Drugstore Cowboys

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Pharmaceuticals and Personal Care Products in Surface Waters: Case Study of Chattahoochee River

Company Profile

Environmental and Water Quality Engineering Firm

Staff Expertise:

Matt Andrews	Env. Engineering
Sam Haffey	Computer Science
Joe Lin	Chemical Engineering
Alex Machairas	Civil Eng.

Statement of Problem

- Occurrence and fate of pharmaceuticals and personal care products (PPCP) in surface waters
  - An emerging issue in environmental science
- Sources:
  - Wastewater Treatment Plant (WWTP) discharges (Main)
  - Agricultural runoff
  - Soil Leaching to Groundwater
- Presence in finished municipal drinking water
  - Drinking water treatment plant (DWTP) intake downstream of WWTP outfall

Project Objectives

- Explore fate and transport in both natural processes and drinking-water treatment processes
- Utilize data to support our conclusions
  - USGS data
  - CDC data
  - Data we collect
  - Other data
- Make engineering recommendations with regards to chemicals of interest

Project Tasks

- Select group of compounds
  - Choose from those identified as present in the CDC & USGS data
  - Choose compounds detectable by available methods
- Design sampling strategy
  - Samples should correspond to DWTP residence time
  - Varying times of day for WWTP effluent
- Travel to Atlanta to collect samples

IAP Trip

- Travel to Atlanta, GA for 1-4 weeks in January, 2004
- Objectives:
  - Talk with CDC personnel about data collection methods
  - Conduct our own field surveys on the Chattahoochee River

Possible Pitfalls

- Concentrations generally near detection limit
  - Even though they are present they may be difficult to detect
  - Available detection methods may have higher detection limit
- River will have higher flow during January
  - CDC & USGS samples taken during summer (Low flow period)
  - Increased flow will further dilute concentrations.

Backup Plan

- Attempt to make conclusions from CDC & USGS data
- Supplement CDC/USGS data with bench scale analysis (Alexandros will discuss in detail)

Current Research

- Studies by USGS and Centers for Disease Control
  - Pharmaceuticals, Hormones & other organic wastewater contaminants in U.S. Streams, 1999-2000: A National Reconnaissance; US Geological Survey
  - Centers for Disease Control study on Chattahoochee watershed – 1999
- Analogous Research Conducted in Europe – ENVIRPHARMA conference 2003.

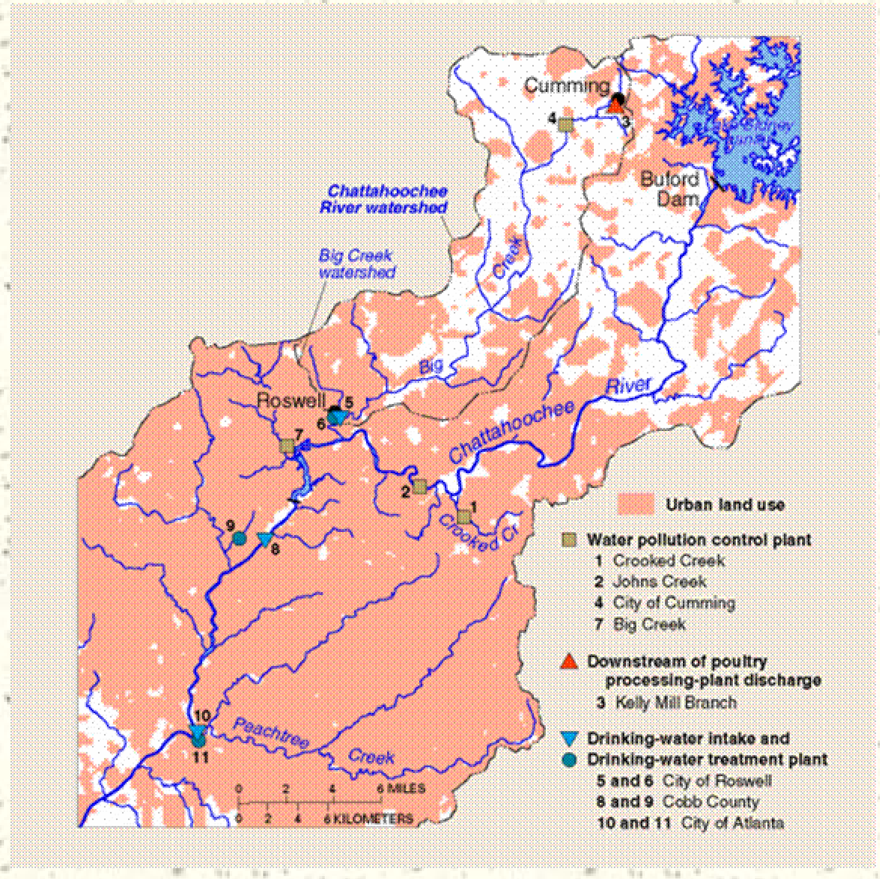
USGS Data

- Study conducted in effluent-dominated streams across US
  - States Covered
    - Georgia , Iowa, Illinois, Minnesota , Massachusetts, Missouri, New Jersey, Ohio, Oklahoma, Oregon, Texas
- Looked for and detected a variety of pharmaceutical compounds, hormones, and personal care products
- Data was collected to show presence of compounds in environment
  - Single samples Collected on specific days at specific sites.
    - Time series not available
- Conclusion: Good start to identify compounds of interest, but not useful in determining specific behavior

CDC Data

- Data collected in Chattahoochee, GA watershed - Atlanta metropolitan area.
- Chattahoochee: Effluent dominated river system with DW intakes downstream of WWTP outfalls.
- CDC Samples taken from WWTP effluent, DWTP intake and finished drinking water.

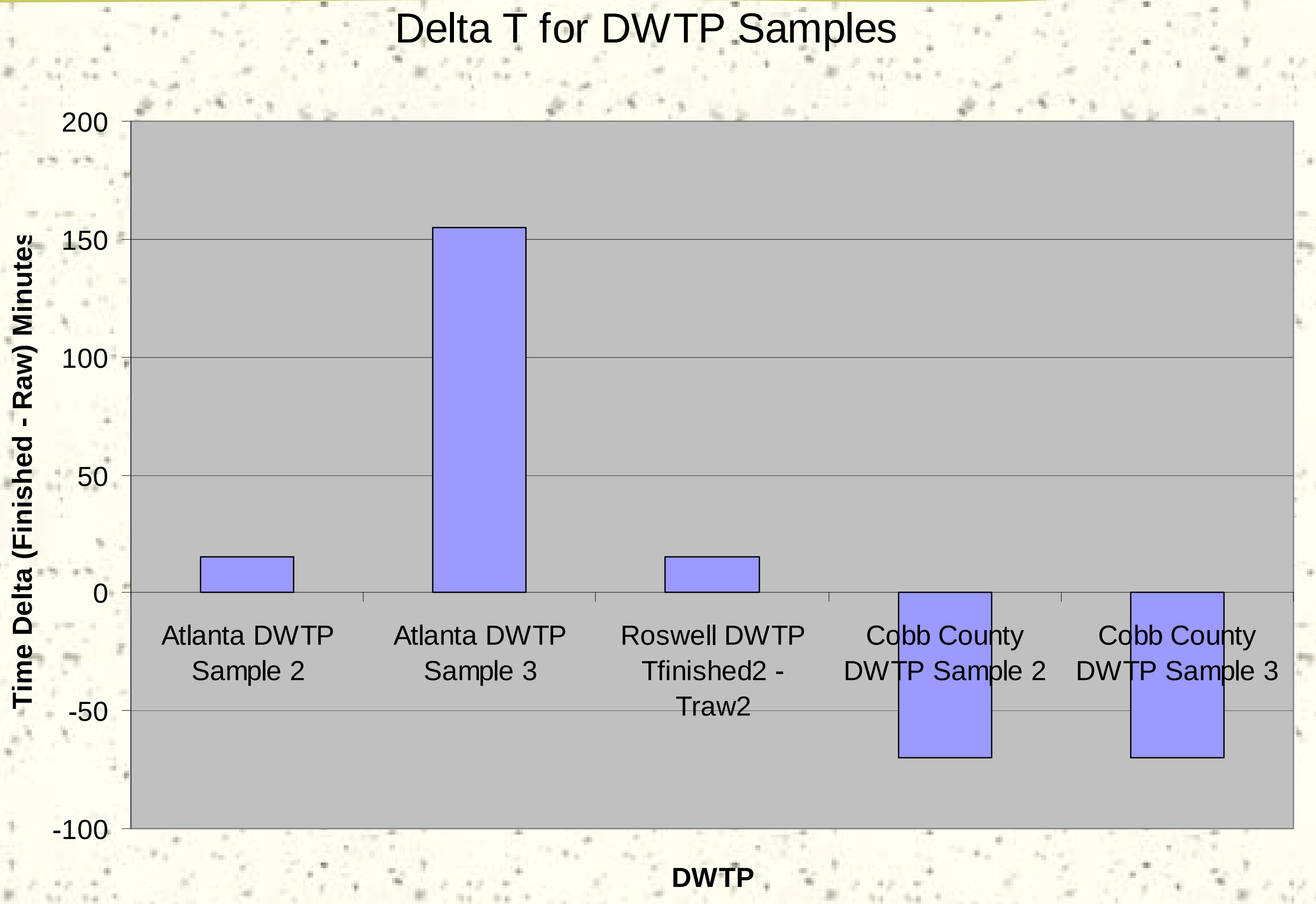
CDC Sample sites



CDC Data

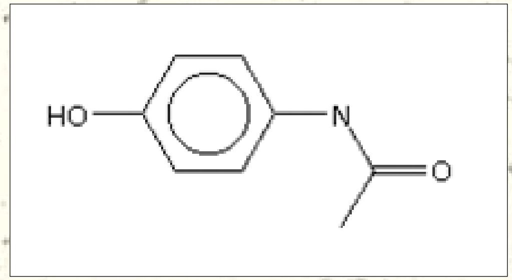
- Sample results tell more about compound behavior
  - Detections in WWCP, Raw & finished drinking water can be compared along same stretch of river.
- Still the samples cannot be related to processes
  - Samples taken at same DWTP show no consistent time difference between raw & finished samples
  - Some concentrations increased between raw & finished samples
  - Difficulties exist in analyzing the effectiveness of treatment

CDC Samples (Residence Time)



Chemicals of Interest

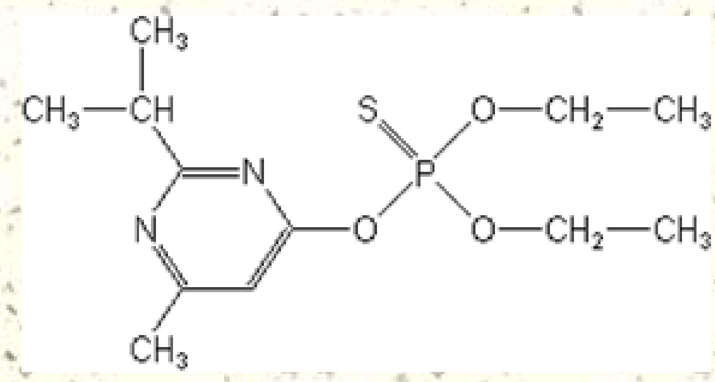
- Acetaminophen
  - Formula: $C_8H_9NO_2$
  - MW: 151.16 g/mol
  - CAS #: 103-90-2
  - Chemical Structure:



  - References: USGS (Kolpin et al)
  - Usage: Analgesic and antipyretic
  - Brand Names: Tylenol

Chemicals of Interest

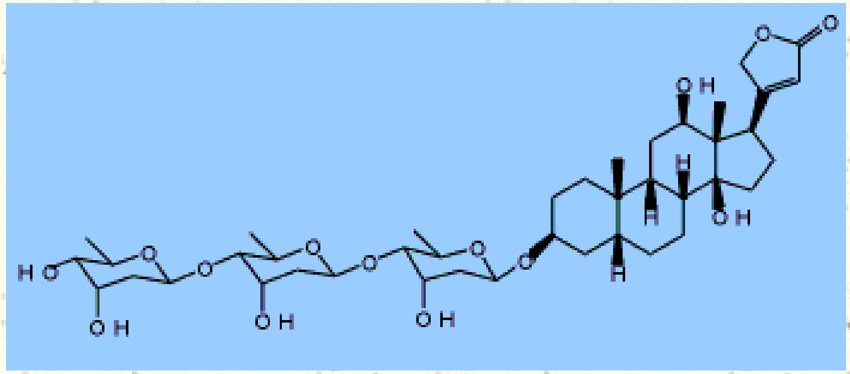
- Diazinon
- Formula: $C_{12}H_{21}N_2O_3PS$
- MW: 304.4 g/mol
- CAS #: 333-41-5
- Chemical Structure:



- References: CDC dataset,USGS (Kolpin et al), Heberer (2002)
- Usage: agricultural and household insecticide/pesticide

Chemicals of Interest

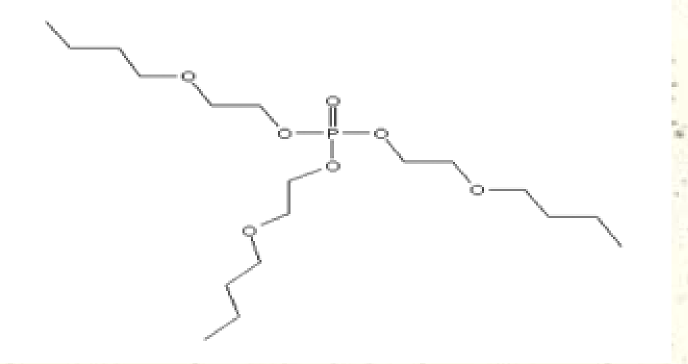
- Digoxin
- Formula: $C_{41}H_{64}O_{14}$
- MW: 780.94 g/mol
- CAS #: 20830-75-5
- Chemical Structure:



- References: CDC dataset,USGS (Kolpin et al), Heberer (2002)
- Usage: treatment of congestive heart failure/ abnormal heart rhythm
- Brand Names: Lanoxin

Chemicals of Interest

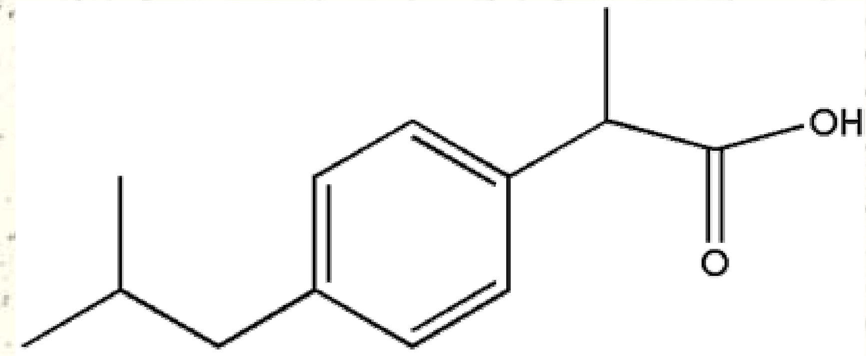
- Ethanol, 2-butoxy-,phosphate
  - Formula: $C_{18}H_{39}O_7P$
  - MW: 398.47 g/mol
  - CAS #: 78-51-3
  - Chemical Structure:



  - References: CDC dataset,USGS (Kolpin et al)
  - Usage: plasticizer

Chemicals of Interest

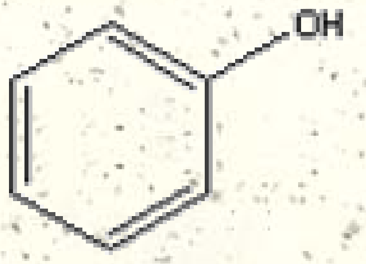
- Ibuprofen
  - Formula: $C_{19}H_{23}NO_2$
  - MW: 297.4 g/mol
  - CAS #: 15687-27-1
  - Chemical Structure:



  - References: USGS (Kolpin et al),Heberer (2002)
  - Usage: Anti-inflammatory
  - Brand Names: Advil

Chemicals of Interest

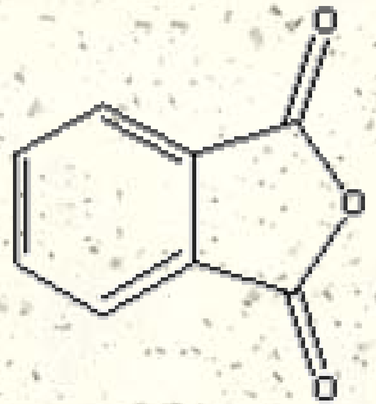
- Phenol
  - Formula: C_6H_5OH
  - MW: 93.9 g/mol
  - CAS #: 108-95-2
  - Chemical Structure:



  - References: CDC dataset,USGS (Kolpin et al), Heberer (2002)
  - Usage: Manufacture of plastics/synthetics, disinfectant products

Chemicals of Interest

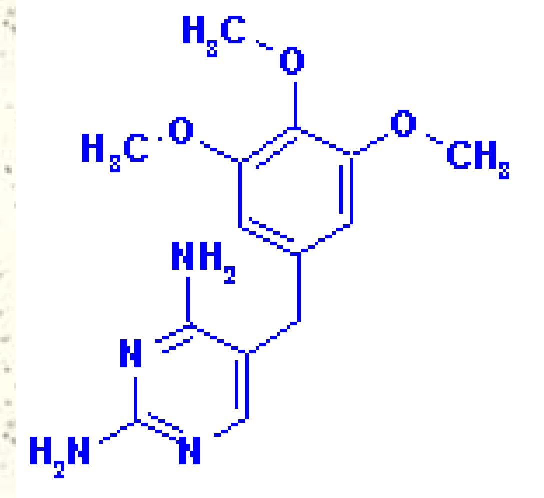
- Phthalic anhydride
- Formula: $C_8H_4O_3$
- MW: 148.11 g/mol
- CAS #: 85-44-9
- Chemical Structure:



- References: CDC dataset,USGS (Kolpin et al), Heberer (2002)
- Usage: Production of plastics/plasticizers, flame retardants

Chemicals of Interest

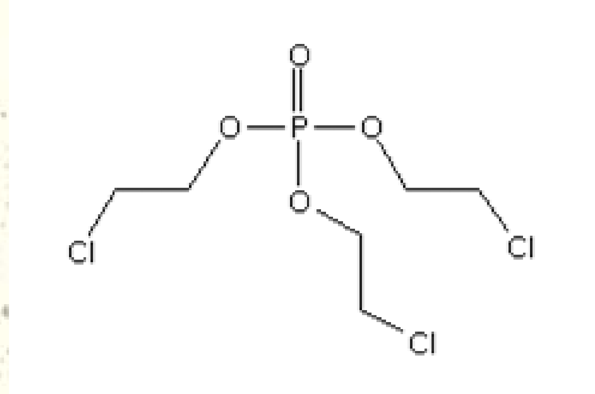
- **Trimethoprim**
- Formula: $C_{14}H_{18}N_4O_3$
- MW: 290.32 g/mol
- CAS #: 738-70-5
- Chemical Structure:



- References: CDC dataset, USGS (Kolpin et al)
- Usage: Antibiotic

Chemicals of Interest

- Tri(2-chloroethyl) phosphate
  - Formula: $C_6H_{12}C_{l3}O_4P$
  - MW: 285.49 g/mol
  - CAS #: 115-96-8
  - Chemical Structure:



  - References: CDC dataset,USGS (Kolpin et al)
  - Usage: fire retardant

Individual Contributions

Matt - Natural Attenuation Processes

Investigation of Natural Attenuation Processes

- General Project Objective: Study the fate and transport of pharmaceuticals and personal care products in natural surface waters
- Applications:
  - Improvements to Drinking Water Treatment Design
  - More ecologically friendly flame retardants

Investigation of Natural Attenuation Processes

- **Testing:** Longitudinal variation in chemical concentration along stretch of Chattahoochee River
  - Measure concentration at several locations along river
  - Develop profile of chemical transport in river
  - Investigate mechanisms of chemical removal/degradation in Chattahoochee River

Investigation of Natural Attenuation Processes

- Questions to Answer Before Testing:

  How are chemicals reaching the river and it what form/quantity?

  What are the characteristics of flow in particular stretch of Chattahoochee River?

  What are the physical properties of these chemicals that will affect their fate/transport in surface waters?

  What degradation/removal processes are likely to affect presence of chemicals?

  Examples: Photolysis, Sorption, Biodegradation

Investigation of Natural Attenuation Processes

Applications:

- Improving water treatment system design
  - Must effective natural processes utilized by treatment
  - Chemicals surviving natural degradation likely to survive drinking water treatment
- More environmental friendly flame retardants

Individual Contributions

Alex – Bench Scale Modeling

Bench Scale Modeling-Why the need?

- Existing data show presence but do not offer any insight on degradation processes (in the environment or in a DWTP)
- Under current political climate it is very hard to get permission to measure in a DWTP
- Concentrations in DWTPs are near the detection limit – need for higher artificial concentrations

Bench Scale Modeling-What is the Plan?

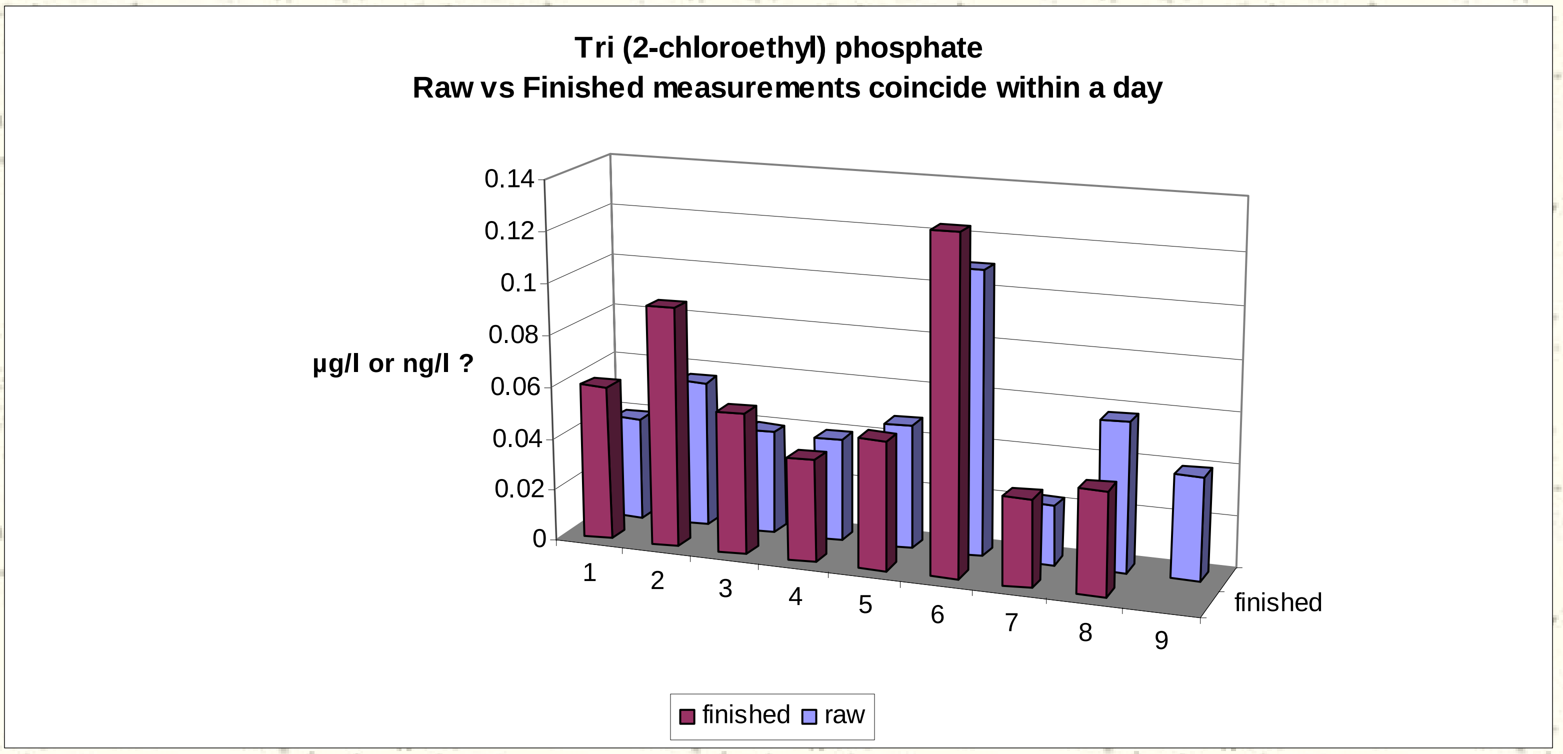
- Set up a bench scale DWTP and have as inflow water with high concentrations of the selected chemicals

- Take consistent measurements at the various stages -> Provide knowledge for removal at each separate process

Bench Scale Modeling-Options (1)

- Water at the intake can be:
  - Raw (Charles River)
  - Tap
  - Distilled
- Full scale or selected stages
  - Existing Studies show that most chemicals are not affected by sedimentation + filtration
  - Probably only photolysis will do something

Bench Scale Modeling-Options (2)



Bench Scale Modeling-Options (3)

- Set up a bench scale that consists of:
  - a mixing tank (for the chemicals)
  - a mixing tank for the addition of H_2O_2 and photocatalysts
  - a UV disinfection tank
  - Such a scheme will depend on the formation of •OH
  - Need for use of either distilled or tap water (TSS must be low)

- Set up a full DWTP bench scale
  - Better Scheme
  - More realistic results
  - Can account for real life conditions
  - We will be able to use raw water

Bench Scale Modeling-Considerations

- The lab space must be found and the available inflow rates estimated. The space needs to have adequate sewage capacity.
  - Problem especially in case of full DWTP bench scale
- Construction problems must be addressed
  - If full scale is chosen the bench scale is pretty sophisticated
  - If full scale is chosen serious machinist's work is needed
  - Need for identification of industry standard for UV lights, Flocculants , Material for Filtration etc.

Bench Scale Modeling-Proposal

- Try and set up a full bench scale
  - This will provide more in depth knowledge of the processes that govern the removal of the chemicals, can account for natural attenuation processes
  - Find machinist for specialized work
- Back up scenario: Set up only the UV stage
  - Strong indications from existing data that the other processes do not affect the specified chemicals
  - Easier to set up, More direct results
  - Easier to play around with the various photocatalysts

Individual Contributions

Joe – Drinking Water Treatment

Drinking Water Treatment

- Dilemma: Many studies exist for removal of PPCPs in drinking water processes

- Article: "Future research needs include **more detailed fate and transport data**, **standardized analytical methodology**, *predictive models*, removal kinetics, and determination of the toxicological relevance of trace levels of PPCPs in water."[1]

[1] Snyder et. al, Pharmaceuticals, personal care products, and endocrine Disruptors in water: Implications for the water industry (2003)

“More detailed fate and transport data”

- Alexandros’ plans: gather data in a controlled environment
- Matt’s plans: gather data from processes in nature
- My plans: analyze data from actual water treatment plants

“Standardized analytical methodology”

- My take: take samples, noting the different variables that can be looked at
  - Time intervals
  - Different places along the treatment plant
  - What time of day (e.g. low flow)
  - Where influent comes from

Project Proposal

- Grab samples in an organized matter
  - Equal time intervals
  - Or, more samples during possible peak concentration times
  - Analysis of small amount of compounds
  - Or, analysis of mélange of compounds

Concerns (1/2)

- Data yet to be found
- Short amount of time to gather data
- Analysis of samples possibly hard to come by
- Methodology of taking samples
  - Where? When? What? How?

Concerns (2/2)

- Research similar to my interests already exist
  - E.g. Using GAC to remove organic chemicals (Paune et. al, 1998)
  - Key: differentiate my methods from other research

Goal

- Produce high-quality data
- From this data:
  - Make judgments
    - E.g. Influent: how does this impact the drinking water process?
  - Future use
    - Confirmation that process 'X' removes or does not remove the PPCP.

Individual Contributions

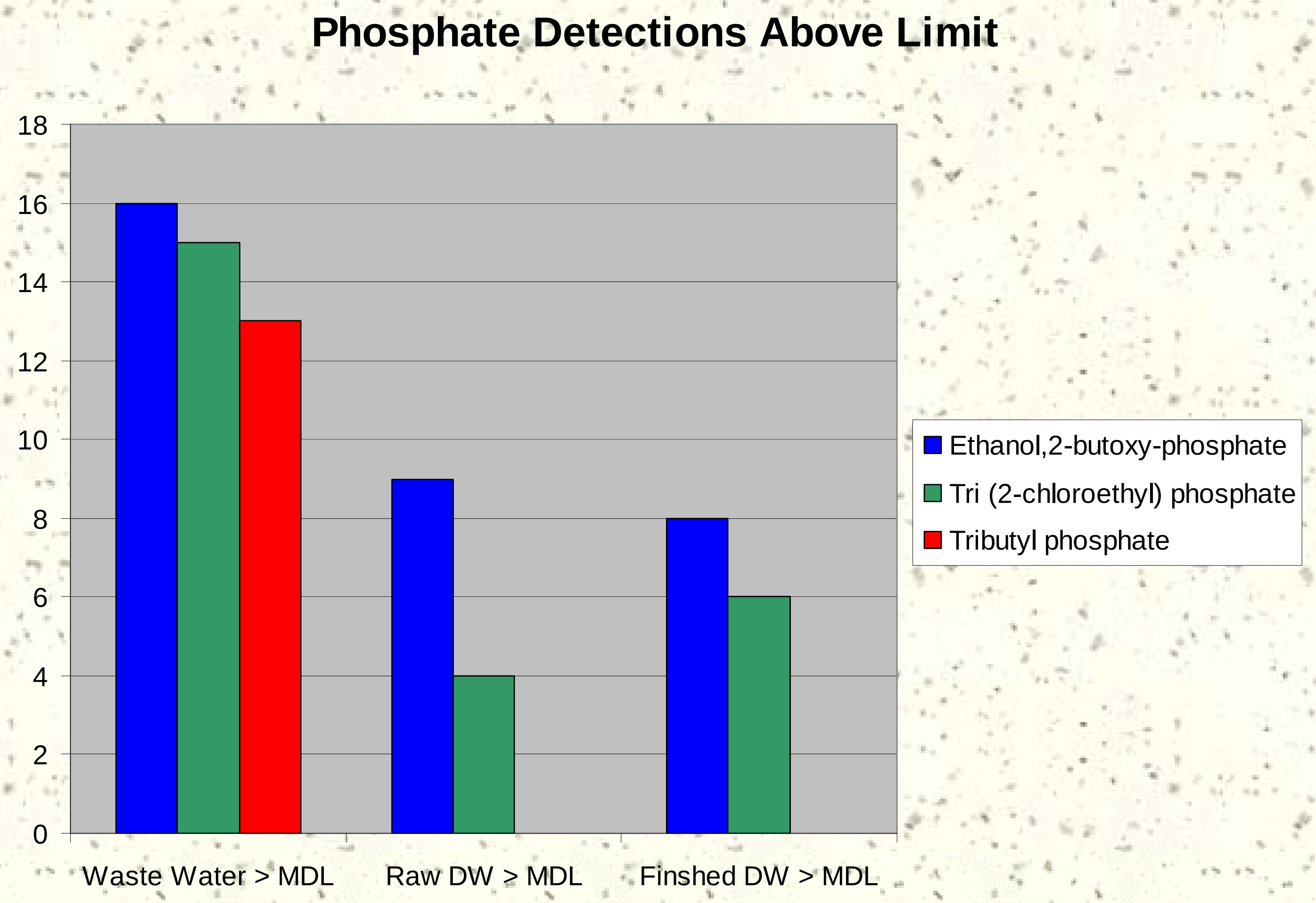
Sam – Modeling Compound Behavior

Modeling Compound Behavior

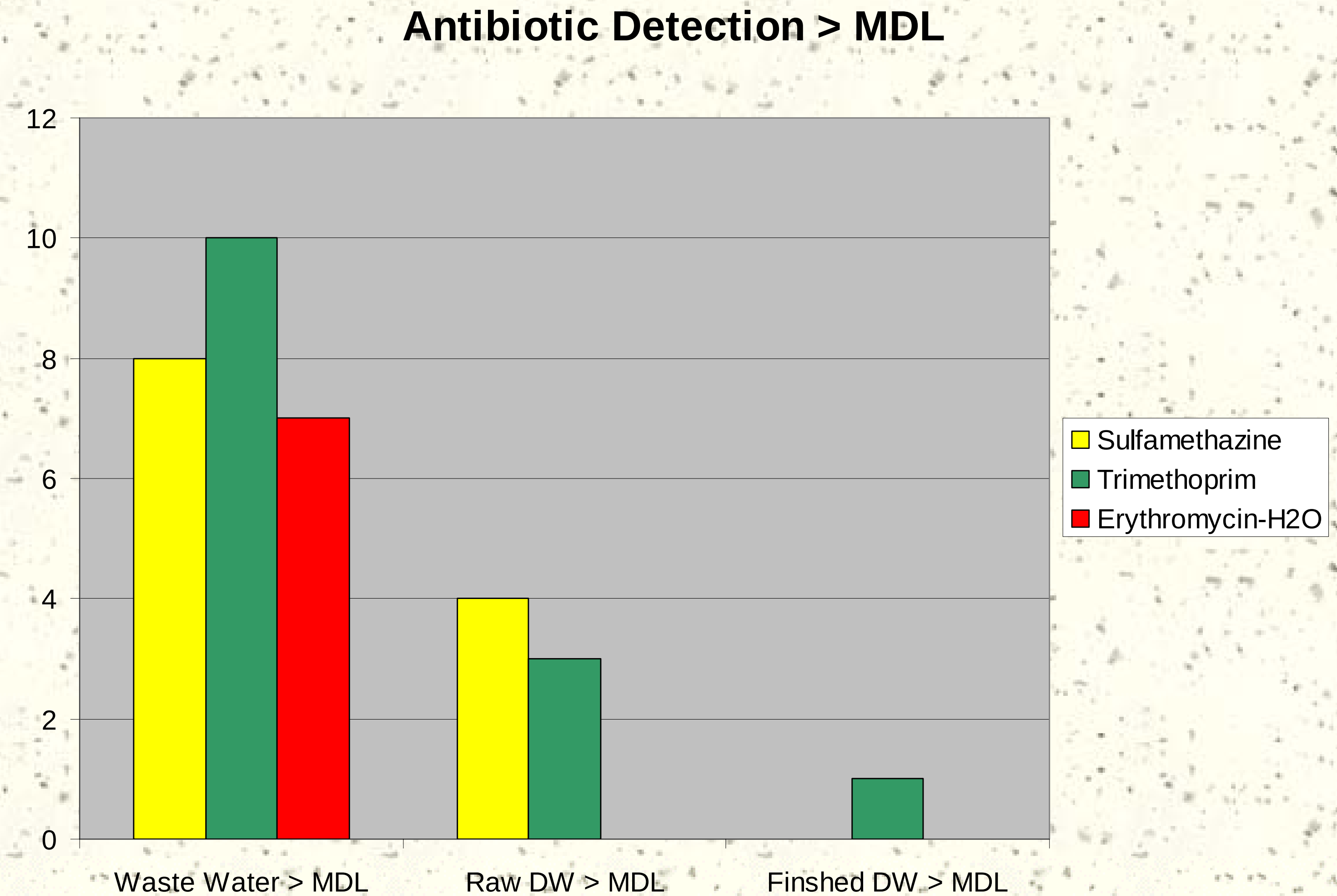
- Identified families of compounds using CDC Data
  - Organo Phosphates
  - Antibiotics
- High Concentrations in Waste Water Effluent
- Varying Concentrations in Raw & Finshed Drinking Water

1 – Looked at data in search of patterns
2- found families of compounds with varying behavior
3- the behavior

Phosphate Detections



Antibiotic Detections



Questions Raised

- Different Chemical Properties
  - Are there differences that cause attenuation of some species?
  - If chemical properties are responsible, could changes be made in manufacture?

- Compounds Surviving River Stretch Survive DWTP
  - Similar behavior in River & DWTP?

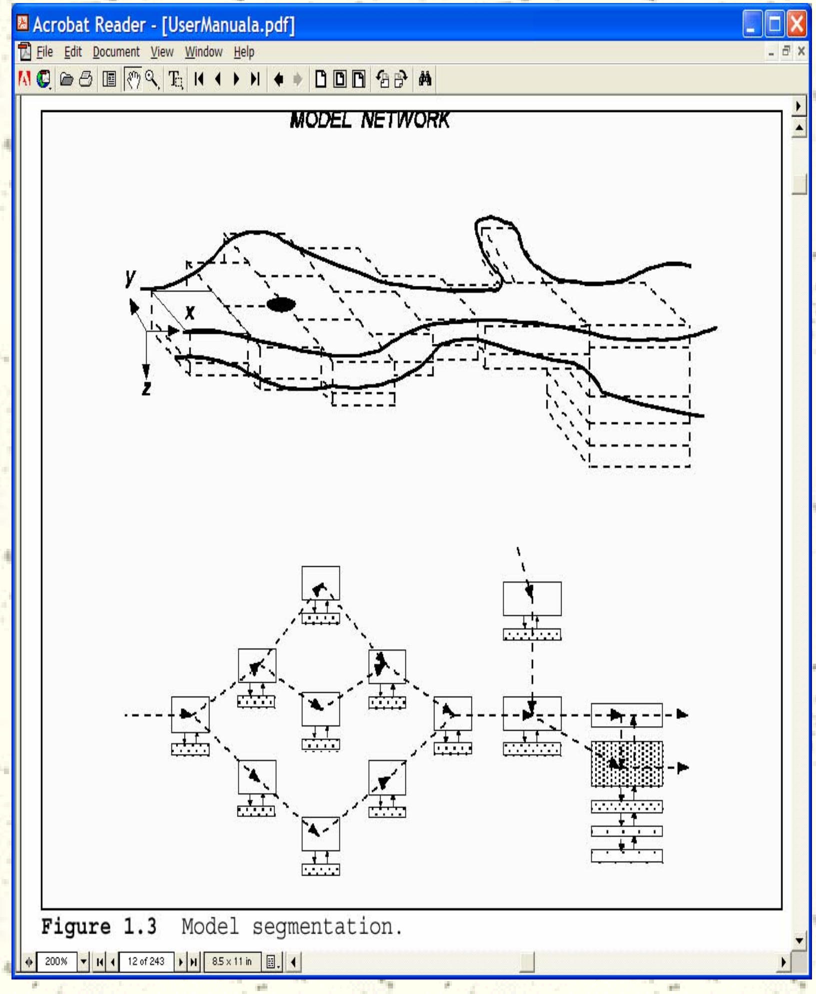
Why?
Is it the case that these chemicals behave the same in DWTP as the do in river

Plan For Answers

- Collect Additional Data from Chatahoochee
  - Possible difficulties
    - Can we perform detections tests?
    - Lowered Concentrations Due to high flow in January
  - Possible Backups
    - Supplement CDC data with data from bench scale
    - Obtaining data from researchers in Europe and US
- Model Behavior in River & DWTP using WASP

Water Quality Analysis Simulation Program

- EPA Customizable Water Quality Model
- Use to model behavior of compounds in both natural channel and DWTP
  - Models river as segments with mixing between them
  - Model DWTP as river without mixing between segments



Next Steps

- Develop Testing Plan for Atlanta
- Compile Detailed list of chemical properties for compounds
- “Back of the Envelope” Model of Behavior
- Begin experimenting with WASP

IAP Trip

- Travel to Atlanta, GA for 1-4 weeks in January, 2004
- Objectives:
  - Talk with CDC personnel about data collection methods
  - Conduct our own field surveys on the Chattahoochee River