Kentucky Water Resources Research Institute
Annual Technical Report
FY 2004

Introduction

The FY 2004 Annual Technical Report for Kentucky consolidates reporting requirements of the Section 104(b) base grant award in a single technical report that includes: 1) a synopsis of each research project supported during the period, 2) a list of related reports, 3) a description of information transfer activities, 4) a summary of student support during the reporting period, and 5) notable achievements and awards during the year.

Research Program

The activities supported by Section 104(b) and the required matching are interwoven into the Kentucky Water Resources Research Institute's total program. Other elements of the program during FY2004 included: 1) the Environmental Systems Graduate Certificate, 2) the Environmental Protection Scholarship Program, and 3) Research, Service and Technology Transfer Activities funded by other sources. Memorandum of Agreement projects with the Kentucky Division of Water included TMDL development for pH, nutrients, and pathogens in several Kentucky streams. Additional projects were funded by the Environmental and Public Protection Cabinet (Environmental Protection Scholarship), the Kentucky Cabinet for Health Services (Technical Support for the Maxey Flats Nuclear Disposal Site and the Paducah Gaseous Diffusion Plant Federal Facilities Agreement and Agreement in Principle), the Kentucky Department of Military Affairs (Technical Support for Environmental Construction and Solid Waste Management), the Kentucky River Authority (Watershed Management Services), the National Institute of Environmental Health (Superfund Public Outreach Program), and east Kentucky PRIDE (Personal Responsibility in a Desirable Environment) Water Quality Assessment. In addition, the Institute was instrumental in the development of the Kentucky Research Consortium for Energy and the Environment, a collaborative program of the University of Kentucky, Murray State University, and the University of Louisville. Creation of the consortium was directed by Lindell Ormsbee who became Director of the Kentucky Water Resources Research Institute in July 2004. $5 million in Federal Funds (Department of Energy) have been secured for research on environmental assessment and cleanup evaluation at the Paducah Gaseous Diffusion Plant over the next several years.

Four research projects were selected for support provided by the 104(b) FY 2004 program funding. Investigators included faculty/research staff at the University of Kentucky (Elskus 2004KY41B, Rowe 2004KY44B, and Paylor 2004KY45B) and at Western Kentucky University (Kenworthy 2004KY43B). Project synopses for the four investigations follow.

Linking chemical tolerance to reproductive resilience: CYP1A as a metric for predicting fish species distributions in chemically impacted habitats

Basic Information

Title:	Linking chemical tolerance to reproductive resilience: CYP1A as a metric for predicting fish species distributions in chemically impacted habitats
Project Number:	2004KY41B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	6th
Research Category:	Biological Sciences
Focus Category:	Toxic Substances, Water Quality, Ecology
Descriptors:	PCBs, monitoring, endocrine disruptors, bioindicators
Principal Investigators:	Adria Anne Elskus

Publication

1. Brammell, Benjamin F., David J. Price, Wesley J. Birge, and Adria A. Eslkus, 2004, Apparent Lack of CYP1A1 Response to High PCB Body Burdens in Fish from a Chronically Contaminated PCB Site, Marine Environmental Research, 58(2004), p. 251-255.
2. Brammell, Benjamin F., Eleana M. Harmel, John A. Hitron, Xabier Arzuaga, David J. Price, Wesley J. Birge, and Adria A. Elskus, 2005, Induction of Pollutant Metabolizing Enzymes in Lepomis Species Following PCB and PAH Exposure, in Proccedings Kentucky Water Resources Annual Symposium, March 3, 2005, Kentucky Water Resources Research Institute, Lexington, Kentucky, p. 85.
3. Brammell, Benjamin F., Eleana M. Harmel, J. Andrew Hitron, Xabier Arzuaga, David J. Price, Wesley J. Birge, and Adria Elskus, 2004, Induction of Pollutant Metabolizing Enzymes in Lepomis Species Following PCB and PAH Exposure, in Proceedings Society of Environmental Toxicology and Chemistry, 25th Annual Meeting, November 14-18, 2004, Portland Oregon, SETAC, p. 269.

Problem and Research Objectives

Polychlorinated biphenyls (PCBs) are ubiquitous aquatic pollutants with significant toxic effects in both humans and fish. In our previous KWRRI-funded projects (2002KY1B, 2003KY17B), we found both sediments and fish in the Town Branch-Mud River (TB/MR) system in Kentucky to be highly contaminated with PCBs, despite extensive remediation efforts by the state and others to remove these chemicals. We also found resident fish in the TB/MR system had developed resistance to some of the toxic effects of these chemicals, including induction of the biomarker enzyme, CYP1A. Based on research in our laboratory and others, we **hypothesized** that there is a mechanistic link between resistance to PCB mediated induction of CYP1A and resistance to the deleterious effects of PCBs on reproductive function.

Original objectives: 1) Determine if PCB-resistant resident populations in Town Branch have altered reproductive function compared to non-resistant populations of the same and different species; 2) Determine whether species abundance reflects species-specific ability to develop resistance; 3) Determine whether altered regulation of the pollutant-metabolizing enzyme, CYP1A (a defining characteristic of PCB-resistance in fish) is mechanistically linked to reproductive function.

Methodology

We were unable to pursue two of our original objectives due to unexpected remediation of our field site which resulted in a massive disturbance of the entire Town Branch study area. The remediation occurred in April 2004 and involved removal of large amounts of sediment from the bottom and banks of Town Branch stream leading to a virtual absence of fish in the study area. This development forced us to abandon objective 2 (a field survey of resident species) and modify objective 1. Objective 3 remained, but we had to switch to a non-resident fish species to address it.

Modified objective # 1: Determine whether acquired resistance to PCBs, as measured by altered expression of CYP1A, results in resistance to the endocrine disrupting effects of PCBs.

Modified Methodology

To meet the new objective 1, we modified our original method, evaluating endocrine function in PCB-resistant and responsive resident TB/MR fish, to use PCB-resistant and PCB-responsive populations of the killifish (*Fundulus heteroclitus*). For the killifish study, we chose thyroid function, instead of reproductive function, as the endocrine endpoint. Briefly, killifish were depurated, treated with PCBs or vehicle, and evaluated for CYP1A activity, circulating levels of the thyroid hormone T3, T4 and activity of UDP-GT, an enzyme involved in thyroid hormone metabolism.

Original objective #3: To determine whether altered regulation of the pollutant-metabolizing enzyme, CYP1A (a defining characteristic of PCB-resistance in fish) is mechanistically linked to reproductive function.

Modified Methodology
To meet objective 3, we used rainbow trout, instead of TB/MR resident species, as the source of hepatocytes to evaluate PCB effects on reproductive function. As originally proposed, we used green sunfish as the PCB-resistant species. No other major changes in methodology were made.

Principal Findings and Significance

In fish, resistance to PCBs is characterized, in large part, by the ability of PCBs to induce the biomarker enzyme, CYP1A. We asked whether resistance to PCB-induction of CYP1A indicates resistance to the toxic effects of PCBs, specifically, their endocrine-disrupting effects. If this proved to be the case, CYP1A might be used as an indicator of response to chemicals that affect both CYP1A and endocrine function.

Our results suggest that resistance to PCB induction of the biomarker, CYP1A, may reflect resistance to the endocrine-disrupting effects of PCBs. Our *in vivo* studies with resistant and responsive killifish suggest that fish which are resistant to induction of CYP1A by PCBs may also be resistant to the deleterious effects of PCBs on thyroid hormone metabolism, based on UDP-GT and T4 levels (T3 assays are currently underway). Because inter-individual variability was higher than expected, the thyroid hormone data must be considered preliminary, indicating trends, not statistical differences.

Preliminary data from our *in vitro* studies with rainbow trout and green sunfish hepatocytes confirm our earlier *in vivo* studies that green sunfish, as a species, are resistant to PCB induction of CYP1A while rainbow trout are responsive. Completion of the egg-yolk protein analysis from these *in vitro* studies (expected June 2005) will determine if lack of CYP1A response to PCBs protects fish from reproductive disruption by PCBs, specifically, suppression of egg-yolk protein production by PCB treatment.

Fine sediment source areas and in-channel sediment storage in the Upper Green River Basin, KY

Basic Information

Title:	Fine sediment source areas and in-channel sediment storage in the Upper Green River Basin, KY
Project Number:	2004KY43B
Start Date:	3/1/2004
End Date:	8/31/2005
Funding Source:	104B
Congressional District:	KY 2nd
Research Category:	Water Quality
Focus Category:	Non Point Pollution, Sediments, Water Quality
Descriptors:	soil erosion, aquatic habitat, sediment supply
Principal Investigators:	Stephen Kenworthy

Publication

1. Kenworthy, Stephen, 2005, Landscape Attributes Affecting Sediment Production and Sediment Delivery in the Upper Green River Basin, in Proceedings Kentucky Water Resources Annual Symposium, March 3, 2005, Kentucky Water Resources Research Institute, Lexington, Kentucky, p. 23.

Problem and Research Objectives

Fine sediment pollution is an important water quality concern in the Commonwealth of Kentucky. Fine sediment accumulation can lead to degradation of aquatic ecosystems as a result of habitat alteration or because of contaminants and nutrients bound to sediments. As part of the US Department of Agriculture Conservation Reserve Enhancement Program (CREP), state and federal funds have been committed to reduce by 10% the amount of sediment, pesticides, and nutrients entering the Upper Green River between Green River Lake and Mammoth Cave National Park. These funds are targeted to support the implementation of soil conservation practices in the Upper Green River Basin, and emphasize the environmental and ecological importance of fluxes of sediment and sediment-bound contaminants into riparian zones and channels. In order to monitor and evaluate the effectiveness of these conservation efforts, management agencies require information on the spatial pattern of potential agricultural and non-agricultural sediment sources and on the quantity and distribution of fine sediment stored in the stream channel network.

The scientific objectives of the research are to identify potential sources of fine sediment in the Upper Green River Basin CREP area and to explain the distribution of fine sediment storage in terms of the spatial pattern of source areas and the geomorphic controls on in-channel and riparian sediment deposition. The work will provide a detailed assessment of the potential supply of fine sediment from agricultural and non-agricultural portions of the CREP area, based on the integration of digital landscape data with field surveys of sediment storage and potential sediment delivery pathways. Field surveys of the pattern of fine sediment storage within the Green River and major tributary valleys will facilitate identifying portions of the landscape that are important sediment sources and will also provide information on long-term patterns of fine sediment routing through the watershed. This information will be valuable to the CREP partner agencies and to individual program participants in assessing the effectiveness of conservation practices in specific locations, and will serve as critical habitat data for resource management agencies charged with protecting aquatic biota in the Green River and Mammoth Cave system.

Methodology

The project includes documenting the spatial distribution of fine (< 2mm) sediment stored in the channel and riparian zone of the Green River and its major surface tributaries. Field surveys of a stratified sample of channel reaches determine locations and volumes of in-channel fine sediment storage. Reaches will be delimited and selected on the basis of geomorphic factors such as valley slope and width that can influence patterns of sediment storage. Large samples of bed material will be sieved in the field to determine fine sediment content. Subsamples of the fine fractions will be retained for laboratory grain-size analysis.

A GIS-based spatial analysis of topography, geology, soils, land use, and soil conservation practices will be used to assess the sediment production potential of

different subwatersheds and landscape units within the study area. This analysis of source areas will be overlaid on the patterns of sedimentation observed in the field to assess the relationship between sediment storage patterns and the distribution of likely sediment sources. Although it is usually difficult to link sedimentation at a given location conclusively to a particular source area, the downstream pattern of sediment transport in fluvial systems constrains potential source areas. The pattern of sediment sources and sediment deposition will be analyzed and explained in terms of landscape attributes affecting the delivery of eroded soil to channels (e.g. presence and type of conservation practices) and fluvial transport mechanisms that control patterns of sediment deposition (such as flow regime and channel morphology). Observed correlations between the volume of sediment stored in study reaches and descriptors of the number and (along-channel) distance of potential upstream sediment sources will provide one test of the spatial coherence of the patterns of sediment supply and storage within the drainage network. Additional field observations of sediment delivery pathways in land areas identified as potential sediment sources will be used to refine the assessment of sediment supply and soil conservation practices.

Principal Findings and Significance

Because field data collection efforts were limited by high flow conditions during late summer and fall of 2004, findings reported here are preliminary. Despite the likelihood of significant reduction in fine sediment supply to the tailwater reach of the main channel of Green River between Green River Lake and the confluence of Russell Creek, bed material samples in this portion of the river contain relatively large proportions (> 10%) of sand, suggesting that the small tributaries entering along this reach supply considerable amounts of fine sediment. Bed material samples from larger tributary streams also contained large sand fractions, suggesting that the Green River is a fairly fines-rich system in its current state. Additional sediment sampling during summer 2005, especially in the lower reaches of the CREP area, will complete the assessment of in-channels fine sediment abundance in the study area. Synthesis of the landscape-attribute analysis with the field surveys of fine sediment storage is ongoing and will be described in detail in the project completion report, along with recommendations for resource management agencies charged with protecting aquatic biota in the Green River and Mammoth Cave system.

Assessing groundwater age, regional flowpaths, and hydrochemical evolution of the Knox Group Aquifer in the Bluegrass Region of Kentucky

Basic Information

Title:	Assessing groundwater age, regional flowpaths, and hydrochemical evolution of the Knox Group Aquifer in the Bluegrass Region of Kentucky
Project Number:	2004KY44B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	KY 6th
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Hydrogeochemistry, Water Supply
Descriptors:	stable isotopes, Chlorine-36, brine
Principal Investigators:	Harry Rowe

Publication

Problem and Research Objectives

The Cambro-Ordovician Knox Group dolomites of Kentucky are host to a regionally extensive aquifer system that could potentially play an important role in future water resource developments in the region. Preliminary water quality assessments, based largely on total dissolved solids concentrations from wells drilled into the Knox Group, identify large portions of the aquifer as being saline. However, a freshwater portion of the aquifer in the central Bluegrass Region is potentially useful for rural and suburban supplies. The study expands on previous work in order to 1) define the age of Knox Group ground waters along locally-inferred flowpaths, 2) identify regional flowpaths, including important recharge-discharge zones, and 3) characterize the evolution of ground water within the Knox Group. The research relies largely upon isotopic tracers to uncover differences in ground water characteristics that can be used to infer ground water age and the processes that alter water chemistry. A clearer understanding of flow regime and rates of ground water movement within the Knox Group aquifer will yield a more effective strategy for exploitation of water resources within the Bluegrass Region.

Ground water recharge into, transport within, and discharge out of the Knox Group aquifer is complex due to regional (Cincinnati Arch) and localized (fault zone, jointing) structural controls and because of the high salinity of formation waters (brines). The study seeks to provide a stronger temporal and spatial context by which to view ground water transport through a regionally-extensive deep aquifer, increasing the potential for strategic exploitation of the aquifer. The investigation is largely geochemistry-based, and relies on the ability to acquire samples that can yield meaningful information on the age of waters across the region. The project focuses on three objectives: 1) Age-dating and geochemically characterizing ground waters along a localized North-South transect and defining flowpaths in what is hypothesized to be a dominant recharge area (the Kentucky River valley along the southern border of Jessamine County and the well-constrained fault zones in southern and eastern Jessamine County); 2) Age-dating and geochemically characterizing waters along a North-South transect from eastern Madison County, in the southern Bluegrass Region, to Boone County, in the northern Bluegrass Region, cutting across the central Bluegrass (Clarke, Bourbon, Fayette, Harrison, and Grant Counties) toward a hypothesized discharge zone (the various salt licks that outcrop in the northern Bluegrass Region); and, 3) Defining spatial variations and mixing between freshwater and brines along an East-West transect across the Cincinnati Arch, largely within the inner Bluegrass region.

Methodology

Field Methodology: Existing wells must be prepared for sampling. Pumps and piping systems must be removed from wells where they are not in working condition. Equipment required for this process includes the Kentucky Geological Survey hydraulic pump-hoist truck as well as equipment, purchased during the term of the award, necessary to manipulate well pump and piping systems (pipe clamps and pipe pullers). Once the piping has been removed, each well is video taped using the Kentucky Division of Water's downhole camera. The condition of well walls and the static water level must

be accurately determined before sampling. A deep groundwater pumping system is needed to obtain the most representative water sample possible. This infrastructure does not currently exist in the state of Kentucky, but such a system has been designed in conjunction with Kentucky Irrigation in Lexington, Kentucky.

Analytical Methodology: Bulk geochemical and stable isotopic concentrations will be analyzed in the Environmental Research and Teaching Laboratory (ERTL) at the University of Kentucky. Accelerator mass spectrometry (AMS) analyses of ^{36}Cl will be performed at the Center for Accelerator Mass Spectrometry-Lawrence Livermore National Laboratory (CAMS-LLNL). $^{87}Sr/^{86}Sr$ analyses will be performed on a Finnigan MAT-262 thermal ionization mass spectrometer (TIMS) housed at Stanford University. U-series analyses will be performed at the University of Illinois at Chicago (UIC) using a Canberra Alpha Analyst alpha counter (Table 1).

TABLE 1: Proposed analyses, tracer properties, and analysis locations.

Analysis	**Tracer Properties**	**Analysis Location**
metals	water chemistry, water-rock interaction, mixing	ERTL, UK
anions	water chemistry, water-rock interaction, mixing	ERTL, UK
dissolved organics	water chemistry, water-rock interaction, mixing	ERTL, UK
D and ^{18}O of water	water origin, mixing	ERTL, UK
^{13}C of dissolved inorganic carbon	water chemistry, water-rock interaction, mixing	ERTL, UK
^{34}S and ^{18}O of dissolved sulfate	redox history, mixing	ERTL, UK
$^{234}U/^{238}U$	redox history, water-rock interaction, mixing	UIC
$^{87}Sr/^{86}Sr$	water-rock interaction, mixing	Stanford University
^{36}Cl dating	ground water age, mixing	CAMS-LLNL

Bulk geochemical and isotopic modeling of Knox Group waters (speciation, mixing, water-rock interactions) will be accomplished using PHREEQCI, a downloadable freeware program provided and supported by the USGS. Project investigators are familiar with using PHREEQCI to model water evolution and mixing. Associated analytical methods have been developed for the project.

Principal Findings and Significance

1) Well Locations: Extensive ground truthing has revealed that only 23 of the 71 recorded Knox wells in the central Kentucky region are viable candidates for this study. Forty-eight wells were eliminated because they no longer exist or they have been plugged. Only 4 of the remaining wells have working pumps. The other 19 wells either lack pumping systems, or the existing pumps no longer function.

2) Analytical Infrastructure: Analytical techniques and methodologies have been developed so that sample analysis can proceed. Two trips to the University of Illinois at Chicago have allowed researchers to learn ^{36}Cl dating and U-series analytical techniques. Extraction techniques for obtaining dissolved sulphate samples have been provided by Dr. Barry Maynard at the University of Cincinnati. The equipment for these processes has been assembled and is now housed in Rowe's lab at the University of Kentucky.

3) Field Sampling Infrastructure: The ability to obtain representative samples from deep groundwater wells lacking dedicated pumping systems does not currently exist at the University of Kentucky. A mobile pumping system that would allow Knox wells to be appropriately purged and sampled has been designed by the investigators. The system consists of a pump attached to a winch-controlled hosing system that would be permanently installed on a flat bed trailer and towed behind a standard pick-up truck or SUV. Kentucky researchers with potential interest in such a groundwater sampling system are being asked to help support purchase of this system.

4) Development of a Local Meteoric Water Line: Rowe has been sampling local meteoric waters which have then been analyzed in ERTL. A permanent meteoric sampling device has been developed and will be installed so that continuous meteoric water samples can be gathered.

Characterizing pollution impacts to urban karst aquifers from artificial and enhanced recharge

Basic Information

Title:	Characterizing pollution impacts to urban karst aquifers from artificial and enhanced recharge
Project Number:	2004KY45B
Start Date:	3/1/2004
End Date:	2/28/2005
Funding Source:	104B
Congressional District:	KY 6th
Research Category:	Ground-water Flow and Transport
Focus Category:	Groundwater, Non Point Pollution, Water Quality
Descriptors:	hydrogeochemistry, storm runoff, lawn chemicals, wastewater
Principal Investigators:	Randall L. Paylor, James C. Currens

Publication

Problem and Research Objectives

Urbanization on Kentucky's karst landscape has increased pollution problems associated with springs in the region. The main objective for the project was to monitor three urbanized karst springs in the Inner Bluegrass Region that have previously shown anomalously high base flow levels, and to test for a suite of hydrologic parameters and contaminants. Detailed discharge and contaminant testing were intended to help quantify groundwater impacts resulting from urban recharge potentially originating from infrastructure leakage.

Russell Cave Spring and McConnell Spring in Lexington, and Big Spring in Versailles were originally proposed as the target urban monitoring points. Monitoring of the McConnell Spring basin was moved to Prestons Cave Spring for the study as that is the final resurgence point for the McConnell aquifer. McCalls Spring, draining a non-urbanized area near Lawrenceburg, was added as a control monitoring point.

Methodology

The three main data gathering tasks included: 1) ambient field water quality monitoring, 2) sample collection for laboratory analysis to evaluate suspected urban runoff constituents, and 3) collecting more extensive discharge measurements from urban springs than had previously been accomplished.

A bi-weekly monitoring schedule was originally proposed, with additional testing planned during at least two storm events to document first flush effects and high-flow loads. Field measurements included temperature, pH, conductivity, and turbidity. Stage recorders were installed at each spring, and discharge rating curves were calculated in order to determine mass fluxes of contaminants and analyze hydrograph anomalies.

Chemical constituents chosen for laboratory analysis were based on similar previous studies of surface water and ground water impacts in urban areas. Metals, BTEX, nitrate, orthophosphate, chloride, fluoride, optical brightener, caffeine, and the herbicide 2,4-D were originally proposed for monitoring. 2,4-D was replaced by simazine because of better detection limits and the widespread use of simazine for urban applications in the study area.

2004 turned out to be a poor year for the study because base-flow conditions were needed for characterization of urban effects at low flow. Above normal precipitation throughout most of the year resulted in a change in the monitoring plan from the original bi-weekly schedule. Near base flow conditions occurred a few times between August and October 2004, and then again during February 2005. Although this reduced the total number of sampling runs from the original plan, the results were adequate to make the proposed characterizations. Eight base flow sampling events and two high flow samplings were conducted at each of the four springs. Discharge measurements were conducted 14 times during the study at each spring.

Principal Findings and Significance

Caffeine, orthophosphate, and optical brightener showed a strong inverse correlation with discharge in the three urban springs, with r^2 values approaching 0.9. Fluoride and simazine showed a moderately strong inverse correlation with urban spring discharge, and nitrate and chloride both showed weak inverse correlations with discharge in the three urban springs. Fluoride, which may have been from natural sources and chloride, which may have been derived from salting of the nearby highway, were noted in the control spring (McCalls). Both BTEX and metals showed a moderate positive correlation with discharges at all springs.

Constituent	Range of Results
Caffeine	ND to 9.2 micrograms/liter
Fluoride	ND to 2.4 milligrams/liter
Chloride	7.4 to 78 milligrams/liter
Orthophosphate	ND to 0.11 milligrams/liter
Optical Brightener	ND to 422 fluorescence units
Nitrate	0.12 to 3.8 milligrams/liter
Simazine	ND to 0.36 micrograms/liter

The chemical results suggest that base-flow at urban springs is augmented by leaking infrastructure – both water supply lines and sewage disposal lines. Results also suggest that storm flow from impervious surfaces into swallow holes and sinks provide the highest hydrocarbon and metal concentrations with first-flush runoff. Big Spring in Versailles had the highest levels of most of the constituents analyzed, with Prestons Cave Spring a close second. Russell Cave Spring showed only moderate levels of contaminants – probably due to the fact that only about 45 percent of its recharge area is urbanized.

Fourteen sets of discharge measurements were used to evaluate the volume of excess recharge within the urban areas. Urbanization appears to have radically altered the hydrographs of the studied springs. Storm events were followed almost immediately by flood spikes at Prestons Spring and Big Spring, with Russell Cave Spring showing a short lag time from peak rainfall to peak discharge, and McCalls a normal lag time and broader curve. Prestons Spring and Big Spring discharge dropped rapidly after the rainfall ceased, but the Russell Cave recession curve was less steep, and McCalls showed a typical recession slope.

Normalized base level discharges were calculated for each spring based upon their recharge areas. Average normalized base flow for Bluegrass Region springs during this period was approximately 0.09 cubic feet per second per square mile (cfsm) (0.98 $l/s/km^2$). Big Spring showed the most significant deviance, with the lowest measured

normalized flow during the study at 0.5 cfsm (5.5 l/s/km^2). Prestons Spring normalized base flow was as low as 0.35 cfsm (3.8 l/s/km^2), and Russell Cave Spring base flow was 0.2 cfsm (2.2 l/s/km^2). This suggests that artificial urban recharge accounts for about 82% of Big Spring discharge, 74% of Prestons Spring discharge, and 55% of Russell Cave Spring discharge during low flow conditions.

Occurrence and Distribution of Mercury in Mammoth Cave National Park - Phase II

Basic Information

Title:	Occurrence and Distribution of Mercury in Mammoth Cave National Park - Phase II
Project Number:	2003KY18B
Start Date:	3/1/2003
End Date:	9/30/2004
Funding Source:	104B
Congressional District:	Kentucky 2nd
Research Category:	Water Quality
Focus Category:	Groundwater, Sediments, Solute Transport
Descriptors:	karst, bioaccumulation, biomagnification
Principal Investigators:	Cathleen Joyce Webb

Publication

Problem and Research Objectives

Atmospheric deposition of mercury from power plants is currently of great concern throughout the country and is slated for increased regulation in the future. Coal-fired power plants were the largest unregulated source of mercury emissions in the United States prior to 2005, accounting for one-third of all anthropogenic mercury releases to the atmosphere. There are 18 existing coal-burning power plants in Kentucky and 6 proposed constructions or expansions in the Commonwealth of Kentucky since October 1999 to meet a growing national demand for electricity. A significant increase in atmospheric deposition of mercury at Mammoth Cave National Park (MCNP) is anticipated. Addition of more mercury emission sources in the region will increase the probability that MCNP may be impacted by a larger geographical distribution of coal-fired power plants. Kentucky's power plants generate approximately nine x 10^9 kg of ash per year. The Peabody Thoroughbred Power Plant is one of the proposed new power plants and is slated for construction at a site 74 km west of MCNP. If built, this plant will be the fourth largest emitter of mercury in Kentucky and is expected to emit over 190 kg of mercury, over 6 x 10^6 kg /year of NO_x (maximum 30-day rolling average of 0.08 lbs/MMBTU) and 11 x 10^6 kg/year of SOx (maximum 0.167 lbs/MMBTU per each unit based on a 30-day rolling average and maximum 24-hour block average of 0.410 lbs/MMBTU) per the final Kentucky Division for Air Quality permit dated October 11, 2002. There is little current data that can be used to predict the potential impact on MCNP and the karst ecosystem. Determination of mercury levels in MCNP and the factors that affect mercury levels and distribution is critical.

The specific objectives of this research project are to: (1) establish the extent, occurrence, distribution, and speciation of mercury in groundwater, surface water and sediments in Mammoth Cave National Park, including storm events, (2) examine the bioaccumulation and ecological impacts of mercury in surface, subsurface, and aquatic organisms at the Park, (3) investigate the fate and transport characteristics of mercury in a karst aquifer system, and (4) determine the TMDL of mercury at the Park.

Methodology

Approximately 60 mL samples of unfiltered water were transported to Materials Characterization Center, Western Kentucky University for total Hg analysis. Sample preparation included transferring 30 mL of the sample to a 50 mL container and adding 7.5 mL of 33% v/v HCl and 1 mL 0.1N $KBr/KBrO_3$. Samples were then diluted to 50 mL with ultra-high DI water. The concentration of mercury in water samples was determined by PS Analytical fluorescence spectrometry.

Sediment samples of 25-30 grams were oven-dried for 24 hours to remove excess water. The samples were then homogenized and prepared for analysis by drying the homogenized samples in a 105˚C oven overnight. A 1.000 g sample was transferred to a sample tube and 1.0 mL water and 3 to 4 aluminum oxide anti-bump granules were added. Approximately 12 mL 33% HCl and 4 mL 70% HNO_3 (aqua regia) were run down the side of the tube carefully. The sample was heated at 140˚C for 20 minutes, followed by an addition of 5 mL of water. The sample was then gently refluxed for an additional 10 minutes. After heating, it was diluted with water to 100 mL and filtered using Whatman 541 filter paper. Finally, 10 mL of the filtered aqua regia extract was pipetted and diluted with water to 100 mL and analyzed for total mercury.

Water and sediment samples were digested using EPA methods 245.1 and 245.5. The concentrations of total mercury were analyzed by EPA method 1631: Mercury in Water by Oxidation, Purge and Trap, and Cold Vapor Atomic Absorption Spectrometry (CVAAS). This method consists of three essential steps: oxidation of Hg species to reactive mercury (Hg^{2+}), reduction of Hg^{2+} to elemental mercury (Hg^0), and detection of Hg^0 by CVAAS.

Principal Findings and Significance

Mercury concentrations in upstream and downstream water sample locations sampled monthly from July 2002 through February 2005 are shown in Figure 1. Mercury levels are evenly distributed throughout the upstream and downstream portions of the river. Mercury levels in water are low (5-13 ppt) since mercury preferentially binds to sediments and organic matter. Samples taken from Buffalo Spring Creek (BSBC) and Big Spring (BSBS) sites showed higher levels of Hg in water. Statistical analysis using unpaired t-test was performed to determine the p value. Analysis compared mercury levels at all the sampling sites and indicated that the p values are greater than 0.05. Therefore, variations in mercury concentrations at all the sampling sites are statistically insignificant.

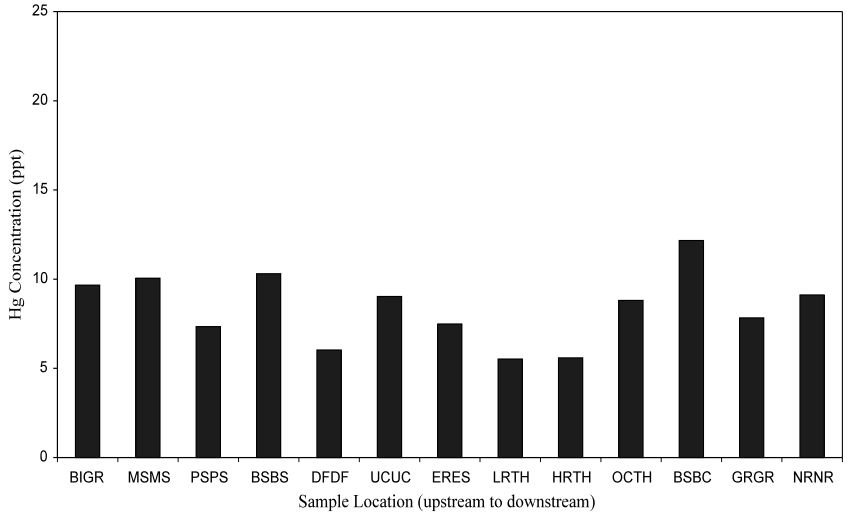

Figure 1. The average mercury concentration in each water sample location sampled monthly from July 2002-February 2005.

The sediments were collected seasonally as weather and river water levels permitted. Over the sampling period, the average mercury concentration at all of the sample sites ranged from 15-70 ppb. A rough correlation was observed between mercury levels in the water and mercury in the sediment. The sample location BSBC had the highest levels of mercury in both water and sediment. Mercury levels in sediments varied more widely from location to location than in water and are on the average 33,987 times higher.

To date, biological samples have been collected from freshwater drum, large mouth bass, *M. Salmoides*, Asiatic clam, *Cirbicula fluminea*, mayflies and bats. The concentrations of Hg are shown in Table 1. The 0.6 ppm Hg level found in the muscle of the Large Mouth Bass illustrates the potential threat of bioaccumulation of mercury in the food chain. The 0.233 ppm Hg concentration in the muscle of the freshwater Drum demonstrates biomagnification because

these fish are long-lived bottom feeders. Observed levels of mercury in fish and clam samples are comparable to values observed in other studies.

Sample Name	May Flies	Drum Liver	Drum Muscle	Large Mouth Bass Liver	Large Mouth Bass Muscle	Asiatic Clam
Hg (mg/kg) ppm	0.0025	0.2030	0.2330	0.2300	0.6000	0.0520

Table 1. Mercury concentrations in biological samples collected at the Park.

Hair samples from adult male bats of five different species captured at Long Cave, MCNP were analyzed for mercury (Table 2). These species have bioaccumulated significant levels of mercury with *Pipistrellus subflavus* having the highest Hg concentration. Mercury in the range of 3-4 ppm was detected in hair samples from two endangered mammals, Gray bat (*Myotis grisescens*) and Indiana bat (*Myotis sodalis*).

Species (*Scientific Name*)	**Sample Composition (Adult Males)**	**Hg (ppm)**
Indiana Bat (*Myotis sodalis*)	6	3.82
Gray Bat (*Myotis grisescens*)	5	4.20
Big Brown Bat (*Eptesicus fuscus*)	9	5.00
Eastern Pipistrelle (*Pipistrellus subflavus*)	8	6.60
Little Brown Bat (*Myotis lucifugus*)	7	4.90
Little Brown Bat (*Myotis lucifugus*) (Duplicate)	7	4.10

Table 2. Mercury concentrations in the fur of adult male bats of 5 different species.

Batch tests were performed to determine if limestone sequesters mercury and acts as a potential sink for mercury removal. Two sizes of Kentucky limestone (< 0.5 mm and 1-2 mm) were examined to see if limestone is efficient in removing mercury. Samples of the limestone were placed in labeled round-bottom flasks. Blanks with 100 mL of de-ionized water also were prepared. Batch experiments were conducted with 50 ppt inorganic mercury. The initial pH of the standard mercury solution was adjusted to 8 using sodium hydroxide. All samples were secured to a wrist shaker and agitated for 48 hours. The samples were allowed to settle for 30 minutes. The final solutions were filtered with a 0.45 m filter. The pH and conductivity of the final solutions were measured. Standard, blank and duplicate samples were run for each batch test for QA-QC. The samples were analyzed for total mercury. The results showed that varying amounts of limestone of two different sizes removed 97% of mercury. Therefore, it can be concluded that limestone indeed has the potential to act as a major sink for inorganic Hg.

Information Transfer Program

The Information Transfer Program of KWRRI has numerous components including lectures, seminars, symposia, workshops, and publications.

04/08/2004 National Ground Water Association Darcy Lecture: Dr. Allen M. Shapiro, USGS, Recent Advances in Characterizing Ground-Water Flow and Chemical Transport in Fractured Rock from Cores to Kilometers (co-sponsored with the University of Kentucky Department of Geological Sciences)

04/22/2004 Storm Water Control Strategies for Kentucky (Municipal Stormwater Program Overview, sessions on Public Education and Participation, and APWA Teleconference on Silt and Sediment Control Practices), University of Kentucky (additional video conference sites provided at University of Louisville, Murray State University, Western Kentucky University, and Northern Kentucky University). Sponsors included Watershed Watches of Kentucky, Kentucky Waterways Alliance, Kentucky Division of Water, Lexington Fayette Urban County Government, Tetra Tech, Inc., and KWRRI.

Tetra Tech, Inc., 2004, Kentucky Erosion Prevention and Sediment Control Field Guide. Funding for the project was provided in part by a grant from the U.S. Environmental Protectin Agency through the Kentucky Division of Water Nopoint Source Section as authorized by the Clean Water Act Amendments of 1987, Section 319(h) Nonpoint Source Implementation Grant #C9994861-01. James Kipp, Associate Director of the Kentucky Water Resources Research Institute, served on the technical review committee during development of the field guide. A platform presentation describing these efforts was also presented at the annual water resources symposium: Becker, Jory, Richard Walker and Barry Tonning, 2005, Update of Kentucky Best Management Practices for Construction Activities, in Proceedings Kentucky Water Resources Annual Symposium, March 3, 2005, Kentucky Water Resources Research Institute, Lexington, Kentucky, p. 71.

May is designated as Kentucky Water Awareness Month. This observance is an educational program of the University of Kentucky Cooperative Extension Service, Environmental and Natural Resource Issues Task Force (Kipp serves on the task force). The program promotes overall water awareness for the citizens of Kentucky. Program materials are developed each year at the state level and distributed to each of the 120 county extension offices. Packet materials include new publications, teaching guides, fact sheets, radio scripts, and news releases. In 2004, over 7000 individuals were reached through this program. A poster describing the effort was also presented at the annual water resources symposium: Abnee, Amanda and Ashley Osborne, 2005, Kentucky Water Awareness Month Education Program, in Proceedings Kentucky Water Resources Annual Symposium, March 3, 2005, Kentucky Water Resources Research Institute, Lexington, Kentucky, p. 91.

07/26-30/2004 Salt River Watershed Academy for Educators co-sponsored with the University of Louisville, Jefferson County Public Schools, Blackacre State Nature Preserve, Jefferson County Metro Parks, Kentucky Department of Fish and Wildlife Resources, Bernheim Forest and Arboretum, Kentucky Partnership for Environmental Education, Tracy Farmer Center for the Environment, and Cooperative Extension. Two 104B researchers funded in 2003 (Coyne and Webb) spoke to the group and suggested ways that middle school teachers can bring university research into the classroom. Educators participated in hands-on activities to enhance their knowledge about watersheds and investigated the physical, chemical, biological, and human influences on watershed quality. A platform presentation describing the effort was also presented at the annual water resources symposium: Hanley, Carol, David Wicks, Russ

Barnett, and Stephanie Jenckins, 2005, Salt River Watershed Academy for Educators, in Proceedings Kentucky Water Resources Annual Symposium, March 3, 2005, Kentucky Water Resources Research Institute, Lexington, Kentucky, p. 69.

07/27-28/2004 Building Healthy Watersheds: Kentucky Watershed Roundtable. Sponsors included Bluegrass PRIDE, East Kentucky PRIDE, Kentucky Division of Water, Kentucky Waterways Alliance, Southeast Watershed Forum, Tennessee Valley Authority, U.S. Geological Survey, and Kentucky Water Resources Research Institute. Conference objectives included: (1) raising awareness of watershed issues and resources, (2) leveraging resources by building trust and forging links among partners, and (3) providing tools to support watershed and community development. The 207 participants represented a mix of local, state, federal, and private sector professionals, nonprofit and citizen groups, and interested individuals. Final Report Building Healthy Watersheds: Kentucky Watershed Roundtable, December 2004, Kentucky Waterways Alliance, Inc., Munfordville, Kentucky, 50 p.
http://www.kwalliance.org/news/roundtable2004finalreport.pdf

08/03-05/2004 A three-day, two night pilot resident 4-H Water Camp was conducted at Land Between The Lakes. Fifteen 5th and 6th graders from Kentucky and Tennessee participated in activities related to key water concepts. Specific objectives were to: (1) create a multi-state program for youth, (2) enhance partnerships and collaboration between neighboring states and various agencies and organizations, and (3) develop a camp manual that could be used in other states in the Southern Region of Extension. Partners in planning the effort included EPA Region IV's Watershed Education Network, US Forest Service, Tracy Farmer Center for the Environment, Cooperative Extension at both the University of Kentucky and the University of Tennessee, and KWRRI. A platform presentation describing the effort was made at the annual water resources symposium: Osborne, Ashley and Amanda Abnee, 2005, Multi-State 4-H Water Camp, in Proceedings Kentucky Water Resources Annual Symposium, March 3, 2005, Kentucky Water Resources Research Institute, Lexington, Kentucky, p. 67.

09/21/2004 GSA Hydrogeology Division Birdsall-Dress Lectures. Barbara Bekins, USGS, Menlo Park, (1) The Influence of Hydrogeology on 25 Years of Natural Attenuation at a Crude Oil Spill Site, and (2) Hydrogeology and the Weak Nature of Plate Boundary Faults (local arrangements co-sponsored with the University of Kentucky Department of Geological Sciences).

10/12-13/2004 Coal 2020 - Burning Questions. Sponsored by Cinergy Corporation, University of Kentucky, and Eastman Chemical Company. Lindell Ormsbee, KWRRI Director, served as the moderator for Panel II: How Shall We Ensure Sustainability? Coal and the Environment.

10/13/2004 Earth Science Week Open House in conjunction with the Kentucky Geological Survey, and the Tracy Farmer Center for the Environment. KWRRI set up and staffed an Enviroscape (demonstrating nonpoint source pollution) for the open house.

Cyberseminars provided through the Consortium for the Advancement of Hydrologic Sciences, Inc. (CUAHSI) were made available by the KWRRI on the campus of the University of Kentucky for interested faculty, staff, students, and local professionals upon request.

The Kentucky Water Resources Annual Symposium was held March 3, 2005. Although the date of the event fell outside of FY2004, most of the planning and preparation occurred during the fiscal year. This one-day event recognized the 40-year history of the institutes program. Past directors (Billy Barfield and Lyle Sendlein) shared their perspectives on the successes and strengths of the program during the opening

plenary session. This was followed by two concurrent sessions for the remainder of the day that included a total of 36 platform presentations. Eleven poster presentations were also included as a part of the program. There were 154 registrants for the conference. Abstracts were printed as a proceedings volume and distributed to all participants: Proceedings Kentucky Water Resources Annual Symposium, 2005, Kentucky Water Resources Research Institute, March 3, 2005, Kentucky Water Resources Research Institute, Lexington, Kentucky, 94 p.

Publication of the quarterly newsletter WATERWORKS continued in 2004 and the institute's web site was maintained: **www.uky.edu/WaterResources/**

The Association of State Dam Safety Officials (ASDSO) is a national, non-profit association dedicated to the improvement of dam safety through research, education, and communication. The national office is located in Lexington, Kentucky and the unit is affiliated administratively with the University of Kentucky through the Kentucky Water Resources Research Institute. In addition to technical seminars held regionally and nationally, ASDSO also maintains a clearinghouse of books, videos, articles, and CDs on subjects related to dam safety. The association web site is: http://www.damsafety.org

The Ohio River Basin Commission seeks to improve the water resources and land programs in member states. The commission endeavors to contribute to the formation of a comprehensive, coherent, and coordinated national water policy that recognizes interstate water issues and the primary role of the states in water resources planning and management in the Ohio River basin. The ORBC cosponsors the Institutes annual symposium. Its office is located in Lexington, Kentucky and the unit is affiliated administratively with the University of Kentucky through the Kentucky Water Resources Research Institute.

Student Support

Student Support					
Category	**Section 104 Base Grant**	**Section 104 RCGP Award**	**NIWR-USGS Internship**	**Supplemental Awards**	**Total**
Undergraduate	7	0	0	0	7
Masters	4	0	0	0	4
Ph.D.	1	0	0	0	1
Post-Doc.	1	0	0	0	1
Total	13	0	0	0	13

Notable Awards and Achievements

Ashely Dockery received third prize for her poster presentation at the Annaul Sigma Xi Student Research Conference, Western Kentucky University, Bowling Green, Kentucky, 2005. The title of her poster was "Occurrence and Distribution of Mercury in Mammoth Cave National Park" Project Number: 2003KY18B, PI: Cathleen Joyce Webb

University of Kentucky Cooperative Extension Service Publication IP-73, Living Along a Kentucky Stream, won a Certificate of Excellence at the American Society of Agronomy in 2004. Jim Kipp, Associate Director of the Kentucky Water Resources Research Institute, served on the review committee during the development of this publication. http://www.ca.uky.edu/agc/pubs/ip/ip73/ip73.pdf

SETAC Travel Award, Fall 2004, $500, 2004KY41B, PI: Adria Elskus

The Kentucky Environmental Quality Commission, a seven-member citizen advisory board, works to strengthen the public role in addressing environmental problems in the Commonwealth. The commission was created under state law to: 1) facilitate public discussion and resolution of environmental issues, 2) monitor environmental trends and conditions, 3) promote partnerships to protect the environment for future generations, and to 4) serve as an advisory board to the governor and other state officials on environmental matters. Commissioners represent industry, environmental, governmental, and academic communities. KWRRI Director, Lindell Ormsbee, was Chair of the Commission in 2004 and currently continues to serve in that role.

Publications from Prior Projects

1. 2001KY1982B ("Retirement and Restoration of Forest Roads in Steep Terrain: Influence on Nonpoint Source Pollution and Hillslope Hydrology") - Articles in Refereed Scientific Journals - Kolka, R. K. and M. F. Smidt, 2004, Effects of Forest Road Amelioration Techniques on Soil Bulk Density, Surface Runoff, Sediment Transport, Soil Moisture and Seedling Growth, Forest Ecology and Management, 202 (2004) 313-323.