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Characterization of TOX Produced During Disinfection Processes

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A Research Proposal submitted to the American Water Works Association Research Foundation

16 July 2001

Project Abstract

PROJECT TITLE: Characterization of TOX Produced During Disinfection Processes

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OBJECTIVES: (1) to determine the nature and chemical characteristics (e.g., size, charge, hydrophobicity, structural features) of the unknown fraction of the total organic halogen (UTOX) produced during chlorination and alternative disinfection processes (i.e., chloramination, chlorine dioxide, ozone disinfection), (2) to assess the impact of treatment on removal of UTOX precursors; (3) to assess the stability of UTOX in a model distribution system and (4) to determine the best TOX protocol for use with IC analysis for the purposes of discriminating between TOCl, TOBr and TOI..

EXPECTED RESULTS: This research will make two major contributions to the field of drinking water treatment. First, it will clarify methodology for the characterization of TOX in finished waters. Second, it will provide a detailed, yet broad-based perspective on the chemical and physical characteristics of the unidentified halogenated organic byproducts of drinking water disinfection. This information will have important implications to the assessment of potential human health effects of unidentified TOX (UTOX) compounds. The results of this study will be presented in a final project report as well as in published journal articles.

APPROACH: This work will be conducted in several phases; and it builds upon the latest fundamental advancements in NOM characterization. First, a series of TOX methodology studies (Task 1) will be undertaken. This is needed to validate existing TOX methods before they can be reliably applied to the analysis of TOBr and TOI. Next, a broad survey of North American utilities will be conducted (Task 2). This will involve the collection of waters of diverse quality and geographic location for laboratory treatment with 5 basic disinfection scenarios (chlorination, chloramination, both with and without preozonation, and chlorine dioxide). Analysis of these samples for TOX species and known DBPs will allow the PIs to better assess the full range of UTOX occurrence and the raw water characteristics that are associated with higher levels. In addition, distribution system samples will be fractionated according to hydrophobicity and molecular size, and then analyzed for UTOX. This will help in assessing the likelihood that UTOX compounds are biologically active. Task 3 focuses on factors influencing UTOX concentrations, especially engineering factors. This task will examine impacts of pretreatment, and post treatment as well as chemical conditions during disinfection on ultimate UTOX concentrations. The final phase (4) will be directed to the application of advanced chemical techniques (borrowed from the humics researchers) to the characterization of UTOX. This will include analysis of bulk disinfected waters (Task 4a), and analysis of carefully fractioned samples (Task 4b). A set of three promising and complementary techniques will be used: TMAH thermochemolysis GC/MS, electrospray ionization high resolution MS, and CuO oxidation GC/MS & LC/MS.

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Project Description

Background

Despite nearly 3 decades of research on the formation of halogenated disinfection byproducts in drinking water, there still remains a large fraction of material that has not been identified. We know that there are many unknown chlorinated and brominated byproducts, thanks to the development of the total organic halide (TOX) analyzer. This instrument and its associated methodology, is capable of measuring all or nearly all of the organically-bound chlorine, bromine and iodine in a disinfected water sample. By comparing the TOX values with the halides attributed to known identifiable byproducts (trihalomethanes, haloacetic acids, etc.) we can estimate the unknown TOX (abbreviated here as UTOX).

Researchers have been attempting to close the TOX gap for many years by identifying more and more of the UTOX. When using free chlorine, the trihalomethanes (THMs) and the haloacetic acids (HAAs) can together comprise as much as 50% of the TOX. Although large in number, other identified groups of halogenated byproducts account for very little of the remaining 50%. Efforts to identify more of these and to account for more of the TOX are ongoing. One of the most complete and recent compilations of DBPs can be found in the review article by Richardson (1998).

Although the earliest work on DBP and TOX centered on the use of free chlorine, more attention has recently been paid to the alternative disinfectants. These have gained favor largely because of the DBP issue. For example, chloramination is becoming more widely used in the US as utilities re-evaluate their operations in light of the new DBP/microbial cluster of regulations. A recent survey has shown that 29.4% of medium and large US utilities were using chloramines as of 1998, as compared to 20% in 1989 (Connell et al., 2000). Chloramines offer many potential advantages over chlorine, most notably lower THM and HAA levels (Bryant et al., 1992). Nevertheless, chloramination has been shown to produce substantial amounts of TOX, which increases from hours to days (Johnson & Jensen, 1986; Stevens et al., 1989). The amount of TOX produced has been shown to be greater at lower pHs. Stevens also showed that a similar trend exists for THM formation, in direct contrast with the behavior for free chlorination. Also, with certain types of activated aliphatic compounds, reaction with chloramines is nearly as fast as the analogous reaction with free chlorine (McKnight and Reckhow, 1992).

Symons and co-workers (1996) conducted a detailed study of chloramination and DBP formation under the sponsorship of AWWARF. Symons' data support the earlier findings of Jensen that an especially large fraction of the TOX formed by chloramines are not in the form of the common DBPs (i.e., THMs, HAAs). These authors found that only 10-35% of the TOX could be accounted for by these major byproducts.

One question that persists with chlorimination centers on the potential significance of the unidentified TOX. There are indications that chloramination produces mostly high molecular weight TOX (e.g., Johnson & Jensen, 1986). The higher MW material might not be toxicologically significant due to membrane transport issues (ILSI, 1998).

Another widely used alternative disinfectant is ozone. Due to its lack of stability, ozone is not used as a residual disinfectant in the US. However, it is becoming more common as a primary disinfectant, preceeding free chlorination or chloramination. Ozone, itself, does not produce chlorinated organic byproducts. However, it can oxidize ambient bromide or iodide and produced TOBr and TOI compounds. It will also modify the organic precursors so that upon subsequent chlorination or chloramination, the DBP yields are altered.

Preozonation has been known for many years to result in both increases and decreases in subsequent THM formation during free chlorination. This is a result of complex set of sequential reactions who's ultimate outcome depends on the pH's at various points, the ozone dose, the bicarbonate concentrations, the reaction time, and the nature of the NOM ((Riley at al., 1978; Reckhow and Singer, 1984). The case for TOX formation is similarly complex, but most observers have reported decreases as a result of preozonation. Symons and co-workers have presented some data that indicates similar effects of preozonation when chloramines are used instead of free chlorine.

It's clear that in this time of rapid changes in US disinfection practice, we need to acquire a better understanding of the importance of unidentified byproducts. The TOX measurement gives us a window on to these compounds. If we cannot identify them at a structural level, we must use the TOX measurement to characterize them in a way that can help engineers, toxicologists and regulators make intelligent decisions.

Research Objectives and Scope

Objectives of this research are: (1) to determine the nature and chemical characteristics of the unknown fraction of the total organic halogen (UTOX) produced during chlorination and alternative disinfection processes (i.e., chloramination, chlorine dioxide, ozone disinfection), (2) to assess the impact of treatment on removal of UTOX precursors; (3) to assess the stability of UTOX in a model distribution system and (4) to determine the best TOX protocol for use with IC analysis for the purposes of discriminating between TOCl, TOBr and TOI.

Experimental Design

General Approach

To make best use of limited funds, it was decided that all controlled disinfection experiments be conducted at bench scale, whereas general treatment impacts could be better assessed using samples from operating full-scale plants. The use of pilot scale treatment processes were deemed to be inappropriate for this work for the following reasons:

- We're looking at homogeneous solution chemistry, no need to worry about scale
- One of the PIs (Reckhow) has extensive experience with parallel pilot and bench scale DBP formation studies & the two match each other very well
- Possible exception would be use of in-situ chloramines, but the issue of mixing will be avoided by using pre-formed chloramines
- Bench scale is much more cost effective

Standard IC analysis of furnace pyrolysates will be used for TOCl, TOBr and TOI analysis. Dionex IC using chemical suppression will be used. This is well-established methodology, and will not be investigated further. However, the adsorption/pyrolysis protocols will be studied.

In general, all disinfected samples will be analyzed for the full suite of specific halogenated byproducts, and residual disinfecant species. This includes the neutral extractables (including all 10 THMs, the haloacetonitriles, haloketones, etc.) and all 19 haloacetic acids. All samples will be further analyzed for TOX, and its halogen-specific fractions, TOCl, TOBr and TOI. The halide-based difference between the specific compound analysis and the bulk OX

analysis will then be used to calculate unknown TOX (UTOX). This can be further resolved into unknown TOCl, unknown TOBr, and unknown TOI.

Specific Tasks
Task 1: Preliminary Assessment of TOX Method Performance

Research Questions:
- How do the various commercial TOX analyzers compare with respect to TOX (TOCl, TOBr and TOI recovery, and halide ion (Cl, Br and I) rejection?
- What is the best combination of analyzer, and PAC for this project?
- How well do the various analyzers/protocols work when combined with IC analysis?

One of the PIs (Reckhow) has been involved with TOX analysis since its early use in the US in the 1970s. He has also served as the joint task force chair for the TOX method in Standard Methods. Through 20+ years of experience with this method (including several different commercial instruments, GAC types, etc.), it has become evident that some careful validation needs to be included in a TOX-oriented study such as this one. For example, halide rejection has always been a concern, especially with the heavier halides (Reckhow et al., 1990). Recovery of standard solutions of TOX compounds can vary substantially from one analyzer to another. Problems such as these will be even more of concern as more attention is focused on bromine-containing and especially iodine-containing organic compounds.

This first portion of task 1 will involve the analysis of known solutions of chlorine, bromine and iodine containing HAAs, THMs and other compounds. Each will be run on the two analyzers at UMass (Euroglass and Dohrmann) using the standard activated carbon, as well as other TOX carbons that are commercially available. Final determination will be by IC (to get TOCl, TOBr, and TOI) as well as microcoulometric detection (standard TOX). The comparison between these two analyzers is quite important, because they represent the two different approaches that have been used in commercial instruments. One uses oxygen with carbon dioxide as an auxiliary gas (Dohrmann). The other uses only oxygen (Euroglass). This distinction is important for two reasons. First the oxidative environments in the two systems are different, so pyrolysis reactions may proceed in different ways. It is important to know if this impacts recovery of TOCl, TOBr or TOI. Second, the use of carbon dioxide results in excessive interference in IC analysis of the halides. Minear and coworkers were forced to purge much of the dissolved CO_2, thereby creating new opportunities for loss of HX, or sample contamination. By comparing results with the Euroglass instrument, we may be able to invoke a simpler and more robust approach that doesn't need a pre-IC purge step.

Task 1a Summary: Model compound Testing

Select several model TOX compounds for testing (which include Cl, Br and I atoms)
- HAAs
- THMs
- others

Analyze model TOX compounds for TOX, TOCl, TOBr and TOI using
- Different commercial analyzers
- Prepared using different PACs and different adsorption protocols

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The second group of Task 1 experiments will make use of two contrasting groups of precursors for production of unknown TOX that can be used to test the methodologies. Our approach is to pick a water that has NOM with a substantial autochthonous content and another dominated by allochthonous or pedogenic material. Both should have a substantial TOC, so that a high yield of TOX is obtained. It's also important that neither has a high bromide level. This will better permit us to evaluate the impacts of added bromide. The waters selected for this task are raw waters from Tulsa's Jewell plant and from the city of Winnipeg. The former is largely allochthonous and the latter is heavily autochthonous as evidenced by their SUVA values (Table 1). These two waters represent extremes when considering the range of values noted for the ICR plants as shown in Figure 2 (differences between the TOC and SUVA for Figure 2 and Table 1 are due to small differences in the averages versus the median values).

Table 1: Comparative Raw Water Quality for Task 1 Waters (average values)

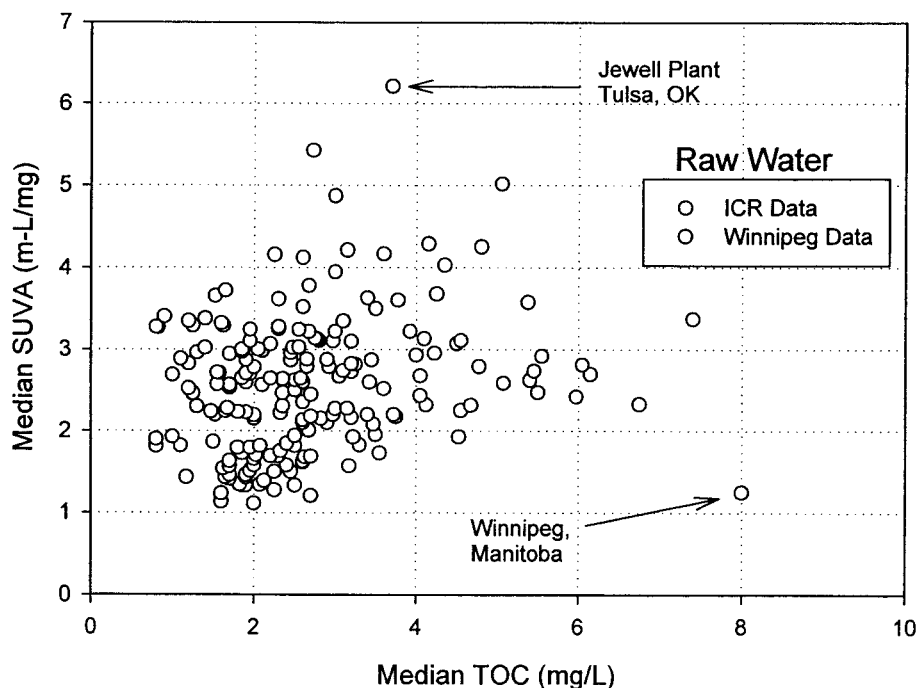| Parameter	Tulsa, OK (Jewell Plant) Raw Water	Winnipeg, Manitoba, Raw Water
TOC (mg/L)	3.8	8.0
SUVA (L/mg-m)	5.5	1.3
UV abs (cm^{-1})	0.21	0.10
Hardness (mg/L)	142	83
Alkalinity (mg/L)	113	81
Bromide (mg/L)	0.065	low
pH	7.9	8.2
Turbidity (NTU)	22	1.0

Figure 1: Distribution of Raw Water NOM Characteristics for 195 Large US Plants (Summarized from ICR data), also showing Winnipeg.

The waters used in Task 1b will be treated with chlorine after being dosed with varying levels of bromide and iodide ion. The purpose is to form a range of unknown brominated and iodinated byproducts (contrasting with the known ones from Task 1a) which can be tested for relative recovery by the various TOX protocols. Additional experiments will be run where the halide ions are added after quenching the chlorine. The purpose here is to see if bromide or iodide ions will interfere with TOX measurements using these protocols. The end result will be a clearer picture of the comparative merits of the TOX and OX species protocols, as well as some important data on the impacts of inorganic halide on TOX speciation.

All samples will be analyzed for the full suite of specific halogenated byproducts, and residual disinfecant species. This includes the neutral extractables (including all 10 THMs, the haloacetonitriles, haloketones, etc.) and all 19 haloacetic acids. All samples will be further analyzed for TOX, and its halgen-specific fractions, TOCl, TOBr and TOI.

Task 1b Summary: TOX Methodology & Raw Water Studies[1]

Select two contrasting waters of moderate to high TOC
- Winnipeg (low SUVA)
- Tulsa (high SUVA)

Dose each with chlorine under the following conditions
- Varying levels of bromide added prior to chlorination
- Varying levels of iodide added prior to chlorination
- Varying levels of bromide added after chlorine is quenched
- . Varying levels of iodide added after chlorine is quenched

Analyze for TOX, TOCl, TOBr and TOI using:
- Different commercial analyzers
- Prepared using different PACs and different adsorption protocols

Analyze for Specific DBPs

Task 2: Survey of unknown TOX formation in disinfected waters
Research questions:
- How much unknown TOX (UTOX) is formed?
- How wide is the variation/range? How do raw water characteristics affect UTOX?
- What is the impact of preozonation on UTOX formation?
- How do the three residual disinfectants compare with respect to UTOX formation when applied to different water types?
- Do treatments aimed at minimizing known DBPs also control UTOX?
- What are the size and hydrophobicity characteristics of UTOX produced by full-scale system?

Task 2 is intended to generate data on the range of UTOX values that may be observed in waters across North America. The first step will be to identify about two dozen waters of differing quality (considering various combinations of TOC, SUVA, bromide/iodide, alkalinity/hardness, and region) for study. This will be done using available data (ICR and other sources) and in consultation with the AWWARF project officer and the PAC. Once selected, raw waters and finished waters will be collected from each site at different points throughout the

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[1] These will also serve to meet some of the objectives of Task 3

project period. These will be shipped to UMass[2] for treatment with disinfectants and chemical analysis. At UMass each will be treated with the five disinfection scenarios (chlorine, chloramine, both with an without preozonation, and chlorine dioxide). A standard set of protocols will be used for all samples (see Table 2). All samples will then be quenched and analyzed for the full suite of DBPs (THM[3], HAAs, TOX, TOCl, TOBr and TOI).

Table 2: Task 2 Test Conditions

	Standard conditions
Bromide/Iodide	Ambient
pH	Ambient
Pre-O_3 dose	1 mg-O_3/mg-C
Free Cl_2 target residual	1.5 mg/L
Chloramine target residual	2.5 mg/L
Cl_2/N ratio	4.5 g/g
ClO_2 dose	1.5 mg/L
Free Cl_2 Contact Time	12 hr
Disinfectant Contact Time	48 hr
Temp	20°C

At the same time, a characteristic distribution water sample will be collected from each of the Task 2 plants, quenched and shipped to UMass. This will be analyzed for the full suite of DBPs. In addition, a portion of this sample will be fractionated based on molecular size (ultrafiltration) and hydrophobicity (hydrophobic resin adsorption). The resulting fractions will be analyzed for the full set of DBPs as well. The intention is to develop a database on the general character (e.g., hydrophobicity and apparent molecular weight) of UTOX in North American waters.

Task 2 Summary: Survey of unknown TOX formation in disinfected waters

Group raw waters (across US, Canada) based on:
- TOC
- SUVA
- Bromide and Iodide
- Alkalinity and hardness
- Geographical Region/watershed ecosystem characteristics

Select one or several from each category and treat with each of the following disinfectants at a fixed dose, pH and reaction time
- Chlorine
- Chloramines
- Chlorine dioxide
- Ozone & chlorine
- Ozone and chloramines

Collect Distribution System sample from each of these systems for comparison, and fractionate (analytical scale) using the following techniques:
- Size (ultrafiltration)

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[2] Many utilities have been contacted about potential collaboration for TOX/DBP study. To date, all have indicated that they are willing to conduct sampling and ship samples at their own cost, in return for learning more about their own water quality characteristics and DBP formation.

[3] Note that for the purpose of this research project, all THM analysis will be accompanied by determination of other neutral extracables (e.g., haloacetonitriles, haloketones, chloropicrin)

- Hydrophobicity (hydrophobic resin adsorption)

For each of these tests, the following will be measured
- TOX (separating TOCl, TOBr, and TOI)
- THMs and other neutral extractables
- Haloacetic Acids

Task 3: Conditions affecting UTOX formation and destruction

Research Questions:
- How much of a role does pH adjustment play in UTOX formation?
- What impacts are expected from pretreatment on UTOX formation (e.g., UTOX precursors and removability)?
- How susceptible is UTOX to degradation by corrosion products and pipe surfaces?
- How will the presence of reactive chemicals (disinfectants and corrosion control chemicals), and especially bases and nucleophiles (e.g., phosphates, hydroxide, iron species) in distribution systems affect UTOX?

The purpose of phase 3 is to determine the impact of a variety of treatment conditions (pretreatment, disinfection conditions, post-treatment) on UTOX concentration. In Task 3a, a smaller set of water samples will be selected from the phase 2 plants. Selection criteria will be based on raw water characteristics and UTOX yields and characteristics. An attempt will be made to include a set of waters that adequately captures the full range of behavior as observed in phase 2. These waters will be treated with the same combinations of disinfectants as used in Task 2, but some additional experimental variations will be used. These include variations in pH, bromide level and iodide level. In addition laboratory pretreatments will be performed on each water to study the impact of ultrafiltration, alum coagulation, and UV irridiation on subsequent UTOX formation. Finally, a additional set of experiments will be performed on disinfected samples to test UTOX stability. These will involve addition of NaOH (to a pH of 11), phosphates and silicates in separate experiments. These are all nucleophiles that may be effective at dehalogenating UTOX (expecially TOBr and TOI).

Task 3a Summary: Bench-scale Studies

Select a subset of waters from Task 2 for this work[4]

Treat as in Task 2, but add the following additional variations:
- range of pHs (5 to 10)
- with and without added bromide
- with and without added iodide

Treat as in Task 2, but pre-treat or fractionate to examine precursors
- Pre-treated with UF
- Pre-treated with alum coagulation
- Pre-treated with UV irradiation

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[4] Task 1a raw water studies will serve to partly meet the objectives of Task 3

> *Treat as in Task 2, but post-treat or fractionate to examine TOX stability*
> - Post-treated with NaOH to pH 11
> - Post-treated with phosphates, silicates or other corrosion control chemicals

Task 3b will make use of MWRA's experimental pilot plant and pipe loop system. This is a series of pipe loops that were comprised from old mains removed from the Boston distribution system. They were originally employed to study the impacts of certain pretreatment and corrosion control strategies on corrosion, corrosion byproducts and biological growths. The MWRA has agreed to run their system for the purpose of testing the stability of UTOX in a real distribution system environment. We will look at several disinfection scenarios, including simple chlorination, chloramination, ozonation/chlorination, and ozonation/chloramination. These will be treated with realistic doses of corrosion control chemicals and then pass through the pipe loops. MWRA has agreed to conduct standard WQ testing while these tests are in progress. In addition, we will collect samples for analysis of the full suite of DBPs. This will provide valuable information on UTOX stability that goes beyond the simple chemical studies in Task 3a.

Task 3b Summary: Studies with MWRA Pipe Rack

Use Cosgrove Raw Water and treat with various disinfectants
- Chlorine
- Chloramine
- Both with and without preozonation

Treat with varying corrosion control chemicals
- Per MWRA protocols

Measure UTOX into and out of pipe racks

Task 4: Advanced characterization of unknown TOX
Research Questions:
- What are the chemical & physical characteristics of this UTOX?
- To what extent does it have the right size/charge/stability properties to cross cell membranes?
- To what extent does it have the right size/charge/stability properties to be removed by subsequent treatment?
- Are there structural features in UTOX that are sufficiently abundant so that they can be identified or used as a marker?
- Are there chemical structures in UTOX that indicate of the origin of its precursors?

The purpose of task 4 is to borrow some of the most promising advanced techniques from the field of NOM characterization, and to apply these to the problem of UTOX. The selected methods include TMAH thermochemolysis, ESI/MS, and CuO oxidation with GC/MS & LC/MS. The first two are relatively new techniques that have been pioneered by one of the PIs (Hatcher). These have been employed quite successfully in the last few years for the characterization of NOM in drinking water. The last one is an older technique with some new elements added. It has traditionally been one of the most useful approaches to the characterization of humic substances. The three represent a complementary group. One is largely a reductive technique (TMAH), another (CuO method) is oxidative, and the third (ESI) is

relatively non-degradative. None of these techniques has been applied to the focused study of halogenated NOM as proposed here. In task 4a these techniques will be applied directly to the bulk disinfected waters. Task 4b carries this further by means of preparative-scale extraction and fractionation protocols prior to advanced chemical analysis.

In task 4a we will collect a subset of waters from Task 2, and treat these in the laboratory using the 5 major disinfection scenarios (chlorine, chloramines, both with and without preozonation, and chlorine dioxide). Each will be extracted or lyophilized as needed and analyzed by the selected advanced methods.

Task 4a Summary: Characterization of Bulk UTOX

Select a few waters from Task 2
Apply the 5 disinfection scenarios to each on large volumes of the waters.
- Chlorine
- Chloramines
- Chlorine dioxide
- Ozone & chlorine
- Ozone and chloramines

Analyze each of the fractions Methods of Analysis
- Standard DBP and OX analysis
- TMAH-thermochemolysis GC/MS
- Electrospray Ionization / High Resolution MS
- CuO Oxidation & LC/MS & GC/MS

Task 4b will incorporate preparative-scale fractionation into the experimental design for task 4a. Because of the labor-intensive nature of this fractionation, only the two most common disinfection scenarios can be examined. We propose to treat a water selected from the task 2 studies with chlorine and another aliquot of the same water with chloramines. Based on the Task 2 and task 4a results, we may decide to add some inorganic bromide or iodide to this water. Laboratory disinfection will be done in a large bulk sample (about 300L) which will then be subject to preparative scale resin extraction followed by UF fractionation of each of the resin extracts. This will result in about 24 separate fractions based on combinations of size, charge and hydrophobicity. All will be analyzed by standard OC (TOC, UV-Vis absorbance) and DBP analysis (TOX, TOCl, TOBr, TOI, THM, HAA). Some of the fractions will have a large abundance of organic carbon, and those fractions will be analyzed by the advanced techniques. Special attention will be paid to those fractions that are considered to be likely candidates for passive transport through biological membranes.

Task 4b Summary: Characterization of Fractionated UTOX

Select a "typical" water from Task 2
Apply the 2 major residual disinfectants to two large volumes of the water.
- Chlorine
- Chloramines

Fractionate each based on hydrophobic behavior and charge.
- Use preparative-scale resin extraction (XAD-4/XAD-8, cation & anion exchangers).
- Elute and analyze total eluant as well as size fractionated (UF) eluant.

Sub-fractionate each of the above fractions based on size.
- Use laboratory ultrafiltration

Detailed Experimental Methods

Laboratory Treatments

Chlorination/chloramination procedures

Chloramination and chlorination will be conducted by widely used methodology. Generally, reagents are added in the form of concentrated solutions under conditions of high-speed mixing. Symons and co-workers (1996) have concluded that the exact nature of this mixing is not of primary importance in simulating full-scale chloramination with bench-scale experiments. Nevertheless, to avoid any possible complication of this type, we propose to use pre-formed chloramines. These are produced by careful mixing of concentrated solutions of sodium hypochlorite and ammonium chloride. This is done at low temperatures, and at a controlled pH (). Experience with this approach at UMass has shown that relatively stable and pure solutions of monochloramine can be produced in this way.

Ozonation Procedures

When required for task 2,3&4 studies, samples will be ozonated in a semi-batch system. Ozone is generated from pure oxygen by means of a laboratory corona discharge generator. The ozone/oxygen product gas is introduced into a 2-L glass reaction vessel containing the water to be treated. Flow is controlled with an electronic flow controller, and the ozone content is monitored by direct UV absorbance spectrophometry. The gas is mixed with the sample by a porous quartz frit. Off-gas is re-directed through a spectrophotomer for determination of ozone content. A membrane ozone electrode (Orbisphere) is fitted into the side of the glass reactor so aqueous ozone concentration can be continuously monitored. Ozone transferred is determined from the flow rates and the differences in ozone content in the applied gas versus the off-gas.

Chlorine Dioxide Treatment

When required, samples will be preoxidized with chlorine dioxide in a batch reactor. The reaction will be conducted at darkness in BOD bottles in absence of air in order to avoid the possible loss of oxidant or volatile by-products produced during the course of the reaction (flasks will be filled up).

Chlorine dioxide will be freshly generated as needed. Aqueous solutions will be prepared from the gaseous chlorine dioxide generated from the acidification (i.e. sulfuric acid) of a solution of sodium chlorite. In order to avoid the presence of trace chlorine in the chloride dioxide stock solution, chlorine will be removed from the gas stream by a $NaClO_2$ scrubber. Concentration in chlorine dioxide of solutions prepared using this protocol were found to range from 3 to 4 g/L of ClO_2. The concentration of the chlorine dioxide stock solution will be checked before each use using the LSB method as developed by Bubnis and others.

Chlorine dioxide typically reacts with most reducing agents through a one-electron transfer, thus, chlorite is considered to be the principal oxidation by-products and generally represents 50 to 70 % of the initial chloride dioxide. Based on this and due to the MCL and

MRDL established for chlorite, the practical upper limit for chloride dioxide would be approximately 1.5 mg/L.

Ultrafiltration
Ultrafiltration will be used for assessing apparent molecular size of TOX compounds. Samples will be treated using a stirred 300-mL Amicon pressure cells under a nitrogen atmosphere. We will use membranes rated at 1K and 10K Daltons. These will be applied in a parallel configuration. The smaller UF membrane will be used to determine those TOX molecules that are most likely to pass through biological membranes. It has been proposed that the low MW TOX contains the toxicologically important compounds The 10K UF membrane will help determine which TOX molecules are of sufficient size as to be considered macromolecular for the purposes of physical and chemical treatment processes (e.g., coagulation, adsorption).

Chemical Analysis
Total Organic Carbon
Total organic carbon (TOC) will be measured on nearly all samples in this research. It will be measured by the high-temperature combustion method (APHA et al., 1999). At UMass a Shimadzu 5000 will be used for these measurements.

Residual Chlorine (Free and Combined)
Residual chlorine will be measured by titrimetric DPD methodology (4500-Cl, D and F: APHA et al., 1999). We will be measuring residual chlorine species on all samples collected for DBP analysis.

THMs and other Neutral Extractables
Trihalomethanes and other neutral extractables (haloacetonitriles, haloketones, chloropicrin, etc.) will be measured on all disinfected samples and controls. We will use the standard micro-extraction method with GC and electron capture detection (ECD) (APHA et al., 1999). This method will be expanded to include the 6 iodinated THMs, and as many iodinated neutral extractables as possible given availability of standards.

Haloacetic Acids
The full suite of haloacetic acids will be measured along with the THMs whenever samples are disinfected. Haloacetic acids will be measured by the micro-extraction method with methylation and separation/detection by GC with ECD. More specifically, we will use the acidic methanol derivatization (US EPA method 552.2) which avoids the use of highly-toxic reagents as required for the diazomethane method. Acidic methanol has proven to give better and more reliable recoveries of all HAA9 species, especially the brominated forms (Pat Fair, personal communication, 2000) The existing method will be expanded to include the 6 iodinated trihaloacetic acids, the 3 iodinated dihaloacetic acids and monoiodoacetic acid. This results in a total of 19 HAAs.

Total Organic Halide
Total organic halide (TOX) will be measured on nearly all of the samples in this study. Task 1 analyses (at UMass) will employ a Euroglass instrument as well as a Dohrmann DX-20

unit. Subsequent tasks will use whichever is selected in Task 1 as the most appropriate for this work. Both instruments operate under the standard GAC adsorption, pyrolysis and coulometric detection scheme. However, one (Dohrmann) uses a carbon dioxide auxiliary gas, and the other (Euroglass) doesn't. Methodology generally follows that established in Standard Methods (APHA et al., 1999).

In addition we will be measuring TOCl, TOBr and TOI as separate fractions of the TOX. This is done by trapping the HX vapor in the pyrolysis tube gases, and subjecting these to inorganic halide analysis by ion chromatography. This approach has been used by a small number of researchers over the past 20 years. However, Minear is one of the few to actually publish a specific methodology (e.g., see: Echigo et al., 2000). They used a heated transfer line, which was also flushed after each sample. We plan to take the same approach. As mentioned above, the Euroglass TOX analyzer does not use a CO_2 auxiliary gas, which should prove to be an advantage over the Dohrmann instrument (used by Minear) as carbon dioxide will interfere with halide analysis by IC.

Inorganic halide analysis will be conducted with a dedicated Dionex instrument. This uses chemical suppression technology, and is equipped with an autosampler and data system.

Hydrophilic/Hydrophobic Content

The analysis of hydrophobic and hydrophilic content will be performed on all Task 3 waters subject to the extensive chloramination studies. Non-ionic resin fractionation by XAD resin adsorption chromatography will be used to determine the DOC distribution of operationally defined hydrophobic, transphilic and hydrophilic DOC fractions. The methodology was scaled down from the design employed by Aiken et al. (1992). Two sequential columns containing XAD-8 and XAD-4 resins are used to adsorb (the column distribution coefficient, $k'_{0.5r}$, is set equal to 50 for both XAD-8 and XAD-4 resins, $V_{0.5r} = 2V_0(1+k'_{0.5r})$ with V_0: Void volume) hydrophobic and transphilic DOC, respectively. The XAD-8 resin is an acrylic ester polymer and the XAD-4 resin is a styrene divinylbenzene copolymer. Phosphoric acid was used to acidify samples to pH ~ 2 prior to application to the columns. Acidified samples are first passed through a column containing XAD-8 resin at an approximate flow rate of 2 mL/min, and then subsequently passed through an additional column containing XAD-4 resin at the same flow rate. DOC measurements of influents and effluents of columns were used to perform a carbon mass balance, which yielded hydrophobic, transphilic and hydrophilic DOC fractions. Hydrophobic DOC are compounds that adsorb onto XAD-8 resin, transphilic DOC are compounds that adsorb onto XAD-4 resin, and hydrophilic DOC are compounds that pass through both columns.

Preparative-scale fractionation based on hydrophobicity and charge

Samples used for Task 4b will be subject to preparative-scale fractionation. The proposed scheme will used resin extraction to produce 8 major fractions based on hydrophobic behavior and organic charge. The organic extraction system will consist of three resin columns connected in series in accordance with the method of Leenheer and Noyes[5]. The first column is filled with DAX-8 resin[6], a nonionic acrylic ester resin (Figure 2). The second column is filled with a cation exchange resin, MSC-IH, and the third column with Duolite A-7, an anion

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Leenheer, Jerry A. and Noyes, T. I. A Filtration and Column-Adsorption System for Onsite concentration and Fractionation of Organic Substances from Large Volumes of Water. Washington, D.C.: U.S. Government Printing Office; 1984(U.S. Geological Survey Water Supply Paper; 2230).

[6] This is equivalent to the older XAD-8 resin.

exchange resin. All resin columns will be cleaned according to methods developed by Leenheer and co-workers. Two-liter glass liquid chromatography (LC) columns (Spectrum Chromatography Products, Dallas, TX) with Teflon end plates are to be used.

A total volume of about 300 liters of water will be pumped through the extraction system at a flow rate of 150 mL/min. The water will be pumped through two cartridge filter units (Balston Co., Haverhill, MA) with glass fiber filters rated at 25 µm and 0.3 µm pore size and then through the column and fractionation system. The effluent from the columns will be collected for subsequent recovery of the unretained hydrophilic neutral fraction.

The three resin columns will be separately desorbed to recover the organic fractions after completion of the adsorption run. Weak hydrophobic acids are to be desorbed from the DAX- 8 column with a 0.1 N NaOH solution, followed by a deionized water rinse in the upflow direction. The eluant (1.5 liters) is immediately neutralized to pH 7 with H_2SO_4 to prevent alkaline oxidation and hydrolysis. Hydrophobic bases (5 liters) will be desorbed from the DAX-8 column with a 0.1 N HCl solution. Hydrophobic neutrals are then recovered from the DAX-8 column by Soxhlet extraction of dried DAX-8 resin after desorption of hydrophobic bases and weak hydrophobic acids.

Hydrophilic bases will be desorbed from the MSC-1H column with a 1.0 N NaOH solution and deionized water rinse. As before, the eluate (7 liters) is neutralized to pH 7 with H_2SO_4 to prevent alkaline oxidation and hydrolysis. Strong hydrophobic acids and hydrophilic acids are desorbed from the anion exchange column, Duolite A-7, by recycling a mixture of 10 N NaOH and deionized water through the column. Recycling is stopped when the pH of the eluant reaches 11.5, after which the column is rinsed with deionized water.

One of the PIs (Reckhow) has use this fractionation scheme for the study of NOM in raw waters (Forge Pond, MA; Wachusett Reservoir, MA; Lake Gaillard, CT) and in treatment and distribution systems (New Haven, CT; Boston, MA).
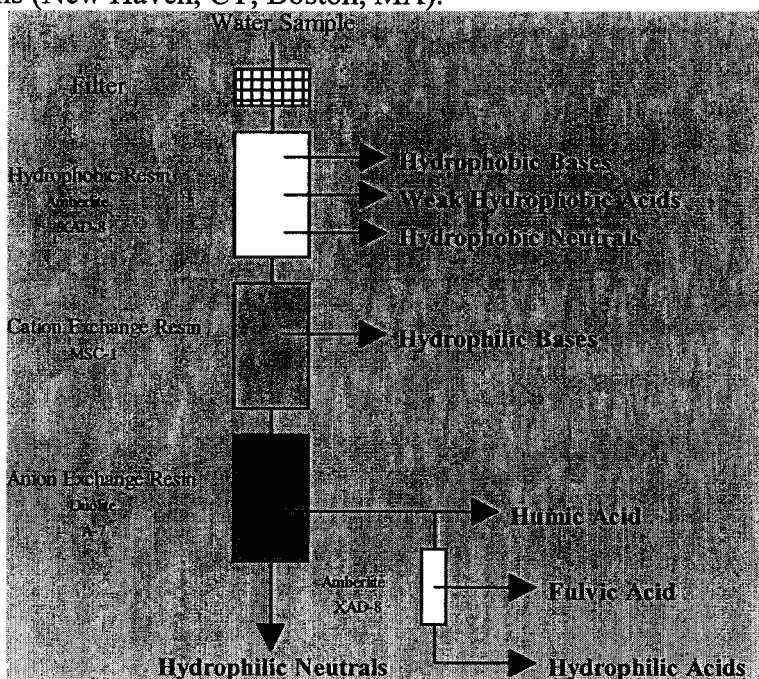

Figure 2. Preparative-scale resin fractionation scheme

Specific and Delta UV Absorbance

We propose to measure the full UV-Visible absorbance spectrum for all waters prior to treatment with disinfectants. UV Spectroscopy has been extensively used in studying humic substances. Specific UV absorbance at 254 nm is widely used to assess the humic content of NOM. Though their UV spectra are often featureless, the ratio of absorbance at 465 nm to 665 nm (i.e., E_4/E_6 ratio) has been successfully used as an indictor for the degree of humification and aromaticity of NOM (Stevenson, 1995; Chen at al., 1977). The E_4/E_6 ratio decreases with increasing molecular weight and condensation of aromatic constituents. Molar absorptivity at 280 nm of NOM is also indicative of humification and molecular size (Chin et al., 1994; Chin et al., 1997).

Korshin and co-workers have shown that there are certain wavelengths (ca. 272 nm) that present especially strong correlations between absorbance and formation of TOX following chlorination (Korshin et al., 1996). We will measure UV absorbance (full range of wavelengths) before and after disinfection on all samples. All absorbance measurements will be made at UMass a Hewlett-Packard diode array spectrophometer.

TMAH thermochemolysis for characterization of chlorinated DOM

One technique for investigating chlorinated DOM molecular composition is the tetramethylammonium hydroxide (TMAH) thermochemolysis GC-MS procedure, developed by Challinor (1989, 1995). This method has been useful for investigating the molecular composition of organic matter in several recent studies of humic substances (HS) (Chefetz et al., 2000; del Rio et al., 1998; Hatcher & Clifford, 1994; Hatcher et al., 1996; Martin et al., 1995; McKinney et al., 1996; McKinney & Hatcher, 1996; Zang et al., 2000) and DOM (del Rio *et al.*, 1998; Mannino & Harvey, 2000; van Heemst *et al.*, 2000; Wetzel *et al.*, 1995). The TMAH reaction serves both as a degradative technique as well as a derivatization technique. Labile C-O bonds such as esters, amide bonds, some ether bonds with α-hydroxy groups (β-O-4 bonds in lignin), and to some extent glycosidic bonds, are cleaved resulting in fragments. This degradation occurs mainly through a base-catalyzed hydrolysis reaction. Acidic protons, such as those found on carboxylic acids and phenols, are methylated whereas esters are transesterified into the corresponding methyl esters (Filley et al., 1999). The results are products of increased volatility that can be separated and analyzed using GC-MS.

We believe the TMAH thermochemolysis GC-MS procedure is a valuable technique for studying the structural composition of DOM as a result of the numerous polar functionalities often excluded from the analytical window using other degradative GC-MS techniques. For example, CuO oxidation has been found to be particularly useful to study lignin-derived material in DOM. However, to the authors' knowledge other biogenic contributions to DOM have not been represented by this approach aside from short chain fatty acids (<6 carbon units) (Ertel et al., 1984; Hautala et al., 1997; Hautala et al., 1998; Hyotylainen et al., 1997; Louchouarn et al., 2000). Pyrolysis GC-MS has also been useful for structural studies of DOM (Bruchet *et al.*, 1990; Schulten, 1999; van Heemst *et al.*, 1996; van Heemst *et al.*, 1999). However, substantial amounts of CO and CO_2 are produced during pyrolysis, which result from the polar functionalities that are important structural features of DOM (Saiz-Jimenez, 1994). These may be retained with the TMAH GC-MS technique since sub-pyrolysis temperatures are used (250°C) and since methylation deactivates polarity and the tendency to undergo thermal transformations.

We have recently employed this method to examine the changes in DOM accompanying the passage of stream waters through plug-flow bioreactors and water inflow at water treatment

facilities being subjected to various different treatment technologies including chlorination, ozonation, and GAC sorption. In these studies we first established protocols for quantitative measurements of TMAH products (Frazier et al., 2001a) on DOM isolated by rotovaporization and lyophilization of the water samples. We then applied the quantitative methodologies to assess the changes being sought for the various applications above. Figure 3 shows the chromatograms of TMAH products associated with changes in DOM induced by the various treatment technologies at the Norristown, PA facility. Figure 4 displays the quantitative data obtained from the chromatograms and plotted as differences in concentrations induced by each treatment. From these data, we can assess quantitatively the efficacy of treatment in removal of various constituents of the DOM.
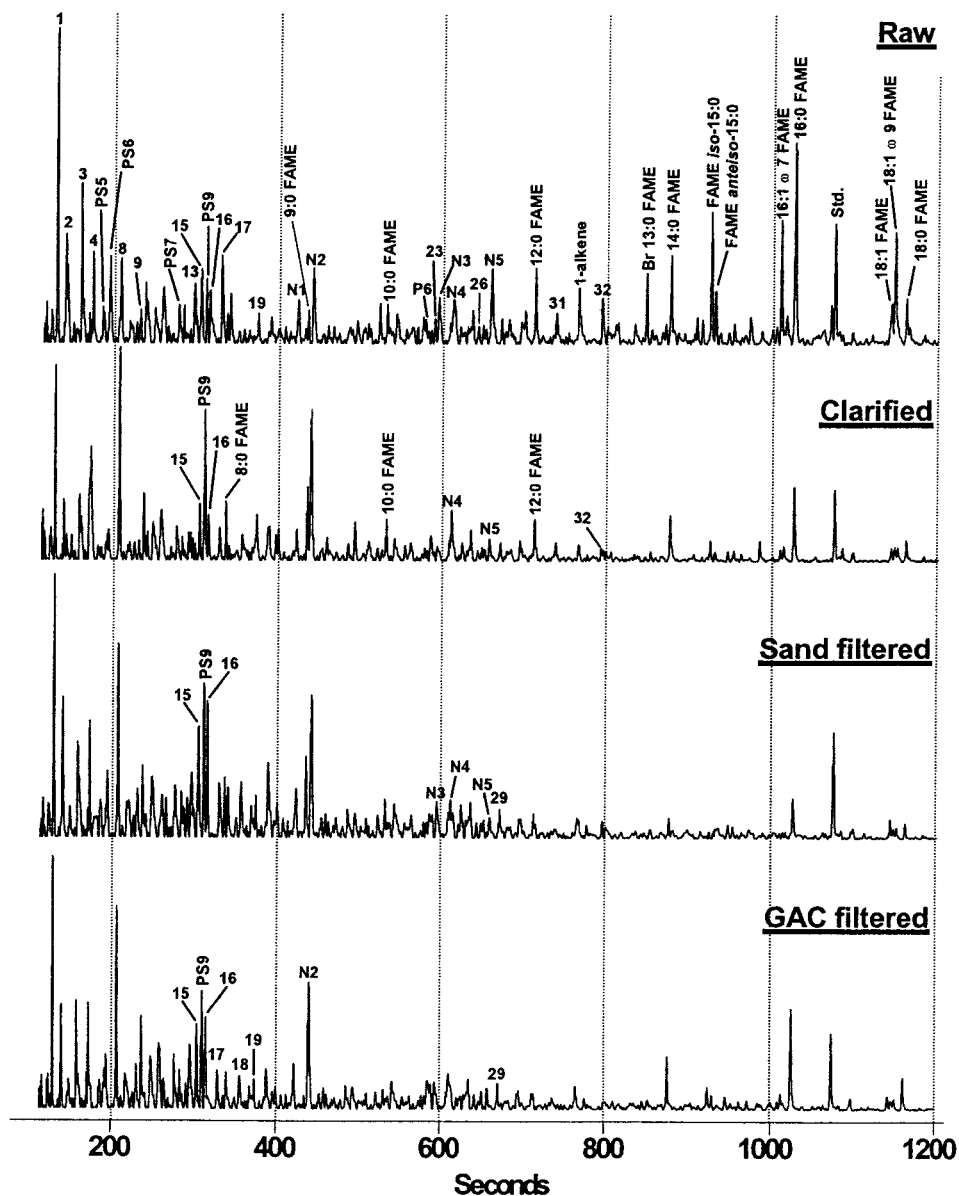

Figure 3.   GC chromatograms of TMAH thermochemolysis products from DOM isolated from various points in the Norristown, PA water treatment facility.
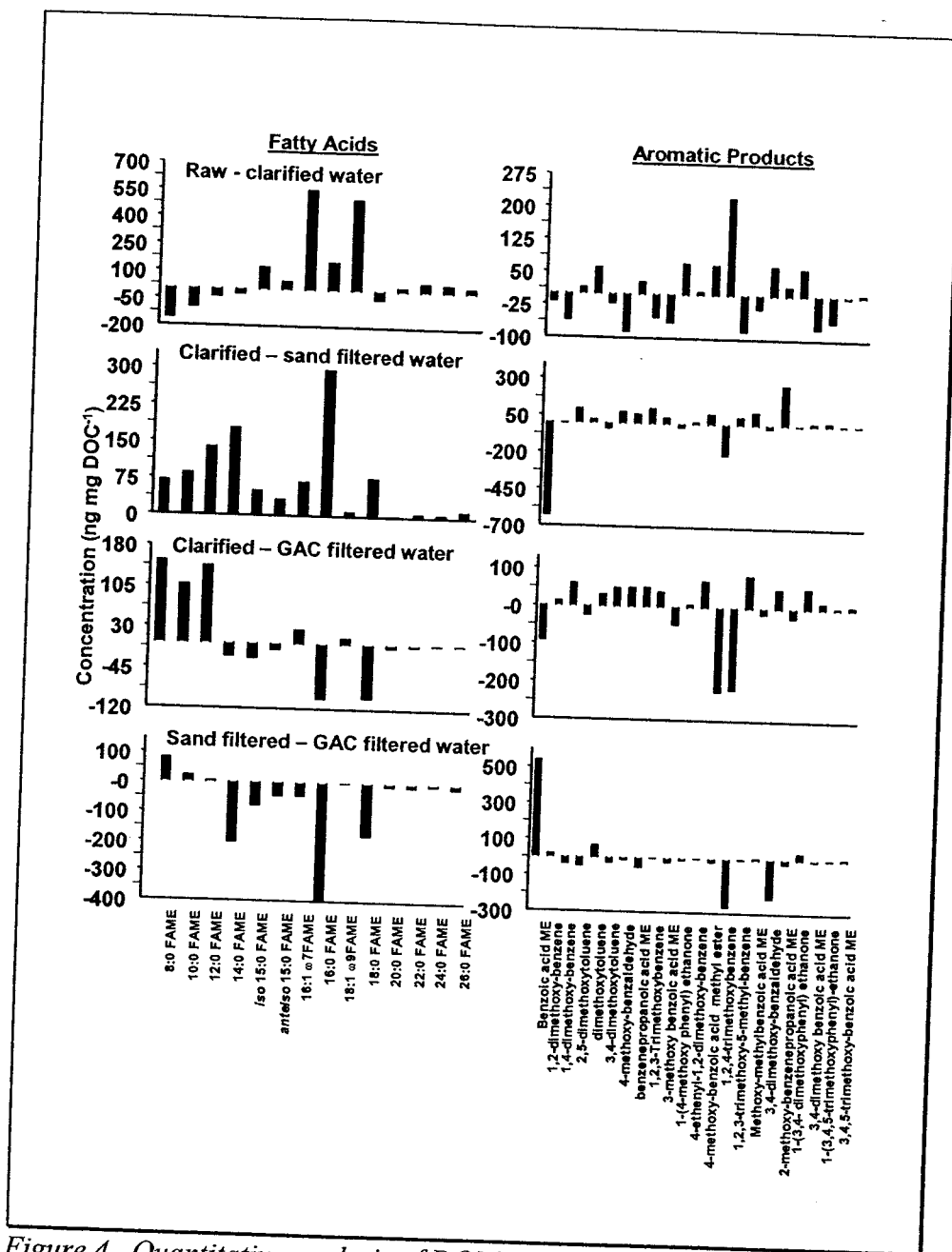
18

Figure 4. Quantitative analysis of DOM isolated from water collected at various points in the Norristown, PA treatment facility presented as differences in concentration induced by passage of the water through the various treatments.

A drawback to the TMAH procedure is that natural methoxy groups, such as those found in lignin, cannot be distinguished from those introduced during the TMAH reaction and that the strong base can remove Cl atoms from structural entities in chlorinated DOM by simple subtitution reactions. However, these drawbacks can be overcome by using the new ^{13}C-labeled TMAH thermochemolysis GC-MS procedure. [13]C TMAH thermochemolysis maintains the same degradative and derivatization characteristics as that of unlabeled TMAH (Filley et al., 1999). However, ^{13}C TMAH thermochemolysis relies on ^{13}C labeled methyl groups in TMAH as the

methylating agent so that naturally occurring methoxy groups can be distinguished from those produced during the TMAH thermochemolysis procedure. The position of the labeled methoxy group (or natural phenolic or hydroxyl precursor position) can often be determined by analysis of the mass spectral fragmentation patterns. Filley *et al.* (1999) demonstrated that there are minimal exchange reactions (<4%) with preexisting methoxy groups on TMAH products. This procedure yields vastly more information than that provided by other wet chemical degradation techniques for two reasons. Not only are chemically and thermally labile functionalities stabilized by methylation and thus the products more closely resemble their precursors (functionalities often not seen using other degradative techniques), but by using the ^{13}C TMAH procedure, one can more accurately identify the structure of the precursor prior to derivatization. We have recently employed this approach to evaluate the transformation of DOM into biodegradable DOM on plug-flow bioreactors (Frazier et al., 2001). By the combined use of TMAH and ^{13}C-TMAH thermochemolysis we determined that the indigenous bacteria preferentially degrade and demethylate lignin. This is contrary to present belief that bacteria cannot demethylate lignin on time scales of a few hours.

In the case of chlorinated DOM, we can employ a dual methylation procedure, the first using diazomethane to methylate the hydroxyl functional groups with natural abundance methyls and the second using the ^{13}C-labeled TMAH to remove Cl and replace it with a labeled methyl. Mass spectrometry of resulting products will allow us to define the positions of Cl atoms in fragments of the molecular structure. This approach has never been attempted and we are anxious to evaluate its ability to define the character of chlorinated sites in portions of chlorinated DOM.

Electrospray Ionization Mass Spectrometry for characterization of chlorinated DOM

Electrospray ionization (ESI) mass spectrometry is a novel technique that has been applied recently to the characterization of humic substances (McIntyre et al., 1997; Fievre et al., 1997; Brown and Rice, 1999; Solouki et al., 1999; Leenheer et al., 2001; Plancque et al., 2001; Kujawinski et al., 2001). ESI is a "soft" ionization technique in which ionizable compounds such as proteins, polar molecules, and humics become charged by the action of a volatilizing nebulizer spray. This process has been shown not to fragment the components of similar molecules, such as proteins (Gaskell, 1997). Intuitively, it is thought that humic substances will remain intact as well. This assumption is crucial considering the debate on whether humic substances are high molecular weight macromolecules or aggregates of noncovalently linked molecules (Piccolo and Conte, 2000) such as sugars, carbohydrates, and fatty acids.

We propose to apply ESI ionization coupled to a quadrupole time of flight mass analyzer to identify and describe chlorinated DOM structures. We already have applied solid phase extraction and mass spectrometry to get molecular level information of DOM. The initial data for DOM analysis by this method is shown in Figure 5. The ESI-QqTOF method is capable of achieving resolving powers in excess of 10,000, which is sufficient to resolve many of the peaks in the spectrum of DOM. The molecular weight distribution from this spectrum is consistent with reported spectra of fulvic acid from natural water (Plancque et al., 2001). This fact is very encouraging because fulvic acid should have a lot of common structures with DOM prepared in this protocol. From this study, we conclude that there are many series of molecules with differences of 2H, O, CH_2 and H_2O, which could be an explanation for observed peak patterns (Brown and Rice, 1999).

Much higher resolving power can be attained for humic substances with other techniques such as Fourier transform ion cyclotron resonance (FT ICR) mass spectrometry (Brown and Rice, 1999; Kujawinski et al., 2001). The QqTOF analyzer is chosen because of its robust and sensitive nature and ability to show little mass discrimination over a relatively wide range of masses. Several types of adducts are possible, such as H^+, Na^+, K^+, and NH_4^+, but only H^+ and Na^+ are expected in these samples as demonstrated previously (Kujawinski et al., 2001). The sodium ion would be expected as a result of extraction in sodium hydroxide. However, it appears that the peaks in these samples is expected to consist mostly of hydrogen adducts. In our protocol, DOM will be isolated from water by solid phase extraction. In this way, we can reduce or eliminate sodium adduct peaks, with the resulting spectrum characterized by peaks reflecting primarily H^+ adducts. This is very crucial to identifying chlorinated DOM.

One particular feature of high resolution mass spectrometry is the ability to separate compounds having relatively large mass defects, especially chlorine-containing compounds that have two isotopes each having a large negative mass defect. This property will allow us to clearly identify a DOM component containing chlorine. Without interfering ions, carbon (12.0000 amu), nitrogen (14.0031 amu), hydrogen (1.0078 amu) and oxygen (15.9949 amu) would be the main elemental composition of DOM, and their exact mass numbers in any sort of added proportions are close to their nominal mass numbers (maximum difference is 0.0078). Compared to these elements, chlorine (34.9689), bromine (78.9183) and iodine (126.9045) have much larger mass defect (minimum difference is 0.0311). Substitution of any of main elements with halogen will change the mass defect of DOM molecules. By comparing the mass defect patterns in the spectra of natural and chlorinated DOM, we can determine the contribution of halogenated molecules. From the high-resolution data, we should be able to identify the elemental composition of individual halogenated molecules. These identified molecules then can be subjected to MS/MS analysis for structural elucidation (Plancque et al., 2001).
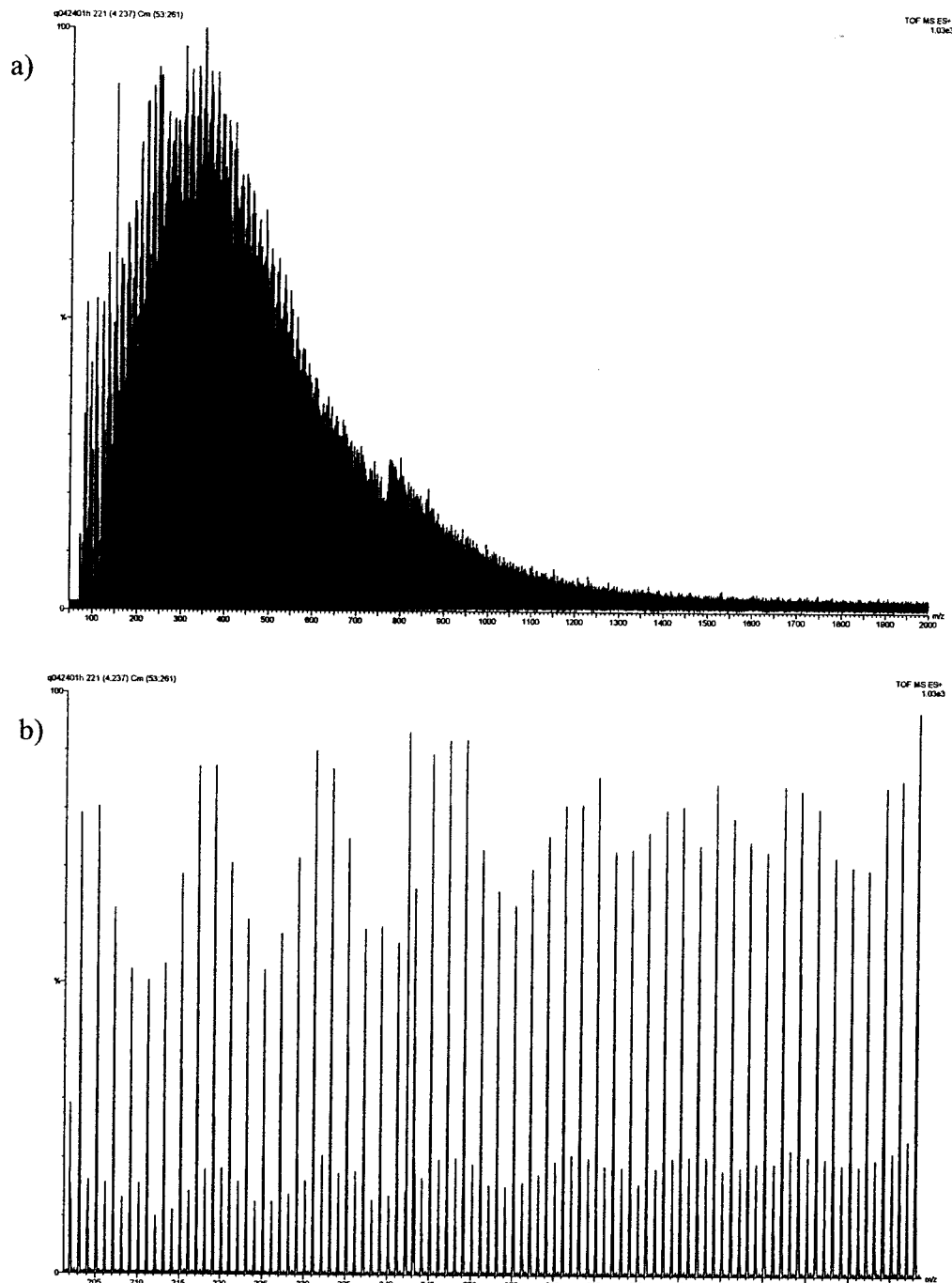
Figure 5. Analysis of DOM isolated from water ESI mass spectrometry. a) Whole spectrum in the mass range between 50 and 2000 is shown. b) Expanded region between 200 and 305 is presented.

CuO Oxidation and Product Analysis by GC/MS and LC/MS

Oxidative degradation methods have been used along with GC/MS for the characterization of NOM since the early 70s. While many different oxidants have proven successful in preserving structural features in degraded NOM, CuO oxidation has probably been

the most useful (Christman et al., 1983; Ertel et al., 1984; Hautala et al., 1997; Hautala et al., 1998; Hyotylainen et al., 1997; Liao et al., 1983; Louchouarn et al., 2000). Using this technique, researchers from both Ertel's laboratory and Christman's laboratory have clearly identified a range of lignin-based structures in aquatic NOM. Cupric oxide methods are mild and have been reported to preserve 25-75% of such lignin structures in environmental samples.

We propose to use the alkaline CuO conditions employed by both of these research groups The degradation products will then be derivatized with trimethylsilyl groups and analyzed by GC/MS in accordance with standard protocols (Hedges & Ertel, 1982). We also propose to examine use of LC/MS analysis without sample derivatization. In this case the sample would have to be desalted by passage through a cation exchange column in the hydrogen form prior to analysis.

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Applications Potential

The applications of this proposed research touch on five areas related to disinfection byproduct control: (1) methods for assessing DBP concentrations and characterizing these compounds, (2) impacts of pretreatment on DBPs, (3) impacts of disinfection conditions on DBPs, and (4) impacts of post treatment conditions on DBP stability. This research also has two important regulatory applications: (1) information on occurrence of unknown TOX (UTOX), and (2) information on the likely biological activity of UTOX.

The applications that are of most direct interest to utilities pertain to those first 4 that focus on measurement and control. This research will take some important steps in expanding the tools available to utilities for assessing the unknown DBPs. First, this work will further develop and test a protocol for measurement of TOCl, TOBr and TOI in treated waters. While methods currently exist, they have been developed in research labs on an "ad hoc" basis. This work will help to establish these as robust and optimized procedures. Second, a set of advanced characterization tools will be applied to the problem of UTOX. This will give an opportunity to assess their usefulness for other researchers as well as for drinking water utilities. Some method refinement will naturally occur, as part of this work.

Treatment-related applications will primarily come out of the task 3 work. This set of experiments will shed light on the effectiveness of selected drinking water treatment technologies as a means of controlling organic precursors to UTOX. Other experiments will assess the impacts pH changes, and addition of corrosion control chemicals on the ultimate levels of UTOX expected at the consumer's tap. Finally, the pipe loop studies will help in determining the potential for UTOX decomposition in the presence of reactive pipe surfaces.

Regulatory applications pertain to the significance of UTOX as a threat to public health. Results from this study will help toxicologists assess the threat posed by UTOX compounds based on its molecular size distribution, its charge, and its hydrophobic characteristics. These data will also add to the small data set on UTOX occurrence.

Quality Assurance/Quality Control

General Approach

Quality assurance is an essential and integral part of a research study. The purpose of the QA plan is to insure that valid and reliable procedures are used in collecting and processing the research data. The procedures outlined are designed to eliminate or reduce errors in experiments, sample preparation and handling, and analytical methods. Emphasis will be given throughout the project to incorporate the plan into the research project by all research personnel.

Any equipment and experimental procedure that are used to provide numerical data will be calibrated to the accuracy requirements for its use. Records shall be kept of all calibrations. Calibration schedules will be established for all aspects of physical and chemical measurements and will be strictly enforced. Physical standards and measuring devices will have currently valid calibrations, traceable to national standards. Chemical standards will be prepared using state-of-the-art analytical methods and materials of known purity (the highest purity available). Calibrations and standards obtained externally will adhere to the requirements for internal standards.

As a general rule, experiments will be replicated to assure reproducibility. All data reported will include a statement of its uncertainty, and the means for the determination and assignment of such limits. Standard reference materials will be used for this purpose where possible. Statistically established confidence limits and an analysis of sources of systematic error will be used in the absence of experimental demonstration of limits of inaccuracy.

All data will be subject to review by the principal investigators before release. The analysts involved will sign reports as well as all who review them. All signers attest that the data and associated information contained in the report are believed to be correct and that all quality assurance requirements have been fulfilled, unless exceptions are approved and noted. Careful and detailed laboratory records by each analyst will be maintained, including source of reagents, meticulously detailed procedures, instrument and conditions of analysis, failed experiments, etc. Data output will be archived.

Regular meetings will be held to review the results and project progress, and to plan further experiments. The results will be analyzed promptly and published in scientific journals. The experimental and analytical procedures will be reviewed for their performances and changes will be made as necessary. The quality assurance program as described above will be strictly enforced.

Quality Assurance Objectives

The precision, accuracy and method detection limits will be evaluated, and where there are existing methods, held within the control limits set forth in the accepted references (e.g.,APHA et al., 1999; USEPA-EMSL, 1990; ASTM, 1994). In addition to the analysis of sample replicates, approximately 10 percent of the time involved in analytical determinations will be devoted to quality control. The precision of each test is determined through analysis of sample replicates. These are commonly presented in the form of control charts (e.g. Section 1020B of APHA et al., 1999).

The accuracy of each analysis will be determined by measuring spike recoveries in the matrix of interest. The relative errors will be calculated and will be considered acceptable if they

fall within the control limits determined for the particular test. For new methods developed under this research, we will have to establish criteria on acceptable control limits. In general, a test will not be deemed useful if its precision or accuracy is found to be equal to or greater than 20% of the highest values observed. Where possible, external performance standards will also be run. This serves as a measure of accuracy both for the analysis and for standard preparation.

Data generated by the QA program will be incorporated into a Quality Control (QC) method that will monitor the fluctuations in precision and accuracy so that chance or assignable causes of error can be determined. Control charts such as X-charts for simple successive samples or cumulative sum techniques will be employed to record both precision and accuracy data (Taylor, 1987).

Procedures

General sample collection and handling will be in accordance with the guidelines of Section 1060 of Standard Methods (APHA et al., 1999). All previously established analytical methods used in the research will follow approved methods in the standard compilations (e.g., ,APHA et al., 1999; USEPA-EMSL, 1990, or ASTM, 1994).

Reagent grade chemicals or higher quality when needed will be used throughout the research. Super-Q water (purified by reverse osmosis, deionization, and carbon adsorption) or equivalent will be used for preparation of reagents, sample blanks, and dilution water. Where necessary, this water will be further purified using batch UV irradiation. All glassware used in the experiments and in analytical analyses will be thoroughly cleaned with a chromium-free sequence of detergent, oxidant and acid to prevent interferences from trace organics.

Chromatographic analyses will be standardized by the use of carefully prepared solutions of known standards. In general, non-aqueous primary stocks will be kept in a -10°C freezer and discarded after two months. Duplicate primary stocks will be prepared regularly, as a check against degradation of the primary stock. Data quality objectives for this work will be assured by: (1) use of blanks; (2) use of an internal standard; (3) analysis of duplicates; (4) determination of spike recovery; (5) analysis of a matrix standard; (6) monitoring of response factors; and (7) monitoring for spurious peaks.

Three types of blanks will be run daily or with each set of samples: (1) reagent blanks, composed of the extracting solvent(s) and internal standard; (2) Laboratory water blanks; and (3) Field blanks. This last type of blank is prepared by transporting laboratory reagent to the study site, and transferring it to a labeled sample vial at the time of general sample collection.

An internal standard will be used to control for solvent evaporation and variable injection volume. Most samples will be run in duplicate. If they differ by more than the acceptable range, additional GC or LC injections will be made. If there still exists a significant problem, either the original sample will be re-extracted or the data will be discarded.

Spike recoveries will be determined for each analyte/method. Matrix standards will be prepared and analyzed with each method. These may be test-specific, but many types of DBP tests will make use of a bulk sample of raw drinking water (depending on the particular sample being studied). This would be treated with the oxidant of interest under well-defined conditions. Control charts are prepared and continually updated for this type of matrix standard. Data falling outside of the control limits require that the method be re-tested in order to bring it back under control. Calibration response factors will be monitored and compared from one day to the next. Significant changes in either these response factors or in the spike recoveries will be considered

cause for method re-evaluation. Finally, general QA requires that all chromatograms be manually inspected for spurious peaks. When such peaks are observed, potential sources must be investigated. If the problem cannot be corrected, the data may have to be discarded.

This outlines our general QA philosophy for chromatographic and other methods. Many specific details relating to the individual procedures may be found in the cited references, and other particulars will have to be adopted as new methods are developed.

Sampling Custody

In most cases analyses will be performed immediately upon return from the field or after preparation of samples in the laboratory. Problems with sample custody will be minimized, because the same people will both receive (or sometimes, collect) the samples, and analyze them. In general sample collection, handling, and preservation will be in accordance with the guidelines of Section 1060 of Standard Methods (APHA et al., 1999).

Data Reduction, Validation and Reporting

To ensure the accuracy and permanency of collected data, all research data will be recorded with permanent ink in a bound notebook and all QC data (precision, accuracy) will be recorded in instrument log notebooks. Summary QC graphs and tables will be reviewed at least quarterly by the PI to observe noteworthy trends or inconsistencies. These will be maintained in loose leaf notebooks for subsequent use in preparing quarterly or final reports. Major concerns and conclusions will be reported to the Project Officer via the project reports.

Laboratory data books will have a carbon so that a file copy of raw data can be placed in safe storage in the event that the book is lost or destroyed. At the end of the project, all bound data books and any loose-leaf data will be stored by the project team for at least ten years. Summary data files will be put on magnetic media so that statistical analysis of the data can be done. The two laboratories have several microcomputers that can be used for this purpose.

Schedule

The project is proposed to begin as soon as possible, and continue for 2.5 years of data collection and analysis, and 0.5 years of final report preparation, and revision. If the winning team is selected by AWWARF, and contracts can be signed by the end of September, we would be happy to begin on November 1st. Otherwise the starting date would have to be adjusted accordingly. The timeline below is based on a presumed November 1, 2001 starting date. This would make September 30, 2003 as the date that the final progress report would be submitted, marking the end of data collection. The full project report would then be submitted in draft form, 2 months later and in final form by October 31, 2004.

Task Name	2001	Qtr 1, 2002	Qtr 2, 2002	Qtr 3, 2002	Qtr 4, 2002	Qtr 1, 2003	Qtr 2, 2003	Qtr 3, 2003	Qtr 4, 2003	Qtr 1, 2004	Qtr 2, 2004	Qtr 3, 2004	Qtr 4
Task 1: TOX Method Performance													
Task 1a: Model Compound Testing													
Task 1b: TOX & Raw Water Studies													
Winnipeg Studies													
Tulsa Studies													
Task 2: UTOX Survey													
Task 3: UTOX Formation and Destruction													
Task 3a: Bench-scale studies													
Task 3b: MWRA pipe loop studie													
Task 4: Advanced Characterization of UTC													
Task 4a: Bulk studies													
Task 4b: Fractionated Studies													
Progress Reports													
Final Report													

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Statement of Qualifications

The proposed work will be conducted by two research partners, University of Massachusetts and Ohio State University, with substantial analytical assistance from the participating Utilities. This work will be distributed as summarized in the section on "General Division of Labor", below. Additional description follows in the subheading, "Project Management and Time Commitments".

General Division of Labor

Tasks 1-3 and 4b will be the primary responsibility of UMass, however, Ohio State will provide valuable assistance in the detailed experimental design and interpreation of results. Ohio State will have primary responsibility for task 4a.

This division of labor is summarized below by research partner in bulleted list form.

University of Massachusetts

- Primary responsibility for TOX methods studies (Task 1)
- Experimental survey of North American utilities (Task 2)
- Bench-scale studies with North American raw & treated waters (Task 3), focusing on existing US technologies, e.g.,
    - Effects of pretreatments
    - Effects of disinfection conditions
    - Effects of post treatment
- Assistance with task 4 studies
    - Advanced analysis with CuO oxidation
    - Fractionation treatments in task 4b

Ohio State University

- Assist with TOX methodology
- Assistance with experimental survey of North American utilities (Task 2)
- Advanced characterization methods for task 4, except CuO oxidation
    - TMAH thermochemolysis
    - ESI/MS (high resolution)
    - Sample extraction and preparation for all task 4a studies
- Overall assessment of task 4 data, and interpretation of characterization results

Participating Utilities

- Collection and shipping of waters for survey; and for bench-scale tests (if selected)
- Provide routine WQ data on raw and treated waters
- Operation of distribution pipe network, and associated chemical analyses (MWRA only)