Drugstore Cowboys, Inc.

Flame retardant chemicals in the Chattahoochee River

Company Profile

- Statement of Purpose –

  Serve the needs of the public and our client by providing expert analysis and guidance in the characterization and remediation of surface water environments contaminated by pharmaceuticals, personal health care products, and other synthetic chemicals

- Specialization –

  Multi-faceted approach to surface water remediation, utilizing the diverse background and expertise of our employees to effectively treat a variety of contaminated sites

Company Employees

- Matt Andrews – Chief Environmental Engineer

  Expertise – Environmental fate and transport of organic and synthetic pollutants in aqueous systems (groundwater, river, estuarine, and coastal environments). Extensive experience implementing innovative solutions to complex remediation projects

- Samuel Haffey – Chairman, Computer Science Department

  Expertise – Software Engineering, Data Management Architecture, Computer-Enhanced Environmental Modeling.

Company Employees

- Joe Lin – Director, Chemical Engineering Department

  Expertise – Chemical processes: thermodynamics, kinetics, mass/energy balances. Knowledgeable of specific chemistry occurring for PPCPs and OWCs.

- Alexandros Machairas –Chief Executive Officer , Civil Engineering Division

  Expertise – Water Resources,Environmental Fluid Mechanics, Surface & Groundwater Hydrology

Statement of Problem

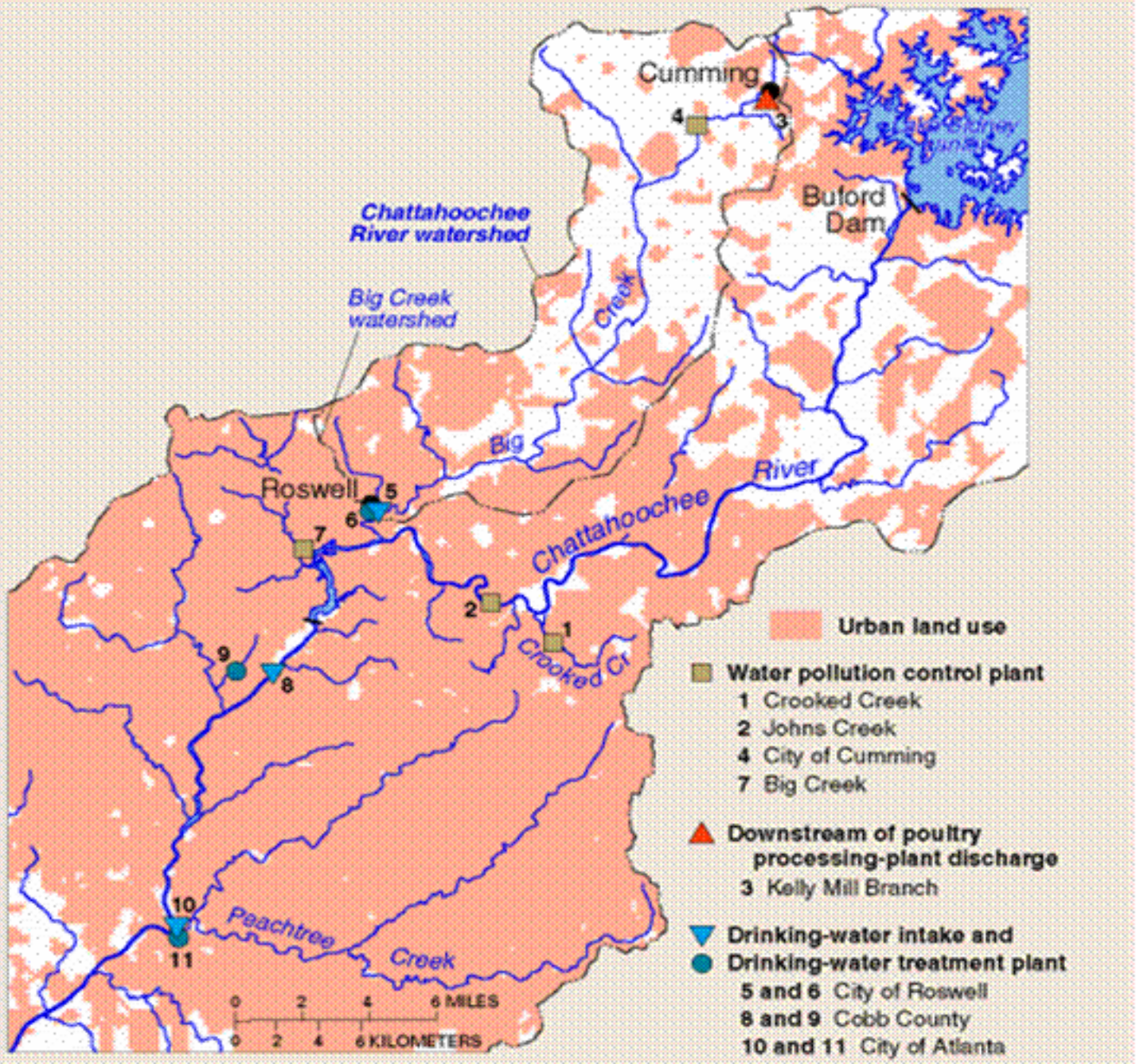
- Occurrence & fate of pharmaceuticals, personal care products, and flame retardants in natural surface waters an emerging issue in environmental science.
- Main Source – Wastewater Treatment Plant (WWTP) discharge
- Detection in municipal drinking water of particular concern for public health
- Effect on aquatic organisms uncertain yet presumed to be of concern, even at low concentrations

Published Research

- Studies by USGS and the Center for Disease Control obtained accurate low level concentration measurements in surface waters
- Analogous Research Conducted in Europe – ENVIRPHARMA conference 2003
- Ongoing research seeking to characterize toxic effect of these compounds on natural aquatic environments

CDC Data

- Concentrations collected for over 100 compounds along 50 mile stretch of Chattahoochee River Basin, from Buford, GA to Atlanta, GA
- Measurements taken for WWTP discharge and both intake and outflow at drinking water treatment plants (DWTP)
- Permits comparison of concentrations along continuous stretch of river.
- Suffers from a lack of sampling repetition and trends are difficult to extract

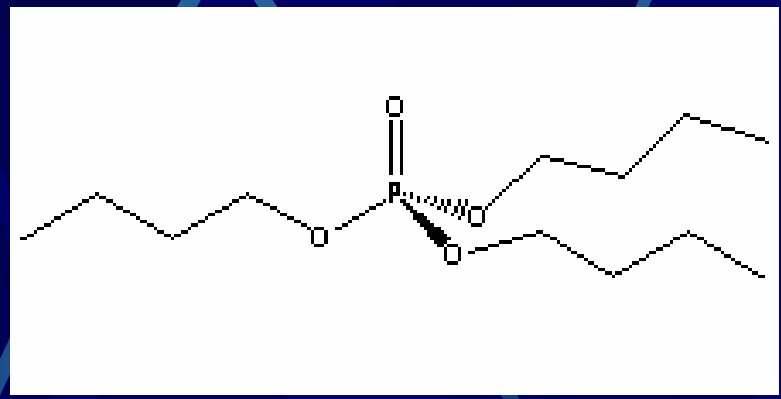

Cumming
4
3
Buford
Dam
Chattahoochee
River watershed
Big Creek
watershed
Creek
Big
River
Chattahoochee
Roswell
5
6
7
2
1
Crooked Cr
9
8
10
11
Peachtree
Creek
0 2 4 6 MILES
0 2 4 6 KILOMETERS
Urban land use
Water pollution control plant
1 Crooked Creek
2 Johns Creek
4 City of Cumming
7 Big Creek
Downstream of poultry
processing-plant discharge
3 Kelly Mill Branch
Drinking-water intake and
Drinking-water treatment plant
5 and 6 City of Roswell
8 and 9 Cobb County
10 and 11 City of Atlanta

Chemical Selection

- 3 Phosphate Esters:
  - Phosphotriesters
    - Tributyl phosphate
    - Tri (2-butoxyethyl) phosphate
    - Tri (2-chloroethyl) phosphate
- Comparable structure and associated properties
- Relatively high level of detection in CDC-USGS data

Tributyl Phosphate (TBP)

- Properties
  - Formula: $C_{12}H_{27}O_4P$
  - MW (g/mol): 266
  - Chemical Structure:



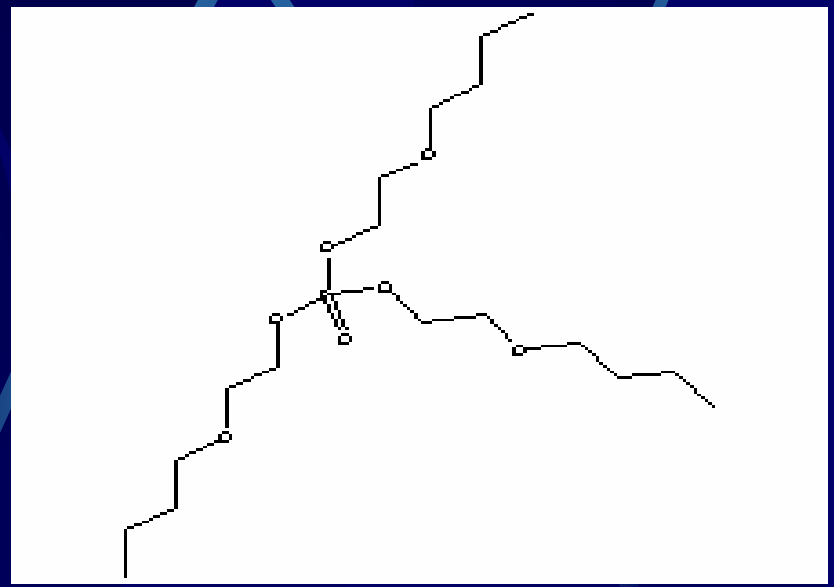
- Toxicology
  - Affecting transpiration from tree leaves
  - Long-term exposure effects not studied

Tributyl Phosphate (TBP)

- Manufacture process
  - Reaction of phosphorus oxychloride and n-butanol (1:3)
  - Uses: Flame retardant, plasticizer
    - Recently: recovery of Uranium ores (Thomas et al, 1998)
- Production
  - 2500-4000 tonnes produced in 1985

Tri (2-butoxyethyl) phosphate (TBEP)

- Properties
  - Formula: $C_{18}H_{39}O_7P$
  - MW (g/mol): 398
  - Chemical Structure:



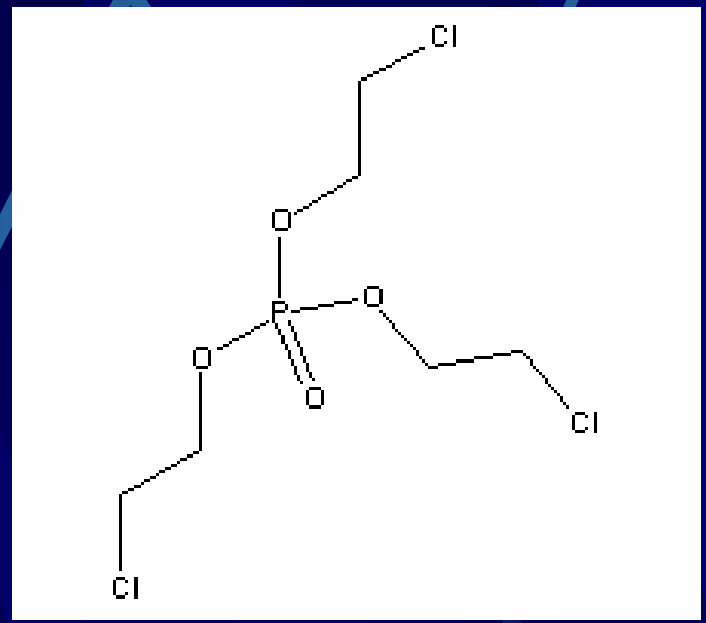
- Toxicology
  - Generally found to be non-toxic in humans
  - Long-term exposure effects not studied

Tri (2-butoxyethyl phosphate (TBEP)

- Manufacture process
  - Rxn of phosphorus oxychloride and 2-butoxyethanol (1:3)
  - Uses: Household product, flame retardant
    - Cleaners: Up to 8% TBEP
- Production
  - Approximately 6000 tonnes produced in 2000

Tri (2-chloroethyl) phosphate (TCEP)

- Properties
  - Formula: $C_8H_{12}PO_4Cl_3$
  - MW (g/mol): 278
  - Chemical Structure:



- Toxicology
  - Carcinogenic effects on mice
  - Long-term exposure effects not studied

Tri (2-chloroethyl) phosphate (TCEP)

- Manufacture process
  - Reaction of phosphorus oxychloride with ehtylene oxide (1:3)
  - Uses: Flame retardant, plasticizer
    - Products: Resins, such as casting of bathtubs and pipes

- Production
  - Decline in use, as TCEP is not recognized as a good flame retardant anymore
  - Below 4000 tonnes in 1998

Phosphate Ester Loading

- Approximate loading into Chattahoochee River:
  - TBP and TCEP in USA: 2000 m^3/year
  - TBEP in USA: 3000 m^3/year
  - Population of Atlanta area: 2.8 million
  - Population of United States: 280 million
  - Thus, 20 - 30 m^3/year produced of each chemical
- Average volumetric flow of Chattahoochee River: 20×10^8 m^3/year

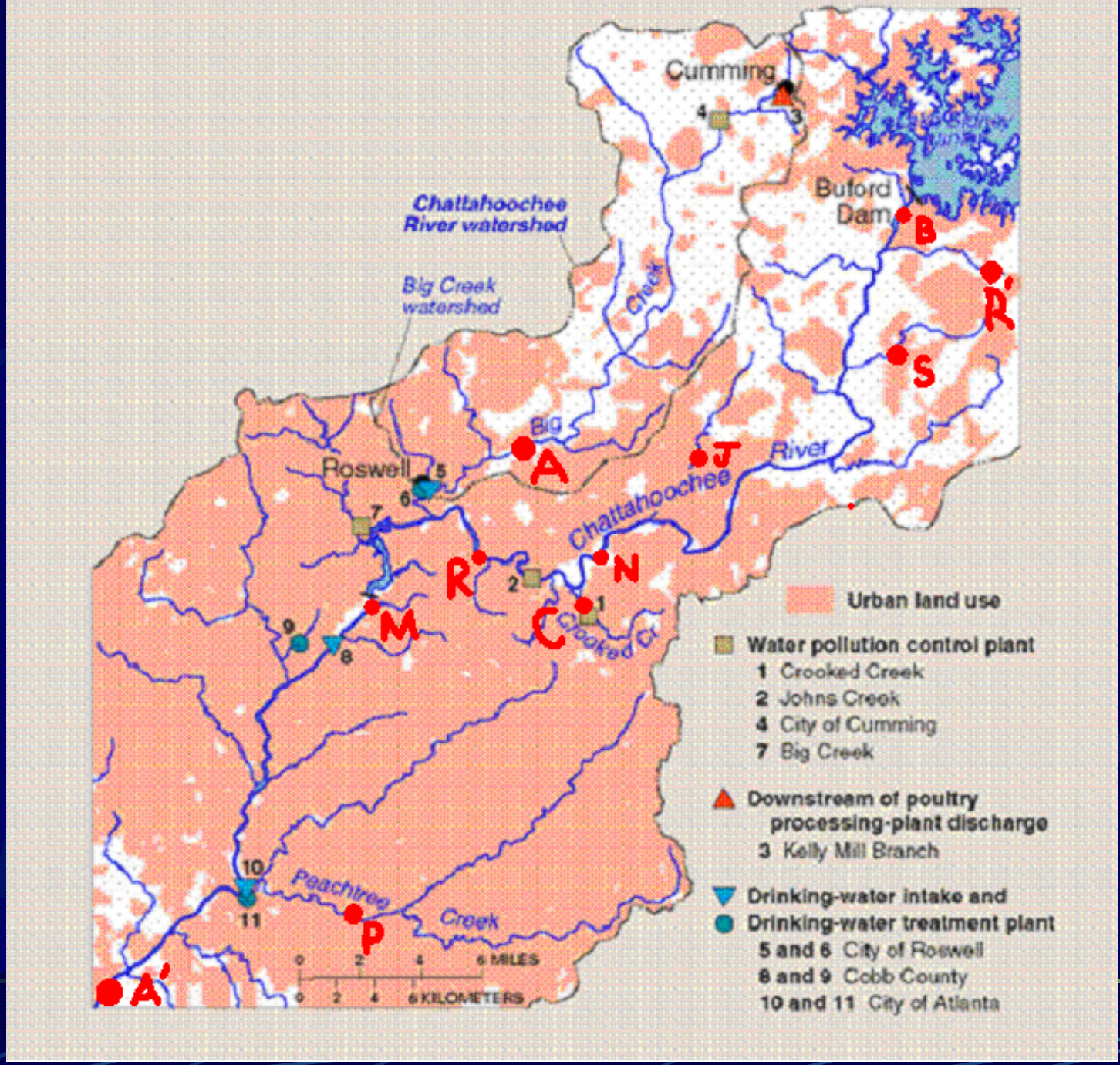
Phosphate Ester Loading

- Conclusion: ~10 - 15 ppb in river
  - Actual concentrations are .1 – 2 ppb
  - Overestimation due to all production going into streams

Chattohoochee River Characteristics

- General Description:
  - Length of 48 miles from Buford to Atlanta, GA
  - Landscape predominantly forestland
  - Flow oscillates with power generation schedule at Buford Dam (550 to 7500 cfs, average 2100 cfs)

- Flow Characteristics
  - Flow rates determined from USGS stream gages stationed along Chattahoochee and several tributaries
  - WWTP and DWTP flows based on average operation


Cumming
Buford Dam
Chattahoochee River watershed
Big Creek watershed
Big Creek
Roswell
Chattahoochee River
Crooked Cr
Peachtree Creek
A
A'
B
B'
C
J
M
N
P
R
S
Urban land use
Water pollution control plant
1 Crooked Creek
2 Johns Creek
4 City of Cumming
7 Big Creek
Downstream of poultry processing-plant discharge
3 Kelly Mill Branch
Drinking-water intake and
Drinking-water treatment plant
5 and 6 City of Roswell
8 and 9 Cobb County
10 and 11 City of Atlanta
0 2 4 6 MILES
0 2 4 6 KILOMETERS

Chattahoochee River Characteristics

- "Black Box" mass balance
  - Wastewater discharge only phosphate source considered
  - Flows based on average January stream gage readings
  - Average CDC concentrations combined with river flow to determine concentration in river
  - Allows for estimation of rate of removal from natural sinks

Potential Natural Removal Processes

- Sorption
- Volatilization
- Photodegradation
- Hydrolysis
- Bioaccumulation
- Biodegradation

- Time Scale: 1-1.5 days

Sorption

- Estimated yearly sediment load from USGS turbidity data collected upstream of Atlanta.
  - 4 X 10^8 kg/year
- Calculated K_{oc} based on average organic carbon content and instantaneous partition equilibrium
- Estimated levels of removal minimal compared to that anticipated in river

Volatization

- TBP and TBEP have low Henry's constants (high solubility) such that volatization is negligible
- TCEP volatization is more significant
  - Toxinet: half-life of ~20 days for a model river

Photodegradation

Two types of Photodegradation

- Direct
  - No available uv/vis absorption spectrum
  - TBP estimated absorption at λ=200nm
  - Negligible degradation
- Indirect
  - Mainly by creation and attack by hydroxyl radicals
  - Estimated mean concentration for $OH\cdot \sim 10^{-16}$ M
  - $k = 10^{10}\ M^{-1}\ sec^{-1}$ for TBP
  - half life ~ 8 days (TBP)

Hydrolysis

- Two types of hydrolysis:
  - Substitution of esters or halides with hydroxyl ions
- Most likely to occur at high (basic) pH values, however river water and drinking water are usually an acidic or neutral pH
- EPA: TBP half-life for hydrolysis: ~130 days
- Ishikawa et al: 100% of TBP and TCEP remained after 24 hours at low to neutral pH

Bioaccumulation

- Uptake of chemical into the organic tissue of aquatic organism, either through water or food
- Usually presented as bioconcentration factor (BCF), empirically linked to K_{ow} constant for particular species
- Studies have shown TCEP and TBEP exhibit low BCF in test fish species and is unlikely to appreciably bioaccumulate
- TBP uptake and metabolism has been demonstrated in several fish species with half lives similar to that observed in river

Biodegradation

- Biological transformation of a chemical, which often serves as food source for bacterial culture
- TBP shown to degrade with half lives on the order of a few days, consistent with the rate of removal observed in the river
- Considered most likely removal mechanism in Chattahoochee River

Plan of Action

- Continued literature research
  - Develop more complete water and pollutant balance models for Chattahoochee River
  - More thorough understanding of major removal mechanisms within river

Plan of Action

- Atlanta Site Visit
  - Field sampling analysis – tailored to exploring role of major degradation processes in phosphate removal
  - Drinking water treatment plant exploration
  - Meet with CDC staff to discuss data collection methods and results from their testing

Plan of Action

- Data Analysis
  - Interpret data collected from field samples
  - Develop computer modeling system
  - Investigate hydroxyl radical attack effects
- Prepare presentation
  - Submit final written report
  - Deliver oral presentation

Schedule

- December: Experiment development
  - Prepare testing goals and strategies
  - Make travel arrangements and obtain testing supplies
- January: Trip to Atlanta
  - Meet with CDC personnel
  - Conduct field experiments
- February: Analysis of Data
  - Further literature research
  - Analyze and interpret data collected from field tests
- March – April: Conclusions
  - Draw conclusions from work completed
  - Prepare presentation and report of findings

Budget

- Drugstore Cowboys Bill Rate: $25/hr
- Anticipated work hours:

Matt Andrews	1000 hours
Samuel Haffey	1000 hours
Joe Lin	1000 hours
Alexandros Machairas	1000 hours
Total billed:	$100,000

Budget

- Trip costs
  - Testing Supplies: $200
  - Airline Expenses: $1000
  - Lodging: $800
  - Total: $2000
- Sample Analysis costs
  - Analysis Fees: $1000
- Total Anticipated Budget: $103,000

Final Remarks

- Flame retardants and other synthetic mixtures in the environment is a hot current issue
- Our competitive advantage is our experienced, diverse staff fully capable of successfully completing investigatory analysis
- Please visit our website for more details:
  web.mit.edu/andrewsm/www/DrugstoreCowboys.htm