Regional Water Quality NEWSLETTER

DATE: Report for May 2013
A Tempe, Glendale, Peoria, Chandler, Phoenix, ADEQ, CAP, SRP, Epcor
ASU Regional Water Quality Partnership

http://enpub.fulton.asu.edu/pwest/tasteandodor.htm

SUMMARY: EVALUATION AND RECOMMENDATIONS

1. MIB and geosmin levels are < 10 ng/L everywhere, even for Chandler WTP which had been experiencing high geosmin levels for the past several months.
2. Drought conditions are setting in. Lake Powell on the Colorado River, which stores water for Arizona and the CAP canal, is at 47% full. Total inflows for the water year 2013 are only at 47% of average and 53% of last years higher inflows. Rivers feeding Lake Powell also have reduced streamflows.
3. Our team recently performed a round-robin of analytical measurements of Sucralose with 5 labs through the southwestern USA. Sucralose is an artificial sweetener and is being used as a wastewater tracer. The average concentration of sucralose in wastewater effluent was around 50,000 ng/L (50 ug/L), which is far higher than pharmaceuticals. Sucralose is quite persistent in the environment and we recommend it as a tracer.
4. SRP awarded our team a project to map out potential forest fire zones in Arizona that may impact our drinking water supply. As a start to this work, included is a description of how past extreme events have impacted our drinking water.

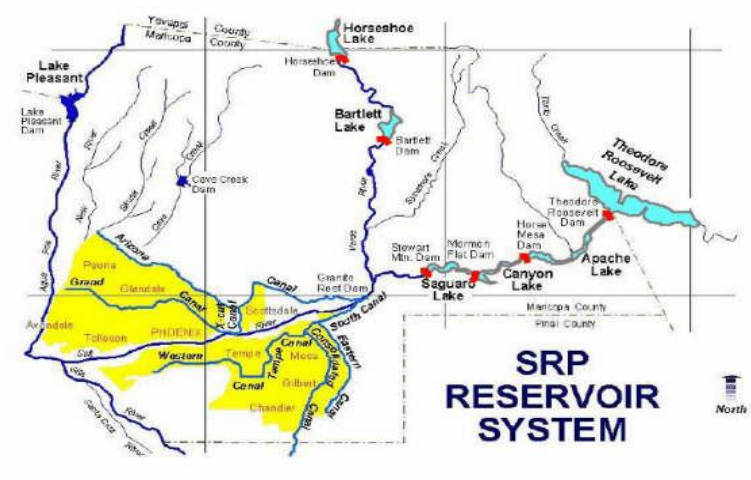
Quick Update of Water Supplies for May 2013
(during day of sampling – May 6th)

Source	Trend in supply	Discharge to water supply system	Flow into SRP Canal System	Dissolved organic carbon Concentration (mg/L) **
Salt River	Reservoirs at 62% full	165 cfs	600 cfs into **Arizona Canal**	4.0 mg/L
Verde River	Reservoirs At 68% full	625 cfs	343 cfs into **South Canal** **(77% Verde River Water)**	4.1 mg/L
Colorado River	Lake Pleasant is full (Lake Powell is 47% full)	Lake Pleasant is filling water into the CAP canal	188 cfs of **CAP water** into Arizona Canal	2.8 mg/L
Groundwater	Generally increasing due to recharge	371 cfs pumping by SRP	371cfs **Groundwater Pumping** into SRP Canals	0.5 to 1 mg/L

*Concentration of these taste and odor compounds in the upper [lower] levels of the terminal reservoir (Saguaro Lake on the Salt River; Bartlett Lake on the Verde River; Lake Pleasant on the CAP system

**Concentration of DOC in the terminal reservoir
*** On paper cities are receiving CAP water in the SRP canals, but as a method of "paying back" from the last drought for excess CAP deliveries – SRP is delivering wet water only from the Salt and Verde Rivers
Data from the following websites:

- http://www.srpwater.com/dwr/
- http://www.cap-az.com/index.php/departments/water-operations/lake-pleasant
- http://lakepowell.water-data.com/



CAP
CENTRAL ARIZONA PROJECT

DATE: May 6, 2013

TO: Distribution

FROM: Brian Henning, CAP Water Control Manager

SUBJECT: Summer 2013 Lake Pleasant Operating Plan

CAP's summer 2013 operating strategy will be similar to the last two years. In an effort to maximize CAP's energy resources, releases will begin in May and continue into September. In previous years, CAP avoided Lake Pleasant releases in September altogether to avoid water quality problems. However, experience has shown we can continue releases until Mid-September without issue.

In order to supply customers with the best quality water, CAP's operational strategy will be to make all releases exclusively from the lower gates all summer. Refilling of Lake Pleasant will begin around October 1. The lake level is projected to drop from elevation 1687 to elevation 1641 by the end of September.

The operating plan is to continuously pump from the west end of the CAP system, supplementing Lake Pleasant releases with pass-through pumping of Colorado River water. About 500 cfs of Colorado River water may be blended with Lake Pleasant releases. Pumping operations may change based on energy market conditions. The west end pumping may be reduced and Lake Pleasant releases may be increased for short periods of time between June and the end of summer, so the two water sources may be blended in varying amounts. For the benefit of our M&I users, treatment plants will be given as much advance notice as possible of all changes in water sources.

CAP maintenance at the west pumping plants will not affect pass-through pumping this summer. Half-plant outages are scheduled for early July through August.

CAP Operations will notify customers of any unscheduled changes as early as possible, so I hope this summer's operation will bring no surprises. If you have any further questions, you may contact me at (623) 869-2567, or Doug Crosby at (623) 869-2426.

Dissolved Organic Carbon In Reservoirs and Treatment Plants

DOC = Dissolved organic carbon
UV254 = ultraviolet absorbance at 254 nm (an indicator of aromatic carbon content)
SUVA = UV254/DOC
TDN = Total dissolved nitrogen (mgN/L)

Due to equipment issues – this month we only have UV254 data

Reservoir Samples

Table 4 - Reservoir Samples – May 7, 2012

Sample Description	Location	UV254 (1/cm)
Havasu (April)		0.054
Lake Pleasant (April)	Epilimnion	0.049
	Hypolimnion	0.048
Verde River	@ Tangle	0.069
Verde River	@ Beeline Hwy	0.102
Bartlett Reservoir	Epilimnion (15')	0.156
	30'	0.148
	Hypolimnion (60')	0.161
	90'	0.131
	120'	0.119
	150'	0.109
Saguaro Lake	Epilimnion (15')	0.079
	Epi - Duplicate	0.079
	30'	0.084
	Hypolimnion (60')	0.075
	75'	0.074
	90'	0.069
Salt River	@ Blue Point Bridge	0.067

Table 5 - Upper Reservoir Quarterly Samples – May 8, 2013
Samples are listed in upstream to downstream order

Sample Description	Location	UV254 (1/cm)
Roosevelt	Epilimnion	0.097
	Hypolimnion	0.088
	Epilimnion	0.089
	Hypolimnion	0.072
Apache	Epilimnion	0.068
	Hypolimnion	0.063
	Epilimnion	0.065
	Hypolimnion	0.062
Canyon	Epilimnion	0.078
	Hypolimnion	0.081
	Epilimnion	0.080
	Hypolimnion	0.076
Saguaro Lake	Epilimnion	0.079
	Epi - Duplicate	0.079
	Hypolimnion	0.075

Organic Matter in Canal

Table 3 - Rivers and Canals – May 6, 2013

Sample Description	UV254 (1/cm)
Waddell Canal	0.048
Anthem WTP Inlet	0.048
Union Hills Inlet	0.045
CAP Salt-Gila Pump Station (January)	0.052
CAP Mesa Turnout (January)	0.050
CAP Canal at Cross-connect	not accessible
Salt River @ Blue Pt Bridge	0.067
Verde River @ Beeline	0.102
AZ Canal above CAP Cross-connect	0.093
AZ Canal below CAP Cross-connect	0.073
AZ Canal at Highway 87	0.075
AZ Canal at Pima Rd.	0.077
AZ Canal at 56th St.	0.077
AZ Canal - Central Avenue	0.082
AZ Canal - Inlet to Glendale WTP	0.072
AZ Canal - Inlet to GreenwayWTP	0.072
South Canal below CAP Cross-connect	0.000
Head of the Tempe Canal	0.071
Tempe Canal - Inlet to Tempe's South Plant	0.030
Head of the Consolidated Canal	0.070
Middle of the Consolidated Canal	0.052
Chandler WTP – Inlet	0.052

Organics at the Water Treatment Plants

Table 2 - Water Treatment Plants – May 6, 2013

Sample Description	UV254 (1/cm)
Union Hills Inlet	0.045
Union Hills Treated	0.030
Tempe North Inlet	0.079
Tempe North Plant Treated	0.049
Tempe South Inlet	0.030
Tempe South Plant Treated	0.017
Greenway WTP Inlet	0.072
Greenway WTP Treated	0.035
Glendale WTP Inlet	0.072
Glendale WTP Treated	0.035
Anthem WTP Inlet	0.048
Anthem WTP Treated	0.046
Chandler WTP Inlet	0.052
Chandler WTP Treated	0.034

Taste and Odor

MIB, Geosmin and Cyclocitral are compounds naturally produced by algae in our reservoirs and canals, usually when the water is warmer and algae are growing/decaying more rapidly. They are non toxic, but detectable to consumers of water because of their earthy-musty-moldy odor. The human nose can detect these in drinking water because the compounds are semi-volatile. Since compounds are more volatile from warmer water, these tend to be more noticable in the summer and fall. The human nose can detect roughly 10 ng/L of these compounds. Our team collects samples from the water sources and raw/treated WTP samples. We usually present all the data when concentrations start to exceed 5 ng/L.

- Data for this month on the next pages. MIB and geosmin levels are very low now. As the water warms and sunlight hours increase, MIB levels in the lakes near the surface are beginning to increase.
- We are now sampling a few residences for MIB and Geosmin. In Tempe, on the ASU campus the MIB and geosmin levels are < 2 ng/L. This sampling will be in line with better understanding what customers are really observing.
- This is a HUGE change for the Consolidated canal and Chandler WTP, which had been experiencing very high geomsin levels (see graph below) since January. There are still 15 groundwater wells operating along the Consolidated Canal above the WTP, but geosmin levels have dropped to nearly zero. We thought this might be associated with a return flow canals from the Eastern Canal, but working with Chandler we never were exactly able to identify the culprit source of geosmin this winter. This month additional samples were collected from a residence in Chandler of a person complaining of T&O issues. The MIB & Cyclocitral concentrations inside/outside the house were < 2 ng/L. The geosmin concentrations were 2.3 ng/L inside the house (5 ng/L outside the house). Either this consumer is very sensitive, or the T&O issue was from other compounds.

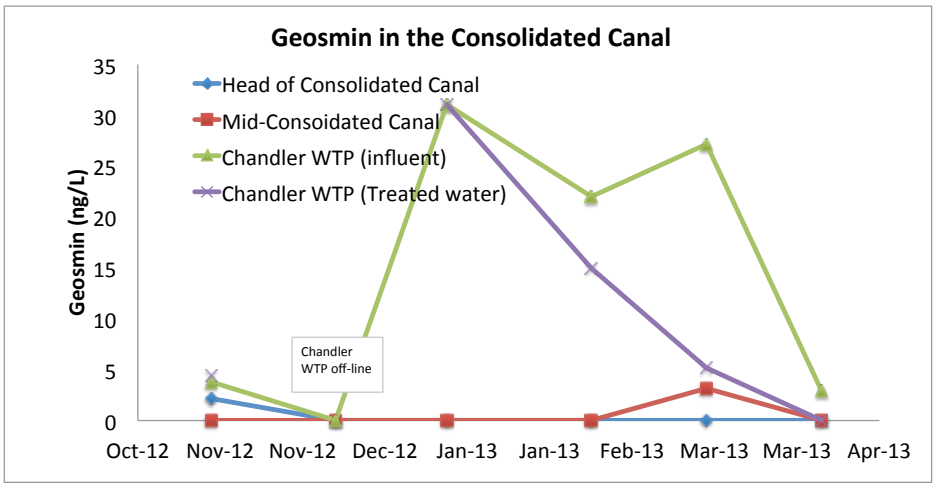


Table 2 - Water Treatment Plants – May 6, 2013

Sample Description	MIB (ng/L)	Geosmin (ng/L)	Cyclocitral (ng/L)
Union Hills Inlet	<2.0	<2.0	<2.0
Union Hills Treated	<2.0	<2.0	<2.0
Tempe North Inlet	<2.0	<2.0	<2.0
Tempe North Plant Treated	2.5	<2.0	<2.0
Tempe South WTP	<2.0	<2.0	<2.0
Tempe South Plant Treated	<2.0	<2.0	<2.0
Anthem Inlet	<2.0	<2.0	<2.0
Anthem Treated	<2.0	<2.0	<2.0
Chandler Inlet	<2.0	6.1	<2.0
Chandler Treated	<2.0	3.3	<2.0
Greenway WTP Inlet	2.1	24.1	<2.0
Greenway WTP Treated	<2.0	<2.0	<2.0
Glendale WTP Inlet	<2.0	<2.0	<2.0
Glendale WTP Treated	<2.0	<2.0	<2.0

Table 3 - Canal Sampling – May 6, 2013

System	Sample Description	MIB (ng/L)	Geosmin (ng/L)	Cyclocitral (ng/L)
CAP	Waddell Canal	<2.0	<2.0	<2.0
	Union Hills Inlet	<2.0	<2.0	<2.0
	CAP Canal at Cross-connect			
AZ Canal	Salt River @ Blue Pt Bridge	2.4	<2.0	<2.0
	Verde River @ Beeline	3.0	<2.0	<2.0
	AZ Canal above CAP Cross-connect	2.7	<2.0	<2.0
	AZ Canal below CAP Cross-connect	<2.0	<2.0	<2.0
	AZ Canal at Highway 87	2.2	<2.0	<2.0
	AZ Canal at Pima Rd.	2.0	<2.0	<2.0
	AZ Canal at 56th St.	<2.0	<2.0	<2.0
	AZ Canal - Central Avenue	2.1	<2.0	<2.0
	AZ Canal - Inlet to Glendale WTP	<2.0	<2.0	<2.0
	Head of the Consolidated Canal	2.1	<2.0	<2.0
	Middle of the Consolidated Canal	2.0	<2.0	<2.0
South Tempe Canals	South Canal below CAP Cross-connect	2.6	<2.0	<2.0
	Head of the Tempe Canal	2.3	<2.0	<2.0
	Tempe Canal - Inlet to Tempe's South Plant	<2.0	<2.0	<2.0
	Mesa Turnout (April)	<2.0	<2.0	<2.0
	Salt-Gila Pump (April)	<2.0	<2.0	<2.0

Table 4 - Reservoir Samples – May 7, 2013

Sample Description	Location	MIB (ng/L)	Geosmin (ng/L)	Cyclocitral (ng/L)
Lake Pleasant (April)	Eplimnion	**<2.0**	**<2.0**	**<2.0**
Lake Pleasant (April)	Hypolimnion	**2.2**	**<2.0**	**<2.0**
Verde River @ Beeline		**3.0**	**<2.0**	**<2.0**
Bartlett Reservoir	Epilimnion	**8.8**	**9.6**	**<2.0**
Bartlett Reservoir	Epi-near dock	**8.8**	**11.6**	**<2.0**
Bartlett Reservoir	Hypolimnion	**<2.0**	**<2.0**	**<2.0**
Salt River @ BluePt Bridge		**2.4**	**<2.0**	**<2.0**
Saguaro Lake	Epilimnion	**2.6**	**<2.0**	**<2.0**
Saguaro Lake	Epi - Duplicate	**2.1**	**<2.0**	**<2.0**
Saguaro Lake	Epi-near dock	**2.5**	**<2.0**	**<2.0**
Saguaro Lake	Hypolimnion	**<2.0**	**<2.0**	**<2.0**
Lake Havasu (April)		**<2.0**	**<2.0**	**<2.0**
Verde River at Tangle Creek (April)		**<2.0**	**<2.0**	**<2.0**
Roosevelt at Salt River Inlet (April)		**<2.0**	**<2.0**	**<2.0**

Quarterly Lake Sampling - May 8, 2012

Sample Description	Location	Location	MIB (ng/L)	Geosmin (ng/L)	Cyclocitral (ng/L)
Roosevelt Lake	Site 1	Eplimnion	2.9	<2.0	<2.0
Roosevelt Lake	Site 1	Hypolimnion	<2.0	<2.0	<2.0
Roosevelt Lake	Site 2	Eplimnion	<2.0	<2.0	<2.0
Roosevelt Lake	Site 2	Hypolimnion	<2.0	<2.0	<2.0
Apache Lake	Site 1	Eplimnion	4.3	<2.0	<2.0
Apache Lake	Site 1	Hypolimnion	<2.0	<2.0	<2.0
Apache Lake	Site 2	Eplimnion	2.0	<2.0	<2.0
Apache Lake	Site 2	Hypolimnion	<2.0	<2.0	<2.0
Canyon Lake	Site 1	Eplimnion	4.3	5.2	<2.0
Canyon Lake	Site 1	Hypolimnion	<2.0	<2.0	<2.0
Canyon Lake	Site 2	Eplimnion	3.1	<2.0	<2.0
Canyon Lake	Site 2	Hypolimnion	2.3	<2.0	<2.0

Pharmaceuticals and Human Tracers

Our team recently performed a round-robin of analytical measurements of Sucralose with 5 labs through the southwestern USA. Sucralose is an artificial sweetener and is being used as a wastewater tracer. The average concentration of sucralose in wastewater effluent was around 50,000 ng/L (50 ug/L), which is far higher than pharmaceuticals. Sucralose is quite persistent in the environment and we recommend it as a tracer. The methods we use now for sucralose are a direct injection into a LC/MS instrument, which reduces the time involved in solid phase extraction sample preparation, but also reduces interferences from other organics in the extracts. This is especially important for sucralose because it can be difficult to ionize. Of course, we practice isotope dilution during these measurements to get good data too. If you are interested in learning more, please let us know. We are measuring Sucralose on our quarterly lake samples. (additional data and details are in Appendix A)

Impact of Extreme Climate Events on Water Quality: a case study of dissolved organic carbon in the Phoenix Metropolitan Water Supply

Climate change potentially leads to increased periods of drought, heavy precipitation events, and increased water temperatures. The dry climate and extremes in weather events associated with the Southwestern U.S. (drought, flash floods, forest fires, etc.) provide an opportunity to evaluate the impact of climate change on water quality at a large scale. The dissolved organic carbon (DOC) concentration in the three main water supplies for the Phoenix metropolitan area (Salt River, Verde River, and Colorado River via the Central Arizona Project (CAP)) was monitored from 1999 to 2010.

Monthly water samples from both the epilimnion and hypolimnion of each reservoir were collected and analyzed for a range of characteristics including dissolved organic carbon (DOC) concentration. The fluctuations in DOC over this 11 year period were examined in relation to weather events. Combining historic water quality data with stream gauge flows monitored by the USGS using a carbon mass balance model illustrated the impact of spring runoff following unusually heavy winter snowpack and extreme weather events (drought, monsoons, first flush and forest fires) on DOC concentration. Understanding the changes in concentration and type of DOC associated with extreme weather events will help water treatment plant operators to better anticipate, prepare for and treat impacted water.

Additionally, as climate change continues to progress, concern over long periods of droughts and/or flash flooding may lead to construction of additional reservoirs to supplement water supplies and attenuate flooding. Each of the source water systems for Phoenix includes a uniquely operated terminal reservoir just upstream of the metropolitan area. The differences in these reservoirs provide further insight into the impacts of reservoir operation on the impacts of climate change to water quality. The Bartlett Lake reservoir located along the Verde River operates most similarly to a natural lake system, with river water and a smaller upstream reservoir with a low hydraulic retention time and was most strongly impacted by extreme weather events. The CAP Lake Pleasant reservoir was less impacted because it is operated as an offline reservoir with inflow and outflow primarily controlled by the CAP. The Saguaro Lake is a terminal reservoir of a series of reservoirs utilized for hydroelectric generation and includes recirculated water pumped for Saguaro Lake to preceding reservoirs. It's longer HRT provided the clearest attenuation weather-caused DOC concentrations.

3.1 Results and Discussion

3.3.1 Organic Matter Trends in Major Reservoirs of Arizona

The variations of DOC concentrations are plotted against time in Figure 3.2. The difference is long term trends of DOC concentrations in these three reservoirs during the study period from 1999 to 2010, the yearly average DOC in Saguaro Lake increased from 3 mg/L to 5 mg/L with two higher levels observed in 2005 and 2008 (yearly average DOC = 5.7 and 5.5 mg/L, respectively). In terms of seasonal variation, the average DOC concentration was 5.0 ± 0.4 mg/L during May to October and was 4.5 ± 0.2 mg/L during November to April. UVA254 absorbance varied from 0.084 to 0.099 within a year. The yearly variation of DOC in Saguaro Lake was less than observed in other reservoirs (Figure 3.2a), which can be attributed to the hydrological management and operational mode of multiple-lake system for Salt River leading to longer retention times and DOC stability (i.e. impact of extreme events were attenuated).

In contrast the long-term DOC trend in Bartlett Lake showed a strong variation and the average DOC increased from 2 mg/L to 4 mg/L over the last ten years (Figure 3.2b). With respect to seasonal variation, the average DOC concentration varied little (3.6 ± 0.3 mg/L May to October and 3.3 ± 0.4 mg/L November to April). UVA254 absorbance varied from 0.07 to 0.13 within a year. In 2003, 2005, 2008, and 2010, high DOC concentrations and variation were observed.

For Lake Pleasant, the yearly averaged DOC showed some increase from 3 to 3.8 mg/L over the study period with less yearly variation than Bartlett Lake(Figure 3.2c). The average DOC concentration Showed slight seasonal variation from 3.8 ± 0.2 mg/L (May to October) to 3.4 ± 0.1 mg/L (November to April). UVA254 absorbance varied from 0.05 to 0.06 within a year. High DOC concentrations were measured in 2003 and 2005. The relatively stable DOC concentrations in Lake Pleasant are likely due to the relatively long hydraulic residence time (400 days) as well as its operation as off-stream reservoir (i.e. not subject to the same impact of extreme weather events on water quality of in-line reservoirs/natural lakes).

The temporal pattern of inflows and DOC concentrations into each reservoir on an average monthly basis are presented in Figure 3. 3. The highest inflow to Bartlett Lake occurred during January to March of each year and accounted for 55% of yearly inflow. The highest DOC concentrations followed in March and June (~ 4 mg/L) most likely based on increased algal activity during the warmer months and with the increased nutrients brough in by the previous increased flows (Figure 3.3a). As a terminal reservoir, the impact of spring runoff on DOC and even inflow on water quality at Saguaro reservoir would be expected to be highly attenuated. However, increased releasing from upstream reservoir to meet summer power demands resulted in the main inflow during a year was occurring during late spring to early fall (June to August) (Figure 3.3b). DOC followed a similar trend with the highest average monthly concentration of 5.5 mg/L in June. There was very low inflow to Lake Pleasant during summer when water is typically released into the CAP canals, and the highest inflows from November to February (Figure 3.3c). The highest DOC concentrations were again observed during summer. However, the concentrations were fairly constant compared with the inline reservoirs. . The DOC concentrations increased during summer in all three reservoirs. In contrast, the UVA254 absorbance and SUVA values were low during summer and tended to increase at the beginning of the year; for all three reservoirs. Regression analyses using DOC, UVA254, or SUVA values as a function of logarithmic transformed inflow for the three reservoirs showed poor relationships for most of the combinations. However, for Bartlett Lake, a strong correlation ($R^2 = 0.74$; slope = 1.3) was found between SUVA value and log inflow; indicating that Bartlett Lake inflows during spring runoff bring in significant amount of terrestrial DOM (as evidenced by SUVA values).

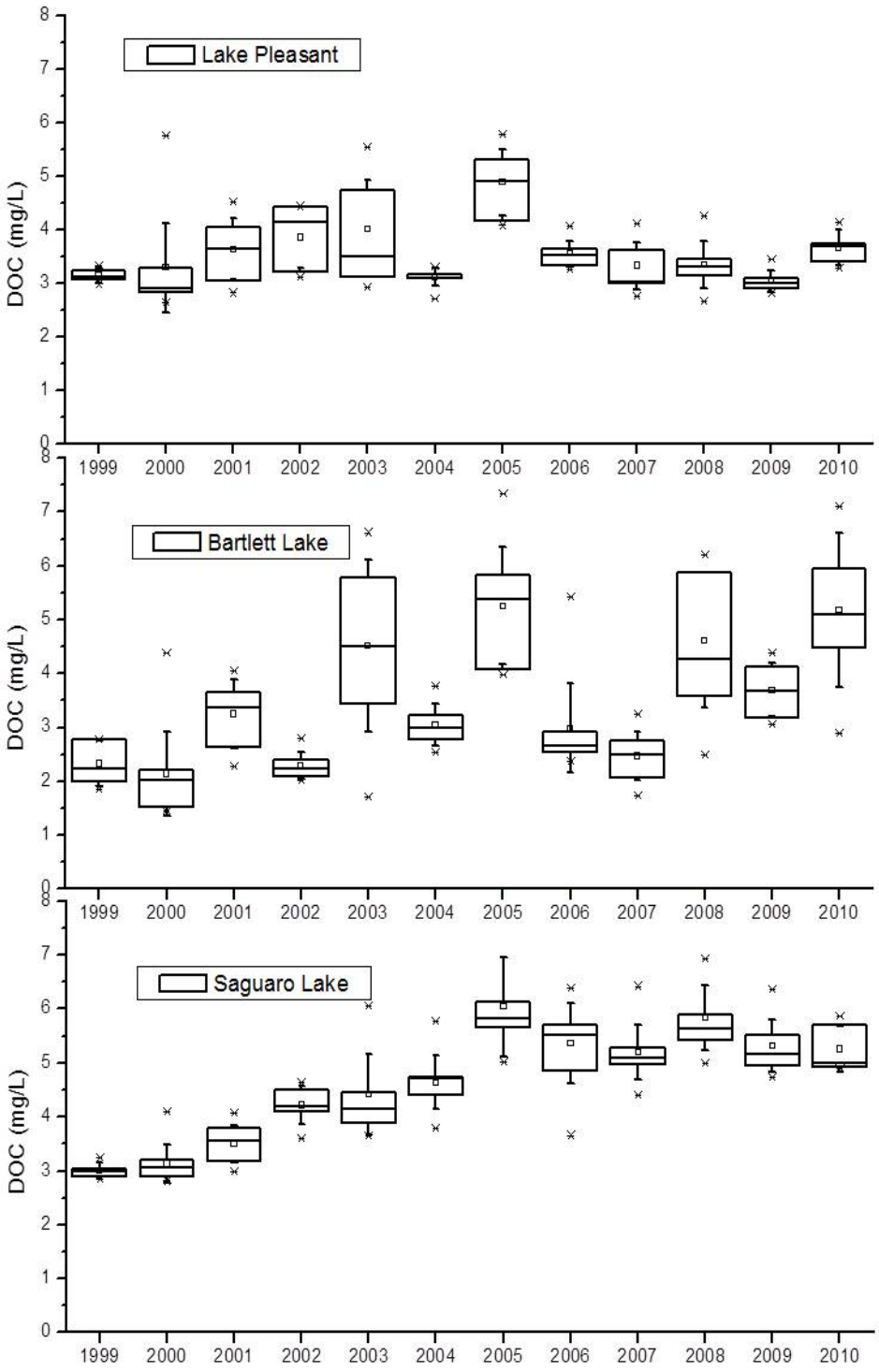


Figure 3. 1 Long-term DOC concentration variations of three reservoirs during study period (1999 to 2010).

Appendix A
Round-Robin Summary

1.0 Introduction

The goal of the analysis was to assess the variability of sucralose measurements within wastewater effluent. Previously reported sucralose values within the U.S. range from 2,800 to 40,000 ng/l. The study site was City of xxx, an advanced 18 MGD treatment facility. Treatment includes … The effluent is discharged to two recharge sites and the Salt River. Final effluent samples were collected and shipped on March 5th. Due to the range of analytical methods of the participants, the samples were not pre-treated. In response to sucralose previously being measured at Xxx WWTP an order of magnitude lower than other published WW effluents, a spiked sample was added. Each of the five participants analyzed two samples; (1) xxx WWTP Eff and (2) Xxx WWTP Eff + Spike. The following summary will detail the results of the round-robin analysis.

2.0 Participants

- Confidential for now
-

3.0 Methods

3.1 Analytical Methods across Participants

To maintain confidentiality, the above participants will be assigned number-ID's randomly. The table below displays the analysis performed by each lab. Lab #2 reported results for two different methods. Several labs provided details regarding sample preparation and analysis, this information can be found in the appendix.

Table 1: Analytical Methods

Lab-ID	Type of Analysis
1	LC/MS-MS by Direct Injection (ESI Negative)
2_1	LC/MS-MS by SPE (ESI Positive)
2_2	LC/MS-MS by Direct Injection (ESI Positive)
3	LC/MS-MS by SPE
4	LC/MS-MS by SPE (ESI Positive)
5	LC/MS-MS by Direct Injection (ESI Positive)

3.2 Evaluation

Results were evaluated according to ISO 5725-2 "Accuracy (trueness and precision) of measurement method and results." Due to the low number of samples all no samples were excluded from the results, therefore tests were not conducted to test for consistent bias or high variances. Repeatability standard deviation (S_r), standard deviation between laboratories (S_L) and reproducibility standard deviation (S_R) were calculated from the mean squares within group (MSW) and mean squares between groups (MSB). MSW and MSB were calculated using one-way analysis of variance (ANOVA). Reported results should be taken with caution due to the low number of samples involved in the analysis between groups (N=2 for each lab).

4.0 Results

4.1 Average Sucralose Concentration by Lab

Figure 1: Xxx WWTP Effluent

Figure 2: Xxx WWTP Effluent + Spike

4.2 Overall Sucralose Trends

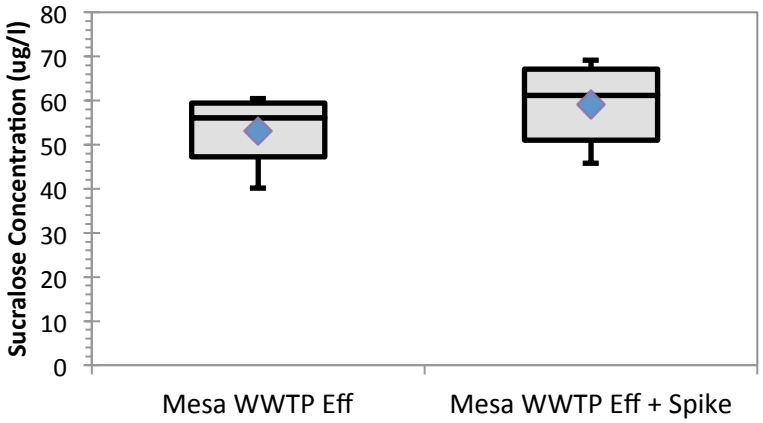


Figure 3

Legend: top and bottom of box= 75th and 25th percentiles respectively; top and bottom of whisker = 90th and 10th percentiles respectively; line across inside of box= median(50th percentile).

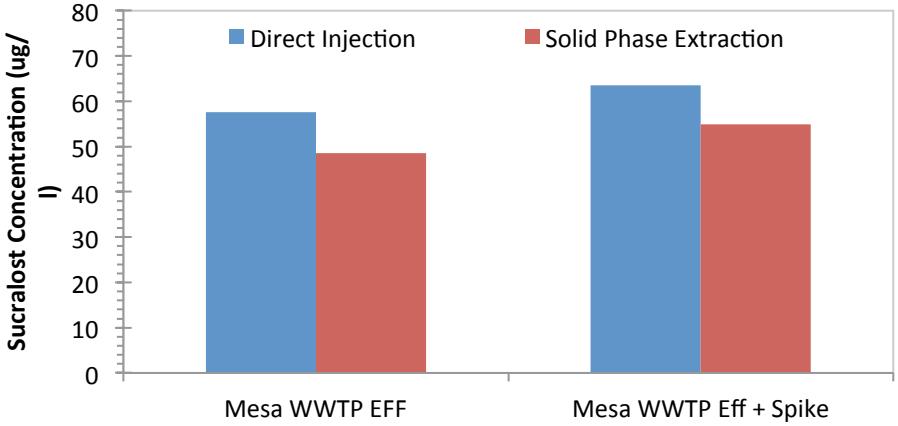


Figure 4

4.3 Repeatability, between-laboratory standard deviation and reproducibility

Table 2: Repeatability and Reproducibility (all participants)

	S_r (ug/l)	S_L (ug/l)	S_R(ug/l)
Xxx WWTP Eff	1.5	6.7	6.9
Xxx WWTP Eff + Spike	1.6	8.1	8.2

Table 3: Repeatability and Reproducibility (omitting datasets outside of ± 1 St Dev)

	S_r (ug/l)	S_L (ug/l)	S_R(ug/l)
Xxx WWTP Eff	1.7	4.5	4.8
Xxx WWTP Eff + Spike	1.7	6.3	6.5

Appendix: Detailed Lab

LAB 1

ANALYTICAL METHOD FOR SUCRALOSE BY LC/MS/MS USING DIRECT INJECTION

SUMMARY OF METHOD

Filtered (0.45 μm) water samples are injected directly onto a 2.0 mm C18 reversed phase HPLC column equipped with a 2.0 mm C18 guard column. The mass spectrometer is operated under electrospray negative ion mode. Sucralose is identified by matching both the retention time and the MS/MS transition in the samples with those in authentic standards. The tentative minimum reporting limit is 0.2 μg/L (200 ng/L).

I. Autosampler

HTC PAL autosampler from Leap Technologies is used. Injection volume is 50 μL.

II. LC parameters

Agilent 1100 LC system is used. The analytical column is Phenomenex Luna C18 (2) column (150 x 2 mm, 5 μm particle size). The guard column is Phenomenex C18 (4 x 2.0 mm). The LC gradient is shown in Table 1. Solvent A is 0.05% formic acid (v/v) in 90% water: 10% MeOH. Solvent B is 0.05% formic acid (v/v) in MeOH. The column is kept at ambient temperature.

Table 1. LC Gradient

Time (min)	Solvent A	Solvent B	Flow Rate (μL/min)
5.00 (equilibration)	100	0	400
0.00	100	0	400
1.00	100	0	400
1.50	30	70	400
1.51	30	70	400
11.00	0	100	400
13.00	0	100	400
13.50	100	0	400
14.00	100	0	400

III. MS parameters

AB/SCIEX API 4000 triple quadrupole MS/MS system is used in the electrospray negative ion mode. The instrument operating conditions are listed in Table 2. The precursor/product ion pairs for sucralose and sucralose-d_6, and the retention times are listed in Table 3. Sucralose is identified by matching both the retention time and MS/MS transition in the samples with those in authentic standards.

Table 2. MS/MS Instrument Operating Conditions.

Collision gas	6 psi
Curtain gas	20 psi
Ion source gas 1	50 psi
Ion source gas 2	50 psi
Ion spray voltage	-4500 V
Temperature	550°C
Entrance potential	10 V

Table 3. Compound-Dependant Parameters for Sucralose.

Compound	Retention Time (min)	Precursor Ion	Product Ion	Declustering potential	Collision energy	Collision cell exit potential
Sucralose	4.77	395	359	-85	-14	-11
Sucralose-d_6	4.77	401	365	-75	-15	-8

LAB 2

METHODS OF ANALYSIS

Direct Injection Analyses. An internal standard (Carbamazpine d-10) was added to 125 mL of each water sample. One milliliter of each sample was transferred to glass vials and an aliquot of 100 µL was directly injected onto the triple quadrupole instrument and analyzed by the method described below.

Sample Extraction (SPE). An off-line SPE was used for the pre-concentration of the water samples. All the extraction experiments were performed using an automated sample preparation with extraction columns system (GX-271 ASPEC, Gilson, Middleton, WI, USA) fitted with a 25-mL syringe pump for dispensing the water samples through the SPE cartridges. Water samples were extracted with Oasis HLB cartridges (200 mg, 6mL) obtained from Waters (Milford, MA, USA). The cartridges were conditioned with 4 ml of methanol followed by 6 ml of HPLC-grade water at a flow rate of 1 ml/min. The water samples (100mL) were loaded at a flow rate of 10 mL/min. Elution of the analytes from the cartridge was carried out with 6 mL of methanol. The solvent was evaporated to 0.5-mL with a stream of nitrogen at a temperature of 45 ºC in a water bath using a Turbovap concentration workstation (Caliper Life Sciences, Mountain View, CA, USA). The samples were transferred to vials and analyzed by LC/MS-MS.

Mass spectrometry analyses (LC/MS-MS). The separation of the water extracts was carried out using an HPLC system (consisting of vacuum degasser, autosampler and a binary pump) (Agilent Series 1290, Agilent Technologies, Santa Clara, CA, USA) equipped with a reversed phase C_{18} analytical column of 50 mm x 2.1 mm and 1.8 µm particle size (Zorbax Eclipse Plus). Column temperature was maintained at 25 ºC. The injected sample volume was 15 µL. Mobile phases A and B were acetonitrile and water with 0.1% acetic acid, respectively. The optimized chromatographic method held the initial mobile phase composition (10% A) constant for 1.7 min, followed by a linear gradient to 100% A after 10 min. The flow-rate used was 0.4 mL/min. A 4-min post-run time was used after each analysis. This HPLC system was connected to a triple quadrupole mass spectrometer Model 6460 Agilent (Agilent Technologies, Santa Clara, CA, USA) equipped with electrospray Jet Stream technology operating in positive ion mode, using the following operation parameters: capillary voltage: 4000 V; nebulizer pressure: 45 psig; drying gas: 10 L/min; gas temperature: 250 ºC; sheath gas flow: 11 L/min; sheath gas temperature: 350 ºC; nozzle voltage: 0. Two transitions were recorded for sucralose (419→221) and (419→239). Collision energy was set at 15V for both transitions. The data recorded was processed with Mass Hunter software (Agilent Technologies).

LAB 4

Sample Preparation

All samples were filtered with 0.7 µm GF/F filters within one week of sample receipt. 50 ml sample was then spiked with an isotopically labeled standard (Sucralose-d6) at a concentration of 200 ng/L in the sample. The samples were then extracted using a Dionex Autotrace. Briefly, 200 mg hydrophilic-lipophilic balance (HLB) cartridges from Waters Corporation (Millford, MA) were first preconditioned with 5 ml of MTBE, followed by 5 ml of methanol and 5 ml of ultrapure water. The 50 mL samples were then loaded onto the cartridge at 15 ml/min, after which the cartridges were rinsed with ultrapure water followed by nitrogen drying for 30 minutes. The analytes were then eluted with 5 ml of methanol followed by 5 ml of 10/90 (v/v) methanol/MTBE solution into 15 ml graduated conical tubes. The eluent was then blown down to less than 100 µl using nitrogen TurboVap from Zymark Corporation (Hopkinton, MA) followed by reconstitution to 1 ml using methanol. This final extract was then transferred to 2-mL autosampler vials for analysis on the instrument.

Sample Analysis

An Agilent 1290 binary pump (Palo Alto, CA) with metal solvent fittings was used for all analyses. The ZORBAX Eclipse Plus reverse phase, rapid resolution HD column (2.1x50 mm) was used to separate analytes in both the positive electrospray ionization (ESI) modes. Two solvents comprising 0.1% formic acid in ultrapure water (A) and 0.1% formic acid in 100% Acetonitrile (B) were used. A flowrate of 400 µl/min was chosen and the gradient run was as follows: 5% B was held for 1.5 min, followed by a linear increase to 20% B at 3 min. Further linear increases to 45% B at 4 min and 65% B at 6.1 min followed. At 7 min, the gradient was linearly increased to 100% organic and held till 7.45 min when it was bought back to the initial condition of 5% B. A post-run time of 1.45 min was performed to allow the column to re-equilibriate. This resulted in a total run-time of 9.90 min for analysis of all the ESI positive analytes. Sucralose was analyzed using an Agilent (Santa Clara, CA) 6460 triple quadrupole mass spectrometer. Two transitions were monitored with the most abundant chosen as the quantifier (419-239) and second transition being a qualifier (419-221). In addition the sucralose d-6 (425-243) was also monitored and both compounds were detected at a retention time of 4.01 min. Data analysis was performed using Agilent Mass Hunter (Ver 5.00) with the isotope dilution method used for quantification of all samples.