Think before you Drink: The Occurrence of Organic By-Products in the Disinfection of Natural Waters

Brian C. DeSchuytner '00, Kathryn A. Greer '00, Karen M. Miller '00, Michael Orchowski '00, Rebecca L. Sangster '00

Abstract

To some extent, the municipal water chlorination/disinfection process itself introduces contaminants (in the form of organohalogen compounds) into the water supply. This is of interest because several disinfection by-products, such as trihalomethanes (THMs), are suspect carcinogens. In order to estimate their by-product formation potential, samples taken from local waters sources were chlorinated at levels several times those used by water distributors to disinfect raw drinking waters. Volatile organics were extracted from all samples using the Supelco^{TM} Solid Phase MicroExtraction technique. This is a new technique which uses an adsorbent fused silica fiber to collect organics from solution. After sample adsorption, the fiber can be desorbed directly into the injection port of the GC/MS for analysis. It was found that the local water supplies show considerable variation in by-product formation potential and that this variation is correlated with levels of humic acids naturally present in the waters. It was also found that the Supelco^{TM} Solid Phase MicroExtraction technique is highly susceptible to chemical contamination across runs and that the fiber can be unstable at temperatures encountered in the injection port of the GC/MS.

Introduction

The History

The United States was one of the first countries to adopt chlorine as a means of water disinfection. By 1914, the first water health standard had been instituted by the U.S. Public Health Service. This standard recommended the use of chlorine to control pathogenic species potentially present in water supplies (Putnam & Wiener, 1995). Previously, drinking waters were only disinfected after pathogens had been discovered in the water supply.

In order to meet current drinking water regulations, disinfection must consist of two stages: primary and secondary. Primary disinfection is the eradication of microorganisms present in the raw water. Secondary disinfection is the use of a disinfectant residual in the water to prevent the regrowth of these biological contaminants. Nearly a century after its introduction, Cl_2 is still the most widely used disinfectant, it is nearly unrivaled in its potency as both a primary and secondary disinfectant (National, 1996).

Cl_2 dissolves in solution by the following mechanism (Gonzalez, *et al.*, 1996):

$$Cl2 + H2O \rightarrow HOCl + H+ + Cl-$$
$$HOCl \rightarrow H+ + OCl-$$

The OCl^- ion is able to disrupt cell walls and diffuse into a cell, interfering with cellular respiration and cytoplasmic transport. It is also able to destroy nucleic acids, thus inactivating any viruses present in the water supply (Montgomery, 1985). The disinfection process is not specific and can be used to control pathogenic bacteria, viruses, slime molds, algae, and fungi that would otherwise clog water distribution systems.

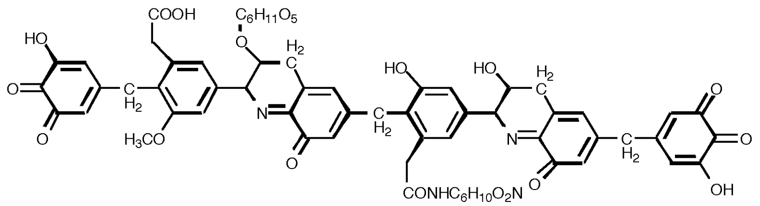
The disinfecting properties of chlorine are not what initially made it so attractive to water suppliers. While the need for water free from biological contamination was certainly recognized, it was the aesthetic appeal of chlorine that secured for it a distinguished place in the annals of water disinfection technology. Even biological contaminant free water contains natural organic material in the form of humic acids, which account for its yellowish tinge. These humic acids are the products of the natural decay of aquatic plant life. The advantage of chlorine over other methods of disinfection was that it could be used to bleach humic acids out of the water. The need to make drinking water appealing was not trivial. Water distributors had to be sure that their customers would not turn to other, possibly less safe, water sources purely for aesthetic reasons (Minear & Amy, 1996).

Ironically, it was the ability of chlorine to destroy these humic acids that ultimately led to its fall from grace. In 1974 Johannes Rook demonstrated that Amsterdam drinking water had a high concentration of chloroform and other trihalomethanes (THMs) (Minear & Amy, 1996). Bellar independently identified THMs as the by-products of municipal water chlorination. Bellar and colleagues found THMs in municipal water supplies at concentrations as high as 37 to 150 µg/L. They also determined that surface water sources produced higher levels of THMs than did ground water sources (Bellar, *et al.*, 1974). In 1981, R.F. Christman isolated chloroform, among other by-products, upon reaction of aquatic humic acid material with HOCl (Christman, *et al.*, 1981).

Interest in the study of THM formation has stemmed primarily from the biological implications of their presence in drinking water. Bellar found the oral lethal dose of chloroform in mice to be 120 mg/kg (Bellar, *et al.*, 1974). While this value is much higher than the µg levels found in any of his water samples, even low concentrations of chloroform in drinking water have been shown to increase the likelihood of several types of cancer. A study done over the years 1968 to 1970 by Alavanja, Goldstein, and Susser which surveyed the occurrence of gastrointestinal (GI) and urinary tract cancer in seven New York counties found that areas which used chlorinated water exhibited a "statistically significant increase in GI and urinary tract cancer mortality" (Alavanja, *et al.*, 1978).

In addition, the 1995 Great Lakes Basin Cancer Risk Assessment Study found that long term consumption of chlorinated water led to an increased risk of bladder and possibly colon cancer (Deputy). These findings were supported by the Iowa Women's Health Study, released in 1997 by Doyle and colleagues, which showed a correlation between chloroform in chlorinated water and an increased risk of colon cancer. An increase in melanoma and lung cancer was also observed. Doyle asserted that THMs "appear to exhibit tumor-promoting activity," and that this is most likely due to the production of intermediates in THM metabolism which are capable of reacting with DNA (Doyle, *et al.*, 1997). It has also been postulated that exposure to volatiles in water through inhalation may be as large or larger than through ingestion alone (Putnam & Wiener, 1995). A hypothesis which, if proven, may have implications toward the use of chlorine in swimming pools as well as drinking water.

Humic acid model proposed by Dragunov (Jug).



Reproduced from Jug, Student Seminar.

Figure 1

The Chemistry

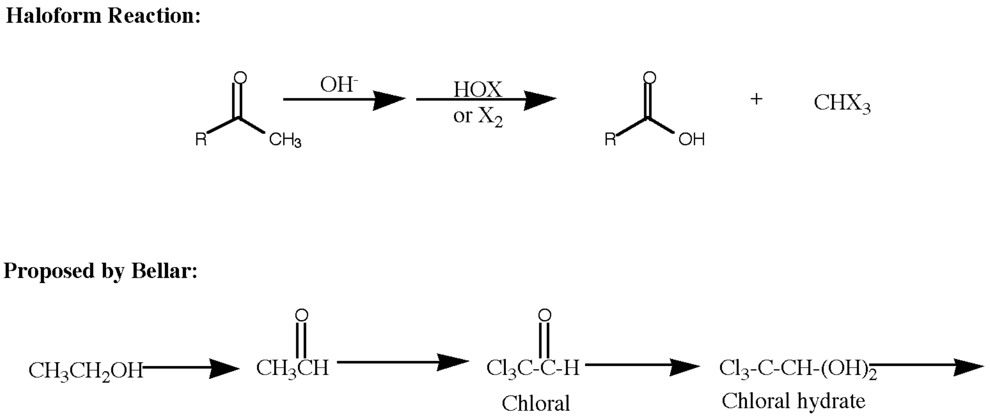
Chlorination by-products (CBPs) originate from reaction of the hypochlorous acid (HOCl) used in water treatment with the humic acids found in abundance in natural waters. Humic acids are complex, polyelectrolytic, nonvolatile molecules of molecular weight 500-5000 amu with oxygen-containing functional groups capable of reacting with HOCl via various mechanisms to cause break down of its structure. A model of humic acid structure can be seen in Figure 1.

CBPs can be assembled into two groups: volatile and nonvolatile. The most prevalent volatile by-products are the THMs (chloroform, dibromochloromethane, bromodichloromethane, and bromoform). Yet the TOX (total organic halogen) content of any given sample has been shown to be 5 to 10 times greater than values for THMs alone (Kühn & Sontheimer, 1979). Other volatile CBPs include haloketones, haloacetonitriles, halophenols, carbon tetrachloride, and chlorinated ethylene (Faust & Aly, 1983). The most significant nonvolatile by-products are the di- and trihaloacetic acids (DCAAand TCAA) (Jug, 1998).

Several mechanisms have been proposed for the formation of chloroform and other THMs during chlorination. The simplest involves the haloform reaction, in which a methyl ketone is converted, in the presence of base, to a carboxylic acid and a molecule of THM. Evidence for this mechanism came with the discovery that THM formation levels increase with pH. This supports the hypothesis that THM formation via the haloform reaction is base-catalyzed. Another mechanism, proposed by Bellar, shows formation from an alcohol of a chloral hydrate, which can then generate a molecule of chloroform. Both mechanisms can be seen in Figure 2. In addition, Figure 3 suggests some molecular structures found in humic acids that are most likely responsible for chloroform formation.

Several variables have been found to affect chloroform formation. In 1979, A. A. Stevens released a study which showed that chloroform formation increased with temperature, pH, and concentration of Br^- and I^-. In addition, he found that samples containing higher levels of bromine, mostly due to intrusion of sea water, were more likely to contain or produce brominated THMs (Stevens, 1979). THMs also exhibit seasonal variation, due to the variable nature of their humic acid precursors. Median values of THM concentration (in μg/L) throughout the year have been

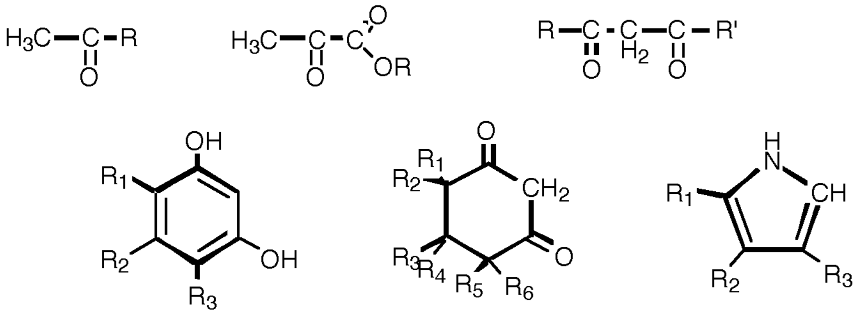
Two Possible Mechanisms for the Formation of THMs from Chlorination of Organic Compounds



$$CH_3CH_2OH \longrightarrow CH_3\overset{O}{\overset{\|}{C}}H \longrightarrow Cl_3C\text{-}\overset{O}{\overset{\|}{C}}\text{-}H \longrightarrow Cl_3\text{-}C\text{-}CH\text{-}(OH)_2 \longrightarrow CHCl_3$$

Figure 2

Molecular Structures Most Likely Responsible for Chloroform Formation



Reproduced from Morris and Baum, Ann Arbor Science.

Figure 3

reported as follows: Spring - 34, Summer - 44, Fall - 40, Winter - 30 (Krasner, *et al.*, 1989). THMs also undergo daily fluctuation, showing highest concentration in the early morning. It has been hypothesized that such fluctuation occurs because more THMs are formed at night when water demands are low, but they are flushed from distribution systems in the early morning when water use rises again (Faust & Aly, 1983).

The links between THMs and cancer have launched two efforts among drinking water distributors: one seeks to find chlorination alternatives, and the other to decrease formation of THMs during chlorination through removal of organic precursors. The most obvious way to accomplish the latter is to remove as many of the organics in the raw water as possible before chlorination. Gross organic material can be removed by simple filtration, often using a sand filter. Smaller particles can be removed by dispersing a coagulant, such as alum, into the water. The coagulant forms a gelatinous material when it contacts the water and traps small particles of organic material to be filtered out in the gel. The City of Lebanon uses such a method to reduce disinfection by-products (DBPs), as well as to remove foul tastes and odors. Another possible method for reducing THMs in treated water involves pre-oxidation with permanganate (Miller, 1993). To this day, however, no municipal system uses pre-oxidation to reduce DBPs.

Although disinfection with chlorine gas or sodium hypochlorite remains the most popular method for water treatment in the United States (71% of large, and 85% of small water systems in the US (Miller, 1993)), other oxidants have been gaining popularity in Europe. Initially these were used to control odor and taste problems, although alternative disinfectants have now become a popular way for water systems to deal with DBPs. The most common of these is chlorine dioxide gas. It has about 70% of the oxidation power of chlorine gas but produces different by-products. Chlorine dioxide is an oxidizing, rather than chlorinating agent, and thus it tends not to form THMs. Nonetheless, it has its own problems. Chlorine dioxide is difficult and expensive to generate, making it out of reach for many small water systems. It also produces a wide range of DBPs, including the chlorite and chlorate ions, as well as a number of ketones and aldehydes that are not yet fully known (Guttman-Bass, *et al.*, 1987). The chlorate and chlorite by-products are of most interest, as the similar bromate ion has been shown to be carcinogenic. A comprehensive study on chlorine dioxide by-products has never been done, though it has been shown to reduce the mutagenicity of Lake Kinnereth water (Guttman-Bass, *et al.*, 1987). Hanover water is disinfected with chlorine dioxide.

The Purpose

With such a broad range of options for study, we needed to narrow the scope of our research down quite a bit. We hoped to run a study that would investigate several points and have both a local and a global impact. On the global side, we wanted to confirm the formation and origin of water chlorination by-products. This was accomplished by over-chlorinating a known sample of an ideal humic acid, resorcinol, and testing for by-products. Second, we wanted to investigate formation potentials (FPs) for a variety of water source types including deionized water, moving surface water, and still surface water. On the local side, we wanted to evaluate our local water systems’sources, as well, to distinguish our study from the multitude of studies done previously. We did this by taking raw and tap water samples from Hanover and Lebanon, simply running the tap samples, and running both raw and chlorinated raw samples, and then analyzing them.

Although we have only scratched the surface of investigating water disinfection by-products, we hope that our study will be of some use to our local communities. In the future, a possible investigation of coagulants’ utility in reducing disinfection by-product formation could be in order, or perhaps a fuller investigation of alternative disinfectants.

Methods

Sampling

A glass jar was rinsed with the water to be sampled, and then filled completely to no headspace. These samples were taken with no headspace because THMs are extremely volatile compounds. When possible, samples were taken in the early morning from the center of the sampled body of water.

Supelco^{TM} Solid Phase MicroExtraction (Supelco^{TM}, 1998)

The Supelco system consists of a retractable fused silica fiber held within a needle. When the fiber is placed in a sample with organic components, they adsorb to the solid phase coated silica fiber. The coating of our particular fiber was 100 μm polydimethylsiloxane, which is very good for collecting polar, volatile organic compounds. The fiber can be directly injected to the GC/MS, where the components are desorbed into the injection port of the GC.

Some of the water sample was used to fill a 5 mLvial and the vial was capped with a penetrable lid of Teflon leaving zero headspace. The penetrable cap was punctured with the needle and then the fiber was immersed in the sample for a period of 24 hours. All samples were stirred magnetically.

Samples of the straight water were run as controls. These controls were compared to chlorinated formation potentials from the same sources. Formation potentials involved chlorinating at 25 mg/L (McClellan, *et al.*, 1996) for 24 hours. This procedure was used in an attempt to maximize by-product formation. In addition to area water samples, control runs were carried out on distilled water and a chlorinated solution of resorcinol, a model humic acid compound.

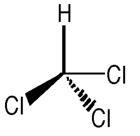
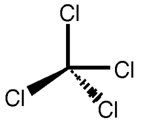
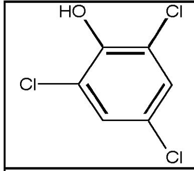
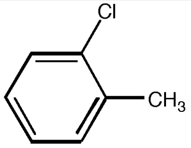
Chlorination of a Model Humic Acid

Following a procedure used by Boyce (1980), the humic acid model resorcinol (1,3-dihydroxybenzene) was treated with chlorine in a ten-fold molar excess for an extended amount of time in an attempt to achieve maximum formation potential of organic by-products. It was hoped that compounds formed in this chlorination could be compared to future by-products generated by chlorination of area water samples.

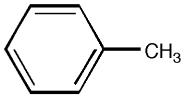
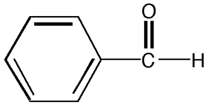
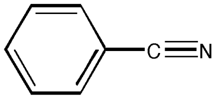
Chlorination of Area Water Samples

With resorcinol data in hand, preparations were made to begin chlorination of samples from area waters. Chlorination reactions involved mixing equal volumes of water sample and standard chlorine solution diluted to a concentration of 25 mg/Lin phosphate buffer. Buffer solutions at both pH 7.0 and pH 8.5 were prepared from KH_2PO_4 and Na_2HPO_4 and were used in order to maintain constant pH throughout the chlorination. All chlorinations were done at 25 mg/L and pH 7.0 unless otherwise indicated. Results obtained using Supelco^{TM} MicroExtraction and GC/MS analysis are presented in the following tables and charts (see next two pages).

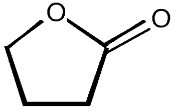
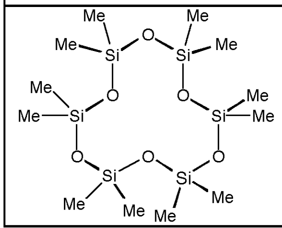
Sample Name	Chloroform?	Abundance	Other Compounds Identified with Quality > 90 %
Resorcinol	yes	800,000	Butyrolactone Toluene Benzaldehyde Benzonitrile Dodecamethylcyclohexasiloxane
River Control	yes	175,000	Butyrolactone 4-bromo-1,1'-biphenyl
River Formation Potential	yes	75,000	Butyrolactone Dodecanal
Pool	no	-	Butyrolactone Dodecamethylcyclohexasiloxane Benzenthiol
Occom Control	no	-	Butyrolactone Butanoic Acid Anhydride
Occom Formation Potential (25 mg/L)	yes	160,000	Butyrolactone Toluene Benzaldehyde Nonanol 1,3,5,7-cyclooctatetraene
Deionized	yes	25,000	Butyrolactone Toluene Benzaldehyde Benzonitrile Dodecanoic Acid Tetradecanoic Acid
Hanover Plant Control	yes	25,000	Butyrolactone
Hanover Plant Formation Potential	yes	40,000	Butyrolactone Benzaldehyde Diethyltoluamide Urea
Hanover Tap	no	-	Butyrolactone
Lebanon Plant Control	no	-	Butyrolactone
Lebanon Plant Formation Potential	yes	170,000	Butyrolactone Toluene Buty-1,2-benzenedicarboxylic Acid
Mink Brook Control	no	-	Butyrolactone
Mink Brook Formation Potential	yes	65,000	Butyrolactone Aniline Benzeneacetaldehyde
Occom Formation Potential (300 mg/L)	yes	700,000	Butyrolactone Carbon Tetrachloride 1-chloro-2-methylbenzene 2,4,6-trichlorophenol

	**Chloroform**: Most common DBP, as well as a suspect carcinogen. Found in all chlorinated samples (except , surprisingly, the swimming pool), as well as deionized water, the River control and Hanover raw water. These samples probably contained it due to needle contamination.
	**Carbon Tetrachloride:** Known DBP, found in the super-chlorinated Occom sample. Former dry-cleaning solvent that was banned in most industrial uses due to its ability to cause cancer. Causes liver and kidney damage.
	**2,4,6-trichlorophenol**: Found in super-chlorinated Occom sample. Suspect carcinogen, as well as an eye/skin irritant.
	**1-chloro-2-methylbenzene**: Found in super-chlorinated Occom sample. Non-carcinogenic, but a strong irritant.

Significant Chlorination Byproducts

	**Toluene**: Found in resorcinol and deionized sample. Not a known chlorination by-product. In high concentrations it can cause central nervous system depression.
	**Benzaldehyde**: Found in resorcinol, Occom and Hanover raw chlorinations, as well as in the deionized sample. Eye/skin irritant and CNS depressant. Chronic exposure can lead to liver damage.
	**Benzonitrile:** Found in resorcinol and deionized sample. Eye and skin irritant.

Suspected Distilled Water Contaminants

	**Butyrolactone**: Commonly used in coatings industry. Found in every sample and suspected to have leaked from the fiber.
	**Dodecamethylcyclohexasiloxane:** Also suspected to have come off of the fiber because of its polydimethylsiloxane composition.

Suspected Fiber Contaminants

Safety information from Cornell MSDS Database.

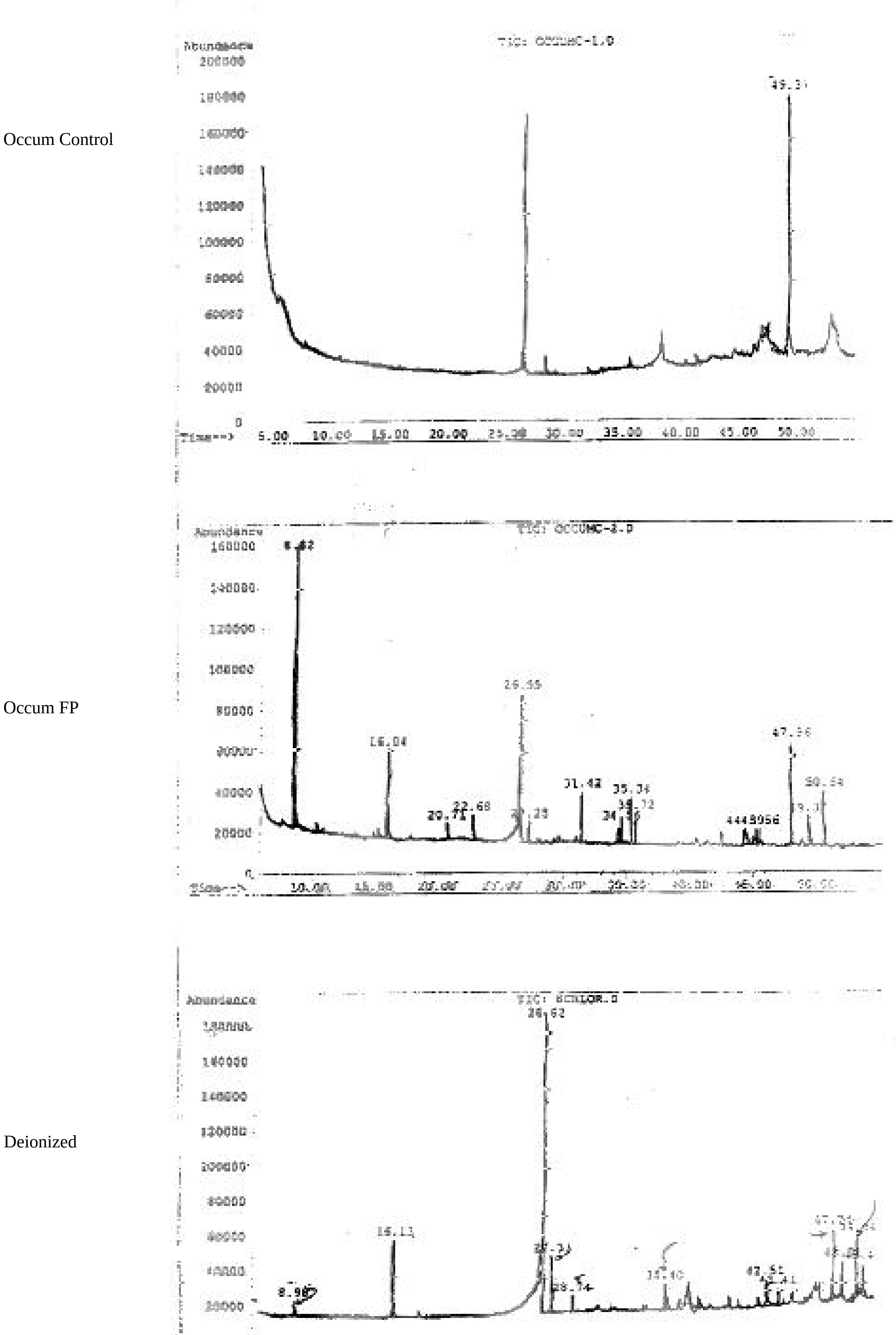
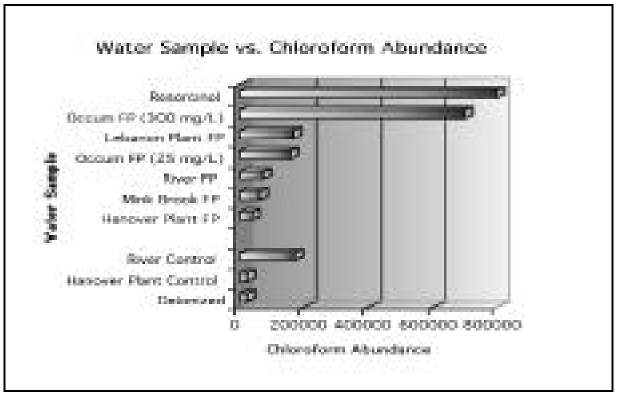


Figure 4: A Comparison of GC Plots



Discussion of Results

Resorcinol

Our model humic acid, resorcinol, served as a worst-case scenario chlorination. Similar results would be expected from a water supply saturated in humic acids and having a massive CBP formation potential. Indeed, gas chromatography showed a large abundance of chloroform, the largest on the table, in fact. This is to be expected from a compound able to undergo the same reactions as humic acids upon chlorination and confirms the already established connection between trihalomethanes and humic acid degradation. GC/MS analysis also identified toluene, benzaldehyde, benzonitrile, butyrolactone, and dodecamethylcyclohexasiloxane in the sample.

These last two compounds are very likely associated with the Supelco^{TM} fiber and are not chlorination by-products. Butyrolactone is used in the coating industry and may be a component of the fiber itself. This theory is well substantiated in that butyrolactone is found in every water sample analyzed with the Supelco^{TM} SPME technique. Because butyrolactone is found in every sample and can be associated with the fiber, its importance is negligible, and it will not be mentioned further.

Dodecamethylcyclohexasiloxane is similar to dodecamethylcyclopentasiloxane, a known product of solid waste incinerators (Jay & Steiglitz, 1995). However, the link from resorcinol to solid waste incineration is tenuous at best. Dodecamethylcyclohexasiloxane is also similar to the polydimethylsiloxane which coats the needle and adsorbs organic matter for analysis (Supelco^{TM}, 1998). Possibly it is the product of fiber degradation and ring fusion of polydimethylsiloxane.

Toluene, benzaldehyde, and benzonitrile were also identified with high quality. It is disturbing that these compounds are present in the sample. They are not by-products of the chlorination process. Other studies on resorcinol had been able to isolate multiple by-products only prior to the reaction "end point." After that time, chloroform was the only known compound isolated; everything else had been completely broken down to form THMs (Christman, *et al.*, 1978).

The possibility that these aromatic compounds were present as impurities on the GC/MS column was considered. However, if this were the case, then they would appear in all samples, not just those chlorinated in the laboratory. It is more likely that these aromatics were present as deionized water contaminants in the standard chlorine solution and buffer solution used in chlorinating resorcinol and other compounds. Most of the FPsamples show at least one of these three compounds. Because the Supelco^{TM} fiber is optimized for the analysis of polar volatile organics such as THMs, it is conceivable that all of these compounds existed to some extent in each sample due to contamination, but the fiber is not sensitive enough to dependably adsorb all of them in every sample.

River

The River control and FP are not in agreement with the expectation that chloroform would not be present in unchlorinated water. The River control yielded a high abundance of chloroform, more than the FP by a factor of approximately 2.4. Although natural sources of chloroform are well-documented, the levels observed in the River control are large enough to suggest that other factors are involved. It is thought that the presence of chloroform in the control is the result of fiber contamination. The resorcinol run was performed just prior to the River control. Some residual chloroform may have remained in the fiber after the resorcinol run and desorbed during the River control run. The River FP, performed with a different fiber to avoid contamination, gave a smaller but still significant abundance of chloroform. Also found in the control and FP were 4-bromo-1,1'-biphenyl and dodecanal, respectively. Literature searches did not implicate these two compounds as CBPs.

After the possibility of fiber contamination was recognized, the assembly was cleaned by running blank GCs. This consisted of injecting the fiber into the GC/MS and desorbing without first adsorbing a sample.

Pool

The pool sample was one of the first runs performed. Again, dodecamethylcyclohexasiloxane was identified. The other identified peak belonged to benzenethiol. It is difficult to make conclusions about roles for benzenethiol as a putative DBPbecause it is not adsorbed by the needle with peak efficiency. The fact that no chloroform was found in the pool sample even though the pool is routinely disinfected with chlorine is of great importance. The pool sample was taken late in the day, after swimmers had already agitated the water for several hours. It is possible that all of the volatile THMs had already evaporated by the time of sampling. Another factor may be the lack of humic acids in the pool. Negligible amounts of humic acids would generate negligible amounts of chloroform even in a heavily chlorinated environment.

Occom

The Occom control/FP pair shows results far more agreeable with expectation. The control shows no chloroform, but does possess at least one compound of undetermined origin. This is shown in the table of results. The FP shows not only a high abundance of chloroform but also several other compounds that are not known CBPs. Two of these (toluene and benzaldehyde) were also present in the deionized water sample.

Deionized Water

Deionized water was expected to function as a control sample. Curiously, far more compounds were identified in it than in any FP. It contained dodecanoic acid and tetradecanoic acid, compounds that are, themselves, associated with solid waste incineration (Jay & Steiglitz, 1995). Deionized water also contained chloroform (perhaps due to fiber contamination from the super-chlorinated GC run immediately before and discussed below), toluene, benzaldehyde, and benzonitrile. These compounds are usually found in chlorinated samples, as well. Samples that were not chlorinated to 25 mg/L in pH 7 phosphate buffer show no traces of these compounds. This suggests that contamination of samples resulted from the deionized water used in the buffer and standard chlorine solutions. Comparisons of GC plots between an FP/control pair and deionized water show that the non-by-product peaks recorded in the FP sample have analogous peaks in the deionized water. The obvious exception is chloroform, since its presence in the deionized water has been attributed to fiber contamination. A comparison of GC plots is presented in Figure 4.

After the deionized water run, the fiber was replaced with another for fear that it had sustained damage during the super-chlorination of the immediately preceding sample. Fiber contamination seemed to generate false positive tests for chloroform and this was to be avoided.

Hanover

The Hanover control shows a minimal amount of chloroform, certainly lower than that present in any FP. It is most likely due to contamination of the fiber because at this point the fiber had been used previously but not cleaned. Chlorination of the raw water gave chloroform, benzaldehyde, diethyltoluamide, and urea. Benzaldehyde was a component of the resorcinol sample and a deionized water contaminant. Diethyltoluamide is a potent insect repellent. Urea is a component of urine. These compounds are not similar to THMs or other CBPs.

Hanover tap water showed no chloroform. This is to be expected because Hanover water is disinfected with ClO_2, not Cl_2. As mentioned, ClO_2 is less prone to THM formation than Cl_2. Decanal was identified with high quality. Since ClO_2 is known to produce a variety of aldehydes and ketones as DBPs, it is possible that decanal forms as a result of the disinfection process for Hanover water.

Lebanon

The Lebanon control/FPpair conformed to expectations with regard to chloroform. The control showed no detectable levels of chloroform, while the FP yielded chloroform in high abundance. The FPshowed detectable levels of toluene, probably due to contamination.

Mink Brook

The last area to be listed as a control/FP pair in the results is Mink Brook. As expected, the control contained no chloroform. The FP showed high levels of chloroform and two other non-volatile compounds of undetermined origin not previously detected.

Occom Revisited

Finally, the last piece of data in the table is the Occom super-chlorination. This sample was chlorinated at nearly 13 times the normal FPlevel (approximately 100 times the level used by water distributors). The GC/MS showed not only chloroform, but carbon tetrachloride, 1-chloro-2-methylbenzene, and 2,4,6-trichlorophenol. All of these have been described as chlorination by-products in prior research (Faust & Aly, 1983). None of these, except for chloroform, were found in the Occom FP at 25 mg/L. This suggests that several CBPs other than chloroform occur in such minuscule levels that they are not detectable at chlorination levels on the order of 25 mg/L. Unfortunately, chlorination of the sample at the level of 310 mg/L severely contaminated the fiber. Despite the impressive results, damage to the fiber and the need for extra cleaning precluded the adoption of this level of chlorination as the standard technique.

Conclusions

Due to the limitations of the fiber, such as its questionable usefulness in collecting non-THM organic compounds, it is only possible to make conclusions based on the levels of chloroform found in each sample. Both the River FP and the Mink Brook FP displayed similar chloroform levels (abundancies of 75,000 and 65,000, respectively). The samples collected from stagnant water sources: Occom and Lebanon Plant, showed much higher levels of chloroform (160,000 and 170,000, respectively). The Hanover Plant uses a combination of streams and ground water wells as its water supply, it is not included in this generalization.

Based on the idea that chloroform is produced by the reaction of free chlorine with humic acids, it is reasonable to conclude that there exist fewer humic acids in moving rivers and streams than exist in stagnant bodies such as Occom or the Lebanon reservoir. In fact, moving bodies of water often display less plant life than stationary ones and thus contain less decaying organic matter to give rise to humic acids. Graph 1 displays the striking change in chloroform abundance with water sample.

Also of interest is the fact that the City of Lebanon's water supply is known to contain massive amounts of dissolved organic carbon (comparable to Occom Pond). This drives up the THM formation potential of their water. In order to counter this problem, the Lebanon water plant adds a coagulant to its raw water in order to remove as many humics and other THM precursors as possible before chlorination.

Unfortunately, problems in establishing a single ion monitoring (SIM) or quantification set up on the GC/MS precluded the quantitative analysis of chloroform formation. However, quantification would mean little, as the formation potential of water at 25 mg/L free chlorine is not a particularly useful number. It is clearly not indicative of the total amount of humic acids present because successively higher levels of free chlorine generated successively higher levels of chloroform. It is also not an accurate measure of the total amount of CBPs, as anywhere from 5 to 10 times as much chlorine is bound into other forms of organic carbon which can be subjected to gas chromatography only with great difficulty (Chlorination, 1978).

Other problems resulted from the fact that the Supelco^{TM} literature is somewhat lacking in regard to the specific characteristics of the fiber. The fiber coating equilibrates with the surrounding solution, binding volatile organics. It is unclear if the fiber can become saturated in high concentrations of chloroform-, yielding results that do not vary linearly over the range of chloroform concentrations encountered. This could be tested by conducting adsorption runs of standard THM solutions of varying concentration, but these tests would take several days to one week to complete. The problem was realized far too late in the term to be effectively resolved.

The amount of organics collected on the fiber depends to a high degree on the affinity of the fiber for different compounds. It is possible, indeed probable, that abundancies on the GC/MS can not be directly related to concentrations in solution. In fact, THM standard runs suggested that the fiber even binds different THMs with differing affinities. This creates peaks of differing abundance on the GC plot even when concentrations in solution are identical. This further complicates accurate quantification of the data without the generation of time-consuming calibration curves. Fortunately, since the fiber was left in contact with the solution for the same amount of time during each run, it can be assumed that equivalent amounts of sample were desorbed into the injector port on the GC/MS. This means that, at the very least, abundancies are directly comparable among GC/MS runs.

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ABOUT THE AUTHORS

Brian C. DeSchuytner ‘00 is a biophysical chemistry major. He is currently working as a research assistant in Professor Thomas Spencer's lab. This summer he will be interning in the natural products division at Wyeth-Ayerst Research.

Kathryn A. Greer ‘00 is a women's studies major, and a chemistry minor. She is hoping to work in the non-profit sector after graduation, preferably in the area of women in science.

Karen Miller ‘00 a chemistry major, and a drama minor. She has done independent research in organic chemistry with both Professors Gordon Gribble and David Lemal and plans to write a Senior Honors thesis next year based on some of this work. Upon graduation, Karen plans to pursue a graduate program in Synthetic Organic Chemistry.

Michael Orchowski ‘00 is a double major in Chemistry and Government. He hails from the Philadelphia area and hopes to pursue a career in Environmental Law after he leaves Dartmouth. In addition to his chemical research with the Glueck group, he is active in Sigma Nu, sits on the CFS executive committee as a programming liasion and writes for Policy Perspectives Quarterly.

Rebecca L. Sangster ‘00 wants to go to med school. She is majoring in biophysical chemistry. She also plays field hockey.