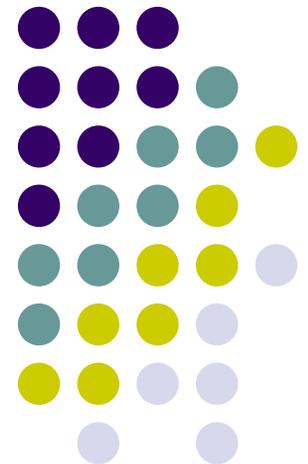


DRUGSTORE COWBOYS INC.
**PHOSPHATE ESTERS IN
CHATTAHOOCHE RIVER**

FINAL PRESENTATION



STATEMENT OF PROBLEM



- Occurrence and fate of Organic Wastewater Contaminants (OCWs) in Chattahoochee River
- Explore fate and transport in both natural processes and drinking-water treatment processes

Existing Studies



- USGS National Reconnaissance (1999-2000)
- CDC study at Chattahoochee River (summer 1999)



USGS study

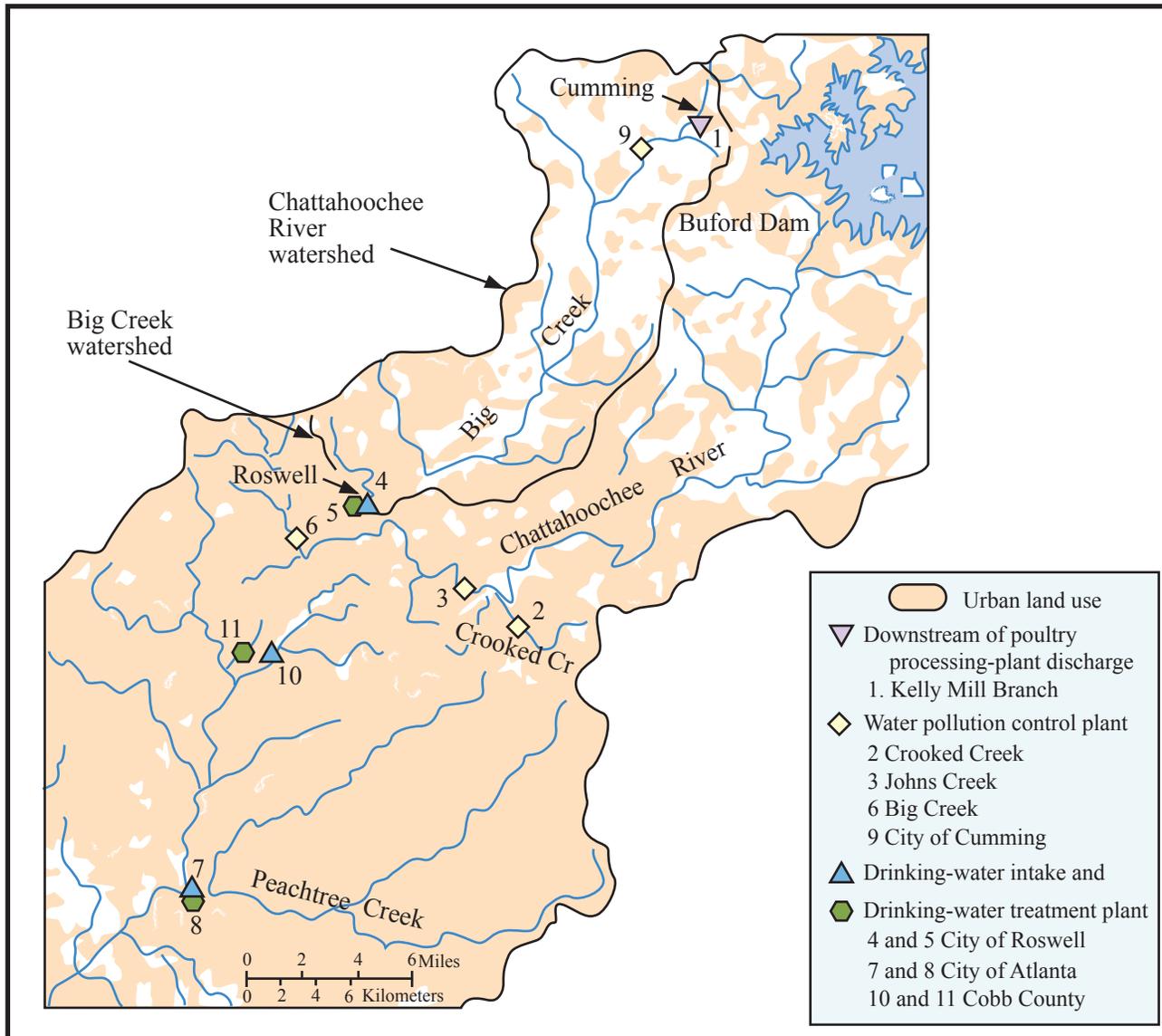
- Sampled 139 streams in 30 states
- Sampled for 95 Organic Wastewater Contaminants
- OCWs present at ~80% of streams sampled
- Very low concentrations (order of ng/l) but surprisingly high because most are man made compounds
- Persistence in natural environment

CDC study



- 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)
- Revealed Significant Presence of OCWs

Area of Study



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Magnitude of problem

- OCWs are currently present at low concentrations but their release in the environment is expected to continue
- Unknown effects in human health, potential risk of long term exposure
- Pharmaceutical compounds and their metabolites gravest fear
- Hot current scientific problem
- On going research Through-out the world

Selection of Phosphate Esters

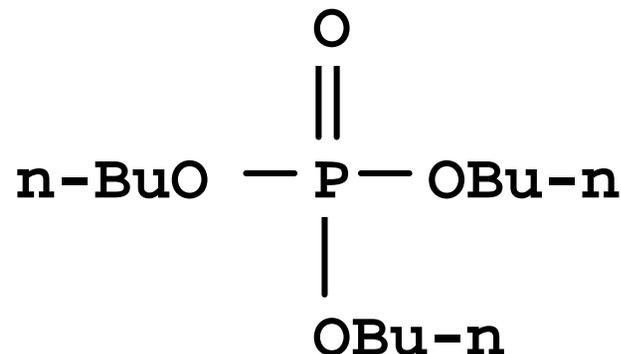


- 3 Phosphate Esters:
 - Tributyl phosphate
 - Tri (2-butoxyethyl) phosphate
 - Tri (2-chloroethyl) phosphate
- Comparable structure and associated properties
- Relatively high level of detection in CDC-USGS data



Tributyl Phosphate (TBP)

- Properties
- Formula: $C_{12}H_{27}O_4P$
- MW (g/mol): 266
- Chemical Structure:
- Uses: Flame Retardant,Plastisizer
- Annual Production:2500-4000 tonnes in 1985



Tri (2-butoxyethyl) phosphate (TBEP)



- Properties

- Formula: $C_{18}H_{39}O_7P$

- MW (g/mol): 398

- Chemical Structure: $n\text{-BuO}-\text{CH}_2-\text{CH}_2-\text{O}-\text{P}(=\text{O})(\text{O}-\text{CH}_2-\text{CH}_2-\text{OBu-n})_2$

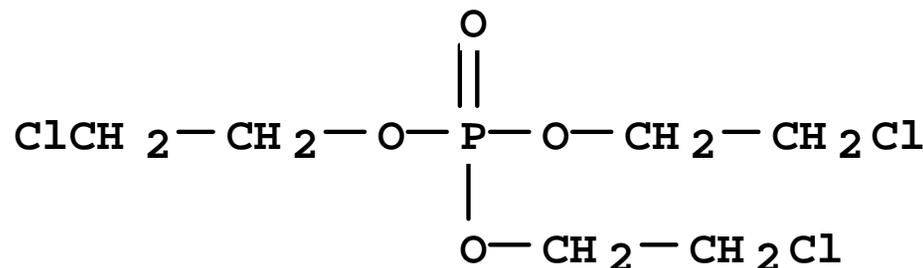
- Uses: Flame Retardant, household product

- Annual Production: 6000 tonnes in 2000

Tri (2-chloroethyl) phosphate (TCEP)



- Properties
- Formula: $C_8H_{12}PO_4Cl_3$
- MW (g/mol): 278
- Chemical Structure:
- Uses: Flame Retardant,Plastisizer
- Annual Production: <4000 tonnes in 1998

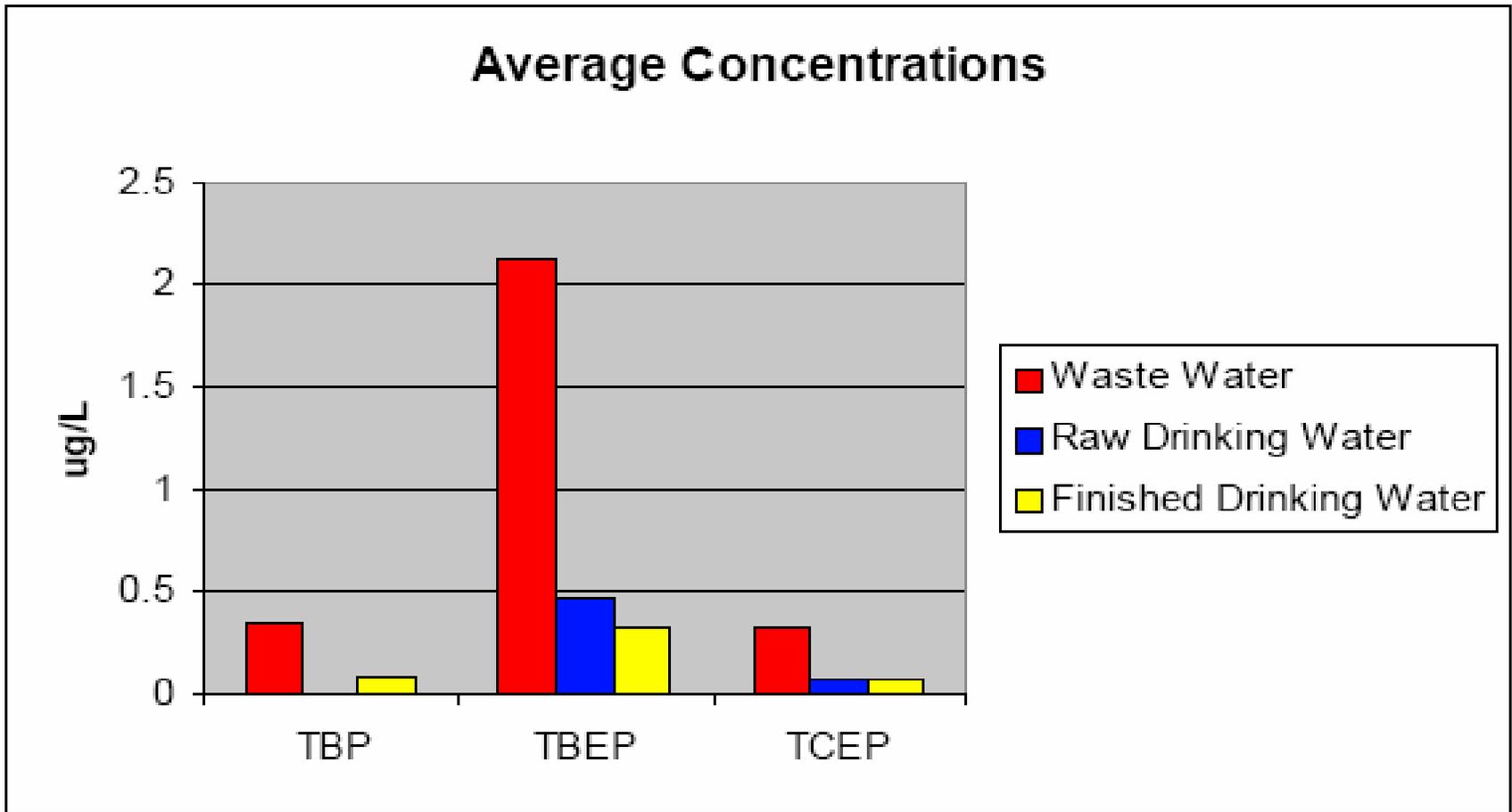


CDC data on phosphate esters



- Present at detectable conc's in most sampling sites
- Significant persistence in the river environment
- Present even after drinking-water treatment

CDC data on phosphate esters



Drugstore Cowboys Inc. initial approach to the problem



- Create a “black box” mass balance model
- Determine the magnitude of each natural attenuation process occurring
- Identify the most promising ones and research them in depth

Chattahoochee 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



Black Box Model

- 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



Estimation of annual loading

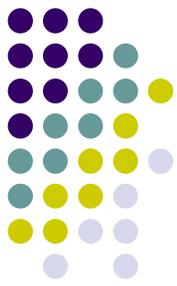
- Approximate loading into Chattahoochee River:
 - TBP and TCEP in USA: 2000 m³/year
 - TBEP in USA: 3000 m³/year
 - Population of Atlanta area: 2.8 million
 - Population of United States: 280 million
 - Thus, 20 - 30 m³/year produced of each chemical
- Average volumetric flow of Chattahoochee River: 20 x 10⁸ m³/year
- Conclusion: ~10 - 15 ppb in river
 - Actual concentrations are .1 – 2 ppb
 - Overestimation due to all production going into streams

Potential Natural Removal Processes



- Sorption
 - Volatilization
 - Photodegradation
 - Hydrolysis
 - Bioaccumulation
 - Biodegradation
-
- Time Scale: 1-1.5 days

Estimates of influence of each process



- Our simple calculations provide insight in the removal magnitude

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

Discussion of Estimates: What they reveal



- The only processes that seem to affect the phosphate esters are biodegradation and sorption to sediments
- Especially for biodegradation great uncertainty exists and further sampling is needed. But it is the most promising one



In situ investigation

- A visit to Chattahoochee river was decided that is needed
- Provide Additional sampling 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

A troubled River



- Pristine conditions upstream





A troubled river

- The situation near Atlanta is quite different
- I AM MISSING PICTURE



Sampling and Lab work

- Extensive Sampling was done
- Carefully chosen sampling locations and protocol
- Sampling done in a way to reveal biodegradation effects
- Significant amount of work done at our “state of the art” laboratory

Sampling and Lab work



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Valuable Experiences

- Nobody realized at first the problems associated with field work and sampling
- Great logistical problems
- Countless possible sources of experimental error
- The most sophisticated sampling project undertaken up to now from MEng
- Overall highly successful
- Without Pete Shanahan's help it couldn't have been done