Regional Water Quality Issues:
Algae and Associated Drinking Water Challenges

Workshop – September 2011

A Cooperative Research and Implementation Program
Arizona State University (Tempe, AZ)
Paul Westerhoff
Chao-An Chiu, Jacelyn Rice, Kyle Doudrick, David Hanigan

Salt River Project
Central Arizona Project
City of Tempe
City of Peoria
City of Glendale
City of Chandler
Arizona Water

Agenda

Purpose: Provide a forum to review and discuss on-going regional water quality issues, in particular algae-associated issues.

- **830 am** — **Snacks and coffee**
- **845 am** — **Introductions and key questions**
- **900am** — **Water Quality Update and Overview (Westerhoff)**
- **925am** — **Taste and Odors in Canals – Will it ever happen again? (Westerhoff)**

Water Supplies in light of climate changes

- **935am** — **Water quality responses under different climatic situations (Chiu)**
- **905-10am** — **Stretch**
- **1005 am** — **How much wastewater is in our drinking water supply (Rice)**
- **1015am** — **Groundwater – how do we deal with nitrate (Doudrick)**

Treatment of organics and T&O using Activated carbon

- **1040am** — **In-situ GAC regeneration: Progress and a Path Forward (Chiu)**
- **1055am** — **Jar Testing with PAC (Hanigan)**

Open Discussion on research needs for next year and feedback

1130am — **Workshop concludes**

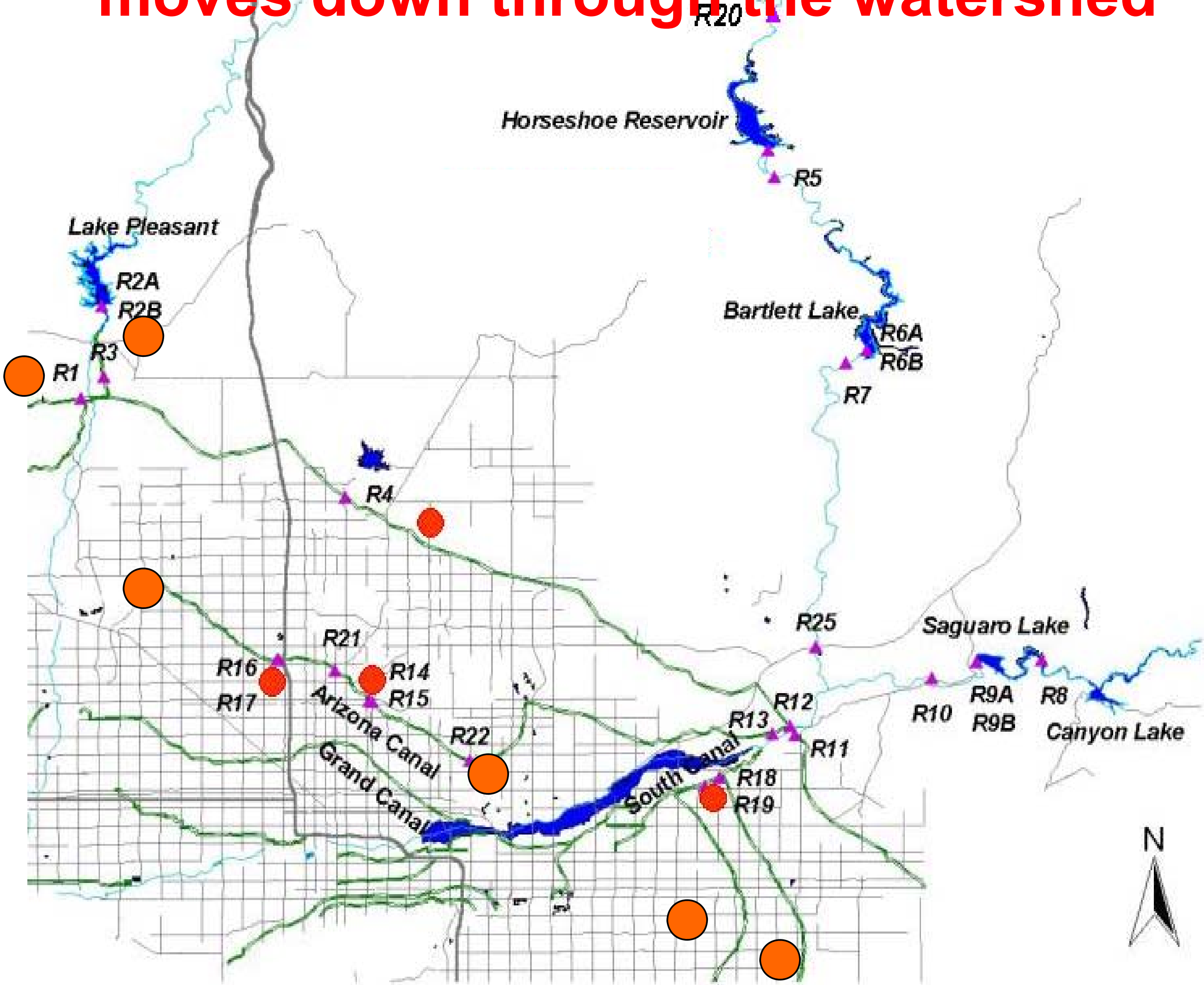
Introductions

Name?

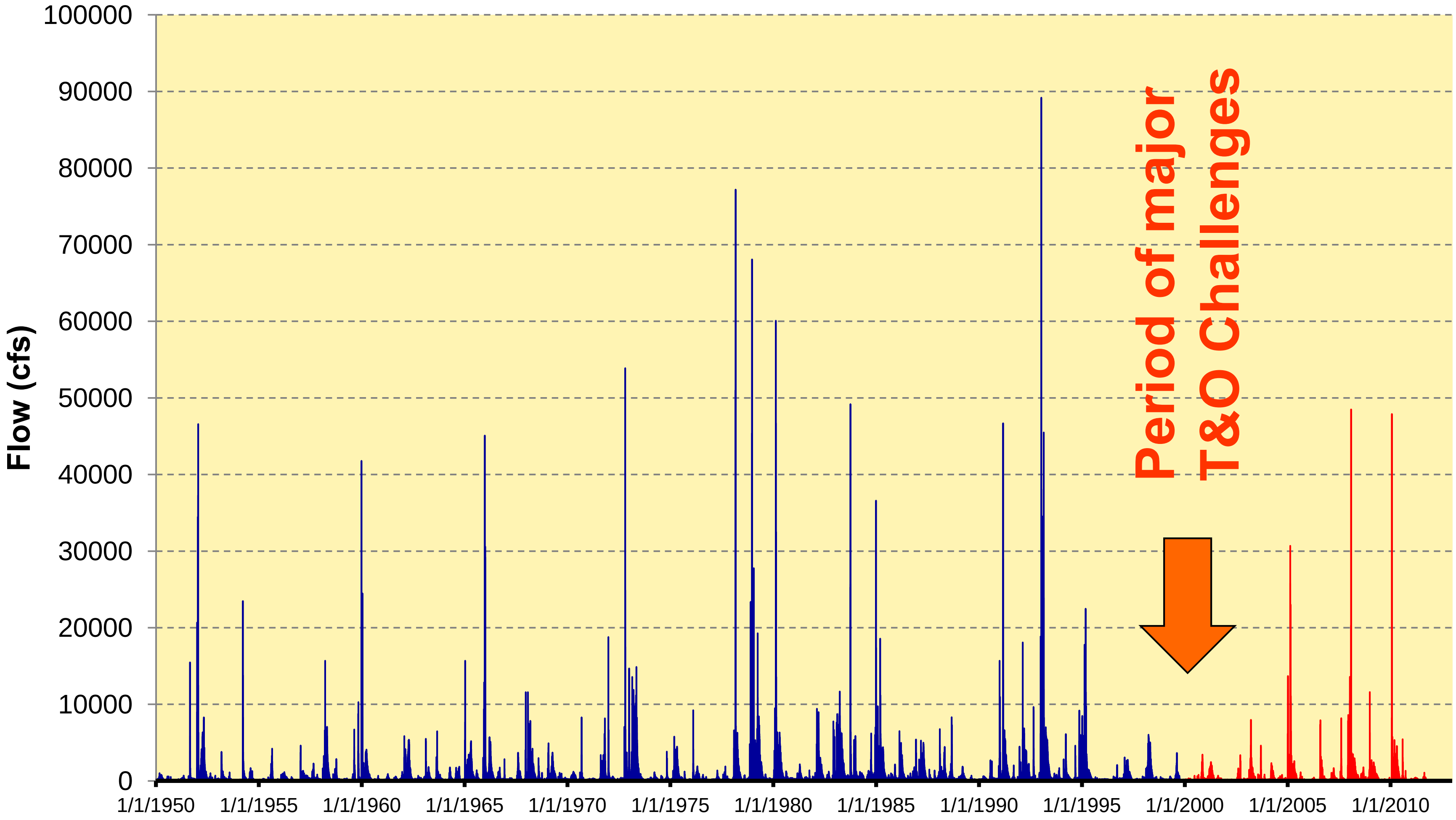
Affiliation?

What do you want to hear today?

Workshop will present results as water moves down through the watershed

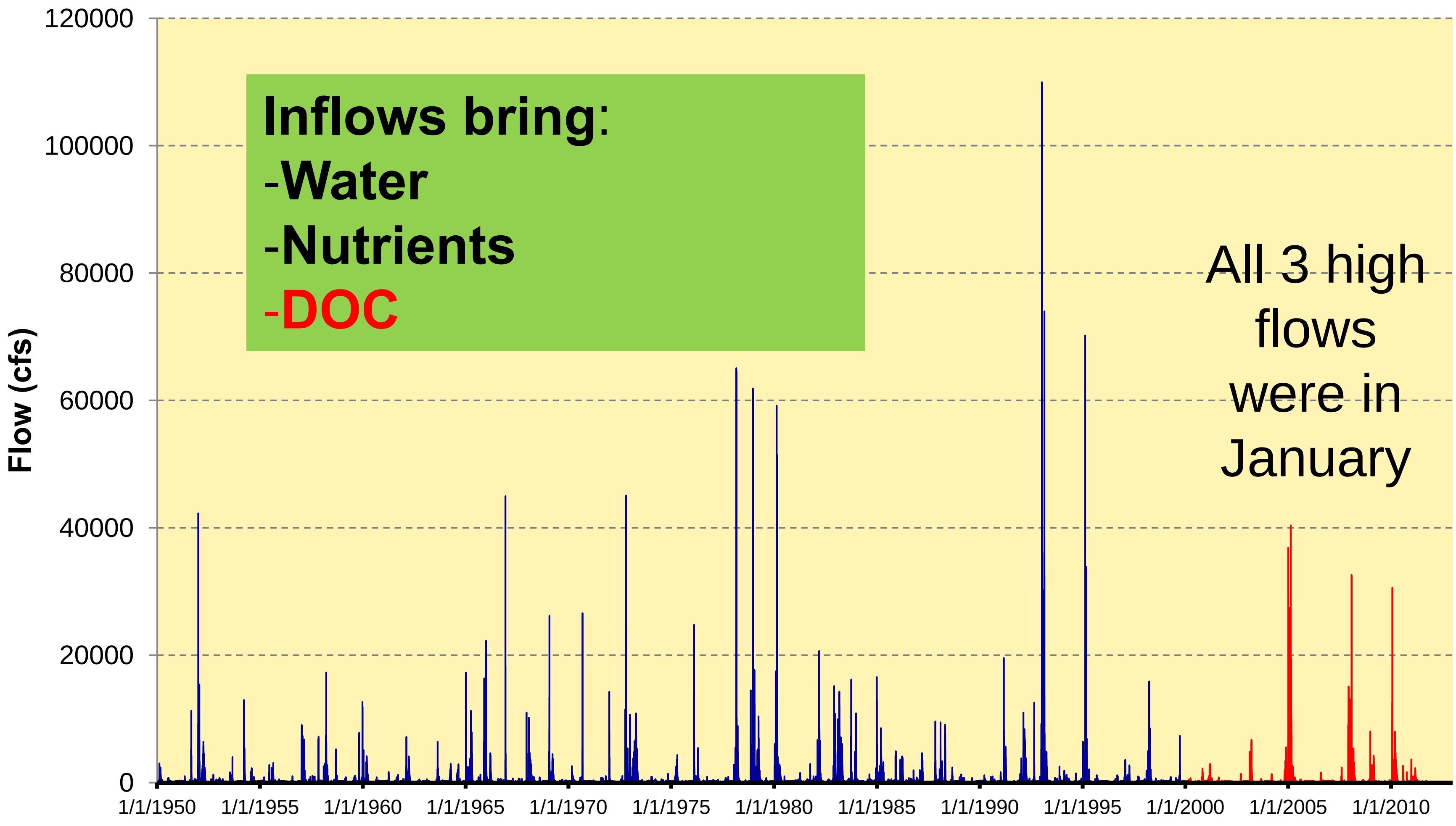


Salt River Above Roosevelt

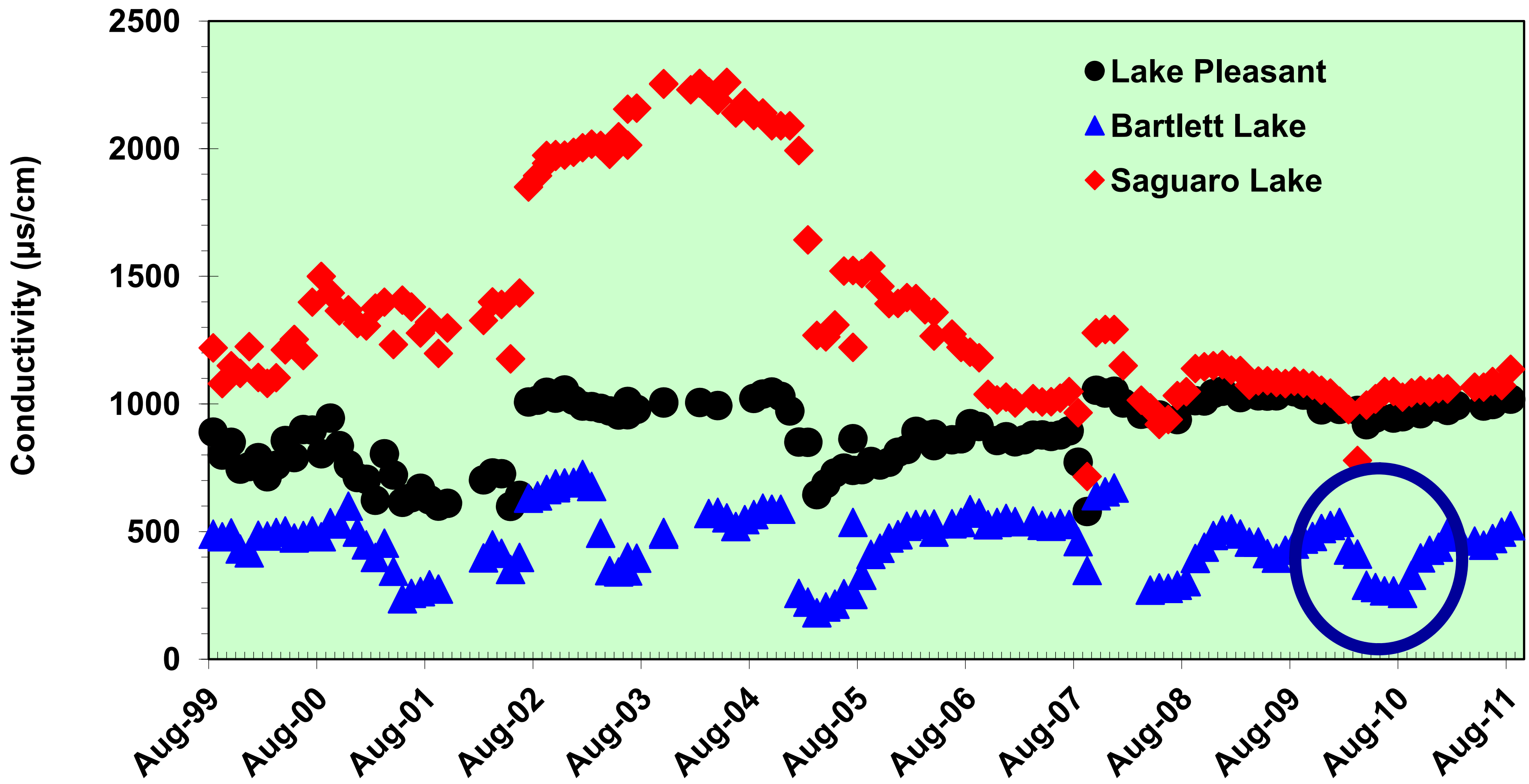


High flows are between Dec 15-Mar 31 usually

Verde River Above Horseshoe Reservoir (at Tangle Creek)

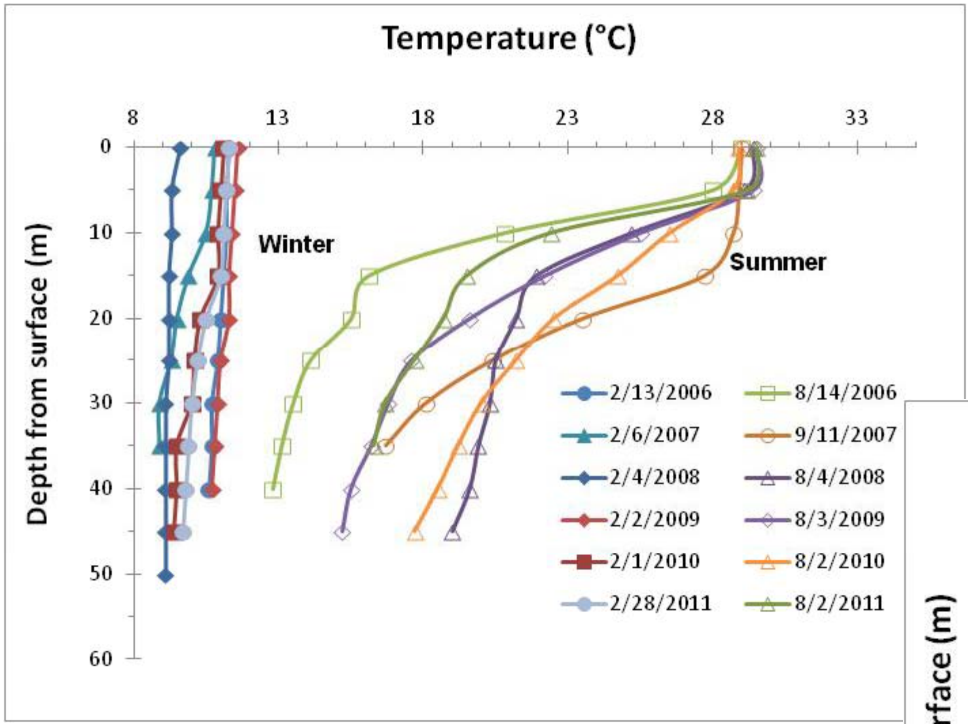


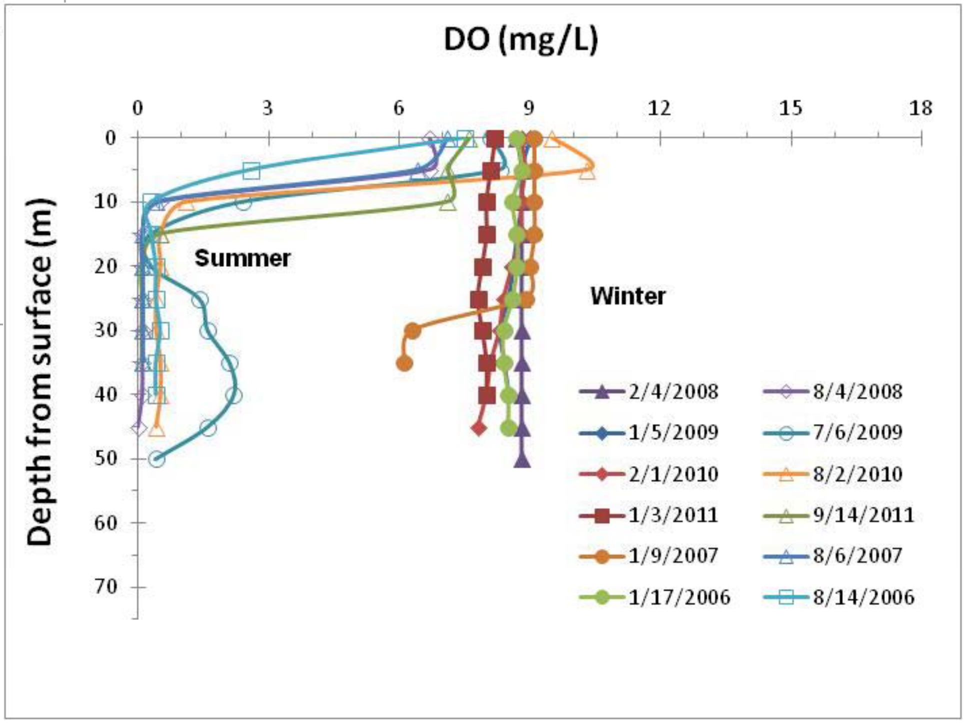
Hydrology Affects Water Quality (conductance can affect algal dominance)



Reservoir Stratification over the years

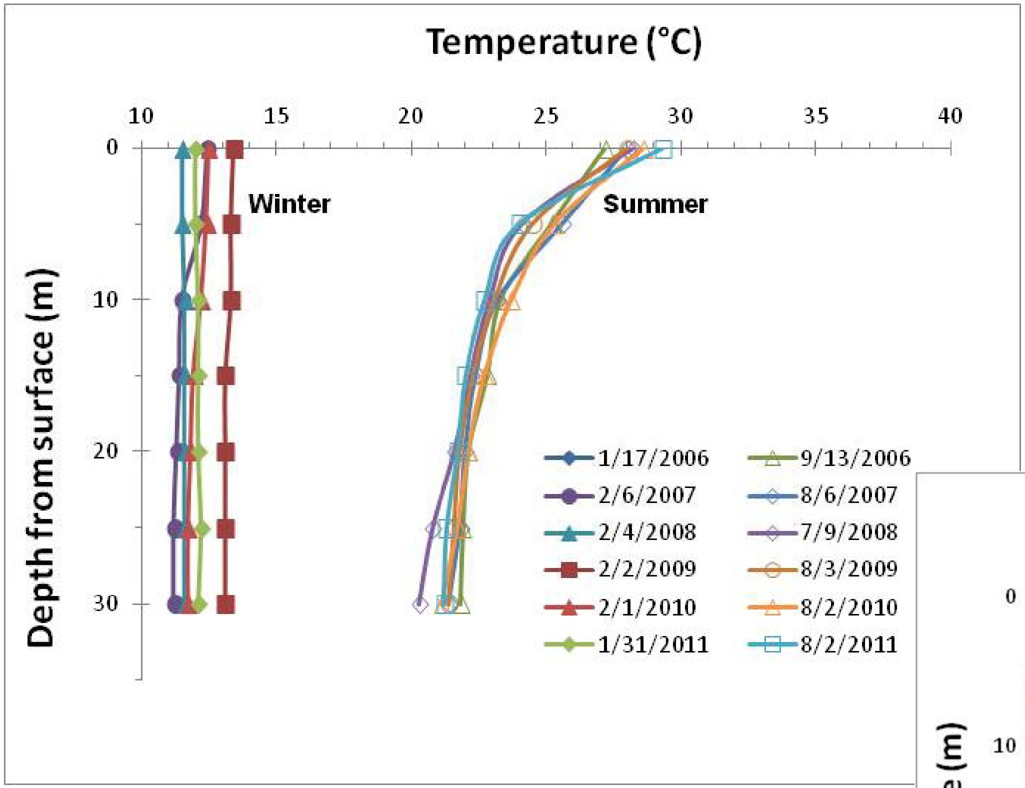
Bartlett Lake winter & summer

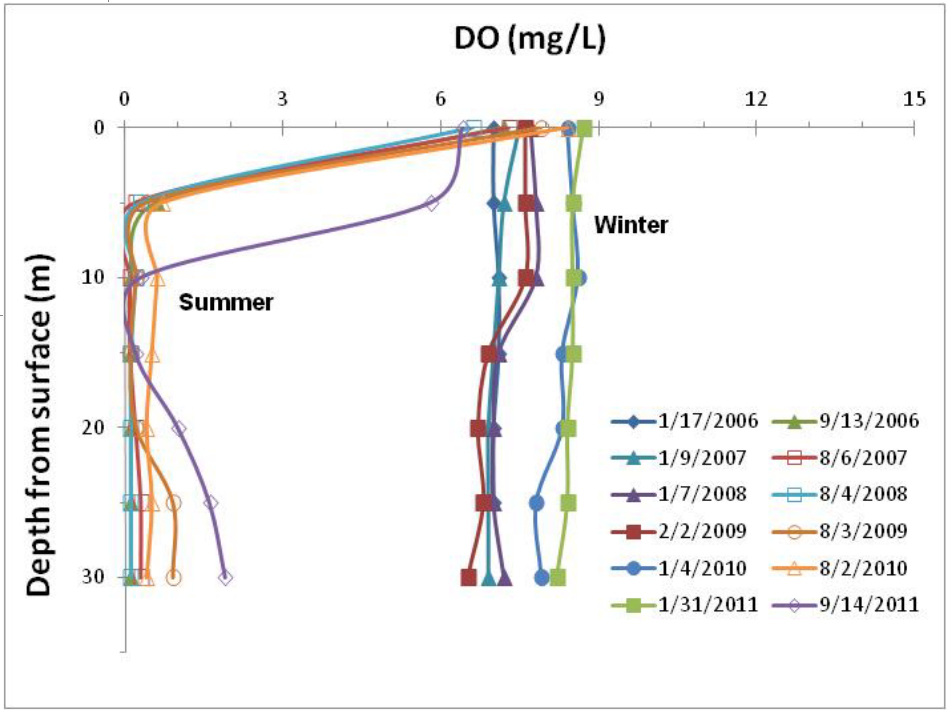




Reservoirs are destratifying

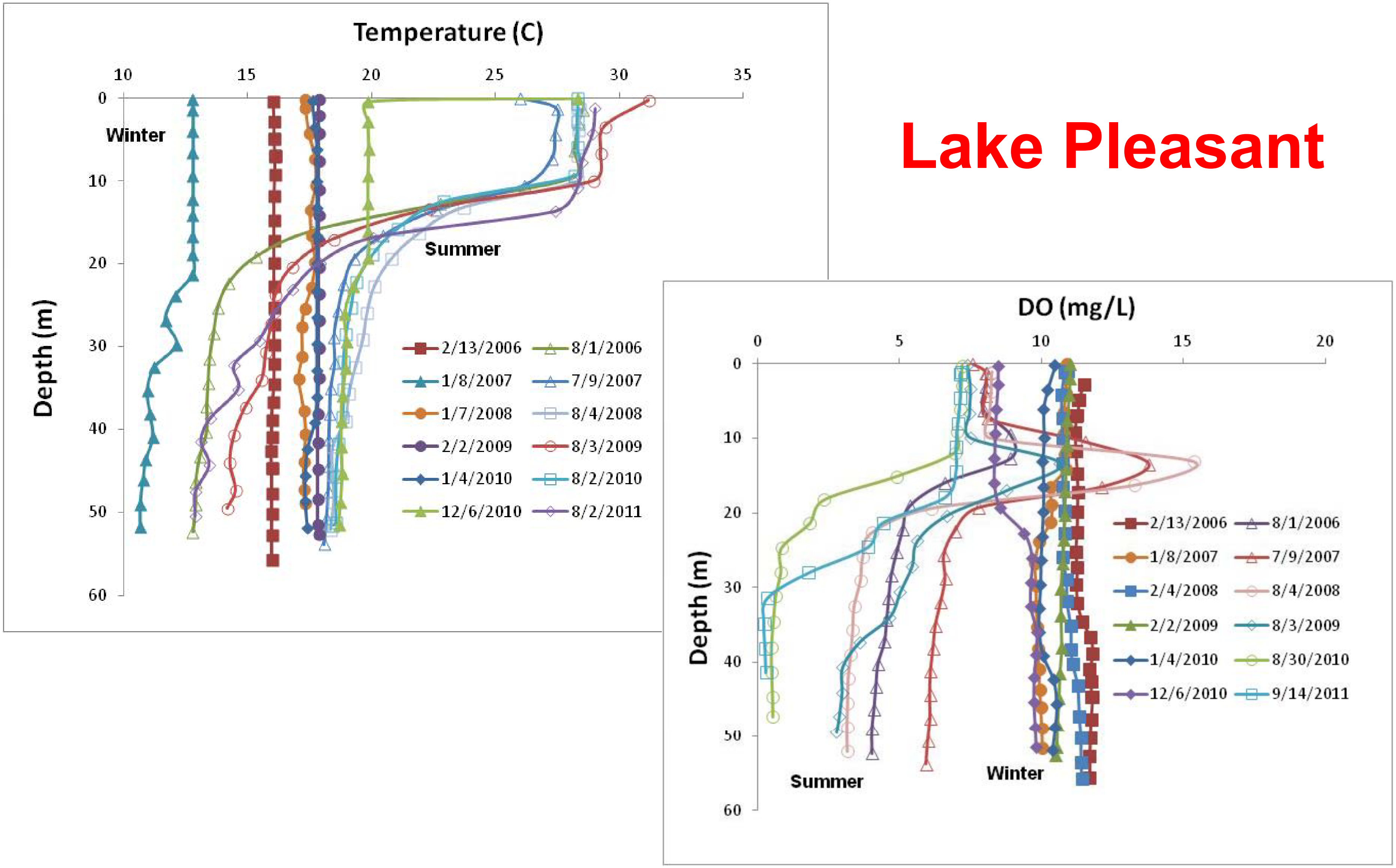
Saguaro Lake



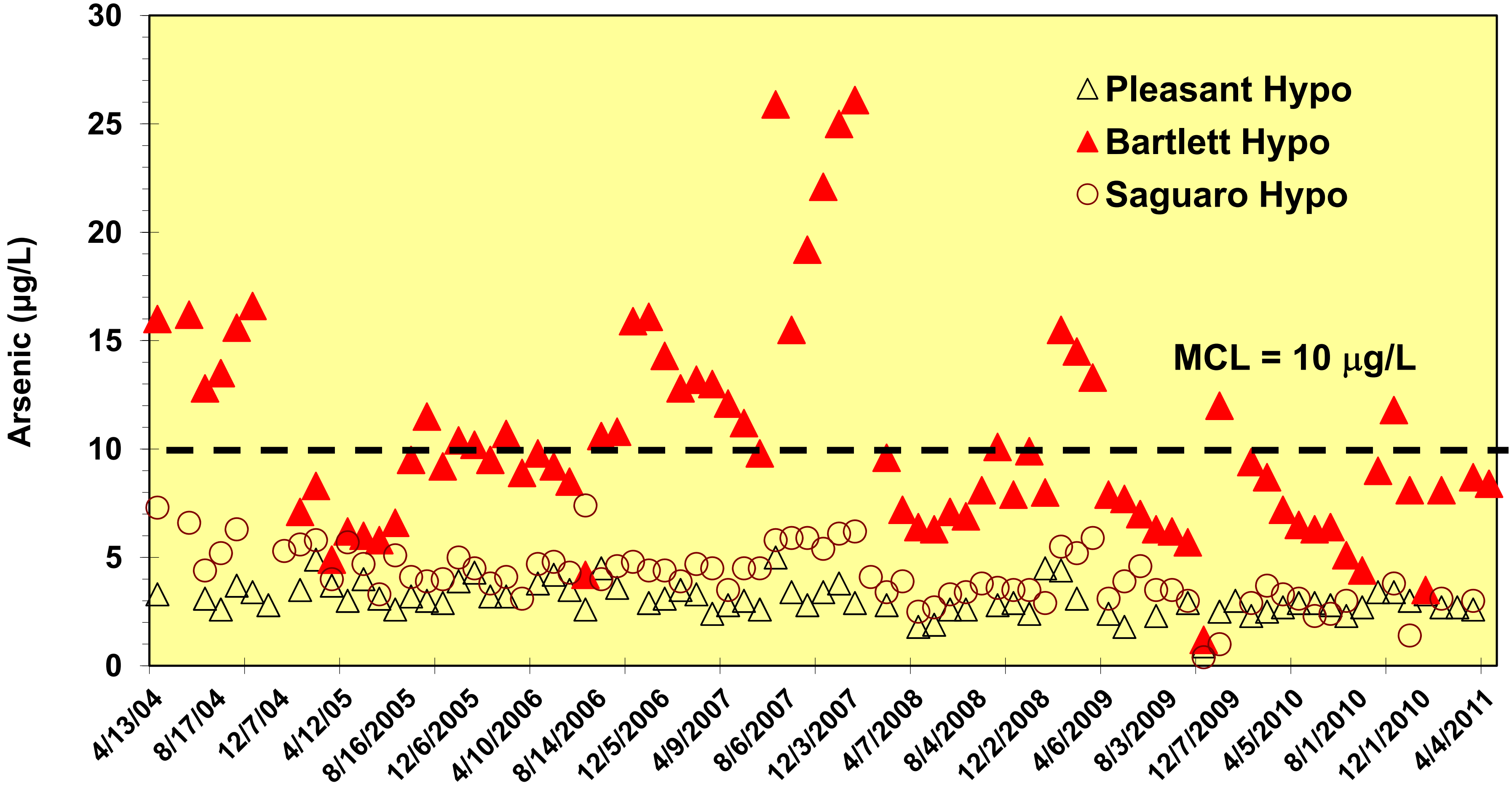


Reservoir Conditions Affect Water Quality

Lake Pleasant

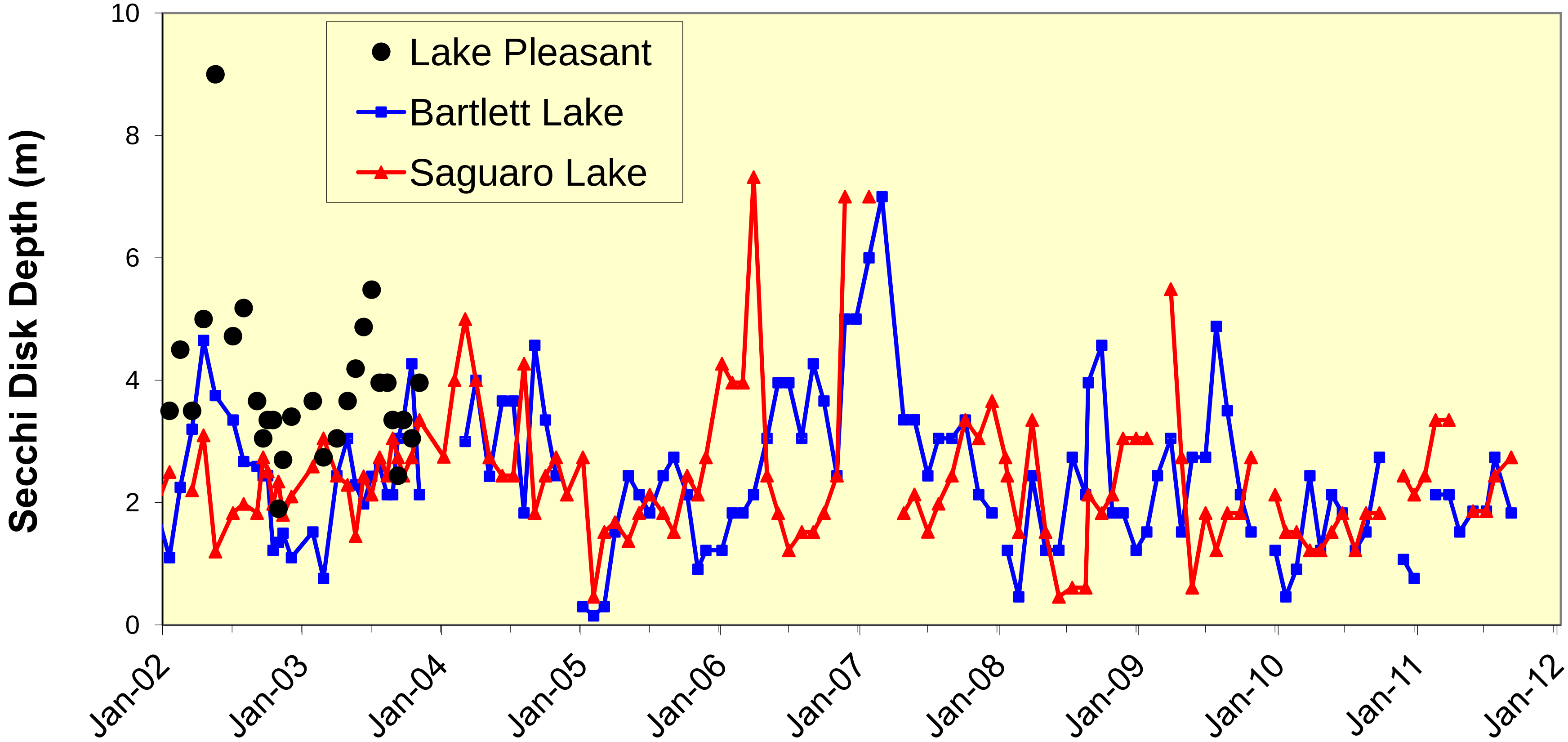


Arsenic



30
25
20
15
10
5
0
Arsenic (µg/L)
Pleasant Hypo
Bartlett Hypo
Saguaro Hypo
MCL = 10 µg/L
4/13/04
8/17/04
12/7/04
4/12/05
8/16/2005
12/6/2005
4/10/2006
8/14/2006
12/5/2006
4/9/2007
8/6/2007
12/3/2007
4/7/2008
8/4/2008
12/2/2008
4/6/2009
8/3/2009
12/7/2009
4/5/2010
8/1/2010
12/1/2010
4/4/2011

Secchi Disk Depth Influenced by Inorganic Suspended Sediment and/or Organic Biomass

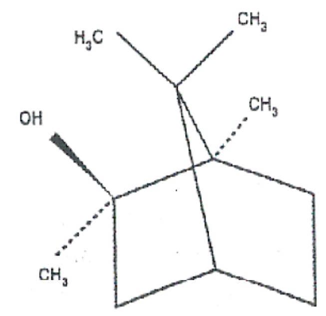
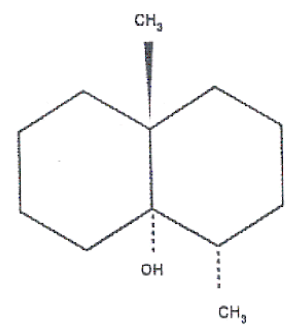


Low values in Bartlett: Jan-Feb due to rains

Low values in Saguaro: early summer due to algae blooms

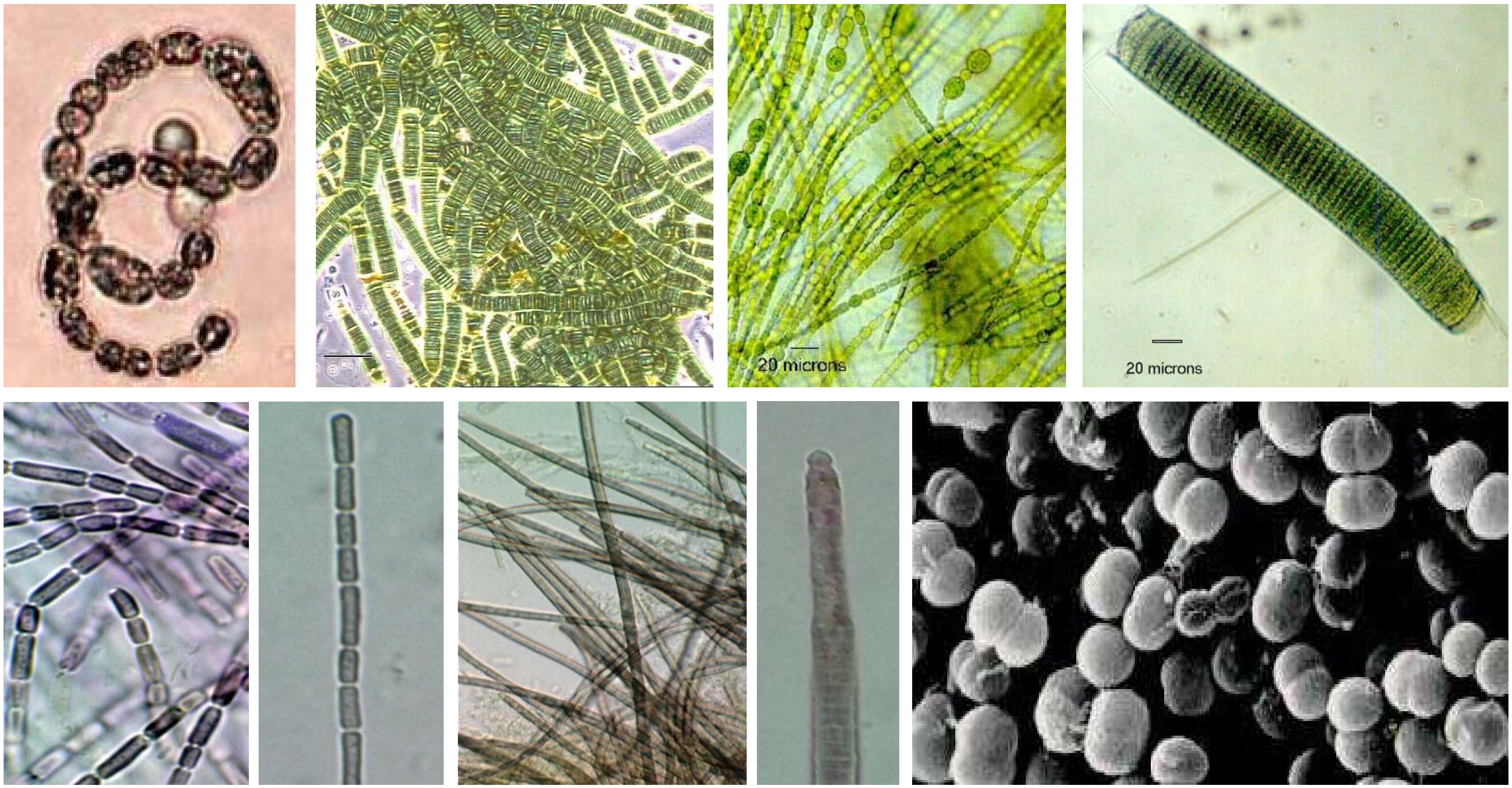
Common Algal T&O Compounds

- Taste threshold ~ 10 ng/L
- Chlorine residual can "mask" odors
- T&O is a worldwide issue affecting the publics "confidence" in drinking waters, but is not regulated

Parameter	MIB (2-methyisoborneol)	Geosmin
Full Name	(1-R-exo)-1,2,7,7-tetramethyl bucyclo-[2,2,1]-heptan-2-o1	tran-1, 10-dimethyl-trans-9-decalol
Molecular Formula	$C_{11}H_{20}O$	$C_{12}H_{22}O$
Molecular Weight	168 g-mole^{-1}	182 g-mole^{-1}
Boiling Point	197 ^{o}C	165 ^{o}C
Aqueous Solubility	195 mg/L	150 mg/L
K_{ow}	3.13	3.7
Henry's Law Constant	5.76×10^{-5} atm m^{3}-mole^{-1}	6.66×10^{-5} atm m^{3}-mole^{-1}
Structure		

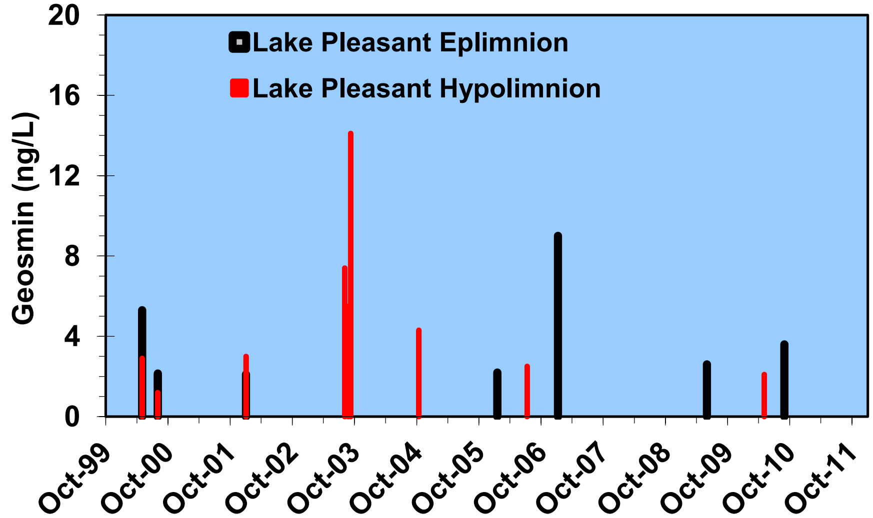
Source: (Pirbazari et al. 1992)

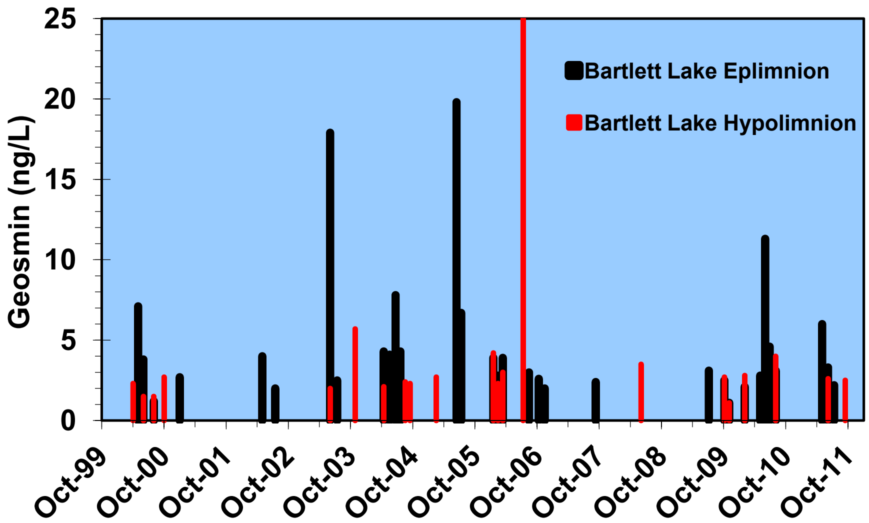
Possible MIB/geosmin producing cyanobacteria

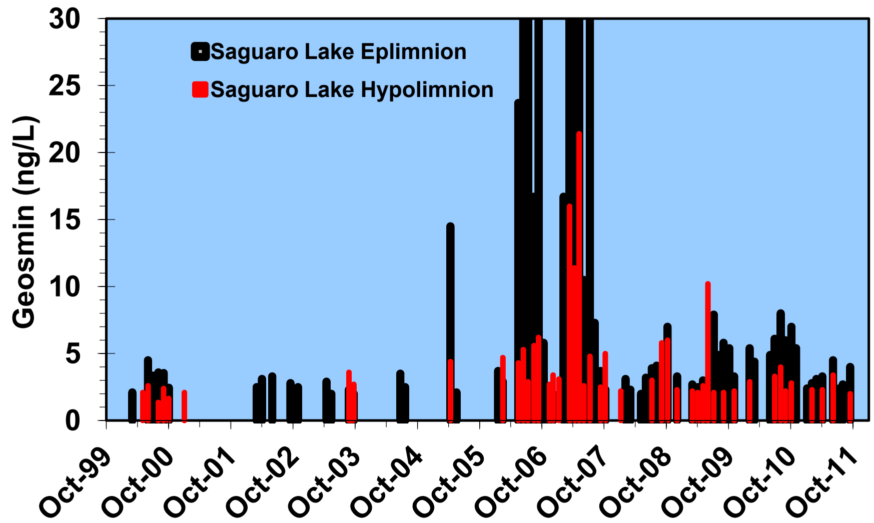


On our website:
INTERACTIVE TAXONOMIC GUIDE
http://enpub.fulton.asu.edu/pwest/tasteandodor.htm

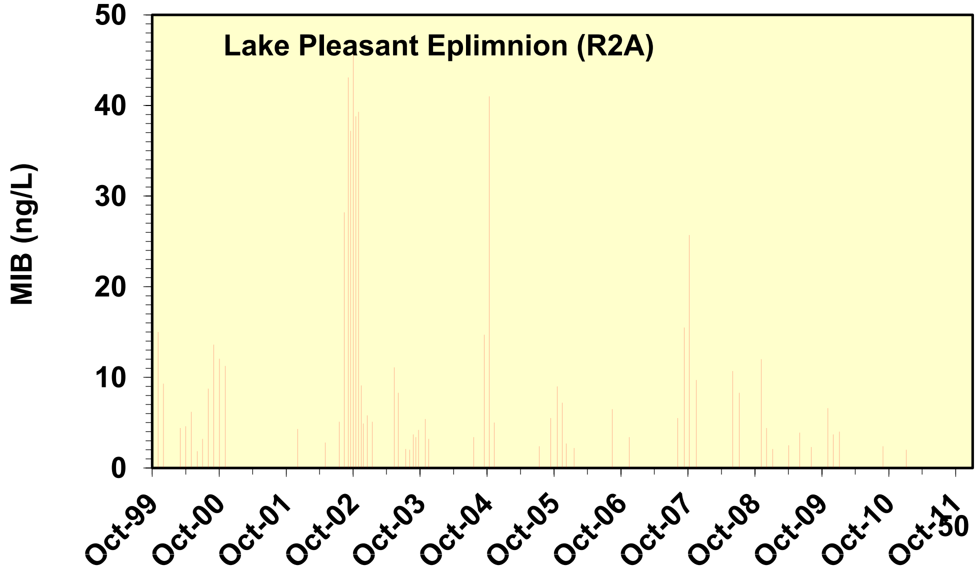
Geosmin Data

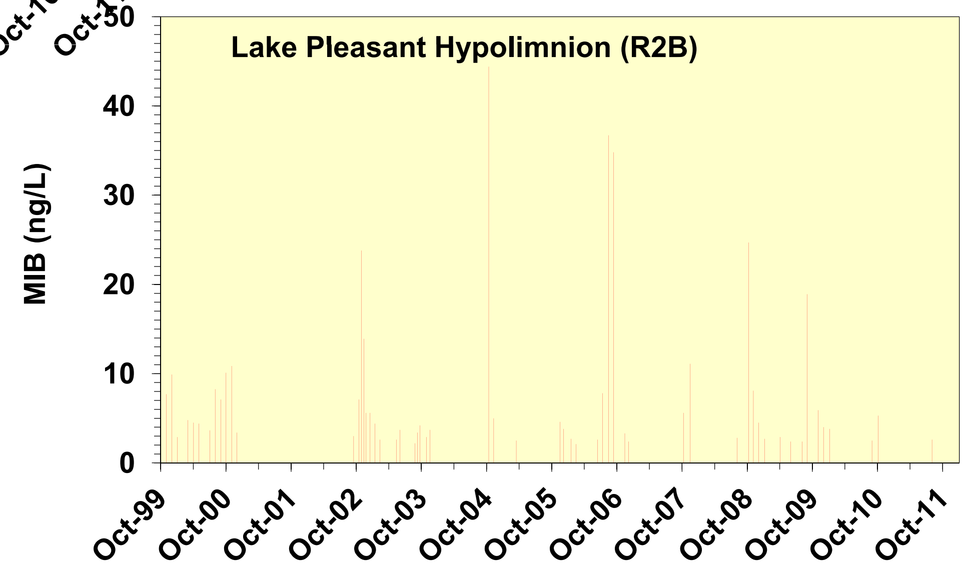




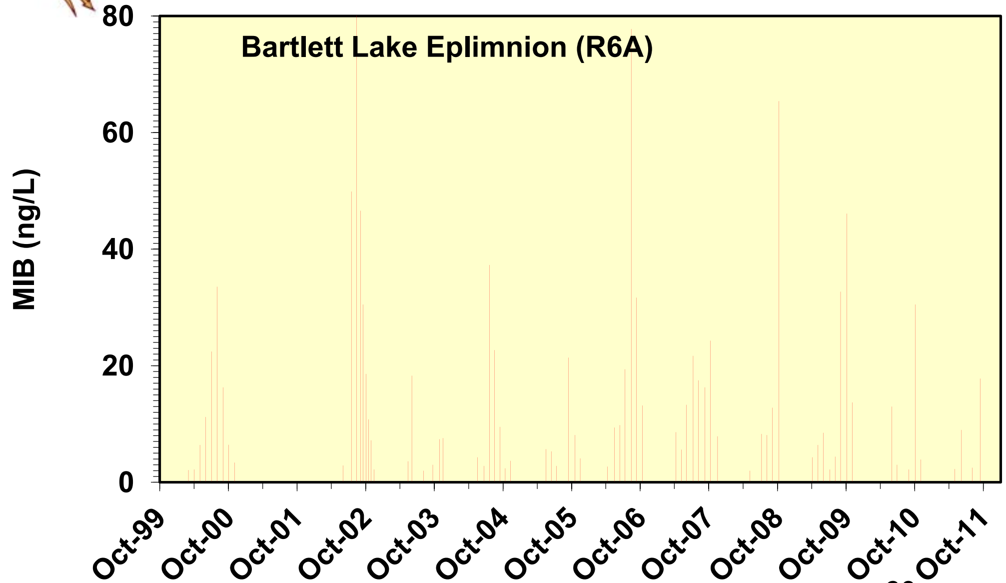


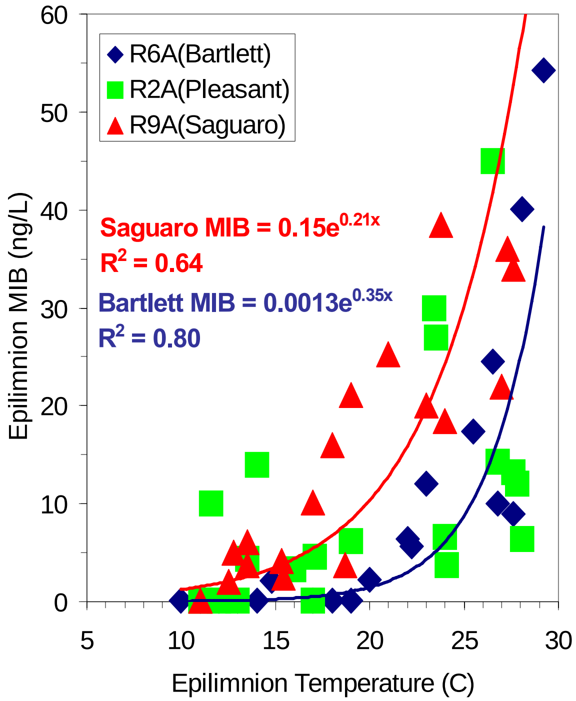
MIB Data – Lake Pleasant

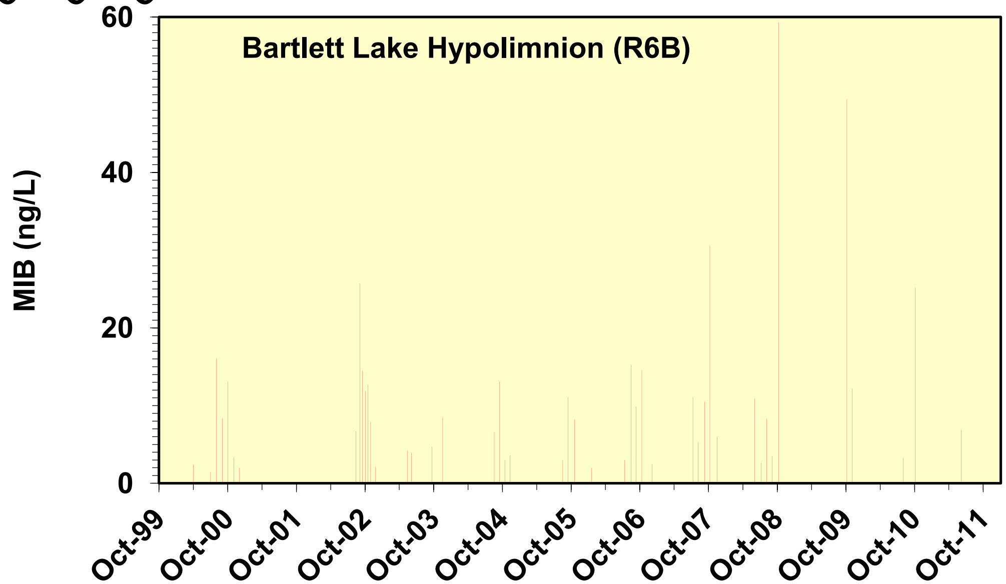




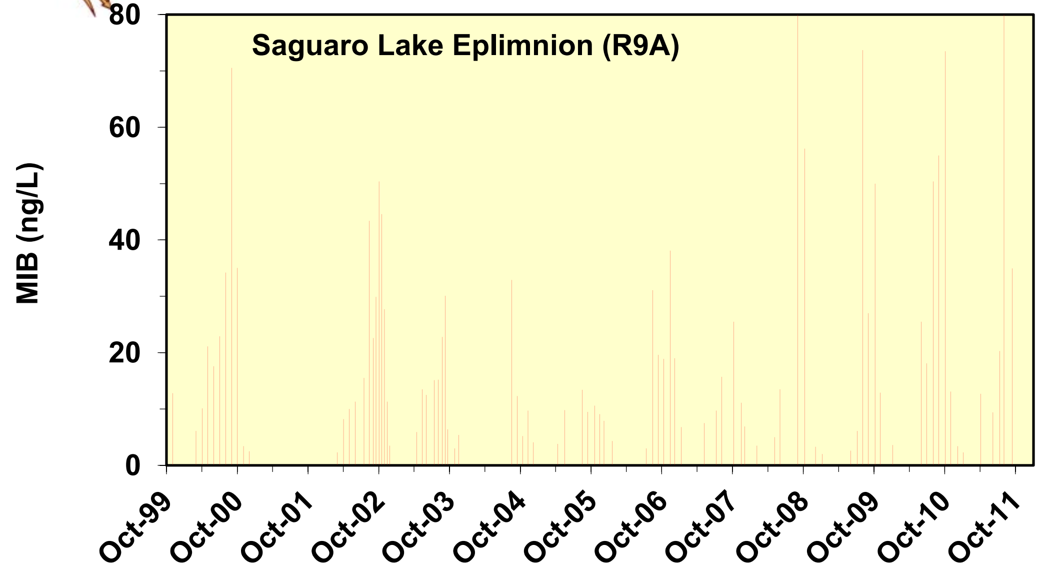
MIB Data – Bartlett Lake

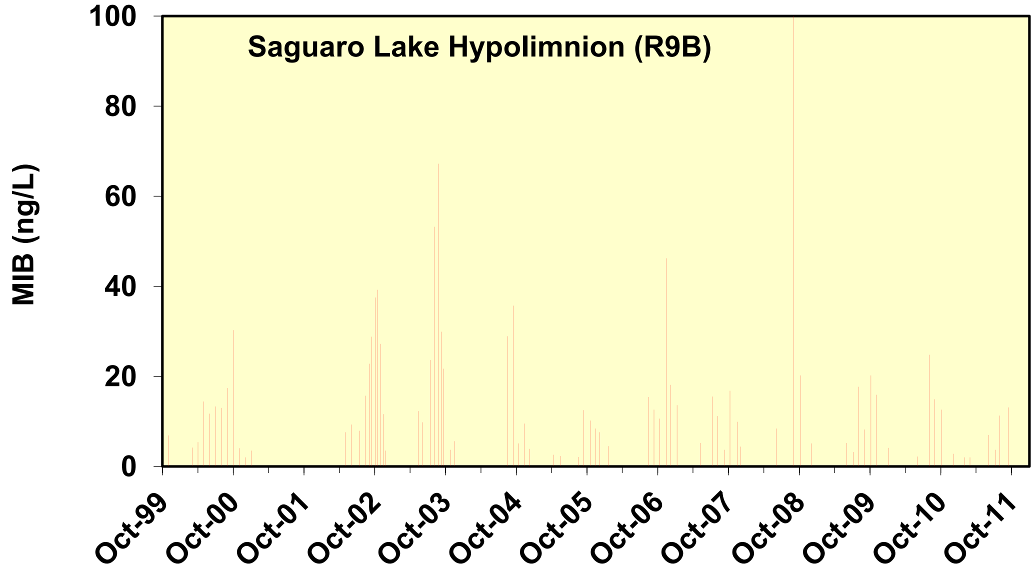






MIB Data – Saguaro Lake



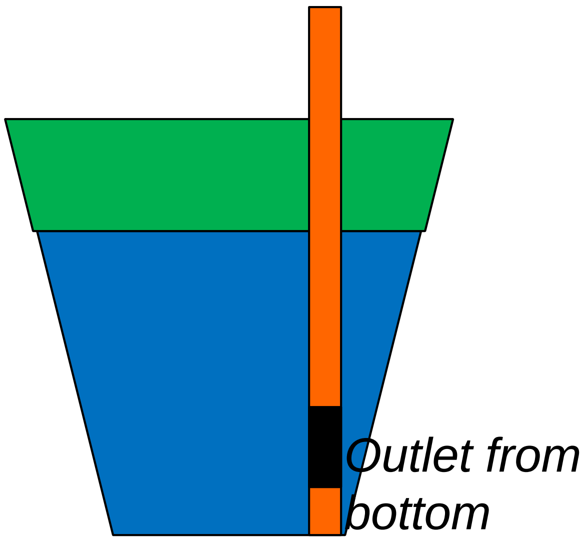


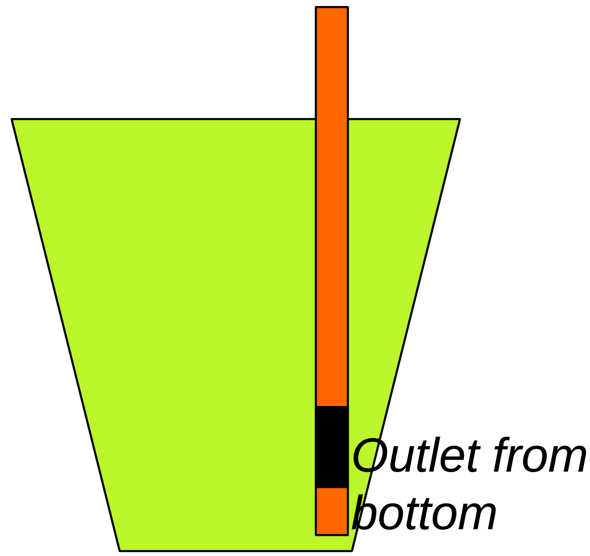
Cells die and settle into darkness

Most Recent Data (Sept 14)

Sample Description	Location	MIB (ng/L)	Geosmin (ng/L)	Cyclocitral (ng/L)
Lake Pleasant (August11)	Eplimnion	**<2.0**	**<2.0**	**<2.0**
Lake Pleasant (August11)	Hypolimnion	**2.6**	**<2.0**	**<2.0**
Verde River @ Beeline				
Bartlett Reservoir	Epilimnion	**17.8**	**<2.0**	**<2.0**
Bartlett Reservoir	Epi-near dock	**22.9**	**<2.0**	**<2.0**
Bartlett Reservoir	Hypolimnion	**<2.0**	**2.5**	**<2.0**
Salt River @ BluePt Bridge		**7.6**	**3.7**	**<2.0**
Saguaro Lake	Epilimnion	**34.9**	**4.0**	**<2.0**
Saguaro Lake	Epi - Duplicate	**35.0**	**4.1**	**<2.0**
Saguaro Lake	Epi-near dock	**32.9**	**5.9**	**<2.0**
Saguaro Lake	Hypolimnion	**13.1**	**2.0**	**<2.0**

Lake Destratification





Thermally Stratified

-Algae & MIB are on top

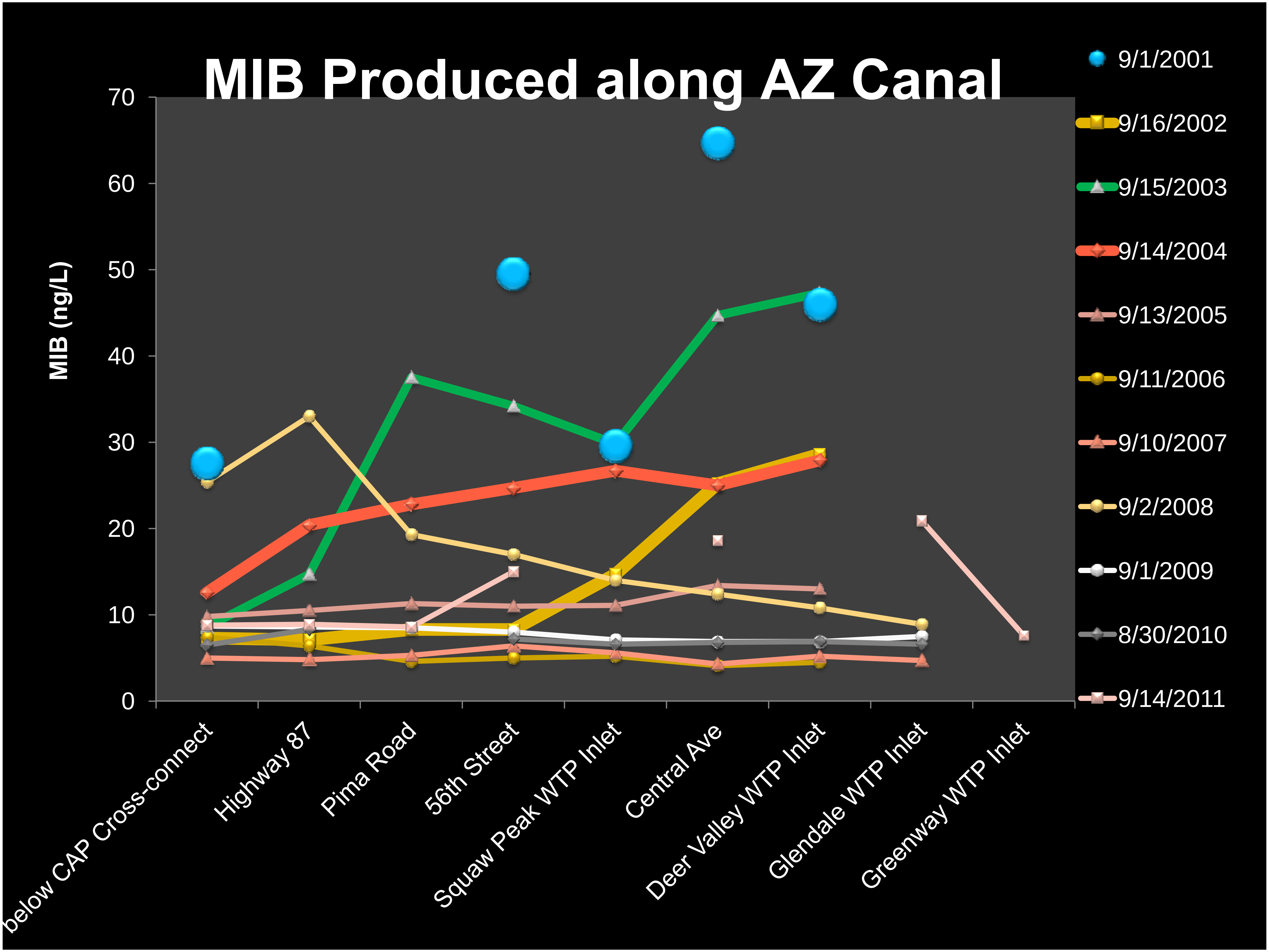
-Dead cells sink and release MIB

Post-stratification

-Algae & MIB mix with depth

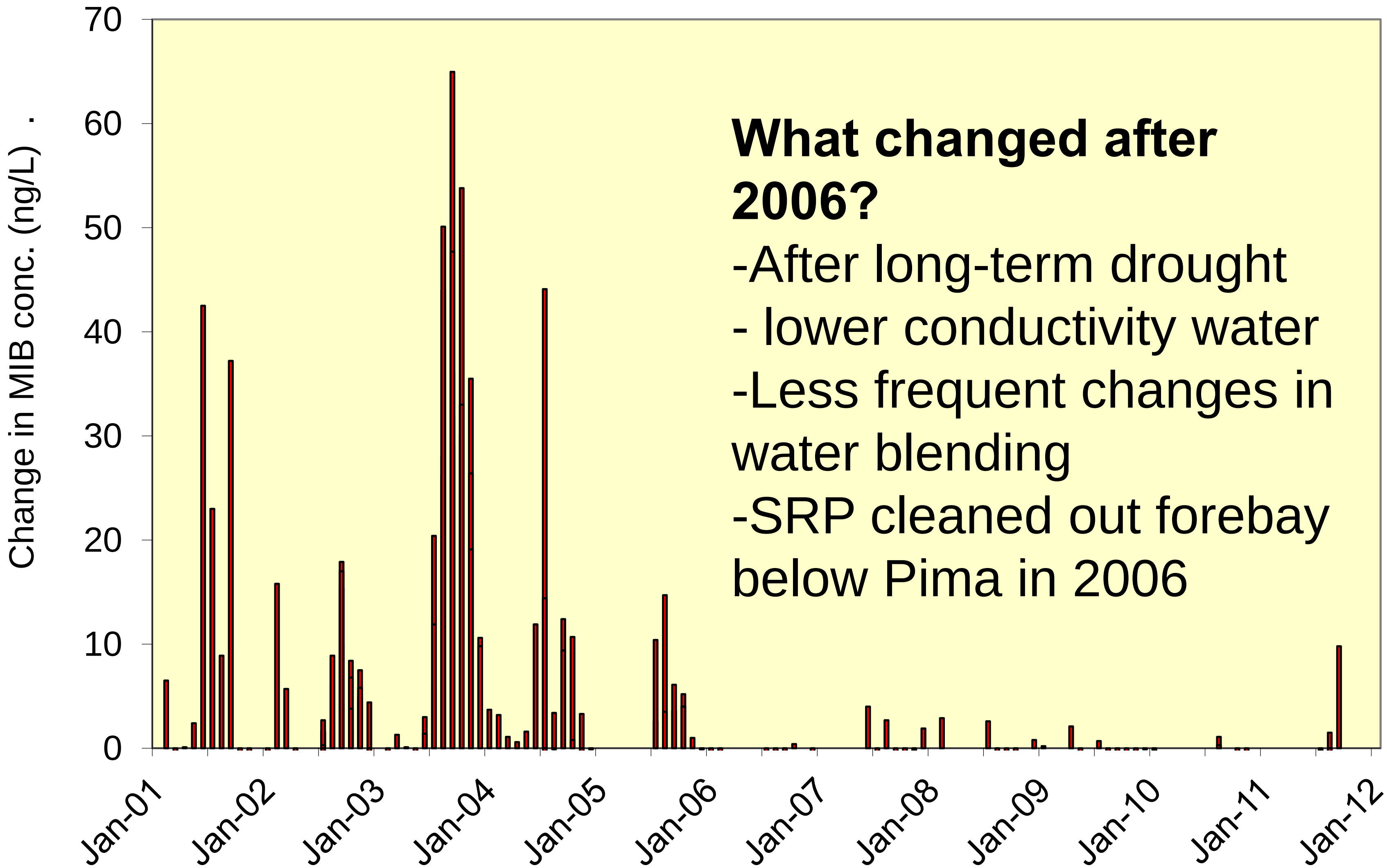
-Increased MIB in outlet

-Food and O2 fuels rapid biodegradation



MIB Produced along AZ Canal
MIB (ng/L)
0
10
20
30
40
50
60
70
below CAP Cross-connect
Highway 87
Pima Road
56th Street
Squaw Peak WTP Inlet
Central Ave
Deer Valley WTP Inlet
Glendale WTP Inlet
Greenway WTP Inlet
9/1/2001
9/16/2002
9/15/2003
9/14/2004
9/13/2005
9/11/2006
9/10/2007
9/2/2008
9/1/2009
8/30/2010
9/14/2011

MIB Growth in AZ canal from below X-Con to Central Ave.



What changed after 2006?

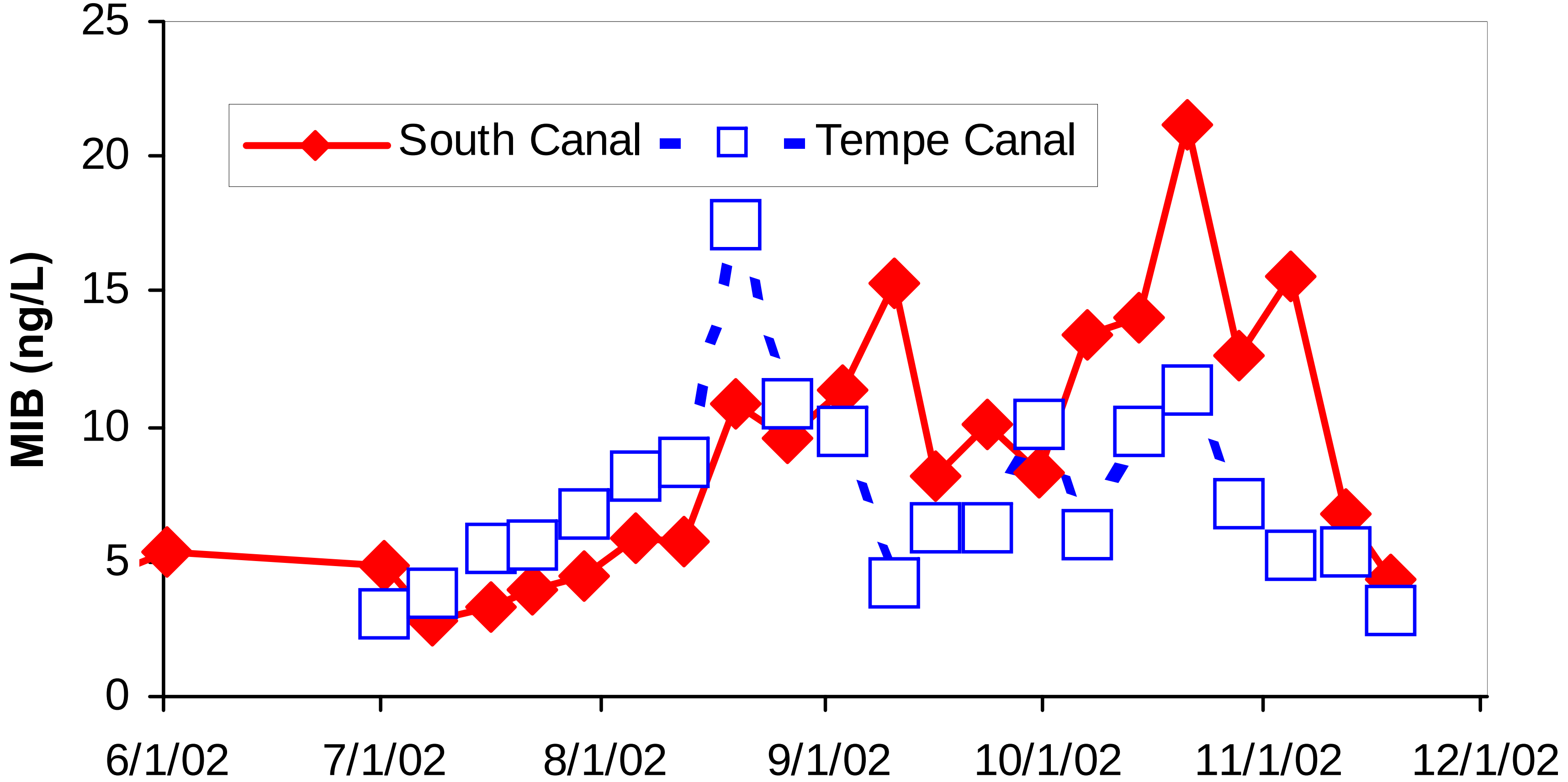
-After long-term drought

- lower conductivity water

-Less frequent changes in water blending

-SRP cleaned out forebay below Pima in 2006

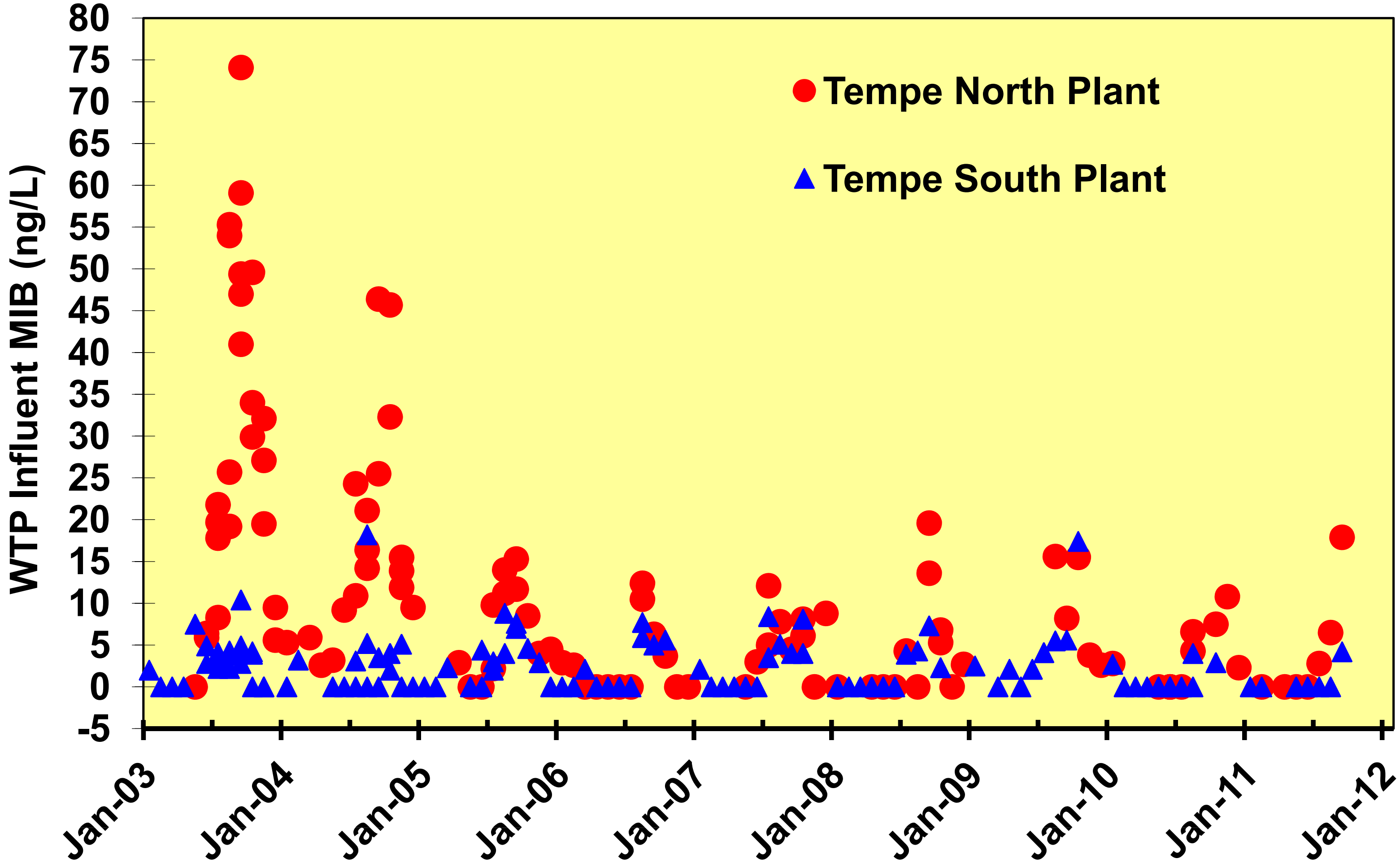
South and Tempe Canal - Summer 2002



Algae Removal Demonstrations (July 2004)

Copper Application

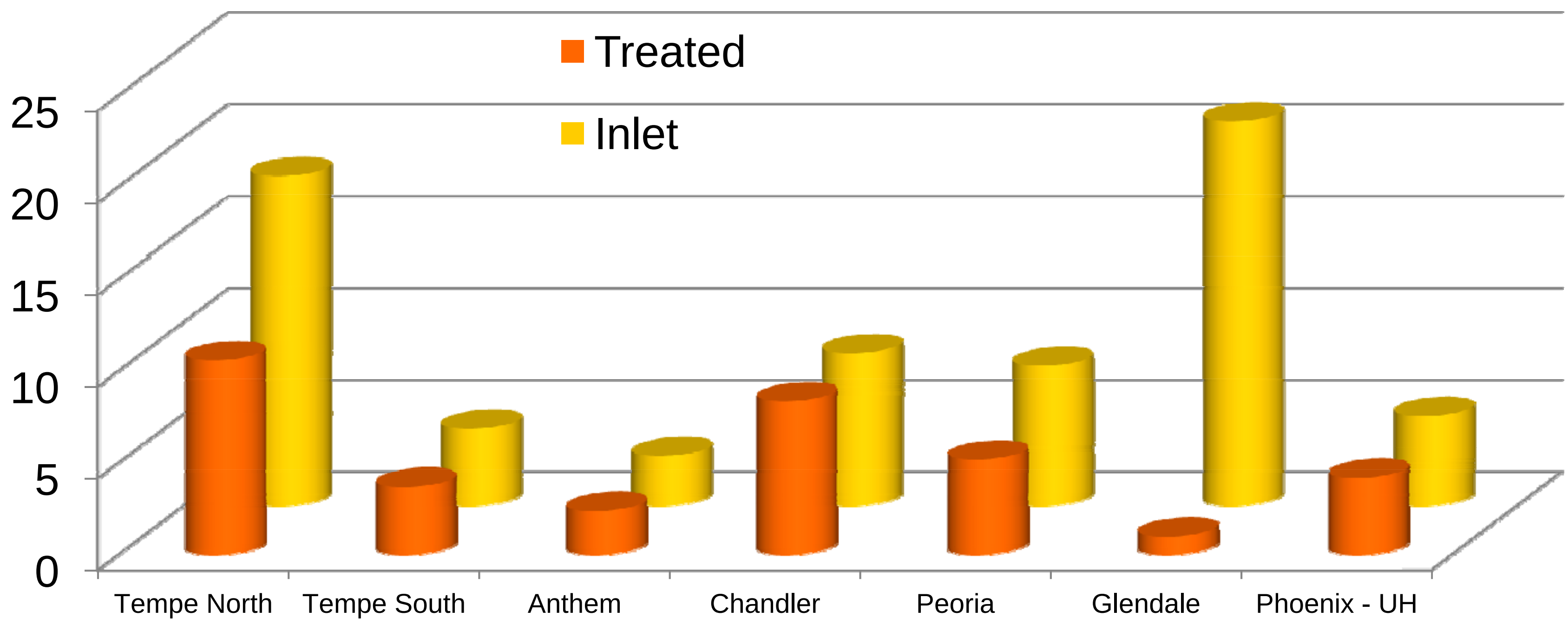
MIB levels higher in AZ Canal system compared against South Canal system



T&O Production Trend Summary

- Significant MIB production potential in the Arizona Canal between Pima and Central
- Historically geosmin production in Consolidated canal – but no MIB or geosmin change this year

MIB Removal at WTPs (September 2011)

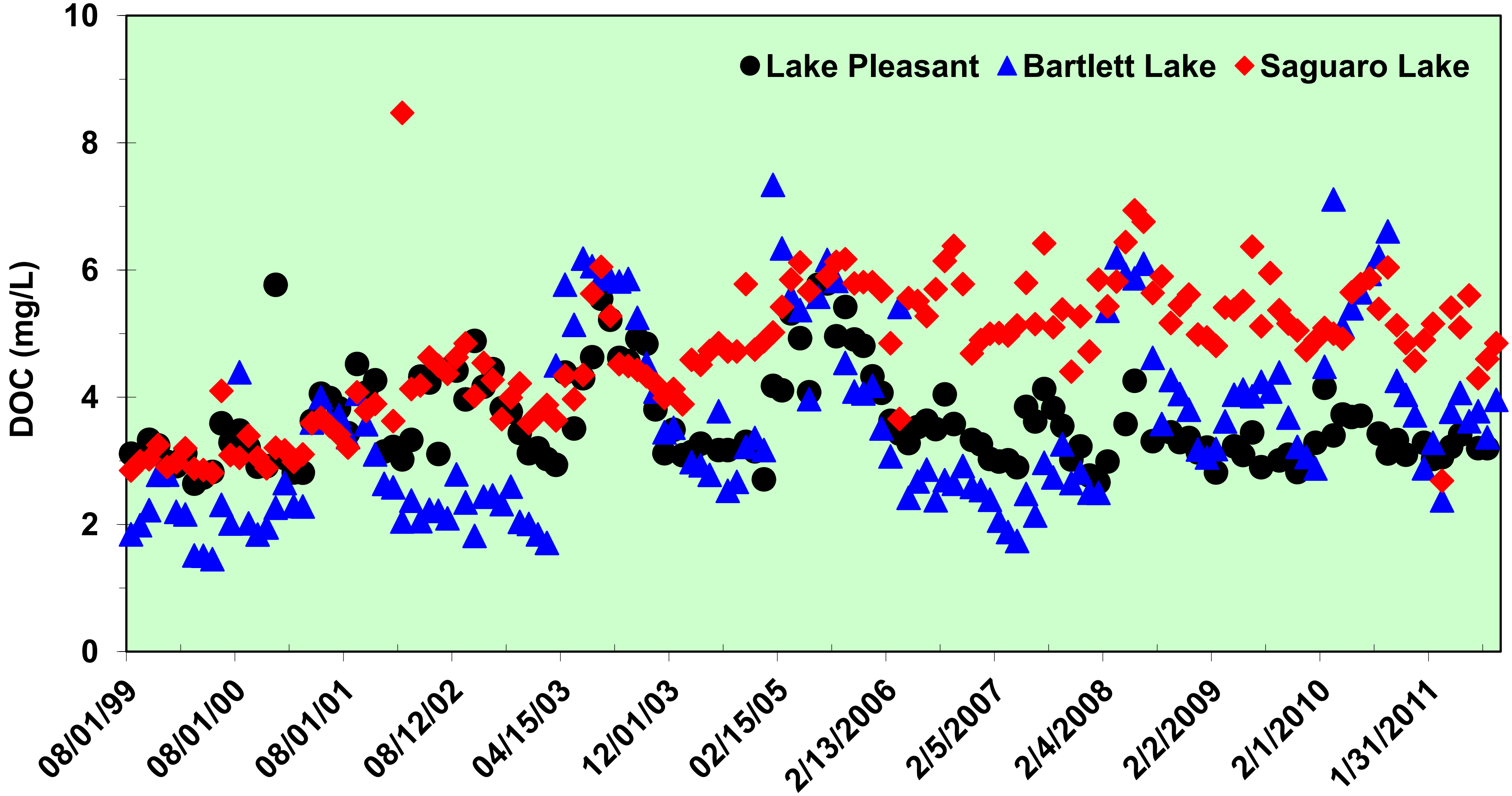


Tempe Tap Water MIB = 13 ng/L; Geosmin = 3 ng/L

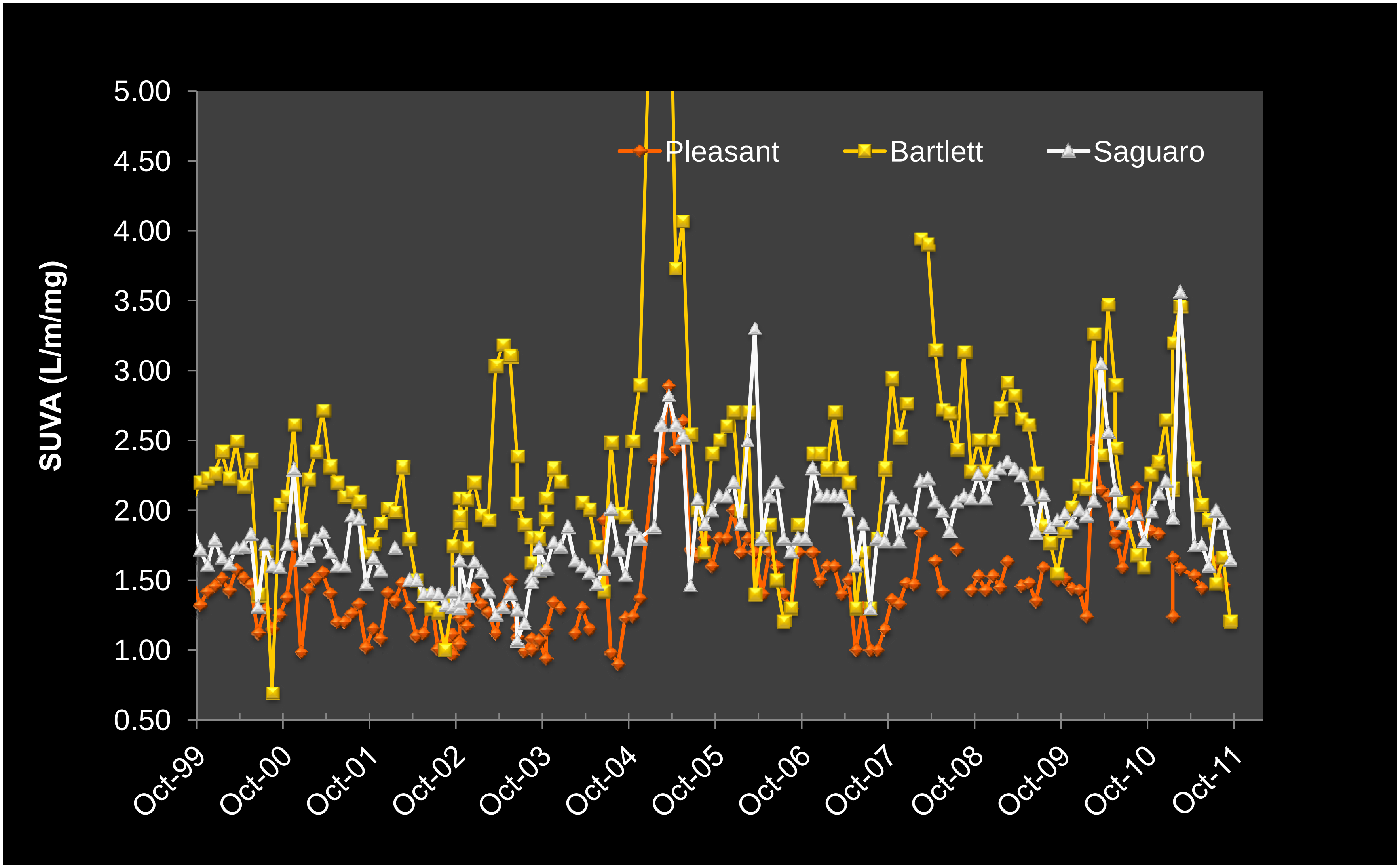
T&O Trends

- Saguaro Lake has consistently produced highest levels of T&O
- Verde River can produce T&O below Bartlett Reservoir
- Minimal production of T&O in canals over past ~ 5 years
  - Prior > 50 ng/L MIB or geosmin could form in canals
  - Significant MIB production potential in the Arizona Canal between Pima and Central
  - Historically geosmin production in Consolidated canal – but no MIB or geosmin change this year

Up-stream reservoirs attenuate DOC



Specific UV Absorbance at 254 nm



Roosevelt Lake

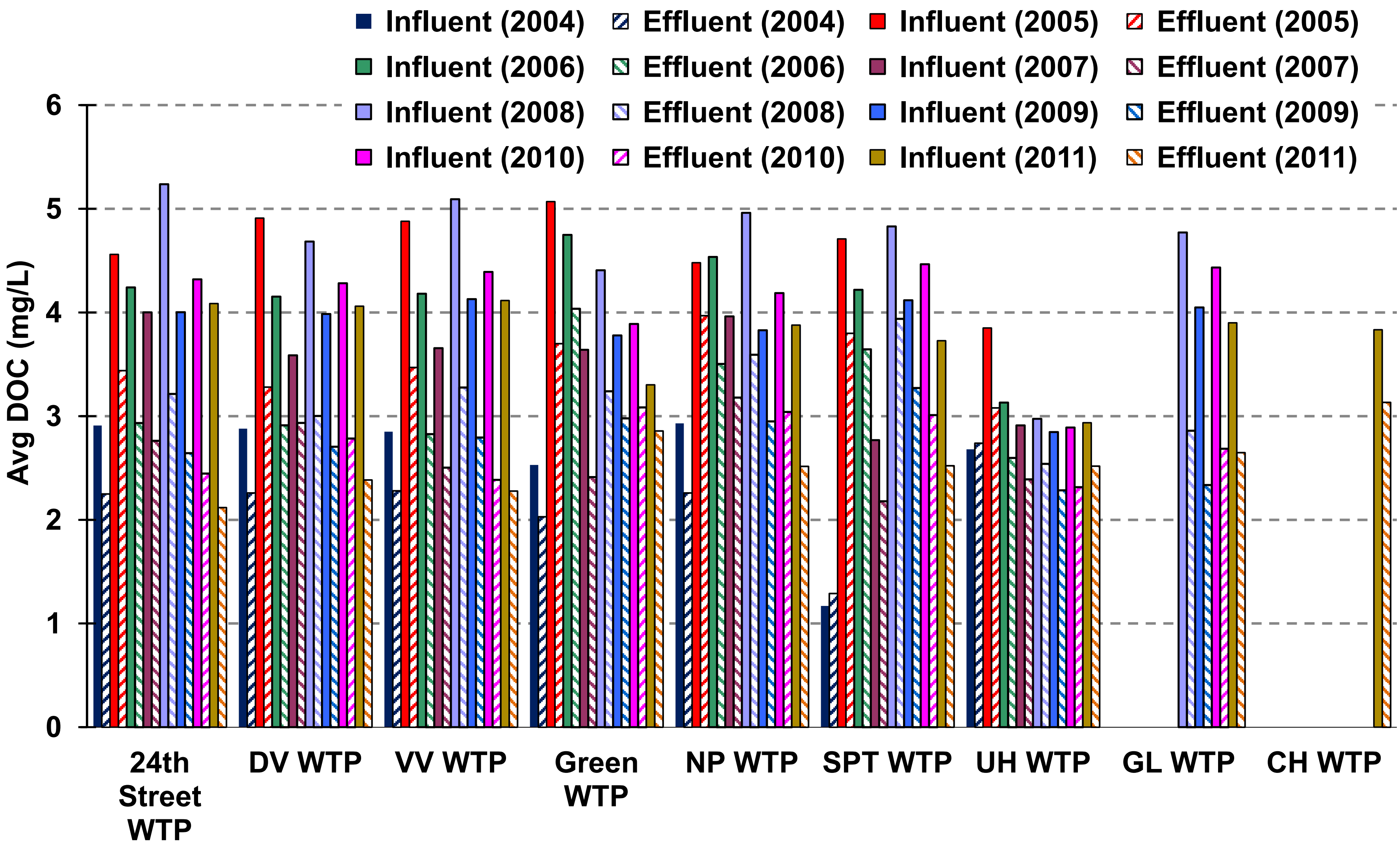
- 2003 (August) DOC = 4.9 mg/L
- 2005 data (April)
  - DOC = 6.7 mg/L
  - SUVA = 2.8 (L/mg-m)

2009	*January*	*May*
DOC =	4.2 mg/L	4.2 mg/L
SUVA =	2.6 (L/mg-m)	2.3 (L/mg-m)

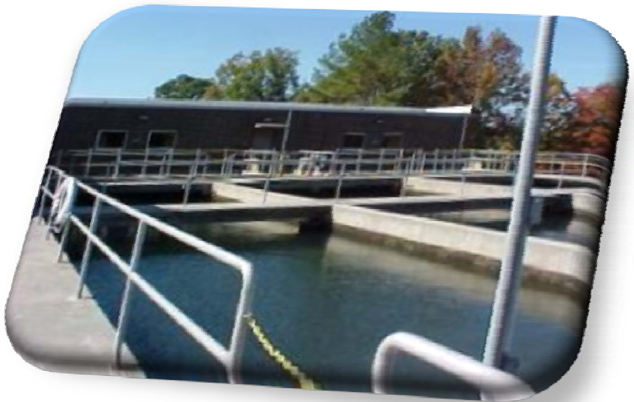
2011 data	*July*	*Sept**
DOC =	3.6 mg/L	4 mg/L
SUVA =	1.7 (L/mg-m)	1.7 (L/mg-m)

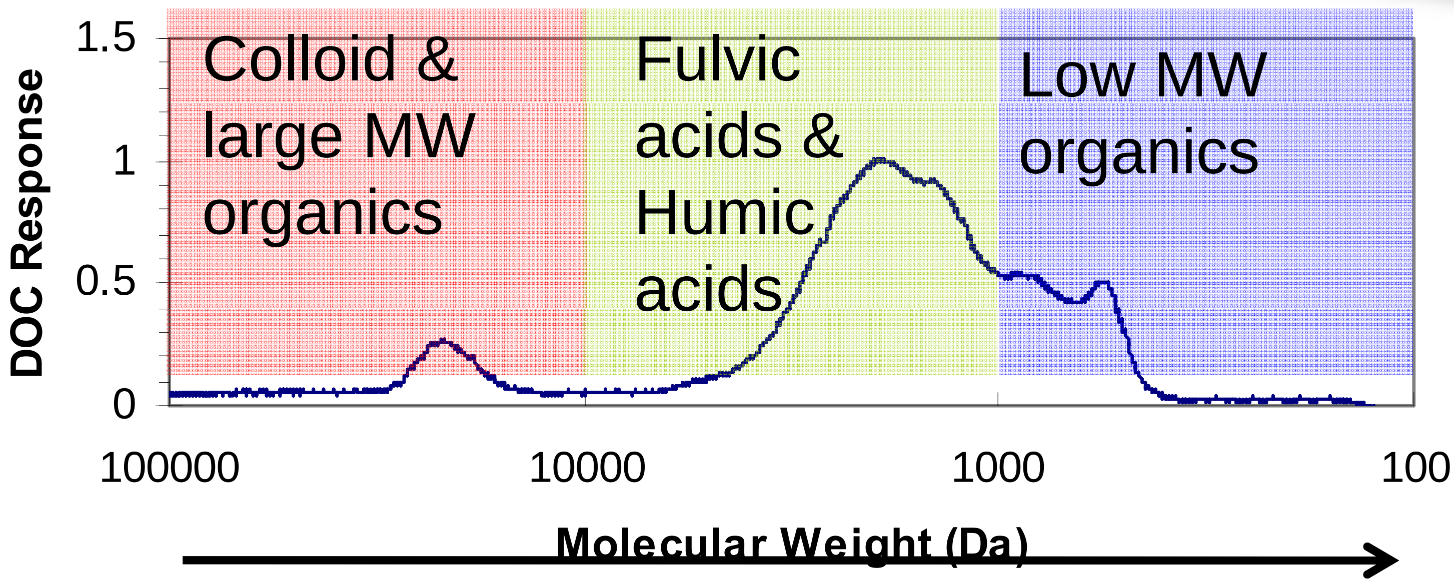
- *MIB: 25 ng/L (epi) & 2 ng/L (hypolimnion)

DOC Removal by WTP



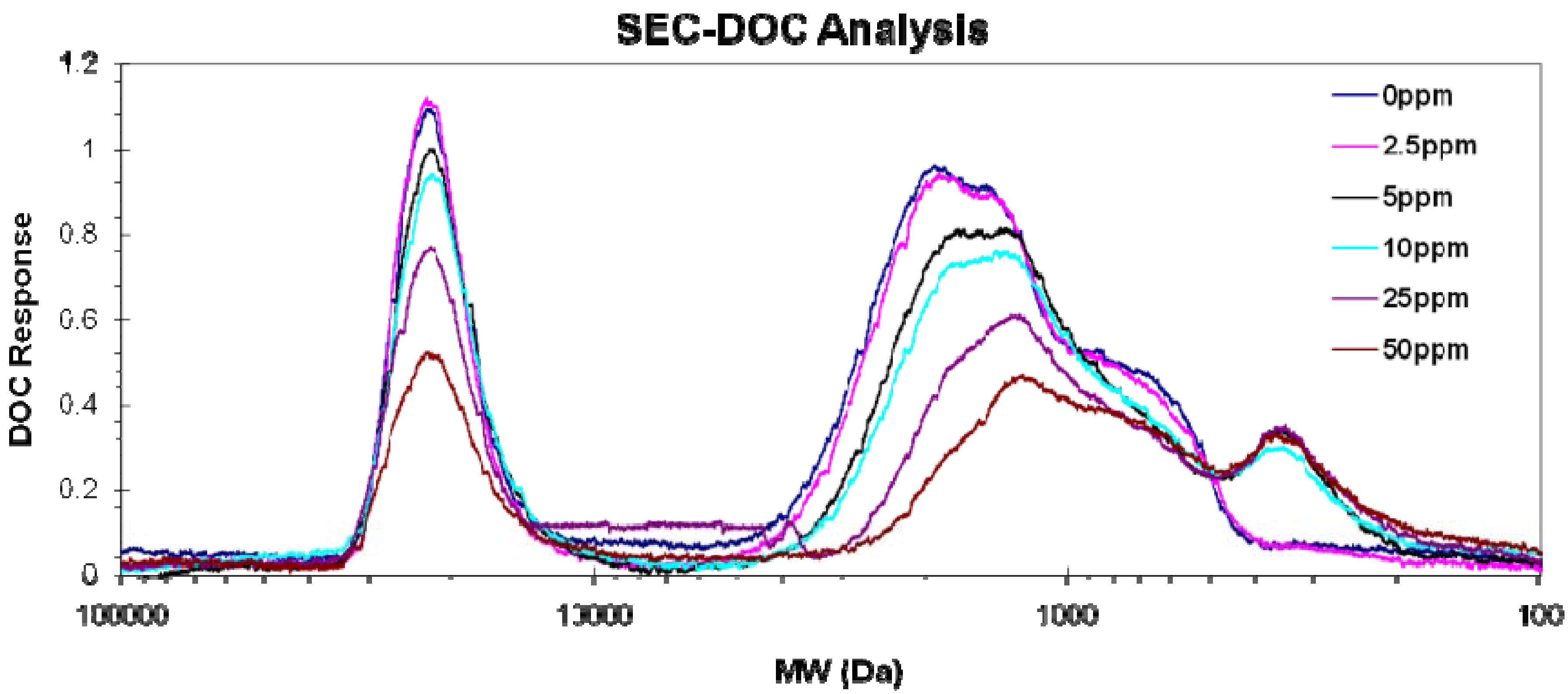
Removal of Size Fractions by Different Unit Processes



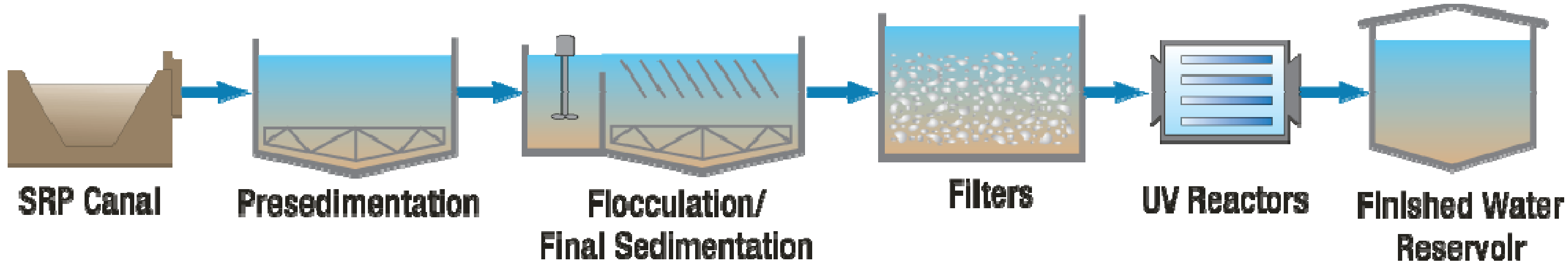


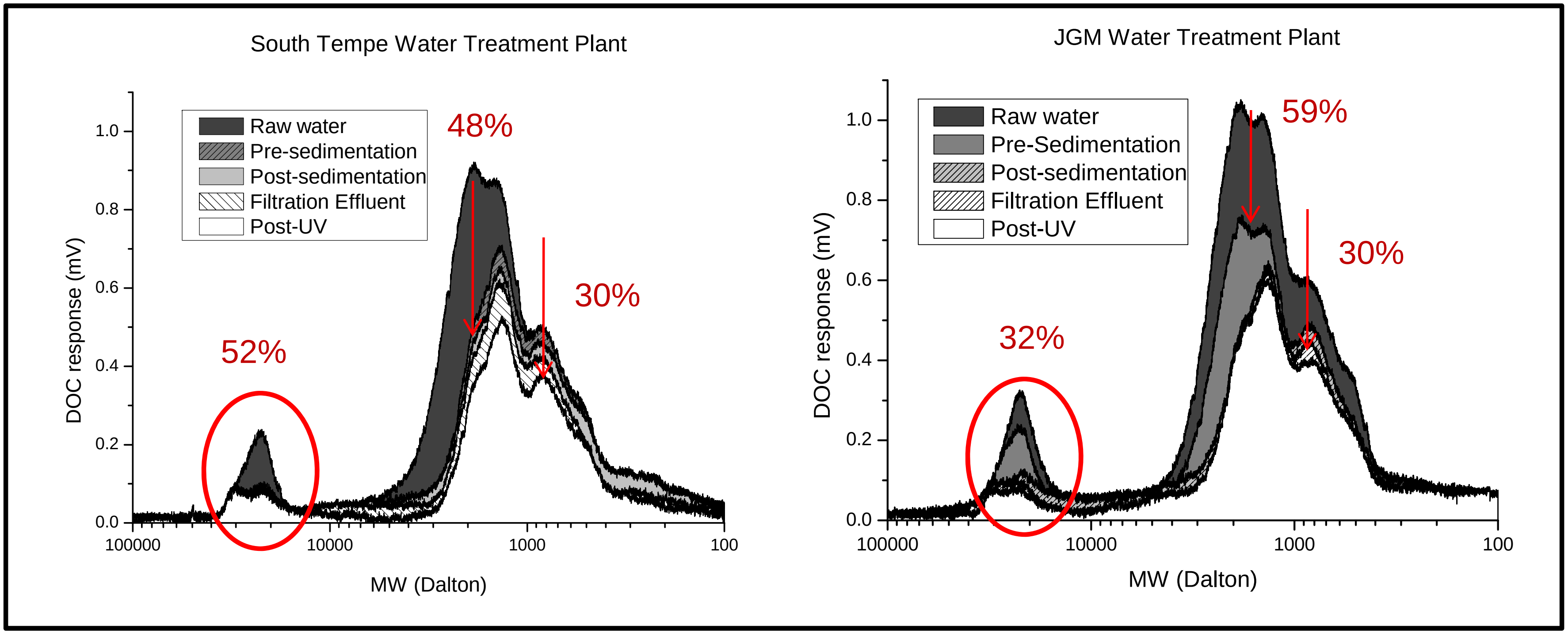
Time series of in-line DOC signal output

Coagulation Dose Impacts Organic Size Distribution

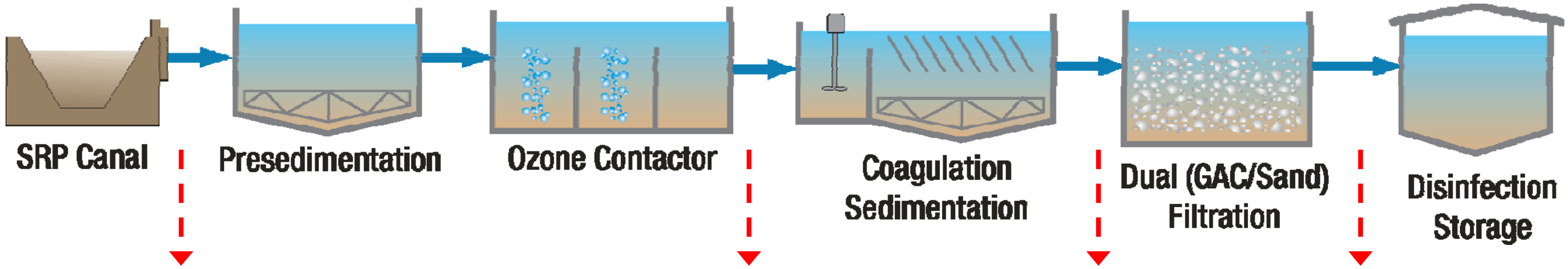


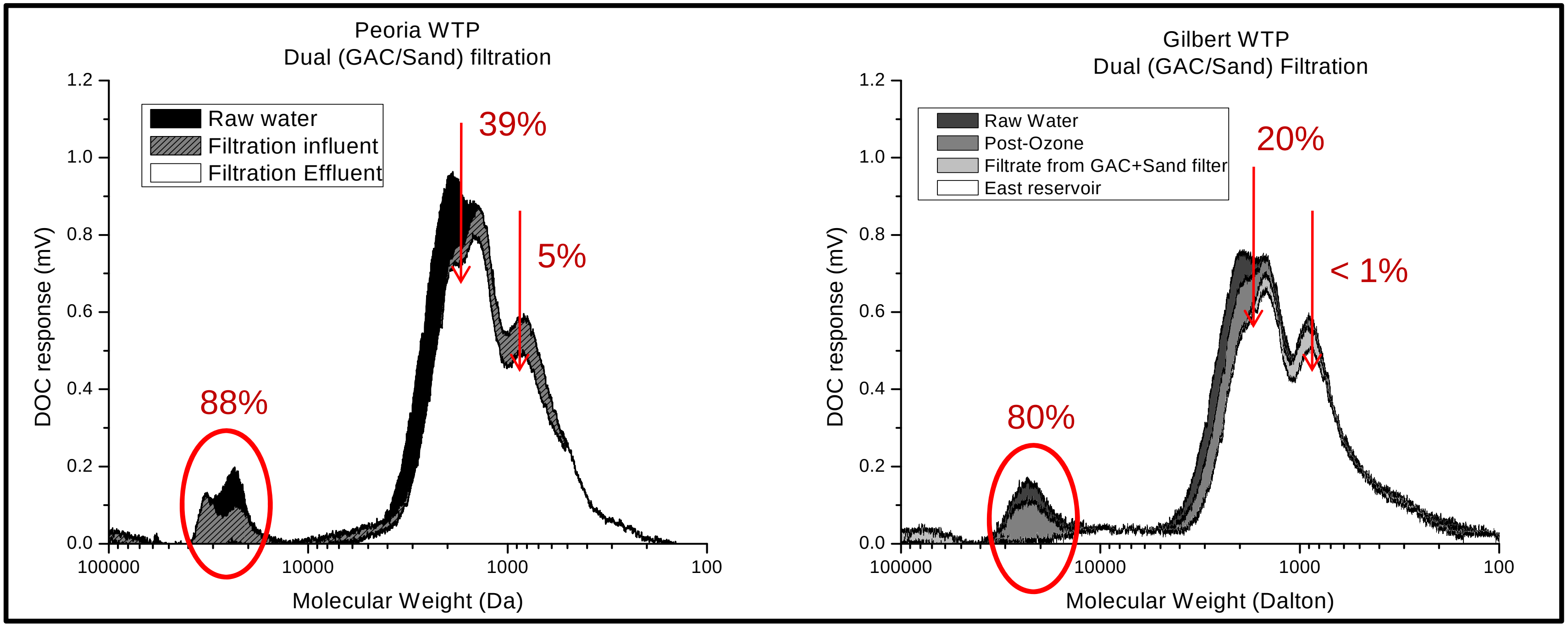
Tempe WTPs DOC Responses





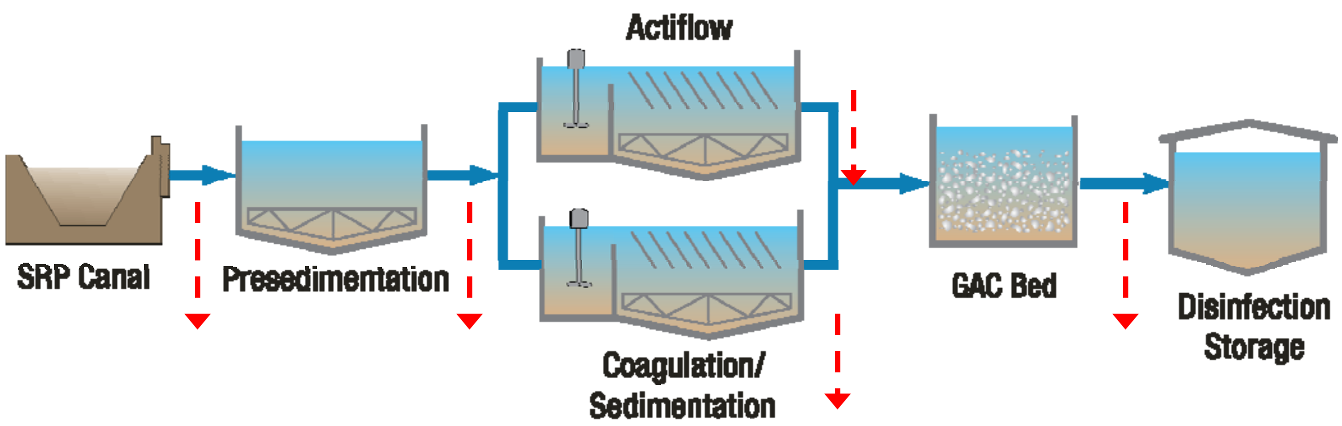
Peoria and Gilbert WTP

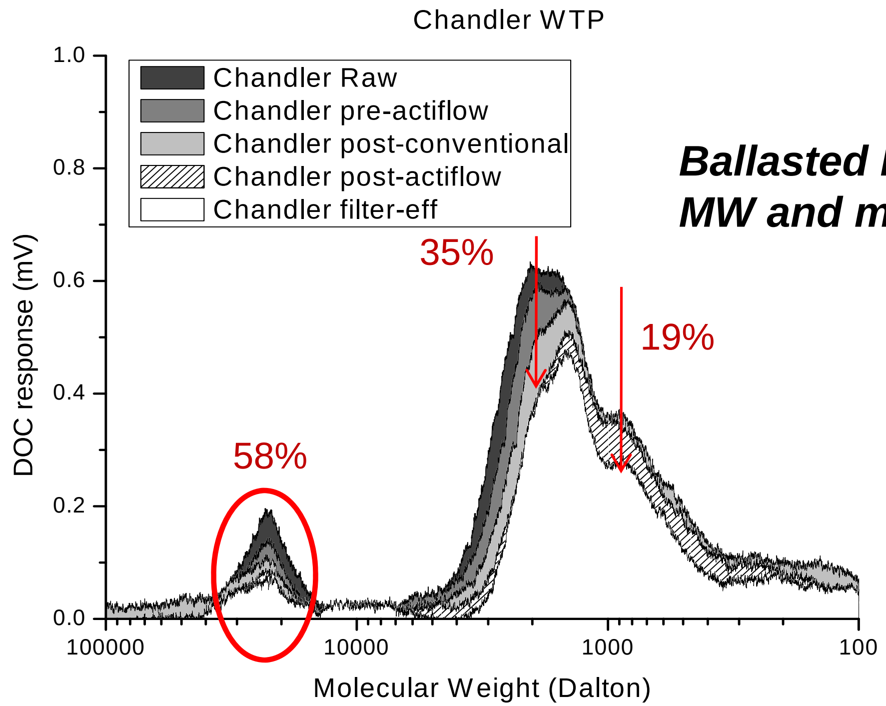




Ozonation helps breakdown of large MW OM but won't remove DOC significantly

Chandler Pecos SWTP Actiflo vs. Conventional Processes

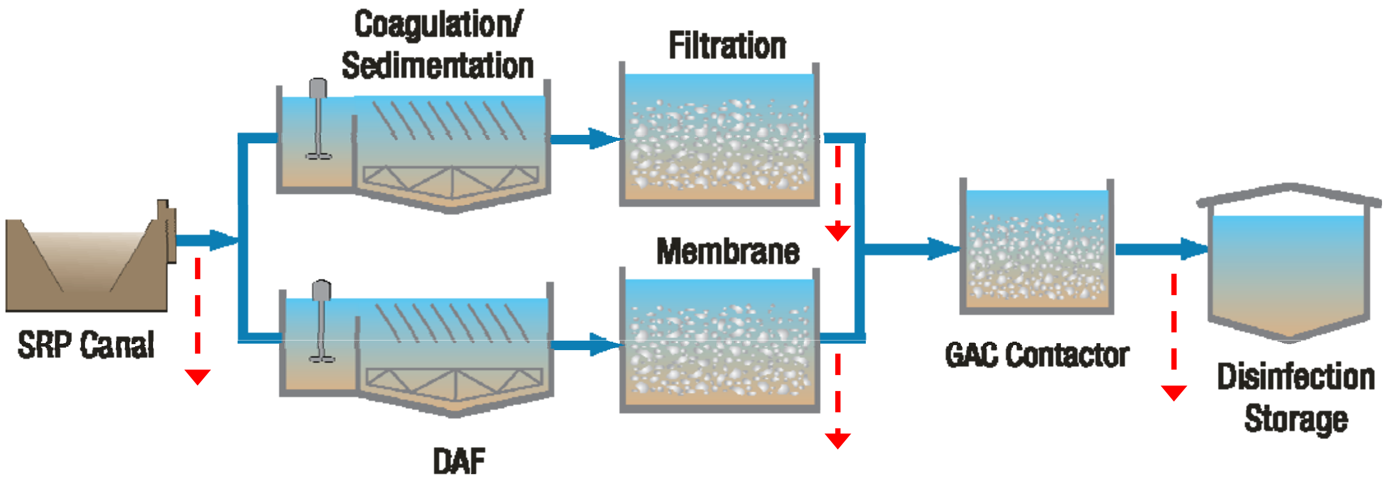


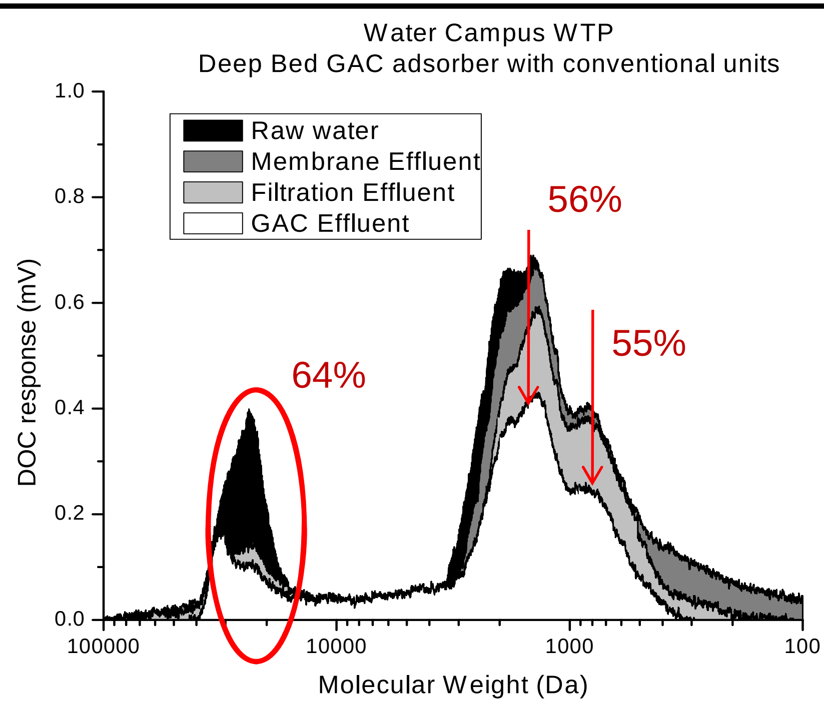


Ballasted Flocc helps in removing of large MW and medium MW organic matters.

Fractional Removal	Large MW	Medium MW
Ballasted Flocc	58%	40%
C/F/S	30%	30%

Membrane Filtration vs. Conventional Processes with GAC Contactors

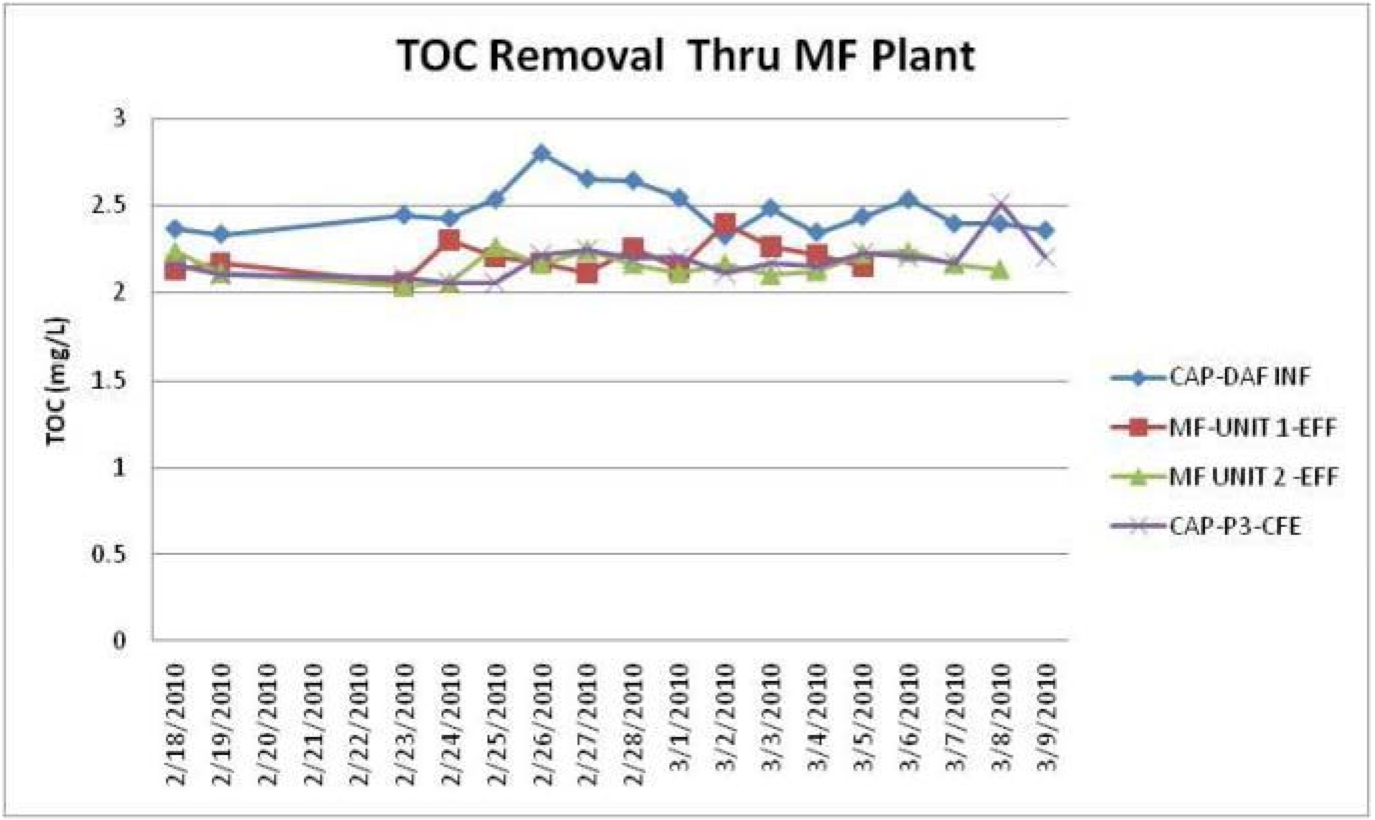




- ***Membrane filtration enhances the removal of large MW OM.***
- ***GAC removes medium and low MW OM further.***

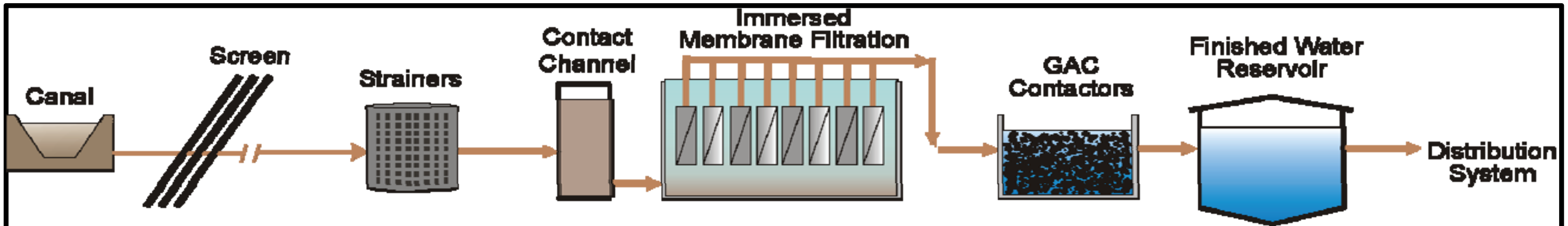
Fractional Removal	Large MW	Medium MW	Low MW
Membrane	51%	19%	< 1%
C/F/S	44%	35%	< 1%
GAC	-	56%	55%

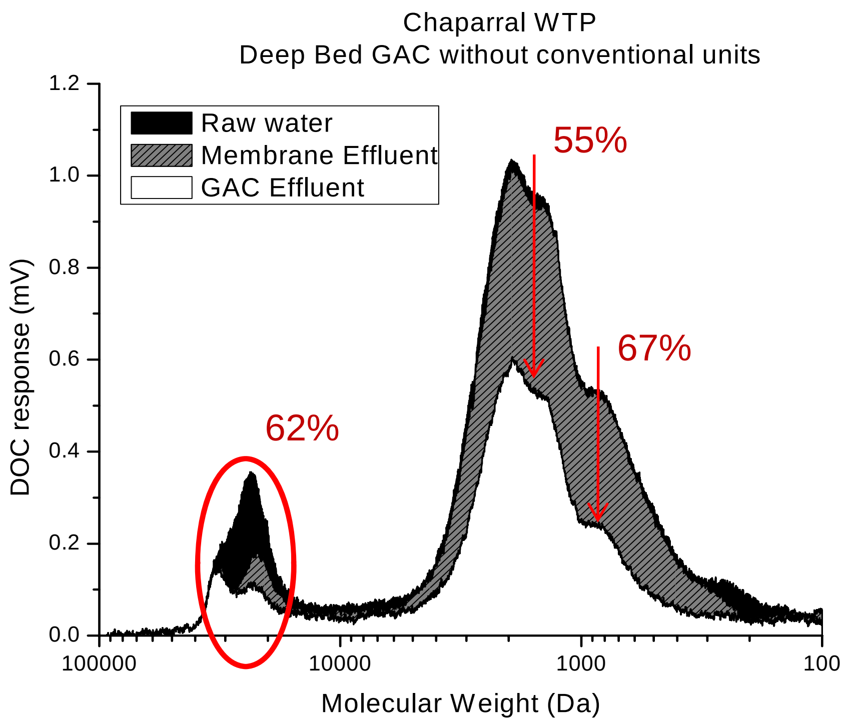
Membranes Remove Some TOC



Major benefit of membranes is multi-barrier approach for pathogen reduction

Membrane Filtration with GAC Contactors (Scottsdale)





- ***Membrane filtration enhances the removal of large MW OM but not medium and small MW OM.***
- ***GAC removes medium and low MW OM further.***

DOC Summary

- DOC levels in Lakes right now
  - Bartlett Lake (Verde River): 3.6 mg/L
  - Saguaro Lake (Salt River): 5.0 mg/L
  - Lake Pleasant (CAP): 3.4 mg/L
- Limited impact from Wallow Fire on DOC in Roosevelt Lake (yet)
- Winter rains is what transport most of the DOC into the reservoirs
- Each unit process removes different size fractions of organic matter

ASU

Last Years Workshop

- **Potential Influences of Climate Change on Arizona Water Supply (A. Ellis) conclusions:**
  - Region has warmed over the past century & projected to warm during remainder of 21st century – little uncertainty
  - Regional precipitation has changed little over the past century; recent drought of early 2000s evidenced in a trend back to long-term mean
  - Much uncertainty in projected precipitation during rest of the century – majority of GCM-GHG models => less precipitation
  - •Virtually all local-to-regional hydrologic projections (indicate less runoff (-10% to -20%), but with a large range of potential outcomes (+23% to –45%)

Water Supplies in light of climate changes

- We looked at information & comments from last years workshop on what it means for water quality during extreme events, potentially more wastewater influences during droughts and potentially greater reliance on groundwater

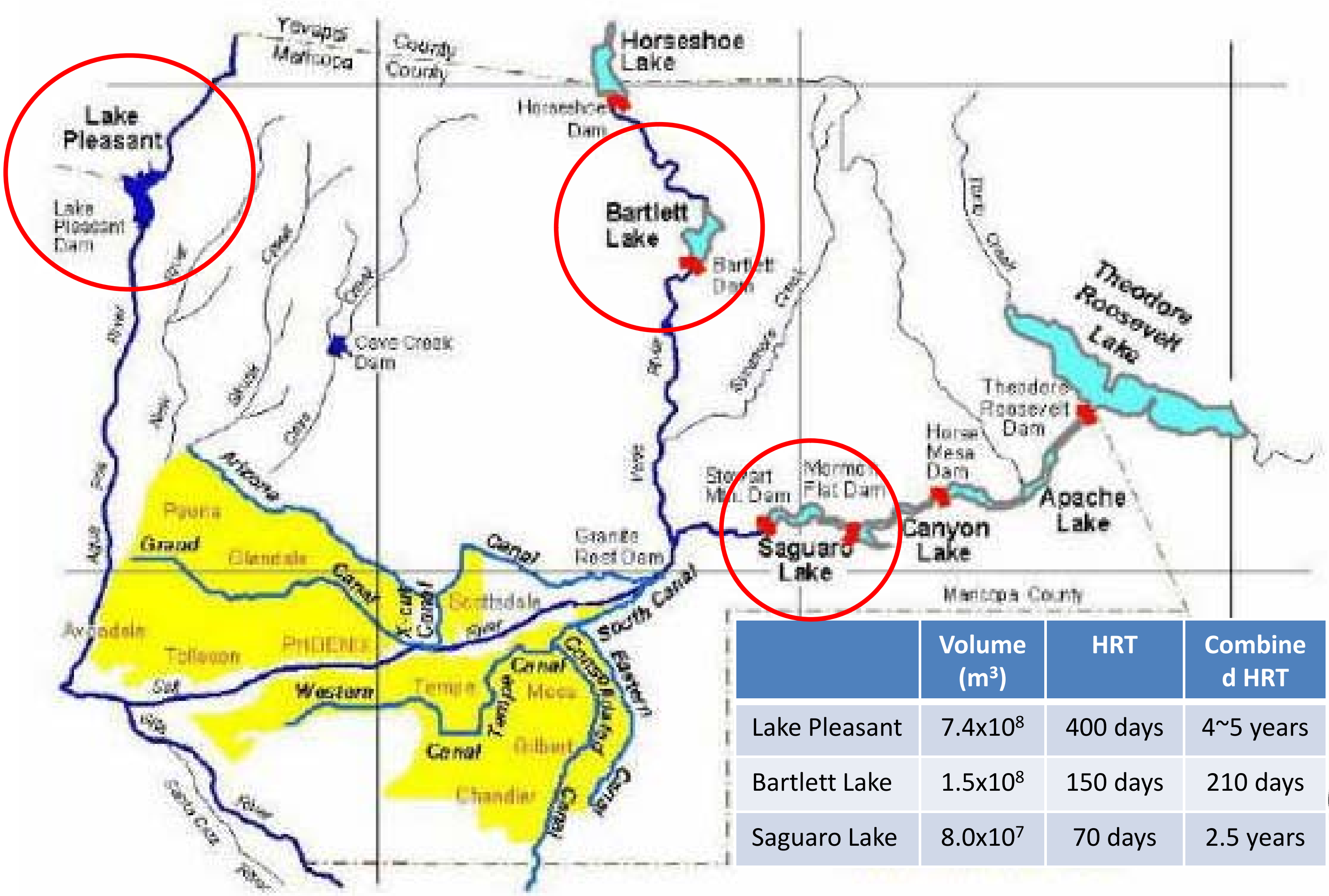
Water Quality Responses under Different Climate Situations

Chao-An Chiu
Paul Westerhoff
Arizona State University
School of Sustainable Engineering and The Built Environment
Civil, Environmental and Sustainable Engineering

Headlines

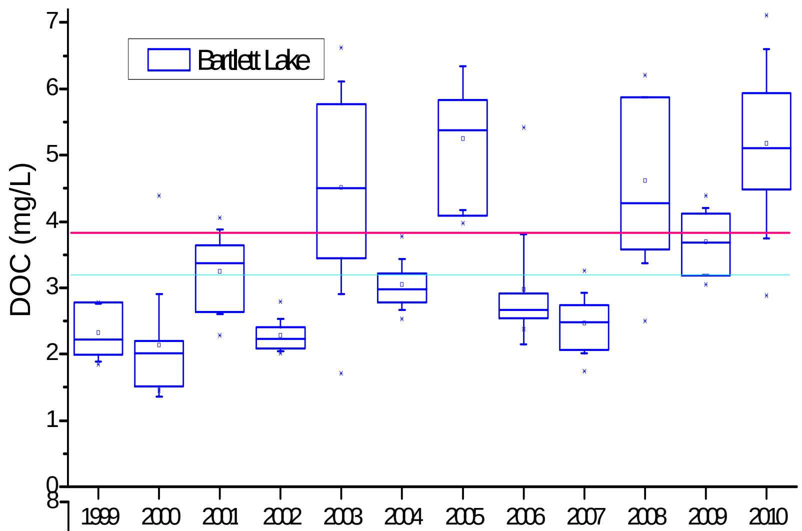
- Long-term (1999-2010) DOM trend in SRP and CAP reservoirs.
- Annual DOM and inflow profiles for three reservoirs.
- Spring flush and loading of DOC mass – example of Bartlett Lake (Verde River)
  - early storm
  - dry duration antecedent to first flush.
- In Case of extreme climate scenarios.

SRP and CAP Reservoir System

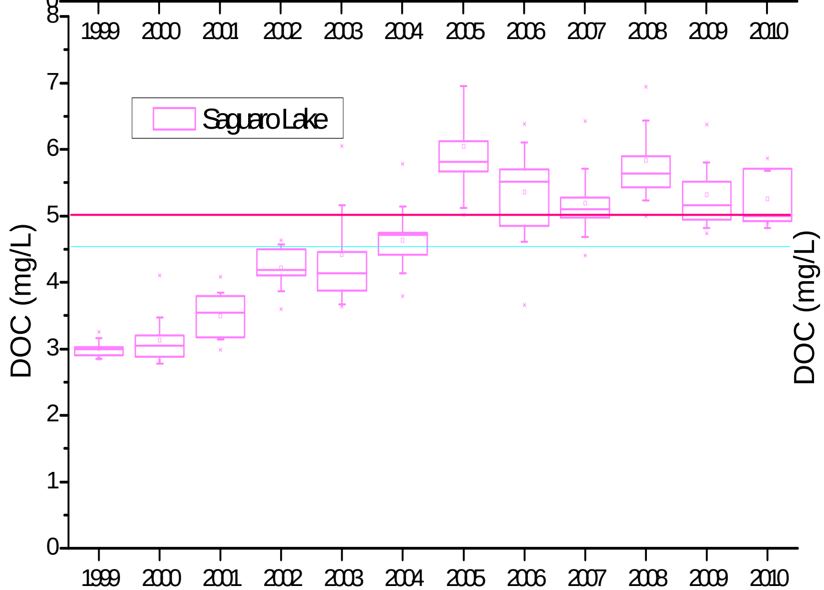


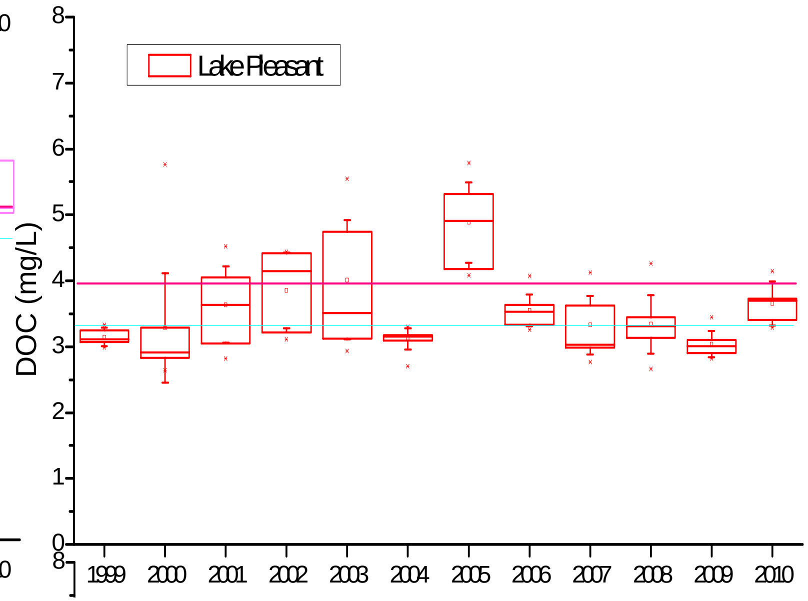
	Volume (m^3)	HRT	Combined HRT
Lake Pleasant	7.4×10^8	400 days	4~5 years
Bartlett Lake	1.5×10^8	150 days	210 days
Saguaro Lake	8.0×10^7	70 days	2.5 years

Long-Term DOC Trends



- Lake pleasant – Some variation
- Saguaro Lake – Low variation with increasing trend of DOC.
- Bartlett Lake – largest variation with increasing trend of DOC

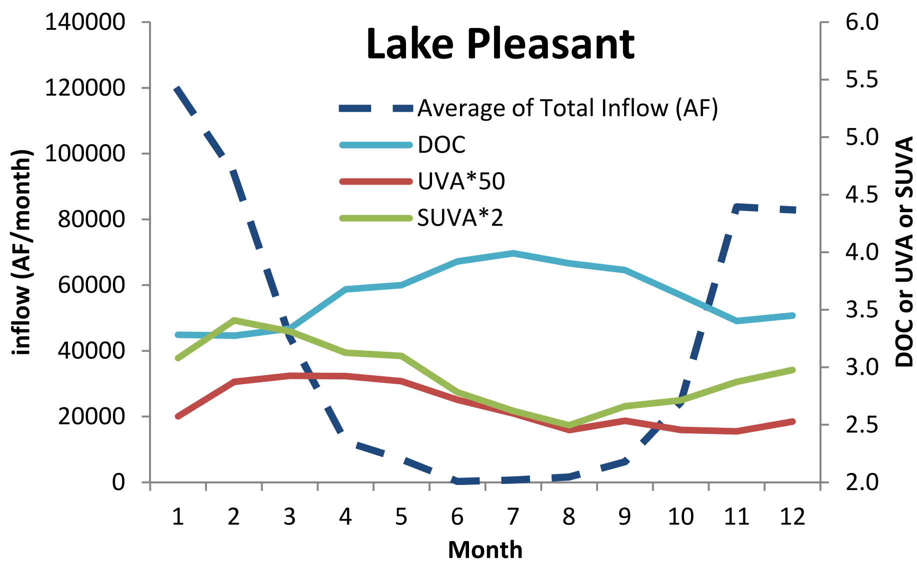




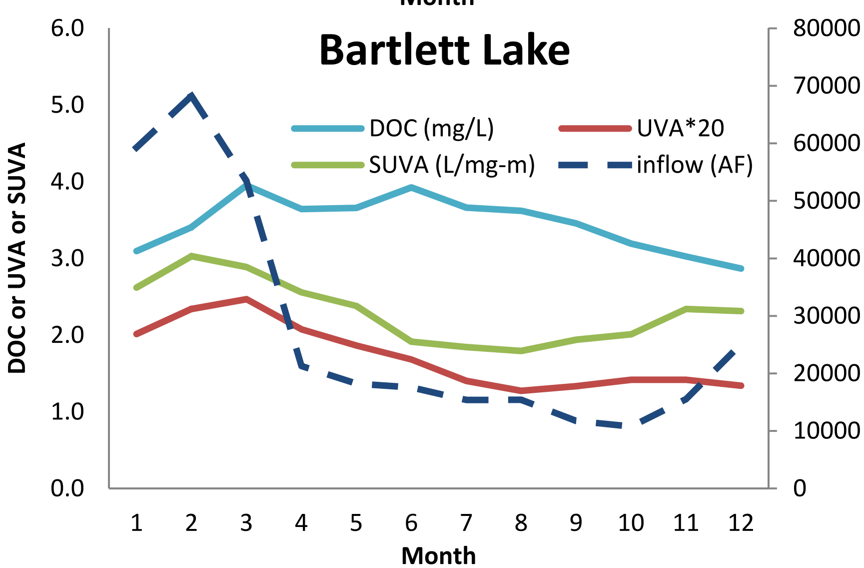
Annual DOM and inflow profiles

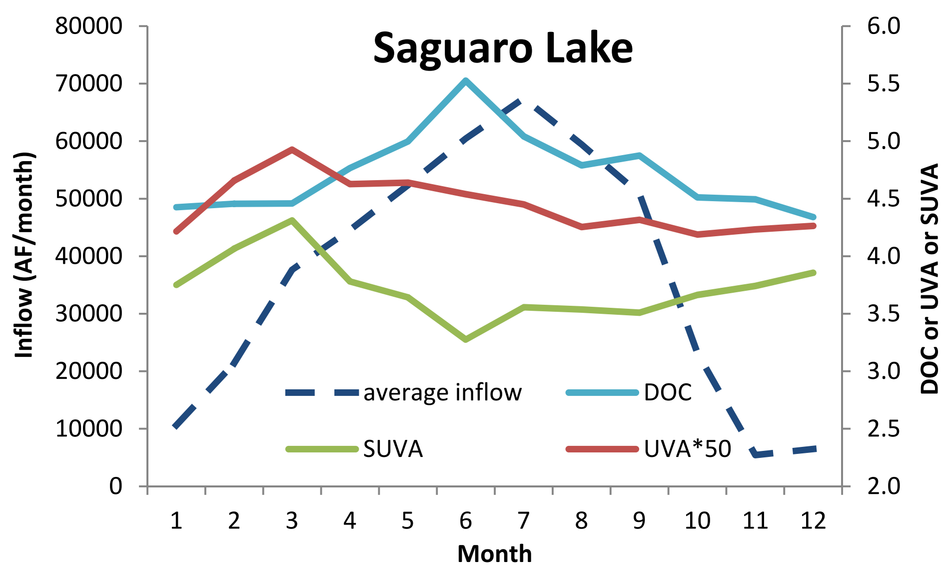
- Sources of inflow:
  - Snowmelt (early spring);
  - precipitation (storm or monsoon).
- Higher UV254 or SUVA value shows
  - Higher aromatic content;
  - Higher terrestrially-derived DOM;
  - Higher DBP formation potential.

Annual Average DOM conc. and Inflow



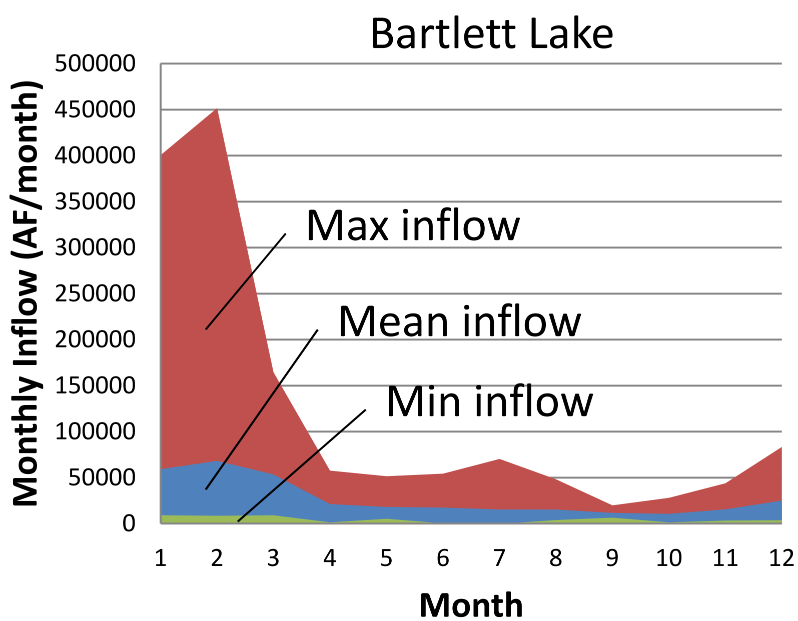
- DOC increased during summer due to in-lake bioactivities.
- Summer inflow might bring autochthonous DOM into Saguaro Lake from lake upstream.
- Early spring inflow brought in terrestrial materials.

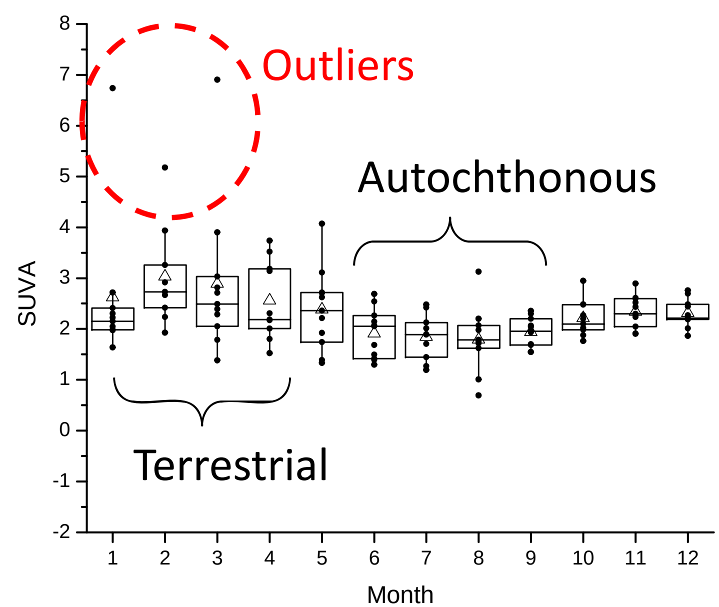




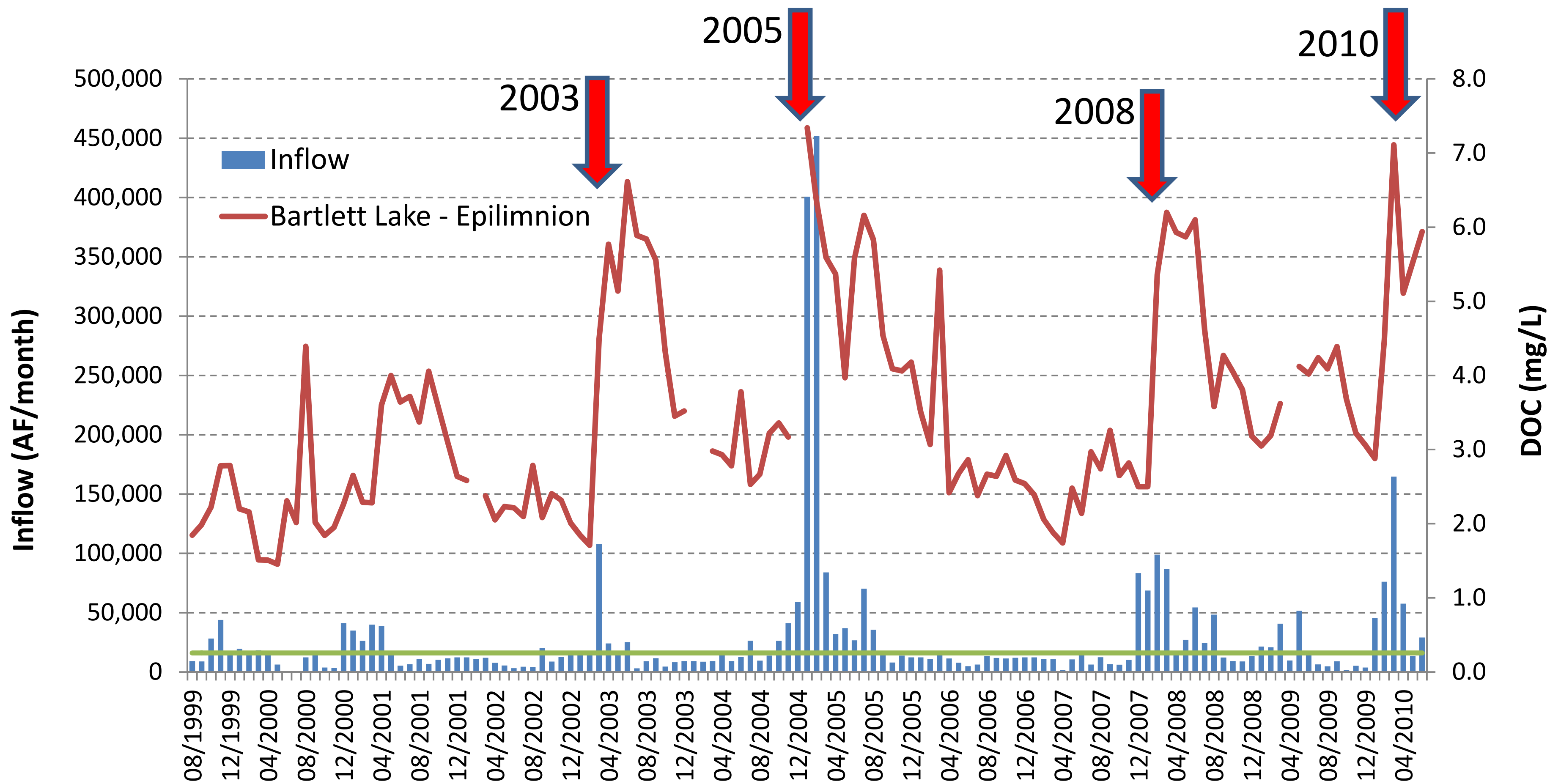
Higher Variation = Vulnerable ?

- Less variation of summer DOM content – autochthonous production.
- Higher variation of DOM content during early spring with some extremely high value (outliers).





Inflow vs. DOC concentration in Bartlett Lake over time

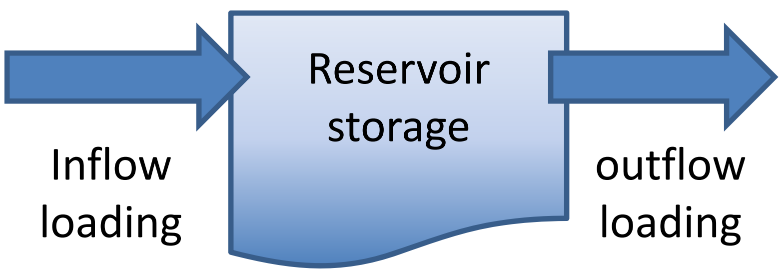


While we only interested in data during early spring …

How to calculate mass of DOC loading?

- Main assumption:
  - Autochthonous DOM is negligible
  - Biological reaction is negligible
  - Evaporation is negligible
  - Water is well mixed vertically

$$\text{Inflow loading of DOC mass (kg)} = (\text{Storage}_{final} - \text{Storage}_{initial}) + \text{outflow loading}$$



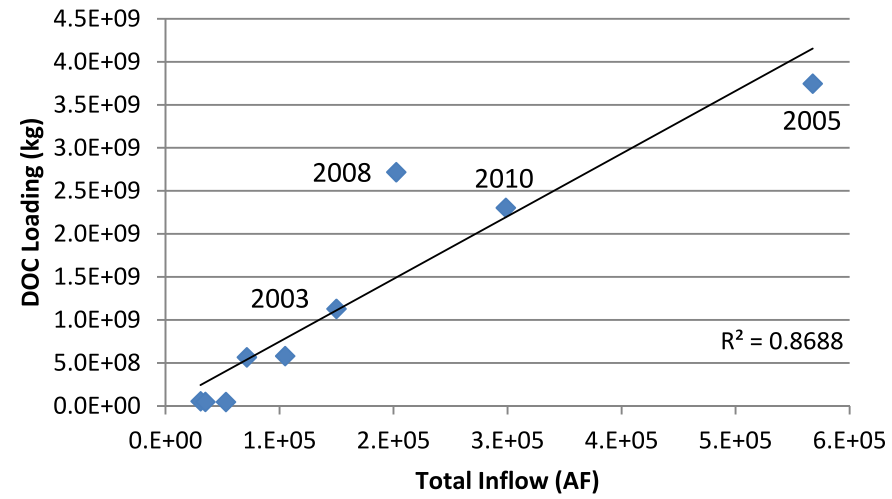
Define of Dry Duration (DD) Antecedent

- Criteria: Average of total inflow volume (Ave_{inflow}) except inflow volume > 50% of reservoir volume.
- If month total inflow < Ave_{inflow} then this month is identified as “Dry month”, opposite as “Wet month”.
- Total amount of “Dry month” between “Wet month” before February is defined as “Dry Duration (DD)” antecedent to February.
- This “DD” factor is used to adjust the inflow (Adj_{inflow}) by:

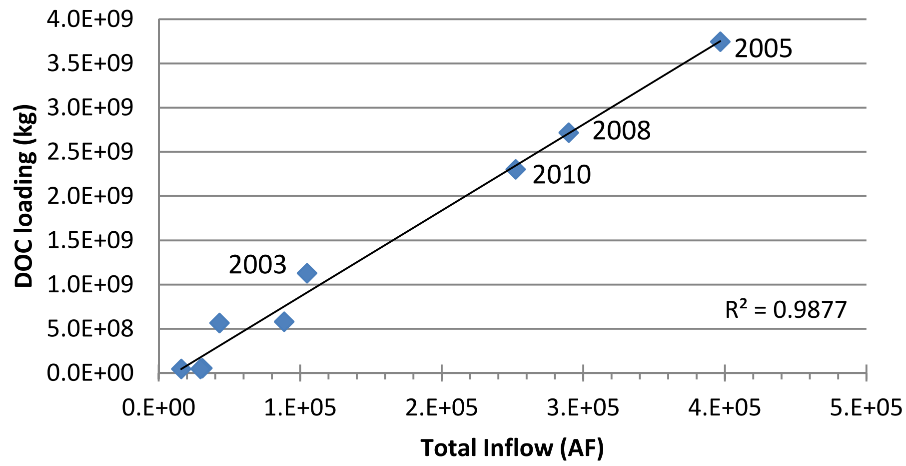
$$Adj_{\text{inflow}} = Inflow(AF) \times \log_{10}(DD)$$

Relationship between DOC mass loading and inflow in spring

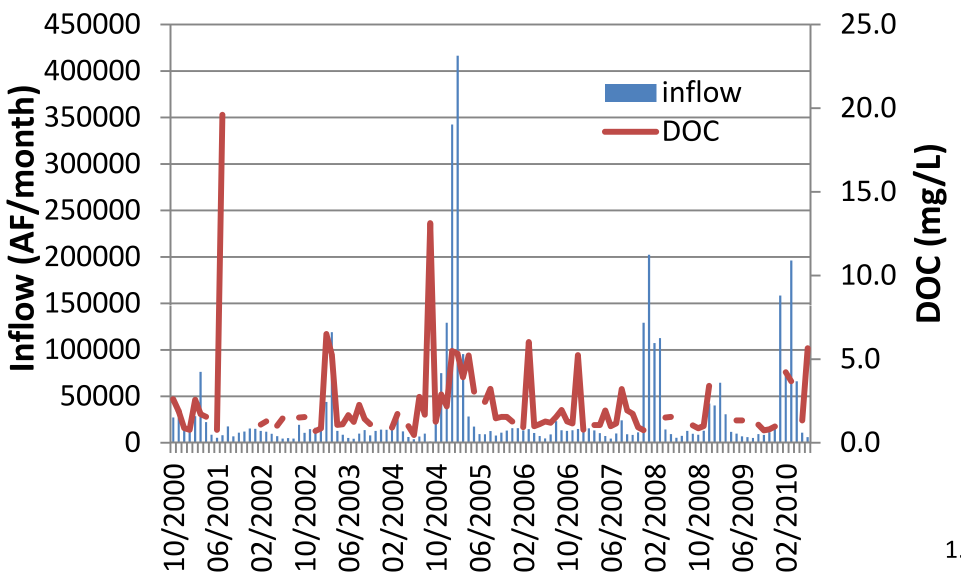
Year	Dry duration antecedent to Feburary (month)	Total inflow btw Feb to Apr (AF)	Inflow DOC loading from Feb to Apr (kg)
2000	2	52,967	47141853
2001	7	104,894	580783475
2002	10	30,798	55712055
2003	5	149,925	1129276819
2004	7	34,959	48202614
2005	5	567,593	3746193620
2006	6	36,608	-23670489
2007	18	23,317	-494959
2008	27	202,355	2717621946
2009	4	71,326	566331116
2010	7	298,422	2303591268

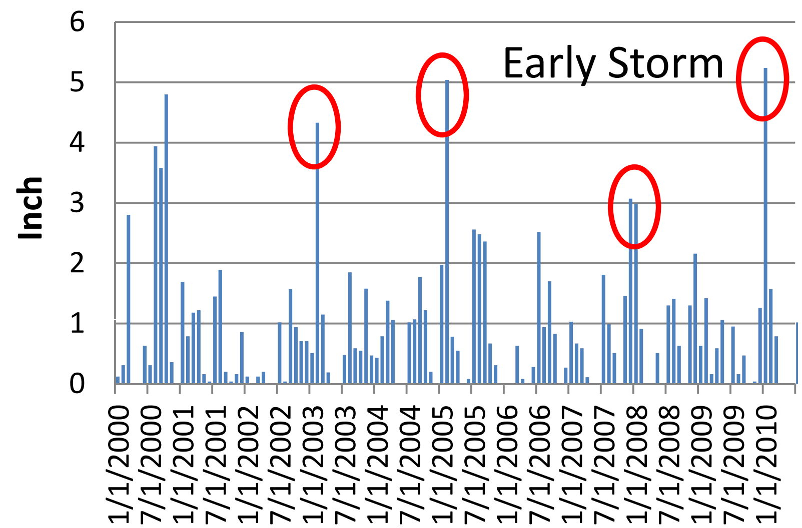


Adjusted by factor of dry duration

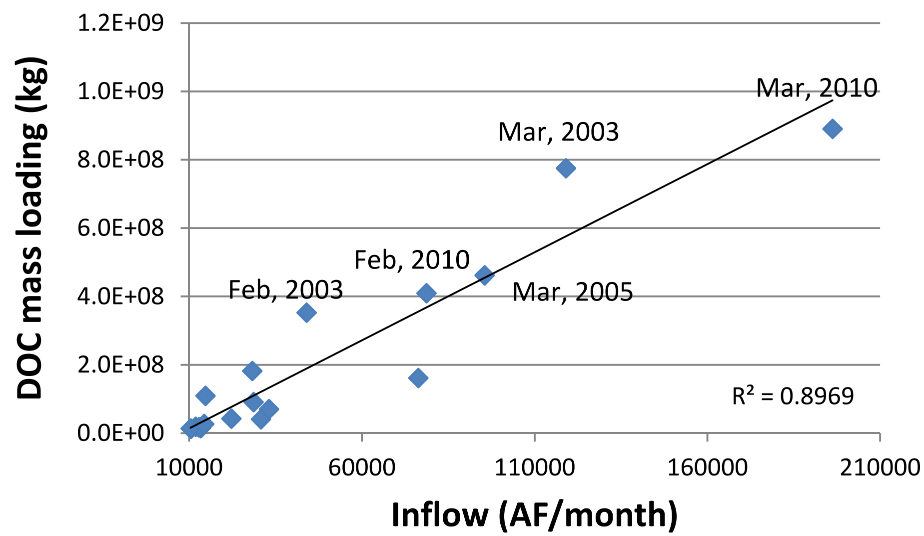


From another view of inflow and DOC mass loading – Verde River at Tangle creek





- Loading of DOC mass strongly correlated with inflow volume in early spring.
- Early storm occurred could increase DOC mass loading.
- Lack of 2008 DOC data.

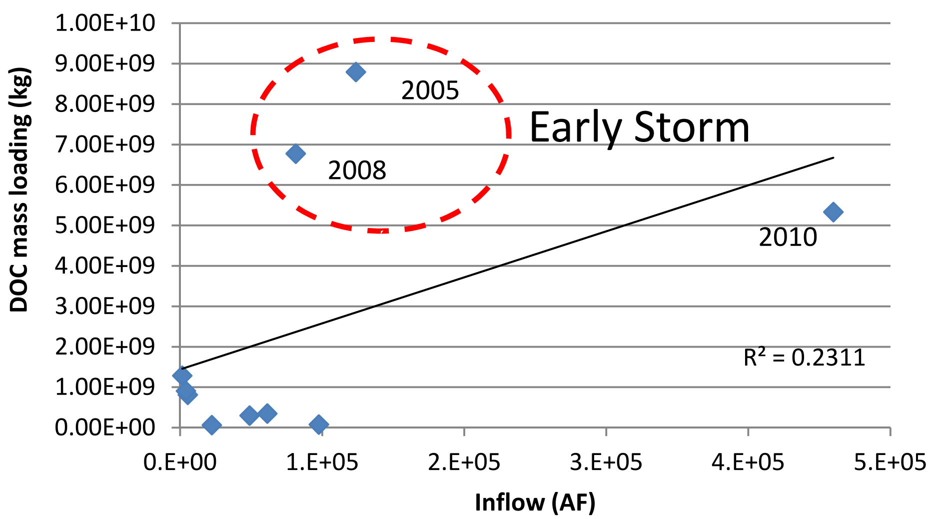


What did we observed in Bartlett Lake of Verde River system

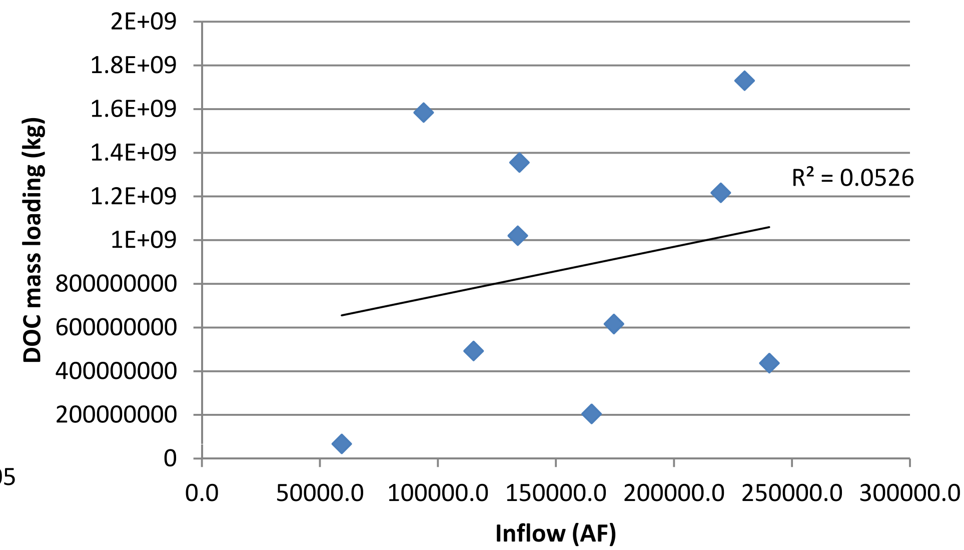
- Loading of DOC mass into Bartlett Lake is strongly correlated to inflow volume during early spring (Feb to Apr).
- Early storm of 2003, 2005, 2008, and 2010 brought more DOC mass into Bartlett Lake than other years.
- Long term of dry duration might result in loss of DOC mass from reservoir.
- In 2008, Spring flush after long dry duration brought more DOC mass into Bartlett Lake even though the total inflow was not as high as 2010.

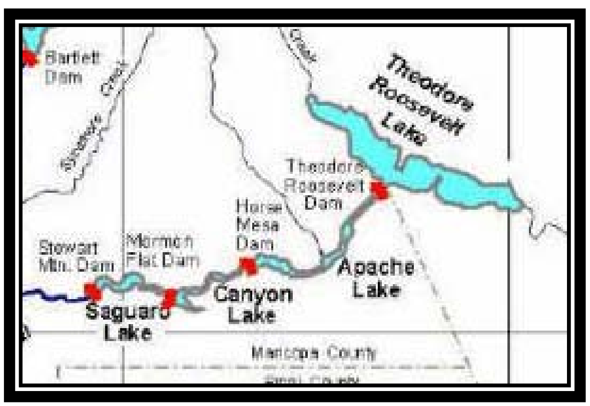
How about Saguaro Lake and Lake pleasant

Saguaro Lake

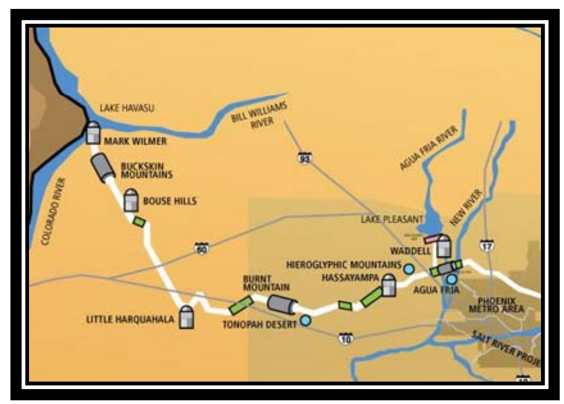


Lake Pleasant

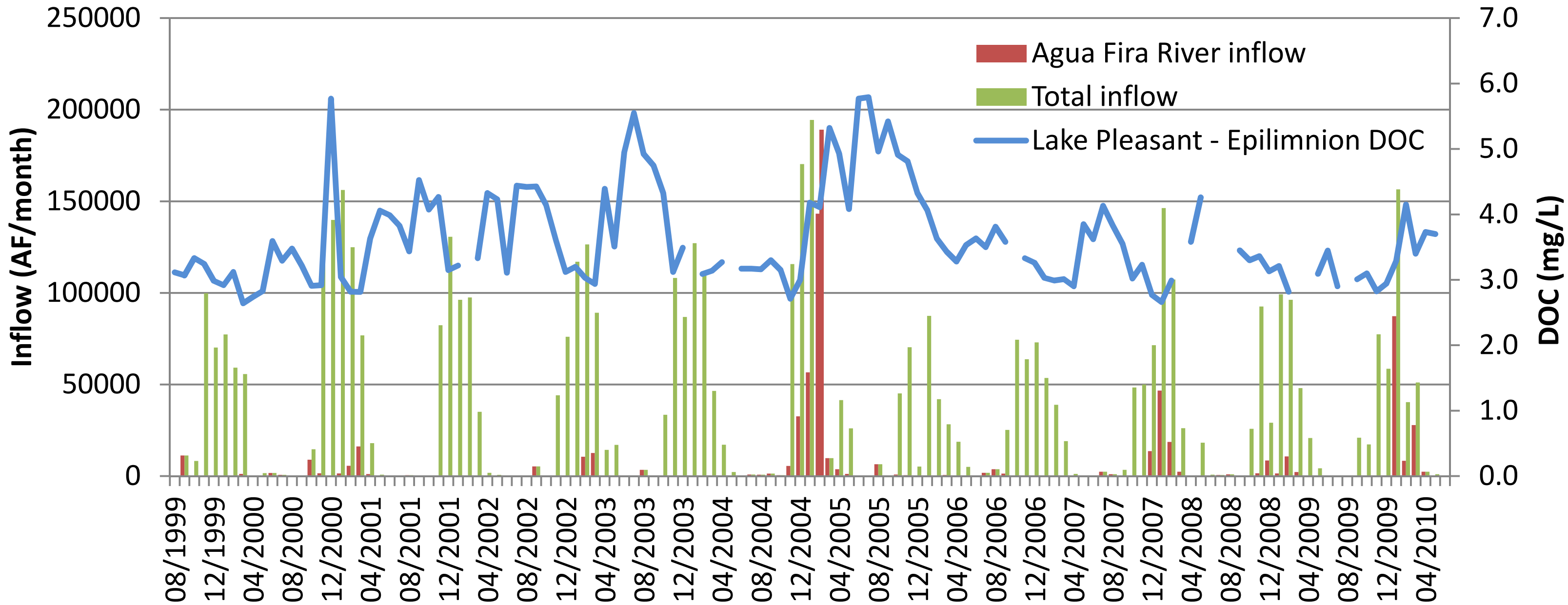


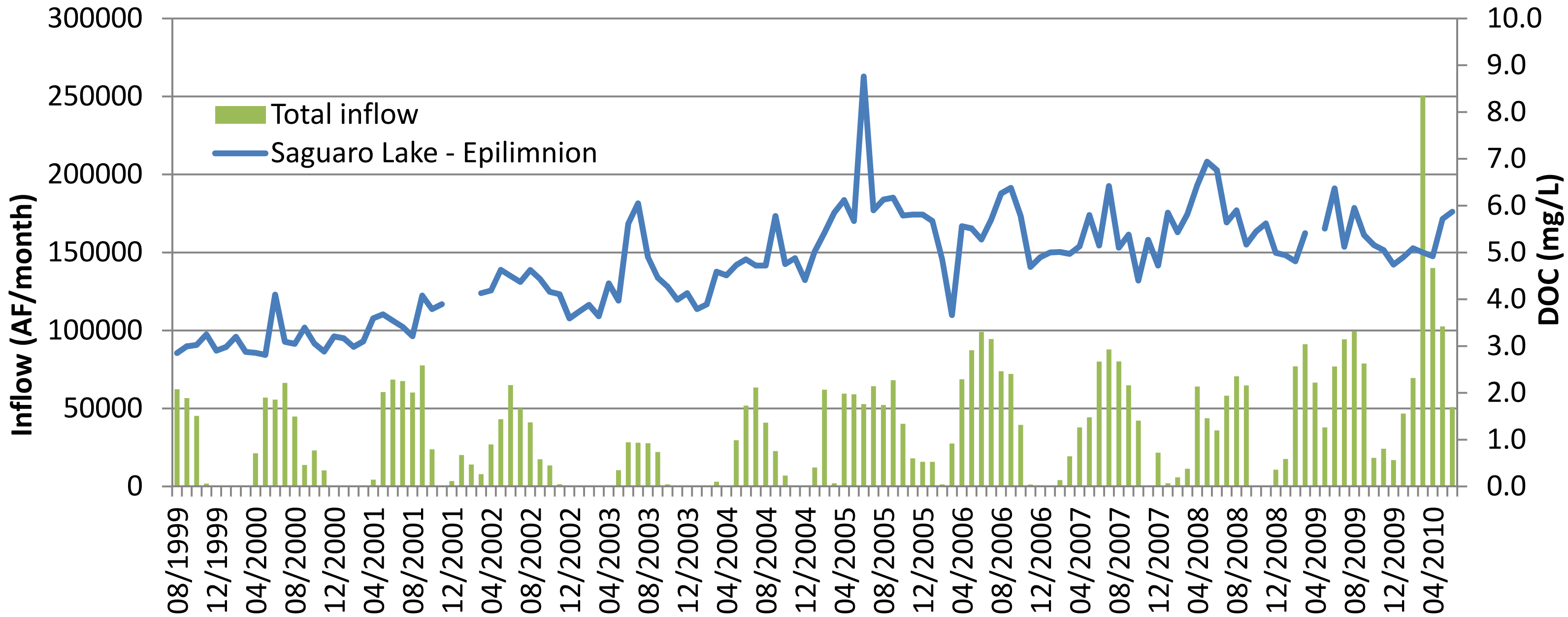


Salt River Lake system



Lake Pleasant (off-stream)





Inflow of these two lakes were regulated and relatively constant.

Take home messages

- DOC loading early of the year was associated to spring flush and impacted by early storm significantly.
- Multi-lake system (Salt River) – less impact by spring flush and early storm; in-lake autochthonous production is major concern (longer HRT).
- Single-lake system (Verde River) – vulnerable to spring flush and early storm.
- Dry duration antecedent to spring flush could increase the terrestrial DOM loading, especially in extreme case.

In Case of extreme climate scenarios




- Wildfire events
- 2005 phoenix water boil (early storm)
- Drought duration antecedent to first flush
- Long HRT vs. short HRT reservoir system.
- Expected impact:
  - Muddy water
  - High in DOC and UVA material
  - High chlorine demand
  - High in DBPs formed in drinking water
- The rain after a long drought!!

How Much Wastewater is in Our Drinking Water?

Presented By: Jacelyn Rice

NSF Award # 0855802

http://www.worldchanging.com/archives/008372.html

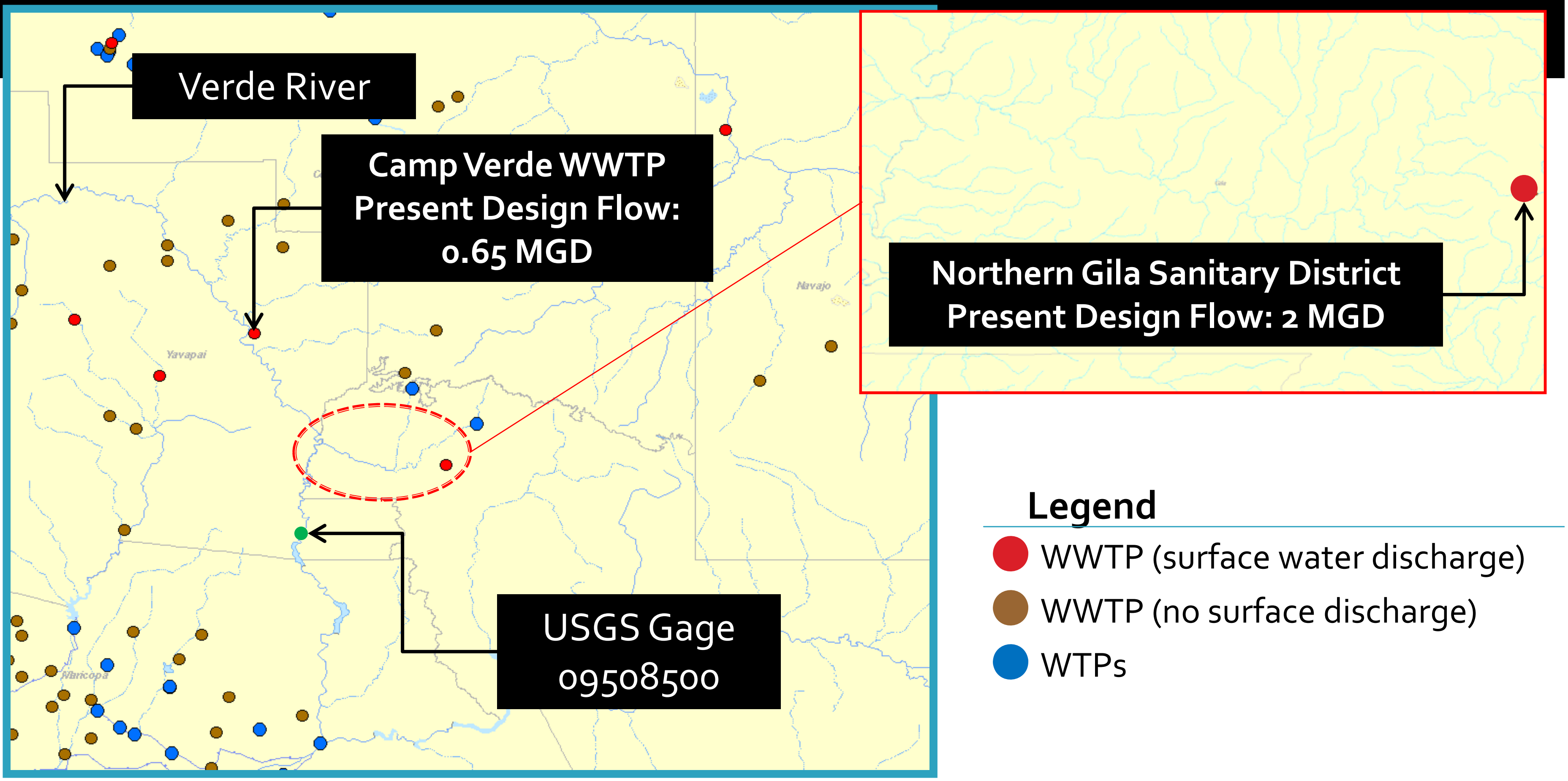
Why?

- Contaminants of Emerging Concern
- Possible tool for analysis/studies on WW impacts
- Implications on public perception
- Potential source of DBP Precursors

Salt and Verde River Watersheds

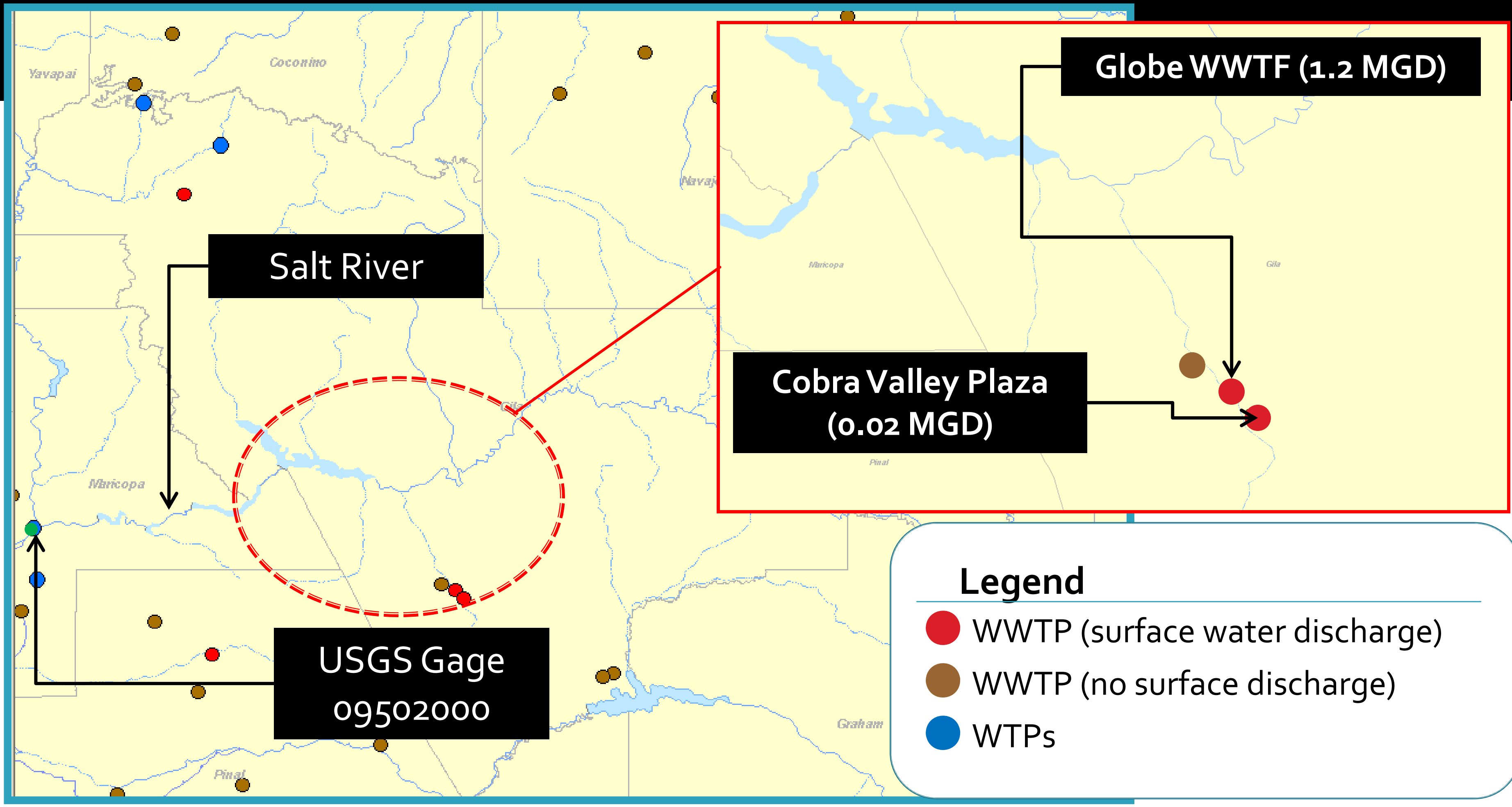
http://upload.wikimedia.org/wikipedia/commons/5/5a/Salt_River_Map.jpg

Verde River



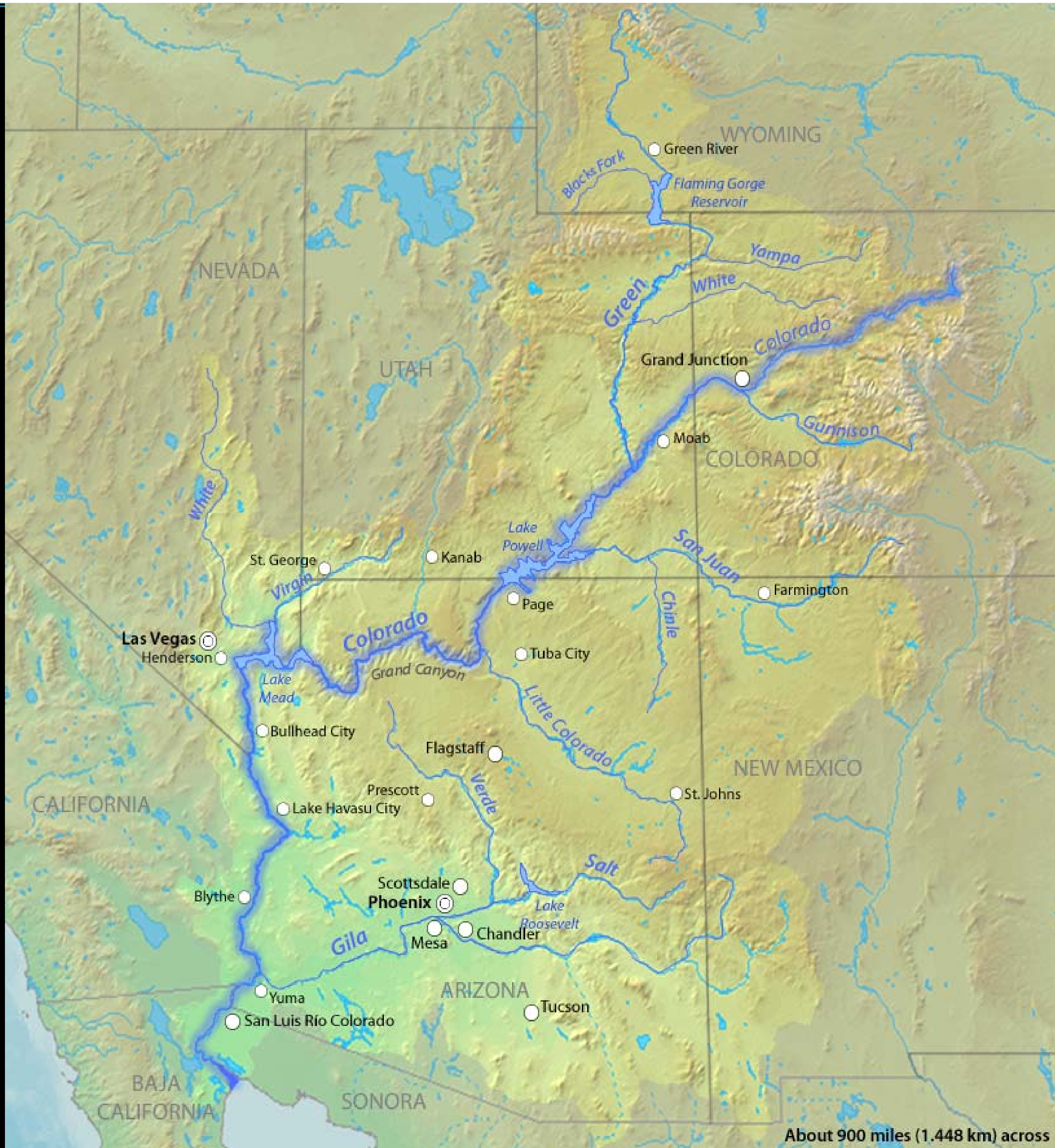
Discharge Statistic	Flow(CFS)	% WW
25th percentile	129	3.2%
Mean	220	1.9%

Salt River



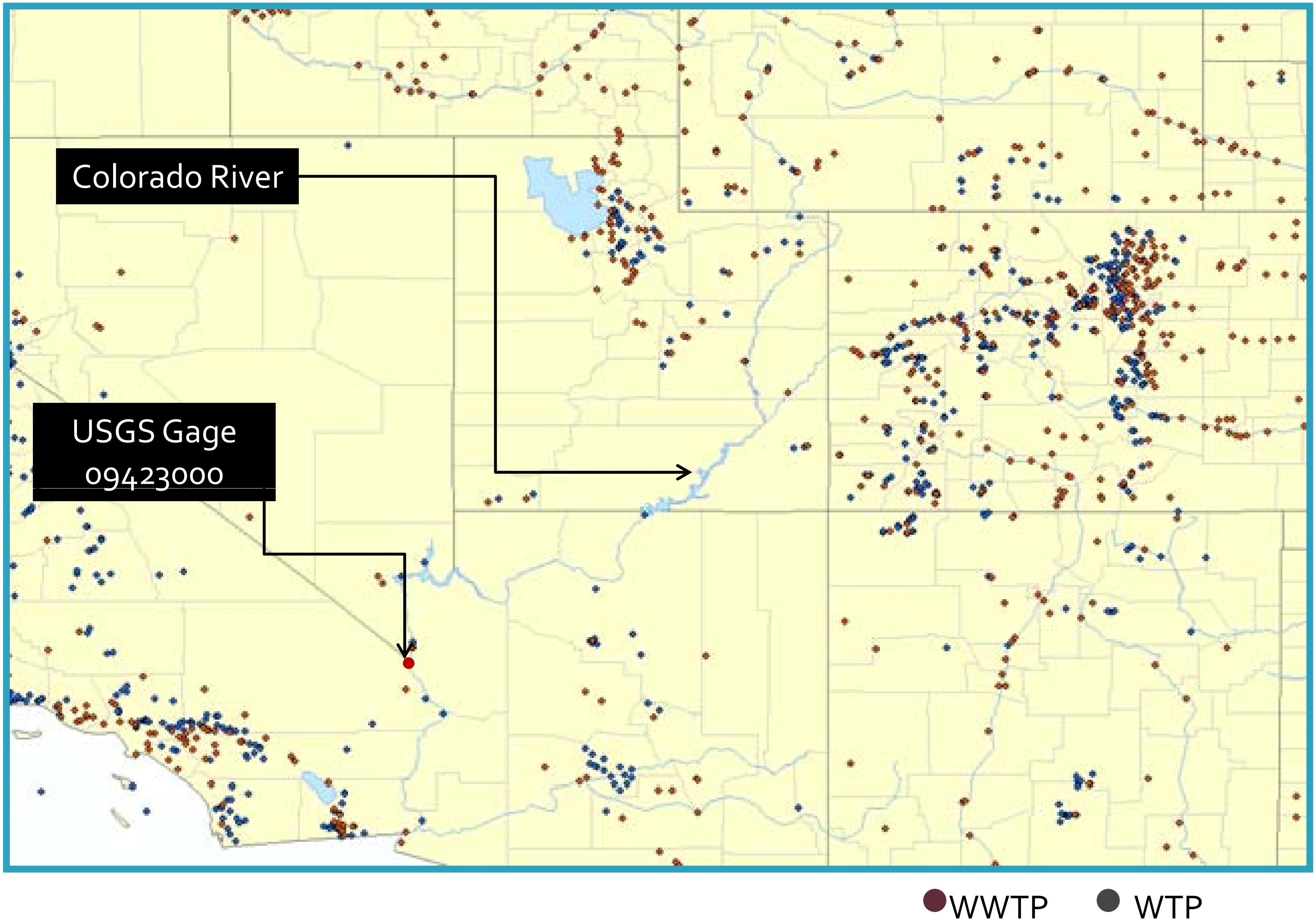
Discharge Statistic	Flow (CFS)	% WW
25th percentile	573	0.3%
Mean	923	0.2%

Colorado River



http://upload.wikimedia.org/wikipedia/commons/9/9d/Coloradorivermapnew.jpg

Colorado River (GIS)



Colorado River WWTPs Breakdown

State	#WWTPs in Drainage	2004 Q_{Design} (MGD)
Wyoming	13	6.27
Colorado	79	69.71
Utah	12	29.40
Arizona	2	2.74
New Mexico	3	7.40
Nevada	4	151.75
TOTAL	113	267.27

**2010 Census Data for Las Vegas Metro Area: 1.95 Million People
Current Flows are possibly closer to 195 MGD (assuming 100 gpcd)**

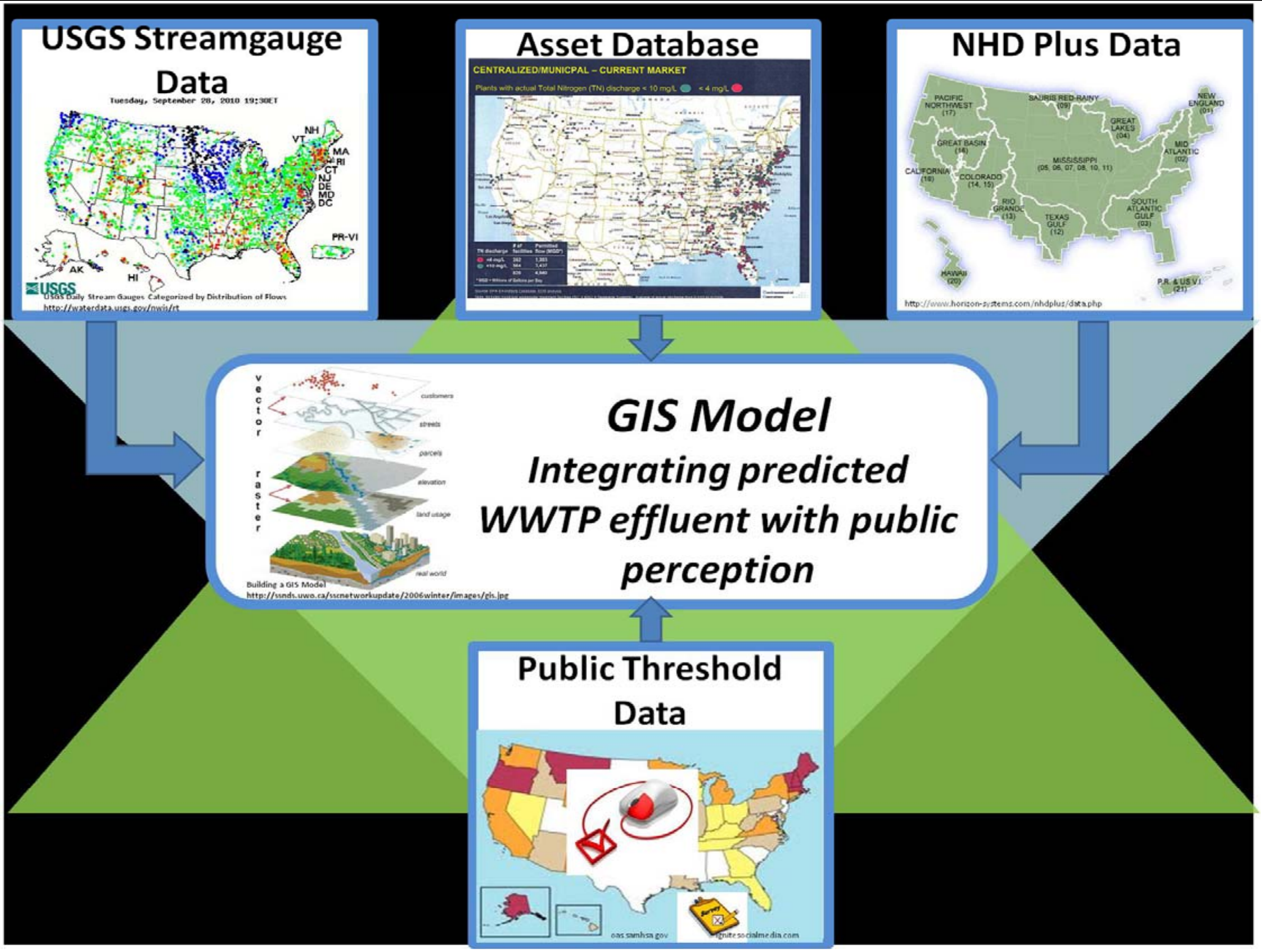
Colorado River WW%

Discharge Statistic	Daily Discharge (CFS)	Worst Case (all upstream)	Only Las Vegas
Max (1983)	39600	1.0%	0.5%
75th Percentile	14200	2.7%	1.5%
Mean	13000	3.0%	1.6%
25th Percentile	10600	3.7%	2.0%
Min (1905)	4520	8.6%	4.6%

So…. Is this Important?

- Is treated WW effluent in our drinking water Bad?
- Does this change ones perception of the water quality or safety?
- What is your social perception? Did this presentation change your perception?

Developing a National View



Wastewater Tracers

- What makes a good environmental tracer?
  - Constituent should be present whenever the pollutant is present
  - Compound should not accumulate on its own
  - Concentration of compound should be directly related to degree of pollutant
- Tracers
  - Caffeine
  - Sucralose

Sucralose Occurrence across Valley

(Concentration: ppt)	Sucralose	Caffeine
	Mean, detected	Mean, detected
Salt Rvier at Blue Point Bridge	5	19
Verde River at Beeline Highway	13	14
CAP Canal at Waddle Canal	180	17
WTP-Influent (example of 1)	15	14
WTP-Sedimentation (example of 1)	8	13
WTP-Effluent (example of 1)	11	11
WWTP-Raw (example of 1)	5,400	51,000
WWTP-Effluent (Activated Sludge)	2,800	47
GRUSP Measure Well #1	3	8
GRUSP Measure Well #2	3	5
GRUSP Measure Well #3	92	6

Photocatalysis: A new treatment option for nitrate mitigation

Kyle Doudrick

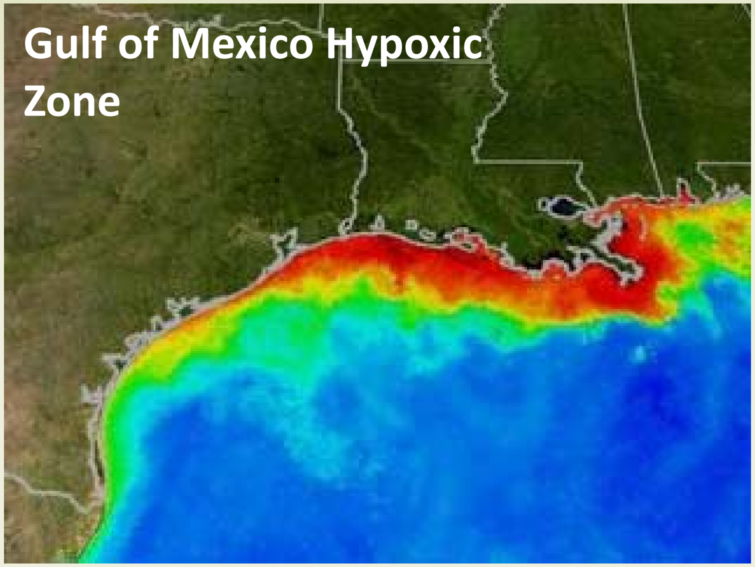
Ting Yang & Paul Westerhoff

Kiril Hristovski (ASU-Poly)

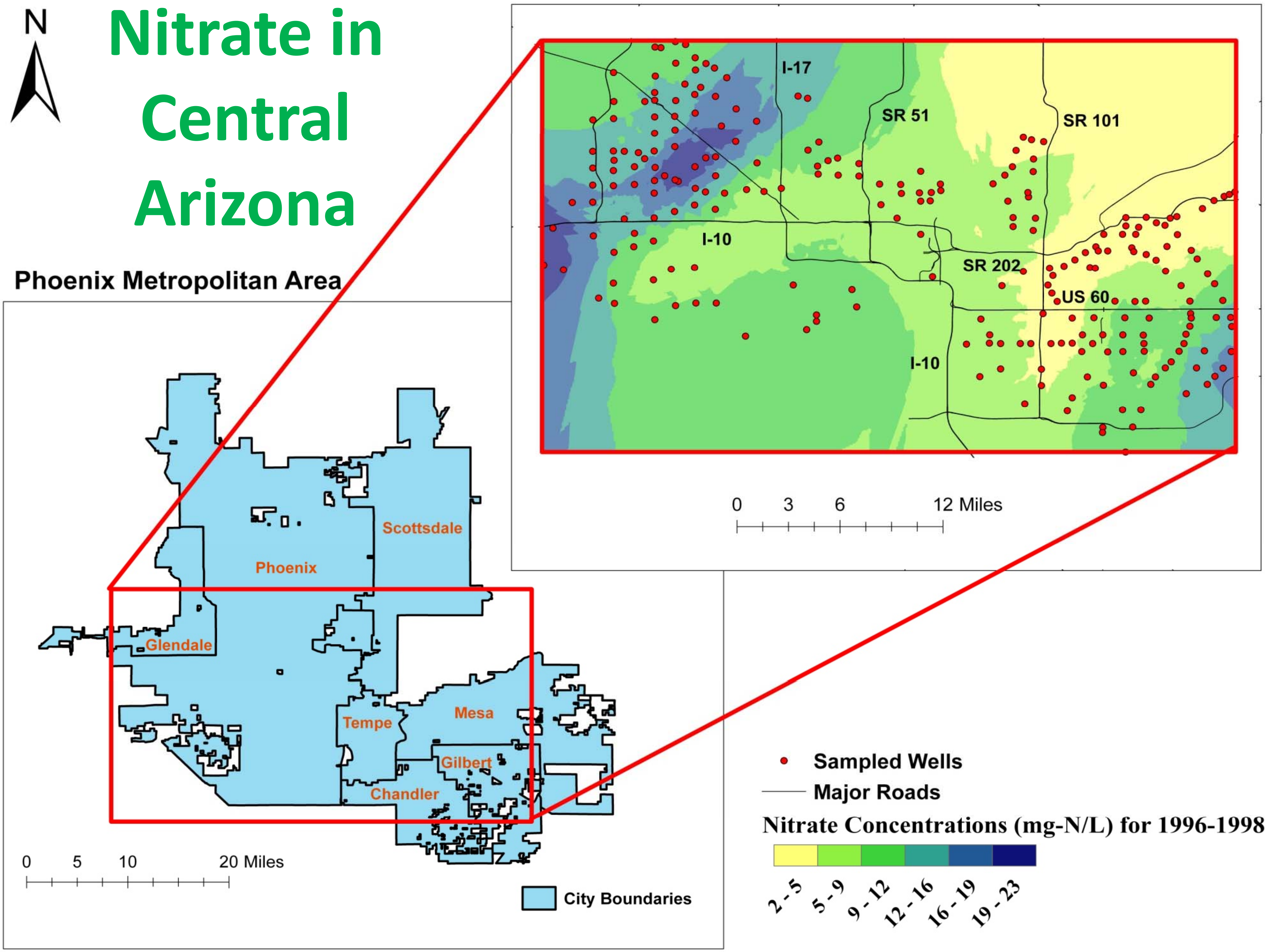
Funding by

Objectives

- 20% of drinking water wells in rural areas in the U.S. are above the EPA MCL (10 mg-N/L)
- Main cause of eutrophication in the Gulf of Mexico
- Develop a new nitrate mitigation technology
- Examine the potential for pilot scale applications



Nitrate in Central Arizona



Nitrate Treatment Technologies

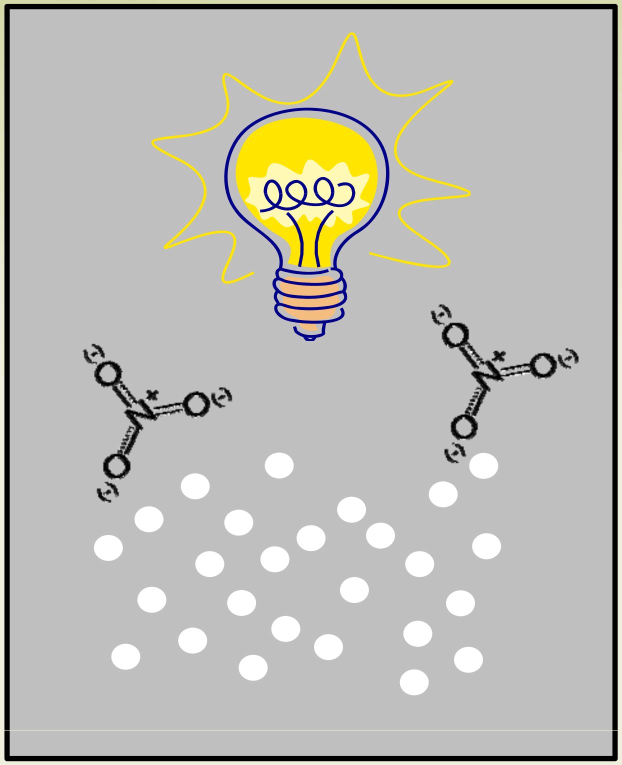
- Glendale currently uses IX treatment that produces nitrate-laden brine
- IX brine is costly to dispose
- They have investigated biological denitrification pilot scale and currently uses IX treatment as a Water Research Foundation (AwwaRF) Project with ASU (Bruce Rittmann)

Treatment Technology	Advantages	Disadvantages
Ion Exchange	Simple, cost-effective, low-maintenance for smaller applications	Disposal/treatment of brines, toxic by-products, not good for high TDS waters
Biological Denitrification	Non-toxic by-product, large applications, high concentrations, more cost effective than brine disposal	Electron donor required (H2 or organic carbon), possible microbial contamination, high-maintenance, start-up times

Novel Solution

- Photocatalysis (light activated catalysts)

- Advantages
  - Non-biological
  - Low maintenance
  - On/off
- Disadvantages
  - Still in research stage
  - Energy cost for UV light



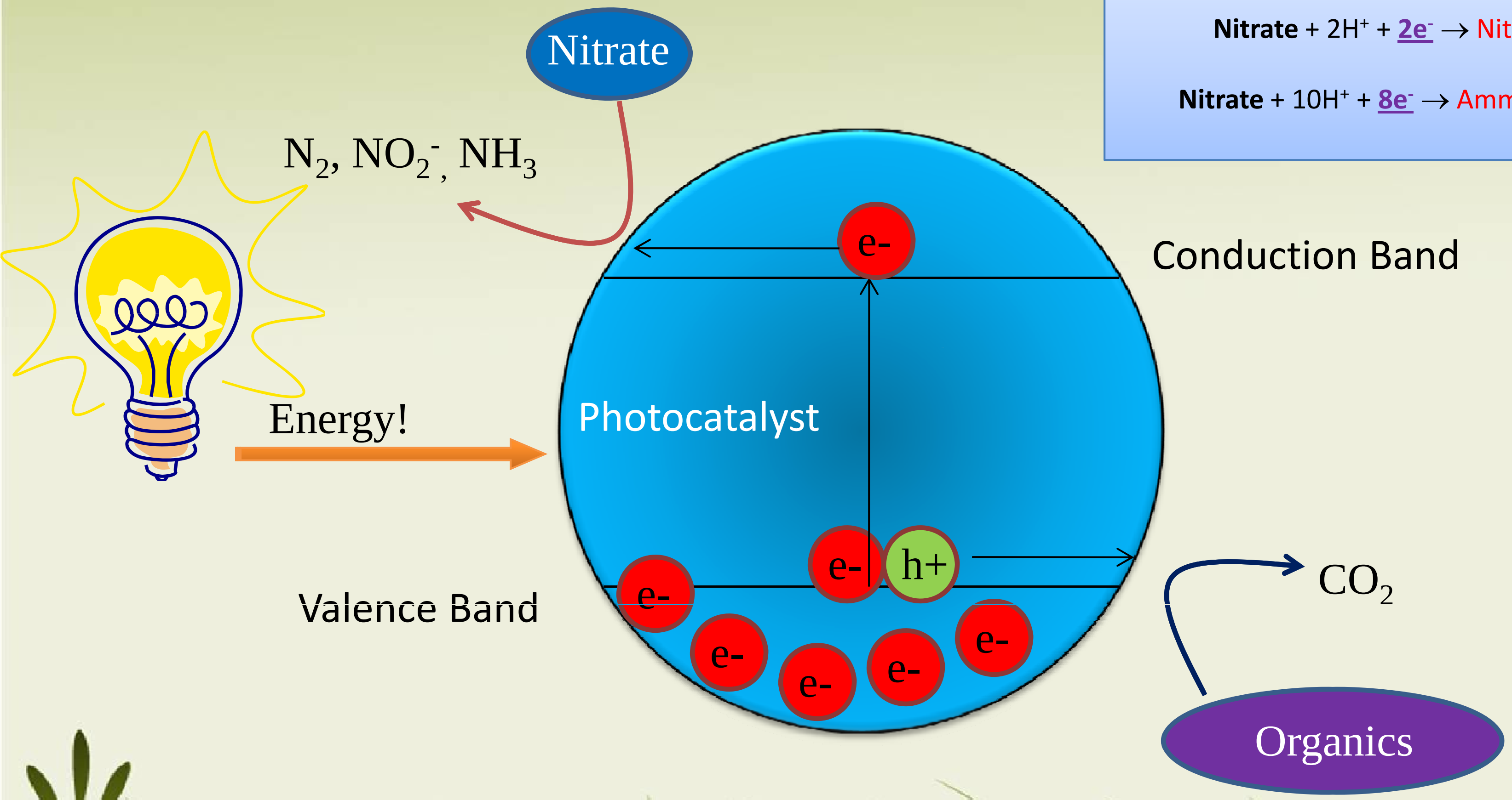
Photocatalyst Mechanisms

By-products

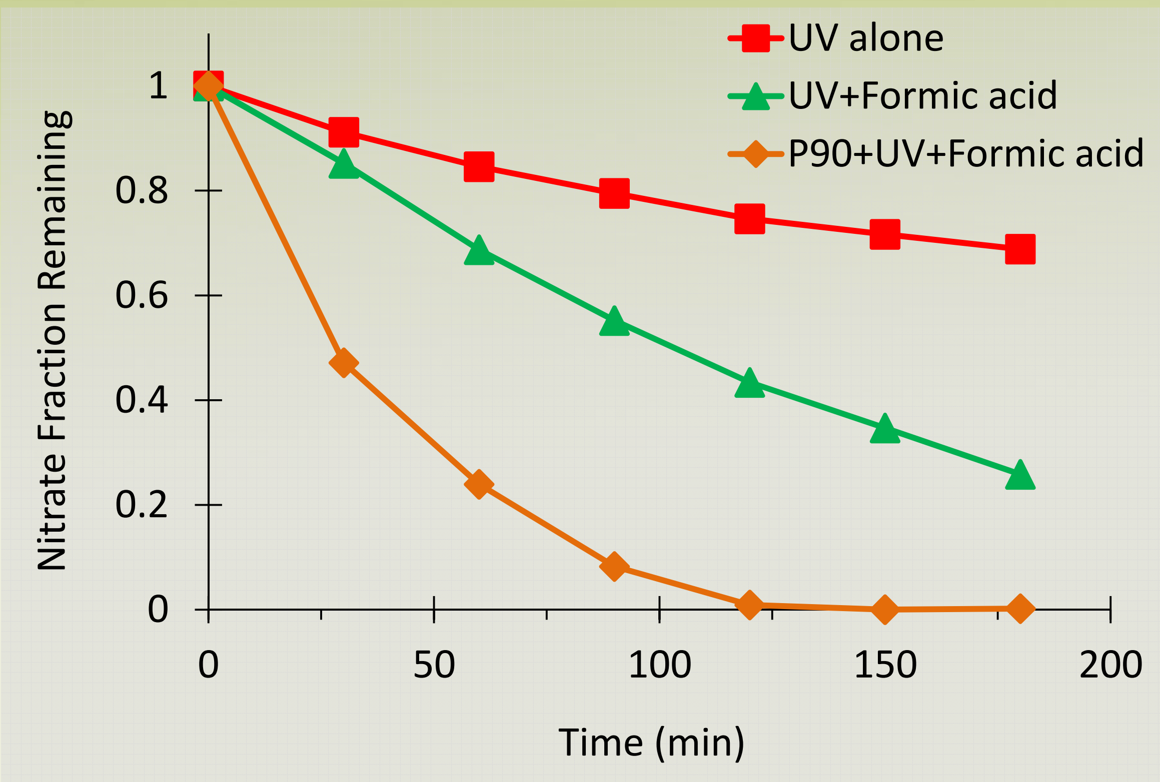
2**Nitrate** + 12H^+ + 10e^- → Nitrogen gas + 6H_2O

Nitrate + 2H^+ + 2e^- → Nitrite + H_2O

Nitrate + 10H^+ + 8e^- → Ammonia + 3H_2O



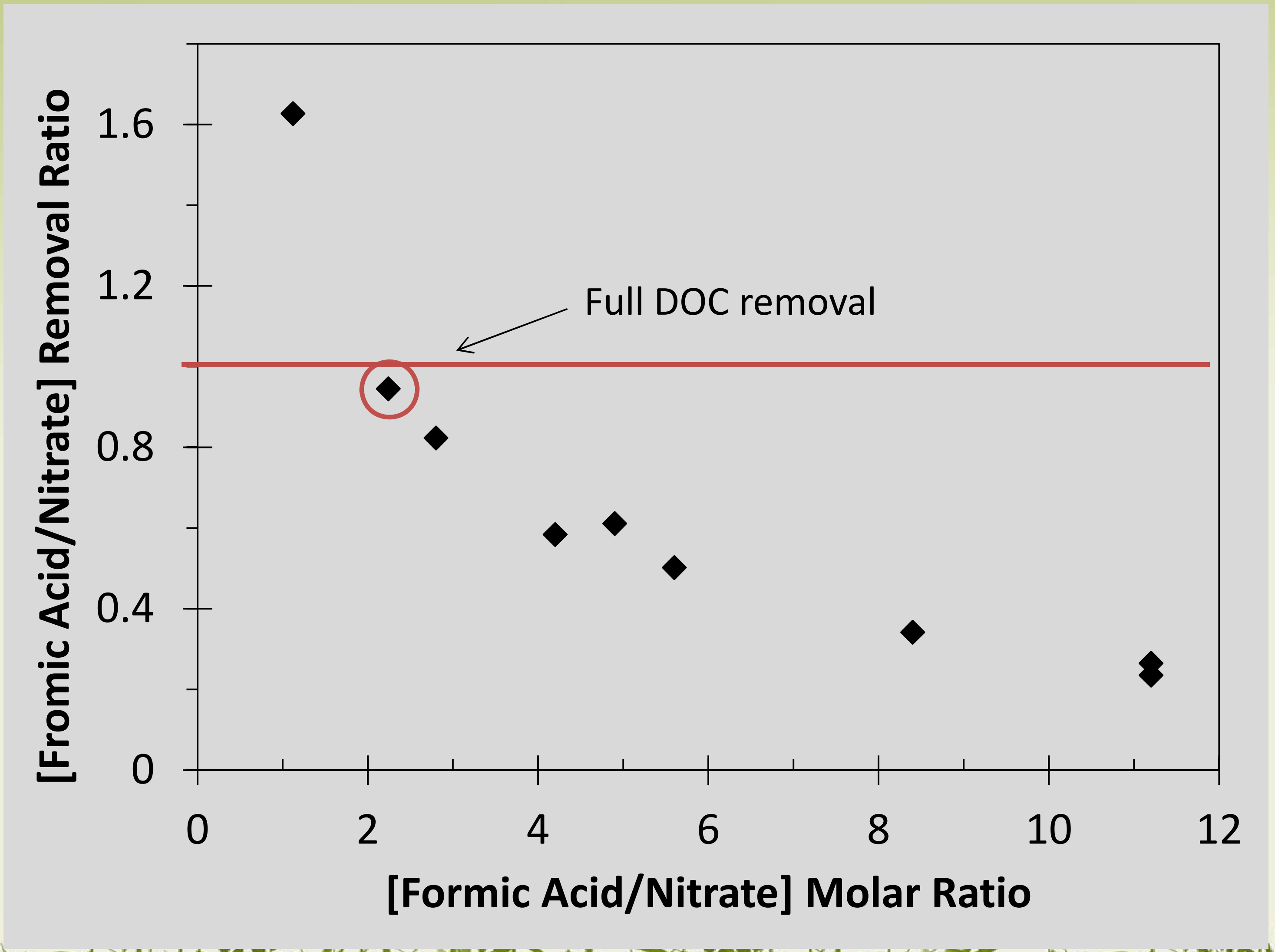
Nitrate removal in DI water



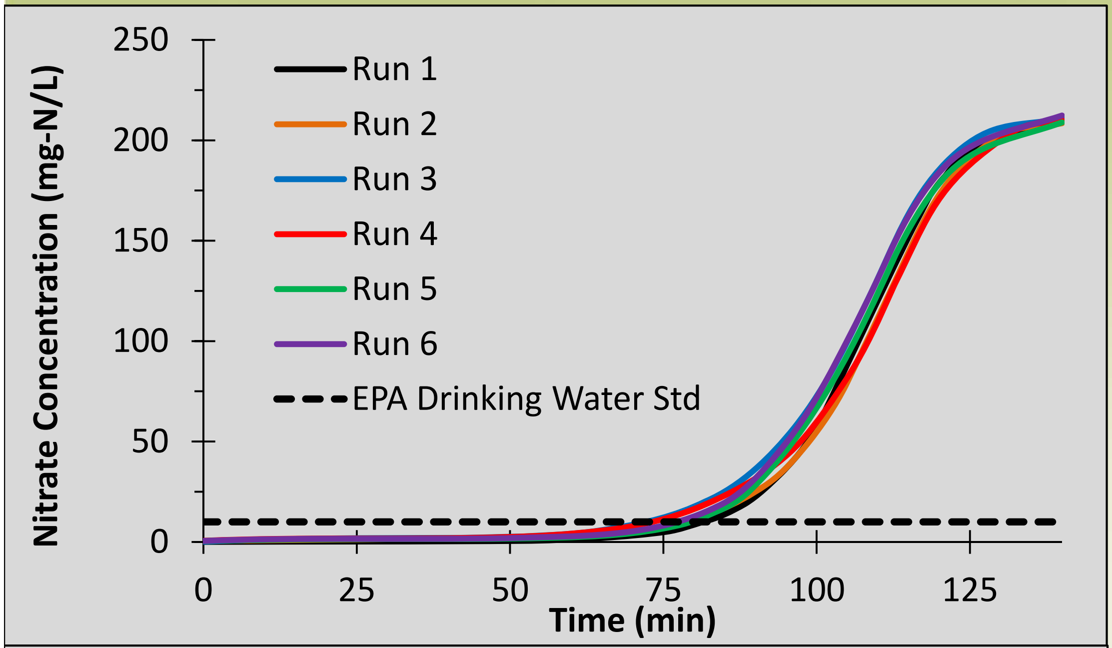
By-products

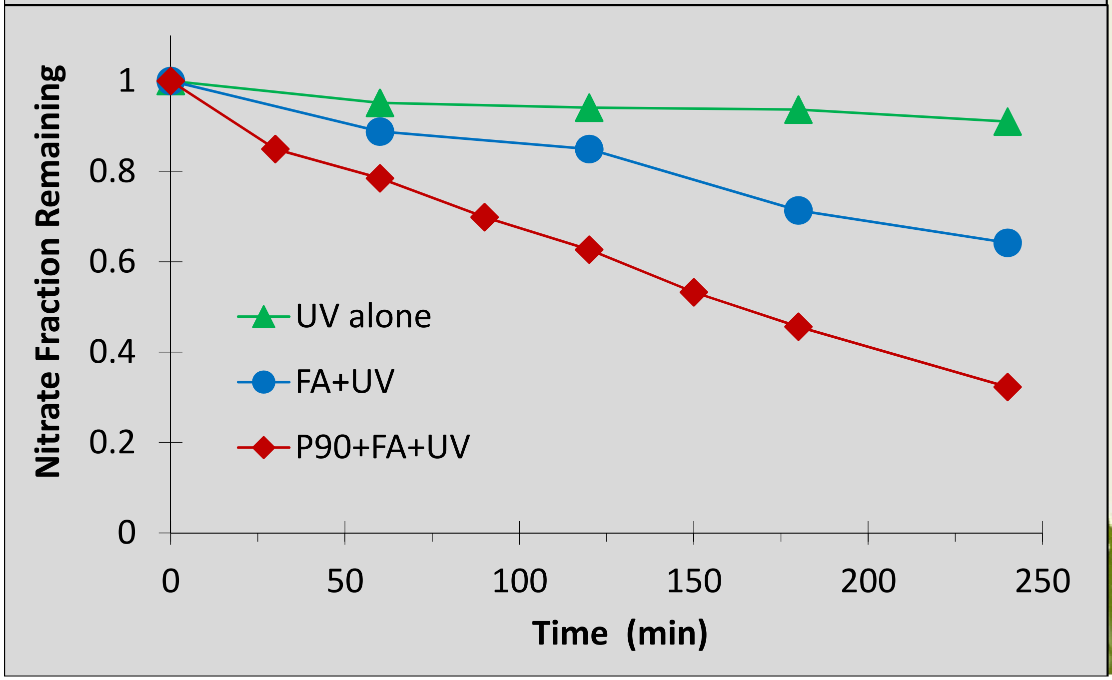
- UV alone
  - Nitrite
- UV+Formic
  - Nitrogen gas
- P90+UV+Formic
  - Nitrogen gas
  - ~15% Ammonia

DOC (Formic acid) Management



IX Brine Treatment





Looking Forward…

2009
Preliminary experiments comparing commercial TiO_2 photocatalysts

2010
Exploration of new photocatalysts for improved nitrate removal rates

2011
IX brine treatment preliminary studies

NSF funding awarded to expand study

2012-
New materials

Pilot-scale testing

<u>Current Partners</u>:
- Glendale, AZ
- Salt River Project
- 3 Private Companies

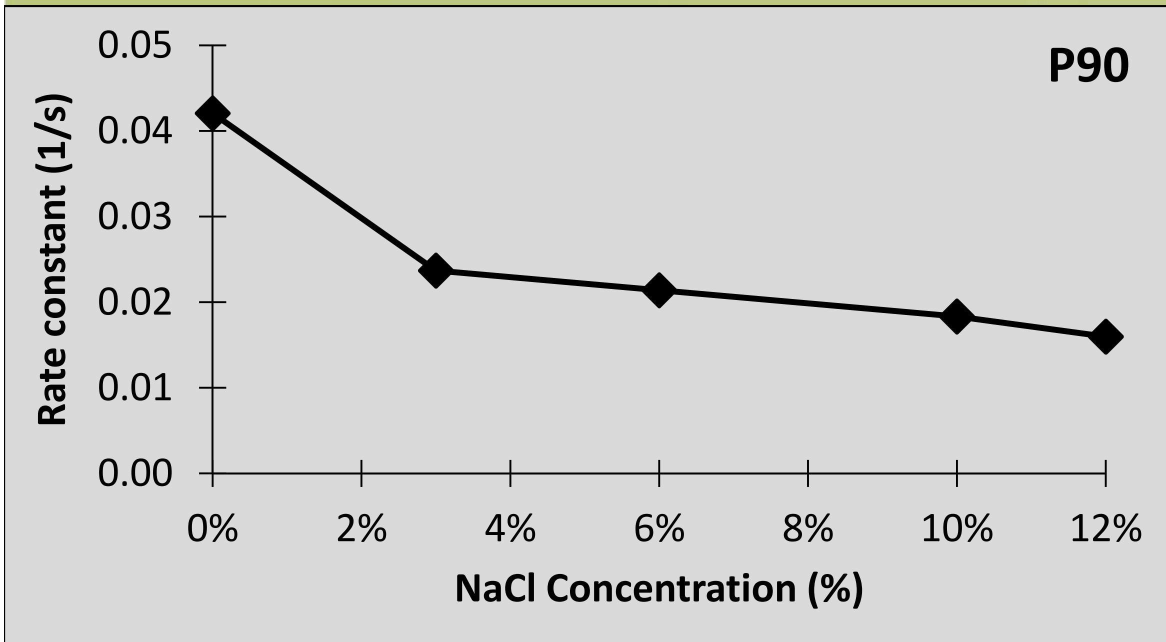
Thank You

Future Research

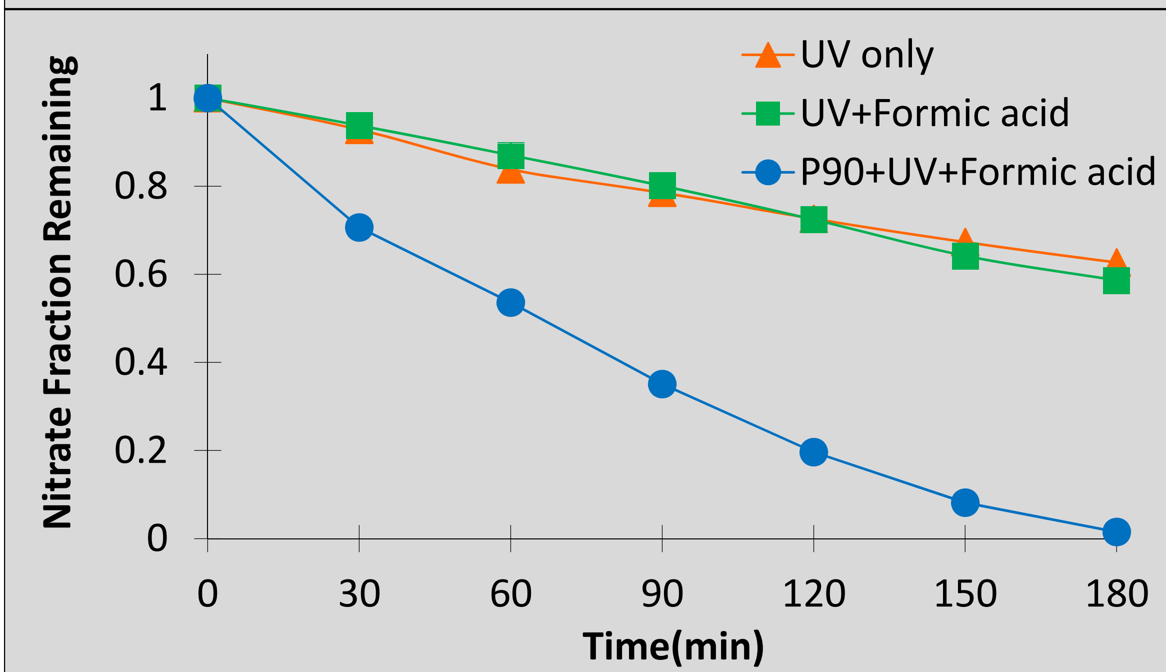
- Test in ion exchange brine
- Scale up to pilot
- Synthesis of new photocatalysts for:
  - Activity/Selectivity at neutral pH
  - Water as an electron donor

PhotoCat® system

Puralytics Shield ®



Increasing NaCl concentration decreases the rate of nitrate removal with P90



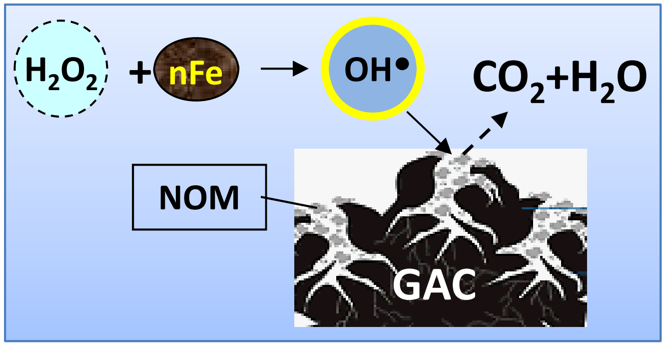
12% NaCl: Formic acid does not improve nitrate removal rate without a catalyst

In-situ GAC Regeneration: Progress and Path Forward

Chao-An Chiu
Paul Westerhoff
Arizona State University
School of Sustainable Engineering and The Built Environment
Civil, Environmental and Sustainable Engineering

In-Situ GAC Regeneration

- What concept is?

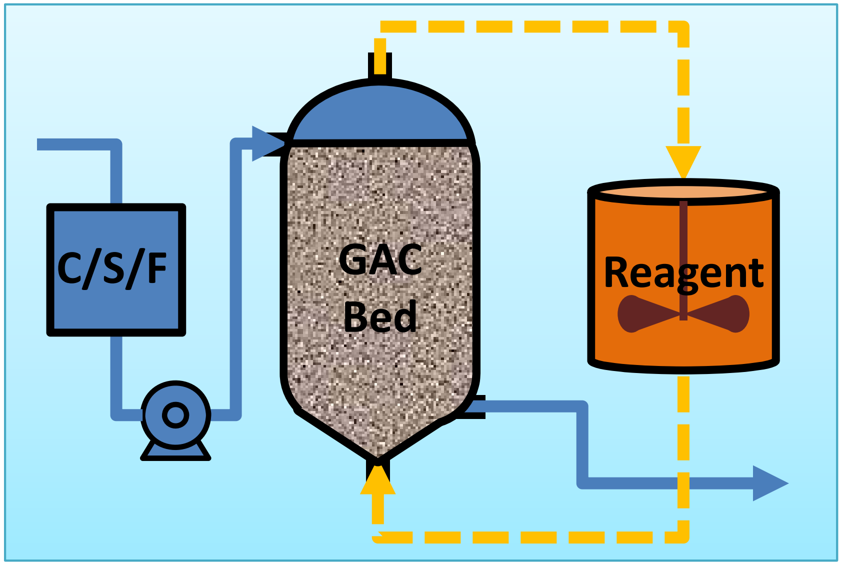


What does it replace?

- Operate to near complete breakthrough;
- GAC remove;
- GAC off-site transportation;
- GAC thermal regeneration;
- Transport back to site;
- GAC back-installation;
- Attrition replacement (at least 10%);
- 4-6 weeks downtime.

- Envision Process -

- Reagent preparation;
- In-column contact with GAC;
- Reagent washout;
- GAC back to operation;
- 1-2 days downtime;
- <u>May have frequent regeneration (weeks) to make GAC more effective during peak THM control needs.</u>



In-Situ GAC Regeneration for Surface Water Treatment Plant
(Timeline for Implementation)

2009

Literature Study and Nano-Fe Synthesis

- Nano-Fe can be synthesized easily by hydrolysis of $FeCl_3$ in hours and preserved for months.

2010

Feasibility and Batch Test

- Nano-Fe produced by 7% $FeCl_3$ can oxidize organics sorbed onto GAC in an hour.
- Nano-Fe can be recycled and reused.
- No-Slurry formed after oxidization.

2011

In-Situ GAC Regeneration Test

- Nano-Fe can recover >80% GAC sorption capacity.
- > 5 runs of sorption-regeneration can be performed.
- Nano-Fe can be used for regeneration of GAC saturated with low conc. organics.

2012

Demonstrate with NOM and DBPs control

2013

Pilot Study

Full Scale Study

Implementation Full Scale

In-situ saturated GAC regeneration Small-Scall Test

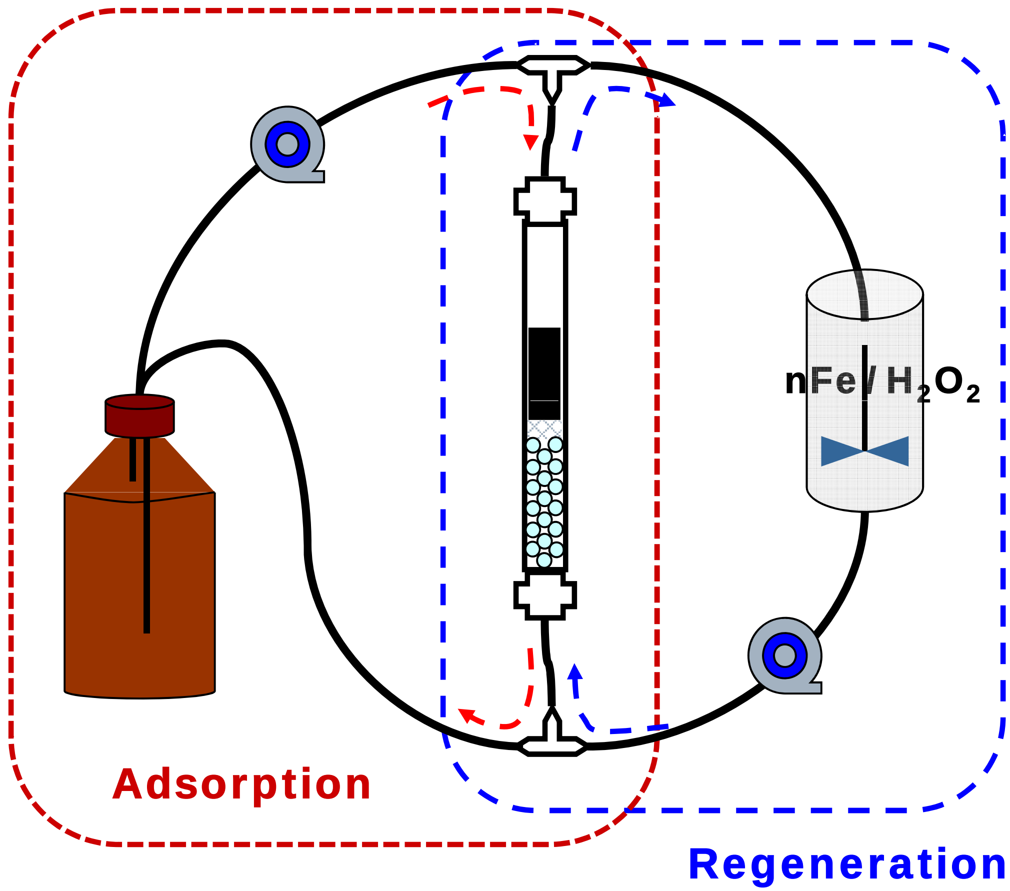
Three Stages:

A. Adsorption Stage
   - Fresh GAC
   - Downflow mode
   - Enforced adsorption

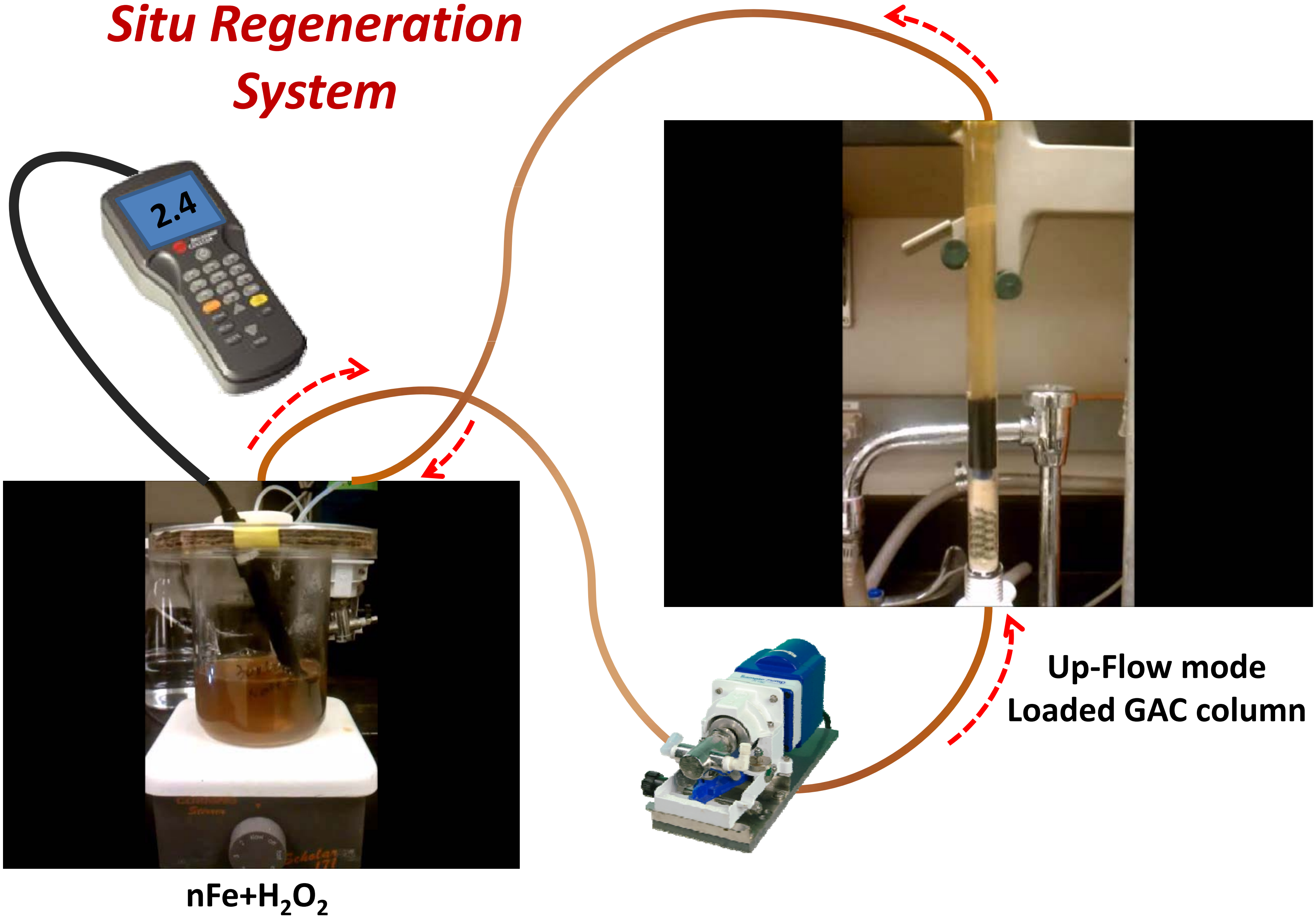
B. In-situ Regeneration Stage
   - Upflow mode
   - In-situ
   - 30 minutes

C. Re-Adsorption Stage
   - Regenerated GAC
   - Downflow mode
   - Enforced adsorption

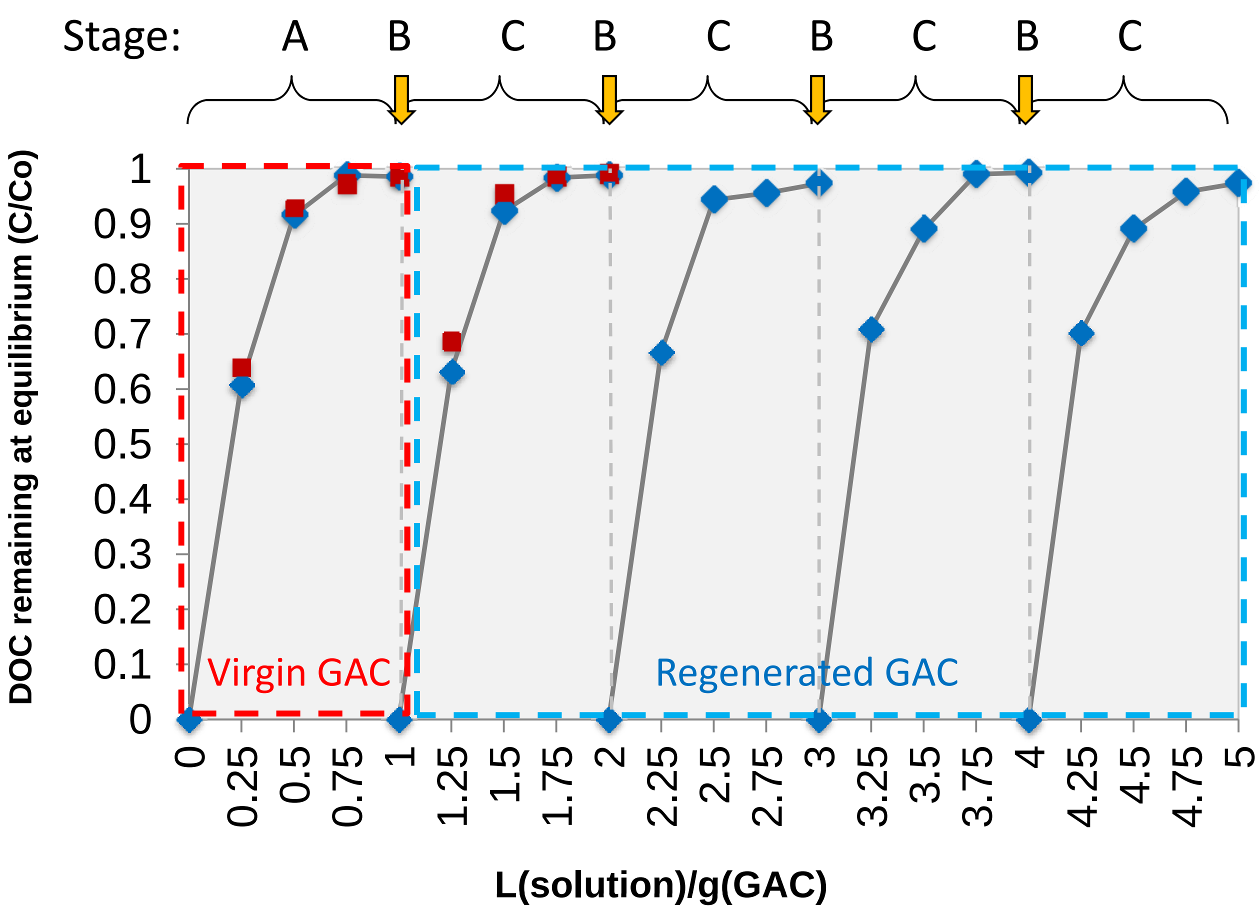
Comparison of GAC adsorption capacity between stage A and C.



Demonstration of In-Situ Regeneration System



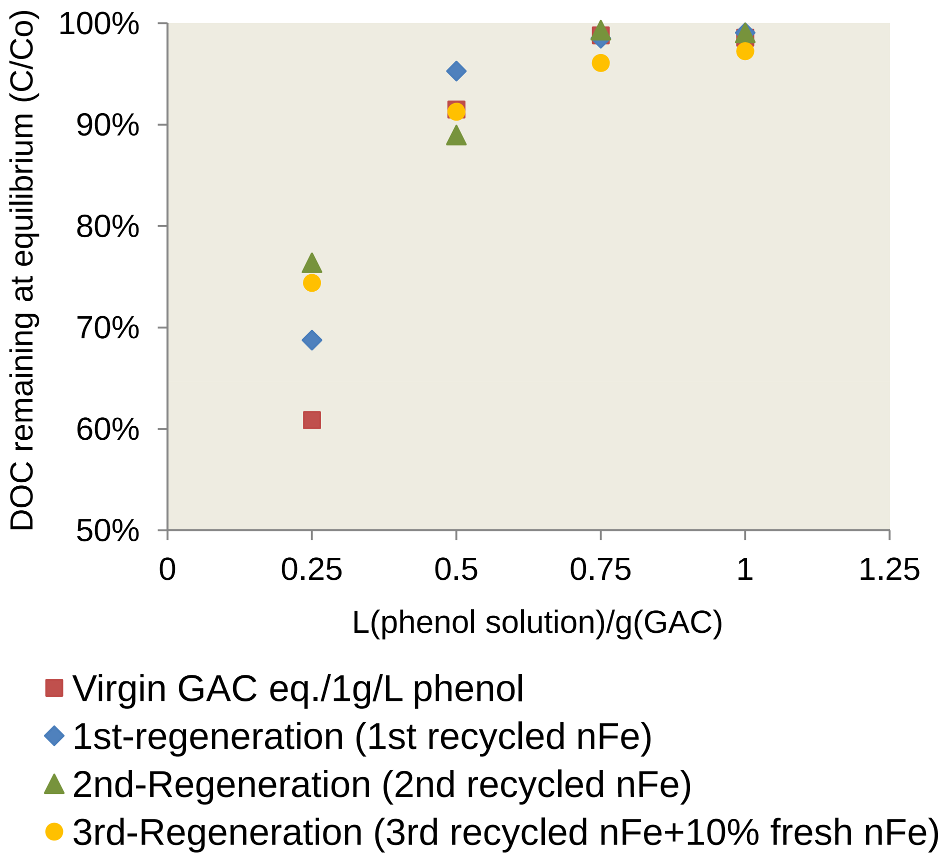
Representative Results



- GAC adsorption capacity was recovered.
- Stage A-B-C can be repeated for 5 runs.
- Duplicate results (red dot) confirmed the feasibility.

Adsorption of phenol (1000 mg/L) onto virgin and in-situ regenerated GAC.

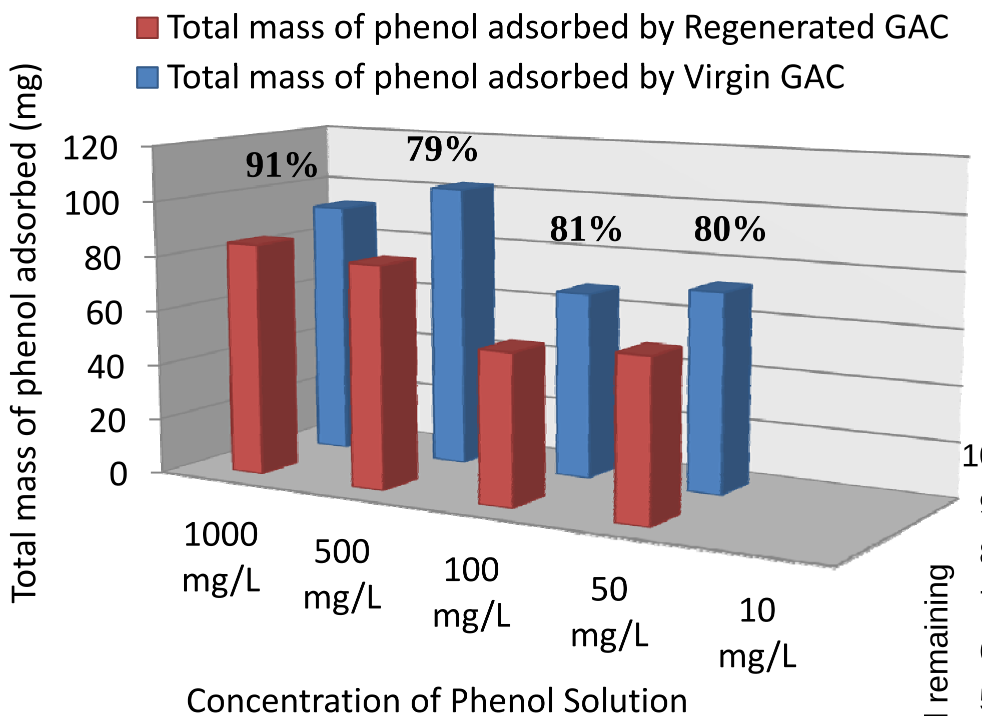
Test for recycle and reuse of nano-Fe

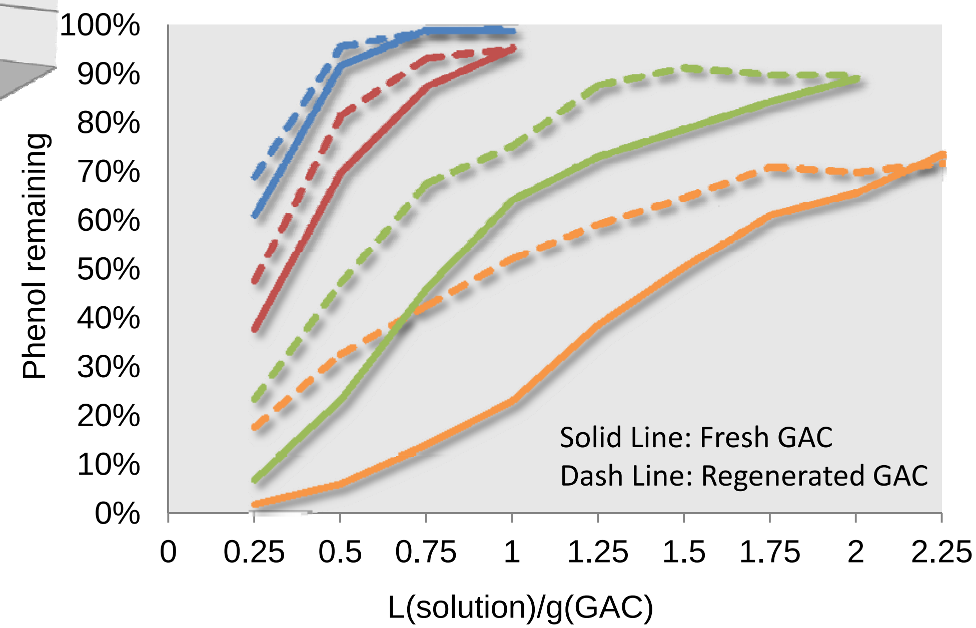


Recycle of Nano-Fe

- Simple pH adjustment
  - pH > 5 → aggregation
  - pH < 2 → re-dispersion
- Measurement of iron concentration shows no iron loss after reaction.
- Nano-Fe can be recycled and performed as fresh nano-Fe.

In-situ regeneration of GAC adsorbing different PHENOL concentrations





Comparison for Regeneration Efficiency of Sorption Capacity

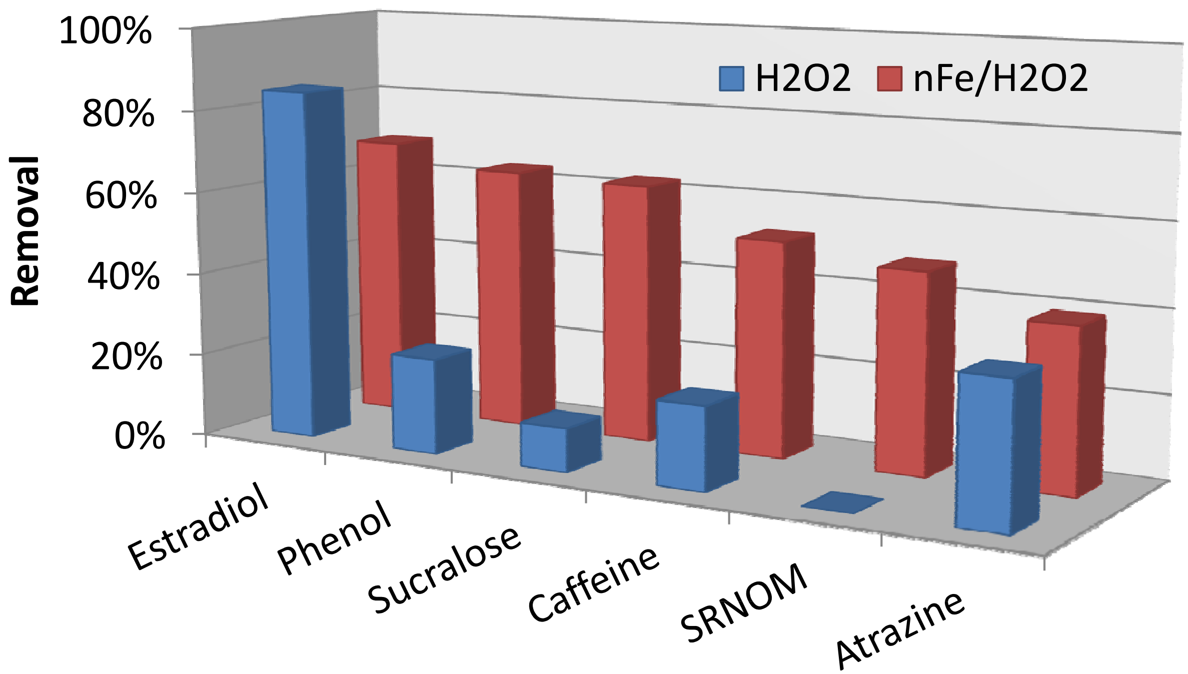
$$Efficiency(E) = \frac{\sum_{i=1}^{n}\left[(C_{0,i} - C_{eq,i}) \times V_i\right]_{Virgin}}{\sum_{i=1}^{n}\left[(C_{0,i} - C_{eq,i}) \times V_i\right]_{regenerated}} \times 100$$

More Adsorption-Regeneration Cycles →

Lower adsorbate concentration ↓

Regeneration condition		Efficiency (E) of Adsorption Capacity Recovery			
		1st cycle	2nd cycle	3rd cycle	4th cycle
Adsorbate (phenol) Iron nanocatalyst	1000ppm Fresh	92%	93%	85%	90%
Adsorbate (phenol) Iron nanocatalyst	1000ppm Recycled	77%	74%	81%	
Adsorbate (phenol) Iron-nanoparticles	1000ppm Fresh	81%			
Adsorbate (phenol) Iron-nanoparticles	500ppm Fresh	79%			
Adsorbate (phenol) Iron-nanoparticles	100ppm Fresh	80%			
Adsorbate (phenol) Iron-nanoparticles	50ppm Fresh	81%			
Adsorbate (phenol) Iron-nanoparticles	10ppm Fresh				

Next Step – Demonstrate In-situ Regeneration with NOM and PPCP



Why Pharmaceuticals?
Are they significant in surface water?

Summary and Timeline for Implementation

2009

Literature Study and Nano-Fe Synthesis

- Nano-Fe can be synthesized easily by hydrolysis of $FeCl_3$ in hours and preserved for months.

2010

Feasibility and Batch Test

- Nano-Fe produced by 7% $FeCl_3$ can oxidize organics sorbed onto GAC in an hour.
- Nano-Fe can be recycled and reused.
- No-Slurry formed after oxidization.

2011

In-Situ GAC Regeneration Test

- Nano-Fe can recover >80% GAC sorption capacity.
- > 5 runs of sorption-regeneration can be performed.
- Nano-Fe can be used for regeneration of GAC saturated with low conc. organics.

2012

Demonstrate with NOM and DBPs control

2013

Pilot Study

Full Scale Study

Implementation Full Scale

Jar Testing with PAC

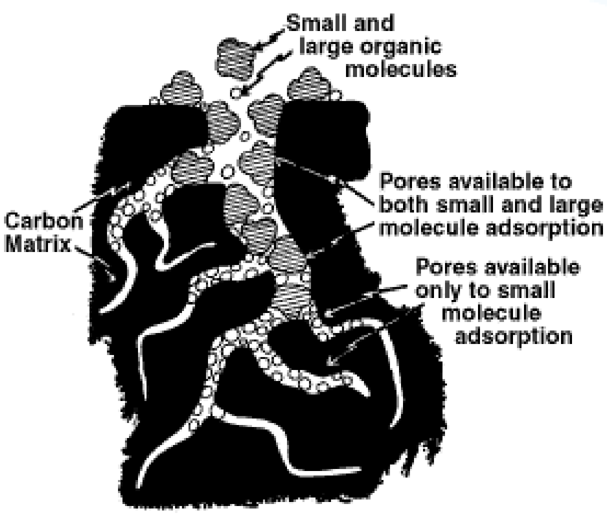
How to & Results with S-PAC

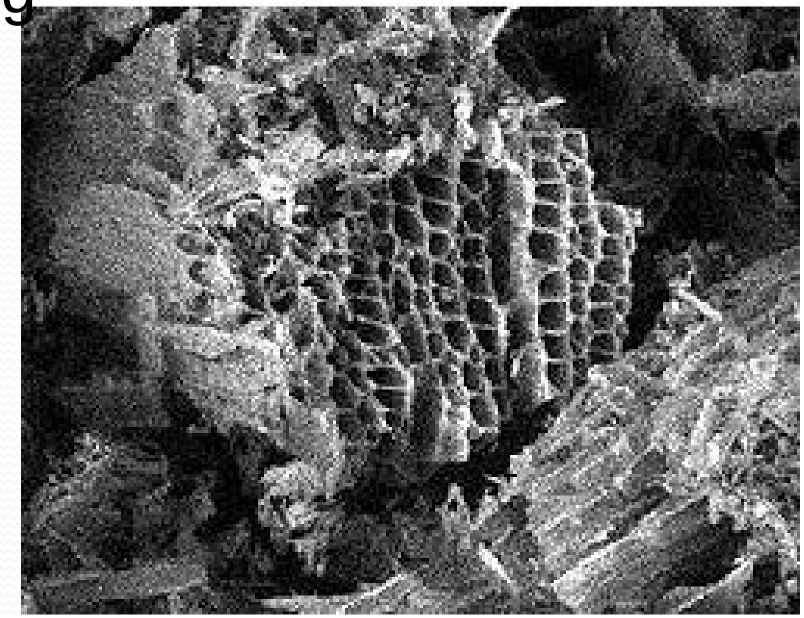
David Hanigan
Ph.D. Student

S-PAC provided by Detleff Knappe / Univ of N. Carolina

PAC

- Carbon that has been "activated"
  - Common carbon sources: Coal, peat, wood
  - Activation generates an extremely porous structure that is beneficial for adsorption
  - Surface areas of 500-2000 m^2/g
    - Football field=5300 m^2





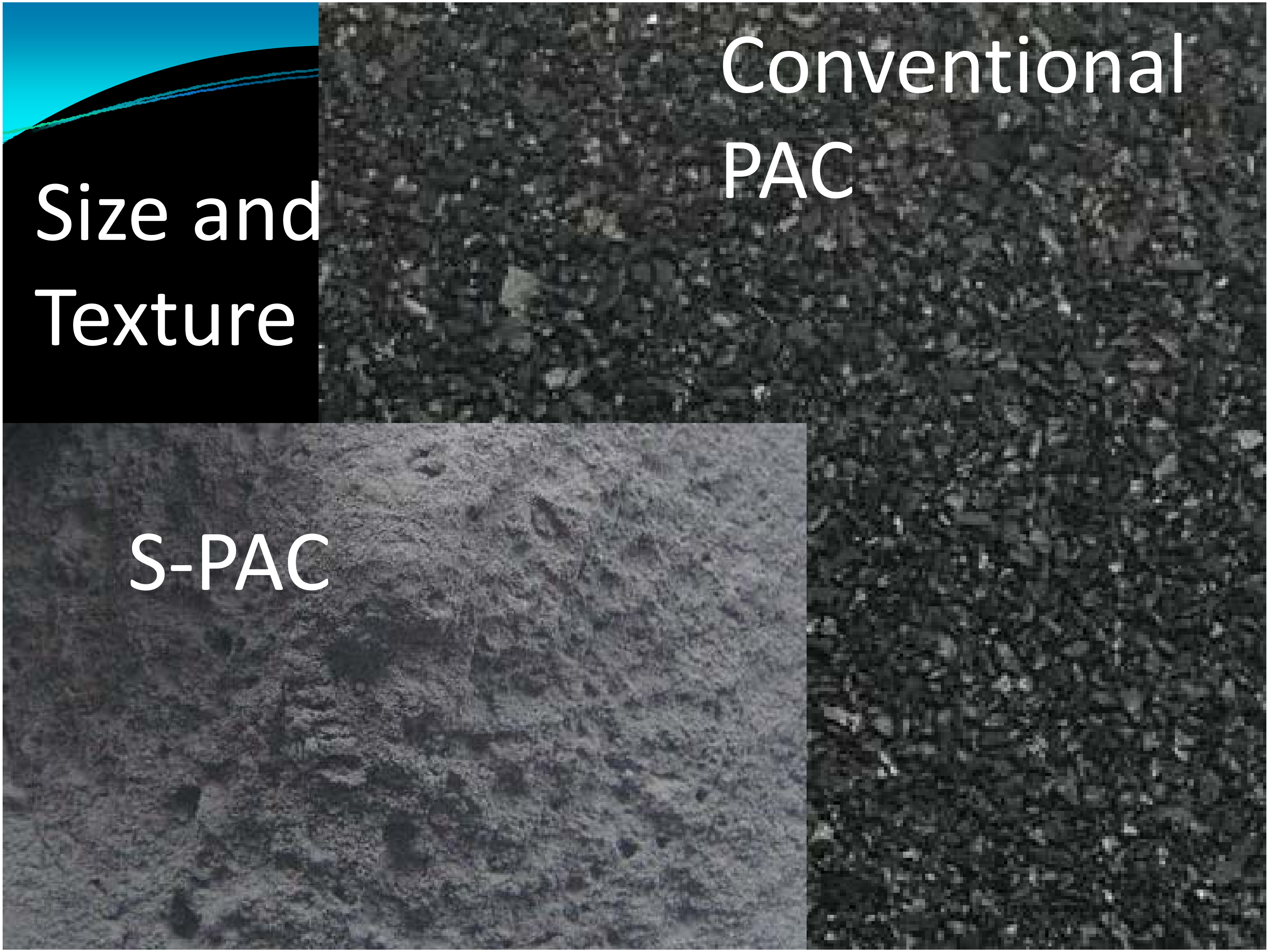
Uses in Water Treatment

- Taste and odor organics
  - MIB, Geosmin, Cyclocitral
- Performs best on certain organics:
  - High molecular weight (large)
  - Aromatic (unsaturated bonds)
  - Hydrophobic (nonpolar, not attracted to water)
- Nontraditional uses
  - DBP precursors (THM, HAA, NDMA?)

It's a matter of size

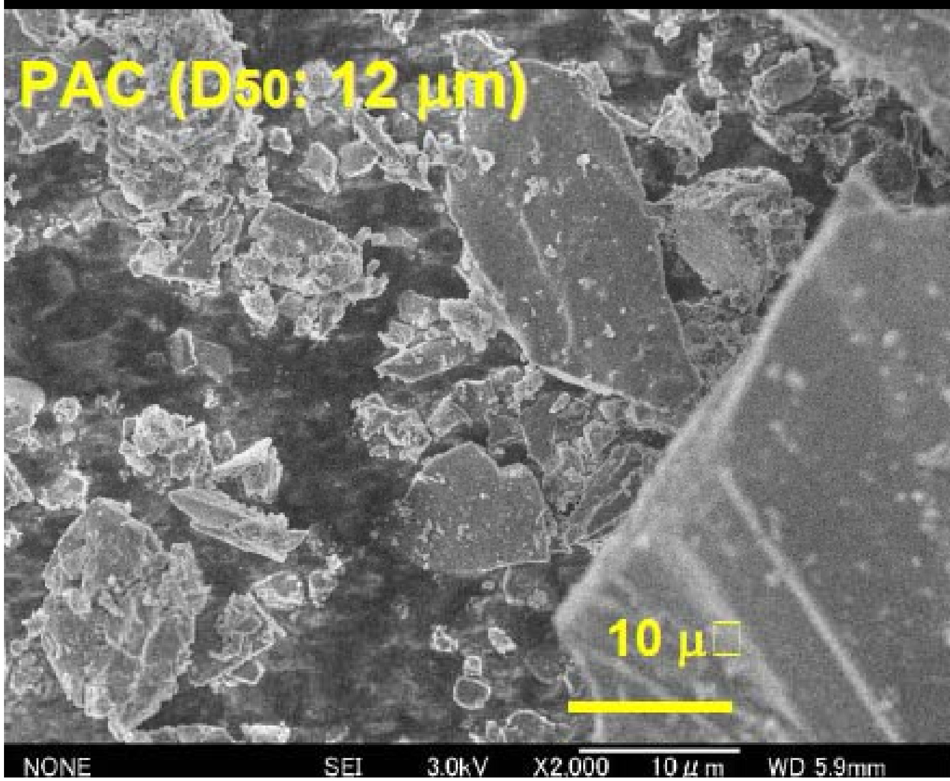
- GAC
  - Usually used in a packed column
  - Can be regenerated
  - **Particle size ~500-2000 micron**
- PAC
  - Not recovered, removed by coagulant or filters
  - Can be used in older facilities not designed for GAC beds
  - Sometimes used seasonally for THM/HAA precursor reduction
  - **Particle size generally less than 100 micron**
- S-PAC
  - Similar to PAC, with **particle size ~0.3 micron**

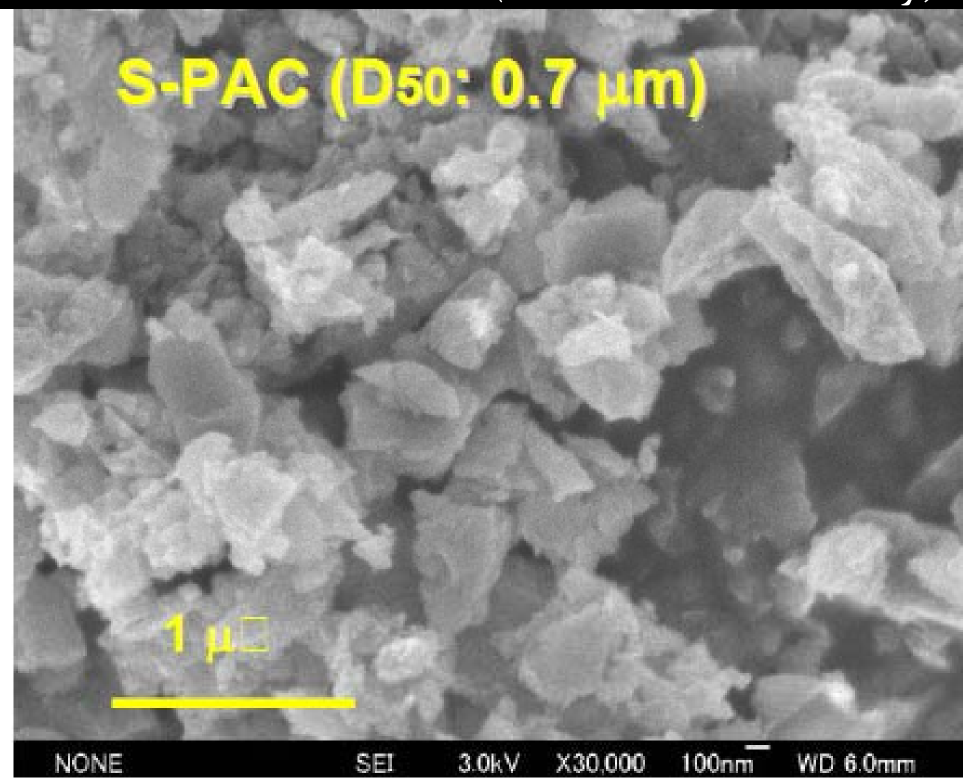
Size and Texture



SEM Images

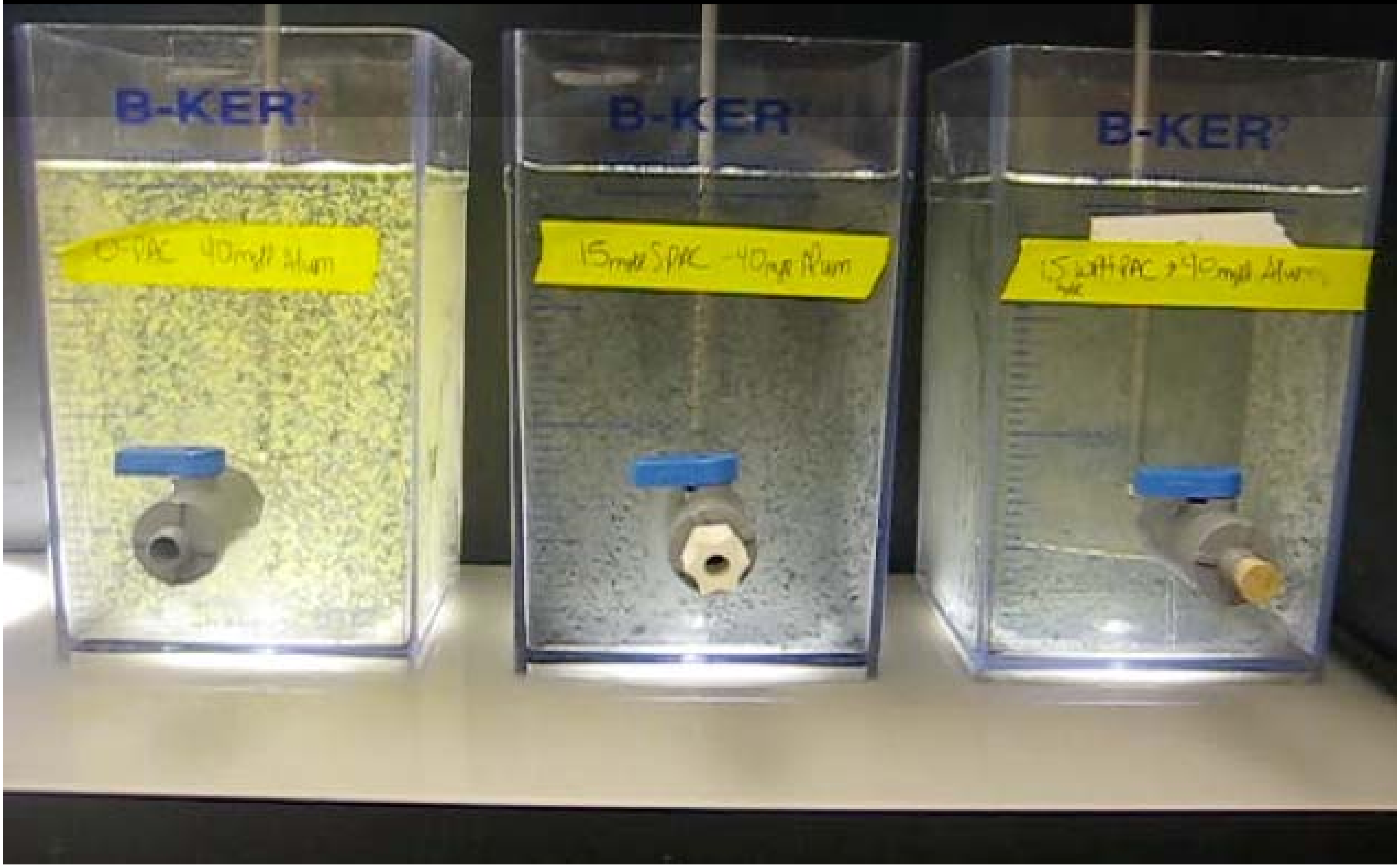
Source: Matsui, Yoshida, Ando, Matsushita (Hokkadio University)



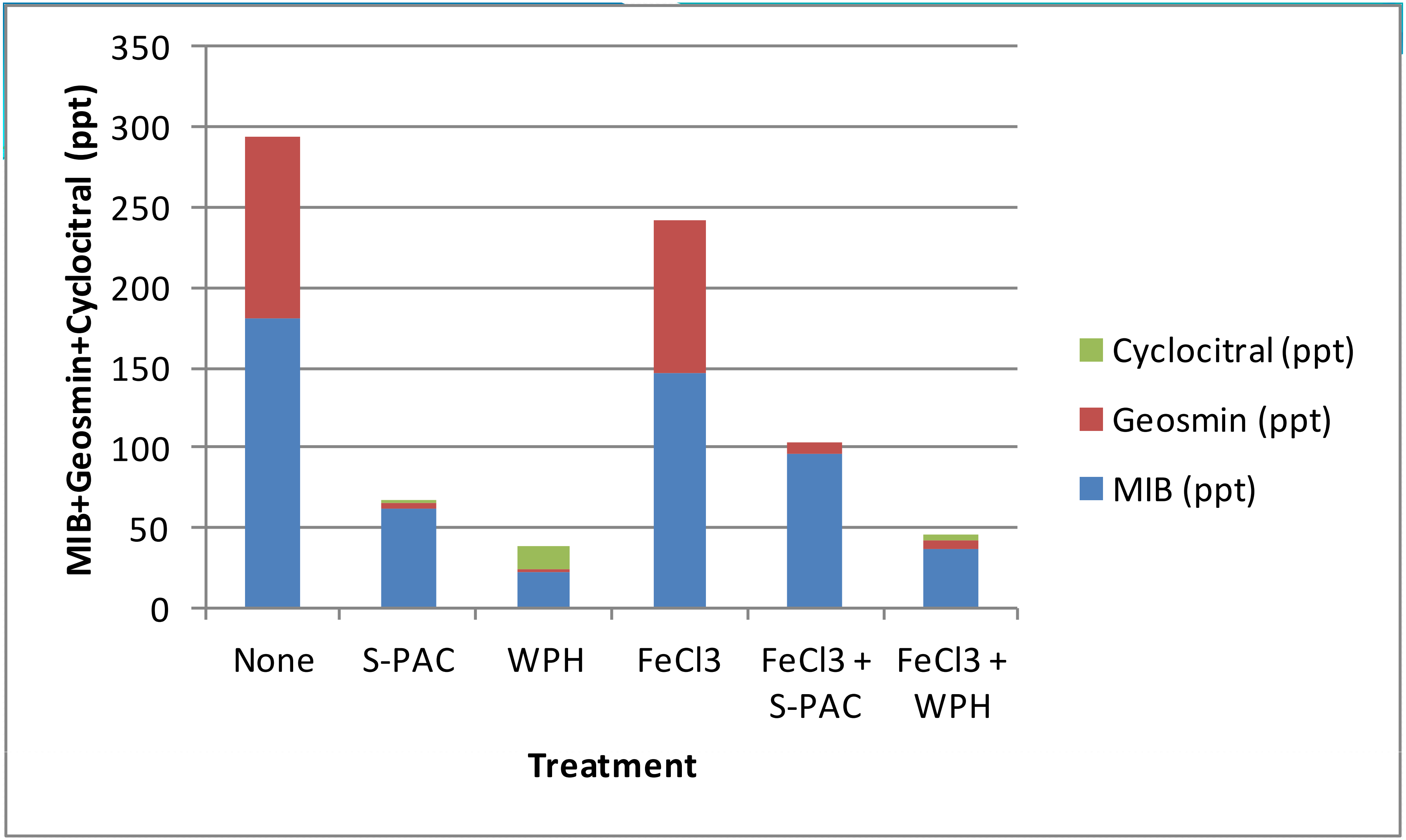


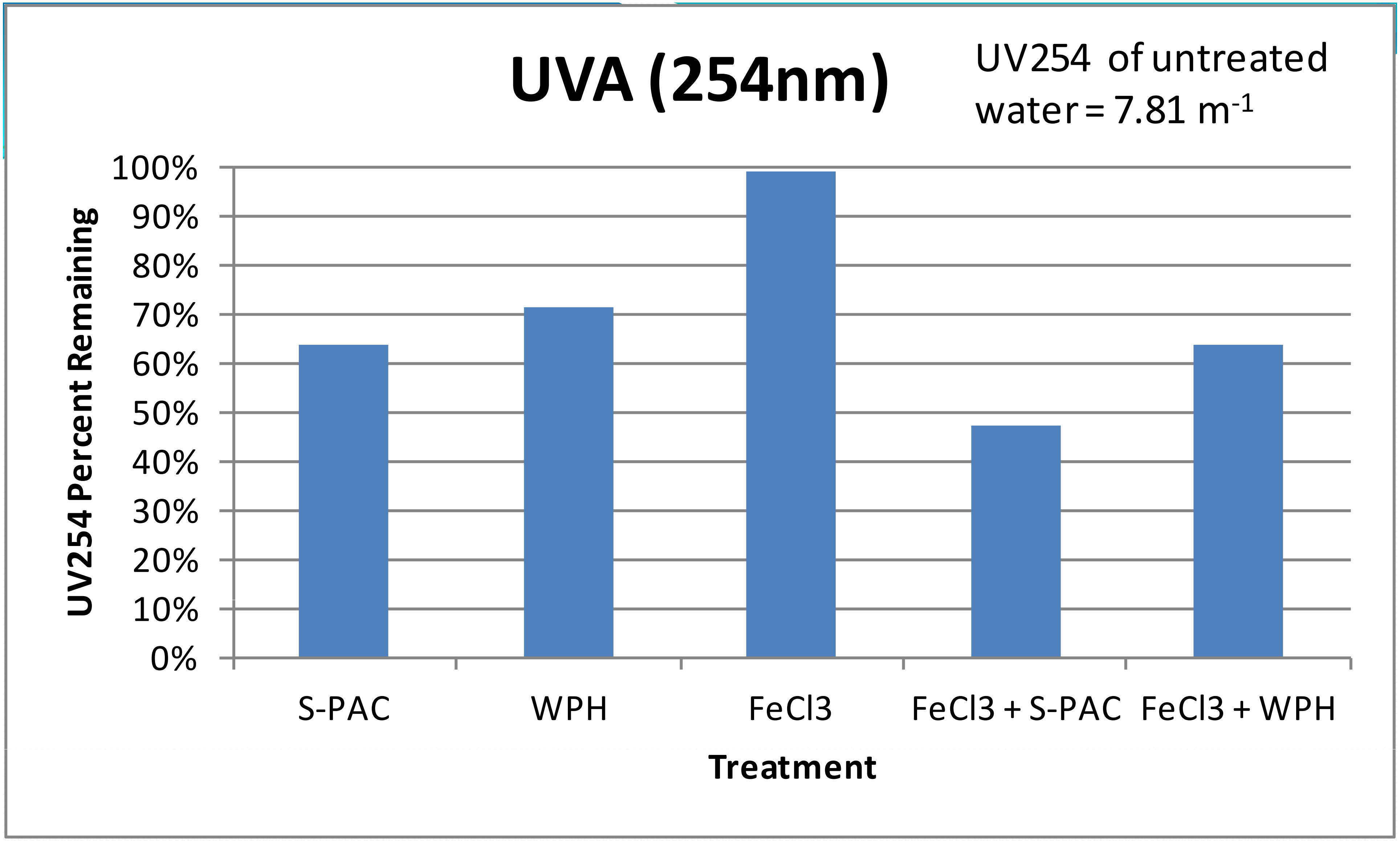
Jar Tests

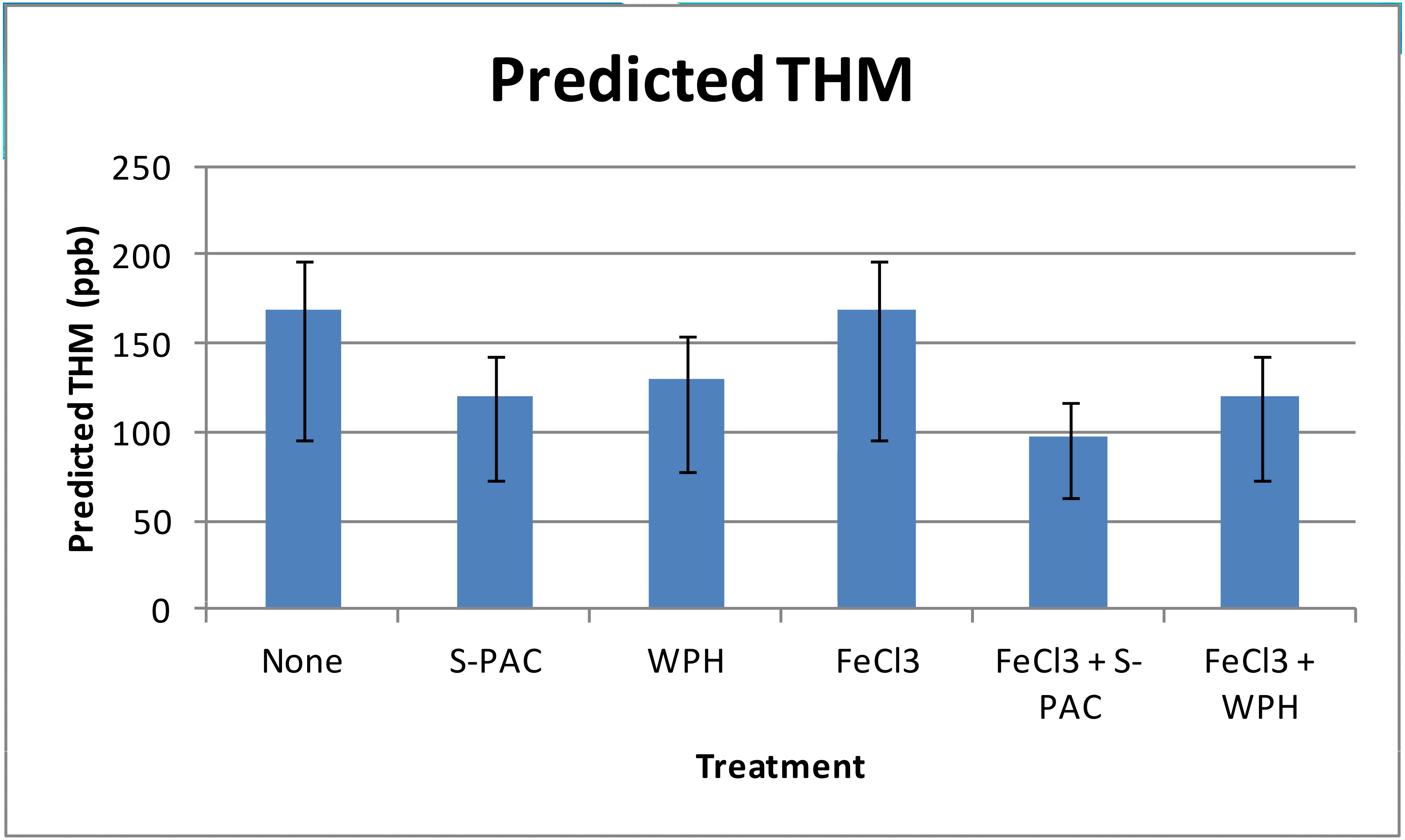
- Commonly used for finding optimum coagulation dosage
- Instead, used in this study to compare S-PAC to WPH with and without coagulation (ferric chloride) for UVA, MIB, geosmin removal
- Saguaro Lake water spiked with MIB and Geosmin
- Add PAC (15 mg/L), mix for 30 min (100rpm)
- Add ferric (40mg/L) (2 min rapid mix)
- Floc/Sedimentation (~30 rpm) for 30 min
- Filtered (0.2 micron)
- Analyzed for UVA, Geosmin, MIB, cylcocitral
  - MIB spike contains methanol so cannot analyze for TOC


B-KER2
B-KER2
B-KER2


B-KER2
0-PAC 40 mg/l FeCl3
1 LITER
B-KER2
15 mg/l WDH-PAC 40 mg/l FeCl3
1 LITER
B-KER2
15 mg/l S-PAC 40 mg/l FeCl3
1 LITER


MIB+Geosmin+Cyclocitral (ppt)
350
300
250
200
150
100
50
0
None
S-PAC
WPH
FeCl3
FeCl3 + S-PAC
FeCl3 + WPH
Treatment
Cyclocitral (ppt)
Geosmin (ppt)
MIB (ppt)

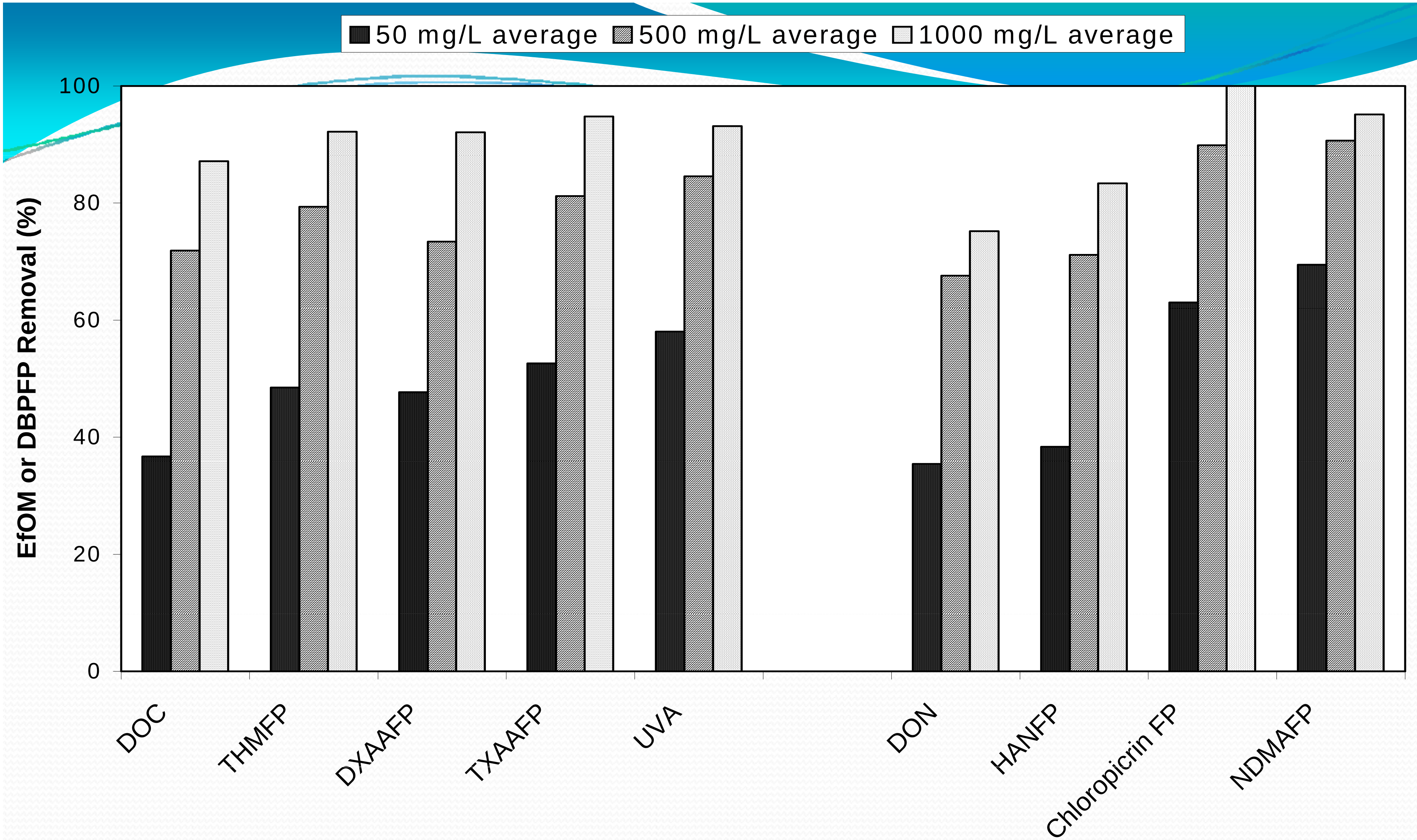

UVA (254nm)
UV254 of untreated water = 7.81 m-1
UV254 Percent Remaining
100%
90%
80%
70%
60%
50%
40%
30%
20%
10%
0%
S-PAC
WPH
FeCl3
FeCl3 + S-PAC
FeCl3 + WPH
Treatment



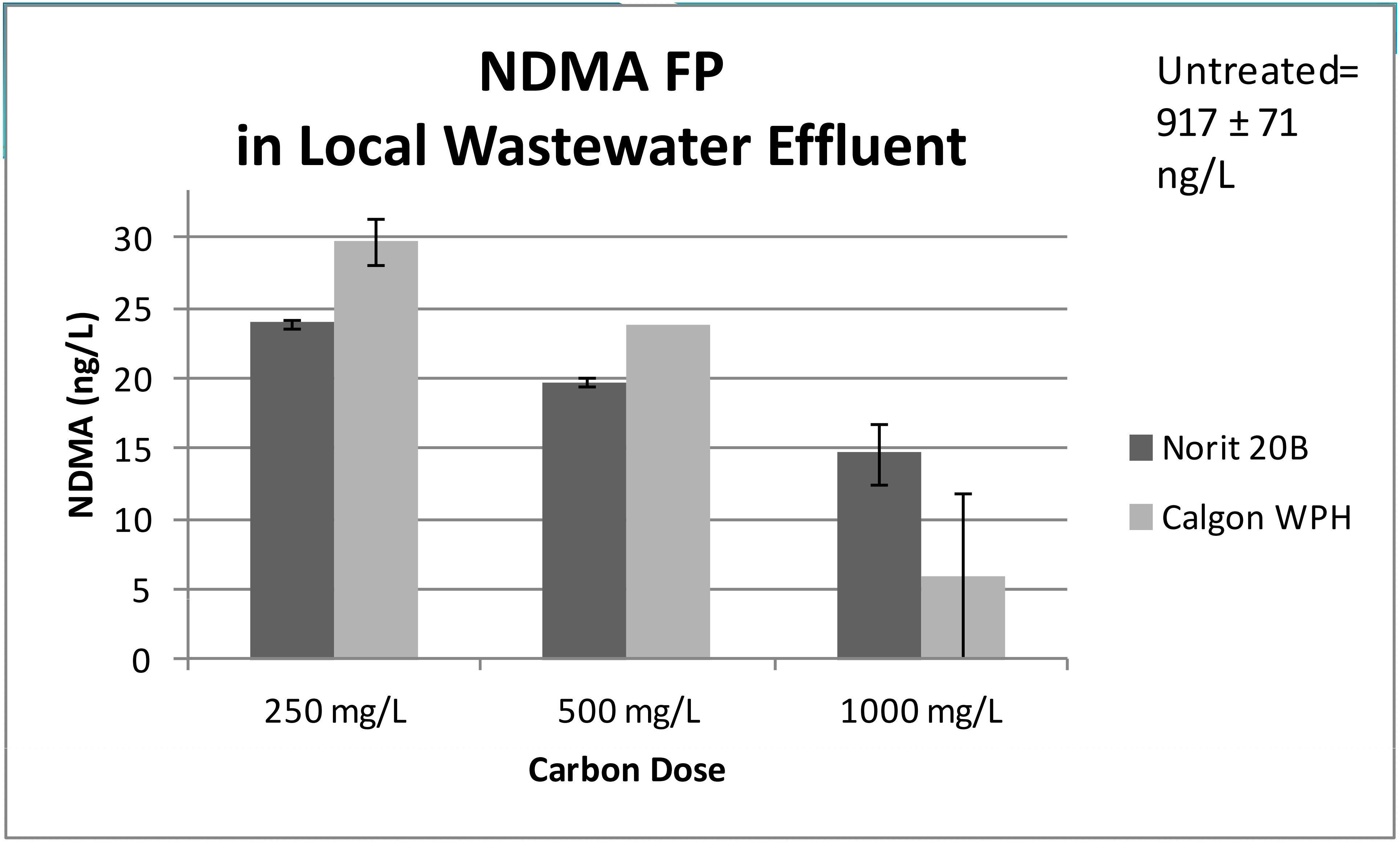
- Based on linear relationship between UV254 and THM developed by several authors summarized in Chowdhury and Champagne, 2007
- R^2 between .77 and .91

Conclusions and Future Research

- S-PAC has a smaller particle size than regular WPH
- S-PAC removes less taste and odor compounds than WPH under similar experimental conditions
- S-PAC removes a larger amount of UV absorbing material than WPH under similar conditions
- A greater removal of UV absorbing material generally results in reduced THM and HAA formations.
- Future work
  - Can S-PAC/PAC/GAC reduce NDMA formation in drinking waters impacted by wastewater?



- EfOM and DBP precursor average removal after equilibration **(7d)** at three activated carbon dosages (all four EfOMs evaluated with 50 mg/L of PAC, the SMPs and the Nogales WWTP evaluated with 500 mg/L of PAC, and the Southerly WWT Center and the Metro District/North Complex evaluated with 1000 mg/L of PAC, all Calgon WPM) (HAAFP results for the 50 mg/L test of Southerly WWT Center not included [data out of control]) *(Kranser et al., 2007)*



- Samples are from secondary effluent
- PAC contact time is 3 hr.

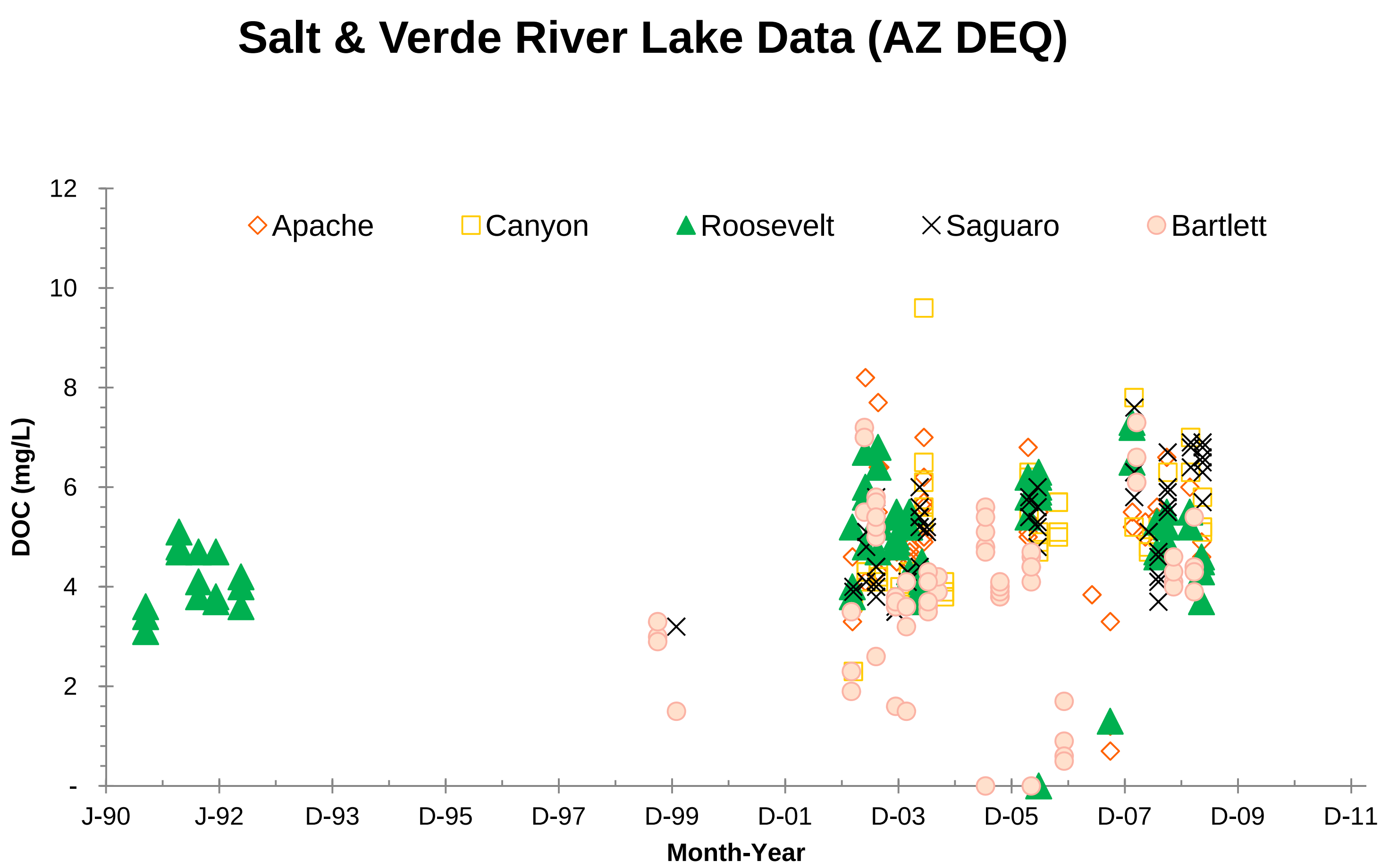
Building Long-Term Datasets from Multiple Sources

Linking data is an increasing opportunity/challenge within scientific communities

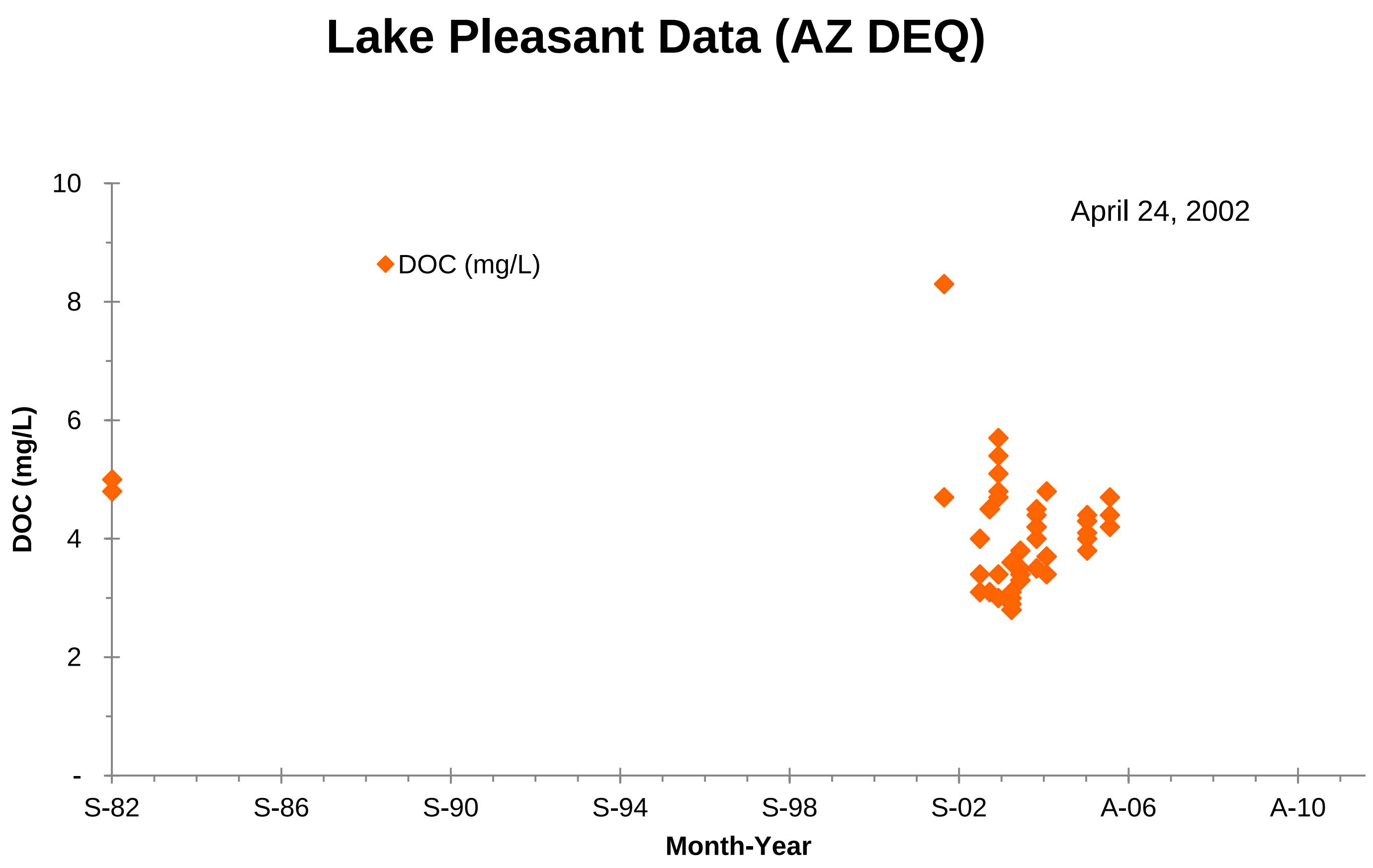
We want to start with our water supply – it has been fascinating

We want your help to expand our dataset

Example Data

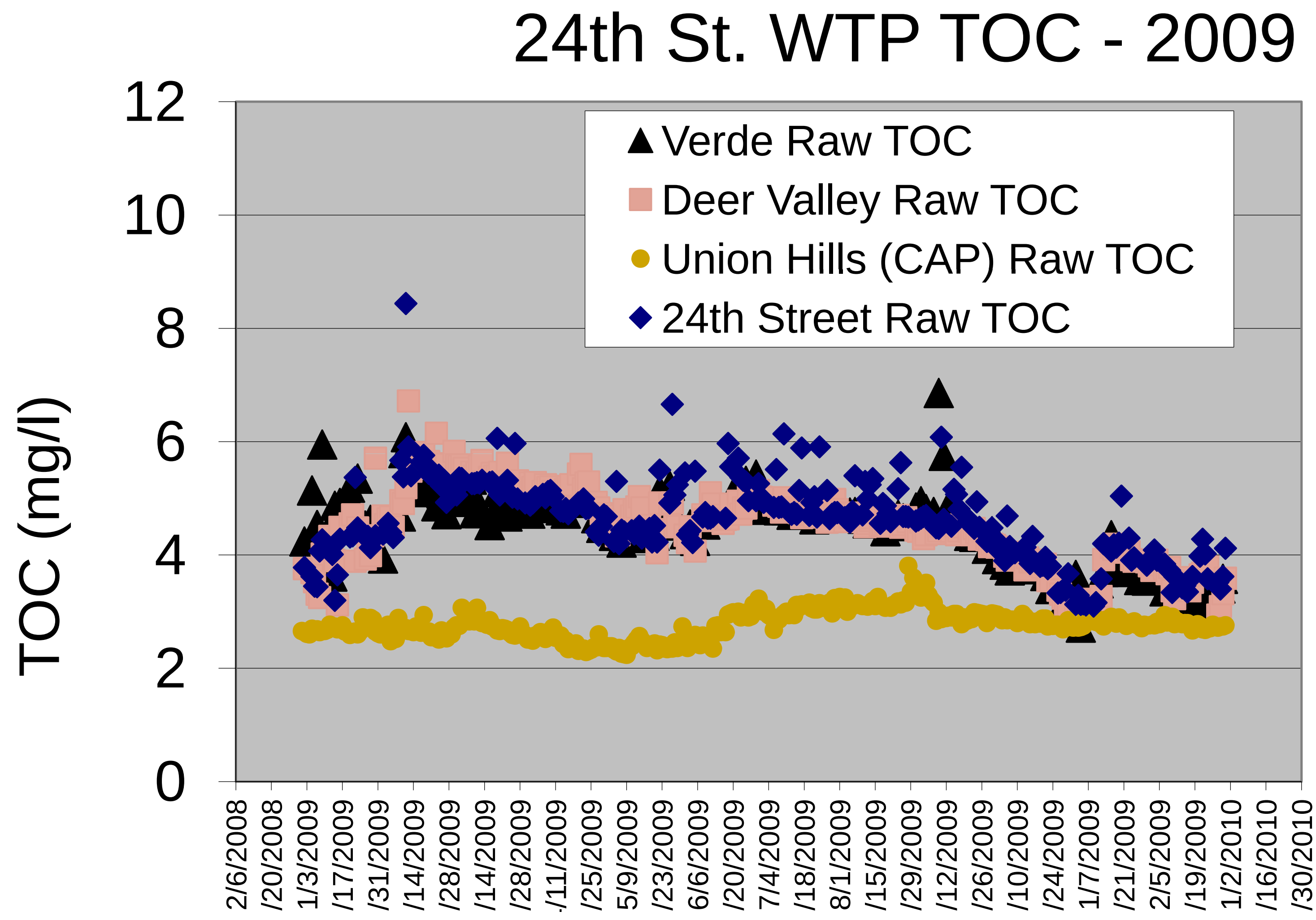


We want to include all CAP data too

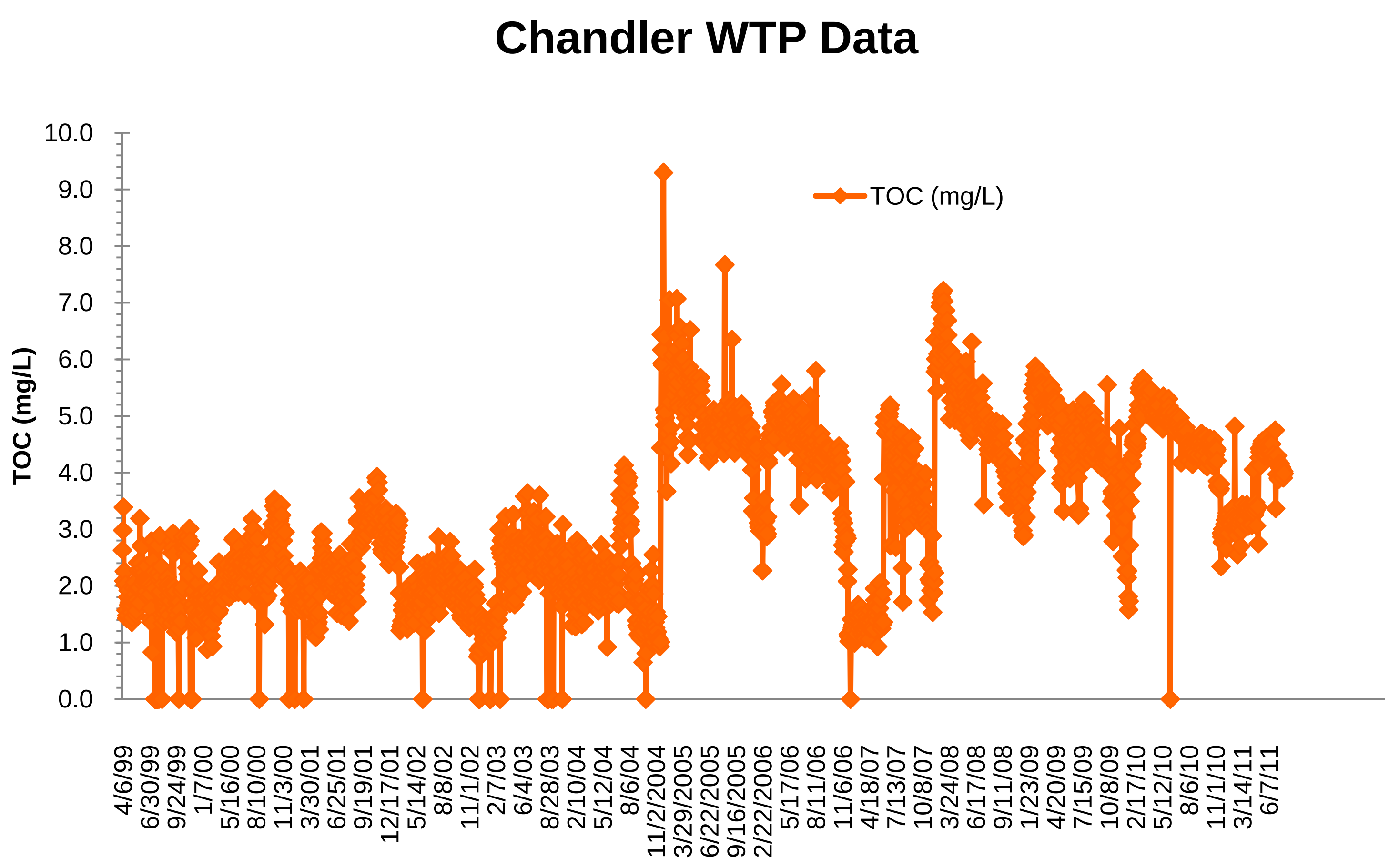


Mesa CAP Plant sees large increases in operational chemical costs seasonally despite similar bulk water qualities – why?

Treatment plants have this type of data For how many years is it electroncially available?



If cities have data – Should our project continue to measure this at each WTP?



Discussion

- 10 years ago TOC data was not measured as frequent as today – it would seem we can streamline canal sampling if this type of data is being collected and focus on the watershed?
- We could instead focus on molecular weight changes for example
- What type of Organic matter data over time would help your facilities?

General Discussion

- We plan to continue lake monitoring – as that is the most requested information
- We plan to continue MIB/Geosmin monitoring
- What other monitoring is critical for you?
- Is anyone using S::can and should we get it into the monitoring network?
- With a gradual shift towards GAC what issues are you having?
- What would you like to see us initiate and eventually seek outside funding?
- Open floor….