inland Empire Paper



Findings

- Discharger Specific Mineralization Rates for Dissolved Phosphorus
  - Biological Treatment, Membrane Bioreactor, Tertiary Membrane, Dual Sand Filtration
    - First Order Rate Kinetics That Can Be Used in Spokane River Model
      - 1, 2 and 3 Pool Models
        - 2 and 3 Pool Models Correlated Better Than 1 Pool
    - Gamma Model
      - 2 Parameter Continuous Probability Distribution
- Determined Bioavailability of Nitrogen and Phosphorus in Effluent from Nutrient Removal Facilities
- Characterizes Effluent Composition
  - P Composition from Bioavailable Phosphorus (BAP) Experiments
  - N Composition from Bioavailable Nitrogen (BAN) Experiments

Conclusions

Phosphorus

- Bioassay Experiments Can Describe P Mineralization Rates
  - Easy Incorporation of First Order Decay Kinetics into Water Quality Models
    - Gamma Model May be Better
- 16% to 63% Dissolved P Recalcitrant

Nitrogen

- Cell Growth Bioassay Not Suitable for Bioavailable N Analysis
  - Dissolved N Uptake More Reliable
- 32% to 84% Dissolved N Recalcitrant

- Further Research Into Recalcitrant N and P Fractions and Potential Connection to Larger Molecular Sizes




Applications

Spokane River

Dissolved Oxygen Total Maximum Daily Load (TMDL)

- 8 mg/l Dissolved Oxygen Standard Not Met in Lake Spokane
  - Allowable 0.20 mg/l D.O. Depression
    - Washington Dissolved Oxygen Water Quality Standards Are Restrictive
      - Standards allow for a small depression in natural dissolved oxygen levels for all human activities (<0.2 mg/L) if a waterbody is naturally lower than the state's numerical oxygen standard
- Very Low Effluent P Limits
  - TMDL WLA: Total Phosphorus 36 ug/L Idaho/42 ug/L Washington

BAP Relevance?

- Significant For Ultra Low Effluent P (<100 ug/L) Circumstances
  - >50% Effluent P Recalcitrant in Most Cases

Lake Spokane Algae Bloom. Source: Washington Department of Ecology October 2004 Draft TMDL

Nutrient Bioavailability and Permitting

Potential Applicability

- Low N (<5 mg/L) and Low P Effluent (< 100 ug/L)
  - Refractory/Slowly Degradable N and P
    - Not Biodegradable in Treatment
    - Reduced Bioavailability (<50%)
- Effluent Limits Based on Bioavailability
  - Total Reactive P (TRP)?
    - Avoids Recalcitrant Constituents

Example Nitrogen NPDES Permit

LOTT Budd Inlet Plant Effluent Limits

- *Total Inorganic Nitrogen (TIN) 2 mg/L*

Under Consideration

- *Onondaga Lake TMDL, Syracuse, NY*
  - *Onondaga County & NYDEC*
- *Spokane River DO TMDL*
  - *Spokane County (Washington Ecology)*

S1.B.a Alternate effluent limits for oxygen consuming pollutants demonstrated to be equivalent to DO TMDL baseline effluent limits in S1.A (option 1)

Parameter	Seasonal Limit Applies March 1 to October 31 See notes f and g
Carbonaceous Biochemical Oxygen Demand (5-day) ($CBOD_5$)	133.4 pounds/day (lbs/day) average
Total Phosphorus (as P) March 1 to Oct. 31	3.34 lbs/day average

Total Ammonia (as NH_3-N)	Seasonal Limit	Maximum Daily Limit
For "season" of March 1 to March 31	1067.5 lbs/day average	16 mg/L
For "season" of April 1 to May 31	66.7 lbs/day average	16 mg/L
For "season" of June 1 to Sept. 30	16.7 lbs/day average	8 mg/L
For "s[illegible]	[illegible]	[illegible]

Parameter	Average Monthly [a]	Average Weekly [b]
Carbonaceous Biochemical Oxygen Demand (5-day) ($CBOD_5$) November 1 through February 29	2.0 milligrams/liter (mg/L) [illegible] pounds/day (lbs/day)	---

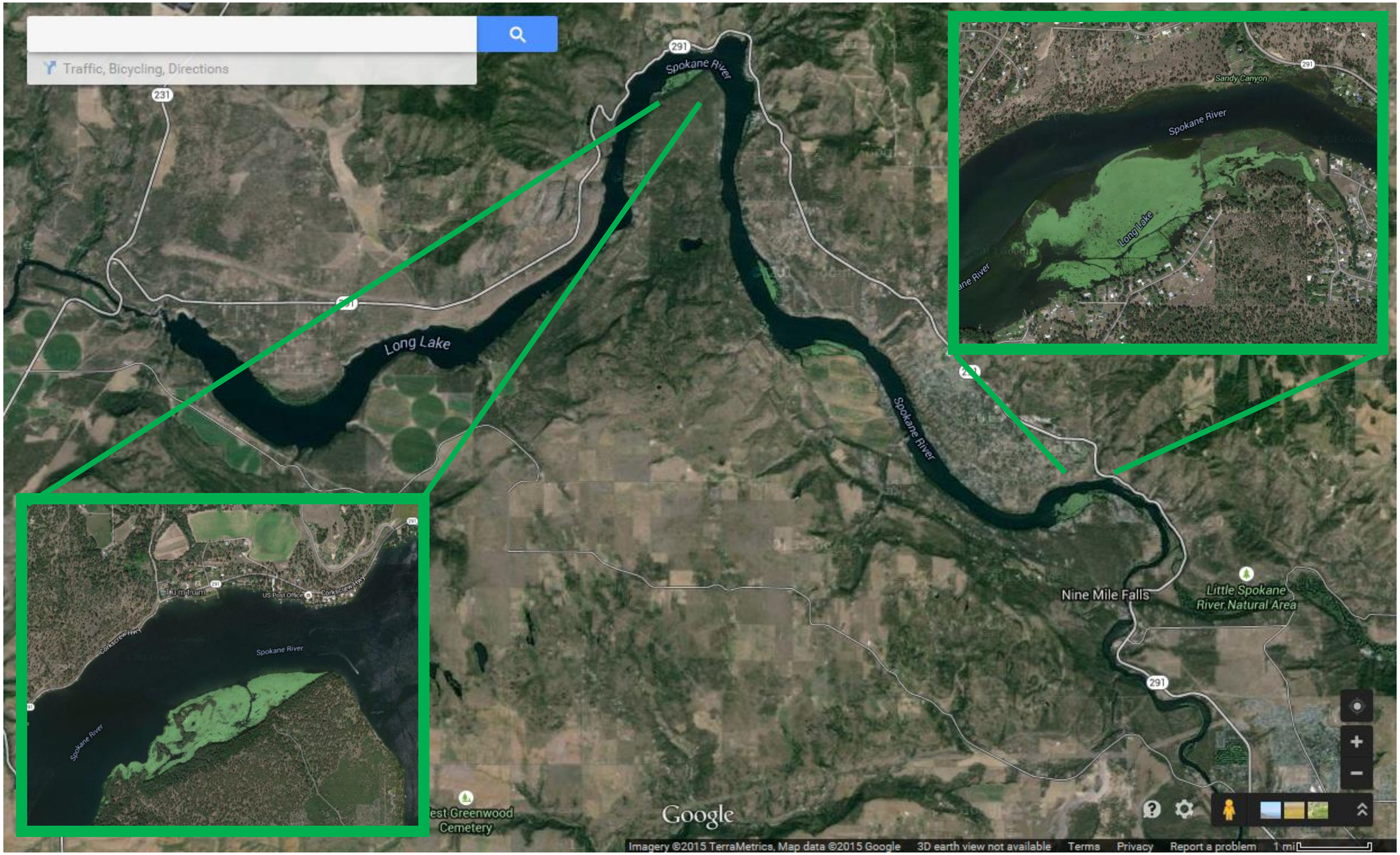
Permit Footnote: "[g]Future adjustments to the final effluent based on demonstrated pollutant equivalencies or non bioavailable P will be implemented as major modifications requiring public notice and comment"

Bioavailability Considerations and Treatment Process Design

- Influent Wastewater Characteristics
  - Potential Sources of Dissolved Organics and Recalcitrant Species
    - Industrial Loadings, etc.
- Treatment Process Selection
  - Single v. Multiple Stage Processes
  - Biological P Removal v. Chemical
    - Biosolids Land Application and P-Index Controlled Application Rates
- Generation of Recalcitrant Species within Treatment Processes
  - Solids Processing and Anaerobic Digestion?
- Treatment for Removal of Recalcitrant Nutrient Species
  - Humic Substances and Humic-Metal-P Complexes (HMEP)?
    - Convert to Something That Can Be Removed in Treatment?
      - Advanced Oxidation Processes (AOP) (UV + Peroxide) → Coagulate & Filter?

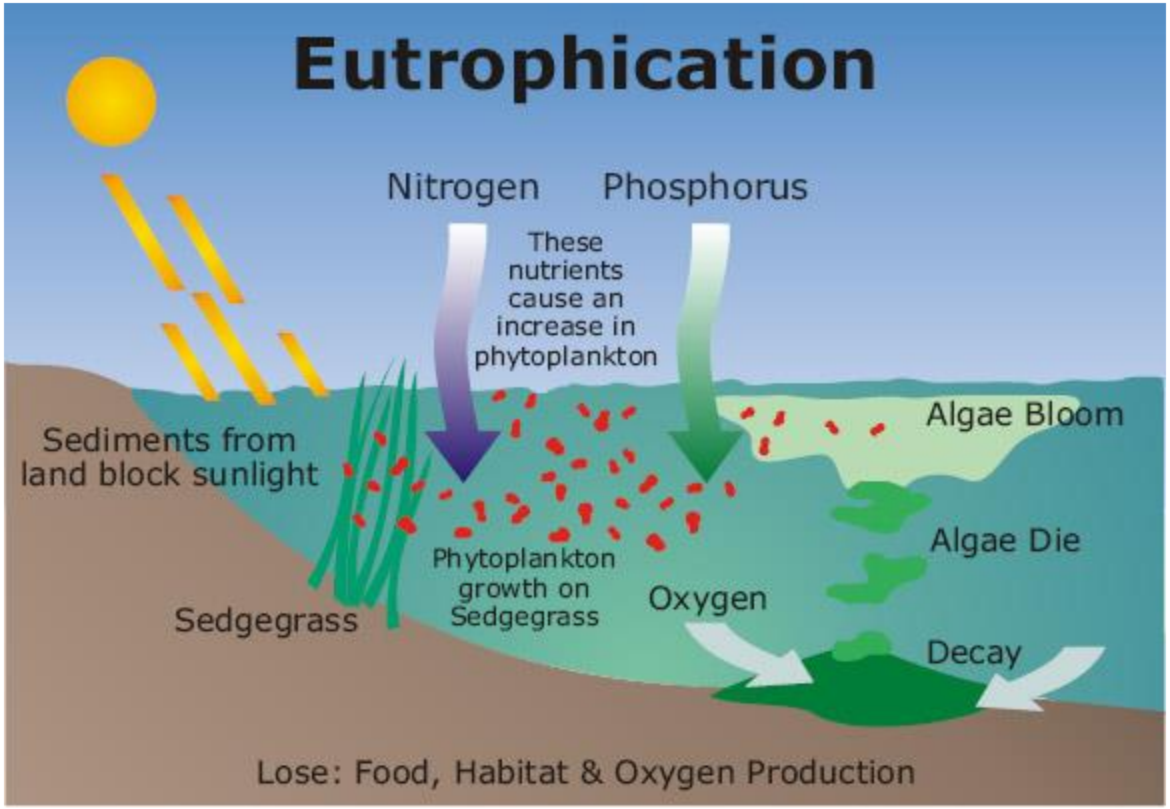
Bioavailability Considerations and Water Quality

- Observations of Eutrophication



Basis for Water Quality Modeling

- Eutrophication Process
  - Nutrients (Nitrogen and Phosphorus) promote algae blooms
  - Algae die and consume oxygen



Source: Ohio Wesleyan University

Water Quality Monitoring Data to Construct Models

- Collect samples and analyze in the laboratory
- Per Washington Ecology
  - River and Stream Water Quality Monitoring
    - » http://www.ecy.wa.gov/programs/eap/fw_riv/rv_main.html
- Routinely measured indicators are:
  - ammonia (SM4500NH3H)
  - nitrate plus nitrite (SM4500NO3I)
  - nitrogen, total (SM4500NB)
  - phosphorus, soluble reactive (SM4500PG)
  - phosphorus, total (SM4500PH)
  - conductivity (SM2510B)
  - suspended solids (SM2540D)
  - fecal coliform bacteria (SM9222D)
  - oxygen (SM4500OC)
  - temperature (thermistor)
  - flow (at most stations)
  - pH (EPA150.1)
  - turbidity (SM2130)
  - metals (bimonthly, at a few stations) (EPA200.8, 245.7)

Water Quality Models

- Water Quality Models are Tools to Relate the Measured Parameters
  - Example: CE-QUAL-W2

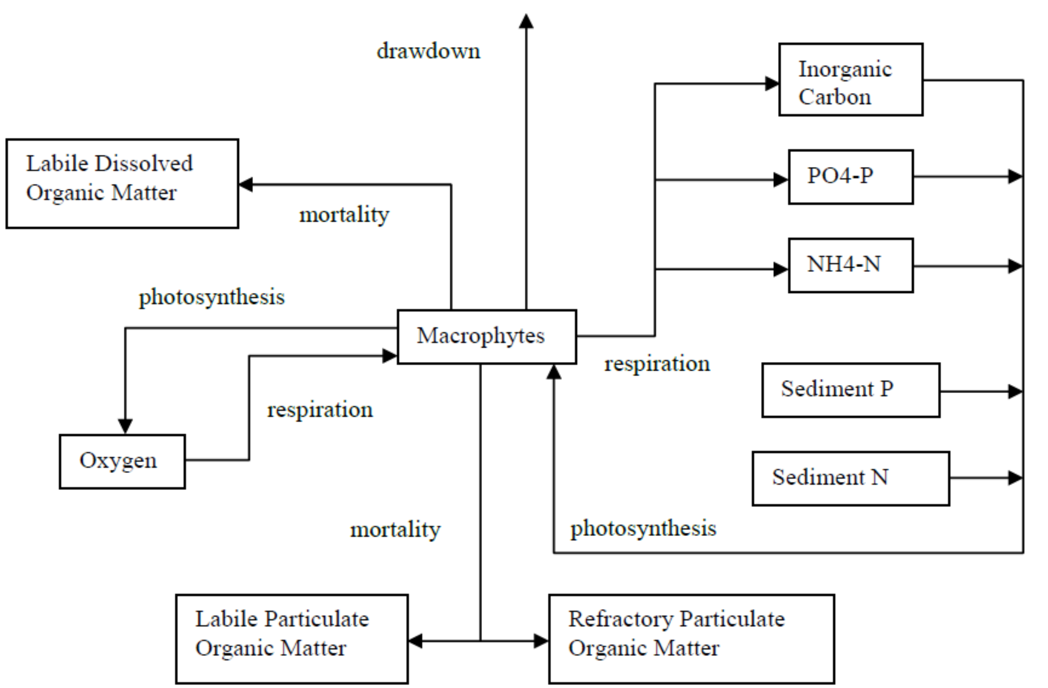


Figure 15. Nutrient fluxes for the macrophyte compartment in CE-QUAL-W2.

Summary of Receiving Water Model Capabilities to Simulate Nutrient Species and Refractory Compounds

Model Label or Name Acronym	Current Capabilities	Opportunities for Enhanced Application and Potential Refinements
	Simplistic Models	
Mass Balance	Data Assessment Technique. Incapable of Simulating Nutrient Species.	Limited Potential.
Empirical	Data Assessment Technique. Incapable of Simulating Nutrient Species.	Limited Potential.
	Mechanistic Models	
AQUATOX	Capable of Nutrient Species Simulation. Bioavailability reflected with input of SRP and refractory organic phosphorus.	Provide Data on Refractory Compounds. Improve documentation and explanation in the model interface and user manual about nutrient species options. Provide multiple options for nutrient speciation and coefficient conversion rates.
CE-QUAL-ICM	Nutrient Speciation and Refractory Compounds.	Provide Data on Refractory Compounds.
CE-QUAL-RIV1	Capable of Nutrient Species Simulation.	Provide Data on Nutrient Species.
CE-QUAL-W2	Nutrient Speciation and Refractory Compounds. Bioavailability reflected with input of SRP and organic phosphorus associated with BOD.	Provide Data on Refractory Compounds. Model can divide point source phosphorus loads into as many unavailable compartments as desired. Set an upper bound mineralization rate for weakly bioavailable compounds. Requires monitoring data to calibrate mineralization rates.
DELWAQ	Nutrient Speciation and Refractory Compounds.	Provide Data on Refractory Compounds.
EFDC/HEM-3D	Nutrient Speciation and Refractory Compounds.	Provide Data on Refractory Compounds.
MIKE	Capable of Nutrient Species Simulation.	Provide Data on Nutrient Species.
RCA	Nutrient Speciation and Refractory Compounds.	Provide Data on Refractory Compounds.
QUAL2K	Capable of Nutrient Species Simulation. Bioavailability reflected with input of Soluble Reactive Phosphorus (SRP) only.	Provide Data on Nutrient Species. Add options for nutrient speciation with point source input specification. Add options for mineralization with rates input specification.
WASP7	Capable of Nutrient Species Simulation.	Provide Data on Nutrient Species.

CE-QUAL-W2

Need Data

Incorporate into CE-QUAL-W2 Water Quality Model

- ***"The model can track multiple organic matter fractions and nutrient fractions associated with the organic matter fractions separating these into both particulate and dissolved and refractory and labile. For example, one can have a CBOD group and the CBOD-N and CBOD-P associated with one discharger and these could be refractory – the same discharger could also use another CBOD group that has the same C, N, and P fractions that are labile. Similarly for dissolved and particulate versions of each of these. Since the model can have as many CBOD groups as one wants, then there is no limit to the amount of slicing and dicing and tracking one can do for the speciation of organic matter!"***
  - Scott Wells, Portland State University, CE-QUAL-W2 model developer

- ***"….there is no limit to the amount of slicing and dicing and tracking one can do for the speciation of organic matter!"***

Water Quality Model Inputs

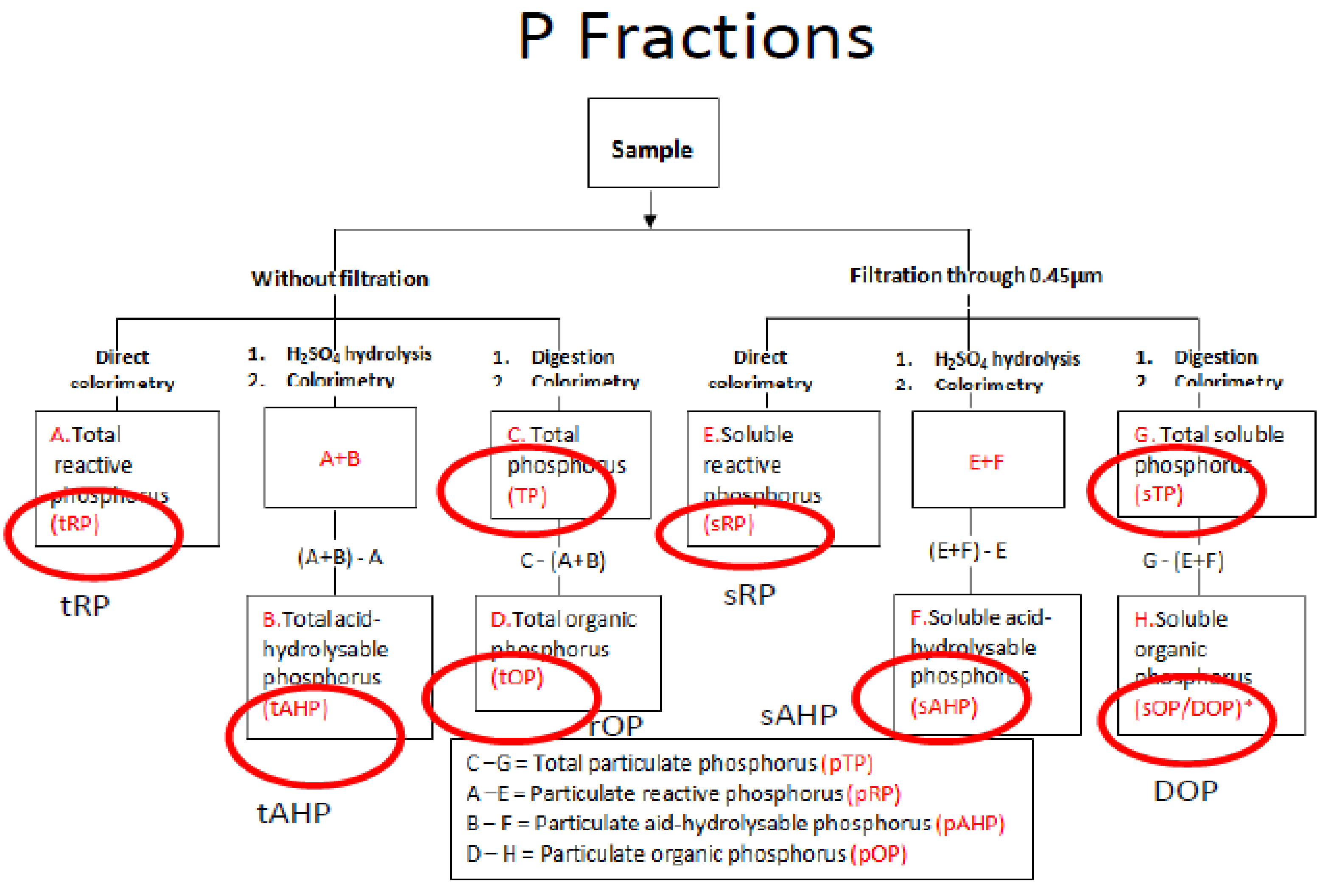
- Inputs Generally Align with Parameters That are Measured

CIN CON	CINBRC	CINBRC	CINBRC	CINBRC	CINBRC CINBRC CINBRC CINBRC CINBRC
TDS	ON	ON	ON	ON	Total dissolved solids or salinity
TRACER	ON	ON	ON	ON	Generic constituent 1 - tracer
AGE	OFF	OFF	OFF	OFF	Generic constituenT 2 - residence time
COL1	ON	ON	ON	ON	Generic constituent 3 - coliform group 1
COL2	ON	ON	ON	ON	Generic constituent 4 - coliform group 2
ISS1	ON	ON	ON	ON	Inorganic suspended solids group 1
ISS2	ON	ON	ON	ON	Inorganic suspended solids group 2
ISS3	ON	ON	ON	ON	Inorganic suspended solids group 3
PO4	ON	ON	ON	ON	Inorganic dissolved phosphorus
NH4	ON	ON	ON	ON	Ammonium
NO3	ON	ON	ON	ON	Nitrate-nitrite
DSI	ON	ON	ON	ON	Dissolved silica
PSI	ON	ON	ON	ON	Particulate biogenic silica
FE	ON	ON	ON	ON	Iron
LDOM	ON	ON	ON	ON	Labile dissolved organic matter
RDOM	ON	ON	ON	ON	Refractory dissolved organic matter
LPOM	ON	ON	ON	ON	Labile particulate organic matter
RPOM	ON	ON	ON	ON	Refractory particulate organic matter
CBOD1	ON	ON	ON	ON	Carbonaceous BOD group 1
CBOD2	ON	ON	ON	ON	Carbonaceous BOD group 2
CBOD3	ON	ON	ON	ON	Carbonaceous BOD group 3
CBOD1-P	ON	ON	ON	ON	Carbonaceous BOD-P group 1
CBOD2-P	ON	ON	ON	ON	Carbonaceous BOD-P group 2
CBOD3-P	ON	ON	ON	ON	Carbonaceous BOD-P group 3
CBOD1-N	ON	ON	ON	ON	Carbonaceous BOD-N group 1
CBOD2-N	ON	ON	ON	ON	Carbonaceous BOD-N group 2
CBOD3-N	ON	ON	ON	ON	Carbonaceous BOD-N group 3
ALG1	ON	ON	ON	ON	Algal group 1
ALG2	ON	ON	ON	ON	Algal group 2
ALG3	ON	ON	ON	ON	Algal group 3
DO	ON	ON	ON	ON	Dissolved oxygen
TIC	ON	ON	ON	ON	Total inorganic carbon mg/l as C
ALK	ON	ON	ON	ON	Alkalinity mg/l as CaCO3
ZOO1	ON	ON	ON	ON	Zooplankton
LDOM_P	ON	ON	ON	ON	Total P in labile dissolved organic matter
RDOM_P	ON	ON	ON	ON	Total P in refractory dissolved organic matter
LPOM_P	ON	ON	ON	ON	Total P in labile particulate organic matter
RPOM_P	ON	ON	ON	ON	Total P in refractory particulate org matter
LDOM_N	ON	ON	ON	ON	Total N in labile dissolved organic matter
RDOM_N	ON	ON	ON	ON	Total N in refractory dissolved organic matter
LPOM_N	ON	ON	ON	ON	Total N in labile particulate organic matter
RPOM_N	ON	ON	ON	ON	Total N in refractory particulate org matter

Model Data Needs

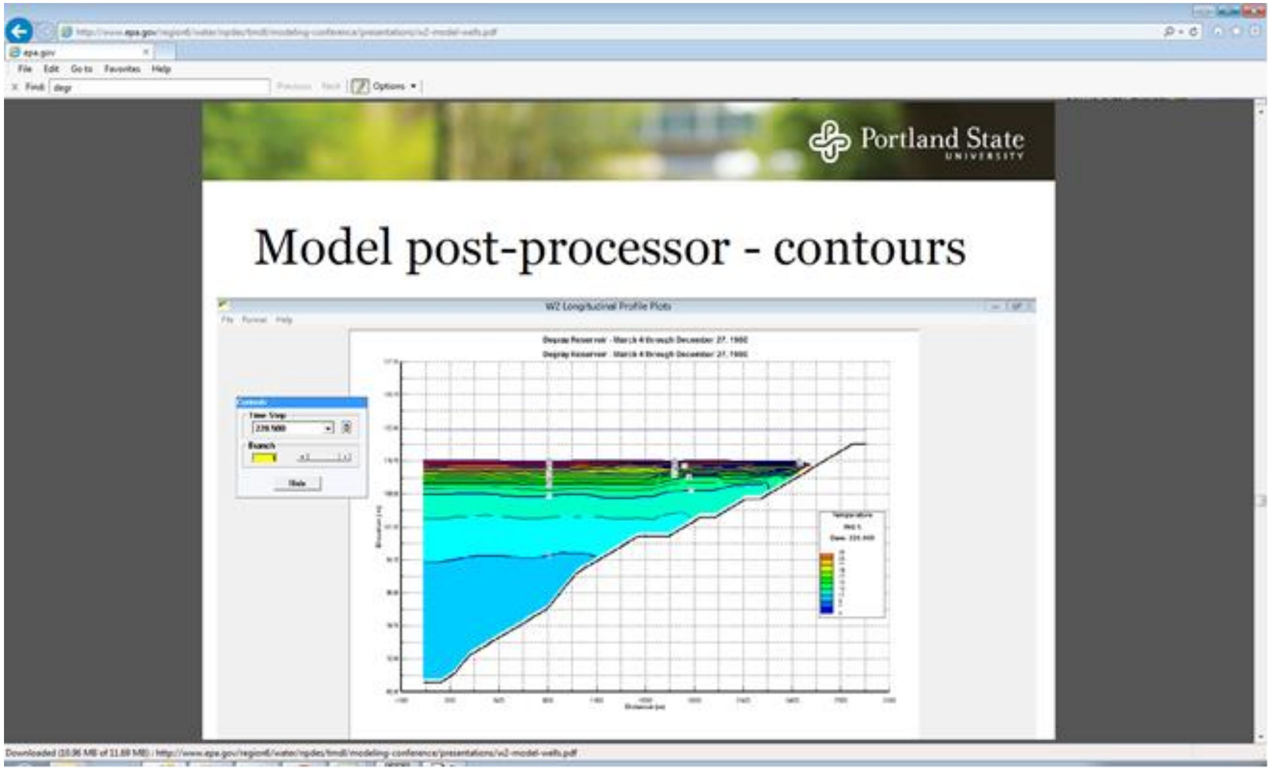
- Model entries for ambient and effluent nutrient loadings can reflect nutrient speciation and refractory organic compounds, providing that the data are available to characterize effluent discharges and ambient waters
- **BAP Studies Directly Inform WQ Model Needs**

P Speciation Terminology



Water Quality Model Test of Sensitivity to BAP Inputs

- CE-QUAL-W2 Example Model
  - DeGray Reservoir, AR
    - ~15 Miles Long
    - ~60 Feet Dee
    - Model Period ~1 year

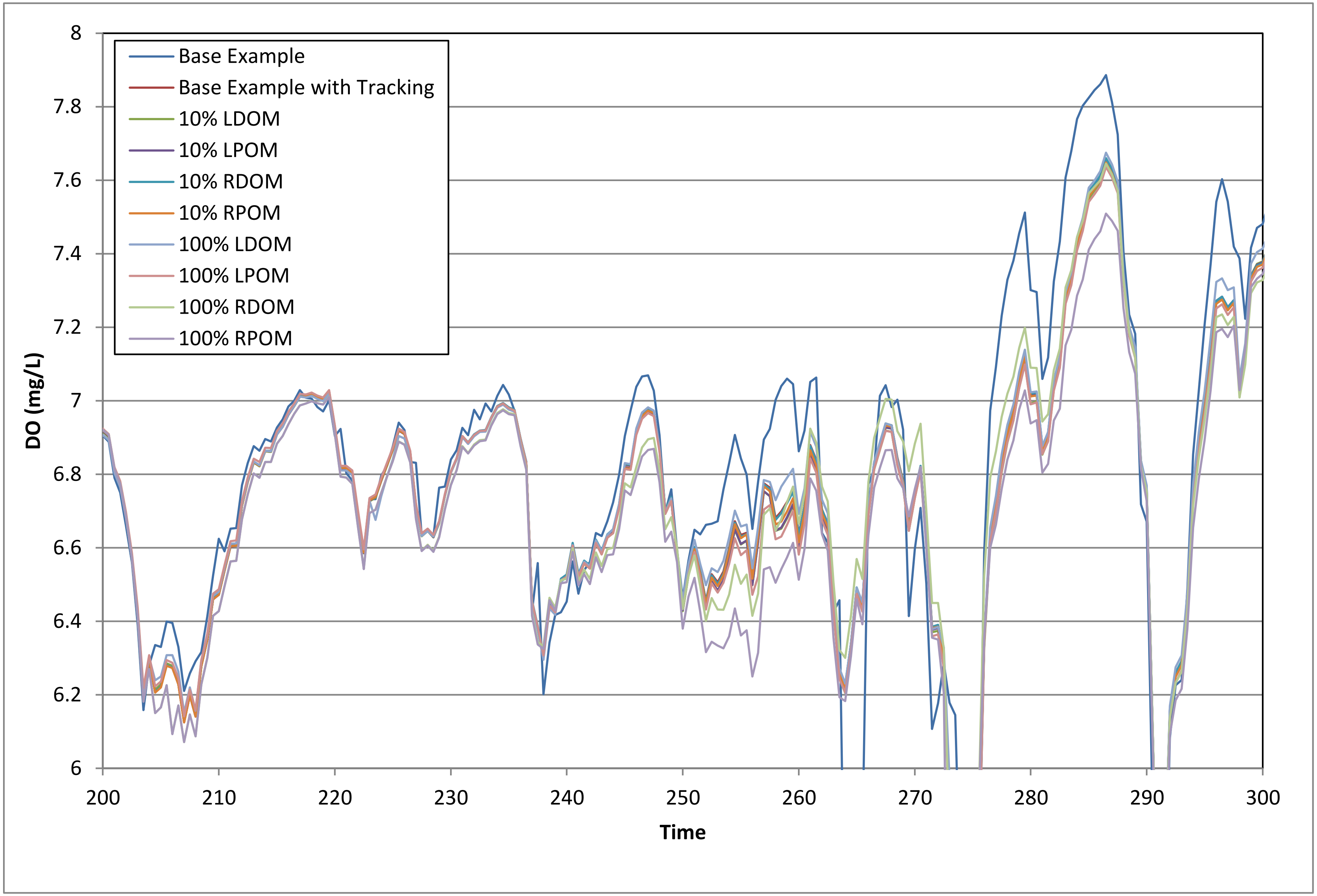


Model Scenarios to Explore Dissolved Oxygen Sensitivity to Changes in P Bioavailability

- Difference in dissolved oxygen in a reservoir when 10- and 100-percent of the SRP is entered as
  - Labile dissolved
  - Labile particulate
  - Refractory dissolved
  - Refractory particulate

Example Dissolved Oxygen Sensitivity Results to Changes in P Bioavailability in Lowermost Segment of Reservoir

Dissolved Oxygen Range From 6 to 8 mg/L



Time: Julian day 200 (July 19th) to Julian day 300 (October 27th)

Water Environment Research Foundation (WERF) Bioavailable Phosphorus (BAP) Reports

David L. Clark, HDR Engineering, Inc.
dclark@hdrinc.com
May 21, 2015