

Courtesy of Matt Andrews, Sam Haffey, Joe Lin, and Alexandros Machairas. Used with permission.

# Proposal for Chattahoochee River Water Quality Study

Drug Store Cowboys Inc.

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## **Introduction**

During the summer of 1999 the U.S. Center for Disease Control (CDC), in cooperation with the United States Geological Survey (USGS), performed an extensive sampling study of the Chattahoochee River Basin along a fifty-mile stretch just north of Atlanta, Georgia. The purpose of the study was to measure concentrations of several pharmaceuticals, personal care products (PPCPs), and organic wastewater compounds (OWCs) at several sites within the basin. In particular, the focus was on major point sources to the river, namely wastewater treatment plant effluents, along with concentrations both within the river at the point of intake for drinking water treatment and post-wastewater treatment discharge. The CDC performed a preliminary statistical analysis of the data resulting from the study, and is now seeking an environmental engineering firm to complement this work by lending their unique perspective and carrying out their own study of the data. The CDC has expressed interest in having their data evaluated from an engineering point of view in hopes of drawing sound, well-supported conclusions. One especially desired result is to have a surface water quality model developed that accurately depicts the fate and transport of PPCPs and OWCs in the Chattahoochee River.

A Request for Proposal was released by the CDC in early September, 2003 with a December 5, 2003 response deadline. Drugstore Cowboys, Inc. is pleased to submit a proposal for the investigatory analysis of pollutant loading and transport in the Chattahoochee River. In conjunction with the submitted written proposal a regularly updated website outlining Drugstore Cowboys, Inc.'s efforts thus far can be found at <http://web.mit.edu/andrewsm/www/DrugstoreCowboys.htm>.

### **Company Profile**

Drugstore Cowboys, Inc. is a young and prosperous environmental engineering consulting firm with expertise in a wide range of environmentally related topics. We take pride in developing and implementing innovative and environmentally friendly solutions

to pressing environmental problems, while remaining mindful of the current demand for sustainable development.

Four experienced senior engineers, Matthew Andrews, Joseph Lin, Samuel Haffey, and Alexandros Machairas, comprise Drugstore Cowboys, Inc. All have the educational and professional background that allows them to provide solutions to the most demanding problems. In addition, Drugstore Cowboys, Inc., through their collaboration with the Department of Civil and Environmental Engineering at the Massachusetts Institute of Technology (MIT), has established a panel of expert advisors comprised of distinguished members of MIT's academic community. This panel includes Dr. Eric Adams, Dr. Peter Shanahan, Dr. Philip Gschwend, and Dr. Tina Voelker.

Because each member of Drugstore Cowboys, Inc. brings a different background to the company, we bring a competitive advantage in that our company can analyze a situation through many different perspectives. This allows Drugstore Cowboys, Inc. to design remediation schemes and develop best management practices that attack the problem in question thoroughly. Thus, our company can ensure the CDC that the solutions we propose are viable, and will not become a problem in the future.

The resumes of our senior engineers are attached in the Appendix.

### **The Selected Family of Chemical Compounds – Phosphate Esters**

After careful consideration of the available data, extensive literature review, and deliberation over maximizing the possible positive impact of our findings, Drugstore Cowboys, Inc. proposes to investigate the fate of a group of phosphate esters.

This group is comprised of three phosphate esters: tributyl phosphate (TBP, CAS # 126-73-8), tri(2-chloroethyl) phosphate (TCEP, CAS # 115-96-8), and tri(2-butoxyethyl) phosphate (TBEP, CAS # 78-51-3). Drugstore Cowboys, Inc. has chosen these phosphate esters based on the following reasons:

- The CDC-USGS study detected these compounds in most of the samples.
- Many other studies report the presence of these compounds in surface water and drinking water.
- The phosphate esters exhibit some similar chemical characteristics, where other chemicals in the CDC-USGS study having a high percentage of detection did not exhibit similar properties.
- They are widely used as flame-retardants, plasticizers, and other various products.
- They exhibit significant presence in the environment.
- To our knowledge, there has not been any prior research on their fate in the aquatic environment.

Analytical methods with high accuracy are available for measuring their concentration even in the order of parts per trillion.

### **The Objective of the Drugstore Cowboys, Inc. Group Study**

The main objective of the proposed study is to identify the natural degradation processes that most greatly affect the selected phosphate esters in the aquatic environment and to confirm this identification with analysis of the known data and the Drugstore Cowboys Inc.'s own data (to be collected in January 2004). Our first objective has been completed, with a thorough analysis located later in this report. Ultimately the completion of the main objective will lead to the development of a water quality model for the Chattahoochee River that can possibly be developed and generalized for other watersheds.

Another objective of this study is to investigate the fate of the phosphate esters in drinking water treatment plants (DWTPs). Specifically, the Drugstore Cowboys took samples within the Chattahoochee Water Treatment Plant in Atlanta, GA. The presence of the phosphate esters after each major process will be studied. In addition, the intake of

the plant comes from the Chattahoochee River, which also adds to the surface water analysis noted above.

Finally, the last objective set forth by Drugstore Cowboys, Inc. is to investigate the possibility of substantial removal of the selected phosphate esters in DWTPs by minor alterations to the existing treatment process. Advanced Oxidation Processes will be tested, and if effective, discussion of implementation through traditional disinfection schemes like ozonation or UV disinfection will follow.

# **Background**

## **Emergence of Pharmaceuticals & Personal Care Compounds as Potential Environmental Contaminants**

One of the main current concerns is the increasing occurrence of pharmaceuticals and personal care compounds in the natural water environment. The problem was first identified in the late seventies, and throughout the last twenty years, there have been an increased number of reported occurrences of these chemical compounds in natural water systems.

The concentrations measured range from being on the order of a few nanograms per liter in surface waters to a few micrograms per liter in wastewater effluents. These concentrations do not pose an immediate threat to the environment and human health but are alarming. The reason why pharmaceuticals have been a major concern is that they are highly active compounds that are engineered to be persistent and that the effects of long exposure to them are not understood. Besides pharmaceuticals, other major groups of anthropogenic organic chemical compounds have been detected in the water environment in comparable concentrations.

One of these groups is the phosphate esters that are primarily used as flame-retardants and plasticizers. Even though their nature and use suggest that they would be mainly found in industrial effluents, they have been reported in a wide range of water systems and even in drinking water distribution networks.

## **History of Extensive Research to Identify the Occurrence of Man-Made Chemicals**

Since the early eighties, studies reporting the occurrence of anthropogenic organic chemicals in the water environment were made in Europe. They mainly focused on identifying the occurrence of pharmaceuticals and their metabolites in river and lake

systems. Around the same time, studies in Japan revealed the presence of industrial organic chemicals in surface waters and in municipal and industrial wastewaters. In Canada studies as early as 1979 identified anthropogenic organic chemicals in drinking water.

In response to the emerging environmental concerns regarding OWCs, the U.S Geological Survey conducted in 1999-2000 the first nationwide reconnaissance of the occurrence of these chemical compounds in U.S. streams and rivers (Kolpin et al., 2002). The results were alarming since OWCs were found in 80% of the streams sampled.

Following the findings of the USGS reconnaissance, the Centers for Disease Control and the USGS initiated a study to determine the occurrence of commonly used pharmaceuticals and OWCs in surface and drinking waters of a large metropolitan city. The selected study site was a portion of the Chattahoochee River and one of its tributary streams, Big Creek, located north of Atlanta, Georgia.

To the best of our knowledge, this is currently the most extensive study conducted in the United States and the only one that provides information on the occurrence of the selected chemicals in a river system and in the treatment processes. Again the findings are alarming since a substantial number of OWCs and pharmaceuticals were detected in finished drinking water at comparable concentrations to those found in the river system before drinking water treatment plant uptakes.

## **Reported Occurrences of the Selected Organophosphates**

### **Drinking Water**

Reports of occurrence of the selected organophosphates exist from as early as 1979 in a national survey of Canadian drinking water. The concentrations reported were 0.2 to 62 ng/L for TBP, 1.1 to 560 ng/L for TBEP and 0.3 to 13.8 ng/L for TCEP (HSDB Database, 2003).



All three of the selected organophosphates have been identified as present in the drinking water at the CDC survey.

### **Surface Waters**

TBP has been reported in surface waters in the U.S. (CDC, 2000), Japan, Spain, Italy, Germany, Switzerland, and the U.K. (HSDB Database, 2003). Reported concentrations are below the level of 1 µg/L.

TBEP has been reported in surface waters in the U.S. (Kolpin et al., 2002). Reported concentrations are up to a few micrograms per liter.

TCEP has been reported in surface waters in the U.S. (Kolpin et al., 2002).

### **Treatment Plant Effluents**

In a comprehensive survey of wastewater from 4000 industrial and publicly owned treatment works (POTWs) sponsored by the Effluent Guidelines Division of the U.S. EPA, TBP was identified in various types of industrial discharge. The maximum industrial effluent concentrations were 13.5 ppm in the organics and plastics industry and 10.0 ppm in the paint and ink industry (HSDB Database, 2003).

### **Groundwater**

TBP and TCEP have been reported present in the groundwater at concentrations up to 200 ng/L in the U.S, Spain, and the Netherlands (HSDB Database, 2003).

## **Detailed Description of Selected Phosphate Esters**

An extensive knowledge of the properties, manufacture, and uses of the compounds is essential to developing an understanding of their presence in the environment. With an in-depth understanding of the physical and chemical properties, analysis of possible sinks in the environment becomes possible. Insight into the manufacture and use of the compounds is necessary to evaluate the loads on the environment.

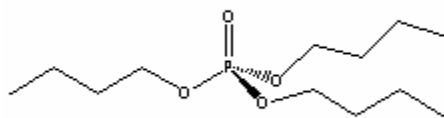
The three compounds being studied are tributyl phosphate, tri(2-butoxyethyl) phosphate and tri(2-chloroethyl) phosphate. They are members of the phosphate ester family of chemicals, which are the most predominant phosphate-containing flame retardants in use. Organophosphate flame retardants represent twenty percent of the worldwide production of flame retardants (Environmental Health Criteria-192, 1997). In general, the organophosphate flame retardants work by breaking down into phosphoric acid and other components upon heating. The phosphoric acid forms a char on the surface of the material being burned, thus shielding the substance from being burned by the heat and stopping the release of volatiles being combusted. In addition, free radicals are formed and released into the vapor phase. The free radicals compete for the materials being oxidized in the combustion reaction, thereby reducing the intensity of the flame (Environmental Health Criteria-192, 1997).

In addition to its flame retarding capabilities, these phosphate esters are used in a variety of other distinct ways as described in the following.

## Tributyl Phosphate

### Physical Properties

The chemical formula for TBP is  $C_{12}H_{27}O_4P$ , and its structure is shown in Figure 1. At room temperatures, TBP is a colorless and odorless liquid. It is non-explosive and non-flammable, but rather breaks down before reaching its boiling point (Environmental Health Criteria-112, 1991). Since we are primarily concerned with the presence of these organophosphates in water, a useful property is maximum solubility, which for TBP is 280 mg/L. A Henry's Law constant, defined as a ratio of a chemical's equilibrium concentration in air and water, is used to quantify a chemical's tendency to partition between the two media. A low Henry's Law constant indicates a strong desire to remain in the water while a large value would be associated with highly volatile compounds. TBP, with a vapor pressure of 0.00113 mmHg and Henry's Law constant of  $1.41 \times 10^{-6}$  atm-m<sup>3</sup>/mole (both at 20°C) indicates that partitioning to the air is not a significant removal mechanism (SRC, 2003).



**Figure 1 Chemical structure of TBP**

### Manufacture and Uses

TBP is manufactured for use in plastics, floor finishes, hydraulic fluids and ore extraction processes, primarily for its flame resistant properties. TBP is manufactured through the reaction of butyl alcohol and phosphorous oxychloride (HSDB Database, 2003). It is manufactured under the brand names Phosflex 4, Skydrol LD-4, Celluphos 4, and Disphamol 1 TBP (Environmental Health Criteria-112, 1991).

Manufacturers include Pfletz & Bauer Inc., Akzo Nobel, Acros Organics USA, Chem Service, Inc., ICN Biomedicals, Wako Chemicals USA, Inc., Albright & Wilson Ltd., A & K Petroleum Ind. Ltd., Ashland Chemical Co., Bayer AG, Commercial Solvent Corp., East Coast Chemicals Co., FMC Corporation, McKesson Chemical Co., Mobay Chemical Co., Mobile Chemical Co., Monsanto Chemical Co., Rhone-Poulenc Co., Protex (SA) Stauffer Chemical Co., Tenneco Organics, Daihachi Chemical Ind. Co., and Nippon Chemical Ind. Co. Ltd. (Chem Sources, 2003; Environmental Health Criteria–112, 1991).

Our best data concerning the amount manufactured is that in 1985 approximately 2700-4000 tonnes were produced worldwide (Environmental Health Criteria–112, 1991). Data regarding the production of phosphorous oxychloride states that approximately 40,000 tonnes of phosphorous oxychloride were produced in 2001 (The Innovation Group, Chem Profiles, 2003). Since the largest consumers of phosphorous oxychloride are producers of phosphate esters for the plastics industry, we estimate that at least as much as the 1985 estimate is in production today (The Innovation Group, 2003). Therefore we will use the 1985 production figure as a lower bound for the yearly worldwide production of TBP in 2003.

TBP has many uses, and we feel that it is important to have an understanding of each of these uses in order to adequately evaluate the pathways TBP takes before entering the Chattahoochee River. The majority of TBP (forty to sixty percent) is used in fire-resistant hydraulic fluid for aircraft (Environmental Health Criteria–112, 1991). A 1988 study estimated that approximately 45,000 aircraft industry workers were exposed to TBP for an average of 30 minutes to two hours per week (Environmental Health Criteria–112, 1991). The presence of several airports in the Atlanta vicinity makes this a probable pathway for TBP to enter the wastewater stream.

The second most prevalent use of TBP is as a plasticizer for plastics and vinyl resins. It is a preferred plasticizer due to its dual capability as a plasticizer and flame retardant in plastics. Use in plastics is a possible pathway into the environment as TBP can leach

from plastics into water, although this seems more likely to occur through landfill leachate than through wastewater treatment plant outfalls.

TBP is also used as an antifoaming agent in paper coatings, lithographic inks, rubber-based paint, and floor polishes (Environmental Health Criteria–112, 1991). Its use in floor polishes indicates another possible pathway into the water system. TBP is used less predominantly as a solvent for cellulose esters, lacquers, and natural gums. It is used in the blending of material that is difficult to dissolve such as lithographic inks and is used in the preparation of agricultural herbicides and fungicides (Environmental Health Criteria–112, 1991). An interesting, emerging use of TBP is in the recovery of uranium ores from reactor products. This use of TBP has become increasingly significant in recent years (Thomas et al., 1998; Environmental Health Criteria–112, 1991).

### **Health Effects & Toxicity**

The estimated oral lethal dose of TBP is between one ounce and one pint for a 150 pound person (HSDB Database, 2003). Most direct encounters with significant quantities of TBP occur through dermal contact by airline mechanics or workers in TBP production plants. Skin irritation is reported in most cases and headaches and dizziness have been reported due to exposure to TBP vapor (HSDB Database, 2003).

Although there have been no fatal effects to humans, animals poisoned with TBP have displayed neurological effects such as weakness and dyspnea (difficulty in breathing). Poisoning of rats with TBP resulted in pulmonary edema (fluid entering the lungs) (HSDB Database, 2003).

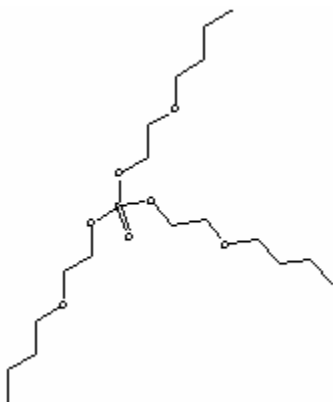
TBP's most dramatic effects are to plant life. TBP has been shown to increase the drying rate of leaves and plants exposed to TBP stopped respiring (Environmental Health Criteria–112, 1991).

The above studies deal with levels of TBP far greater than those identified in the water concentrations in the Chattahoochee River. No data were found concerning the effects of prolonged exposure at the levels encountered in the Chattahoochee.

## **Tri(2-butoxyethyl) Phosphate**

### **Physical Properties**

The chemical formula for TBEP is  $C_{18}H_{39}O_7P$ , and its structure is shown in Figure 2. At room temperatures it is a light-colored, viscous fluid with an odor of butyl. It is a high-boiling and non-flammable substance (Environmental Health Criteria–218, 2000). TBEP, with a vapor pressure of  $2.5 \times 10^{-8}$  mmHg and Henry's Law constant of  $1.2 \times 10^{-11}$  atm- $m^3$ /mole (both at 20°C) would indicate that partitioning to the air is not a significant removal mechanism. This is further evidenced by TBEP's relatively large solubility in water, 1100 mg/L (SRC, 2003) TBEP has the potential for a high level of sorption to suspended sediment in the river system due to its high organic carbon partition coefficient, which is reported as a log  $K_{oc}$  of 4.38 (Environmental Health Criteria–218, 2000).



**Figure 2 Chemical structure of TBEP**

## **Manufacture and Uses**

Tri(2-butoxyethyl) phosphate is manufactured for use in floor polishes and as a plasticizer in rubbers and plastics, primarily for its flame resistant properties. TBEP is manufactured through the reaction of butoxyethanol and phosphorous oxychloride and stripping hydrochloric acid in excess of butoxyethanol (Environmental Health Criteria–218, 2000). It is manufactured under the brand names Kronitex KP-140, KP-140, Phosflex T-BEP, Phosflex 176C, and Amgard TBEP (Environmental Health Criteria–218, 2000).

Manufacturers include City Chemical LLC, Pfletz & Bauer Inc., Akzo Nobel, Acros Organics USA, Chem Service, Inc., Scientific Polymer Products Inc., Ashland Distribution Company, ICN Biomedicals, Wako Chemicals USA, Inc., Tokyo Kasei Kogyo Co. Ltd., Transol Chemicals Ltd., Wilhelm E.H. Biesterfeld, Polycor Chemicals, Akulu Marchon Ltd, Blagden Chemical Specialties Ltd., and NBS Biologicals Ltd. (Chem Sources, 2003).

Our best data concerning the amount manufactured is that in 2000 approximately 6000 tonnes were produced worldwide (Environmental Health Criteria–218, 2000). These data are recent enough that we will use it as our estimate for the yearly environmental load.

TBEP has many particular uses and we feel it is important to have an understanding of each of these in order to adequately evaluate the pathways TBEP takes to enter the Chattahoochee River. The most likely pathway TBEP takes into the wastewater system is through its use in floor polishes. TBEP adds elasticity and gloss to floor polishes. The increased elasticity increases the leveling and spreading properties of the polish. It is a component of several household floor polishes, including such familiar names as Mop & Glo and Brilliance, in concentrations as high as eight percent (Household Products Database, 2003). Disposal of wastewater after floor polishing is an obvious pathway to municipal wastewater systems.

TBEP is also used as an antifoam agent and solvent for complex organic compounds such as resins, waxes, poly acrylates, and acrylic copolymers (Environmental Health Criteria–218, 2000). However these are highly specialized functions and probably represent an insignificant amount of the TBEP that escapes to the river system.

TBEP is used as a plasticizer in specialty rubber used in seals, gaskets, hoses, and shoe laces. Leaching of TBEP from these items, especially hoses, could present a significant pathway into the river system. Its use as a plasticizer in rubber seals has resulted in the previous contamination of blood samples (HSDB Database, 2003) and is worth noting in order to avoid contamination of proposed river water samples.

TBEP has been detected in dust in offices in the United States at concentrations of approximately 15 ng/m<sup>3</sup>. It is estimated that as many as 200,000 office workers have been exposed to TBEP through the inhalation of office dust (Environmental Health Criteria–218, 2000).

### **Health Effects & Toxicity**

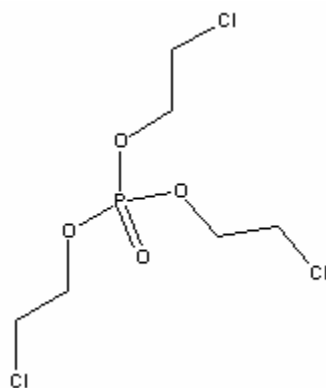
The effect of TBEP on humans has been only sparsely examined, with very few studies dedicated to long term exposure. One dermatology study did demonstrate TBEP to be a mild skin irritant (HSDB Database, 2003). However significant testing has been done to determine its non-human toxicity. Among other effects it has been found to reduce the production of red blood cells in rats and chickens (Environmental Health Criteria–218, 2000). No studies have been performed to evaluate the effect of chronic exposure, long term toxicity, or carcinogeneticity. Considering this it is possible that the chronic exposure through drinking water could have detrimental effects.



## Tri(2-chloroethyl) phosphate

### Physical Properties

The chemical formula for TCEP is  $C_6H_{12}Cl_3O_4P$  and its structure is shown in Figure 3. At room temperatures it is a clear, colorless liquid with a slight odor. It decomposes at temperatures above  $220^{\circ}C$ . (Environmental Health Criteria–209, 1998) TCEP has a maximum solubility in water of 8000 mg/L. In order to analyze the magnitude of loss from the river system to the atmosphere we note the vapor pressure of .0613 mmHg and a Henry's Law constant of  $3.29 \times 10^{-6}$  atm-m<sup>3</sup>/mole (SRC, 2003). TCEP, with a vapor pressure of 0.0613 mmHg and Henry's Law constant of  $3.29 \times 10^{-6}$  atm-m<sup>3</sup>/mole (both at  $20^{\circ}C$ ) would indicate that partitioning to the air is not a significant removal mechanism. This is further evidenced by TCEP's large solubility in water, 8000 mg/L (SRC, 2003).



**Figure 3 Chemical structure of TCEP**

### Manufacture and Uses

Tri(2-chloroethyl) phosphate is manufactured for use as a fire retardant and plasticizer in liquid unsaturated polyester resins and PVC and as a fire resistant back coating for textiles. TCEP is manufactured through the reaction of phosphorous oxychloride with ethylene oxide followed by subsequent purification (Environmental Health Criteria–209,

1998). It is manufactured under the brand names Celanese Celluflex CEF, Celluflex CEF, Disflamoll TCA, Fyrol CEF, Fyrol CF, Genomoll P, Niax 3CF, Niax Flame retardant 3 (nospa)CF, Hosta flam UP 810, Amgard TCEP, Tolgard TCEP, Antiblaze TCEP, Levagard EP, and Nuogard TCEP (Environmental Health Criteria–209, 1998).

Manufacturers include City Chemical LLC, Pflatz & Bauer, Inc., Akzo Nobel Functional Chemical, Acros Organics USA, Chem Service Inc., ICN Biomedicals Inc., Crescent Chemical Co. Inc., Wako Chemicals USA Inc., ABCR GmbH & Co. KG, Beckmann Chemikalien KG, Tokyo Kasei Kogyo Co. Ltd., ICN Biomedicals Inc., Crescent Chemical Co. Inc., Transol Chemicals Ltd., and Albright & Wilson Ltd. (Chem Sources, 2003).

TCEP production was at its height in the late 1980's, peaking at 9000 tonnes a year in 1989. However, since then its demand has steadily declined due to its propensity to decompose and it has been replaced with other phosphate ester flame retardants (Environmental Health Criteria–209, 1998). The latest figures we were able to obtain regarding its current production is below 4000 tonnes in 1997 (Environmental Health Criteria–209, 1998). However even with declining use it is still the most prevalent of the flame retardants being studied here.

TCEP has many uses and we feel it is important to have an understanding of each of these in order to adequately evaluate the pathways TCEP takes to enter the Chattahoochee River. TCEP has several uses that provide ready pathways into the municipal wastewater stream. TCEP is used as fire retardant in liquid unsaturated polyester resins (Environmental Health Criteria–209, 1998). The normal concentration is two to five percent in these resins. (Jiangdu Dajian Chemical Factory, 2003) The resins are used in the casting of bathtubs, spas, and pipes. It is possible that leaching from these surfaces could provide a pathway into the environment.

An even more likely source is the use of TCEP as a back-coating for textiles used in furniture and protective clothing (Environmental Health Criteria–209, 1998).

Maintenance and cleaning of these products and subsequent disposal of the wastewater used in the process could provide a pathway to the wastewater treatment plant (WWTP).

TCEP is also used in cellulose ester compounds and coatings (Environmental Health Criteria–209, 1998) that are used for sampling filters and photographic film. However, we estimate that this represents an insignificant percentage of the TCEP that ends up in the wastewater stream.

Historical use of TCEP was as a flame-retarding component of rigid polyurethane foams (Environmental Health Criteria–209, 1998). The decomposition of TCEP caused the discontinuation of this chemical as a flame-retardant. The use of rigid polyurethane foam in insulation for refrigerators and houses requires that it be rather long lived. Drugstore Cowboys, Inc. estimates that its use in these products began to decline after 1989 as represented by it falling off its peak in that year. It is quite feasible that a substantial amount of this foam is still in use and this could be a major source to the river system. In fact, similar to TBEP, TCEP has been detected in household dust (Environmental Health Criteria–209, 1998). This could likely be from the decomposition of these foams.

### **Health Effects & Toxicity**

In tests regarding bioconcentration, TCEP was found to accumulate in the brains of rats, and with repeated exposure was found to have adverse effects on the brain, liver, and kidneys. It is also known to adversely affect the reproduction rates of rats and mice (HSDB Database, 2003).

As with TBEP, few studies have been conducted to identify health effects to humans as a result of TCEP exposure. Given that there is no toxicological data for the effects of TCEP on humans, TCEP is not classified a carcinogen. The fact that it is not classified does not clear us of danger and in our opinion the fate and transport of TCEP should be studied in order to have the maximum information on it in the event that future toxicological studies reveal detrimental health effects as the result of TCEP exposure.

## **Chattahoochee River Characteristics**

The Chattahoochee River originates in Union County, Georgia, just south of the Tennessee border. The river traverses Georgia in a southwestwardly direction, passing the city of Atlanta, comprising a portion of the Alabama-Georgia border, and eventually terminating in Lake Seminole along the Georgia-Florida border. The Chattahoochee River extends a total of 698 kilometers, draining a basin of 22,714. square kilometers, 70 percent of which lies in the state of Georgia (GDNR, 1997).

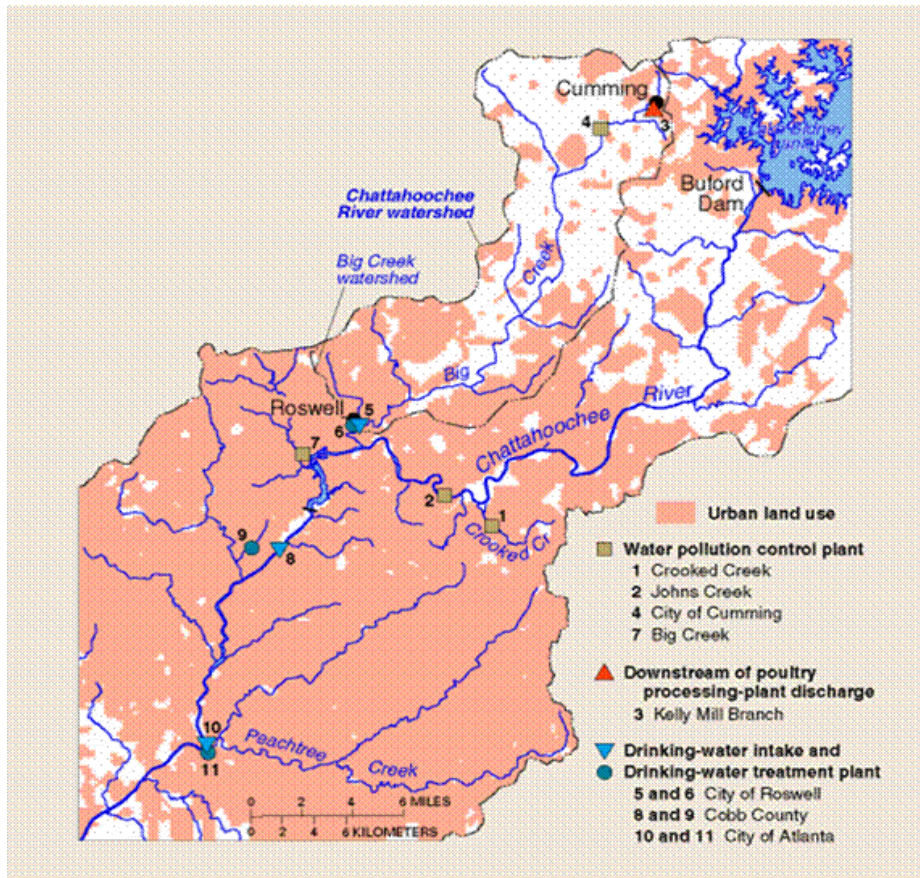
The basin climate is typical for its latitude and longitude, with temperatures ranging from 4°C in the winter to 27°C in the summer, and an average annual precipitation of 138 centimeters (Stamey, 1998). A majority of the Chattahoochee River Basin is covered by forestland, with the exception of the more urbanized landscape as the river passes the metropolitan area of Atlanta.

The reach of river upon which the Centers for Disease Control chose to focus lies in the Upper Chattahoochee River Basin, originating at Buford Dam and meandering approximately 77 kilometers south to the City of Atlanta water works facility, located just north of downtown Atlanta, at the mouth of Peachtree Creek (see Figure 4). Two hydroelectric dams are located within this reach. The first, Buford Dam, is located at the most upstream boundary of the reach and creates Lake Sydney Lanier. Lake Lanier is over 190 square kilometers and stores close to 3 cubic kilometers of water (GDNR, 1998). The Morgan Falls Dam is located approximately 56 kilometers down stream of Buford Dam. Morgan Falls dam creates the smaller, Bull Sluice Lake reservoir, which covers an area of around 2.4 square kilometers and has no significant storage (GDNR, 1998). In addition the reach contains a designated national recreation area, Chattahoochee River National Recreation Area, which is a popular trout fishing hole and water sport destination.

In addition to a source of hydroelectric energy, The Chattahoochee River serves as the main source of municipal drinking water for more than 2 million people in metropolitan Atlanta. The river and its tributaries also receive treated sewage effluent from local wastewater treatment plants. Thirteen municipal drinking water treatment plants use the river or its tributaries as source water, and seventeen municipal wastewater treatment plants discharge effluent into one of the rivers in the watershed. Four drinking water intakes lie downstream of a wastewater outfall with the result that a substantial percentage of the drinking water originates from wastewater (CDC, 2000). It is this fact that makes this reach of the Chattahoochee River suitable for this examination.

To produce the data set that was the impetus for this study, the CDC collected water samples in this reach of the Chattahoochee. The sample set was made up of samples taken in the effluent streams of four wastewater treatment plants, downstream of a fifth, at the intakes of three drinking water treatment plants, and of finished water from these same three plants. Each sampling location was sampled three separate times and each sample was analyzed for the three phosphate esters being studied here. The results, although indicating the consistent presence of the selected organophosphate esters, varied greatly in magnitude. Still the data was used to construct a first approximation mass balance.

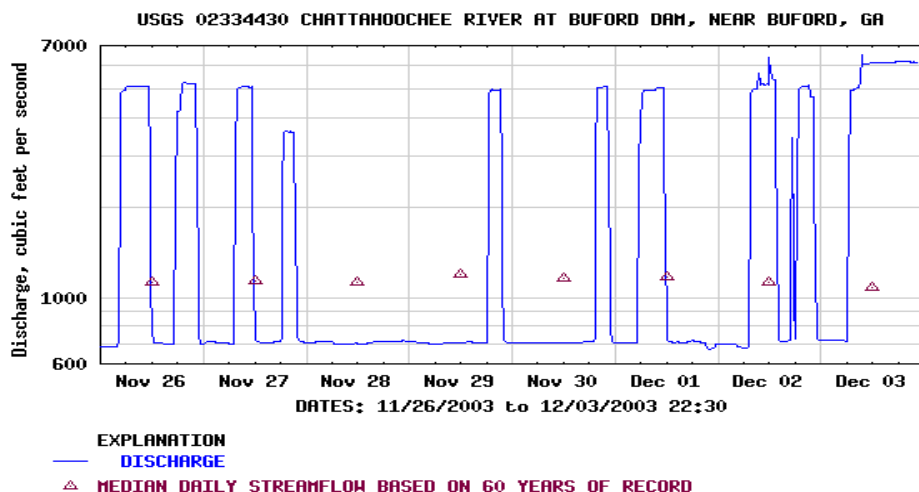
A “black box” mass balance must be constructed before the natural attenuation processes can be considered as a means of determining the fate of the three phosphate esters in this stretch of the Chattahoochee River. The initial “black box” mass balance is only concerned with bookkeeping the major sources (wastewater treatment plant discharges) and sinks (water treatment plant intakes) of the organophosphate pollutants. Missing mass identified in this accounting indicates the possible location and magnitude of natural organophosphate sinks. The information will be used to focus later research on only those mechanisms likely to cause the observed discrepancies. Four features must be well understood in order to create this balance: the flow rates of the river, its tributary inflows, the location of wastewater discharges and the concentration of the three organophosphates in the discharges



**Figure 4: CDC test sites along Chattahoochee River (CDC, 2000)**

Flow exiting Buford Dam averages about 57 cubic meters per second, but the fluctuation is considerable, owing to the hydropower production schedule. Figure 5 highlights the typical oscillation experienced in daily discharge from Buford Dam.

Flow data were collected at all points along the Chattahoochee River and its tributaries where the USGS has stream gages set up and monitored (See Appendix A for map). Most of these stream gages are well established; flow records date back several decades in some instances. To complete the mass balance, the average flow for the month of January was recorded, as this is the best estimate of flow rates to be expected when experiments are to be conducted in January 2004.



**Figure 5: Typical discharge profile for Buford Dam (USGS, 12/03/2003)**

An average concentration for each organophosphate, in each treated effluent stream entering the river, was computed from the concentrations detected in the three samples taken in the effluent stream. The average effluent concentration was then coupled with typical discharge rates for each of the wastewater treatment plants to yield approximations of the amount of each compound entering the Chattahoochee River. Drinking water treatment plant intake concentrations were determined within the river itself, allowing downstream concentrations to be compared with loadings from WWTPs upstream. The comparison resulted in estimates of compound mass removed between recording stations (See Appendix A for a chart depicting concentration approximations within the Chattahoochee River). Knowing the approximate amount missing enables an analysis of which degradation processes are capable of such removal.

Further analysis will seek to enhance the “black box” model, attempting to prepare a more complete water balance in conjunction with the organophosphate balance so as to better understand the organophosphate concentrations downstream of the wastewater treatment plants and throughout the test section of river. This will involve the incorporation of rainfall, evaporation, land runoff, and groundwater flux models. This will allow a more precise estimate of the magnitude of the organophosphate sinks, which will presumably be identified through our study of the natural degradation mechanisms undergoing organophosphate removal in the Chattahoochee River.

# Presence of Phosphate Esters in Chattahoochee River System

The CDC-USGS survey of the treatment plants along the Chattahoochee River revealed the significant presence of phosphate esters. Tributyl phosphate, tri(2-butoxyethyl) phosphate, and tri(2-chloroethyl) phosphate were consistently present in detectable concentrations. A summary of the detections in this data set is displayed in Figure 6.

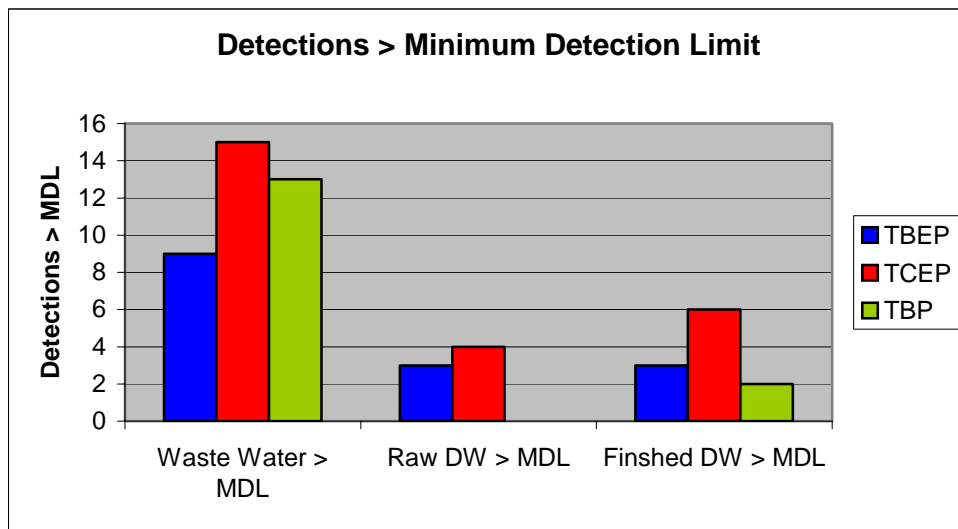


Figure 6

**Total detections of phosphate esters out of 33 samples**

**(Note: The number of wastewater samples was 15, for raw drinking water nine, and for finished drinking water nine.)**

Although it is clear from the histogram that the number of detections is reduced between the wastewater effluent and the drinking water intakes, the data suggest that contamination by these phosphate esters is not completely removed by drinking water treatment. For this reason we feel it is important to understand more thoroughly the fate and transport of these compounds.



## **Major Point Sources**

The CDC survey tested for concentrations of various compounds contained in pharmaceuticals and household products. The tests were conducted at the outfalls of wastewater treatment plants, at the intakes of drinking water treatment plants, and in samples of the finished drinking water from DWTP. The municipal water system plants are set up along the river in such a way that the DWTP intakes are downstream from the WWTP outfalls. See Figure 4 for locations.

The data suggest that detectable concentrations of the three phosphate esters are making it through the WWTP treatment and being discharged into the Chattahoochee River. To some extent, the compounds are surviving the stretch of the river between the WWTP outfalls and the DWTP intakes and are detectable in the drinking water. Although non-point sources are a possibility, we feel that the most appropriate way to approach the problem is by assuming that the concentrations being provided by the major point sources indicated above will be orders of magnitude larger than any non-point source. Therefore, the fate and transport of the three phosphate esters can be modeled as originating from major point sources.

Recently, non-point sources have been suggested to be important (Frick and Zaugg, 2003). This in the end may prove to be useful, as possible high concentrations of the phosphate esters without a major point source can be accounted for.

## **Estimated Annual Loads**

Given the significant presence of the three phosphate esters, it is important to estimate an annual load to the Chattahoochee River system of each chemical. Drugstore Cowboys, Inc. used an estimated annual production of 6000 tonnes/year for TBEP and approximately 4000 tonnes/year for both TCEP and TBP. Given an approximate population for the area being studied of 2.8 million (US Census Bureau, 2003) and assuming that the majority of the compounds are used in the United States (population

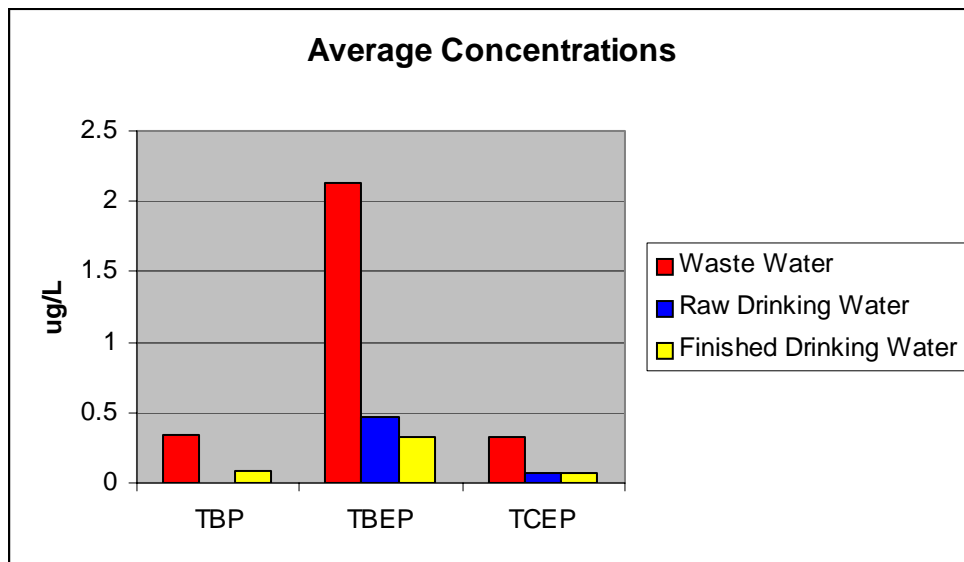
approximately 280 million) Drugstore Cowboys, Inc. can come up with an approximate annual load for each of the compounds on the Chattahoochee River system. For these calculations, Drugstore Cowboys, Inc. assumed that 50% of the worldwide production of these compounds is used in the United States. An example of the calculations done to estimate the annual load is displayed here

- TBEP:  $((3000 \text{ tonnes/year}) / 280,000,000 \text{ persons}) * 2,800,000 \text{ persons in area} = 30 \text{ tonnes / year}$

With these calculations, Drugstore Cowboys, Inc. determined an estimated annual load for the other two compounds being studied of 20 tonnes/year for TBP and TCEP. The annual average daily flow of the Chattahoochee River at (gaging station) is (value) cfs (USGS, 2003). Thus, a rough estimate of the volumetric flow rate of the Chattahoochee River is  $20 \times 10^8$  cubic meters per year with a mass of  $20 \times 10^8$  tonnes per year. Thus, the approximate concentration of TBP and TCEP in the Chattahoochee River is approximately 1 part per  $10^8$ , or 10 parts per billion. Even though the concentrations measured by the CDC ranged from approximately 100 parts per trillion to two parts per billion, the above analysis overestimates the actual values because it assumes that all phosphate ester produced that year also became waste in the same year. If only five percent of the phosphate ester produced went into waste, then this analysis would match up well with the actual concentrations.

In addition, we expect that the concentration of TBEP will be relatively higher than predicted because its use in household cleaners provides an easy access pathway to the municipal WWTP. We expect the TCEP loads to be somewhat higher due to its past use in polyurethane foams that are probably still in use today. TCEP should also display higher relative concentrations due to its past production peak of 9000 tonnes/year, leading us to believe that there is a more substantial amount of it still present in the population.

The CDC data seem to agree with our predicted annual loads. The graph in Figure 7 displays the average of the detected concentrations for the three compounds. As expected, TBEP concentrations were the highest followed by TCEP. TBP displays the lowest concentration due to its use in specialized industry. However, it is still likely that some will be disposed of improperly; this is represented by the concentrations we observe.



**Figure 7**  
**Average concentrations of phosphate esters measured by CDC**

### Missing Mass

From the histogram above, it is apparent that a sink exists between the WWTP outfalls and the DWTP intakes. Identification of this sink is of major importance to determine the fate of the missing mass in the environment. Determining the nature of the sink in the Chattahoochee River system could also lead us to identify a drinking water treatment process most effective in removing phosphate esters. Since drinking water treatment processes tend to mimic natural attenuation processes, we feel this is of major importance considering that drinking water treatment appears ineffective at removing the compounds at the concentrations present in the Chattahoochee River.

## Possible Fates of the Phosphate Esters

There are many possible ways that the phosphate esters can disappear in the aquatic environment. These include:

- Volatization
- Sorption to sediment
- Photodegradation
- Hydrolysis
- Bioaccumulation
- Biodegradation

Whether any of these ways can affect the disappearance rate of the phosphate esters is discussed below.

### Volatization

From (SRC, 2003), the Henry's Law constant for TBP is  $1.5 \times 10^{-7}$  atm-m<sup>3</sup>/mol, and  $1.2 \times 10^{-11}$  atm-m<sup>3</sup>/mol for TBEP. This corresponds to negligible amounts of loss to the atmosphere from surface waters. However, for TCEP, the Henry's Law constant is  $3.3 \times 10^{-6}$  atm-m<sup>3</sup>/mol, which can result in an appreciable amount of volatilization. SRC states that the half-life of TCEP in a model river (1 meter deep, flowing 1 m<sup>3</sup>/sec with a velocity of 3 meter/second) is approximately 20 days. Since this is an order of magnitude greater than the residence time in the river between the WWTP outfalls and the DWTP intakes we will assume that we can neglect as a significant sink of TCEP. (NOTE: this assumes the residence time in Bull Sluice Lake (at Morgan Falls) is also  $\ll$  than 20 days).

## Sorption

Chemicals dissolved in water may partition to solid surfaces encountered during transport in the fluid system. Organic compounds tend to have an affinity to partition to organic carbon. The ratio according to which the chemical partitions between the solid and aqueous phase is described by a partition coefficient.

In addition to dissolved compounds, rivers tend to carry solids suspended in water. Suspended solid particles may contain organic carbon and dissolved organics can partition onto the organic carbon. Once sorbed to the surface of these particles the particles can become a sink for the compound by settling out of the flow and depositing the chemicals on the riverbed.

The partition coefficient for phosphate esters to organic carbon,  $K_{oc}$ , can be approximated using their partition coefficient between octanol and water,  $K_{ow}$ , and the following equation (Hemond and Fechner-Levy, 2000):

$$\text{Log } K_{oc} = 0.544 \log K_{ow} + 1.377$$

The organic carbon partition coefficients for TBP, TBEP, and TCEP are listed below, where only an octanol-water coefficient was available (TBP, TCEP), the above equation was used to approximate  $K_{oc}$ .

- $\text{Log } K_{oc, \text{TBP}} = 3.55$  (Environmental Health Criteria, 112)
- $\text{Log } K_{oc, \text{TBEP}} = 4.38$  (Environmental Health Criteria, 218)
- $\text{Log } K_{oc, \text{TCEP}} = 2.30$  (Environmental Health Criteria, 209)

The amount of each compound that partitions to the organic carbon is given by the equation

$$C_{\text{water}} * f_{\text{oc}} * K_{\text{oc}} = C_s$$

Where  $C_{\text{water}}$  is the concentration in water,  $f_{\text{oc}}$  is the percentage by mass of organic carbon in the suspended particles, and  $C_s$  is the concentration of phosphate ester sorbed to suspended solids. A fair estimate of the amount of organic carbon in particles suspended in the Chattahoochee is 1% (Hemond and Fechner-Levy, 2000).

To calculate the sorbed concentration for each compound, the assumption of equilibrium is used. Using this value we will estimate the annual sorbed mass of the compound by multiplying this value by the annual sediment load in the river. We assume this process does not reach equilibrium due to constant fluctuation in stream flow and WWTP discharge rate; this estimated value most likely overestimates the sorbed mass. Therefore, we will regard this value to be an order of magnitude estimate (e.g. a factor of ten).

Two USGS stream gages measure turbidity in the Chattahoochee River system above the DWTP intakes at Atlanta: one at Norcross upstream from the confluence of the Chattahoochee and the Crooked Creek, and one at Crooked Creek where it runs into the Chattahoochee at Norcross. The USGS records turbidity in NTU, and we used the approximate conversion 1 NTU = 1 mg/L suspended solid to convert from turbidity to suspended solid.

The Chattahoochee gage at Norcross recorded a mean of 178 mg/L suspended solid in 2002, and the Crooked Creek gage recorded a mean of 261 mg/L of suspended solid. Taking into account the average flows recorded at these gages, a total of 181 mg/L of solids are suspended in the Chattahoochee below the confluence with Crooked Creek. An average streamflow at the Roswell gage downstream from the confluence of the Chattahoochee and Crooked Creek is 58,000 Liters per second. Therefore according to the average measurements listed above,  $4 \times 10^8$  kg of suspended solid per year pass this point in the river. This, multiplied by the sorbed concentration, gives an estimate of how much of each phosphate ester is lost to the suspended sediment.

The Chattahoochee's River regime is controlled by the upstream hydroelectric plant at Burford Dam. The power plant is operated for a few hours per day, leading to artificial flooding events in the river. The flow is therefore controlled by the propagation of this diurnal flood events cycle. Consequently, the concentration of contaminants in the river is unsteady spatially and temporarily due to the above flood events. All of the existing measurements were taken at low-flow season, and at times that wastewater accounted for a large percent (~50%) of the total flow. These concentrations cannot be readily transformed to an equivalent average concentration due to the lack of knowledge of the input loads for every WWTP. In our calculations we will use an estimated effective average concentration of the order of 0.5 µg/l because the sediment suspension and transport probably occurs when the flood waves are propagated downstream.

Therefore, according to these assumptions, 7.2 tonnes TBP/year, 48 tonnes TBEP/year, and that 0.4 tonnes TCEP/year are lost to sorption in the Chattahoochee River. As stated above, the assumptions lead to overestimation of sorbed mass. We can assume that this estimation is at least an order of magnitude too large. Extensive experimental measurements must be made to more accurately quantify this sink, but our analysis clearly shows that sorption is a major potential sink for the phosphate esters.

## **Photodegradation**

### **Direct Photodegradation**

Direct photodegradation is the process where chemical compounds absorb light and undergo transformations.

For the phosphate esters of interest, Drugstore Cowboys, Inc. has not been able to locate any published information for the UV/visible absorption spectrum. Extensive literature review has been made on this subject, including searching through MIT's organic compounds reference books, but no absorption spectrum has been found. The only

relevant information that we were able to find is a summary of the UV spectrum absorption for TBP.

Due to their structure, phosphate esters are not expected to absorb light in the visible spectrum, therefore direct photodegradation as a sink will not be accounted for in our overall analysis of the fate of the selected phosphate esters in the Chattahoochee River.

To verify this decision, a simple calculation for the absorbance of light for TBP follows. For wavelength of 200 nm, TBP has a molar extinction coefficient of  $3.4 \times 10^{-20}$   $\text{cm}^2/\text{molecule}$  (Rewick et al., 1986). Beer's law gives light absorbance:

$$A_{(\lambda)} = \log_{10} \frac{I_0}{I} = \epsilon_{(\lambda)} \cdot C \cdot l$$

where  $\epsilon_{(200\text{nm})} = 3.4 \times 10^{-20} \frac{\text{cm}^2}{\text{molecule}}$ . Manipulating the units of  $\epsilon(\lambda)$  to yield  $\text{M}^{-1}\text{cm}^{-1}$ , and using some typical values for Chattahoochee River (depth 3 m, and concentration of TBP  $\sim 1\mu\text{g/L}$ ), we have:  $A_{(200\text{nm})} = 2.31 \times 10^{-11}$ , which is negligible.

In addition, because the wavelength used above is in the UV spectrum (where organic compounds typically exhibit stronger absorbance, it can be argued that direct photodegradation is not a major sink for the selected phosphate esters.

### **Indirect Photodegradation**

Indirect photodegradation occurs in natural surface waters due to the existence of highly reactive species that are formed photochemically and go on to degrade chemical compounds. The most important species in indirect photodegradation is the hydroxyl radical,  $\text{OH}\cdot$ . Hydroxyl radical is formed by many processes, amongst which are photochemical production of hydrogen peroxide  $\text{H}_2\text{O}_2$  and consequently disassociation in two hydroxyl radicals, and the Fenton Reaction.



The highly reactive hydroxyl radical is present in surface waters at levels of the order of  $10^{-16} \text{ M} \sim 10^{-17} \text{ M}$  (Hemond and Fechner-Levy, 2000; Schwarzenbach et al., 2003). Even though these concentrations are very small due to its significant reactivity it is a major source of degradation of chemical compounds in surface waters.

A rough estimation of the half-lives of the selected phosphate esters due to degradation by hydroxyl radical attack will be calculated. All the assumptions made in the following lead to an underestimation half-lives.

### **TBP**

For the reaction of TBP with hydroxyl radical there is a known reaction rate of  $k = 10^{10} \text{ M}^{-1}\text{sec}^{-1}$  (Notre Dame Radiation Laboratory, 2003). The reaction rate comes from the Radiation Chemical Data Center at Notre Dame University and has been obtained for  $\text{pH} = 1.2$ . It is known that hydroxyl radical has a stronger reaction potential in strongly acidic aqueous solutions so any half-life calculated with this rate is shorter than the actual one.

$$\frac{d[\text{TBP}]}{dt} = -k[\text{OH}\cdot][\text{TBP}] = -k'[\text{TBP}]$$

$$\text{where } k' = 10^{-16} \times 10^{10} \text{ sec}^{-1}$$

Therefore the estimated half-life is:

$$t_{1/2} = \frac{0.693}{k'} = 693000 \text{ sec} \approx 8 \text{ days}$$

### **TCEP & TBEP**

To our knowledge there is no tabulated reaction rate with hydroxyl radical for TCEP and TBEP. In order to estimate a half-life for these compounds, Drugstore Cowboys, Inc. will regard the reactions with hydroxyl radicals as diffusion-limited reactions because the eventual half-life found will be the lower bound.

In diffusion-limited reactions, the reaction rate constant, assuming equal molar radii and molecular diffusion coefficients, is:

$$k_d = \frac{8}{3} \frac{kT}{n} N_A 10^3 \text{ (M}^{-1} \text{ sec}^{-1}\text{)}$$

where  $k$  is the Boltzmann's constant,  $T$  absolute temperature, and  $n$  the dynamic viscosity of water. Using some typical environmental values, the reaction rate is  $k_d \approx 7 \cdot 10^9 \text{ M}^{-1} \text{ sec}^{-1}$

Using the above reaction rate, we get:

$$\frac{d[\text{TCEP}]}{dt} = \frac{d[\text{TBEP}]}{dt} = -k[\text{OH}\cdot][\text{Org-P}] = -k'[\text{Org-P}]$$

where  $k' = 10^{-16} \times 7 \cdot 10^9 \text{ sec}^{-1}$

Therefore, the estimated half-life for both compounds is:

$$t_{1/2} = \frac{0.693}{k'} = 990000 \text{ sec} \approx 11.5 \text{ days}$$

## Hydrolysis

Two classes of pollutants in surface waters are most likely to undergo hydrolysis. These are the esters and the alkyl halides (Hemond and Fechner-Levy, 2000). In saturated phosphorus atoms (ones without a hydrogen atom directly connected to the phosphorus atom), such as the phosphate esters Drugstore Cowboys, Inc. is examining, the ester is attacked by  $S_N2$  nucleophilic substitution. This changes the phosphotriester into a phosphodiester, and so on, until the molecule turns back into a phosphate ion (Thomas, 1998). Alkyl halides also have  $S_N2$  substitution, where the alkyl halide turns into an alcohol. Alkyl halides are a much better leaving group than the esters because of the stability of the halide ion. Virtually all ester and alkyl halide substitution is caused by the hydroxyl ion because it is a much better substitution-catalyzer for saturated phosphorus atoms than  $H_2O$ . Thus, phosphate ester hydrolysis is usually characterized as a base-catalyzed reaction (Schwarzenbach, 2003).

Overall, hydrolysis does not seem to be a significant factor over the time scales and pH values for the Chattahoochee River. In Ishikawa and Baba (1988), hydrolysis of TBP and TCEP was measured for a range of pH from 2 to 12 and at a reactant concentration of 0.1 mg/L. For TBP, 100% of the chemical remained after one day for all range of pH. For TCEP, 100% of the chemical remained after one day for pH 2 to 8. At pH 10, ~95% remained, and at pH 12, ~40% remained. But, because the time scale of river flow is approximately one to one and a half days, and because the pH of river water seldom approaches basic values, hydrolysis is not a factor in the Chattahoochee River for either TBP or TCEP.

In the Environmental Protection Agency chemical testing of TBP (U.S. EPA, 1989), hydrolysis was specifically tested for a period of 30 days at pH 3, 7, and 11, using a concentration of 10 mg/L. The average amount remaining was 85.6%, which would mean a half-life of approximately 130 days. In Brown et al. (1975), the estimated half-life of TCEP is 100 days, and “the chlorine may hydrolyze moderately rapid with a half-life of 38 days based on the half-life of ethyl chloride.” This idea goes back to the possible  $S_N2$  nucleophilic substitution of the ester group or only substitution of the halogen group, which is in general a better leaving group. No pH values were indicated in this test.

No specific data could be found for TBEP, but Muir (1984) indicates that phosphate esters do not hydrolyze at pH 5-7, but are more likely to degrade under more alkaline conditions; therefore, TBEP will most likely follow the same trends discussed above.

### **Bioaccumulation**

Bioaccumulation, or the accumulation of pollutant chemicals in aquatic organisms from both water and food, is another potential sink for the three organophosphates. This can present a serious risk to humans and other higher-order organisms if substantial amounts of a harmful compound are ingested by a particular organism and rather than metabolized, are concentrated within the organism's tissue lining or blood. A

*bioconcentration factor* (BCF) is usually used as a means of measuring chemical uptake by an organism, and is defined as the ratio of a chemical's concentration in an organism to the chemical's aqueous concentration (Hemond and Fechner-Levy, 2000). Considering only a partitioning model is particularly useful for hydrophobic chemicals that readily migrate between animal tissue and water, and is a function of both the chemical's octanol-water partitioning coefficient,  $K_{ow}$ , and the fish's lipid content. More detailed kinetic models are sometimes implemented that take into account the dynamics of ingestion, excretion, and other processes associated with metabolism by the organism (Hemond and Fechner-Levy, 2000).

In the Chattahoochee River Basin, a diverse collection of fish fauna exists, with over 104 species representing 22 families observed (Couch, 1996). The largest number of species (31) is from the minnow family Cyprinidae, with large numbers of sunfishes, catfishes, and suckers present as well (Georgia DNR, 1997). The Georgia Department of Natural Resources also stocks trout in this section of the Chattahoochee River in support of recreational opportunities in the metropolitan Atlanta area.

A small number of experiments have been conducted to assess the bioconcentration of the three phosphate chemicals in various fish species. Killifish and goldfish were tested under TCEP concentrations of a few parts per million for several days of continuous exposure (Sasaki, 1981). Another test was conducted with killifish using concentrations on the order of tens of micrograms per liter (CITI, 1992). Both tests resulted in a low BCF, leading to the conclusion that the likelihood of bioaccumulation of TCEP is low. Similar results were found for TBEP using a carp species (CITI, 1992). For TBP, a BCF of 190 was determined from an empirical correlation with  $\log K_{ow}$ , which has a published value of approximately 4.00. This leads to a moderate potential for bioconcentration in aquatic organisms (Saeger, 1979). A similar conclusion was found while studying bioconcentration in killifish and goldfish, in which half-lives of 58 and 100 hours, respectively, were observed (Sasaki, 1981). Both of these species metabolize and eliminate the phosphate ester from their systems, so observed BCFs are lower than predicted. In a separate test conducted with carp, high amounts of TBP uptake were also

observed (CITI, 1992). From these results, it can be concluded that only TBP has the potential for substantial removal from the water column via uptake and subsequent breakdown and/or bioaccumulation.

### **Biodegradation**

Biodegradation involves the biological transformation of pollutant chemicals into other, usually less toxic compounds. Through successive breakdown, most organic compounds are eventually reduced to water, inorganic salts, and carbon dioxide in a process known as mineralization (Hemond and Fechner-Levy, 2000). When supplied with appropriate nutrients and oxygen, specialized aerobic bacteria can consume and degrade pollutant chemicals as their primary food source.

Biodegradation of TBP is believed to follow the same intermediate transformation pathway as when chemically hydrolyzed, moving first to dibutyl then monobutyl phosphate before converting into butanol and finally phosphoric acid (Macaskie and Rosenberg, 1991). A separate study also determined that the degradation pathway for phosphate esters most likely includes a stepwise enzymatic hydrolysis to orthophosphate and the phenolic or alcohol moieties, which themselves undergo further degradation (Barret et al., 1969).

One particular study conducted at the University of Birmingham explored the breakdown of TBP in hopes of harnessing the resultant enzymatically liberated phosphate as a mechanism for precipitating uranyl ions from aqueous solution. (Thomas and Macaskie, 1996). In this experiment, river water taken from the Mersey River at Warrington (U.K.) was diluted with a feed solution to eight percent by volume then supplied with TBP at a solution concentration of 0.53 g/L (overall concentration of 2 mM) to serve as the sole carbon and phosphorous source. The aqueous solution was then inoculated with bacteria *Pseudomonas* and allowed to adjust to the new medium. A moderate length lag phase (~2 weeks) was followed by steady TBP consumption of  $37 \mu\text{mol hr}^{-1} \text{mL}^{-1}$ . Hence, TBP was utilized for growth by TBP-supplemented pseudomonad cultures (see Figure 1D – Thomas and Macaskie, 1996).

*Pseudomonads* were found to be the most persistent bacteria species when TBP was the sole phosphorous source (Rosenberg and Alexander, 1979). *Acinetobacter* was found to respond in a similar fashion, although at a slower rate (150 µg/mL TBP over 28 days) (Stoner and Tien, 1995).

In a separate publication, the effect of different parameters on TBP biodegradation, such as temperature, pH, and metal and ion addition, was identified (Thomas and Macaskie, 1997). Acid-mine drainage water was treated with the same feed solution and presented with TBP at the same concentration as the previous experiments (Thomas and Macaskie, 1996). Optimal results were found at a temperature of 30°C and pH of 7, with  $0.48 \pm 0.03$  mM residual TBP after 50 hours, corresponding to roughly 75 percent TBP removal. The presence of sulfate ions and specific metals such as copper, cadmium, nickel, cobalt, and manganese either reduced or completely inhibited biodegradation. Also, the introduction of a competing carbon source, such as kerosene (tested because of its role as a diluent in nuclear fuel processing), can severely reduce TBP biodegradation by inhibiting oxygen intake or trapping TBP, thereby removing it as a site for bacterial growth.

An in-depth analysis of solubility, octanol-water partition coefficient, and biodegradability was conducted for 11 phosphate esters, including TBP (Saeger, 1979). The study found that five of these compounds, including TBP, underwent complete primary biodegradation in river die-away tests in less than seven days. Two separate semi-continuous activated sludge (SCAS) tests were conducted for TBP. In one test, TBP was added at a rate of  $3 \text{ mg L}^{-1} 24\text{hr}^{-1}$ , with 96 percent biodegradation over 13 days. A second study, using a feed rate of  $13 \text{ mg L}^{-1} 24\text{hr}^{-1}$ , yielded  $56 \pm 21$  percent degradation over a 3-week period, demonstrating that TBP biodegradation may increase with decreased loading. A follow-up CO<sub>2</sub> evolution study was undertaken to determine the extent of biodegradability, with almost all phosphate esters essentially undergoing complete mineralization. The study concluded that naturally occurring mixed microbial

populations in surface waters will degrade commercial phosphate esters such as TBP (Saeger, 1979).

Further studies by Thomas, Macaskie, and Dick, to be researched shortly, will hopefully add insight into the biodegradability of TBP as well as TBEP and TCEP. A report completed for the time period of spring 1999 to spring 2000 analyzed indicator bacteria such as *Escherichia coli* (*E. coli*) and *enterococci* in the tributary streams of the Upper Chattahoochee River and could possibly give insight into bacterial loading within this region (Gregory and Frick, 2001). Given the results of these past toxicological experiments, biodegradation is a potentially significant mechanism for natural degradation of organophosphates in surface waters and will be one of our focal points in future studies on the Chattahoochee.

## Major Potential Sink

Table 1 summarizes our analysis of half-lives.

Table 1. Summary of half-life analysis.

Type	Half-Life (days)	Notes
Volatization	20	Only for TCEP; TBP & TBEP negligible
Photodegradation	8-12	In reality, half-lives are most likely higher
Hydrolysis	100-130	Half-life of Chlorine atom is around 38 days
Bioaccumulation	3-4	BCF is very low, so may not be a large factor
Biodegradation	2-28	Depends highly on type of bacteria

(Note: Sorption is not included because it does not technically have a half-life)

To put some meaning into these numbers, Drugstore Cowboys, Inc. estimated the residence time for a particle to travel down the Chattahoochee River. This estimate can be found with the volumetric flow rate, the distance traveled, and the hydraulic cross-section area. The volumetric flow rate is 2000-3000 cubic feet per second. The distance traveled from Buford Dam to Atlanta is 48 miles, and the hydraulic cross-section area is approximately 1000 square feet. This leads to a residence time of 1-1.5 days.

Thus, biodegradation and bioaccumulation seem to be the major potential sinks in the Chattahoochee River, since the other processes have considerably longer half-lives than the residence time of the river.

Further research that Drugstore Cowboys, Inc. will perform includes considering the effects from other minor sinks, such as recharge from or discharge to groundwater. Plus, dilution factors must be considered when sampling directly from the river as opposed to the outfalls of a WWTP.



## **In Situ Investigation at the Chattahoochee River**

To examine more closely the life cycle of the phosphate esters, the Drugstore Cowboys will travel to Atlanta in order to supplement the CDC-USGS data from the summer of 1999.

Sampling sites will include areas where the original data were taken, but will also have sites that correspond to the major potential natural sinks in the process. This will most likely include sites in the Chattahoochee River itself, as opposed to the outfalls at WWTPs and intakes and finished samples at the DWTPs. Other sites will come within an actual DWTP, with the intention of examining how DWTP processes affect the removal of the phosphate esters. Plus, since the CDC-USGS data only took samples upstream of Atlanta, valuable information may also lie downstream of Atlanta. These potential sites are being discussed among the clients and Drugstore Cowboys Inc., in hopes of gathering the best data to complement the natural and treatment processes being analyzed.

Sampling styles are still being hashed out among Drugstore Cowboys Inc., but will suit the analytical method(s) that will detect the concentrations of phosphate esters in the waters. The preferred method comes from (Kolpin et al., 2002), using a whole-water continuous liquid-liquid extraction with capillary gas chromatography/mass spectrometry analysis. One major note is that the method requires at least one liter of sample for each analysis, since the concentrations of the phosphate esters are in the order of ng/L.

Most costs of the project will come from the large amount of sampling bottles, the analysis costs, the possible use of a craft to move along the Chattahoochee River, and hotel fees. Assuming a stay of two weeks, the total cost will most likely be under \$5,000 for these four items. Other fees will come from travel expenses, such as transportation and food.

## **Drugstore Cowboys, Inc. Proposed Further Investigation**

### **Natural Attenuation Processes**

Mathew Andrews will focus on the natural attenuation processes driving the removal of the three phosphates in the river. Utilizing his expertise in environmental transport processes, Mr. Andrews will analyze the factors that contribute to natural degradation. In particular, he will focus on the mechanisms of sediment sorption, bioaccumulation and biodegradation, previously noted to be potential major sinks for phosphate compounds in surface waters. Field testing along the Chattahoochee River will be conducted to augment his ongoing literature research.

A thorough understanding of the factors involved in the fate of these compounds in the surface water environment can be incorporated into the modeling work of Mr. Haffey. Additionally, the concepts derived from the natural environment may be applicable in the manufactured water treatment system, which will be the focus of Mr. Lin's work. Parallels may be drawn between the natural system and the manufactured water system, which ultimately lead to improvements in water treatment efficiency.

By developing a logical justification for the observed fate of flame retardant compounds in the environment, recommendations can perhaps be made for chemicals which are more readily degraded in the surface water environment while maintaining the necessary flame retarding capability.

## **Investigation into a Drinking Water Treatment Plant**

In addition to taking samples along the Chattahoochee River, Joseph Lin plans to take samples in a DWTP or a WWTP. Each of the processes within the plant will be examined from a chemical perspective. For example, disinfection in a chemical plant involves the use of chlorine; is there any form of hydrolysis within disinfection that may affect the removal of the phosphate esters?

Depending on the DWTP that Mr. Lin will have access to, he will examine the chemistry of (Adams et al., 2002; Paune et al., 1998):

- Metal Salt Coagulation: The use of aluminum sulfate and ferric sulfate is intended to coagulate particles, but may have different effects on the phosphate esters.
- Lime Softening: The use of soda ash to lower the hardness due to calcium and magnesium. Do the extra carbonate molecules promote hydrolysis?
- Granulated Activated Carbon and Powdered Activated Carbon Sorption: This method is very useful in removal of hydrophobic organic chemicals.
- Ozonation: Diffusing ozone into the waters, usually done as a substitution to chlorination.
- Ion exchange: Although used rarely in practice, strong-acid cation and strong-base anion resins are used.
- Other processes that may involve chemical removal of the phosphate esters.

Plus, WWTP chemistry involves:

- Aeration: Diffusion of oxygen, usually done after the primary sedimentation stage. In some instances, phosphate removal occurs depending on the type of bacteria.

- Polymer/ferric chloride addition: Promotes coagulation. The question is where the phosphate esters end up, whether it is hydrolyzed, goes into the sludge, or stays in the water.
- Chlorination
- Other processes that may involve chemical removal of the phosphate esters-.

The samples will most likely be taken at low-flow periods, which depend on the flow from the dams upstream of the Chattahoochee River. As noted in the in situ investigation section, one-liter samples will be necessary for each analysis. Details of the methodology for collecting samples will be determined by the time Mr. Lin travels to Atlanta in January 2004.

## **Computer Model of Phosphate Ester Fate and Transport**

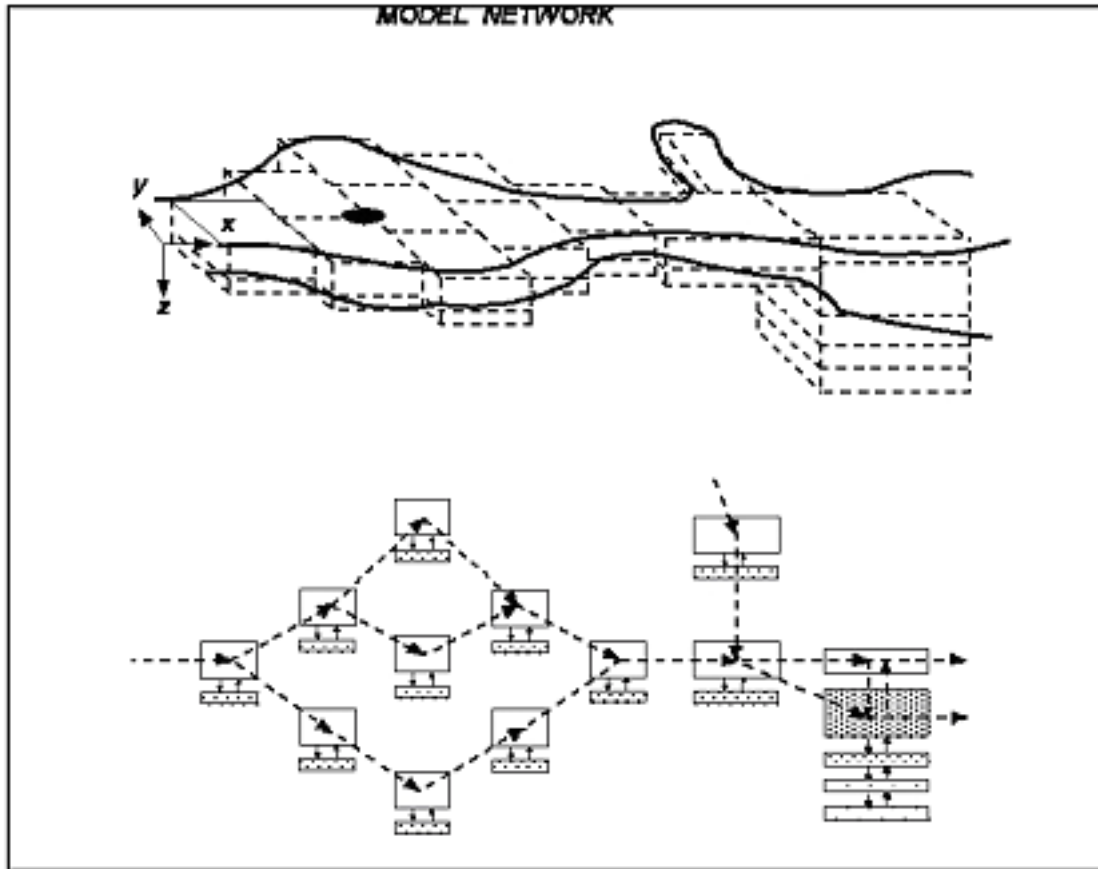
Samuel Haffey will develop a computer model that strives to predict the behavior of the selected phosphate esters within the Chattahoochee River. Mr. Haffey's background in computer science makes him the most suitable choice for this portion of the project. The computer model will combine data on specific characteristics of the Chattahoochee River with properties of the compounds to predict their behavior.

A computer simulation modeling the fate and transport of the phosphate esters in the Chattahoochee River can help describe present water quality conditions. The current set of data gathered by the CDC in addition to data that will be gathered by the project team provides information on concentrations at specific points in the system. The computer simulation can help to interpolate between these sample points and give a greater understanding of the concentrations that can be encountered at any point along the river system.

The model can also serve to provide site-specific predictions. The projected increase in the production and use of at least two of the phosphate esters being studied indicates that concentrations may increase over the coming years. A model is useful for predicting the effect that increased loads will have on the Chattahoochee River and where we can expect the accumulation of the phosphate esters. Furthermore, the predictions provided by the model can be extrapolated to provide predictions on the effect of phosphate ester loads on other river systems. Given the pervasive presence of phosphate esters in the environment, these extrapolated predictions could prove very useful for further studies.

Mr. Haffey proposes using the Environmental Protection Agency's water quality analysis code, Water Quality Analysis Simulation Program (WASP5) (Ambrose, Wool & Martin, 1993), to construct the model for the fate and transport of the phosphate ester compounds in the Chattahoochee River. Data from the CDC-USGS survey as well as data the project team will collect during January will be used to calibrate the model.

The WASP5 code models the hydraulic system as a series of control volumes linked together through mixing processes. Each control volume represents a segment of the river with defined transport, loading and transformation processes. The control volumes are linked together to form a model of the river system. (Ambrose, Wool & Martin, 1993)



**Figure 8**  
**Graphic Representation of WASP5 Model (Ambrose, Wool & Martin, 1993)**

Using the same kinetic model of the phosphate esters used in the model of the Chattahoochee River discussed above, we propose to further use the WASP5 code to model the drinking water treatment processes being performed at the DWTPs drawing water from the Chattahoochee River. This will be achieved by defining the tanks in the drinking water treatment process as control volumes with no mixing. This model will provide insight into ways of improving the treatment process to more efficiently remove the phosphate esters as well as provide predictions as to how the process will behave with varying concentration levels.

## **Engineering a Viable solution for removal of phosphate esters at DWTPs**

Alexandros Machairas will investigate the possibility of removal of the selected phosphate esters at traditional Drinking Water Treatment Plants with small alterations of existing treatment processes.

The focus of his research will be on identifying possible ways of altering existing widely used treatment processes with a feasible cost that will provide substantial results. His preliminary considerations target the chemical degradation of the phosphate esters by hydroxyl radical attack. These considerations rise from the fact that some of the traditional disinfection processes, like ozonation or ultraviolet irradiation can be easily altered to produce a significant amount of hydroxyl radicals.

In order to investigate the above possibility, funding will be required so that necessary experiments are performed that will tabulate the reaction rate of hydroxyl radical with the phosphate esters of interest at relevant pH levels. The experiments most probably will be performed in a batch reactor with a known hydroxyl radical concentration. The hydroxyl radical will be produced through a Fenton reaction, and the phosphate esters will be introduced at spiked concentrations.

The production of hydroxyl radicals in the previously mentioned treatment processes can be increased in many ways. For UV disinfection, one approach could be to introduce  $H_2O_2$  that breaks down to produce hydroxyl radicals. At ozonation tanks, the introduction of  $H_2O_2$  can increase the naturally occurring hydroxyl radicals and therefore enhance the degradation processes. Another solution is the irradiation of ozonation tanks with UV light to enhance the production of hydroxyl radicals.

In addition, Mr. Machairas will do an extensive literature review that will provide necessary information for the estimation of the degradation potential for the above processes. For example, a necessary value is the average irradiation intensity at UV disinfection tanks.

The goal of his research will be to explore the potential of the above mentioned engineering solutions at addressing the emerging concerns relating to the occurrence of xenobiotic organic compounds in surface waters and their mitigation to drinking water.



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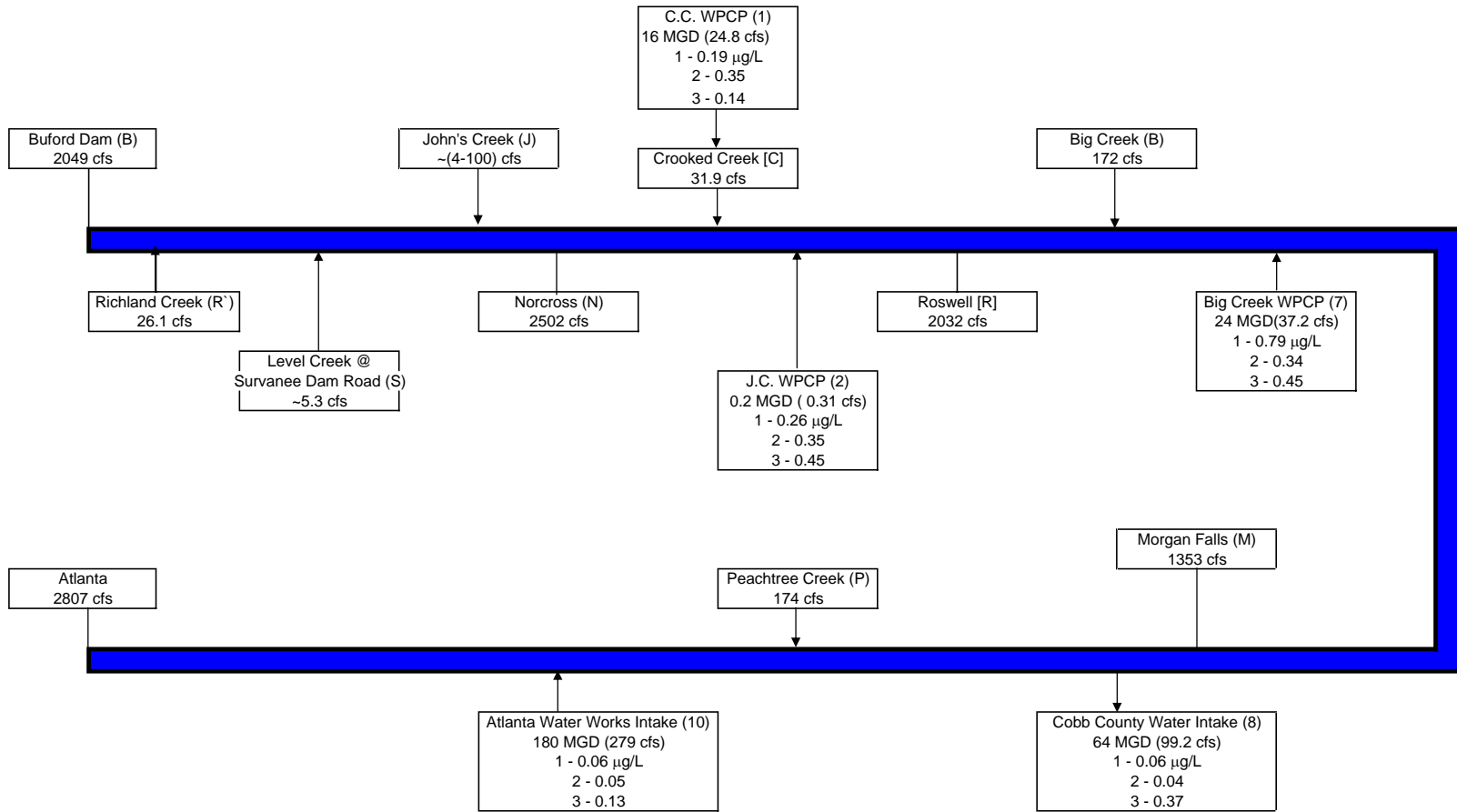
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**Appendix A**

**Chattahoochee River (Buford to Atlanta)**



Key: 1 = tributyl-phosphate  
 2 = tri(2-chloroethyl) phosphate  
 3 = ethanol, 2-butoxy-,phosphate

**Big Creek (Cummings to Roswell)**

