CALIFORNIA DEPARTMENT OF WATER RESOURCES
CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

REMOVAL OF NDMA, EDCS AND PPCPS IN SOUTH DELTA WATER

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CALIFORNIA DEPARTMENT OF WATER RESOURCES
CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

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ABBREVIATIONS

Abbreviation	Term
BAF	Biologically Active Filtration
BB	Bottle Broken
BCAA	Bromochloroacetic Acid
BDCAA	Bromodichloroacetic Acid
BDCM	Bromodichloromethane
BPA	Bisphenol A
CAN	Chloroacetonitrile
CBZ	Carbamazepine
CCWD	Contra Costa Water District
CDBAA	Chlorodibromoacetic Acid
CDBM	Chlorodibromomethane
CDPH	California Department of Public Health
CDWR	California Department of Water Resources
CNM	Chloronitromethane
DBAA	Dibromoacetic Acid
DBPs	Disinfection Byproducts
DCAA	Dichloroacetic Acid
DCAN	Dichloroacetonitrile
DCNM	Dichloronitromethane
DIN	Dissolved Inorganic Nitrogen
DOC	Dissolved Organic Carbon

DON	Dissolved Organic Nitrogen
EBCT	Empty Bed Contact Time
EDC	Endocrine Disrupting Compound
E2	17β-estradiol
EE2	17α-ethinylestradiol
GAC	Granular Activated Carbon
HAA	Haloacetic Acid
HAA_7FP	Formation Potential – Sum of Seven HAAs
HPC	Heterotrophic Plate Counts
MBAA	Monobromoacetic Acid
MCAA	Monochloroacetic Acid
MDL	Method Detection Limit
NA	Not Available
NDBA	N-nitrosodibutylamine
NDEA	N-nitrosodiethylamine
NDMA	*N*-nitrosodimethylamine
NDPA	N-nitrosodiphenylamine
NMEA	N-nitrosomethylethylamine
4-NP	4-nonylphenol
NPYR	N-nitrosopyrrolidine
NPIP	N-nitrosopiperidine
PPCP	Pharmaceuticals and Personal Care Products
QAPP	Quality Assurance Project Plan
RL	Reporting Limit
SCVWD	Santa Clara Valley Water District

SSRIs	Serotonin Reuptake Inhibitors
SMX	Sulfamethoxazole
SUVA	Specific UV Absorbance
TBAA	Tribromoacetic Acid
TCAA	Trichloroacetic Acid
TCAN	Trichloroacetonitrile
TCNM	Trichloronitromethane
TDN	Total Dissolved Nitrogen
THM	Trihalomethane
THM_4FP	Formation Potential – Sum of Four THMs
TOC	Total Organic Carbon
TOX	Total Organic Halide
WTP	Water Treatment Plant
WRF	Water Research Foundation

REMOVAL OF NDMA, EDCS AND PPCPS IN SOUTH DELTA WATER

1.0 INTRODUCTION AND BACKGROUND

The San Francisco Bay/Sacramento-San Joaquin Delta (Delta) Estuary and Suisun Marsh are located at the confluence of California's two major river systems, the Sacramento River and San Joaquin River, and San Francisco Bay. The Delta is a source of drinking water to over 23 million Californians. Deterioration of the Delta source water quality due to xenobiotic inputs (e.g., agricultural drains and other surface discharges), and increased freshwater diversions is a growing concern for drinking water users. In particular, users must consider the possibility of significantly deteriorated water quality during a severe drought event. As such, Delta water utilities must be prepared for both the presence of existing contaminants (e.g., pesticides and nutrients) at significantly greater concentrations than currently observed, as well as trace organic compounds that are of emerging concern (e.g., endocrine disrupting compounds (EDCs), and pharmaceuticals and personal care products (PPCPs)). An additional concern with treatment of Delta waters is the formation of disinfection byproducts (DBPs) including trihalomethanes (THMs), haloacetic acids (HAAs), *N*-nitrosodimethylamine (NDMA) and other nitrosamines. There is a need for Delta utilities to understand the treatment effectiveness of existing treatment processes as well as other advanced treatment processes that may be implemented in the future.

This study focused on water quality in the South Delta and treatment of this source water. The South Delta generally encompasses the area between Franks Tract to the area south of Clifton Court Forebay. Delta utilities including Contra Costa Water District (CCWD) and Santa Clara Valley Water District (SCVWD) rely on the South Delta for source water. The experimental phase of this project was conducted with water from the CCWD's Bollman Water Treatment Plant (WTP). The plant is located in the City of Concord, California (Contra Costa County). A vicinity map is shown in Figure 1. Bollman WTP receives water from the Contra Costa Canal, which conveys Delta water from Rock Slough and/or Old River. At the time of this study, Rock Slough and Old River were CCWD's two major intakes. Since then, the Middle River intake has been constructed and began operating in 2010. All water treated at the Bollman WTP is conveyed through the Contra Costa Canal before treatment. Mallard Reservoir, a forebay to the treatment plant, contains water diverted from the Contra Costa Canal. The Bollman WTP operates using Mallard Reservoir, the Contra Costa Canal, or a blend of both.

Source water quality at the Bollman WTP is similar to other locations where municipal supplies are diverted from the South Delta. It is important to note that the experimental phase of this project was designed to illustrate the effectiveness of treatment technologies at removing trace organics in South Delta water. The project involved spiking trace organics

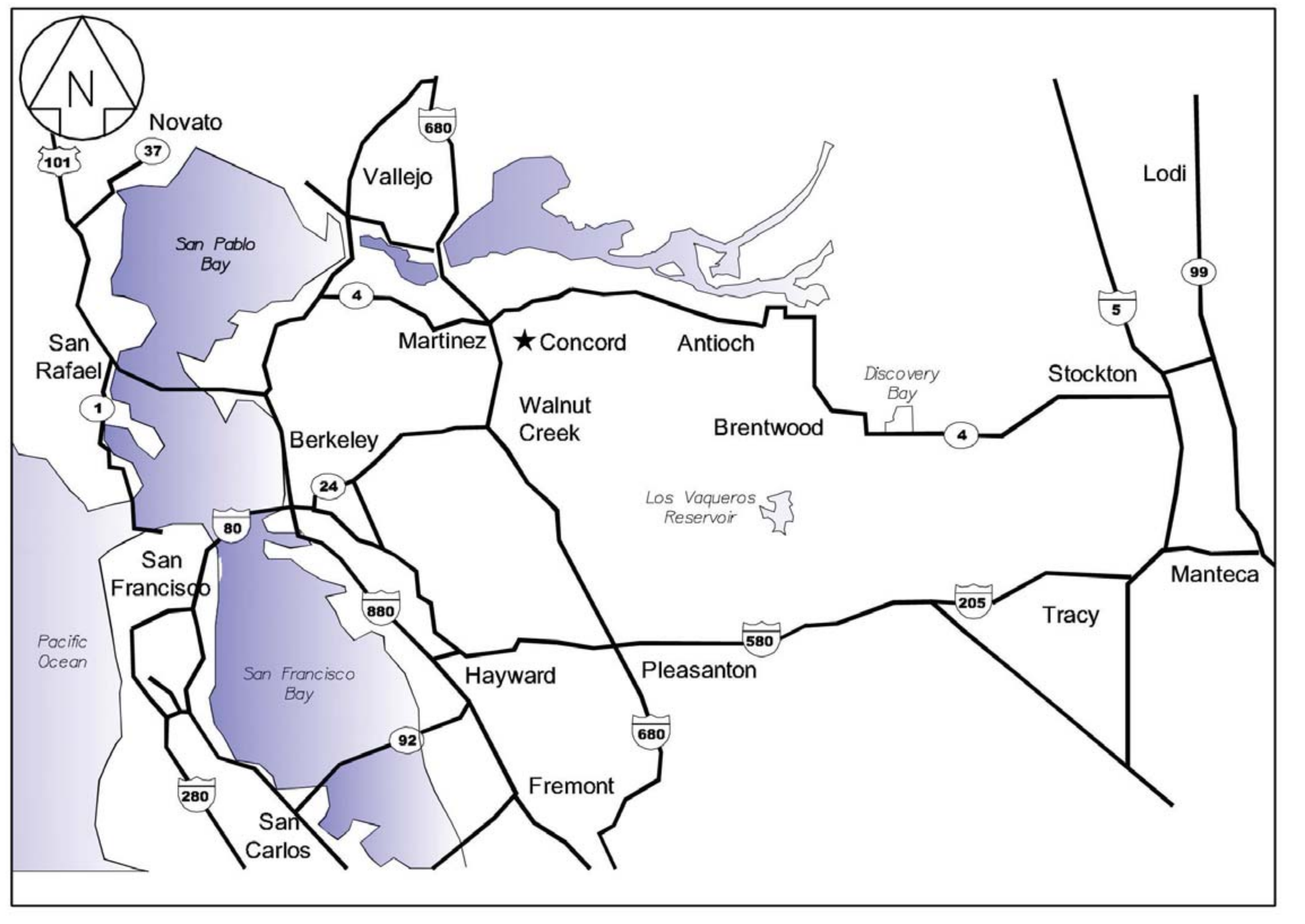

Figure 1
VICINITY MAP
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and evaluating treatment removal efficiencies. Therefore, the data collected in this project represents a simulation of treatment response to trace contaminants added to South Delta water and does not represent actual water quality produced at the Bollman WTP.

This project was funded through Proposition 50 grant funds. The funding was administered through the California Department of Water Resources (CDWR) and project oversight was provided by the California Department of Public Health (CDPH).

2.0 STUDY OBJECTIVES AND ORGANIZATION OF THE REPORT

The primary objective of the study was to examine selected potential treatment options for removal of trace organics. To meet this objective, a comprehensive research plan consisting of a series of research tasks was developed, as described as follows:

- Literature Review on Occurrence – A literature review on the occurrence of trace organics in Delta source water was conducted to determine which compounds were most commonly found in the Delta, and the concentrations of these compounds. The results of the literature review informed the decision on which compounds should be tested in the experimental phase of the project.

- Literature Review on Treatment Process Performance – A literature review on potential treatment plant processes and the effectiveness of these processes at removing trace organics was conducted. The results of this literature review were considered in the selection of treatment processes that were tested in the experimental phase of the project.

- Screening Analysis – A screening analysis of South Delta water was conducted to evaluate the presence of specific trace organics. The results of this site specific data collection effort were used combination with the literature review on occurrence to determine which compounds should be tested in the experimental phase of the project.

- Pilot Scale Testing of Selected Treatment Processes – Pilot scale testing of selected treatment processes was conducted to evaluate the effectiveness of treatment processes at removing trace organic contaminants. In order to better quantify process removal efficiencies, trace organics were spiked into the feed water to the treatment processes. The results of the pilot tests were used to compare the effectiveness of individual processes including ozone, perozone, biologically active filtration (BAF), and nanofiltration membranes. In addition, the data allowed evaluation of the combined effectiveness of some of these processes, including ozone followed by BAF and perozone followed by BAF. Overall, the pilot scale tests, provided site specific data on treatment process performance.

While the primary objective of the study focused on the removal of trace organics, one of the secondary objectives focused on DBP formation. The formation of DBPs is and ongoing challenge for Delta utilities, and this study provided an opportunity to examine the formation of both conventional and emerging DBPs from existing treatment processes as well as other advanced treatment processes that may be implemented in the future. This secondary objective of the study involved examining the overall performance of selected treatment processes with respect to DBP formation. To meet this objective, the research plan included bench scale disinfection tests and quantification of the formation of DBPs, as described as follows:

- Conventional Bench Scale DBP Formation Potential Tests – Formation potential tests were conducted on samples collected from pilot train feed water, after individual treatment processes, and from the finished water. These results allowed a relative comparison of the conventional DBP formation potential across the various treatment trains tested.

- Bench Scale Simulated Final Disinfection Tests – Bench scale disinfection tests were conducted on the finished water of the pilot test trains. In this case, disinfection tests were conducted, as part of, and in accordance with procedures and methods of a concurrent Water Research Foundation study. These results provided more detailed information on the formation of conventional and emerging DBPs, based on disinfection conditions/practices similar to those used at CCWD.

Another secondary objective of the study was to examine some of the operational issues associated with implementing nanofiltration. Delta utilities considering implementation of nanofiltration were interested in understanding more about some of the operational challenges associated with this treatment technology. To meet this objective, the fouling potential, impacts of chloramines for the purpose of controlling biofouling, and power demands of the pilot scale NF membranes were investigated, as described as follows:

- NF Membrane Fouling Potential – Water quality data were collected to estimate the potential for different types of fouling, including particulate fouling, mineral fouling, biofouling and organ fouling.

- Impacts of Chloramine use on DBP Formation – The contribution of DBP formation related to the use of chloramine to control biofouling of the NF membrane was quantified.

- Power Demands – Power demands of the pilot scale NF membrane process were measured to provide an estimated of the power demands of NF as compared to other advanced treatment processes.

The sections of this report describe the components of the overall research plan and the findings of the analysis, as follows:

- Section 3 – Literature review
- Section 4 – Screening analysis and selection of target compounds tested at the pilot scale
- Section 5 – Pilot scale testing of trace organic removal, evaluation of DBP formation, and evaluation of NF membrane performance.
- Section 6 - Summary of major conclusions of the study
- Section 7 – Future research

3.0 LITERATURE REVIEW

A literature review was conducted focusing on previous studies of the occurrence of trace organics in drinking water supplies, and research on the removal of trace organics by drinking water treatment processes. The literature review findings, along with other information, were used to select the pilot scale process trains and to identify the target compounds for the investigation.

The literature review was completed in early 2008. As discussed, the findings of the literature review were used to refine the experimental plan for the pilot tests. Therefore, it was completed in advance of the pilot testing, which began in Spring 2008. Since this time, there has been numerous studies on occurrence and removal of trace organics. Some of the most significant studies include Drewes et al. (2001), Cooper et al. (2010), Guo et al. (2010), and Kim and Tanaka (2010).

Throughout the literature review and subsequent sections of the report, concentrations of trace organics are presented. Because these compounds occur at low levels in source and treated waters, there are frequent reports of concentration below method detection limits (MDL) or below reporting limits (RL). Reference to DL or RL is consistent with the source of the data/information. EPA and CDPH definitions, respectively, are as follows:

- Method Detection Limit (MDL): The MDL is the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero, and is determined from analysis of a sample in a given matrix containing the analyte. Appendix A contains the necessary equations for calculating method detection limits. (40 CFR part 136, Appendix B, rev.1.11)

- Reporting Limit (RL): The RL is the lowest concentration at which an analyte can be detected in a sample and its concentration can be reported with a reasonable degree of accuracy and precision.

3.1 Occurrence of Trace Organics in Delta Source Waters

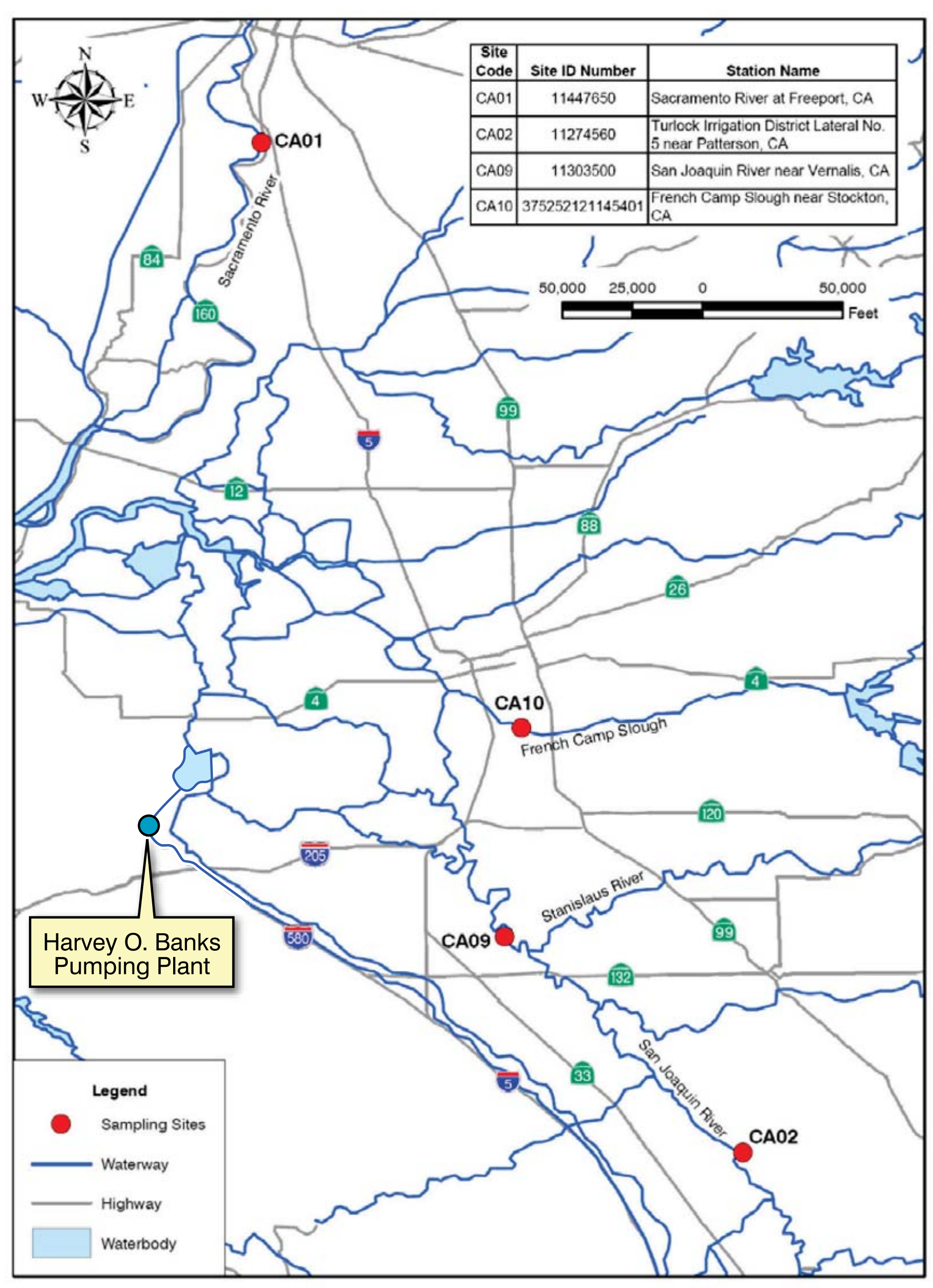
Historically, the Delta has been monitored for a limited number of pesticides and industrial chemicals. Data for these compounds are collected by DWR three times per year at the H.O. Banks Headworks, located south of Clifton Court Forebay as shown in Figure 2. Table 1 presents a summary of data collected between 1998 and 2003. In addition to these data, CCWD monitors approximately once per year for alachlor, atrazine and lindane from CCWD source waters, specifically Old River and Rock Slough. Between 2002 and 2006 all alachlor, atrazine and lindane concentrations were below the RLs of 1μg/L, 1μg/L, and 0.2 μg/L, respectively.

Table 1 Results of DWR Sampling for Selected Contaminants
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Constituent	Result	Reporting Limit (μg/L)
Alachlor	All results < RL	0.05
Atrazine	All results < RL	0.02
Lindane	All results < RL	0.01
Dichlorprop	All results < RL	0.1
Metolachlor	All results < RL	0.2, 0.05 (1)

Note:
RL = Reporting Limit
(1) For one of the sampling events the reporting limit was reported as 0.05 μg/L.

With respect to the trace organic compounds that are characterized as EDCs and PPCPs, there are limited data on the occurrence of the compounds in Delta waters. The most comprehensive study was conducted by the United States Geological Survey (USGS) and Kolpin et al (2002) (USGS (2002), Kolpin et al. (2002)). The most relevant Delta sampling locations (see Figure 3) are the Sacramento River at Freeport (USGS Site 11447650), Turlock Irrigation District Lateral No. 5 near Patterson (USGS Site 11274560), San Joaquin River near Vernalis (USGS Site (11303500), and French Camp Slough near Stockton (USGS Site 375252121145401). Composite samples from between 4 and 6 vertical profiles were collected from each site. Most sites were sampled once during the 1999 to 2000 study period and results are presented in Table 2. Due to the influence that the Sacramento River and San Joaquin River have on source water quality of Delta utilities, the data from the Sacramento River at Freeport and the San Joaquin River near Vernalis sites were identified as being most representative of "existing water quality". Compounds above the RLs at the Sacramento River and/or San Joaquin River sampling locations are shaded in gray in Table 2.



Site Code	Site ID Number	Station Name
CA01	11447650	Sacramento River at Freeport, CA
CA02	11274560	Turlock Irrigation District Lateral No. 5 near Patterson, CA
CA09	11303500	San Joaquin River near Vernalis, CA
CA10	375252121145401	French Camp Slough near Stockton, CA

Figure 2
MAP OF THE DELTA SHOWING THE H.O. BANKS PUMPING PLANT LOCATION AND SELECTED SAMPLING SITES FOR THE USGS (2002) STUDY
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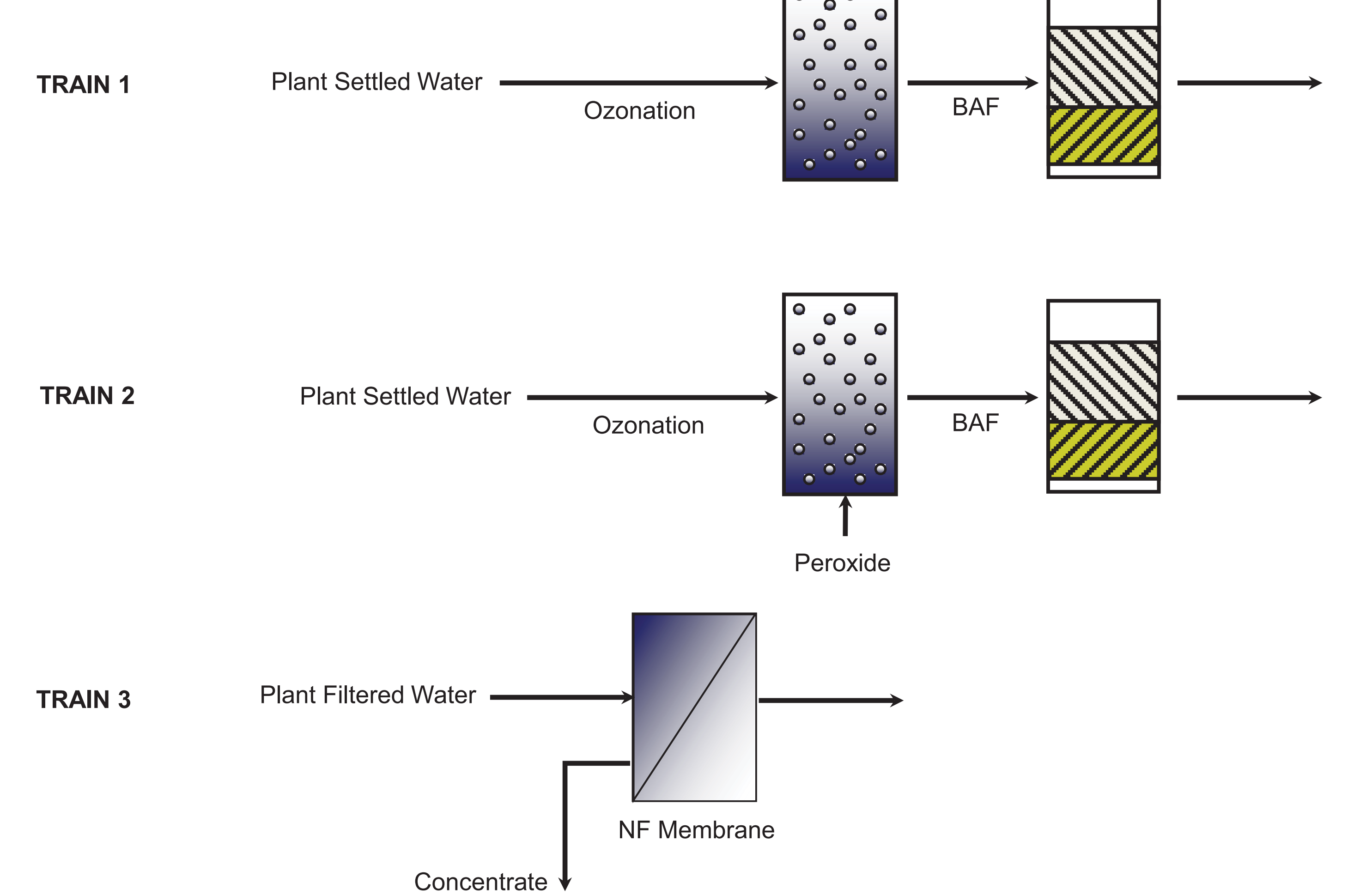

Figure 3
PILOT TESTING TREATMENT TRAINS
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Table 2	Contaminant Concentrations from the USGS (2002) Study Removal of NDMA, EDCs and PPCPs in South Delta Water California Department of Water Resources California Department of Public Health			
Constituent	**Sacramento River at Freeport (μg/L)**	**Turlock Irrigation District Lateral No. 5 near Patterson (μg/L)**	**French Camp Slough near Stockton (μg/L)**	**San Joaquin River near Vernalis (μg/L)**
Steroids				
17-β Estradiol	<0.005	0.002	-	-
Estrone	<0.005	<0.005	-	-
19-norethisterone	<0.005	0.113	-	-
Mestranol	0.011	<0.005	-	-
Estriol	<0.005	0.01	-	-
PPCPs				
Sulfamethoxazole	<0.023	<0.023	<0.023	<0.023
Gemfibrozil	<0.015	0.031	<0.015	<0.015
Ibuprofen	<0.018	0.16	<0.018	<0.018
Triclosan	<0.040	0.06	<0.040	0.01 E
Caffeine	<0.080	0.38	<0.060	0.08
Tris (2-chloroethyl) phosphate	<0.040	0.02 E	<0.040	<0.040
4-Nonylphenol	<0.500	<0.500	<0.500	<0.500
DEET	<0.040	0.06	-	-
Pesticides and Industrial Chemicals				
Bisphenol A	<0.090	<0.090	<0.090	0.06 E
Lindane (γ-BHC)	<0.500	0.01 E	<0.500	<0.500
Note: E = Estimated				

Snyder et al. (2007) sampled the source water and finished water of a Delta water treatment plant for EDCs, PPCPs and pesticides. The results of this study are presented in Table 3. Most analytes were present below the RLs in the raw and finished water. Compounds detected above the RLs in both raw water samples are shaded in gray in Table 3.

Combining data from these two studies, leads to a subset of trace organic compounds that occurred in Delta waters at concentrations above analytical reporting limits. The subset of compounds is presented in Table 4.

Table 3 EDC and PPCP Concentrations in the Source Water and Finished Water of a Delta Water Treatment (Snyder et al. 2007)
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Description	Raw	Raw Duplicate	Finished	Distribution System
Analyte	**ppt**	**ppt**	**ppt**	**Ppt**
Sulfamethoxazole	3.1	3.3	3.0	<0.25
Atenolol	12	8.2	<0.25	<0.25
Trimethoprim	0.25	<0.25	<0.25	<0.25
Fluoxetine	<0.50	<0.50	<0.50	<0.50
Norfluoxetine	<0.50	<0.50	<0.50	<0.50
Meprobamate	3.9	4.6	1.5	1.3
Dilantin	1.5	2.4	<1.0	<1.0
Carbamazepine	2.0	1.6	<0.50	<0.50
Atrazine	5.5	5.9	0.99	0.58
Diazepam	<0.25	<0.25	<0.25	<0.25
Linuron	4.1	4.0	<0.50	<0.50
Atorvastatin	<0.25	<0.25	<0.25	<0.25
o-Hydroxy atorvastatin	<0.50	<0.50	<0.50	<0.50
p-Hydroxy atorvastatin	<0.50	<0.50	<0.50	<0.50
Risperidone	<0.25	<0.25	<0.25	<0.25
Enalapril	<0.25	<0.25	<0.25	<0.25
Gemfibrozil	0.91	0.91	<0.25	<0.25
Bisphenol A	<5.0	<5.0	<5.0	<5.0
Simvastatin	<0.25	<0.25	<0.25	<0.25
Simvastatin hydroxy acid	<0.25	<0.25	<0.25	<0.25
Diclofenac	<0.25	1.0	<0.25	<0.25
Naproxen	0.72	0.59	<0.50	<0.50
Triclosan	1.5	1.4	1.2	<1.0
Testosterone	<0.50	<0.50	<0.50	<0.50
Progesterone	<0.50	<0.50	<0.50	<0.50
Estrone	0.44	0.43	<0.2	<0.2
Estradiol	<0.5	<0.5	<0.5	<0.5
Ethynylestradiol	<1.0	<1.0	<1.0	<1.0
Genistein	<1.0	<1.0	<1.0	<1.0
Daidzein	<1.0	<1.0	<1.0	<1.0

Table 3 EDC and PPCP Concentrations in the Source Water and Finished Water of a Delta Water Treatment (Snyder et al. 2007)
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Description	Raw	Raw Duplicate	Finished	Distribution System
Analyte	**ppt**	**ppt**	**ppt**	**Ppt**
Formononetin	<1.0	<1.0	<1.0	<1.0
Biochanin A	<1.0	<1.0	<1.0	<1.0
Apigenin	3.1	2.8	<1.0	<1.0
Naringenin	<1.0	<1.0	<1.0	<1.0
Coumestrol	<1.0	<1.0	<1.0	<1.0
Chrysin	1.7	2.4	<1.0	<1.0
Matairesinol	<5.0	<5.0	<5.0	<5.0
Equol	<10	<10	<10	<10
Glycitein	<1.0	<1.0	<1.0	<1.0
BHA	<25	<25	<25	<25
BHT	<25	<25	<25	<25
DEET	<25	<25	<25	<25
octylphenol	<25	<25	<25	<25
Benzophenone	<25	<25	<25	<25
□-BHC	<10	<10	<10	<10
□-BHC	<10	<10	<10	<10
□-BHC	<10	<10	<10	<10
TCEP	<50	<50	<50	<50
TCPP (Fyrol PCF)	<50	<50	<50	<50
Diazinon	<10	<10	<10	<10
□-BHC	<10	<10	<10	<10
Traseolide	<25	<25	<25	<25
Galaxolide	<25	<25	<25	<25
Tonalide	<25	<25	<25	<25
Vinclozolin	<10	<10	<10	<10
Metolachlor	28	27	<10	<10
Musk Ketone	<25	<25	<25	<25
Octachlorostyrene	<10	<10	<10	<10
Butylbenzyl phthalate	<50	<50	<50	<50
Methoxychlor	<10	<10	<10	<10
Dioctyl phthalate	<50	172	59	53
Nonylphenol	<50	<50	<50	<50

Table 4 Compounds Detected in Delta Waters Based on Koplin et al. (2002) and Snyder et al. (2007) Removal of NDMA, EDCs and PPCPs in South Delta Water California Department of Water Resources California Department of Public Health	
Compound	**Compound**
Mestranol	Atrazine
Triclosan	Linuron
Caffeine	Gemfibrozil
Bisphenol A	Estrone
Sulfamethoxazole	Naproxen
Atenolol	Apigenin
Meprobamate	Chrysin
Dilantin	Metolachlor
Carbamazepine	

The compounds listed in Table 4 provided a starting point for selecting compounds to target for treatability testing at the pilot-scale. Other considerations included past research on treatability, a desire to experimentally capture compounds exhibiting a wide variety of physical and chemical properties, and the availability of analytical methods.

3.2 Removal of Trace Organic Compounds in Drinking Water Processes

The existing treatment train at CCWD's Bollman WTP includes prechlorination, pH depression, alum coagulation/flocculation, conventional sedimentation, intermediate ozonation, and dual media (Granular Activated Carbon (GAC)/sand) filtration. The GAC/sand filtration process is biologically active (i.e., biologically active filtration (BAF)). CCWD also practices chloramination as secondary disinfection. Several other Bay Area utilities also employ intermediate ozonation followed by BAF.

The treatment plants in the Bay Area were not designed specifically for the removal of the trace organic compounds. Furthermore, the majority of these contaminants are not regulated and are therefore not regularly monitored. Thus, the effectiveness of the existing processes of the Bay Area utilities to remove these compounds is not well understood. While it is not possible to test for every conceivable trace contaminant, work has shown that structural similarities between compounds can be exploited to predict their removal during some water treatment processes with fairly good certainty (Lei et al., 2007).

Listed in Table 5 are qualitative treatment efficacies for the removal of pesticides, steroids, and PPCPs of several technologies that are employed or may be considered by Delta utilities.

Table 5 Anticipated Effectiveness of Various Treatment Technologies for Removing Pesticides, Steroids and PPCPs
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Treatment Technology	Anticipated Effectiveness				References
	General	Pesticides	Steroids	PPCPs	
Flocculation/ Sedimentation (alum or ferric coagulants)	Removes hydrophobic compounds.	Poor	Poor	Poor	Ternes, et al., (2002) Snyder, et al., (2003)
Ozonation	Removes aromatic compounds and aliphatic compounds with thiol, amine, hydroxyl and carboxyl functional groups	Variable[1]	Excellent	Variable[1]	Ternes, et al., (2002) Huber, et al., (2003) Alum, et al., (2004) Westerhoff, et al. (2005) Hua, et al. (2006) Snyder, et al. (2006) Ning, et al. (2007) Snyder, et al. (2007)
Perozone (ozone with peroxide)	Hydroxyl radical based oxidation, more powerful and less selective oxidant than ozone.	Excellent	Excellent	Variable[1]	Ternes, et al., (2002) Huber, et al., (2003) Acero, et al. (2003) Snyder, et al. (2007)
Biological GAC filtration	Operating as GAC, removes hydrophobic compounds, operating as BAC, removes biodegradable organics.	Variable[1]	Variable[1]	Variable[1]	Fuerhacker, et al., (2001) Snyder, et al., (2003) Snyder, et al. (2005) Jiang, et al. (2006) Fukuhara, et al. (2006) Snyder, et al. (2007)
Membrane Filtration (inclusive of microfiltration, nanofiltration, and reverse osmosis)	Removes compounds through size exclusion and hydrophobic adsorption	Good	Variable[1]	Variable[1]	Nghiem, et al. (2004) Kosutic, et al. (2005) Yoon, et al., (2006) Snyder, et al (2006) Khan et al. (2004) Snyder, et al. (2007)

Note:
(1) "Variable" effectiveness means that the effectiveness ranged from poor to good in the studies cited.

The results of the literature review on the effectiveness of various treatment technologies was used to define the treatment processes to be evaluated in this study. The literature suggests that ozonation and BAF may effectively remove some trace organic compounds. The literature also suggests that the combination of ozone and peroxide (perozone), and membrane treatment (nanofiltration and reverse osmosis) are effective technologies for removing some trace organic compounds. While the literature review formed the basis for selecting processes to be tested at the pilot scale, the feasibility of implementing new treatment technologies in Delta utilities was also considered. Since several utilities currently employ intermediate ozonation followed by BAF, the addition of peroxide for advanced oxidation could be implemented relatively easily. In addition, nanofiltration (NF) membranes could be added to these treatment processes as a polishing step before disinfection. The following discussion includes additional information on the effectiveness of the ozone, perozone, BAF, and NF membranes.

3.2.1 Ozone and Perozone

Ozone and perozone can both be used to remove trace organic compounds, however their effectiveness varies. Ozone reacts more efficiently with compounds containing amine groups, phenolic groups, and unsaturated carbon structures in general. There are many trace compounds, however, that are relatively slow to react with ozone. Snyder et al. (2007) summarized the removal of selected trace organics at 2 and 24 minutes of ozone contact time. Table 6 presents the summarized results.

When hydrogen peroxide is combined with ozone, hydroxyl radicals are formed. These radicals are stronger oxidants than ozone itself, and generally react with contaminants more universally and more quickly than ozone. For example, X-ray contrast media is relatively unreactive towards ozone, but can be more effectively oxidized using perozone (Ternes et al., 2003). However, while perozone may provide faster and more consistent removal of the broad range of trace contaminants, it is a more expensive and complicated process. Furthermore, there is currently no disinfection credit for the hydroxyl radical, since the hydroxyl radicals react too indiscriminately to be an effective disinfectant.

3.2.2 Biologically Activated Filtration

Researchers have shown that adsorption on granulated activated carbon provides good removal for trace organics (Kim et al., 2007). However, most Delta utilities that employ BAF, operate these filters in biologically active mode. This mode of operation will greatly reduce the number of adsorptive sites on the carbon surface and therefore reduce removal through that mechanism. However, the microbial communities that develop on the carbon surface can reduce contaminant concentrations through biotransformation (Al-Rifai et al. (2007)). In biologically active mode, easily-biotransformed compounds will be preferentially removed.

Table 6	Summary of Minimum Percent Removal of Selected Trace Contaminants by Ozonation (adapted from Snyder et al. 2007) Removal of NDMA, EDCs and PPCPs in South Delta Water California Department of Water Resources California Department of Public Health			
2 Minutes Contact Time	**24 Minutes Contact Time**			
>95% Removal	**>80% Removal**	**50-80% Removal**	**20-50% Removal**	**<20% Removal**
Acetaminophen	Androstenedione	DEET	Atrazine	TCEP
Carbamazepine	Caffeine	Diazepam	Iopromide	
Diclofenac	Pentoxifylline	Dilantin	Meprobamate	
Erythromycin-H_20	Progesterone	Ibuprofen		
Estradiol	Testosterone			
Estriol				
Estrone				
Ethynylestradiol				
Fluoxetine				
Gemfobrozil				
Hydrocodone				
Naproxen				
Oxybenzone				
Sulfamethoxazole				
Triclosan				
Trimethoprim				

Snyder et al. (2007) summarized the removal of trace organics through BAF pilot testing. In general, the removal efficiencies of the trace organics tested were low. Table 7 presents a summary of the results.

3.2.3 Nanofiltration

Removal of trace organics through nanofiltration has been well studied. Removals range from approximately 30 percent to more than 95 percent (Kim et al. (2007); Yoon et al. (2006). Nanofiltration works both by size exclusion and by adsorption onto the membrane surface. Therefore, both hydrophobic and large compounds will be preferentially removed (Yoon et al. (2006)).

Snyder et al. (2007) summarized the removal of trace organics through NF for three different systems. Most of the removal efficiencies of the trace organics tested ranged from 50 to 80 percent. Table 8 presents a summary of the results.

Table 7 Summary of Biological Processes Pilot Scale Testing (adapted from Snyder et al. 2007)
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

>95% Removal	>80% Removal	50-80% Removal	20-50% Removal	<20% Removal
Fluoxetine (1)	Benzo[a]pyrene(1)	Progesterone(1)	Androstenedione (1)	Acetaminophen (1)
	DDT (1)		Erythromycin-H_20(1)	Atrazine (2)
			Fluorene (1)	Caffeine (2)
			Ibuprofen (2)	Carbamazepine (2)
			Testosterone (1)	DEET (2)
			Triclosan (1)	Diazepam (1)
			Trimethoprim (1)	Diclofenac (1)
				Dilantin (2)
				Estriol (1)
				Estrone (1)
				Ethynylestradiol (1)
				Galaxolide (2)
				Gemfobrozil (1)
				Hydrocodone (1)
				Iopromide (2)
				Lindane (1)
				Meprobamate (2)
				Metolachlor (1)
				Musk Ketone (1)
				Naproxen (1)
				Oxybenzone (1)
				Sulfamethoxazole(1)

Notes:

(1) Based on pilot testing of a biologically active anthracite filter (BAF) that was not used for adsorption

(2) Based on the BAF (see Note 1) and full scale GAC beds that were operated in biological mode

Table 8	Summary of NF membrane testing (adapted from Snyder et al. 2007) Removal of NDMA, EDCs and PPCPs in South Delta Water California Department of Water Resources California Department of Public Health		
>80% Removal	**50-80% Removal**	**20-50% Removal**	**<20% Removal**
Benzo[a]pyrene	Androstenedione	Acetaminophen	
DDT	Atrazine	Naproxen	
Erythromycin	Caffeine		
Fluorene	Carbamazepine		
Fluoxetine (Prozac)	DEET		
Iopromide	Diazepam		
Musk Ketone	Diclofenac		
Oxybenzone	Dilantin		
Triclosan	Estradiol		
	Estriol		
	Estrone		
	Ethynylestradiol		
	Galaxolide		
	Gemfobrozil		
	Hydrocodone		
	Ibuprofen		
	Lindane		
	Meprobamate		
	Metolachlor		
	Pentoxifylline		
	Progesterone		
	Sulfamethoxazole		
	TCEP		
	Testosterone		
	Trimethoprim		

4.0 SCREENING ANALYSIS OF TRACE ORGANICS IN THE DELTA

Two initial screening sampling events for trace organic compounds present in the Delta water were performed. Samples were drawn from CCWD's Old River intake on October 15, 2007. Samples were also drawn from the Bollman WTP influent on February 25, 2008. The

purpose of the screening sampling was to help to refine the selection of compounds to be analyzed for treatability in the pilot-scale testing. This sampling approach allowed evaluation of the different water sources that are used to supply the Bollman WTP. These locations capture a range of sources with varying anthropogenic inputs. During the screening analysis, samples were taken from the sampling locations and analyzed for the compounds listed in Table 9. NDMA was not included in the screening analysis because it had already been identified as a compound that would be studied at the pilot scale.

Table 9 Compounds Included in Screening Sampling
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Class	Compound
Acidic Drugs	Gemfibrozil
	Acetaminophen
	Ibuprofen
	Naproxen
Neutral Drugs	Carbamazepine
	Caffeine
	Cotinine (nicotine metabolite)
	Trimethoprim
Estrogens & Xenoestrogens	17α-ethinylestradiol (EE2)
	17β-estradiol (E2)
	Estrone (E1)
	4-nonylphenol
Plasticizers	Bisphenol-A
Antibacterial Agents	Triclosan
	Triclocarban
Sulfonamide Antibiotics	Sulfamethoxazole
	Sulfapyridine
Synthetic Musks	HHCB (Galaxolide)
	AHTN (Tonalide)
	DPMI (Cashmeran)
	ATII (Traseolide)
	ADBI (Celestolide)
	AHMI (Phantolide)
	Musk xylene
	Musk ambrette
	Musk moskene
	Musk tibetene

Table 9 Compounds Included in Screening Sampling Removal of NDMA, EDCs and PPCPs in South Delta Water California Department of Water Resources California Department of Public Health	
Class	**Compound**
	Musk ketone
Beta Blockers	Propranolol
	Metoprolol
	Atenolol
	Sotolol
Selective Serotonin Reuptake Inhibitors	Fluoxetine and norfluoxetine
	Venlafaxine and O-desmethyl venlafaxine
	Citalopram and desmethyl citalopram
	Sertraline and desmethyl sertraline
	Bupropion
	Paroxetine
X-ray Contrast Media	Iopromide
Pesticides	Atrazine
	Simazine

4.1 Sampling Procedures

At each sampling location grab samples were taken for EDCs/PPCPs/industrial chemicals testing, iopromide testing, and pesticide testing in the volumes of 7L, 3L, and 3L, respectively. Additionally, field blank samples were taken for each test at each sampling location. Samples were sent to Trent University and MWH for analysis. More detailed sampling and shipment procedures are outlined in Appendix H.

4.2 Sample Analysis of Screening Compounds

Trent University did not have capabilities to analyze all compounds listed in Table 9, and therefore samples were also sent to MWH Labs for analysis. Some of the analyses offered by MWH labs are inclusive of a group of compounds. Therefore, as a result, some compounds were analyzed both at Trent University and MWH labs. Detailed protocols for the analysis of each class of compounds analyzed at Trent University are provided in Appendix C. Methods used by MWH labs are referenced in Appendix D. The data gathered from the screening analysis was not statistically analyzed as the purpose of the screening analysis was to simply determine the potential presence of the various trace organic compounds listed in Table 9, such that appropriate compounds could be selected for the pilot testing phase of the study.

4.3 Screening Analysis Results

Of the screening compounds analyzed (listed above in Table 9), those present in detectable concentrations, from at least one of the laboratories, are presented in Table 10 for both the fall and winter sampling events. Differences in the analytical results from Trent University and MWH labs are attributed to differences between samples (i.e., separate samples were collected and sent to the individual labs) and to analytical variability between laboratories.

Table 10 Screening Analysis Data For Detectable Compounds
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Compound Category	Sample Location / Laboratory [1] =>	Old River: Trent University (µg/L)	Old River: MWH (µg/L)	Bollman Intake: Trent University (µg/L)	Bollman Intake: MWH (µg/L)
Acidic drugs	Acetaminophen	0.012	0.076	ND	0.041
	Ibuprofen	0.011	ND	ND	0.001
	Gemfibrozil	ND	0.018	0.020	0.007
Neutral drugs	Cotinine	0.006	ND	0.009	ND
	Caffeine	0.016	0.024	0.028	ND
	Carbamazepine	0.004	ND	0.003	ND
	Trimethoprim	0.005	ND	ND	ND
Beta-blockers	Atenolol	0.011	ND	0.023	ND
	Metoprolol	0.005	ND	ND	ND
Antibacterials	Triclosan	0.005	ND	0.035	ND
Sulfonamide Antibiotics	Sulfamethoxazole	ND	0.018	ND	0.005
Musks	Galaxolide	0.017	ND	NA	ND
Plasticizers	Bisphenol-A	3.485 [2]	ND	ND	ND
Estrogens & xenoestrogens	4-Nonylphenol	0.006	ND	ND	ND
	Estrone	0.016	ND	ND	0.001
Pesticides	Simazine	ND	ND	ND	0.060

Notes:

(1) For some compounds, analyses were conducted at both Trent University and MWH labs. Differences in the analytical results from Trent University and MWH labs are attributed to differences between samples (i.e. separate samples were collected and sent to the individual labs) and to analytical variability between laboratories.

(2) Based on results from the MWH lab and the other sample, this value is a suspected outlier.

4.4 Selection of Target Compounds

The criteria for selecting target compounds included:

- Variability in structure, properties, and expected variability in removal by ozone, perozone, NF, and biofiltration
- Occurrence of compound or similar compound in Delta water and/or Bollman WTP influent
- Availability of analytical method for detection and quantification
- Ability to legally purchase/obtain compounds for testing
- Consistency with past research

The compounds selected were:

- Gemfibrozil - Acidic pharmaceutically active compound (PhAC) that is negatively charged at neutral pH. Represents a large class of acidic drugs that are commonly detected in surface water
- Carbamazepine - Neutral psychoactive drug that is persistent in the environment and has unique properties that may affect its removal by ozone and ozone peroxide
- Caffeine - Neutral psychoactive drug that is commonly found in surface water and has unique properties that affects its removal by NF
- Atenolol - Beta blocker that is positively charged at neutral pH which makes it a unique compound for removal by NF
- Bisphenol-A - Neutral industrial chemical (plasticizer) that has a unique structure (e.g., phenol), is commonly detected in surface water, and is an EDC
- Atrazine - Neutral, and heavily used pesticide that is commonly detected in surface water and groundwater
- Sulfamethoxazole - Neutral (slightly positive depending on pH) antimicrobial that is commonly detected in surface water
- Estrone - Neutral steroidal hormone and EDC that was previously detected in Delta waters

Of the compounds presented in Table 9, the following compounds were eliminated from the target compound list:

- Mestranol - Eliminated based on availability of analytical methods and because it has properties and reported removal similar to other hormones (e.g., estrone, 17β-estradiol)
- Dilantin, Apignen, and Chrysin - Eliminated based on availability of analytical methods

- Linuron - Eliminated based on availability of analytical methods
- Naproxen - Eliminated because it has properties and reported removal similar to other acidic drugs. (e.g., gemfibrozil and ibuprofen)
- Metolachlor - Eliminated because it has properties and reported removal similar to other compounds selected (e.g., atrazine)
- 17β-estradiol (E2) - Neutral, relatively hydrophobic steroidal hormone and EDC that is commonly detected in surface water. Deleted due to similarity to estrone and because it was not previously detected in Delta waters.
- Meprobamate - Eliminated based on difficulty in acquiring sufficient amounts of the chemical.
- All of the selective serotonin reuptake inhibitors (SSRIs) - Neutral compounds that have not been well studied.

During the course of the literature review, additional compounds were identified that were added to the target compound list. These compounds were added to broaden the range of types and properties of compounds tested, to challenge the selected treatment processes, and/or to investigate the removal of compounds that have not been as well documented in past studies. The compounds include:

- Ibuprofen - Acidic PhAC that is commonly found in surface water samples. Similar to gemfibrozil but smaller size makes it interesting for NF testing
- 4-Nonylphenol – Neutral, relatively hydrophobic industrial chemical and by-product of surfactants that is commonly found at relatively high concentrations in surface water. As a surfactant, it has unique properties including a distinct hydrophilic and hydrophobic portion of its structure.
- Iopromide - Neutral, large molecular weight, X-ray contrast media. Considered to be persistent in the environment and not well studied.
- Synthetic musk (musk ketone) – Neutral, hydrophobic compounds that are not well studied and have unique properties.
- Triclosan - Neutral antimicrobial agent that is commonly found in Delta waters.

The list of target compounds and compound characteristics are presented in Table 11.

The list of target compounds is presented in Table 12 along with reported occurrence in Delta waters and expected removal based on the literature review. As discussed, some of the compounds are more likely to be present in Delta waters. In addition, results of the literature review suggest that there will be variability in the removal efficiencies of the compound by the treatment technologies.

Table 11 Target Compounds for the Pilot Testing Experiments
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Compound	CAS#	Structure	Formula	MW (g/mol)	log K_{ow}[1,2]	pK_a[2]	Charge[1]	Class of Compound	Grouping for Study
Gemfibrozil	25812-30-0		$C_{15}H_{22}O_3$	250.3	2.1	4.8	Negative	PhAC - Cholesterol Control	Hydrophilic, Ionic (negative)
Ibuprofen	15687-27-1		$C_{13}H_{18}O_2$	206.3	1.2	4.4	Negative	PhAC - Analgesic	Hydrophilic, Ionic (negative)
Estrone	53-16-7		$C_{18}H_{22}O_2$	270.3	3.1	10.4	Neutral	Steroid	Hydrophobic neutral
Triclosan	3380-34-5		$C_{12}H_7Cl_3O_2$	289.6	4.8	NA	Neutral	Antibacterial agent	Hydrophilic neutral
4-Nonylphenol	25154-52-3		$C_{15}H_{24}O$	220.4	5.8	NA	Neutral	Surfactant, byproduct of APE degradation	Hydrophobic neutral
Bisphenol-A	80-05-7		$C_{15}H_{16}O_2$	228.3	3.4	9.7	Neutral	Industrial chemical, plasticizer	Hydrophobic neutral
Iopromide	73334-07-3		$C_{18}H_{24}I_3N_3O_8$	791.1	-2.1	NA	Neutral	X-ray contrast media	Hydrophilic neutral
Sulfamethoxazole	723-46-6		$C_{10}H_{11}N_3O_3S$	253.3	0.9	5.7	Neutral (<10% positive)	Antibiotic	Hydrophilic neutral (slightly positive)

Table 11 Target Compounds for the Pilot Testing Experiments
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Compound	CAS#	Structure	Formula	MW (g/mol)	log $K_{ow}^{1,2}$	pK_a^2	Charge[1]	Class of Compound	Grouping for Study
Musk Ketone	81-14-1		$C_{14}H_{18}N_2O_5$	294.3	4.3	NA	Neutral	Synthetic fragrance	Hydrophobic neutral
Atenolol	29122-68-7		$C_{14}H_{22}N_2O_3$	266.3	0.2	9.6	Positive	PhAC - Beta blocker	Hydrophilic, Ionic (positive)
Caffeine	58-08-2		$C_8H_{10}N_4O_2$	194.2	-0.07	10.4	Neutral	PhAC - Stimulant	Hydrophilic neutral
Carbamazepine	298-46-4		$C_{15}H_{12}N_2O$	236.3	2.45	13.9	Neutral	PhAC - Anti-epileptic, anti-depressant	Hydrophobic neutral
Atrazine	1912-24-9		$C_8H_{14}ClN_5$	215.7	2.6	1.7	Neutral	Pesticide	Hydrophobic neutral

Notes:
(1) At neutral pH
(2) pK_a and Log K_{ow} are values obtained from Environmental Science Database SRC Physprop

Table 12 List of Preliminary Target Compounds and Anticipated Removals Based on Literature Review
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Compound	Type	Measured Occurrence	Expected NF Removal	Expected Ozone Removal	Expected Perozone Removal
Gemfibrozil	PhAC	Yes	Good (>95%)	Moderate (50 -70%)	Good (>90%)
Ibuprofen	PhAC	No	Good (>95%)	Poor to moderate (20 - 50%)	Good (>90%)
Estrone	Hormone	No	Good (>90%)	Good (>90%)	Good (>90%)
Triclosan	Antimicrobial	Yes	Moderate to good (70 - 90%)	Moderate (50 -70%)	Good (>90%)
4-Nonylphenol	Degradation by-product	No	Moderate to good (70 - 90%)	Moderate (50 -70%)	Good (>90%)
Bisphenol-A	Plasticizer	Yes	Moderate to good (70 - 90%)	Moderate (50 -70%)	Good (>90%)
Iopromide	X-ray contrast media	No	Good (>90%)	Poor to moderate (20 - 50%)	Moderate (50 - 70%)
Sulfamethoxazole	Antibiotic	Yes	Good (>90%)	Good (>90%)	Good (>90%)
Musk Ketone	Musk	NA	Good (>90%)	Poor to moderate (20 - 50%)	Poor to moderate (20 - 50%)
Atenolol	PhAC	Yes	Moderate to good (70 - 90%)	Poor to moderate (20 - 50%)	Poor to moderate (20 - 50%)
Caffeine	PhAC	Yes	Moderate to good (70 - 90%)	Good (>90%)	Good (>90%)
Carbamazepine	PhAC	Yes	Good (>90%)	Good (>90%)	Good (>90%)
Atrazine	Pesticide	Yes	Good (>90%)	Poor to moderate (20 - 50%)	Poor to moderate (20 - 50%)

5.0 ADVANCED TREATMENT PILOT STUDY

Experiments were performed using three different pilot-scale treatment trains at the Bollman WTP. This section outlines the pilot experiments including equipment, target compounds, sampling procedures, test conditions, and testing location.

5.1 Pilot Testing Phases and Equipment

5.1.1 Pilot Testing Phases

The study focused on the treatment efficacy of three treatment trains, as shown in Figure 3, and was conducted in three phases:

- Phase 1: Treatment train #1 includes feed water from the effluent of the full scale sedimentation basins followed by ozonation and then followed by BAF. This treatment train includes processes currently employed at the full scale treatment plant (at the Bollman WTP and at other Delta utilities). The objective of evaluating this treatment train was to assess the ability of these existing processes to remove trace organics. The experimental plan was designed to allow evaluation of the removal efficiencies of ozonation and BAF, and the cumulative removal achieved by the treatment train.
- Phase 2: Treatment train #2 includes feed water from the effluent of the full scale sedimentation basins followed by ozone/peroxide (perozone) and then followed by BAF. Some Delta utilities are interested in advanced oxidation due to the relative ease of adding peroxide to existing ozonation processes (and common, seasonal taste and odor issues in Delta water). The objective of evaluating this treatment train was to assess the ability of existing processes, with the relatively minor modification of adding peroxide, at removing trace organics. The experimental plan was designed to allow evaluation of the removal efficiencies of perozone and BAF, and the cumulative removal achieved by the treatment train.

Phase 3: Treatment train #3 includes NF membranes. In this phase, the feed water to the pilot was full-scale filtered water. The objective of this treatment train was to evaluate the removal of trace organics achieved by the NF membrane without upstream treatment of the spiked target compounds by ozonation and BAF. This was achieved by spiking the target compounds in the feed water (full scale- filtered water) to the NF membranes. For Delta utilities interested in nanofiltration, this treatment train provides information on the effectiveness of NF membranes at removing trace organics.

As a secondary focus, the operation of the NF membrane was documented.

This evaluation included assessment of fouling potential, impacts of chloramines for the purpose of controlling biofouling, and power demands. To evaluate fouling potential, water quality data were collected before in the feed water, permeate and brine waste of the NF membranes. The water quality parameters included organics, mineral and biological constituents, selected to assess various types of fouling potential. To evaluate the impacts

of chloramines for the purpose of controlling biofouling, samples were collected in the feed water to the NF membranes pre- and post-chloramination, and in the NF permeate. These samples were subject to DBP formation potential tests. Power demands were estimated based on measurements of the cumulative power demand while the NF membrane process was in operation.

5.1.2 Ozone Pilot

The ozone pilot plant, shown in Figure 4, was provided by Intuitech, Inc. (Ozone Module Z100, Salt Lake City, Utah). The unit consisted of 5 ozone contactor columns in series, however only 3 contactor columns were considered as part of the reactor. The first column was considered the influent tank, and ozone was applied to the second column. The third and fourth columns provided additional contact time, and the fourth column overflowed to the fifth column, which was considered the effluent tank. The pilot ozone system was operated to mimic the operation of the Bollman plant, which applies ozone to achieve a 0.5-log *Giardia* and 2-log virus inactivation. At the time of the pilot testing, this amounted to a 0.5 - 1.6 milligrams per liter (mg/L) applied ozone dose, resulting in a 0.2 - 0.3 mg/L ozone residual after 8 minutes of contact time. The ozone skid was equipped with a data logger that recorded the ozone gas feed rate, the ozone concentration in the gas, the water flow rate, and the ozone residual concentration. The ozone residual was measured via UV adsorption at the effluent of the ozonation process (the top of the fourth column) for the purpose of calculating CT.

The ozone generator on the ozone skid was set to run at 65 percent of its maximum output. The air/ozone gas flow rate into the feed column was set at 5.0 standard cubic feet per hour (SCFH) (+/- 0.5 SCFH). The settled water from the full-scale sedimentation basins was fed through the ozone system at a rate of 5 gpm to achieve the desired 8 minutes of contact time in the three columns representing the ozone contactor in the pilot system. The theoretical contact time (T) was calculated using the volumetric flowrate and the cumulative volume of the columns. Offline instrumentation was used to verify the performance of the ozone residual analyzer. This process involved comparing the ozone concentration provided by the pilot's online analyzer with a sample measurement obtained utilizing a HACH AccuVac ampules with HACH DR test kits (indigo trisulfonate method).

5.1.3 Peroxide Addition

Peroxide was added to the influent (bottom) of the fourth column of the ozone contactor, as shown in Figure 5, to generate hydroxyl radicals. An important parameter for peroxide addition is the molar ratio of peroxide to ozone. Snyder et al. (2007) cited past studies that suggested that improved removal of some organics occurred with the addition of hydrogen peroxide at 0.4 to 0.7 mg peroxide/ozone. This is equivalent to a molar ratio of approximately 0.5 to 0.9 peroxide to ozone. Therefore, an intermediate molar ratio of 0.7

Figure 4
INTUITECH OZONE MODULE Z100
SET UP ON SITE AT BOLLMAN WTP
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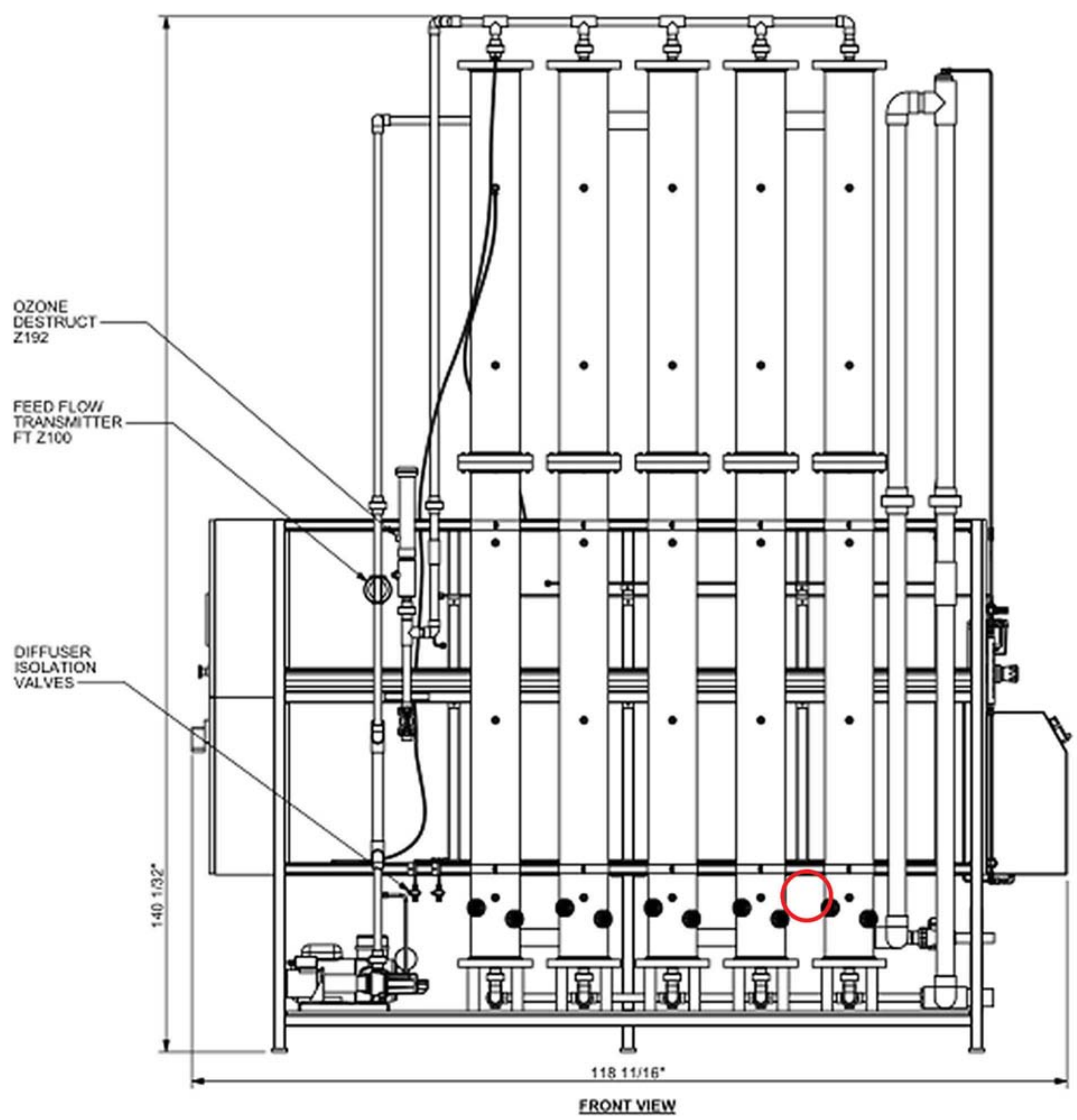

Figure 5
LOCATION OF HYDROGEN PEROXIDE DOSING PORT ON OZONE SKID
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was selected for this study. If peroxide and ozone were simultaneously dosed at a given location, then the peroxide dose would be based on the ozone dose. However, in this study, peroxide was dosed after ozone, at an intermediate location in the ozone contractor. Therefore, the peroxide dose was based on the ozone residuals entering the fourth column of the reactor, the peroxide dosing location. Given that ozone residuals entering the fourth column were typically in the range of 0.04 – 0.14 mg/L, peroxide doses were therefore in the order of 0.03 – 0.10 mg/L.

A solution of 0.05 percent hydrogen peroxide in settled feed water was created and fed into the system at a rate of 7 +/- 0.5 mL/min. This rate was controlled using a laboratory peristaltic pump (Model Number 7553-80, Cole Parmer Instruments, Vernon Hills, Illinois) and size 14 Neoprene tubing.

5.1.4 BAF Skid

Carollo provided a BAF skid, shown in Figure 6, that included three filter columns, each 4 inches in diameter and 14 feet tall. Exhausted GAC was obtained from the full-scale filters at the Bollman WTP and used in the filter skid system to try to promote removal by biodegradation as opposed to by adsorption. The 4-inch diameter column has been found to provide performance representative of full-scale filters, with minimal wall effects, when the pilot and full-scale filters share the same bed depth and media size. The filters contained approximately 4 feet of GAC overlying 10 inches of sand bedding and were operated at a filter flow rate 0.52 gallons per minute (gpm) (approximate filter loading rate of 6 gpm/ft^2). The cumulative maximum flow rate through the filters (all columns) was approximately 1.56 gpm. The BAF was operated as a biological process, consistent with operation of the full-scale filtration system at the Bollman WTP. The empty bed contact time (EBCT) for the GAC phase was 6.1 min.

The BAF pilot units were backwashed with filtered water from the skid that was stored in an effluent tank on the filter skid. While the Bollman WTP filters are backwashed at a frequency of at least once every 72 hours, the pilot system was only backwashed once per week since the system was not operating on a 24 hour per day basis.

5.1.5 Spiral Wound Nanofiltration Skid

Spiral wound NF membranes and a skid were provided by Dow and Harn R/O Systems, respectively. This system is shown in Figure 7. Dow's FILMTEC Desalting NF membranes were a demonstration scale unit that allowed for evaluation of operation and water quality data that is scalable to full scale treatment (Filmtec Corporation, Model Number 11361, NF-4040, Chicago, Illinois).The pilot skid, provided by Harn R/O Systems, was made of two separate stages, each with identical membranes, only the first stage containing 4 membrane units while the second held 3 membrane units. Due to a lack of pressure between the feed holding tank and the inlet to the prefilter system, a booster pump was used to pressurize the water through the prefilters. The prefilter effluent was then further

Figure 6
BAF PILOT SKID SET UP ON SITE AT BOLLMAN WTP
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Figure 7
HARN R/O NANOFILTRATION PILOT SYSTEM
CALIFORNIA DEPARTMENT OF WATER RESOURCES
CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

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pressurized via the main high pressure pump and passed through the first stage membrane filters. The concentrate from the first stage was then re-pressurized by the inter-stage booster pump, and passed through the second stage membrane filters. The first and second stage permeates were combined to give the total permeate flowrate.

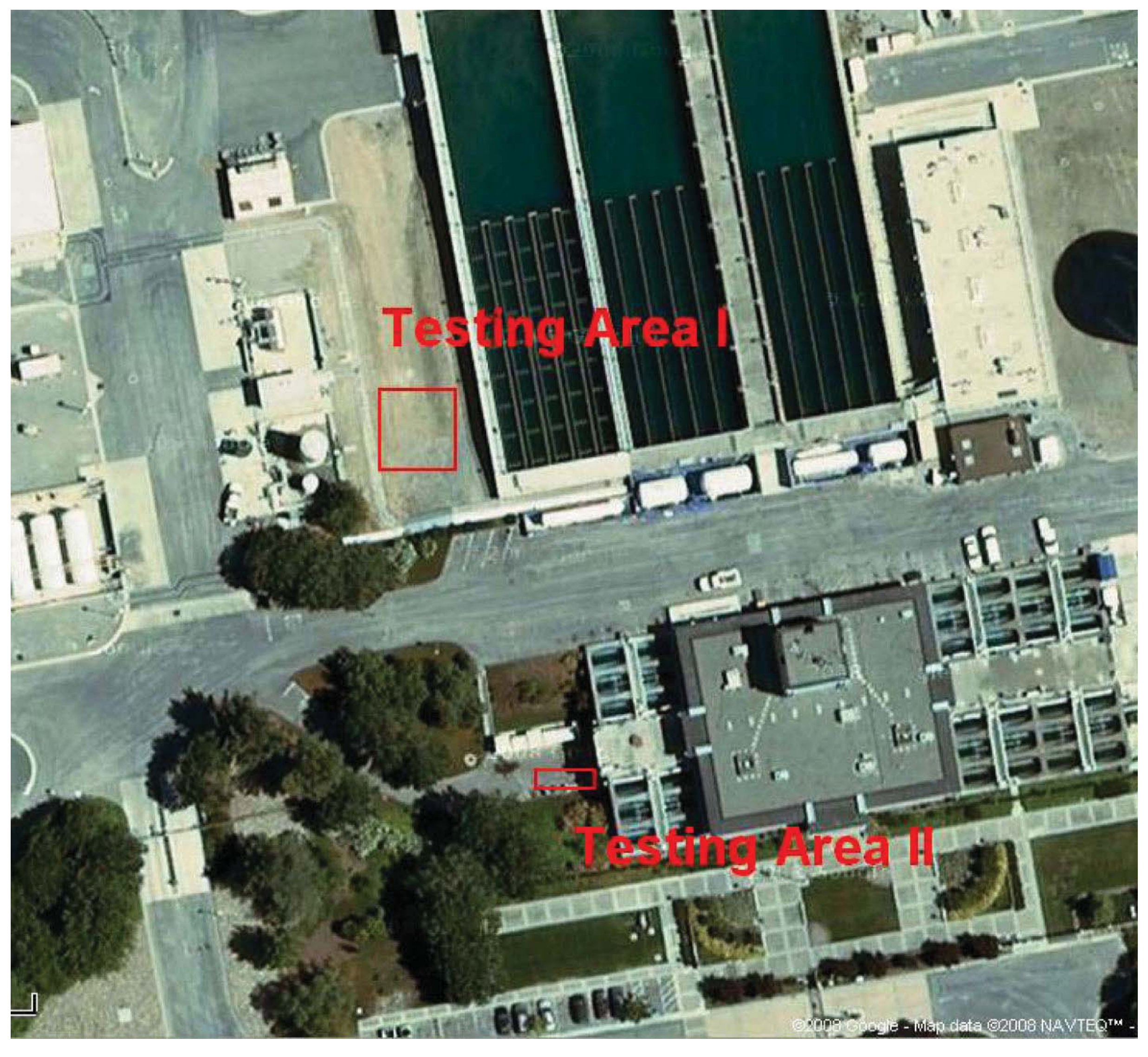
To avoid biofouling of the membrane the feed water to the pilot was dosed with chloramines. Chloramines were effectively dosed by adding free chlorine in the form of sodium hypochlorite, along with ammonia. The 5 percent sodium hypochlorite, and the 19 percent ammonia solutions were provided by CCWD from Bollman's stock chemicals, and were dosed at 4 mL/min and 2 mL/min, respectively. This gave a chlorine to ammonia-nitrogen ratio of 3:1 by weight. The free chlorine contact time was minimized by dosing the chlorine and ammonia into the feed tank supplying the full-scale filtered water with a pH of 7.2. This simulated the addition of pre-formed chloramines. Based on the 3:1 chlorine to ammonia-nitrogen ratio, and the water's pH, it is assumed that the dominant form of chloramine present was monochloramine (NH_2Cl).

Chloramines were dosed continuously at a target level of 3 mg/L as total chlorine. The dosing rates were routinely monitored on a daily basis using a chlorine HACH colorimeter test kit to measure both the total and free chlorine concentrations. The chloramines were briefly turned off during the sampling events such that the chloramine addition would not interfere with the bench scale disinfection testing, or with the spiked trace organic compounds.

5.2 Pilot Testing Location

At the Bollman WTP facility, two separate testing areas were set up for the pilot plant systems as shown in Figure 8. Testing Area I was situated in an open gravel area on the west side of the plant's sedimentation basins. Settled water was pumped from the outlet zone of the west sedimentation basin to a 55 gallon inlet holding tank. From the inlet tank the water passed through an inline static mixer, to aid with blending added chemicals, on its way to the inlet of the ozone pilot skid. After passing through the ozone contactors the water would flow into an inter-stage holding tank before being pumped up to the top of the filtration columns on the filter skid. The effluent from the GAC/sand filters was then pumped into a discharge tank. The water was removed from Testing Area I when it was pumped into a second holding tank located in Testing Area II from where it was ultimately discharged to the sanitary sewer.

Testing Area II was located at the west side entrance to the filter gallery. The water used in Phase 3 had already been treated at the plant (full-scale) by coagulation/sedimentation, ozonation, and BAF. The water was taken from the filter effluent, and initially held in a holding tank that would feed to the inlet of the NF pilot skid. The NF effluent, both the permeate and the concentrate water, was discharged to a combined 280 gallon holding



SOURCE:
Google Maps, 2008.

Figure 8
PILOT TESTING AREAS I AND II
AT THE BOLLMAN WTP, CONCORD, CALIFORNIA
CALIFORNIA DEPARTMENT OF WATER RESOURCES
CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

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tank (along with the Testing Area I effluent). The contents of this combined discharge tank were ultimately disposed of via the sanitary sewer.

5.3 Pilot Operations and Monitoring

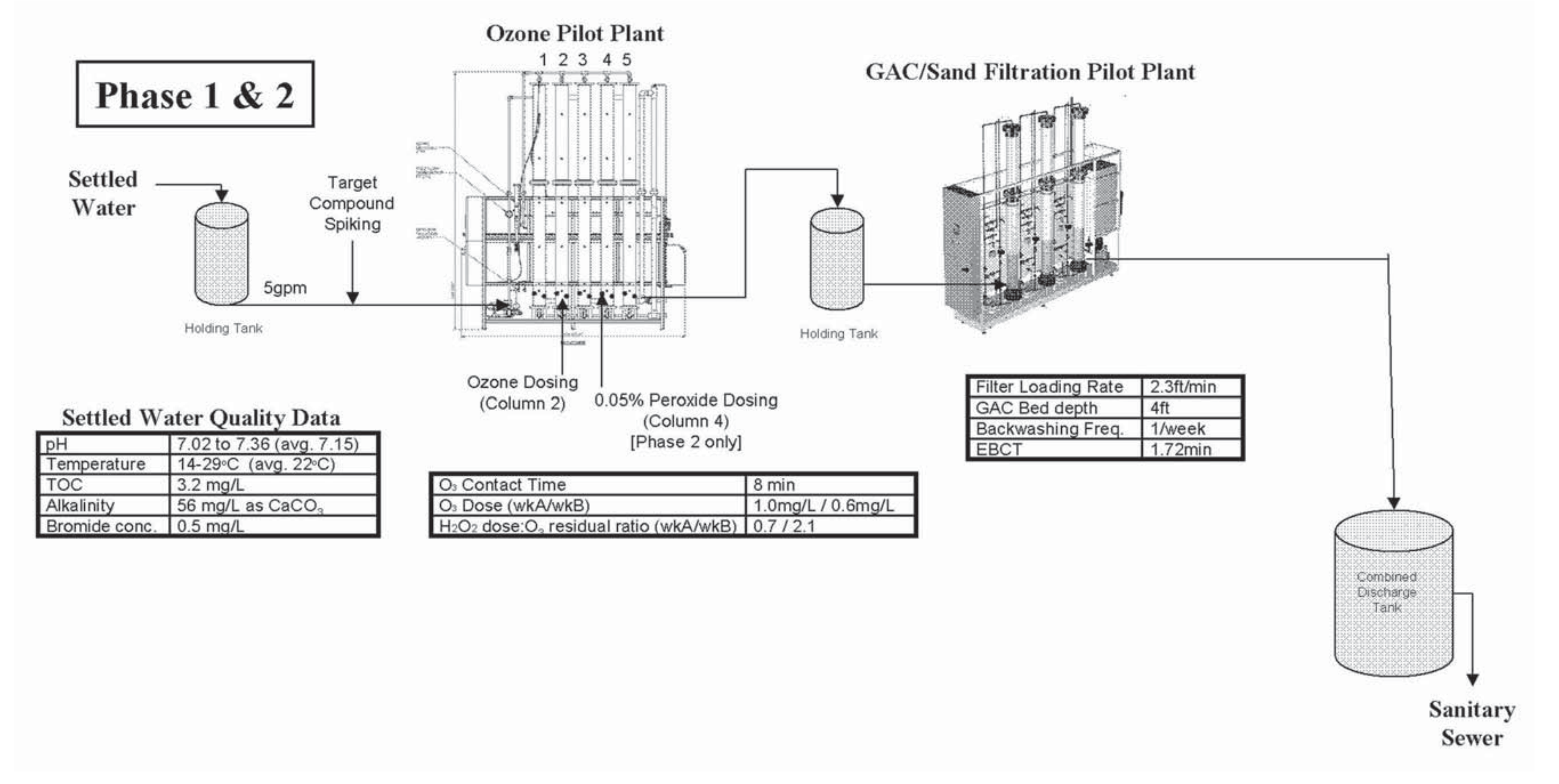
Figure 9 (Figures 9a and 9b) present a detailed schematic of the three treatment trains tested in Phases 1 through 3, and includes the experimental conditions. One critical operational condition was the target compounds were spiked into the feed water of the treatment trains. This approach was taken to obtain measurable results from the experiments. because the historical concentrations of the compounds of interest in Delta water were generally too low and method detection limits were too high for removals to be accurately measured across pilot treatment trains. Details on the spiking procedures are provided in Section 5.4. It should be noted that the spiked concentrations were approximately 50 to 100 times greater than concentrations detected in Delta waters.. In addition, it was anticipated that the relatively high concentrations of target compounds would lead to detectable concentrations in the treated water.

5.3.1 Phases 1 & 2

Upon start-up of the system, various tests were conducted to ensure that the pilot plant performance was similar to full-scale performance and that the pilot units were operating properly.

The target ozone residual was 0.2 to 0.3 mg/L after 8 minutes of contact time. The ozone gas feed rate, the ozone concentration in the gas, the water flow rate, and the ozone residual in the process effluent were measured daily. Significant variation existed in the water temperature over the course of every day of operation, and as a result the amount of dissolved ozone in the water was difficult to stabilize. Typically, over the course of the day (in the month of June), the feed water temperature was observed to rise from high 60’s (degrees Fahrenheit) in the early morning to low 80’s in the late afternoon. The ozone concentration was inversely related to the temperature fluctuation: as the temperature increased, the solubility of the ozone in the water decreased.

A number of the ozone production operating parameters were set at fixed values since a process control was not available to regulate the parameters in real-time to produce the target residual. Because each of the sampling events (1A, 1B, etc) took place at approximately the same time on each of the days, the parameter values were set to achieve the target residual based on the typical temperature for that time in the day (mid-70s range). These parameter values mainly consisted of the ozone generator power set point, set at 65 percent of its maximum capacity, and the ozone gas flow rate, set at 5.0 SCFH (+/- 0.5 SCFH). The water flow rate through the ozone columns was automatically regulated through an auto control set point of 5 gpm. The Feed Gas and the Off Gas measurements were typically in the ranges of 9 – 19 g/Nm^3 and 2 – 8 g/Nm^3, respectively; and were measured with Mini-HiCon Ozone Analyzers (IN USA Inc, Needham, MA, USA).



pH	7.02 to 7.36 (avg. 7.15)
Temperature	14-29°C (avg. 22°C)
TOC	3.2 mg/L
Alkalinity	56 mg/L as $CaCO_3$
Bromide conc.	0.5 mg/L

O_3 Contact Time	8 min
O_3 Dose (wkA/wkB)	1.0mg/L / 0.6mg/L
H_2O_2 dose:O_3 residual ratio (wkA/wkB)	0.7 / 2.1

Filter Loading Rate	2.3ft/min
GAC Bed depth	4ft
Backwashing Freq.	1/week
EBCT	1.72min

Figure 9a
PILOT TESTING TREATMENT TRAINS - PHASE 1 AND 2 AND EXPERIMENTAL CONDITIONS
CALIFORNIA DEPARTMENT OF WATER RESOURCES
CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

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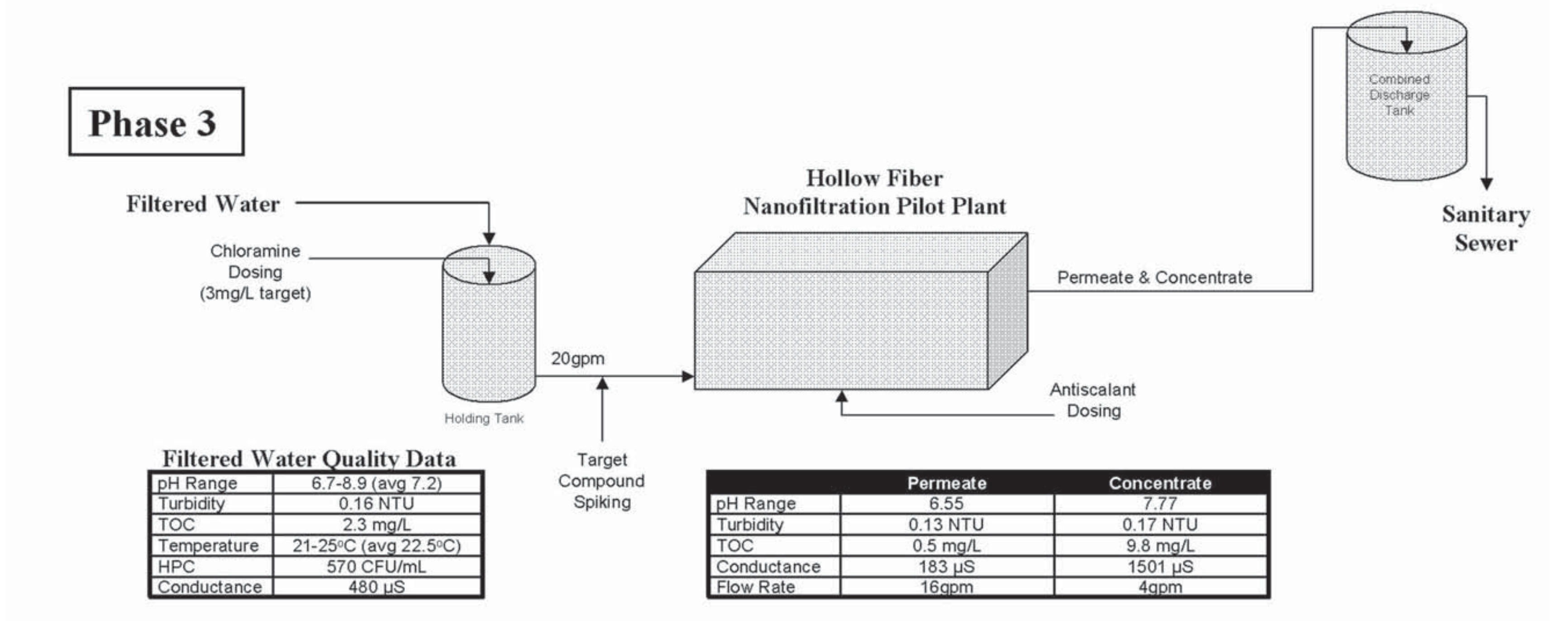

pH Range	6.7-8.9 (avg 7.2)
Turbidity	0.16 NTU
TOC	2.3 mg/L
Temperature	21-25°C (avg 22.5°C)
HPC	570 CFU/mL
Conductance	480 µS

	Permeate	Concentrate
pH Range	6.55	7.77
Turbidity	0.13 NTU	0.17 NTU
TOC	0.5 mg/L	9.8 mg/L
Conductance	183 µS	1501 µS
Flow Rate	16gpm	4gpm

Figure 9b
PILOT TESTING TREATMENT TRAINS - PHASE 3 AND EXPERIMENTAL CONDITIONS
CALIFORNIA DEPARTMENT OF WATER RESOURCES
CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

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An additional quality control test was to ensure that the acetone used as a solvent for the spiking solutions of the analytes did not affect ozone demand as the analytes were spiked into the flow. The tests showed that ozone residuals were the same regardless of whether the analyte solution was being spiked, indicating that the acetone (and analytes themselves) had a negligible impact on ozone demand.

5.3.2 Phase 3

The NF unit start up involved exposing the membrane to the full-scale filtered water while simultaneously making refinements to the operating conditions including the flux rates, operating pressures, and recovery rates. Start-up testing of the NF system included collecting TOC, turbidity, and HPC samples of the filtered water and the NF permeate. Additionally, silt-density index (SDI) measurements were obtained to monitor the stability of the feed water and the pre-filter unit.

Due to variation in the full-scale filtered feed water, the oxidation-reduction potential (the ORP) could not be used as a measure of the total or free chlorine available in the system as originally anticipated. As a result, the chlorine and chloramine levels were monitored manually by the operator utilizing a handheld chlorine HACH colorimeter test kit. The membrane skid was not equipped with a data logger, and therefore operating parameters such as pH, conductivities, fluxes, and recoveries, were manually recorded by the operator on a semi-daily basis for each stage of the system.

The target total flowrate through the system was 20 gpm, with an 80 percent flux rate across the membrane. Therefore, a total permeate flowrate of 16 gpm and a concentrate flowrate of 4 gpm were targeted. The filtration system was split into 2 stages, with an interstage booster pump raising the pressure in between the 2 stages. The target permeate flowrate from the first stage was 11 gpm, and the remaining 5 gpm as the second stage permeate. Following prefiltration, and prior to entering the first stage of membrane filters, the influent was dosed with an anti-scalant chemical, provided by Harn R/O Systems. The anti-scalant was applied at the recommendation of the manufacturer.

Some of system's typical parameter ranges are outlined in Table 13.

Additionally, a mass balance on the NF results was performed as a check by combining the permeate and concentrate concentrations and comparing this value to the influent concentration. In general, the influent and effluent concentrations were roughly equivalent. The results of this are discussed and presented in Appendix A.

5.4 Spiking Procedures

A concentrated solution of the target compounds was provided by Trent University. The spiking concentration was determined based on the literature review, the expected removals for the various processes presented in Table 12, and Trent University's detection

Table 13 NF Parameters Range of Operation
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Parameter	Typical Operating Range (& Average)
Oxidation-Reduction Potential (ORP)	342 – 795 mV (490 mV)
Feed water pH	6.7 – 8.9 (7.2)
Feed water Temperature	20.9 – 24.9 ^{o}C (22.5 ^{o}C)
Inlet Feed Pressure	86 – 104 psi (95 psi)
% Recovery	79.0 – 80.6% (79.9%)
Feed Conductivity	377 – 606 uS (445 uS)
Permeate Conductivity	113 – 257 uS (148 uS)
% Rejection	57.6 – 73.0% (67.6%)

levels. Expected NF removals ranged from 70 to greater than 99 percent for certain compounds (e.g., ibuprofen, gemfibrozil, iopromide). Removal of certain compounds (e.g., estrone, bisphenol-A) by the perozone process and to a lesser extent ozone was expected to be greater than 95 percent. Because Trent University's quantification levels are between 10 - 25 nanograms/liter (ng/L), the spiking range for the pilot study was approximately 1 microgram/liter (μg/L) in order to quantify compounds that are 99 percent removed in the treated water.

The solvent for the spiking compounds was acetone. The spiking solution was prepared in batches for each test of the pilot trains. The concentrated target compounds were added to the spiking tank containing plant settled water. The spiking solution was dosed into the feed water of the pilot using laboratory peristaltic pumps (Model Number 7553-80, Cole Parmer Instruments, Vernon Hills, Illinois). In Phases 1 and 2 the target compounds were spiked into the full scale settled water, which was the feed water to the pilot-scale ozone system. In Phase 3, the target compounds were spiked into the full scale filtered water, which was used as feed water to the NF membranes.

In addition to spiking the target compounds, the influent of the pilot was spiked with a salt solution. The ion solution composition was such that the influent to the pilots for each phase contained bromide at a concentration of 0.4 mg/L. This was the "medium" bromide level used for Water Research Foundation (WRF) Project #3004 (Advanced Treatment of Estuarine Water Supplies). In estuarine waters, bromide concentrations typically change along with concentrations of other constituents such as chloride and sulfate. Consistent with WRF project #3004, chloride was spiked at 119 mg/L. Iodide was spiked at a 10:1 bromide to iodide ratio (by weight), at a concentration of 0.04 mg/L. This ratio was based on recent studies designed to examine the formation of iodinated DBPs (Karanfil et al 2011). All ions were added to the ion spiking tank containing the feed water to the pilot units. The ion spiking solution was pumped into the feed water of the pilot.

5.5 Sampling and Analysis Procedures

For Phase 1 and 2, a concentrated solution of the spiking compounds was fed to the pilot influent for a minimum of 4 hours (approximately 7.5 retention times) before sampling. For Phase 3 the concentrated spiking solution was dosed for a minimum of 8 hours before sampling. Sampling events took approximately 4 hours, such that the total spiking time of trace organic compounds ranged from 8 to 12 hours per sampling event. Upon completion of sampling, the feed pump was turned off and ambient water fed through the pilot for a minimum of 7 days. Sampling events occurred weekly, allowing time to establish the baseline operating conditions for the next testing sampling event, and each train was tested twice, under the same operating conditions, during the testing phase. These sampling events are referred to as “A “ and “B” (e.g. Phase 1A and Phase 1B). The sampling locations for each pilot train are presented in Figure 10.

These sampling locations are described as follows:

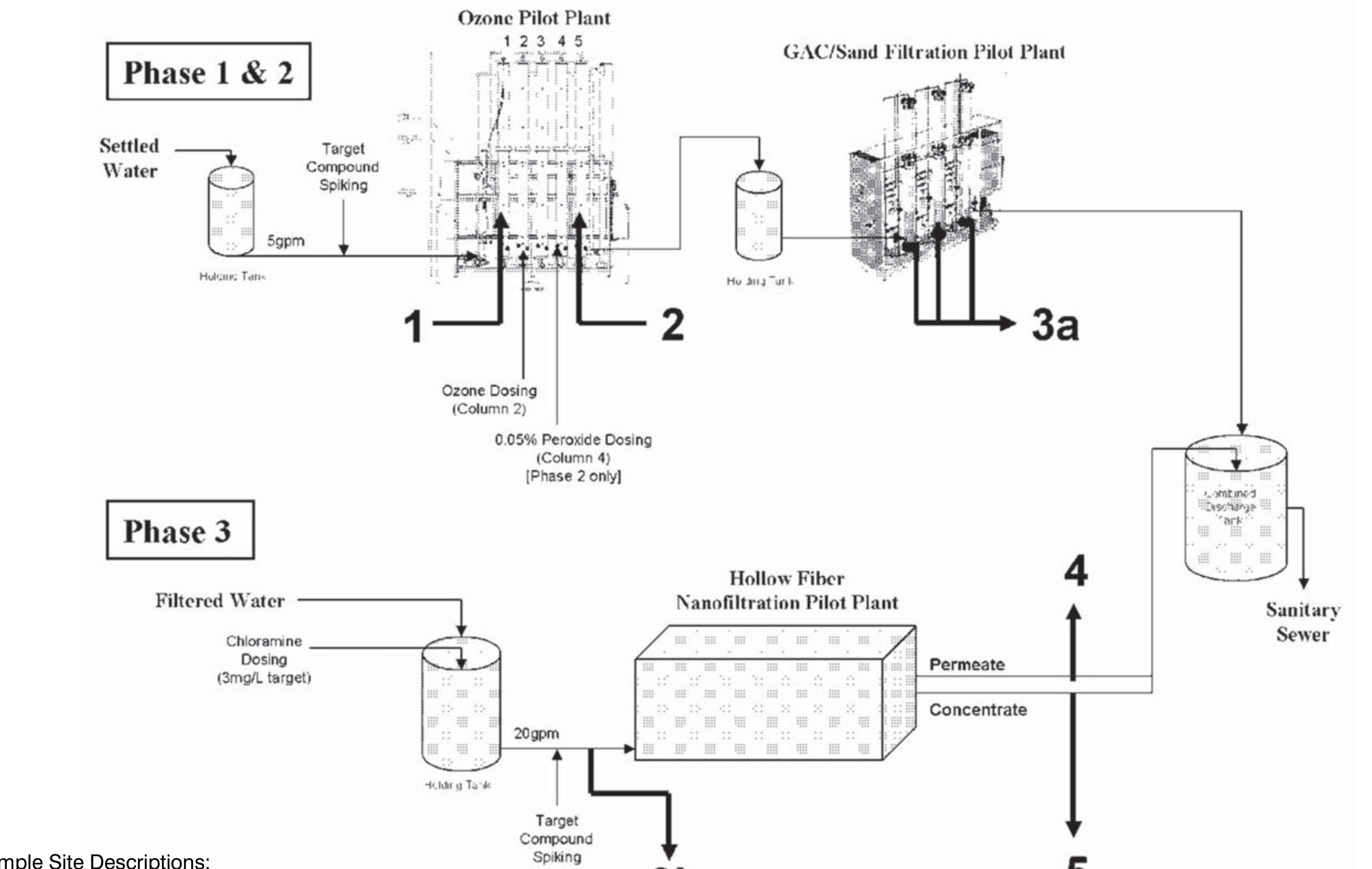
- Sampling locations 1 and 3b are immediately downstream of injection of trace organic compounds and prior to any treatment.
- Sampling locations 2, and 3a are post ozonation, and post BAF, respectively. Sampling locations 4 is post NF membrane treatment (membrane filtrate).
- Sampling location 5 is the membrane concentrate.
- Of the treated water samples collected from the pilot at locations 3a, 3b and 4, a portion were shipped to Duke University and University of Toronto for additional bench scale disinfection tests.

Parameters analyzed at each sampling location are presented in Appendix B.

Chloramines were added in the NF feed water (used to control biofouling), however, this chemical feed was turned off during testing. In a full scale treatment system, where a NF membrane follows a biological process the water may need to be subject to chloramination to prevent biofouling. To assess the contribution of the addition of chloramine for the purpose of controlling biofouling, on DBP formation, additional samples were collected after chloramine addition was resumed.

The sample analyses for the pilot test experiments were conducted at several laboratories/universities, as shown in Table 14.

The conventional parameters and parameters related to membrane fouling/performance were analyzed by CCWD and the operator per the methods listed in Appendix E. Heterotrophic plate counts and DBP formation potential tests were conducted at University of Toronto. Appendix G includes the relevant analytical methods for the analyses. Simulated distribution system tests were conducted at Duke University. DBPs and organic nitrogen were analyzed per the Quality Assurance Project Plan (QAPP) for WRF project



Sample Site Descriptions:

1 Downstream of injection of trace organic compounds and prior ozone or perozone

2 Post ozone

3a Post BAF

3b Downstream of injection of trace organic compounds and prior NF membranes

4 Post NF membranes (membrane permeate)

5 NF membrane concentrate

Figure 10
PILOT SCALE TREATMENT TRAIN SAMPLING LOCATIONS
CALIFORNIA DEPARTMENT OF WATER RESOURCES
CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

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Table 14	Location of Sample Analysis for the Pilot Experiments Removal of NDMA, EDCs and PPCPs in South Delta Water California Department of Water Resources California Department of Public Health
Analysis Category	**Laboratory**
Conventional (except organic nitrogen)	CCWD
Membrane Fouling/Performance	CCWD
Heterotrophic Plate Counts	University of Toronto
DBPs (and organic nitrogen)	Duke University [1]
DBPs	University of Toronto
EDCs, PPCPs, Industrial Chemicals	Trent University
Pesticides	MWH Labs

Notes:

(1) The principal investigator for WRF project #4019 (Karl Linden) is currently employed at the University of Colorado. However, at the time of the study, Karl Linden was employed at Duke University and the bench scale DBP tests were conducted at Duke University.

#4019 (Linden et al. 2010). Appendix F includes the relevant analytical methods for the analyses. EDCs, PPCPs, and industrial chemicals were analyzed at Trent University. Only the target compounds were analyzed, and Appendix C includes the analytical methods. Atrazine was analyzed by MWH. The analytical method for atrazine is included in Appendix D.

5.6 Quality Control

A number of actions were taken during the experimental setup, sampling, and analytical testing to ensure that the results obtained were as accurate as possible. These precautions included:

- calibration of dosing pumps,
- flushing sampling ports prior to sample extraction,
- sample collection methods,
- including field blank and duplicate samples,
- observing the detection limits of the analytical capabilities, and
- performing a mass balance on the NF system.

Detailed descriptions of these techniques can be found in Appendix A.

5.7 Pilot Scale Results & Discussion

5.7.1 General Physical and Chemical Water Quality

A number of conventional water quality parameters were measured at each sampling port for every phase of the project. The results for Phase 1 and 2 (A and B) were averaged

together to give the data presented In Table 15. The results for Phase 3 (A and B) were also averaged together and are presented in Table 16.

Table 15 General Water Quality Parameters – Phases 1 and 2
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Parameters	Units	Sampling Location		
		Settled Water, Post-spike	Ozone/ Perozone Effluent	BAF Effluent
pH		7.2	7.2	7.2
Turbidity	NTU	0.40	0.45	0.32
UV_{254}	cm^{-1}	0.049 (1)	0.036 (1)	0.032 (1)
		0.05 (2)	-	0.0345 (2)
Specific Conductance	µS	621	618	620
Alkalinity	mg/L as $CaCO_3$	56	55	54
Hardness	mg/L as $CaCO_3$	115	115	116
Bromide	mg/L	0.5	-	0.5
Chloride	mg/L	105	-	105
Nitrate	mg/L as NO_3-N	<2.0	-	<2.0
Ammonia	mg/L as NH_3	<0.1	<0.1	<0.1
TDN (2)	mg/L as N	0.57	-	0.58
DIN (2)	mg/L as N	0.25	-	0.27
DON (2)	mg/L as N	0.32	-	0.31
TOC	mg/L	3.2	3.1	2.8
DOC (2)	mg/L	4.0	-	3.8
SUVA (3)	L/mg-m	1.24	-	0.92
Heterotrophic Plate Counts	CFU/mL	3576	183	5636

Notes:
(1) Analyzed at CCWD.
(2) Analyzed at Duke University.
(3) SUVA calculated based on DOC and UV results from Duke University.

In general, the settled water quality results in Table 15 were consistent or greater than median settled water and filtered water quality at CCWD (based on the analysis of water quality in Briggs et al, 2007). Parameters with greater than median concentrations included turbidity, UV absorbance and TOC. The pilot processes of ozonation followed by BAF, achieved reduction in UV absorbance, TOC, DOC and turbidity. The relatively high HPC concentration in the BAF effluent, as compared to the settled water and the ozone/perozone effluent, suggests that the BAF pilot was biologically active.

Table 16 General Water Quality Parameters – Phase 3
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Parameters	Units	Sampling Location: Filter effluent, Post-Spike	Permeate	Concentrate
pH		7.2	6.6	7.8
TSS	mg/L	0.69	0.94	1.75
Turbidity	NTU	0.158	0.125	0.169
UV_{254}	cm^{-1}	0.021 (1)	0.001	0.097
		0.019 (2)	-	-
Specific Conductance	μS	480	183	1501
Alkalinity	mg/L as $CaCO_3$	44	14	163
Hardness	mg/L as $CaCO_3$	90	17	380
Bromide	mg/L	0.45	0.3	0.95
Chloride	mg/L	76.5	45.5	195
Sulfate	mg/L	63	3.25	305
Fluoride	mg/L	0.1	<0.1	0.6
Nitrate	mg/L as NO_3-N	<2.0	<2.0	<2.0
Ammonia	mg/L as NH_3	0.1	<0.1	0.35
TDN (2)	mg/L as N	0.59	0.24	-
DIN (2)	mg/L as N	0.36	0.19	-
DON (2)	mg/L as N	0.23	0.05	-
Phosphate	mg/L	<0.2	<0.2	0.4
TOC	mg/L	2.3	0.5	9.8
DOC (2)	mg/L	2.3	0.51	-
SUVA (3)	L/mg-m	0.84	0.07	-
Heterotrophic Plate Counts	CFU/mL	570	177	-

Notes:
(1) Analyzed at CCWD
(2) Analyzed at Duke University
(3) SUVA calculated based on DOC and UV results from Duke University

In Table 16, the filtered effluent that provided the feed water to the NF membranes was from the full-scale BAFs. The NF membranes achieved reductions in specific conductance, alkalinity, hardness, bromide, chloride, sulfate, UV absorbance, TOC and DOC.

5.7.2 Removal of Trace Organic Compounds

The overall removal efficiencies for the target trace organics are presented in Table 17 as the percent removed by each treatment train. Since the treatment trains could contain multiple treatment stages (e.g. ozone followed by BAF), the percent removals by the downstream treatments (e.g. BAF) are based on the percent removal of the compounds that had passed through the upstream process. For example, if ozone removed 92 percent of a compound, and BAF removed half of the remaining 8 percent, the percent removal through BAF is shown as 50 percent, and total treatment train removal is shown as 92 percent + 4 percent = 96 percent removal.

As noted previously, sampling events A and B were intended to be replicate events, with the same experimental conditions for the two events. Inadvertently, sampling events 1B and 2B (the second week of Phases 1 and 2) were completed with a lower ozone dose (0.5-0.7 mg/L) than sampling events 1A and 2A (1 mg/L). This deviation from the experimental plan was due to difficulties in maintaining a constant ozone dose from the ozone generator, under conditions where there were significant air temperature swings. However, this variation demonstrated a dose-response relationship, and this can be seen by comparing the ozone removal efficiencies for 1A and 1B or 2A and 2B (see sections 5.7.3.1 and 5.7.3.2).

5.7.2.1 Ozonation

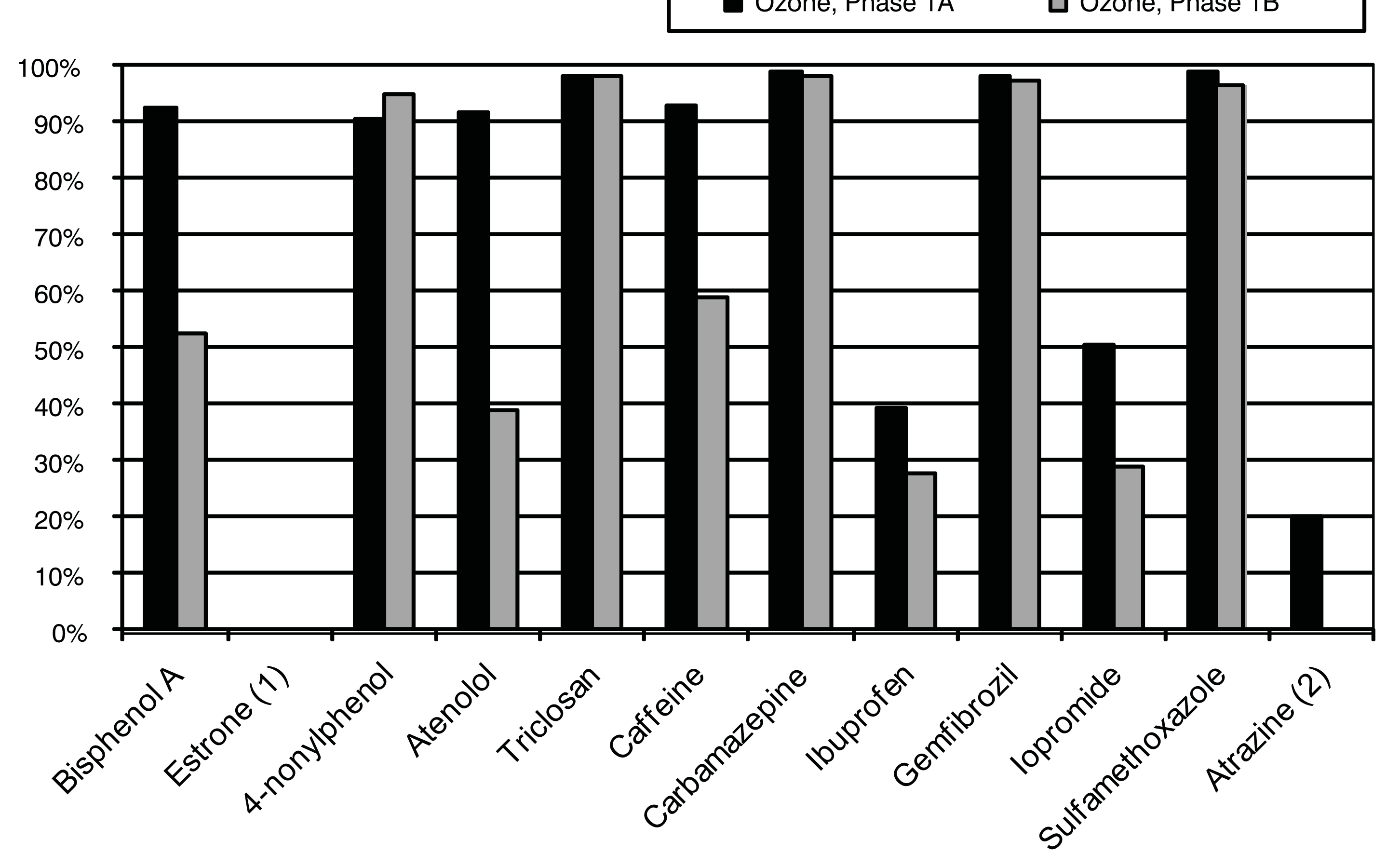
The removal efficiency of each compound by the ozone pilot system during Phase 1 is shown in Figure 11. In Phase 1A, eight out of eleven compounds were removed at 90 percent or greater. Three compounds, iopromide, ibuprofen, and atrazine, were removed at rates ranging from 20 percent to 50 percent. These results suggest that these compounds are relatively resistant to treatment by ozonation at the dose of 1 mg/L, and with the water quality conditions for the Phase 1 testing. The removal efficiencies in Phase 1A are higher than those in Phase 1B as a result of the higher applied ozone dose in week A (1.0 mg/L) relative to week B (0.5-0.7 mg/L). While this variation in ozone dose prevents analysis of the reproducibility of the treatment train, it demonstrates a dose-response relationship.

In Phase 1B, five compounds still exhibited over 90 percent removal, 4-nonylphenol, triclosan, carbamazepine, gemfibrozil, and sulfamethoxazole. Three compounds, BPA, atenolol, and caffeine show ozone dose dependence. In Phase 1A these three compounds were removed at 90 percent or greater, while in Phase 1B, removals ranged from 40 percent to 60 percent.

Table 17 Summary of Removal Efficiencies by Process
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

Phase	Process	BPA	Estrone	4-NP	Atenolol	Triclosan	Caffeine	CBZ	Ibuprofen	Gemfibrozil	Iopromide	SMX	Atrazine
1A	Ozone	92%	NA	>91%[4]	92%	>98%[4]	93%	>99%[4]	39%	98%	50%	>99%%[4]	20%
	BAF	44%	NA	-[2]	84%	-[2]	50%	-[2]	55%	10%	31%	-[2]	75%
	Overall	96%	NA	>91%[4]	99%	>98%[4]	96%	>99%[4]	73%	98%	66%	>99%%[4]	80%
1B	Ozone	52%	NA	>95%[4]	39%	>98%[4]	59%	98%	28%	97%	29%	96%	BB
	BAF	96%	NA	-[2]	82%	-[2]	77%	0%	>44%	0%	0%	43%	BB
	Overall	98%	NA	>95%[4]	89%	>98%[4]	90%	98%	>60%	97%	29%	98%	60%
2A	Perozone	94%	NA	>93%[4]	83%	>99%[4]	91%	>99%[4]	45%	98%	13%	>99%%[4]	20%
	BAF	32%	NA	-[2]	-89%[3]	-[2]	>88%[4]	-[2]	62%	0%	14%	-[2]	75%
	Overall	96%	NA	>93%[4]	68%	>99%[4]	>99%[4]	>99%	79%	97%	26%	>99%%[4]	80%
2B	Perozone	97%	95%	87%	18%	>99%[4]	2%	99%	14%	67%	36%	96%	0%
	BAF	0%	20%	>28%[4]	81%	-[2]	87%	>17%[4]	65%	54%	27%	25%	67%
	Overall	96%	96%	>91%[4]	85%	>99%[4]	87%	>99%[4]	70%	85%	53%	97%	67%
3A	NF	86%	>93%[4]	>33%[1,4]	>92%	>97%[4]	80%	97%	>99%[4]	98%	>96%%[4]	>99%%[4]	92%
3B	NF	80%	>93%[4]	>30%[1,4]	>93%	>96%[4]	92%	97%	>99%[4]	>98%[4]	>97%%[4]	96%	93%

Notes:
NA = Data not available due to poor sample recovery.
BPA = Bisphenol A; 4-NP = 4-nonylphenol; CBZ = carbamazepine; SMX = Sulfamethoxazole
BB = Sample bottle broken.
(1) The spiked concentration was low for this compound and the effluent concentration was below the detection limit. Therefore, the removal efficiency was calculated based on a low influent concentration and the detection limit concentration for the effluent sample.
(2) Denotes that non-detect levels were measured in the influent sample of the process and therefore removal rates could not be calculated.
(3) The effluent concentration for the perozone process was less than the effluent concentration of the BAF process and therefore a negative removal efficiency was calculated.
(4) Removal rates denoted as greater than (">") are shown where a detectable influent concentration was measured but a less than detectable effluent concentration was measured. Therefore, the removal efficiency was calculated by assuming that the effluent concentration was equivalent to the detection limit.



NOTES:
(1) Data not available
(2) Broken bottle for Phase 1B
Phase 1A Ozone Dose = 1 mg/L
Phase 1B Ozone Dose = 0.5 to 0.7 mg/L

Figure 11
PERCENT REMOVAL BY OZONE: PHASE 1A AND 1B
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Compounds in Phase 1A that were relatively resistant to ozonation were also removed at relatively low removal efficiencies in Phase 1B.

Previously reported removal efficiencies by ozone for the compounds tested by Snyder et al. (2007) were similar to those observed in Phase 1A.

5.7.2.2 Perozone

The results of the perozone treatment experiments are shown in Figure 12. As a result of the different ozone doses in Phase 2A and 2B, the resulting ratios of peroxide dose to ozone residual were 0.7 molar ratio for Phase 2A, and 2.1 molar ratio from Phase 2B.

In both Phases 2A and 2B, the ozone residuals concentrations were low. Such low ozone residual concentrations, regardless of the peroxide concentration, will result in very little hydroxyl radical formation. Phase 2A represents a typical ozone dose for Delta utilities, with an intermediate dosing location for peroxide. The low ozone residual in Phase 2A suggests that if Delta utilities wanted to practice advanced oxidation with perozone, then the ozone dose or the ozone contact time prior to peroxide addition would need to be adjusted.

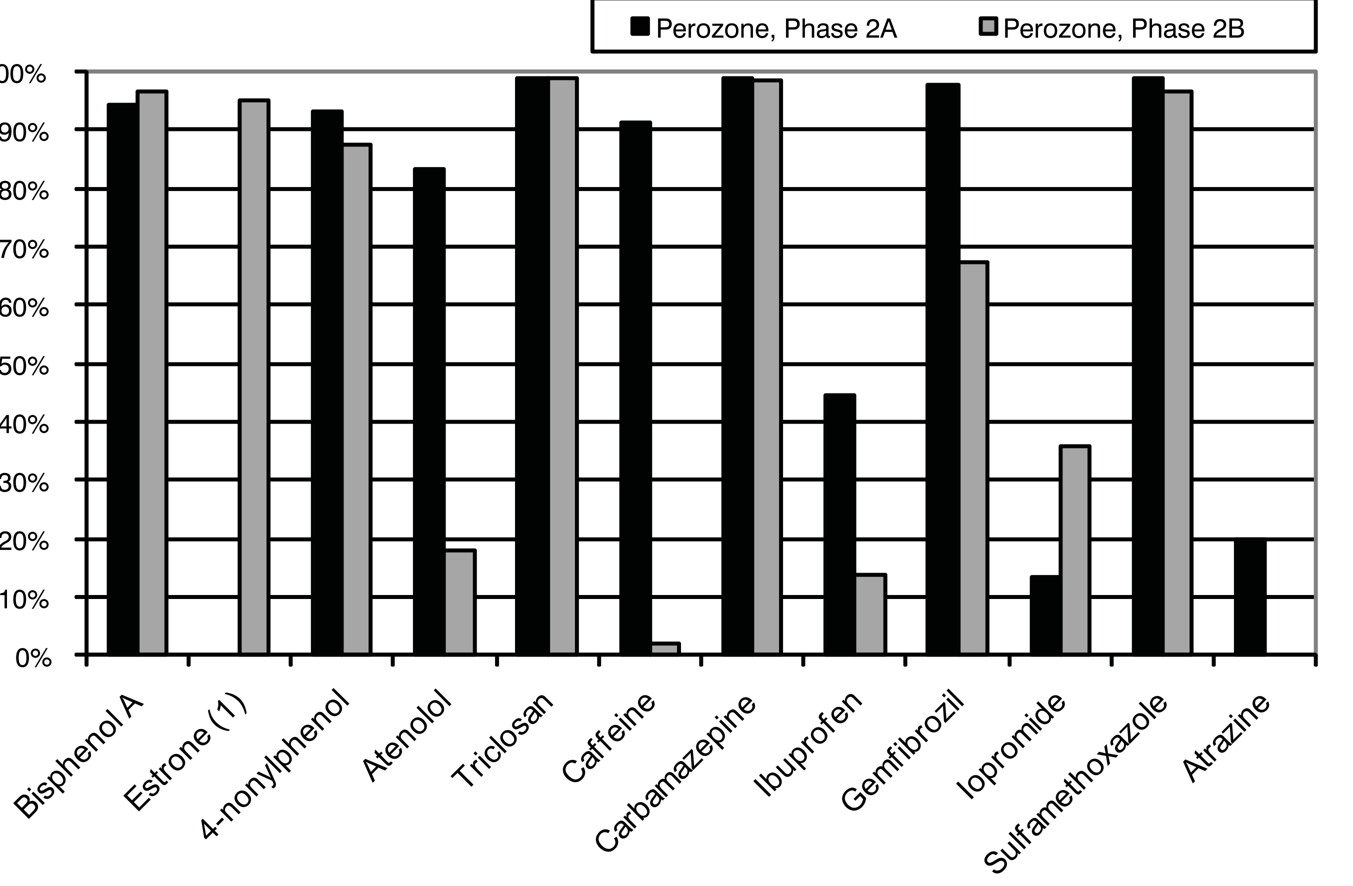
Differences in the ozone doses and resulting peroxide to ozone residual ratios were observed for some compounds. Similar removals were achieved in Phases 2A and 2B for bisphenol-A, 4-nonylphenol, triclosan, carbamazepine, and sulfamethoxazole. Greater removals were achieved in Phase 2A as compared to 2B for atenolol, caffeine, ibuprofen, gemfibrozil and atrazine.

In this study, the perozone results generally matched the ozone results closely at the greater ozone dose, as shown in Figure 13 (comparison of Phase 1A and 2A). One exception, was iopromide, where the removal by ozone was greater than the removal by perozone.

Figure 14 shows the results of Phases 1B and 2B. Some differences were observed between Phase 1B and 2B, where some compounds, including atenolol, caffeine, ibuprofen and gemfibrozil had lower removals in Phase 2B as compared to Phase 1B. This is possibly due to the shorter ozone contact time in Phase 2B as compared to Phase 1B. The opposite was observed for bisphenol-A, where greater removal was observed in Phase 2B as compared to Phase 1B.

5.7.2.3 BAF

The additional removal achieved by BAF in addition to removal by ozone/perozone is presented in Figures 15, and 16, for Phases 1A and 1B, respectively. The contribution of the BAF process to compound removal is observed by comparing the ozonated effluent with the BAF effluent. For compounds that were well removed by ozonation (>90 percent), the BAF process did not significantly contribute to the overall treatment train removal efficiency (<5 percent additional removal).



Notes:

(1) Data not available for Phase 2A

Atrazine removal in Phase 2B = 0%

Phase 2A ozone dose = 1 mg/L, Peroxide/ozone residual molar ratio = 0.7

Phase 2B ozone dose = 0.5 to 0.7 mg/L, Peroxide/ozone residual molar ratio = 2.1

Figure 12

PERCENT REMOVAL BY PEROZONE: PHASE 2A AND 2B

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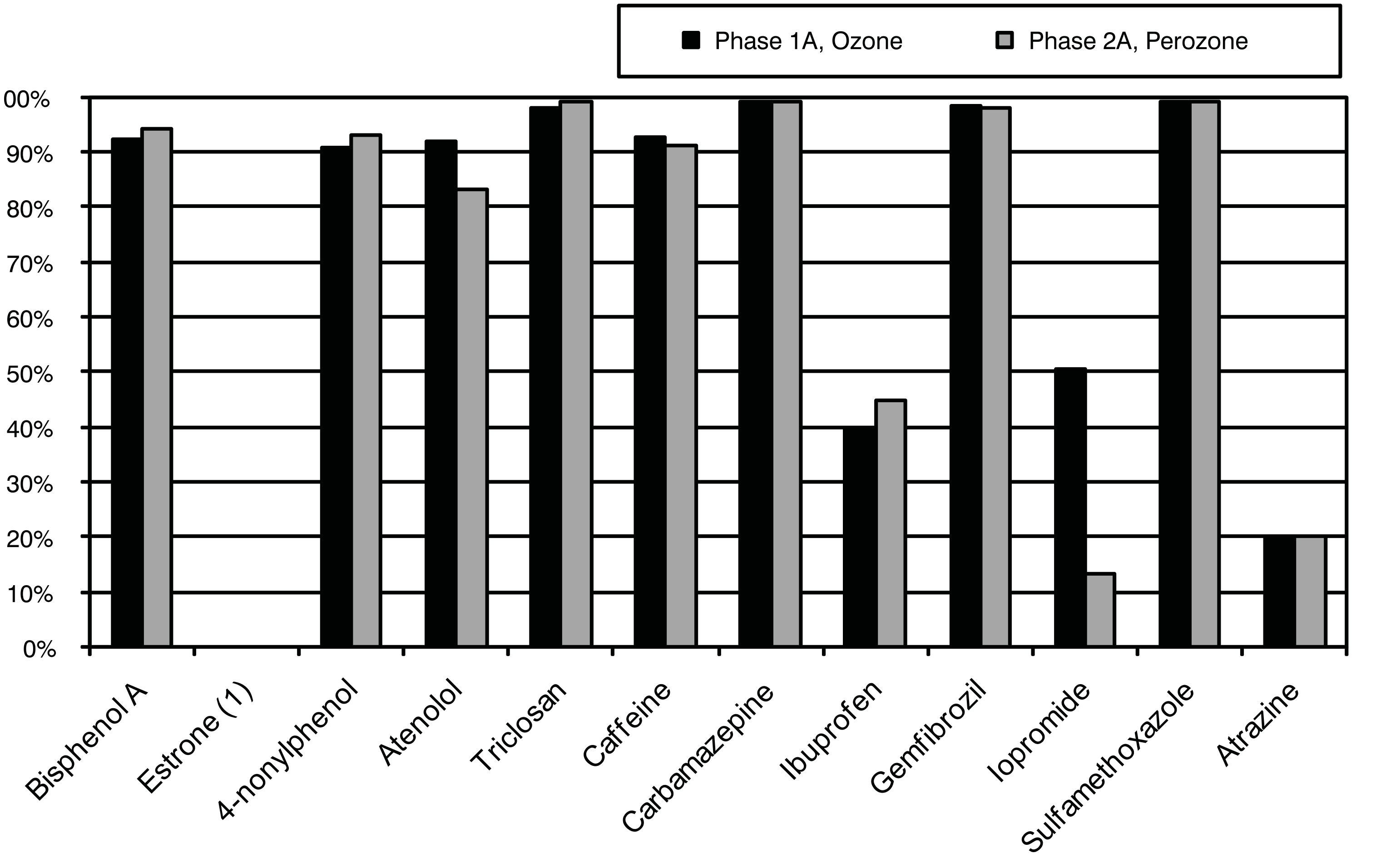

Notes:

(1) Data not available

Phase 1A ozone dose = 1 mg/L

Phase 2A ozone dose = 1 mg/L, Peroxide/ozone residual molar ratio = 0.7

Figure 13
PERCENT REMOVAL BY OZONE AND PEROZONE: PHASE 1A AND 2A
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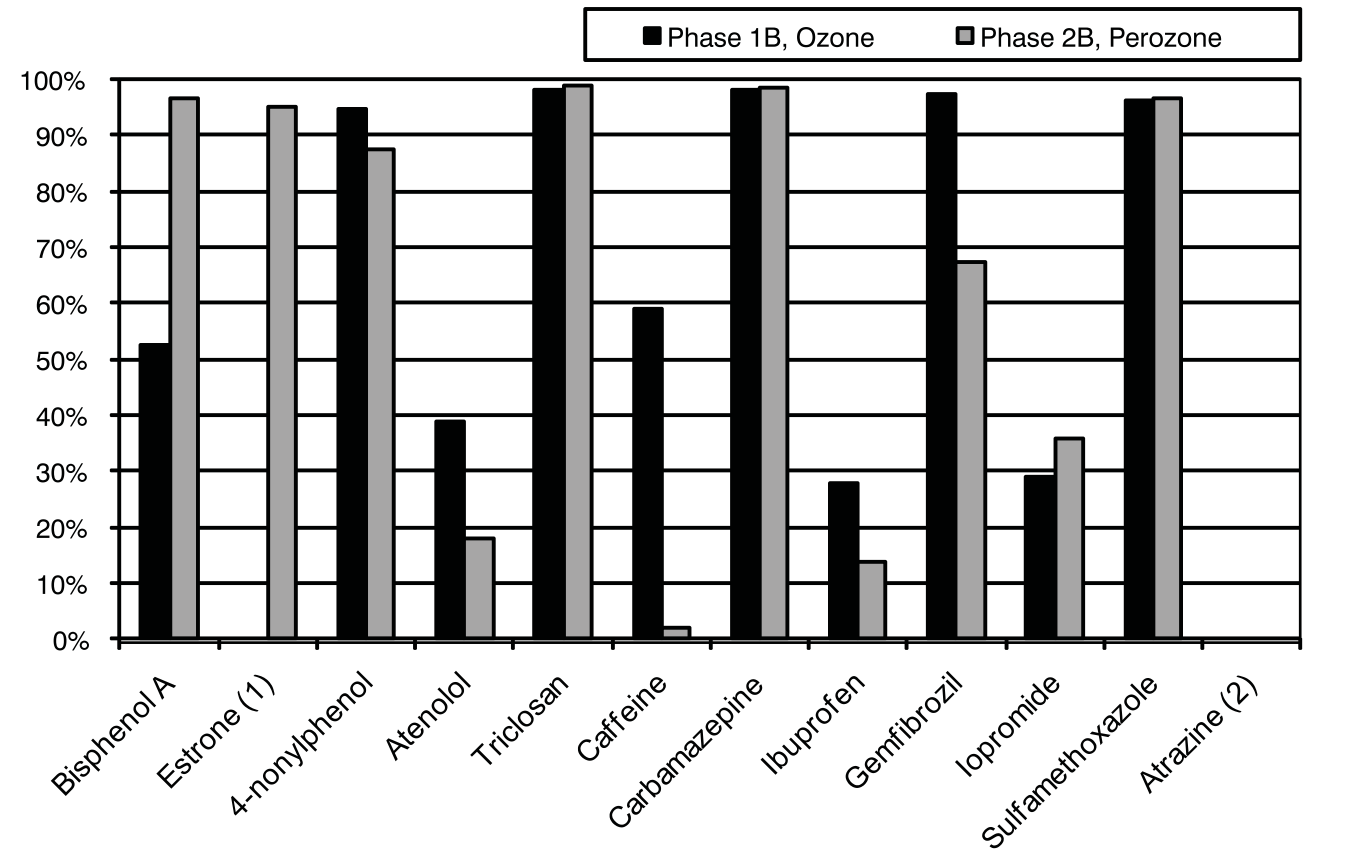

Notes:

(1) Data not available

(2) Broken bottle in Phase 1B and 0% removal in Phase 2B

Figure 14
PERCENT REMOVAL BY OZONE AND PEROZONE: PHASES 1B AND 2B
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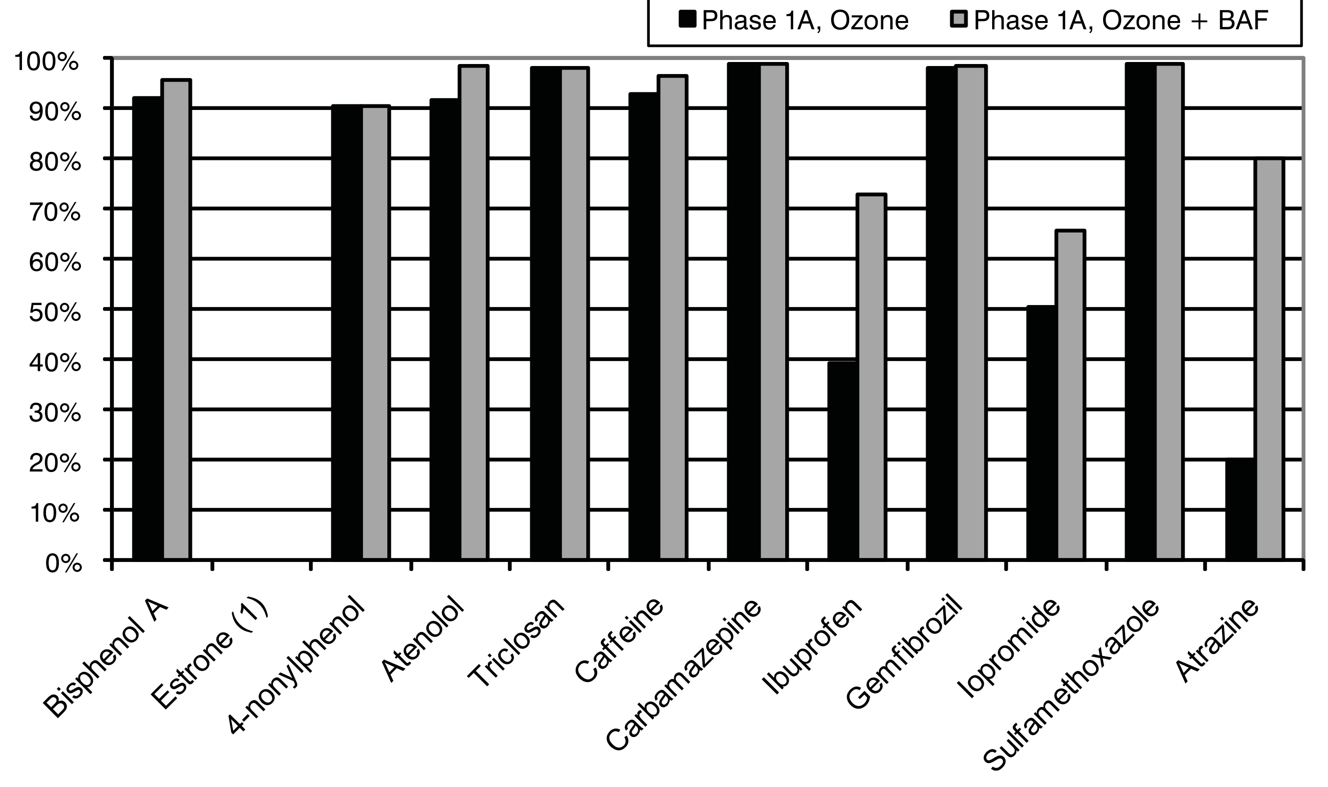

Notes:
(1) Data not available

Figure 15
PERCENT REMOVAL BY OZONE AND BAF: PHASE 1A
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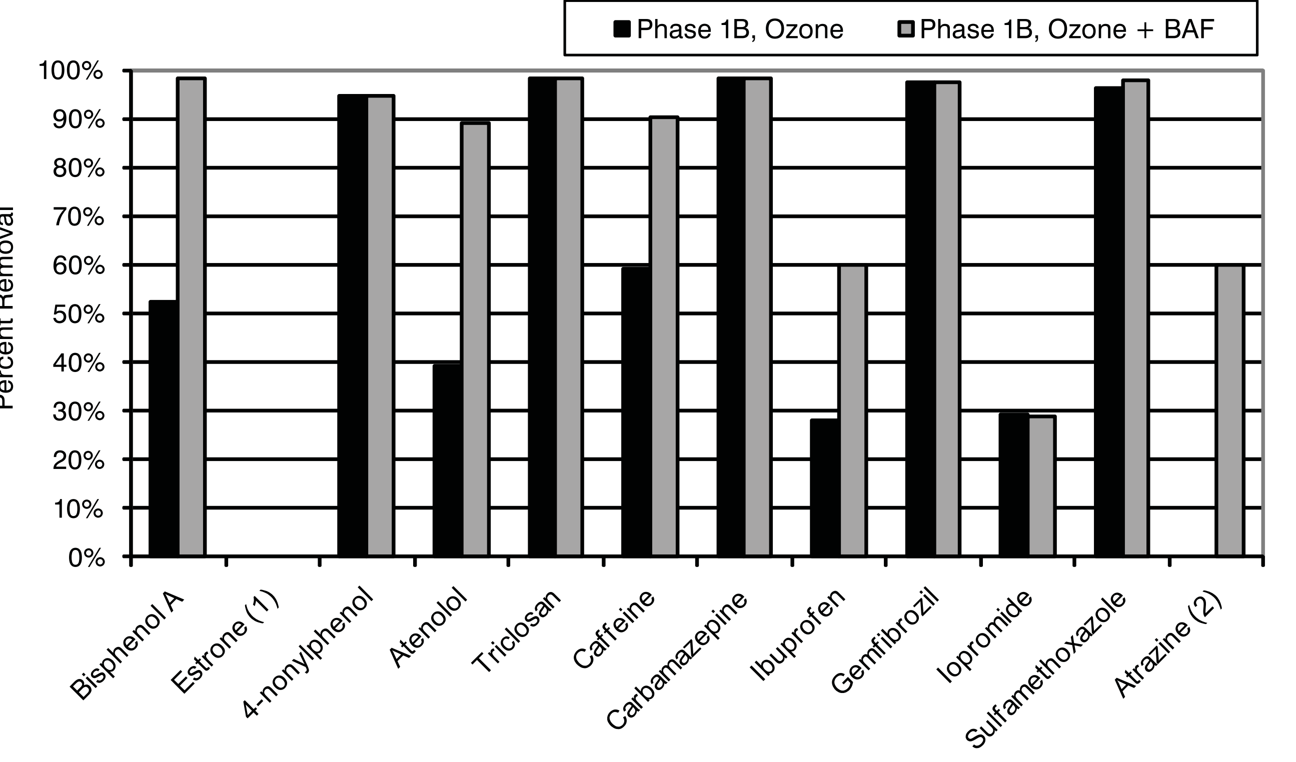

Notes

(1) Data not available

(2) Broken bottle for Phase 1B

Figure 16

PERCENT REMOVAL BY OZONE AND BAF: PHASE 1B

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For the relatively ozone resistant compounds, or compounds that were not well removed at the lower ozone dose, the BAF contributed to the overall process train performance. Table 18 presents the removal efficiencies by the BAF only, in each sampling event of Phases 1 and 2, as well as removal efficiencies reported in the literature. For many compounds, a wide range of removal efficiency was observed. Some of this variability is due to the calculation method, where if the BAF effluent was below the detection limit then the detection limit concentration was used to calculate a removal efficiency.

Table 18 Removal Efficiency by BAF in Phases 1 and 2
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

	Removal (%)					Removal (%)	
	1A	**1B**	**2A**	**2B**	**Range**	**Biological Mode GAC Beds (2)**	**Adsorption Mode GAC Beds (3)**
Bisphenol A	44	96	32	0	0 - 96	-	
Estrone	-	-	-	20	20 - 20	-	
4-nonylphenol	-	-	-	28 (1)	28 - 28	-	
Atenolol	84	82	0	81	0 - 84	-	
Triclosan	-	-	-	-	-	-	
Caffeine	50 (1)	77	88 (1)	87	50 - 88	<1 - 36	>44
Carbamazepine	-	0	-	17 (1)	0 - 17	3.4	>54
Ibuprofen	55	44	62	65	44 - 65	52 - >58	>9
Gemfibrozil	10	0	0	54	0 - 54	-	>16
Iopromide	31	0	14	27	0 - 31	<1 - 14	>69
Sulfamethoxazole	-	43	-	25	25 - 43	-	>83
Atrazine	75	-	75	67	67 - 75	5.9	>99

Notes:
(1) BAF effluent concentrations were below the detection limit. Therefore, the detection limit value was used to calculate a removal efficiency.
(2) Range of removal efficiencies for granular activated carbon beds that are operated in biological mode (Snyder et al., 2007).
(3) Removal efficiencies for granular activated carbon beds that are regularly regenerated (Snyder et al, 2007)

Table 18 includes literature values (Snyder et al, 2007), for two granular activated carbon beds that are operated in biological mode at two full scale drinking water treatment plants. Both utilities, use Calgon Filtrasorb-300 and -820 respectively, and operate in biological mode where the TOC removal capabilities have been exhausted. Table 18 also includes literature values (Snyder et al, 2007), for one granular activated carbon bed that is operated in adsorption mode at a full scale drinking water treatment plant. This plant uses Calgon Filtrasorb-400. Removal efficiencies observed for the pilot BAF for caffeine, atrazine,

carbamazepine, and gemfibrozil were greater than the literature values for the GAC beds operated in biological mode. While exhausted GAC from the Bollman WTP full-scale filter beds was used in the pilot BAF, it is possible that some of the removal observed at the pilot scale was due to adsorption. If this is the case, then it would be expected that in practice over a longer period of time, the GAC would be exhausted with respect to sorption of these compounds and that removal efficiencies would potentially be lower.

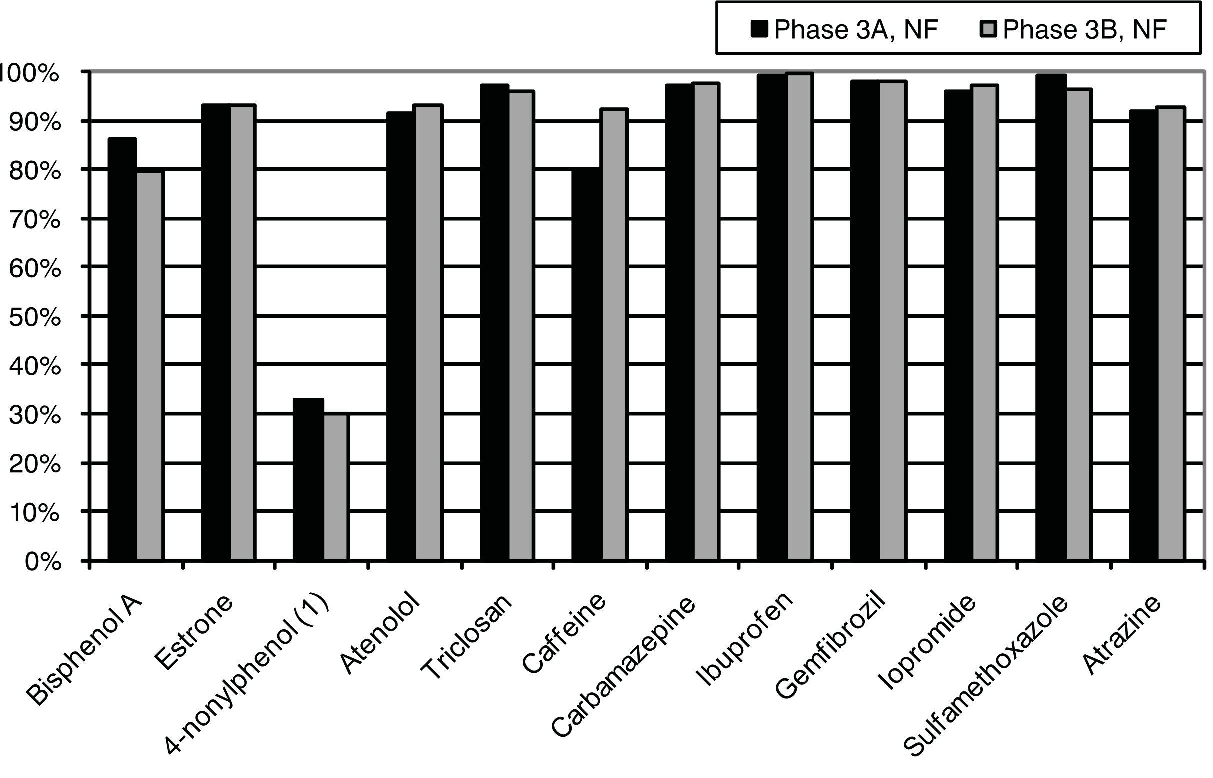
5.7.2.4 Nanofiltration

Figure 17 presents the results for Phase 3, where the removal efficiency of NF was evaluated. In Phases 3A and 3B, NF achieved >90 percent removal of estrone, atenolol, triclosan, carbamazepine, ibuprofen, gemfibrozil, iopromide, sulfamethoxazole and atrazine. Greater than 80 percent removal was achieved for bisphenol-A and caffeine. In comparison, Snyder et al (2007) reported NF removal efficiencies ranging from 50 percent to 80 percent for atrazine, estrone, carbamazepine, ibuprofen and sulfamethoxazole. For 4-nonylphenyl, the spiked dose was low and the permeate concentration was below the detection limit. Therefore, the 4-nonylphenyl removal by NF was at least 30 percent, but may have been greater if a greater spiked dose was achieved in the influent to the membrane.

Figure 18 presents a comparison between Phase 1A and Phase 3A. This allows comparison of pilot results representing the existing treatment process train and a process train that includes NF as a polishing step. Figure 18 includes the removal achieved by the ozone process alone, and the cumulative removal achieved by ozone followed by BAF. As noted previously, the removal achieved by BAF pilot may be an overestimate of long-term performance at the full scale. Most of the compounds tested were removed at 90 percent or greater with the combined processes of ozonation and BAF (representing the existing treatment process train), with the majority of the removal attributed to the ozonation process. Exceptions included ibuprofen, atenolol and atrazine, which were shown to be relatively ozone resistant compounds. These three compounds were well removed by NF.

5.7.3 <u>Summary of Trace Organics Removal</u>

The Phase 1 pilot tests were designed to simulate existing treatment processes at CCWD and other Delta utilities. Almost all (8 out of 11) of the target compounds were well removed by ozonation (>90 percent) at an ozone dose similar to current practices at the Bollman WTP. These results demonstrate the effectiveness of ozonation for trace organics removal, and suggest that at a dose similar to 1 mg/L, Delta utilities are already achieving good removal of trace organics. Three of the target compounds were not well removed by ozonation, including ibuprofen, iopromide and atrazine. The BAF process contributed to improved removal of these three compounds. However, the removal of the BAF pilot may



Notes:

(1) For 4-nonylphenyl, the spiked dose was low and the permeate concentration was below the detection limit. This allowed calculation of a minimum removal efficiency of approximately 30%.

Figure 17
PERCENT REMOVAL BY NANOFILTRATION: PHASES 3A AND 3B
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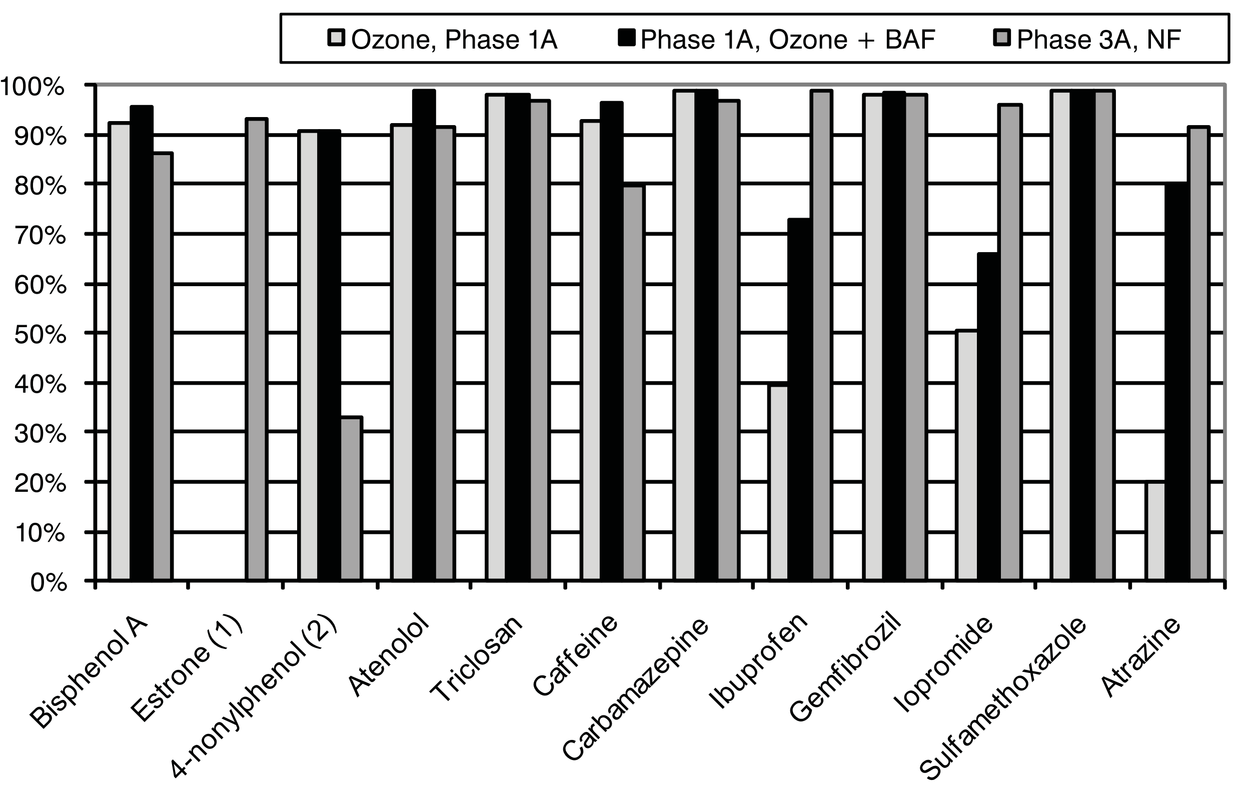

Notes:

(1) Data not available for Phase 1A.

(2) For 4-nonylphenyl, the spiked dose was low and the permeate concentration was below the detection limit. This allowed calculation of a minimum removal efficiency of approximately 30%.

Figure 18
PERCENT REMOVAL BY OZONE AND BAF, AND BY NF: PHASE 1A AND 3A
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be an overprediction of the removal that would be achieved over the long term at a full-scale process. At lower ozone doses, there was evidence of dose dependence for three compounds, including bisphenol-A, atenolol, and caffeine. These results have implications for Delta utilities that may modify ozone doses in response to changes in water quality. Again, the BAF contributed to overall improved removal of these compounds, but may not be representative of long-term, full-scale performance.

The Phase 2 pilot tests examined the effects of adding peroxide at an intermediate location within the ozone contactor. This pilot train was designed to evaluate the benefits of implementing peroxide addition for trace organics removal, which would be a relatively minor change that could be made at some Delta utilities. In this study, the perozone results generally matched the ozone results. However, this may be in part due to the low ozone residual concentrations at the point of peroxide addition, and the likelihood that advanced oxidation was not achieved in the pilot tests. The low ozone residual under the 1 mg/L dosing condition suggests that if Delta utilities wanted to practice advanced oxidation with perozone, then ozone dose or the ozone contact time prior to peroxide addition would need to be adjusted.

The Phase 3 pilot studies allowed evaluation of NF membranes, only, as the target compounds were spiked upstream of the NF membranes. NF membranes removed almost all target compounds at greater than 90 percent removal, including the ozone resistant compounds, ibuprofen, iopromide, and atrazine. Greater than 80 percent removal of bisphenol-A and caffeine was achieved. These results demonstrate the effectiveness of NF membranes as a technology for trace organics removal.

5.8 Bench Scale Disinfection Testing Results

While the primary objective of the study focused on the removal of trace organics, one of the secondary objectives focused on DBP formation. The formation of DBPs is an ongoing challenge for Delta utilities, and this study provided an opportunity to examine the formation of both conventional and emerging DBPs from existing treatment processes as well as other advanced treatment processes that may be implemented in the future.

As part of this study, two types of bench scale disinfection tests were conducted:

The first type of bench scale tests, described in Section 5.8.1, were conventional formation potential tests conducted on samples collected from the pilot train feed water, after individual treatment processes, and from the finished water. Data collected from these tests allowed a relative comparison of the reduction in conventional DBP formation by treatment process and across the treatment trains.

The second type of bench scale tests, described in Section 5.8.2, were conducted on the finished water of the pilot test trains. These tests were conducted as part of a concurrent Water Research Foundation Study, and included analysis of conventional and emerging

DBPs formed in the finished water of the three treatment trains. The data collected from these tests allowed a relative comparison of DBP formation across the three treatment trains. For these tests, the formation of the emerging (and unregulated) DBPs are of particular interest, as Delta utilities don't often have the opportunity to obtain this type of data.

It is important to note that experimental conditions for these two types of bench scale disinfection tests were different and the results in Sections 5.8.1 and 5.8.2 are not comparable.

5.8.1 Conventional Bench Scale DBP Formation Potential Tests

Bench scale DBP formation potential tests were conducted at the University of Toronto's Drinking Water Research Group laboratory. These tests focused on measuring conventional THMs and HAAs formed in samples collected from the pilot trains after chlorine addition. These results provide a baseline understanding of how the treatment trains compare with respect to removal of THM and HAA precursors. In addition, the formation potential tests were conducted on water collected from several locations within the treatment trains, and therefore allowed a relative comparison of the effectiveness of the individual treatment processes for removing THM and HAA precursors.

These bench scale tests were not intended to simulate disinfection practices at CCWD or the formation of DBPs in the Bollman WTP finished water or distribution system. The formation potential tests were conducted according to Standard Methods 5710B: Trihalomethane Formation Potential (THMFP), and 5710 D: Formation of Other Disinfection By-Products. In brief, water samples from each phase of the pilot plant tests were chlorinated at pH 7.0 and 22°C for 7 days at a chlorine concentration that yielded a 7 day residual in the range of 3-5 mg/L (See appendix G for method details). In these tests, the residual chlorine concentration ensures that the DBP formation is not chlorine limited, and therefore represents the maximum DBP formation given the temperature, pH, and incubation time of the tests.

The DBP measurements included chlorinated/brominated THMs and HAAs. The THMs included chloroform, bromodichloromethane (BDCM), chlorodibromomethane (CDBM), and bromoform. THM_4 is the sum of these compounds and is a regulated concentration. The HAAs included monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), monobromoacetic acid (MBAA) and dibromoacetic acid (DBAA) and bromochloroacetic acid (BCAA), Bromodichloroacetic acid (BDCAA), chlorodibromoacetic acid (CDBAA), and tribromoacetic acid (TBAA). HAA_9 is the sum of these nine compounds. HAA_5 is the sum of DCAA, TCAA, MCAA, MBAA, and DBAA, and is a regulated concentration. .

There was a problem with the HAA_9 measurements. Two of the compounds, monochloroacetic acid and monobromoacetic acid—showed unrealistically high concentrations in some samples ranging up to 145 μg/L. Considerable efforts were made without success in the laboratory to try to identify problems with the analysis that could lead to such high concentrations. Unfortunately a mass spectrometer was not available to confirm potential problems such as coelution of the two HAAs with unknown compounds. It is the judgment of the researchers that despite any evidence of problems with the analytical method, that the monochloro- and monobromoacetic acid results be discounted because such high values are not realistic based on experiences elsewhere. Furthermore, given the normally very small contributions of these two compounds to HAA_9, it is suggested that "HAA_7" (i.e. ignoring monochloro- and monobromoacetic acid) can be used as an acceptable surrogate to identify the impact of the pretreatment on HAA formation.

The THM_4 and HAA_7 formation potentials (THM_4FP and HAA_7FP) are presented in Tables 19 and 20, and Figure 19. The results indicated that oxidation with ozone and perozone resulted in similar reductions in the DBPFP. Ozone reduced THM_4FP by approximately 14 percent relative to the formation potential in the settled water, while perozone reduced THM_4FP by approximately 18 percent. Similarly, HAA_7FP was reduced by 16 percent and 5 percent using ozone and perozone, respectively. There were not enough samples collected to warrant a full statistical analysis of this data, however the general message that ozone and perozone reduced DBPFP by approximately 10-15 percent is consistent with observations from other studies (Mowat et al., 2005).

Table 19 THM_4FP Results for Phase 1, 2 and 3
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

	Phase 1			Phase 2			Phase 3	
DBP	1 Settled Water (ppb)	2 Ozone Effluent (ppb)	3a BAF Effluent (ppb)	1 Settled Water (ppb)	2 Perozone Effluent (ppb)	3a BAF Effluent (ppb)	3b NF Influent (ppb)	4 NF Permeate (ppb)
Chloroform	72	47	30	63	36	34	26	7
BDCM	186	161	128	173	148	134	132	88
CDBM	118	113	93	122	107	101	108	59
Bromoform	28	27	24	32	28	28	22	4
THM_4	**404**	**348**	**276**	**389**	**320**	**298**	**289**	**158**

Figure 19
THM_4FP AND HAA_7FP FOR PHASES 1, 2, AND 3
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CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

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Table 20	HAA_7FP Results for Phase 1, 2 and 3 Removal of NDMA, EDCs and PPCPs in South Delta Water California Department of Water Resources California Department of Public Health							
	Phase 1			Phase 2			Phase 3	
DBP	1 Settled Water (ppb)	2 Ozone Effluent (ppb)	3a BAF Effluent (ppb)	1 Settled Water (ppb)	2 Perozone Effluent (ppb)	3a BAF Effluent (ppb)	3b NF Influent (ppb)	4 NF Permeate (ppb)
DCAA	62	42	30	56	49	29	27	8
TCAA	20	12	6	15	11	6	14	5
BCAA	42	42	27	49	47	32	8	1
BDCAA	38	33	22	48	46	34	26	2
DBAA	18	11	8	18	14	9	5	0
CDBAA	33	27	23	38	36	26	10	<MDL
TBAA	9	9	8	13	13	10	<MDL	<MDL
HAA_7	**222**	**177**	**124**	**237**	**215**	**146**	**90**	**15**

The BAF also contributed to a reduction in DBPFP. THM_4FP was reduced by approximately 21 percent and 7 percent across the BAF when preceded by ozone and perozone, respectively, while HAA_7FP was reduced by approximately 30 percent across the BAF for both ozone and perozone pretreatments. The total organic carbon reduction across the BAF was 10 percent (Table 15), suggesting that the BAF process was selectively removing THM and HAA precursors.

Nanofiltration was found to be effective for reducing the DBPFP. The THM_4FP was found to be reduced by 45 percent in nanofilter permeate relative to the NF influent, while the HAA_7FP decreased by 83 percent. This decrease in formation potential is related to the reduction in TOC across the nanofilter, which was 82 percent (see Table 16). In comparison to the BAF effluent in Phases 1 and 2, the overall THM_4FP and HAA_7FP in the NF permeate were lower. It should be noted that the feed water to the ozone/perozone and BAF pilot train was the full-scale settled water and that the feed water to the NF pilot was the full scale BAF effluent. Therefore, these results are not directly comparable, but provide some insight into the quality of NF permeate if the NF filters were used as a polishing step after the existing BAFs.

5.8.2 Bench Scale Simulated Final Disinfection Tests

A series of bench scale disinfection tests were conducted at Duke University as part of WRF Project #4019. The objective of WRF Project #4019 was to investigate how the addition of UV disinfection may affect the formation of regulated, known but unregulated, and currently unknown DBPs when chlorination or chloramination is coupled with UV. The

results presented in this report do not include any of the results for samples that were also exposed to UV disinfection. For results on all the disinfection scenarios see Linden et al. (2010).

It is important to note that due to differences in the experimental conditions of the bench scale tests described in section 5.8.1 and in this section, the results are not comparable. As described previously, the concurrent WRF study (WRF Project #4019) provided an opportunity to obtain data on both conventional and emerging DBPs, and that this is valuable information for Delta utilities.

The results in this report are limited to two disinfection scenarios. The first analysis measured the DBP concentrations in the finished water from the treatment trains, with no disinfectant added at the bench scale, and therefore these samples represents the "control" condition. Note that the feed water to the pilot units is from the full scale Bollman WTP, and that pre-chlorination is practiced at the full scale. The second analysis investigated the DBP formation potential of the finished water from the treatment trains subject to bench-scale disinfection.

The bench scale disinfection tests involved chlorination at pH 8.5 using 2 mg/L free chlorine for 13 minutes, followed by application of ammonia to convert the remaining chlorine to monochloramine. This chloraminated sample water was then held for 24 or 72 hours. For Phases 1A and 2A, the holding time was 24 hours. However, after reviewing the data, the researchers decided to increase this hold time to determine if this change would lead to formation of more DBPs at detectable concentrations. Therefore, for all other phases (1B, 2B, and 3), the hold time was 72 hours. The samples treated with chlorine and ammonia are referred to as the "treated" samples. The bench scale disinfection scenario was designed to be similar to disinfection practices at the Bollman WTP. However, the bench results are not intended to be a predictive tool for the formation of DBPs at the full scale. The results provide information on the relative concentrations of both regulated and unregulated DBPs formed under conditions that are similar to disinfection practices at the full scale.

Each sample was analyzed for the following DBPs:

- THMs – THM_4 and iodinated THMs.
- HAAs – HAA_9 and iodinated acids
- Nitrogenous DBPs - Nitrosamines, HANs, and HNMs. Measured nitrosamines include NDMA, N-nitrosomethylethylamine (NMEA), N-nitrosodiethylamine (NDEA), N-nitrosodiphenylamine (NDPA), N-nitrosodibutylamine (NDBA), N-nitrosopyrrolidine (NPYR), and N-nitrosopiperidine (NPIP). Measured HANs included trichloroacetonitrile (TCAN), dichloroacetonitrile (DCAN), and chloroacetonitrile (CAN). Measured HNMs included dichloronitromethane (DCNM), chloronitromethane (CNM), and trichloronitromethane (TCNM).

- Haloketones - Two haloketones 1,1-dichloropropanone (1,1-DCP) and 1,1,1-trichloropropanone (1,1,1-TCP).

- Total organic halides (TOX) – TOX was measured and the unknown TOX percentage was calculated.

While iodinated THMs and HAAs were analyzed, it was not possible to quantify the concentrations of the iodinated compounds based on the analytical results. For this reason, results and discussion on iodinated DBPs are not included.

5.8.2.1 Ozone/Perozone and BAF

The DBP formation in samples treated with ozone or perozone prior to BAF were similar. However, the difference in experimental conditions, 24 hours hold time versus 72 hours hold time, resulted in differences in the DBP formation. Therefore, samples from Phases 1A and 2A were averaged, and samples from Phases 1B and 2B were averaged.

5.8.2.1.1 THMs

THM_4 formation is presented in Table 21, and Figure 20. Accounting for the THM_4 in the control samples, the THM_4 ranged from approximately 40 ppb to 75 ppb for the 24 and 72 hour hold times. Figure 21 shows that for Phases 1 and 2 (regardless of hold time), the THM_4 formation is dominated by bromoform and CDBM. At bromide concentrations of approximately 0.4 mg/L, the importance of the more brominated THMs is illustrated in these results.

Table 21 Individual and THM_4 Formed in Each Testing Phase
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

	Phase 1A/2A (ppb)		Phase 1B/2B (ppb)		Phase 3A-Permeate (ppb)	
Compound	**Control**	**Treated**	**Control**	**Treated**	**Control**	**Treated**
Chloroform	6.0	10.2	7.3	7.5	6.0	4.6
BDCM	5.0	11.2	7.5	14.6	6.0	5.3
CDBM	3.9	14.1	4.4	29.6	3.3	4.0
Bromoform	0.7	21.4	0.1	43.8	0.1	4.3
THM_4	**16**	**57**	**19**	**95**	**15**	**18**

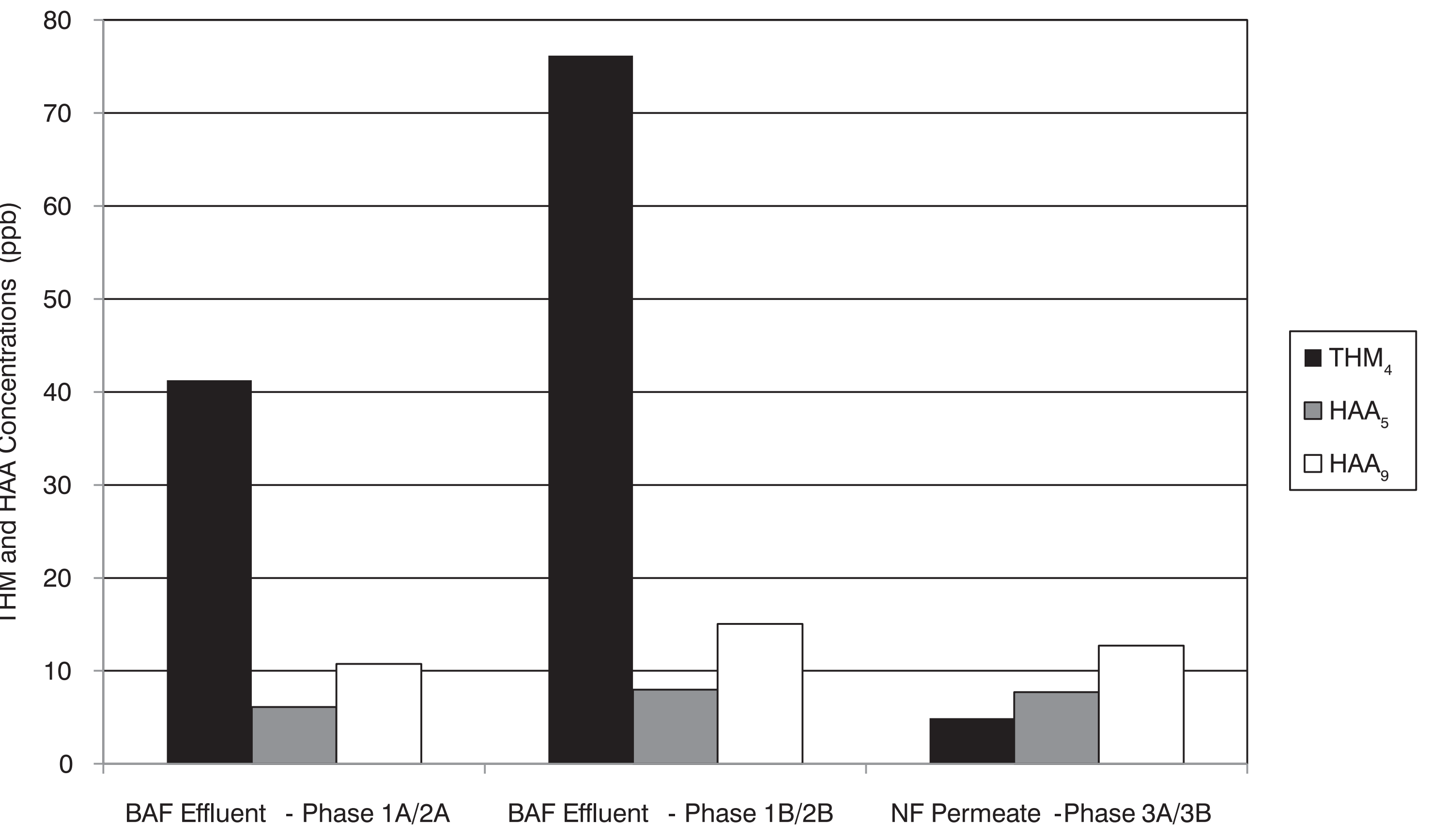

Figure 20
THM_4, HAA_5, AND HAA_9 FORMED IN CHLORAMINATED SAMPLES
CALIFORNIA DEPARTMENT OF WATER RESOURCES
CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

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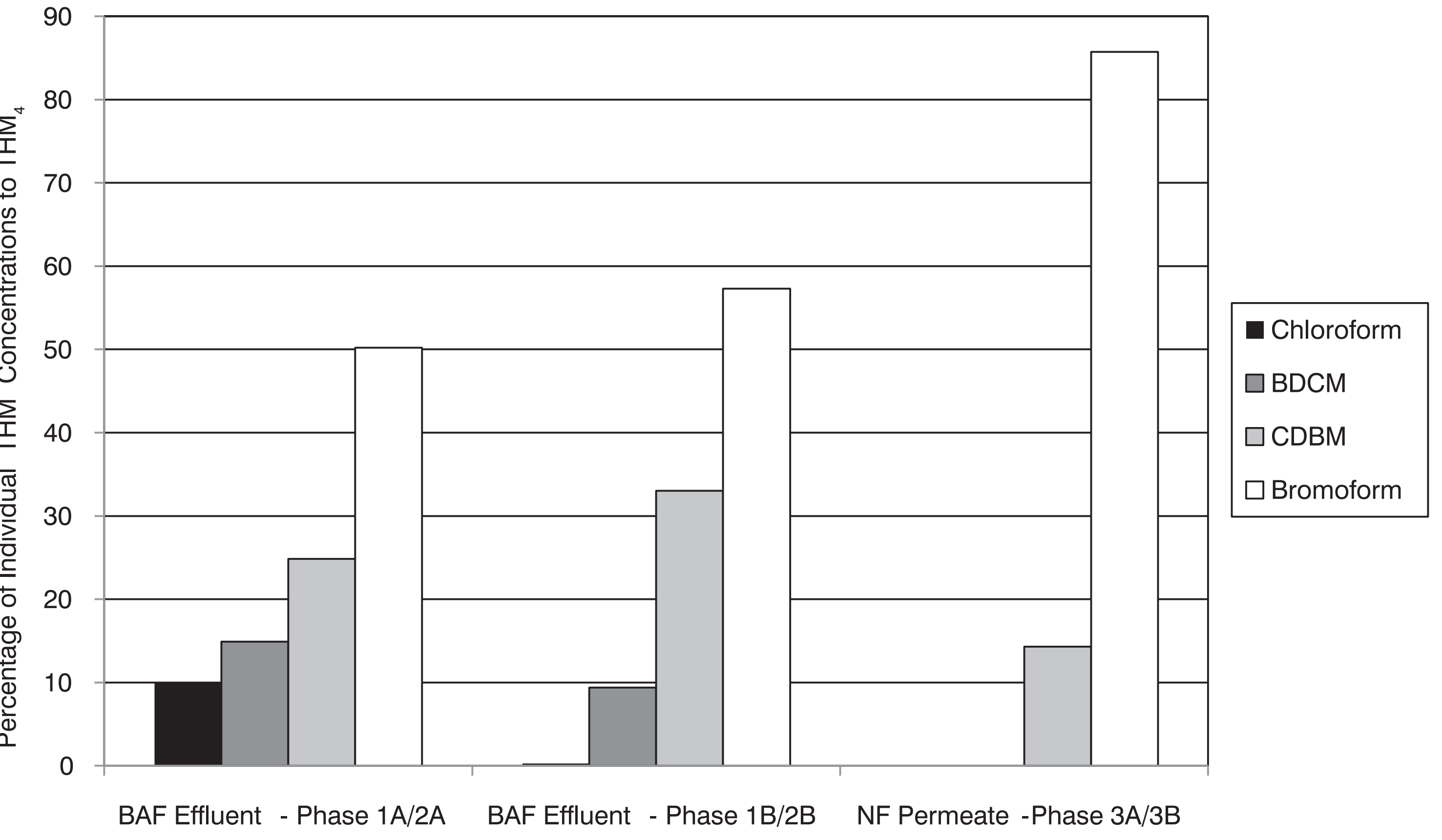

Figure 21
PERCENTAGE CONTRIBUTION OF INDIVIDUAL HMs TO THM_4 FORMED IN CHLORAMINATED SAMPLES
CALIFORNIA DEPARTMENT OF WATER RESOURCES
CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

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5.8.2.1.2 HAAs

HAA formation, in terms of HAA_5 and HAA_9, is presented in Table 22 and Figure 20. Similar to the THM_4 concentrations, the HAA_5 and the HAA_9 were greater for the samples held for 24 and 72 hours. HAA_9 concentrations were two- to three-fold higher than HAA_5. The individual HAAs that contribute to the HAA_5 are show in Figure 22. This figure shows that for Phases 1 and 2 (regardless of hold time) HAA_5 formation is dominated by DBAA, with contributions ranging from approximately 60 to 70 percent. Similar to the results for THMs, the more brominated HAAs dominate the distribution of HAA_5 formed.

Table 22 Individual HAAs, HAA_5 and HAA_9 Formed in Each Testing Phase
Removal of NDMA, EDCs and PPCPs in South Delta Water
California Department of Water Resources
California Department of Public Health

	Phase 1A/2A (ppb)		Phase 1B/2B (ppb)		Phase 3A-Permeate (ppb)	
Compound	**Control**	**Treated**	**Control**	**Treated**	**Control**	**Treated**
MCAA	0.6	0.6	0.6	0.6	0.6	0.6
MBAA	0.4	0.5	0.4	1.2	0.4	1.0
DCAA	0.6	1.7	0.6	0.8	0.6	1.9
BCAA	0.5	2.6	0.7	3.3	0.4	3.0
TCAA	1.3	1.5	0.8	0.9	0.4	0.5
DBAA	0.4	4.1	0.6	6.0	0.4	4.1
BDCAA	2.1	3.2	1.5	3.0	1.4	2.2
CDBAA	4.2	4.9	3.9	5.4	3.4	4.0
TBAA	5.7	6.4	6.1	7.6	4.0	4.8
HAA_5	**1.7**	**7.8**	**1.0**	**9.0**	**0.8**	**8.5**
HAA_9	**14.1**	**24.8**	**13.2**	**28.2**	**10**	**23**

5.8.2.1.3 Nitrogenous DBPs

Linden et al (2010) noted that the nitrate concentrations were sufficiently high to generate nitrogen containing DBPs measurable by the analytical methods that were employed. In addition, organic nitrogen and nitrite are also important nitrogenous DBP precursors. The results presented in Table 23, are limited to compounds where a detectable concentration was measured in at least one sample. Therefore, the results are limited to one HAN and two nitrosamines. Accounting for the concentrations in the control samples, DCAN formation was not important in Phases 1 and 2. Accounting for the concentrations in the control samples, approximately 2 ppt of NDMA was formed in the treated samples in Phases 1 and 2. While there was formation of NDMA observed, the concentrations were low. The California Public Health Goal and the California Notification Levels are 3 ng/L (3 ppt) and 10 ng/L (10 ppt), respectively.

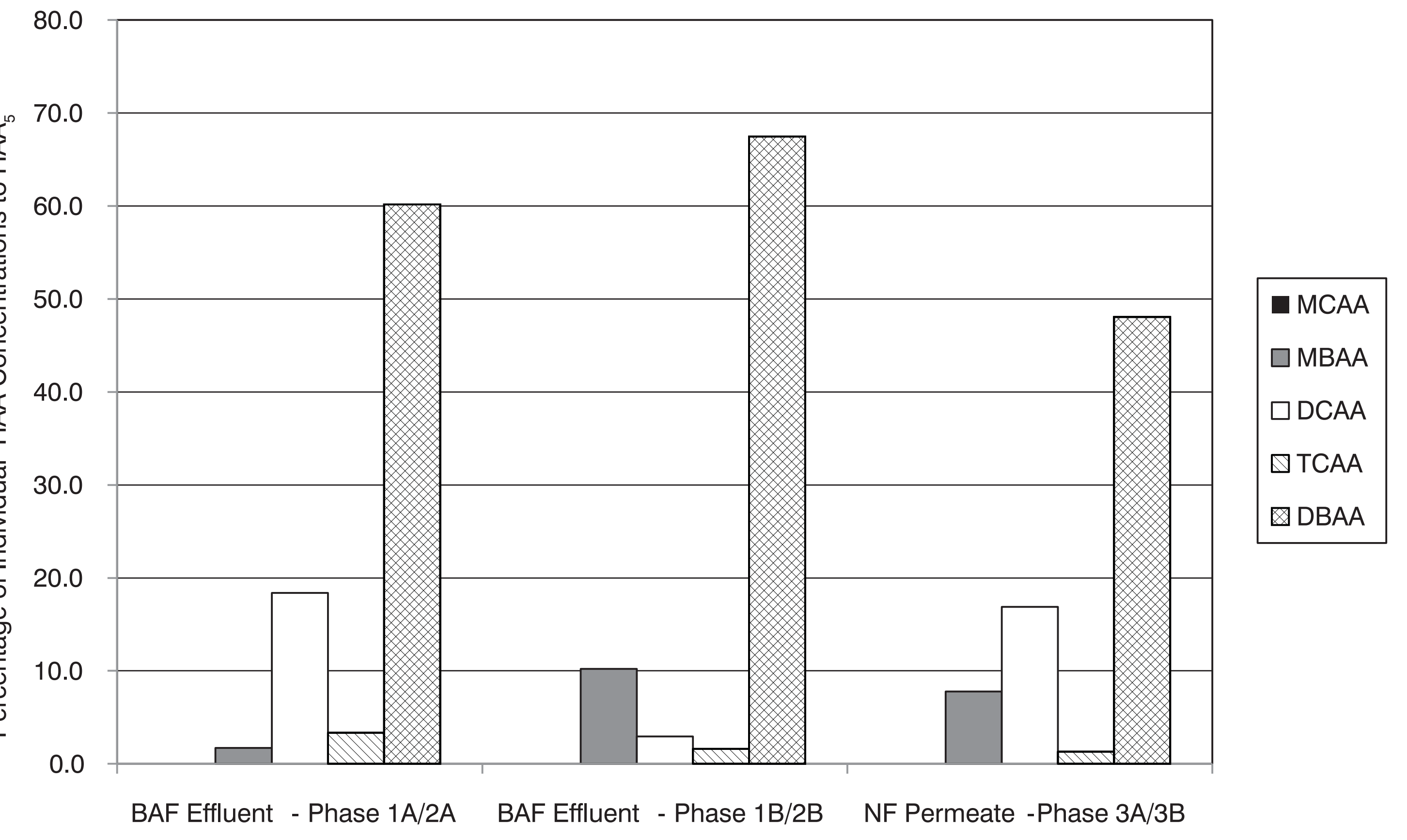

Figure 22
PERCENTAGE CONTRIBUTION OF INDIVIDUAL HAAs TO HAA_5 FORMED IN CHLORAMINATED SAMPLES
CALIFORNIA DEPARTMENT OF WATER RESOURCES
CALIFORNIA DEPARTMENT OF PUBLIC HEALTH

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Table 23	Nitrogenous DBPs Formed in Each Testing Phase Removal of NDMA, EDCs and PPCPs in South Delta Water California Department of Water Resources California Department of Public Health					
	Phase 1A/2A		**Phase 1B/2B**		**Phase 3A-Permeate**	
Compound	**Control**	**Treated**	**Control**	**Treated**	**Control**	**Treated**
DCAN (ppb)	<0.4	0.42	0.4	0.41	0.4	0.4
NDMA (ppt)	<2.0	4	<2.0	4.3	<2.0	2.3
DMNA (ppt)	<2.0	<2.0	<2.0	<2.0	3.5	4.7

Notes:
DCAN detection limit is 0.4 ppb.
Nitrosamines detection limit is 2.0 ppt.

5.8.2.1.4 Haloketones and TOX

The two haloketones 1,1-dichloropropanone (1,1-DCP) and 1,1,1-trichloropropanone (1,1,1-TCP) were only detected in phases 1A and 2A, which suggests that they form within 24 hours and may not be stable over 72 hours.

The unknown total organic halide (TOX) percentages were calculated in the control and treated samples. In Phases 1 and 2 the control and treated TOX percentages ranged from 16 percent to 66 percent, and 52 percent and 80 percent, respectively.

5.8.2.2 Nanofiltration

The DBP formation potentials in Phase 3A and 3B were similar, and averaged results are presented in this section.

5.8.2.2.1 THMs

THM_4 formation results are presented in Table 21 and in Figures 20 and 21. The THM_4FP of the treated sample from the permeate of the membranes is similar to that of the control sample. Table 20 and Figure 20 show low THM_4 formation relative to the BAF effluent in both Phases 1 and 2. Figure 21 shows that the THM_4 formation is dominated, 85 percent, by the formation of bromoform. In comparison, the bromoform formed from the BAF effluent samples in Phases 1 and 2 ranged from approximately 50 to 60 percent. This is likely due to the more efficient removal of TOC relative to bromide. This leads to a relatively increased bromide to TOC ratio, which results in relatively more bromoform formation (on a percentage basis).

5.8.2.2.2 HAAs

The HAA formation results are presented in Table 22 and in Figures 20 and 22. The HAA_5 and the HAA_9 are similar in Phases 1, 2 and 3. Similar to Phases 1 and 2, the dominant

HAA contributing to the HAA_5 is DBAA. In the filter permeate DBAA accounted for approximately 50 percent of HAA_5.

5.8.2.2.3 Nitrogenous DBPs

Nitrogenous DBP results are presented in Table 23. Accounting for the concentrations in the control samples, DCAN was not formed at detectable concentrations, and low concentrations of NDMA and DMNA were formed. NDMA concentrations formed were below the California Public Health Goals and Notification Levels.

5.8.2.2.4 Haloketones and TOX

The two haloketones analyzed were both formed at concentrations below the detection limit in samples from the permeate of the NF membrane.

The TOX percentage was not calculated due to loss of sample integrity.

5.8.3 Summary of DBP tests

The conventional DBP formation potential tests showed that the ozone plus BAF treatment train and the perozone plus BAF treatment train led to similar THMFPs and HAAFPs. THM_4FP and HAA_7FP were reduced through the treatment train processes, with reductions by ozone and perozone ranging from 7 percent to 30 percent. The BAF process accounted for approximately 10 percent TOC removal and therefore also contributed to THM_4FP and HAA_7FP reduction. The NF membranes achieved 78 percent TOC removal and led to THM_4FP and HAA_7FP reductions of 45 percent to 83 percent.

The results from the bench scale simulation of final disinfection tests allowed evaluation of the formation of THM and HAA species and numerous other unregulated DBPs. Results of Phases 1 and 2 showed that DBP formation in samples treated with ozone or perozone prior to BAF were similar. For both the ozone plus BAF and the perozone plus BAF treatment trains, the THM_4 formation was dominated by bromoform and CDBM. At bromide concentrations of approximately 0.4 mg/L, the importance of the more brominated THMs was illustrated in these results. Similar trends were observed in the HAA_5 results. In both Phases 1 and 2, the HAA_5 formation was dominated by DBAA.

In Phases 1 and 2, most nitrogenous DBPs were formed at less than the detection limit. Exceptions include the formation of DCAN, NDMA, and DMNA, but these were formed at low concentrations, less than the California Public Health Goal of 3 ng/L. Other DBPs were formed in the treated water in Phases 1 and 2, with measurable concentrations of unknown TOX.

For the permeate of the NF membranes, THM_4 and HAA_5 formation were both dominated by the more brominated species. Most nitrogenous DBPs were not formed at detectable concentrations. Low concentration of NDMA were formed, at concentrations below the California Public Health Goals and Notification Levels.

Comparing to Phases 1 and 2, the Phase 3 results showed lower THM_4 formation, but similar HAA_5 formation. This may be due to the importance of TOC concentration in the formation of THMs as compared to HAAs. In addition, the THM_4 formed in the NF permeate showed a greater dominance by bromoform as compared to the THM_4 formed in the BAF effluent. This is likely due to the more efficient removal of TOC relative to bromide. This leads to a relatively increased bromide to TOC ratio, which results in relatively more bromoform formation (on a percentage basis).

5.9 NF Membrane Operational Testing

As a secondary objective of the study, this part of the study was designed to investigate some of the operational challenges associated with NF membrane filtration. The performance of the NF membranes in terms of contaminant removal, in addition to the trace organic contaminants discussed previously in this report, was evaluated. In addition, data were collected to assess NF membrane fouling potential, impacts of chloramines, and power demands.

5.9.1 NF Membrane Performance

The data presented in Table 24 provides information on the performance of the membranes with respect to removal of contaminants in addition to the trace organics that were the primary objective of this study. In addition, Section 5.8 includes a discussion of DBP formation in the permeate of the NF membranes, when membranes are incorporated as a polishing step after the existing BAF. However, membranes could be used at different stages in the treatment process, and therefore, the general performance of the NF membranes with respect to DBP precursor removal, in particular, is of interest. Table 24, is based on the data presented in Table 16 and provides a summary of pollutant removal efficiencies achieved by the NF membranes.

5.9.2 Fouling Potential

One operational issue with membranes is various types of fouling that can negatively impact membrane performance and/or increase O&M demands (i.e. maintenance and chemicals).

5.9.2.1 Particle Fouling

Spiral wound NF membranes, like the ones used in this study, are designed to remove dissolved salts from water. While they are able to remove particles, they are not designed for this, and high concentrations of solids and particles will damage the NF membrane elements. The particle content of the NF feed water must therefore be quite low. As shown in Table 16, turbidity is generally low and within the range that would be acceptable to an NF process. TSS is also reported and appears low, however NF users are not accustomed to using this as a measure of fouling potential. The Silt Density Index (ASTM D4109-07) is a more accepted approach to assessing the potential for particulate fouling.

Table 24	NF Membrane Removal Efficiencies for Selected Contaminants Removal of NDMA, EDCs and PPCPs in South Delta Water California Department of Water Resources California Department of Public Health			
		Sampling Location		
Parameters	Units	Filter Effluent, Post-spike	Permeate	Percent Removal (%)
UV_{254}	cm^{-1}	0.021	0.001	95%
Bromide	mg/L	0.45	0.3	33%
Chloride	mg/L	76.5	45.5	41%
TDN	mg/L as N	0.59	0.24	59%
DIN	mg/L as N	0.36	0.19	47%
DON	mg/L as N	0.23	0.05	78%
TOC	mg/L	2.3	0.5	78%
DOC	mg/L	2.3	0.51	78%
SUVA	L/mg-m	0.84	0.07	92%

5.9.2.2 Mineral Fouling

Mineral fouling of an NF membrane is a result of concentrating the sparingly soluble salts in the raw water feed to the NF system. Typical salts that result in mineral fouling (a.k.a., scaling) are calcium carbonate, calcium sulfate, barium sulfate, strontium sulfate, silica, calcium fluoride and calcium phosphate. The concentration of these salts in the concentrate stream determines the fouling potential. This potential may be controlled either by controlling the concentration of these salts (i.e., by controlling the NF Process recovery rate), and to some extent by adding a scale inhibitor. Scale inhibitors however, are only effective to a certain extent. The data presented in Table 16 indicates that the fouling potential for calcium carbonate, calcium sulfate and calcium fluoride was within the range that is acceptable for NF applications. Additional data is required to determine fouling potential for other salts. Measured concentrations of barium, strontium, and silica would also provide information on mineral fouling potential.

5.9.2.3 Organic Fouling

TOC is a measure used to determine the possible fouling potential of an NF feed water. As presented in Table 16 (and Table 24), at 2.3 mg/L, the TOC concentration is quite low and therefore suggests minimal potential for organic fouling.

5.9.2.4 Biological Fouling

HPC is a crude measure of biological activity that may be used to determine the biological fouling potential of an NF feed water. The HPC count reported in Table 16 is adequately

low (nearly the range that is acceptable for drinking water quality). Chloramines were used to minimize the potential for biofouling the pilot membranes. Therefore, there is limited information on biofouling potential in the absence of chloramines.

5.9.3 Impacts of Chloramines Used for Biofouling Control

One potential treatment concern is the use formation of THMs and HAAs as a result of using chloramines to minimize biological fouling of the membranes. To assess this potential source of DBPs, an additional set of DBP measurements were undertaken during Phase 3. For one week prior to each sampling event chloramines were dosed into the NF system at a rate of 3 mg/L. The chlorine and ammonia were dosed simultaneously into a 280 gallon tank containing plant filtered water which served as the NF feed supply. THM and HAA samples of the plant filtered water, before and after chloramination, as well as samples of the NF permeate were collected before shutting off the chloramine dosing for each trace organics experimental sampling event. The THM and HAA concentrations, resulting from chloramination, were measured and are presented in Table 25. When discounting the monochloroacetic acid results as before (see section 5.8.1), it is evident that THM and HAA formation in the presence of monochloramine alone is negligible.

5.9.4 Power Demands

One operational concern with NF membranes is power consumption. To address this issue, power demand data were collected during operation of the NF membranes. Over the course of the 3 weeks of experimentation the amount of power consumed was 1,287 kWh (or 4.63MJ). The high pressure pumps are the system's major power consumers and consist of the initial booster pump (running consistently at 60.0Hz), the main R/O high pressure pump (at 26.6Hz), and the interstage booster pump (at ~19.6Hz). At the stated normal operating conditions, providing 20 gpm with an 80 percent flux rate, the system required approximately 173-183 kW of power.

A reverse osmosis system provides a reasonable comparison for power demands. Based on the recorded NF power demands, a unit power demand of approximately 2,600 kWh/million gallons (MG) was calculated. The power demands of a reverse osmosis system is estimated at approximately 20 percent greater than the NF membranes.

5.9.5 Summary of NF Membrane Operational Tests

In this study, membranes were piloted as a polishing step to the existing full scale process train. In addition to being an effective tool for removing target compounds, the NF membranes showed significant removal of organic carbon, organic nitrogen and SUVA. In addition, bromide was removed at 33 percent. The study was not designed to provide a thorough evaluation of membrane fouling potential, but based on the collected data, fouling does not appear to be a major issue given the quality of the BAF effluent. However, limited information is known about biofouling due to the use of chloramines to control biofouling of

Table 25	THM and HAA Concentrations in Filtered, Pre-Chloraminated, or Nanofiltered Water Removal of NDMA, EDCs and PPCPs in South Delta Water California Department of Water Resources California Department of Public Health		
Phase 3 THM/ HAA Concentrations (ppb)			
Sample Location	**NF influent, pre-chloramination (1)**	**NF influent, post-chloramination (1)**	**NF permeate**
DBP Compound	Average	Average	Average
Chloroform	4	2	3
BDCM	3	2	2
CDBM	3	2	2
Bromoform	<MDL	<MDL	<MDL
THM_4	**10**	**6**	**7**
HAA_9	19.2	25.2	18.4
MCAA	18.6	24.5	18.4
MBAA	n.a.	n.a.	n.a.
DCAA	<MDL	n.a.	n.a.
TCAA	n.a.	n.a.	n.a.
BCAA	0.6	0.7	n.a.
BDCAA	n.a.	n.a.	n.a.
DBAA	n.a.	n.a.	n.a.
CDBAA	n.a.	n.a.	n.a.
TBAA	n.a.	n.a.	n.a.
AA_7	**0.6**	**0.3**	**0.3**

Note:

(1) The full scale filtered water was used as the feed water to the NF membranes (NF influent). To control biofouling, the NF influent was dosed with chloramines prior to the NF membranes. Samples of the NF influent water were collected before (pre-chloramination) and after (post-chloramination) the chloramine dosing location.

the pilot scale membranes. The use of chloramines in the NF feed to control biofouling was not shown to be an issue with respect to DBP formation.

6.0 CONCLUSIONS

The primary objective of the study was to examine selected potential treatment options for removal of trace organics. Pilot scale testing of selected treatment processes was conducted to evaluate the effectiveness of treatment processes at removing trace organic contaminants. The results of the pilot tests were used to compare the effectiveness of individual processes including ozone, perozone, BAF, and NF membranes. In addition, the

data allowed evaluation of the combined effectiveness of some of these processes, including ozone followed by BAF and perozone followed by BAF.

One of the secondary objectives included examining the overall performance of selected advanced treatment processes and the formation of DBPs. The formation of DBPs is an ongoing challenge for Delta utilities, and this study provided an opportunity to examine the formation of both conventional and emerging DBPs from existing treatment processes as well as other advanced treatment processes that may be implemented in the future. This secondary objective of the study involved examining the overall performance of selected treatment processes with respect to DBP formation. To meet this objective, the research plan included bench scale disinfection tests.

Another secondary objective of the study was to examine some of the operational issues associated with implementing NF membranes. Delta utilities considering implementation of nanofiltration were interested in understanding more about some of the operational challenges associated with this treatment technology. To meet this objective, the fouling potential, impacts of chloramines for the purpose of controlling biofouling, and power demands of the pilot scale NF membranes were investigated.

It is important to recognize that almost all of the target compounds tested at the pilot scale are currently not regulated. Many of the DBPs analyzed are also not currently regulated. The study provides a baseline understanding of the performance of existing processes and selected advanced processes for trace organics removal, and to a certain degree, formation of DBPs. It was not intended to be a thorough investigation of advanced treatment processes that would form the basis for future planning. Therefore, the information in this report should be considered a portion of the body of information that should be considered in any decision making processes related to the implementation of advanced treatment technologies.

Major conclusions of the study are:

Trace Organics Removal

- The Phase 1 pilot tests were designed to simulate existing treatment processes at CCWD and other Delta utilities. Almost all (8 out of 11) of the target compounds were well removed by ozonation (>90 percent) at an ozone dose similar to current practices at the Bollman WTP. The majority of the removal was attributed to the ozonation process. These results demonstrate the effectiveness of ozonation for trace organics removal, and suggest that at a dose similar to 1 mg/L, Delta utilities are already achieving very good removal of trace organics.

- The lowest removals by ozonation, ranging from 20 to 50 percent, were measured for ibuprofen, iopromide and atrazine, suggesting that these compounds are relatively ozone resistant. The BAF process contributed to improved removal of these three compounds. However, the removal achieved by the BAF pilot may be an

overprediction of the removal that would be achieved over the long term at a full-scale process.

- At lower ozone doses, there was evidence of dose dependence for three compounds, including bisphenol-A, atenolol, and caffeine. These results suggest that ozonation may not be as effective for trace organics removal at doses lower than 1 mg/L. These results have implications for Delta utilities that may modify ozone doses in response to changes in water quality.

- The Phase 2 pilot tests examined the effects of adding peroxide at an intermediate location within the ozone contactor. The perozone results generally matched the ozone results but this may be a result of the experimental conditions during testing, where it is suspected that there was not sufficient ozone residual to achieve advanced oxidation with the addition of peroxide. The low ozone residual under the 1 mg/L dosing condition at the point of peroxide addition suggests if Delta utilities wanted to practice advanced oxidation in this configuration, the ozone dose or the ozone contact time prior to peroxide addition would need to be adjusted.

- The Phase 3 pilot studies allowed evaluation of NF membranes, only, as the target compounds were spiked upstream of the NF membranes. NF membranes removed almost all target compounds at greater than 90 percent removal, including the ozone resistant compounds, ibuprofen, iopromide, and atrazine. The NF membranes were effective at removing all of the target compounds, including the relatively ozone resistant compounds. Greater than 80 percent removal of bisphenol-A and caffeine was achieved. These results demonstrate the effectiveness of NF membranes as a technology for trace organics removal.

DBP Formation

- Similar results for THMFP and HAAFP were observed for the Phase 1 and Phase 2 treatment trains. The existing ozonation followed by BAF process was shown to reduce THM_4FP and HAA_7FP through the reduction of DBP precursors.

- THM_4FP and HAA_7FP were lower in the NF permeate than in the BAF effluent. The performance of the NF membranes in reducing THM_4FP and HAA_7FP is attributed to the 78 percent reduction in TOC that was achieved by the NF membranes.

- Regardless of the treatment process train, THM formation and HAA formation were dominated by the more brominated species. THM formation was dominated by bromoform and HAA formation was dominated by DBAA. At a bromide concentration of approximately 0.4 mg/L, these results suggest the importance of bromide in the distribution of individual THMs and HAAs in the regulated summed values of THM_4 and HAA_5.

- As compared to the BAF effluent, the THMs formed in the NF permeate showed greater percentages of bromoform. This is likely due to the more efficient removal of TOC relative to bromide. This leads to a relatively increased bromide to TOC ratio, which results in relatively more bromoform formation (on a percentage basis).

- Regardless of the treatment process train, most nitrogenous DBPs were formed at less than the detection limit, and the nitrogenous DBPs that were formed, were formed at low concentrations, less than the California Public Health Goal of 3 ng/L.

Membrane Performance

- The NF membranes achieved good removal of organic carbon, organic nitrogen and SUVA, with removal efficiencies of 78 percent, 78 percent and 92 percent, respectively. These results illustrate the effectiveness of NF membranes for removing DBP precursors.

- The NF membranes achieved some bromide removal, which is important because the DBPs formed were dominated by brominated species.

- Based on analysis of water quality data, NF membrane fouling potential does not appear to be a major issue given the quality of the BAF effluent. However, the potential for biofouling warrants further investigation.

- The use of chloramines to control biofouling of the NF membranes did not contribute significantly to the formation of THMFP and HAAFP.

In general, the findings of this study contribute to the information on treatment technologies that are in the "toolbox" of technologies that Delta water purveyors may consider to address future regulations and changes in water quality. The information presented in this report should be used in conjunction with other information on treatment process performance, feasibility, costs, energy demands, etc, in the process of evaluating treatment processes for future use by Delta water purveyors.

7.0 FUTURE RESEARCH

The study findings provide a baseline understanding of the performance of existing processes and selected advanced processes for trace organics removal, DBP formation and some of the operational challenges associated with NF membranes. The study findings also provide a basis for identifying future research topics that Delta utilities may be interested in investigating. Potential future research topics include:

- Investigation of trace organics removal at ozone doses lower than 1 mg/L, in order to further evaluate and quantify the ozone dose dependence observed in this study. For Delta utilities that modify ozone doses in response to changes in source water quality

may be interested in understanding the effects of changing ozone dose on trace organics removal.

- Further investigation of the potential benefits of adding peroxide at an intermediate location in the ozone contactor. In Phase 2 of this study, it is not likely that advanced oxidation was achieved due to the low ozone dose at the location of peroxide addition. Delta utilities that may be interested using peroxide at an intermediate location, may be interested in further investigation of the parameters that affect advanced oxidation (ozone dose, contact time, and location of peroxide addition) and the potential benefits of advanced oxidation with respect to trace organics removal.

- Further investigation of optimizing the intermediate oxidation processes at Delta utilities for the purposes of achieving disinfection credit, oxidation of trace organics and minimizing DBP formation. This research could involve evaluation of ozone and perozone and the use of perozone followed by an ozone polishing step. The optimization study would need to evaluate these processes over a range of source water quality conditions.

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APPENDIX A – PILOT TESTING QUALITY CONTROL

Appendix A - Pilot Testing Quality Control

Sample Handling and Shipping

For all samples sent to the University of Colorado, Trent University, and MWH labs, appropriate shipping and handling procedures were followed.

Following sample collection, all sample bottles were immediately placed in coolers containing frozen ice bricks. Sufficient packing material and bubble wrap were included in each cooler to prevent the glass sample containers from breaking during shipment. Each shipment of coolers was accompanied by a chain-of-custody form. These forms included sample identification numbers, date and time of collection, name and signature of the sampler, and the analysis to be conducted on each sample. The samples were shipped overnight to the appropriate laboratory. Upon receipt of the samples, the integrity of the sample containers was assessed. The chain of custody forms would then be completed with the date and time sample was received, name and signature of the individual who received the sample, and any remarks on the status of samples will be reported. Upon receipt, the samples were stored at 4 degrees Celcius in darkness or processed immediately.

Calibration of Dosing Pumps

The peristaltic pumps that were used for dosing specific chemical solutions into the system were calibrated to specific flow rates prior to dosing initiation. The flow rates were set, and then reconfirmed, through a series of at least three volumetric displacement tests. These tests consist of using a known volume of liquid as the dosing source, and measuring the decrease in volume over a set time period. Typically these dosing rates were measured in milliliters per minute.

Flushing the sampling ports

At each sample port, prior to filling the initial sample bottle, at least one liter of water was allowed to leave the port uncollected to ensure that each sample port was flushed with the desired sample water. Additionally, if a sample port was left closed for a duration of approximately one minute or more, it was subsequently re-flushed prior to taking further samples.

Sample collection

Special consideration was taken in filling each different set of sample bottles. If no preservative was included in the bottle, such as with the samples collected for in-house testing at the CCWD laboratory, the bottle could be rinsed with the sample water prior to completely filling the bottle.

Other considerations included filling the sample bottles by allowing water to run down the inside wall of the bottle, thereby decreasing the turbulence and the resulting aeration of the sample.

Most importantly, special consideration was taken to ensure that sample bottles containing pre-measured preservative were not overfilled, which would have resulted in loss of preservative.

Field Blanks

Field blank samples were collected during each of the sampling events and sent to Trent University for EDC analytical testing. Seven bottles, each 1 L in volume, were filled with de-ionized (DI) water, which was provided by the CCWD analytical laboratories. The de-ionized water was preserved with 1 g/L of sodium azide. Each of these 7 field blanks were exposed to atmospheric conditions, within relatively proximity of the sampling ports, for the duration of filling a 1 L sample bottle.

Duplicate Samples

A duplicate sample was collected from each sampling port for each sampling event. Three 2.36 litre samples, each preserved with 1 g/L sodium azide, was collected at each sample port and stored at the CCWD facility under refrigerated conditions (< 4°C). These samples were collected as back up samples, should some of the 1 L sample bottles being shipped to Trent University break during transit.

Detection Limits

The analytical capabilities at Trent University are limited at a measure of detection of 10ng/L. This detection limit value was used as the assumed value where any non-detect measurements were reported (i.e. the actual measured value was less than the detection limit).

Nanofiltration Mass Balances

A mass balance on the NF results was performed as a check. In units of g/day the influent and effluent mass flowrates of each compound are displayed in Figure A.1 and Figure A.2 for weeks A and B respectively. Generally, the mass flows of each compound in and out of the system are similar, although not always exactly the same. One mechanism which might account for lower flow rates leaving the system is adsorption of compounds onto the membrane filters.

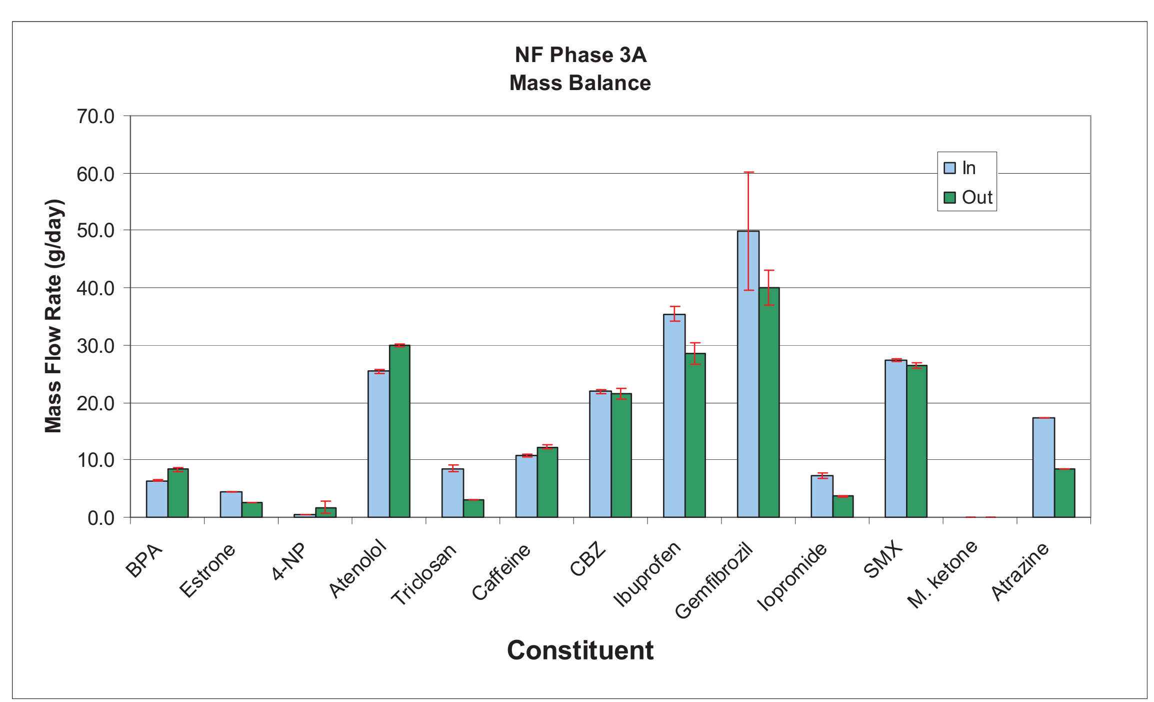

Figure A.1. Nanofiltration Mass Balance for Phase 3 – Week A

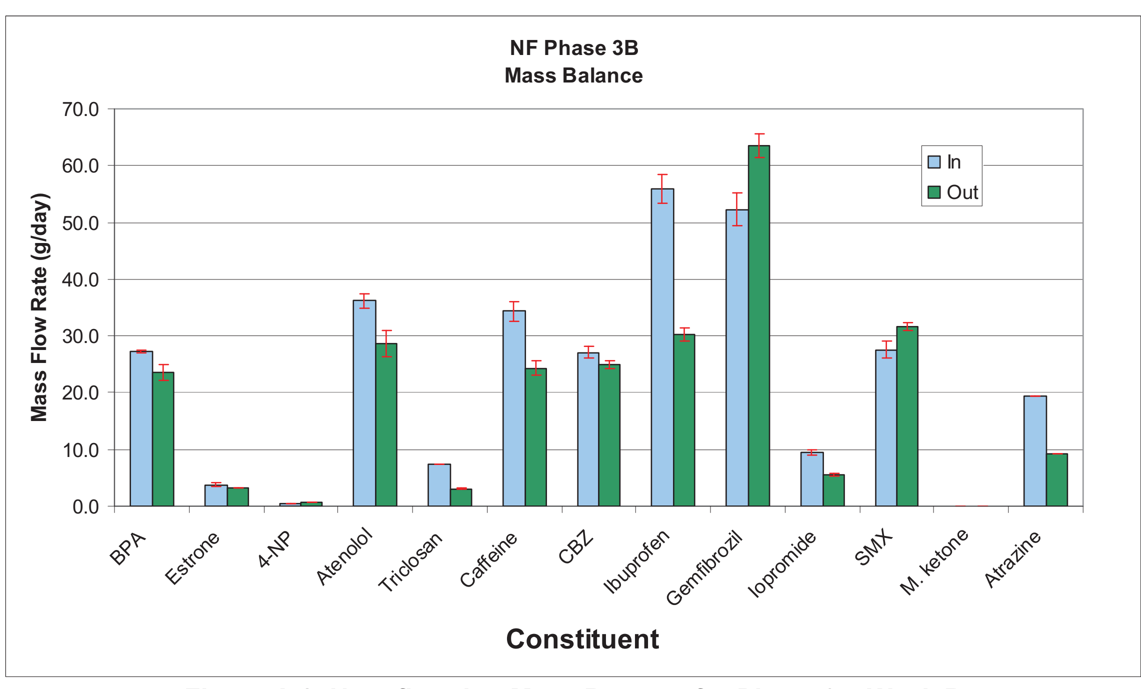

Figure A.2. Nanofiltration Mass Balance for Phase 3 – Week B

APPENDIX B – PILOT SYSTEM SAMPLING LOCATIONS

APPENDIX B: PILOT SYSTEM SAMPLING LOCATIONS

Table 1. Sampling Locations and Analytical Tests for Phase 1			
	Sampling Location		
Parameter	**1**	**2**	**3a**
Conventional Parameters			
Temperature	X	X	
pH	X	X	
Turbidity	X	X	X
TOC	X	X	X
UV	X	X	X
Specific Conductance	X		X
Bromide	X		X
Chloride	X		X
Alkalinity	X		X
Hardness	X		X
Ozone		X	
Organic Nitrogen			X
Heterotrophic Plate Counts		X	X
Membrane Fouling/Performance			
TSS			
Calcium			
Magnesium			
Sodium			
Potassium			
Ammonia			X
Barium			
Strontinum			
Nitrate			X
Fluoride			
Phosphate			
Silica			
Boron			
Manganese (T&D)			
Iron (T&D)			
Aluminum			

Table 1. Sampling Locations and Analytical Tests for Phase 1

	Sampling Location		
Parameter	**1**	**2**	**3a**
Sulfate			
DBPs			
Bromate and iodate	X	X	X
THM4 and iodinated THMs[1]			X
HAA9 and Iodoacids[1]			X
Haloketones[1]			X
Oxyhalides[1]			X
Total Organic Halides (and speciation)[1]			X
NDMA and other nitrosamines[1]	X	X	X
EDCs, PPCPs, Industrial Chemicals			
Target Compounds	X	X	X

Notes:

(1) Samples from site 3a were collected and sent to Duke University and University of Toronto for bench scale DBP testing. Analyses for these compounds were conducted post-disinfection at the bench scale.

Table 2. Sampling Locations and Analytical Tests for Phase 2			
	Sampling Location		
Parameter	**1**	**2**	**3a**
Conventional			
Temperature	X	X	
pH	X	X	
Turbidity	X	X	X
TOC	X	X	X
UV	X	X	X
Specific Conductance	X		X
Alkalinity	X		X
Hardness	X		X
Bromide	X		X
Chloride	X		X
Ozone		X	
Organic Nitrogen			X
Heterotrophic Plate Counts		X	X
Membrane Fouling/Performance			
TSS			
Calcium			
Magnesium			
Sodium			
Potassium			
Ammonia			X
Barium			
Strontinum			
Nitrate			X
Fluoride			
Phosphate			
Silica			
Boron			
Manganese (T&D)			
Iron (T&D)			
Aluminum			
Sulfate			
DBPs			
Bromate and iodate	X	X	X

Table 2. Sampling Locations and Analytical Tests for Phase 2			
	Sampling Location		
Parameter	**1**	**2**	**3a**
THM4 and iodinated THMs[1]			X
HAA9 and Iodoacids[1]			X
Haloketones[1]			X
Oxyhalides[1]			X
Total Organic Halides (and speciation)[1]			X
NDMA and other nitrosamines[1]	X	X	X
EDCs, PPCPs, Industrial Chemicals			
Target Compounds	X	X	X

Notes:

(1) Samples from site 3a were collected and sent to Duke University and University of Toronto for bench scale DBP testing. Analyses for these compounds were conducted post-disinfection at the bench scale.

Table 3. Sampling Locations and Analytical Tests for Phase 3			
	Sampling Location		
Parameter	**3b**	**4**	**5**
Conventional			
Temperature	X		
pH	X		
Turbidity	X		
TOC	X	X	
UV	X	X	
Specific Conductance	X	X	X
Alkalinity	X	X	X
Hardness	X	X	X
Bromide	X	X	X
Chloride	X	X	X
Ozone			
Organic Nitrogen	X	X	
Heterotrophic Plate Counts	X		
Membrane Fouling/Performance			
TSS	X	X	X
Calcium	X	X	X
Magnesium	X	X	X
Sodium	X	X	X
Potassium	X	X	X
Ammonia	X	X	X
Barium	X	X	X
Strontinum	X	X	X
Nitrate	X	X	X
Fluoride	X	X	X
Phosphate	X	X	X
Silica	X	X	X
Boron	X	X	X
Manganese (T&D)	X	X	X
Iron (T&D)	X	X	X
Aluminum	X	X	X
Sulfate	X	X	X
DBPs			
Bromate and iodate			
THM4 and iodinated THMs[1]	X	X	

Table 3. Sampling Locations and Analytical Tests for Phase 3			
	Sampling Location		
Parameter	**3b**	**4**	**5**
HAA9 and Iodoacids[1]	X	X	
Haloketones[1]	X	X	
Oxyhalides[1]	X	X	
Total Organic Halides (and speciation)[1]	X	X	
NDMA and other nitrosamines[1]	X	X	
EDCs, PPCPs, Industrial Chemicals			
Target Compounds	X	X	X

Notes:

(1) Samples from site 3b and 4 were collected and sent to Duke University and University of Toronto for bench scale DBP testing. Analyses for these compounds were conducted post-disinfection at the bench scale.

APPENDIX C – ANALYTICAL METHODS USED BY TRENT UNIVERSITY

APPENDIX C– ANALYTICAL METHODS USED BYTRENT UNIVERSITY

The protocols used for the analysis of each class of compounds are provided below.

A1. Acidic Pharmaceuticals

Water or wastewater samples are spiked with stable isotope surrogates and then extracted using the SPE procedures described in the SOP (below). The extracts are evaporated using the Savant apparatus to almost dryness and reconstituted in 50:50 methanol/water to a volume of 0.5 mL.

A series of acidic drug standards was prepared with different concentrations of gemfibrozil, ibuprofen, and fixed concentrations (50 ng/mL), of ibuprofen (propionic) $^{13}C_3$, gemfibrozil-D6, as internal standards. A linear calibration curve was developed from the drug standards. The acidic pharmaceuticals were analyzed by Micromass Quattro LC triple-quadrupole mass spectrometer fitted with a Z-spray electrospray interface. Instrument control, data acquisition and processing were performed using Masslynx 3.4 software. The target compounds were analyzed in negative ion mode with the capillary voltage at 3.0 kV. Multiple reaction monitoring was employed for analyte quantitation (Table 1). The collision-induced dissociation (CID) was carried out using 8.0×10^{-4} mbar of UHP argon as collision gas. The source temperature was 80°C and the desolvation temperature was 300°C. Nitrogen was used as both the nebulizing and the desolvation gas at flow rates of 50 and 500 Lh^{-1}, respectively. The cone voltage and collision energy were optimized for each individual analyte (Table 1). A dwell time of 200 ms per ion pair was used and the inter-channel delay was 0.01 s.

Chromatographic separation was conducted on a Waters model 2690 HPLC system with a Genesis C18 column (150 × 2.1 mm i.d., 4μm) at a flow rate of 0.2 mL/min. The mobile phase A and B consisted of 40:60 acetonitrile-methanol and 20 mM aqueous ammonium acetate, respectively, which were degassed by an in-line vacuum degasser. The applied gradient elution was as follows: mobile phase A was increase from 40% to 98% within 8 min, held at 98% for 7 min and then decreased to 40% over 2 min. The column was kept at room temperature and the injection volume was 25 μL.

Table A1: Analytical conditions for acidic drugs.

Compound	MRM transition (precursor> product)	Retention time (min)	Collision energy (eV)	Cone voltage (V)	Internal standard
Gemfibrozil	249 > 121	10.72	12	30	Gemfibrozil-D6
Ibuprofen	205 > 161	8.73	7	22	Ibuprofen -^{13}C3
Iopromide	790 > 127	2.02	12	40	Ibuprofen -^{13}C3

Compound	MRM transition (precursor> product)	Retention time (min)	Collision energy (eV)	Cone voltage (V)	Internal standard
Gemfibrozil-D6	255 > 121	10.72	12	30	
Ibuprofen -^{13}C3	208 > 163	8.73	7	22	

Standard Operating Procedures for Extraction of Acidic Drugs

Sample Preparation

1. Vacuum filter an appropriate volume of aqueous sample (e.g. wastewater, surface water) through a 1.5µm glass-fiber filter.
2. Pour filtered sample into glass container. If there are 3 replicates, prepare 3 separate aliquots.
3. Acidify samples to pH=2.0 by adding 3.5M H_2SO_4.
4. Spike the samples with surrogate standards (Table 1) and mix.
5. The water samples are now ready to be extracted by SPE, but the SPE cartridges must first be pre-conditioned.
6. Clean all equipment before extracting a different sample.

SPE Cartridge Pre-conditioning

1. Place the cartridges on top of the SPE manifold and begin to condition each of them sequentially with 6 mL acetone, 6 mL methanol, and 6 mL HPLC grade water adjusted to pH 2.0 with 3.5 M H_2SO_4. DO NOT LET THE CARTRIDGES GO DRY.
2. Once conditioned, the samples can be passed through the cartridges.

Extraction

1. The Teflon tubes that connect the samples to the SPE manifold must first be cleaned with Methanol, and then rinsed with HPLC water.
2. Attach one clean tube to each of the cartridges, and then place the other end in one of the samples. Clearly label all of the cartridges.
3. The water samples should be passed through the SPE cartridges at a rate of approximately 10 mL/min.
4. Rinse each of the sample bottles with approx. 10 mL of pH=2.0 distilled water and pass the rinsings through the cartridge.
5. At this point, ensure the solid phase material is kept wet by trapping the last rinse in the cartridge. Once all samples have passed through, let the cartridges go dry for a one minute in order to remove unwanted water.
6. The Teflon tubing should be quickly removed. Wash procedure: first wash cartridges with 3 mL 1% formic acid aqueous solution then 3 mL of 1% ammonium hydroxide aqueous solution

7. A 15mL collection tube should be placed under the sample in order to collect the eluate. Small Teflon “Guides” must be placed under the top of the manifold, so the samples are properly guided into the 15 mL collection tube.
8. IMMEDIATELY wet the cartridges with approx. 3 mL of 2% ammonium hydroxide in methanol. Let stand for 10 minutes and then slowly drain into the 15 mL collection tubes. Repeat twice, first with 2% ammonium hydroxide in methanol and then with pure methanol, letting each 3 mL aliquot stand in the cartridge for 10 minutes. A total of approx. 9mL of methanol is used to elute the samples.

A2. Neutral Pharmaceuticals

Water or wastewater samples are spiked with stable isotope surrogates and extracted using SPE procedures described in the SOP (below). The extracts are evaporated using the Savant apparatus to almost dryness and reconstituted in 50:50 methanol/water to a volume of 0.5 mL.

A series of neutral drugs are prepared with different concentrations of caffeine, cotinine, carbamazepine and fluoxetine, together with fixed concentrations of caffeine-^{13}C3 (50 µg/L), cotinine-D3 (50 µg/L), carbamazepine-D10 (50 µg/L) and trimethoprim-D5 (50 µg/L) as internal standards. A linear calibration curve is developed from the drug standards. The neutral pharmaceuticals are analyzed by the LC-MS/MS system consisting of the Agilent 1100 series binary pump and autosampler and QTrap mass spectrometer (MDS SCIEX, Toronto) equipped with APCI source operated by Analyst 1.4. Using Analyst 1.4, multiple reaction monitoring (MRM) with unit resolution on both of the first and second analyzer is selected for data acquisition in the positive-ion mode and nitrogen was used as curtain, nebulizer, auxiliary and collision gas. The mass spectrometric parameters are optimized as follows: curtain gas 20 psi, nebulizer gas 70 psi, auxiliary gas 15 psi, corona discharge needle current 2.0 µA, probe temperature 470°C, interface heater on, CAD gas 5. Collision energy and declustering potential are determined for each compound separately. The dwell time for each MRM transition is set at 200 ms.

Chromatographic separation is conducted on a Genesis C18 (150 × 3 mm, 4µm) column at the flow rate of 0.5 mL/min. The mobile phases consisted of 10mM ammonium acetate aqueous solution (A) and acetonitrile (B). The target analytes are separated using the following linear gradient elution profile at room temperature: mobile phase B was increased from the initial 5% to 20% over 4 min and reached 95% at 12 min; it remains at 95% for the next 3 min and then ramped back to 5% within 2 min. The column is kept at room temperature and the injection volume is 20 µL.

Table A2: Analytical conditions for neutral pharmaceuticals.

Compound	MRM transition (precursor>product)	Retention Time (min)	Declustering Potential (V)	Collision Energy (eV)
Caffeine	195 > 138	7.43	47	25
Carbamazepine	237 > 194	10.88	40	28
Cotinine	177 > 80	7.06	40	40
Trimethoprim	310 > 148	12.60	15	17
Caffeine-$^{13}C3$	198 > 140	7.42	47	25
Carbamazepine-D10	247 > 204	10.86	25	30
Cotinine-D3	180 > 80	7.08	40	40
Trimethoprim-D5	315 > 44	12.60	15	17

Standard Operating Procedures for Extraction of Neutral Drugs

Sample Preparation

1. Vacuum filter an appropriate volume of aqueous sample (e.g. wastewater, surface water) through a 1.5μm glass-fiber filter.
2. Pour filtered sample into glass container. If there are 3 replicates, prepare 3 separate aliquots.
3. Adjust pH of all samples to pH=7.5 by adding 1.0 M NaOH.
4. Spike the samples with surrogate standards (Table 1) and mix.
5. The water samples are now ready to be extracted by SPE, but the SPE cartridges must first be pre-conditioned.
6. Clean all equipment before extracting a different sample.

SPE Cartridge Pre-conditioning

7. Place the cartridges on top of the SPE manifold and begin to condition each of them sequentially with 6 mL acetone, 6 mL methanol, and 6 mL HPLC grade water adjusted to pH 7.5. DO NOT LET THE CARTRIDGES GO DRY.
8. Once conditioned, the samples can be passed through the cartridges.

Extraction

9. The Teflon tubes that connect the samples to the SPE manifold must first be cleaned with Methanol, and then rinsed with HPLC water.
10. Attach one clean tube to each of the cartridges, and then place the other end in one of the samples. Clearly label all of the cartridges.
11. The water samples should be passed through the SPE cartridges at a rate of approximately 10 mL/min.

12. Rinse each of the sample bottles with approx. approx. 10mL of pH=7.5 distilled water and pass the rinsings through the cartridge.
13. At this point, ensure the solid phase material is kept wet by trapping the last rinse in the cartridge. Once all samples have passed through, let the cartridges go dry for a one minute in order to remove unwanted water.
14. The Teflon tubing should be quickly removed and a 15mL collection tube should be placed under the sample in order to collect the eluate. Small Teflon "Guides" must be placed under the top of the manifold, so the samples are properly guided into the 15 mL collection tube.
15. IMMEDIATELY wet the cartridges with approx. 3 mL of methanol. Let stand for 10 minutes and then slowly drain into the 15 mL collection tubes. Repeat twice, letting each 3 mL aliquot of methanol stand in the cartridge for 10 minutes. A total of approx. 9mL of methanol is used to elute the samples.

A3. Sulfonamide Antibiotics

Water or wastewater samples are spiked with stable isotope surrogates and extracted using the SPE procedures described in the SOP (below). The extracts are evaporated using the Savant apparatus to almost dryness and reconstituted in 40:60 methanol/water to a volume of 0.5mL.

A series of standards are prepared with different concentrations of sulfamethoxazole and sulfapyridine as well as a fixed concentration of sulfamethoxazole-13C6 (50 µg/L) and sulfamethazine-13C6 (50 µg/L) as internal standards. A linear calibration curve is developed from the drug standards. The sulfonamide antibiotics with an LC-MS/MS system consisting of the Agilent 1100 series binary pumps and autosampler and QTrap mass spectrometer (MDS SCIEX, Toronto) equipped with APCI source operated by Analyst 1.4. Using Analyst 1.4, multiple reaction monitoring (MRM) with unit resolution on both of the first and second analyzer is selected for data acquisition in the positive-ion mode and nitrogen was used as curtain, nebulizer, auxiliary and collision gas. The mass spectrometric parameters are optimized as follows: curtain gas 15 psi, nebulizer gas 70 psi, auxiliary gas 15 psi, corona discharge needle current 2.0 µA, probe temperature 460°C, interface heater on, CAD gas 5. Collision energy and declustering potential are determined for each compound separately. The dwell time for each MRM transition is set at 200 ms.

Chromatographic separation is conducted on a Genesis C18 (150 × 3 mm, 4µm) column at the flow rate of 0.5 mL/min. The mobile phases consisted of 0.1% formic acid aqueous solution (A) and acetonitrile (B), respectively. Sulfonamides are separated using the following linear gradient elution profile at room temperature: the mobile phase B was initially held at 3% for 0.5 min, increased to 24% at 1 min, then further increased to 43% at 10 min and held at 43% for 2 min. Iit reaches 95% at 13 min and is held for 3

min. Afterwards, B is ramped back to 3% at 17 min. The column is kept at room temperature and the injection volume is 20 μL.

Table A3: Analytical conditions for sulfonamide anitbiotics.

Compound	MRM Transition	Retention Time (min)	Declustering Potential (V)	Collision Energy (eV)
Sulfapyridine	250 > 156	5.80	30	20
Sulfamethoxazole	254 > 156	8.65	30	20
Sulfamethoxazole-$^{13}C_6$	260 > 162	8.64	30	20
Sulfamethazine-13C6	285 > 186	8.25	30	20

Standard Operating Procedures for Extraction of Sulphonamide Antibiotics

Sample Preparation

1. Vacuum filter an appropriate volume of aqueous sample (e.g. wastewater, surface water) through a 1.5μm glass-fiber filter.

2. Pour filtered sample into glass container. If there are 3 replicates, prepare 3 separate aliquots.

3. Adjust all 7 samples to pH=3.0 by adding 3.5M H_2SO_4.

4. Add Na_2EDTA to samples (1 g per L). Mix until completely dissolved.

5. Spike the samples with surrogate standards (Table 1) and mix.

6. The water samples are now ready to be extracted by SPE, but the SPE cartridges must first be pre-conditioned.

7. Clean all equipment before extracting a different sample.

SPE Cartridge Pre-conditioning

8. Place the cartridges on top of the SPE manifold and begin to condition each of them sequentially with 6 mL acetone, 6 mL methanol, and 6 mL 50mM Na_2EDTA aqueous solution (pH 4.0) (Note: at pH 3.0, Na2EDTA precipitates). Let Na_2EDTA aqueous solution stay in the cartridge for at least 1 hr and replace it with new Na_2EDTA aqueous solution every 15 min. DO NOT LET THE CARTRIDGES GO DRY.

9. Once conditioned, the samples can be passed through the cartridges.

Extraction

10. The Teflon tubes that connect the samples to the SPE manifold must first be cleaned with Methanol, and then rinsed with HPLC water.

11. Attach one clean tube to each of the cartridges, and then place the other end in one of the samples. Clearly label all of the cartridges.

12. The water samples should be passed through the SPE cartridges at a rate of approximately 5 mL/min.

13. Rinse each of the sample bottles with approx. 10mL of pH=3.0 distilled water and pass the rinsings through the cartridge.

14. At this point, ensure the solid phase material is kept wet by trapping the last rinse in the cartridge. Once all samples have passed through, let the cartridges go dry for a one minute in order to remove unwanted water.

15. The Teflon tubing should be quickly removed and a 15mL collection tube should be placed under the sample in order to collect the eluate. Small Teflon "Guides" must be placed under the top of the manifold, so the samples are properly guided into the 15 mL collection tube.

16. IMMEDIATELY wet the cartridges with approx. 3 mL of methanol. Let stand for 10 minutes and then slowly drain into the 15 mL collection tubes. Repeat twice, first with pure methanol and then with 2% ammonium hydroxide in methanol, letting each 3 mL aliquot stand in the cartridge for 10 minutes. A total of approx. 9mL of methanol is used to elute the samples.

A4. Triclosan

Water or wastewater samples are spiked with a stable isotope surrogate and then extracted using the SPE procedure described in the SOP (below). The extracts are evaporated using the Savant apparatus to almost dryness and reconstituted in 50:50 methanol/water to a volume of 0.5 mL.

A series of standards are prepared with different concentrations of native compound and a fixed concentration (50 ng/mL) of the surrogate, triclosan-$^{13}C_{12.}$ A linear calibration curve is developed from the drug standards. The surrogate standard is added to sample extracts and blank samples. The LC-MS analysis in selected ion mode (SIM) is performed on a Micromass Quattro LC triple-quadrupole mass spectrometer fitted with a Z-spray electrospray interface. Instrument control, data acquisition and processing are performed using Masslynx 3.4 software. Triclosan is eluted on a Waters model 2690 HPLC system with a Genesis C18 column (150 × 2.1 mm i.d., 4μm) at a flow rate of 0.2 mL/min. The mobile phase A and B consists of acetonitrile and water, respectively, which were degassed by an in-line vacuum degasser. The applied gradient elution is as follows: mobile phase A is increased from 55% to 98% within 3 min, held at 98% for 7 min and then decreased to 55% over 2 min. The column is kept at room temperature and the injection volume is 25 μL. Selected ion monitoring (SIM) in the negative-ion

mode is employed to analyze triclosan, which in this case is the deprotonated molecular ion. The source temperature is 100°C and the desolvation temperature is 300°C, and nitrogen is used as both nebulizer and desolvation gas at flow rate of 70 and 500 Lh^{-1}, respectively. The cone voltage is kept at 20 V, a dwell time of 200 ms is used and the inter-channel delay was 0.01 s.

Table A4: Analytical conditions for Trisclosan.

Compound	SIM	Retention Time (min)
Triclosan	287	8.82
Triclosan-$^{13}C_{12}$	299	8.82

Standard Operating Procedure for Extraction of Triclosan

Sample Preparation

1. Vacuum filter an appropriate volume of aqueous sample (e.g. wastewater, surface water) through a 1.5μm glass-fiber filter.
2. Pour filtered sample into glass container. If there are 3 replicates, prepare 3 separate aliquots.
3. Adjust all samples to pH=6.0 by adding 3.5M H_2SO_4.
4. Spike the samples with surrogate standard (Table 1) and mix.
5. The water samples are now ready to be extracted by SPE, but the SPE cartridges must first be pre-conditioned.
6. Clean all equipment before extracting a different sample.

SPE Cartridge Pre-conditioning

7. Place the cartridges on top of the SPE manifold and begin to condition each of them sequentially with 6 mL EtOAc-acetone (50:50), 6 mL methanol, and 6 mL HPLC grade water adjusted to pH=6.0. DO NOT LET THE CARTRIDGES GO DRY.
8. Once conditioned, the samples can be passed through the cartridges.

Extraction

9. The Teflon tubes that connect the samples to the SPE manifold must first be cleaned with Methanol, and then rinsed with HPLC water.
10. Attach one clean tube to each of the cartridges, and then place the other end in one of the samples. Clearly label all of the cartridges.
11. The water samples should be passed through the SPE cartridges at a rate of approximately 5 mL/min.

12. Rinse each of the sample bottles with approx. approx. 10 mL of pH=6.0 distilled water and pass the rinsings through the cartridge.
13. At this point, ensure the solid phase material is kept wet by trapping the last rinse in the cartridge. Once all samples have passed through, let the cartridges go dry for a one minute in order to remove unwanted water.
14. The Teflon tubing should be quickly removed. Wash procedure: first with 3 mL of 10:90 water-methanol and then 5 mL of 1% ammounium hydroxide aqueous solution.
15. A 15mL collection tube should be placed under the sample in order to collect the eluate. Small Teflon "Guides" must be placed under the top of the manifold, so the samples are properly guided into the 15 mL collection tube.
16. IMMEDIATELY wet the cartridges with approx. 2 mL of EtOAc-acetone (50:50). Let stand for 10 minutes and then slowly drain into the 15mL collection tube. Repeat twice, letting each 2 mL aliquot of EtOAc-acetone (50:50) stand in the cartridge for 10 minutes. A total of approx. 6mL of EtOAc-acetone (50:50) is used to elute the samples.

A5. Synthetic musks

Water or wastewater samples are spiked with two stable isotope surrogates (AHTN-D3; musk xylene-D15) and then extracted using the procedures described in the SOP (below). The extracts are evaporated to almost dryness and reconstituted in ethyl acetate to a volume of 0.5 mL.

A series of musk standards are prepared with different concentrations of the analytes (Table A5) and fixed concentrations (50 ng/mL), of AHTN-D3 and musk xylene-D15) as internal standards in ethyl acetate. A linear four point calibration curve is developed from the drug standards. Musks are analyzed by GC-MS using a Varian 3800 GC, equipped with a Varian 1079 injector, a Varian 8410 autosampler, and a Varian Saturn 2200 ion trap mass spectrometer (Palo Alto, CA, USA) operated in Selected Ion Storage (SIS) mode. Separation is achieved on a 30m Varian FactorFour™ (VF-5ms) capillary column (0.25mm i.d., 0.25µm film). Helium is used as a carrier gas. The temperature program is 50 ºC, hold for 1.5 min, 10 ºC/min to 150 ºC, 2 ºC/min to 190 ºC, 25 ºC/min to 290 ºC and hold for 10 min. The injector temperature is set at 275 ºC. Injection (2 µL) is performed in the split/splitless mode using a splitless time of 0.75 min with constant column flow of 1.0 mL/min. The capillary column is coupled directly to the ion source which is operated in electron impact (EI) ionization mode. The transfer line and ion trap temperature are 250 ºC and 200 ºC, respectively. For SIS mode operation, the axial modulation voltage was 4.0 volts.

In order to increase detection sensitivity and selectivity, the total analysis time was divided into 8 acquisition segments. Table 1 lists the GC/MS-SIS parameters used for quantitation using an external standard. In all cases, 3 ions with high intensity are

selected for monitoring, and both retention time and ion ratios are used for identification (Table A5). Peak areas are used for quantification.

Table A5: Analytical conditions for GC-MS-SIS analysis of synthetic musks.

Segment[a]	Start, min	End, min	Analyte	Retention time,[b] min	Quan Ions	Ion ratios,[b]%
1	0.00	14.0	Solvent Delay			
2	14.0	19.0	DPMI	14.79	191, 135, 163	28.3 28.0
3	19.0	21.1	ADBI	20.19	229, 173, 244	20.7 18.2
4	21.1	23.5	AHDI	21.48	229, 187, 230	22.2 18.2
5	23.5	25.4	MUSK AMBRETTE	24.07	253, 251, 254	26.9 12.6
			ATII	24.60	215, 173, 216	34.8 18.6
			HHCB	24.67	243, 213, 244	42.0 19.3
			MUSK XYLENE	24.98	282, 265, 251	20.8 30.2
			AHTN	25.06	243, 187, 244	33.4 21.1
6	25.4	27.0	MUSK MOSKENE	25.92	263, 264, 261	14.8 10.3
7	27.0	28.5	MUSK TIBETENE	27.71	251, 252, 234	13.9 2.6
8	28.5	31.4	MUSK KETONE	29.48	279, 294, 191	15.4 10.4

[a] The total acquisition time (31.4 min.) is divided into 8 segments.
[b] Both retention time and ion ratios are used for identification.
[c] An external standard calibration method is used for quantification.

Standard Operating Procedures for Extraction of Synthetic Musks

Sample Preparation

1. Vacuum filter an appropriate volume of aqueous sample (e.g. wastewater, surface water) through a 1.5μm glass-fiber filter.
2. Pour filtered sample into glass container. If there are 3 replicates, prepare 3 separate aliquots.
3. Spike the samples with surrogate standards (Table 1) and mix.
4. Extract by liquid-liquid partitioning into 100 mL hexane in a 2 L separatory funnel. Repeat two more times and combine the extract.
5. Dry the combined extract by filtering through sodium sulfate (solvent washed) packed into a Buchner funnel with a glass wool plug.
6. Concentrate the extract using a rotary evaporator to ~ 2 mL for clean up by gel permeation chromatography.

Gel-Permeation Chromatography (GPC)

1. To clean-up the extracts, a GPC column is prepared with Bio-Beads S-X (Bio-Rad Laboratories, CA, USA).
2. Load the extract onto the GPC column, followed by hexane rinses. Do not let the column go dry.
3. Elute the column with a mobile phase of hexane and ethyl acetate (1:1, V/V) at an elution rate of 3-4 mL/min.
4. Collect two fractions: Fraction A (75 mL) and Fraction B (75 mL).
5. Discard Fraction A and save Fraction B for further silica gel cleanup.

Silica-gel Cleanup

1. Pack 5 g of silica gel (60-200 mesh, hexane washed and activated at 200 °C) into a glass chromatographic column (300 mm long x 10 mm ID, with glass wool at the bottom and a PTFE stopcock). Top the column with 2 g sodium sulfate (granular, anhydrous).
2. Pre-wet the column with hexane, and then load the sample on top of the silica gel column, followed by rinses. Do not let the column go dry.
3. Elute the column with a volume of 60 mL ethyl acetate, followed by 50 mL acetone.
4. Combine the eluate and concentrate to a final volume of 0.5 mL of ethyl acetate using a rotary evaporator and Savant vacuum system.

A6. Estrogens

Water or wastewater samples are spiked with stable isotope surrogates and then extracted using the SPE procedures described in the SOP (below). The phenolic fraction is evaporated using the Savant apparatus to almost dryness and reconstituted in 50:50 methanol/water to a volume of 0.5 mL.

A series of acidic drug standards are prepared with different concentrations of estradiol, ethinylestradiol, estrone, bisphenol A, and 4-n-nonylphenol, and fixed concentrations of ethinylestradiol $^{13}C_2$, estradiol $^{13}C_2$, bisphenol A $^{13}C_2$ and 4-n-nonylphenol-d4 as internal standards. A linear calibration curve is developed from the drug standards.

The phenolic estrogens (except for nonylphenol) are analyzed by LC-MS/MS using a Micromass Quattro LC triple-quadrupole mass spectrometer fitted with a Z-spray electrospray interface. Instrument control, data acquisition and processing are performed using Masslynx 3.4 software. The target compounds are analyzed in negative ion mode with the capillary voltage at 3.0 kV. Multiple reaction monitoring was employed for analyte quantitation (Table 1). The collision-induced dissociation (CID) was carried out using 3.0×10^{-4} mbar of UHP argon as collision gas. The source temperature was 80°C and the desolvation temperature was 300°C. Nitrogen was used as both the nebulizing and the desolvation gas at flow rates of 70 and 600 Lh^{-1}, respectively. The transitions monitored, cone voltages and collision energies were optimized for each individual analyte (Table A6). A dwell time of 200 ms per ion pair was used and the inter-channel delay was 0.01 s.

Chromatographic separation is conducted on a Waters model 2690 HPLC system with a Genesis C18 column (150 × 2.1 mm i.d., 4μm) at a flow rate of 0.2 mL/min. The mobile phase B and D consist of 40:60 water and methanol respectively, which are degassed by an in-line vacuum degasser. The applied gradient elution was as follows: mobile phase D was increased from 60% to 100% within 5 min, held at 100% for 10 min and then decreased to 60% over 2 min and left to re-equilibrate. The total run time is 30 minutes. The column is kept at room temperature and the injection volume was 20 μL.

4-n-nonylphenol was analyzed by LC-MS/MS using an Agilent 1100 series binary pump and autosampler and QTrap mass spectrometer (MDS SCIEX, Toronto) equipped with APCI source operated by Analyst 1.4 software. Using Analyst 1.4, multiple reaction monitoring (MRM) with unit resolution on both of the first and second analyzer is selected for data acquisition in the positive-ion mode and nitrogen was used as curtain, nebulizer, auxiliary and collision gas. The mass spectrometric parameters are optimized as follows: curtain gas 20 psi, nebulizer gas 70 psi, auxiliary gas 15 psi, corona discharge needle current 2.0 μA, probe temperature 470°C, interface heater on, CAD gas 5. The transitions monitored, collision energies and declustering potentials are optimized for each analyte. The dwell time for each MRM transition is set at 500 ms.

Chromatographic separation is conducted on a Genesis C18 (150 × 2.1 mm i.d., 4μm) at a flow rate of 0.2 mL/min. The mobile phases consisted of water (A) and methanol (B). The target analytes are separated using the following linear gradient elution profile at room temperature: mobile phase B is increased from the initial 20% to 100% over 5 min, and it remained at 100 % for the next 17 min and then ramped back to 20% within 2 min,

and left at 20% for re-equilibration. The total runtime is 34 minutes. The column is kept at room temperature and the injection volume was 20 µL.

Table A6: Analytical conditions for phenolic estrogens

Compound	MRM transition (precursor> product)	Retention time (min)	Collision energy (eV)	Cone voltage (V)
Bisphenol A	226.8 > 211.9	7.40	18	40
Bisphenol A 13C12	239.1 > 224.2	7.40	18	40
Estrone	269.0 > 144.8	8.82	38	60
Estradiol	270.9 > 144.8	8.72	48	52
Estradiol 13C2	273.0 > 144.8	8.72	48	52
Ethinylestradiol	295.0 > 144.8	8.63	40	60
Ethinylestradiol 13C2	297.1 > 144.8	8.63	40	60

Standard Operating Procedures for Extraction of Estrogens

Sample Preparation

1. Vacuum filter an appropriate volume of aqueous sample (e.g. wastewater, surface water) through a 1.5µm glass-fiber filter.
2. Pour filtered sample into glass container. If there are 3 replicates, prepare 3 separate aliquots.
3. Adjust the pH of the samples to pH=8.0 by adding 10 % NH_4OH.
4. Spike the samples with surrogate standards (Table 1) and mix.
5. The water samples are now ready to be extracted by SPE, but the SPE cartridges must first be pre-conditioned.
6. Clean all equipment before extracting a different sample.

SPE Cartridge Pre-conditioning

7. Place the cartridges (OASIS MAX SPE cartridges, 6 mL, 500 mg) on top of the SPE manifold and begin to condition each of them sequentially with 6 ml DCM, 6 ml MeOH, 6 ml 0.1 M NaOH in water, and 6 ml distilled water. DO NOT LET THE CARTRIDGES GO DRY.
8. Once conditioned, the samples can be passed through the cartridges.

Extraction

9. The Teflon tubes that connect the samples to the SPE manifold must first be cleaned with methanol, and then rinsed with HPLC water.
10. Attach one clean tube to each of the cartridges, and then place the other end in one of the samples. Clearly label all of the cartridges.
11. The water samples should be passed through the SPE cartridges at a rate of approximately 10 mL/min.
12. Rinse each of the sample bottles with approx. 10 mL of pH=8.0 distilled water and pass the rinsings through the cartridge.
13. At this point, ensure the solid phase material is kept wet by trapping the last rinse in the cartridge. Once all samples have passed through, let the cartridges go dry for a one minute in order to remove unwanted water.
14. The Teflon tubing should be quickly removed. Wash the cartridge with 2 mL of a solution of 25 mM NH_4OH in water. Let the cartridge aspirate to dryness for about 20 min with vacuum.
15. A 15 mL collection tube should be placed under the sample in order to collect the eluate. Small Teflon “Guides” must be placed under the top of the manifold, so the samples are properly guided into the 15 mL collection tube.
16. Elute the cartridge into two fractions as follows:
17. *Neutral fraction:*
18. Elute the cartridge with 2 ml MeOH at a flow rate of about 1 ml/min. After elution aspirate the cartridge to dryness.
19. Then, elute the cartridge with 3 × 2 mL DCM at a flow rate of about 1 ml/min. After each elution step, aspirate the cartridge to dryness.
20. Combine the two fractions.
21. *Phenolic fraction:*
22. Elute the cartridge with 3 × 3 mL MeOH/MTBE/formic acid (86/10/4, v/v/v) at a flow rate of about 1 ml/min. After each elution step, aspirate the cartridge to dryness.
23. For both fractions, evaporate to almost complete dryness. Reconstitute the sample with 0.5 mL methanol.

A7. Selective Serotonin Reuptake Inhibitors (SSRIs)

Water or wastewater samples were spiked with stable isotope surrogates and then extracted using the SPE procedures described in the SOP (below). The extracts were evaporated using the Savant apparatus to almost dryness and reconstituted in methanol to a volume of 0.5 mL.

A series of SSRI drug standards was prepared with different concentrations of the analytes (Table A7) and fixed concentrations (50 ng/mL), of venlafaxine-D10, citaporam-D4, fluoxetine-D5, paroxetine-D6 and sertraline-D3 as internal standards. A linear

calibration curve was developed from the drug standards. Analysis of SSRIs is performed with the Applied Biosystems/Sciex Q-Trap mass spectrometer and Agilent 1100 HPLC system. The HPLC column is a Dynatec C-18 column (150 × 2.1 mm i.d.) operated at a mobile phase flow rate of 0.2 ml/min. The mobile phases are: A (10 mM ammonium acetate in water) and B (10 mM ammonium acetate in 95 % acetonitrile /water (v/v)). The elution gradient is as follows: mobile phase B increase from 5 % to 100 % within 12 min and then hold for 6 min, then decrease to 5 % by 2 min and hold for 15 min.

The mass spectrometer is operated with the APCI source in positive ion mode. Nitrogen is used as the nebulizer, drying, curtain and collision gases. Detection is by tandem mass spectrometry in multiple reaction monitoring (MRM) mode. The APCI source operational parameters are: TEM: 300°C; CUR:10; GS1: 60; GS2:5; CAD: 5; NC:3 and ihr: ON.

Table A7: Analytical conditions for SSRIs

Compound	Transition Monitored	Rt (min)	Declustering Potential (V)	Entrance Potential (V)	Collision cell Entrance potential (V)	Collision Energy (eV)	Internal Standard
O-Desmethyl venlafaxine	264>44	12.7	28	3	10	36	Venlafaxine-d10
Venlafaxine	278>58	13.2	26	6	14	42	Venlafaxine-d10
Bupropion	240>164	13.4	28	6	8	15	Venlafaxine-d10
Desmethyl citalopram	311>109	13.9	38	8	14	40	Citalopram-d4
Citalopram	325>109	14.4	42	8	20	36	Citalopram-d4
Paroxetine	330>70	14.9	36	8	12	50	Paroxetine-d6
Norfluoxetine	296>134	15.1	16	4	8	8	Fluoxetine-d5
Fluoxetine	310>44	15.6	22	4	12	28	Fluoxetine-d5
Desmethyl sertraline	292>159	16.0	18	2	16	30	Sertraline-d3
Sertraline	306>159	16.7	26	4	22	34	Sertraline-d3
Venlafaxine-D10	288>58	13.2	26	6	14	42	
Citalopram-D4	329>113	14.4	42	8	20	36	
Paroxetine-D6	336>76	14.9	36	8	12	50	
Fluoxetine-D5	315>44	15.6	22	4	12	28	
Sertraline-D3	309>159	16.7	26	4	22	34	

Standard Operating Procedures for Extraction of SSRIs

Sample Preparation

1. Vacuum filter an appropriate volume of aqueous sample (e.g. wastewater, surface water) through a 1.5μm glass-fiber filter.
2. Pour filtered sample into glass container. If there are 3 replicates, prepare 3 separate aliquots.

3. Acidify samples to pH=2.5 by adding concentrated HCl.
4. Spike the samples with surrogate standards (Table 1) and mix.
5. The water samples are now ready to be extracted by SPE, but the SPE cartridges must first be pre-conditioned.
6. Clean all equipment before extracting a different sample.

SPE Cartridge Pre-conditioning

1. The SPE enrichment is performed with Waters OASIS MCX SPE cartridges (6 cc, 150mg). Place the cartridges on top of the SPE manifold and begin to condition each of them sequentially with 6 mL acetone, 6 mL methanol, and 6 mL HPLC grade water adjusted to pH 2.0 with 3.5 M H_2SO_4. DO NOT LET THE CARTRIDGES GO DRY.
2. Once conditioned, the samples can be passed through the cartridges.
3. Extraction
4. The Teflon tubes that connect the samples to the SPE manifold must first be cleaned with methanol, and then rinsed with HPLC water.
5. Attach one clean tube to each of the cartridges, and then place the other end in one of the samples. Clearly label all of the cartridges.
6. The water samples should be passed through the SPE cartridges at a rate of approximately 5 mL/min.
7. Rinse each of the sample bottles with approx. 10 mL of distilled water and pass the rinsings through the cartridge.
8. At this point, ensure the solid phase material is kept wet by trapping the last rinse in the cartridge. Once all samples have passed through, let the cartridges go dry for a one minute in order to remove unwanted water.
9. The Teflon tubing should be quickly removed. IMMEDIATELY wash the cartridge with 2 mL 0.1 M HCl in water. Let the cartridge aspirate to dryness for about 30 min with vacuum.
10. Further wash the cartridge with 3 × 3 ml of DCM at a flow rate of 1 ml/min. After each wash step, let the cartridge aspirate to dryness. After the final wash, let the cartridge aspirate to dryness for about 30 min with vacuum.
11. Elute the analytes from the cartridge with 3 × 3 mL of a solution of 5 % NH_4OH in methanol (5v/ 95v) and collect the eluant in a centrifuge tube.
12. Evaporate the eluant just to dryness and reconstitute the sample to 0.5 mL with methanol. Transfer the sample to an autosampler vial with an insert for LC-MS/MS analysis.

A8. Beta Blocker Extraction and Analysis

Water or wastewater samples Are spiked with deuterated surrogates and then extracted using the SPE procedures described in the SOP (below). The extracts were evaporated

using the Savant apparatus to almost dryness and reconstituted in 20:80 methanol/water to a volume of 0.5 mL.

Beta-blocker pharmaceuticals are analyzed by Micromass Quattro LC triple-quadrupole mass spectrometer fitted with a Z-spray electrospray interface. Instrument control, data acquisition and processing were performed using Masslynx 3.5 software. The target compounds are analyzed in positive ion mode with the capillary voltage at 3.0 kV. Multiple reaction monitoring is employed for analyte quantitation (Table A8). The source temperature was 80°C and the desolvation temperature was 300°C. Nitrogen is used as both the nebulizing and the desolvation gas at flow rates of 70 and 600 Lh^{-1}, respectively. The cone voltage and collision energy are optimized for each individual analyte (Table A8). A dwell time of 200 ms per ion pair is used and the inter-channel delay was 0.01 s.

Chromatographic separation is conducted on a Waters model 2695 HPLC system with a Genesis C18 column (150 × 2.1 mm i.d., 4μm) at a flow rate of 0.2-0.3 mL/min. The mobile phase A and B consist of acetonitrile and 20 mM aqueous ammonium acetate, respectively, which were degassed by an in-line vacuum degasser. The applied gradient elution is as follows: mobile phase A was increased from 20% to 95% at 0.2 mL/min within 6 min, held at 95% at 0.3 mL/min for 4 min and then decreased to 20% at 0.2 mL/min for 6 min. The column is kept at room temperature and the injection volume was 20 μL.

Table A8: Analytical conditions for Beta Blockers

Compound	Retention Time	Transition 1 (Strongest)	Transition 2	Cone Voltage	Collision Energy
Atenolol	2.99	267 → 145	267 → 190	30 V	22 eV
Atenolol-d7	3.01	274 → 145	274 → 190	30 V	22 eV
Sotalol	3.36	273 → 255	273 → 213	15 V	13 eV
Sotalol-d6	3.38	279 → 261	279 → 214	15 V	13 eV
Nadolol	4.27	310 → 254	310 → 201	30 V	20 eV
Metoprolol	7.03	268 → 133	268 → 159	30 V	25 eV
Propranolol	7.91	260 → 116	260 → 183	30 V	22 eV
Propranolol-d7	7.91	267 → 117	267 → 189	30 V	22 eV

Standard Operating Procedure for Extraction of Beta-Blockers

Sample preparation

1. Vacuum filter an appropriate volume of aqueous sample (e.g. wastewater, surface water) through a 1.5μm glass-fiber filter.

2. Pour filtered sample into glass container. If there are 3 replicates, prepare 3 separate aliquots.
3. Adjust all samples to pH 3.0 by adding 3.5 M H_2SO4.
4. Spike the samples with surrogate standards and mix.
5. The water samples are now ready to be extracted by SPE, but the SPE cartridges must first be pre-conditioned.
6. Clean all equipment before extracting a different sample.

SPE Cartridge Pre-conditioning

1. Place the cartridges (Waters Oasis MCX cartridge, 6 mL/150 mg) on top of the SPE manifold and begin to condition each of them sequentially with 6 mL methanol and 10 mL HPLC grade water of pH 3.0. DO NOT LET THE CARTRIDGES GO DRY.
2. Once conditioned, the samples can be passed through the cartridges.

Extraction

1. The Teflon tubes that connect the samples to SPE manifold must first be cleaned with methanol, and then rinsed with HPLC water.
2. Attach one clean tube to each of the cartridges, and then place the other end in one of the sample containers. Clearly label all of the cartridges.
3. The water samples should be passed through the SPE cartridges at a rate of approximately 10 mL/min.
4. Rinse each of the sample bottles with approx. 10 mL of pH 3.0 HPLC water and pass the rinses through the cartridge.
5. At this point, ensure the solid phase material is kept wet by trapping the last rinse in the cartridge. Once all samples have passed through, let the cartridges go dry for one minute in order to remove unwanted water.
6. The Teflon tubing should be quickly removed. The cartridges are further washed with 6 mL methanol.
7. A 15 mL collection tube should be placed under the sample in order to collect the eluate. Small Teflon “Guides” must be placed under the top of the manifold, so the samples are properly guided into the 15 mL collection tube.
8. IMMEDIATELY wet the cartridges with approx. 3 mL 5% ammonium hydroxide in methanol. Let stand for 10 min and then slowly drain into the 15 mL collection tube. Repeat twice, letting each 3 mL aliquot of 5% ammonium hydroxide in methanol stand in the cartridge for 10 min. A total of approx. 9 mL of 5% ammonium hydroxide in methanol is used to elute the samples.

APPENDIX D – ANALYTICAL METHODS USED BY MWH

MWH LABORATORIES

Standard Operating Procedure
for the Determination of Emerging Organic Pollutants in Environmental Matrices by Liquid Chromatography Mass Spectrometry in Tandem Analysis (LC-MS-MS)
EDC2

The standard operating procedure for the analysis of endocrine disrupting compounds used by MWH Laboratories is a confidential method. Therefore, the standard operating procedure is not included in this document. Information on this method can be obtained by contacting MWH Laboratories.

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METHOD 525.2

DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

Revision 2.0

J.W. Eichelberger, T.D. Behymer, W.L. Budde - Method 525,
Revision 1.0, 2.0, 2.1 (1988)

J.W. Eichelberger, T.D. Behymer, and W.L. Budde - Method 525.1
Revision 2.2 (July 1991)

J.W. Eichelberger, J.W. Munch, and J.A. Shoemaker
Method 525.2 Revision 1.0 (February, 1994)

J.W. Munch - Method 525.2, Revision 2.0 (1995)

NATIONAL EXPOSURE RESEARCH LABORATORY
OFFICE OF RESEARCH AND DEVELOPMENT
U.S. ENVIRONMENTAL PROTECTION AGENCY
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METHOD 525.2

DETERMINATION OF ORGANIC COMPOUNDS IN DRINKING WATER BY LIQUID-SOLID EXTRACTION AND CAPILLARY COLUMN GAS CHROMATOGRAPHY/MASS SPECTROMETRY

1.0 SCOPE AND APPLICATION

1.1 This is a general purpose method that provides procedures for determination of organic compounds in finished drinking water, source water, or drinking water in any treatment stage. The method is applicable to a wide range of organic compounds that are efficiently partitioned from the water sample onto a C_{18} organic phase chemically bonded to a solid matrix in a disk or cartridge, and sufficiently volatile and thermally stable for gas chromatog-raphy. Single-laboratory accuracy and precision data have been determined with two instrument systems using both disks and cartridges for most of the following compounds:

Analyte	MW[1]	Chemical Abstract Services Registry Number
Acenaphthylene	152	208-96-8
Alachlor	269	15972-60-8
Aldrin	362	309-00-2
Ametryn	227	834-12-8
Anthracene	178	120-12-7
Atraton	211	1610-17-9
Atrazine	215	1912-24-9
Benz[a]anthracene	228	56-55-3
Benzo[b]fluoranthene	252	205-82-3
Benzo[k]fluoranthene	252	207-08-9
Benzo[a]pyrene	252	50-32-8
Benzo[g,h,i]perylene	276	191-24-2
Bromacil	260	314-40-9
Butachlor	311	23184-66-9
Butylate	317	2008-41-5
Butylbenzylphthalate	312	85-68-7
Carboxin[2]	235	5234-68-4
Chlordane components		
alpha-Chlordane	406	5103-71-9
gamma-Chlordane	406	5103-74-2
trans-Nonachlor	440	39765-80-5
Chlorneb	206	2675-77-6
Chlorobenzilate	324	510-15-6
Chlorpropham	213	101-21-3
Chlorothalonil	264	1897-45-6

Analyte	MW[1]	Chemical Abstract Services Registry Number
Chlorpyrifos	349	2921-88-2
2-Chlorobiphenyl	188	2051-60-7
Chrysene	228	218-01-9
Cyanazine	240	21725-46-2
Cycloate	215	1134-23-2
Dacthal (DCPA)	330	1861-32-1
4,4'-DDD	318	72-54-8
4,4'-DDE	316	72-55-9
4,4'-DDT	352	50-29-3
Diazinon[2]	304	333-41-5
Dibenz[a,h]anthracene	278	53-70-3
Di-n-Butylphthalate	278	84-74-2
2,3-Dichlorobiphenyl	222	16605-91-7
Dichlorvos	220	62-73-7
Dieldrin	378	60-57-1
Diethylphthalate	222	84-66-2
Di(2-ethylhexyl)adipate	370	103-23-1
Di(2-ethylhexyl)phthalate	390	117-81-7
Dimethylphthalate	194	131-11-3
2,4-Dinitrotoluene	182	121-14-2
2,6-Dinitrotoluene	182	606-20-2
Diphenamid	239	957-51-7
Disulfoton[2]	274	298-04-4
Disulfoton Sulfoxide[2]	290	2497-07-6
Disulfoton Sulfone	306	2497-06-5
Endosulfan I	404	959-98-8
Endosulfan II	404	33213-65-9
Endosulfan Sulfate	420	1031-07-8
Endrin	378	72-20-8
Endrin Aldehyde	378	7421-93-4
EPTC	189	759-94-4
Ethoprop	242	13194-48-4
Etridiazole	246	2593-15-9
Fenamiphos[2]	303	22224-92-6
Fenarimol	330	60168-88-9
Fluorene	166	86-73-7
Fluridone	328	59756-60-4
Heptachlor	370	76-44-8
Heptachlor Epoxide	386	1024-57-3
2,2', 3,3', 4,4', 6-Heptachloro-biphenyl	392	52663-71-5
Hexachlorobenzene	282	118-74-1
2,2', 4,4', 5,6'-Hexachloro-biphenyl	358	60145-22-4

Analyte	MW[1]	Chemical Abstract Services Registry Number
Hexachlorocyclohexane, alpha	288	319-84-6
Hexachlorocyclohexane, beta	288	319-85-7
Hexachlorocyclohexane, delta	288	319-86-8
Hexachlorocyclopentadiene	270	77-47-4
Hexazinone	252	51235-04-2
Indeno[1,2,3,c,d]pyrene	276	193-39-5
Isophorone	138	78-59-1
Lindane	288	58-89-9
Merphos[2]	298	150-50-5
Methoxychlor	344	72-43-5
Methyl Paraoxon	247	950-35-6
Metolachlor	283	51218-45-2
Metribuzin	214	21087-64-9
Mevinphos	224	7786-34-7
MGK 264	275	113-48-4
Molinate	187	2212-67-1
Napropamide	271	15299-99-7
Norflurazon	303	27314-13-2
2,2', 3,3', 4,5', 6,6'-Octachloro-biphenyl	426	40186-71-8
Pebulate	203	1114-71-2
2,2', 3', 4,6'-Pentachlorobiphenyl	324	60233-25-2
Pentachlorophenol	264	87-86-5
Phenanthrene	178	85-01-8
cis-Permethrin	390	54774-45-7
trans-Permethrin	390	51877-74-8
Prometon	225	1610-18-0
Prometryn	241	7287-19-6
Pronamide	255	23950-58-5
Propachlor	211	1918-16-7
Propazine	229	139-40-2
Pyrene	202	129-00-0
Simazine	201	122-34-9
Simetryn	213	1014-70-6
Stirofos	364	22248-79-9
Tebuthiuron	228	34014-18-1
Terbacil	216	5902-51-2
Terbufos2	288	13071-79-9
Terbutryn	241	886-50-0
2,2', 4,4'-Tetrachlorobiphenyl	290	2437-79-8
Toxaphene		8001-35-2
Triademefon	293	43121-43-3
2,4,5-Trichlorobiphenyl	256	15862-07-4
Tricyclazole	189	41814-78-2

Analyte	MW[1]	Chemical Abstract Services Registry Number
Trifluralin	335	1582-09-8
Vernolate	203	1929-77-7
Aroclor 1016		12674-11-2
Aroclor 1221		11104-28-2
Aroclor 1232		11141-16-5
Aroclor 1242		53469-21-9
Aroclor 1248		12672-29-6
Aroclor 1254		11097-69-1
Aroclor 1260		11096-82-5

[1]Monoisotopic molecular weight calculated from the atomic masses of the isotopes with the smallest masses.
[2]Only qualitative identification of these analytes is possible because of their instability in aqueous matrices. Merphos, carboxin, disulfoton, and disulfoton sulfoxide showed instability within 1 h of fortification. Diazinon, fenamiphos, and terbufos showed significant losses within seven days under the sample storage conditions specified in this method.

Attempting to determine all of the above analytes in all samples is not practical and not necessary in most cases. If all the analytes must be determined, multiple calibration mixtures will be required.

1.2 Method detection limit (MDL) is defined as the statistically calculated minimum amount that can be measured with 99% confidence that the reported value is greater than zero[1]. The MDL is compound dependent and is particularly dependent on extraction efficiency and sample matrix. MDLs for all method analytes are listed in Tables 3 through 6. The concentration calibration range demonstrated in this method is 0.1-10 µg/L for most analytes.

2.0 SUMMARY OF METHOD

Organic compound analytes, internal standards, and surrogates are extracted from a water sample by passing 1 L of sample water through a cartridge or disk containing a solid matrix with a chemically bonded C_{18} organic phase (liquid-solid extraction, LSE). The organic compounds are eluted from the LSE cartridge or disk with small quantities of ethyl acetate followed by methylene chloride, and this extract is concentrated further by evaporation of some of the solvent. The sample components are separated, identified, and measured by injecting an aliquot of the concentrated extract into a high resolution fused silica capillary column of a gas chromatography/mass spectrometry (GC/MS) system. Compounds eluting from the GC column are identified by comparing their measured mass spectra and retention times to reference spectra and retention times in a data base. Reference spectra and retention times for analytes are obtained by the measurement of calibration standards under the same conditions used for samples.

The concentration of each identified component is measured by relating the MS response of the quantitation ion produced by that compound to the MS response of the quantitation ion produced by a compound that is used as an internal standard. Surrogate analytes, whose concentrations are known in every sample, are measured with the same internal standard calibration procedure.

3.0 DEFINITIONS

3.1 Internal Standard (IS) -- A pure analyte(s) added to a sample, extract, or standard solution in known amount(s) and used to measure the relative responses of other method analytes and surrogates that are components of the same solution. The internal standard must be an analyte that is not a sample component.

3.2 Surrogate Analyte (SA) -- A pure analyte(s), which is extremely unlikely to be found in any sample, and which is added to a sample aliquot in known amount(s) before extraction or other processing, and is measured with the same procedures used to measure other sample components. The purpose of the SA is to monitor method performance with each sample.

3.3 Laboratory Duplicates (LD1 and LD2) -- Two aliquots of the same sample taken in the laboratory and analyzed separately with identical procedures. Analyses of LD1 and LD2 indicate precision associated with laboratory procedures, but not with sample collection, preservation, or storage procedures.

3.4 Field Duplicates (FD1 and FD2) -- Two separate samples collected at the same time and place under identical circumstances, and treated exactly the same throughout field and laboratory procedures. Analyses of FD1 and FD2 give a measure of the precision associated with sample collection, preservation, and storage, as well as with laboratory procedures.

3.5 Laboratory Reagent Blank (LRB) -- An aliquot of reagent water or other blank matrix that is treated exactly as a sample including exposure to all glassware, equipment, solvents, reagents, internal standards, and surrogates that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents, or the apparatus.

3.6 Field Reagent Blank (FRB) -- An aliquot of reagent water or other blank matrix that is placed in a sample container in the laboratory and treated as a sample in all respects, including shipment to the sampling site, exposure to sampling site conditions, storage, preservation, and all analytical procedures. The purpose of the FRB is to determine if method analytes or other interferences are present in the field environment.

3.7 Instrument Performance Check Solution (IPC) -- A solution of one or more method analytes, surrogates, internal standards, or other test substances used to evaluate the performance of the instrument system with respect to a defined set of method criteria.

3.8 Laboratory Fortified Blank (LFB) -- An aliquot of reagent water or other blank matrix to which known quantities of the method analytes are added in the laboratory. The LFB is analyzed exactly like a sample, and its purpose is to determine whether the methodology is in control, and whether the laboratory is capable of making accurate and precise measurements.

3.9 Laboratory Fortified Sample Matrix (LFM) -- An aliquot of an environmental sample to which known quantities of the method analytes are added in the laboratory. The LFM is analyzed exactly like a sample, and its purpose is to determine whether the sample matrix contributes bias to the analytical results. The background concentrations of the analytes in the sample matrix must be determined in a separate aliquot and the measured values in the LFM corrected for background concentrations.

3.10 Stock Standard Solution (SSS) -- A concentrated solution containing one or more method analytes prepared in the laboratory using assayed reference materials or purchased from a reputable commercial source.

3.11 Primary Dilution Standard Solution (PDS) -- A solution of several analytes prepared in the laboratory from stock standard solutions and diluted as needed to prepare calibration solutions and other needed analyte solutions.

3.12 Calibration Standard (CAL) -- A solution prepared from the primary dilution standard solution or stock standard solutions and the internal standards and surrogate analytes. The CAL solutions are used to calibrate the instrument response with respect to analyte concentration.

3.13 Quality Control Sample (QCS) -- A solution of method analytes of known concentrations which is used to fortify an aliquot of LRB or sample matrix. The QCS is obtained from a source external to the laboratory and different from the source of calibration standards. It is used to check laboratory performance with externally prepared test materials.

4.0 INTERFERENCES

4.1 During analysis, major contaminant sources are reagents and liquid- solid extraction devices. Analyses of field and laboratory reagent blanks provide information about the presence of contaminants.

4.2 Interfering contamination may occur when a sample containing low concentrations of compounds is analyzed immediately after a sample containing relatively high concentrations of compounds. Syringes and splitless injection port liners must be cleaned carefully or replaced as needed. After analysis of a sample containing high concentrations of compounds, a laboratory reagent blank should be analyzed to ensure that accurate values are obtained for the next sample.

5.0 SAFETY

5.1 The toxicity or carcinogenicity of chemicals used in this method has not been precisely defined; each chemical should be treated as a potential health hazard, and exposure to these chemicals should be minimized. Each laboratory is responsible for maintaining awareness of OSHA regulations regarding safe handling of chemicals used in this method. Additional references to laboratory safety are cited[2-4].

5.2 Some method analytes have been tentatively classified as known or suspected human or mammalian carcinogens. Pure standard materials and stock standard solutions of these compounds should be handled with suitable protection to skin, eyes, etc.

6.0 EQUIPMENT AND SUPPLIES (All specifications are suggested. Catalog numbers are included for illustration only.)

6.1 All glassware must be meticulously cleaned. This may be accomplished by washing with detergent and water, rinsing with water, distilled water, or solvents, air-drying, and heating (where appropriate) in a muffle furnace. Volumetric glassware should never be heated to the temperatures obtained in a muffle furnace.

6.2 Sample Containers -- 1 L or 1 qt amber glass bottles fitted with Teflon-lined screw caps. Amber bottles are highly recommended since some of the method analytes are very sensitive to light and are oxidized or decomposed upon exposure.

6.3 Volumetric Flasks -- Various sizes.

6.4 Laboratory or Aspirator Vacuum System -- Sufficient capacity to maintain a minimum vacuum of approximately 13 cm (5 in.) of mercury for cartridges. A greater vacuum (66 cm [26 in.] of mercury) may be used with disks.

6.5 Micro Syringes -- Various sizes.

6.6 Vials -- Various sizes of amber vials with Teflon-lined screw caps.

6.7 Drying Column -- The drying tube should contain about 5-7 g of anhydrous sodium sulfate to prohibit residual water from contaminating the extract. Any small tube may be used, such as a syringe barrel, a glass dropper, etc. as long as no sodium sulfate passes through the column into the extract.

6.8 Analytical Balance -- Capable of weighing 0.0001 g accurately.

6.9 Fused Silica Capillary Gas Chromatography Column -- Any capillary column that provides adequate resolution, capacity, accuracy, and precision (Section 10.0) can be used. Medium polar, low bleed columns are recommended for use with this method to provide adequate chromatography and minimize column bleed. A 30 m X 0.25 mm id fused silica capillary column coated with a 0.25 µm bonded film of polyphenylmethylsilicone (J&W DB-5.MS) was used to develop this method. Any column which provides analyte separations equivalent to or better than this column may be used.

6.10 Gas Chromatograph/Mass Spectrometer/Data System (GC/MS/DS)

6.10.1 The GC must be capable of temperature programming and be equipped for splitless/split injection. On-column capillary injection is acceptable if all the quality control specifications in Section 9.0 and Section 10.0 are met. The injection tube liner should be quartz and about 3 mm in diameter. The injection system must not allow the analytes to contact hot stainless steel or other metal surfaces that promote decomposition.

6.10.2 The GC/MS interface should allow the capillary column or transfer line exit to be placed within a few mm of the ion source. Other interfaces, for example the open split interface, are acceptable as long as the system has adequate sensitivity (see Section 10.0 for calibration requirements).

6.10.3 The mass spectrometer must be capable of electron ionization at a nominal electron energy of 70 eV to produce positive ions. The spectrometer must be capable of scanning at a minimum from 45-450 amu with a complete scan cycle time (including scan overhead) of 1.0 second or less. (Scan cycle time = total MS data acquisition time in seconds divided by number of scans in the chromatogram). The spectrometer must produce a mass spectrum that meets all criteria in Table 1 when an injection of approximately 5 ng of DFTPP is introduced into the GC. An average spectrum across the DFTPP GC peak may be used to test instrument performance. The scan time should be set so that all analytes have a minimum of five scans across the chromatographic peak.

6.10.4 An interfaced data system is required to acquire, store, reduce, and output mass spectral data. The computer software must have the capability of processing stored GC/MS data by recognizing a GC peak within any given retention time window, comparing the mass spectrum from the GC peak with spectral data in a user-created data base, and generating a list of tentatively identified compounds with their retention times and scan numbers. The software must also allow integration of the ion abundance of any specific ion between specified time or scan number limits, calculation of response factors as defined in Section 10.2.6 (or construction of a linear regression calibration curve), calculation of response factor statistics (mean and standard deviation), and calculation of concentrations of analytes using either the calibration curve or the equation in Section 12.0.

6.11 Standard Filter Apparatus, All Glass or Teflon Lined -- These should be used to carry out disk extractions when no automatic system or manifold is utilized.

6.12 A manifold system or an automatic or robotic commercially available sample preparation system designed for either cartridges or disks may be utilized in this method if all quality control requirements discussed in Section 9.0 are met.

7.0 REAGENTS AND STANDARDS

7.1 Helium Carrier Gas -- As contaminant free as possible.

7.2 Liquid-Solid Extraction (LSE) Cartridges -- Cartridges are inert non-leaching plastic, for example polypropylene, or glass, and must not contain plasticizers, such as phthalate esters or adipates, that leach into the ethyl acetate and methylene chloride eluant. The cartridges are packed with about 1 g of silica, or other inert inorganic support, whose surface is modified by chemically bonded octadecyl (C_{18}) groups. The packing must have a narrow size distribution and must not leach organic compounds into the eluting solvent. One liter of water should pass through the cartridge in about two hours with the assistance of a slight vacuum of about 13 cm (5 in.) of mercury. Section 9.0 provides criteria for acceptable LSE cartridges which are available from several commercial suppliers.

The extraction disks contain octadecyl bonded silica uniformly enmeshed in an inert matrix. The disks used to generate the data in this method were 47 mm in diameter and 0.5 mm in thickness. Other disk sizes are acceptable and larger disks may be used for special problems or when sample compositing is carried out. As with cartridges, the disks should not contain any organic compounds, either from the matrix or the bonded silica, which will leach into the ethyl acetate and methylene chloride eluant. One L of reagent water should pass

through the disks in five to 20 minutes using a vacuum of about 66 cm (26 in.) of mercury. Section 9.0 provides criteria for acceptable LSE disks which are available commercially.

7.3 Solvents

7.3.1 Methylene Chloride, Ethyl Acetate, Acetone, Toluene, and Methanol -- High purity pesticide quality or equivalent.

7.3.2 Reagent Water -- Water in which an interference is not observed at the method detection limit of the compound of interest. Prepare reagent water by passing tap water through a filter bed containing about 0.5 kg of activated carbon or by using a water purification system. Store in clean, narrow-mouth bottles with Teflon-lined septa and screw caps.

7.4 Hydrochloric Acid -- 6N.

7.5 Sodium Sulfate, Anhydrous -- (Soxhlet extracted with methylene chloride for a minimum of four hours or heated to 400°C for two hours in a muffle furnace.)

7.6 Stock Standard Solutions (SSS) -- Individual solutions of surrogates, internal standards, and analytes, or mixtures of analytes, may be purchased from commercial suppliers or prepared from pure materials. To prepare, add 10 mg (weighed on an analytical balance to 0.1 mg) of the pure material to 1.9 mL of methanol, ethyl acetate, or acetone in a 2 mL volumetric flask, dilute to the mark, and transfer the solution to an amber glass vial. If the analytical standard is available only in quantities smaller than 10 mg, reduce the volume of solvent accordingly. Some polycyclic aromatic hydrocarbons are not soluble in methanol, ethyl acetate, or acetone, and their stock standard solutions are prepared in toluene. Methylene chloride should be avoided as a solvent for standards because its high vapor pressure leads to rapid evaporation and concentration changes. Methanol, ethyl acetate, and acetone are not as volatile as methylene chloride, but their solutions must also be handled with care to avoid evaporation. If compound purity is confirmed by the supplier at >96%, the weighed amount can be used without correction to calculate the concentration of the solution (5 µg/µL). Store the amber vials at 4°C or less.

7.7 Primary Dilution Standard Solution (PDS) -- The stock standard solutions are used to prepare a primary dilution standard solution that contains multiple analytes. Mixtures of these analytes to be used as primary dilution standards may be purchased from commercial suppliers. Do not put every method analyte in a single primary dilution standard because chromatographic separation will be extremely difficult, if not impossible. Two or three primary dilution standards would be more appropriate. The recommended solvent for these standards is

acetone or ethyl acetate. Aliquots of each of the stock standard solutions are combined to produce the primary dilution in which the concentration of the analytes is at least equal to the concentration of the most concentrated calibration solution, that is, 10 ng/µL. Store the primary dilution standard solution in an amber vial at 4°C or less, and check frequently for signs of degradation or evaporation, especially just before preparing calibration solutions.

7.8 Fortification Solution of Internal Standards and Surrogates -- Prepare an internal standard solution of acenaphthene-D_{10}, phenanthrene-D_{10}, and chrysene-D_{12}, in methanol, ethyl acetate, or acetone at a concentration of 500 µg/mL of each. This solution is used in the preparation of the calibration solutions. Dilute a portion of this solution by 10 to a concentration of 50 µg/mL and use this solution to fortify the actual water samples (see Section 11.1.3 and Section 11.2.3). Similarly, prepare both surrogate compound solutions (500 µg/mL for calibration, 50 µg/mL for fortification). Surrogate compounds used in developing this method are 1,3-dimethyl-2-nitrobenzene, perylene-D_{12}, and triphenylphosphate. Other surrogates, for example pyrene-D_{10} may be used in this solution as needed (a 100 µL aliquot of this 50 µg/mL solution added to 1 L of water gives a concentration of 5 µg/L of each internal standard or surrogate). Store these solutions in an amber vial at 4°C or less. These two solutions may be combined or made as a single solution.

7.9 GC/MS Performance Check Solution -- Prepare a solution in methylene chloride of the following compounds at 5 ng/µL of each: DFTPP and endrin, and 4,4'-DDT. Store this solution in an amber vial at 4°C or less. DFTPP is less stable in acetone or ethyl acetate than it is in methylene chloride.

7.10 Calibration Solutions (CAL1 through CAL6) -- Prepare a series of six concentration calibration solutions in ethyl acetate which contain analytes of interest (except pentachlorophenol, toxaphene, and the Aroclor compounds) at suggested concentrations of 10, 5, 2, 1, 0.5, and 0.1 ng/µL, with a constant concentration of 5 ng/µL of each internal standard and surrogate in each CAL solution. It should be noted that CAL1 through CAL6 are prepared by combining appropriate aliquots of a primary dilution standard solution (Section 7.7) and the fortification solution (500 µg/mL) of internal standards and surrogates (Section 7.8). All calibration solutions should contain at least 80% ethyl acetate to avoid gas chromatographic problems. IF ALL METHOD ANALYTES ARE TO BE DETERMINED, TWO OR THREE SETS OF CALIBRATION SOLUTIONS WILL LIKELY BE REQUIRED. Pentachlorophenol is included in this solution at a concentration four times the other analytes. Toxaphene CAL solutions should be prepared as separate solutions at concentrations of 250, 200, 100, 50, 25, and 10 ng/µL. Aroclor CAL solutions should be prepared individually at concentrations of 25, 10, 5, 2.5, 1.0, 0.5, and 0.2 ng/µL. Store these solutions in amber vials in a dark cool

place. Check these solutions regularly for signs of degradation, for example, the appearance of anthraquinone from the oxidation of anthracene.

7.11 Reducing Agent, Sodium Sulfite, Anhydrous -- Sodium thiosulfate is not recommended as it may produce a residue of elemental sulfur that can interfere with some analytes.

7.12 Fortification Solution for Recovery Standard -- Prepare a solution of terphenyl-D_{14} at a concentration of 500 µg/mL in methylene chloride or ethyl acetate. These solutions are also commercially available. An aliquot of this solution should be added to each extract to check on the recovery of the internal standards in the extraction process.

8.0 SAMPLE COLLECTION, PRESERVATION, AND STORAGE

8.1 Sample Collection -- When sampling from a water tap, open the tap and allow the system to flush until the water temperature has stabilized (usually about two minutes). Adjust the flow to about 500 mL/min. and collect samples from the flowing stream. Keep samples sealed from collection time until analysis. When sampling from an open body of water, fill the sample container with water from a representative area. Sampling equipment, including automatic samplers, must be free of plastic tubing, gaskets, and other parts that may leach interfering analytes into the water sample. Automatic samplers that composite samples over time should use refrigerated glass sample containers if possible.

8.2 Sample Dechlorination and Preservation -- All samples should be iced or refrigerated at 4°C and kept in the dark from the time of collection until extraction. Residual chlorine should be reduced at the sampling site by addition of 40-50 mg of sodium sulfite (this may be added as a solid with stirring or shaking until dissolved) to each water sample. It is very important that the sample be dechlorinated prior to adding acid to lower the pH of the sample. Adding sodium sulfite and HCl to the sample bottles prior to shipping to the sampling site is not permitted. Hydrochloric acid should be used at the sampling site to retard the microbiological degradation of some analytes in water. The sample pH is adjusted to <2 with 6 N hydrochloric acid. This is the same pH used in the extraction, and is required to support the recovery of acidic compounds like pentachlorophenol.

8.2.1 If cyanizine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in the stored sample. Samples collected for cyanazine determination MUST NOT be dechlorinated or acidified when collected. They should be iced or refrigerated as described above and analyzed within 14 days. However,

these samples MUST be dechlorinated and acidified immediately prior to fortification with internal standards and surrogates, and extraction using the same quantities of acid and sodium sulfite described above.

8.2.2 Atraton and prometon are not efficiently extracted from water at pH 2 due to what appears to be their ionization in solution under acidic conditions. In order to determine these analytes accurately, a separate sample must be collected and dechlorinated with sodium sulfite, but no acid should be added. At neutral pH, these two compounds are recovered from water with efficiencies greater than 90%. The data in Tables 3, 4, 5, 6, and 8 are from samples extracted at pH 2.

8.3 Holding Time -- Results of the time/storage study of all method analytes showed that all but six compounds are stable for 14 days in water samples when the samples are dechlorinated, preserved, and stored as described in Section 8.2. Therefore, samples must be extracted within 14 days. If the following analytes are to be determined, the samples cannot be held for 14 days but must be extracted immediately after collection and preservation: carboxin, diazinon, disulfoton, disulfoton sulfoxide, fenamiphos, and terbufos. Sample extracts may be stored at 4°C for up to 30 days after sample extraction.

8.4 Field Blanks

8.4.1 Processing of a field reagent blank (FRB) is recommended along with each sample set, which is composed of the samples collected from the same general sample site at approximately the same time. At the laboratory, fill a sample container with reagent water, seal, and ship to the sampling site along with the empty sample containers. Return the FRB to the laboratory with the filled sample bottles.

8.4.2 When sodium sulfite and hydrochloric acid are added to samples, use the same procedure to add the same amounts to the FRB.

9.0 QUALITY CONTROL

9.1 Quality control (QC) requirements are the initial demonstration of laboratory capability followed by regular analyses of laboratory reagent blanks, laboratory fortified blanks, and laboratory fortified matrix samples. A MDL should be determined for each analyte of interest. The laboratory must maintain records to document the quality of the data generated. Additional quality control practices are recommended.

9.2 Initial Demonstration of Low Disk or Cartridge System Background -- Before any samples are analyzed, or any time a new supply of cartridges or disks is

received from a supplier, it must be demonstrated that a laboratory reagent blank (LRB) is reasonably free of contamination that would prevent the determination of any analyte of concern. In this same experiment, it must be demonstrated that the particle size and packing of the LSE cartridges or the preparation of the disks are acceptable. Consistent flow rate with all samples is an indication of acceptable particle size distribution, packing, and proper preparation.

9.2.1 A source of potential contamination is the liquid-solid extraction (LSE) cartridge or disk which could contain phthalate esters, silicon compounds, and other contaminants that could prevent the determination of method analytes[5]. Although disks are generally made of an inert matrix, they may still contain phthalate material. Generally, phthalate esters can be leached from the cartridges into ethyl acetate and methylene chloride and produce a variable background in the water sample. If the background contamination is sufficient to prevent accurate and precise measurements, the condition must be corrected before proceeding with the initial demonstration.

9.2.2 Other sources of background contamination are solvents, reagents, and glassware. Background contamination must be reduced to an acceptable level before proceeding with the next section. In general, background from method analytes should be below the method detection limits.

9.2.3 One L of water should pass through a cartridge in about two hours with a partial vacuum of about 13 cm (5 in.) of mercury. Using full aspirator or pump vacuum, approximately five to 20 minutes will normally be required to pass one liter of drinking water through a disk. The extraction time should not vary unreasonably among LSE cartridges or disks.

9.3 Initial Demonstration of Laboratory Accuracy and Precision -- Analyze four to seven replicates of a laboratory fortified blank containing each analyte of concern at a suggested concentration in the range of 2-5 µg/L. This concentration should be approximately in the middle of the calibration range, and will be dependent on the sensitivity of the instrumentation used.

9.3.1 Prepare each replicate by adding sodium sulfite and HCl according to Section 8.2, then adding an appropriate aliquot of the primary dilution standard solution, or certified quality control sample, to reagent water. Analyze each replicate according to the procedures described in Section 11.0.

9.3.2 Calculate the measured concentration of each analyte in each replicate, the mean concentration of each analyte in all replicates, and mean accuracy (as mean percentage of true value) for each analyte, and the precision (as relative standard deviation, RSD) of the measurements for each analyte.

9.3.3 For each analyte and surrogate, the mean accuracy, expressed as a percentage of the true value, should be 70-130% and the RSD should be $<30\%$. If these criteria are not met, locate the source of the problem, and repeat with freshly prepared LFBs.

9.3.4 Analyze seven replicate laboratory fortified blanks which have been fortified with all analytes of interest at approximately 0.5 µg/L. Calculate the MDL of each analyte using the procedure described in Section 13.1.2[1]. It is recommended that these analyses be performed over a period of three or four days to produce more realistic method detection limits.

9.3.5 Develop and maintain a system of control charts to plot the precision and accuracy of analyte and surrogate measurements as a function of time. Charting of surrogate recoveries is an especially valuable activity since these are present in every sample and the analytical results will form a significant record of data quality.

9.4 Monitor the integrated areas of the quantitation ions of the internal standards and surrogates in continuing calibration checks (see Section 10.3). In laboratory fortified blanks or samples, the integrated areas of internal standards and surrogates will not be constant because the volume of the extract will vary (and is difficult to keep constant). But the ratios of the areas should be reasonably constant in laboratory fortified blanks and samples. The addition of 10 µL of the recovery standard, terphenyl-D_{14} (500 µg/mL), to the extract is recommended to be used to monitor the recovery of the internal standards in laboratory fortified blanks and samples. Internal standard recovery should be in excess of 70%.

9.5 With each batch of samples processed as a group within a 12-hour work shift, analyze a laboratory reagent blank to determine the background system contamination. Any time a new batch of LSE cartridges or disks is received, or new supplies of other reagents are used, repeat the demonstration of low background described in Section 9.2.

9.6 With each batch of samples processed as a group within a work shift, analyze a single laboratory fortified blank (LFB) containing each analyte of concern at a concentration as determined in Section 9.3. If more than 20 samples are

included in a batch, analyze a LFB for every 20 samples. Use the procedures described in Section 9.3.3 to evaluate the accuracy of the measurements. If acceptable accuracy cannot be achieved, the problem must be located and corrected before additional samples are analyzed. Add the results to the on-going control charts to document data quality.

Note: If the LFB for each batch of samples contains the individual PCB congeners listed in Section 1.0, then a LFB for each Aroclor is not required. At least one LFB containing toxaphene should be extracted for each 24 hour period during which extractions are performed. Toxaphene should be fortified in a separate LFB from other method analytes.

If individual PCB congeners are not part of the LFB, then it is suggested that one multi-component analyte (toxaphene, chlordane or an Aroclor) LFB be analyzed with each sample set. By selecting a different multi-component analyte for this LFB each work shift, LFB data can be obtained for all of these analytes over the course of several days.

9.7 Determine that the sample matrix does not contain materials that adversely affect method performance. This is accomplished by analyzing replicates of laboratory fortified matrix samples and ascertaining that the precision, accuracy, and method detection limits of analytes are in the same range as obtained with laboratory fortified blanks. If a variety of different sample matrices are analyzed regularly, for example, drinking water from groundwater and surface water sources, matrix independence should be established for each. Over time, LFM data should be documented for all routine sample sources for the laboratory. A laboratory fortified sample matrix should be analyzed for every 20 samples processed in the same batch. If the recovery data for a LFM does not meet the criteria in Section 9.3.3., and LFBs show the laboratory to be in control , then the samples from that matrix (sample location) are documented as suspect due to matrix effects.

9.8 With each set of samples, a FRB should be analyzed. The results of this analysis will help define contamination resulting from field sampling and transportation activities.

9.9 At least quarterly, analyze a quality control sample from an external source. If measured analyte concentrations are not of acceptable accuracy (Section 9.3.3), check the entire analytical procedure to locate and correct the problem source.

9.10 Numerous other quality control measures are incorporated into other parts of this procedure, and serve to alert the analyst to potential problems.

10.0 CALIBRATION AND STANDARDIZATION

10.1 Demonstration and documentation of acceptable initial calibration is required before any samples are analyzed and is required intermittently throughout sample analysis as dictated by results of continuing calibration checks. After initial calibration is successful, a continuing calibration check is required each day or at the beginning of each period in which analyses are performed not to exceed 12 hours. Additional periodic calibration checks are good laboratory practice. It is recommended that an additional calibration check be performed at the end of each period of continuous instrument operation, so that all field sample analyses are bracketed by a calibration check standard.

10.2 Initial Calibration

10.2.1 Calibrate the mass and abundance scales of the MS with calibration compounds and procedures prescribed by the manufacturer with any modifications necessary to meet the requirements in Section 10.2.2.

10.2.2 Inject into the GC/MS system a 1 µL aliquot of the 5 ng/µL solution of DFTPP, endrin and 4,4'-DDT. If desired, the endrin and DDT degradation checks may be performed simultaneously with the DFTPP check or in a separate injection. Acquire a mass spectrum that includes data for m/z 45-450. Use GC conditions that produce a narrow (at least five scans per peak) symmetrical peak for each compound (Section 10.2.3.1 and Section 10.2.3.2). If the DFTPP mass spectrum does not meet all criteria in Table 1, the MS must be retuned and adjusted to meet all criteria before proceeding with calibration. A single spectrum or an average spectrum across the GC peak may be used to evaluate the performance of the system. Locate any degradation products of endrin (endrin ketone [EK] and endrin aldehyde [EA]) and 4,4'-DDT (4,4'-DDE and 4,4'-DDD) at their appropriate retention times and quantitation ions (Table 2). Endrin ketone can be located at ≈1.1 to 1.2 times the endrin retention time with prominent m/z 67 and 317 ions in the mass spectrum. If degradation of either endrin or DDT exceeds 20%, maintenance is required on the GC injection port and possibly other areas of the system before proceeding with the calibration. Calculate percent breakdown using peak areas based on total ion current (TIC) as follows:

% 4,4'-DDT breakdown =

$$\frac{\sum \text{ TIC area of DDT degradation peaks (DDE+DDD)}}{\sum \text{ TIC area of total DDT peaks (DDT+DDE+DDD)}} \times 100$$

% endrin breakdown=

$$\frac{\sum \text{ TIC area of endrin degradation peaks (EA+EK)}}{\sum \text{ TIC area of total endrin peaks (endrin+EA+EK)}} \text{ x } 100$$

10.2.3 Inject a 1 µL aliquot of a medium concentration calibration solution, for example 0.5-2 µg/L, and acquire and store data from m/z 45-450 with a total cycle time (including scan overhead time) of 1.0 second or less. Cycle time should be adjusted to measure at least five or more spectra during the elution of each GC peak. Calibration standards for toxaphene and Aroclors must be injected individually.

10.2.3.1 The following are suggested multi-ramp temperature program GC conditions. Adjust the helium carrier gas flow rate to about 33 cm/sec. Inject at 45°C and hold in splitless mode for one minute. Heat rapidly to 130°C. At three minutes start the temperature program: 130-180°C at 12°/min.; 180-240°C at 7°/min.; 240-320°C at 12°/min. Start data acquisition at four minutes.

10.2.3.2 Single ramp linear temperature program suggested GC conditions. Adjust the helium carrier gas flow rate to about 33 cm/sec. Inject at 40°C and hold in splitless mode for one minute. Heat rapidly to 160°C. At three minutes start the temperature program: 160-320°C at 6°/min.; hold at 320°C for two minutes. Start data acquisition at three minutes.

10.2.4 Performance Criteria for the Calibration Standards -- Examine the stored GC/MS data with the data system software.

10.2.4.1 GC Performance -- Anthracene and phenanthrene should be separated by baseline. Benz[a]anthracene and chrysene should be separated by a valley whose height is less than 25% of the average peak height of these two compounds. If the valley between benz[a]anthracene and chrysene exceeds 25%, the GC column requires maintenance. See Section 10.3.6.

10.2.4.2 MS Sensitivity -- The GC/MS/DS peak identification software should be able to recognize a GC peak in the appropriate retention time window for each of the compounds in the calibration solution, and make correct

identifications. If fewer than 99% of the compounds are recognized, system maintenance is required. See Section 10.3.6.

10.2.5 If all performance criteria are met, inject a 1 µL aliquot of each of the other CAL solutions using the same GC/MS conditions. Calibration standards of toxaphene and Aroclors must be injected individually.

10.2.5.1 Some GC/MS systems may not be sensitive enough to detect some of the analytes in the two lowest concentration CAL solutions. In this case, the analyst should prepare additional CAL solutions at slightly higher concentrations to obtain at least five calibration points that bracket the expected analyte concentration range.

10.2.6 Calculate a response factor (RF) for each analyte of interest and surrogate for each CAL solution using the internal standard whose retention time is nearest the retention time of the analyte or surrogate. Table 2 contains suggested internal standards for each analyte and surrogate, and quantitation ions for all compounds. This calculation is supported in acceptable GC/MS data system software (Section 6.10.4), and many other software programs. The RF is a unitless number, but units used to express quantities of analyte and internal standard must be equivalent.

Note: To calibrate for multi-component analytes (toxaphene and Aroclors), one of the following methods should be used.

Option 1 - Calculate an average response factor or linear regression equation for each multi-component analyte from the combined area of all its component peaks identified in the calibration standard chromatogram, using two to three of the suggested quantitation ions in Table 2.

Option 2 - Calculate an average response factor or linear regression equation for each multi-component analyte using the combined areas of three to six of the most intense and reproducible peaks in each of the calibration standard chromatograms. Use an appropriate quantitation ion for each peak.

$$RF = \frac{(A_x)\ (Q_{is})}{(A_{is})\ (Q_x)}$$

where: A_x = integrated abundance of the quantitation ion of the analyte
A_{is} = integrated abundance of the quantitation ion internal standard
Q_x = quantity of analyte injected in ng or concentration units
Q_{is} = quantity of internal standard injected in ng or concentration units.

10.2.6.1 For each analyte and surrogate, calculate the mean RF from the analyses of the six CAL solutions. Calculate the standard deviation (SD) and the relative standard deviation (RSD) from each mean: RSD = 100 (SD/M). If the RSD of any analyte or surrogate mean RF exceeds 30%, either analyze additional aliquots of appropriate CAL solutions to obtain an acceptable RSD of RFs over the entire concentration range, or take action to improve GC/MS performance. See Section 10.3.6.

10.2.7 As an alternative to calculating mean response factors, use the GC/MS data system software or other available software to generate a linear regression calibration by plotting A_x /A_{is} vs. Q_x.

10.3 Continuing Calibration Check -- Verify the MS tune and initial calibration at the beginning of each 12-hour work shift during which analyses are performed using the following procedure.

10.3.1 Inject a 1 µL aliquot of the 5 ng/µL solution of DFTPP, endrin, and 4,4'-DDT. Acquire a mass spectrum for DFTPP that includes data for m/z 45-450. Ensure that all criteria in Section 10.2.2 are met.

10.3.2 Inject a 1 µL aliquot of a calibration solution and analyze with the same conditions used during the initial calibration. It is recommended that the concentration of calibration solution be varied, so that the calibration can be verified at more than one point.

Note: If the continuing calibration check standard contains the PCB congeners listed in Section 1.0, calibration verification is not required for each Aroclor. Calibration verification of toxaphene should be performed at least once each 24 hour period.

10.3.3 Demonstrate acceptable performance for the criteria shown in Section 10.2.4.

10.3.4 Determine that the absolute areas of the quantitation ions of the internal standards and surrogate(s) have not changed by more than 30% from the

areas measured in the most recent continuing calibration check, or by more than 50% from the areas measured during initial calibration. If these areas have decreased by more than these amounts, adjustments must be made to restore system sensitivity. These adjustments may require cleaning of the MS ion source, or other maintenance as indicated in Section 10.3.6, and recalibration. Control charts are useful aids in documenting system sensitivity changes.

10.3.5 Calculate the RF for each analyte and surrogate from the data measured in the continuing calibration check. The RF for each analyte and surrogate must be within 30% of the mean value measured in the initial calibration. Alternatively, if a linear regression is used, the calculated amount for each analyte must be ±30% of the true value. If these conditions do not exist, remedial action should be taken which may require recalibration. Any field sample extracts that have been analyzed since the last acceptable calibration verification should be reanalyzed after adequate calibration has been restored.

10.3.5.1 Because of the large number of compounds on the analyte list, it is possible for a few analytes of interest to be outside the continuing calibration criteria. If analytes that missed the calibration check are detected in samples, they may be quantified using a single point calibration. The single point standards should be prepared at concentrations that produce responses close (±20%) to those of the unknowns. If the same analyte misses the continuing calibration check on three consecutive work shifts, remedial action MUST be taken. If more than 10% of the analytes of interest miss the continuing calibration check on a single day, remedial action MUST be taken.

10.3.6 Some Possible Remedial Actions -- Major maintenance such as cleaning an ion source, cleaning quadrupole rods, replacing filament assemblies, etc. require returning to the initial calibration step.

10.3.6.1 Check and adjust GC and/or MS operating conditions; check the MS resolution, and calibrate the mass scale.

10.3.6.2 Clean or replace the splitless injection liner; silanize a new injection liner.

10.3.6.3 Flush the GC column with solvent according to manufacturer's instructions.

10.3.6.4 Break off a short portion (about 1 m) of the column from the end near the injector; or replace GC column. This action will cause a change in retention times.

10.3.6.5 Prepare fresh CAL solutions, and repeat the initial calibration step.

10.3.6.6 Clean the MS ion source and rods (if a quadrupole).

10.3.6.7 Replace any components that allow analytes to come into contact with hot metal surfaces.

10.3.6.8 Replace the MS electron multiplier, or any other faulty components.

11.0 PROCEDURE

11.1 Cartridge Extraction

11.1.1 This procedure may be carried out in the manual mode or in the automated mode (Section 6.12) using a robotic or automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's operating instructions, but follow this procedure. If the manual mode is used, a suggested setup of the extraction apparatus is shown in Figure 1A. The reservoir is not required, but recommended for convenient operation. Water drains from the reservoir through the LSE cartridge and into a syringe needle which is inserted through a rubber stopper into the suction flask. A slight vacuum of approximately 13 cm (5 in.) of mercury is used during all operations with the apparatus. About two hours should be required to draw a liter of water through the cartridge.

11.1.2 Elute each cartridge with a 5 mL aliquot of ethyl acetate followed by a 5 mL aliquot of methylene chloride. Let the cartridge drain dry after each flush. Then elute the cartridge with a 10 mL aliquot of methanol, but DO NOT allow the methanol to elute below the top of the cartridge packing. From this point, do not allow the cartridge to go dry. Add 10 mL of reagent water to the cartridge, but before the reagent water level drops below the top edge of the packing, begin adding sample to the solvent reservoir.

11.1.3 Pour the water sample into the 2 L separatory funnel with the stopcock closed, add 5 mL methanol, and mix well. If a vacuum manifold is used instead of the separatory funnel, the sample may be transferred directly

to the cartridge after the methanol is added to the sample. (Residual chlorine should not be present as a reducing agent should have been added at the time of sampling. Also the pH of the sample should be about 2. If residual chlorine is present and/or the pH is >2, the sample may be invalid.) Add a 100 µL aliquot of the fortification solution (50 µg/mL) for internal standards and surrogates, and mix immediately until homogeneous. The resulting concentration of these compounds in the water should be 5 µg/L.

11.1.4 Periodically transfer a portion of the sample into the solvent reservoir. The water sample will drain into the cartridge, and from the exit into the suction flask. Maintain the packing material in the cartridge immersed in water at all times. After all of the sample has passed through the LSE cartridge, draw air or nitrogen through the cartridge for 10 minutes.

11.1.5 Transfer the 125 mL solvent reservoir and LSE cartridge (from Figure 1A) to the elution apparatus if used (Figure 1B). The same 125 mL solvent reservoir is used for both apparatus. Rinse the inside of the 2 L separatory funnel and the sample jar with 5 mL of ethyl acetate and elute the cartridge with this rinse into the collection tube. Wash the inside of the separatory funnel and the sample jar with 5 mL methylene chloride and elute the cartridge, collecting the rinse in the same collection tube. Small amounts of residual water from the sample container and the LSE cartridge may form an immiscible layer with the eluate. Pass the eluate through the drying column (Section 6.7) which is packed with approximately 5-7 g of anhydrous sodium sulfate and collect in a second vial. Wash the sodium sulfate with at least 2 mL methylene chloride and collect in the same vial. Concentrate the extract in a warm water bath under a gentle stream of nitrogen. Do not concentrate the extract to less than 0.5 mL, as this will result in losses of analytes. Make any volume adjustments with ethyl acetate. It is recommended that an aliquot of the recovery standard be added to the concentrated extract to check the recovery of the internal standards (see Section 7.12).

11.2 Disk Extraction

11.2.1 This procedure was developed using the standard 47 mm diameter disks. Larger disks (90 mm diameter) may be used if sample compositing is being done or special matrix problems are encountered. If larger disks are used, the washing solvent volume is 15 mL, the conditioning solvent volume is 15 mL, and the elution solvent volume is two 15 mL aliquots.

11.2.1.1 Extractions using the disks may be carried out either in the manual or automatic mode (Section 6.12) using an

automatic sample preparation device. If an automatic system is used to prepare samples, follow the manufacturer's operating instructions, but follow this procedure. Insert the disk into the filter apparatus (Figure 2) or sample preparation unit. Wash the disk with 5 mL of a 1:1 mixture of ethyl acetate (EtAc) and methylene chloride (MeCl2) by adding the solvent to the disk, drawing about half through the disk, allowing it to soak the disk for about a minute, then drawing the remaining solvent through the disk.

Note: Soaking the disk may not be desirable when disks other than Teflon are used. Instead, apply a constant, low vacuum in this Section and Section 11.2.1.2 to ensure adequate contact time between solvent and disk.

11.2.1.2 Pre-wet the disk with 5 mL methanol (MeOH) by adding the MeOH to the disk and allowing it to soak for about a minute, then drawing most of the remaining MeOH through. A layer of MeOH must be left on the surface of the disk, which should not be allowed to go dry from this point until the end of the sample extraction. THIS IS A CRITICAL STEP FOR A UNIFORM FLOW AND GOOD RECOVERY.

11.2.1.3 Rinse the disk with 5 mL reagent water by adding the water to the disk and drawing most through, again leaving a layer on the surface of the disk.

11.2.2 Add 5 mL MeOH per liter of water to the sample. Mix well. (Residual chlorine should not be present as a reducing agent should have been added at the time of sampling. Also the pH of the sample should be about 2. If residual chlorine is present and/or the pH is >2, the sample may be invalid.)

11.2.3 Add 100 µL of the internal standard and surrogate compound fortification solution (50 µg/mL) to the sample and shake or mix until the sample is homogeneous. The resulting concentration of these compounds in the water should be 5 µg/L.

11.2.4 Add the water sample to the reservoir and apply full vacuum to begin the extraction. Particulate-free water may pass through the disk in as little as five minutes without reducing analyte recoveries. Extract the entire sample, draining as much water from the sample container as possible. Dry the disk by maintaining vacuum for about 10 minutes.

11.2.5 Remove the filtration top, but do not disassemble the reservoir and fritted base. If a suction flask is being used, empty the water from the flask, and insert a suitable collection tube to contain the eluant. The only constraint on the sample tube is that it fit around the drip tip of the fritted base. Reassemble the apparatus.

11.2.6 Add 5 mL of ethyl acetate to the sample bottle, and rinse the inside walls thoroughly. Allow the solvent to settle to the bottom of the bottle, then transfer it to the disk. A disposable pipet or syringe may be used to do this, rinsing the sides of the glass filtration reservoir in the process. Draw about half of the solvent through the disk, release the vacuum, and allow the disk to soak for a minute. Draw the remaining solvent through the disk.

Note: Soaking the disk may not be desirable if disks other than Teflon are used. Instead, apply a constant, low vacuum in this Section and Section 11.2.7 to ensure adequate contact time between solvent and disk.

11.2.7 Repeat the above step (Section 11.2.6) with methylene chloride.

11.2.8 Using a syringe or disposable pipet, rinse the filtration reservoir with two 3 mL portions of 1:1 EtAc:MeCl2. Draw the solvent through the disk and into the collector tube. Pour the combined eluates (Section 11.2.6 through Section 11.2.8) through the drying tube (Section 6.7) containing about 5-7 g of anhydrous sodium sulfate. Rinse the drying tube and sodium sulfate with two 3 mL portions of 1:1 EtAc:MeCl2 mixture. Collect all the extract and washings in a concentrator tube.

11.2.9 While gently heating the extract in a water bath or a heating block, concentrate to between 0.5 mL and 1 mL under a gentle stream of nitrogen. Do not concentrate the extract to less than 0.5 mL, since this will result in losses of analytes. Make any volume adjustments with ethyl acetate. It is recommended that an aliquot of the recovery standard be added to the concentrated extract to check the recovery of the internal standards (see Section 7.12).

11.3 Analyze a 1 µL aliquot with the GC/MS system under the same conditions used for the initial and continuing calibrations (Section 10.2.3).

11.4 At the conclusion of data acquisition, use the same software that was used in the calibration procedure to tentatively identify peaks in predetermined retention time windows of interest. Use the data system software to examine the ion abundances of components of the chromatogram.

11.5 Identification of Analytes -- Identify a sample component by comparison of its mass spectrum (after background subtraction) to a reference spectrum in the user-created data base. The GC retention time of the sample component should be within five seconds of the retention time observed for that same compound in the most recently analyzed continuing calibration check standard.

11.5.1 In general, all ions that are present above 10% relative abundance in the mass spectrum of the standard should be present in the mass spectrum of the sample component and should agree within absolute 20%. For example, if an ion has a relative abundance of 30% in the standard spectrum, its abundance in the sample spectrum should be in the range of 10-50%. Some ions, particularly the molecular ion, are of special importance, and should be evaluated even if they are below 10% relative abundance.

11.5.2 Identification is hampered when sample components are not resolved chromatographically and produce mass spectra containing ions contributed by more than one analyte. When GC peaks obviously represent more than one sample component (i.e., broadened peak with shoulder(s) or valley between two or more maxima), appropriate analyte spectra and background spectra can be selected by examining plots of characteristic ions for tentatively identified components. When analytes coelute (i.e., only one GC peak is apparent), the identification criteria can be met but each analyte spectrum will contain extraneous ions contributed by the coeluting compound.

11.5.3 Structural isomers that produce very similar mass spectra can be explicitly identified only if they have sufficiently different GC retention times. See Section 10.2.4.1. Acceptable resolution is achieved if the height of the valley between two isomer peaks is less than 25% of the average height of the two peak heights. Otherwise, structural isomers are identified as isomeric pairs. Benzo[b] and benzo[k]fluoranthene may be measured as an isomeric pair. MGK 264 is made up of two structural isomers. These are listed separately in the data tables.

11.5.4 Each multi-component analyte can be identified by the presence of its individual components in a characteristic pattern based on the relative amounts of each component present. Chromatograms of standard materials of multi-component analytes should be carefully evaluated, so that these patterns can be recognized by the analyst.

12.0 DATA ANALYSIS AND CALCULATIONS

12.1 Complete chromatographic resolution is not necessary for accurate and precise measurements of analyte concentrations if unique ions with adequate intensities are available for quantitation. In validating this method, concentrations were calculated by measuring the characteristic ions listed in Table 2. If the response of any analyte exceeds the calibration rage established in Section 10.0, dilute the extract and reanalyze.

12.1.1 Calculate analyte and surrogate concentrations, using the multipoint calibration established in Section 10.0. Do not use daily calibration verification data to quantitate analytes in samples.

$$C_x = \frac{(A_x)\ (Q_{is})}{(A_{is})\ RF\ V}$$

where: C_x = concentration of analyte or surrogate in µg/L in the water sample

A_x = integrated abundance of the quantitation ion of the analyte in the sample

A_{is} = integrated abundance of the quantitation ion of the internal standard in the sample

Q_{is} = total quantity (in micrograms) of internal standard added to the water sample

V = original water sample volume in liters

RF = mean response factor of analyte from the initial calibration. RF is a unitless value

12.1.2 Alternatively, use the GC/MS system software or other available proven software to compute the concentrations of the analytes and surrogates from the linear regression established in Section 10.0. Do not use daily calibration verification data to quantitate analytes in samples.

12.1.3 Calculations should utilize all available digits of precision, but final reported concentrations should be rounded to an appropriate number of significant figures (one digit of uncertainty). Experience indicates that three significant figures may be used for concentrations above 99 µg/L, two significant figures for concentrations between 1-99 µg/L, and one significant figure for lower concentrations.

12.2 To quantitate multi-component analytes (toxaphene and Aroclors), one of the following methods should be used.

Option 1 - Calculate an average RF or linear regression equation for each multi-component analyte from the combined area of all its component peaks identified in the calibration standard chromatogram, using two to three of the suggested quantitation ions in Table 2.

Option 2 - Calculate an average response factor or linear regression equation for each multi-component analyte using the combined areas of three to six of the most intense and reproducible peaks in each of the calibration standard chromatograms.

When quantifying multi-component analytes in samples, the analyst should use caution to include only those peaks from the sample that are attributable to the multi-component analyte. Option 1 should not be used if there are significant interference peaks within the Aroclor or toxaphene pattern. Option 2 was used to generate the data in Table 6.

13.0 METHOD PERFORMANCE

13.1 Single laboratory accuracy and precision data (Tables 3-6) for each listed analyte (except multi-component analytes) were obtained at a concentration of 0.5 µg/L and/or 5 µg/L in reagent water utilizing both the disk and the cartridge technology and two different GC/MS systems, an ion trap and a quadrupole mass spectrometer. Table 8 lists accuracy and precision data from replicate determinations of method analytes in tap water using liquid-solid cartridge extractions and the ion trap mass spectrometer. Any type of GC/MS system may be used to perform this method if it meets the requirement in Sect. 6.10 and the quality control criteria in Section 9.0. The multi-component analytes (i.e., toxaphene and Aroclors) are presented in Tables 5 and 6. The average recoveries in the tables represent six to eight replicate analyses done over a minimum of a two-day period.

13.1.2 With these data, the method detection limits (MDL) in the tables were calculated using the formula:

$$MDL = S\ t_{(n-1,\ 1-alpha\ =\ 0.99)}$$

where: $t_{(n-1,1-alpha\ =\ 0.99)}$ = Student's t value for the 99% confidence level with n-1 degrees of freedom

n = number of replicates

S = standard deviation of replicate analyses

13.2 Problem Compounds

13.2.1 Some polycyclic aromatic hydrocarbons (PAH), including the labeled PAHs used in this method as internal standards, are rapidly oxidized and/or chlorinated in water containing residual chlorine. Therefore, residual chlorine must be reduced at the time of sampling. These same types of compounds, especially anthracene, benz[a]anthracene, and benzo[a]pyrene, are susceptible to photodegradation. Therefore, care should be taken to avoid exposing standards, samples, and extracts to direct light. Low recoveries of some PAH compounds have been observed when the cartridge or disk was air dried longer than 10 minutes (Section 11.1.4 and Section 11.2.4). Drying times longer than 10 minutes should be avoided, or nitrogen may be used to dry the cartridge or disk to minimize the possible oxidation of these analytes during the drying step.

13.2.2 Merphos is partially converted to DEF in aqueous matrices, and also when introduced into a hot gas chromatographic injection system. The efficiency of this conversion appears to be unpredictable and not reproducible. Therefore, merphos cannot be quantified and can only be identified by the presence of DEF in the sample.

13.2.3 Several of the nitrogen and/or phosphorus containing pesticides listed as method analytes are difficult to chromatograph and appear as broad, asymmetrical peaks. These analytes, whose peak shapes are typically poor, are listed in Table 7. The method performance for these analytes is strongly dependent on chromatographic efficiency and performance. Poor peak shapes will affect the linearity of the calibration curves and result in poor accuracy at low concentrations. Also listed in Table 7 are data generated at a mid-concentration level for these analytes. In most cases, the data at this concentration meet the quality control criteria requirements of the method.

13.2.4 Phthalate esters and other background components appear in variable quantities in laboratory and field reagent blanks, and generally cannot be accurately measured at levels below about 2 µg/L. Subtraction of the concentration in the blank from the concentration in the sample at or below the 2 µg/L level is not recommended because the concentration of the background in the blank is highly variable.

13.2.5 Atraton and prometon are not efficiently extracted from the water at pH 2 due to what appears to be their ionization occurring in solution under acidic conditions. In order to determine these analytes accurately, a separate sample must be collected and dechlorinated with sodium sulfite, but no HCl should be added at the time of collection. At neutral pH, these two compounds are recovered from water with efficiencies greater

than 90%. The data in Tables 3, 4, 5, 6, and 8 are from samples extracted at pH 2.

13.2.6 Carboxin, disulfoton, and disulfoton sulfoxide were found to be unstable in water and began to degrade almost immediately. These analytes may be identified by this method but not accurately measured.

13.2.7 Low recoveries of metribuzin were observed in samples fortified with relatively high concentrations of additional method analytes. In samples fortified with approximately 80 analytes at 5 µg/L each, metribuzin was recovered at about 50% efficiency. This suggests that metribuzin may break through the C-18 phase in highly contaminated samples resulting in low recoveries.

13.2.8 If cyanazine is to be determined, a separate sample must be collected. Cyanazine degrades in the sample when it is stored under acidic conditions or when sodium sulfite is present in the stored sample. Samples collected for cyanazine determination MUST NOT be dechlorinated or acidified when collected. They should be iced or refrigerated and analyzed within 14 days. However, these samples MUST be dechlorinated and acidified immediately prior to fortification with internal standards and surrogates, and extraction using the same quantities of acid and sodium sulfite described in Section 8.0.

14.0 POLLUTION PREVENTION

14.1 This method utilizes liquid-solid extraction (LSE) technology to remove the analytes from water. It requires the use of very small volumes of organic solvent and very small quantities of pure analytes, thereby eliminating the potential hazards to both the analyst and the environment involved with the use of large volumes of organic solvents in conventional liquid-liquid extractions.

14.2 For information about pollution prevention that may be applicable to laboratory operations, consult "Less Is Better: Laboratory Chemical Management for Waste Reduction" available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington, D.C. 20036.

15.0 WASTE MANAGEMENT

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particu-larly the hazardous waste identification rules and land disposal restrictions. The laboratory using this method has the respons-ibility to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance

is also required with any sewage discharge permits and regulations. For further information on waste management, see "The Waste Management Manual for Laboratory Personnel", also avail-able from the American Chemical Society at the address in Section 14.2.

16.0 REFERENCES

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2. "Carcinogens - Working With Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

3. "OSHA Safety and Health Standards, General Industry", (29CFR1910), Occupational Safety and Health Administration, OSHA 2206, (Revised, January 1976).

4. "Safety in Academic Chemistry Laboratories", American Chemical Society Publication, Committee on Chemical Safety, 3rd Edition, 1979.

5. Junk, G. A., M. J. Avery, J. J. Richard. "Interferences in Solid-Phase Extraction Using C-18 Bonded Porous Silica Cartridges", Anal. Chem. 1988, 60, 1347.

17.0 TABLES, DIAGRAMS, FLOWCHARTS, AND VALIDATION DATA

TABLE 1. ION ABUNDANCE CRITERIA FOR BIS(PERFLUORO-PHENYL)PHENYL PHOSPHINE (DECAFLUOROTRIPHENYL-PHOSPHINE, DFTPP)

Mass (M/z)	Relative Abundance Criteria	Purpose of Checkpoint[1]
51	10-80% of the base peak	Low-mass sensitivity
68	<2% of Mass 69	Low-mass resolution
70	<2% of Mass 69	Low-mass resolution
127	10-80% of the base peak	Low- to mid-mass sensitivity
197	<2% of Mass 198	Mid-mass resolution
198	Base peak or >50% of Mass 442	Mid-mass resolution and sensitivity
199	5-9% of Mass 198	Mid-mass resolution and isotope ratio
275	10-60% of the base peak	Mid- to high-mass sensitivity
365	>1% of the base peak	Baseline threshold
441	Present and < Mass 443	High-mass resolution
442	Base peak or >50% of Mass 198	High-mass resolution and sensitivity
443	15-24% of Mass 442	High-mass resolution and isotope ratio

[1]All ions are used primarily to check the mass measuring accuracy of the mass spectrometer and data system, and this is the most important part of the performance test. The three resolution checks, which include natural abundance isotope ratios, constitute the next most important part of the performance test. The correct setting of the baseline threshold, as indicated by the presence of low intensity ions, is the next most important part of the performance test. Finally, the ion abundance ranges are designed to encourage some standardization to fragmentation patterns.

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
Internal Standards				
Acenaphthene-d10 (#1)	7:47	7:01	164	
Chrysene-d12 (#2)	21:33	18:09	240	
Phenanthrene-d10 (#3)	11:37	10:13	188	
Surrogates				
1,3-Dimethyl-2-Nitrobenzene	5:16	4:33	134	1
Perylene-d12	26:60	21:31	264	3
Triphenylphosphate	20:25	17:25	326/325	3
Target Analytes				
Acenaphthylene	7:30	6:46	152	1
Alachlor	12:59	11:24	160	2
Aldrin	14:24	12:31	66	2
Ametryn	13:11	11:35	227/170	2
Anthracene	11:50	10:24	178	2
Aroclor 1016		7:30-14:00	152/256/292	2
Aroclor 1221		6:38-11:25	152/222/256	2
Aroclor 1232		6:38-13:54	152/256/292	2
Aroclor 1242		6:38-15:00	152/256/292	2
Aroclor 1248		8:47-15:00	152/256/292	2
Aroclor 1254		11:00-18:00	220/326/360	2
Aroclor 1260		13:10-21:00	326/360/394	2
Atraton	10:31	9:25	196/169	1
Atrazine	10:49	9:38	200/215	1/2
Benz[a]anthracene	21:31	18:08	228	3
Benzo[b]fluoranthene	25:33	20:44	252	3
Benzo[k]fluoranthene	25:45	20:48	252	3
Benzo[g,h,i]perylene	31:16	24:18	276	3
Benzo[a]pyrene	25:24	21:25	252	3
Bromacil	13:46	12:03	205	2
Butachlor	16:25	14:16	176/160	2
Butylate	6:60	6:23	57/146	1
Butylbenzylphthalate	19:39	16:53	149	2/3
Carboxin	17:37	15:13	143	2
Chlordane, (alpha-Chlordane)	16:43	14:28	375/373	2/3

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
Chlordane, (gamma-Chlordane)	16:19	14:05	373	2/3
Chlordane, (trans-Nonachlor)	16:47	14:30	409	2/3
Chlorneb	7:47	7:05	191	1
Chlorobenzilate	18:22	15:52	139	2
2-Chlorobiphenyl	7:53	7:08	188	1
Chlorpropham	9:33	8:36	127	1
Chlorpyrifos	14:10	12:23	197/97	2
Chlorothalonil	11:38	10:15	266	2
Chrysene	21:39	18:13	228	3
Cyanazine	14:14	12:28	225/68	2
Cycloate	9:23	8:26	83/154	1
DCPA	14:20	12:30	301	2
4,4'-DDD	18:40	16:05	235/165	2
4,4'-DDE	17:20	14:59	246	2
4,4'-DDT	19:52	17:00	235/165	2
DEF	17:24	15:05	57/169	2
Diazinon	11:19	10:05	137/179	2
Dibenz[a,h]anthracene	30:32	23:47	278	3
Di-n-Butylphthalate	13:49	12:07	149	2
2,3-Dichlorobiphenyl	10:20	9:12	222/152	1
Dichlorvos	5:31	4:52	109	1
Dieldrin	17:35	15:09	79	2
Di(2-Ethylhexyl)adipate	20:11	17:19	129	2/3
Di(2-Ethylhexyl)phthalate	22:11	18:39	149	2/3
Diethylphthalate	8:68	7:53	149	1
Dimethylphthalate	7:13	6:34	163	1
2,4-Dinitrotoluene	8:08	7:22	165	1
2,6-Dinitrotoluene	7:19	6:40	165	1
Diphenamid	14:52	12:58	72/167	2
Disulfoton	11:43	10:22	88	2
Disulfoton Sulfone	16:28	14:17	213/153	2
Disulfoton Sulfoxide	6:09	5:31	97	1
Endosulfan I	16:44	14:26	195	2
Endosulfan II	18:35	15:59	195	2
Endosulfan Sulfate	19:47	16:54	272	2
Endrin	18:15	15:42	67/81	2
Endrin Aldehyde	19:02	16:20	67	2
EPTC	6:23	5:46	128	1
Ethoprop	9:19	8:23	158	1

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
Etridiazole	7:14	6:37	211/183	1
Fenamiphos	16:48	14:34	303/154	2
Fenarimol	23:26	19:24	139	3
Fluorene	8:59	8:03	166	1
Fluridone	26:51	21:26	328	3
HCH, alpha	10:19	9:10	181	1
HCH, beta	10:57	9:41	181	2
HCH, delta	11:57	10:32	181	2
HCH, gamma (Lindane)	11:13	9:54	181	2
Heptachlor	13:19	11:37	100	2
Heptachlor epoxide	15:34	13:29	81	2
2,2',3,3',4,4',6-Heptachlorobiphenyl	21:23	18:04	394/396	3
Hexachlorobenzene	10:27	9:15	284	1
2,2',4,4',5,6'-Hexachlorobiphenyl	17:32	15:09	360	2
Hexachlorocyclopentadiene	5:16	5:38	237	1
Hexazinone	20:00	17:06	171	2
Indeno[1,2,3-cd]pyrene	30:26	23:43	276	3
Isophorone	4:54	4:10	82	1
Merphos	15:38	13:35	209/153	2
Methoxychlor	21:36	18:14	227	3
Methyl Paraoxon	11:57	10:22	109	2
Metolachlor	14:07	12:20	162	2
Metribuzin	12:46	11:13	198	2
Mevinphos	5:54	6:19	127	1
MGK 264 - Isomer a	15:18	13:00	164/66	2
MGK 264 - Isomer b	14:55	13:19	164	2
Molinate	8:19	7:30	126	1
Napropamide	16:53	14:37	72	2
Norflurazon	19:31	16:46	145	2
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	21:33	18:11	430/428	3
Pebulate	7:18	6:40	128	1
2,2',3',4,6-Pentachlorobiphenyl	15:37	13:33	326	2
Pentachlorophenol	11:01	9:45	266	2
Permethrin, cis	24:25	20:01	183	3
Permethrin, trans	24:39	20:10	183	3
Phenanthrene	11:41	10:16	178	2
Prometon	10:39	9:32	225/168	2

TABLE 2. RETENTION TIME DATA, QUANTITATION IONS, AND INTERNAL STANDARD REFERENCES FOR METHOD ANALYTES

Compound	Retention Time (min:sec) A[a]	Retention Time (min:sec) B[b]	Quantitation Ion	IS Reference #
Prometryn	13:15	11:39	241/184	2
Pronamide	11:19	10:02	173	2
Propachlor	9:00	8:07	120	1
Propazine	10:54	9:43	214/172	2
Pyrene	16:41	14:24	202	2
Simazine	10:41	9:33	201/186	2
Simetryn	13:04	11:29	213	2
Stirofos	16:20	14:11	109	2
Tebuthiuron	8:00	7:16	156	1
Terbacil	11:44	10:24	161	2
Terbufos	11:14	9:58	57	2
Terbutryn	13:39	11:58	226/185	2
2,2',4,4'-Tetrachlorobiphenyl	14:02	12:14	292	2
Toxaphene		13:00-21:00	159	2
Triademefon	14:30	12:40	57	2
2,4,5-Trichlorobiphenyl	12:44	10:53	256	2
Tricyclazole	17:15	14:51	189	2
Trifluralin	9:31	8:37	306	1
Vernolate	7:10	6:32	128	1

[a]Single-ramp linear temperature program conditions (Section 10.2.3.2).
[b]Multi-ramp linear temperature program conditions (Section 10.2.3.1).

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
<u>Surrogates</u>					
1,3-Dimethyl-2-Nitrobenzene	5.0	4.7	3.9	94	
Perylene-d12	5.0	4.9	4.8	98	
Triphenylphosphate	5.0	5.5	6.3	110	
<u>Target Analytes</u>					
Acenaphthylene	0.50	0.45	8.2	91	0.11
Alachlor	0.50	0.47	12	93	0.16
Aldrin	0.50	0.40	9.3	80	0.11
Ametryn	0.50	0.44	6.9	88	0.092
Anthracene	0.50	0.53	4.3	106	0.068
Aroclor 1016	ND	ND	ND	ND	ND
Aroclor 1221	ND	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND	ND
Aroclor 1448	ND	ND	ND	ND	ND
Aroclor 1254	ND	ND	ND	ND	ND
Aroclor 1260	ND	ND	ND	ND	ND
Atraton[a]	0.50	0.35	15	70	0.16
Atrazine	0.50	0.54	4.8	109	0.078
Benz[a]anthracene	0.50	0.41	16	82	0.20
Benzo[b]fluoranthene	0.50	0.49	20	98	0.30
Benzo[k]fluoranthene	0.50	0.51	35	102	0.54
Benzo[g,h,i]perylene	0.50	0.72	2.2	144	0.047
Benzo[a]pyrene	0.50	0.58	1.9	116	0.032
Bromacil	0.50	0.54	6.4	108	0.10
Butachlor	0.50	0.62	4.1	124	0.076
Butylate	0.50	0.52	4.1	105	0.064
Butylbenzylphthalate	0.50	0.77	11	154	0.25
Carboxin	5.0	3.8	12	76	1.4
Chlordane (alpha-Chlordane)	0.50	0.36	11	72	0.12
Chlordane (gamma-Chlordane)	0.50	0.40	8.8	80	0.11
Chlordane (trans-Nonachlor)	0.50	0.43	17	87	0.22

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Chlorneb	0.50	0.51	5.7	102	0.088
Chlorobenzilate	5.0	6.5	6.9	130	1.3
2-Chlorobiphenyl	0.50	0.40	7.2	80	0.086
Chlorpropham	0.50	0.61	6.2	121	0.11
Chlorpyrifos	0.50	0.55	2.7	110	0.044
Chlorothalonil	0.50	0.57	6.9	113	0.12
Chrysene	0.50	0.39	7.0	78	0.082
Cyanazine	0.50	0.71	8.0	141	0.17
Cycloate	0.50	0.52	6.1	104	0.095
DCPA	0.50	0.55	5.8	109	0.094
4,4'-DDD	0.50	0.54	4.4	107	0.071
4,4'-DDE	0.50	0.40	6.3	80	0.075
4,4'-DDT	0.50	0.79	3.5	159	0.083
Diazinon	0.50	0.41	8.8	83	0.11
Dibenz[a,h]anthracene	0.50	0.53	0.5	106	0.010
Di-n-butylphthalate	ND	ND	ND	ND	ND
2,3-Dichlorobiphenyl	0.50	0.40	11	80	0.14
Dichlorvos	0.50	0.55	9.1	110	0.15
Dieldrin	0.50	0.48	3.7	96	0.053
Di(2-ethylhexyl)adipate	0.50	0.42	7.1	84	0.090
Di(2-ethylhexyl)phthalate	ND	ND	ND	ND	ND
Diethylphthalate	0.50	0.59	9.6	118	0.17
Dimethylphthalate	0.50	0.60	3.2	120	0.058
2,4-Dinitrotoluene	0.50	0.60	5.6	119	0.099
2,6-Dinitrotoluene	0.50	0.60	8.8	121	0.16
Diphenamid	0.50	0.54	2.5	107	0.041
Disulfoton	5.0	3.99	5.1	80	0.62
Disulfoton Sulfone	0.50	0.74	3.2	148	0.070
Disulfoton Sulfoxide	0.50	0.58	12	116	0.20
Endosulfan I	0.50	0.55	18	110	0.30
Endosulfan II	0.50	0.50	29	99	0.44
Endosulfan Sulfate	0.50	0.62	7.2	124	0.13
Endrin	0.50	0.54	18	108	0.29
Endrin Aldehyde	0.50	0.43	15	87	0.19

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
EPTC	0.50	0.50	7.2	100	0.11
Ethoprop	0.50	0.62	6.1	123	0.11
Etridiazole	0.50	0.69	7.6	139	0.16
Fenamiphos	5.0	5.2	6.1	103	0.95
Fenarimol	5.0	6.3	6.5	126	1.2
Fluorene	0.50	0.46	4.2	93	0.059
Fluridone	5.0	5.1	3.6	102	0.55
HCH, alpha	0.50	0.51	13	102	0.20
HCH, beta	0.50	0.51	20	102	0.31
HCH, delta	0.50	0.56	13	112	0.21
HCH, gamma (Lindane)	0.50	0.63	8.0	126	0.15
Heptachlor	0.50	0.41	12	83	0.15
Heptachlor Epoxide	0.50	0.35	5.5	70	0.058
2,2',3,3',4,4',6-Heptachlorobiphenyl	0.50	0.35	10	71	0.11
Hexachlorobenzene	0.50	0.39	11	78	0.13
2,2',4,4',5,6'-Hexachlorobiphenyl	0.50	0.37	9.6	73	0.11
Hexachlorocyclopentadiene	0.50	0.43	5.6	86	0.072
Hexazinone	0.50	0.70	5.0	140	0.11
Indeno[1,2,3-cd]pyrene	0.50	0.69	2.7	139	0.057
Isophorone	0.50	0.44	3.2	88	0.042
Methoxychlor	0.50	0.62	4.2	123	0.077
Methyl Paraoxon	0.50	0.57	10	115	0.17
Metolachlor	0.50	0.37	8.0	75	0.090
Metribuzin	0.50	0.49	11	97	0.16
Mevinphos	0.50	0.57	12	114	0.20
MGK 264 - Isomer a	0.33	0.39	3.4	116	0.040
MGK 264 - Isomer b	0.17	0.16	6.4	96	0.030
Molinate	0.50	0.53	5.5	105	0.087
Napropamide	0.50	0.58	3.5	116	0.060
Norflurazon	0.50	0.63	7.1	126	0.13
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	0.50	0.50	8.7	101	0.13
Pebulate	0.50	0.49	5.4	98	0.080
2,2',3',4,6-Pentachlorobiphenyl	0.50	0.30	16	61	0.15

TABLE 3. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Pentachlorophenol	ND	ND	ND	ND	ND
Permethrin, cis	0.25	0.30	3.7	121	0.034
Permethrin, trans	0.75	0.82	2.7	109	0.067
Phenathrene	0.50	0.46	4.3	92	0.059
Prometon[a]	0.50	0.30	42	60	0.38
Prometryn	0.50	0.46	5.6	92	0.078
Pronamide	0.50	0.54	5.9	108	0.095
Propachlor	0.50	0.49	7.5	98	0.11
Propazine	0.50	0.54	7.1	108	0.12
Pyrene	0.50	0.38	5.7	77	0.066
Simazine	0.50	0.55	9.1	109	0.15
Simetryn	0.50	0.52	8.2	105	0.13
Stirofos	0.50	0.75	5.8	149	0.13
Tebuthiuron	5.0	6.8	14	136	2.8
Terbacil	5.0	4.9	14	97	2.1
Terbufos	0.50	0.53	6.1	106	0.096
Terbutryn	0.50	0.47	7.6	95	0.11
2,2',4,4'-Tetrachlorobiphenyl	0.50	0.36	4.1	71	0.044
Toxaphene	ND	ND	ND	ND	ND
Triademefon	0.50	0.57	20	113	0.33
2,4,5-Trichlorobiphenyl	0.50	0.38	6.7	75	0.075
Tricyclazole	5.0	4.6	19	92	2.6
Trifluralin	0.50	0.63	5.1	127	0.096
Vernolate	0.50	0.51	5.5	102	0.084

ND = Not determined.

[a]Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-Dimethyl-2-Nitrobenzene	5.0	4.6	2.6	93	
Perylene-d12	5.0	4.8	1.6	95	
Triphenylphosphate	5.0	5.0	2.5	101	
Target Analytes					
Acenaphthylene	0.50	0.47	8.4	94	0.12
Alachlor	0.50	0.50	5.8	100	0.087
Aldrin	0.50	0.39	13	78	0.16
Ametryn	0.50	0.38	28	76	0.32
Anthracene	0.50	0.49	13	98	0.18
Aroclor 1016	ND	ND	ND	ND	ND
Aroclor 1221	ND	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND	ND
Aroclor 1248	ND	ND	ND	ND	ND
Aroclor 1254	ND	ND	ND	ND	ND
Aroclor 1260	ND	ND	ND	ND	ND
Atraton[a]	0.50	0.07	139	19	0.29
Atrazine	0.50	0.60	3.7	119	0.065
Benz[a]anthracene	0.50	0.38	6.1	76	0.070
Benzo[b]fluoranthene	0.50	0.61	2.5	121	0.046
Benzo[k]fluoranthene	0.50	0.61	27	122	0.50
Benzo[g,h,i]perylene	0.50	0.69	1.4	138	0.029
Benzo[a]pyrene	0.50	0.58	6.1	116	0.11
Bromacil	0.50	0.49	23	99	0.34
Butachlor	0.50	0.63	2.1	127	0.039
Butylate	0.50	0.50	4.9	99	0.073
Butylbenzylphthalate	0.50	0.78	5.5	156	0.13
Carboxin	5.0	2.7	12	54	0.98
Chlordane (alpha-Chlordane)	0.50	0.37	5.5	74	0.061
Chlordane (gamma-Chlordane)	0.50	0.40	4.2	80	0.050
Chlordane (trans-Nonachlor)	0.50	0.45	7.8	90	0.11
Chlorneb	0.50	0.51	7.3	100	0.11
Chlorobenzilate	5.0	7.9	8.4	156	2.0

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
2-Chlorobiphenyl	0.50	0.42	1.9	84	0.023
Chlorpropham	0.50	0.68	5.4	134	0.11
Chlorpyrifos	0.50	0.61	6.5	119	0.12
Chlorothalonil	0.50	0.59	6.5	116	0.11
Chrysene	0.50	0.35	3.6	71	0.038
Cyanazine	0.50	0.68	15	136	0.31
Cycloate	0.50	0.53	4.9	106	0.077
DCPA	0.50	0.55	4.5	110	0.073
4,4'-DDD	0.50	0.67	14	137	0.28
4,4'-DDE	0.50	0.48	4.9	96	0.070
4,4'-DDT	0.50	0.93	3.2	187	0.090
Diazinon	0.50	0.56	6.8	109	0.11
Dibenz[a,h]anthracene	0.50	0.61	15	122	0.28
Di-n-Butylphthalate	ND	ND	ND	ND	ND
2,3-Dichlorobiphenyl	0.50	0.46	8.1	93	0.11
Dichlorvos	0.50	0.54	5.6	108	0.092
Dieldrin	0.50	0.52	7.8	104	0.12
Di-(2-ethylhexyl)adipate	ND	ND	ND	ND	ND
Di(2-ethylhexyl)phthalate	ND	ND	ND	ND	ND
Diethylphthalate	0.50	0.66	10	132	0.20
Dimethylphthalate	0.50	0.57	8.3	114	0.14
2,4-Dinitrotoluene	0.50	0.54	5.7	109	0.093
2,6-Dinitrotoluene	0.50	0.48	4.9	96	0.071
Diphenamid	0.50	0.60	3.8	118	0.067
Disulfoton	5.0	4.8	9.4	96	1.3
Disulfoton Sulfone	0.50	0.82	2.8	164	0.070
Disulfoton Sulfoxide	0.50	0.68	8.9	136	0.18
Endosulfan I	0.50	0.65	10	132	0.20
Endosulfan II	0.50	0.60	21	122	0.38
Endosulfan Sulfate	0.50	0.67	6.1	133	0.12
Endrin	0.50	0.58	18	116	0.31
Endrin Aldehyde	0.50	0.51	16	101	0.24
EPTC	0.50	0.50	3.8	100	0.056
Ethoprop	0.50	0.69	2.3	138	0.048
Etridiazole	0.50	0.74	4.0	149	0.090

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Fenamiphos	5.0	6.3	8.8	124	1.6
Fenarimol	5.0	7.5	5.5	150	1.2
Fluorene	0.50	0.47	8.1	94	0.11
Fluridone	5.0	5.7	4.5	114	0.77
HCH, alpha	0.50	0.54	12	107	0.20
HCH, beta	0.50	0.57	17	112	0.28
HCH, delta	0.50	0.61	8.2	120	0.15
HCH, gamma (Lindane)	0.50	0.62	6.6	124	0.12
Heptachlor	0.50	0.40	12	80	0.14
Heptachlor Epoxide	0.50	0.36	8.7	71	0.093
2,2',3,3',4,4',6-Heptachlorobiphenyl	0.50	0.36	13	71	0.14
Hexachlorobenzene	0.50	0.47	8.3	95	0.12
2,2',4,4',5,6'-Hexachlorobiphenyl	0.50	0.41	11	83	0.13
Hexachlorocyclopentadiene	0.50	0.42	12	84	0.16
Hexazinone	0.50	0.85	5.6	169	0.14
Indeno[1,2,3-cd]pyrene	0.50	0.69	2.4	138	0.050
Isophorone	0.50	0.41	4.2	83	0.052
Methoxychlor	0.50	0.58	1.9	117	0.033
Methyl Paraoxon	0.50	0.62	14	122	0.25
Metolachlor	0.50	0.38	7.5	75	0.084
Metribuzin	0.50	0.54	3.9	107	0.062
Mevinphos	0.50	0.72	3.7	143	0.079
MGK 264 - Isomer a	0.33	0.40	8.8	119	0.10
MGK 264 - Isomer b	0.17	0.17	5.9	103	0.030
Molinate	0.50	0.53	3.2	105	0.050
Napropamide	0.50	0.64	5.9	126	0.11
Norflurazon	0.50	0.70	4.2	141	0.089
2,2',3,3',4,5',6,6'-Octachloro-biphenyl	0.50	0.51	4.2	102	0.064
Pebulate	0.50	0.48	5.8	96	0.084
2,2',3',4,6-Pentachlorobiphenyl	0.50	0.35	4.2	70	0.044
Pentachlorophenol	2.0	1.9	16	95	.89
Permethrin,cis	0.25	0.32	3.3	126	0.031
Permethrin,trans	0.75	0.89	1.9	118	0.051

TABLE 4. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE QUADRUPOLE MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Phenathrene	0.50	0.48	5.0	95	0.071
Prometon[a]	0.50	0.21	66	45	0.44
Prometryn	0.50	0.46	24	93	0.33
Pronamide	0.50	0.58	7.1	113	0.12
Propachlor	0.50	0.49	5.4	98	0.079
Propazine	0.50	0.59	5.0	117	0.088
Pyrene	0.50	0.40	3.2	79	0.038
Simazine	0.50	0.60	10	120	0.18
Simetryn	0.50	0.41	15	83	0.19
Stirofos	0.50	0.84	3.2	168	0.081
Tebuthiuron	5.0	9.3	8.6	187	2.4
Terbacil	5.0	5.0	11	100	1.7
Terbufos	0.50	0.62	4.2	123	0.077
Terbutryn	0.50	0.46	23	94	0.32
2,2',4,4'-Tetrachlorobiphenyl	0.50	0.40	7.4	79	0.088
Toxaphene	ND	ND	ND	ND	ND
Triademefon	0.50	0.73	7.2	145	0.16
2,4,5-Trichlorobiphenyl	0.50	0.44	5.3	89	0.071
Tricyclazole	5.0	6.8	12	137	2.4
Trifluralin	0.50	0.62	2.6	124	0.048
Vernolate	0.50	0.51	3.4	100	0.051

ND = Not determined.

[a]Data from samples extracted at ph 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-Dimethyl-2-Nitrobenzene	5.0	4.9	8.4	98	
Perylene-d12	5.0	4.3	18	86	
Triphenylphosphate	5.0	4.8	13	96	
Target Analytes					
Acenaphthylene	0.50	0.50	8.8	100	0.13
Alachlor	0.50	0.58	4.0	115	0.069
Aldrin	0.50	0.42	3.5	85	0.045
Ametryn	0.50	0.46	3.3	91	0.045
Anthracene	0.50	0.42	3.8	84	0.048
Aroclor 1016	1.0	1.1	4.4	113	0.15
Aroclor 1221	ND	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND	ND
Aroclor 1248	ND	ND	ND	ND	ND
Aroclor 1254[a]	1.0	1.1	17	110	0.56
Aroclor 1260	1.0	0.96	9.3	96	0.27
Atraton[c]	0.50	0.35	11	70	0.12
Atrazine	0.50	0.55	5.0	109	0.081
Benz[a]anthracene	0.50	0.43	7.3	85	0.093
Benzo[b]fluoranthene	0.50	0.44	16	88	0.21
Benzo[k]fluoranthene	0.50	0.34	22	68	0.23
Benzo[g,h,i]perylene	0.50	0.38	31	76	0.35
Benzo[a]pyrene	0.50	0.36	21	73	0.23
Bromacil	0.50	0.45	9.1	90	0.12
Butachlor	0.50	0.67	12	133	0.24
Butylate	0.50	0.52	5.2	104	0.082
Butylbenzylphthalate[b]	5.0	5.7	7.7	114	1.4
Carboxin	0.50	0.58	22	117	0.38
Chlordane, (alpha-Chlordane)	0.50	0.47	12	95	0.17
Chlordane, (gamma-Chlordane)	0.50	0.50	10	99	0.16
Chlordane, (trans-Nonachlor)	0.50	0.48	11	96	0.16

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Chlorneb	0.50	0.51	8.1	103	0.13
Chlorobenzilate	0.50	0.61	9.7	123	0.17
2-Chlorobiphenyl	0.50	0.47	4.8	94	0.068
Chlorpropham	0.50	0.55	8.1	109	0.13
Chlorpyrifos	0.50	0.50	2.4	99	0.035
Chlorothalonil	0.50	0.62	5.3	123	0.098
Chrysene	0.50	0.50	9.2	99	0.14
Cyanazine	0.50	0.49	13	97	0.19
Cycloate	0.50	0.52	7.6	103	0.12
DCPA	0.50	0.55	7.2	109	0.12
4,4'-DDD	0.50	0.52	3.6	103	0.055
4,4'-DDE	0.50	0.41	5.8	81	0.070
4,4'-DDT	0.50	0.54	2.4	108	0.039
Diazinon	0.50	0.37	2.7	75	0.030
Dibenz[a,h]anthracene	0.50	0.37	29	74	0.32
Di-n-Butylphthalate[b]	5.0	6.2	4.6	124	0.89
2,3-Dichlorobiphenyl	0.50	0.45	5.8	90	0.079
Dichlorvos	0.50	0.53	8.0	106	0.13
Dieldrin	0.50	0.50	10	100	0.15
Di(2-Ethylhexyl)adipate	0.50	0.59	18	117	0.31
Di(2-Ethylhexyl)phthalate[b]	5.0	6.5	6.6	130	1.3
Diethylphthalate	0.50	0.63	15	126	0.28
Dimethylphthalate	0.50	0.51	9.5	102	0.14
2,4-Dinitrotoluene	0.50	0.45	18	91	0.24
2,6-Dinitrotoluene	0.50	0.40	17	80	0.20
Diphenamid	0.50	0.55	6.5	111	0.11
Disulfoton	0.50	0.62	9.8	124	0.18
Disulfoton Sulfone	0.50	0.64	3.5	128	0.068
Disulfoton Sulfoxide	0.50	0.57	8.6	114	0.15
Endosulfan I	0.50	0.60	6.1	121	0.11
Endosulfan II	0.50	0.64	3.9	128	0.074
Endosulfan Sulfate	0.50	0.58	5.4	116	0.093
Endrin	0.50	0.62	18	124	0.34
Endrin Aldehyde	0.50	0.58	8.7	116	0.15
EPTC	0.50	0.53	7.7	105	0.12

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Ethoprop	0.50	0.62	10	124	0.19
Etridiazole	0.50	0.61	6.5	122	0.12
Fenamiphos	0.50	0.67	12	133	0.24
Fenarimol	0.50	0.74	11	148	0.25
Fluorene	0.50	0.49	9.0	98	0.13
Fluridone	5.0	5.2	2.5	105	0.39
HCH, alpha	0.50	0.55	6.8	109	0.11
HCH, beta	0.50	0.54	5.3	107	0.085
HCH, delta	0.50	0.52	3.1	105	0.049
HCH, gamma (Lindane)	0.50	0.53	5.3	105	0.084
Heptachlor	0.50	0.50	4.1	100	0.061
Heptachlor Epoxide	0.50	0.54	8.2	108	0.13
2,2',3,3',4,4',6-Heptachloro-biphenyl	0.50	0.45	11	90	0.15
Hexachlorobenzene	0.50	0.41	6.0	82	0.074
2,2',4,4',5,6'-Hexachloro-biphenyl	0.50	0.40	15	80	0.18
Hexachlorocyclopentadiene	0.50	0.34	13	68	0.13
Hexazinone	0.50	0.80	5.6	159	0.14
Indeno[1,2,3-cd]pyrene	0.50	0.36	28	71	0.30
Isophorone	0.50	0.54	7.9	107	0.13
Methoxychlor	0.50	0.58	7.7	115	0.13
Methyl Paraoxon	0.50	0.85	3.7	170	0.094
Metolachlor	0.50	0.58	4.8	117	0.085
Metribuzin	0.50	0.54	14	108	0.22
Mevinphos	0.50	0.47	12	95	0.17
MGK 264 - Isomer a	0.33	0.38	9.5	113	0.11
MGK 264 - Isomer b	0.16	0.18	5.4	105	0.029
Molinate	0.50	0.55	5.2	111	0.086
Napropamide	0.50	0.63	10	127	0.20
Norflurazon	0.50	0.82	3.8	165	0.093
2,2',3,3',4,5',6,6'-Octachloro-biphenyl	0.50	0.49	19	99	0.28
Pebulate	0.50	0.56	6.1	112	0.10

TABLE 5. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
2,2',3',4,6-Pentachlorobiphenyl	0.50	0.43	8.7	86	0.11
Pentachlorophenol	2.0	2.4	10	119	0.72
Permethrin,cis	0.25	0.45	3.2	179	0.043
Permethrin,trans	0.75	1.1	2.2	153	0.074
Phenanthrene	0.50	0.48	4.8	96	0.069
Prometon[c]	0.50	0.24	27	48	0.20
Prometryn	0.50	0.46	3.0	92	0.041
Pronamide	0.50	0.56	5.3	113	0.089
Propachlor	0.50	0.56	8.6	112	0.14
Propazine	0.50	0.52	4.3	103	0.066
Pyrene	0.50	0.47	11	95	0.16
Simazine	0.50	0.48	8.8	96	0.13
Simetryn	0.50	0.48	2.9	96	0.042
Stirofos	0.50	0.80	3.9	160	0.093
Tebuthiuron	0.50	0.67	7.4	134	0.15
Terbacil	0.50	0.59	12	119	0.22
Terbufos	0.50	0.46	11	92	0.15
Terbutryn	0.50	0.48	2.6	97	0.038
2,2',4,4'-Tetrachlorobiphenyl	0.50	0.40	6.4	81	0.077
Toxaphene	10	11	4.9	118	1.7
Triademefon	0.50	0.73	6.4	146	0.14
2,4,5-Trichlorobiphenyl	0.50	0.44	3.3	88	0.043
Tricyclazole	0.50	0.63	16	127	0.31
Trifluralin	0.50	0.62	13	124	0.24
Vernolate	0.50	0.50	9.3	101	0.14

[a]Seven replicates.
[b]Seven replicates in fortified tap water.
[c]Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Surrogates					
1,3-dimethyl-2-nitrobenzene	5.0	4.9	10	98	
perylene-d12	5.0	4.9	4.5	98	
triphenylphosphate	5.0	5.9	8.1	117	
Target Analytes					
Acenaphthylene	0.50	0.51	4.5	102	0.068
Alachlor	0.50	0.54	6.6	108	0.11
Aldrin	0.50	0.45	6.3	90	0.085
Ametryn	0.50	0.41	23	82	0.29
Anthracene	0.50	0.39	15	79	0.18
Aroclor 1016	0.20	0.25	4.7	123	0.040
Aroclor 1221	0.20	0.26	6.1	130	0.054
Aroclor 1232	0.20	0.24	4.7	121	0.042
Aroclor 1242	0.20	0.26	4.9	129	0.043
Aroclor 1248	0.20	0.24	4.1	118	0.038
Aroclor 1254	0.20	0.22	3.7	110	0.028
Aroclor 1260[a]	0.20	0.21	2.2	108	0.018
Atraton[d]	0.50	0.10	46	21	0.14
Atrazine	0.50	0.56	4.6	111	0.076
Benz[a]anthracene	0.50	0.44	7.4	88	0.098
Benzo[b]fluoranthene	0.50	0.50	9.1	100	0.14
Benzo[k]fluoranthene	0.50	0.46	2.2	91	0.031
Benzo[g,h,i]perylene	0.50	0.47	7.9	95	0.11
Benzo[a]pyrene	0.50	0.44	12	89	0.16
Bromacil	0.50	0.49	4.4	99	0.066
Butachlor	0.50	0.66	5.1	132	0.10
Butylate	0.50	0.50	5.4	100	0.082
Butylbenzylphthalate[b]	5.0	5.7	7.7	114	1.4
Carboxin	0.50	0.40	38.1	79	0.45
Chlordane, (alpha-Chlordane)	0.50	0.50	4.3	101	0.065
Chlordane, (gamma-Chlordane)	0.50	0.51	7.2	102	0.11
Chlordane, (trans-Nonachlor)	0.50	0.52	6.2	104	0.097
Chlorneb	0.50	0.54	6.3	108	0.10

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Chlorobenzilate	0.50	0.59	9.7	117	0.17
2-Chlorobiphenyl	0.50	0.50	4.7	100	0.070
Chlorpropham	0.50	0.55	4.7	111	0.079
Chlorpyrifos	0.50	0.54	11	109	0.18
Chlorothalonil	0.50	0.59	4.4	119	0.079
Chrysene	0.50	0.48	6.1	96	0.088
Cyanazine	0.50	0.52	8.3	105	0.13
Cycloate	0.50	0.51	4.1	102	0.063
DCPA	0.50	0.53	3.2	105	0.051
4,4'-DDD	0.50	0.63	16	127	0.31
4,4'-DDE	0.50	0.48	3.7	96	0.054
4,4'-DDT	0.50	0.58	7.2	117	0.13
Diazinon	0.50	0.50	4.5	101	0.068
Dibenz[a,h]anthracene	0.50	0.47	9.9	94	0.14
Di-n-Butylphthalate[b]	5.0	5.7	3.3	115	0.59
2,3-Dichlorobiphenyl	0.50	0.50	2.6	100	0.039
Dichlorvos	0.50	0.50	8.7	99	0.13
Dieldrin	0.50	0.53	7.0	106	0.11
Di(2-Ethylhexyl)adipate[b]	5.0	5.4	7.5	107	1.3
Di(2-Ethylhexyl)phthalate[b]	5.0	5.7	2.6	114	0.46
Diethylphthalate	0.50	0.68	5.0	137	0.10
Dimethylphthalate	0.50	0.51	5.0	102	0.077
2,4-Dinitrotoluene	0.50	0.30	8.1	59	0.072
2,6-Dinitrotoluene	0.50	0.28	6.4	56	0.054
Diphenamid	0.50	0.56	6.4	112	0.11
Disulfoton	0.50	0.70	5.3	139	0.11
Disulfoton Sulfone	0.50	0.64	5.9	128	0.11
Disulfoton Sulfoxide	0.50	0.60	3.8	119	0.068
Endosulfan I	0.50	0.61	4.9	122	0.089
Endosulfan II	0.50	0.66	6.1	131	0.12
Endosulfan Sulfate	0.50	0.57	9.0	115	0.16
Endrin	0.50	0.68	7.9	137	0.16
Endrin Aldehyde	0.50	0.57	2.8	114	0.048
EPTC	0.50	0.48	5.2	97	0.076
Ethoprop	0.50	0.61	7.5	122	0.14

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Etridiazole	0.50	0.54	4.2	108	0.067
Fenamiphos	0.50	0.67	10	133	0.20
Fenarimol	0.50	0.59	5.8	118	0.10
Fluorene	0.50	0.53	3.4	106	0.054
Fluridone	5.0	5.2	2.3	104	0.16
HCH, alpha	0.50	0.55	5.0	110	0.083
HCH, beta	0.50	0.54	4.1	109	0.068
HCH, delta	0.50	0.53	3.6	106	0.058
HCH, gamma (Lindane)	0.50	0.50	3.2	100	0.047
Heptachlor	0.50	0.49	4.0	98	0.059
Heptachlor Epoxide	0.50	0.50	3.2	100	0.048
2,2',3,3',4,4',6-Heptachlorobiphenyl	0.50	0.46	7.3	92	0.10
Hexachlorobenzene	0.50	0.49	3.4	97	0.049
2,2',4,4',5,6'-Hexachlorobiphenyl	0.50	0.50	5.3	99	0.079
Hexachlorocyclopentadiene	0.50	0.37	9.3	73	0.10
Hexazinone	0.50	0.75	4.2	150	0.094
Indeno[1,2,3-cd]pyrene	0.50	0.48	7.3	96	0.10
Isophorone	0.50	0.51	4.3	102	0.066
Methoxychlor	0.50	0.52	6.7	104	0.10
Methyl Paraoxon	0.50	0.75	4.5	151	0.10
Metolachlor	0.50	0.57	3.2	114	0.054
Metribuzin	0.50	0.53	5.7	107	0.090
Mevinphos	0.50	0.56	6.2	112	0.10
MGK 264 - Isomer a	0.33	0.38	6.7	113	0.076
MGK 264 - Isomer b	0.16	0.18	5.3	110	0.029
Molinate	0.50	0.53	3.8	105	0.060
Napropamide	0.50	0.58	7.9	116	0.14
Norflurazon	0.50	0.71	4.3	142	0.091
2,2',3,3',4,5',6,6'-Octachlorobiphenyl	0.50	0.47	5.3	94	0.076
Pebulate	0.50	0.56	7.1	112	0.11
2,2',3',4,6-Pentachlorobiphenyl	0.50	0.49	4.0	97	0.059
Pentachlorophenol	2.0	2.2	15	111	1.0
Permethrin,cis	0.25	0.37	3.1	149	0.035

TABLE 6. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS OF THE METHOD ANALYTES IN REAGENT WATER USING LIQUID-SOLID C-18 DISK EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc. (µg/L)	Mean Observed Conc. (µg/L)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	MDL (µg/L)
Permethrin,trans	0.75	0.84	1.6	112	0.039
Phenanthrene	0.50	0.49	6.3	97	0.092
Prometon[d]	0.50	0.16	63	32	0.30
Prometryn	0.50	0.46	23	91	0.32
Pronamide	0.50	0.56	3.9	111	0.064
Propachlor	0.50	0.58	5.7	115	0.098
Propazine	0.50	0.53	4.7	106	0.074
Pyrene	0.50	0.52	5.2	104	0.080
Simazine	0.50	0.54	2.8	107	0.045
Simetryn	0.50	0.36	20	71	0.22
Stirofos	0.50	0.72	3.7	144	0.080
Tebuthiuron	0.50	0.67	7.9	133	0.16
Terbacil	0.50	0.64	12	129	0.23
Terbufos	0.50	0.57	6.8	113	0.11
Terbutryn	0.50	0.46	24	93	0.34
2,2',4,4'-Tetrachlorobiphenyl	0.50	0.46	7.4	91	0.10
Toxaphene[c]	10	12	2.7	122	1.0
Triademefon	0.50	0.71	7.3	142	0.16
2,4,5-Trichlorobiphenyl	0.50	0.48	4.5	97	0.066
Tricyclazole	0.50	0.65	14	130	0.27
Trifluralin	0.50	0.59	7.8	117	0.14
Vernolate	0.50	0.50	3.2	99	0.047

[a]Six replicates.
[b]Seven replicates in fortified tap water.
[c]Seven replicates.
[d]Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.

TABLE 7. ACCURACY AND PRECISION DATA FROM EIGHT DETERMINATIONS AT 5 µg/L IN REAGENT WATER OF POORLY CHROMATOGRAPHED NITROGEN AND PHOSPHOROUS CONTAINING PESTICIDES

	Ion Trap Mass Spectrometer				Quadrupole Mass Spectrometer			
	Cartridge		Disk		Cartridge		Disk	
Compound	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)	Relative Standard Deviation (%)	Mean Method Accuracy (% of True Conc.)
Fenamiphos	7.7	99	4.5	108	6.1	103	8.8	124
Fenarimol	2.0	104	10	110	6.5	126	5.5	150
Fluridone	2.5	105	2.3	104	3.6	102	4.5	114
Hexazinone	4.2	106	9.7	116	5.3	104	8.3	127
Norflurazon	4.1	111	9.6	119	3.2	98	11.1	113
Stirofos	8.2	114	12	124	4.1	110	11.1	125
Tebuthiuron	9.5	119	5.3	145	13	136	8.6	182
Triademeton	7.8	113	10	128	3.7	100	9.8	118
Tricyclazole	16	81	9.5	99	19	92	12	137

TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc.	Mean	% RSD	% REC
Acenaphthylene	5.0	5.2	5.3	104
Alachlor	5.0	5.5	6.9	110
Aldrin	5.0	4.4	14	88
Ametryn	5.0	4.2	3.4	83
Anthracene	5.0	4.3	5.2	87
Aroclor 1016	ND	ND	ND	ND
Aroclor 1221	ND	ND	ND	ND
Aroclor 1232	ND	ND	ND	ND
Aroclor 1242	ND	ND	ND	ND
Aroclor 1248	ND	ND	ND	ND
Aroclor 1254	ND	ND	ND	ND
Aroclor 1260	ND	ND	ND	ND
Atraton[a]	5.0	2.2	28	43
Atrazine	5.0	5.6	6.2	111
Benz[a]anthracene	5.0	4.9	8.8	97
Benzo[b]fluoranthene	5.0	5.7	7.5	114
Benzo[k]fluoranthene	5.0	5.7	2.9	113
Benzo[g,h,i]perylene	5.0	5.6	7.1	113
Benzo[a]pyrene	5.0	6.1	4.6	121
Bromacil	5.0	3.5	5.1	69
Butachlor	5.0	5.4	7.5	109
Butylate	5.0	5.1	4.5	102
Butylbenzylphthalate	5.0	7.2	8.3	144
Carboxin	5.0	1.0	23	20
Chlordane, (alpha-Chlordane)	5.0	5.2	8.9	104
Chlordane, (gamma-Chlordane)	5.0	5.1	8.0	102
Chlordane, (trans-Nonachlor)	5.0	5.6	7.4	111
Chlorneb	5.0	5.2	3.0	105
Chlorobenzilate	5.0	5.7	4.4	114
2-Cchlorobiphenyl	5.0	5.8	5.4	115
Chlorpropham	5.0	6.3	4.9	127
Chlorpyrifos	5.0	5.3	7.2	107
Chlorthalonil	5.0	5.4	9.9	108
Chrysene	5.0	5.5	3.9	110
Cyanazine	5.0	6.1	13	122
Cycloate	5.0	5.6	1.5	112
DCPA	5.0	5.4	5.0	107
4,4'-DDD	5.0	5.3	6.5	105

TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc.	Mean	% RSD	% REC
4,4'-DDE	5.0	5.2	6.6	104
4,4'-DDT	5.0	5.6	9.6	111
Diazinon	5.0	4.9	8.7	98
Dibenz[a,h]anthracene	5.0	5.9	7.5	118
Di-n-Butylphthalate	5.0	6.2	4.6	124
2,3-Dichlorobiphenyl	5.0	5.3	7.4	106
Dichlorvos	5.0	2.8	7.3	56
Dieldrin	5.0	5.3	7.2	105
Di(2-Ethylhexyl)adipate	5.0	6.7	10	134
Di(2-Ethylhexyl)phthalate	5.0	6.5	6.6	130
Diethylphthalate	5.0	6.4	7.4	127
Dimethylphthalate	5.0	5.8	7.1	116
2,4-Dinitrotoluene	5.0	4.2	8.7	84
2,6-Dinitrotoluene	5.0	4.1	8.5	82
Diphenamid	5.0	5.2	7.7	104
Disulfoton	5.0	2.5	33	50
Disulfoton Sulfone	5.0	5.5	7.4	110
Disulfoton Sulfoxide	5.0	9.4	11	188
Endosulfan I	5.0	5.5	11	109
Endosulfan II	5.0	5.3	9.6	106
Endosulfan Sulfate	5.0	5.3	7.8	106
Endrin	5.0	6.1	3.9	121
Endrin Aldehyde	5.0	5.1	9.1	102
EPTC	5.0	5.1	2.1	102
Ethoprop	5.0	6.3	4.2	125
Etridiazole	5.0	5.8	7.5	117
Fenamiphos	5.0	5.9	22	119
Fenarimol	5.0	7.1	3.3	141
Fluorene	5.0	5.7	5.2	114
Fluridone	5.0	6.2	9.0	125
HCH, alpha	5.0	5.9	2.6	118
HCH, beta	5.0	5.3	8.4	106
HCH, delta	5.0	5.3	5.2	106
HCH, gamma (Lindane)	5.0	5.3	6.9	107
Heptachlor	5.0	4.7	8.7	93
Heptachlor Epoxide	5.0	5.2	7.7	105
2,2',3,3',4,4',6-Heptachlorobiphenyl	5.0	5.1	6.9	103
Hexachlorobenzene	5.0	4.6	7.4	93

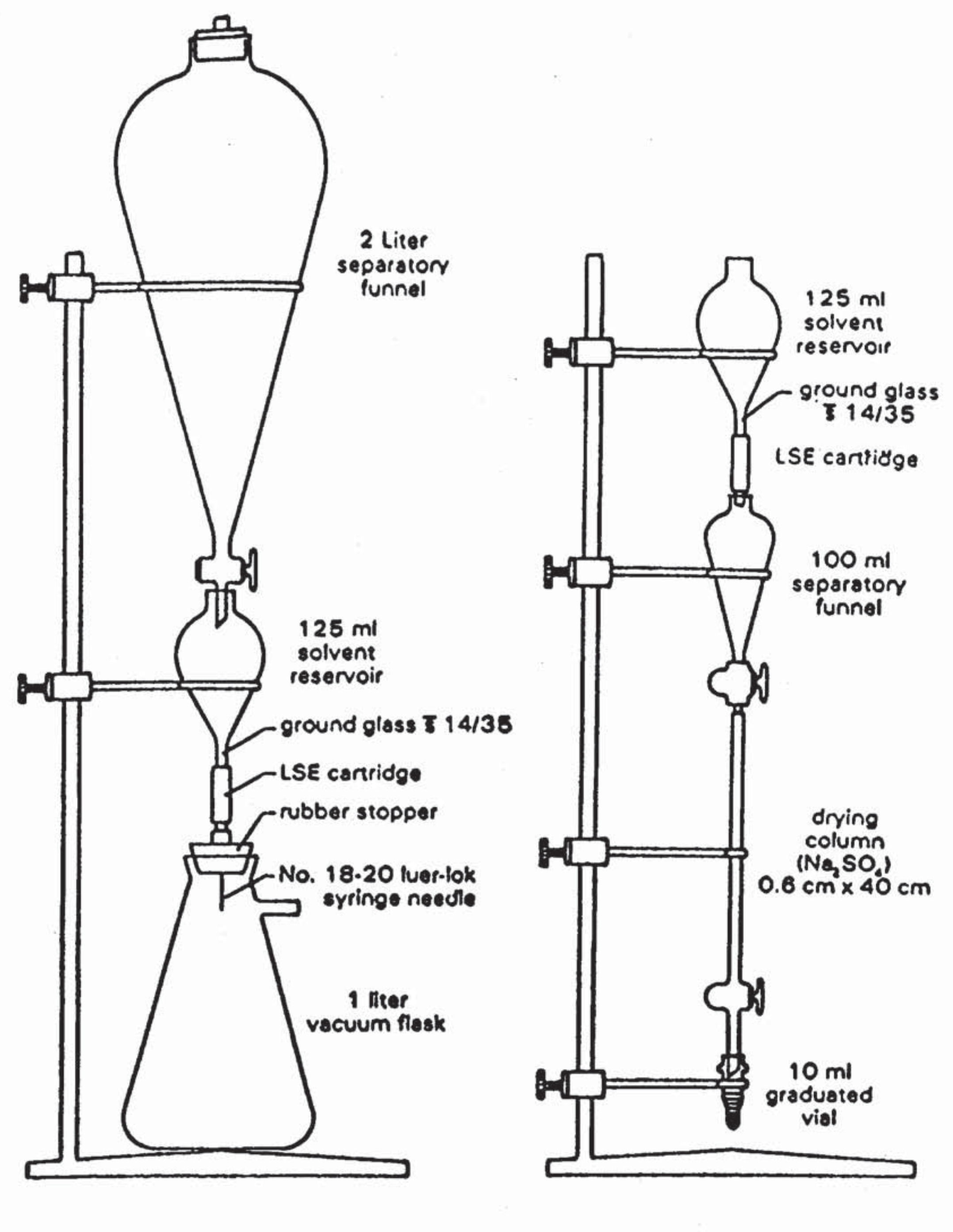
TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

Compound	True Conc.	Mean	% RSD	% REC
2,2',4,4',5,6'-Hexachlorobiphenyl	5.0	5.6	8.1	112
Hexachlorocyclopentadiene	5.0	6.0	4.8	120
Hexazinone	5.0	6.9	6.3	138
Indeno[1,2,3-cd]pyrene	5.0	6.8	7.7	135
Isophorone	5.0	4.9	12	99
Methoxychlor	5.0	5.6	4.9	112
Methyl Paraoxon	5.0	5.6	11	111
Metolachlor	5.0	5.6	7.7	111
Metribuzin	5.0	2.1	5.8	42
Mevinphos	5.0	3.3	1.6	67
MGK 264 - Isomer a	3.3	3.6	6.2	107
MGK 264 - Isomer b	1.7	1.8	7.6	110
Molinate	5.0	5.5	1.5	110
Napropamide	5.0	5.3	8.9	106
Norflurazon	5.0	6.7	7.2	135
2,2',3,3',4,5',6,6'-Octaclorobiphenyl	5.0	4.9	6.9	97
Pebulate	5.0	5.3	3.1	106
2,2',3',4,6-Pentachlorobiphenyl	5.0	5.3	8.1	107
Pentachlorophenol	20.	33	4.9	162
Permethrin, cis	5.0	3.3	3.5	130
Permethrin, trans	5.0	8.5	2.2	113
Phenanthrene	5.0	5.5	4.0	109
Prometona[a]	5.0	2.0	25	40
Prometryn	5.0	4.5	4.3	89
Pronamide	5.0	5.7	5.3	115
Propachlor	5.0	6.2	4.0	124
Propazine	5.0	5.6	4.9	113
Pyrene	5.0	5.2	6.7	104
Simazine	5.0	6.0	9.0	120
Simetryn	5.0	3.9	7.0	78
Stirofos	5.0	6.1	12	121
Tebuthiuron	5.0	6.5	9.7	130
Terbacil	5.0	4.0	5.5	79
Terbufos	5.0	4.5	8.4	90
Terbutryn	5.0	4.3	6.5	86
2,2',4,4'-Tetrachlorobiphenyl	5.0	5.3	4.3	106
Toxaphene	ND	ND	ND	ND
Triademefon	5.0	6.0	12	121

TABLE 8. ACCURACY AND PRECISION DATA FROM SEVEN DETERMINATIONS OF THE METHOD ANALYTES IN TAP WATER USING LIQUID-SOLID C-18 CARTRIDGE EXTRACTION AND THE ION TRAP MASS SPECTROMETER

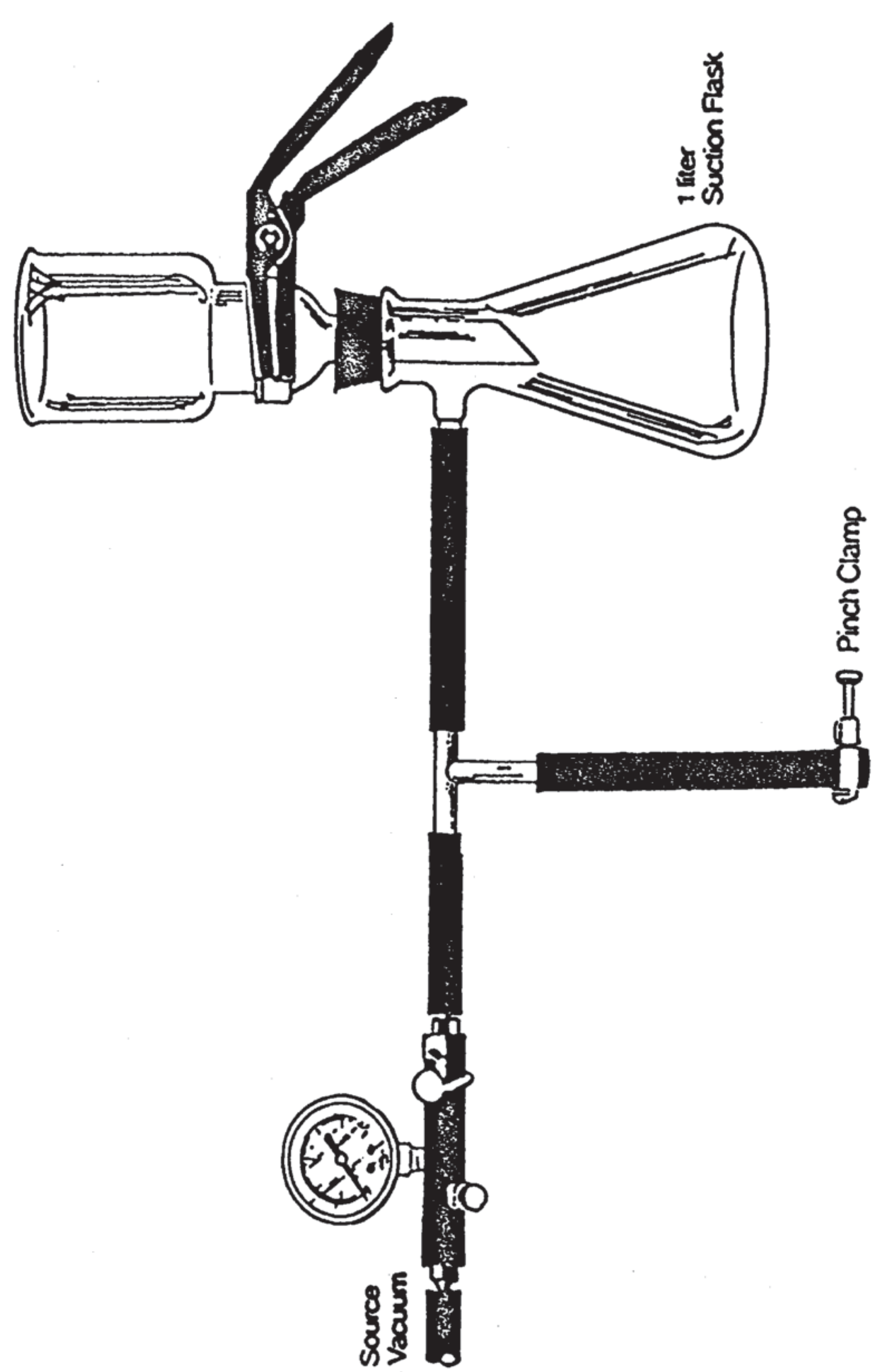
Compound	True Conc.	Mean	% RSD	% REC
2,4,5-Trichlorobiphenyl	5.0	5.2	5.1	103
Tricyclazole	5.0	4.8	5.2	96
Trifluralin	5.0	5.9	7.8	119
Vernolate	5.0	5.4	3.3	108

[a]Data from samples extracted at pH 2 - for accurate determination of this analyte, a separate sample must be extracted at ambient pH.



A. Extraction apparatus B. Elution apparatus

FIGURE 1. CARTRIDGE EXTRACTION APPARATUS


1 liter
Suction Flask
Pinch Clamp
Source
Vacuum

APPENDIX E – ANALYTICAL METHODS USED BY CCWD

Appendix E - Analytical Methods used by CCWD

The conventional parameters as well as the membrane performance and fouling parameters will be analyzed by CCWD per the methods listed in Table E.1.

Table E.1 CCWD Analytical Methods

Parameter	Method
Conventional Parameters	
pH	Standard Methods, pH (4500-H^+)/Electrometric Method
Turbidity	Standard Methods, Turbidity (2130/Nephelometric)
TOC	EPA 415.2
UV	Standard Methods, UV 254 Absorbance, 5910
Specific Conductance	EPA 120.1
Bromide	The procedure used in CCWD's lab is equivalent to Standard Methods, 20th edition, 429 and EPA method 300.0.
Chloride	The procedure used in CCWD's lab is equivalent to Standard Methods, 20th edition, 429 and EPA method 300.0.
Alkalinity	Standard Methods, Alkalinity (2320 B)/Titration Method
Iodide	EPA 200.7
Hardness	Standard Methods, Hardness (2340 C)/EDTA Titration Method
Ozone	Hach Method 8311 (Colorimetric), EPA Equivalent Method
Membrane Fouling/Performance	
TSS	EPA 160.2
Calcium	The procedure used in CCWD's lab is equivalent to Standard Methods, 20th edition, 3111 B and EPA method 215.1.
Magnesium	EPA 200.7
Sodium	EPA 273.1
Potassium	EPA 200.7
Ammonia	Standard Methods, Ammonia (4500-NH3)/Selective Electrode Method.
Barium	EPA 208.1

Table E.1 CCWD Analytical Methods	
Parameter	**Method**
Strontinum	EPA 200.7
Nitrate	The procedure used in CCWD's lab is equivalent to Standard Methods, 20th edition, 429 and EPA method 300.0.
Fluoride	EPA 340.2
Phosphate	The procedure used in CCWD's lab is equivalent to Standard Methods, 20th edition, 429 and EPA method 300.0.
Silica	EPA 200.7
Boron	EPA 200.7
Manganese (T&D)	The procedure used in CCWD's lab is equivalent to Standard Methods, 20th edition, 3113 B and EPA method 243.2 with appropriate matrix modifiers.
Iron (T&D)	The procedure (furnace method) used in CCWD's lab is equivalent to Standard Methods, 20th edition, 3113 B and EPA method 236.2 with appropriate matrix modifiers. The procedure (flame method) used in CCWD's lab is equivalent to Standard Methods, 20th edition, 3111 B and EPA method 236.1.
Aluminum	The procedure used in the CCWD's lab is equivalent to Standard Methods, 20th edition, 3113 B and EPA method 202.2 with appropriate matrix modifiers.
Sulfate	The procedure used in CCWD's lab is equivalent to Standard Methods, 20th edition, 429 and EPA method 300.0.

ALKALINITY (TITRATION METHOD)

INTRODUCTION:

The alkalinity of water is its acid-neutralizing capacity. It is the sum of all the titratable bases. The measured value may vary significantly depending upon the end-point pH used. Alkalinity is a measure of an aggregate property of water and can be interpreted in terms of specific substances only when the chemical composition of the sample is known. Because the alkalinity of many surface waters is primarily a function of carbonate, bicarbonate, and hydroxide content, it is taken as an indication of the concentration of these constituents. (Standard Methods, Alkalinity (2320 B)/Titration Method.)

INTERFERENCES:

Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response. Allow additional time between titrant additions to let electrode come to equilibrium or clean the electrodes occasionally. Do not filter, dilute, concentrate, or alter sample.

APPARATUS:

1. pH meter (Beckman 200)
2. pH electrode, 0-14 pH, 0-80 °C (Beckman 39841)
3. Magnetic stirrer
4. TFE-coated stir bars
5. 150 mL polyethylene beakers
6. 25 mL automatic buret
7. Wash bottle
8. Blotting tissues

REAGENTS:

1. Phosphate buffer, pH 7.00 (VWR #34180-650 or equivalent)
2. Phthalate buffer, pH 4.00 (VWR #34180-264 or equivalent)
3. Carbonate buffer, pH 10.0 (Baxter #H7592-10 or equivalent)
4. pH 6.0 and 8.0 secondary standardization checks
5. Saturated potassium chloride (KCl) with AgCl solution
6. Standard sulfuric acid 0.0200N titrant (Ricca 38200 or equivalent)
7. Deionized (DI) water

PROCEDURE:

1. Turn power on. Press mode until meter is in "pH" mode.
2. Rinse pH probes with DI water, blot and immerse in a beaker of pH 7.00 buffer standard, adjusting magnetic stirrer to a slow speed.
3. Press "STD" and wait for meter to lock on (number will stop blinking). Remove probes, rinse with DI water and blot with tissue.
4. Place probes into a beaker with pH 10 standard. Press “STD” and wait for meter to lock on.
5. Place probes in pH 8.0 to confirm the calibration. Press “pH” to read the sample pH.
6. Place probes in a beaker containing 100 mls of sample and a magnetic stirrer. Press “pH” to read sample pH. Adjust magnetic stirrer for complete mixing of sample contents.
7. Set the H2SO4 titrant level in buret to 0.0 mL.
8. Titrate slowly until pH reaches 4.5. This is the end-point for the Total Alkalinity analysis.

REPORTING RESULTS:

Alkalinity, mg/L as $CaCO_3$ = (A)(N)(50000)/(sample volume, mL)

where, A=mL standard acid used

N=normality of standard acid

QUALITY CONTROL:

No general statement can be made about precision because of the great variation in sample characteristics. The precision of the titration is likely to be much greater than the uncertainties involved in sampling and sample handling before the analysis. In the

range of 10-500 mg/L, when the alkalinity is due entirely to carbonates or bicarbonates, a standard deviation of 1 mg $CaCO_3$/L can be achieved.

AMMONIA (SELECTIVE ELECTRODE METHOD)

INTRODUCTION:

In waters and wastewaters the nitrogen forms of greatest interest are nitrate, nitrite, ammonia, and organic nitrogen. These forms of nitrogen are used in the nitrogen cycle by biological organisms in the environment and there concentrations are rate limiting in the production of algae and other plant life. Ammonia is produced largely from of natural organic mater and by hydrolysis of urea. At some water treatment plants ammonia is added to form combined chlorine and ammonia residual, which form mono- and dichloramines.

The ammonia-selective electrode uses a hydrophobic gas-permeable membrane to separate the sample solution from an electrode internal solution of ammonium chloride. This method is applicable to the measurement of 0.03 to 1400 mg/L NH_3-N in potable and surface waters, and domestic and industrial wastes. Sample distillation is unnecessary, and color and turbidity do not affect the measurement. (Standard Methods, Ammonia (4500-NH3)/Selective Electrode Method.)

INTERFERENCES:

High concentrations of dissolved ions affect the measurement, and amines are a positive interference. Mercury and silver interfere by complexing with ammonia. Do not stir the standards or samples so rapidly that air bubbles are sucked into the solution because they will become trapped on the electrode membrane.

APPARATUS:

1. Selective ion analyzer ThermoOrion Model 720A)
2. Automatic temp compensation probe (Orion ATC #917005)
3. Ammonia electrode (Orion Model 9512)
4. Magnetic stirrer, stir bars
5. 150 mL polyethylene beakers
6. 100 mL graduated cylinder
7. 100 mL volumetric flask
8. 1000 mL volumetric flask

REAGENTS:

1. Reagent grade, ammonia-free, de-ionized water
2. Ammonia pH-adjusting ISA solution (Orion 95-12-11)
3. 1000 ppm Nitrogen (1.22mg as NH3) stock solution
4. 1.0 ppm Nitrogen standard make-up solution (Dilute 100 ul of 1000 ppm stock solution brought to 100 mL with deionized (DI) water in a 100-mL volumetric flask)
5. 0.5 ppm Nitrogen standard (Dilute 50 ul of 1000 ppm stock solution to 100 mL with DI water in a 100-mL volumetric flask)
6. 0.1 ppm NH_4Cl standard (Dilute 10 ul of 1000 ppm stock solution brought to 1000 mL with DI water in a 1000-mL volumetric flask)
7. Internal filling solution (Orion 95-10-02)

8. 0.05 M NH_4Cl soaking solution (Dissolve 2.675 g reagent grade NH_4CL in 100 mL DI water, diluting to 1000 mL in a volumetric flask)

PROCEDURE:

Standardizing the meter:

1. Place selective ion meter in the "Concentration" mode. 2. Prepare standards with ionic activities (or concentrations)which bracket the range of anticipated samples (normally 0.1 ppm and 1.0 ppm).
2. Measure 100 mL of the lower concentration standard into a beaker, insert the electrodes, add 2 mL of ISA, and press "Calibrate" enter number of standards used for calibration (minimum 3) and press "YES."4.After 3 minutes or when display has stabilized, key in the exact value of the first standard concentration and press "YES."
3. Blot dry probes and insert into next standard.
4. Repeat steps 3 and 4 for remaining calibration standards.
5. Key in the exact value of the last standard and press "Enter." The meter will then calculate the slope and y-intercept, which the slope must be between –54 and –60.9. The meter has now been entered a multi-point calibration series into its memory and is ready to read samples.

Direct measurement of samples

1. Measure 100 mL of sample into a beaker, immerse the electrode and turn on stirrer, and add 2 mL of ISA. Press measure and allow 3 minutes for reading stabilization.
2. Record mg/L nitrogen (N) concentration off the meter as displayed.
3. Rinse probe with nanopure water and blot dry before running next sample. Repeat steps 1 and 2 above for the rest of the samples

REPORTING RESULTS:

The selective-ion meter concentration is reported as mg/L nitrogren [Co(N)]. If concentration falls within standardized range, report to the nearest 0.1 mg/L. If the concentration falls below 0.1 mg/L, record as "<0.1 mg/L." To report concentration as mg/L ammonia [Co(NH_3-N)], multiply by 1.21.

QUALITY CONTROL:

Be sure that standard solutions and samples are at the same temperature and contain a total level of dissolved species less than 1 M. A 1° C difference in temperature will give rise to about a 2% measurement error. The ammonia-selective electrode responds slowly below 1 mg/L NH_3-N; hence, use longer times of electrode immersion (3-5minutes) to obtain stable readings.

Store samples in the refrigerator for no more than 24 hours when holding for analysis. Keep beakers containing standards and samples covered between measurements. Insulate the sample from the heat generated by the magnetic stirrer.

Add the pH-adjusting ISA solution to the sample or standard just before analysis. If after addition of 2 mL of ISA the sample remains clear, add ISA in increments of 1 mL until a blue color remains. Alkaline samples should be measured at once, frozen or preserved with H_2SO_4 to a pH <2 for future analysis.

For low-level measurements, keep the electrode in a pH 4 buffer between measurements. Do not store overnight in a pH 4 buffer.

For overnight storage or over a weekend, the electrode tip should be immersed in a 0.05 M standard without added NaOH. If the electrode is stored indefinitely, disassemble completely and rinse the inner body, outer body, and bottom cap with deionized water. Dry and reassemble electrode without the internal filling solution or membrane.

Assembling the electrode:

1. Remove the top cap of the electrode and lift out inner body.
2. Pour out old internal filling solution if present and remove bottom cap.
3. Rinse the cap, inner, and outer body with DI water.
4. Carefully remove and separate a new membrane from the pale blue packing paper. Lay membrane over the bottom opening of the outer body and gently wrap, holding in place with fingers. Screw cap firmly on outer body. Be careful not to wrinkle or tear membrane. Pre-assembled membrane screw caps are also available.
5. Fill outer body with 2.5 mL of internal filling solution.
6. Insert inner body inside the outer body and screw on top cap.
7. After assembly, allow the electrode to stand for thirty minutes in the internal filling solution.

TOTAL HARDNESS (EDTA TITRIMETRIC METHOD)

INTRODUCTION:
Originally, water hardness was understood to be a measure of the capacity of water to precipitate soap. Soap is precipitated chiefly by the calcium and magnesium ions present. In conformity with current practice, total hardness is defined as the sum of the calcium and magnesium concentrations, both expressed as calcium carbonate, in mg/L. (Standard Methods, Hardness (2340 C)/EDTA Titration Method.)

INTERFERENCES:
Some metal ions interfere by causing fading or indistinct end point or by stoichiometric consumption of EDTA. Reduce this interference by adding certain inhibitors before titration. Suspended or colloidal organic matter also may interfere with the end point.

APPARATUS:

1. 25 mL automatic buret
2. Magnetic stirrer
3. TFE-coated stir bars
4. Indicator (HACH Univer™1 Hardness Reagent)
5. Standard 0.0100M EDTA titrant (Ricca #2700 or equivalent)

PROCEDURE:

1. Select a sample volume that requires less than 15 mL EDTA titrant and complete titration within 5 minutes, measured from time of indicator addition. (A 50 mL water sample is normally sufficient for an effective titration.)
2. Add one scoop (one scoop = 1 g) of indicator to sample. Adjust mixer to a brisk mixing speed.

3. Titrate with EDTA until color changes from a wine red to a definite blue end-point.

REPORTING RESULTS:

Total Hardness (EDTA), as mg CaCO3/L = (A)(B)(1000)/(sample volume, mL)

where: A = mL of titrant

B = mg CaCO3 equivalent to 1.00 mL EDTA titrant (=1)

QUALITY CONTROL:

Because the titrant extracts hardness-producing cations from soft-glass containers, store in polyethylene (preferable) or borosilicate glass bottles. Compensate for gradual deterioration by periodic restandardization and by using a suitable correction factor.

TOTAL SUSPENDED SOLIDS

INTRODUCTION:

"Total suspended solids" is the term applied to the material residue left on the glass fiber filter and its subsequent drying in an oven at a defined temperature. Total suspended solids includes the portion of total solids retained by a glass fiber filter.

A well-mixed sample is filtered through a weighed standard glass-fiber filter and the residue retained on the filter is dried to constant weight in an oven at 103 to 105°C. The increase in weight of the filter represents the total suspended solids. If the suspended material clogs the filter and prolongs filtration, the difference between the total solids and the total dissolved solids may provide an estimate of the total suspended solids. (Standard Methods, Total Suspended Solids (2540-D).)

INTERFERENCES:

Exclude large floating particles or submerged agglomerates of nonhomogeneous materials from the sample if it is determined that their inclusion is not desired in the final result. Because excessive residue on the filter may form a water-entrapping crust, limit the sample size to that yielding no more than 200 mg residue. For samples high in dissolved solids, thoroughly wash the filter to ensure removal of the dissolved material. Prolonged filtration times resulting from filter clogging may produce high results owing to excessive solids capture on the clogged filter.

APPARATUS:

1. glass-fiber filter discs, 47 mm (Whatman 934-AH)
2. aluminum weighing dish, 57 mm (VWR Cat # 952-0142)
3. filtration funnel (Gelman Cat # 4201, 47 mm)
4. filtration manifold system with vacuum
5. drying oven (Thelco Precision Laboratory Oven)
6. analytical balance (Mettler AE 200)
7. dessicator (Boekel)
8. 100 mL graduated cylinder
9. centigrade thermometer
10. forceps

PROCEDURE:

1. Check the calibration of the balance by weighing a certified 100 gram and one gram mass, and record on the data sheet.
2. Check the thermometer to insure that the oven temp is 104C. Do not rely on digital temp readout on the oven.
3. Insert a filter disk with wrinkled side up in the filtration funnel. Apply vacuum and wash disk with three successive 20-mL portions of DI water. Continue suction to remove all traces of water, and discard washings. Transfer filter to an aluminum weighing dish.
4. Dry in an oven at 103 to 105°C for 1 hour. Store dish in dessicator until needed. Weigh immediately before use, recording the tare weight of the dish & filter to the nearest 0.1 mg.
5. Using forceps, place the filter back on the filter funnel. Apply vacuum and wet filter with a small volume of DI water to seat it. Measure 100 mL of a well-mixed sample and pour into filter funnel.
6. Wash with three successive 10-mL volumes of DI water, allowing complete drainage between washings and continue suction for about 3 minutes after filtration is complete. Carefully remove the filter from the funnel and transfer back to original weighing dish.
7. Place in drying oven and allow to dry sample for at least 1hour at 103 to 105°C.
8. Cool dish in dessicator to balance temperature.
9. Weigh filter and dish to the nearest 0.1 mg and repeat cycle of drying, cooling, dessicating, and weighing until a constant weight is obtained, or until weight loss is less than 4% of previous weight or 0.5 mg, whichever is less.

REPORTING RESULTS:

$$\text{mg Suspended Solids/L} = \frac{(A - B) \times 1000}{\text{sample volume, mL}}$$

where: A = weight of filter & dish + dried residue, mg
B = weight of filter & dish, mg

QUALITY CONTROL:
Use resistant-glass or plastic bottles, provided that the material in suspension does not adhere to container walls. Begin analysis as soon possible because of the impracticality of preserving the sample. Refrigerate sample at 4°C until analysis to minimize microbiological decomposition of solids.

pH (ELECTROMETRIC METHOD)

INTRODUCTION:
The measurement of pH is one of the most important and frequently used tests in water chemistry. The basic principle of electrometric pH measurement is determination of the activity of the hydrogen ions by potentiometric measurement using a standard hydrogen electrode and a reference electrode. (Standard Methods, pH (4500-H+)/Electrometric Method.)

INTERFERENCES:
The glass electrode is relatively free from interference from color, turbidity, colloidal matter, oxidants, reductants, or high salinity, except for a sodium error at pH>10. Soaps, oily matter, suspended solids, or precipitates may coat the glass electrode and cause a sluggish response.

pH measurements are affected by temperature in two ways: mechanical effects that are caused by changes in the properties of the electrodes and chemical effects caused by equilibrium changes. In the first instance, the Nernstian slope increases with increasing temperature and electrodes take time to achieve thermal equilibrium. This can cause long-term drift in pH. Because chemical equilibrium affects pH, standard pH buffers have a specified pH at indicated temperatures. Always report temperature at which pH is measured.

APPARATUS:
1. pH meter (Beckman 200)
2. pH electrode, 0-14 pH, 0-80 °C (39841)
3. Magnetic stirrer
4. TFE-coated stir bars
5. 150 mL-polyethylene beakers
6. Wash bottle
7. Blotting tissues

REAGENTS:
1. Phosphate buffer, pH 7.00 (VWR #34180-650 or equivalent)
2. Phthalate buffer, pH 4.00 (VWR #34180-264 or equivalent)
3. Carbonate buffer, pH 10.00 (Baxter #H7592-10 or equivalent)
4. pH 6.0 and 8.0 standards to confirm calibration
5. Saturated potassium chloride (KCl) solution
5. Deionized (DI) water

PROCEDURE:
1. Turn power on. Press mode until meter is in "pH" mode.
2. Rinse pH probes with DI water, blot and immerse in a beaker of pH 7.00 buffer standard, adjusting magnetic stirrer to a slow speed.
3. Press "2nd" and then "CAL" button. When display reaches specified pH value and the screen shows "READY", press "YES". "P2" will show on the screen. If the specified value for the buffer is not reached, press the "SETUP" button and enter correct value. If the value is correct, press "YES".
4. Remove probes, rinse with DI water and blot with tissue.
5. Place probes into pH 4 or 10 buffer. When the display reaches the specified pH value and the screen shows "READY", press "YES". If the specified value is not reached, press "SETUP" and enter correct value. If value is correct, press "YES" and the % SLOPE is displayed.
6. Remove probe, rinse and blot; immerse in 100 mL of sample and press "MEASURE" and allow meter to stabilize (it will display "READY"). Recheck stability of that value by pressing "MEASURE" once again and wait for "READY". Read and record pH to the nearest 0.1 pH unit.

REPORTING RESULTS:

A precision of ±0.02 pH unit and an accuracy of ±0.05 pH unit can be achieved. However, ±0.1 pH unit represents the limit of accuracy under normal conditions, especially for measurement of water and poorly buffered solutions. Report pH values to the nearest 0.1 pH unit.

QUALITY CONTROL:
Use a 6.0 or 8.0 (depending on range of calibration) to check calibration. Acceptable ranges for calibration checks are 5.9 to 6.1 for the 6.0 standard and 7.9 and 8.1 for the 8.0 standard.

TURBIDITY (NEPHELOMETRIC METHOD)

INTRODUCTION:
Clarity of a natural body of water is a major determinant of the condition and productivity of that system. Turbidity in water is caused by suspended matter, such as clay, silt, finely divided organic and inorganic compounds, and plankton and other microscopic organisms. Turbidity is an expression of the optical property that causes light to be scattered and absorbed rather than transmitted in straight lines through the sample. Historically, the standard method for determination of turbidity has been based on the Jackson candle turbidimeter; however, the lowest turbidity value that can be measured directly on this instrument is 25 units. Because there is no direct relationship between the intensity of light scattered at 90° angle measured by a nephelometer and Jackson candle turbidity, there is no valid basis for the practice of calibrating a nephelometer in JTU. (Standard Methods, Turbidity (2130/Nephelometric).)

INTERFERENCES:
Turbidity can be determined for any water sample that is free of debris and rapidly settling coarse sediments. Dirty glassware, the presence of air bubbles, and the effects of vibrations that disturb the surface visibility of the sample will give false results. "True color," that is, water color due to dissolved substances that absorb light, causes measured turbidities to be low. This effect usually is not significant in the case of treated water.

APPARATUS:
1. Turbidimeter (Hach 2100 N Turbidimeter)
2. Sample cells (Hach #21003)

REAGENTS:
1. 4000 NTU Formazin standard (Hach #2461)
2. Turbidity free water (Nanopure or equivalent)
3. Gelex 2° calibration standards.

PROCEDURE:
1. Instrument should be on, in Auto-range.
   Single averaging on, ratio off if turbidity is less than 40NTU..
2. Check the calibration of the turbidimeter with the 2° standard which most closely matches the range of turbidity for the sample. If result
   is not within 10% of the stated value, notify lab supervisor.
3. Thoroughly shake sample. Wait until air bubbles disappear and pour sample into sample cell.
4. Wipe down the sides of the sample cell with a kimwipe (do not use

paper towels, they will scratch the cell), making sure to remove any finger prints or smudges on the side of the sample cell.

5. Apply a thin coat of silicone oil to the cell & wipe with a velvet cloth.
6. Report the turbidity directly from the instrument when stable.

REPORTING RESULTS:

Report turbidity readings as follows:

Range, NTU-	Nearest NTU
0-1.0	0.05
1-10	0.1
10-40 1	
40-100	5
100-400	10

For comparison of water treatment efficiencies, estimate turbidity more closely than is specified above.

Uncertainties and discrepancies in turbidity measurements make it unlikely that two or more laboratories will duplicate results on the same sample more closely than specified.

QUALITY CONTROL:

1. Calibrate meter quarterly with primary formazin standard. (See Instrument Owner's Manual).

UV_{254}

INTRODUCTION:

Some organic compounds commonly found in water, such as lignin, tannin, humic substances, and various aromatic compounds strongly absorb ultraviolet (UV) radiation. UV absorption is a useful surrogate measure of organic constituents in water. Strong correlations may exist between UV absorption and organic carbon content, color, and precursors of THMs and other disinfection by-products (DBPs). UV_{254} analysis has been shown to be a useful parameter in developing DBP predictive behavior.

UV absorbing organic constituents in a sample absorb UV light proportionally to their concentration. Samples are analyzed at ambient pH and are filtered (0.45μ) through a pre-washed filter assembly or centrifuged for 10 minutes at 3000 rpm. A spectrophotometer is used at wavelength 254 nm to determine the absorption of the sample.

INTERFERENCES:

The primary interferences are from colloidal particles, UV absorbing organics other than those of interest, and UV absorbing inorganics, notably ferrous iron, nitrate, nitrite, and bromide. Some oxidants and reducing agents, such as ozone, chlorate, chlorite, chloramines, and thiosulfate, will also absorb UV light at 254 nm.

APPARATUS:

1. Thermo Spectronic, model Genesys 10
2. Filter assembly: 0.45μ or glass fiber filter of nominal pore size (1-1.5μm), 4.7 cm diameter.
3. Thermo IEC Centra CL2 centrifuge.

REAGENTS:
1. Organic-free water, nanopure or equivalent containing <0.3 mg/L DOC.
2. Potassium hydrogen biphthalate (KHP) standard.

PROCEDURE:
1. Select sample volume on the basis of the cell path length or dilution required to produce a UV absorbance of between 0.005 and 0.900. For most applications a 25 ml sample size is sufficient.
2. Prepare 0.65, 6.5, and 65 mg/L KHP standards.
3. Place samples in centrifuge tubes and spin for 10 minutes at 3000 rpm.
4. Turn on spectrophotometer and allow to warm up. Set wavelength to 254 nm and adjust spectrophotometer to read zero absorbance with organic-free water blank.
5. Measure UV absorbance at 254 nm of at least two filtered portions of sample at room temperature.
6. Analyze KHP solutions of known absorbance to verify calibration of spectrophotometer using the following equation:

$$UV_{254}\,(cm^{-1}) = 0.0144\ KHP\ (\text{as mg/L C}) + 0.0018$$

REPORTING RESULTS:
Report UV_{254} results as cm^{-1} using the following equation:

$$UV_{254}\,(cm^{-1}) = [A/b] \times D$$

where b = cellpath length (cm), A = mean absorbance measured, and D = dilution factor resulting from dilution with organic-free water.

QUALITY CONTROL:
Run 2 replicates of each filtered sample. Analyze every tenth sample in duplicate to assess method precision. Check system baseline UV absorbance at least after every ten samples by measuring the absorbance of an organic-free water blank. A non-zero absorbance reading for the blank may indicate the need for cell cleaning, or variation in the spectrophotometer response caused by heating or power fluctuations over time.

ANIONS BY IC (CHLORIDE, NITRATE, NITRITE, PHOSPHATE, SULFATE, BROMIDE)

INTRODUCTION:
Monitoring for anions is done for process monitoring, regulatory monitoring, raw water monitoring and lead detection. The procedure used in CCWD's lab is equivalent to Standard Methods, 20th edition, 4110B and EPA method 300.0.

INTERFERENCES:
High concentrations of any one ion interferes with the retention time of other ions. Dilution of samples will overcome many interferences. Any substance that has a retention time coinciding with that of any anion to be determined will interfere with the determination; however, no substance has been noticed to date.

APPARATUS:

Dionex DX-600 Ion Chromatograph:

1. Spectrophotometer: Wavelength: 215 nm
2. Gradient Pump Module
3. Conductivity Meter: Temperature setting 1.7
4. Anion separator column (Dionex AS4A)
5. Guard column (Dionex AG4A)
6. Anion Self-Regenerating Suppressor (ASRS-1)

REAGENTS:

1. Deionized Nanopure water
2. Eluant solution, sodium bicarbonate-sodium carbonate, 1.7mM $NaHCO_3$-1.8mM Na2CO3: Dissolve 0.2856 grams of $NaHCO_3$ and 0.3812 grams of Na2CO_3 in water and dilute to 2 liters
3. Gases:
   Helium, grade 4.5
   Nitrogen, grade 4.8
4. Standard anion solutions; a five point calibration is used to calibrate the instrument. The following are the concentrations of each of the five standards used:
   Stock solutions are as follows:
   - Chloride, 1000 ppm
   - Nitrate, 1000 ppm as Nitrogen
   - Nitrite, 1000 ppm as Nitrite ogen
   - Phosphate, 1000 ppm
   - Sulfate, 1000 ppm
   - Bromide, 1000 ppm

   a. Standard 1
      1) Fluoride, 500 uL of 1000 ppm stock standard to 100 mL
      2) Chloride, 5 mL of 1000 ppm stock standard to 100 mL
      3) Nitrate, 500 uL of 1000 ppm stock standard to 100 mL
      4) Nitrite, 500 uL of 1000 ppm stock standard to 100 mL
      5) Phosphate, 500 ul of 1000 ppm stock standard to 100 mL
      6) Sulfate, 5 mL of 1000 ppm stock standard to 100 mL
      7) Bromide, 500 uL of 1000 ppm stock standard to 100 mL

   b. Standard 2
      1) Fluoride, 300 uL of 1000 ppm stock standard to 100 mL
      2) Chloride, 4 mL of 1000 ppm stock standard to 100 mL
      3) Nitrate, 300 uL of 1000 ppm stock standard to 100 mL
      4) Nitrite, 300 uL of 1000 ppm stock standard to 100 mL
      5) Phosphate, 300 uL of 1000 ppm stock standard to 100 mL
      6) Sulfate, 4 mL of 1000 ppm stock standard to 100 mL
      7) Bromide, 300 uL of 1000 ppm stock standard to 100 mL

   c. Standard 3
      1) Fluoride, 100 uL of 1000 ppm stock standard to 100 mL.
      2) Chloride, 3 mL of 1000 ppm stock standard to 100 mL.
      3) Nitrate, 100 uL of 1000 ppm stock standard to 100 mL.

4) Nitrite, 100 uL of 1000 ppm stock standard to 100 mL.
5) Phosphate, 100 uL of 1000 ppm stock standard to 100 mL.
6) Sulfate, 3 mL of 1000 ppm stock standard to 100 mL.
7) Bromide, 100 uL of 1000 ppm stock standard to 100 mL

d. Standard 4
1) Fluoride, 50 uL of 1000 ppm stock standard to 100 mL
2) Chloride, 2 mL of 1000 ppm stock standard to 100 mL
3) Nitrate, 50 uL of 1000 ppm stock standard to 100 mL
4) Nitrite, 50 uL of 1000 ppm stock standard to 100 mL
5) Phosphate, 50 uL of 1000 ppm stock standard to 100 mL
6) Sulfate, 2 mL of 1000 ppm stock standard to 100 mL
7) Bromide, 50 uL of 1000 ppm stock standard to 100 mL

e. Standard 5
1) Fluoride, 25 uL of 1000 ppm stock standard to 100 mL
2) Chloride, 1 mL of 1000 ppm stock standard to 100 mL
3) Nitrate, 25 uL of 1000 ppm stock standard to 100 mL
4) Nitrite, 25 uL of 1000 ppm stock standard to 100 mL
5) Phosphate, 25 uL of 1000 ppm stock standard to 100 mL
6) Sulfate, 1 mL of 1000 ppm stock standard to 100 mL
7) Bromide, 25 uL of 1000 ppm stock standard to 100 mL

PROCEDURE:

1. Turn on instrument including the computer, autosampler, conductivity detector, UV/Visible Detector, gradient pump, and degas module by clicking on the “equilibrate” button. System remains pressurized by gases.
2. Create a sample list by doing a “save as” on an old file. Modify list to reflect actual sample set.
3. Allow the conductivity to come to equilibrium before proceeding with the analysis. Use pull-down menu to select “batch” and start run.

REPORTING RESULTS:

1. Chromatography data handling with the Dionex DX-600 uses Linear Regression to generate the best fit line of concentration and conductivity and absorption. The Least Squares Fit test for linearity is calculated by the computer during a calibration run and the information is resident in memory on the computer. To calibrate you must select “S” for standard. The method for anions is ANIONS.MET and must be identified in the method column for each standard in the schedule. Once the schedule is completed and saved, simply run the schedule like you would a sample with a defined schedule.
2. The following are the linear relationships for the anions; these results may change from month to month, but they should always serve as an approximate of any result run on the IC.

	Conductivity	UV/Visible
Fluoride	C = 5.4E-8 X + -0.2	N/A
	r2 = 0.99	
Chloride	C = 6.4 E-8 X + 1.1	N/A
	r2 = 0.999	
Phosphate	C = 3.7 E-7 X + 0.03	N/A

	r2 = 0.999	
Sulfate	C = 1.0 E-7 X + 1.8 r2 = 0.999	N/A
Nitrate	C = 1.7 E-7 X + 0.2 r2 = 0.999	C = 8.6 E-5 X + -0.01 r2 = 0.999
Nitrite	C = 8.8 E-8 X + 0.3 r2 = 0.996	C = 8.0 E-5 X + -0.1 r2 = 0.9999
Bromide	C = 2.3E-7 X + 0.0 r2 = 0.9999	C = 0.0009X + 0.008 r2 = 0.9999

QUALITY CONTROL:

1. Calibration of the instrument should be done within the hold time period of analyte.
2. Every set of samples should include a blank and a mid-range check-standard from a secondary source. The percent difference in standard value and the analytical value should not exceed 10%; if the difference is greater than this, the instrument is considered out of control and requires troubleshooting or re-calibration.
3. A spiked sample shall be run and the recovery calculated. The recovery shall not exceed +/- 20%.

APPENDIX F – ANALYTICAL METHODS USED BY WRF PROJECT 4019 – DUKE UNIVERSITY

Bench Scale Dsinfection Tests – Duke University WRF Project 4019

Bench Scale Disinfection Experimental Conditions

Water samples were collected throughout June and July, at different locations along a pilot plant operated in Contra Costa, CA (Contra Costa Water District - CCWD) by Carollo Engineers. Table 1 summarizes the dates and locations of water samples collected from CCWD and Table 13 the water quality for those waters.

Table 1. CCWD Treatment Summary.

Phase	Date collected at CCWD	Location/CCWD treatment
1A	6/2/2008	Ozone
2A	6/3/2008	Ozone/peroxide
1B	6/9/2008	Ozone
2B	6/10/2008	Ozone/peroxide
3A – FE	6/30/2008	Pre-nanofiltration
3A – NF	6/30/2008	Post-nanofiltration
3B – FE	7/7/2008	Pre-nanofiltration
3B –NF	7/7/2008	Post-nanofiltration

In Phase 1A and 1B, the settled plant water was run through an ozone contactor, then GAC, after which it was sampled.

In Phase 2A and 2B, the settled plant water was run through an ozone/peroxide contactor, then GAC, after which it was sampled.

In Phase 3A and 3B, the settled plant water was run through a nanofiltration membrane and samples were taken pre (FE – filtered effluent) and post nanofiltration (NF).

Table 2 presents a summary of the disinfection schemes for the samples collected at CCWD. Each sample number in Table 2 represents the UV dose and chlorination combination listed. This sample treatment matrix was performed for every water tested from CCWD during each of their pilot runs.

Table 2. UV treatment and chlorination scheme of CCWD water

Sample #	UV dose (mJ/cm^2)	Target chlorine schedule
1 (control)	0	0
2	0	CCWD*
3	0	1 mg/l
4	LP 400	CCWD
5	MP 400	CCWD
6	MP 400	1 mg/l
7	MP 100	CCWD
8	LP 400	1 mg/l
* CCWD chlorination scheme: adjust pH to 8.5, add free chlorine at 2 mg/L for 13 minutes, add measured amount of ammonia to form chloramines. Hold for 24 or 72 hours. All samples were treated with 72 hr of chlorination except that of 1A and 2A, which were treated with 24 hr of chlorination.		

Bench Scale Disinfection Analytical Methods

Basic Water Quality

Ammonia was measured using Hach method TNT 830 with a valid measurement range of 0.015 to 2.0 mg-N/L. A Shimadzu TOC-V_{CSH} with attached TMN-1 unit was used to determine total organic carbon (TOC) and total nitrogen (TN) simultaneously. Free chlorine was measured using Hach DPD method 8021with a valid measurement range of 0 to 2.0 mg-Cl_2/L. Dissolved organic nitrogen (DON) or total organic nitrogen (TON) was calculated mathematically by subtracting inorganic nitrogen species (ammonia, nitrate, and nitrite) from total nitrogen or total dissolved nitrogen.

Disinfection Byproducts

Disinfection byproducts were measured by the University of Colorado, Yale University and University of North Carolina. These methods are described herein.

Disinfection Byproducts – University of North Carolina

Haloacetic acids, trihalomethanes, trichloronitromethane, tribromonitromethane, haloacetamides, haloacetonitriles, chloral hydrate, and two haloketones (1,1-dichloropropanone and 1,1,1-trichloropropanone) were liquid-liquid extracted with methyl tert-butyl ether (MtBE) and analyzed on a Hewlett-Packard 5890 gas chromatograph with ^{63}Ni electron capture detector, as described by EPA Method 552.2 and Chinn et al. (2007). A Zebron (Phenomenex, Torrance, CA) ZB-1 capillary column (30 m length, 0.25 mm inner diameter, 1.0-µm film thickness) was used for separation of compounds. Trihalomethanes, halonitromethanes, haloacetonitriles, chloral hydrate and haloketones were analyzed by the following temperature program: oven held at 35°C for 22 min, increased at 10°C/min to 145°C and held for 2 min, increased at 20°C/min to 225°C and held for 10 min, then increased at 20°C/min to 260°C and held for 5 min. Injection volume was 2 µL in splitless/split mode, injection temperature was 117°C and detector temperature was 290°C. Haloacetamides were co-extracted with the trihalomethanes and other

halogenated byproducts (not including haloacetic acids), but analyzed with a separate oven temperature program: held at 37°C for 1 min, increased at 5°C/min to 110°C and held for 10 min, then increased at 5°C/min to 280°C. Injection volume was 2 µL, injector temperature was 200°C and detector temperature was 300°C. Haloacetic acids were analyzed using the following oven temperature program: initial temperature was 37°C, held for 21 min, increased at 5°C/min to 136°C, held for 3 min, increased at 20°C/min to 250°C and held for 3 min. Injection volume was 1 µL, injector temperature was 180°C and detector temperature was 300°C. Samples were analyzed in duplicate and 1,2-dibromopropane was used as an internal standard. The minimum reporting limit (MRL) for each of the halogenated volatile species was 0.10 µg/L, and for haloacetic acids, the MRL ranged from 0.4 to 4 µg/L for individual species. Figures A.1-A.3 and Tables A.1-A.3 presented in appendix A show chromatograms and retention times for the halogenated DBPs suite, haloacetamides, and haloacetic acids (in their derivatized methyl ester forms). Tables 3-5 present names and acronyms of each of the DBPs measured by the University of North Carolina.

Table 3 Abbreviations for suite of halogenated DBPs

Abbreviation	Compound
Cl_3CH	chloroform
TCAN	trichloroacetonitrile
DCAN	dichloroacetonitrile
$BrCl_2CH$	bromodichloromethane
CH	chloral hydrate (trichloroacetaldehyde)
11DCP	1,1-dichloropropanone
TCNM	trichloronitromethane (chloropicrin)
Br_2ClCH	dibromochloromethane
BCAN	bromochloroacetonitrile
Cl_2ICH	dichloroiodomethane
111TCP	1,1,1-trichloropropanone
Br_3CH	bromoform
DBAN	dibromoacetonitrile
BrClICH	bromochloroiodomethane
TBNM	tribromonitromethane (bromopicrin)
Br_2ICH	dibromoiodomethane
ClI_2CH	chlorodiiodomethane
BrI_2CH	bromodiiodomethane
I_3CH	iodoform

Table 4 Haloacetamide abbreviations

Abbreviation	Compound
BrAM	bromoacetamide
Cl_2AM	dichloroacetamide
BrClAM	bromochloroacetamide
Cl_3AM	trichloroacetamide
Br_2AM	dibromoacetamide
ClIAM	chloroiodoacetamide
$BrCl_2AM$	bromodichloroacetamide
BrIAM	bromoiodoacetamide
Br_2ClAM	dibromochloroacetamide
Br_3AM	tribromoacetamide
I_2AM	diiodoacetamide
ClAA	chloroacetic acid
BrAA	bromoacetic acid
Cl_2AA	dichloroacetic acid
BrClAA	bromochloroacetic acid
Cl_3AA	trichloroacetic acid
Br_2AA	dibromoacetic acid
$BrCl_2AA$	bromodichloroacetic acid
Br_2ClAA	dibromochloroacetic acid
Br_3AA	tribromoacetic acid

Disinfection Byproducts – Yale University

The nitrosamine standards were purchased from Accustandard (New Haven, CT). The NDMA-d_6 internal standard was purchased from Cambridge Isotope Laboratories. All nitrosamines that were analyzed excluding the internal standard were provided in a combined EPA 521 mix at 2000 µg/mL in methylene chloride. The nitrosamines in the EPA 521 mix included nitrosodimethylamine (NDMA), nitrosomethylethylamine (NMEA), nitrosodiethylamine (NDEA), nitrosodibutylamine (NDBA), nitrosopyrrolidine (NPYR), nitrosopiperidine (NPIP), and nitrosodipropylamine (NDPA). The NDMA-d_6 was provided as a stock solution at 1000 µg/mL in methylene chloride. Dimethylnitramine, the nitrated analogue of NDMA, has recently been synthesized in Dr. Mitch's laboratory through a modified method described in Mezyk *et al.,* 2006.

Analysis of the nitrosamines and dimethylnitramine (DMNA) were conducted according to EPA 521 and summarized below. Experimental samples were first quenched and 500 mL samples were shipped on ice to Yale. After injection of d_6-NDMA for isotope dilution analysis, samples were extracted through solid-phase extraction cartridges containing activated carbon. Samples were left dry for ~ 30 min and then extracted with ~ 12 mL of methylene chloride. Anhydrous sodium sulfate was then added to these samples to remove residual water from the

extract. The methylene chloride fraction was then removed from the salt and blown down to ~ 0.5 mL under nitrogen and analyzed by gas chromatography tandem mass spectrometry (GC/MS/MS; Agilent DB-1701, 30 m × 0.32 mm × 1 μm column) using chemical ionization (methanol) and large volume injection. The column temperature was held at 35°C for 3 min, ramped up to 130°C at 4°C/min and held for 3 min, ramped up to 210°C at 40°C/min and held for 5 min, and ramped up to 250°C at 40°C/min and held for 0.5 min. The injection port temperature was initially set at 37°C and ramped to 250°C over time. Standards were prepared fresh by spiking known concentrations of nitrosamines/nitramines and NDMA-d_6 into 1 mL of methylene chloride and analyzed on the GC/MS/MS. Parent and daughter ions of analyzed species are presented in Table 5

Table 5 Parent and Daughter Ions for Quantitation of Nitrosamines/Nitramines using GC/MS/MS (chemical ionization with methanol)

Compound	Parent Ion (m/z)	Daughter Ions (m/z)
NDMA	75	44+47+58
NDMA-d_6	81	50+64
DMNA	91	44+45
NMEA	89	61
NDEA	103	75
NDPA	131	89
NPIP	115	69
NPYR	101	55
NDBA	159	57

Quality Assurance Project Plan
AwwaRF Project #4019

Impact of UV Location and Sequence on Byproduct Formation

November 2007

Submitted by
Karl Linden, PI
University of Colorado - Boulder
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A1 – TITLE AND APPROVAL SHEET

Title of the Plan: Quality Assurance Project Plan for AwwaRF Project #4019 on "**Impact of UV Location and Sequence on Byproduct Formation**"
Names of the Organizations Implementing the Project: Water Resources Research Institute at the North Carolina State University, University of Colorado - Boulder, University of North Carolina at Chapel Hill, Yale University.
Effective Date of the Plan: October 2007 - April, 2010

Approving Officials	Name, Title, Organization	Signature, Approval Date
Organization's Project Manager	Alice Fulmer, Project Manager, Awwa Research Foundation	
PAC* Member (EPA Representative)	Jean Munch, USEPA	
PAC Member	James P. Malley, Jr. UNH	
PAC Member	Christine Cotton, Malcolm Pirnie	
PAC Member	Carla Glaser, NYC DEP	
Principal Administrator	David Moreau, Director, Water Resources Research Institute, NC State University	
Principal Investigator	Karl G. Linden, Professor, University of Colorado	
Co-Principal Investigator	Howard Weinberg, Assistant Professor, University of North Carolina	
Co-Principal Investigator	William A. Mitch, Assistant Professor, Yale University	
Research Associate	Detlef Knappe, NC State University	
Technical Advisory Committee	David A. Reckhow, Professor, University of Massachusetts,	
Technical Advisory Committee	Susan A. Richardson, USEPA	

*PAC = Project Advisory Committee

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A3 – DISTRIBUTION LIST

Alice Fulmer	Awwa Research Foundation
Jean Munch	United States Environmental Protection Agency
James P. Malley Jr.	University of New Hampshire
Christine Cotton	Malcolm Pirnie
Carla Glaser	New York City Department of Environmental Protection
David Moreau	NC Water Resources Research Institute, NC State
Karl Linden	University of Colorado-Boulder
Howard Weinberg	University of North Carolina
William A. Mitch	Yale University
Detlef Knappe	NC State University
David Reckhow	University of Massachusetts
Susan Richardson	United States Environmental Protection Agency

A4 – PROJECT/TASK ORGANIZATION

The figure below shows the project team organization and responsibilities. Karl Linden (University of Colorado –CU)) will be the Principal Investigator (PI) and be responsible for project management, including interacting with the AwwaRF Project Manager regarding contractual issues, reporting, and billing, assuring all tasks are conducted during the scheduled timeframes, and facilitating interactions between team members. Dr. Linden is the QA/QC project manager. The PI will also be responsible for: (1) coordination of a project kick-off meeting, (2) preparation and submission of status and periodic reports and responses to PAC comments, and (3) draft and final reports. Dr. Linden will be responsible for carrying out the utility surveys, bench scale disinfection experiments, and coordinating the field testing campaigns. At Yale University (YU), William Mitch will be responsible for guiding the experiments and analyses on the formation of nitrosamine byproducts. At University of North Carolina (UNC) Howard Weinberg will be responsible for guiding the experiments and analyses on the formation of chlorinated and oxidation byproducts in bulk waters and in waters reconstituted from fractionated Natural Organic Matter.

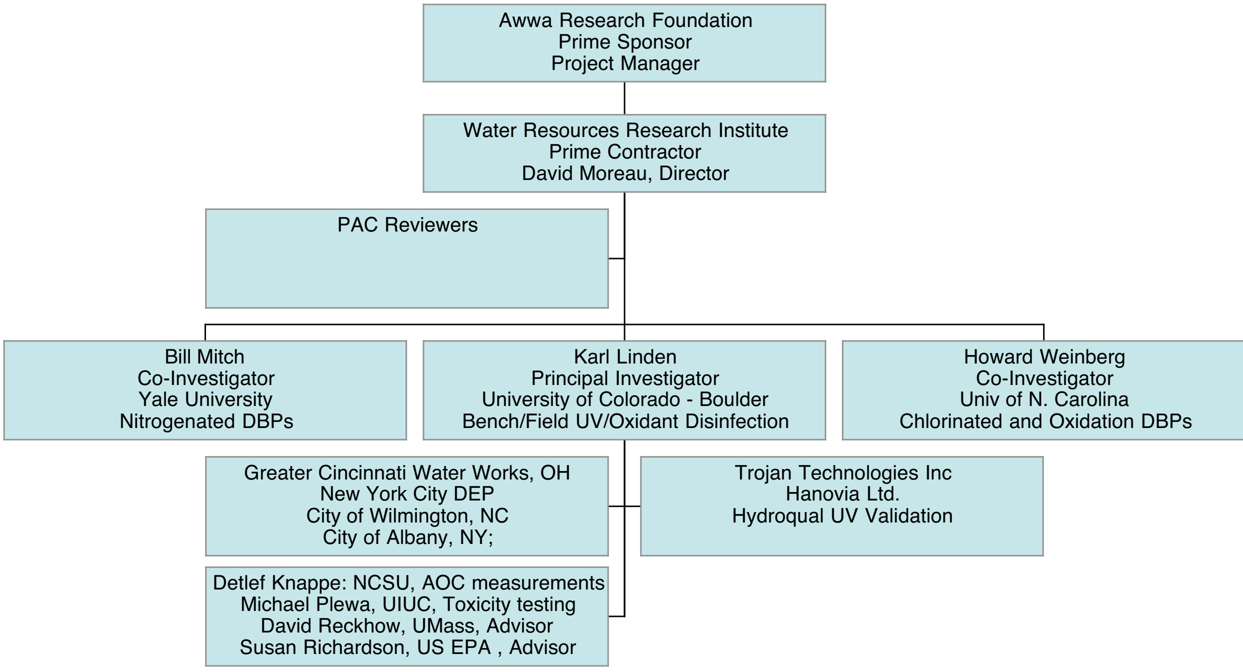

Figure 1: Project Team Organization and Responsibilities

Dr. Detlef Knappe will provide analyses of the AOC at NC State (NCSU). Dr. Plewa at the University of Illinois (UIUC) will provide toxicity testing of specific byproducts.

Waters for various aspects of the UV DBP testing will be provided by water utilities including Greater Cincinnati Waterworks, City of Wilmington NC, City of Albany NY, and New York City. Hydroqual will provide a site for field scale testing with UV disinfection reactors provided by Trojan Technologies and Hanovia Ltd.

A Technical Advisory Committee (TAC) will be used to provide advice on specific areas of expertise to the project team. David Reckhow and Susan Richardson will both serve as technical advisors to this research project.

The primary communication challenge is ensuring that the results accruing from different sections of the project occurring concurrently are efficiently disseminated to team members so that the work plan can be altered to target the most promising research directions. Communication among team members will occur by email (e.g., bi-weekly), through bi-monthly teleconference calls, and by face-to-face meetings (e.g., semi-annually). Data will be shared between the PI and co-PIs electronically.

A5 – QUALITY OBJECTIVES AND CRITERIA

The project team will follow a quality assurance/quality control (QA/QC) program to ensure that accurate, precise, and nonbiased data are produced. The QA/QC program includes the analysis of method blanks, calibration curves, replicates, and laboratory-fortified samples, and the performance of method detection limit (MDL) studies. This project encompasses formation pathway studies as well as occurrence of byproducts during disinfection treatment. The occurrence study often will require detection of analytes near the lower limits of what is analytically feasible. As concentrations approach these lower limits, analytical uncertainties increase. Detection within complex matrices will also be required. For formation pathway studies, precursor concentrations can be adjusted to balance the benefits obtained from operating at higher concentrations against the need to maintain precursor concentrations at levels close to those that might be anticipated under treatment conditions. Moreover, analyses can be conducted in clean (e.g., deionized water) matrices. The project team will develop analytical methods capable of achieving MDLs appropriate to each type of study. These will be referred to hereafter as the "low-level" and "high-level" analytical methods. Low-level analytical methods will require more stringent QA/QC procedures than high-level methods.

Low-Level QA/QC Protocols

Analytical methods will be approved for use following the successful demonstration of the following:

- Method blanks
- Calibration curves with at least 5 points over the range of concentrations of anticipated interest for the study
- Duplicate analyses within 25% relative standard deviation
- Greater than 75% recovery in laboratory fortified spike samples in representative waters
- MDL determinations (based upon the standard deviation of 7 replicate standards whose concentration is roughly 3 times larger than the anticipated MDL).

When used for the occurrence, analyses will include a minimum of:

- 5 point standard curve
- 1 duplicate and matrix spike analysis per 10 samples

High-Level QA/QC Protocols

Analytical methods for formation pathway studies will be approved following the demonstration of the following:

- Method blanks
- Calibration curves over the range of anticipated interest for the study
- Duplicate analyses within 20% relative standard deviation
- Greater than 80% recovery in laboratory fortified spike samples in representative waters (1 each). Note this is only applicable to methods applied to waters not based on deionized water samples.
- MDL determinations (based upon the standard deviation of 7 replicate standards whose concentration is roughly 3 times larger than the anticipated MDL).

When used for formation pathway studies, analyses will include a minimum of:

- 3 point standard curve
- 1 duplicate or replicate analysis per 10 samples. Note that for formation pathway studies, replicate samples will be used in preference to duplicate samples. Replicate samples refers to the performance of a reaction under identical conditions in a separate reaction vessel. Duplicate analysis refers to the analysis of a second aliquot retrieved from the same reaction vessel. Acceptance criteria for duplicate analyses will be 20% relative percent difference. Acceptance criteria for replicate analyses will be 25% relative percent difference. Note that for formation pathway studies, large changes in concentration (i.e., order of magnitude) are targeted.

Table 1 provides target MDLs, and proposed analytical methods for low and high level analytical methods for this project. Details on the experimental plan are provided in the Scope of Work (as indicated in Section B1) and not repeated here. Information on sampling methods is in Section B2.

TABLE 1. PROPOSED ANALYTICAL METHODS FOR DBPS

Analyses	Method	Analytes	Target MDL	Preservative
Oxidation Byproducts	Kuo et al., 1996	Carboxylic Acids	1 µg/L	ethylene diamine
	Modified EPA Method 556	Aldehydes	0.1 µg/L	sodium azide
	Weinberg et al. 2002	Aldo/Keto Acids	0.1 µg/L	sodium azide
	Khan & Weinberg, 2006	Epoxides	0.1 µg/L	sodium azide
	Klassen et al., 1994	Peroxides	0.1 µg/L	pH 4
NOM Characterization	Excitation-emission matrix fluorescence			
	Standard Method 5310B	TOC	100 µg/L	HCl to pH 2
	Standard Method 5910	UV_{254}	NA	HCl to pH 2
Halogenated Byproducts	EPA Method 551.1	THMs,	0.05 µg/L	$(NH_4)_2SO_4$
		Chloral hydrate	0.05 µg/L	ascorbic acid
	Weinberg et al. 2002	Haloketones	0.05 µg/L	ascorbic acid
	Modified EPA 552	HAA9 + Iodoacids	0.5 µg/L	azide plus $(NH_4)_2SO_4$
	Modified EPA 326	Oxyhalides	10 µg/L	ethylene diamine
	Sclimenti et al., 1995	CNCl and CNBr	0.5 µg/L	ascorbic acid
	Pfaff and Brockhoff, 1990	chlorite	5 µg/L	ethylene diamine
	Weinberg & Yamada, 1998	Bromate/iodate	0.1 µg/L	ethylene diamine
	Onstad and Weinberg, 2005	MX	0.01 µg/L	azide plus $(NH_4)_2SO_4$
	Standard Method 5320	TOX	5 µg/L	$(NH_4)_2SO_4$
N-DBPs	Pfaff and Brockhoff, 1990	Nitrite	5 µg/L	ethylene diamine
		Nitrate	5 µg/L	ethylene diamine
		Total Organic N	50 µg/L	HCl to pH 2
	Schreiber and Mitch, 2006b	Nitrosamines		Ascorbic acid
	Joo and Mitch, accepted	Halonitromethanes		Ascorbic acid, pH 3.5

A6 – SPECIAL TRAINING/CERTIFICATION

Each of the organizations that will be doing laboratory analyses and/or bench-scale studies (i.e., CU, YU, UNC, NCSU, UIUC) will be responsible for utilizing staff with the appropriate background and training for the required work, and for providing specialized training when required (e.g., for graduate students). Individuals will not have to be certified, but must prove competency through an initial demonstration of ability to perform the analyses and adherence to other requirements in the QAPP specific to their position.

A7 – DOCUMENTS AND RECORDS

When the QA Project Plan is initially approved or updated, Karl Linden will ensure that all parties on the distribution list (Section A3) get a copy. Electronic copies will be distributed to all personnel affiliated with the project.

The following reports will be submitted to the AwwaRF project manager. A brief status summary will be submitted every three months during the research phase of the project. A more detailed technical summary will be submitted with every other report (every six months). The draft, final report will be submitted in the first quarter of 2010. The final report will be submitted in the second quarter of 2010.

The project team will maintain all project files, including raw data files and spreadsheets, for a period of not less than three years following the completion of the project.

B1 – EXPERIMENTAL DESIGN

The details of the Experimental Design are presented in the previously submitted Scope of Work – please refer to that document.

B2 – SAMPLING METHODS

Karl Linden will have primary responsibility for coordinating the collection of samples from utilities and QA/QC approval for all parameters collected in the field. Sampling instructions sheets will be prepared for each water treatment plant. These sheets will include a list of sample bottles enclosed in each sample kit, and detailed sampling and shipping instructions. Large ziplock bags will be used to separate all of the sample bottles that will need to be collected at a specific location. The instructions will note that the sampling staff should not rinse the bottles before filling and to not overfill, because most of the bottles (in particular, for the DBPs) contain a dechlorination agent and/or preservative. Samples will be shipped overnight in ice chests with frozen Blue Ice. In case of questions, two contacts (with telephone numbers and e-mail addresses) will be provided for each research facility. These instructions will be sent (by e-mail or FAX) one week before the sample date, and a hardcopy will be included in the sample kits, which will be sent to the utility several days prior to the sample date.

Sulfuric acid solutions for acid preservation contained in bottles are placed in small white boxes located usually along with the red-capped sample bottles in the ice chests packs. These acid kits include an eye dropping amber bottle, two additional plastic eyedroppers in case of breakage, and a set of pH test strips. The excess space in the box is filled with Styrofoam peanuts, taped shut, and double bagged with bubble wrap. Labels are used to denote the contents of the box as hazardous where appropriate.

<u>Sample Preservation</u>

Each of the samples will be preserved as outlined in appropriate methods such as *Standard Methods* (APHA, 1998) and presented in Table 1 and/or as discussed below. Sample preservation and holding times will be evaluated as appropriate during the evolution of analytical methods in our laboratories.

<u>Holding Times</u>

All of the samples will be stored in the laboratory at 4ºC and will be extracted within holding times either as established in the literature (e.g. APHA, 1998; Munch and Hautman, 1995) or as determined in our laboratories. For example, many analytes (e.g., the DBPs) will be analyzed for within two weeks

B3 – SAMPLE HANDLING AND CUSTODY

Sample bottles will be labeled at each research facility with the name of the utility and treatment plant, the date of sampling, the sample location, and the name of the analyte.

Glass sample bottles will be shipped in "bubble-pack" bags to prevent breakage. For most analytical fractions (in particular, the DBPs), multiple bottles will be provided (in part) as "back-up" samples. If a TOC, UV, or bromide glass sample bottle is broken, the "missing" analyte can be analyzed from sample aliquots remaining from samples collected for other analytes with compatible preservatives. Plastic bags filled with styrofoam "peanuts" will also be included in the ice chests so that (1) the bottles will not bounce around during transit and (2) the bottles will not directly touch the Blue Ice and freeze. The ice chests will be secured with strapping tape. Each ice chest will also include a pre-filled out airbill for overnight return delivery as well as chain of custody documentation and detailed sample collection instructions.

Upon receipt at each research facility, samples will be logged in. A project-wide unified sampling identification will be used for all three laboratories in the study.

B4 – ANALYTICAL METHODS

Analytical methods anticipated for use in this study are listed in Table 1 and examples are summarized briefly below.

Yale University

Nitrosamines and Dimethylnitramine

High-level (Schreiber and Mitch, 2005): The high-level method will be applied to NDMA and dimethylnitramine formation pathway studies, where dimethylamine will serve as a spiked model precursor. The targeted method detection limits will be 10 ng/L. Chlorination reactions (1 L) will be halted by the addition of ascorbic acid. Deuterated d_6-NDMA will be injected to serve as a surrogate standard. The solution will be extracted immediately with 0.4 g of Ambersorb 572 resin beads by stirring with a Teflon-coated magnetic stir bar for 2 h for recovery of the *N*-nitrosamines (Guo et al., 2004). The sample will be filtered and set aside to air-dry overnight. The dry resin will be extracted with 4 mL methylene chloride for 3 h. After decanting the methylene chloride, the methylene chloride will be concentrated to 1 mL by blowing down under nitrogen gas. The concentrated extracts will be measured by GC/tandem MS with methanol CI. NDMA concentrations will be assessed by comparison with a standard curve following correction for extraction efficiencies using deuterated d_6-NDMA as a surrogate standard. Concentrations of other nitrosamines will be corrected using recoveries determined by separate recovery experiments. Dimethylnitramine will be added as an analyte to this method.

Low-level: Yale University will use EPA Method 521 when analyzing waters not spiked with dimethylamine as a precursor. However, Yale will modify the method for the analysis of dimethylnitramine.

Chloronitromethane, dichloronitromethane, trichloronitromethane (chloropicrin)

High and Low-level: Yale University uses a GC-ECD method for quantifying these analytes (Joo and Mitch, accepted). Briefly, samples collected in 25 mL headspace-free vials are quenched with freshly-prepared ascorbic acid at a concentration of 30 mg/L. The pH of the solution is reduced to 3.7. The samples are transferred to 40 mL vials and shaken with 4 mL of MtBE for 10 min. The MtBE layer is analyzed by GC-ECD using a DB-1701 column. Method detection limits are ~ 1 nM (~ 0.2 μg/L for chloropicrin).

Nitromethane

High and Low-level: Yale University will investigate whether the GC-ECD method used for chloronitromethanes can be adapted for the analysis of nitromethane. In the event that this method can not be modified, Yale University will investigate the use of a headspace SPME extraction method followed by GC-MS in the electron impact mode for nitromethane.

4-nitrosophenol, 2-nitrophenol, 3-nitrophenol and 4-nitrophenol

High-level: As these are the hypothesized products of the model precursor, phenol, they will only be analyzed in samples spiked with phenol. Therefore, only a high-level analysis will be developed. Yale University will investigate the use of EPA Method 625, a GC-MS method, for these analytes. Reported method detection limits are in the low mg/L range for 2-nitrophenol and

4-nitrophenol. Yale will attempt to modify this method to analyze for 3-nitrophenol and 4-nitrosophenol.

University of North Carolina

Quality assurance manuals are available at UNC which include detailed information on methods and procedures, and can be furnished upon request. As an example, the method for haloacetamide analysis is presented below.

Haloacetamide analysis using LLE-GC-ECD method

Materials :

Reagents:

•Ethyl Acetate (Omnisolv, 99.8%), EM Science (Gibbstown, NJ, USA) •L-ascorbic acid certified ACS: Fisher Scientific (Fair Lawn, NJ, USA•Sodium Sulfate powder anhydrous (Na_2SO_4, >99%): ACROS Organics (Fair Lawn, NJ, USA),

Standards:

•Standard Stock Solution:

2-Chloroacetamide (CAM, 98%): Aldrich (St Louis, MO, USA) 2-Bromoaetamide (BAM, 98%): Aldrich (St Louis, MO, USA)

2,2-Dichloroacetamide (DCAM; 98%): Aldrich (St Louis, MO, USA)

2,2-Dibromoacetamide (DBAM; 98%): Aldrich (St Louis, MO, USA)

2,2,2-Trichloroacetamide (TCAM; 99%): Aldrich (St Louis, MO, USA)

•Internal Standard Stock Solution: 1,2-dibromopropane (1,2-DBP) neat standard, >99%, Aldrich (Milwaukee, WI, USA)

Daily working standards

•Haloacetamide standard diluted solutions:

- Individual haloacetamide primary dilutions (~2mg/mL; Table 2): prepared by weighing out a appropriate amount (mg) of individual haloacetamide standard stock solutions and injecting into a 2mL-volumetric flask containing 2mL of ethyl acetate (EtAc)

Table 2. Individual haloacetamide primary dilutions

Individual haloacetamides	Abbreviation	Mass of individual haloacetamide standard stock solutions (mg)	Individual haloacetamide concentrations (mg/mL)
2-Chloroacetamide	CAM	4.98	2.49
2-Bromoacetamide	BAM	2.37	1.19
2,2-Dichloroacetamide	DCAM	5.24	2.62
2,2-Dibromoacetamide	DBAM	3.68	1.84
2,2,2-Trichloroacetamide	TCAM	6.43	3.22

- Mixed haloacetamide secondary dilution (~0.25mg/mL; Table 3): prepared by injecting an appropriate volume (mL) of each individual haloacetamide primary dilutions using a micropipette, into a 2mL-volumetric flask containing 2mL of EtAc

Table 3. Mixed haloacetamide secondary dilution

Individual haloacetamides	Abbreviation	Volume of individual haloacetamide primary dilutions (mL)	Individual haloacetamide concentrations (mg/mL)
2-Chloroacetamide	CAM	0.2	0.25
2-Bromoacetamide	BAM	0.4	0.24
2,2-Dichloroacetamide	DCAM	0.2	0.26
2,2-Dibromoacetamide	DBAM	0.3	0.28
2,2,2-Trichloroacetamide	TCAM	0.2	0.32

- Mixed haloacetamide tertiary dilution (~10mg/L; Table 4): prepared by injecting 80µL of the mixed haloacetamide secondary dilution using a micropipette, into a 2mL-volumetric flask containing 2mL of EtAc

Table 4. Mixed haloacetamide tertiary dilution

Individual haloacetamides	Abbreviation	Individual haloacetamide concentrations (mg/mL)
2-Chloroacetamide	CAM	9.96
2-Bromoacetamide	BAM	9.48
2,2-Dichloroacetamide	DCAM	10.48
2,2-Dibromoacetamide	DBAM	11.04
2,2,2-Trichloroacetamide	TCAM	12.86

•1,2-DBP Internal Standard Diluted Solutions:

- Primary dilution at 2mg/mL: prepared by weighing out 10mg of 1,2-DBP and injecting into a 5mL-volumetric flask containing 5mL of EtAc

- Secondary dilution at 100µg/mL: prepared by injecting 250µL of 1,2-DBP primary dilution using a micropipette, into a 5mL-volumetric flask containing 5mL of EtAc - Tertiary dilution at 50µg/L: prepared by injecting 250µL of 1,2-DBP secondary dilution using a micropipette, into a 500mL-volumetric flask containing 500mL of EtAc

Water sample collection and preparation:

Collect water in 1L amber glass bottles containing 40mg of L-ascorbic acid headspace-free. Keep below 10 degrees Celsius during transport in coolers and immediately place in refrigerator at 4 degrees Celsius upon receipt at laboratory and after completing chain of custody documentation. Samples should be extracted within 10 days of collection.

Preparation of calibration standards:

Add the appropriate amounts (Table 5) of the mixed haloacetamide tertiary dilution (at ≈10mg/L, in EtAc) to a 100mL volumetric flask of one of the water samples. The actual concentrations of the individual haloacetamides are given in Table 6.

Table 5. Preparation of calibration standards in a 1:50 diluted RO water sample

Standard name	Volume of mixed haloacetamide tertiary dilution (µL)	Calibration standard concentration (µg/L)
Std 0	0	0
Std 1	10	1
Std 5	50	5
Std 10	100	10

Table 6. Actual concentrations of individual haloacetamides in calibration standards (µg/L)

Standard name	CAM	BAM	DCAM	DBAM	TCAM
Std 0	0.00	0.00	0.00	0.00	0.00
Std 1	1.00	0.95	1.05	1.10	1.29
Std 5	4.98	4.74	5.24	5.52	6.43
Std 10	9.96	9.48	10.48	11.04	12.86

Liquid-liquid extraction:

Put **20mL** of each standard added to aqueous sample (spiked or not) into each of three 40mL vials.

Add **4g of Na_2SO_4 anhydrous powder** (dried in oven at 400°C and stocked in dessicator). Shake the vial to dissolve Na_2SO_4, and then set down

Add **5mL of internal standard tertiary dilution** (1,2-DBP at 50µg/L in EtAc) and shake for 1 min.

Transfer the organic layer to a GC-vial. Cap with crimp topper and store in freeze (-20°C).

GC-ECD analysis on a Hewlett-Packard GC5890 Series II:

- Injector:

Syringe size = 10µL; Injection volume = 2µL

Wash solvent = EtAc; Pre-injection washes = 3; Post-injection washes = 3; Pumps = 3

Temperature injector = 180°C; Injection splitless

- Oven/Column:

Oven equil. time = 3 min; Oven max T°C = 300°C

Column type = DB1 (Agilent), 30.0m length, 0.25mm diameter, 0.25µm film thickness

Gas = He; Flow column = 1mL/min; Pressure column = 11.3 psi

Split flow = 1mL/min; Split ratio = 1:1

- Detector:

Type = ECD (Electron Capture Detector)

Temperature detector = 300°C

- Temperature program (Total time = 59.60 min)

	Velocity (°C/min)	Temperature (°C)	Time (min)
Initial	-	37	1
Level 1	5	110	10
Level 2	5	280	0

Quality Control

Standard addition is the method used for calibration and quantitation. Precision is measured as the average and coefficient of variation (%CV) of the triplicate analyses of each sample and should be less than 10%. The %CV of all the internal standard responses for the complete set of samples must be less than 15%. Individual samples responsible for elevating this value above the threshold should be flagged and considered suspect.

A calibration check standard is prepared in the mid-range of the standard calibration curve and is injected every 10 samples. If the detector response for this sample varies more than 10% from the previous injection, all samples analyzed between the two injections are flagged for investigation.

Each sample bottle set is accompanied by replicate field and travel blanks

North Carolina State University

New Assimilable Organic Carbon Method

Assimilable organic carbon (AOC) concentrations will be measured by a new flow-cytometric method that utilizes a natural consortium of bacteria from a local lake water (Hammes and Egli 2005), using a protocol developed at EAWAG (Berger *et al.* 2005).

- Results at EAWAG showed that the addition of sodium thiosulfate for quenching of ozone residuals did not affect AOC concentration measurements (Berger *et al.* 2005).
- Effect of incubation time on AOC results. For a natural consortium of bacteria obtained from a Swiss surface water, EAWAG results suggest that a 2-day incubation time is typically required at 30°C to reach the stationary phase. On this basis, a 3-day incubation time at 30°C was recommended for AOC tests. For the natural microbial consortium that will be used in this study (obtained from natural water source described below), growth curves will be developed at 30°C to identify the required incubation time to reach the stationary phase.
- Determination of yield factor using acetate and a synthetic AOC mixture (Table 8). In the AOC context, yield factors have traditionally been developed for the growth of bacteria on acetate (e.g., van der Kooij 1992). However, yield factors can be higher for other carbon sources and for solutions containing a mixture of carbon sources. Therefore, yield factors will be determined in this study for both acetate and a synthetic AOC mixture (Table 8). Yield factors (cells/µg of acetate-C or cells/µg of C in AOC mixture) obtained with the natural microbial consortium to be used in this study (obtained from University Lake in Carrboro, NC) will be compared to those obtained at EAWAG for a natural

microbial consortium obtained from a Swiss surface water. The yield factors will be used to benchmark this new AOC procedure against previously used AOC protocols.

Each AOC experiment will be conducted in triplicate and both positive and negative controls will be included. Positive controls (ultrapure water plus mineral buffer [Table 7] plus AOC mixture [Table 8]) will be used to verify that the inoculum behaves similarly in all experiments while negative controls (ultrapure water plus mineral buffer) will be used to verify absence of AOC contamination from glassware and/or sample handling steps. All samples will be delivered to NC State University by Duke investigators on ice within 2 hours of performing the UV or post-chlorination exposures. Upon receipt of samples at NC State University, samples will be immediately analyzed for total cell counts and AOC.

Table 7. Composition of mineral buffer stock solution (1 μL buffer stock solution will be added per mL of sample prior to AOC analysis)

Mineral Salt	Stock Solution Concentration
$(NH_4)_2SO_4$	1.0 g/L
$MgSO_4$	50 mg/L
$CoCl_2 \cdot 6H_2O$	4.1 mg/L
$ZnCl_2$	2.1 mg/L
KH_2PO_4	3.0 g/L
K_2HPO_4	7.0 g/L

Mineral Salt	Stock Solution Concentration
KCl	0.2 g/L
NaCl	0.1 g/L
$CuCl_2 \cdot 2\,H_2O$	5.4 mg/L
$MnSO_4 \cdot 7\,H_2O$	5.0 mg/L
$(NH_4)_6Mo_7O_{24} \cdot 4H_2O$	1.3 mg/L
$FeSO_4 \cdot 7\,H_2O$	1.0 mg/L

Table 8. Composition of synthetic AOC mixture stock solution (EAWAG recipe)[a].

Organic Acids (mM)		**Sugars** (mM)		**Amino Acids** (mM)			
Pyruvate	0.54	Glucose	0.54	Alanine	0.08	Leucine	0.16
Oxalate	0.54	Ribose	0.54	Arginine	0.16	Lysine	0.16
Formate	0.54	Fructose	0.54	Asparagine	0.10	Methionine	0.13
Acetate	0.54	Xylose	0.54	Aspartic acid	0.10	Phenylalanine	0.23
Succinate	0.54	Maltose	0.54	Cysteine	0.08	Proline	0.13
		GlcNAc[b]	2.7	Glutamine	0.13	Threonine	0.10
				Glutamic acid	0.13	Tryptophan	0.29
				Glycine	0.05	Tyrosine	0.23
				Histidine	0.16	Valine	0.13
				Isoleucine	0.16		

[a] C:N molar ratio = 10:1
[b] GlcNAc = N-acetyl glucosamine

Method for quantifying total cell counts. Total cell counts will be determined using a nucleic acid staining/flow cytometry procedure as previously described (Hammes and Egli 2005). Briefly, 1-mL samples will be amended with lysis buffer and directly stained with 10 μg/mL SYBR Green stain (Molecular Probes), and incubated in the dark for at least 20 min before measurement. Flow cytometric analyses and cell sorting will be performed at the NC State

University Flow Cytometry and Cell Sorting Laboratory using green fluorescence as trigger. Staining results for several samples will be compared to epifluorescence microscopy (Nikon Optiphot) using the appropriate filter sets. Results will be reported as number of cells per mL.

AOC method. For AOC analyses, the procedure depicted in Figure 2 will be followed. Briefly, about 50 mL of sample (raw water, finished water, distribution system sample) will be filtered through rinsed, 0.22-µm PVDF filters (Millipore) and collected in a baked AOC-free glass beaker. To assure that filters do not add AOC, filters will be rinsed overnight with 2-3 liters of AOC-free water (Berger *et al.* 2005). The sample is then evenly distributed among three baked AOC-free, 20-ml glass vials and inoculated with the natural microbial consortium (see below for a description of the method that will be used to obtain the inoculum). The required inoculation volume will be based on the cell count of the inoculum. The inoculated sample will be incubated at 30ºC until the stationary phase is reached (determined during method standardization).

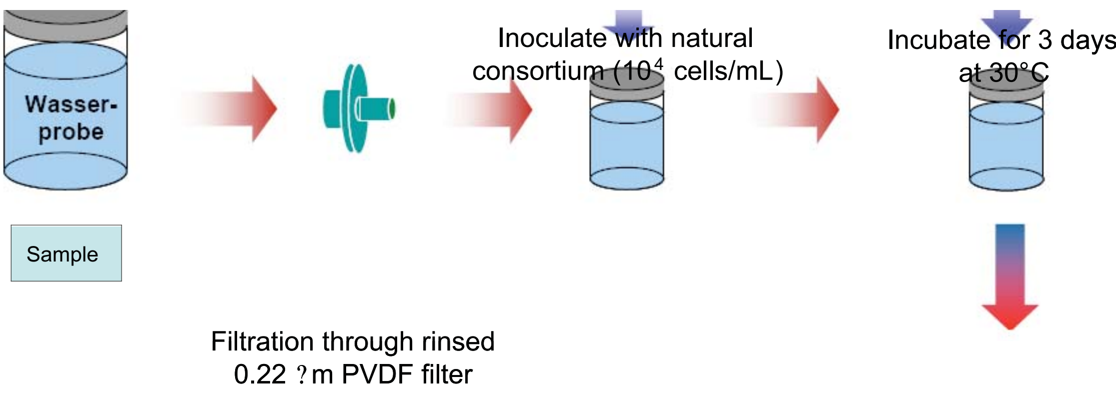

Figure 2. Depiction of AOC methodology (after Berger *et al.* 2005).

Method for obtaining natural microbial consortium. The natural consortium will be obtained from a local water source (University Lake Reservoir, Carrboro, NC). To obtain the inoculum, 100 mL of lake water will be filtered through rinsed, 0.22-µm PVDF membrane filters (Millipore). The filtrate will be inoculated with 100 µL of unfiltered lake water and incubated at 30ºC for 14 days (Hammes and Egli 2005). This time is sufficiently long to assure maximum growth as well as AOC depletion. The cells will be harvested by centrifugation and afterwards re-suspended in HPLC water amended with a mineral buffer. The re-suspended cells will be incubated for 7 more days to assure that no residual AOC is present in the inoculum. To determine the cell concentration of the inoculum, a sub-sample will be taken, stained with SYBRGreen, and analyzed by flow-cytometry.

Based on EAWAG experience, the inoculum can be stored for at least eight months at 4ºC. Sufficient fresh inoculum will be prepared to be able to inoculate all samples that will be collected at any one time. To verify that the inoculum behaves similarly throughout the experimental period, positive controls (ultrapure water plus mineral buffer plus AOC mixture [Table 8]) will be included with each sample batch.

For AOC tests, all glassware and screw caps will be cleaned according to the procedure described in *Standard Methods* (APHA, 1998). For example, borosilicate glass vials will be washed with detergent, rinse thrice in deionized water, submerged overnight in 0.2 N HCl, and again rinsed thrice in deionized water. Upon washing and rinsing, removal of trace carbon from glassware will be achieved by baking all glassware at 550ºC for 6 hours. Prior to baking, glassware will be covered with aluminum foil. Baked glassware will be stored for a maximum of one week. Screw caps with TFE-lined septa will be soaked in 10% sodium persulfate solution at 60ºC for at least 1 hour, rinsed twice with deionized water, and air-dried. Carbon-free pipette tips will be used following rinsing with ultrapure water and dry-sterilizing at 100°C for 3 h (Charnock and Kjonno 2000). All AOC samples will be analyzed in triplicate, and triplicate positive and negative controls will be included with each sampling event.

B5 – INSTRUMENT/EQUIPMENT TESTING, INSPECTION, AND MAINTENANCE

Required maintenance of all instruments and equipment will be done in accordance with manufacturer's guidelines. Instruments will be visually checked for proper operation on a daily basis when in use. Maintenance logs of routine inspections and corrective active will be kept.

Where available, some analytical instruments have service contracts with an outside vendor to provide troubleshooting and replacement parts to keep the systems running like new. In addition, some contracts allow for one yearly preventative maintenance visit in which the instrument is serviced and performance specifications are tested.

B6 – INSTRUMENT/EQUIPMENT CALIBRATION AND FREQUENCY

Calibration curves are established with a sufficient number of standards to determine linearity and/or nonlinear regression. If criteria are not met, steps are taken immediately to identify and correct this situation. When the level of an analyte is greater than that of the highest standard in the calibration curve, the sample is diluted and rerun. In some cases, samples are run both straight and diluted in order to quantity a series of analytes over a wide range of concentrations. Calibration curves will be run at least once every sampling session. GC-ECD and GC-MS instrumentation have performance evaluation standards prepared daily from stock solutions stored at -15°C in MtBE or hexane and themselves prepared fresh every month. The purpose of these standards is to monitor instrument performance over time and a log of detector response is maintained together with signal to noise values for these standards injected at a concentration in the range of 10-100 pg on column. When detector response differs by a value of more than three standard deviations of the mean of all data obtained to that point in time, the stock solution is remade if more than one month old. If after reinjection the performance bias is repeated, the analyst/operator will have the choice to run a set of calibration standards and determine if the level of the practical quantitation limit is compromised or not. If it is, the instrument will be shut down and cleaned and not be available for continued analysis until quality control criteria are re-established. In our laboratories, we maintain two to three instruments that can perform the same analyses functions so that project downtime is minimized during these occurrences.

B7 – INSPECTION/ACCEPTANCE OF SUPPLIES AND CONSUMABLES

Project staff at each laboratory/test site will be responsible for the inspection and acceptance of supplies and consumables. When standards/solvents are received the appropriate member of staff logs receipt into our record book together with the lot or batch number. The staff member initials and dates the bottle label. The bottle is stored according to category and type as defined in the laboratory safety plan. Before use, aliquots of extraction solvents are transferred to autosampler vials and analyzed by the instruments for which their extracts are intended. If contaminated, they are returned to the supplier. After use, the solvent bottles are stored in secondary containers with caps bound by Teflon tape.

Standards are used to prepare stock solutions and analyzed within 7 days of receipt with results compared to the supplied specifications.

B8 – NON-DIRECT MEASUREMENTS

During each sampling event, sample information sheets will be prepared for each water treatment plant. These sheets will be used to record water quality and operational information at the time of sampling. The information sheets will be sent out in advance of sampling, as well as in the sample kits. When a utility's response is incomplete or questionable, the project team will make follow-up inquiries (e.g., by phone or e-mail) to complete or correct information on the sheets.

B9 – DATA MANAGEMENT

Each of the research facilities will store original copies of all paper and electronic files. Results data will be entered into Excel spreadsheets. Karl Linden will be the primary responsible party for approving the data at CU. At YU, William Mitch will be responsible for approving the data. At UNC, Howard Weinberg will be responsible for approving the data.

C1 – ASSESSMENTS AND RESPONSE ACTIONS

All calibration and QC data will be generated and initially reviewed by the analysts. The analysts will be responsible for assuring that all calibrations have been conducted on the equipment and instruments at the beginning of each set of analyses or other measurements. The analysts will be responsible for ensuring that instrument systems are in control and that QA objectives for accuracy and precision are being met. If any QC data are outside of the acceptance criteria, samples will be re-analyzed. If an analytical method is no longer able to produce accurate and precise data, the analyst will investigate the cause of the problem and re-optimize the method if needed. These actions will be taken before any new samples will be analyzed. If there is any other problem, the data will be flagged with a data qualifier and the qualifier will be included and explained in the project database. Before data are tabulated and reported as final, the QA officer at each laboratory will review all electronic spreadsheets for accuracy and compare to raw data for validation of data entry,

C2 – REPORTS TO MANAGEMENT

Data and associated QC information will be summarized by the analysts and presented to the individuals responsible for approving the data. Analysts will report significant QA problems and recommended solutions to the same individuals at each research facility.

The following reports will be submitted to the AwwaRF project manager. A brief status summary will be submitted every three months during the research phase of the project according to the project schedule. A more detailed technical summary will be submitted with every other report (every six months). The draft, final report will be submitted in the first quarter of 2010. The final report will be submitted in the second quarter of 2010.

D1 – DATA REVIEW, VERIFICATION, AND VALIDATION

The data will be reviewed by the members of the project team at each research facility for assessment of validity and conformance with QA Project Plan objectives. Decisions to reject data (e.g., data out of control) will be made by the project team. Although there will be no formal "sign-off" sheets *per se*, written documentation will be kept with the data.

D2 –VERIFICATION AND VALIDATION METHODS

Sample data will also be recorded in Excel files with the relevant sample identification information. As discussed in Section B10, data from the analysts will be conveyed to members of the project team via Excel spreadsheets and will then be combined into summary spreadsheets.

Members of the project team will validate that the data are consistent with expected results based on hypotheses originally proposed or developed during the course of the study. If data are not consistent with expected results, the data will be rechecked. For example, if a DBP is detected at an atypically high value, the analyst will be asked to determine if this could be due to an interference problem and to see if the result can be confirmed (or not) with a second GC method or with MS confirmation. Alternatively, if a DBP is not detected that was expected, the analyst will be asked to determine if this could be due to the elution of the compound somewhat outside the normally expected retention time window.

Any justification for rejecting potential outlier data will be recorded in the “comment” field associated with the data where possible.

D3 – RECONCILIATION WITH USER REQUIREMENTS

As discussed in Section D2, project team members will use professional judgment in identifying suspect data. Issues with suspect data will be communicated with the analysts and corrective action determined. If issues with suspect data are not resolved, this information will be communicated with other members of the project team.

Analysis and modeling of data can be conducted with and without outlier data. A single or several extremely outlying data values can have a substantial adverse impact on both the sample mean and sample standard deviation. Thus, data analysis in this project will also include nonparametric statistics (e.g., cumulative probability distributions, box-and-whisker plots). The latter method uses data summaries based on sorting and counting (e.g., median, 25th to 75th percentile), which are more resistant to outliers. That is, significant outliers that constitute a small part of the data set can have only a small effect on the summary statistics.

Data for compounds that are reported as below the MRLs (i.e., "left-censored" data) also complicate the issue of how to compute parametric summary statistics such as the mean and sample deviation. Because nonparametric statistic methods do not require an assumed parametric distribution of the data, cases below the MRL can be handled. The data in the sample set are sorted in ascending order of magnitude, starting with less than MRL data. In this method, the median or 25th percentile value can either be a measured number or a "non detect" (i.e., less than the MRL).

Progress reports and the final report will document how data are reconciled with the project requirements.

E – USEFUL ABBREVIATIONS

AC	activated carbon
amu	atomic mass unit
APHA	American Public Health Association
AwwaRF	American Water Works Association Research Foundation
BAN	bromoacetonitrile
BDCAN	bromodichloroacetonitrile
BDCM	bromodichloromethane
Br	bromine
Br^-	bromide
C	carbon
CAN	chloroacetonitrile
CE	cellulose ester
CI	chemical ionization
Cl	chlorine
Cl_2	chlorine
CNBr	cyanogen bromide
CNCl	cyanogen chloride
CNX	cyanogen halides
COD	chemical oxygen demand
Co-PI	co-principal investigator
CU	University of Colorado-Boulder
Da	Daltons
DBAN	dibromoacetonitrile
DBCM	dibromochloromethane
DBNM	dibromonitromethane
DBP	disinfection by-product
DBPFP	disinfection by-product formation potential
DCAN	dichloroacetonitrile
DCNM	dichloronitromethane
DHANs	dihalogenated haloacetonitriles
DIN	dissolved inorganic nitrogen
DMA	dimethylamine
DOC	dissolved organic carbon
DON	dissolved organic nitrogen
DQOs	data quality objectives
DW	drinking water
DWS	drinking water supply
DWTP	drinking water treatment plant
ECD	electron-capture detector
EEM	excitation-emission matrix
EI	electron impact

FP	formation potential
GAC	granular activated carbon
GC	gas chromatography
GC/ECD	gas chromatography/electron capture detector
GC/MS	gas chromatography/mass spectrometry
HANs	haloacetonitriles
HAN4	the sum of the four haloacetonitriles in the Information Collection Rule
HAN9	the sum of the nine haloacetonitriles
HAs	haloacetaldehydes
HNMs	halonitromethanes
HNO_3	nitric acid
HPLC	high-pressure liquid chromatograph
H_2SO_4	sulfuric acid
ICR	Information Collection Rule
ICP/MS	inductively coupled plasma/mass spectrometry
I-THMs	iodinated trihalomethanes
LIMS	laboratory information management system
LLE	liquid/liquid extraction
LWL	lower warning level
MDL	method detection limit
MMA	monomethylamine
MRL	minimum reporting level
MS/MS	mass spectrometry/mass spectrometry
MSA	methanesulfonic acid
MW	molecular weight
MWCO	molecular weight cutoff
m/z	mass/charge
N	nitrogen
N_2	nitrogen gas
N/D	nitrification/denitrification
N-DBP	nitrogenous disinfection by-product
NDBA	N-nitrosodibutylamine
NDEA	N-nitrosodiethylamine
NDMA	N-nitrosodimethylamine
NDPA	N-nitrosodiphenylamine
NH_2Cl	monochloramine
$NHCl_2$	dichloramine
NH_3	ammonia
NH_3-N	ammonia nitrogen

NH_4^+	ammonium ion
NMEA	N-nitrosomethylethylamine
NMOR	N-nitrosomorpholine
NPIP	N-nitrosopiperidine
NPYR	N-nitrosopyrrolidine
NO_2^-	nitrite
NO_3^-	nitrate
NOM	natural organic matter
O_2	oxygen
OCl^-	hypochlorite
OM	organic matter
org-N	organic nitrogen
P	phosphorus
PAC	project advisory committee
PDMS	polydimethylsiloxane
PI	principal investigator
PN	particulate nitrogen
QAPP	quality assurance project plan
QA/QC	quality assurance/quality control
RO	reverse osmosis
SEC	size exclusion chromatography
SM	standard method
SPE	solid-phase extraction
SS	suspended solids
SUVA	specific ultraviolet absorbance
TAC	technical advisory committee
TBAN	tribromoacetonitrile
TCAN	trichloroacetonitrile
TCNM	trichloronitromethane (chloropicrin)
TDN	total dissolved nitrogen
THMs	trihalomethanes
THM4	the sum of the four regulated trihalomethanes
THMFP	trihalomethane formation potential
TKN	total Kjeldahl nitrogen
TMA	trimethylamine
TN	total nitrogen
TOC	total organic carbon
TSS	total suspended solids
TTHMs	total trihalomethanes
UF	ultrafiltration

UNC	University of North Carolina at Chapel Hill
USEPA	United States Environmental Protection Agency
UV	ultraviolet
UVA	ultraviolet absorbance
UWL	upper warning level
WQL	water quality laboratory
WQS	water quality standards
WTP	water treatment plant
XAD	extraction resin
YU	Yale University

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APPENDIX A
Sampling Sheet Instructions

To: Sample Collector at City of Wilmington NC (Wilm)

From: Karl Linden, University of Colorado-Boulder (CU),
William Mitch, Yale University (YU), and
Howard Weinberg, University of North Carolina at Chapel Hill (UNC)

Subject: Instructions for Collection and Shipment of Water Samples

The samples you are about to collect are for an American Water Works Association Research Foundation (AwwaRF) study of disinfection by-products (DBPs). You are being requested to collect samples of water from your water treatment plant (WTP) and watershed. Additional details about the samples and the collection methods are described in the following pages.

Please measure the temperature, pH, and chlorine residual at the sampling locations and record the information on the enclosed **SAMPLE INFORMATION SHEETS**. Also, provide additional information as requested on these sheets for the day of sampling.

Please collect the samples on *Put Date Here*. Please note that the sample bottles are pre-prepared and some of them contain preservatives. Please DO NOT rinse the bottles before collection of the samples. Please use caution in handling the bottles, as some of the preservatives may be corrosive.

We will provide you with results of these measurements during the course of the project. Thank you very much for your assistance in this matter.

SAMPLING INSTRUCTION SHEETS (continued)

Note: this is just an example of the type of Instructions that will be provided

A. Sample Locations

Sampling at XXX WTP (XX):

1. Plant **influent** (**INFL**) (*before recycle*)

Samples for UNC:

Analytical fraction	Sample bottle	Number of bottles	Acid addition per bottle
TOC	125-mL amber glass	1	None
DOC	125-mL amber glass	1	None
ULTRA VIOLET	125-mL amber glass	1	None
BROMIDE	60-mL amber glass	1	None
IODINE TOTAL	60-mL amber glass	1	None
AMMONIA TOTAL SALICY	500-mL plastic	1	None
ALK/EC/TH	500-mL plastic	1	None
PEDBP	60-mL clear glass	3	None
HAA (9)	125-mL amber glass	2	None
DBPFP-3	1-L glass	2	None
NITROSAMINES	1-L glass	2	None

Samples for YU:

Analytical fraction	Sample bottle	Number of bottles	Acid addition per bottle
Nitrosamines	1-L amber glass	1	None

Samples for CU:

Analytical fraction	Sample bottle	Number of bottles	Acid addition per bottle
TOC	125-mL amber glass	1	None
DOC	125-mL amber glass	1	None
ULTRA VIOLET	125-mL amber glass	1	None

B. Sample Collection Method

(1) If the faucet has an aerator, please remove it before collecting the samples. Let the water run freely from the tap for five minutes before you begin filling bottles, so you are taking water from the main and not water that has been settling in the pipes.

(2) Slowly fill the sample bottles allowing the water to flow down into the bottles at a slight angle to reduce the possibility of aerating the samples. Remove each bottle from the tap when the water reaches the rim. **DO NOT RINSE THE BOTTLES BEFORE FILLING AND DO NOT OVERFILL, BECAUSE MOST OF THE BOTTLES CONTAIN A DECHLORINATION AGENT AND/OR PRESERVATIVE.**

(3) Cap each bottle making certain that the hard shiny Teflon side of the septum (e.g., for the 40-mL glass bottles) is against the water. Do not over tighten because the caps break easily.

(4) Invert each bottle to check for air bubbles. If air is present, re-open the bottle and add a few more drops of water. Reseal and check as before.

(5) For one of the analytical fractions (i.e., LLE_GC), the samples need to be acidified to a pH ~3-4. (**THESE SAMPLE BOTTLES ALL HAVE RED CAPS SO THEY ARE EASY TO IDENTIFY.**) A small bottle of a 0.5 molar (M) solution of sulfuric acid (H_2SO_4) has been provided with the ice chests and sample bottles. *Prior to the sampling, please determine how much acid is needed for your water.* Test strips to make sure that the pH value lies between 3 and 4 have been provided with the ice chest and sample bottles. **AS SOON AS POSSIBLE AFTER SAMPLING, PLEASE ADD THE APPROPRIATE AMOUNT OF ACID TO EACH OF THE SAMPLE BOTTLES FOR THE LLE_GC ANALYTICAL FRACTION.** Reseal and gently shake the bottles to mix the acid into the samples.

C. Sample Shipping

(1) Put the bottles into “bubble-pack” bags and seal the tops. Where noted, separate out the samples for shipping to specific locations. (**NOTE: THE BLUE ICE MUST BE PUT IN A FREEZER AT LEAST ONE DAY IN ADVANCE OF SAMPLING.**) Add plastic bags filled with styrofoam “peanuts” to the ice chest so that (1) the bottles will not bounce around during transit and (2) the bottles are not directly touching the Blue Ice. Please return the **SAMPLE INFORMATION SHEETS** with the requested information on operations and water quality in a sealed plastic bag and place in the laboratory ice chests. Close the ice chests and **SECURE WITH STRAPPING TAPE**.

(2) It is essential that the samples are kept cold until we receive them, so ship the ice chests on the same day the samples are collected via Federal Express (guaranteed next morning delivery). Use the enclosed Federal Express airbills. **YOU WILL NEED TO CALL FEDERAL EXPRESS EARLY IN THE DAY TO ARRANGE A PICK-UP TIME TO ENSURE OVERNIGHT DELIVERY.**

D. Questions

If you have any questions, please call or email one of the following:

- *List appropriate contact person for samples*

XXXXX, XX
XXXXX, XX
XXXXX, XX

APPENDIX B
General Sample Bottle Cleaning Procedures

The water used for the laboratory goes through a multistage purification system to provide both deionized (DI) laboratory grade water and polished water, referred to as Super-Quality (Super-Q) water. The DI system consists of softening, reverse osmosis, granular activated carbon filtration, ion exchange resin filtration, and particle filtration. The purified water is continuously circulated through a loop system and is returned to a supply tank. The Super-Q water is generated from the DI system treatment by applying additional carbon and ion exchange steps using a Millipore SuperQ System. This polished water flows into a separate loop supplying separate sinks and equipment. For trace level analytes, this polished water is feed through an additional Milli-Q-UV treated system that provides resistivity of 18 MΩ-cm or greater.

Glassware Washing:

Hand Wash

1. Detergent wash (50% Liqui-nox in hot tap water)
2. Rinse with tap water until no suds are detected
3. Rinse 3X with de-ionized water (DI)
4. Rinse 3X with Super-Q water
5. Air dry

Machine Wash

1. Wash cycle 4 minutes (Alcojet detergent at 170 F)
2. Tap water rinse cycle 4 minutes at 170 F
3. DI rinse 4 minutes at ambient temperature
4. Super-Q rinse 4 minutes at ambient temperature

Plasticware:

All 500 mL plastic bottles intended for Water Quality background parameters (ex. ammonia, alkalinity, hardness, conductivity) is used new from the manufacturer.

Organic Carbon Testing Glassware:

TOC/DOC Bottles (125 mL amber glass)

1. Machine wash (see above)
2. Place in metal baking pan with aluminum foil cover
3. Bake in annealing oven at 400 C
4. Cap and store

TOC/DOC Septa & Caps

1. Detergent wash (50% Liqui-nox in hot tap water)
2. Rinse with tap water until no suds are detected
3. Rinse 3X with de-ionized water (DI)
4. Rinse 3X with Super-Q water

5. Bake in 180 C oven for 1 hour (septa only)
6. Air dry caps

Organic Analysis Glassware:

One of two procedures will be followed:

1. After rinsing with Super-Q water, glassware will be baked in a muffle furnace at 400 C for at least 3 h.
2. When the number of glassware items is too large to pass through a muffle furnace, the following cleaning procedure will be used:

40 and 60 mL vials (Examples: LLE, PEDBP, EPA Method 551)

1. Hand wash (see above)
2. Rinse 2X with tap water
3. Rinse 2X with de-ionized water (DI)
4. Rinse 2X with Super-Q water
5. Machine wash can be used if vials are placed in plastic racks/baskets
6. Place vials in metal baking pan with aluminum foil cover
7. Bake in 180 C oven for at least 30 minutes
8. Allow to cool, cover with aluminum foil

Septa & Caps

1. Detergent wash (50% Liqui-nox in hot tap water)
2. Rinse 2X with tap water
3. Rinse 2X with de-ionized water (DI)
4. Rinse 2X with Super-Q water
5. Bake in 180 C oven for 1 hour (septa only)
6. Air dry caps

High-Level:

After rinsing with deionized water, glassware will be baked

APPENDIX G – ANALYTICAL METHODS USED BY UNIVERSITY OF TORONTO

Appendix G – Analytical Methods use by University of Toronto

HETEROTROPHIC PLATE COUNT (POUR PLATE METHOD)

INTRODUCTION:
The Heterotrophic Plate Count (HPC) Method is a direct quantitative measurement of the viable aerobic and facultative anaerobic bacteria in a water environment, that are capable of growing on the selected plating medium. Each colony that develops on or in the agar medium originates theoretically from one bacterial cell. The application of this procedure in the lab will be for both treated and raw water samples. A detailed explanation of the HPC Analysis can be found in *Standard Methods*, 20th edition (9215).

INTERFERENCES:
The HPC technique provides a method for monitoring changes in the bacteriological quality of finished water throughout the distribution system as well as the possible existence of cross-connections, sediment accumulations and other problems within the distribution lines. Total bacterial densities greater than 500 organisms per mL in the HPC analysis may be an indicator of coliform suppression or desensitization of quantitative tests for coliform. Although this simple technique is a useful tool for determining the bacterial density of a given sample, there are several factors that contribute to interference in the test.

a. No total count procedure yields the true number because not all viable bacteria cells in the water sample can reproduce under a single set of cultural conditions imposed in the test.
b. Clumps of organisms in the water sample, which are not broken up by shaking, result in underestimates of bacterial density since an aggregation of cells will appear as one colony on the growth medium.

APPARATUS AND MATERIALS:
1. Incubator that maintains 35 ± 0.5 °C. Temperature should be checked and recorded twice daily at least four hours apart
2. Water bath set at 44 - 46 °C for tempering agar
3. Dark-field colony counter
4. Hand tally for enumeration
5. Sterile glass reusable 1 mL serological pipet (Pyrex Brand cat. #13-676, or equivalent)
6. Sterile disposable plastic 100 X 15 mm petri dishes (VWR cat. #25384-070, or equivalent)

REAGENTS:
1. R2A Agar (Difco # 218263, or equivalent)

PROCEDURE:
1. Preparation of Agar
   a. Rehydrate R2A agar by dissolving 18.2g into 1L nanopure water. Heat with frequent agitation and boil for 1 minute to completely dissolve the media.
   b. Pour approximately 250 mL portions into screw top bottles and cap loosely.

c. Autoclave bottles for 15 min at 121 °C and 15 psi; remove promptly.

d. For agar being used within the next three hours, place bottles in the water bath; maintained at 44 - 46 °C.

f. Agar that is not being used on the day it is made can be capped tightly and stored in the refrigerator for up to 3 months.

2. Preparation of Plates
   a. Prepare duplicate plates for each sample tested. Label all plates with location and date with a lab marker and arrange plates in a reasonable order.
   b. Determine the proper aliquot to be used for a given sample (1 mL for treated water, 0.1-1.0 mL for raw water). If the approximate CFU/mL for a given raw water sample is unknown, 0.1 and 1.0 mL of sample should be plated to yield a countable number of colonies. Duplicate plates should be prepared for each of the two sample aliquots.
   c. Vigorously shake the sample before each transfer is made. Aseptically pipet the determined aliquot from the sample into the bottom of each petri dish. For each sample, use a separate sterile pipet to transfer sample to each set of petri dishes. If pipetting 1.0 mL, after delivery, touch the tip once to a dry spot in the dish.

3. Pouring Agar Plates
   a. Melted agar is tempered in a 44 - 46 degrees C water bath before pouring. Agar is melted only once and held no longer than 3 hours.
   b. Flame the lip of the agar bottle before pouring each set of plates. After samples have been added to each plate add 10 - 12 mL of the melted agar. Swirl the inoculated medium gently until the media completely covers the bottom of the plate. Avoid splashing the inside cover.
   c. Check the sterility of each bottle of melted agar by pouring a sterile empty plate at the beginning and end use of each bottle. Cover and incubate with other samples. Discard data if either the before or after control have more than 3 colonies on either control plate.
   d. Check for room air purity by pouring agar into a plate. Leave plate uncovered for 15 minutes. Cover and incubate with other samples.
   e. Discard all sample results if more than 15 colonies are detected ont eh air control plate.

4. Incubation of Plated Samples
   a. After the agar plates have hardened on a level surface (usually within 10 minutes), invert the plates and immediately incubate at 35 ± 0.5 °C.
   b. Incubate tests for 48 ± 3 hours.
   c. Stacks of plates are arranged to allow circulation between stacks. Do not stack plates more than 4 high.

5. Counting and Recording Colonies
   a. After the required incubation period, examine plates in the dark-field colony counter and use a hand tally for enumeration. Record the number of colonies per plate and calculate the average of the two replicate plates and record this as CFU/mL (colony forming units per mL).

b. Count estimations on crowded plates: with less than 10 colonies/cm^2, count the colonies in 13 squares (7 consecutive horizontal and 6 consecutive vertical--omitting the duplicate square) and multiply by 4.32. With more than 10 colonies/cm^2, count 4 representative squares, average the count per cm^2 and multiply by 57. Record as: *CFU/mL est*.
c. Plates containing a spreader must be reported on the data sheet. If spreaders exceed one-half of the total plate area, the plate is not used. Report as: *No results, spreader*.

REPORTING RESULTS:

a. Report HPC as CFU/mL.
b. HPC should be rounded to the number of significant figures obtainable in the procedure: 1 significant figure for 0-9 actual plate counts, 2 significant figures for 10-99 actual plate counts, and 3 significant figures for 100-300 actual plate counts.

QUALITY CONTROL:

a. Agar before and after control plates are used to check sterility of the media. Data is rejected if either control has more than 3 colonies.
b. Room air is checked by exposing an uncovered agar plate for 15 minutes. If there are more than 15 colonies on this plate, sample results are discarded.
c. If two or more analysts are available each analyst counts a set of plates monthly. Laboratory personnel should be able to duplicate their own count on the same plate within 5% and the counts of other analysts within 10%. If analyst's counts do not agree, review counting procedures for analyst error.

TOTAL ORGANIC CARBON (TOC) BY PERSULFATE OXIDATION METHOD

INTRODUCTION:

Measurement of Organic carbon in raw water is the most important indication of precursors to the production of carcinogenic compounds caused by disinfection. Analyzing TOC in the plant influent, sedimentation basin, applied water and after filtration is an effective tool to monitor the treatment plant performance and disinfection by-product formation. The persulfate-ultraviolet oxidation procedure is a reliable method to analyze TOC where even refractory organic compounds can be detected with good accuracy. The method first removes inorganic carbon by purging an acidified sample with nitrogen then the organic carbon is oxidized by sodium persulate and ultraviolet radiation. The purge stream from the persulfate-ultraviolet reactor passes through a non-dispersive infrared analyzer that detects the carbon dioxide in the sample stream. (Standard Methods, 20th edition, Total Organic Carbon (5310 C).)

INTERFERENCES:

Major interferences with this procedure are inorganic carbon and refractory organic compounds. Inorganic carbon is removed from the sample by first acidifying to a pH less than 2.0 and purging with carrier gas.

APPARATUS:

Tekmar Dohrman Phoenix 8000 TOC analyzer and STS 8000 autosampler.

REAGENTS:

1 Phosphoric acid, 21%.

3. Sodium persulfate, 10% and phosphoric acid, 5%
4. Standards: Stock standard 1000 ppm,
5. Carrier gas Grade 5 Nitrogen.
6. Nano-pure water.

PROCEDURE:

1. Preparation of phosphoric acid, 21%
    a. Measure 74 mL of 85% phosphoric acid (H3PO4) into the rinsed one liter acid bottle.
    b. Add 375 mL nano-pure water and stir.
2. Preparation of sodium persulfate, 10% and phosphoric acid, 5%.
    a. Weigh 50 grams of 98+% sodium persulfate (Na2S2O8) into rinsed one liter persulfate bottle.
    b. Add 15 mL of 85% phosphoric acid (H3PO4).
    c. Add 425 mL of nano-pure water and stir until solids are dissolved.
3. From the Tekmar TOC Talk software click on the “Setup” pull down menu then scroll down and click on the “Instrument” button. Turn on the Phoenix 8000 TOC analyzer by clicking on the “Ready” then the “OK” button.
4. Click on the “Run” pull down menu then scroll down and click on the “Sample Setup” button. Enter the sample information for the analytical run. After all the information has been entered click on “Save/Use” button.
5. Make up a standard calibration curve as follows:
    a. 5.0 ppm = 0.5 mL of 1000 ppm standard into a 100 mL volumetric flask fill to the mark with nano-pure water.
    b. 2.5 ppm = 0.25 mL of 1000 ppm standard into a 100 mL volumetric flask fill to the mark with nano-pure water.
    c. 0.5 ppm = 0.05 mL of 1000 ppm standard into a 100 mL volumetric flask fill to the mark with nano-pure water.
    d. Verification = 0.05 mL of 1000 ppm standard into a 100 mL volumetric flask fill to the mark with nano-pure water.
6. Pour standards into 40 mL amber vials and place them in the autosampler in their perspective locations.
7. Make a 1.0 ppm spike sample by adding 42 uL of 1000 ppm stock standard into the appropriate sample vial and mix. Place the vial in the appropriate sample location n the autosampler.
8. Check pH of samples prior to analysis to verify pH<2. Document in calibration logbook and on COC.
9. Place the 40 mL sample vials in the appropriate autosampler locations according to the sample information listed in the Sample Set up page and click on the start button.
10. After all of the standards have been run and before the samples are run initiate the new calibration curve by clicking on the “Results” pull down menu followed by “Calibration” button. Scroll down to the standard results that were just run and click on them. Next click on the “Recall” button then the “OK” button.
11. Wait for the samples to finish. The results will be printed out at the end of the run.

QUALITY CONTROL:

1. The least squares regression coefficient for the calibration curve must be equal to 0.999 or higher.

2. Quality control checks shall be run on 10% of the samples and include a blank, verification sample, sample duplicate and spike recovery.
3. Verification of accuracy must use a separate stock standard than the calibration curve and have a recovery of between 80 to 120%.
4. Matrix spikes must have a recovery of between 80 and 120% and the duplicate sample must not vary from the first sample by more than 20%.

Trihalomethane Formation Potential (THMFP)

Method: Standard Methods 5710 B: Trihalomethane Formation Potential (THMFP)

Prepared by: Dania Chehab, DWRG, Department of Civil Engineering, University of Civil Engineering (April, 2008)

General Description

The sample is treated with excess free chlorine and allowed to react at room temperature for 7 days to reach completion. Samples are buffered and treated with enough chlorine to allow for a residual concentration of 3 to 5 mg/L at reaction completion. THMs are extracted by liquid-liquid extraction and analysed.

Apparatus

250 mL glass bottles with Teflon-lined caps
25 or 40 mL glass vials with Teflon-lined caps
pH meter

Reagents

5 mg Cl_2/mL hypochlorite dosing solution (store in amber bottle)
pH 7.0 phosphate buffer
100 mg/mL sodium sulphite solution (prepare every 2 weeks)
0.039 mg/mL 3, 5-dihydroxy-benzoic acid (not stable – prepare before each use)
All reagents are prepared using Milli-Q water

Procedure

Estimate Chlorine Demand

Pipet 5 mL chlorine dosing solution into 250 mL bottle, fill with Milli-Q water, cap with Teflon-lined cap, and shake well. Determine initial chlorine concentration (C_I) by titrating 100 mL of this solution with 0.025 N sodium thiosulphate.

Pipet 5 mL phosphate buffer and 5 mL chlorine dosing solution into a second 250 mL bottle, fill with Milli-Q, cap, and shake well. Store in the dark for at least 4 hours at room temperature, then determine residual chlorine concentration (C_R) by titrating 100 mL of this solution with 0.025 N sodium thiosulphate.

The estimated chlorine demand (D_{Cl}) is the difference between C_I and C_R.

Sample Chlorination

Adjust pH to 7.0 ± 0.2 using concentrated HCl or NaOH if sample contains more than 200 mg/L alkalinity or acidity.
Determine volume of dosing solution required (V_D):

$$V_D = \frac{D_{Cl} + 3}{5} \times \frac{V_s}{1000}$$

Where: V_D = volume of dosing solution required (mL)
D_{Cl} = estimated chlorine demand (mg Cl_2/L)
V_s = volume of sample bottle (mL)

Add 1 mL phosphate buffer per 50 mL sample to sample bottle and fill with sample. Seal immediately with Teflon-lined cap, shake well, and store in the dark at room temperature for 7 days.

After 7 days, add 0.1 mL sulphite solution to 25 mL vial and fill carefully with sample. Seal with Teflon-lined cap.

Follow SOP for trihalomethane analysis.

Storage
Store at 4°C for up to 7 days; bring sample to room temperature before analysis.

Quality Control
Run one reagent blank with each batch of samples.

Reference:
Clescert, L., Greenberg, A. and Eaton, A. 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association. Washington. USA.

Standard Methods 6232 B. Liquid-Liquid Extraction Gas Chromatographic Method

Prepared by: Walt Bayless, DWRG, Department of Civil Engineering, University of Civil Engineering (May 16, 2002)

General Description

Sample is extracted to an organic (Pentane or MTBE) and then injected into a gas chromatograph (GC) equipped with an electron capture detector (ECD). GC is set as follows:

Method: THM2K1 (Quangfang's method)
Column: 30m x 025mm x 1 □m DB-5 Capillary column
Injection: 3 □m splitless injection
Injector Temperature: 200 C
Detector Temperature: 300 C
Carrier Gas: Helium, 1.2 mL/min at 35 C
Oven Temperature: 40 C for 14 min
Increase by 4 C/min to 95 C
Increase by 60 C/min to 200 C

Apparatus
Gas chromatograph equipped with an electron capture device HP 5890 series II GC
Retort stand
Rack for vials with cover
40 mL clear vials, with Teflon lined caps
2 mL GC vials with caps
Pasteur pipettes

Reagents
Methyl-tert-butyl ether (MTBE)
Sodium Sulfate (Na_2SO_4)

Procedure
Blanks Transfer 23 mL Milli-Q water into 40 mL vials, process alongside samples

Working Solution
Prepare working solution (10 μg/mL) as follows:
Fill a 5 mL volumetric flask with methanol
Add 25 μL of THM stock (2000 μg/mL each – Supleco 48140-U) to volumetric flask
Top flask to 5 mL and cap with glass stopper

Standards (8.7 μg/L)
Add 20 μL of working solution to 23 mL Milli-Q water, process alongside samples

Distribute blanks and standards every 10 samples

Samples

1. Transfer sample to 40 mL vial.
2. Add 1 tsp Na_2SO_4 salt (half scoop).
3. Add 4 mL MTBE.
4. Cap sample, ensure cap is on tight.
5. Shake sample to ensure the salt is evenly distributed, place sample on its side on the counter.
6. Repeat steps 1-5 for remaining samples, including blanks and standards.
7. Replace all the vials into the tray and shake for 2 minutes.
8. Let samples stand for 10 minutes to allow for phase separation.
9. For the next step, ensure that when moving vials DO NOT induce any mixing and ensure no water is extracted.
10. Using a 5” pasteur pipette extract 2 mL the organic layer and place in 2 mL GC vial and cap.
11. Repeat for each sample using a new pipette for each sample.
12. Place vials into GC auto sampler tray and prepare sequence as per GC SOP using THM2K1 method.

Storage
Samples should be preserved using 1 mg ammonia chloride and stored in 20 mL vials with TFE caps and no headspace. When stored at 4 C samples are good for 14 days.

Quality Control
Include solvent at start of GC run to ensure there is no contamination present
Include a blank and standard every 10 samples. Recovery should be between 80 and 120%.

Output Analysis
Sample chromatographs must be analyzed using the GC software. From the run status screen the THM2K1 method must be loaded. Click on “Method”, “Load” and then select THM2K1 from the list. To analyze samples click on “Data Analysis”, “Main Screen”. From the file menu open the appropriate chromatogram. Select “Integration”, “Integrate”. After the software has interpreted the data click on “Reports”, “Print Report”.

Reference:
Clescert, L., Greenberg, A. and Eaton, A. 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association. Washington. USA.

General Disinfection Byproduct Formation Potential (DBPFP)

Prepared by: Dania Chehab, DWRG, Department of Civil Engineering, University of Civil Engineering (April, 2008)

Standard Methods 5710 D: Formation of Other Disinfection By-Products (DBPs)

The sample is treated with excess free chlorine and allowed to react at room temperature for 7 days to reach completion. Samples are buffered and treated with enough chlorine to allow for a residual concentration of 3 to 5 mg/L at reaction completion. DBPs are extracted by liquid-liquid extraction for analysis.

Apparatus
250 mL glass bottles with Teflon-lined caps
25 or 40 mL glass vials with Teflon-lined caps
pH meter

Reagents
Refer to Trihalomethane Formation Potential SOP and Procedure section for DBP-specific quenching agents

Procedure
Procedure and methodology for general DBP formation potential tests are the same as those for THM formation potential; refer to Trihalomethane Formation Potential SOP, using the appropriate quenching agent.

Disinfection Byproduct	Quenching Solution	Additional Instructions
Trihalomethanes	Sodium sulphite	
HAAs	Ammonium chloride	Add 4 drops ammonium chloride to 250 mL bottle and fill with sample. Just before acidifying and extracting sample, add 1 mL sodium sulphite solution to the 250 mL sample.

Storage
Store at 4°C for up to 7 days; bring sample to room temperature before analysis.

Quality Control
Run one reagent blank with each batch of samples.

Reference:
Clescert, L., Greenberg, A. and Eaton, A. 1998. Standard Methods for the Examination of Water and Wastewater, 20th ed. American Public Health Association. Washington. USA.

APPENDIX H – SCREENING ANALYSIS SAMPLING SHIPMENT PROCEDURES

Appendix H - Screening Analysis Sampling and Shipment Procedures

EDCs, PPCPs, Industrial Chemicals

Seven 1 L grab samples were collected from the screening sampling locations for each sampling event. The samples containers were pre-cleaned amber glass bottles, pre-labeled with the sample date, sample location, sample identification number, the analysis to be performed, and the laboratory to which the sample was shipped.

The concentrations of trace organic compounds in the collected samples were expected to be very low (parts per trillion (ppt)). To reduce the potential for contamination, sample collectors were non-smokers, and refrained from using lotions, perfumes, sunscreen, and lip balm prior to sample collection. In addition, nitrile gloves were worn by the sample collectors.

To evaluate for potential sample contamination, field blanks were included in each sampling event. Deionized water in the pre-cleaned 1 L amber glass sample bottles (total of 7 bottles) served as the field blanks. Field blanks were preserved with one gram of sodium azide per liter. The field blank sample bottles were opened by the sampler on site, exposed to the ambient air, and closed while the screening samples were collected.

Following sample collection, the sample bottles were preserved with one gram of sodium azide per liter. The samples and field blanks were then placed in coolers containing frozen ice bricks. Sufficient packing material and bubble wrap was included in the cooler to prevent the glass sample containers from breaking during shipment. Each cooler contained a chain-of-custody form that included sample identification number, date and time sample was collected, name and signature of sampler, and the analysis to be conducted on each sample. The samples were shipped overnight to Trent University and were analyzed for all screening parameters except atrazine, simazine and iopromide which were analyzed at MWH Labs. Sampling and shipping procedures for these compounds followed MWH protocols and are described below.

Upon sample reception at the laboratories, the integrity of the sample containers were assessed. The chain of custody forms were then completed with the date and time sample was received, name and signature of the individual who received the sample, and any remarks on the status of samples will be reported. Upon receipt, the samples will be stored at 4 degrees C in darkness or processed immediately.

Iopromide

Three 1 L grab samples were collected from the screening sampling location for each sampling event. Another three 1 L samples were filled with deionized water to provide a field blank. Samples were collected in pre-cleaned amber glass bottles. The sample bottles were pre-labeled with the sample date, sample location, sample identification

number, the analysis to be performed, and the laboratory to which the sample is to be shipped. All sample bottles contained ascorbic acid and copper sulfate for sample preservation.

To evaluate for potential sample contamination, a pre-filled blank was included in each sampling event. The field blank sample bottles were opened by the sampler on site, exposed to the ambient air, and closed while the screening samples are collected.

Following sample collection, the samples and field blanks will then be placed in coolers containing frozen ice bricks. Sufficient packing material and bubble wrap will be included in the cooler to prevent the glass sample containers from breaking during shipment. Each cooler will contain a chain-of-custody form that includes sample identification number, date and time sample was collected, name and signature of sampler, and the analysis to be conducted on each sample. The samples will be shipped overnight to MWH Labs.

Upon sample reception at the laboratories, the integrity of the sample containers will be assessed. The chain of custody forms will then be completed with the date and time sample was received, name and signature of the individual who received the sample, and any remarks on the status of samples will be reported. Upon receipt, the samples will be stored at 4 degrees C in darkness or processed immediately.

Pesticides (atrazine and simazine)
An almost identical procedure was followed for the sampling of pesticides as was described for Iopromide sampling. The variation in the pesticide sampling procedure is that sample bottles contained hydrochloric acid, instead of copper sulfate/ascorbic acid, for sample preservation.