

# Determining the Removal Effectiveness of Flame Retardants from Drinking Water Treatment Processes

by

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
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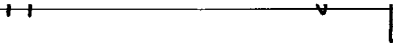
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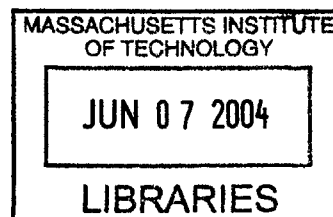
  
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## **ABSTRACT**

Low concentrations of xenobiotic chemicals have recently become a concern in the surface water environment. The concern expands to drinking water treatment processes, and whether or not they remove these chemicals while going through the treatment plant. In this study, the concentrations of organophosphoric acid triester flame retardants tributyl phosphate, tri(2-chloroethyl) phosphate, and ethanol, 2-butoxy-, phosphate (3:1) were measured after major treatment processes at the Chattahoochee Drinking Water Plant in Atlanta, Georgia, USA.

The findings indicated significant removal of all three organophosphate triesters after the pre-treatment chemical addition of sodium hypochlorite. The interaction of sodium hypochlorite and organophosphate triesters, through oxidation, was suspected to be the reason for the removal.

Second, the concentrations of tri(2-chloroethyl) phosphate after the filtration stage and at the clearwell were much greater than values after the sedimentation stage, and were well above the concentration measured at the intake. Exposure to the chemicals within the treatment plant was the chief potential reason for the heightened concentrations.

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# 1. Introduction

## *1.1 Pollutants in the Water: Current Regulations and its Fallacies*

History indicates that mankind has dumped pollutants into surface water and groundwater environments for a very long time. In the 1950's, water quality became a hot topic within the United States community due to the large amounts of toxic chemicals being dumped without any regulation (Nazaroff and Alvarez-Cohen, 2001). This, along with other general environmental concerns for air and land quality, led Congress to pass the first major environmental act: the Clean Air Act in 1970. This act also led to the formation of the Environmental Protection Agency (EPA). Soon after, Congress passed the first version of the Clean Water Act (CWA) in 1972, the Safe Water Drinking Water Act (SDWA) in 1974, and many other regulations that limited the amount of pollutants being discharged into the environment.

The CWA and SDWA focused, and still currently focus, on water quality. In the current CWA, the state issues a permit that either limits the effluent concentration of a specific pollutant or the total mass of pollutants released. This permit may be given to anyone who discharges some water effluent into a surface or groundwater environment. The permits are specific to each building, as a wastewater treatment plant (WWTP) will have many more chemical effluent limits than an industry that has an effluent stream with only one hazardous chemical.

The SDWA develops drinking water quality standards for drinking water treatment plants (DWTPs), through similar methods of the CWA. For example, the SDWA requires a minimum of 99.99% of viruses be killed from raw water to finished water in the drinking water treatment process, either through chlorination, filtration, or a combination of both (Nazaroff and Alvarez-Cohen, 2001). Although these two acts regulate a wide variety of chemicals and other criteria items (e.g. BOD, TSS, fecal coliform, heat), strict limits only apply for chemicals that are known to be harmful. This can be problematic for chemicals

that may be harmful to humans or the environment, but have yet to be deemed toxic. Current regulations have placed limits on many of these chemicals, but the stringency of the limit may be quite lax. Or, some chemicals are not regulated due to the lack of information available about them. What is being done to impose more stringent limits on these chemicals being discharged into surface water and groundwater environments? Before answering this question, we must first introduce these potentially harmful chemicals.

## ***1.2 The Emerging Issue: Xenobiotic Chemicals Produced Only Through Anthropogenic Methods***

Most chemicals that have not been regulated enough are chemicals that are produced only through synthetic methods and are not naturally in the environment. Some types of chemicals, such as endocrine-disrupting compounds (e.g. estrogen) and poly-chlorinated biphenyls (PCBs), have received much attention due to their bioactivity and/or toxicity and persistence in the environment. But, some other chemicals still need more attention pertaining to their transport and transformations in the environment. These include chemicals used in everyday life, like drugs, fragrances, and household cleaners, or chemicals indirectly used by humans, such as flame retardants and plasticizers.

### **1.2.1 Motivation to Study these Chemicals: An Environmental Life Cycle Analysis of the Phosphate Triesters**

The EPA (US EPA, 2004) has put together a very descriptive diagram concerning the environmental life cycle of chemicals in the environment. Please refer to Appendix A for a detailed picture. This paper demonstrates many different ways of releasing the chemicals through human use. First, someone may dispose or excrete the chemicals. From this point, there are different locations into which the chemical will be introduced, such as groundwater or sewer systems. If the chemicals have a high degree of persistence after traveling through these places, they may end up in surface waters such as rivers and lakes. These surface waters are used by DWTPs, treated, and sent to the customer. Then, if these chemicals are not treated within the DWTP, humans may end up putting these chemicals into their system. Therefore, humans are eventually consuming these

chemicals, even if they were first not intended for human consumption! Although the concentrations measured are quite small (on the order of 1 part per billion to 1 part per trillion), this may potentially be a problem, as the human body is not accustomed to consuming various drugs, fragrances, and plasticizers. This may also lead to bioaccumulation, as was found with PCBs (ATSDR, 2004).

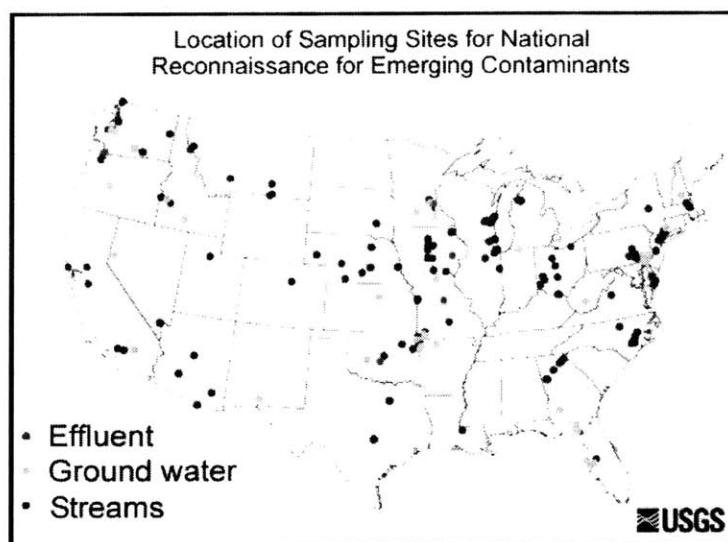
### **1.2.2 Brief History of Research Completed Pertaining to these Chemicals**

During the 1970's and 80's, studies showed that widely used pharmaceuticals such as caffeine, nicotine, and aspirin were present in wastewater effluents and the surface waters that these sources discharge into. But, there was no or little advancement in these studies over the next 15 years (Daughton, 2004). Only during the past five to ten years did the presence of these chemicals in the environment become an issue again.

The resurgence began in Europe during the mid-1990s, resulting in the formation of different conferences (e.g. ENVIRPHARMA) and groups, such as Poseidon, a German-based group focused on “the removal of pharmaceuticals and personal care products in sewage and drinking water facilities to improve the indirect potable water reuse” (European Community, 2003). Not much later, these chemicals became a more pressing issue in the United States. No specific date can be pointed to what initiated this resurfacing, but an example comes from Hutzinger (2000), which had a comprehensive article pertaining to the presence of pharmaceuticals and personal care products in the environment. In addition, an important paper that caught the attention of many was a national reconnaissance paper headed by the United States Geological Survey (USGS) (Kolpin et al., 2002). The USGS sampled 139 sites across the United States where concentrations of organic wastewater compounds (OWCs) were most likely to be present (Figure 1). The findings were quite eye-catching, as 80% of the sites sampled had at least one of the OWCs being tested for. In addition, the mean amount of OWCs in sites containing OWCs was six, a significant quantity. Because the survey only looked for 95 OWCs, there is a good possibility that other chemicals may be there but were not surveyed. Thus, this paper demonstrated the presence of OWCs in the environment,



where no region was left untouched. Now, with this information, the next step is to find different ways to utilize this data.



**Figure 1: Locations where the USGS surveyed in Kolpin et al. (2002). Source: Stackelberg and Lippincott (undated).**

### 1.2.3 Issues Concerning these Chemicals

Thus, in the pursuit of understanding these xenobiotic chemicals to a greater extent, one must ask how to attack this issue beyond finding the presence of these chemicals in the environment. Daughton (2004) proposes that people of various education backgrounds must examine the problem. The chemist may study the chemical properties or environmental fates, such as volatilization, biodegradation, hydrolysis, and photodegradation. In addition, because the concentrations of the chemicals are likely to be very low (i.e. in the order of 0.01 to 100 parts per billion (Kolpin et al., 2002), the chemist must also determine good analytical techniques to measure these concentrations. The toxicologist must understand if these low concentrations affect human health at all; a comprehensive study is currently ongoing (Syracuse Research Corporation, 2003). The policy maker has the important job of regulating and enforcing the effluent limits. With even more information, the policy maker can also use regulations to promote the use of safer alternative chemicals or ban the use of the chemical altogether if necessary.

The engineer also must be involved in the problem. For example, if the engineer is examining a surface water environment, he or she could conduct a full life cycle analysis from cradle to grave like the one done discussed in section 1.2.1. Or, one can do a mass balance analysis on just part of the full life cycle, such as a specific river or a DWTP. For example, if one is to do a mass balance analysis on a specific river, the inflows, outflows, sources, and sinks must be determined. This involves many different challenges, such as finding major natural attenuation processes (Andrews, 2004) or creating a computer model that simulates the flow of the river (Haffey, 2004). This same concept can also be done within a DWTP, where one may evaluate the effectiveness of drinking water treatment plants to remove or contribute (?) to the concentrations.

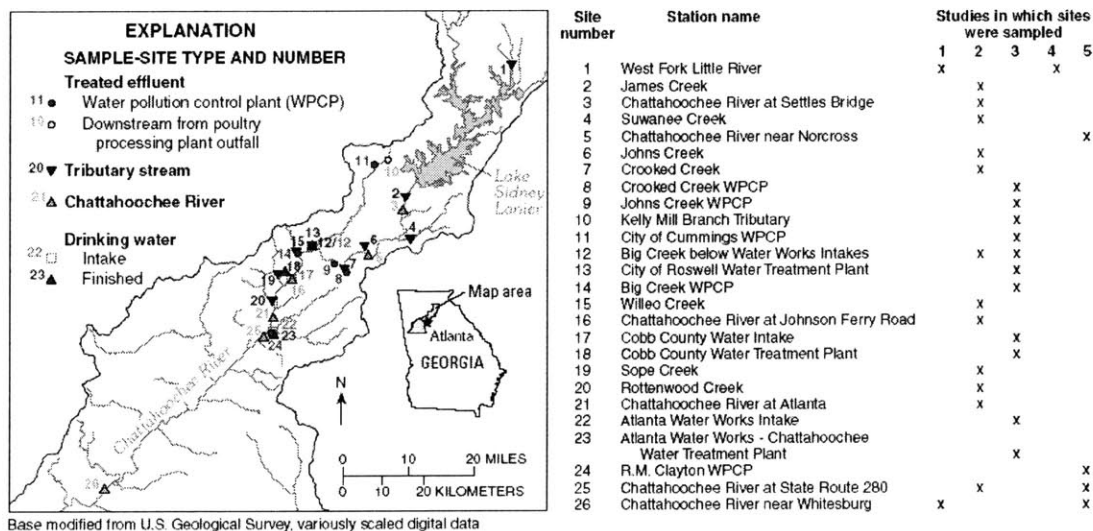
## 2. Location, Chemicals, and Processes Focused on in this Study

### 2.1 Location Focus: The Upper Chattahoochee River Basin

The upper Chattahoochee River basin, which is from Lake Sidney Lanier to downtown Atlanta, GA, was chosen as the study site for this paper. This was chosen due to previous USGS studies conducted in this region.

#### 2.1.1 Summary of Previous USGS Studies Done on the Chattahoochee River Basin

Frick and Zaugg (2003) compiled data of OWCs measured in Kolpin et al. (2002), Frick et al. (2001), and Henderson et al. (2001), and Gregory and Frick (2001). All data focused on the upper Chattahoochee River basin, with the exception of the Chattahoochee River site near Whitesburg, GA (site 26) (Figure 2).



**Figure 2 Sampling sites from Frick and Zaugg (2003). 25 of 26 sampling sites were in the upper Chattahoochee River basin.**

All of the sampling was conducted between 1999 and 2002. Sampling was done along the river, in tributaries of the river, at WWTP intakes and effluents, and at DWTP intakes and effluents.

### **2.1.1.1 Description of Frick et al. (2001) and Henderson et al. (2001)**

Study 3 from Figure 2 comprises the sites sampled in Frick et al. (2001) and Henderson et al. (2001) These studies were done simultaneously, and were jointly sponsored by the Centers for Disease Control (CDC) and the USGS. Sampling methods were the same as Kolpin et al. (2002), and all sampling was completed in the summer of 1999. The findings were quite similar to Stackelberg and Lippincott (undated) and Kolpin et al., where detectable concentrations of many OWCs were found in most sampling sites. Every type of OWC (e.g. detergents, plasticizers, pharmaceuticals, etc.) had similar detection frequencies, and were found at levels ranging from 10 to 2000 parts per trillion. Frequencies of some of the detections are in the next sections. In addition, the specific sampling times, sampling points, and concentrations measured at each site were also available from the authors.

## ***2.2 Chemical Focus: Organophosphate Triesters***

The three chemicals picked for the study reported in this thesis were tributyl phosphate (TBP), tri(2-chloroethyl) phosphate (TCEP), and ethanol, 2-butoxy-, phosphate (3:1) (TBEP). These chemicals were chosen because:

- Due to time constraints of this group project, multiple families could not be chosen.
- These three organophosphates were frequently detected in previous USGS studies. From Stackelberg and Lippincott (undated), TCEP was detected in 50% of all samples, and TBEP was in 38%. Within the WWTP intake water, TCEP were detected in 12 of 12 samples, and TBP and TBEP was detected in 10 of 12 samples. From Kolpin et al. (2002), TCEP was detected in 57.6% of 85 samples, and TBEP was detected in 45.9% of 85 samples. From Frick and Zaugg (2003), TCEP and TBP were detected in 100% of 13 WWTP effluent samples and TBEP was detected in 38% of the 13 samples. In addition, for the DWTP samples taken in Frick and Zaugg, the percentage of detections for

all three phosphate triesters actually increased from raw water to finished water! (Table 1)

- The three chemicals all have similar structure. This study focuses only on phosphate triesters. A phosphate triester is comprised of a phosphorus atom, with four oxygen atoms bonded to the atom: one doubly-bonded, and the other three singly-bonded. Each of the three singly-bonded oxygen atoms has an organic group attached to it. Specifically, the phosphate triesters studied in this paper are phosphotriesters, where the functional group is identical for each three oxygen atoms.
- The chemicals are widely used as flame retardants, plasticizers, in floor polishes, and for many other purposes. Thus, there was good reason to believe that these compounds will be in the Chattahoochee River when the sampling was done in January 2004.
- The author did not find any studies that specifically discussed the fate of TBP, TCEP, or TBEP in drinking water treatment processes.

**Table 1 Percent Detections at Specific Sites. Note that the numbers in parentheses are the number of samples taken for each type. Source: Frick and Zaugg (2003)**

Chemical	Reporting Limit (ug/L)	Treated Effluent	Tributary Stream		Chattahoochee River		DWTP	
		WWTP % (13)	Baseflow % (9)	Wet Weather % (17)	Baseflow % (8)	Wet Weather % (7)	Intake % (9)	Finished % (8)
TBP	0.04	100	0	7/9	43	0/4	0	25
TCEP	0.04	100	33	82	50	57	56	75
TBEP	0.07	38	22	82	13	43	33	38

## 2.4.2 Description of the Phosphate Triesters

### 2.4.2.1 The Phosphate Triesters' Main Use – Flame Retardants

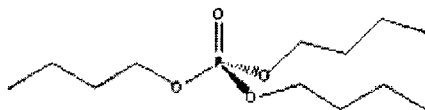
Organophosphate flame retardants represent 20% of worldwide production of flame retardants (World Health Organization, 1997). When the flame retardants are put into a fire, they break down into phosphoric acid and other components upon heating. The resulting phosphoric acid forms a char on the burning surface, resulting in less surface

area available as fuel; this acid also reduces the release of volatiles. Both of these phenomena reduce the intensity of the flame.

The problem with these flame retardants is not when they are used, but when they are not used. For example, the organophosphates may be in very small concentrations in a person's clothing. Through washing of the clothes, the organophosphates go into a waste stream, thus starting the possible chemical transport into the environment. Other uses, as described in the following sections, also cause the phosphate triesters to get into the environment.

#### 2.4.2.2 TBP

TBP has an n-butyl group attached to each of the single-bonded oxygen atoms.



**Figure 3 Chemical Structure of TBP.**

Some of the important chemical properties are (Syracuse Research Corporation (2003), Risk Assessment Information System (2004), and World Health Organization (2001):

- Liquid at room temperature, miscible with water and chloroform.
- Boiling point: 289 °C. Melting point: -79 °C.
- Log  $K_{ow}$  = 4.
- $K_{oc}$  = 1900 L/kg.
- Solubility in water at 20 °C: 280 mg/L
- Henry's Law constant:  $6.13 \times 10^{-6}$  (dimensionless)
- Density: 0.973 – 0.983 mg/L at 25 °C

- Vapor pressure: 0.00349 mm Hg at 20 °C

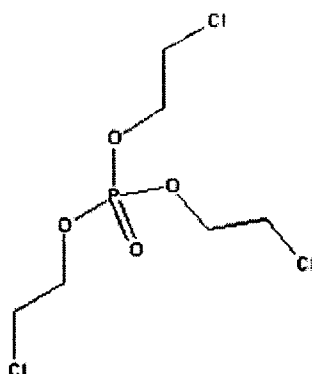
TBP is made through the reaction of phosphorus oxychloride ( $\text{POCl}_3$ ) and butyl alcohol (World Health Organization, 1991). There is little information on the production of TBP. The Environmental Protection Agency requires any company producing at least 10,000 pounds of a chemical to report to them through the Inventory Update Rule (IUR). From the 2002 IUR, the production of TBP in the United States was between 1 and 10 million pounds. Three companies (Akzo Nobel Functional Chemicals, LLC; Ferro Corporation; Great Lakes Chemical Corp.) produced at least 10,000 pounds of TBP that year (US EPA, 2002). Chemical Sources International, Inc. (2004) lists 21 companies in the United States that produce TBP, but only Akzo Nobel was listed in this website among the three companies that produced more than 10,000 pounds in 2002. Thus, the production volume within the United States may be significantly more than the reported volume.

About 40-60% of TBP is used in fire-resistant hydraulic fluid for aircraft. In addition, TBP is used in floor finishes, as plasticizers, and in ore extraction processes. These uses can easily lead to the discharge of TBP into the environment. For example, TBP may be leached from floor finishes during floor cleaning and thus goes into the sewage system.

Toxicity information of TBP is also quite sparse. Animals exposed to TBP have displayed neurological problems such as dyspnea (i.e. difficulty in breathing), but the amount of TBP in their system was not indicated. For humans, TBP is suspected to be a kidney toxicant and a neurotoxicant (Environmental Defense, 2003). The chronic dermal reference dose (RfD) currently is 0.1 mg/kg-day (Risk Assessment Information System, 2004).

#### **2.4.2.3 TCEP**

TCEP has a 2-chloroethyl group attached to each of the single-bonded oxygen atoms. TCEP has different chemical properties because of the chlorine atom end group, as shown in Figure 4.



**Figure 4 Chemical Structure of TCEP.**

Major chemical properties:

- Liquid at room temperature, miscible with water and chloroform.
- Boiling point: 330 °C. Melting point: -35 °C.
- $\text{Log } K_{ow} = 1.44$ .
- $K_{oc} = 300 \text{ L/kg}$ .
- Solubility in water at 20 °C: 7000 mg/L.
- Henry's Law constant:  $1.04 \times 10^{-6}$  (dimensionless)
- Density: 1.425 mg/L at 20 °C
- Vapor pressure: 0.000391 mm Hg at 20 °C

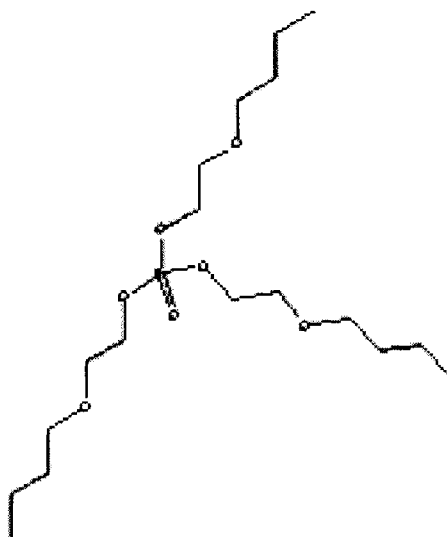
TCEP is made through the reaction of phosphorus oxychloride and ethylene oxide, followed by subsequent purification (World Health Organization, 1998). Brown et al. (1975) indicated that the United States produced 29.4 million pounds and consumed 25.5 million pounds of TCEP. Twelve million of the 25.5 million consumed was used as a flame retardant, and the other 13.5 million was used in synthetic lubricants and hydraulic fluids. In 1997, the estimated demand was 9 million pounds, a significant decline in use compared to Brown et al. In the 2002 IUR, TCEP production in the United States was 1-10 million pounds. This production volume is based on the reports of two companies, Akzo Nobel and Great Lakes Chemical (US EPA, 2002). TCEP is also used as a plasticizer in PVC and resins.



TCEP is known to be a carcinogen (recognized in 1992 by California through Proposition 65 (2004)), and is suspected to be a reproductive, kidney, and liver toxicant. The current chronic dermal RfD is 0.15 mg/kg-day.

#### 2.4.2.4 TBEP

TBEP has a 2-butoxyethyl group attached to the single-bonded oxygen atoms (Figure 5).



**Figure 5 Chemical Structure of TBEP.**

Major chemical properties:

- Liquid at room temperature, miscible with water and chloroform.
- Boiling point: 200-230 °C. Melting point: -70 °C.
- Log  $K_{ow}$  = 4.38.
- $K_{oc}$  = 24000.
- Solubility in water at 20 °C: 1100-1300 mg/L.
- Henry's law constant:  $1.20 \times 10^{-6}$  (dimensionless).
- Density: 1.02 mg/L at 20 °C.
- Vapor pressure:  $2.8 \times 10^{-8}$  mm Hg at 20 °C

TBEP is made through the reaction of phosphorus oxychloride with butoxyethanol (World Health Organization, 2000). The World Health Organization estimated production to be between 11-13 million pounds, but no year was cited. In the 2002 IUR, the production volume was 10-50 million pounds, reported by two companies (Akzo Nobel and Great Lakes Chemical). The 1994 and 1998 IUR also report a 10-50 million pound range (US EPA, 2002). This range is larger than the 1-10 million pound range for TBP and TCEP; therefore, the loading into the surface water environment may be much larger than the loadings for TBP and TCEP. In addition to using TBEP as a flame retardant, it is a component of some household cleaners and floor polishes (NIH, 2003). Other uses for TBEP are as a plasticizer and as a solvent for resins. There are no recognized or suspected human health hazards associated with TBEP according to Environmental Defense (2003).

#### **2.4.3 Estimating the Presence of the Organophosphate Triesters in the Upper Chattahoochee River Basin**

From the known production volume ranges given by the 2002 IUR, one can estimate how much of the phosphate triesters exist in the upper Chattahoochee River basin. First, the estimated concentrations of TBP will be done. In this calculation, the author assumed:

- That the annual production volume range was all used in the United States.
- That all of the people in the United States use the phosphate triesters evenly. For instance, because Atlanta has approximately 1% of the United States population, it uses 1% of the phosphate triesters produced.
- The Chattahoochee River flow was  $20 \times 10^8 \text{ m}^3/\text{year}$ .
- That 10% of all phosphate triester used in a year gets into the Chattahoochee River.

With these assumptions, the estimated concentrations in the Chattahoochee River are approximately 0.2 to 2  $\mu\text{g}/\text{L}$ . This is quite close to many of the values reported in previous USGS surveys. TCEP would have the same approximate concentration as TBP because it has the same production volume range in the 2002 IUR. TBEP, on the other

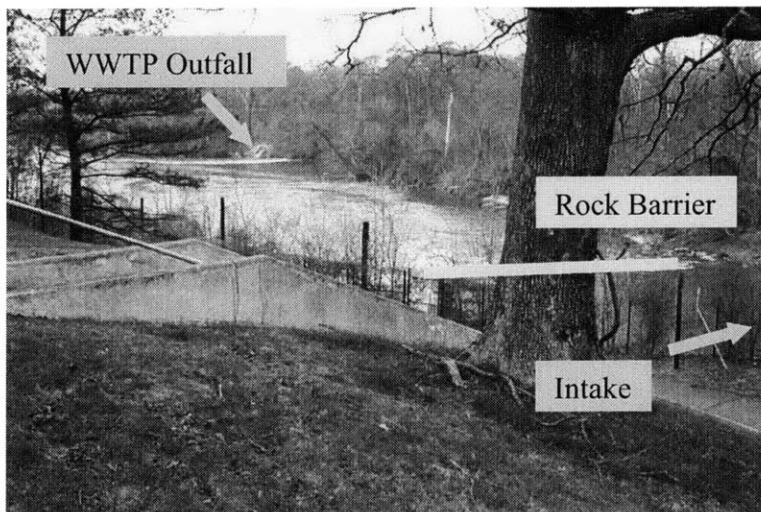
hand, would have approximate concentrations of 2 to 10  $\mu\text{g/L}$  due to the higher production volume range than TBP and TCEP. The concentrations for TBEP in the USGS surveys were not as high as estimated. Yet, the main conclusion from these calculations is that the concentrations already measured do make sense.

## ***2.5 Thesis Focus: Processes in the Chattahoochee Drinking Water Treatment Plant, Atlanta, GA***

The author decided to study the fate of these phosphate triesters in a drinking water treatment facility. This thesis specifically examines the major treatment processes at the Chattahoochee Water Treatment Plant (CWTP). An overview of the Atlanta Water Works system, which includes the CWTP, is located in Appendix B. To summarize the system, the CWTP is one of three major DWTPs located in the downtown Atlanta area. The Hemphill Water Treatment Plant is the main DWTP, which distributes approximately 200 million gallons per day (MGD), as opposed to the CWTP, which distributes 65 MGD.

### **2.5.1 Description of Sampling Sites in the CWTP**

#### **2.5.1.1 Intake**



**Figure 6** Location of WWTP outfall compared to the location of the intake. A rock barrier prevents wastewater effluent from entering the intake.

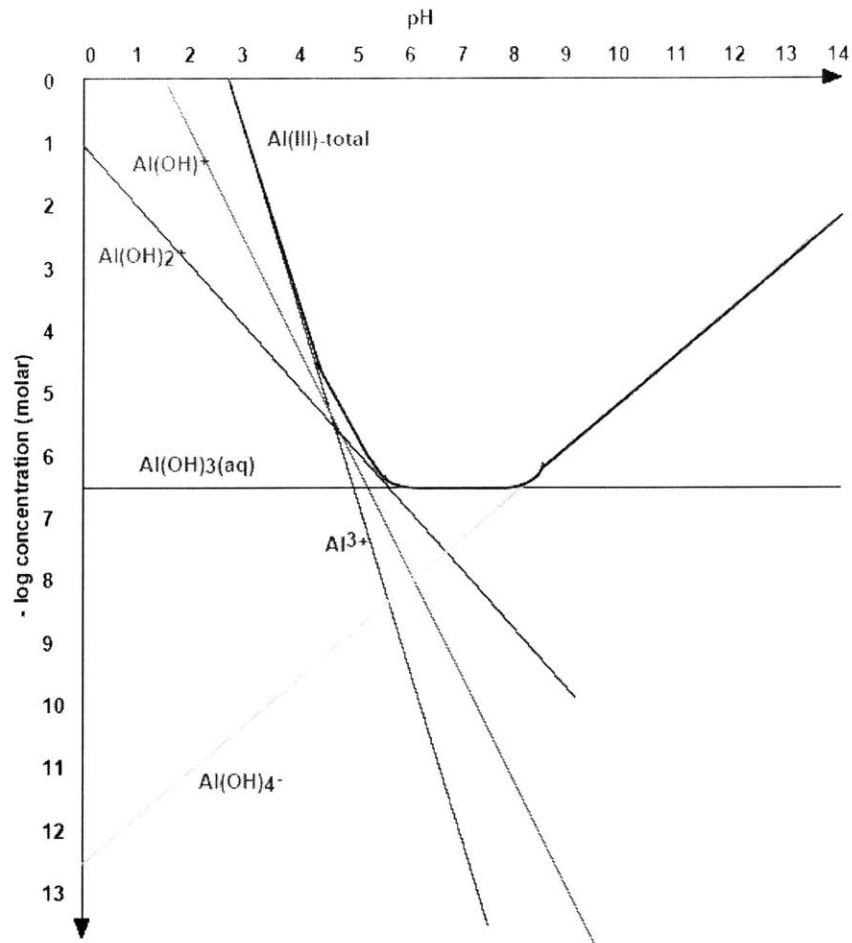
The intake water of the CWTP comes from the Chattahoochee River. The major sources of the phosphate triesters are four major WWTPs that discharge their effluent upstream of the CWTP: Crooked Creek Water Pollution Control Plant (WPCP), Johns Creek WPCP, the City of Cummings WPCP, and the Big Creek WPCP (see Figure 2 for locations with respect to the CWTP, site 23 in Figure 2). The R.M. Clayton WPCP, which is the main wastewater treatment facility for the Atlanta area, has its outfall located approximately half a mile past the intake. To prevent this effluent from contaminating the intake, a rock formation was added between the two sites (Figure 6).

### **2.5.1.2 Addition of Aluminum Sulfate and Sodium Hypochlorite**

The raw water travels via pipeline approximately 1000 feet from the intake to a pre-treatment chemical addition area, where solutions of aluminum sulfate (alum) and sodium hypochlorite are added.

Aluminum sulfate promotes the coagulation of colloidal particles into flocs. In drinking water treatment plants, this mainly happens through three different mechanisms: charge neutralization through adsorption of oppositely charged ions, inter-particle bridging, and precipitate enmeshment. Inter-particle bridging is where the coagulant forms a polymer chain with two or more particles. Enmeshment is the trapping of particles when the colloidal floc forms or when the floc is settling.

Aluminum sulfate, when in the aqueous phase, dissociates into the aluminum and sulfate ions. Depending on the pH of the water, the aluminum ion will undergo hydrolysis, thus adding hydroxyl ions (Figure 7). At pH 6-8, which are the usual pH values in the CWTP, the solubility of aluminum is quite low and aluminum will thus precipitate out. This precipitate will also include the potential flocs.

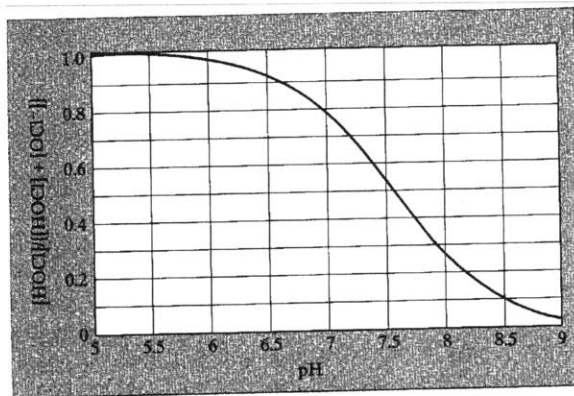


**Figure 7 Diagram of solubility of different aluminum hydroxides exist at different pH values. For pH 6-8, the Al(OH)<sub>3</sub> solubility is the highest. Source: Danish University of Pharmaceutical Sciences (2003).**

Coagulation is an important step to lower the turbidity in water. For an initial turbidity of 10 NTU, the final turbidity after using coagulation, flocculation, and filtration is 0.2 NTU, while the final turbidity after using only filtration is 5 NTU. (ASCE/AWWA, 1990 and Nazaroff and Alvarez-Cohen, 2001). This applies to the CWTP as well, where the average turbidity of raw water is about 15 NTU.

Sodium hypochlorite (NaOCl) is used to disinfect the water. Disinfection this early in the treatment sequence is not uncommon, as a typical drinking water treatment plant will have a pre-treatment chlorine addition (to keep a chlorine residual within the treatment plant) along with a post-treatment chlorine addition (to keep a chlorine residual within

the distribution system). Sodium hypochlorite, when added to water, dissociates into a single positive-charge sodium ion and a single negative-charge hypochlorite ion. This hypochlorite ion becomes hypochlorous acid (HOCl) as long as a certain pH is maintained below about 7 (Figure 8). Hypochlorous acid reacts with bacteria to kill the bacteria. Hypochlorous acid also reacts with different chemicals. For example, hypochlorous acid can react with hydrogen sulfide (which is toxic, and also has a bad smell), converting it to less toxic products. But, hypochlorous acid also reacts with natural organic substances to produce trihalomethanes, a undesirable product (Nazaroff and Alvarez-Cohen, 2001).



**Figure 8 Curve of pH versus fraction of hypochlorous acid concentration over the free chlorine concentration. Source: Nazaroff and Alvarez-Cohen (2001).**

Because the hypochlorite ion is basic, the addition of sodium hypochlorite increases the pH in the water. But, at the CWTP, the pH is affected more by the addition of alum. For instance, the intake water's pH is usually between 6.8 and 7. After the addition of alum (typically at a dose of 10 mg/L for a turbidity of 15 NTU) and sodium hypochlorite (typically at a dose of 3-4 mg/L), the pH is usually between 6.2 and 6.5. In addition, a high fraction of hypochlorous acid is maintained in the sedimentation basin, which usually has an effluent pH of 6.6.

In addition to pH, one must also examine the disinfection kinetics within the treatment plant. Watson's law proposes that  $C * t_c = b$ , where C is the free chlorine concentration,  $t_c$  is the contact time, and b is a constant (Nazaroff and Alvarez-Cohen, 2001). Values of b have been tabulated for specific amounts of bacteria kill. For example, the free chlorine

concentration at the CWTP is always at least 0.5 mg/L in the sedimentation basins. Using this number, and assuming a pH of 7 and a 4-hour residence time in the basin, the value of **b** is 120 min-mg/L. Because there is a 4-log kill of bacteria when **b** is equal to 20 min-mg/L at pH 7, this implies that there is a 24-log kill in the sedimentation basin with **b** equal to 120. Thus, bacteria are sufficiently killed in the treatment plant even before the post-chlorine addition.

### **2.5.1.3 Flocculation/Sedimentation**

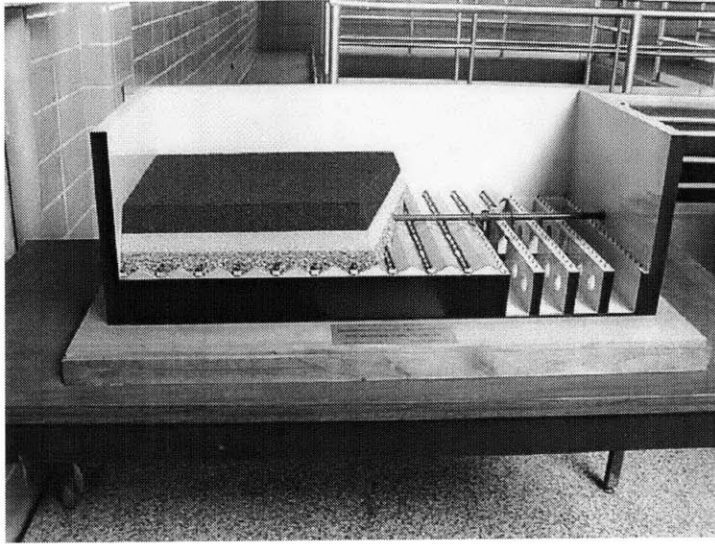
After the addition of alum and sodium hypochlorite, the water goes through a flocculation and sedimentation phase. Flocculation is the thorough mixing of the water to promote the collision of colloidal particles, as discussed in the previous section. The mixing in this stage is slow enough, though, such that the flocs do not break apart.

Sedimentation is the quiescent flow of the water for a long time. This allows larger-diameter particles (e.g., particles formed from flocculation) to settle to the bottom of the tank. To find out what size particles will settle out in the sedimentation process, the flow rate into the plant, the surface area of the basin, and the height of the basin are needed. During mid-January 2004, the average flow rate was around 35 MGD, the numbers of basins in service was 4 (out of 6), and each sedimentation basin is 188 feet long, 88 feet wide, and 14 feet deep. Given the volume of a single sedimentation basin, the residence time in the basin is approximately 4 hours. With a depth of approximately 5 meters, most particles 30  $\mu\text{m}$  in diameter or larger will settle and be collected by the sludge collectors at the bottom of the basin.

### **2.5.1.4 Filtration**

After the sedimentation phase, the effluent goes through a filtration phase. Filtration is required under federal regulations in any DWTP where the intake comes from surface water. The purpose of filtration is to remove smaller particles that sedimentation could not take care of. Each of the 13 filters at the CWTP uses a dual-media filter, where the

top layer is anthracite coal, and the next layer is sand. A bottom gravel layer does not contribute to the filtering due to its large pore size, but is there to help keep the denser particles near the bottom (Figure 9). The sand is comprised to two types, with 1" of larger-diameter torpedo sand above 12" of finer sand.



**Figure 9 Scale model of the dual-media filter used at the CWTP.**

Dual-media filters are preferred to a single-media sand filter because there is less maintenance required. For instance, during backwashing of sand filters (done to remove buildup of particles), heavier sand would tend to settle toward the bottom. Thus, the finer and less dense particles migrate towards the top of the filter, making for a very effective filter up top, but a very ineffective filter everywhere else. The result is less effective filtration and higher head loss. But, by using a dual-media filter, the denser, finer particles stay near the bottom during backwashing, while the less dense and coarser particles stay near the top. This keeps the filter effective for long periods of time.

At the CWTP, a filter is backwashed when one of three parameters is exceeded: head loss, turbidity, or time. If the head loss is above 6 feet, the filter is backwashed. If the effluent turbidity is above 0.30 NTU, the filter is backwashed. Lastly, if the time since the last backwash exceeds 72 or 120 hours (depending on the filter size), the filter is backwashed.



### 2.5.1.5 Post-Chemical Addition

After filtration, there is a post-chemical addition phase, where fluoride, phosphoric acid, lime, and more sodium hypochlorite are added. Fluoride is added to promote stronger teeth when the water is consumed. Phosphoric acid is added to prevent corrosion in the piping distribution system. These two chemicals are added according to required effluent concentrations.

Lime promotes precipitation of some specific metals, such as calcium and magnesium, in the solid forms such as calcium carbonate ( $\text{CaCO}_3$ ). These solids are collected in the clearwell, located in between the post-treatment addition and the piping distribution system. The approximate clearwell residence time at the CWTP is around 40 minutes, which is sufficient time for these solids to precipitate and settle to the bottom collectors. Lime also has a second purpose of increasing the pH from a filter pH of approximately 6.6 to a final value of 7.0 to 7.2. The pH value controls the addition of lime, as pH control is more important than removing the metals. In fact, the hardness of the water, which is a measure of the positive multi-charged ions, such as the calcium and magnesium ion, is already quite soft before entering the plant, as the hardness is 12 mg/L, while a 20 mg/L hardness in tap water is considered soft.

Lastly, more sodium hypochlorite is added to achieve a 1.1-1.3 mg/L residual during the fall and early spring, a 1.7-1.9 mg/L residual during the summer and early fall, and a 1.4-1.6 mg/L residual at all other times. These numbers were picked to maintain a required 0.2 mg/L residual in the farthest part of the distribution system. Because the pH is between 7.0 and 7.2, there is still a sufficient amount of hypochlorous acid to continue the disinfection process in the piping distribution system.

### 3. Materials and Methods

All field sampling was conducted at the CWTP in Atlanta, GA on January 14, 2004. A total of ten 3.8-liter samples were collected after major treatment steps in the CWTP. Then, the samples were reduced to 400 mL extracts of chloroform through liquid-liquid extraction. Subsequent reductions to 50-200  $\mu$ L resulted in the final extract volume.

The JEOL GCmate semi-high resolution gas chromatograph/mass spectrometer was used for the analysis. After obtaining total ion current (TIC) chromatograms from JEOL's Shrader data acquisition and data reduction software, peaks were obtained for the three organophosphate triesters and an injection standard. Using these peak values, the mass of the organophosphate triesters was found by:

$$M_{organophosphatetriester} = \left( \frac{Peak_{organophosphatetriester}}{Peak_{inj.std}} \right) \cdot M_{inj.std} \cdot \left( \frac{R_{injstd}}{R_{organophosphatetriester}} \right) \quad (1)$$

Where Peak is the peak value, M is the mass in the sample vial (units of pg), and R is the counts per unit mass of chemical (1/pg). Dividing this mass by the sample size (3.8-liters) resulted in the concentrations.

See Appendices C and D for details concerning fieldwork and labwork procedure, observations, errors, and for formation of equation 1.

## 4. Results and Discussion

There were three major observations from the values presented in the tables and figures below: after the pre-treatment chemical addition step, the concentrations of the organophosphate triesters decreased significantly compared to the intake concentrations; the concentrations of TCEP increased significantly after filtration and at the final effluent; and, there was no measurable removal of the chemicals after the sedimentation phase.

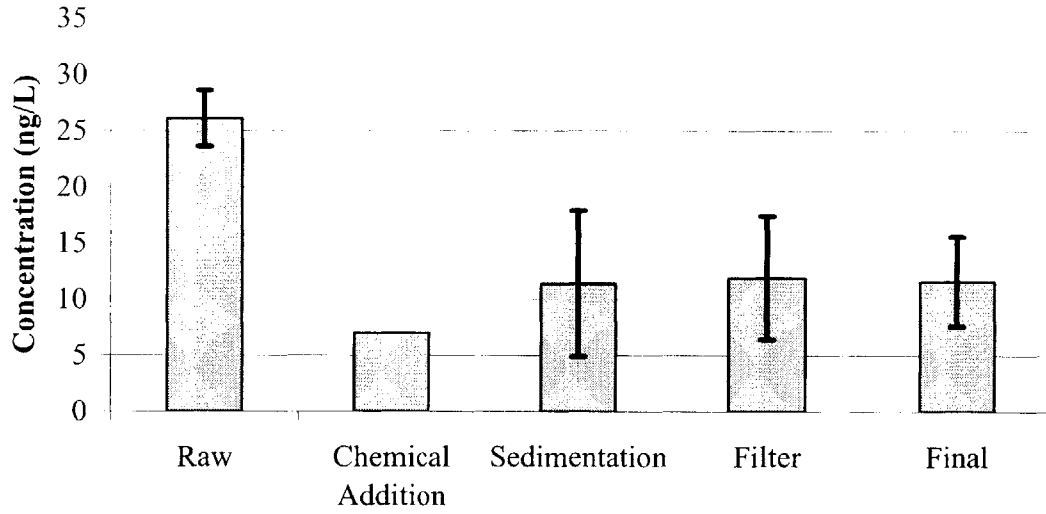
### 4.1 Measured Concentrations of the Organophosphate Triesters

**Table 2 Concentrations of the Samples (Units: ng/L)**

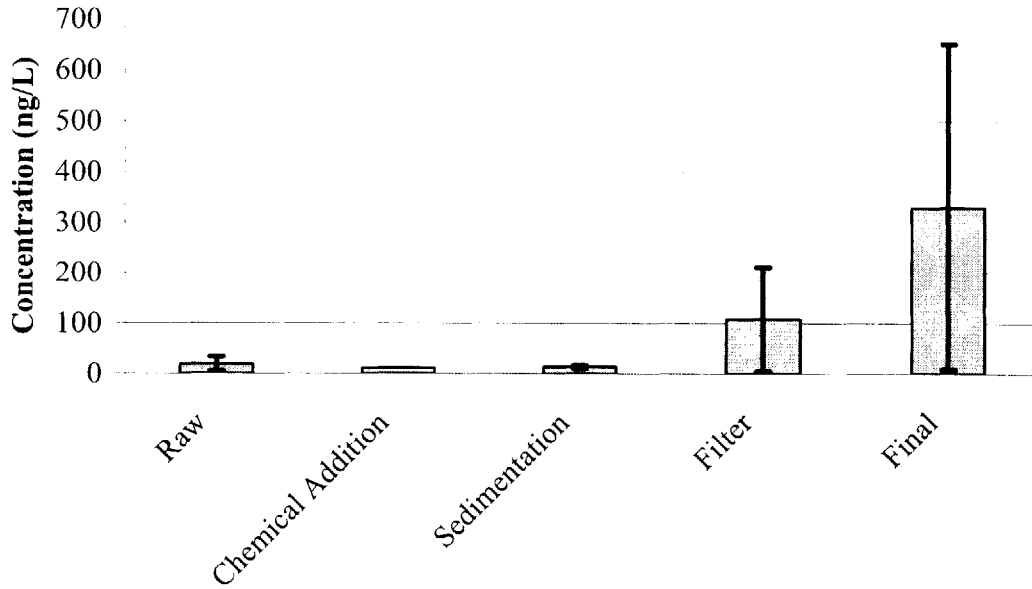
Sample Name	TBP	TCEP	TBEP
Raw #1	24	5	118
Raw #2	29	34	120
Chemical Addition #1	BR	BR	BR
Chemical Addition #2	7	11	18
Sedimentation #1	18	17	13
Sedimentation #2	5	10	21
Filter #1	17	43	ND
Filter #2	6	211	38
Final #1	16	8	10
Final #2	8	651	23

Note: BR = bad run, ND = no detection (< 1 ng/L for this study. See Appendices C and D for determination of no detection limit). Chemical Addition #1 dried up multiple times during the Cambridge laboratory work, resulting in invalid concentrations.

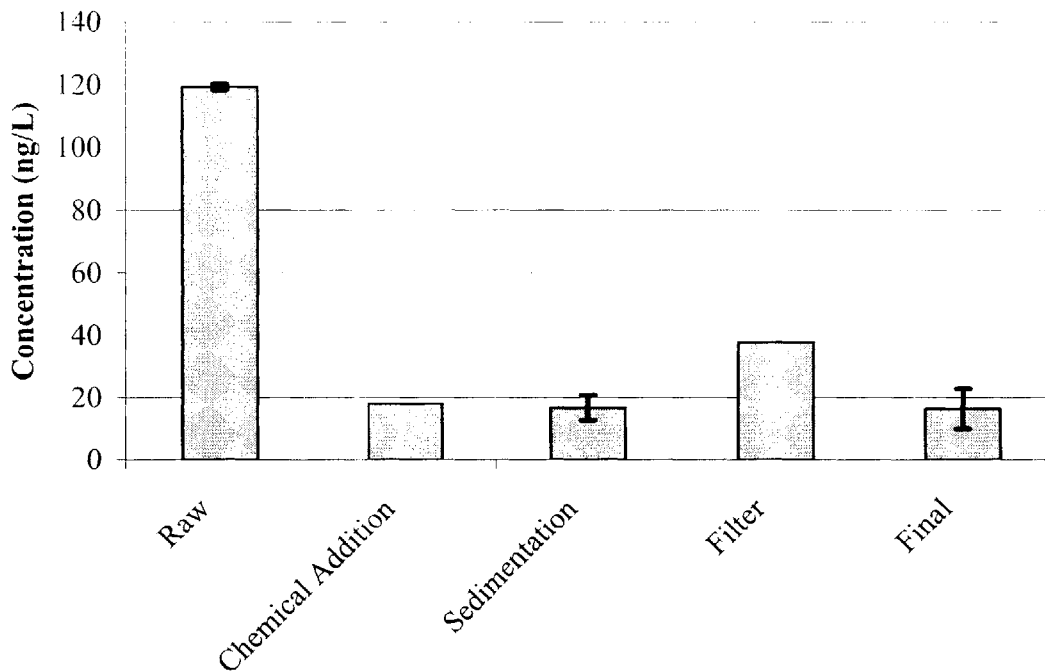
The concentration values were averaged (Figure 10, Figure 11, Figure 12). Error bars indicated the range of concentration values measured for each site. No error bars were indicated for sites and chemicals for which there was one value (i.e. either there was a bad run or no detection for the other value).



**Figure 10** Average concentration of TBP measured in this study. Error bars indicated range of values measured.



**Figure 11** Average concentration of TCEP measured in this study.



**Figure 12 Average concentration of TBEP measured in this study.**

## ***4.2 Comparison to Other Findings***

Now that the concentrations had been found, the author explored how well his numbers compared to other findings.

### **4.2.1 Analysis of Data from Frick et al. (2001) and Henderson et al. (2001)**

In Frick and Zaugg (2003), the percentage of detections, the number of samples, the reporting limit, and the maximum concentrations detected were the only parameters listed. But, a little more information can be extracted by looking at the raw numbers from Henderson et al. (2001) and Frick et al. (2001) For example, these two studies also took samples from the CWTP. Thus, the author directly compared these numbers to his own (Table 3):

**Table 3 Comparison of Samples from Frick et al. (2001) and Henderson et al. (2001) (these are the July-September 1999 samples) compared to the January 2004 samples. Concentrations in (ug/L)**

Chemical Name	Sample Date	Atlanta Intake	CWTP Finished
TBP	Jul-99	< 0.06	< 0.06
	Aug-99	< 0.06	0.093
	Sep-99	< 0.06	< 0.06
	Jan-04	0.026	0.012
TCEP	Jul-99	< 0.04	0.06
	Aug-99	0.057	0.093
	Sep-99	< 0.04	0.055
	Jan-04	0.019	0.33
TBEP	Jul-99	0.26	< 0.07
	Aug-99	< 0.07	0.3
	Sep-99	< 0.07	< 0.07
	Jan-04	0.119	0.016

Note: the values highlighted in yellow were values there were above the detection limit. The January 2004 concentrations were based on one sample from the intake and two samples from the finished water.

The values found in Frick et al. and Henderson et al. are comparable to the January 2004 samples. One interesting observation was that TCEP was detected in all finished water samples, and was also detected in the Final #2 sample. Therefore, the heightened concentrations may be due to plastics contributed from the plant. But, the numbers are close to the detection limit, and no error bars are available for the USGS data. Further research should look at taking more samples, to gather more points. In addition, these further samples should look at different times of the year to examine different loadings into the CWTP.

The finished samples had a higher percentage of detections than the raw water (Table 1). But, this is based on three different treatment plants, one of which is the CWTP. The author does not know what the other two treatment plants, the Cobb DWTP and Roswell DWTP, have in their major treatment processes to make any conclusive judgments. But, if more information about the plants is found, then some conclusions about the CWTP

could be deduced. For example, if the other two plants have no plastic components, but still have detections of the phosphate triesters, then plastic contact may not be as important in the CWTP.

#### **4.2.2 Comparison with Frick and Zaugg (2003), Stackelberg and Lippincott (undated), and Kolpin et al. (2002)**

Section 2 discussed the detection percentages of the phosphate triesters in other USGS surveys. Because the sampling sites vary in so many different ways, making any specific judgments would be quite difficult. For example, Stackelberg and Lippincott only sampled sites within New Jersey, which may have much different loadings than in the Atlanta area. But, one good conclusion from the USGS data was that the values found from the January 2004 samples were within the range of concentrations found in the USGS studies.

#### **4.2.3 Comparison with Haffey (2004)**

Haffey (2004) developed a computer model to follow the transport and transformations of TBP, TCEP, and TBEP in the Chattahoochee River. Haffey used values from Frick et al. (2001) and Henderson et al. (2001) to estimate the loadings coming from major WWTPs. In conclusion, his estimated values compared favorably with the average concentration measured by the author (Table 4)

**Table 4 Comparison of the author's intake concentrations compared to modeled values from Haffey (2004). Note that Haffey's numbers were average concentrations for the modeled day. Units: ng/L.**

	Lin	Haffey (2004)
TBP	26	24
TCEP	19	20
TBEP	119	148

### ***4.3 Discussion of Trends after Pre-Treatment Chemical Addition***

The concentrations of the phosphate triesters drop off significantly after the pre-treatment chemical addition. There was 73% removal of TBP, 42% removal of TCEP, and 85% removal of TBEP after the pre-treatment chemical addition stage (Figure 10, Figure 11, Figure 12)

#### **4.3.1 Errors in Values Due to Over-Drying of the Samples**

In the case of full drying, there may have been some concern for high concentrations in the air of the vial. Using TBP, because it has the highest vapor pressure of the three organophosphate triesters studied, the density of TBP in air can be calculated with the following equation:

$$\rho_{TBP,air} = \rho_{air} \frac{MW_{TBP}}{MW_{air}} \frac{VP_{TBP}}{VP_{air}}$$

Where  $\rho$  is the density (g/L), MW is the molecular weight (g/mol), and VP is the vapor pressure (mm Hg). If the chloroform fully dried, there would be some lipids formed on the bottom of the vial, at approximately 1% of the total organic carbon, or approximately 40  $\mu\text{g}$  in this study. In addition, the mass of TBP in the vial was approximately 400 ng. Therefore, according to Raoult's law, the vapor pressure of TBP in the vial was approximately  $400 \text{ ng}/40 \mu\text{g} = 1\%$  of the vapor pressure of TBP. Because the vial's temperature was close to 20 °C, the vapor pressure of TBP from Section 2.4.2.2 can be used. Therefore, the vapor pressure of TBP in the vial was  $3.5 \times 10^{-5}$  mm Hg. Using the density of air of 1.2 g/L, a molecular weight of air of 29 g/mol, and a vapor pressure of air at atmospheric pressure (760 mm Hg), the approximate equilibrium density of TBP in the air was 0.5  $\mu\text{g}/\text{L}$ . In a 15-mL vial, the most TBP that can be in this volume was 8 ng. Therefore, the full drying of the samples should not be of concern for TBP, as 2% of the mass at most was lost. For TCEP and TBEP, the vapor pressures of the pure liquid were much lower than TBP. Thus, the full drying of these compounds should not be of concern for TCEP and TBEP. Full drying occurred in the 15 mL vial for Chemical Addition #1 and #2, and Sedimentation #1 and #2.



### 4.3.2 Interactions of Phosphate Triesters with Aluminum Sulfate

To figure out what pathways may cause phosphate triesters to directly or indirectly interact with aluminum sulfate, the author first referred to the methods of coagulation: charge neutralization through adsorption of oppositely charged ions, inter-particle bridging, and precipitate enmeshment. Because the aluminum was mainly  $\text{Al}(\text{OH})_3$  (s) (Figure 7), and because the phosphate triesters themselves were neutrally charged in water, charge neutralization should not be a significant interaction. Inter-particle bridging may result if the phosphate triesters were sorbed to the colloidal particles. To find out how effective this phenomenon may have been, one can compute what percent of the chemical will sorb onto the organic carbon. The average total organic carbon (TOC) during January 2004 at the CWTP intake was 1.6 mg/L (Kopanski, 2004, personal conversation). One assumption was made: all the TOC precipitated out of the water due to the aluminum sulfate addition. Starting with the definition of the organic carbon partition coefficient (Karickhoff et al., 1979, and Chiou et al., 1979):

$$K_{oc} = \frac{C_{oc}}{C_{water}} \quad (5)$$

where  $C_{water}$  is the concentration of the chemical in the water (mg chemical/L water), and  $C_{oc}$  is the concentration in the organic carbon (mg chemical/kg organic carbon), the concentration of chemical in the organic carbon can be found. Therefore, if there was  $1.6 \times 10^{-6}$  kg organic carbon per liter of intake water:

$$C_{sorbed} = C_{oc} \cdot TOC \quad (6)$$

$$C_{sorbed} = C_{water} \cdot K_{oc} \cdot TOC \quad (7)$$

where  $C_{sorbed}$  is the concentration of chemical sorbed per liter of intake water. Now, using TBEP's  $K_{oc}$  value of 24000 L/kg, and using a concentration of 1 mg/L of TBEP:

$$C_{sorbed} = 1 \frac{\text{mg}}{\text{L}} \cdot 24000 \frac{\text{L}}{\text{kg}} \cdot 1.6 \cdot 10^{-6} \frac{\text{kg}}{\text{L}} \quad (8)$$

$$C_{sorbed} \approx 0.04 \frac{\text{mg}}{\text{L}} \quad (9)$$

Thus, the most that can be adsorbed for TBEP was about 4% of the concentration in the water. TBP and TCEP will have even lower percentages because of their much lower  $K_{oc}$  values (1900 and 300 L/kg, respectively).

Last, the organophosphate triesters may be trapped in the flocs through precipitate enmeshment. Assuming an aluminum sulfate concentration of 10 mg/L in the water after addition, one may also assume that all 1.6 mg/L of TOC precipitates with the aluminum sulfate. But, if both aluminum sulfate and TOC precipitate (a total of 11.6 mg/L), this was still only about 1% of the total water mass. Therefore, the interactions due to precipitate enmeshment were small, if negligible.

Aluminum oxides are also known to catalyze the hydrolysis of *p*-nitrophenyl phosphate (PNPP) (Baldwin et al., 1995). But, the chemical structure of PNPP differs greatly from the phosphate triesters studied in this thesis, as PNPP is a monoester. That leaves the phosphate moiety available for acid/base reactions and ionic interactions with oxides. From Schwarzenbach et al. (2003), hydrolysis of the phosphate triesters happens under neutral and basic pH conditions. But, the fastest reacting of the phosphate triesters listed, triphenyl phosphate, has a half-life of 320 days at pH 7, which is a comparable pH to the CWTP. This half-life is significantly longer than the 10-minute residence time from the intake to after the pre-treatment chemical addition.

#### **4.3.3 Interactions of Phosphate Triesters with Sodium Hypochlorite**

Sodium hypochlorite may interact with the phosphate triesters through the subsequent hypochlorite ion produced when sodium hypochlorite is initially added to the water. There may be a nucleophilic substitution of the phosphate triester, where the hypochlorite ion attacks the phosphorus atom. Yet, this process is similar to the hydrolysis discussion in the previous section, where hydrolysis is deemed negligible to the removal of the organophosphate triesters.

Oxidation of the sodium hypochlorite with the phosphate triesters was another potential interaction. The hypochlorous ion and the hypochlorous acid generated from the sodium

hypochlorite, along with a hydroxyl ion, may attack the hydrogen atoms on the phosphate triesters, leaving a hydroxyl group. To find the potential rate of removal, assume the reaction occurred in first order with the hypochlorous acid (or hypochlorite ion), and first order with the organophosphate triester. The concentration of hypochlorous acid was approximately  $10^{-4}$  M, and the concentration of TBP was the fraction of the TOC, which is approximately  $10^{-4}$  M. In addition, the half-life for a second order reaction where the concentrations are similar is (Purdue University, undated):

$$t_{1/2} = \frac{1}{k \cdot 10^{-4} M}$$

where  $t_{1/2}$  is the half life (second),  $k$  is the rate constant ( $M^{-1}/\text{second}$ ), and the  $10^{-4}$  M concentration is from the two concentrations noted above. Harrison et al. (1976) indicate that the rate constant for pyrene with hypochlorous acid is  $34.4 M^{-1}/\text{second}$  at  $20^\circ\text{C}$  and a pH above 6.6. For a pyrene concentration of  $10^{-4}$  M, this would indicate a half time of approximately 300 seconds. Even though the phosphate triesters do not have similar composition to pyrene, all are organic compounds, with hydrogen atoms that are available for attack. The author cannot confirm how fast the reaction may take place, but a bench-scale experiment involving the phosphate triesters and sodium hypochlorite at similar pH values and concentrations at the CWTP would suffice to find out if there were any interactions.

Therefore, the reasons for removal and for the different amounts of removal for each chemical were inconclusive. To better quantify the results, a suggestion for further research would be to simulate the CWTP's pre-treatment chemical addition by adding aluminum sulfate and sodium hypochlorite at similar conditions, and determine whether there was significant removal after 10 minutes (i.e. the residence time from the intake to after the pre-treatment chemical addition).

#### ***4.4 Discussion of TCEP Concentrations of Filter #2 and Final #2***

The TCEP concentrations of Filter #2 and Final #2 were significantly larger than other values found. The concentrations were one to two orders of magnitude above the Raw,

Chemical Addition, and Sedimentation samples. There were a few reasons why this may happen. There may have been some laboratory errors. Or, there may have been phosphate triester contamination in the treatment plant. Alternatively, these two samples may have been collected at a period of high phosphate concentration. One may also hypothesize that there was some formation of the phosphate triesters through reaction during the filtration and post-treatment chemical addition phase.

#### 4.4.1 Laboratory Issues

First, problems may occur in the laboratory work. Looking at the runs completed on March 5, 2004, Filter #2, Final #2, and Roswell 2-24 all had very high peak sizes compared to other peak sizes that day for TCEP (Table 5) This trend was also abnormal compared to other days' runs, where there were no large spikes in any specific chemical. Therefore, laboratory issues may be a source of error.

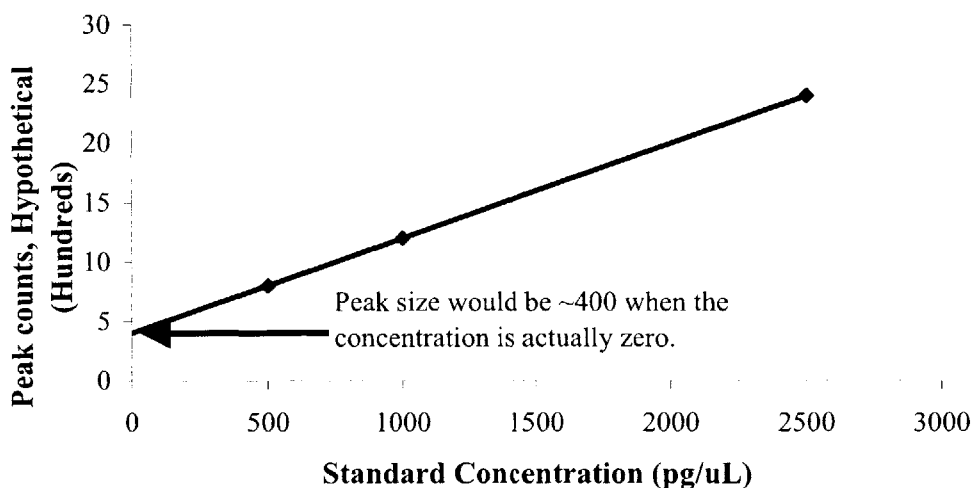
**Table 5 Peak sizes for the March 5th, 2004 runs. Even though the samples have much larger numbers than the standards, the TCEP values highlighted are much larger than the other two phosphates studied.**

			10:58	12:16	18:11	16:18
Date	Time	Sample Name	TBP (99.3)	TCEP (63.2)	TBEP (57.3)	Inj Std (130)
5-Mar	3:13	500 std	952	508	435	11190
5-Mar	3:43	2500 std	5319	3954	1415	12518
5-Mar	4:13	1000 std	1804	1159	653	12071
5-Mar	4:43	Filter #2	2659	<b>56935</b>	5654	135115
5-Mar	5:14	Final #2	2177	<b>119214</b>	2328	91733
5-Mar	5:44	1000 std	2971	2981	1055	29503
5-Mar	6:13	Roswell 2-0	443	3563	6217	76694
5-Mar	6:43	Roswell 2-5	2006	2749	12561	171698
5-Mar	7:13	Roswell 2-24	4337	<b>75433</b>	10859	143456
5-Mar	7:43	1000 std	8533	6264	2967	64315
5-Mar	8:13	Spike #3	43778	27838	71997	723040
5-Mar	8:43	1000 std	6291	5669	1648	51761

One hypothesis for the abnormal numbers was that a peak might have formed even though none of the compound existed. When calculating the concentrations, the assumption that the peak size was zero at zero concentration was done due to runs

completed beforehand (Appendices D and K). But, if this was not true, there may be measured concentrations when none actually existed. To find out whether this was true, the author examined the three standard runs at the beginning of the day of March 5. From section 4, the standards generally formed a linear isotherm and had an approximately zero intercept when counts versus standard concentration was plotted. But, on that day, there might have been a large positive y-axis intercept (Figure 13). When the concentration was extrapolated to zero, there was still a peak measured.

But, this was not the case for the standards run on March 5, as there were negative intercepts for two of the three chemicals. The third one had a small intercept, and thus could not account for the large peak size.



**Figure 13 Graph of hypothetical situation where a peak may be measured when the concentration of the phosphate triesters was actually zero.**

Another hypothesis was that the peaks measured are not from the organophosphates. To check this, one must look at the confirmation ion that was also measured during the GC/MS runs. The findings were that the peaks measured did, in fact, come from the organophosphates, unless some other compounds that elute at the same time as the organophosphates and fragment with the same base peak ion and confirmation ion.

There were other ways in which phosphate triester may be added. During much of the field and lab work, aluminum foil was used to prevent exposure to plastics. But, the aluminum foil itself may have phosphate triesters, as they are also used as lubricants! Because the aluminum foil was never washed before using, there could be significant amounts of phosphate triester being added into the samples. But, for this study, every sample had a significant exposure to aluminum foil, and the Final #2 and Filter #2 samples were not exposed significantly more than the other samples. This idea also was relevant to plastic cap exposure and exposure due to the rubber septum used in the GC/MS vial

Therefore, there was no concrete explanation for these large numbers. But, from what work had been done, these numbers may actually be that large. Further samples need to be taken at those sites and more runs need to be set up on those samples to make better conclusions. In addition, to check the interactions of the injection standard with the gas chromatographer versus the interactions of the phosphate triesters with the gas chromatographer, one should conduct standard additions of the phosphate triesters.

#### **4.4.2 Drinking Water Treatment Plant Issues**

Second, the author examined the possibility the TCEP may have been contributed from the plant itself. One main concern during the whole sampling process was exposure to any plastic material because the phosphate triesters in the plastics may leach into the water (i.e. they are used as plasticizers in resins and PVC piping). For example, in our sampling procedures, all plastic caps were lined with aluminum foil before capping the bottles, jars, or vials to prevent plastic exposure. But, what kind of exposure to plastics existed in the CWTP?

According to the author's findings, there does not seem to be any exposure to plastics in the filtration stage. The filter bottoms were made of steel and concrete, with no plastic materials involved. The only exposure to plastics during the post-treatment chemical addition came from the plastic day tanks in which the phosphoric acid and fluoride were

held (i.e. the lime and sodium hypochlorite were dispensed directly from the holding tanks). But, the supervisor at the CWTP, Tom Kopanski (2004), indicated that the day tanks need to be replaced, especially the fluoride tanks. Thus, the day tanks may have deteriorated such that plastic material would get into the liquid fluoride. Thus, there was a chance that leaching of phosphate triesters into the water may be occurring.

In addition, the day tanks must contribute a significant amount of TCEP into the water to account for the increase. Assuming a 100 ng/L increase in TCEP concentration, and assuming 40 MGD  $\approx 160 \times 10^6$  L/day, there would need to be 16 g/day of TCEP, or approximately 5 kg/year of TCEP contributing to the final effluent. Further research should look into the composition of the plastic day tanks, and the concentrations of phosphate triesters in each of the day tanks.

Another contribution may come from the anthracite coal in the filter. Anthracite coal is a type of granulated activated carbon (GAC), where GAC has been found to remove TBP and TBEP (Paune et al., 1998). But, the filters at the CWTP may have had different conditions than the ones presented in Paune et al. First, the author cannot confirm how long the anthracite coal had been in the filter since the last (re)activation. Second, he also cannot confirm how long the filter had been used since the last backwashing. Last, he cannot find information on how effective the removal of phosphate triesters were when exposed to the anthracite coal for only a small period of time (e.g., if the total residence time was 20 seconds in the filter, the exposure to coal was at most 20 seconds). Further research must determine the effectiveness of removing or adding the chemicals with those three considerations in mind.

#### **4.4.3 Timing of Samples Issues**

The author explored the possibility of variations in concentrations due to the time of sample. Filter #2 was collected five minutes after Filter #1, and Final #2 was collected five minutes after Final #1. Due to such a large change in concentration (Table 2), the chances of detecting such different compositions in such a short time difference does not

seem possible. Therefore, one can be quite sure that time variances could not have been the main problem for these samples. But, to confirm this, more samples should be taken to study the time variance effects.

#### **4.4.4 Reactions that May Form the Phosphate Triesters within the Filtration and Post-Treatment Chemical Addition Stage**

Forming the phosphate triesters through reaction during the filter and post-treatment chemical addition was not feasible. To form an ester, an alcohol reacts with a carboxylic acid, producing an ester along with a water molecule. If formation were to occur, there would have to be no presence of water to drive the reaction. Instead, water was amply present. Therefore, the formation reaction should not occur in water.

In conclusion, the plant may be contributing to the addition of TCEP, either due to the day tanks or from other exposures, such as the anthracite coal. Laboratory issues, issues with timing of the samples, and issues concerning reactions were small or negligible.

#### ***4.5 Discussion of Other Samples***

After sedimentation, the concentration values indicate there is no measurable removal or addition for TBEP and TCEP. But, TBP has an increase in concentration. This may occur due to flocs breaking up in the coagulation stage, resulting in the sorbed TBP going back into the water. Yet, this result is inconclusive without exactly knowing what goes on in the pre-treatment chemical addition phase. Further research must either take more samples at the CWTP after flocculation and sedimentation, or try to simulate the plant conditions of those two processes through bench-scale experiments.

TBP does not exhibit any significant removal or addition after filtration and post-treatment chemical addition. This should be the case if there is no plant exposure (either through the anthracite coal or plastics in the day tanks), no reaction in the filter, and no time variability.



TBEP does have a small increase after filtration. Thus, all filtration discussion for TCEP in section 4.4 also applies to TBEP. TBEP does not exhibit any significant removal or addition after post-treatment chemical addition.

## **5. Conclusions, Suggestions for Further Study, and Recommendations When Conducting Further Study**

In the CWTP, there appeared to be removal of the organophosphate triesters after the addition of aluminum sulfate and sodium hypochlorite. Addition of hypochlorous acid and hypochlorite ion may be the reason for the removal. Contributions from the plant were most likely to be the cause the addition of the phosphate triesters at the final effluent.

Much of the research conducted by the author could be expanded upon. First, a bench-scale version of the pre-treatment chemical addition should be done. This includes the addition of sodium hypochlorite and aluminum sulfate into water, thoroughly mixing the solution, and finding out if there is any removal of phosphate triesters.

Other studies have been suggested throughout the paper. For example, the different times of the day or year should be looked at, as the loadings of phosphate triesters into the plant may vary temporally. The composition of the plastics in the day tanks should be examined for phosphate triesters. If these triesters are in them, one should test if there is leaching into the fluoride or phosphoric acid tanks. Further testing should also be done on the aluminum foil, the plastic caps, and the fatty blobs mentioned in Appendix D.

Further research should determine the effectiveness of GAC in removing phosphate triesters. In addition, other types of potential DWTP process such as advanced oxidation processes should also be studied to check for removal of phosphate triesters (Machairas, 2004).

If further samples are to be collected, one should find another phosphate triester that is of similar composition. Then, a small known amount of this phosphate triester should be added to the original samples to determine the efficiency of transferring the studied phosphate triesters from water to chloroform. In addition, trying different injection standards would be useful for determining the interactions of the phosphate triesters and

the stationary phase within the GC column. Last, the LLE process done in Atlanta has the possibility of being done faster with better laboratory equipment.

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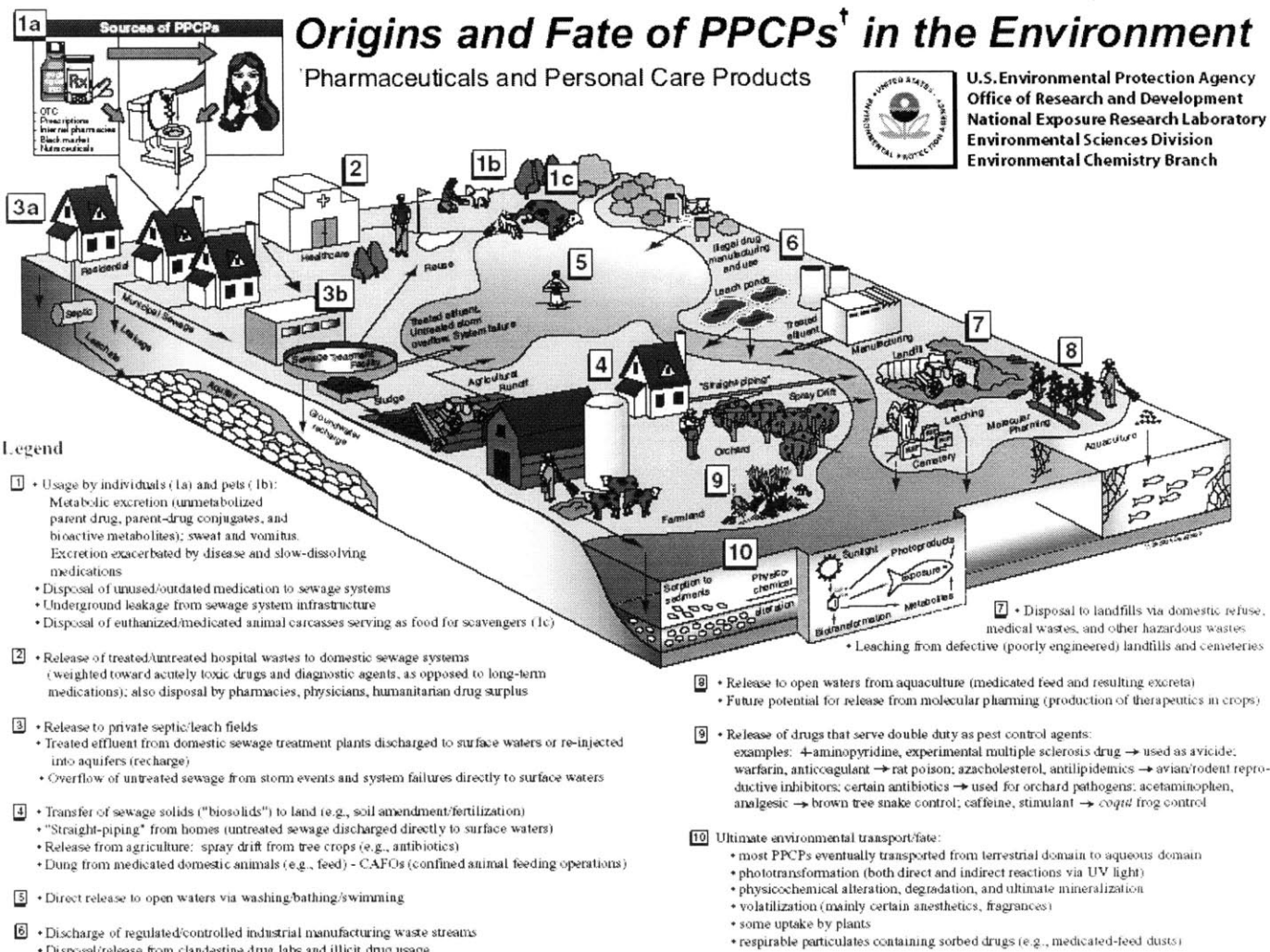
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**APPENDICES**



**APPENDIX A Origins and Fate of Pharmaceuticals and  
Personal Care Products in the Environment (US EPA, 2004)**



**APPENDIX B Atlanta Water Quality Report 2002 WSID  
1210001 (City of Atlanta, 2002)**

# Atlanta Water Quality Report 2002 WSD 1210001

The City of Atlanta Department of Watershed Management is pleased to provide the 2002 Water Quality Report (WQR). During 2002, your community's drinking water met or exceeded all safety and quality standards set by the State of Georgia and U.S. Environmental Protection Agency (EPA).

Annually, we collect over 12,000 samples of untreated (raw) and treated (finished) water and conduct over 50,000 tests, screening for more than 150 potential contaminants. The regulated substances that were detected are listed in the Water Quality Table. The presence of these contaminants in the water does not necessarily indicate that the water poses a health risk. The water also was tested for hundreds of undetected compounds.

## Our Monitoring Program

The Safe Drinking Water Act (SDWA) requires water systems to monitor for unregulated parameters in order to assist the EPA in determining where certain contaminants occur and whether additional regulations may be necessary.

In 1998, the City of Atlanta participated in a monitoring program called the Information Collection Rule (ICR). Monitoring data from this program (WQ Table) shows the presence of disinfection byproducts as a result of the reaction between chlorine and naturally occurring organic matter in the water.

Based on the results from water systems throughout the United States, new regulations have gone into effect. Our current monitoring results meet the new regulations. (WQ Table Organic Contaminants)

In 2002, the first round of monitoring was conducted for additional "unregulated parameters" under a program called the Unregulated Contaminant Monitoring Rule (UCMR). None of the "unregulated contaminants" for which the federal or state rules require monitoring were detected in our water system.

## Sources of Your Water

Each day, the Atlanta water system provides approximately 120 million gallons of treated drinking water to nearly 1 million residents in the metropolitan Atlanta area.

All the water processed is surface water that is pumped from the Chattahoochee River. The raw water intake for the Chattahoochee and Hemphill Water Treatment Plants is located on the Chattahoochee River, north of Peachtree Creek.

The Chattahoochee Plant receives the water directly from the river. The Hemphill Plant processes raw water that has been pumped from the river to a reservoir.

These two plants supply about 75 percent of Atlanta's drinking water. The remaining water is supplied by the Atlanta-Fulton County Water Treatment Plant, which also processes water from the Chattahoochee River. This plant supplies treated (finished) water to the northeast area of our distribution system.

## Citizen Participation Program

The City of Atlanta has an ongoing Citizen Participation Program to educate and inform citizens of water quality issues and infrastructure projects that are designed to improve water treatment and delivery systems. The program also includes a public education initiative to encourage water conservation and source water protection.

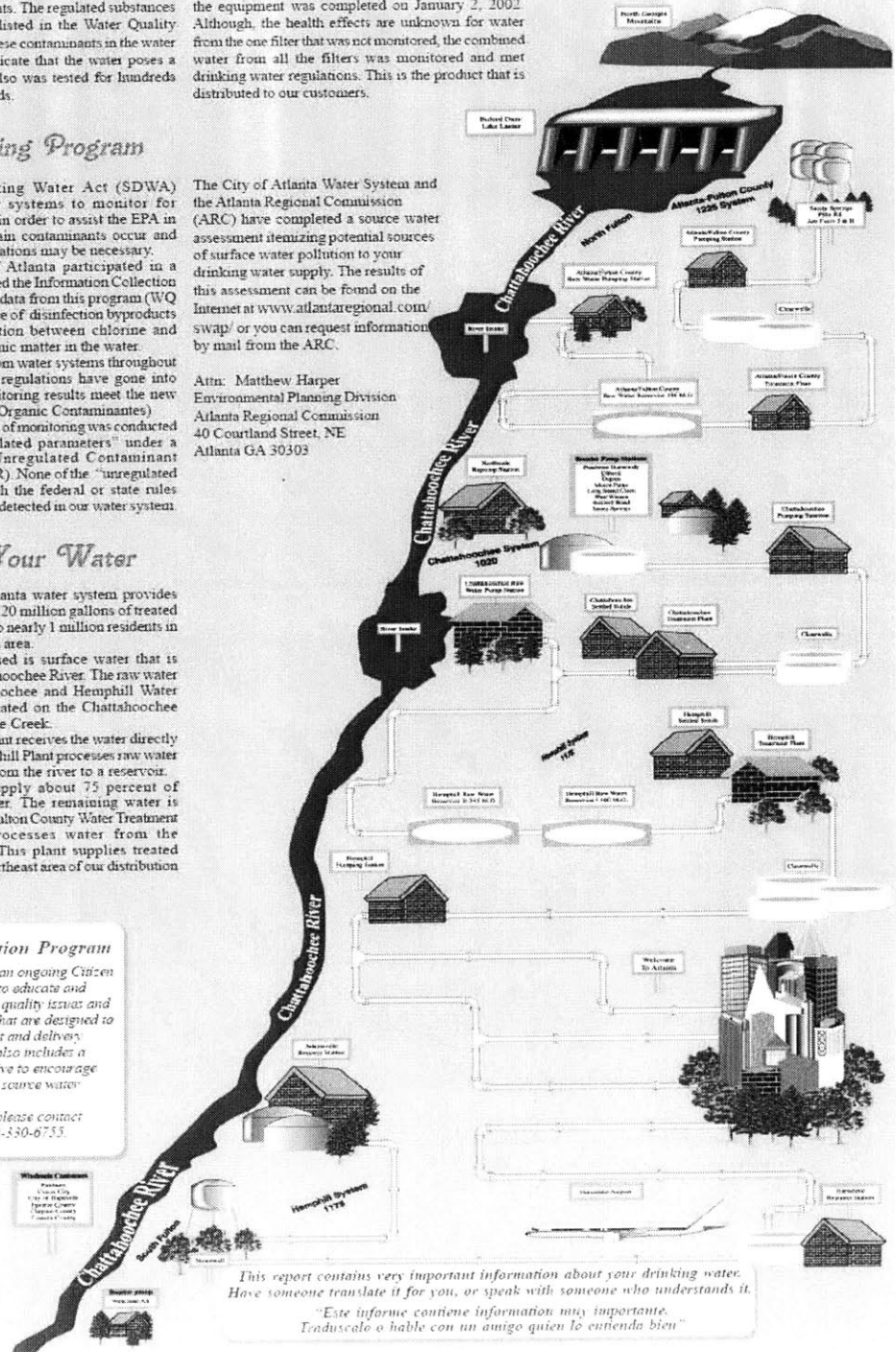
For more information, please contact Martin Johnson at 404-330-6753.

Although we experienced no violations related to water quality in 2002, new federal regulations require continuous monitoring of drinking water for turbidity at each of our 28 individual filters. On January 1, 2002, an overnight mechanical failure on one of the filters' continuous monitoring systems occurred.

Manual monitoring in accordance with the new regulation was not conducted, and therefore, the monitoring requirement was not met. The repair on the equipment was completed on January 2, 2002. Although, the health effects are unknown for water from the one filter that was not monitored, the combined water from all the filters was monitored and met drinking water regulations. This is the product that is distributed to our customers.

Notification of this incident was distributed to the public on July 1, 2002.

The City of Atlanta Bureau of Water is pleased to have the opportunity to serve you in the future. Our goal is to provide our customers with the level of water service they expect and deserve. The Bureau's mission is to provide high quality, dependable drinking water at the lowest possible cost.



The City of Atlanta Water System and the Atlanta Regional Commission (ARC) have completed a source water assessment identifying potential sources of surface water pollution to your drinking water supply. The results of this assessment can be found on the Internet at [www.atlantaregional.com/swap/](http://www.atlantaregional.com/swap/) or you can request information by mail from the ARC.

Attn: Matthew Harper  
Environmental Planning Division  
Atlanta Regional Commission  
40 Courtland Street, NE  
Atlanta GA 30303

This report contains very important information about your drinking water. Have someone translate it for you, or speak with someone who understands it.

*"Este informe contiene información muy importante. Tradúscalo o hable con un amigo quien lo entienda bien"*

## **APPENDIX C Field and Lab Work in Atlanta, GA**

Field sampling and subsequent lab work were completed in Atlanta, GA during January 2004. A total of ten 3.8-liter samples were collected after major processes in the CWTP. Then, the samples were reduced to 400 mL of chloroform for liquid-liquid extraction. These 400 mL extracts were brought back to Cambridge to finish the necessary lab work and to find the concentrations of the organophosphate triesters.

### ***C.1 Sampling Conducted***

#### **C.1.1 Description of Samples Taken at the Chattahoochee Water Treatment Plant**

On January 14, the author sampled at five different sites within the plant. In addition to collecting at the plant's intake, the sites corresponded to the completion of a major drinking water treatment process. For each site a 3.8-liter sample was taken along with a duplicate taken directly after the first sample, resulting in a total of 10 samples. The five sites were the 'Raw' water from the Chattahoochee River (note: the quoted words were the label names for that site), after pre-treatment 'Chemical Addition' (i.e. addition of alum, sodium hypochlorite), after 'Sedimentation'/Flocculation, after going through filtration (site labeled as 'Filter'), and the 'Final' finished water (i.e. after addition of lime, phosphoric acid, fluoride, sodium hypochlorite, and after going through the clearwell). All samples were grab samples (i.e. the samples were not composite, or time-averaged, samples), and were taken from spigots that were hooked up to the major process, as opposed to grabbing the samples directly from the treatment process. For example, the Sedimentation sample did not involve dipping a bucket into the sedimentation tank to grab the sample.

#### **C.1.2 Sampling Procedure for the Raw and Chemical Addition Samples**

The following procedure was used for the Raw and Chemical Addition samples:

- Turn on sampling spigots. Let water run for a minute to clear out any residue in the piping system..
- Using a 1-liter graduate cylinder, grab water sample. Record volume.
- Place sample into 4-liter amber bottle.
- Grab more samples until 3.8 liters are grabbed.
- Line the mouth of the 4-liter amber bottle with aluminum foil, then cap the bottle.
- Take bottle outside as quickly as possible for chloroform addition.

### **C.1.2.1 Major Observations and Sources of Error**

Steel funnels assisted the transfer from the graduated cylinder to the amber bottle. Raw #1 was sampled at 9:05 am, with its duplicate, Raw #2, taken at 9:10 am. Chemical Addition #1 was taken at 9:15 am, and Chemical Addition #2 was taken at 9:20 am.

The reason our group used chloroform will be explained in more detail in section C.3.3, but the reason for acting quickly was to stop any biological processes going on in the water. There was 200 mL of chloroform added to each of the four samples at the CWTP.

A source of error is the measurements of the 1-liter graduated cylinder samples. The size of the error for each 1-liter sample is 10 mL, which is the distance between tick marks on the graduated cylinder. Because four 1-liter samples are collected, the error is approximately 40 mL, or about 1% of the total sample.

### **C.1.3 Sampling Procedure for the Sedimentation, Filter, and Final Samples**

The following procedure was used for the Sedimentation, Filter, and Final samples:

- Because the sampling spigots continuously have water running through them, there is no need to wait before taking the sample.
- Using a 1-liter graduate cylinder, grab water sample. Record volume.

- Place sample into 4-liter amber bottle.
- Grab more samples until 3.8 liters are grabbed.
- Line the mouth of the 4-liter amber bottle with aluminum foil, then cap the bottle.

### **C.1.3.1 Major Observations and Sources of Error**

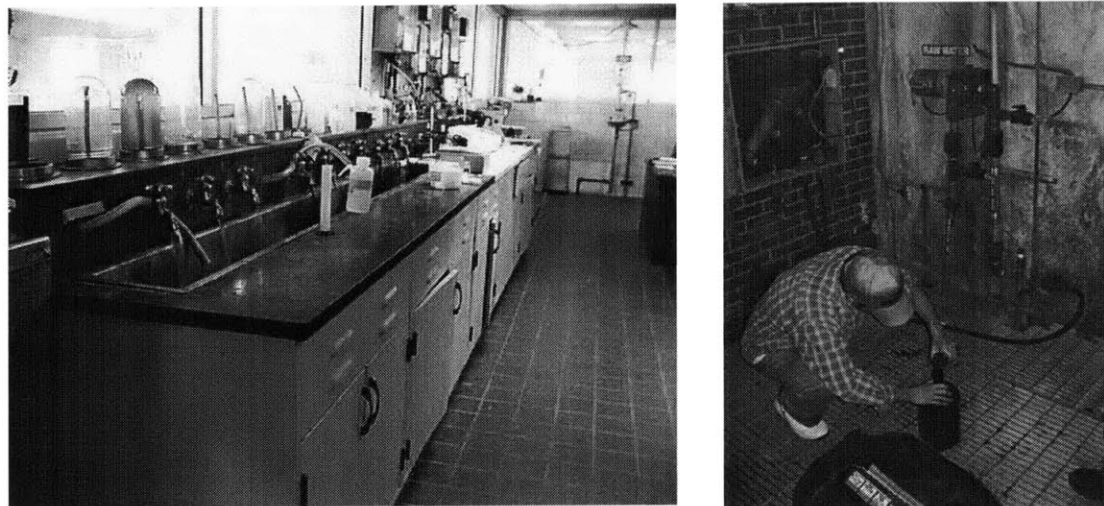
Sedimentation #1 and #2 were taken at 1:15 and 1:20 pm, four hours after the Chemical Addition samples. This was done because the author wanted to follow the same parcel of water such that time variances did not affect the results. Thus, the author waited four hours to take the sample because the residence time in the sedimentation basin was estimated to be 4 hours in section 2. In contrast, the residence time from the Raw sample to the Chemical Addition sample was approximately 5 minutes, the residence time from Sedimentation to Filter was less than a minute, and from Filter to Final was approximately 40 minutes.

Filter #1 and #2 were taken at 1:30 pm and 1:35 pm, and Final #1 and #2 were taken at 1:45 and 1:50 pm. See Figure 14 for what the sampling spots looked like.

One source of error comes from the Final #1 and #2 samples. Unfortunately, the author did not know the residence time between the Filter and Final samples before conducting the samples. Thus, the “same parcel of water” concept may be off by approximately 30 minutes for this sample. 30 minutes, though, should not affect the concentrations too greatly.

The sources of error for the Raw and Chemical Addition samples also apply for the Sedimentation, Filter, and Final samples: the piping distribution should not contaminate the water, and the volume of the samples has approximately a 1% error.

Because the Sedimentation, Filter, and Final samples have had sufficient contact time with the sodium hypochlorite, all biological processes have been stopped. Thus, the 200 mL of chloroform did not have to be added as soon as possible.



**Figure 14 Left: Sampling location of Sedimentation, Filter, and Final samples. Right: Location of the Raw sample. The Chemical Addition sample was taken in the same area.**

### ***C.2 Sampling along the Chattahoochee River***

In addition to sampling at the CWTP, sampling was done along the Chattahoochee River. The sampling was completed on January 15 and 16, 2004. A total of 27 river-water samples were collected. Please refer to Andrews (2004) for more details about the sampling procedure, observations, and errors.

### ***C.3 Lab Work Done in Atlanta, GA***

After collecting the samples, the main objective was to reduce the 3.8-liter water samples to 400-mL chloroform extracts, using liquid-liquid extraction (LLE). LLE involves the transfer of organic compounds from one fluid to an immiscible organic solvent through thorough contact with the two fluids. The main reason for doing this work in Atlanta and not back in Cambridge was that bringing 37 4-liter bottles back to Massachusetts was not practical.



### **C.3.1 Description of Lab Workspace**

Because the CDC did not have lab space for our group, all lab work was done at an affiliate's porch. Although this choice may seem like an unsuitable place to be working with hazardous chemicals, this was the most suitable choice for many reasons. First, because chloroform is quite dangerous to breathe, finding a well-ventilated area was required. Thus, any indoor site was not viable. Second, the lab space should be easily accessible, should have some kind of security, and should not be too visible to the public; our affiliate's house fit all three of these criteria.

Two major issues with an outdoor lab were darkness and weather. Because the porch did not have sufficient lighting, work was limited to daylight hours. In addition, fate smiled upon the group, as there was sunshine every day except for the last day, when a small amount of rain fell.

### **C.3.2 Overview of the Procedure**

First, each sample was dosed with either 200 mL of chloroform (1<sup>st</sup> extract) or 100 mL of chloroform (2<sup>nd</sup> and 3<sup>rd</sup> extracts) within the amber bottle. Then, the sample was shaken thoroughly to promote contact of the chloroform with the water. Because there was pressure buildup in the bottle during shake and bake, the bottle was vented frequently to prevent excessive pressure buildup. After shaking the bottle for 5 to 10 minutes, the sample was allowed to rest for approximately 10 minutes to allow the two liquids to separate. Last, the chloroform was extracted by putting a graduated pipette into the bottom of the amber bottle, and then pipetted into a 500-mL amber jar. This was done in 25-mL increments until the chloroform was removed.

The whole process was repeated three times for each water sample. The first dose used 200 mL of chloroform, while the second and third dose used 100 mL each. Three doses were used because the overall efficiency of transferring the organic compounds from water to chloroform increases significantly after each extraction. For example, if only one

dose was used, about 90% of all organic compounds would be transferred from the water to the chloroform. For two doses, the efficiency would increase to 99%, and could be up to 99.9% for three doses. Note that the 90% efficiency is only an approximation; refer to Appendix D for details.

### **C.3.3 Why Use Chloroform as the Organic Solvent?**

The group had a variety of choices from which pick the organic solvent used in the LLE. Chloroform was chosen because:

- As stated before, chloroform stops all on-going biological processes.
- Chloroform is a common solvent used in normal LLE processes.
  - o One reason this is true is because chloroform is denser than water. This was advantageous because this makes the extraction process easier. Any undesired water would float to the top of the graduated pipette, and would not be put into the 500 mL amber jar.
- For chloroform, organic compounds stay dissolved in the liquid phase instead of evaporating.
- The cost of chloroform is similar to other organic solvents used for LLE.

### **C.3.4 Procedure**

This was the procedure used to conduct the LLE on the samples:

- If there is no chloroform currently in the water sample, measure out 100 mL of chloroform using a 100 mL graduated cylinder.
- If there is no chloroform currently in the water sample, add the 100 mL of chloroform to the 3.8-liter water sample.
- Start shaking the amber bottle to promote more chloroform-water contact. Because the plastic caps do not provide a sufficient seal on the bottle when combined with the aluminum foil, use one hand to put a seal on the mouth of the bottle. See Figure 15 for details.

- During the first minute of shaking, release hand from the mouth of the bottle to release air every few seconds. The chloroform-water contact causes pressure buildup in the bottle, and an excessive amount of pressure will cause liquid to be forced out.
- Continue shaking until five minutes have elapsed.
- Let the bottle rest for at least 10 minutes such that the chloroform and water can separate back into their own phases.
- After settling, use a 25-mL graduated pipette to remove the chloroform from the water sample. Because chloroform is denser than water, stick the graduated pipette to the bottom of the bottle, and remove ~25 mL of chloroform.
- Transfer this chloroform into a 500-mL amber jar. Excess water will be in the graduated pipette. Do not put this in the jar. Instead, put this water back into the original water sample.
- When at the last extraction, take out as much as possible. Having large amounts of water within the graduated pipette is fine, since the user can carefully pipette out only the chloroform, and put the rest of the water back into the original water sample.
- Repeat this process two more times. For the first time that the extraction is done, add 200 mL of chloroform. For the second and third extractions, add 100 mL of chloroform.



**Figure 15 Finding the best method to conduct the shaking of the sample involved holding the bottle in a nearly horizontal position as shown, while swirling the bottle to promote maximum chloroform-water contact.**

### **C.3.5 Major Observations and Sources of Error**

The sample size collected was 3.8 liters, which compares to 1-liter samples collected in Kolpin et al. (2002). Thus, the sensitivity of analysis will be approximately 4 times larger than Kolpin et al. See section C.3.7 for more details concerning detection limit analysis.

Because the hands were used as a seal for the shaking process, there were small amounts of liquid that came out due to an insufficient seal. In addition, small amounts of liquid were also forced out of the bottle due to pressure buildup. The total amount of liquid lost after all three shaking sessions was approximated to be 10-20 mL.

During transfer of the chloroform from the amber bottle to the amber jar, small amounts of chloroform came out of the pipette. If this chloroform came out of the pipette while the pipette was still in the bottle, there would be less chloroform in the pipette than recorded. In addition, this chloroform that came out would then be extracted again. Thus, this chloroform may explain why some recordings may have recorded above 100 mL when only 100 mL were added. Other possibilities for recordings above 100 mL may be from temperature differences during the day, resulting in chloroform solubility differences in the water. Or, the initial dose may have been 101 or 102 mL, for example.

If chloroform came out of the pipette when outside of the bottle, but not into the jar, the chloroform was lost. The amount lost due to this process was estimated to be 1-10 mL of chloroform.

During the last pipetting for each of the three extractions, there was a colloidal layer separating the chloroform-water interface. Most of the time, the group members put this colloidal layer into the jar. The disadvantage of having the colloidal layer was that the colloidal layer might have had a lot of dirt and residue. The advantage of adding the

colloidal layer was that any chloroform in that layer would also be included. Another advantage is that dirt and residue should be included as long as possible (although the dirt and residue must be rid of eventually (Appendix D)) in the water, as it is a component of the water. In addition, Kolpin et al. did not filter their water samples.

### **C.3.6 Cleanup**

After each sample received a dose, the 500-mL amber jar and the 4-liter amber bottle would be covered with an aluminum foil-lined plastic cap. The 25-mL graduated pipettes were then rinsed in the inside and outside with distilled water. As more samples were extracted, the pipettes started to develop residues in the inside, which could not be cleaned using distilled water. To clean the inside of the pipettes, they needed to be soaked in an acidic or a basic solution, which was not brought for the Atlanta lab work. One of the pipettes was replaced about midway through the whole laboratory process, but the other pipette was used during the whole time. The accumulation of the residue leads to a possibility of cross-contamination between samples.

The residual water from the samples was aerated for a few hours to volatilize the saturated chloroform. Once the samples did not smell of chlorine, the samples were then safe for disposal.

### **C.3.7 Reporting Limits, and Why 3.8 Liters was Chosen as the Sampling Size**

Prior to the fieldwork, the field team determined how large a volume would be necessary to be able to detect the phosphate triesters. There was some worry that even though the chemicals were chosen because of their high detection rate, there could always be a possibility of getting no detection. Thus, the desire was to get as large a sample size as possible to increase the sensitivity. From previous studies, the concentrations were approximated to be between 0.01 to 10  $\mu\text{g}/\text{L}$ . To get a reliable reading from the Gas Chromatograph/Mass Spectrometer (GC/MS), the concentrations of the phosphate triesters need to be, at a minimum, at least 500  $\text{pg}/\mu\text{L}$ , or 500  $\mu\text{g}/\text{L}$  in the analyzed

extract. Therefore, one needs to get a 50- to 50,000-fold reduction in volume from the original 3.8-liter sample to the analyzed extract to get any results from the GC/MS analysis. As will be discussed in Appendix D, the 3.8-liter samples will be reduced to approximately 50-200  $\mu\text{L}$ , with a goal of a 100  $\mu\text{L}$  final sample. This would result in a magnification of approximately 20,000- to 80,000-fold. Thus, this is quite close to achieving or exceeds expectations for reliable results, assuming that all concentrations are between 0.01 to 10  $\mu\text{g/L}$ . Some of the results, though, were below 0.01  $\mu\text{g/L}$  (section 4). These results cannot be trusted without some probability of having no detection.

Another way of figuring out the reporting limit would be to look at Kolpin et al. (2002) and Frick and Zaugg (2003). For example, in Kolpin et al., the reporting limit for TCEP is 0.04  $\mu\text{g/L}$ . Because the sample size in the author's work is about four times larger, and because the final sample extract is 10 times smaller, one can infer that the sensitivity for the Atlanta samples will be 40 times greater, which would mean a reporting limit of 0.001  $\mu\text{g/L}$ . Nonetheless, any value that was at least 0.001  $\mu\text{g/L}$  was noted in the results (section 4).

As mentioned before, the largest sampling size was desired to get the greatest sensitivity. Yet, working with a size greater than 3.8 liters would have become too cumbersome. In addition, the magnification is large enough to warrant not using a larger size.

## **APPENDIX C1 AND C2 Laboratory Equipment Used in Atlanta, GA**

### ***C1.1 Equipment Used in the Atlanta Field Sampling Procedure***

1 1-Liter graduated cylinder  
10 4-L amber bottles  
Steel funnels  
Recording material  
Labels as necessary  
Aluminum foil

### ***C1.2 Fluids Used in the Atlanta Field Sampling Procedure***

Water from the drinking water treatment plant  
Chloroform

### ***C2.1 Equipment Used in the Atlanta Laboratory Work***

4-L amber bottles (16 bottles purchased)  
500 mL amber jars (72 jars purchased)  
Aluminum foil  
100 mL graduated cylinders (2 used)  
Cork ring  
25 mL graduated pipettes (3)  
Teflon gloves  
Aluminum pans  
Large steel bucket (approximately 40 L)  
Air pump, as used in aquarium tanks  
Wooden dowels  
Garbage bags, tarp  
Cardboard boxes  
Cooler for storing bottles  
Labeling materials  
Recording materials  
Calculator

### ***C2.2 Fluids Used in the Atlanta Laboratory Procedure***

37 3.8-liter water samples (27 from the Chattahoochee River, 10 from the CWTP)  
Chloroform (32 liters total, in 4-liter amber bottles)  
Distilled water

## APPENDIX D Lab Work Done in Cambridge, MA

The objective of the Cambridge lab work was to determine the concentrations of the phosphate triesters in the original water samples. To do so, the 400-mL chloroform samples prepared in Atlanta were reduced to approximately 100  $\mu\text{L}$  through different evaporation steps. Then, 1  $\mu\text{L}$  of this final sample was analyzed using Gas Chromatography/Mass Spectrometry (GC/MS). Last, the resulting chromatogram produced through the GC/MS analysis would be used to determine the concentrations. This chapter describes the specific procedure used by the author and Andrews (2004) in their collaborative laboratory work. In addition, many of the details were specified through conversations with John MacFarlane (2003, personal conversation).

### *D.1 Reducing the Chloroform Samples from 400 mL to 100 $\mu\text{L}$*

In Atlanta, the 37 water samples collected were reduced from 3.8 liters of water to 400 mL of chloroform through LLE. These 400-mL chloroform samples were brought back to Cambridge in 500-mL amber jars. The samples were then reduced to 100  $\mu\text{L}$  through evaporation.

#### **D.1.1 Why Evaporation of Chloroform Evaporates, but the Organophosphate Triesters Do Not**

In the case of full drying, there may have been some concern for high concentrations in the air of the vial. Using TBP, because it has the highest vapor pressure of the three organophosphate triesters studied, the density of TBP in air can be calculated with the following equation:

$$\rho_{TBP,air} = \rho_{air} \frac{MW_{TBP}}{MW_{air}} \frac{VP_{TBP}}{VP_{air}}$$

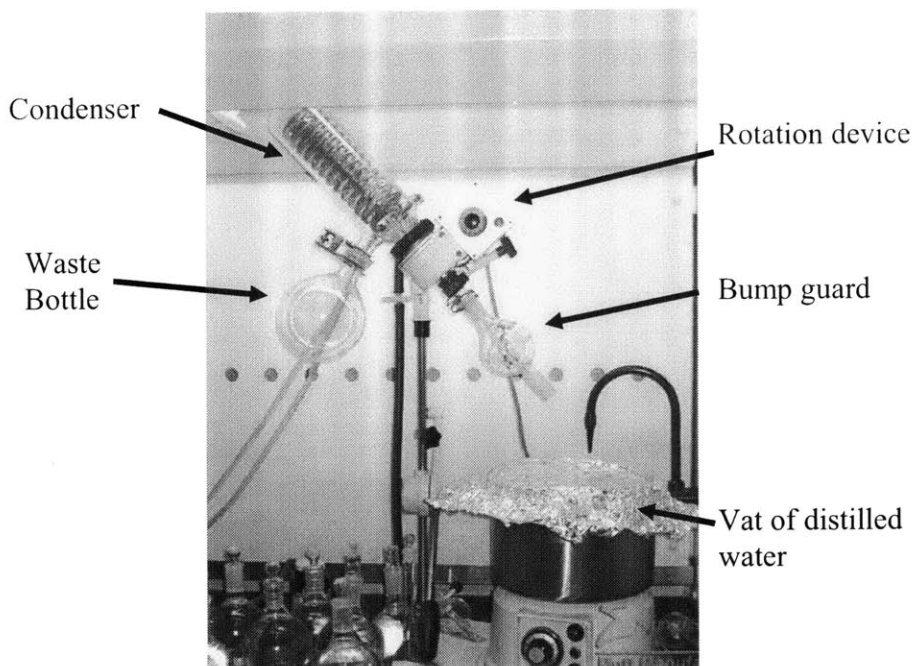
Where  $\rho$  is the density (g/L), MW is the molecular weight (g/mol), and VP is the vapor pressure (mm Hg). If the chloroform fully dried, there would be some lipids formed on the bottom of the vial, at approximately 1% of the total organic carbon, or approximately



40 µg in this study. In addition, the mass of TBP in the vial was approximated at 400 ng. Therefore, according to Raoult's law, the vapor pressure of TBP in the vial was approximately  $400 \text{ ng}/40 \text{ µg} = 1\%$  of the vapor pressure of TBP. Because the vial's temperature was close to 20 °C, the vapor pressure of TBP from section 2.4.2.2 can be used. Therefore, the vapor pressure of TBP in the vial was  $3.5 \times 10^{-5}$  mm Hg. Using the density of air of 1.2 g/L, a molecular weight of air of 29 g/mol, and a vapor pressure of air of 760 mm Hg, the approximate equilibrium density of TBP in the air was 0.5 µg/L. In a vial that was 15 mL, the most TBP that can be in this volume was 8 ng. Therefore, the full drying of the samples should be of some concern for TBP, as the author was uncertain how much TBP was lost into the atmosphere after uncapping the vial. For TCEP and TBEP, the vapor pressures of the pure liquid were much lower than TBP. Thus, the full drying of these compounds should not be of concern for TCEP and TBEP. Full drying occurred in the 15 mL vial for Chemical Addition #1 and #2, and Sedimentation #1 and #2.

### **D.1.2 Going from 400 mL to 2-15 mL: Rotary Evaporation**

The first process that the chloroform goes through is rotary evaporation. Rotary evaporation is used to evaporate the chloroform in a controlled manner until the desired volume is met. A picture of the machine is shown below (cooling water tank and pump not shown) (Figure 16).



**Figure 16** Picture of the rotary evaporation device.

A plastic clamp attaches the sample round-bottom bottle, which looks similar to the one shown on the left side of Figure 16, to the bump guard. The guard is attached to a hollow rod, which itself is held by the rotation device through friction and pressure. Above the rotation device is a condenser, where the coils have cold running water going through them. Last, the round bottle attached to the condenser collects the waste chloroform. Any evaporated chloroform from the original round bottle will go through the guard and the hollow rod, condense on the cool surfaces of the condenser, and flow as a liquid to the waste round-bottom bottle.

Evaporation is done by increasing the temperature, decreasing the pressure, and increasing the liquid surface area through rotation of the bottle. The sample bottle is slightly submerged in the vat of distilled water. Because the boiling point of chloroform is 60 °C, a temperature from 55-70 °C was used for the water temperature, according to how strong the boiling was inside the sample bottle. The pressure is lowered by closing off the system to the atmosphere and applying a vacuum through the use of a pump. This vacuum also helped hold the sample vessel to the rotation device. Last, the rotation of the round-bottom bottle increases the amount of surface area of the solvent available for

evaporation. As the bottle rotates, a thin film forms on the sidewalls due to centripetal forces.

#### **D.1.2.1 Procedure**

The rotary evaporation procedure is as follows:

First, turn on the cooling water and vat to get the desired temperatures before starting the actual evaporation. Remove the vat cover, and add more distilled water into the vat (if necessary) to the required water level.

- Place a 500 mL round-bottom bottle on a cork ring. Starting with the 400 mL of chloroform in the 500 mL amber jar, pour the contents into the round-bottom bottle. If needed, use a glass funnel to assist the pouring. Add boiling stones into the sample bottle.
- Attach the sample bottle to the guard with a plastic clamp. Lower the apparatus such that the sample bottle is slightly submerged in the vat.
- Turn the speed dial to start rotation. Use individual judgment to determine a good speed, so that a thin film develops, but that sloshing of the liquid does not occur in the sample bottle.
- Turn on the pump to start the vacuum. Once the pump is fully on, turn the valve on top of the condenser to close the system from the atmosphere.
- The chloroform should start boiling within a minute or two. Keep watch for controlled boiling and a thin film. Adjust parameters (i.e. speed dial, temperature of vat, raising or lowering apparatus to keep bottle slightly submerged) as necessary. The whole evaporation process takes 10-30 minutes.
- Once the approximate volume is achieved, raise the whole apparatus such that the bottle is out of the vat. This should stop most of the evaporation, as the bottle cools off very quickly when not heated. Turn the speed dial off. Turn off the pump, and then open the condenser valve.

- Carefully take the sample bottle off the guard. Re-cap the sample bottle, and clamp.
- Final samples should be around 2-10 mL.

When done for the day, turn off cooling water and vat. Re-cover the vat with aluminum foil. Clean the bottles as necessary when done.

#### **D.1.2.2 Main Observations and Possible Sources of Error**

When pouring the liquid, there were many small spills due to the shape of the amber jar. The best method to prevent spills was to pour as quickly as possible without overfilling the funnel. The approximate volume lost was 1-10 mL, resulting in a 2-3% error at most.

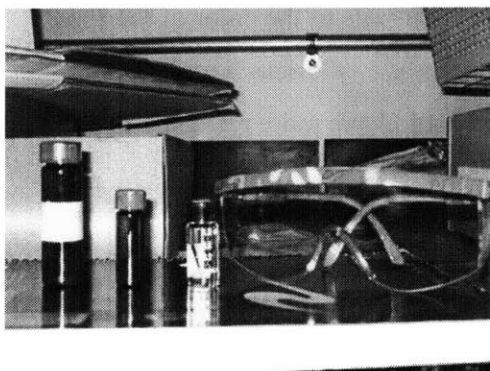
Many times during the evaporation process, the rotation device would intermittently stop turning. This occurred because the hollow rod had moved out of its original position, where the original position has the largest surface area than anywhere else on the hollow rod. Thus, suction and friction between the hollow rod and rotation device was not as strong because there was a little air that could travel between the two. The main way to fix this was to turn off the rotation device, then unclamp the guard and the sample bottle. Then, a sledgehammer was used to gently tap the hollow rod back to the section with the largest surface area, thus making the suction and friction much stronger.

Because the guard was not submerged in the vat, the temperature of the bottle was much lower than the sample bottle. Thus, some chloroform condensed in the guard before making it to the rest of the system. Sometimes, the guard would become too full with chloroform, such that any chloroform evaporated in the sample bottle would be replaced by overflow liquid chloroform from the guard. If this happened, the whole process was turned off, the guard was unclamped, and its contents were disposed. Then, the guard was re-clamped, and the rest of the evaporation was completed.

Possible sources of error would come from a couple instances where sloshing occurred in the sample bottle. Sloshing in the sample bottle may cause some of the chloroform to go into the guard. Some of the phosphate triesters may be in that sloshed chloroform, resulting in some loss. The author cannot recall this happening more than once, though, and a very small amount getting into the guard.

### **D.1.3 Transfer from Round-Bottom Bottle to 15-mL Amber Vial**

The purpose of transferring the remaining chloroform to the 15-mL amber vial is to make the remaining evaporation steps easier. A picture of the vial is shown below (Figure 17).



**Figure 17** Picture of vials used in the Cambridge lab work. From left to right: 15 mL amber glass vial, 3 mL amber glass vial (not used), and 1 mL cone-shaped glass vial.

#### **D.1.3.1 Procedure**

- Place round-bottom bottle on a cork ring, and let bottle cool for a few minutes down to room temperature.
- Remove clamp and cap, and place these two things on aluminum foil to avoid contamination.
- Using a Pasteur pipette, pipette out the remaining chloroform and place into amber vial until all contents are removed from sample bottle. When trying to take out the last amounts of chloroform, tilt the sample bottle slightly such that the

boiling stones are not touching the chloroform. Thus, the last amounts of chloroform can be seen easily, and can be pipetted out.

- Rinse the sample bottle with fresh chloroform. Try to use as little as necessary, while coating all sides with chloroform to pick up as much residue as possible. Pipette this rinse chloroform out, and put into amber vial.
- Top the amber vial with aluminum foil-lined cap. Label sample as needed.
- The sample volume should be ~2-15 mL after this process.

#### **D.1.3.2 Main Observations and Possible Sources of Error**

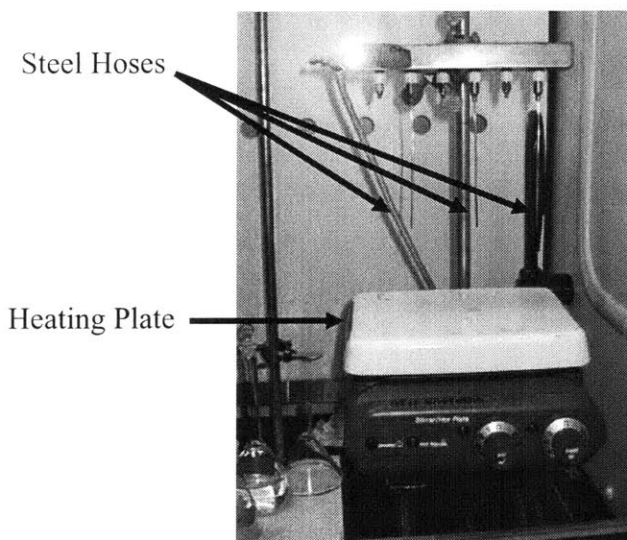
The color of the Raw samples was quite murky; this contrasts to the color of the Final samples, which were nearly colorless (note: chloroform is a colorless liquid at room temperature). This was expected, as the raw water should have more residue compared to the finished water.

Possible sources of error include residue left in the pipette and residue left in the sample bottle. The Pasteur pipette would pick up a lot of the residue left in the sample bottle. But, after transferring the chloroform out of the pipette, some residue would stick in the pipette. Much of this residue could not be taken out of the pipette. In addition, even after rinsing the sample bottom with chloroform, much of the bottle still had a very small layer of residue stuck to it. Even after cleaning out the sample bottle with soap, water, and more chloroform, the residue was still there. Thus, this also affects later samples where the same bottle is used for the rotary evaporation stage. Quantifying this error is tricky, as there is no way of knowing how much of the phosphate triesters were in the residues. But, the residue would have to be taken out at some point, as the GC/MS machine cannot handle solid particles within its system.

#### **D.1.4 Nitrogen Blow Down from 2-15 mL to ~1 mL**

With the labeled 15-mL vials now in hand, the samples were then evaporated in an even more controlled manner by using Nitrogen. Blowing Nitrogen across the surface of the

chloroform promotes mass transfer of the chloroform into the gas phase. These samples were blown down to 1 mL, and were then transferred to a 1-mL vial. The apparatus used is shown in Figure 18.



**Figure 18** Picture of the Nitrogen blow down device. Both the steel hoses' and heating plate's heights can be adjusted as necessary.

#### **D.1.4.1 Procedure**

- Uncap the 15 mL vial, and place in a 10 mL beaker for stability. Place vial under one of the steel hoses.
- Adjust the height of the heating plate and hoses such that the hoses will directly blow Nitrogen into the vial.
- The hoses are connected to a gas tank full of pressurized Nitrogen. First, open the valve that connects the Nitrogen tank with the hoses. Then, turn the Nitrogen tank "on" by turning the tank valve fully. Last, adjust the pressure regulator valve to induce flow through the tank to the hoses. Adjust the regulator valve to get desired flow.
- In addition, turn on the heating plate to add a warm amount of heat. This is done because the Nitrogen flow causes the vial to cool down quickly, retarding the

evaporation process. Thus, to try to keep the vial at a more constant temperature, the vial is heated on the bottom.

- Remove vial when approximately 1 mL is left in the vial. Depending on the starting volume, the process takes 5-30 minutes.

#### **D.1.4.2 Main Observations and Sources of Error**

Up to three samples can be blown down at one time. If the chloroform levels for those three samples varied, the flow of air had to be minimized such that the sample with the highest amount of chloroform had sufficient flow, but the others did not. If the flow was higher, the other samples may get sufficient flow, but the sample with the highest chloroform level would start sloshing.

Heating the bottom of the vial was not very effective, as the vial was usually quite cool after completing the blow down. Yet, heating the vials quickened the evaporation, as the evaporation would have taken an excessive amount of time if not heated.

Sources of error include the drying out of samples. Most of the samples went through the process of going from 400 mL to 1 mL on the same day. Then, the samples were not touched for many days. When Mr. Andrews and the author looked at a few of the samples a few days later, the chloroform was all gone! Thus, some chloroform was added to all dried samples as soon as this was realized, and all 15 mL vials were placed in the refrigerator. As mentioned in section D.1.1, there may have been some losses of the organophosphates after uncapping the vial. This amount cannot be quantified, as the author and Mr. Andrews did not record how long the vials were opened for.

#### **D.1.5 Addition of Sodium Sulfate to Remove any Remaining Water**

Once reducing the sample to 1 mL, sodium sulfate (soda ash) is placed into the 15 mL vial to remove any water that may be in the sample. All water must be removed from the sample because the GC/MS cannot handle water within its system. Using soda ash for the



purpose of removing water is very common because of its ability to hydrate very readily when exposed to water. The resulting salt formed by the soda ash and water keeps its solid state, and any remaining liquid can be removed by decanting, gravity filtration, or in this case, by pipette (Rhodium, 2004).

#### **D.1.5.1 Procedure**

- Add a small amount (~0.5 g) of soda ash to the 1 mL chloroform sample. Swirl the sample to see if clumping forms. If so, add a little more, and swirl until the added soda ash does not clump anymore. This assures that no water remains in the chloroform sample.

#### **D.1.5.2 Major Observations and Sources of Error**

The required amount of soda ash varied for each sample. But, only a couple of samples required the whole bottom of the vial to be covered with soda ash.

Sources of error would be from the complete drying of a sample, or not having enough chloroform to extract for the next process. If there was not enough chloroform, a little bit more chloroform would be added such that there was ~1 mL to extract out.

#### **D.1.6 Transfer from 15 mL Amber Vial to 1 mL Glass Vial, and Nitrogen Blow Down to 100 $\mu$ L**

Now, with about 1 mL of chloroform remaining, the contents in the soda ash-filled vial were placed into a pre-weighed 1 mL glass vial, and then would go through a second Nitrogen blow down until approximately 100  $\mu$ L was reached.

#### **D.1.6.1 Procedure**

- Weigh the 1 mL glass vial, with aluminum foil-lined cap, but without the chloroform sample. Record weight.

- Using a Pasteur pipette, pipette out the remaining chloroform from the 15 mL amber vial into a 1 mL glass vial. To avoid picking up soda ash, shake the soda ash to one side of the vial, and place the pipette on the other side.
- Rinse 15 mL glass vial with a very small amount of chloroform. Pipette out the rinse chloroform and place in the 1 mL vial.
- Place the 1 mL glass vial in a 10 mL glass beaker for stability. Put under steel hoses for a second Nitrogen blow down.
- Reduce volume until  $\sim 100 \mu\text{L}$ , as noted on the markings of the 1 mL vial.
- Weigh glass vial again with chloroform, and record weight.
- Final volume will be between 50 and 200  $\mu\text{L}$ . Label vial as necessary.

#### **D.1.6.2 Major Observations and Possible Sources of Error**

Once the second Nitrogen blow down began, small blobs of fat started to appear in a few samples. This probably happened because there was so little chloroform to keep the fat dissolved in the chloroform. These blobs were removed as carefully as possible, using pokers. Because the blobs were not tested for phosphate triesters, the amount lost due to the removal of these blobs is unknown. Further research should examine these blobs if found in more samples.

The reason for weighing the glass vial before and after the addition of chloroform is to approximate the volume of chloroform before it goes into its final GC/MS vial. The approximate volumes are in Appendix E. The volumes were not necessary to do the subsequent calculations to determine concentrations, but were used to confirm that the volume of 100  $\mu\text{L}$  was roughly attained. Reducing the sample to 100  $\mu\text{L}$  increases sensitivity, as discussed in section 3.

Sources of error may come from the removal of the chloroform from the 15-mL vial. After the complete removal of the chloroform from the 15-mL vial, a very small amount of chloroform may be sticking to the soda ash, and cannot be accessed. Yet, the volume that stuck to the soda ash was probably not too large compared to the volume extracted

out of the vial, as 1 mL was extracted; the author suggests that only ~5% of the 1 mL at most stuck to the chloroform.

### **D.1.7 Transfer from 1 mL Glass Vial to the GC/MS Vial, and Addition of Injection Standard**

One of the last steps before the GC/MS run was to put the final volume of chloroform into a GC/MS vial. Once this step is done, about 10  $\mu$ L of another compound (i.e. the injection standard, which was m-terphenyl in this lab work) is added in the GC/MS vial. The sample is then labeled, and ready for analysis.

#### **D.1.7.1 Procedure**

- Using a 100  $\mu$ L volumetric pipette along with a screw-top bulb, slowly remove the chloroform from the 1 mL glass vial, and transfer directly to the GC/MS vial. Repeat this until all chloroform is transferred.
- Using a 10  $\mu$ L volumetric pipette along with a screw-top bulb, take 10  $\mu$ L of the injection standard stock solution and transfer to the GC/MS vial.
- Label GC/MS vial.
- Refrigerate if not analyzed right away.

#### **D.1.7.2 Major Observations**

The screw-top bulb should not be fully tight before starting a transfer. Instead, it should be slightly loose, so that when the volume goes into the GC/MS vial, the screw-top bulb can then be tightened, thus allowing all of the volume to get out of the volumetric pipette. If not all of the volume was gone after doing this, blowing slightly into the pipette (after being removed from the bulb) caused the volume to leave.

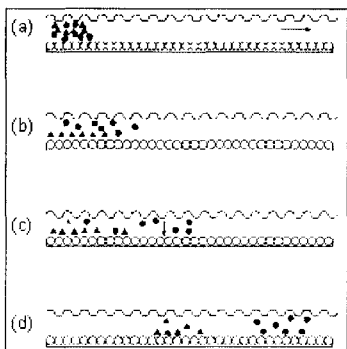
A glass insert was added in the GC/MS vial to hold volumes that are 250  $\mu\text{L}$  or less. If the sample were going to be run, a cap with a rubber septum would be used. If not, a hard cap was used.

The injection standard stock solution used was m-terphenyl in hexane, at a concentration of 1  $\text{ng}/\mu\text{L}$ . From March 9 on, the stock solution was diluted to 200  $\text{pg}/\mu\text{L}$  due to GC/MS sensitivity issues.

## ***D.2 Gas Chromatography/Mass Spectrometry Procedure***

### **D.2.1 How Does a GC/MS Work?**

Gas chromatography, along with mass spectrometry, is one of the most widely used methods to analyze low concentrations of organic compounds. In gas chromatography, 1  $\mu\text{L}$  of the sample goes into an injection port, where it is vaporized and then mobilized by an inert gas (also referred to as the mobile phase). The mobile phase travels through the length of the column, which is lined with an organic material (also referred to as the stationary phase). If the stationary phase is picked correctly, the desired compounds to be analyzed will be slowed down by the stationary phase through interactions (Figure 19). This will result in different elution times coming out of the GC machine (US EPA, 2003). In addition, all of the compound will come out of the GC machine in a discrete band, approximately plus or minus 3 seconds from the elution time.

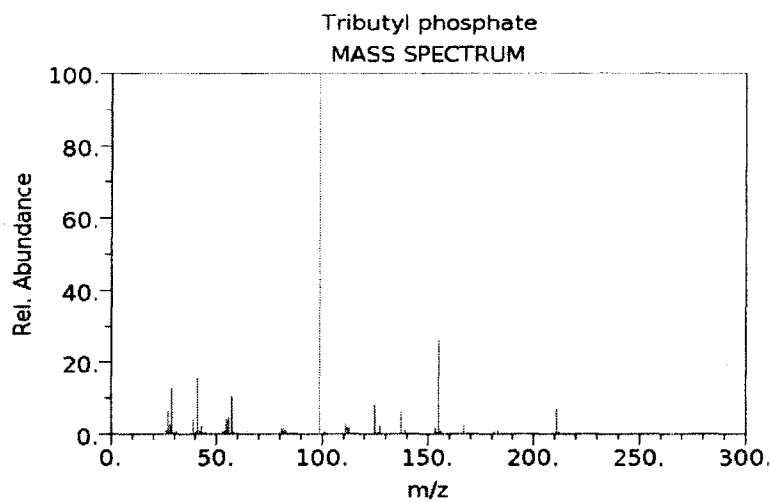


**Figure 19 Simple diagram for how the GC machine works. (a) The compounds are introduced by the mobile phase. (b,c) Compounds that interact more with the stationary phase stay back, and separation starts to occur. (d) The compounds are sufficiently separated, and also stay in discrete bands. Source: US EPA (2003).**

Mass spectrometry analyzes the separated compounds coming out of the GC machine. When the compounds enter the MS machine, an electron beam ionizes them. The loss of an electron generates a charged molecular ion having the same molecular weight as the original molecule. Usually, an electron beam of 20 eV is used to ionize the molecule, while the excess energy from the beam fragments the molecular ion into lower mass to charge ratios (adapted from US EPA, 2003).

The positive ions produced from these ionizations go through the slits of the electron beam and the mass analyzer. These ions are mass analyzed to determine the mass. The negative ions are detected by an electron multiplier, which in turn send out a signal for each type of mass ion. The sum of these signals produces a total ions current (TIC) chromatogram. When a compound goes through the MS, a large number of signals are made, thus producing a peak. These peaks come out at different times according to what happened in the GC machine.

Along with a TIC chromatogram, a mass spectrum is produced for each time. A mass spectrum quantifies how much of each mass ion came out. Due to the significant amount of fragmentation that occurs, each compound has a unique mass spectrum that should be produced every time. These mass spectrums for each compound can usually be found in the GC/MS software or on the web. See Figure 20 for the mass spectrum of TBP, and Appendix G for the mass spectra of TCEP, TBEP, and m-terphenyl. Because multiple compounds may generate their peaks at the same time on the TIC chromatogram, looking at the mass spectrum helps decide what the compound actually is. The ion with the highest peak is also referred to as the base peak.



**Figure 20** Mass spectrum of TBP. Source: NIST (2003)

In this study, the JEOL GCmate semi-high resolution gas chromatograph/mass spectrometer was used. More information on the GC/MS runs used are available in Appendix F.

### **D.2.2 Finding the Mass Spectrums, Peak Times, and Base Peaks for the Organophosphates and the Injection Standard**

Before conducting any runs with the samples, one must find out where the peaks will appear on the TIC chromatogram (that is, the elution times). To do this, a standard with a high concentration (10 ng/μL) of just one of the phosphate triesters was run through the GC/MS. After doing this for each of the phosphate triesters and the injection standard, the elution times were found. TBP eluted at 10 minutes and 58 seconds after injection of the 1 uL, TCEP at 12:16, TBEP at 18:11, and the injection standard at 16:18. Because the elution times were far apart from each other, the peaks formed by the compounds would not overlap. Please look at Appendix H for more details.

But, the concentrations to be measured will be at least an order of magnitude less than the high concentrations used above. Thus, only specific ions are measured to increase sensitivity, as opposed to scanning across the whole mass-to-charge spectrum. Two or

three ions are picked for each compound: the base peak (used later for calculations), and one or two more ions to confirm that what is being measured is actually the compound. For example, in Figure 20, the ions picked are 99.3 (the base peak) and 155.6 (the second highest peak to confirm that the peak is coming from TBP). This same idea was done for each of the four compounds. This type of scanning in the MS machine is called the selected ion monitoring (SIM) method, as opposed to the full scan method used in the high-concentration standards. The SIM method was used for the rest of the samples.

### **D.2.3 Runs: Blanks**

Blanks consisted of chloroform samples that had no foreign organic compounds (i.e. pure chloroform samples). After running these samples through the GC/MS machine, no prevalent peaks were found at the elution times of the phosphate triesters and injection standard. Therefore, the background concentrations from the chloroform do not interfere with the potential peaks formed by the phosphate triesters and injection standard. Please look at Appendix I for details.

### **D.2.4 Runs: Standards**

After running blanks, standards for the phosphates were made. The concentrations of the three standards had 500 pg/ $\mu$ L, 1000 pg/ $\mu$ L, and 2500 pg/ $\mu$ L of all three phosphates. These concentrations were chosen because they would probably be similar to the concentrations in the final samples. In addition, the injection standard had a concentration of 50 pg/ $\mu$ L in each of the three standards. After running these samples, peaks showed up at the correct places, but at different sizes according to the different standard concentrations. The standards determined the number of counts versus unit mass, and determined if there is a Langmuir GC/MS response formed when graphing peak counts versus standard concentrations. After running a significant number of standards, the concentrations were determined to have a linear GC/MS response with a zero intercept,

thus making the value of counts versus unit mass equal to the slope of the line of peak counts versus standard concentration. More discussion is available in section 5.

### **D.2.5 Runs: Determining a Specific Schedule**

After completing the blank runs and standard runs, the samples now needed to be run. After some trial and error, the run schedule for each day was decided to be:

500 Standard

2500 Standard

1000 Standard

Samples (up to 3)

1000 Standard

Samples

1000 Standard...Continue this until all samples finished for that day.

The standards were run in the beginning to determine the counts versus unit mass for that day. The standards in between the samples were used to “clean” the GC from any residual organic compounds still left from the previous run. These standards also had a second use of determining the interactions of the phosphate triesters in the GC stationary phase compared to the injection standard interactions with the GC stationary phase. For example, if the peak size of TBP was 8 times higher than the 1000 ug/L standard run at the beginning of the day, the peak size of the injection standard was also ~8 times higher. Thus, the phosphate triesters interact with the GC column similarly to the m-terphenyl interactions with the GC column. This is important information, as the ratio of the m-terphenyl peak to the phosphate triester peaks are used in calculations. Some examples of runs appear in the Appendix J. All peak values for every run is located in Appendix K.

### **D.2.6 Runs: Spikes**

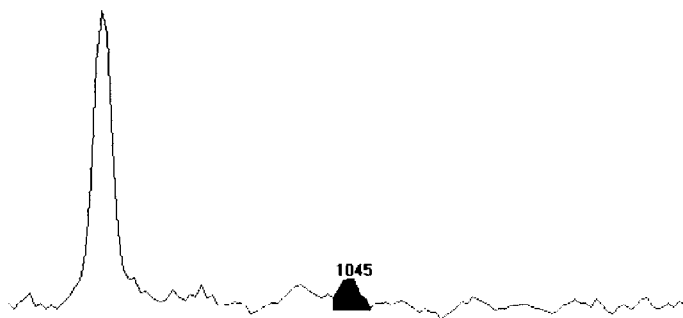


In Cambridge, 200 ng of each phosphate triester was added into a 3.8-liter tap water sample. Then, the whole process done in Atlanta was replicated with this sample, like the shake and bake and the extractions. The sample also went through the whole evaporation process, and was another sample run in the GC/MS. This was done multiple times to accurately determine what the efficiency of removing the phosphate triesters were from the water to the chloroform. Thus, if the peak generated from this run resulted in 120 ng, there would be 60% efficiency in the whole process. This efficiency would be incorporated into the concentrations calculated. For example, if 0.06  $\mu\text{g/L}$  were found in a sample, and there was 60% efficiency, the actual concentration in the river would have been 0.1  $\mu\text{g/L}$ .

### ***D.3 Converting Peak Sizes to Concentrations***

#### **D.3.1 Evaluating Peak Size**

To get the number of counts from the peak, one must first find the base peak of each chemical. After looking at the base peak, the user can either have the software automatically find the peak size or the user can manually pick the peak size. See Figure 21 for details. Whether manually or automatically finding the peak, the software removes any background counts and reports the peak size of the compounds only.



**Figure 21 Example of measuring the peak size of one of the phosphate triesters from the TIC chromatogram.**

Once the peak sizes for each chemical are determined, the next step is to convert these peak sizes to concentrations. Prof. The following equations were used to find the

concentrations (Gschwend, 2003, personal conversation); they involve comparing the peaks of the phosphate triester versus the peak of the injection standard:

$$Peak_{inj.std} = M_{inj.std} \left( \frac{V_{injected\ into\ GC/MS}}{V_{vial}} \right) \cdot R_{inj.std} \quad (1)$$

Where Peak is the peak counts, M is the mass (units of pg) in the vial, V is the volume ( $\mu$ L), and R is the counts per unit mass (1/pg).

The volume of the vial can then be solved for:

$$V_{vial} = \frac{M_{inj.std} \cdot V_{injected\ into\ GC/MS} \cdot R_{inj.std}}{Peak_{inj.std}} \quad (2)$$

Now applying equation 1 to the organophosphate triester, like TBP:

$$Peak_{TBP} = M_{TBP} \left( \frac{V_{injected}}{V_{vial}} \right) \cdot R_{TBP} \quad (3)$$

Substitution of  $V_{vial}$  from equation 3 and rearranging to find  $M_{TBP}$ :

$$M_{TBP} = \left( \frac{Peak_{TBP}}{Peak_{inj.std}} \right) \cdot M_{inj.std} \cdot \left( \frac{R_{injstd}}{R_{TBP}} \right) \quad (4)$$

From data collected, all of the values on the right-hand side can be found:

- Peak (TBP) and Peak (inj.std.) found from TIC chromatogram.
- M (inj.std.) = 10 ng before March 9, and 2 ng at and after March 9.
- R (inj.std.) and R (TBP) determined from standards at the beginning of the day.

The R-value of the injection standards varied quite a bit by day. But, the R-value of the phosphate triesters usually varied by a similar factor. Thus, the ratio of the R-values did not significantly change too much when doing the calculations. In addition, even if the ratio of the R-values significantly changed, the chemicals may as well have different interactions with the GC column for that specific day.

Thus, the mass of TBP in the vial can be found. Dividing that number by the sample size (3.8 liters) resulted in the concentrations. The next section shows the values of these numbers.

### D.3.2 Error Analysis

To place error bars on the samples, Raw #2 was run multiple times through the GC/MS. The three measurements of TBP were quite close, but because of the limited number of runs, the standard deviation may not be quite representative (Table 6). In addition, this multiple-run schedule was done only on Raw #2, so transferring the error bars to other samples may have some fallacies.

**Table 6 Masses of Phosphate Triesters Measured for the Same Sample, Raw #2**

	TBP (ng)	TCEP (ng)	TBEP (ng)
Original mass	200	200	200
Spike 1	520	2000	1200
Spike 2	22	5.5	1400
Spike 3	310	310	740

In addition, the spike samples could also have been used to determine the standard deviations of samples. Unfortunately, the spike samples cannot be used with any confidence for error analysis because the first spike had higher initial amounts of mass that cannot be determined, and the other two spikes had numbers that differed by orders of magnitude.

The inability to determine the statistical reliability of the reported concentrations from the spike standards also means that an efficiency of removing phosphates could not be established with any confidence. Because the efficiency average and standard deviation could not be determined, the variability in the current numbers are probably a little higher than believed, but cannot be quantified.

**Table 7 Masses Found in the three spike samples. Spike 1 cannot be useful because the original mass was not believed to be 200 ng (i.e., the mass was incorrect and not recorded). The other 2 spikes have quite different masses.**

	TBP (ng)	TCEP (ng)	TBEP (ng)
Original mass	200	200	200
Spike 1	520	2000	1200
Spike 2	22	5.5	1400
Spike 3	310	310	740

## APPENDIX E Estimation of Volumes in Vial

Temp Samples: 17 °C
Density Temp: 20 °C

Density of Chloroform (g/mL):	1.492
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	Sample	Empty Vial (g)	Vial w/ Sample (g)	Sample Mass (g)	Volume in Vial (uL) - Scale
WTP	Raw 1	15.1197	15.1815	0.0618	<b>41.4</b>
	Raw 2	14.9633	15.1359	0.1726	<b>115.7</b>
	Ch. Add 1	14.6349	14.9821	0.3472	<b>232.7</b>
	Ch. Add 2	14.9847	15.1111	0.1264	<b>84.7</b>
	Sed 1	15.0727	15.2265	0.1538	<b>103.1</b>
	Sed 2	15.6129	15.7778	0.1649	<b>110.5</b>
	Filter 1	15.3653	15.5954	0.2301	<b>154.2</b>
	Filter 2	15.5167	15.6479	0.1312	<b>87.9</b>
	Final 1	15.2464	15.4974	0.2510	<b>168.2</b>
	Final 2	15.5888	15.7792	0.1904	<b>127.6</b>

### River

Atlanta	Atl 1-0	15.6626	15.7464	0.0838	<b>56.2</b>
	Atl 1-5	15.5637	15.7129	0.1492	<b>100.0</b>
	Atl 1-24	15.0166	15.2162	0.1996	<b>133.8</b>
	Atl 2-0	15.5064	15.7167	0.2103	<b>141.0</b>
	Atl 2-5	15.8068	16.0232	0.2164	<b>145.0</b>
	Atl 2-24	9.0499	9.2624	0.2125	<b>142.4</b>
	Atl 3-0	9.2303	9.457	0.2267	<b>151.9</b>
	Atl 3-5	9.5342	9.7623	0.2281	<b>152.9</b>
	Atl 3-24	15.0246	15.1527	0.1281	<b>85.9</b>

Morgan Falls	MF 1-0	15.6353	15.7931	0.1578	<b>105.8</b>
	MF 1-5	15.154	15.2811	0.1271	<b>85.2</b>
	MF 1-24	15.7411	15.9475	0.2064	<b>138.3</b>
	MF 2-0	15.7122	15.874	0.1618	<b>108.4</b>
	MF 2-5	9.2398	9.4745	0.2347	<b>157.3</b>
	MF 2-24	9.1871	9.4534	0.2663	<b>178.5</b>

Roswell	Ros 1-0	15.402	15.5259	0.1239	<b>83.0</b>
	Ros 1-5	15.0702	15.212	0.1418	<b>95.0</b>
	Ros 1-24	14.7603	14.9218	0.1615	<b>108.2</b>
	Ros 2-0	15.0205	15.23	0.2095	<b>140.4</b>
	Ros 2-5	15.4114	15.5853	0.1739	<b>116.6</b>

Ros 2-24	15.4652	15.6507	0.1855	<b>124.3</b>
Ros 3-0	15.0335	15.2662	0.2327	<b>156.0</b>
Ros 3-5	15.1298	15.315	0.1852	<b>124.1</b>
Ros 3-24	15.5476	15.76	0.2124	<b>142.4</b>

Buford	Buf 1	9.3551	9.7665	0.4114	<b>275.7</b>
	Buf 2	9.2659	9.5055	0.2396	<b>160.6</b>
	Buf 3	9.3442	9.5327	0.1885	<b>126.3</b>

## **APPENDIX F Description of GC/MS Runs**

Equipment Used: JEOL GCmate semi-high resolution gas chromatograph-mass spectrometer.

Run time: 25 minutes.

Initial oven temperature: 70 °C

- After injection, hold temperature for 1 minute.

Final oven temperature: 300 °C

- Linearly ramp temperature from 70 °C to 300 °C from 1 minute to 20 minutes after injection.
- Hold temperature from 20 minutes to 25 minutes after injection.

Carrier gas: Helium

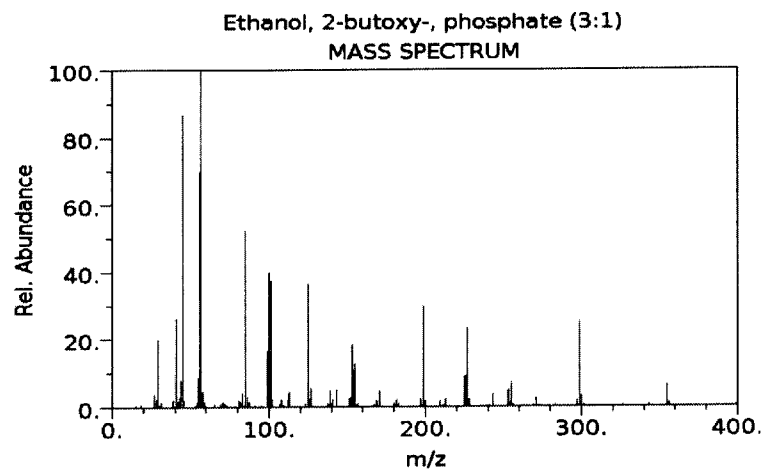
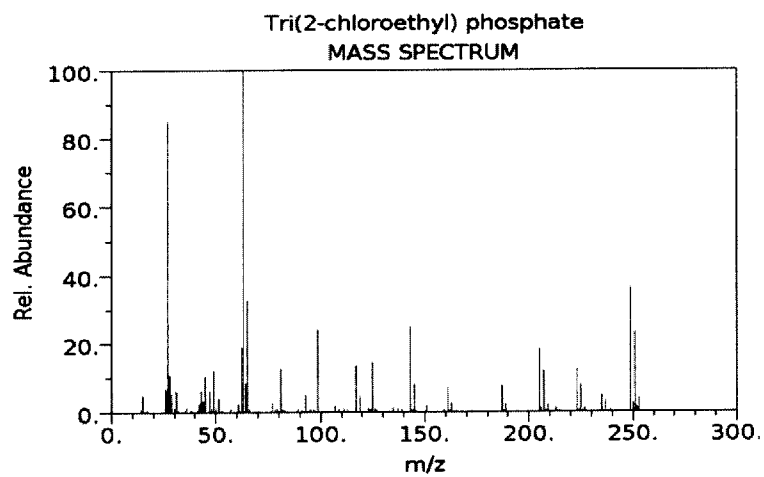
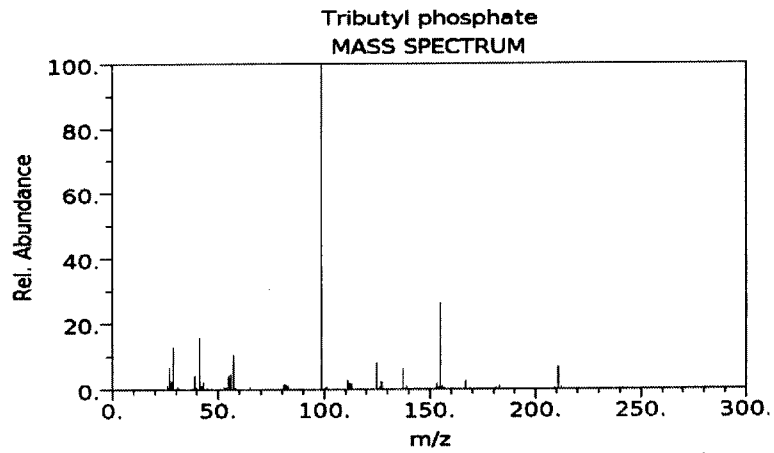
Flow rate: 2 mL/min.

Transfer line temperature: 280 °C

EI impact voltage: 300  $\mu$ Amps

Software Used: JEOL's Shrader software.

## APPENDIX G Mass Spectra for TBP, TCEP, and TBEP (NIST, 2004)



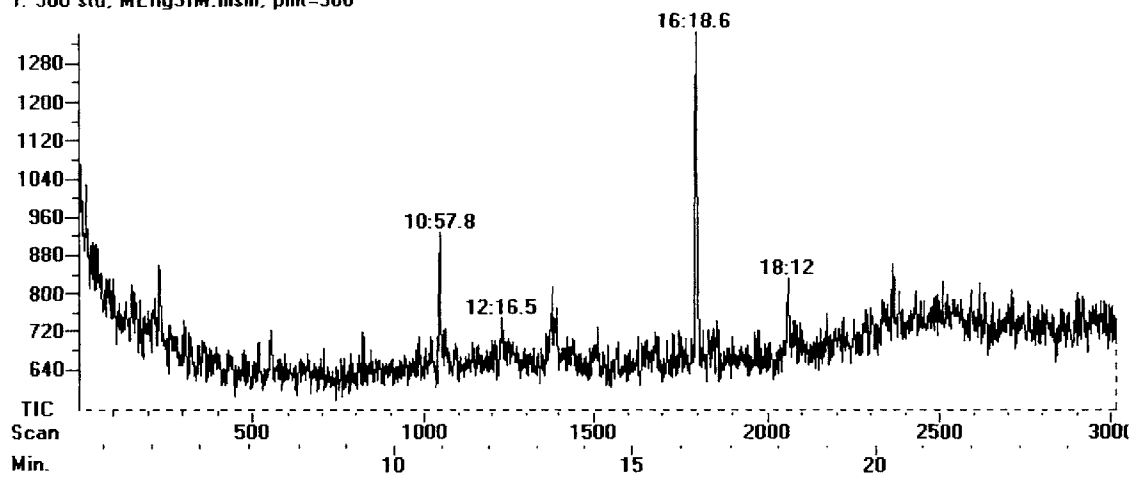


## APPENDIX H Example of Standards Run, and Measuring Peaks

500 pg/ $\mu$ L Standard (March 9, 2004)

030951

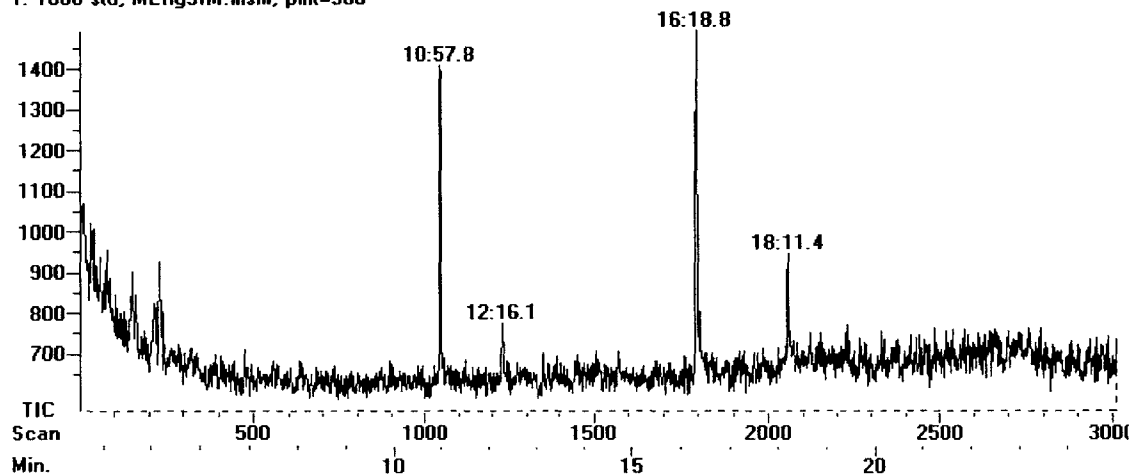
1. 500 std; MEngSIM.msm; pmt=500



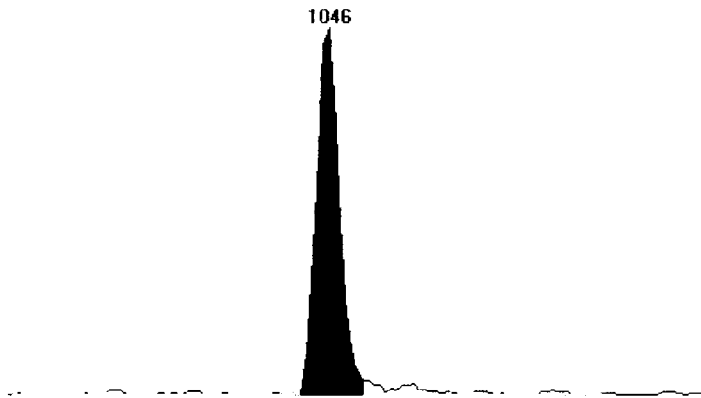
1000 pg/ $\mu$ L Standard (March 9, 2004)

030953

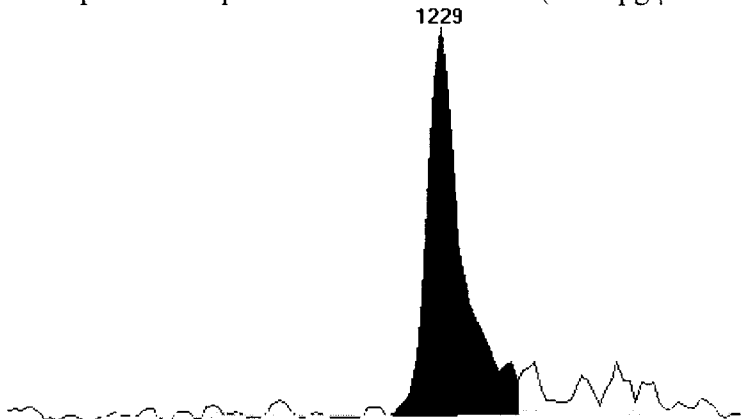
1. 1000 std; MEngSIM.msm; pmt=500



Example of 99.3 peak measured for TBP (2500 pg/ $\mu$ L standard, March 9, 2004)



Example of 63.2 peak measured for TCEP (2500 pg/ $\mu$ L standard, March 9, 2004)

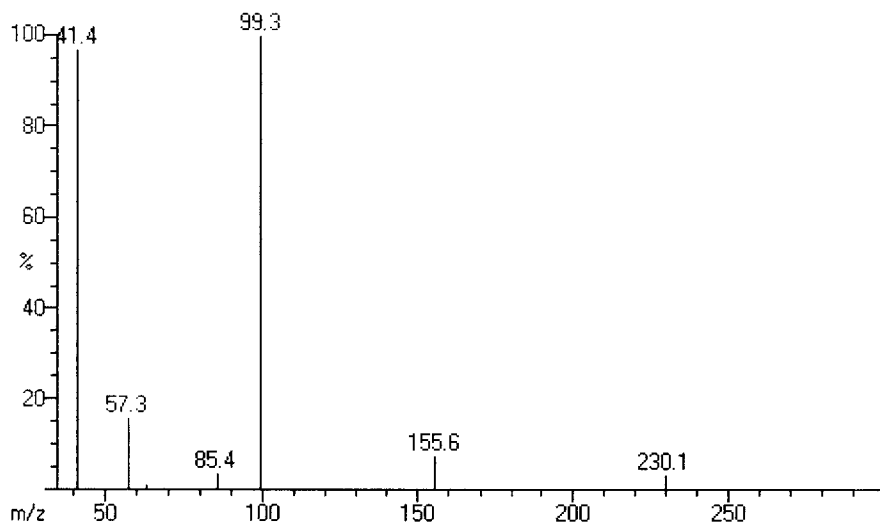


Mass Spectrum for TBP (Using SIM, 2500 pg/ $\mu$ L standard, March 9, 2004)

0309S2

1. 2500 std: MEngSIM.msm; pmt=500

Scan: 1045(984-995, 1081-1092) TIC=1958 Base=.08%FS #ions=7 RT=10:57.5

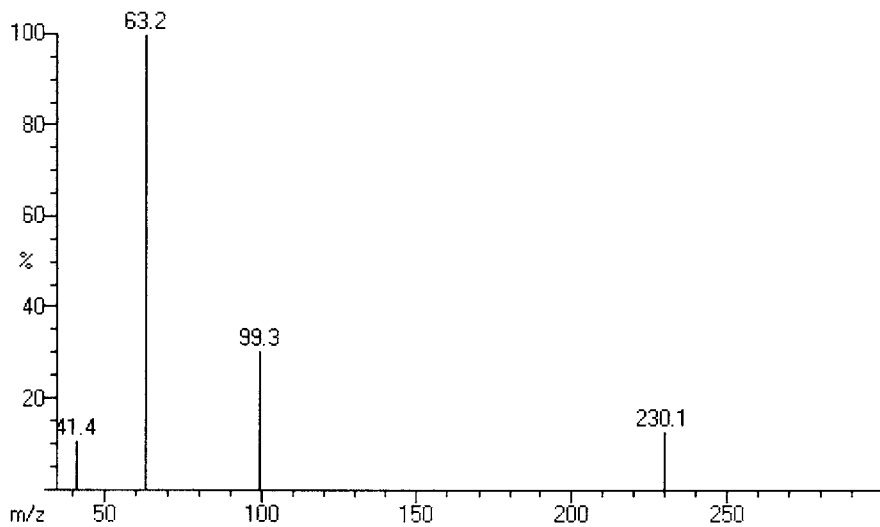


Mass Spectrum for TCEP (Using SIM, 2500 pg/ $\mu$ L standard, March 9, 2004)

0309S2

1. 2500 std: MEngSIM.msm; pmt=500

Scan: 1229(1195-1206, 1279-1290) TIC=462 Base=.03%FS #ions=7 RT=12:16.2

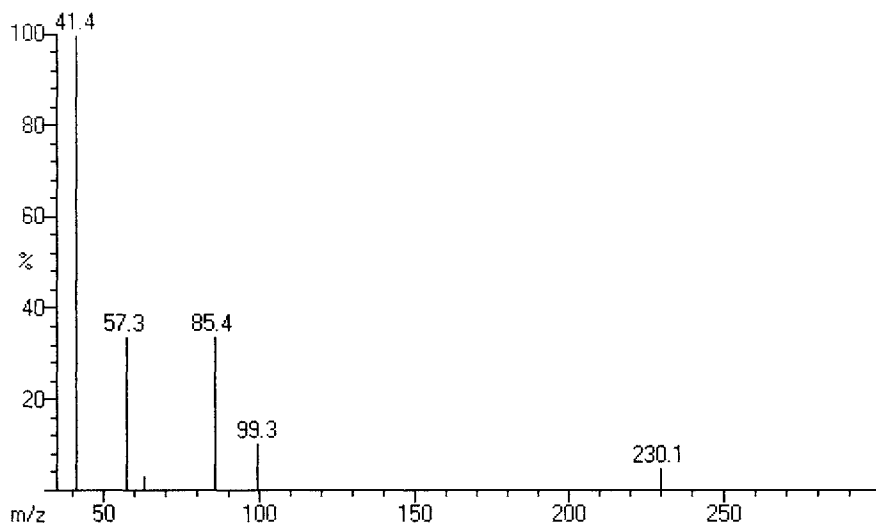


Mass Spectrum for TBEP (Using SIM, 2500 pg/ $\mu$ L standard, March 9, 2004)

0309S2

1. 2500 std; MEngSIM.msm; pmt=500

Scan: 2059(2027-2038, 2102-2113) TIC=668 Base=.03%FS #ions=7 RT=18:11.4

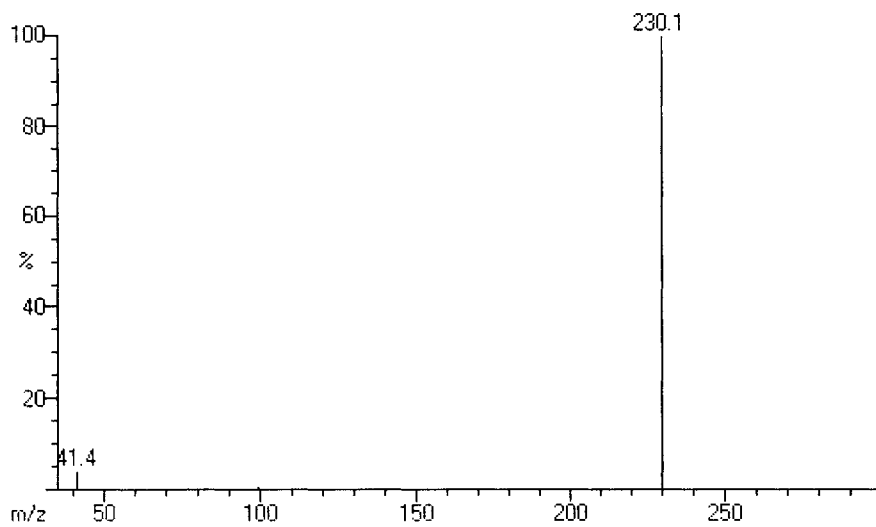


Mass Spectrum for Injection Standard (Using SIM, 2500 pg/ $\mu$ L standard, March 9, 2004)

0309S2

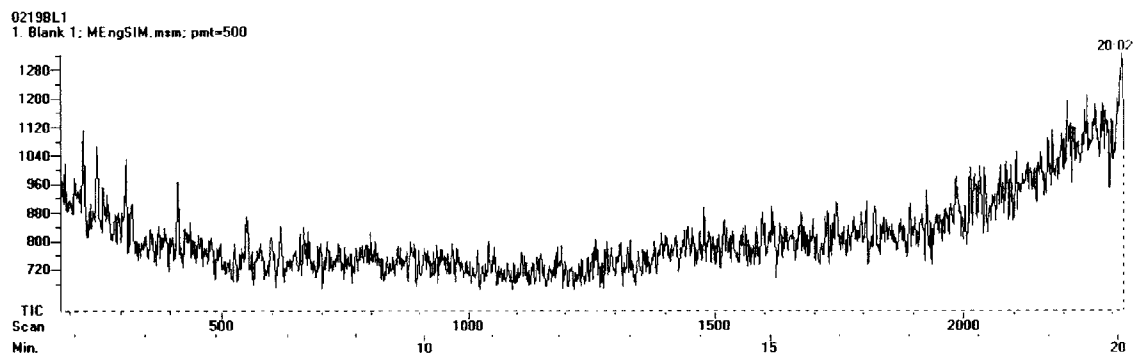
1. 2500 std; MEngSIM.msm; pmt=500

Scan: 1794(1778-1789, 1841-1852) TIC=1030 Base=.09%FS #ions=7 RT=16:18



# APPENDIX I Example of Blank Run

Example of blank run (February 19, 2004)

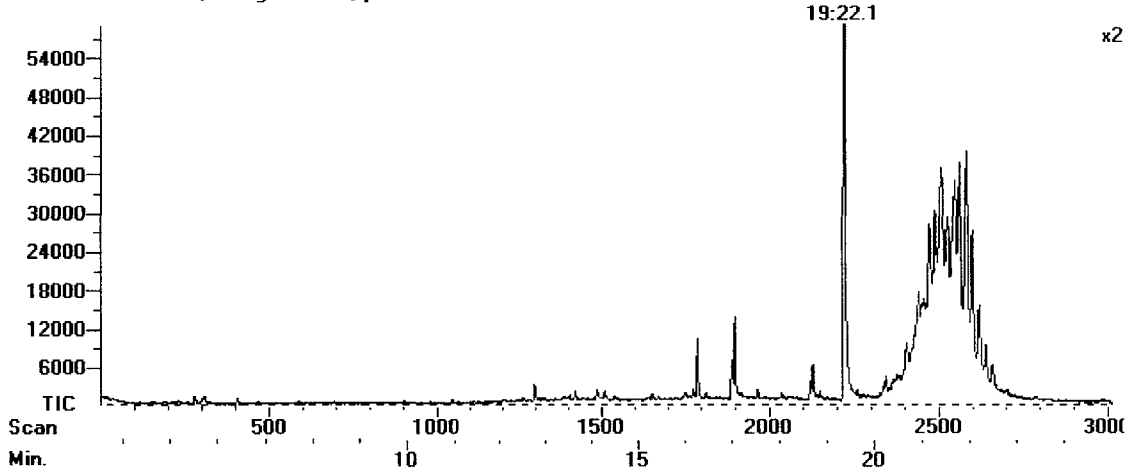


## APPENDIX J Examples of Sample Runs

Example of Sedimentation #2 (March 9, 2004)

0309SED2

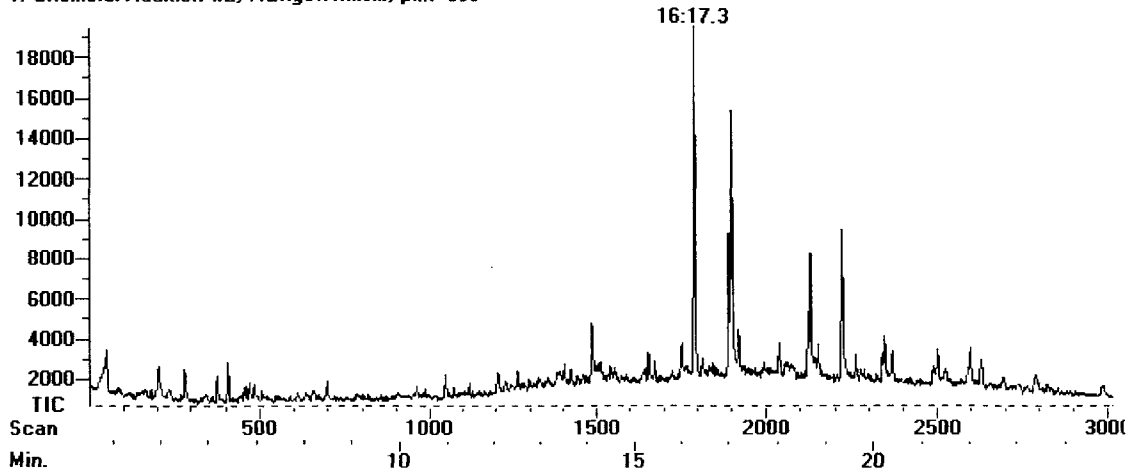
1. Sedimentation #2; MEngSIM.msm; pmt=500



Example of Chemical Addition #2 (March 9, 2004)

0309CH2

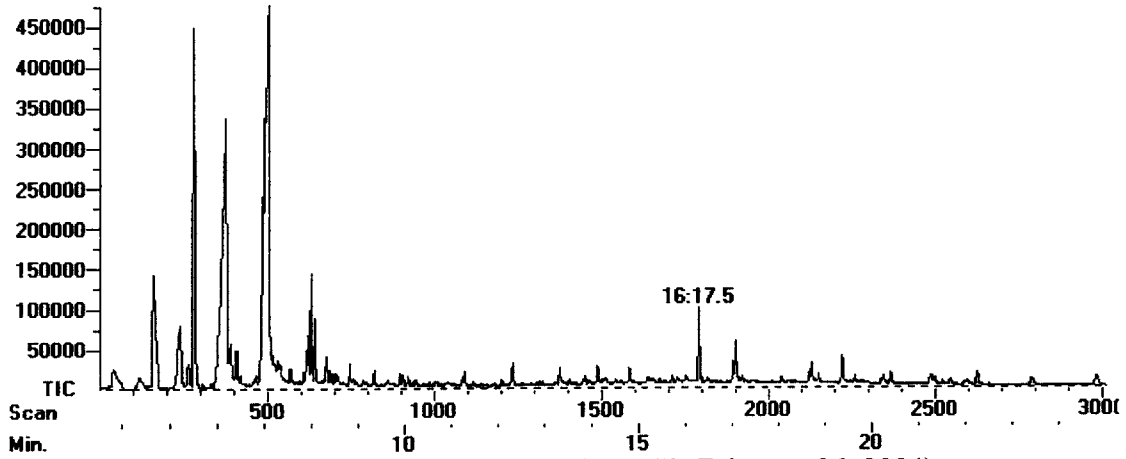
1. Chemical Addition #2; MEngSIM.msm; pmt=500



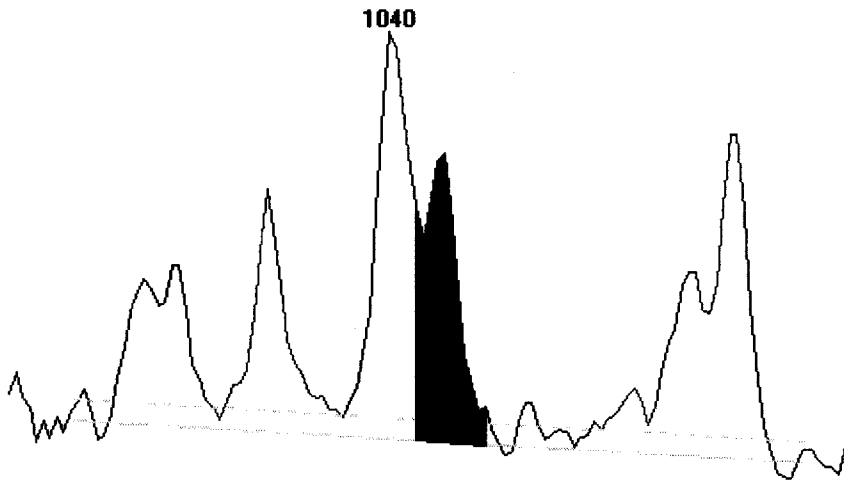
Example Raw #2 (February 26, 2004)

0226RAW3

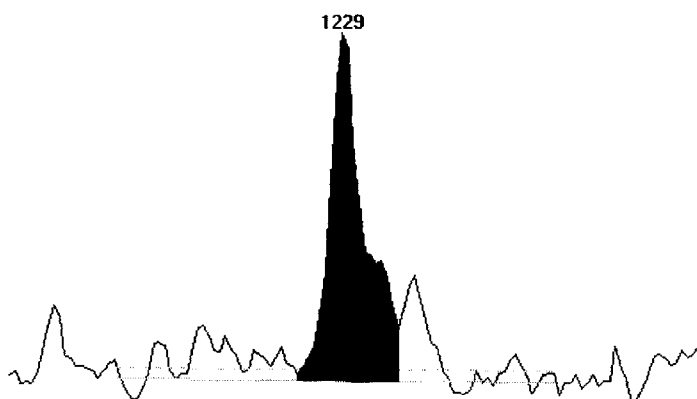
1. Raw #2 with 500pg added; MEngSIM.msm; pmt=500



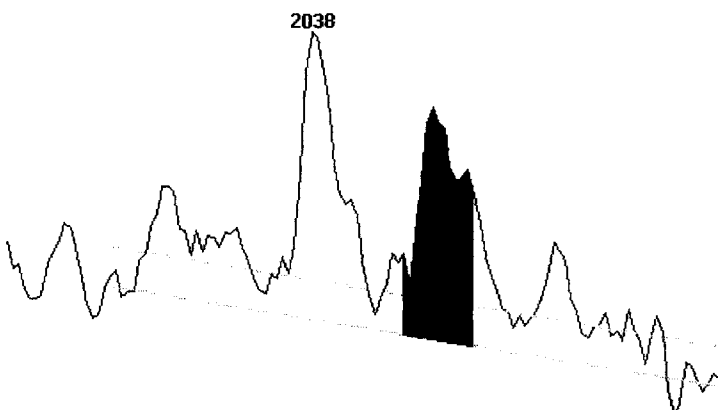
Example of measuring the 99.3 peak for TBP (Raw #2, February 26, 2004)



Example of measuring the 63.2 peak for TCEP (Raw #2, February 26, 2004)

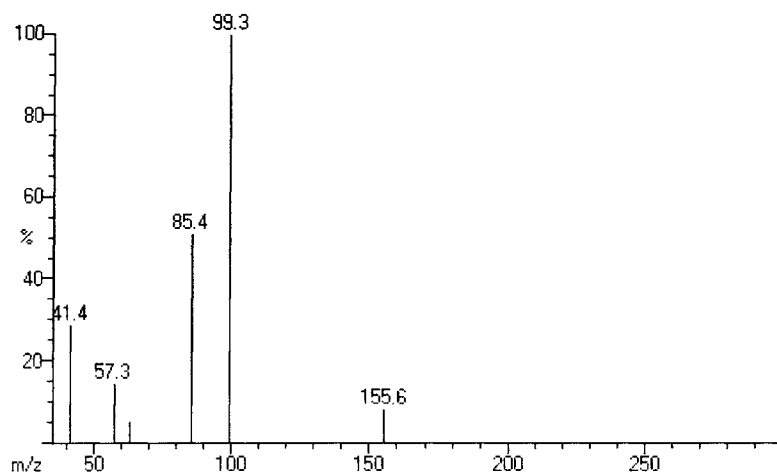


Example of measuring the 57.3 peak for TBEP (Raw #2, February 26, 2004)



Example of TBP mass spectrum (SIM, Raw #2, February 26, 2004)

0226RAW3  
1. Raw #2 with 500pg added; MEngSIM.msm; pmt=500  
Scan: 1048(988-999, 1096-1107) TIC=2562 Base=.12%FS #ions=7 RT=10:59.1



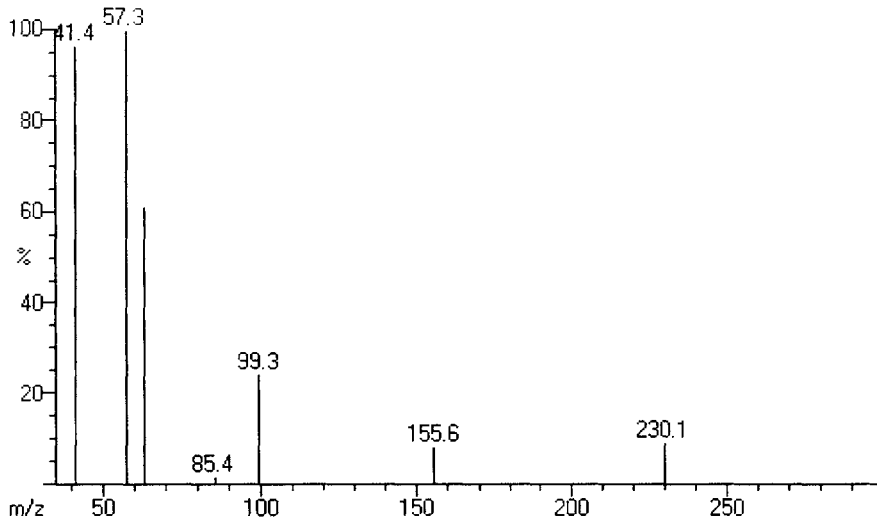


Example of TCEP mass spectrum (SIM, Raw #2, February 26, 2004)

0226RAW3

1. Raw #2 with 500pg added; MEngSIM.msm; pmt=500

Scan: 1229(1183-1194, 1262-1273) TIC=4571 Base=15%FS #ions=7 RT=12:16.6

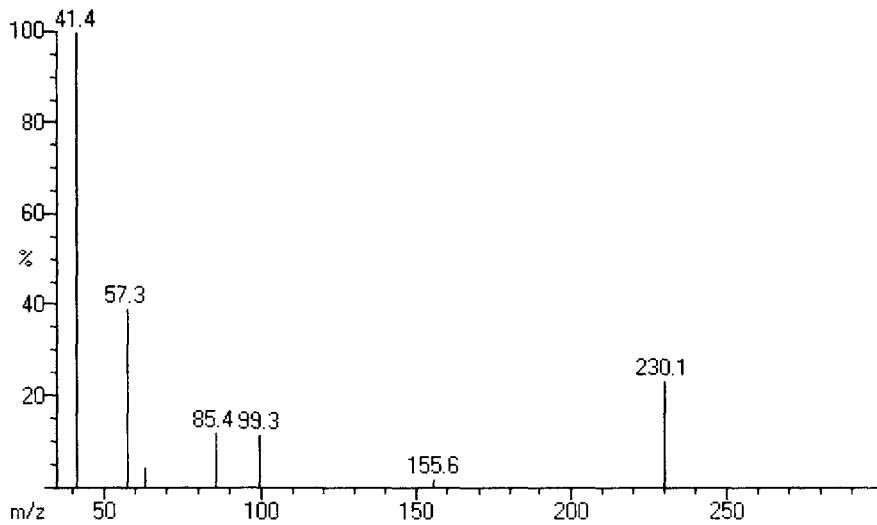


Example of TBEP mass spectrum (SIM, Raw #2, February 26, 2004)

0226RAW3

1. Raw #2 with 500pg added; MEngSIM.msm; pmt=500

Scan: 2060(1998-2009, 2104-2115) TIC=2390 Base=12%FS #ions=7 RT=18:12.2



## APPENDIX K Listing of all Runs Done in the Cambridge Lab

Date	Time	File Name	Sample Name	10:58 TBP (99.3) Background	12:16 TCEP (63.2) Background	18:11 TBEP (57.3) Background	16:18 Inj Std Background		
START OF GC/MS RUNS									
11-Feb	9:19	0211astd	500 std	781	810	915	936	167	474
			57.1 was double peak, hard to get accurate area; 250 peak in use						
11-Feb	10:15	0211bstd	1000 std	1277	693	1692	1463	578	1404
11-Feb	10:47	0211cstd	2500 std	3255	858	4036	1040	1939	1720
11-Feb	11:23	0211ast1	500 std	741	1482	751	1040		
			57.1 and 41.3 unidentifiable						
11-Feb	11:58	0211cst1	2500 std	3872	858	4429	1200	1977	1640
			good peaks						
11-Feb	2:27	0211spk2	Spike #1	93943	2132	809275	3345	1326554	27600
			abnormally high results						
11-Feb	3:04	0211raw1	Raw #1	18832	11802			69437	82161
			double peak for 57.3; couldn't identify TCEP; need to run again, much static last half of analysis						
11-Feb	4:02	0211a101	Atlanta 1-0	62186	52459	191809	15526	1031165	564256
			12:17 for TCEP; 18:13.7 for 57.3; 18:14.1 for 41.4; still identified as compounds						
12-Feb	7:54	0212chl	Blank						
			250 peak in use, no injection standard						
12-Feb	8:44	0212std	500 std	1419	1105	928	1566		
			unidentifiable TBEP, large increase in background after 13 min.; injection standard introduced (230.1), 250 still in use					441642	14050
12-Feb	9:09	0212std1	1000 std	3676	1176	1952	913	1424	8232
			inj std in use, 250 peak in use; 57.3 bad peak, lots of noise						
12-Feb	9:43	0212std2	2500 std	6264	1032	4238	1408	3529	6468
			inj std in use full time, 250 peak removed permanently; TBEP hard to identify						
12-Feb	10:09	0212chl1	Blank						
			looked clear of phosphates						
12-Feb	10:44	0212mrec	Spike #1, Run 2	25408	1176	103770	1540	189903	19228
			for some reason, no inj. std., should have been						
12-Feb	11:09	0212a100	Atlanta 1-0	3651	2322	13739	2210	72338	39312
			no 250 peak: inj std in use					451973	27586

12-Feb	2:06	0212a105	Atlanta 1-5	13065	4752	19758	7872	33266	43846	1427584	107088
12-Feb	2:33	0212std4	500 std TBEP hard to identify with double peak	8324	1430	3008	1512	33588	51091	1123157	22528
12-Feb	2:57	0212chl2	Blank relatively smooth								
12-Feb	3:22	0212raw1	Raw #1 57.3 a double peak, uncertain result	7332	2418	855	1360	17262	24894	1029752	60816
12-Feb	3:46	0212raw2	Raw #2 10:56.5 for 99.3; 12:17.5 for 63.2	59128	31785	12060	4548	32351	50064	1717560	118954
12-Feb	4:11	0212std5	1000 std	36793	3601	8809	1610	8120	23184	1470301	28446
13-Feb	9:29	0213inj	Inj. Std. By itself							430211	5004
13-Feb	9:54	0213std	500 std a lot of noise around 18:12, so results are sketchy; began using 50uL for injection instead of 100uL	2950	1170	1199	1120			101178	3234
13-Feb	10:19	0213std1	1000 std	5335	1064	2290	1200	1956	2740	92376	2112
13-Feb	10:44	0213a124	Atlanta 1-24	1515	1323	1676	1419	3892	6903	442472	18447
13-Feb	11:09	0213std2	1000 std	8033	1288	3549	1162	2462	4202	187639	19578
13-Feb	11:33	0213fin1	Final #1	2247	1917	831	2332			341992	34056
13-Feb	11:58	0213std3	2500 std too much noise last five minutes to discern TBEP data	43576	1440	15468	1440			374625	23298
13-Feb	12:23	0213chl	Blank								
13-Feb	3:37	0213std4	500 std 57.3 had several localized peaks, difficult to discern: starting with this run, all runs are for 30 minutes	7582	1600	2551	1188			291862	5448
13-Feb	4:16	0213r100	Roswell 1-0	43802	20616	109213	16185	304098	117266	1499547	110447
17-Feb	9:37	0217std	1000 std 57.3 not discernable, 41.4 pretty noisy, entire line was full of terrible noise	2943	1989	1735	1980			153438	13734
17-Feb	10:19	0217bl1	Blank								
17-Feb	11:01	0217spk	Spike #1 w/Inj. Std. peaks too high, something wrong	69565	1300	153150	1200	244575	5152	450998	2904



18-Feb	3:59	0218std4	1000 std	34104	1358	1579683	2325	23177	9690	581091	9480
			63.2 is off by ~2 sec, 16:17.9								
19-Feb	9:14	0219std1	1000 std	324609	1526	913129	1540	6779	3528	123839	3939
19-Feb	9:44	0219bl1	Blank								
19-Feb	10:14	0219spk1	Spike #2	18767	1287	12837	1652	25251	6024	25731	5104
19-Feb	10:44	0219inj	Injection Standard							414854	1904
19-Feb	11:14	0219std2	2500 std	19750	1148	204857	1288	5568	2080	166939	1680
19-Feb	11:44	0219m105	Morgan Falls 1-5	6040	4896	14903	6060	33645	21336	1895683	86064
19-Feb	12:14	0219bu1	Buford #1	1643	1826	3963	2370	9354	8840	214097	25848
19-Feb	12:44	0219std3	1000 std	19566	1410	1551377	1876	15917	8214	310523	4128
			63.2 late again on std, 12:17.8								
20-Feb	3:27	0220s1	500 std	1701	984	922	1743	353	1196	88644	2040
			today was all new standards from scratch								
20-Feb	3:57	0220s2	2500 std	9959	1360	6811	1530	2317	1764	118117	2074
20-Feb	4:27	0220s3	1000 std	3124	960	1912	1494	642	990	109553	1935
20-Feb	4:57	0220m124	Morgan Falls 1-24	1147	1920	99566	2338	19181	12060	655327	40044
20-Feb	5:27	0220s4	1000 std	5605	1275	4050	1456	2182	3528	242768	3750
23-Feb	10:52	0223inj	Inj. Std.							49451	2304
26-Feb	8:38	0226s1	500std	905	1377	831	1909	285	1020	68219	2247
26-Feb	9:29	0226s2	2500 std	4164	1120	3169	1328	1238	1118	66580	1836
26-Feb	10:11	0226s3	1000 std	1405	960	962	1312	630	1092	65463	2120
26-Feb	10:45	0226raw3	Raw #2 w/500 pg added	5536	5770	4247	3487	5620	10336	423574	27264
			very rough estimates for TBP and TBEP								
26-Feb	12:21	0226s4	1000 std	3742	1632	3411	1734	1170	2431	161377	3468
26-Feb	1:01	0226s5	1000 std	2528	1106	2719	2025	725	864	134564	1495
26-Feb	1:42	0226raw4	Raw #2 w/1000 pg added	3007	3600	3827	5336	4568	8010	226222	14168

26-Feb	2:23	0226s6	1000 std	6000	1428	4548	1848	1324	1764	193650	1738
27-Feb	14:26	0227s1	500 std.	1481		1149		457		130608	
27-Feb	15:08	0227s2	2500 std.	5926		5125		2387		132130	
27-Feb	15:49	0227s3	1000 std.	2285		1938		880		122408	
27-Feb	16:30	0227raw5	Raw #2 w/2000 pg added	1806		1439		3483		168045	
27-Feb	17:11	0227s4	1000 std.	3371		2751		1162		162876	
27-Feb	17:42	0227r100	Ros. 1, 0 hours	12451		47278		145330		639403	
27-Feb	18:14	0227r105	Ros. 1, 5 hours	8885		14509		43524		872769	
27-Feb		0227r124	Ros. 1, 24 hours	6199		4423		32552		997866	
27-Feb		0227s5	1000 std.	12676		8277		3091		399536	
1-Mar		0301s1	500 std	852		967		632		88011	
1-Mar	10:04	0301s2	2500 std	4564		4114		1906		75877	
1-Mar	10:43	0301s3	1000 std	2199		1927		938		85691	
1-Mar	11:24	0301sed1	Sedimentation #1	2030		1809		738		260645	
1-Mar	12:02	0301fil1	Filter #1	2066		492	ND			270754	
1-Mar	12:44	0301fin1	Final #1 57.3 peak was made on scan count 2057	2022		1028		669		297784	
1-Mar		0301s4	1000 std	7058		4766		2147		198022	
1-Mar	1:57	0301m100	Morgan Falls 1-0 41.3 a sec earlier than 57.3	1075		2989		3397		150175	
1-Mar	2:28	0301m105	Morgan Falls 1-5	944		1971		3973		238108	
1-Mar	3:10	0301m124	Morgan Falls 1-24	881		46507		8160		234841	
1-Mar	3:42	0301s5	1000 std	6462		3817		1521		164006	
1-Mar	4:14	0301buf1	Buford #1	1021		4286		12164		305949	
1-Mar	4:45	0301s6	1000 std	11290		4928		1364		186600	

4-Mar	9:56 0304s1	500 std	899	455	134	2179
4-Mar	11:58 0304s2	2500 std	3240	2080	838	3938
4-Mar	12:36 0304s3	1000 std	1122	542	456	4030
4-Mar	1:14 0304a200	Atlanta 2-0	6250	16238	ND	179268
4-Mar	1:47 0304a205 lotta noise after 15 mins	Atlanta 2-5	907	6939	8156	80976
4-Mar	2:29 0304a224	Atlanta 2-24	2405	10677	11379	71909
4-Mar	3:01 0304s4	1000 std	5784	4245	1672	42956
5-Mar	3:13 0305s1	500 std	952	508	435	11190
5-Mar	3:43 0305s3	2500 std	5319	3954	1415	12518
5-Mar	4:13 0305s2	1000 std	1804	1159	653	12071
5-Mar	5:44 0305s6	1000 std	2971	2981	1055	29503
5-Mar	6:13 0305r200	Roswell 2-0	443	3563	6217	76694
5-Mar	6:43 0305r205	Roswell 2-5	2006	2749	12561	171698
5-Mar	7:13 0305r224	Roswell 2-24	4337	75433	10859	143456
5-Mar	7:43 0305s4	1000 std	8533	6264	2967	64315
5-Mar	8:13 0305spk3	Spike #3	43778	27838	71997	723040
5-Mar	8:43 0305s5	1000 std	6291	5669	1648	51761
5-Mar	4:43 0305fil2 Double peaks at 57.3	Filter #2	2659	56935	5654	135115
5-Mar	5:14 0305fin2 Double peaks at 57.3	Final #2	2177	119214	2328	91733
9-Mar	10:30 0309s1 57.3 a bad double peak, wouldn't count it	500 std	522	444	124	4605
9-Mar	11:00 0309s2	2500 std	3896	2080	961	6327
9-Mar	11:30 0309s3	1000 std	1422	659	396	5871

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9-Mar	12:00	0309sed2	Sedimentation #2	1025	1186	1107	45625
			57.3 and 41.4 probably a ND				
9-Mar	12:30	0309ch2	Chemical Addition #2	2689	2409	1778	83930
9-Mar	1:00	0309s4	1000 std	1889	1902	504	17337
9-Mar	1:30	0309buf2	Buford #2	231	621	2355	45203
			99.3 basically a nodetect, essentially just noise				
9-Mar	2:00	0309buf3	Buford #3	676	508	7505	71630
			57.3 a little shaky				
9-Mar	2:29	0309s5	1000 std	3739	2701	1084	26815
9-Mar	2:59	0309m200	Morgan Falls 2-0	1979	2232	82255	77423
9-Mar	3:53	0309m205	Morgan Falls 2-5	26281	20616	51333	71088
			something's not right, values are way too high				
9-Mar	4:23	0309m224	Morgan Falls 2-24	1223	3815	2544	48037
9-Mar	4:52	0309s6	1000 std	4804	3666	784	31717
10-Mar	10:17	0310s1	500 std	425	620	392	16114
			230.1 double peak				
10-Mar	10:47	0310s2	2500 std	3813	1.27606667	2823	10445
10-Mar	11:17	0310s3	1000 std	1453	1105	633	10550
10-Mar	11:47	0310r300	Roswell 3-0	559	1206	2522	50833
10-Mar	12:17	0310r305	Roswell 3-5	1531	1650	15618	91700
			57.3 and 41.4 probably a ND (took peaks that were near scan 2059)				
10-Mar	12:47	0310r324	Roswell 3-24	525	723	4980	134992
10-Mar	13:16	0310s4	1000 std	7089	4774	2121	63666
10-Mar	13:46	0310a300	Atlanta 3-0	8388	10575	43974	118198
10-Mar	14:16	0310a305	Atlanta 3-5	12367	8957	6179	105013
10-Mar	14:46	0310a324	Atlanta 3-24	11494	5110	13567	215044
10-Mar	15:15	0310s5	1000 std	7570	5161	2424	55736