Disinfection By-product Formation from Water Reuse Practices
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Problem and Research Objectives

Expanding water demands have put increasing pressure on water agencies, city officials, and scientists to develop innovative ideas to seek alternative renewable water supplies. One alternative source of water which is reliable and local is wastewater discharged from Reclaimed water is a viable option. This recycled water is treated to various extents depending on intended use. Historically, recycled water was used primary for land application, either for irrigation or to recharge underlying groundwater through percolation. If a drinking water treatment plant draws water from the same aquifer, this is called indirect potable reuse (IPR). As an alternative, generally due to limits in land area and/or geology, recycled water is treated with advanced processes and injected into an aquifer. However, there is recent interest in eliminating this environmental buffer by connecting the highly treated recycled water directly to a drinking water system. These systems are known as direct potable reuse (DPR) and two such systems have been constructed in the USA (one in New Mexico and one in Texas) and several others are in planning. It is anticipated that potable will become an increasingly important part of water management, especially in the arid Southwest where groundwater is often withdrawn faster than it is replenished by the natural hydrological cycle. Therefore, the significant growth is potable reuse is expected in Arizona, and throughout the Southwest USA, in the near future.

However, there are some notable concerns regarding potable water reuse (PWR). Public acceptance of PWR is challenging, as it is difficult to convince citizens that drinking "treated" wastewater is safe. Citizens should be reassured that utilities are required to ensure that sufficiently low numbers of bacteria leave in the effluent recharge, and that the water is devoid of chemicals at levels of risk to public health. This is accomplished via sufficient disinfection and/or advanced treatment and/or prolonged aquifer percolation time. While utilities emphasize water treatment for harmful biological entities, they sometimes inadvertently create transformation products from trace organic compounds (TOrCs) and from natural organic matter (NOM). Therefore, when ozone, chlorine, UV, and/or chloramines are utilized for disinfection and/or contaminant oxidation, disinfection by-products (DBPs) may form from reactions with organic substances. Since wastewater contains high iodide and bromide concentrations compared to most "natural" waters, PWR can generate unique DBPs and at concentrations atypical for a non-impacted site.

The majority of disinfection byproducts formed during water treatment remains unknown (Krasner, Weinberg et al. 2006). Iodinated and nitrogenous DBPs (IDBPs and NDPBs, respectively) are, by far, the most toxic group of transformation products formed during oxidative water treatment processes (Plewa, Muellner et al. 2008; Richardson, Fasano et al. 2008). Mammalian cell studies have shown that iodoacetic acid is 3.2 and 287.5 times

more cytotoxic in Chinese hamster ovary cells than bromoacetic acid and chloroacetic acid, respectively; and iodoacetic acid is 2.0 and 47.2 times more genotoxic in Chinese hamster ovary cells than bromoacetic acid and chloroacetic acid, respectively (Plewa, Muellner et al. 2008). A commonly detected NDBP is nitrosodimethylamine (NDMA), which has a calculated cancer risk as low as 0.7 ng/L (Mitch, Oelker et al. 2005). However, despite their higher toxicity, IDBPs and NDBPs are not yet regulated. The lack of federal regulation is due in part to limited occurrence data since reliable and sensitive analytical methodologies are not yet commonly available. However, recent advances in analytical technology coupled with commercial availability of purified reference standards are allowing further investigation into this new generation of DBPs. Since wastewater is known to contain elevated levels of iodine and organic nitrogen, the oxidative technologies commonly employed to purify to potable standards can result in elevated levels of IDBPs and NDBPs as compared to a non-impacted potable source water.

The primary objective of this study was to determine the attenuation of TOrC using ozone and the potential formation IDBPs and NDMA in wastewaters that are, or maybe, utilized for potable reuse. In order to achieve this objective, we developed and implemented a novel method for characterizing IDBPs and evaluated the formation potential in actual waters. We further evaluated the formation and fate of NDMA in water under various treatment scenarios.

Methodology

Sample Collection and Preservation

Samples were collected by Tucson Water and Pima County staff in pre-cleaned five gallon polypropylene carboys. The two wastewater samples (Roger Rd and Ina Rd) were quenched within four hours of receipt in the lab with 20 mg/L of sodium thiosulfate and the free chlorine was measured using a Hach DPD kit. Groundwater samples did not have any residual chlorine and thus were not quenched. All samples were stored at 4 ºC till the time of analysis.

Ozonation

Water samples were ozonated at three different doses within five days of collection. A concentrated ozone stock was prepared by bubbling gaseous ozone with a diffuser into ultra-pure water in a specialized liquid-jacketed vessel. The vessel was cooled to 1ºC with ethylene glycol and a recirculating chiller. The resulting ozone stock solution was tested for residual ozone concentration and found to be >40 mg/L. An aliquot of ozone stock solution was then placed into the ozone reaction vessel containing the sample to achieve the desired ozone concentration. The ozone residual was tested using the Indigo method every 30 seconds for the first 2 minutes followed by every minute from 3-10 minutes and every 2 minutes from 10-20 minutes.

The above procedure was performed again to obtain the samples for analysis of nitrosodimethylamine (NDMA), trace organic compounds (TOrCs), disinfection byproducts, bromide (Br^-) and bromate (BrO_3^-). Ozone residual for these samples was

quenched and post-ozonated water remained at ambient temperature for six hours to ensure the ozone was completely consumed.

Groundwater samples were chlorinated and chloraminated to achieve a one ppm residual with a contact time of one day to determine DBP formation potential. The preparation of the chlorine and chloramine (as monochloramine) stocks is described below.

Chlorine Stock Solution

Chlorine stock solution was prepared by diluting a sodium hypochlorite solution (6% available chlorine). Commercial sodium hypochlorite solution was initially diluted and verified by UV spectrometry at 292nm. A molar absorption coefficient of 362 $Lmol^{-1}cm^{-1}$ was used to calculate the measured concentration of the commercial solution. Based on the calculated concentration, sodium hypochlorite solution was added to deionized water to create a desired stock solution concentration.

Monochloramine Stock Solution

Preformed monochloramine stock solution was prepared by combining sodium hypochlorite to ammonium chloride. To create monochloramine, deionized water was put in a volumetric flask and placed on a stir plate. Sodium hydroxide and ammonium chloride at 10g/L were then added. Sodium hypochlorite was then slowly added (drop by drop) to create a N:Cl ratio of 1:1.4. To ensure proper formation, solution was well stirred during the addition of sodium hypochlorite. The solution was then covered with foil to avoid degradation by light.

To confirm the concentration, the solution was verified by UV spectrometry. Absorbance readings at 245 nm and 295nm for NH_2Cl and $NHCl_2$, respectively, were then used to determine exact stock solution concentration.

Chlorination/Chloramination Procedure

1) Prepare bottles (# of bottles = # of samples + blank(s))
2) Prepare chlorine stock solution at 1.4mM.
3) Prepare monochloramine stock solution at 1.4mM.
4) Prepare carbonate buffer at 500mM.
5) Prepare a diluted hydrochloric acid solution for pH adjustments (1M).
6) Fill bottles with sample water.
7) Calculate the dose volume for monochloramine, chlorine, and carbonate buffer based on total volume and desired dose concentration. Remove sample volume based on disinfectant and buffer addition. This step is necessary to ensure final dose concentration is accurate. For example, if 100mL sample volumes, stock solutions at 1.4mM, and a buffer at 500mM were used, 1mL and 0.8mL was removed for disinfectant and buffer addition, respectively.
8) Add carbonate buffer.
9) Add chlorine or monochloramine.
10) Record exact time of dosing.
11) Check for pH and add HCl to obtain a pH of 8.
12) Cap and store in a dark location.

Dissolved Organic Carbon

A Shimadzu TOC-L CSH Total Organic Carbon Analyzer was used to determine the dissolved organic carbon (DOC) of the wastewater samples. The method followed is very similar to standard method 5310(APHA 2012). This instrument incinerates the samples at approximate 680℃ to convert total carbon components to carbon dioxide. The resulting gas is cooled, dehydrated and delivered to a non-dispersive infrared (NDIR) gas analyzer to detect the amount of carbon dioxide. The flow line was washed twice before the first injection of each sample. Sparge gas flow was set as 80mL/min with a sparge time of 1.5 minute. The injection volume was 50 µL.

Stock solutions of TOC were prepared at 1000 mg/L in Milli-Q water and stored at 4 °C. Calibration standard solutions ranging from 1 to 20 mg/L were prepared from the stock solutions. Calibration curves were used only if the linearity was higher than 0.99 and each calibration point had accuracy between 80% and 120%, otherwise the calibration curve was prepared again and reanalyzed.

For DOC analysis, the samples are filtered with a 0.45 µm glass fiber filter before acidification and analysis on the instrument. While TOC samples are not filtered.
Approximately 15 mL of the samples were transferred into 20 mL glass vials for DOC analysis. Then they were acidified to pH 3 or lower using hydrochloric acid (35%). pH test papers were used to determine the final pH. To avoid contamination, all the glassware was pre-furnaced at 550℃ for 5 hours.

To ensure the precision of the measurements, every sample including calibration standards and lab blanks was injected five times, and the average of the three closest measurements was reported. In addition, a quality control sample of known concentration was analyzed with every 10 samples to monitor instrumental accuracy and drift.

Nitrate/Nitrite

Nitrate and nitrite was analyzed using a Dionex ICS-1000 with an AS-22 column set (with AS-22 guard) Ion Chrmatograph (IC).

Trihalomethanes (THMs)

The extraction procedure was based on US EPA Method 555.1. A 10 mL sample volume was extracted with 10mL of methyl-tert-butyl-ether (MTBE). Four grams of sodium sulfate was added for a “salting out” effect and sample vials were vigorously shaken until sodium sulfate was fully dissolved. MTBE extracts were collected and placed into a two ml autosampler vial. For quality control purposes, a laboratory reagent blank and laboratory fortified blank was included with each extraction batch. Each sample was extracted in duplicate with 1,2,3-trichloropropane added as a surrogate.

MTBE extracts were analyzed with an Agilent 7890A Gas Chromatograph equipped with a linearized electron capture detector (ECD), fused silica capillary column, and split/splitless injector. The GC system was equipped with an Agilient HP-5 column (30m x 0.25 mm x 0.25 um).

N-Nitrosodimethylamine (NDMA)

Samples were filtered through 0.7 µm glass fiber filters upon receipt and stored at 4 °C until extraction. The protocol for extraction closely followed that of EPA 521. EnviroCarb coconut charcoal cartridges were used for the solid phase extraction (SPE). Nitrosamines are extracted by passing a 500 ml aliquot sample (spiked with NDMA-d6 as a surrogate) through the SPE cartridge containing 2 g of 80-120 mesh coconut charcoal. Cartridges are conditioned prior to extract by sequential addition of 3 ml methylene chloride, 3 ml methanol (repeated 3 times), followed by 3 ml HPLC grade water, repeated 5 times. Water samples were loaded onto the cartridge at a rate of 10 ml/min. Analytes are eluted from the cartridge using 10 ml of methylene chloride. Residual water was eliminated from sample extract by passing through 5-7 g of anhydrous sodium sulfate. Eluent was then concentrated under a gentle stream of nitrogen to 0.9 ml. Prior to immediate analysis, 20 µl of 500ug/ml NDPA-d14 internal standard is added to the extract.

Nitrosamine analysis was conducted using an Agilent 7000 triple quadrupole mass spectrometer coupled to an Agilent 7890 gas chromatograph. All gases used were ultra-high purity or equivalent. A DB-WAX ETR capillary column from J&W Scientific (30m x 0.25mm ID x 0.25um) was employed for gas chromatographic separation with the following oven temperature program: 40 °C (3 minute hold), heating to 110 °C at 10 °C/min, ramping at 15 °C/min to 200 °C , with a final progression of 40 °C/min to 240 °C. The column was operated at a constant helium flow rate of 1.25 ml/min with injector in splitless mode and held at 200 °C. The MS interface was held at 240 °C, while the source temperature was 200 °C and both quadrupoles maintained at 150 °C. The mass spectrometer was operated in positive chemical ionization mode with nitrogen collision cell gas at 1.5 ml/min, helium quench gas at 2.25 ml/min, and using 20% ammonia as the reagent gas. Analytes were detected in multiple reaction monitoring mode (MRM).

Trace Organic Compounds (TOrCs)

Samples were fortified with a surrogate standard stock to obtain a final concentration of 200 ng/L. Samples were subsequently filtered through 0.2 µm PES syringe filters from GE Whatman. Two sets of samples were prepared: a 1.5 ml sample and a sample diluted 5x with ultrapure water (300µL sample + 1200 µL water) so as to obtain concentrations of all analytes within the linear range of calibration curve. Calibration standards were freshly prepared from a 1 mg/L stock of all target analytes.

TOrC analysis was performed using online solid-phase extraction coupled to an ultra-high performance liquid chromatography-tandem mass spectrometer (UHPLC-MS/MS). This UHPLC-MS/MS method utilizes a polymeric solid phase extraction cartridge that is attached online to an Agilent 1290 Infinity LC, which in turn is coupled to an Agilent 6460 LC/MS Triple Quadrupole system. It utilizes simultaneous positive and negative electrospray ionization (ESI) to provide significant time savings. The method uses a dynamic multiple reaction monitoring (DMRM) mode for even more sensitivity and specificity of detection. Further details on compound and instrument optimized parameters have been published elsewhere(Anumol, Mohsin et al. 2013). Data was processed using the Mass Hunter software and samples were quantified using the isotope

dilution method(Vanderford and Snyder 2006). The analysis of 28 TOrCs was performed on all samples as indicated in
Table1.

Table 1. Trace Organic Compounds Analyzed

Trace Organic Contaminant	Trace Organic contaminant
Atenolol	DEET
Caffeine	Propylparaben
Benzotriazole	Bisphenol A
Trimethoprim	Testosterone
Primidone	Naproxen
Sulfamethoxazole	PFOA
Meprobamate	Estrone
Diphenhydramine	TCPP
Prednisone	Benzophenone
Ditiazem	Ibuprofen
Simazine	Gemfibrozil
Carbamezapine	PFOS
Dexamethasone	Triclocarban
Atrazine	Triclosan

Bromide/Bromate

Sample analysis was performed using an Agilent 7700x inductively coupled plasma mass spectrometer (ICP-MS) that is interfaced with an Agilent 1260 liquid chromatograph (LC). The ICP-MS is operated in helium collision mode, in order to remove the effects of polyatomic interferences. The speciation of bromide and bromate was performed using a Dionex AG-9 HC/AS-9 HC (4 mm) ion chromatography column eluted using an isocratic 10 mM sodium carbonate (flow rate = 1.0 mL/min) solution over the time course of 25 minutes. During the experiment, ion intensities for both ^{79}Br and ^{81}Br are recorded as a function of time, concentrations in water samples are determined by evaluating areas of peaks and comparing these to the areas obtained for calibration standards.

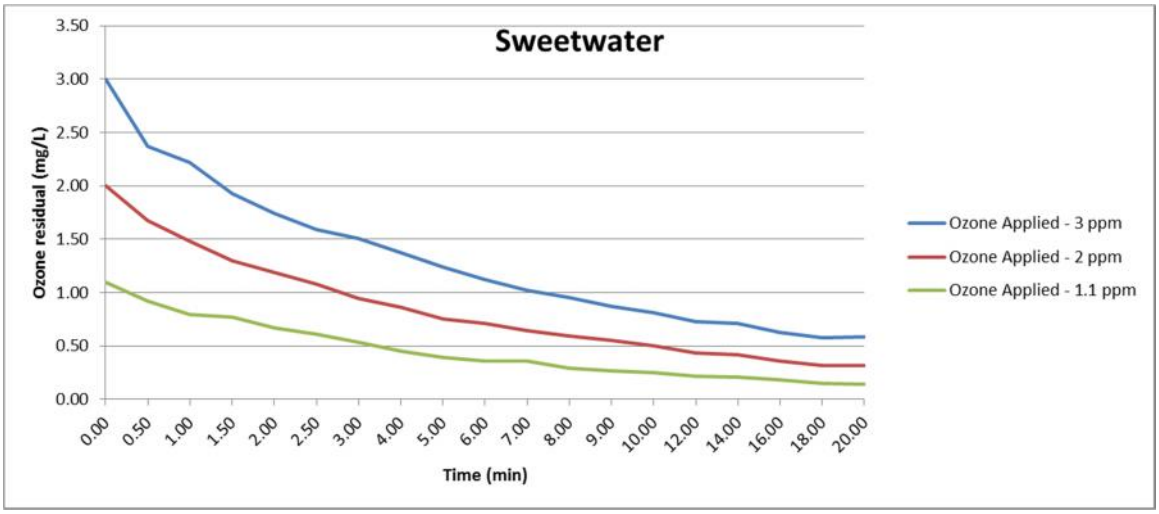
GC-ICP-MS

Samples were split in two, one half was left untreated and the other half was treated with aqueous chloramine. For extraction, 35 mL of these wastewater samples were extracted using 5 mL of MTBE in a modified version of EPA method 551.1. The organic layers were carefully separated and then placed into 2.0 mL amber Agilent GC vials. The organic extracts (1 µL) were then injected into an Agilent 7890A gas chromatograph equipped with 30 m Agilent HP-5 column (320 µm x 0.25 µm) in pulsed splitless injection mode. Oven parameters were 37 °C for 6 minutes, followed by a 10 °C/min rise up to 260 °C followed by an 11 minute hold time. The heated ICP-MS transfer line and the ICP-MS injector were operated at 200 °C. A dilution gas (Ar) flow of 0.39 L/min was used to carry the column outflow through the transfer line. Calibration curves for iodine and bromine were prepared using standards of 1-bromo-4-iodobenzene with concentrations of 0, 1, 2, 5, 10, 25, and 100 ng/mL prepared in MTBE.

Principal Findings and Significance

The Ina Road (IR) effluent DOC was found to be 5.4 mg/L and only exhibited ozone residual at the highest ozone dose applied. The Roger Road (RR) effluent sample had DOC that was extremely high at 10.4 mg/L, which resulted in instantaneous ozone demand greater than all four ozone doses (1, 3, 5, and 7 mg/L). Thus, no ozone residual was detected after the first seconds of application. Conversely, the soil infiltration of Roger Road effluent seems to remove a large amount of DOC as the Sweetwater (SW) sample had DOC of 0.7 mg/L). Thus, ozone applied to SW showed ozone residual at all doses (1, 2, and 3 mg/L) and exhibited relatively slow decay, typical of a low DOC water (Figure 1). Roger Road was also determined to have a high level of nitrite, which consumes ozone at a 1:1 molar rate. Both IR and SW samples had no detectable nitrite. Nitrate at RR was 3.92 mg/L, while IR and SW were 29.5 and 17.7 mg/L, respectively.

Figure 1. Ozone Demand/Decay of Sweetwater Recovery Water



Ozonation of RR and IR effluents produced very low bromate concentrations (Table 2). This is as expected considering the high consumption rate of ozone, which suggestions that bromide is unable to react with ozone because of the relatively low rate constant ($k \sim 10^2$ $M^{-1}s^{-1}$). However, bromate formation was quite high in the SW sample. Interestingly, the bromide reduced almost equivalently indicating that the bromide was converted to bromate on reaction with ozone.

A high concentration of many TOrCs was detected in the RR effluent compared to the IR effluent (Table 3). Most of the TOrCs are attenuated by infiltration though as the SW sample was found to have only four detectable TOrCs. Ozone treatment generally resulted in removal of TOrCs but removals were largely based on the rate constant of the contaminant with ozone (Huber, Gobel et al. 2005; Wert, Rosario-Ortiz et al. 2009).

Table 2. Bromide and Bromate Concentrations During Ozone Experiments

	Roger Rd			
Sample	**No Ozone**	**1 ppm**	**3 ppm**	**5 ppm**
Bromate (ug/L)	BLQ	BLQ	3	2
Bromide (ug/L)	221	209	196	182
	Ina Rd			
Sample	**No Ozone**	**1 ppm**	**3 ppm**	**5 ppm**
Bromate (ug/L)	1	1	1	4
Bromide (ug/L)	176	178	159	148
	Sweet water			
Sample	**No Ozone**	**1 ppm**	**2 ppm**	**3 ppm**
Bromate (ug/L)	BLQ	67	242	394
Bromide (ug/L)	434	283	164	92
BLQ-Below Limit of Quantification				

Table 3. Trace Organic Contaminant Concentrations

	Roger Road					Ina Road					Sweet Water			
Sample (Conc. In ng/L)	**No Ozone**	**1 ppm**	**3 ppm**	**5 ppm**		**No Ozone**	**1 ppm**	**3 ppm**	**5 ppm**		**No Ozone**	**1 ppm**	**2 ppm**	**3 ppm**
Atenolol	1800	1670	1610	1260		450	360	310	220		10	BLQ	BLQ	BLQ
Caffeine	3260	2770	2900	2300		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Benzotriazole	6210	5830	2960	2660		2020	2000	1660	1120		BLQ	BLQ	BLQ	BLQ
Trimethoprim	1090	1140	970	700		260	300	200	110		BLQ	BLQ	BLQ	BLQ
Primidone	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Sulfamethoxazole	1350	1210	970	770		1430	1050	820	490		BLQ	BLQ	BLQ	BLQ
Meprobamate	650	570	580	480		750	679	576	458		BLQ	BLQ	BLQ	BLQ
Diphenhydramine	1720	1550	910	680		810	590	470	410		BLQ	BLQ	BLQ	BLQ
Prednisone	BLQ	BLQ	BLQ	BLQ		100	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Ditiazem	310	280	190	110		260	140	110	70		90	17	16	15
Simazine	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Carbamezapine	310	240	280	130		390	300	190	100		350	BLQ	BLQ	BLQ
Dexamethasone	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Atrazine	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
DEET	400	380	360	300		59	62	50	38		BLQ	BLQ	BLQ	BLQ
Propylparaben	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Bisphenol A	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Testosterone	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Naproxen	500	350	450	240		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
PFOA	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Estrone	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
TCPP	4000	4300	3600	2350		9500	9500	10000	10000		120	140	90	90
Benzophenone	480	590	430	460		200	170	110	110		190	190	60	70
Ibuprofen	170	160	100	78		79	26	22	17		BLQ	BLQ	BLQ	BLQ
Gemfibrozil	4630	4090	4100	2780		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
PFOS	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Triclocarban	BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ		BLQ	BLQ	BLQ	BLQ
Triclosan	980	320	100	80		140	34	19	12		BLQ	BLQ	BLQ	BLQ
BLQ: Below Limit of Quantification														

NDMA formation increased in response to ozone dose in the RR sample (Table 4). The effluent NDMA at RR was also higher than the other two samples (IR and SW). The trend in IR is not clear and further studies may be required. The SW sample had an initial increase in NDMA but did not change at higher ozone doses, suggesting that precursors resulting in NDMA formation likely were completely consumed at the initial ozone dose. Additionally, chlorination and chloramination of SW sample did not result in NDMA formation.

Table 4. NDMA Formation Ozonation (ng/L)

Roger Rd			
No Ozone	1 ppm	3 ppm	5 ppm
17	24	28	31
Ina Rd			
No Ozone	1 ppm	3 ppm	5 ppm
9	7	4	7
Sweet water			
No Ozone	1 ppm	2 ppm	3 ppm
BLQ	4	4	4

BLQ-Below Limit of Quantification

The THMs present in all samples were much lower than the current MCL of 80 µg/L. There was a slight increase in TTHMs on ozonation and chlorination of the SW sample (Table 5).

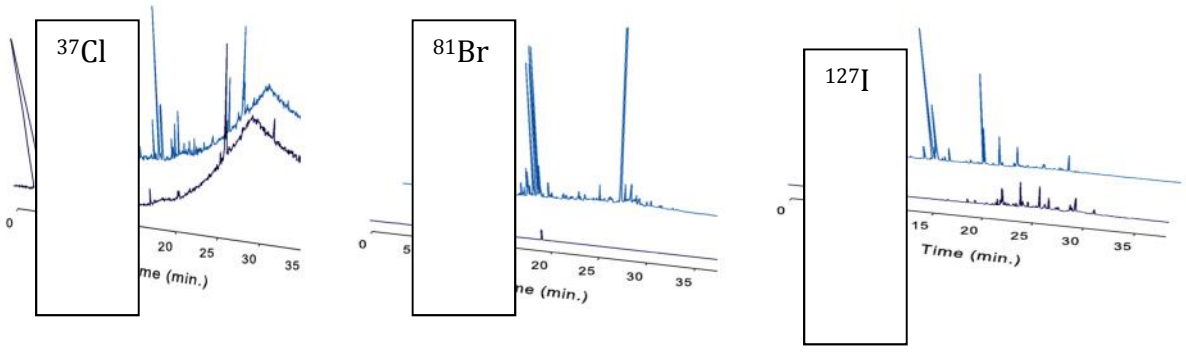
Table 5. Trihalomethane Formation in Sweetwater Sample

Sweetwater					
	Ozone/Chlorine (mg/L)			Ozone/Chloramine	
Compound (Conc. In µg/L)	0/0	1/1	0/1	1/1	0/1
Chloroform	5.8	5.8	5.7	BLQ	BLQ
Dichlorobromomethane	BLQ	9.3	9.0	BLQ	BLQ
Chlorodibromomethane	BLQ	5.3	5.5	BLQ	BLQ
Bromoform	16.1	16.0	15.6	12.5	BLQ
Dichloroiodomethane	BLQ	BLQ	BLQ	BLQ	BLQ
Dibromoiodomethane	BLQ	BLQ	BLQ	BLQ	BLQ
Bromochloroiodomethane	BLQ	BLQ	BLQ	BLQ	BLQ
Chlorodiiodomethane	BLQ	BLQ	BLQ	BLQ	BLQ
Bromodiiodomethane	BLQ	BLQ	BLQ	5.3	5.6
Iodoform	BLQ	BLQ	BLQ	BLQ	BLQ
Tribromochloromethane	BLQ	BLQ	BLQ	BLQ	BLQ
Σ T H M	21.9	36.5	35.9	12.5	0.0

Using GC-ICP-MS, the treatment with chloramine leads to an increase in the concentration of chlorinated, brominated, and iodinated species in the extracts (Figure 2).

Our data reveals several interesting facts. First, there are indeed volatile halogenated organics present in wastewaters prior to chloramination, some of these species are resistant to transformation upon treatment while some are consumed (and likely transformed into new halogenated DBPs). Indeed, it is likely that many non-halogenated organics in the untreated wastewaters are converted into new halogenated DBPs, as well.

Figure 2. GC-ICPMS chromatograms obtained from MTBE extracts prepared from a representative wastewater sample before chloramination (purple line) and after chloramination (blue line).



The effects of chloramination is seen most profoundly in terms of the differences between chromatograms for brominated and iodinated DBPs. There are two reinforcing explanations for this, one dealing with the reactivity of bromide and iodide during oxidative treatments, and the higher sensitivity for detection for I and Br in our assays due to their lower ionization potentials (relative to Cl). A brief summary of our results for a few (of many) halogenated organics in two different wastewaters before and after treatment are shown in Table 6. All CCVs conducted at the end of our analysis provided agreement within 10% of the initial bromine and iodine signal responses for our initial calibration.

Table 6. A simplified table revealing the halogen concentrations in a series of halogenated volatile organics present in extracts that have been prepared from wastewaters before and after chloramination.

Compound name	35 Cl-1	35 Cl-2	35 Cl-3	81 Br-1	81 Br-2	1 BrI-benzen	81 Br-3	127 I-1	127 I-2	7 BrI-benzer	127 I-3
Retention Time (min	15.3	15.8	17.0	15.4	19.0	20.6	25.2	12.2	12.6	20.6	29.0
Sample Name	[Cl], ppb	[Cl], ppb	[Cl], ppb	[Br], ppb	[Br], ppb	[Br], ppb	[Br], ppb	[I], ppb	[I], ppb	[I], ppb	[I], ppb
mtbe BLANK	5.5	6.9	6.2	1.3	0.5	2.4	1.1	0.1	0.3		0.4
Br-I-benzene 1ppb	14.0	4.0	15.8	0.4	0.5	1.3	1.1	0.2	0.2	0.5	0.2
Br-I-benzene 2 ppb	3.6	7.5	3.3	1.5	0.8	1.7	1.0	0.0	0.0	0.8	0.2
Br-I-benzene 5 ppb	17.8	3.5	5.0	0.4	0.1	1.2	0.5	0.2	0.2	2.5	0.5
Br-I-benzene 10 ppb	7.7	13.2	6.0	0.5	0.2	3.0	0.6	0.2	0.3	4.4	0.1
Br-I-benzene 25 ppb	10.6	5.3	5.8	1.3	0.1	7.1	1.6	0.1	0.2	11.9	0.3
Br-I-benzene 100 ppb	8.6	4.1	3.1	0.2	0.2	28.3	0.6	0.1	0.1	44.7	0.5
mtbe BLANK			33.1		2.5		4.2	1.2	0.6		0.6
Sample 1 before	11.8	11.8	56.0	1.1	346.8	3.2	15.6		1.3	4.6	26.0
Sample 1 after	468.7	357.9	69.5	3315.0	293.7		44558.0	169.9	103.4		1.6
Sample 2 before	7.7	11.7	17.0	3.5	3.2		19.0	0.1	0.6	0.7	1.3
Sample 2 after	453.8	261.7	188.1	4819.9	1254.7	1377.7	121428.9	23.5	34.8	18.5	6.6
Sample 3 before	30.7	43.7	33.0	15.4	37.9		100.1	4.1	2.6	1.3	14.8
Sample 3 after	1465.5	130.0	70.9	3388.6	1130.8		126629.7	31.9	103.6	28.5	29.7

Conclusions

This study shows that when local wastewater are ozonated, a great decrease in TOrCs will be observed; however, depending on dose, NDMA formation can be formidable. Conversely, the formation of bromate did not seem significant in wastewaters due to high ozone consumption. NDMA formation was at times significant; however, infiltration seems to have attenuated precursors significantly. The formation of IDBs of known structure were at concentrations far lower than expected. Hoewver, the use of GC-ICP-MS demonstrated that a large number of currently unknown IDBPs and BrDBPs are formed during chloramination. This novel data should be more thoroughly explored using QTOF mass spectrometry and in vitro bioassays. Fortunately, the infiltration of RR water clearly improves water quality at nearly all measures and generally increase treatment performance do improvement in DOC, nitrate, and in ToRC concentrations.

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