REGIONAL WATER QUALITY NEWSLETTER

DATE: Report for October 12, 2006 Samples Collected on October 11, 2006 From the Phoenix, Tempe, Peoria, CAP, SRP – ASU Regional Water Quality Partnership

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

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SUMMARY: EVALUATION AND RECOMMENDATIONS

- 1. MIB and geosmin concentrations are generally < 5 ng/L at the WTPs, but 10-15 ng/L in the reservoirs.
- 2. Bartlett lake remains thermally stratified, which Saguaro is not thermally stratified. There is a possibility for a late season pulse of MIB from Bartlett Lake – however SRP is blending more Salt River water into the canals in order to draw down the water levels in Apache.
- 3. DOC concentrations remain quite high in the SRP system (~ 3 mg/L in Bartlett Lake, 5.8 mg/L in Saguaro Lake) and only slightly lower in the CAP system (~4 mg/L)
- 4. Thanks everyone for a great workshop in September. The slides are posted on our website: <u>http://enpub.fulton.asu.edu/pwest/tasteandodor.htm</u>
- 5. According to SRP: Despite the above normal precipitation during the monsoon, the Valley is in its 11th year of drought.
- 6. At the workshop there was a lot of interest in the antimony leaching from plastic water bottles that municipalities and bottling companies use. So attached is the beginnings of a journal paper we are preparing. Your comments are welcomed. Should your city continue to bottle water in PET plastic bottles?

Table 1 Summary of WTP Operations

	Union Hills	24 th Street WTP	N.Tempe J.G. Martinez	Deer Valley	Greenway WTP	Val Vista	South Tempe	Chandler WTP
Location	CAP	A	Arizona Canal System			South Canal System		
PAC Type and Dose	None	Norit 20B 7ppm (decrease d from 15 ppm due to supply issues)	Norit HDO 14 ppm	Not today	None			
Copper Sulfate	None	None	None	None	None			
PreOxidation	None	None	None	None	Ozone			
Alum Dose Alkalinity pH	12.75 ¹ 127/115 7.0	60 158 6.8	33 ³ 178 7.4	60 103 6.7	30 180 7.3			
WTP Comments								
Raw water DOC % DOC removal ²	17%	34%	23%	30%	35%	33%	22%	
Process recommendations								

¹ Ferric chloride instead of alum
 ² Calculated based upon influent and filtered water DOC
 ³ also adding 3 ppm floc aid

Sample Description	MIB (ng/L)	Geosmin (ng/L)	Cyclocitral (ng/L)
24 th Street WTP Inlet	4.7	2.3	<2.0
24 th Street WTP Treated	4.0	<2.0	<2.0
Deer Valley Inlet	4.5	2.7	3.4
Deer Valley WTP Treated	2.5	2.8	<2.0
Val Vista Inlet	6.2	2.1	<2.0
Val Vista WTP Treated –East	4.9	<2.0	<2.0
Val Vista WTP Treated -West			
Union Hills Inlet	<2.0	<2.0	<2.0
Union Hills Treated	<2.0	<2.0	<2.0
Tempe North Inlet	3.7	2.5	<2.0
Tempe North Plant Treated	2.6	<2.0	<2.0
Tempe South WTP	5.6	<2.0	<2.0
Tempe South Plant Treated	<2.0	<2.0	<2.0
Tempe South Plant Treated (Lab)			
Chandler WTP Inlet			
Chandler WTP Treated	1		
Greenway WTP Inlet	3.2	2.7	<2.0
Greenway WTP Treated	<2.0	<2.0	<2.0

 Table 2 - Water Treatment Plants – October 11, 2006

System	Sample Description	MIB (ng/L)	Geosmin	Cyclocitral
-			(ng/L)	(ng/L)
CAP	Waddell Canal			
	Union Hills Inlet	<2.0	<2.0	<2.0
	CAP Canal at Cross-connect	<2.0	<2.0	<2.0
	Salt River @ Blue Pt Bridge	11.5	3.1	<2.0
	Verde River @ Beeline	4.0	2.6	<2.0
AZ	AZ Canal above CAP Cross-connect	<2.0	<2.0	<2.0
Canal	AZ Canal below CAP Cross-connect	4.1	2.1	<2.0
	AZ Canal at Highway 87	4.1	3.9	6.2
	AZ Canal at Pima Rd.	4.7	3.9	<2.0
	AZ Canal at 56th St.	5.3	2.4	<2.0
	AZ Canal - Inlet to 24 th Street WTP	4.7	2.3	<2.0
	AZ Canal - Central Avenue	4.5	3.4	<2.0
	AZ Canal - Inlet to Deer Valley WTP	4.5	2.7	3.4
	AZ Canal - Inlet to Greenway WTP	3.2	2.7	<2.0
South	South Canal below CAP Cross-connect	5.5	2.3	<2.0
and	South Canal at Val Vista WTP	6.2	2.1	<2.0
Tempe	Head of the Tempe Canal	5.5	2.3	<2.0
Canals	Tempe Canal - Inlet to Tempe's South]		
	Plant	5.6	<2.0	<2.0
	Chandler WTP – Inlet			

 Table 3 - Canal Sampling – October 11, 2006

Table 4 - Reservoir Samples – October 10, 200

Sample Description	Location	MIB (ng/L)	Geosmin (ng/L)	Cyclocitral (ng/L)
Lake Pleasant		CAP will collect samples next week		
Verde River @ Beeline		4.0	2.6	<2.0
Bartlett Reservoir	Epilimnion	13.2	<2.0	<2.0
Bartlett Reservoir	Epi-near dock	10.2	<2.0	<2.0
Bartlett Reservoir	Hypolimnion			
		14.6	<2.0	<2.0
Salt River @ BluePt Bridge		11.5	3.1	<2.0
Saguaro Lake	Epilimnion	18.9	5.8	<2.0
Saguaro Lake	Epi - Duplicate	14.0	5.2	<2.0
Saguaro Lake	Epi-near doc			
		18.6	6.1	<2.0
Saguaro Lake	Hypolimnion			
		10.6	<2.0	<2.0
Verde River at Tangle		<2.0	7.0	<2.0
Havasu				

System	SRP Diversions	САР
Arizona Canal	562	198
South Canal	499	0
Pumping	82	0
Total	1143	198

Table 5 - SRP/CAP OPERATIONS Values in cfs for October 11 2006

SRP is releasing water from both Verde and Salt River Systems. Salt River release from Saguaro Lake: 623 cfs; Verde River release from Bartlett Lake: 429 cfs.

SRP is drawing down Apache Lake – and will continue to use Salt River water released from Saguaro Lake in order to achieve this. Dam repairs/construction will be taking place in Apache Lake.

Canal Dry-up season is coming:

We will be working on portions of the Southside canals from Nov. 17 to Dec. 17 and CANAL WORK STARTS IN NOVEMBER portions of Northside canals from Jan. 5 to Feb. 4. Southside and Northside canals refer to major SRP canals south and north of the Salt River, respectively.

From the SRP Waterways Newsletter (http://www.srpnet.com/water/pdfx/WATERWAYS1006.pdf) :

Rainfall in 2006 has been a tale of contrast. The January-to-May runoff season was the seconddriest in SRP's 103-year history. From June 1 through the end of August, rainfall on the Salt and Verde watershed ranks as the 25th wettest on record, adding approximately 75,000 acre-feet to SRP reservoirs. **Despite the above normal precipitation during the monsoon, the Valley is in its 11th year of drought.**

Central Arizona Project

Below is graph showing the schedule changes in Lake Pleasant water level. Over the next six months water will be pumped into Lake Pleasant from the Wadell Canal to fill the lake.



Below are plots of reservoir stratification. With the cool weather Bartlett Lake should thermally destratify within the next 1-2 weeks if we get a few windy days. Saguaro Lake is thermally destratified already, and as discussed in the workshop is very different from Bartlett Lake because Saguaro Lake is heavily impacted by operations upstream in Apache Lake.





ORGANIC MATTER DATA

DOC concentrations remain quite high in the SRP system (~ 3 mg/L in Bartlett Lake, 5.8 mg/L in Saguaro Lake) and only slightly lower in the CAP system (~4 mg/L)

Sample Description	DOC (mg/L)	UV254 (1/cm)	SUVA
24 th Street WTP Inlet	~4.2	0.082	2.0
24 th Street WTP Treated	2.78	0.033	1.2
Deer Valley Inlet	4.12	0.083	2
Deer Valley WTP Treated	2.90	0.037	1.3
Val Vista Inlet	4.77	0.093	1.9
Val Vista WTP Treated –East	3.21	0.039	1.2
Union Hills Inlet	2.91	0.037	1.3
Union Hills Treated	2.41	0.019	0.8
Tempe North Inlet	4.08	0.082	2.0
Tempe North Plant Treated	3.14	0.040	1.3
Tempe South WTP	4.36	0.092	2.1
Tempe South Plant Treated	3.41	0.051	1.5
Greenway WTP Inlet	4.05	0.0810	2.0
Greenway WTP Treated	2.65	0.0140	0.5

 Table - Water Treatment Plants - October 11, 2006

System	Sample Description	DOC	UV254	SUVA
		(mg/L)	(1/cm)	
CAP				
	Union Hills Inlet	2.91	0.037	1.3
	CAP Canal at Cross-connect	4.28	0.038	0.9
	Salt River @ Blue Pt Bridge	5.40	0.108	2.0
	Verde River @ Beeline	2.80	0.063	2.3
AZ	AZ Canal above CAP Cross-connect	3.04	0.034	1.1
Canal	AZ Canal below CAP Cross-connect	3.75	0.063	1.7
	AZ Canal at Highway 87	3.89	0.068	1.8
	AZ Canal at Pima Rd.	4.29	0.084	1.9
	AZ Canal at 56th St.	4.13	0.081	2.0
	AZ Canal - Inlet to 24 th Street WTP	~4.2	0.082	2.0
	AZ Canal - Central Avenue	4.32	0.083	1.9
	AZ Canal - Inlet to Deer Valley WTP	4.12	0.083	2.0
	AZ Canal - Inlet to Greenway WTP	4.05	0.081	2.0
South	South Canal below CAP Cross-connect	4.93	0.093	1.9
and	South Canal at Val Vista WTP	4.77	0.093	1.9
Tempe	Head of the Tempe Canal	4.39	0.095	2.2
Canals	Tempe Canal - Inlet to Tempe's South			
	Plant	4.36	0.092	2.1

Table - Canal Sampling – October 11, 2006

Table - Reservoir Samples - October 11, 2006

CAP is sampling Lake Pleasant on slightly different days than the other reservoirs.

Sample Description	Location	DOC (mg/L)	UV254 (1/cm)	SUVA
Lake Pleasant (September 13, 2006)	Eplimnion	3.58	0.600	1.70
Lake Pleasant (9/13/06)	Hypolimnion	4.00	0.055	1.40
Bartlett Reservoir	Epilimnion	2.92	0.057	1.9
Bartlett Reservoir	Hypolimnion	3.24	0.057	1.70
Salt River @ BluePt Bridge		5.40	0.108	2.00
Saguaro Lake	Epilimnion	5.78	0.106	1.80
Saguaro Lake	Epi - Duplicate	5.96	0.107	1.80
Saguaro Lake	Hypolimnion	5.83	0.108	1.80
Verde River at Beeline Highway		2.80	0.063	2.3
Verde River at Tangle		1.28	0.038	2.97
Havasu (9/13/06)		2.87	0.036	1.30

ADDITIONAL INFORMATION

Antimony Leaching from PET Plastic Used For Bottled Drinking Water

Paul Westerhoff, Panjai Prapaipong, Everett Shock, Alice Hillaireau

Introduction

Antimony is regulated in municipal drinking water at a maximum contaminant level (MCL) of 6 ppb (μ g/L) by the US Environmental Protection Agency at the European Union set a standard of 5 ppb. The US EPA reports that antimony causes potential health effects (nausea, vomiting, diarrhea) when exposed to levels above the MCL for relatively short periods. Long-term exposure can lead to increased blood cholesterol and decreased blood sugar. The US EPA has not classified antimony as a human carcinogen in water due to lack of studies, although antimony does cause lung cancer in rats. Other research finds similarity in the toxicity between antimony and arsenic, which is a proven carcinogen (Gebel 1997).

Public safety perception and convience trends are resulting in greater usage of bottled water instead of tap water (Allen et al. 1989; Allen and Darby 1994; Ikem et al. 2002; Innes and Cory 2001). While a number of pollutants have been found in bottled waters, this paper focuses on antimony which has been associated with the usage of polyethylene terephthalate (PET) plastic bottle(Shotyk et al. 2006; Suzuki et al. 2000). PET is produced from petroleum monomers (terephthalic acid and ethylene glycol). In order to polymerize the monomers antimony- or gemanium-based catalysts are used. Germanium-based catalysts are more expensive than antinomy-based catalysts, and the later account for more than 90% of the PET manufactured worldwide. There are no regulatory guidelines for germanium in water; germanium has been used in some dietary supplements although its overall human health effects are debatable (Tao and Bolger 1997). PET plastics are visibly clear and a preferred option for bottling "clean" water. PET plastic bottles are used by both private/publicly-owned industry and municipal water agencies.

Because PET plastic bottles are used for drinking water it is important to understand potential environmental factors that influence release of antimony from the catalysts into the water. This may affect the decision of some industries or water agencies to knowingly use PET bottles manufactured using antimony rather than germanium or other types of plastic entirely. Thus the purpose of this paper is to compare the antimony content of several bottled waters purchased in the southwestern USA and to study the effects of storage temperature and exposure to sunlight on antimony release from PET plastic bottles into bottled water.

Results

Comparison of Antimony in Different Brands of Bottled Water

Nine representative samples of bottled water were obtained. All were PET bottles, although some were colorless or had a blue-tint. Antimony concentration was measured at the beginning and end of the three month study (Figure 1). Antimony concentrations ranged from 0.095 to 0.521 ppb (95 to 521 ppt). The average antimony concentration from the nine bottled waters was

 0.195 ± 0.116 ppb at the beginning of the study and 0.226 ± 0.160 ppb three months later. Based upon a Student t-test of these data there is no significance difference over the three month holding time; samples were stored inside at 22 °C. However, the two bottled waters with the highest initial antimony (samples 1 and 9) showed statistically significant increase of 25% to 35% over this holding time.

The observed average antimony concentration of the nine US bottled water samples is comparable with 12 brands of bottled natural waters from Canada (156 ± 86 ppt) and 35 brands in Europe (343 ppt). The antimony concentrations are below the US EPA MCL and EU regulatory limits of 6 ppb (6000 ppt) and 5 ppb, respectively. For reference, a local tap water sample (Tempe, Arizona) was analyzed; the tap water contained 0.146 ± 0.002 ppb of antimony which was also below the MCL.



Figure 1 – Antimony concentrations in purchased bottled water over a three month holding period at room temperature $(22^{\circ}C)$

Antimony Leaching Screening Tests

Initial screening tests to screen the potential of antimony into as-received bottled water was with several bottled water brands, and the results were consistent for each of them. Controls were held at room temperature under fluorescence lights. Insertation of a UV-pen to provide UV irradiation at 254 nm for 6 hours increased antimony concentrations within the bottle from ~ 0.5 ppb to 2.4 to 2.6 ppb. The UV irradiation also heated the water to ~ 40 °C. To screen the effect of temperature separately, holding studies at 4 °C and 80 °C were conducted. Holding the water bottles at 4 °C for 48 hours had no statistical change in antimony concentration of the bottled water. In contrast, holding the water bottles at 80 °C for 48 hours resulted in final antimony concentrations of 8 to 12 ppb, well above the MCL of 6 ppb. The above experiments were repeated at three pH levels (6.3, 7.3 and 8.3) by adding hydrochloric acid or sodium hydroxide to the control (no treatment) and treated (UV, temperature) as-received bottled waters. There was no statistical influence of initial pH on antimony leaching. The largest impact of storage/holding conditions on antimony release from PET plastic into bottled water appeared to be temperature, with perhaps a less significant contribution from UV oxidation. These two parameters were investigated in greater detail.

Effect of Temperature on Antimony Leaching

Because all PET plastic bottles behaved similarly in the screening experiments, only one bottled water brand with the highest initial antimony concentration (brand 9) was used for additional tests. Figure 2 presents the results from temperature-effect antimony leaching tests. Increasing storage temperatures lead to faster rates of antimony leaching into the as-received bottled water. After seven days at 80 °C the antimony concentration reached 14.4 ppb. The rate of change in antimony leaching was best fit by a power function at 60 and 80 °C, rather than first- or second-order reaction kinetics. The rate of antimony leaching decreased as a function of temperature (see Figure 2 inset). At 40 °C antimony leaching could also be fit with a linear model (Sb (ppb) = 0.0017 (time) + 0.39; R²=0.99). In all cases, longer holding times at temperatures above room temperature lead to an increase in antimony concentrations in bottled water.



Influence of temperature on Sb leaching in Arrowhead water bottled in PET plastic

Effect of Sunlight on Antimony Leaching

To investigate the potential influence of sunlight on antimony leaching natural sunlight photolysis kinetic studies were undertaken. Briefly, replicate samples were placed on the roof of a building in August (2006; Tempe, AZ) for up to seven days. One set of samples were wrapped in tin-foil (controls) to be exposed to similar temperature regions as the treated samples (as received bottles with the labels removed). The average temperature based upon morning and afternoon measurements was 35 °C (**GET DATA FROM ALICE**). The final antimony concentrations after seven days had only increased from 0.41 ppb to 0.61 ppb in the treated sample. A linear rate of change in antimony concentration within the bottled water fit the data

the best. Control samples (Sb (ppb) = 0.00095 (time, hour) + 0.41; R²=0.89) had a slightly slower rate of antimony change than treated samples (Sb (ppb) = 0.00128 (time,hour) + 0.41; R²=0.89). Thus the sunlight exposed sample leached antimony at a rate ~ 35% faster than the control sample wrapped in tin foil. This strongly suggests that antimony within the PET plastic is partially affected by sunlight photolysis. The final antimony concentrations after seven days had only increased from 0.41 ppb to 0.61 ppb in the treated sample.

Effect of Different Plastic Materials on Antimony Leaching

The observations above implicate antimony in PET as a source of antimony leaching into bottled waters. So equal surface areas (88 cm²) of three different plastics (clear PET, blue PET and HDPE) were placed in unbuffered nanopure water and placed in 1-L glass bottles. The bottles containing the samples were incubated at 80 °C; water samples were collected over 10 days and analyzed for antimony. The results are shown in Figure 3. The antimony concentration for opaque HDPE sample was not statistically different than the nanopure water control. Therefore the HDPE did not leach antimony. The clear PET leached the most antimony, with less leached from the blue PET. The surface area of clear PET (166 cm²) in contact with water (1L) is 0.166 cm²/cm³. In comparison, the samples illustrated in Figure 2 have a surface area to water ratio of ~0.78 cm²/cm³. The amount of antimony leached in these 1 L tests with 88 cm² of PET is approximately 2.2 ppb, or 16% of the antimony leached (13.9 ppb) from the full bottles illustrated in Figure 2. This value of 16% is very close a value of 21% for the ratio of surface area to volume ratios between the two tests.



Conclusions

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