Water Resources Research Center

Annual Technical Report

FY 2000

Introduction

In the 36th year of the Massachusetts Water Resources Research Center's existence, the Center appears to be playing a substantially larger role in the development of water policy than in the past. Not all the news was good, though. In the spring, the first director of the Center, Bernard Berger, died. He was director from 1965 to 1977. His successor, Dr. Paul Godfrey, has served from 1980 to present and he is now the longest-tenured director at a single water resources institute.

On the state water policy front, the Center's long standing efforts to develop citizen water quality monitoring is rapidly becoming a mainstay of state agency's increasing reliance on volunteer monitoring data to meet state and federal needs. Supplementing the Center's 17 year contribution to high quality data collection by citizen volunteers, the Center has recently been central to the development of the state's lake management policy, development of joint projects between the Executive Office of Environmental Affairs and the University of Massachusetts system, development of a long-range plan for lake and pond management efforts by the state, and development of enhanced guidelines for volunteer monitoring Quality Assurance Project Plans. Future efforts, under discussion, might involve establishing a natural phosphorus baseline for lakes and streams that will aid the state's TMDL response; and a lake classification system that will support the state, volunteer groups and town conservation commissions in selecting appropriate management strategies for lakes. The Center also provides the technical support to volunteer groups through its Massachusetts Water Watch Partnership, recognized as the principal coordinator of volunteer water quality monitoring in Massachusetts and as a principal player in a regional cooperative, the New England Regional Monitoring Cooperative, originally developed with Institute Program funding.

On the research front, the Center's program is quite diverse. Three years ago, the Center initiated support for the examination of improved treatment of airport deicer waste, a topic previously left to limited proprietary industry research even though the main impact is on municipal wastewater treatment systems.

Estuaries are seriously threatened by eutrophication, usually from nitrate input. Many models have been developed but no comparisons had been made to assist the estuary manager in using the most appropriate. The Center funded such a comparison with a very well documented watershed as the basis of the comparison. The results seem destined for development as a web-based tool with follow-on funding.

New projects starting this year are: 1) aimed at developing an improved model of copper toxicity that might ease the burden for many municipalities wastewater treatment facilities by better understanding the relationship between toxicity and copper complexation; and 2) developing cost-effective ways for small drinking water systems to comply with the new stage 2 Federal regulations for minimizing disinfection byproducts.

In a state with a concerned and involved citizenry, multiple state agencies, multiple regional Federal offices, and a plethora of top-notch research universities, communication is essential. Continuing its long-standing effort to improve communication with and between academic researchers, the Center has updated its directory of academic expertise. It is also beginning an effort to create a Massachusetts directory of state and federal agency expertise, an individual to individual connectivity. To everyone's surprise, this has never been attempted previously. It plans to create a similar directory for consulting expertise.

Research Program

Basic Information

Title:	Comparative Toxicity of Formulated Glycol Deicers and Pure Ethylene and Propylene Glycol
Project Number:	MA02
Start Date:	3/1/1999
End Date:	2/28/2001
Research Category:	Engineering
Focus Category:	Toxic Substances, Non Point Pollution, Treatment
Descriptors:	Stormwater, Nonpoint Source Pollution, Deicing Fluids
Lead Institute:	University of Massachusetts
Principal Investigators:	Michael S. Switzenbaum

Publication

PROBLEMS AND RESEARCH OBJECTIVES

With the advent of new regulations concerning aircraft deicing and management of spent aircraft deicing fluids, many airports now face the challenge of maintaining public safety along with environmental protection. Each year large quantities of propylene glycol and ethylene glycol are used to de-ice aircraft. Pavement deicing materials are also used on taxi- and runways. All of these compounds exert large oxygen demands when introduced into natural waterways. In addition, there are toxicity concerns with certain glycols. As a result, the collection and treatment of these wastes is now being mandated by regulatory agencies for protection of both human health and the environment. While numerous alternatives have been proposed for deicing wastewater management, at the present time there is no firm consensus on the best means of managing this significant problem.

This project involves testing of pure ethylene glycol (EG), ethylene glycol based aircraft deicing fluid (EG-ADF), pure propylene glycol (PG) and propylene glycol based aircraft deicing fluid (PG-ADF). Since the PI has been investigating anaerobic treatment of ADFs for the past three years, some experimental data used in this study was collected before the official start of this study (in the Winter and Spring of 1998/99) in anticipation of receiving support for this study. This project officially began during the summer of 1999. The project consists of the following sets of experiments:

1. Anaerobic biodegradation experiments for PG, PG-ADF, EG, and EG-ADF.
2. Anaerobic kinetic experiments for PG, PG-ADF, EG, and EG-ADF
3. Anaerobic toxicity testing on triazoles (which are used in ADF formulation), and
4. Aerobic activity testing

Principal Findings and Significance

The toxicity of Union Carbide ethylene glycol based types I and IV aircraft deicing fluids (EG-ADF Types I and IV) were compared to pure ethylene glycol (EG). Also Octagon propylene glycol based types I and IV aircraft deicing fluids (PG-ADF Types I and IV) were compared to pure propylene glycol (PG). Both sets of comparison were performed in batch tests. Continuous flow stirred tank reactors were used for the anaerobic portion of the tests; a sequential batch reactor was used for the aerobic testing. Cultures were acclimated to the substrates and then tested in batch loadings by measuring chemical oxygen demand over time. It was found that additives in aircraft deicing fluid inhibit the anaerobic degradation process. Additives in both PG-ADF and EG-ADF lowered the extent of degradation and slowed the degradation rate when compared with pure glycols. These differences became more pronounced as the feed concentrations were increased.

Although propylene glycol based aircraft deicing fluids (PG-ADFs) are being successfully degraded in an anaerobic attached growth process (with activated carbon biofilm carriers) at the Albany International Airport, bench scale suspended growth completely mixed reactors were unable to be acclimated to PG-ADFs. Because of the difficulties encountered with the degrading of the PG-ADFs, anaerobic toxicity assays using PG-ADF and pure PG as substrates were performed and compared to pure propylene glycol (PG). It appears that one or more of the additives in the PG-ADFs inhibit the growth of anaerobic, methanogenic microorganisms.

Aerobic microorganisms did not appear to be inhibited by the additives in PG-ADF or EG-ADF.

Basic Information

Title:	Comparisons of models used to estimate land-derived nitrogen loads
Project Number:	MA03
Start Date:	3/1/1999
End Date:	2/28/2001
Research Category:	Water Quality
Focus Category:	Models, Nitrate Contamination, Groundwater
Descriptors:	Model, Nitrogen Loading, Watershed, Land Use, Estuary, Groundwater
Lead Institute:	Marine Biological Laboratory
Principal Investigators:	Ivan Valiela

Publication

Research objectives

The core goal of this proposal was to address the issue of the many untested and quite different models and protocols used in nitrogen loading estimates. We proposed to 1) compare the performance of selected model types versus actual measurements of nitrogen loads from watersheds to receiving estuaries; 2) compare the different models as to components and processes and relative ability to predict measured loads; and 3) present the comparisons and descriptions of the models in a format accessible to stakeholders and other potential users.

Methodology

We started our work by detailed examination of published descriptions of perhaps two dozen models designed to calculate land-derived nitrogen loads to estuaries. We selected to work on a narrower list, based on the following criteria:

1. Availability of clearly stated procedures and data requirements
2. Range of scale of area to which the models were applicable (from single parcel to entire watersheds
3. Range of structure from relatively simple to more complex
4. Inclusion of surface runoff and groundwater as the freshwater delivery mechanism
5. Prediction of either annual nitrogen loads or mean annual dissolved inorganic nitrogen in the water of the receiving estuaries.

We made detailed readings of the published sources for each model, to keep track of the components included in each model, and worked out the protocols needed to use the models to predict either loads or concentrations in a set of Cape Cod estuaries from which we had a substantial data set. These measurements were to be used as the "measured" against which to compare "predictions" made by the various models. We obtained measured estimates of both loads and concentrations.

Before using the "measured" values of either loads or concentrations, we carried out a detailed analysis of the way we calculated "measured loads. To do this, we planned to multiply the average nitrogen concentration found in hundreds of groundwater samples, times the annual recharge of freshwater. The validity of this approach was established by comparing the rates of annual recharge versus freshwater flow rates measured in sets of 9 seepage meters deployed through the seepage face. We established the dimensions of the seepage face by measurements of salinity in the groundwater about to flow through the seepage face. If we found fresh water, we were confident we were within the seepage face.

Principal Findings and Significance

We compared performance of several models used to estimate land-derived nitrogen loads to shallow receiving estuaries. Models included in our comparison differed in complexity and approach, and predicted either loads or concentrations in estuary water. In all cases, we compared model predictions to measured loads or concentrations, as appropriate. Measured nitrogen loads to nine estuaries on Cape Cod, MA, were obtained as the product of mean concentrations in groundwater about to seep into estuaries multiplied by the annual recharge of groundwater. Measured annual mean nitrogen concentrations in estuaries were obtained by extensive sampling surveys. The validity of this procedure to measure loads was verified by comparison against seepage meter data.

Responsiveness of model predictions was generally good: predictions increased significantly as measured values increased in 8 of the 10 models evaluated. Precision of predictions was significant for all models. Three models provided highly accurate predictions; we calculated correction terms that could be applied to predictions from the other models to improve accuracy. Four of the models provided reasonable predictive ability. We ran simulations with somewhat different versions of two of the models; in both cases, the modified versions yielded improved predictions.

The more complex models tended to be more responsive and precise, but not necessarily more accurate or predictive. Simpler models are attractive because they demand less information for use, but models with more comprehensive formulations, and emphasis on processes tended to perform better.

Different models predicted widely different partitioning of land-derived nitrogen loads from wastewater, fertilizers, and atmospheric deposition. This is of concern, because mitigation options would be based on such partitioning of predictions. Choice of model to be used in management decisions or for research purposes therefore is not a trivial decision.

Basic Information

Title:	Sources and behavior of copper-binding compounds in rivers and estuaries
Project Number:	MA2301
Start Date:	4/1/2001
End Date:	3/31/2002
Research Category:	Water Quality
Focus Category:	Toxic Substances, Water Quality, Surface Water
Descriptors:	Humic Substances, Dissolved Organic Matter, Complexation, Copper
Lead Institute:	Massachusetts Institute of Technology
Principal Investigators:	Bettina Margrit Voelker

Publication

Nature, scope, hypotheses to be tested, and objectives of the research

a. Introduction

The concentration at which a heavy metal becomes toxic to an aquatic organism in a given environment depends on which chemical forms, or species, of the metal are present. Current regulatory frameworks only distinguish between “dissolved” (e.g. not retained by a 0.2 mm pore size filter) and “particulate” metal. However, metals in the “dissolved” fraction of a water sample could be associated with inorganic or organic colloids, be complexed by dissolved organic and inorganic ligands, or, in the simplest case, be present as the free ion. In general, biological uptake of a metal is related to the free metal ion concentration, so that complexation by dissolved ligands and formation of colloidal species dramatically lower the bioavailability of a given concentration of total dissolved metal. Natural and effluent waters contain unidentified compounds capable of strongly binding metal ions. Since these compounds are absent in the artificial media used in laboratory toxicity studies, concentrations of metal which show toxic effects to aquatic organisms in such studies could actually be well within safe levels in a given effluent-receiving water. Water quality criteria based on toxicity tests are therefore likely to be more conservative than intended. To address this issue, toxicity tests could be conducted using the receiving waters of specific sites. However, site-specific toxicity tests are time-consuming and expensive, and do not address the possibility of temporal variations in the concentrations of metal-binding compounds.

A chemical-biological model to predict metal toxicity in natural waters, the “Biotic Ligand Model”, has recently been proposed by the Environmental Protection Agency as a new tool for regulators wishing to develop site-specific water quality criteria. Initial efforts to validate the model (Di Toro et al., 2000) have focused on copper, both because copper concentrations frequently exceed currently permitted levels in effluents, and because the decrease in toxicity due to binding by natural compounds tends to be more dramatic for copper than for other metals. At the core of the Biotic Ligand Model is a prediction of the extent of copper complexation in a given water as a function of easily measurable chemical parameters including pH, concentration of dissolved organic carbon, and concentrations of major ions such as calcium, magnesium, and sulfate. The model’s prediction is based on average copper complexation properties of humic substances, the biologically refractory degradation products of higher plants. For the model to be applicable, humic substances must be the copper-binding compounds controlling complexation and must make up a predictable fraction of the dissolved organic carbon (DOC) in the waters in question.

Our abilities both to predict the extent of the Biotic Ligand Model’s applicability and to develop more refined models are limited by our lack of knowledge of the compounds responsible for copper binding in natural waters. In unimpacted freshwater systems, humic substances make up a significant fraction of the DOC pool and are probably the only compounds abundant enough to control copper binding at high (>500 nM) total dissolved copper concentrations. However, there is a growing body of evidence demonstrating that other compounds less abundant than humic substances, for example microbially produced ligands, anthropogenically produced EDTA, and (often colloidal) sulfide complexes, bind a significant fraction of the ambient copper in freshwaters (Breault et al., 1996; Rozan and Benoit, 1999; Xue and Sigg, 1999). In estuaries, the conventional wisdom is that humic substances are rapidly removed by coagulation and precipitation (Sholkovitz and Copland, 1981). In this case, compounds produced by microorganisms *in-situ* may become both the main constituents of the DOC pool and the most important copper-binding compounds. However, removal of humic substances by precipitation may only be significant in Fe-rich waters. Conservative dilution of DOC (Mantoura and Woodward, 1983) and colored dissolved organic matter (Vodacek and Blough, 1997) have been observed in some estuaries, and work using lignin as a tracer of terrestrial humic substances shows that they account for 60% of the total DOM in a southeastern U.S. estuary (salinity = 18%) and up to 20% of total DOM even miles offshore (salinity > 30%) (Moran et al., 1991). It is therefore possible that humic compounds remain significant to copper speciation in estuaries (Kogut and Voelker, submitted). In sewage effluents, compounds other than other humic substances, with unknown copper-binding properties, probably constitute a significant fraction of the dissolved organic carbon, and EDTA and sulfide compounds may be especially important copper-binding compounds. If the copper-binding compounds present in sewage are not humic substances, they may be subject to decomposition (especially by microbes), releasing the copper as they are degraded in the natural water. EDTA may release copper as it equilibrates with colloidal aluminum and iron present in the river water.

In summary, the assumption that humic substances control the extent of copper complexation may be applicable only in low-effluent freshwaters containing high levels of copper. These are in fact the only conditions for which the Biotic Ligand Model has been successfully validated so far. Other approaches may be necessary for predicting copper complexation in estuaries and effluent-rich freshwaters, even when the total dissolved copper concentrations are high. In addition, researchers are just beginning to understand which compounds are responsible for copper binding at much lower total copper concentrations. Predicting copper speciation at nanomolar concentrations of total copper is crucial for understanding its toxicity to many phytoplankton species, which are far more sensitive to copper than fish and other aquatic organisms.

b. Objectives

The goal of this study is to develop a better understanding of the sources and behavior of copper-binding compounds present in natural and effluent waters, in order to increase our ability to predict the extent of copper binding by these compounds. In particular, we will focus on two systems, a river receiving sewage effluent and a relatively unimpacted estuary. In these systems, we plan to address the following questions:

(1) How successful are the Biotic Ligand Model's predictions of copper toxicity in waters affected by sewage input? If the model predictions are inaccurate, what is the

reason for the model’s failure? Does treated sewage contain significant quantities of compounds that affect the copper-binding ability or the humic fraction of DOC in the receiving waters? Do the sewage compounds’ copper-binding properties resemble those of humic substances and is there a simple measurement for determining the humic-like fraction of effluent DOC? Are the copper-binding compounds present in sewage stable in the receiving water?

(2) Do humic substances remain the dominant copper-binding compounds in an estuary in which coagulation and precipitation of humic substances may play only a minor role? If so, does the humic fraction of DOC remain relatively constant, or, alternatively, is there a simple measurement for determining the humic fraction of DOC? If not, is there evidence for *in situ* production of copper ligands by microorganisms?

c. Approach

We will use copper speciation titrations to probe the copper-binding compounds present in the effluent and receiving waters of three Publicly Owned Treatment Works (POTW’s) in the Taunton River watershed in Massachusetts. The results from these titrations can be used to determine whether the sewage compounds can significantly affect copper speciation if mixed with receiving waters in different proportions, or whether only the copper-binding compounds in the receiving waters are important. In addition, we will ascertain whether the input of copper-binding compounds from the POTW’s into the river is proportional to their input of DOC.

If significant input of copper-binding compounds from the POTW’s to the receiving waters are observed, we will examine these compounds’ chemical nature and environmental behavior. To ascertain whether these compounds can be modeled as humic substances, we will compare our measurements of the POTW samples’ copper-binding behavior to predictions by the Biotic Ligand Model. We will also compare different bulk measurements of samples (DOC, UV absorbance) as predictors of the content of copper-binding compounds of samples obtained at different times. In addition, we will isolate the “hydrophobic acid” fraction of the DOC and determine whether most of the copper-binding compounds are associated with this fraction, indicating that they are humic-like. Finally, we will determine whether these compounds are stable with respect to oxidative, microbial, and photochemical processes in the river.

To evaluate the effect of effluent discharge on the accuracy of the Biotic Ligand Model, toxicity tests will be conducted in river water with high and low percentage effluent flow, and compared to model predictions. We will perform copper titrations on the same water samples to determine whether the model’s predictions of copper binding are accurate. The toxicity tests are part of an ongoing project in the Taunton River watershed, whose goals are to validate the Biotic Ligand Model and, if the validation is successful, to apply the model to the development of site-specific water quality criteria for copper. The project is being conducted by the consulting firm ENSR (Acton, MA); they have agreed to share their results with us.

To examine the behavior of copper-binding compounds in an estuary, we chose the Saco River estuary, in southern Maine, as our field site. The Saco River contains moderately high levels of both dissolved organic carbon (DOC) and Fe. A substantial portion of the Fe colloids formed during estuarine mixing aggregate to particles, which mostly do not seem to be removed by settling within this estuary (Mayer, 1982b). A portion of the DOC also forms aggregates, the majority of which remain filtrable (Mayer, 1982a). Removal of terrestrial DOC is therefore likely to be a minor process and we should be able to observe whether terrestrial humic substances remain the most important copper-binding compounds as river water mixes with coastal seawater. We will conduct copper titrations to compare the content of copper-binding compounds in samples from low salinity to high salinity transects and determine whether conservative dilution of these compounds is occurring, or whether a simple metric of humic content, for example DOC and UV absorbance, is a good predictor of the samples' copper-binding ability. To examine the possible impact of biological activity on concentrations of copper-binding content, we will conduct transect studies during seasons of both high and low productivity. If evidence of different sources of copper-binding compounds is observed, we will determine whether these compounds are mostly found in the hydrophobic acid fraction of the samples.

Methods, procedures and facilities

a. Sample collection

Grab samples of discharge of three POTW's (Bridgewater, Mansfield and Middleborough, MA), receiving waters upstream of the POTWs, and Taunton River samples for toxicity studies will be collected during ENSR sampling campaigns, three times under low flow conditions (in summer 2001) and once when higher flow is expected (in April 2001). Samples will be collected in acid-washed Teflon bottles using "clean hands/dirty hands" trace-metal clean sampling techniques. A YSI Model 6920 multi-parameter water quality monitor will be used to measure temperature, specific conductivity, pH, dissolved oxygen, and turbidity in the water before sampling. Additional ancillary measurements needed as input to the Biotic Ligand Model (DOC, calcium, magnesium, chloride, sodium, potassium, alkalinity, sulfate and sulfide) will be performed by ENSR's subcontractors and provided to us.

Water samples from the Saco River will be collected in acid-washed Teflon bottles using Parsons Laboratory's small aluminum boat equipped with an outboard motor. 1-2 liter samples of surface water will be collected from upstream of the boat using a Teflon bottle attached to a PVC pole sampler; this technique minimizes copper contamination of samples (Voelker et al., 2000). Temperature, chlorophyll, dissolved oxygen, turbidity and salinity will be measured at each sampling site using a Hydrolab Datasonde.

Samples from both the Taunton River and Saco River sites will be kept both dark and cool in portable coolers filled with ice, and brought back to Parsons Laboratory (less than two hours' drive from the field sites) for immediate 0.2 mm-filtration. Filtrations will be carried out by pressurizing sample bottles with compressed air or nitrogen to force samples through an on-line 0.2 mm Nuclepore filter connected to the bottles with Teflon tubing (Moffett, 1995). If necessary, samples will be prefiltered through an 8 mm on-line filter. This technique is more gentle and less prone to contamination than use of a vacuum pump.

b. Copper speciation titrations

Cu speciation studies, measuring free copper ion concentrations over a range of total dissolved copper in each sample, will be performed in the lab using several techniques. Competitive ligand exchange (CLE) combined with adsorptive cathodic stripping voltammetry (CLE-ACSV), with the added ligand salicylaldoxime (SA) (Campos and van den Berg, 1994) will be used for titrations at low total copper concentrations (0 to 200 nM added Cu). At higher total copper concentrations, we will use anodic stripping voltammetry (ASV) and chelating resin column partitioning (CRCP) with graphite furnace atomic absorption spectrometry (GFAAS) to determine the extent of copper binding (Bedsworth and Sedlak, 1999; Donat et al., 1994). The theory and practice of these techniques are described in detail in the cited references above; this section addresses only those of our refinements of the techniques which are not part of the usual procedures.

High data precision and a thorough understanding of data reliability are crucial if we are going to interpret differences in Cu titrations from one sample to the next in terms of environmental changes in content and strength of copper-binding compounds. Our analytical protocol is designed to detect and avoid calibration errors, changes in the sample during short-term storage, and incomplete equilibration times.

We have recently developed a new technique for calibrating CLE-ACSV titrations, because previously used techniques cannot distinguish between decreases in method sensitivity due to sample matrix effects from apparent decreases due to weak copper complexation (Kogut and Voelker, submitted; Voelker and Kogut, submitted). Our technique relies on performing calibration titrations using high concentrations of the competing ligand. Since these titrations do not provide information on copper speciation in the samples, additional titrations using lower concentrations of competing ligand must also be performed. We will conduct at least five Cu titrations on each sample using different concentrations of SA (as low as 1 mM and up to 500 mM, if necessary) as the added ligand. Additional titrations using ASV and CRCP-GFAAS will also be performed. The different methods will be applied to span as wide a range as possible in total copper concentration (examining copper speciation in samples containing nanomolar as well as micromolar total dissolved copper), while also insuring that for most values of total dissolved copper, at least two titrations were used to independently determine free copper. Comparison of measured free copper as a function of total copper concentrations obtained from the different titrations can then provide an assessment of the different methods' accuracy and precision.

To assess the effect of 12-36 hour storage at 4˚C on the ligands present, preliminary sampling trips to each field site will be conducted to collect three samples, representing the two "extremes" (e.g. the high salinity and low salinity end members in the Saco River) of a site and a midpoint. Cu titration analysis will be performed on these samples both immediately after sampling and filtering and after both short-term storage and long-term storage (at -20˚C), and the results will be compared.

Preliminary samples will also be used to determine the equilibration times needed to obtain consistent results. Since we expect different kinds of Cu ligands to be present at the different sites, it is crucial that these tests be performed anew at each site. A more extensive sampling trip, collecting samples from 10-20 stations, will then be conducted within a week of the preliminary sampling trip at each site. If even short-term storage is found to change ligand characteristics, fewer samples will be collected so that they can be analyzed immediately.

Whenever equilibration times are found to be short enough, voltammetric titrations will be conducted by successively adding copper to the same sample and measuring current produced at intervals of several minutes. In preliminary analyses of water samples from Boston Harbor, local freshwaters, and humic acid solutions, no change in measured signal occurred between five minutes and twenty-four hours of equilibration time. If longer equilibration times are found to be necessary for some samples, 10 ml of sample will be equilibrated with added Cu (and added ligand, when the competing ligand exchange technique is used) at room temperature in Teflon bottles for appropriate lengths of time before analysis. Added Cu will be in the range of 0-10 uM.

Ionic strength and Ca/Mg competition could affect the conditional stability constants of the natural ligands, which would make it impossible to reliably compare ligand content of Saco River waters collected from a salinity gradient. To eliminate these effects, we will add concentrated salt solutions to each sample to increase its salinity to 35 o/oo. The salt solutions will approximate the ratios of major ions present in seawater (but much more concentrated), cleaned of trace metal contamination using Chelex 100 which has been pretreated to eliminate leaching of ligands (Price et al., 1991). To determine the extent of ionic strength and Ca/Mg effects, we will also conduct titrations in the absence of added salts and compare the results. Boric acid buffer will be added to ensure that all samples are at the same pH (8.3). Total Cu will be measured in each water sample by UV-oxidizing acidified samples, adding buffer to return the pH to 8.3, and performing a titration with SA.

c. Interpretation of Cu titration data.

The goal of many of our copper titration experiments is to compare the relative quantities of copper-binding compounds present in different water samples. To accomplish this, most studies assume that copper binding is described by equilibrium complexation with several types of ligands. "Best fit" total ligand concentrations and conditional stability constants are then extracted from titration data sets. However, in complicated samples, the total ligand concentrations and stability constants chosen by curve-fitting are somewhat arbitrary (that is, different sets of parameters can often fit the data equally well), so that variations of total ligand concentrations obtained from curve fits of titrations of different samples do not necessarily correspond to real variations in ligand content. In a recent modeling study (Voelker and Kogut, submitted) we show that the best way to compare ligand quantities in different water samples is to use FITEQL to determine "best fit" ligand concentrations of several ligand types whose stability constants are not allowed to vary from sample to sample (Cabaniss, 1997). If kinetically inert copper species are present (for example organic or sulfidic colloidal species), they would appear as very strong ligands to this analysis. The fixed-stability-constants method will be applied in our study. To assess whether POTW's represent a significant source of copper-binding compounds to the receiving waters of the Taunton River, ligand content of the effluent and upstream receiving water samples will be determined. In both the Taunton River and Saco River studies, we will also attempt to relate spatial and temporal variations in ligand content of the samples with measurements related to the humic content of the samples: DOC, UV absorbance (determined by spectrophotometer at 300 nm, after removal of Fe colloids using a 0.05 um filter), and possibly DOC in the hydrophobic acid fraction (see below).

In the high percentage effluent and low percentage effluent samples of the Taunton River, we will compare our measurements of copper speciation directly to predictions made by the Biotic Ligand Model. To do this, we have obtained a beta-test version of the software implementation of the model from one of its creators, Robert Santore (HydroQual Inc., Mahwah, NJ). This part of the proposed work will be especially helpful to ENSR's project if the model fails to accurately predict copper toxicity in these waters, because our copper speciation measurements will enable us to decide whether the model's problem is in its chemical component (that is, its prediction of copper speciation in the given water) or in its biological component (prediction of copper toxicity given its aqueous speciation). Furthermore, if the problem is found to be in the chemical component, our measurements can replace model predictions of copper speciation and the biological component of the model can still be used.

d. Toxicity studies

Toxicity tests will be carried out at ENSR's toxicology laboratory in Fort Collins, CO. These tests will determine LC-50 values of copper for fathead minnows in river water samples collected from two sites along the Taunton River, representing high percentage effluent and low percentage effluent conditions, on three different dates. In addition, LC-50 values for the more sensitive species cerio daphnia will be determined for samples collected from each of the two sites on one of these sampling dates.

e. Stability of copper-binding compounds from POTW's in river water

We will simulate the possible decomposition of copper-binding compounds in a number of microcosm experiments. Changes in ligand content will be observed over a time period of several days using copper titrations. Experimental conditions will include: (1) filtered river water mixed with filtered effluent, no light (indicative of abiotic oxidation or ligand exchange reactions); (2) unfiltered river water mixed with unfiltered effluent (indicative of biotic processes, if a poisoned control halts the process, or ligand-exchange reactions involving particles, or sorption processes); and (3) filtered river water mixed with filtered effluent exposed to sunlight (indicative of photochemical processes, if faster than 1). While a detailed study of sink reactions of copper-binding compounds is beyond the scope of this study, the results from these experiments will indicate whether further study of any of these processes if warranted.

f. Isolation of hydrophobic acid fraction of DOC

The hydrophobic acid fraction of the DOC will be isolated by acidifying samples to pH 2 with HCl, passing them through an XAD-8 resin column, and eluting with 0.1 M NaOH (Breault et al., 1996). To convert the isolated material back to the hydrogenated form, a hydrogenated cation-exchange column is placed in series with the XAD-8 resin during elution. DOC is then measured in the eluent to determine the % DOC present in the hydrophobic acid fraction. Copper titrations of both the isolated material and the fraction passing through the XAD-8 can be conducted to determine whether the majority of the ligands are retained by the resin. DOC fractionation studies will take place at the USGS laboratory in Boulder, Colorado, under the supervision of Dr. George Aiken.

Principal Findings and Significance

The project has been underway for only a few months and has no major findings to report at this time.

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Basic Information

Title:	Monitoring disinfection byproducts in drinking water: Strategies for small utilities
Project Number:	MA3341
Start Date:	4/1/2001
End Date:	3/31/2003
Research Category:	Water Quality
Focus Category:	Water Quality, Methods, Toxic Substances
Descriptors:	Trihalomethanes, Monitoring, Modeling, disinfection Byproducts, Haloacetic Acids
Lead Institute:	University of Massachusetts
Principal Investigators:	David Alan Reckhow

Publication

Introduction

On September 6, 2000 US stakeholders in EPA's regulatory negotiation process signed an "agreement in principle" on the Stage 2 M/DBP rules. Under this new agreement utilities of all sizes must monitor for disinfection byproducts and report these data to the appropriate state environmental agency. They will be considered out of compliance if their locational running annual averages (LRAA) exceed the maximum contaminant level (MCL). These MLCs are 80 μg/L for total trihalomethanes (THMs) and 60 μg/L for the sum of 5 haloacetic acids (HAA5).

Despite this federal mandate, most utilities serving fewer than 50,000 people are ill equipped to monitor their own systems for the regulated DBPs. They will be forced to contract with commercial firms to collect samples, analyze for the DBPs and interpret the results. Without in-house analytical and monitoring capabilities for DBPs, smaller utilities can lose some measure of control over their systems. They will also experience delays that could prove costly if they are in danger of falling out of compliance.

If small to medium sized utilities can be given the tools to monitor their DBPs, they will profit in many ways. First they will be able to more quickly respond to excursions in DBP concentrations. Second, they will develop a better in-house understanding of how system operation affects DBP concentrations. Third, they will be less dependent on outside enterprises for meeting their mandate of protecting the public health.

Barriers to in-house DBP monitoring are chiefly related to the sophisticated equipment required to analyze for these compounds and the high level of training needed for operators of that equipment. There are also cost and personnel considerations related to sampling, especially for geographically extended systems. The USEPA requires that formal compliance monitoring be conducted by approved laboratories using established methodology. However, non-compliance monitoring is not constrained in this way. Furthermore, non-compliance monitoring is a critical component in the management of drinking water systems, which is often overlooked by smaller utilities.

A very powerful technique that is just starting to be used by larger utilities is mathematical modeling of DBP formation. Power function models have been widely applied to complex and poorly understood chemical systems such as the reactions between chlorine and disinfection byproduct precursors. An example is the general multiparameter model that includes terms for quantity of organic matter (TOC), reactivity of organic matter (UV abs), time, chlorine dose, pH, bromide and temperature (Amy et al., 1987). A common form of this model is shown below:

$$DBP = \alpha(TOC)^{b}(UV_{254})^{c}(BR + d)^{e}(pH)^{f}(Cl\ dose)^{g}(Time)^{h}(Temp)^{i}$$

This general approach has been applied to large compilations of DBP data obtained from laboratory tests. As a result there is an extensive experience with the use and calibration of these models. Other promising approaches to DBP modeling include the chemical kinetic formulations (e.g., McClellan et al., 2000). These borrow classical chemical kinetic reaction model that take the form of simultaneous differential equations. While more complex, these models are better suited to dynamic systems where concentration are falling as well as rising.

In this research, we propose to combine mathematical modeling with some existing and some new field analytical methods to make DBP monitoring accessible to small and medium sized utilities.

Objectives and Scope

The objectives of this research are 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 include, 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-UV272
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 gas chromatography
8. measurement of DBPs by on-line liquid chromatography

Most of these standard parameters (e.g., TOC, UVA, CR, CD, pH, Q & T) would be measured by means of on-line, low cost, low maintenance devices. Some may require on-site batch testing. All would be measured on-site with methods requiring little operator expertise.

Each of these approaches would be coupled with mathematical DBP formation models to improve the power and scope of the data collected. For example, option #1 would employ the 4 measured parameters in a site-calibrated model to predict THM and HAA concentrations for the particular system. This would require an ordinary PC, and existing computer code.

At the other extreme, is option #8. This would provide actual running data on DBPs, which could also feed into a DBP model. The advantage of coupling this type of data to a model is that it would allow extrapolation of the measured concentrations at one location to other locations in the same system.

Predicted DBPs will be compared to samples collected by UMass researchers and analyzed in the UMass laboratory using EPA-approved GC methods.

Experimental Plan

Experimental Approach

Utility Selection

We will first identify 1 medium-sized utility (10,000 – 50,000 population served) in Massachusetts as the first of two field sites for this work. By starting field work at the medium sized utility, we will be applying some of these new monitoring tools for the first time in an environment that will allow us some measure of flexibility and resources. Medium sized utilities also have a long-term compliance data set that can be used to help validate the models that will be developed in this study. The particular field site will be selected based on the utility profile (size, use of chlorine, type of source water, etc.), logistics (e.g., ability to install on-line devices without substantial structural alterations), and interest on the part of the local officials. A good candidate medium-size utility is Northampton, MA (30,384 served [From the MA DEP database on THM compliance]). The PI has a good working relationship with the Northampton DPW director, and this community has a strong interest in developing its own DBP monitoring program. Furthermore, Northampton has high levels of DBPs, and already has a calibrated distribution system hydraulic model that could be used in the proposed research. The assistance of Tighe & Bond Consulting Engineers will be crucial in overcoming site-specific logistical problems that are certain to present themselves.

Once the work is well underway at the medium sized utility, a small utility (< 10,000) will be chosen for similar study. Again, we will look to Tighe & Bond to provide guidance in this selection. Experience with the medium sized utility will help us determine characteristics we should look for in a small utility to maximize the value of this project. Candidate small utilities are quite numerous in MA. Since there are no substantial DBP databases on MA utilities of this size, we will need to collect such data prior to selecting a field site. A good point of departure is the NEWWA database (see table below). While only a fraction of the small systems are in this source, those that did respond to NEWWA's recent survey are likely to have a substantial amount of water quality data.

Some Small Western MA Community Water Supplies from the NEWWA Database

Community	**Population Served**
Athol	9300
Dalton	7218
Monroe	65
Russell	1400
South Hadley	5800
Stockbridge	2000

Assessment of Existing Data

The first step in working at either site will involve the assessment of existing data related to DBP formation. The medium sized utility will have many years of compliance data, where THMs (and now, HAAs) have been measured by EPA-approved laboratories. For utilities of this size, this generally takes the form of one measurement at each of 4 distribution system locations collected on a quarterly basis. In most cases, these 4 locations do not change from one year to the next. Much less data of this sort are likely to be available for the small utilities.

Additional historical information will be collected on the dates (and specific sampling locations) of the compliance data. The parameters we will seek include: chlorine dose, pH, flow rate, temperature, and chlorine residual. Any existing TOC or UV absorbance data will also be collected, but it’s unlikely that there will be very much (utilities have not been required to collect these data, and they are not generally used for system operation).

The DBP data coupled with historical data will allow us to formulate an initial, crude DBP model. The model is likely to be a power function type that uses flow as a indicator of relative residence time for a given system location:

$$DBP = \alpha(pH)^{f}(Cl\ dose)^{g}(Flow)^{h}(Temp)^{i}$$

If chlorine residual data are available, we could improve the model to include chlorine demand:

$$DBP = \alpha(pH)^{f}(Cl\ demand)^{g}(Flow)^{h}(Temp)^{i}$$

Still none of these models could account for changes in the source water quality, which can be quite important in surface water system, or systems using multiple sources.

On-site Data Collection

Perhaps the most significant aspect of this project is its on-site data collection tasks. Here we will be installing on-line monitoring equipment and deploying on-site batch analytical capabilities (see Table below). The application of many of these technologies to drinking water systems is quite new. For example, the colorimetric THM method is a relatively recent and exciting development that has not yet been widely field tested. The three NOM-related sensors (UV spectrophotometer, UV probe and TOC analyzer) are not commonly used as on-line analyzers in drinking water treatment, although interest in their use is on the rise. The gas chromatographic analyzer has been field tested with hazardous wastes and contaminated groundwater, but not yet with drinking water. Finally, the liquid chromatographic analyzer represents a completely new class of instrument. It will be available for the first time in the summer of 2001. Even those technologies that are well known in drinking water systems (e.g., pH, flow, temperature, and chlorine residual sensors), have not previously been coupled with real-time DBP formation models as proposed here.

Summary of On-site Measurements and Technologies

Technology	**Data**	**on-line, off line**	**Supplier**	**Relative Cost***
Flow Meter	System Flow	On-line	Utility	None
pH Sensor	pH	On-line	Utility	None
Temperature Sensor	Temperature	On-line	Utility	None
Chlorinator Feed Rate	Chlorine Dose	On-line	Utility	None
Colorimetric Analysis	Total THMs	Off-line	Hach	Low
UV spectrophotometer	UV absorbance	Off-line	Hach	Low
UV probe	UV absorbance	On-line	Hach	Low
TOC analyzer	TOC	On-line	Sievers	Medium
Gas Chromatograph	THM species	On-line	Perkin-Elmer	Medium
Liquid Chromatograph	THM and HAA species	On-line	Protasis	High

* those designated “None” are technologies that are normally an essential part of a community water system, so that there is no incremental cost for their use in DBP monitoring.

All analytical measurements (either on-line or off-line) except DBP measurements will be made on the source water at a central location near the entry to the distribution system. The on-site DBP measurements will be made at a representative location in the distribution system. On-line analyzers will be set up so they continuously acquire and store data. The off-line analysis will be performed weekly by utility personnel (in the case of the medium sized utility) and by the UMass graduate student (in the case of the small utility).

Analysis of Samples at UMass Laboratory

Prior to initiation of field monitoring, a bulk water sample will be collected just upstream of chlorination. This will be transported to the UMass laboratory for full kinetic DPB analysis. This particular protocol calls for chlorination of the water under a variety of conditions so that the data can be used for development of a general DBP formation model. Each sample will be analyzed for chlorine residual, UV_{272}, THMs and HAAs. In addition, the unchlorinated water will be analyzed for TOC, UV_{272} and classical UV absorbance (254 nm). The conditions to be explored include:

Variables used in the Full Kinetic DBP Analysis

Parameter	Typical Range
Chlorine dose	0.5 - 4 mg/L
pH	6-9
Temperature	2-25 C
Reaction	2 hrs - 5 days

Once, field monitoring begins, samples will be collected weekly at a representative distribution site for DBP analysis. In addition, bimonthly distribution system synaptic surveys will be conducted. This will include about a dozen sites of contrasting residence times. Also at these times, we will collect a bulk raw water sample. This large-volume sample will be transported to the UMass laboratory for partial kinetic DBP analysis. The protocol calls for laboratory chlorination at the dose used by the utility on the day of collection. The samples will be held at ambient temperature (same as for the day of collection) for a variety of contact times intended to represent the range of distribution system residence times. Each will be analyzed for chlorine residual, UV_{272}, THMs and HAAs by EPA approved methodologies. In addition, the unchlorinated water will be analyzed for TOC, UV_{272} and classical UV absorbance (254 nm)

Data Analysis and Model Development

The data will be analyzed on an as-collected basis. Mathematical DBP formation models will be developed and calibrated based on the total data base and on various sub-sets of the data. These will probably take the form of the previously-discussed power function model. However, chemical kinetic models may also be employed. In either case, careful attention will be paid to the significance of component terms in the models. This will necessarily include a sensitivity analysis. The PI and Dr. McClellan from Tighe & Bond both have experience in the development, calibration and use of both types of models (e.g., McClellan et al., 2000). In particular, Dr. McClellan’s assistance with site-specific models will be crucial in this area.

The accuracy of the calibrated models will be compared with actual DBP measurements made in the UMass laboratory. This will allow us to determine the incremental benefit due to each of the on-site analytical technologies.

Methods

Total Organic Carbon

Total organic carbon (TOC) will be measured on all unchlorinated samples. It will be measured by the high-temperature combustion method (APHA et al., 1999). At

UMass a Shimadzu 5000 will be used for these measurements.

Residual Chlorine

Residual chlorine will be measured by titrimetric DPD methodology (4500-Cl, D and F: APHA et al., 1999). We will be measuring residual chlorine species on all samples collected for DBP analysis.

THMs and other Neutral Extractables

Trihalomethanes and other neutral extractables (haloacetonitriles, haloketones, chloropicrin, etc.) will be measured on all chlorinated samples and controls. We will use the standard micro-extraction method with GC and electron capture detection (ECD) (APHA et al., 1999).

Haloacetic Acids

The full suite of haloacetic acids will be measured along with the THMs whenever samples are chlorinated in the laboratory or collected from the field. Haloacetic acids will be measured by the micro-extraction method with methylation and separation/detection by GC with ECD. More specifically, we will use the acidic methanol derivatization (US EPA method 552.2) which avoids the use of highly-toxic reagents as required for the diazomethane method. Acidic methanol has proven to give better and more reliable recoveries of all HAA9 species, especially the brominated forms (Pat Fair, personal communication, 2000).

Specific and Delta UV Absorbance

We propose to measure the full UV-Visible absorbance spectrum for all waters prior to chlorination/chloramination. UV Spectroscopy has been extensively used in studying humic substances. Specific UV absorbance at 254 nm is widely used to assess the humic content of NOM. Though their UV spectra are often featureless, the ratio of absorbance at 465 nm to 665 nm (i.e., E4/E6 ratio) has been successfully used as an indictor for the degree of humification and aromaticity of NOM (Stevenson, 1995; Chen at al., 1977). The E4/E6 ratio decreases with increasing molecular weight and condensation of aromatic constituents. Molar absorptivity at 280 nm of NOM is also indicative of humification and molecular size (Chin et al., 1994; Chin et al., 1997).

Korshin and co-workers have shown that there are certain wavelengths (e.g., 272 nm) that present especially strong correlations between absorbance and formation of TOX following chlorination (Korshin et al., 1996). We will measure UV absorbance (full range of wavelengths) before and after chloramination on all samples. All laboratory absorbance measurements will be made at UMass using their Hewlett-Packard diode array spectrophometer. We will also consult with researchers at the University of Washington who are currently evaluating the delta-UV methodology under contract with the AWWARF[3].

Principal Findings and Significance

The project has been underway for only a few months and has no major findings to report at this time.

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Basic Information

Title:	The Acid Rain Monitoring Project, Phase IV
Project Number:	NMA01
Start Date:	10/1/2000
End Date:	6/31/2002
Research Category:	Water Quality
Focus Category:	Surface Water, Water Quality, Non Point Pollution
Descriptors:	Acid Deposition, Lakes, Citizen Monitoring, Trends
Lead Institute:	Water Resources Research Center
Principal Investigators:	Paul Joseph Godfrey

Publication

On Earth Day, April 22, 2001, 70 volunteers sampled 192 water bodies, mostly lakes, in Massachusetts as part of the Acid Rain Monitoring Project. They brought their samples to 15 nearby volunteer labs for the first part of the water quality analysis with later analyses to be done at UMASS/Amherst. This is a report of their findings.

The April samples were the first collected by the project since 1993, although the project had developed a ten year database of lake and stream acid sensitivity from 1983-1993. Since the early 1990s, both the State and Federal versions of the revised Clean Air Act have been implemented. However, there has been recent concern expressed by the scientific community that acid rain impacts were not lessening and might even be worsening, primarily because of increased nitrogen oxide emissions from automobiles and trucks. For this reason, the internationally recognized Acid Rain Monitoring Project was reactivated by the Water Resources Research Center at UMASS/Amherst with support from the Department of Environmental Protection, Division of Air Quality. Dr. Paul J. Godfrey, Director of the Water Resources Research Center, has spearheaded the effort since its beginning.

Current results for each water body are posted on the Center's web site at <www.umass.edu/tei/wrrc>. The key question is how the status of lakes has changed since the 1983-93 period. Earlier, Dr. Godfrey expressed hope that the Clean Air Act amendments have resulted in a noticeable improvement in water quality, but one might worry that growth in emissions despite the Clean Air Act amendments has continued to threaten the Commonwealth's lakes.

In the earlier phases of the Acid Rain Monitoring Project, six categories of sensitivity to acid deposition were established. These mostly mimicked similar categories used by the U.S. EPA and state agencies. Basically they apply names to specific ranges of pH and acid neutralizing capacity (ANC) or alkalinity. Acid neutralizing capacity is a natural characteristic of lakes and streams that results from the types of geology and thickness of soils. Calcareous rocks and soil have more ANC, while granites and sand have little to none. If ANC is abundant, as it is in the lower elevations of Berkshire County, additions of acid will be neutralized; but if ANC is nearly non-existent, as it is in many other areas of the state, even small additions of acid will drastically change the acidity of the water body. It is the water bodies that are lowest in ANC that are of greatest concern because a change in acidity, measured by pH, will have severe effects on the flora and fauna of lakes and streams. PH ranges from extremely acid at pH 1 to extremely basic at pH 14, but most of life is content in a narrower range around neutral, pH 7.0. In the northeast, our waters are naturally somewhat acidic with a pH around 6.0-6.5. It is generally agreed that when the pH drops below 5.0, serious effects on the biota are in progress. Species disappear, reproduction fails, heavy metals accumulate, etc. The Acid Rain Monitoring Project sensitivity categories, used since 1983, attempt to capture these features.

Sensitivity Categories	**Alkalinity (mg/l)**
Acidified	≤0 and pH ≤ 5.0
Critical	0-2 or 0 and pH ≤ 5.0
Endangered	>2-5
Highly Sensitive	>5-10
Sensitive	>10-20
Not Sensitive	>20

In a comprehensive survey of nearly all named lakes and streams in Massachusetts, the Acid Rain Monitoring Project found the following:

Acidified	5.5%
Critical	16.7%
Endangered	19.5%
Highly Sensitive	21.2%
Sensitive	20.4%
Not Sensitive	16.7%

The recent sampling consisted of a small random subsample of this larger effort. While the results can be translated into similar percentages for the entire state, this has not yet been done. Similarly, it is desirable to remove the effect of unusual prior weather conditions, such as the heavy snow packs of 2001 and 1993 which store acids until the spring melt. This also has not yet been done. Because the present subsample of lakes is not the same as the comprehensive survey nor has it been adjusted to represent those state-wide percentages, the only fair comparison is between the earlier conditions of these specific lakes and their present condition. The results do allow a <u>preliminary</u> comparison of acid sensitivity in 1983-85, 1992-93 and present for April. If conditions had improved, we should presently see relatively fewer lakes in the acidified through endangered categories and relatively more that are in the highly sensitive to not sensitive categories.

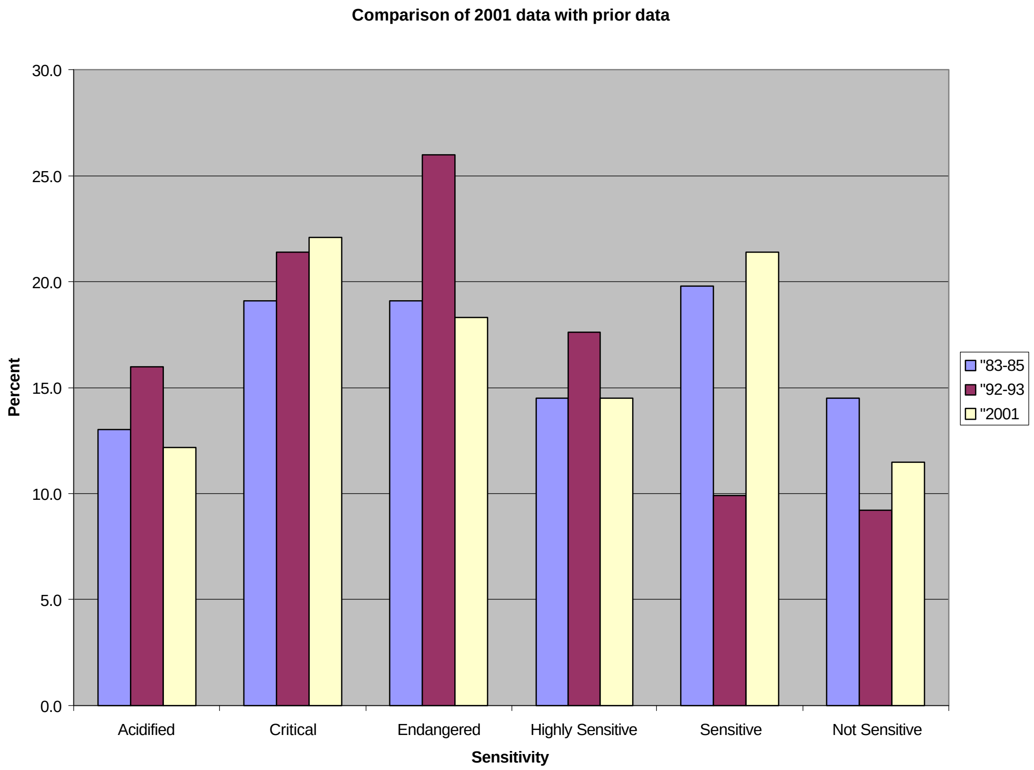
RANDOM LAKES	**%**		
	"83-85	"92-93	"2001
Acidified	13.0	16.0	12.2
Critical	19.1	21.4	22.1
Endangered	19.1	26.0	18.3
Highly Sensitive	14.5	17.6	14.5
Sensitive	19.8	9.9	21.4
Not Sensitive	14.5	9.2	11.5

Overall, there is relatively little change from 1983-85 data to present except that conditions appeared to be worsening by 1992-93 and have been “turned around” since then. These data do not suggest that conditions have improved much since the early 1980s but that we may have avoided worsening conditions. A fairer sense of the degree of change over the past 18 years will occur when the July, October and April, 2002 samples are collected and weather factors are included.”

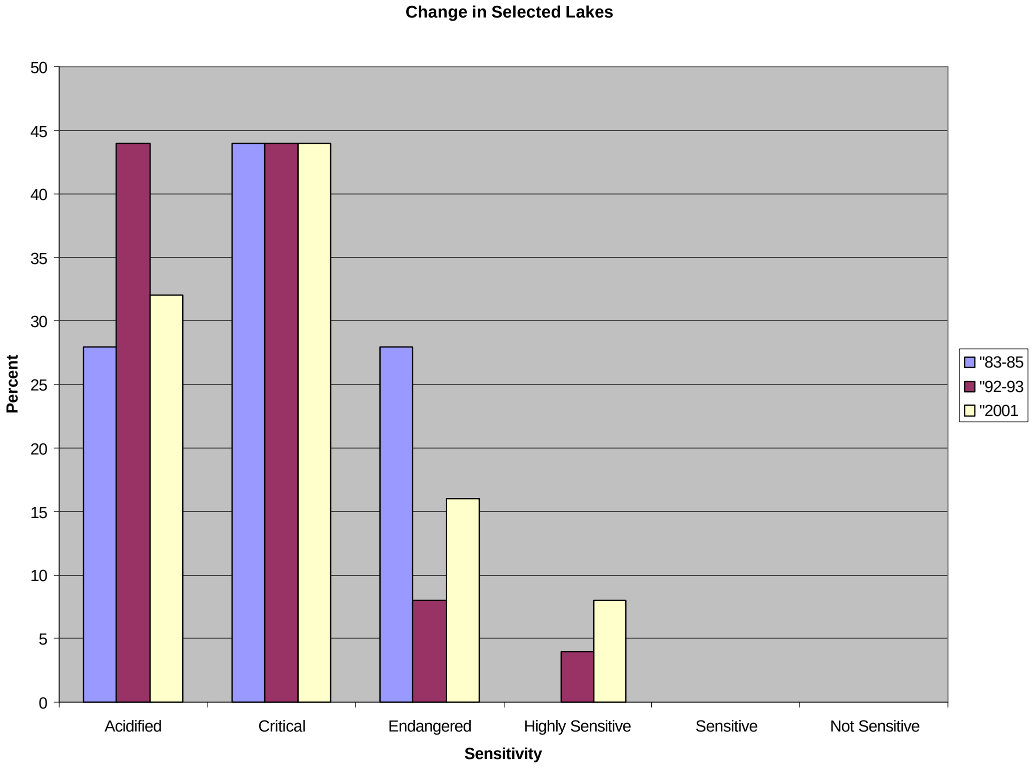
Part of the recent ARM sample collection included 29 lakes and streams that were selected as the best candidates to demonstrate a change in sensitivity. These are water bodies that were acidified, critical or endangered and can be expected to show large changes in pH with relatively small changes in ANC. Again, it would appear that there is relatively little difference between results for 2001 and 1983-85 but that worse conditions exhibited in 1992-93 may have been largely averted.

SELECTED

	"83-85	"92-93	"2001
Acidified	28	44	32
Critical	44	44	44
Endangered	28	8	16
Highly Sensitive		4	8
Sensitive			
Not Sensitive			



In short, these preliminary results appear to suggest that we have not gained any ground on the acid rain problem but, at least, we haven't lost any either. For nearly a decade, many assumed the acid rain problem was solved. It now appears that it was only put on hold. Recent state actions to continue emission reductions and reduce acid rain seem completely justified but more will be needed nationally if we hope to make actual progress.



Basic Information

Title:	Springfield Surface Water Action Monitoring Partnership
Project Number:	NMA02
Start Date:	1/1/2001
End Date:	9/30/2002
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Toxic Substances, Water Quality
Descriptors:	Non-point pollution, mercury, citizen monitoring, subsistence fishing, multicultural
Lead Institute:	Water Resources Research Center
Principal Investigators:	Paul Joseph Godfrey

Publication

***Introduction**:*

The Springfield Surface Water Action Monitoring Program will address three needs. First, the project will address the city's need to discover, monitor and understand the water quality data of its surface water bodies. Second, the project will address the need to present water quality information and health risk advisories in the languages spoken by all who use our water bodies for recreation or sustenance. This information must be presented through outlets that are accessible and practical to these users. Finally, the project partners will address the need to make surface water monitoring and citizen participation in water quality protection sustainable past the term of the grant cycle.

Nationwide, it is estimated that 21,000 water bodies do not meet their designated uses and that 218 million people live within 10 miles of impaired water bodies. The most common reasons for impairment are sediments (17%), nutrients (15%), pathogens (12%) and metals (7%) (D. Brady, EPA, personal communication). Nowhere is this more the case than for the water bodies within the municipal limits of Springfield, Massachusetts (population 156,000). Massachusetts' 303d list of impaired waters includes 7 of the 13 ponds in Springfield and 1 of the 2 streams. Yet, the ponds and streams in Springfield are heavily used by residents for everything from recreation to subsistence fishing.

However, no program currently exists that informs the citizens of the problems and dangers of existing or potential impairment and gives them the informational tools to take appropriate action. Those programs that do exist disseminate information in English only, creating a greater threat for our non-English speaking community which makes up the majority of subsistence fishermen.

We propose to create a program that will provide an initial baseline of information and develop community stewardship that will sustain a monitoring and information transfer program for the whole community, but especially for that segment that most heavily uses the water resources and is most heavily impacted by its impairment. Specifically, information dissemination will focus on the English, Spanish, Vietnamese, and Russian speaking communities.

Contamination of freshwater fish by mercury has become pervasive throughout the northeast. The New England states and all but nine others plus three eastern Canadian provinces (New Brunswick, Nova Scotia and Quebec) have active health advisories that recommend limiting consumption of certain freshwater fish (NESCAUM, 1998). The health concerns focus on two human groups that are most susceptible to excessive mercury consumption: 1) pregnant women and young children and 2) subsistence anglers.

Nearly all of the research attention on mercury deposition, bioaccumulation in the food chain and human consumption has focused on relatively rural and remote environments (NESCAUM, 1997), where anthropogenic inputs were not originally expected to be large. Like acid rain, it has since been learned that emissions of elemental mercury follow a similar wide-spread distribution pattern. However, it is widely agreed that two of the three principal forms of mercury in emissions, divalent and particulate mercury, are likely to be deposited relatively close to the source (NESCAUM, 1997; Nichols, 1996). The main sources of anthropogenic mercury emissions in the Northeast are largely urban sources. Municipal Waste Combustors (45%), Non-utility Boilers (18%), Electric Utility Boilers (13%) comprise 76% of all anthropogenic emissions in the Northeast with other similarly urban sources comprising the remaining 24% (NESCAUM, 1997). Nevertheless, even when studies of mercury accumulation are conducted in an urbanized state like Massachusetts, the focus tends to be on lakes in relatively rural areas (MADEP, 1997). Consequently, the fact that studies on rural lakes and ponds have discovered sufficient problems to issue a statewide caution against fish consumption causes elevated concern for water resources in the immediate local of these primary sources of mercury and other metals.

Existing studies have shown a relationship between elevated concentrations of methyl mercury in fish tissue that are positively correlated with total mercury concentrations, water color, temperature, and dissolved organic carbon and negatively correlated with ANC and pH (Evers and Reaman, 1997, Watras, 1994, Stafford, 1991, Verta, 1994, and Nichols, 1996). In Massachusetts, pH and ecoregion, which encompasses a number of watershed characteristics, were most highly correlated with fish mercury levels (MADEP, 1997) but there was considerable variation among fish species. MADEP also found positive correlations between fish tissue mercury and fish tissue cadmium and selenium for some fish species.

Other studies have shown that point source mercury inputs do not significantly elevate the levels of methyl mercury in a flowing water system until that water flows through riparian wetlands (Waldron et al., in press; Colman et al., 1999). It is known that the primary means of mercury methylation is via the sulfate reducing bacteria (Gilmour et al. 1991). Riparian wetlands, including in-lake weed beds, provide the conditions necessary for mercury methylation. Thus, nutrient and sediment additions to lakes tend to create environments that not only directly impact resource use but may create secondary complications of metal contamination.

Nutrient and sediment problems pervade the Springfield water resources and create the habitat for excessive aquatic plant growth. Many of the ponds have extensive areas of aquatic vegetation; seven are 303d listed as having noxious aquatic plants. One pond (Watershops Pond) was recently dredged to reduce sediment levels and minimize the potential for noxious aquatic plant growth. The variety of riparian wetland/weed beds in Springfield ponds will permit evaluation of the relationship between aquatic weed/shallow sediment area and metal contamination. Analysis of storm inputs will permit separation of direct deposition inputs from watershed inputs. Coupled with mapping of storm drains (currently underway), sources of contamination, silt and nutrients can be statistically isolated and community measures to control inputs established.

Other toxics such as PCBs and chlorinated pesticides are of unknown impact fish tissue concentrations. Sources of PCBs are expected to be atmospheric deposition from waste incineration; sources of chlorinated pesticides are expected to be surface runoff from the urban landscape. The design of storm event monitoring and fish tissue monitoring will capture both toxics and provide further evidence of sources. The proposed study will provide the first information on these compounds for the Springfield area.

Objectives:

1. To determine the baseline chemical and biological characteristics of the water bodies and to determine the baseline levels of nutrients, metals and organic contaminants in the sediments. To determine the current level of mercury, other heavy metals, PCBs and chlorinated pesticides in frequently consumed fish species with the City of Springfield. To determine the extent of nutrient, sediment, and toxic contaminants provided to the water bodies by storm drainage.

Because the eventual goal of the project is to reduce inputs of nutrients, sediment and toxic contaminants from watershed sources and to make a strong case for reduction of atmospheric inputs, it is important to establish current baseline conditions. University graduate and undergraduate students will collect the first year's baseline information consistent with the state's protocols within the Massachusetts Watershed Initiative and will include nutrients and aquatic macrophyte mapping. An accurate bathymetric map will be developed for each water body for future assessment of sedimentation.

Because the pathway for both toxic contamination and nutrient enrichment of aquatic macrophytes is often primarily through the sediments, baseline conditions of the sediments will be determined in the first year. A mid-lake station and at least one littoral site near a storm drain outlet will be evaluated. Further sampling is not anticipated within the project period, but will be part of the long term monitoring plan.

We propose to initiate this effort through a sustainable monitoring program for metal contamination in fish tissue and storm event sampling of nutrients and sediment for the 15 water resources in the Springfield municipality. We expect that this will lead to inclusion of bacterial pathogens within a few years.

2. To inform recreational users of the water bodies and sustenance fishermen, especially those who are non-English speaking, which water bodies present an elevated health hazard. This information will be presented through information outlets most frequented by those effected.

While the Water Resources Research Center is collecting baseline water quality information, the City of Springfield will coordinate the participation of the community in the identification of information dissemination outlets. The project partners will work together to determine locations at each water body where monitoring information can be posted. Further, the partners will identify additional information outlets such as health centers, social service agencies, neighborhood council offices, and water bills where residents of various income levels, and ethnic backgrounds will most easily access the information.

The results of the fish tissue sampling will be adapted to the language used by the State for fish consumption advisories. This information will be translated into three different languages: Spanish, Vietnamese, and Russian. Once the information is translated, it will be placed on signs, in all four languages, and posted at fishing sites identified by the project partners. Some of these signs will be informational kiosks that explain why the consumption of certain fish presents a health risk.

Finally, we will publish a "Guide to Swimming and Fishing in Springfield's Waters" and a guide to stormdrain pollution prevention. These guides will be published in four languages and distributed throughout the city. The recreation guide will include information on where to swim, how to get a fishing license, safe fish consumption practices and a map of the city's water bodies. The stormwater drain guide will describe to people the connection between stormdrains, disposal, and water quality. Specific water quality data for each water body will be included in this brochure.

3. To develop the participation of residents in surface water monitoring as partners in order to ensure the project's long-term sustainability.

Monitoring of water quality has a long history of being inadequately supported despite its obvious fundamental use in all water quality assessments. Massachusetts is no exception. Most water quality monitoring focuses on major river systems on a 7 year rotating cycle with few resources left for smaller tributaries, ponds and lakes or interim monitoring of larger systems. Typically, only a dozen or so of the 2,600 lakes and ponds in the state can be surveyed annually. For some critical issues such as storm event loadings of nutrients and sediment or metal contamination of fish tissue, timing and manpower requirements severely limit what agencies can do.

In the second year, community watershed stewards will be trained by the Massachusetts Water Watch Partnership and will work with the university students to transfer the monitoring responsibility to the community stewards for continuation in successive years.
Successful development of sustainable monitoring efforts have resulted from combinations of citizen interest and motivation with provision of technical information from experienced sources. Over the past decade, an extensive network of citizen volunteers and university and state agency expertise coupled with municipal, industry, state and foundation support has developed through the Massachusetts Water Watch Partnership. The partnership has a series of protocols, accepted by the state, for creating effective local groups and measuring baseline characteristics of rivers and lakes. The elements of the recent EPA Quality Assurance Project Plan guidelines (EPA, 1996) have been the basis for the Partnerships training for more than a decade with equal emphasis on problem prioritization, study design, sample collection, quality control, data management, and presentation of results. The experience gained from a decade of

organizing citizen monitoring that generates information acceptable and used by state and federal agencies will guide this effort to extend our experience in two critical directions: capture of storm event impacts and involvement of non-English speaking or minority sustenance users of the water resources.

During the second year of the project, the project partners will teach local fishermen to be educators to other fishermen in their community. Educational meetings conveying fish consumption information will be held formally in churches and community centers by local fishermen, and informally at the fishing sites.

During a separate- but related- project, volunteers will use City of Springfield maps of all storm drains and their destinations to stencil warning information on all storm drains. During this project, citizen volunteers from each drainage system will be taught to collect water samples at peak drainage flow following significant storm events. The lab results will be correlated with characteristics of the drainage watershed and be provided to community groups at meetings held formally in churches and community centers.

Leaflets will be prepared specifically for the storm drain watersheds for each waterbody that detail the specific findings and encourage residents to minimize activities that contribute to the problem.

***Project Context*:**

The Springfield Surface Water Action Monitoring Project will tie in very closely with three projects currently underway in the city. First, the city is completing a stormwater stenciling program. This program educates residents and businesses about stormwater runoff and safe disposal practices for hazardous wastes. The program also lets each resident and business know which water body their stormdrain empties into.

The second project is an environmental justice pollution prevention program that examines pollution concerns among residents in the Enterprise Community boundary. This program also documents sources of pollution and attempts to find strategies, with the residents and businesses, that will prevent additional pollution and clean existing problems.

The final program is the city's brownfields program. This highly successful program has targeted vacant and contaminated industrial sites all over the city for clean-up and redevelopment. Many of these sites are located near surface water bodies. Through the proposed project, we can determine if any of these sites are impacting water quality and then place a priority on those sites in the brownfields program.

All of these programs are run through the Sustainable Springfield Program. This is an initiative supported by the Mayor to promote Springfield as a clean and healthy place to live and work. Sustainable Springfield distributes a quarterly newsletter and acts as a clearinghouse in the city for environmental technical assistance, coordination and information dissemination.

Approach

This grant is based on one innovation: local control over environmental sampling and analysis and information delivery. Traditionally, we must wait for the State, already overburdened, to conduct the surface water or fish tissue sampling and issue health advisories. Meanwhile, our citizens are placing themselves at risk due to a lack of information. The Springfield Department of Health has never issued a fish consumption advisory for our local surface waters because it has never possessed the tools to do so.

Our innovation is to provide our local agencies, both governmental and non-governmental, with the tools they need to measure and monitor environmental parameters for surface water bodies in Springfield. We will begin by asking the University of Massachusetts, experts in this field, to guide us and teach us on the proper tools and techniques for monitoring. During the grant cycle, the university staff will conduct the sampling of the environmental parameters at regular intervals. During this time, the staff at the University will also teach local agencies and residents to continue the monitoring into the future, making this program sustainable.

Parameters Sampled: Fish

This project will follow the protocols for fish collection and tissue analysis established by the state in a recent statewide survey of heavy metals and PCBs in fish tissue (MADEP, 1997). That survey evaluated total mercury, selenium, arsenic, cadmium, lead, chlorinated pesticides and PCBs in three species of fish from several areas of the state but not including the Springfield eco-region (MADEP, 1994).

The three test species will be yellow perch, largemouth bass and brown bullhead. These species were used in the MADEP 1997 study and will allow comparison with that survey. They are also common in most lakes and ponds in Massachusetts, are favored by anglers and represent predators, pelagic omnivores and bottom-feeding omnivores. Only fish that are larger than the minimum criteria will be collected because these are either the legal limits or the sizes likely to be consumed. The minimum size criteria for yellow perch and brown bullhead is 8 inches (20 cm); for largemouth bass the minimum size criteria is 12 inches (30 cm), the legal minimum size.

Fish will be obtained by electrofishing, gill netting and angling. Contamination of fish samples will be minimized by not allowing fish to rest in the bottom of the boat or on shore, or to be handled by the person operating the boat if the boat was powered by an outboard motor or containing any other gasoline operated engine. Fish will be rinsed in ambient water, placed in a “zip lock” bag and chilled on ice. Fish will be delivered to the laboratory on ice within 24 hours of collection. These handling procedures are consistent with the MADEP 1997 study. Ten individuals of each fish species will be collected from each lake or stream (streams are all slow moving water) if the species is present.

The MADEP study analyzed fish fillets only; this study will consider that multicultural differences exist in the fish portions consumed and will analyze those portions representative of actual fish consumption by Springfield anglers. Project partners will determine fish consumption habits of their constituents.

Fish will be collected in mid to late summer to minimize effects of reproductive cycle effects on water and fat contents.

Fish collection will be done by University of Massachusetts Fisheries Program graduate/undergraduate students for the two years of the study. In the second year, a comparison will be conducted between professionally collected fish and those collected by local anglers following strict protocols but using only angling techniques. If the two methods are comparable, subsequent ongoing efforts will rely on local anglers for continuation of the fish sampling.

Parameters Sampled: Water and Sediment

In a separate city-funded effort, volunteers will be stenciling all storm drains to indicate the eventual pond and river destination of storm water and contaminants. The City of Springfield has compiled storm drainage maps that show the destination of approximately 30,000 storm drains in the city.

Water quality sampling will be of two types. Baseline sampling will be done monthly from April through October by trained professionals and local watershed stewards. To establish baseline conditions in the first year of the project, trained professionals will sample pH, dissolved oxygen, temperature, depth, water transparency, chlorophyll a, total phosphorus and nitrate at a mid-lake site or mid-river. A bathymetric map will be generated from pond soundings and weed beds will be mapped by extent, density and species composition following MADEP procedures. In the second year, the project will begin a transition to use of local watershed stewards. The stewards will be trained in proper collection of water samples and aquatic weed mapping by University staff in the Water Watch Partnership, and the stewards will collect samples in parallel to the trained professionals. In subsequent years, all water quality sampling will be done by the volunteer watershed stewards with annual certification of correct use of protocols. Field sampling methods will follow those approved by USEPA and MADEP for use by volunteer samplers in providing data acceptable for federal and state use.

Sediment samples will be collected only by trained professionals at a mid-lake site and in the outflow area of storm drains. Sampling methodology will exactly follow the state protocol (MADEP, 1997) by using an Ekman dredge to collect the sample with a large subsample collected with a pre-cleaned wide-mouthed glass jar inverted and pushed into the portion of the sediment sample away from the sides of the dredge, then capped with Teflon-lined caps and placed on ice for shipment to the lab. All sediment sampling and handling will follow US EPA protocols (USEPA, 1993a).

Parameters Sampled: Storm Events

Beginning in year one, watershed stewards will collect storm event discharge at storm drainage outfalls. Stewards will be trained to properly collect storm event samples and will collect samples at the peak of storm events that are likely to produce at least ½" of precipitation. The stewards for this task may be different from those trained for mid-lake sampling because one requires constant sample collector availability near the sampling site while the other requires a that the volunteer have access to a boat. Storm water stewards will be certified for sample collection annually.

Storm drainage samples will be analyzed for total phosphorus, nitrate, total mercury, selenium, arsenic, cadmium, and lead**.**

Laboratory Methods

Fish specimens will be processed following US EPA procedures (USEPA, 1993b). In the laboratory, all fish specimens will be held at 4° C prior to dissection and will be dissected within 48 hours of collection. Primarily fish fillets (edible tissue) will be analyzed but other parts may be included to reflect the multiculturalism of sustenance anglers, so fish specimens will not be frozen to avoid rupturing internal organs and contaminating fillets. Fish dissection and homogenization will be conducted in an area dedicated to this task but not complying with class-100 clean room requirements. Such facilities are not required for processing fish samples at the usual ug/g (wet weight) metal concentrations (Bloom, 1995). The left side of the fish will be used for analysis; right side material will be archived for possible future reference

Prior to use, all fish dissection and tissue homogenization equipment and fish sample containers will be washed with a laboratory-grade detergent, rinsed with tapwater, soaked in 50% reagent-grade nitric acid for 12 to 24 h, rinsed with tapwater, rinsed with reagent water and finally rinsed with pesticide-grade isopropanol.

Samples will be analyzed within the recommended holding time of 6 months. The fish will be filleted on precleaned borosilicate glass dissection boards and filleted with high quality stainless steel knives. The skin will be removed after filleting. Sufficient mass of tissue will be removed to meet analytical detection requirements. A duplicate muscle sample will be collected from the other side of the fish, frozen and archived. The sample intended for analysis will either be immediately digested or frozen until analysis. Following similar procedures a sample and duplicate archival sample will be collected for chlorinated pesticides and pcb analysis.

Dissection instruments and work surfaces will be decontaminated between each dissection by rinsing with tap water, washing with detergent, rinsing with tap water, rinsing with reagent water and rinsed with isopropanol. Fillets will be place in individual high-density polyethylene cups with tight fitting covers and frozen at -20°C. Prior to analysis, the entire fillet sample from each fish specimen will be thoroughly homogenized in a food grinder with stainless steel blades.

Analytical Methods

Total mercury will be analyzed using cold vapor atomic absorption spectrometry (US EPA Method 245.6) Analysis of other metals will follow ICP procedures (US EPA 200.7) using a Spectro Model FMD-07. Phosphorus will be analyzed in sediment and water samples using a low level modification of EPA 365.2 that has been approved by MADEP. Spectrophotometric readings will be taken on an Hitachi UV-visible scanning spectrophotometer using a 5 cm cell. organic contaminants will be analyzed by the university of Maine water resources institute laboratory as part of the close network of New England water resources institutes. the lab services of the state of Maine will be used for all fish tissue analysis**.**

Water chemistry parameters will be analyzed according to the procedures listed in the following table.

These procedures have all been approved for use by US EPA Region 1 and MADEP for use in developing data acceptable for state and federal use as described in the Massachusetts Quality Assurance Project Plan Guidebook (Godfrey, in prep).

Parameter	Field Method	Lab Method
Alkalinity	MWWP	MWWP double-end point
Chlorophyll	MWWP	Standard Methods 10200 H
Dissolved Oxygen	MWWP	EPA 360.2
Total Phosphorus	MWWP	MWWP low range based on EPA 365.2
pH	MWWP	EPA 150.1
Transparency	MWWP	
Aquatic Macrophytes	MADEP	

All Standard operating procedures have been reviewed by the quality control offices of EPA Region 1 and Massachusetts Department of Environmental Protection and are approved as acceptable for collection of water quality monitoring data for use by state and federal agencies in the Massachusetts Watershed Initiative.

Appropriate information management, processing, and delivery.

This project was created in response to observed health risks posed to our residents as a result of an information deficit specific to water quality. We have observed that the people of our city pollute waters, not knowing the impact they are having; and we have observed that the people of our city place themselves at risk by using contaminated waters, not knowing what level of contamination that exists. For this project, we propose to disseminate information through information outlets that are frequently observed by people of all ages, incomes, educational levels and languages in a fashion that is easy to understand. This information will inform those who pollute what their impact is on surface waters in Springfield and it will inform those who use the water bodies what, if any, health risks exist at that location.

Delivery of information is frequently offered through internet resources, newspapers and public television. While the internet has taken much of the world by storm, we must acknowledge that access to the internet is not a reality for the majority of the residents in our city. Likewise, we must also recognize that many residents who use our water bodies do not all read English newspapers or watch public television. “Appropriate” is a key word for this proposal. We do not want to collect information that nobody will ever use or understand. We want to deliver information in the most “appropriate” fashion possible.

In order to succeed in this area, we will need the total cooperation of every partner involved. During the first year of the project, the partners will carefully consider how the information must be presented. We will identify tools for information delivery as well as the locations where information will be posted. Emphasis will be placed on locating information at those places where the water bodies themselves are most frequently used. The University of Massachusetts will initially manage and process the data collected. However, during the course of the project, our local health department will be trained to complete similar tasks.

Timely communication of information to the public

The idea of this proposal is not to try to create major media stories on a frequent basis but to develop a routine awareness of water quality much in the manner that we factor weather reports into planning our daily lives. In our experience, a very brief but frequent report on water quality generates ongoing interest and elicits requests for more detailed information. Active questioning by the citizenry is preferable to passive listening. Existing excellent communication with state and nationwide media distributors insure that appropriate articles will be disseminated well beyond the Springfield area.

This routine delivery of information will be completed by the City beyond the term of the grant cycle. As of today, not one local municipality in Massachusetts has issued its own fish consumption advisory. In order to be “timely”, we must be able to undertake the sampling locally so we can post the information quickly. During the course of this project we will work closely with the State to develop a process for information delivery that other municipalities can replicate.

3. Expected Results or Benefits

The philosophy underlying this effort is “knowledge is power”. Citizens and environmental protection advocates alike are inundated with data about the environment that they may or may not understand. Non-English speaking citizens are clearly at an even greater disadvantage when it comes to understanding this data. There is a clear need to transform data into information so that individuals can feel capable of acting to protect their own, and their community’s, health and well being.

In more than a decade of the citizen monitoring movement, it has become clear that communication, involvement and empowerment are the best ways to create true citizen participation in environmental decisions. With non-point source pollution there is little real alternative to finding innovative ways to change people’s attitudes than participation in the process from the beginning and in a role perceived as important. Citizen monitoring also has another benefit: it promotes consensus building and reduces polarization. Citizen monitoring is not a simple task. Partnering with organizations that have the variety of resources needed to inform monitors is the only way to produce sustainable and credible efforts. For this project, experienced and respected partners collaborate in new ways that create expanded partnerships between active participants in innovative environmental solutions with dedicated community motivators.

Short term expected results of the project are:
Local and State knowledge of the baseline surface water quality in Springfield as well as the characterization of stormwater pollutants;

Local and State knowledge of fish tissue contamination and related health risks of consumption;

Established environmental health information outlets for recreation and sustenance water body users, both English and non-English speaking.

Formalized communication between local and state partners who are involved in environmental quality and safety, and the general public that uses the public resources.

Participation of neighborhood organizations in the planning of their own access to environmental health information, leading to their active participation and understanding.

Widespread public education on pollution prevention practices and water pollution impacts.

The long-term expected results of the project are:
More effective efforts to change individuals behavior related to surface water quality, as evidenced by a reduction in dumping of oil down storm drains, improved use of lawn care products, etc.;

Improved community health and safety because residents; regardless of education level, income, or language spoken; will have access to timely water quality information and an understanding of the connection between rainfall and water contamination. Residents will no longer swim and/or fish in contaminated water bodies for lack of knowledge **and** water quality will be improved over time;

Local government ownership over monitoring of surface water quality and information delivery;

Expanded involvement by community residents in government and/or non-profit water protection efforts, as measured by participation at public meetings and the number of advocacy groups;

Improved surface water quality in targeted water bodies;

Inclusion of surface water quality data collection, analysis and dissemination in area school curriculums;

Re-invigoration of local, regional and state government and non-governmental agencies' commitment to protecting surface water bodies in the greater Springfield area; and

Replication of the successes of this project by other communities and community groups in the Pioneer Valley.

4. General Project Information

The Springfield Surface Water Action Monitoring Program will only be successful if each of the partners actively participates. For a management structure, the City of Springfield Planning Department will act as lead and will work closely through a sub-contract with the University of Massachusetts Water Resources Research Center. Each of the other partners will act under the direction of the Department of Planning, but many times work directly with the staff of the University.

Basic Information

Title:	Development of a Quality Assurance Project Plan Guidebook, Standard Operating Procedures and Workshops for Massachusetts
Project Number:	NMA03
Start Date:	3/1/1999
End Date:	6/31/2001
Research Category:	Water Quality
Focus Category:	Water Quality, Surface Water, Management and Planning
Descriptors:	Quality Assurance, Citizen Monitoring, Water Quality
Lead Institute:	Water Resources Research Center
Principal Investigators:	Paul Joseph Godfrey

Publication

Introduction

The Federal Clean Water Act (CWA) requires that each state develop a program to monitor the quality of surface and ground waters and to prepare a 305(b) report every two years to determine the levels of support for specific designated uses of each waterbody. The Executive Office of Environmental Affairs (EOEA) has established the Massachusetts Watershed Initiative to use twenty Basin Teams to monitor water quality on a five year rotating schedule in each of the 27 watersheds in Massachusetts. Due to a limited budget and the large numbers of rivers, lakes, wetlands and coastal / marine areas in Massachusetts to be assessed, only a small fraction of the waters are directly assessed by staff of the Massachusetts Department of Environmental Protection. For example, in the 1995 305(b) report, only 18% of lakes and 17% of rivers were assessed. The number and area of surface waters assessed could be greatly increased if volunteer monitors could be assisted and utilized to collect the data.

Many rivers and lakes are monitored by various volunteer groups, planning agencies, nonprofit groups as well as scientists working for private companies or state agencies. Due to inconsistencies in data collected, data quality, and data availability; these monitoring efforts have not been used to any large degree by either the Basin Teams, or in the past 305(b) reports. Without documented QAPPs, the data may be of limited use to the groups themselves. These data could be more widely used if all groups used Quality Assurance Project Plans with consistent or comparable sets of methods, data quality objectives and data management. In addition, many watershed associations, planning commissions, private consultants and other scientists conduct surveys and use their results to address in local forums problems that they identify. Those who apply to the US Environmental Protection Agency for monies for these surveys are required to supply an approved Quality Assurance Project Plan which includes Standard Operating Procedures. Because the necessary plan is technically difficult for many groups, projects cannot be funded and data is not collected and processed so as to be used and accepted by government agencies and other data users. Additionally, re-writing similar plans repeatedly for each project is an inefficient use of staff time and grant funds. This project will decrease the time and resources spent on writing QAPPs; it will result in more surveys being conducted, and will increase the amount of citizen-collected data that are suitable for 305(b) reports and for use in local forums.

Objectives

The overall objective of this proposed project is to develop a method of assistance that enables a variety of groups in Massachusetts to write Quality Assurance Project Plans for environmental monitoring. These groups include volunteer monitoring groups, watershed, river and lake associations, planning commissions, and other state or private groups. The specific objectives for this demonstration project are to develop guidance documents and workshops that assist monitoring groups in writing QAPPs, for basic river, lake, and/or coastal surveys.

Approach

I. Review current reports and data needs:
    A. Obtain copies of past QAPPs, SOPs, and other related reports (e.g guidance

documents on writing QAPPs). Maintain library, provide copies to interested monitoring groups.

B. Meet with staff from Massachusetts Department of Environmental Protection to determine data needs including data type, frequency, data quality requirements, documentation, data units and reporting formats for inclusion in 305b reports.

C. Meet with staff from US EPA region 1 to discuss format and required elements of the QAPPs, suitable for approval by the EPA.

D. Meet with staff from EOEA Basin Teams and with NGOs in 5 target basins to determine specific data needs for surveys they are planning under the Massachusetts Watershed Initiative.

II. Develop a Guidebook, based on the EPA QAPP Guidebook, that provides significantly more Massachusetts-specific help to groups writing

III. Compile an annotated list of SOPs for the most commonly used monitoring methods in rivers, lakes, and coastal waters, to be used as reference documents by groups preparing QAPPs. The list will include both rigorous and basic methods for some indicators and surveys. This will allow groups that are preparing QAPPs to reference the indicators and methods that match specific data quality objectives (DQOs) of the surveys they are planning. For instance, if a survey is intended to provide information for use a 305(b) report, the QAPP may refer to more rigorous methods, quality control measures, and frequency of sampling than would a QAPP for a similar survey that is intended purely as a public education tool. The list will be annotated to indicate what methods match which DQOs.

The Standard Operating Procedures will follow established methods of Standard Methods or EPA methods and approved methods used by the River Watch Network and the Massachusetts Water Watch Partnership after consultation with DEP and EPA staff.

Principal Findings and Significance

Using the EPA Guidance document on QAPP writing for citizen monitors as a launching point, the Massachusetts Guidebook adds the decade of experience in organizing volunteer monitoring efforts by the Massachusetts Water Watch Partnership and River Watch Network to provide specific guidance on what to include, where to find appropriate resources, and how to select appropriate objectives for various types of projects. Workshops, in the early stages, helped to define the needs of volunteer groups. The Massachusetts Guidebook is backed by world wide web resources, allowing users to immediately view supporting documents and to access Standard Operating Procedures (SOPs). The Guidebook has been extensively reviewed by the Massachusetts Department of Environmental Protection and EPA New England. Several groups have used it to develop their QAPPS. The Guidebook will shortly become the state’s approved guidance on QAPP writing for citizen monitoring projects

Information Transfer Program

Basic Information

Title:	Massachusetts Water Resources Research Center Information Transfer Program, FY2001
Start Date:	3/1/2000
End Date:	2/28/2001
Descriptors:	Directory, Researchers, Massachusetts
Lead Institute:	University of Massachusetts
Principal Investigators:	Paul Joseph Godfrey

Publication

Approximately every five years, the Center updates its listing of academic researchers in Massachusetts. The web sites of all colleges and universities in Massachusetts were visited to obtain up-to-date listings of faculty potentially involved in water resources research. Each of these was sent a one page questionnaire to provide additional information on current research, courses taught and areas of interest. The information on 160 researchers was compiled into the 2001 Directory of Water Resources Research and posted on the Center's web site <www.umass.edu/tei/wrrc> where it may be downloaded. Planned additions to this directory include a directory of state and federal agency researchers and managers and a directory of individuals at consulting firms who are water resources specialists.

Basic Information

Title:	The Massachusetts Water Watch Partnership
Start Date:	7/1/1997
End Date:	6/31/2002
Descriptors:	Citizen Monitoring, Non-point Pollution, Rivers, Lakes, Monitoring, Volunteer, Quality Control
Lead Institute:	Water Resources Research Center
Principal Investigators:	Paul Joseph Godfrey

Publication

The Massachusetts Water Watch Partnership (MassWWP) was formed in 1990 to empower citizens to collect, evaluate, and act on scientifically credible water quality information for the Commonwealth's surface waters. To accomplish this task, we rely on building a partnership with government, industry, educators, conservation organizations and the general public, who lend their respective talents to this effort to achieve practical solutions to water quality problems. The program has grown from working with 15 groups in 1990 to over 80 today. Funded principally through grants from foundations and industry and membership fees until 1999, the program is currently funded principally through contracts with the Massachusetts Executive Office of Environmental Affairs (EOEA), supplemented by grants from the Massachusetts Environmental Trust (MET) and others.

Methodology:

MassWWP services fall into several broad categories:

1) *Workshop and conference series*, which trains volunteers and promotes information sharing on the major aspects of planning and running a monitoring program, from program planning to field and laboratory methods to data management and presentation.
2) *Partnership and network building* to foster productive relationships among volunteer groups and between volunteer programs and governments, business, and other interests.
3) *Special projects* on specific issues, such as satellite imagery and a nationwide Secchi disk survey.
4) *Research* on topics that have potential to enhance the utility of volunteer monitoring programs.
5) *Consultation and advice*, loan of sampling equipment, and other direct services.
6) *Conferences.* MassWWP regularly presents papers and workshops or helps plan water monitoring related conferences around New England and the nation.
7) *Publications.* Development and/or distribution of documents of use to volunteer monitors.
8) *Statewide Coordinator and Western Massachusetts Service Provider*. A principal task of the EOEA support is to provide statewide coordination of citizen water quality monitoring and guide the four current regional service providers. The Water Watch Partnership is also one of the designated regional service providers, covering western Massachusetts.

PRINCIPAL FINDINGS AND SIGNIFICANCE:

Project One: Support to Volunteer Monitoring Network. Funded by EOEA.

Task 1: Coordination between Monitoring Support Centers, support activities of the Volunteer Monitoring Citizens Advisory Committee (CAC):

In FY 2000, a skills matrix was developed after surveying the five Monitoring Support Centers (MSCs) that are sponsored by EOEA to provide assistance to volunteer monitors. In FY 2001, we re-surveyed MSCs (now there are 6), updated the matrix, and posted it on the MSC web page of the MassWWP web site. http://www.umass.edu/tei/mwwp/ . This information was also used to update a set of volunteer monitoring “Yellow Pages” which is sent by mail to clients with no Internet capabilities.

We convened four meetings of the MSCs to share strengths between service centers. The first meeting was held on November 4, 2000, in conjunction with the MassWWP annual volunteer monitoring conference. Meeting notes are posted on our web site.

The second meeting was held on February 22, 2001 and focused on reports by Urban Harbors Institute (UHI) and Charles River Watershed Association (CRWA) on their programs, and on review of MassWWP Data Interpretation handbook. One recommendation coming from this meeting was that MSCs should continue to run QAPP workshops together. This did occur, with a January workshop sponsored by the Merrimack River Watershed Council (MRWC) and run with MassWWP assistance, and a March workshop run jointly by Waquoit Bay National Estuarine Research Reserve (WBNERR), UHI and MassWWP. MSCs offered several suggestions on how MassWWP might improve its data interpretation manual. Subsequently, MassWWP has received some funds from MET (through a grant to the Lakes and Ponds Association West (LAPA West)) to enhance the manual. We anticipate an updated version to be completed in early 2002.

The third meeting took place April 19, 2001 and concentrated on working with Massachusetts Department of Environmental Protection (DEP) watershed monitoring coordinators (WMCs).

The fourth meeting was held May 22, 2001 and the topic covered was database management for volunteer data. This is discussed further below.

The volunteer monitoring CAC met on the same dates as the MSC meetings. Meetings featured discussion of the 2000 River Network report on volunteer monitoring (VM) and developing an implementation strategy for the associated recommendations, laboratory and GIS services, and a data management system and VM – Agency collaboration. Meeting notes, including various recommendations of the CAC, were submitted to EOEA.

MassWWP also serves on the Watershed Initiative Steering Committee, which advises EOEA Secretary Robert Durand on the progress of the Initiative.

Task 2: Provide services statewide to foster the implementation of high quality citizen monitoring efforts.

Information clearinghouse

Training manuals, fact sheets, and training videos are listed and regularly updated on our web page. We announce and distribute existing and new materials at workshops and conferences we attend. We also use our listserv to publicize any new pertinent materials that we hear of from other sources.

Training sessions held by all MSCs are posted on our web site and advertised through our listserv. We created a registration form and added it to the MassWWP web site, on the workshop calendar page. Approximately 75% of our workshop attendees either use this form to register, or send the requested information via email.

We fielded over 150 phone and email requests for advice, contact and other water monitoring related information. We respond either by phone, email, or by mailing materials to those requesting help.

Workshops and presentations (additional workshops offered for Western Massachusetts groups are listed below, under Task 3)

Workshops:

- Aquatic plant and watershed mapping techniques: July 2000 (Hudson) , June 16, 2001 (Spencer).
- QAPP-writing workshop, January 13th, Lawrence.
- Starting a Lake Monitoring Program, January 27th, Leicester.
- Study Design/QAPP workshop February 3rd, Lee.
- Study Design/QAPP workshop March 31st, Carver.
- Macroinvertebrate sampling techniques. July 2000 Amherst; June 2001, Bridgewater.
- Data Presentation: October 2000 & January 2001, Leominster; April 2001, Auburn These focussed on strategies for data presentation on the Web.

Presentations:

- Volunteer monitoring and the Massachusetts Watershed Initiative, April 8, Athol.
- Introduction to macroinvertebrate sampling, May 17, Athol**.**

Quality Assurance Project Plans

MassWWP staff assisted in a DEP-funded project conducted by the Water Resources Research Center to produce a guidebook for writing volunteer monitoring QAPPs, and accompany the guidebook with workshops and followup assistance to monitoring groups. Workshops are listed above. Approximately 15 groups requested and received related assistance, either via answering questions they have about writing QAPPs, or via review of draft QAPPs.

Development of a statewide volunteer monitoring database reporting system

We were charged by EOEA with providing training on the EPA STORET system to MSCs in order build their proficiency in using the system and teaching volunteers in posting data to the system. After discussions with EPA Region I staff in late 2000, we determined that it was premature to offer STORET training, given uncertainty in how practical it is for volunteers to use it at the present time. After consultation with EOEA, we instead organized a May 22 meeting to discuss general questions of data management for volunteer monitors. The primary topic of the meeting was how STORET might be of use in developing a system that meets everyone's needs. EPA, DEP, CZM, MassGIS, Riverways, EOEA and the Monitoring Service Centers were all represented at the meeting. Representatives from EPA described STORET and efforts EPA is undertaking to facilitate its use by volunteer monitoring groups. Based on the discussion at the meeting, we believe there are several important issues to consider:

- STORET appears to be in an ongoing process of development. Several enhancements have recently been added, or are now being added to the system.
- It appears that EPA is achieving only modest success in getting agencies, volunteer monitors, academic institutions and others to use STORET. Massachusetts agencies do not currently contribute data to STORET. EPA itself enters some but not all of its own data into STORET.

- There are concerns about how difficult it will be for monitoring groups to enter data into STORET. The major concerns seem to be: a large "set-up" effort (entering information about the program, type of monitoring done, station location, and other meta data); how much effort is required thereafter to enter data from each sample trip; and whether the hardware and software requirements are too much for groups (e.g. an Oracle interface is required – most groups probably don't have Oracle).
- Several different models have been proposed for how to assist VMs to learn and use STORET. These include regional training programs for groups to use STORET (sponsored by MSCs who themselves will have been trained by EPA); regional working sessions sponsored by MSCs where groups enter their data as they are trained; or office visits by MSCs to assist individual directly in setting up their meta-data "profiles" - thereafter groups would enter their own data. Alternatively, a central organization (or several of them) might receive training and be contracted to enter data for the groups.
- One possible approach is to develop a relatively simple database or spreadsheet package that can house volunteer data and serve as an interface to STORET: groups (or a central organization, as just discussed) would enter their data in such a package and then a central organization would collect the data from several groups and upload it into STORET.

We anticipate working with EOEA, EPA, other MSCs and VMs in FY 2002 to explore these issues further.

Task 3: Volunteer Monitoring Support for Target Watersheds

MassWWP was charged by EOEA to provide service center support to groups in Connecticut, Deerfield, Farmington, Hoosic, Housatonic, and Westfield watersheds

All groups in the service area were contacted early in the fiscal year and asked what assistance they might request of us. In response to their requests, we provided a variety of assistance. Examples include: we provided continuing help to the Deerfield River Watershed Association (DRWA) on web page design, lab establishment, and data presentation options. We also serve on the DRWA Technical Advisory Committee and assisted in data presentation at the State of the Deerfield River Watershed on March 17 and Riverfest on June 9, 2001. We assisted the Hoosic River Watershed Association (HooRWA) in planning a benthic macroinvertebrate (BMI) sampling program and other (i.e. bacterial) monitoring, in preparing its 2000 state of the river conference at which we gave a presentation, and in data presentation for HooRWA's Riverfest May 26, 2001. We attended 11 Watershed Team Meetings in the Connecticut, Housatonic/Hoosic and Deerfield. We assisted the Town of Clarksburg, MA DEM, and Hoosic River Watershed Association to plan a monitoring program on Mausert's Pond in Clarksburg. We provided assistance to Berkshire Regional Planning Commission (BRPC), Onota Lake Association, Hoosic River Watershed Association, and Housatonic Valley Association in writing QAPPs. We advised LAPA-West and wrote a support letter for them on a grant application to Massachusetts Environmental Trust. We helped the Connecticut River Watershed Council & Watershed Team prepare a proposal to the EPA EMPACT program – but this proposal was withdrawn at the last minute when anticipated participation by several municipalities in the Springfield area failed to materialize. We assisted the City of Springfield in implementation of a separate EMPACT project sampling lakes in Springfield.

Western Massachusetts workshops

- We conducted a Laboratory Analysis Techniques workshop for 15 people from 7 groups (13 people, 6 groups from western Mass. service area) March 31, 2001 at UMass Amherst, in collaboration with UMass Environmental Analytical Laboratory.
- We conducted a river sampling training session and a lake sampling training session for groups in the Housatonic watershed on October 3, 2000.
- We conducted a macroinvertebrate training for the Hoosic River Watershed Association in July and August 2000.

Project 2: Regional Monitoring Service Provider Network. Funded by MET MassWWP collaborated with the Waquoit Bay National Estuarine Research Reserve in a project to advance the Regional Service Provider Network (also known as MSC network) with supplemental funds provided by MET. This was a continuation of a grant funded in FY 1999. Project objectives were:

- To advance the development of a *regional service provider (RSP) network* for Massachusetts volunteer monitors.
- To help monitoring groups incorporate three critical elements into their programs: written study designs, annual program reviews, and (as needed), written Quality Assurance Project Plans.
- To facilitate increased communication and collaboration among individual volunteer monitoring programs within a watershed.
- To integrate volunteer monitoring group activities with their associated EOEA-sponsored Watershed Teams.
- To help volunteer monitoring groups establish technical advisory committees (TACs).
- To help volunteer monitors develop data presentation strategies that use the Internet, the web, and a variety of other tools to use water quality data to educate decision makers and the general public on critical issues in each basin.

As these objectives were complementary to the work funded by EOEA, most project activities are described above in the Project 1 report. In addition:

MassWWP assisted the Lake And Pond Association-West (LAPA-West) to develop a set of Standard Operating Procedures for several lake monitoring activities. These were submitted to and approved by the Department of Environmental Protection.

We provided several different types of assistance to help groups establish technical advisory committees (TACs):

- Convening regional or watershed meetings of agencies, volunteer groups and technical experts; providing complementary clearinghouse/networking support to groups who are looking for sources of expert help.
- Serving directly on TACs.

- Written guidance materials on how to establish TACs.
- We held a session on TACs at the November 2000 statewide Clean Water Conference.

Regional / watershed meetings

We helped facilitate several meetings in the Housatonic and Hoosic Basins aimed at increasing intergroup collaboration in watershed planning (including monitoring and providing coordinated technical expertise).

Data Presentation Assistance

In addition to the data presentation workshops listed above, MassWWP developed a package of tips and templates for web designers. This can be found on the MassWWP web site (http://www.umass.edu/tei/mwwp/). A new feature is a web "slide show" that portrays water quality data within the context of an informational presentation about the Deerfield River Watershed Association's monitoring program, recent results, and conclusions drawn by the Association. *Note: This effort was partially funded by a contract with the Massachusetts Watershed Coalition, under funding from the Sudbury Foundation.*

We also completed a test version of an Excel utility that allows groups to enter macroinvertebrate data on a standardized data entry form and then generate any of a variety of graphs of the data with little extra effort. We are in the process of distributing this to groups to test, and preparing a web version of some of the graphs.

Promoting collaboration between state agencies and volunteer monitoring groups

We had a series of meetings with state agency personnel on strategies to effectively integrate volunteer monitors into the Massachusetts Watershed Initiative. A major focus of many of these meetings is the development of watershed-wide collaborations organized by DEP's new Watershed Monitoring Coordinators (WMCs) – positions which were created and filled in early 2001. We produced a report containing recommendations on how that collaboration might proceed, and how Monitoring Support Centers can play a helpful role in advancing effective partnerships.

USGS Summer Intern Program

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	1	0	0	0	1
Masters	1	0	0	0	1
Ph.D.	4	0	0	0	4
Post-Doc.	0	0	0	0	0
Total	0	0	0	0	0

Notable Awards and Achievements

Results from Project MA03, "Comparison of Models Used to Estimate Land-derived Nitrogen Loads has led to development of a proposal, "A User Friendly Aid to Explore Management Options to Lower Nitrogen Loads to Estuaries," a web-based tool to allow users to assess nitrogen loads and management options using any of nine loading assessment protocols. The proposal is submitted to the Cooperative Institute for Coastal and Estuarine Environmental Technology (CICEET)

The Acid Rain Monitoring Project, partially funded by Section 104B between 1983 and 1993, has been restarted with funding from the Mass. Dept. of Environmental Protection and as part of a northeastern region effort by the New England Governors/Eastern Canadian Premiers to assess changes in the acidification status of water bodies since the Clean Air Act Revisions of 1990.

The Center Director is a member of the Executive Office of Environmental Affairs/University of Massachusetts Joint Committee on Watersheds.

The Center Director is a member of the Blue Ribbon Committee on Lakes and Ponds of the Executive Office of Environmental Affairs

Publications from Prior Projects

1. Johnson, Jolen, Nyssa Varney and Michael Switzenbaum. 2001. Comparative Toxicity of Formulated Glycol Deicers and Pure Ethylene and Propylene Glycol. Massachusetts Water Resources Research Center Report No. 174, University of Massachusetts Amherst, MA
2. Valiela, Ivan, Jennifer Bowen, and Kevin Kroeger. 2001. Assessment of models for estimation of land-derived nitrogen loads to shallow estuaries. Massachusetts Water Resources Research Center Report No. 175, University of Massachusetts, Amherst, MA.
3. Godfrey, Paul. 2001. 2001 Directory of Water Resources Expertise in Massachusetts Colleges and Universities. Water Resources Research Center Special Report 30, University of Massachusetts, Amherst, MA

4. Fennessey, Neil M. 2000. Estimating average monthly lake evaporation in the northeast United States. Journal of the American Water Resources Association, Vol 36 (4):759-769
5. New England Regional Monitoring Collaborative. 1999. Following the Flow. NERMC video.
6. New England Regional Monitoring Collaborative. 1999. Watershed Resource Inventories. NERMC video
7. New England Regional Monitoring Collaborative. 1999. Rapid and Intensive Habitat Assessment. NERMC video.
8. New England Regional Monitoring Collaborative. 1999. Benthic Macroinvertebrate Streamside Assessment. NERMC video.
9. New England Regional Monitoring Collaborative. 1999. Intensive Benthic Macroinvertebrate Assessment. NERMC video.
10. New England Regional Monitoring Collaborative. 1999. On-site Non-point Source Pollution Evaluation. NERMC video.
11. Fennessey, Neil M. 1999. Northeast United States: Monthly Reference Evapotranspiration and Monthly Free Surface Evaporation. Massachusetts Water Resources Research Center CD-ROM (2 discs), University of Massachusetts, Amherst, MA.