Metals Releases and Disinfection Byproduct Formation in Domestic Wells Following Shock Chlorination

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Introduction

Shock chlorination is an *in-situ* method for disinfecting water wells contaminated with pathogens and nuisance bacteria. Shock chlorination may increase the concentrations of lead and other trace elements following treatment (Seiler, 2006) and change arsenic concentrations (Gotkowitz, et al, 2008). Much guidance is available for treatment of domestic wells (e.g. http://www.unce.unr.edu/publications/files/nr/2006/FS0668.pdf, last accessed August, 2009). The guidelines recommend contact times (CT: free chlorine concentrations × resting time of the solution) that are very high relative to those used for public water supply treatment, which is appropriate given that treatments occur sporadically, usually in response to perceived problems with water or the health of those who consume water from a well. The procedure typically involves adding sodium hypochlorite solution directly to a well followed by a mixing and resting period of 12-24h. Following treatment, the chlorinated water must be purged prior to resuming use.

Aqueous chlorine (as hypochlorite ion and hypochlorous acid) cleaves carbon-carbon bonds in organic molecules to form disinfection byproducts (DBPs) in two classes: haloacetic acids (HAAs) and trihalomethanes (THMs) (Westerhoff, et al. 2004). HAAs and THMs include carcinogenic organic compounds and have Maximum Contaminant Levels (MCLs) of 0.060 mg/L for HAA5 (the sum of concentrations of monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid and dibromoacetic acid) and 0.080 mg/L for total THM, as specified in the Stage 1 Disinfectants/Disinfection Byproducts Rule (40 CFR, Parts 9, 141 and 142). Trihalomethanes include chloroform, bromodichloromethane, dibromochloromethane, and bromoform.

This poster describes the changes in concentration of Pb, Cu, As, U, gross-α, gross-β, HAA5, THM, and free chlorine (semi-quantitatively measured) resulting from shock chlorination and post-treatment purging of four domestic water wells. Experiments were designed to characterize the net effects of chlorine on short-term release of all of the above chemical constituents in the subsurface, rather than isolating the effects related to well casing or aquifer materials. The study also sought to demonstrate that simple test strips that semi-quantitatively measure the concentration of free chlorine (used for pool and spa maintenance) can be used to indicate that purging has been sufficient to return concentrations of metals and disinfection byproducts to pre-treatment background levels.

Methods and Materials

Study Site

Four wells (Table 1) were selected in the Lahontan Valley, in Nevada (Figure 1). Each well was used for domestic supply prior to being retired for water right acquisition by the US Fish and Wildlife Service. Three were cased with steel (ASTM A135 SCH40 ERW low-carbon steel) and one was cased with polyvinyl chloride casing. The wells were chosen because they had been constructed and used for domestic water supply according to standards and practices commonly used at the time and because they were no longer in service. Each was finished in saturated sands. Well logs indicated that the exteriors of screened intervals on the casing were packed with gravel for wells 182, 167N and 142. No information about well completion was available for well #51. The wells pumped from a stratum of Quaternary valley-fill deposits in the terminus of the Carson River from depths of less than 15 m (50 ft) from the land surface. Infiltration from irrigation and the Carson River have been identified as the main sources of recharge (Glancy, 1986). Water in the aquifer has high but spatially variable concentrations of arsenic (as much as 2100 ppb (Walker, et al 2005)) and uranium (as much as 290 ppb (http://www.atsdr.cdc.gov/HAC/PHA/fallonleukemia2/fln_p1.html, last accessed 8/2009) from contact with sediments and from long-term evapoconcentration (Welch and Lico, 1998). Depth to water (DTW) in the four wells ranged from 1.7 to 5.5 m (5.5 to 18.0 feet) with total well depth ranging from 8.0 to 9.5 m (26.7 to 31.0 feet) (Table 1).

Well Treatment and Purging

A ½ horsepower portable jet pump fitted with a 7.6 m (25 ft) long, 1.9 cm (0.75 in) interior diameter suction line was used for each treatment. The pump was rinsed with distilled, deionized water between uses and allowed to air dry. The outflow line was fitted with a GPI electronic inline flow meter, a flow control valve, and a tee that divided flow between a discharge hose and a flow-through chamber for a YSI model 556MPS (Yellow Springs Instruments, Yellow Springs OH), for real-time measurement of temperature (T (°C)), pH, oxidation-reduction potential (ORP (mV)), and conductivity (C (mS/cm)). The multi-probe was calibrated immediately prior to each stage of field trials, using pH 4.00, 7.00 and 10.00 standards (Fisher Scientific Buffer-Pac, Cat# SB105), a conductivity standard (1000 milli-siemens/cm at 25°C (Yellow Springs Instrument Co. Cat #3167) and an oxidation-reduction potential reference solution (Equipco Inc., part #3682500).

Prior to conducting trials, each well was purged at a rate of 9.5 to 18.9 liters per minute (2.5 to 5.0 gpm) until temperature, pH, ORP, and conductivity readings stabilized (<5% variation in continuous readings), then purged an additional four times the well's standing volume of water. The well volume (WV) was estimated as WV=H×A, with H as the measured height of the water column in the well after the level stabilized following pumping and A as the cross sectional area of the interior of the well casing. Pre-chlorination (designated as IP) water samples were collected for As, Cu, Pb, U, gross-α, gross-β, carbon (as dissolved organic carbon and carbonate), HAA5, and THM. Table 1 presents IP conditions in each well.

Shock Chlorination

Following initial purging, each well was chlorinated to an estimated 200 mg/L as Cl using household bleach (labeled as containing 6% sodium hypochlorite) by adding 8.9 ml (0.3 fl oz) bleach per liter (0.26 gallons) of well volume (Table 1). Pump discharge was circulated back into the well casing for 15 minutes to disperse bleach into solution. Wells were re-capped for at least twelve hours prior to achieve adequate CT.

Sampling

Immediately prior to and during purging temperature, pH, oxidation reduction potential, and conductivity were measured. Prior to purging post-chlorination (PC) samples for As, Cu, Pb, U, gross-α, gross-β, HAA5 and THM were collected using a PTFE dip bailer. The bailer was rinsed with distilled, deionized water and allowed to air dry following use at each site.

Post chlorination purging samples were collected for As, Cu, and Pb at intervals defined by the volume of water purged from each well, including ½, 1, 2, 3, and 4 × WV (designated as 1/2, 1, 2, 3, 4F). After the fourth well volume was pumped, samples were collected for As, Cu, Pb, U, gross-α, gross-β, HAA5 and THM (Table 2).

Samples were stored on ice immediately after collection and submitted within 24 hours to the Nevada State Health Laboratory (University of Nevada School of Medicine, Reno, NV, a certified drinking water analysis laboratory) for analysis (Table 3). All samples were unfiltered. Samples for arsenic, copper, lead and uranium were collected in 500 ml high density polyethylene sample containers provided by the laboratory. All samples were preserved with a nitric acid was at a concentration of 0.15% by mass and transported in a closed container on ice to avoid exposure to sunlight and changes in temperature.

U.S. Fish and Wildlife Service Site Designation (year finished)	Well dia cm (in)	Case material	DTW from land surface m (ft)	WD from land surface m (ft)	Screened interval length m (ft)	Static vol. liters (gal)	pH	Temp °C	Conductivity mS/cm	Oxidation-reduction Potential mV	Bleach added liters (gal)	Treatment duration (hrs)
182 (1975)	15 (6)	PVC	3.4 (11.1)	9.4 (31.0)	4.6-7.9 (15.0-26.0)	110.6 (29.2)	8.50	14.9	0.740	not taken	1.0 (0.3)	20h 25m
167N (1996)	15 (6)	Steel	2.4 (8.0)	9.0 (29.6)	8.2-9.1 (27.0-30.0)	120.0 (31.7)	7.14	16.9	0.345	114.1	1.1 (0.3)	15h 10m
51 (1994)	15 (6)	Steel	1.7 (5.5)	20.4 (67)	18.9-20.4 (62.0-67.0)	171.2 (45.2)	7.27	15.57	0.454	269.7	1.5 (0.4)	24h 20m
142 (1991)	15 (6)	Steel	3.6 (11.8)	8.1 (26.7)	6.4-7.9 (21.0-26.0)	84.8 (22.4)	7.67	16.86	2.093	-123.1	0.7 (0.2)	17h 50m

Table 1: Well characteristics and water physical and chemical characteristics immediately prior to shock chlorination; DTW is depth to water from the land surface, WD is total depth of the well, Static vol. refers to the standing volume of water in a well after water level recovery following the end of pumping. Well diameter, case material, depth to water from the land surface and well depth were recorded at each site. The screened interval length was obtained from well logs available on the Nevada Division of Water Resources (http://water.nv.gov/, last accessed 8/2009).

Figure 1: Left: shock chlorination experiments being conducted in the field; Center: Location of study area, with locations of test wells indicated in circles; Right: simple chlorine test strips evaluated as an indicator of adequate purging

Chlorine test strips

Free chlorine was measured semi-quantitatively with test strips (Figure 1) for swimming pool and spa maintenance (Arch Chemicals, Inc. — HTH line). The test strips indicate free chlorine concentrations in ranges rather than absolute numbers, similar to pH indicator strips. In order to determine the range, a user dips the strip in a solution and compares colors in segregated rectangles with a key. The ranges reported include undetectable (indicated as 0 on the test strip), >0—1 mg/l, >1—2 mg/l, >2—3 mg/l, >3—5 mg/l, >5—10 mg/l and >10 mg/l. We tested the accuracy of the strips using dilutions of sodium hypochlorite solution and determined that they were adequate for distinguishing between the classes noted above (data not shown).

Sample Type	Initial Purge (IP)	Post -Chlorination (PC)	Post- Chlorination Purging (PCP, for ½, 1, 2, and 3well volumes)	Final (4F: 4 well volumes purged)
gross α, gross β, Uranium	√	√		√
Metals (Cu, Pb, As)	√	√	√	√
HAA5, THM	√	√		√
Total Organic Carbon	√			
Chlorine Test Strips		√	√	√

Table 2: Sampling intervals used, with associated chemical constituents measured

Well volumes purged→	0	1/2	1	2	3	4
182 (discharge rate = 14.4 liters per minute (3.8 gpm))						
T (°C)	16.68	15.70	15.69	15.67	15.60	15.65
C (mS/cm)	0.680	0.487	0.560	0.558	0.539	0.549
pH	7.97	7.57	7.70	7.52	7.47	7.58
ORP (mV)	772.6	817.0	810.5	827.9	837.4	828.9
167N (discharge rate = 18.9 liters per minute (5.0 gpm))						
T (°C)	ND	17.1	17.11	17.12	17.1	17.12
C (mS/cm)	2.115	1.225	0.525	0.445	0.420	0.437
pH	8.78	8.38	7.82	7.56	7.27	7.51
ORP (mV)	732.0	786.9	793.2	782.6	791.1	776.9
51 (discharge rate = 14.6 liters per minute (3.9 gpm))						
T (°C)	16.4	14.83	14.96	15.11	15.32	15.17
C (mS/cm)	1.945	1.065	1.083	0.787	0.813	0.772
pH	8.65	8.8	8.5	8.27	8.41	8.42
ORP (mV)	866.5	957.0	962.3	958.5	831.0	586.0
142 (discharge rate = 2.5 liters per minute (0.7 gpm))						
T (°C)	22.40	16.74	16.69	16.63	16.57	16.60
C (mS/cm)	2.257	1.638	2.067	2.041	1.972	1.942
pH	7.56	8.48	8.13	7.71	7.74	7.73
ORP (mV)	704.1	719.0	718.9	-108.7	-123.6	-124.4

Table 3: Physical and chemical characteristics of water in test wells observed during post-chlorination purging (ND: not measured)

Metals (mg/l)	PT	0	½	1	2	3	4
	Well volumes purged						
51							
Arsenic	0.410	0.390	0.380	0.410	0.460	0.460	0.460
Copper	<0.02	0.08	0.08	0.06	<0.02	<0.02	<0.02
Lead	0.003	0.022	0.016	0.012	0.003	0.002	0.003
Cl	<1	>10	>10	>10	>1—2	<1	<1
142							
Arsenic	0.580	0.440	0.460	0.750	0.620	0.590	0.600
Copper	<0.02	<0.02	0.02	<0.02	<0.02	<0.02	0.02
Lead	<0.010	0.010	<0.010	<0.010	<0.010	<0.010	0.010
Cl	<1	>10	>10	<1	<1	<1	<1
167N							
Arsenic	0.019	0.024	0.018	0.019	0.019	0.019	0.019
Copper	<0.02	0.03	0.04	<0.02	<0.02	<0.02	<0.02
Lead	<0.001	0.013	0.008	<0.002	<0.001	<0.001	<0.001
Cl	<1	>10	>10	>10	>3—5	>2—3	>1—2
182							
Arsenic	0.020	0.016	0.016	0.020	0.021	0.021	0.021
Copper	<0.02	0.04	<0.02	<0.02	<0.02	<0.02	<0.02
Lead	<0.001	0.011	0.001	<0.001	<0.001	<0.001	<0.001
Cl	<1	>10	>10	>10	>10	>10	>3—5

Table 4: Trace metal concentrations from pre-treatment (PT) through purging, expressed in number of well volumes pumped. The Maximum Contaminant Levels for arsenic is 0.010 mg/l. Action Levels for lead and copper are 1.3 and 0.015 mg/l, respectively. Samples that contained analytes in concentrations less than the reporting limit (RL) are reported as "<RL." The reporting limit for lead varied according to results of internal laboratory quality control assessments and chemical quality of water samples.

Site	DOC (IP) mg/L	CO_3 (IP) mg/L	HAA5 (IP,PC,4F) µg/L	THM (IP,PC,4F) mg/L
51	2.0	75.1	<1.0, 149.0, 6.5	2.9, 119.3, <0.5
142	15.1	215.8	<1.0, 394.0, <1.0	<0.5, 747.0, <0.5
167N	1.9	47.7	29.0, 645.0, 25.0	<0.5, 355.1, 6.5
182	3.9	49.3	<1.0, 101.0, 128.0	<0.5, 43.7, 70.1

Table 5: DOC and CO3 concentrations following initial purging of test wells (IP), and HAA5 and THM concentrations following IP, post chlorination (PC) and after 4 well volumes had been purged (4F)

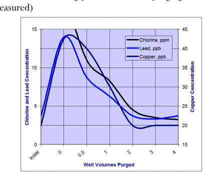

Figure 2a: The concentrations of lead and copper rise after a well is treated with chlorine bleach at 200 ppm. After purging at least two well volumes, concentrations return to pre-treatment levels.

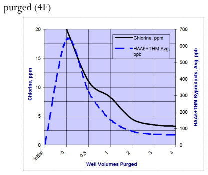

Figure 2b: THM and HAA5 concentrations increase following shock chlorination, but can be removed with adequate purging. THM and HAA5 concentrations follow the same trend during purging.

Results and Discussion

Field measurements

Post-chlorination conductivity measurements were elevated from initial values, and returned to near initial values following purging four well volumes (Table 3). ORP increased above pre-chlorination levels in all wells, as would be expected with the addition of an oxidizer. Throughout the process, pH fluctuated a maximum of 21% from prechlorination observation (well 167N) and a minimum of 6% (well 182).

Chlorine Concentration

The dissipation of free chlorine with purging was hypothesized to be an indicator of dissipation of mobilized trace metals and disinfection byproducts. The concentration of free chlorine decreased in the steel-cased wells to >1—2 ppm free chlorine after four well volumes were pumped (Table 4). Site 182, a PVC-cased well, required that five times the well volume be purged before free chlorine decreased to >3—5 ppm. Site 182 had different well volume related chemical trends than the steel-cased wells following treatment and will be discussed in the section on disinfection byproducts.

Mobilization of Trace Metals

Concentrations of lead and copper in well water increased following shock chlorination, as previously observed and reported by Seiler (2006). Lead concentrations increased up to thirteen-fold and copper concentrations increased up to four-fold following treatment. Concentrations of both decreased to initial levels within two well volumes of purging. The return to background levels corresponded with the decline in free chlorine to >3—5 ppm (Figure 2a, Table 4).

All wells contained arsenic in concentrations that exceeded the MCL (0.010 ppm) prior to treatment. The decline in arsenic concentration in the strong chlorine solution prior to purging was similar to results reported by Gotkowitz et al. (2008). However, the decline was followed by an increase in arsenic above background levels during pumping. After four well volumes, water from one well returned to initial arsenic concentrations, while the others remained elevated by 3—12% higher than initial concentrations.

Uranium and Radionuclides

Samples were analyzed for uranium and gross-α and gross-β radionuclides (data not shown). Uranium concentrations increased at sites 51 and 142 but remained the same or decreased in wells 167N and 187. Concentrations returned to approximately the same as starting levels in all wells after purging four well volumes. Gross-α concentrations changed from the IP to PC sampling steps, increasing in wells 51 and 167N, decreasing in well 142 and remaining approximately the same in well 182. Gross-β concentrations remained approximately the same in all wells at each sampling stage, with concentrations appearing to decrease slightly between the IP and 4F samplings. The maximum change in gross-b concentrations was approximately -9% in well 142.

Disinfection Byproducts and Test Strip Use

Water from wells obtained after treatment, but prior to purging contained concentrations of THM up to ten times the MCL (Table 5). Following the purging of four well volumes, concentrations in two of the steel-cased wells decreased to below the detection limit, demonstrating that the increase in concentration was temporary and can be remediated by purging four well volumes after treatment. In the third steel-cased well, concentrations fell to 6.5 mg/l, approximately 11% of the MCL. Although the concentration was below the MCL, the result suggests that all DBP's had not yet been purged and that further pumping would have been advisable. This may have also been inferred from the chlorine test-strip results, which showed that free chlorine concentrations had not yet returned to background levels after having purged four well volumes of water. Site 182, a PVC-cased well, also retained disinfection byproducts and free chlorine, with concentration of free chlorine (indicated by test strips) >10 ppm after purging 4 WV. Testing for free chlorine at the fifth well volume purged indicated a concentration of >3—5 ppm, though no sampling for THM and HAA5 occurred. PVC polymers may sorb and leach trace metals, organic and phenolic substances, volatile organic chemicals and trihalomethanes (Llopis, 1991; McCaulou et al, 1995). As a result, PVC casings are not recommended for monitoring wells at contaminated sites though they are approved by the National Sanitation Foundation for water supply.

Wells 167N and 51 had HAA5 and THM in detectable concentrations prior to treatment and following purging. Given that HAA5 and THM are formed only by the interaction of free chlorine with carbon compounds resident in the aquifer, this suggests that these wells were treated without our knowledge and possibly not purged prior to our experiments. The groundwater gradient in the region where these wells are located is shallow (approximately .0002 m/m (Maurer et al, 1994)) and given typical hydraulic conductivities and porosities for sands (10^{-3}-10^{-1} cm/sec, 25-50% (Fetter, 1988)), groundwater velocities are expected to be very low (e.g. 12-25 m/yr, based on Darcy's law, scaled by porosity). If the wells were shock chlorinated in months prior to our arrival, it is possible that the HAA5 concentrations resulting from treatment remained stable and, in fact, diffused into aquifer materials, leading to the background levels observed. However, the changes in HAA5 and THM concentrations follow the same pattern as that in the other wells—after treatment but before purging concentrations of HAA5 and THM increased well above background levels (figure 2b). If pre-treatment concentrations of HAA5 and THM were due to prior treatment the results suggest that purging immediately after treatment is a very important step, to avoid persistent contamination of aquifer material with HAA5 and THM.

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