

Current research program for:

## **Dave Reckhow's research group**

### **Current Sponsored Research Projects**

#### ***Chloramines in New York City***

Drinking water utilities around the US have been looking at conversion from chlorine disinfection to chloramines for the purpose of minimizing hazardous disinfection byproducts. As the nation's largest municipal water supplier, New York City DEP's decision concerning chloramines is especially significant. DEP has contracted with UMass through their consultant, Hazen and Sawyer, to assist in making some key assessments in support of their decision process. This research project began in September 2006 and continues through the early of 2009.

There are three main goals of this work:

1. To assess the source and fate of disinfection byproducts (DBPs) in the New York City Water Supply System.
2. To assess compliance options for the anticipated future disinfection byproduct (DBP) regulations.
3. To conduct a comprehensive feasibility study that will look into such chemical treatments as chloramination and/or other treatment methods or operational changes to achieve compliance with anticipated future disinfection byproduct (DBP) regulations.

The following studies are being conducted as part of this research:

1. Characterization of NOM in the Cat/Del and Croton watersheds, and implementation of a program to track seasonal and annual variation in those characteristics which impact DBP formation. Understanding changes in NOM levels and characteristics over time will help DEP manage its raw water supplies to meet a variety of water quality and quantity needs.
2. Determine if operational changes in the NYC water system can lower DBP levels.
3. Studying the effects of chloramination and other methods of meeting the anticipated future disinfection byproduct (DBP) regulations on the New York Water Supply system and the public.

*Principal Researcher: Dr. Junsung Kim; Kirsten Studer*



### ***Aquarion Project Water Treatment (Connecticut)***

This project began in April 2001, and is being conducted entirely by UMass (John Tobiason is the lead faculty PI). We have been working with Aquarion Water Company of CT to help them understand and model their systems for DBP formation. Our initial efforts were at Bridgeport and Stamford, CT. We collected samples at various points and analyzed for THMs and HAAs. We also collected bulk treated water samples for these systems and chlorinated them in the UMass laboratories for kinetic analysis. These were conducted under a range of conditions so that DBP formation models could be

specifically calibrated for the BHC systems. We have also been looking at the impact of various treatment scenarios on NOM and subsequent DBP formation. More recently our efforts have turned to Mystic's Lantern Hill water treatment plant. This water is also complicated by the presence of high iron and manganese levels.

*Principal Researchers: Jill Russell, Melissa Brown*

### **MDC (Boston) Reservoir Project**

Very little data exist on the impact of land use on NOM export. While there are some site-specific estimates of NOM fluxes in the literature, there are no generally-accepted models that can be applied across a heterogeneous basin such as the Wachusett watershed. Even less is known about the effect of land use and geology on NOM characteristics (e.g., hydrophobic behavior, structural components, chemical reactivity). Many of these characteristics have important implications to drinking water treatment (e.g., formation of DBPs, removal by coagulation). Some recent studies in the Sacramento Delta (CA) and the Catskill-Delaware System (NY) have provided early glimpses of how land use might affect critical NOM properties. These must still be viewed as site-specific and not directly applicable to other watersheds.

The objective of the NOM characterization component of this research is to collect data that can be used to link organic loading (nature and quantity) with land use or geological characteristics in the Wachusett watershed. This objective first requires careful assessment of land use and selection of sampling sites based on that information. A few candidate sites have been identified. Some periodic sampling has been conducted that is not linked to precipitation events. Also, episodic (e.g., rain event) sampling is incorporated into the sampling schedule. The data collected for this work will also be used in the Watershed Model Evaluation and Development studies and will support inputs for modeling of NOM fate and transport in a companion Wachusett Reservoir project. This project began in April, 2001, and continues at least through 2007.

*Principal Researcher: Cynthia Castellon*

### **Natural Organic Matter in Springfield's Cobble Mountain Reservoir and Watershed**

The amount of natural organic matter (NOM) in a drinking water source is usually a parameter of concern for the treatment facility. It affects not only the coagulation and filtration process, but also the formation of disinfection byproducts (DBPs) depending on the type and amount of disinfectant used. Typically, an increase of NOM in the source water will translate to higher DBPs in the finished water. Therefore any treatment scheme should attempt to decrease the amount of organic matter in the plant influent prior to disinfection. Optimizing the coagulation addition in the filtration train is one method, but does have its limitations. The best way to reduce the organic load is to prevent it from entering the water by means of source water protection strategies in the watershed.



The Springfield Water and Sewer Commission (SWSC) receives its drinking water from the Cobble Mountain Reservoir, located primarily in the hill towns of Blandford and Granville. The total organic carbon (TOC) entering the treatment plant ranges from 2.5 to 3.5 mg/L. The watershed consists of numerous streams and brooks that feed Cobble Mountain Reservoir. A secondary reservoir, Borden Brook, flows directly into Cobble Mountain. An example of one possible cause of higher levels of organics in the water are the streams entering Borden Brook Reservoir that have extensive wetland areas for med by beaver dams. Results from samples analyzed from these brooks show UV254 levels to be two to three times higher than those with little or no beaver activity. Thought not conclusive it does indicate that the presence of beaver dams is one factor that may influence the amount of dissolved organics entering the water. This fact warrants further research and might ultimately provide evidence leading to wildlife control as a possible strategy for lowering total organic matter in the source water. Other factors also need to be investigated to determine their influence on the presence of organic matter in the source water.

The main research questions posed by this work are:

1. What is the nature of the link between NOM export and land use/ land cover within the Cobble Mountain watershed
2. What are the impacts of beaver activity on NOM export

*Principal Researchers: Boning Liu & Ken Mercer*

### ***Composted Wood Products for Erosion Control***

The experience of state transportation agencies (Maine and Texas) as well as a number of university researchers indicates that compost, particularly from wood waste products, can be effective in preventing erosion of soil and in filtering sediment from bare slopes. Research further suggests that these materials are more effective than conventional erosion control technologies, such as hay bales or silt fence. In addition, certain compost products may in fact offer benefits of adsorbing or absorbing toxic compounds from water runoff.

For these reasons, Massachusetts Highway Department (MHD) is considering using compost filter berms as a standard item for erosion control protection adjacent to wetlands. This requires assurance that the introduction of these materials will not introduce unwanted runoff to these resource areas.

The research is designed to determine the potential impacts of using non-biosolid composts and/or wood waste material as an erosion control measure in wetland areas. In addition, based on the findings of this study, the research will recommend practicable testing protocols for inclusion in the MassHighway Standard specifications to ensure appropriate quality of compost material for use near wetland areas. Specifically, the research will determine what, if any, nutrient, toxicity, or pathogen activity loads the proposed material will contribute to storm water runoff.

*Principal Researchers: Kelvin Wong, Boning Liu*

### ***Pharmaceuticals and Endocrine Disrupters***

Over the last decade, endocrine disruptor compounds (EDC) have been a concern to the U.S. Environmental Protection Agency (US EPA), and more recently, Pharmaceutical compounds (PhAC). EDC's already have been noted to have negative impacts on wild populations, such as sexual development defects known as intersex, and on the distribution of the sex ratio's in exposed populations. PhACs on the other hand, currently have not demonstrated to exhibit acute negative impacts on human health at the levels measured in source waters. However, their long-term chronic effects are not known. Based on the small amount of data collected thus far, there appears to be limited impact to human health directly. However, the public, in terms of the perception of risk, tends to consider any negative risk a bad risk.

The removal of these compounds is an area of active research. Currently, there have been several studies, which have shown the relative performance of common treatment technologies implemented in the water and wastewater industry. Membrane technologies tend to be the most promising with high removals of these compounds from

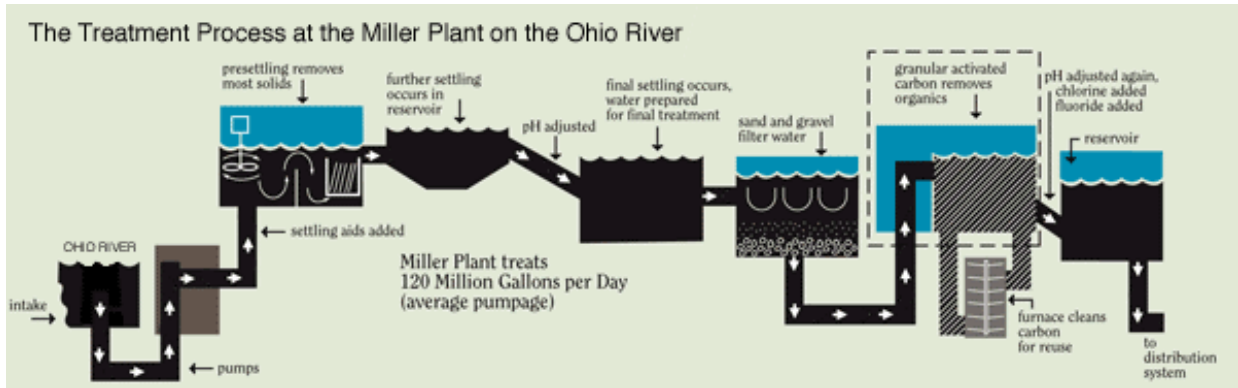
water. Ultrafiltration (1,000 Dalton MWCO) and nanofiltration have shown greater than 70% removal, and reverse osmosis even higher removals. However, these processes still leave the utilities the crisis of how to dispose of these concentrated side streams. Other unit treatment processes such as coagulation, powered activated carbon, biofiltration, chlorination, ultra violet irradiation, and ozonation have demonstrated varied abilities to remove these compounds depending on each compound's chemical properties. Recently, it has become a concern that when these compounds are oxidized, they could yield daughter compounds that are as active as their parent compounds. The initial research program on EDC has focused on the impacts of chlorination and chloramination on loss of parent compound, as well as loss of endocrine activity (by the yeast estrogen screen assay). In addition, daughter products are being documented and degradation pathways evaluated. This portion of the work is supported by the NSF.

It is likely that a multi-barrier approach to treating and ultimately eliminating these compounds will be required. One of the most promising multi-barrier approaches is ozone followed by biofiltration or possibly an advanced oxidation process by which hydrogen peroxide is added prior to ozonation to form hydroxyl radicals which can enhance degradation prior to biofiltration. This treatment could be applied both to water and wastewater facilities to address the EDC and PhAC issue. In this work we will be assessing the effectiveness of ozone/GAC biofiltration at removing a set of selected EDCs. These compounds have been developed based upon the priority listed developed by the Water Research Commission and the American Water Works Research Foundation. These compounds tended to be the most likely to cause adverse human impacts and/or were likely not be removed by conventional water and wastewater treatment processes. This second phase of EDC research will be supported by a consortium of agencies. This work will be done in collaboration with Earth Tech Inc.

*Principal Researchers: Catherine Goodrich; Kirsten Studer*

### ***Special Analytical Program***

With the extensive expertise that exists at UMass-Amherst in the area of drinking water quality and treatment technology, we are frequently asked to provide special assistance in conducting applied research for utilities across the US and Canada. This work is usually an extension of our more fundamental research, whereby we bring to bear some specialized and unique analytical capability to a pilot or full-scale treatment study. Two recent collaborators of this type have been the Greater Cincinnati Waterworks and the City of Reading, MA.



*Principal Researchers: Guanghui Hua, Hans Mentzen, Junsung Kim*

## Recently Completed Research Projects

### ***Characterization of TOX Produced During Disinfection Processes***

This project began in September 2002 and the final report was completed in late 2006. It was one of a cluster of 3 nearly concurrent UMass projects focusing on disinfection byproducts and their precursors, and supported by the American Water Works Association and the US Environmental Protection Agency. This particular project was aimed at exploring the importance of total organic halogen (TOX) in US drinking waters. TOX includes a wide range of potentially toxic compounds, some of which are believed responsible for cancer and reproductive problems in humans. The specific objectives were: (1) to determine the nature and chemical characteristics (e.g., size, charge, hydrophobicity, structural features) of the unknown fraction of the total organic halogen (UTOX) produced during chlorination and alternative disinfection processes (i.e., chloramination, chlorine dioxide, ozone disinfection), (2) to assess the impact of treatment on removal of UTOX precursors; (3) to assess the stability of UTOX in a model distribution system and (4) to determine the best TOX protocol for use with ion chromatographic analysis for the purposes of discriminating between organic chlorine, bromine and iodine.

*Principal Researcher: Guanghui Hua*

### ***Risk Based Prioritization of Disinfection Byproducts***

This project began in early 2003 and the final report was published by AWWARF in November 2006 (the lead PI was Richard Bull of MoBull Consulting). It was one of a cluster of 3 nearly concurrent UMass projects focusing on disinfection byproducts and their precursors, and supported by the American Water Works Association and the US Environmental Protection Agency. This particular project was aimed at developing methods to predict the formation of unknown disinfection byproducts, and to help with



assessment of their health impacts. Estimates of the health risk to the consuming public from by-products of the chlorination of drinking water vary significantly dependent upon whether the data come from toxicological or epidemiological studies. The estimates of risk arrived by summing up the results from toxicological studies of the major identified by-products are considerably less than epidemiological studies attribute to the mixtures of disinfection by-products (DBPs) that are consumed by the public. One potential reason for this discrepancy is that toxicological data is available for only a small fraction of the DBPs produced with chlorination. The inability to associate particular DBPs with the endpoints found in epidemiology studies limits mitigation strategies that are based on alternate disinfectant practice or other physical chemical processes. It is proposed that the gap between toxicological and epidemiological information might be partially bridged by utilizing chemical structure activity relationship (CSAR) tools for predicting formation of novel DBPs. This was followed by using quantitative structure toxicity relationship (QSTR) tools for characterizing the toxicological properties of these DBPs. Prediction of the formation of specific DBPs was based on a search of extant literature on DBP formation and an evaluation of model studies utilizing humic and fulvic acids as substrates. Use was made of minimal structural residues that recur within the structure of humic substances to predict the formation of additional DBPs. The stability of selected putative by-products was assessed under conditions commonly found in drinking water plants. The toxicological characterization of DBPs with established health effects was supplemented by examining the potential toxicological properties of predicted DBPs utilizing QSTR methods, tempered by expert judgment. While such approaches are unlikely to provide definitive evidence of the risk of DBP-induced adverse health outcomes, this process helps in developing priorities for research activities to close the gaps. The principal output of this project was an updateable framework for determining the extent to which toxicological data on individual DBPS risks may be summed to account for findings in epidemiological studies. The framework can be used for assessing potential risks associated with DBP formation using alternative disinfection practices with the main goal of developing a strategy for more efficient study of potential adverse health impacts of disinfection. Finally, the framework was designed to lend itself to being coupled to modeling software for optimizing disinfection practice in individual water supplies.

*Principal Researchers: Dr. Junsung Kim and Hans Mentzen*

### ***Watershed Sources and Long-term Variability of BDOM and NOM as Precursors***

This project began in August 2003, and the final AWWARF report was completed in late 2006. It is the third of 3 concurrent UMass projects focusing on disinfection byproducts and their precursors, and supported by the American Water Works Association and the US Environmental Protection Agency. This particular project was aimed at developing models for the relationship between dissolved organic matter in surface waters and watershed management/characteristics. The project objectives were: (1) to investigate sources, nature, and long-term variability of natural organic matter



(NOM) and biodegradable organic matter (BDOM) in source waters, and (2) to evaluate their impact on the formation of disinfection byproducts (DBPs).

This work was conducted in three major phases or tasks; and it built upon some of the latest fundamental advancements in NOM characterization and origins. In the first phase we conducted an extensive literature review on DBP precursors and BDOM in source waters. We also executed a survey of larger utilities with the objective of finding long-term data sets on precursors and biodegradables in the source water.

Based on this early work, we identified about a dozen utilities for in-depth watershed analysis. These utilities were asked to share their raw water data, as well as a broad range of ancillary information. Bulk raw water samples were then shipped to UMass for some advanced characterization tests. In some cases, many samples were collected at different points within a watershed. At UMass, a suite of organic analyses was conducted (e.g., TOC, DOC, UV abs, CHON, precursor analysis), along with biodegradability test, and a detailed set of NOM fractionation and characterization tests (humic signatures by GC/MS; analysis of acylheteropolysaccharides). This information along with the utility-supplied data was used to develop a set of NOM watershed models. These models make use of modern GIS-based data, and span the range from the empirical to the semi-mechanistic. The modeling effort will ultimately provide insight into NOM sources, degradation processes, NOM characteristics, and impacts of land use and management practices on NOM.

In the last phase, we combined these data sets and models in an effort to provide general guidance for utilities interested in NOM control. We have also started to build a national data base on NOM, its concentrations and characteristics.

*Principal Researchers: Darleen Bryan, Alison Boutin, Greg Devine, Dr. Russell Adams*

### ***Boston / Black&Veatch Water Treatment Project***

This project began in December 2002, and it was part of a larger project that is headed by Black and Veatch engineering consultants. The overall objective was “to compare the relative treatment performance of two treatment schemes (ozone followed by medium pressure UV light and medium pressure UV light alone) for both finished and distributed water quality” in the MWRA (Boston) system. This was a tailored collaboration project funded by the American Water Works Association Research Foundation. Our (UMass) contribution was to provide analytical assistance with the pilot studies. These were conducted at MWRA’s Cosgrove Pilot Facility over a period of about 1 year. We analyzed monthly samples at 6 locations for: neutral extractables (including THMs), HAAs, Aldehydes, and Keto-acids. Some of these were chloraminated in the UMass laboratory prior to analysis.

### ***Winnipeg / CH2M Hill Water Treatment Project***

This project began in March, 2001, with the UMass experimental work beginning about July, 2001. We were part of a larger project that is headed by CH2M Hill engineering consultants. The overall objective was to determine the impact of raw water

quality on UV disinfection efficiency and performance, and to determine the change in DBPs formed from converting to UV primary disinfection in the Winnipeg (Canada) system. This was a tailored collaboration project funded by the American Water Works Association Research Foundation. Our (UMass) contribution was to conduct bench-scale DBP testing and analyze for byproducts. These were conducted at UMass using 40-liter bulk samples shipped 8 times over a period of about 1 year. We examined 4 separate pre-disinfection scenarios, including chlorination, chloramination (2 protocols) and chlorine dioxide treatment. From this point, there was UV disinfection and 3 separate post-disinfection scenarios. For UV treatments, we set up a collimated beam flow-through reactor (on loan from UNH) in our lab. We analyzed all 12 samples in each set for: neutral extractables (including THMs), HAAs, Aldehydes, and Keto-acids. Some of these samples were also be analyzed for Biodegradable Dissolved Organic Carbon (BDOC).

*Principal Researcher: Narayan Venkatesan*

### **Northampton / WRI Water Monitoring Project**

This project began in April 2001, and was being conducted entirely by UMass. The objectives of this research were to develop and test several strategies for non-compliance monitoring of THMs and HAAs in small to medium sized drinking water systems using free chlorine as a residual disinfectant. The particular strategies included, in roughly increasing order of complexity & cost:

1. measurement of chlorine dose, pH, flow rate and temperature, (CD, pH, Q, T), only
2. measurement of chlorine residual (CR), plus CD, pH, Q & T
3. measurement of UV absorbance (UVA) plus CR, CD, pH, Q & T
4. measurement of delta-UV<sub>272</sub>
5. measurement of total organic carbon (TOC) plus UVA, CR, CD, pH, Q & T
6. measurement of DBPs by off-line, on-site colorimetric methods
7. measurement of DBPs by on-line chromatography
8. measurement of NOM fractions by resin adsorption and UV

Most of these standard parameters (e.g., TOC, UVA, CR, CD, pH, Q & T) were measured by means of on-line, low cost, low maintenance devices. Some required on-site batch testing. All could be measured on-site with methods requiring little operator expertise. Each of these approaches were coupled with mathematical DBP formation models to improve the power and scope of the data collected. Predicted DBPs were compared to samples collected by UMass researchers and analyzed in the UMass laboratory. The medium sized utility selected for this work was Northampton, MA..

*Principal Researcher: Bree Carlson*



### ***MWRA (Boston) Chloramine Stability Project***

This project began in January 2002, and was conducted entirely by UMass. The objectives of this research were to determine the stability of chloramines in the MWRA (Boston) system under future treatment scenarios. This involved collection of raw water from Wachusett Reservoir, and treating it in the laboratory with ozone and corrosion control chemicals. Finally, waters were dosed with chloramines under different addition sequences and the residuals are monitored over time. These data was analyzed within the context of existing chemical decay models.

## **Other Ongoing or Planned Research Projects**

### ***Dichloroacetamide (DCAD) in Drinking Water***

1. Improve selectivity and recovery of existing method
  - a. Use of alternative columns to separate DCAD from DCAA
  - b. Use of PFBHA to selectively derivatize DCAD in water??
  - c. Use another extraction solvent which is more specific for DCAD?
2. Measure actual concentrations in drinking water systems
  - a. from finished waters collected in nearby communities
  - b. from samples analyzed for on-going applied research projects (next page)

***DBP formation from Chlorination of Model Compounds  
(following up on Caroline von Stechow)***

1. Identification of the mystery byproduct of the chlorination of Malic Acid
  - c. Use of high resolution GC/MS
  - d. Synthesis and probe MS, or FTIR??
2. Identification of other major byproducts of chlorination and chloramination of model compounds. Many of these will be non-conventional byproducts.
3. Application of the methods used above for analysis of the non-conventional byproducts in samples collected for on-going applied research projects (next page)

***LC/MS Methods for Haloacetic Acids***

1. Use of one of the 2 recently published methods using LC/MS
2. Compare this with conventional GC-ECD method (perhaps taking advantage of on-going projects on the next page which will involve regular HAA analysis by conventional methods)

***NOM Characterization for Wachusett Reservoir Study***

1. Explore LC/MS methods for characterizing natural organic matter
2. Use this method to compare NOM sources in the watershed with NOM in the open reservoir (as part of MDC project)

***Continuation of NPH method for acids by LC/MS (following up on Drs. Angela Gonzalez and Yong Wook Choi)***

1. Improve sensitivity (off-line resin extraction??)
2. Extend method to other compounds
3. Test method with treated drinking waters

*December 14, 2006*