Uptake of Mercury and Relationship to Food Habits of Selected Fish Species in the Shenandoah River Basin, Virginia

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Acknowledgements

<u>Advisory Committee:</u>

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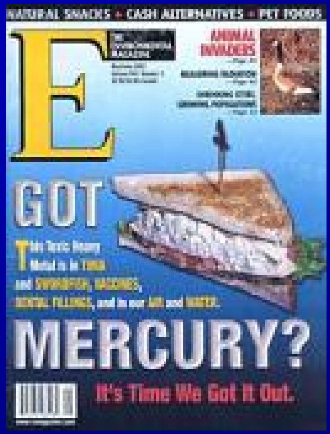
South River Science Team

"Pregnant women eating too much fish; Fetuses may have harmful mercury levels"

"Government advises against eating too much canned tuna; Elevated mercury levels raise alarms"

"High mercury levels found in canned tuna; Average doses may exceed safe limits"

"EPA to offer plan for reducing mercury emissions; Coal-fired power plants would have to cut about 70% from current levels"



"Study finds fish remain focus of concern for high blood mercury levels; But health benefits shouldn't be ignored"

"Mercury damage 'irreversible'; Effects on the brain, heart begin in womb"

"Studies yield contradictory findings on heart disease and fish"

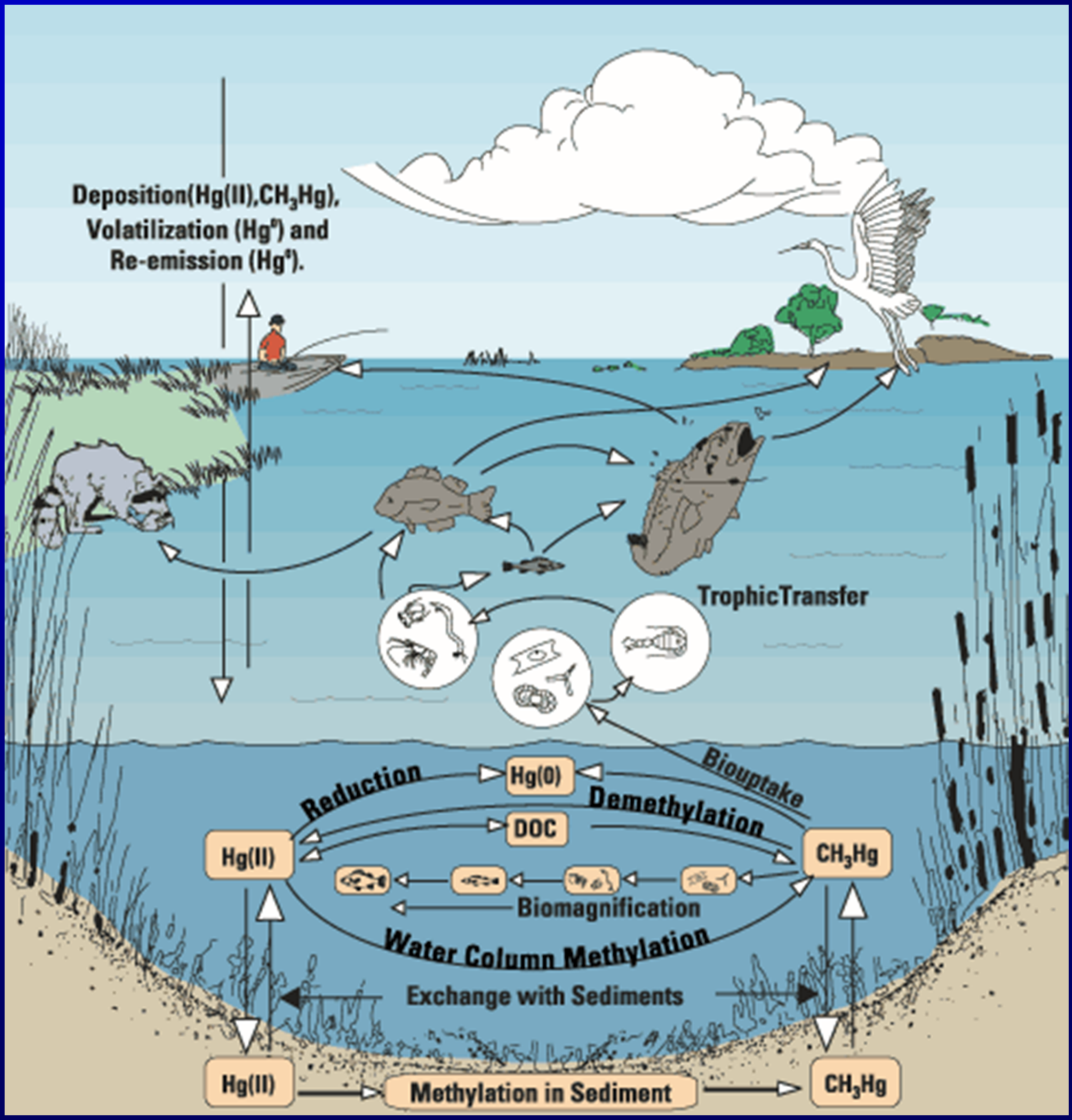
Source: USA Today

What is Mercury?

- Type II heavy metal
- Used in numerous products and control instruments
- Enters aquatic systems through anthropogenic pathways

www.gov.nl.ca

Mercury Bioaccumulation



www.sofia.usgs.gov

Human Health Risks

- Human exposure mainly through fish consumption
- Neurological toxicant and potential carcinogen
- Methylmercury 50-100X more toxic

www.joepattis.com

Fish Consumption Advisories

- U. S. FDA = 1.0 µg/g methylmercury
- 75% advisories issued due to mercury
- Dramatic increase from 1993 to 2002

Shenandoah River Basin

- DuPont
- 100-yr monitoring program
- South River Science Team
- Increasing trends of mercury in fish?

Study Objectives

1. Determine food habits of fish to identify dietary pathways and patterns affecting mercury uptake

2. Determine concentrations of total mercury and methylmercury in common prey items of fish

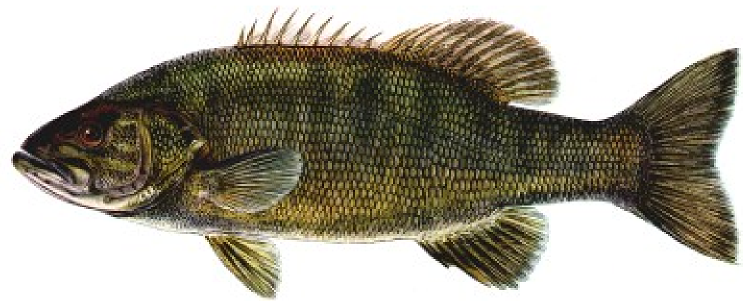
3. Simulate bioaccumulation dynamics of methylmercury in fish communities

4. Assess sexual and seasonal variations of total mercury in smallmouth bass

Selected Fish Species

White sucker

Smallmouth bass



Channel catfish

Redbreast sunfish


Objective 1
Grottoes, VA

Why Study Food Habits?

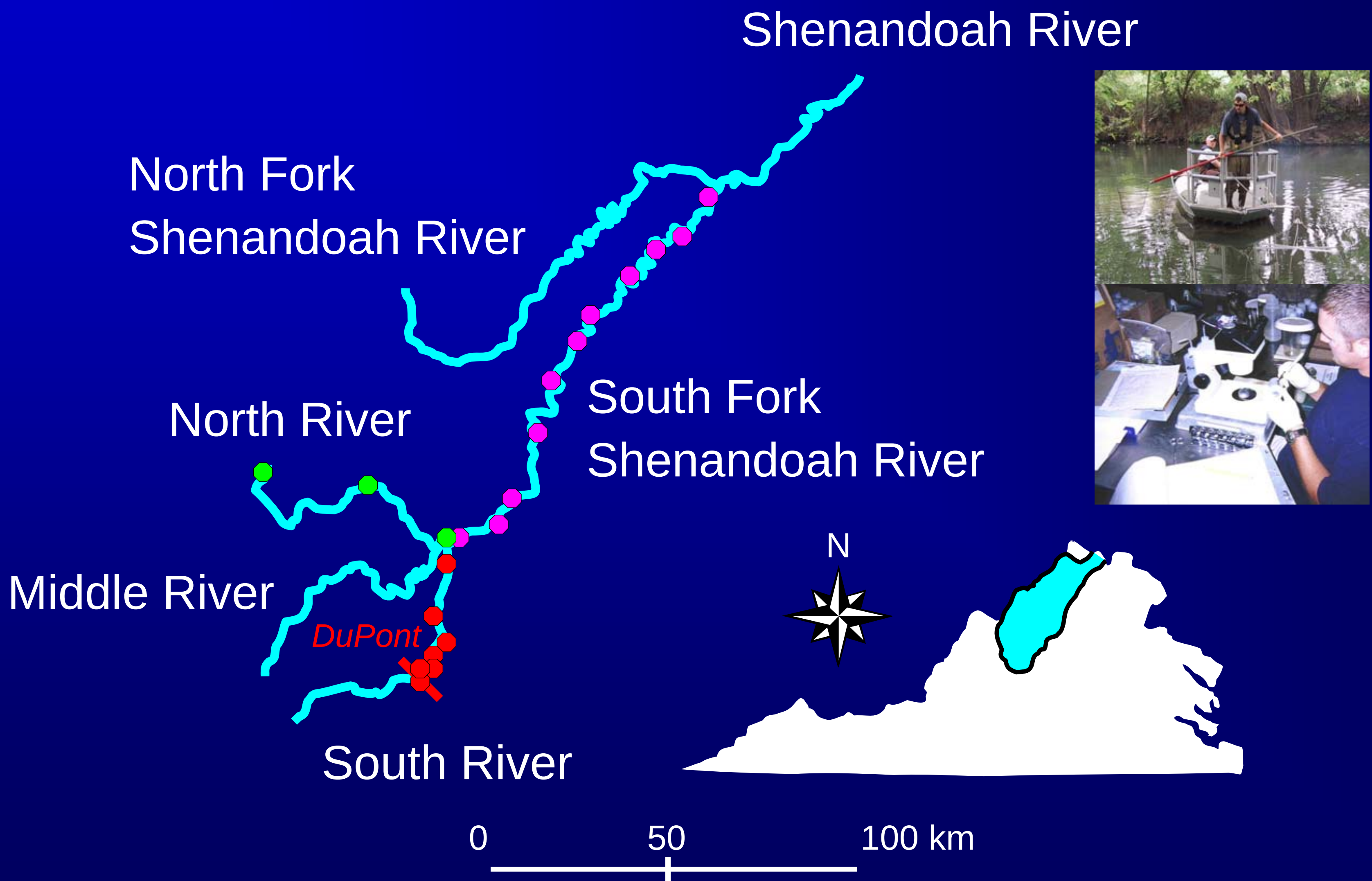
- Useful for bioaccumulation, predator-prey, and bioenergetics studies
- Enables mapping of contaminant flow through aquatic food webs
- Diet of selected fish species in Shenandoah River basin unknown
- Food habits may differ between size classes, seasons, and rivers

Objective 1: Determine food habits of fish to identify dietary pathways and patterns affecting mercury uptake

Tasks

- Identify principal dietary items
- Assess dietary patterns between size classes, seasons, and rivers
- Relate dietary pathways and patterns to mercury uptake

Study Area and Methods



Principal Diet Items

Filamentous algae and fish (84%)

Detritus and aquatic insects (90-93%)

Aquatic insects, crayfish, and fish (87-97%)

Aquatic insects (75-87%)

Dietary Patterns

- Size dependent patterns
- Seasonal patterns
- Spatial patterns

www.webcraft1.com

www.en.wikipedia.org

Conclusions

- Substantial differences in principal diet items and between size classes, seasons, and rivers
- Smallmouth bass feeding at highest trophic level
- Detritus potential source of mercury for white sucker
- Terrestrial insects important link between aquatic and floodplain ecosystems
- Potential reduction in exposure during winter


Objective 2
Burketown, VA

Mercury in Prey Items

- Lower trophic levels serve as important intermediaries in movement of mercury
- Information on mercury in aquatic invertebrates and forage fish widely applicable
- Mercury in prey items of fish rarely studied
- Expensive information to collect!

Objective 2: Determine concentrations of total mercury and methylmercury in common prey items of fish

Tasks

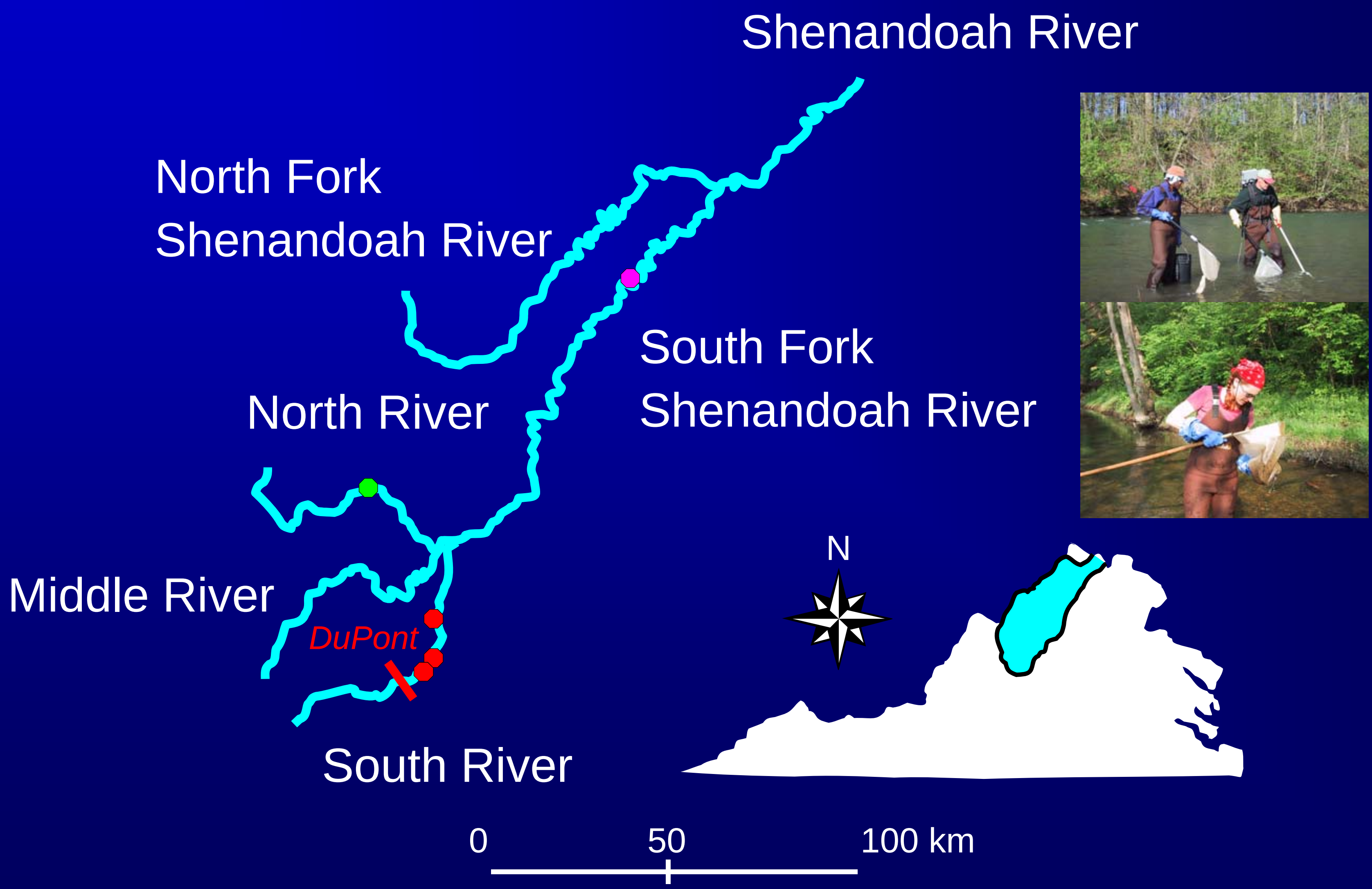
- Establish baseline concentrations of total mercury and methylmercury
- Determine relationship between methylmercury and total mercury
- Identify spatial, trophic, and temporal patterns in concentrations of total mercury

Target Prey Items

South River	S. F. Shenandoah River	North River
	<u>Aquatic Insects</u>	
Coleoptera	Diptera	Coleoptera
Diptera	Ephemeroptera	Diptera
Ephemeroptera	Megaloptera	Ephemeroptera
Odonata	Odonata	Odonata
Trichoptera	Plecoptera	Trichoptera
-	Trichoptera	-
	<u>Terrestrial Insects</u>	
Green June beetle	-	-
	<u>Crustacea</u>	
Crayfish	Crayfish	Crayfish
	<u>Annelida</u>	
Oligochaeta	-	-
	<u>Mollusca</u>	
Asian clam	Asian clam	Asian clam
Gastropoda	Gastropoda	Gastropoda
	<u>Forage Fish</u>	
Common shiner	Margined madtom	Comely shiner
Fantail darter	Redbreast sunfish*	Margined madtom
Margined madtom	Satinfin shiner	Redbreast sunfish*
Redbreast sunfish*	-	-
	<u>Vegetation</u>	
-	Filamentous green alga	-

*Juveniles

Study Area and Methods



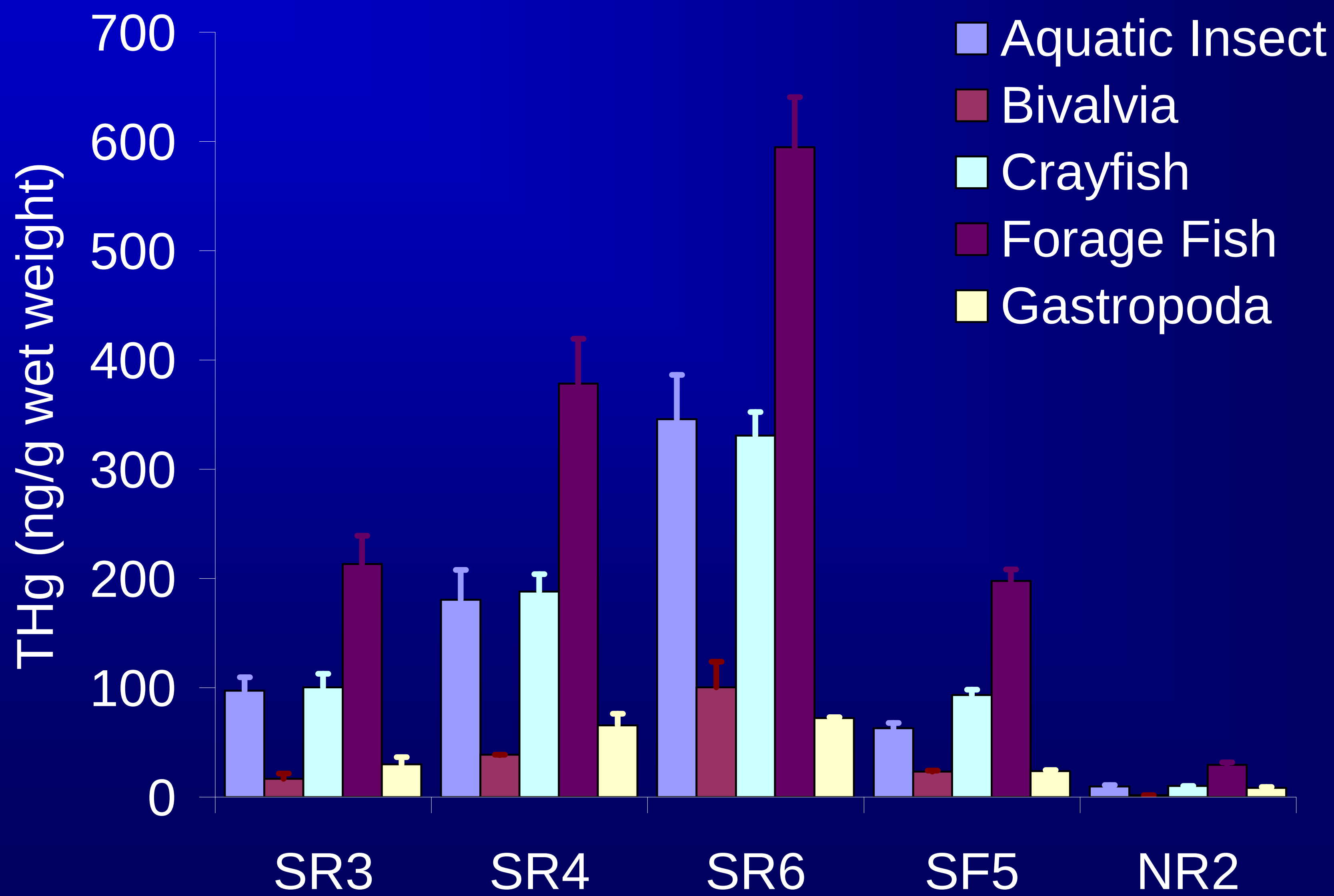
QA/QC Results

- Precision and accuracy within control limits
- Detection limits 0.45 and 1.50 ng/g for total mercury and methylmercury
- No difference in total mercury between brook trout exposure groups
- Water chemistry within normal limits

Total Mercury

- Collected 254 composite samples
- Total mercury in aquatic invertebrates and fish ranged 67-398 and 198-595 ng/g at contaminated sites
- Total mercury in aquatic invertebrates and forage fish were 4 and 29 ng/g at reference

Spatial Patterns

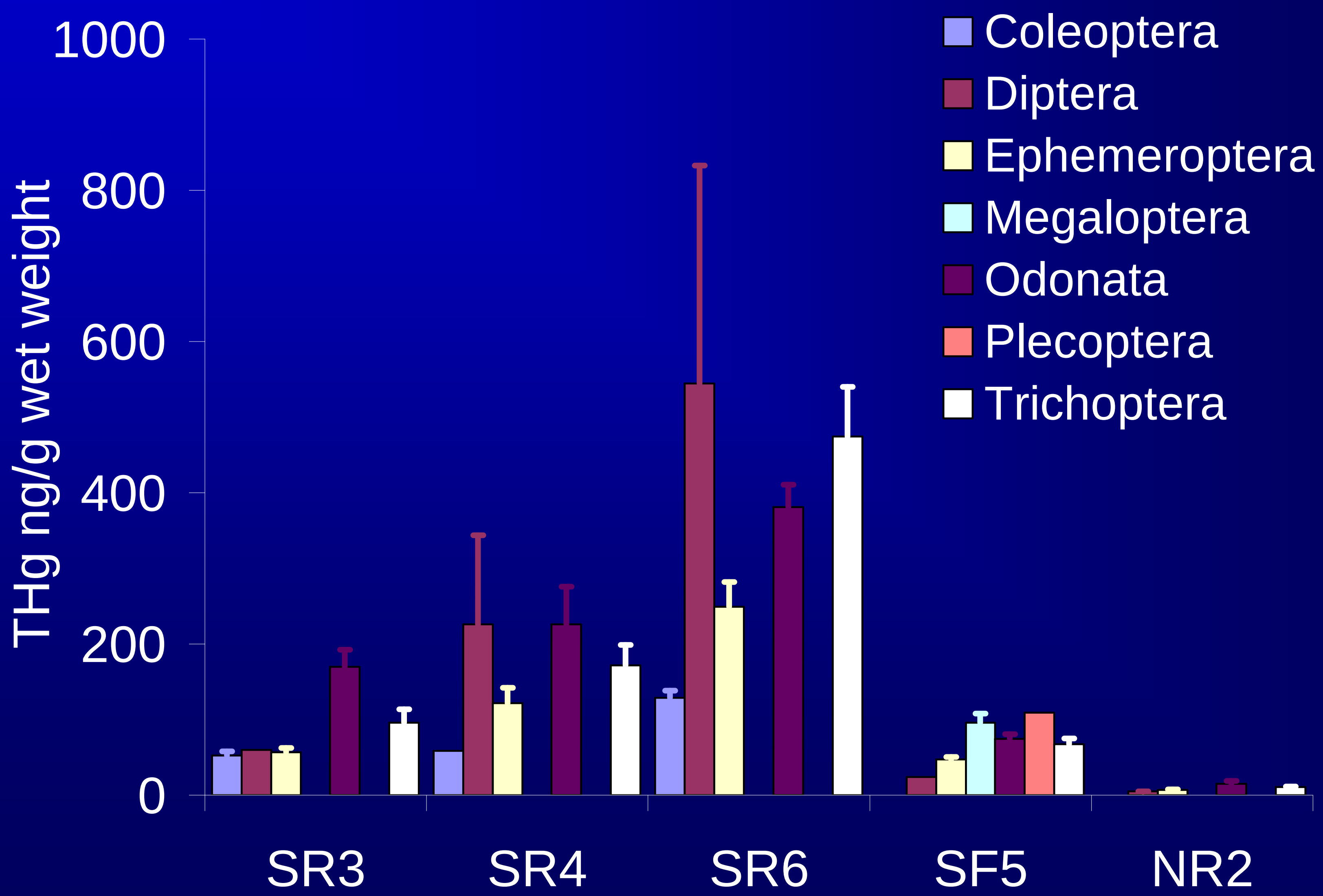


Trophic Patterns
Overall Prey Taxa

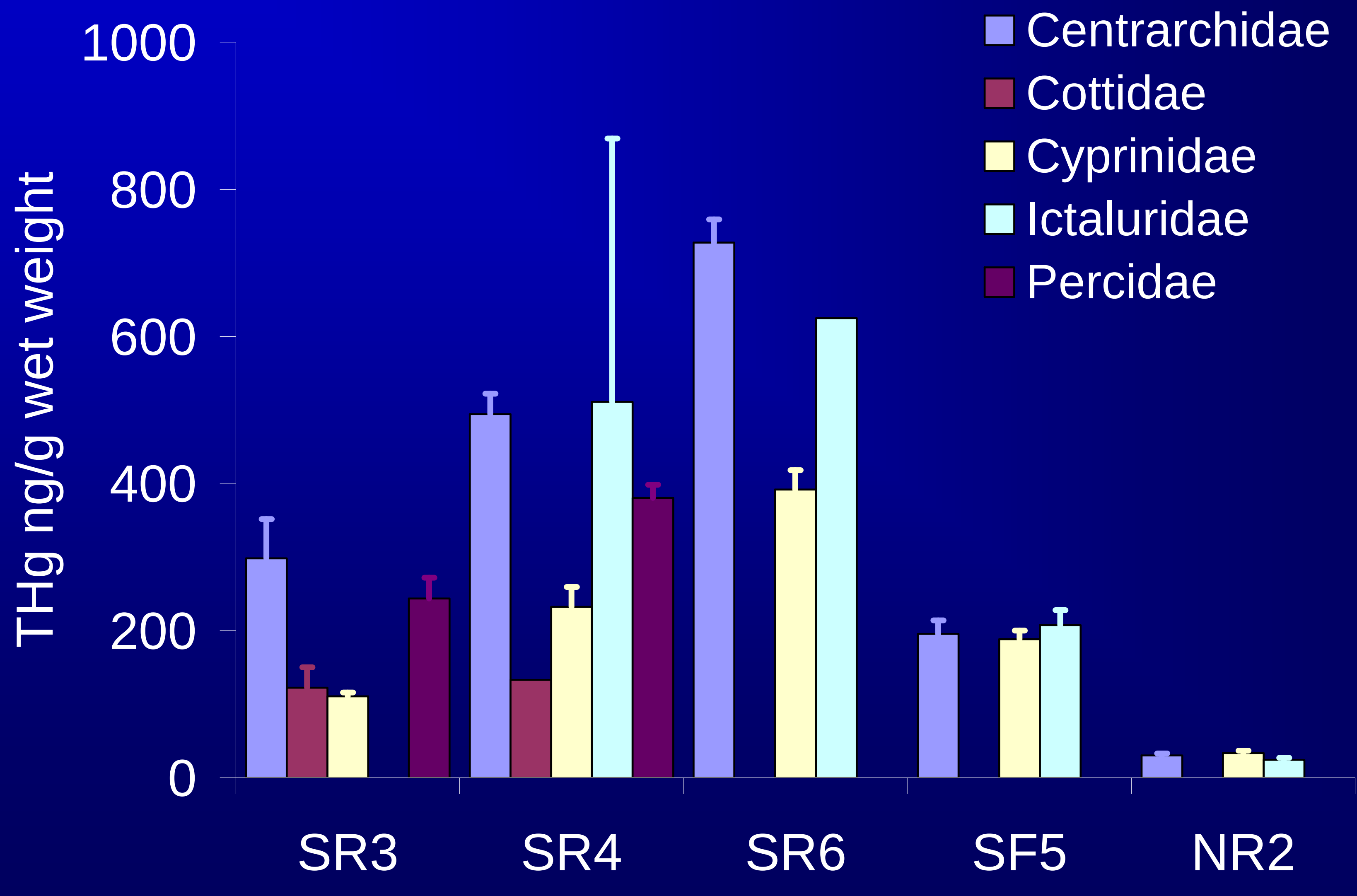
Site	df	KW Statistic	*P*	*Pairwise Comparisons* Aquatic Insect	Bivalvia	Crayfish	Forage Fish	Gastropoda
SR3	4	24.35	0.0001	A	A	AB	B	A
SR4	4	22.96	0.0001	A	A	AB	B	A
SR6	4	23.51	0.0001	A	A	AB	B	A
SF5	4	41.95	<0.0001	A	A	AB	B	A
NR2	4	14.58	0.0056	A	A	AB	B	AB

Trophic Patterns

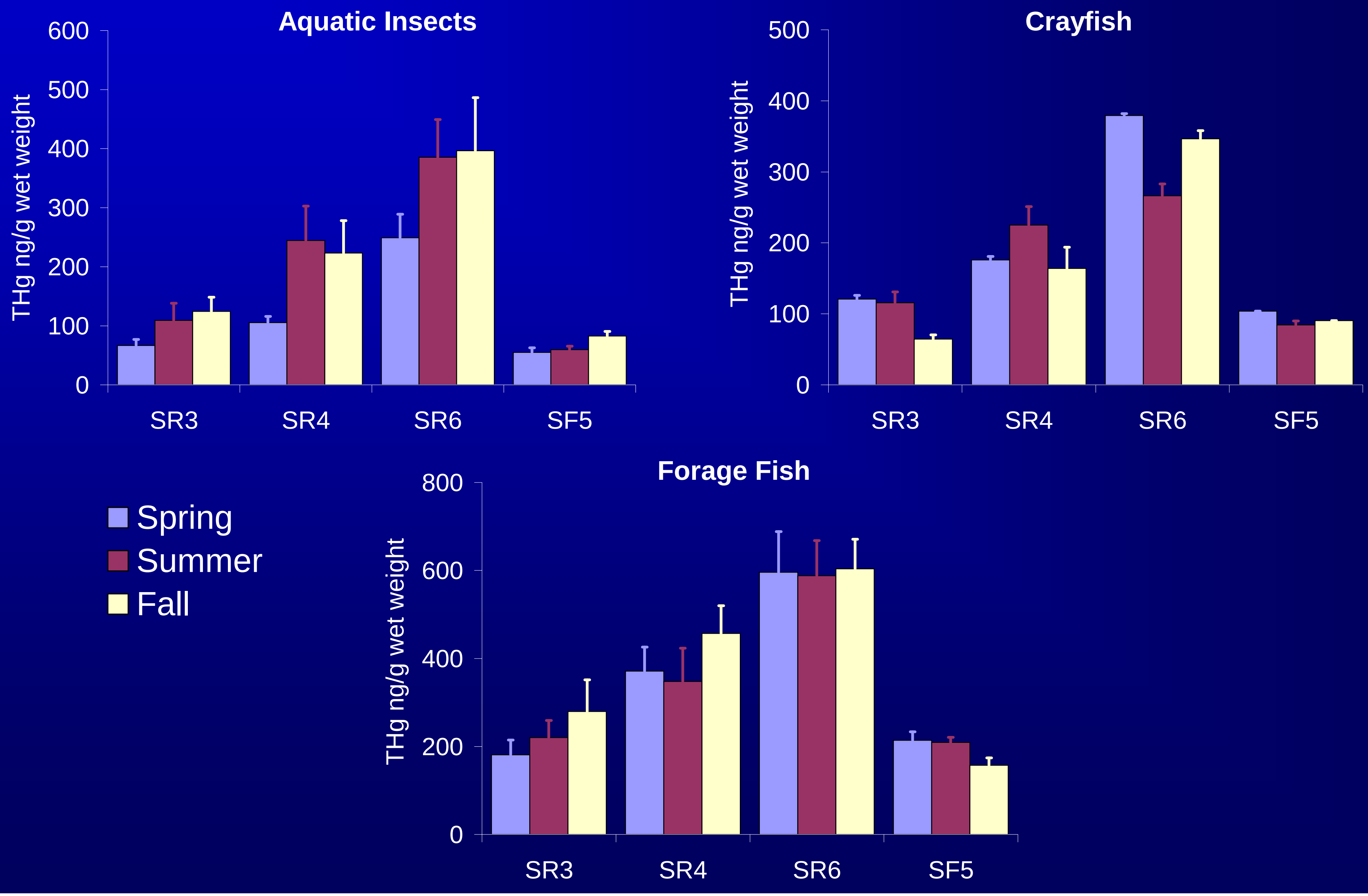
Aquatic Insect Taxa



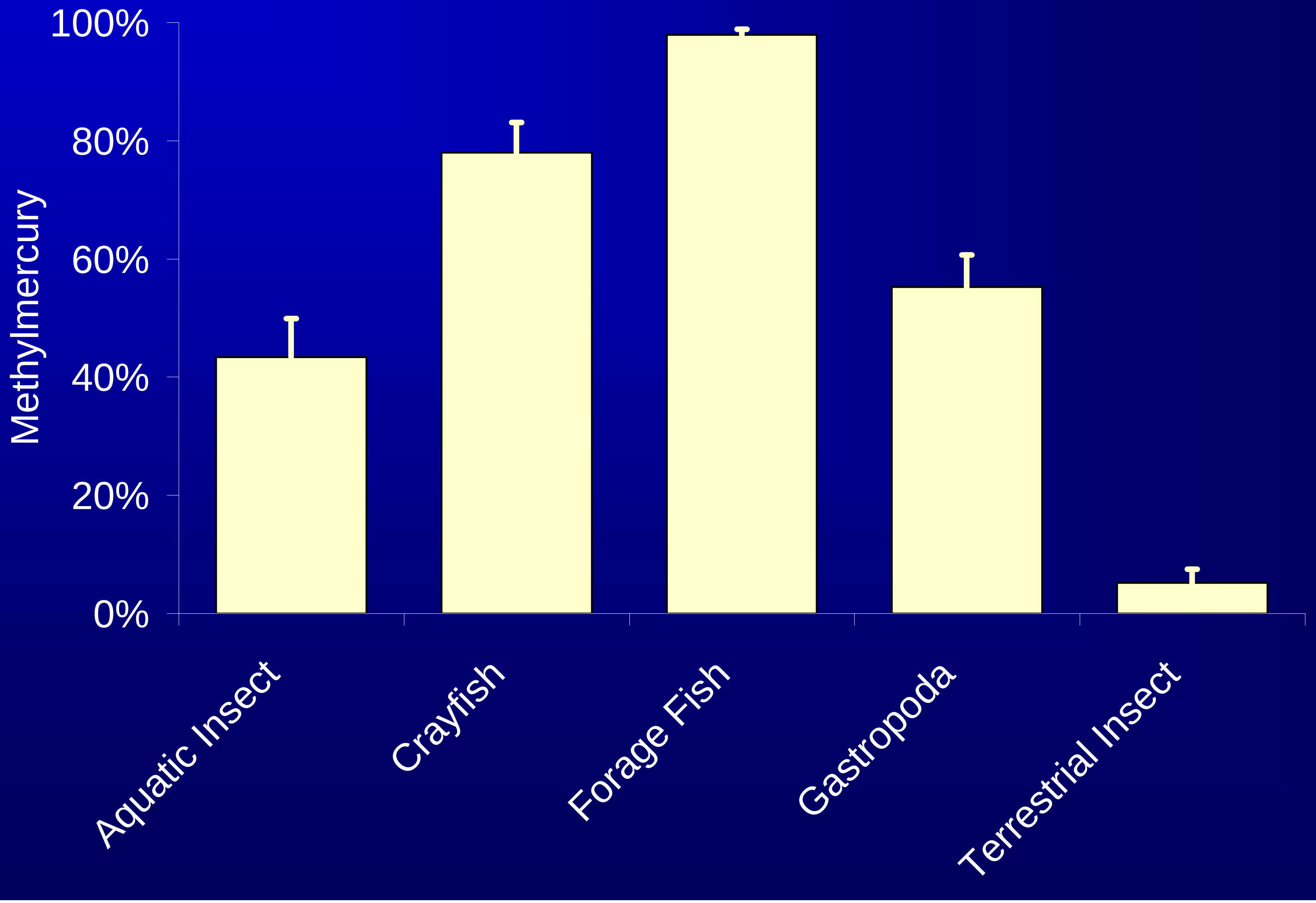
Trophic Patterns
Forage Fish Taxa



Temporal Patterns



% Methylmercury



Conclusions

- Total mercury concentrations lower than reported historically
- Terrestrial insects substantial source of mercury
- Sediment associations important to mercury uptake from physical environment
- Background concentrations identify remediation endpoints

Conclusions

- Spatial patterns similar to that for their predators, sediments, and water
- Trophic differences between insects and fish presumably related to food habits
- Temporal differences not critical to mercury uptake


Objective 3
North Park, Virginia

Bioaccumulation Modeling

- Prediction of mercury essential to assessing ecological and human health risks
- Bioenergetics-based models particularly useful
- Prior studies failed to describe bioaccumulation dynamics in community context
- Aid in model development and provide management guidance prior to costly expenditures

Objective 3: Simulate bioaccumulation dynamics of methylmercury in fish communities

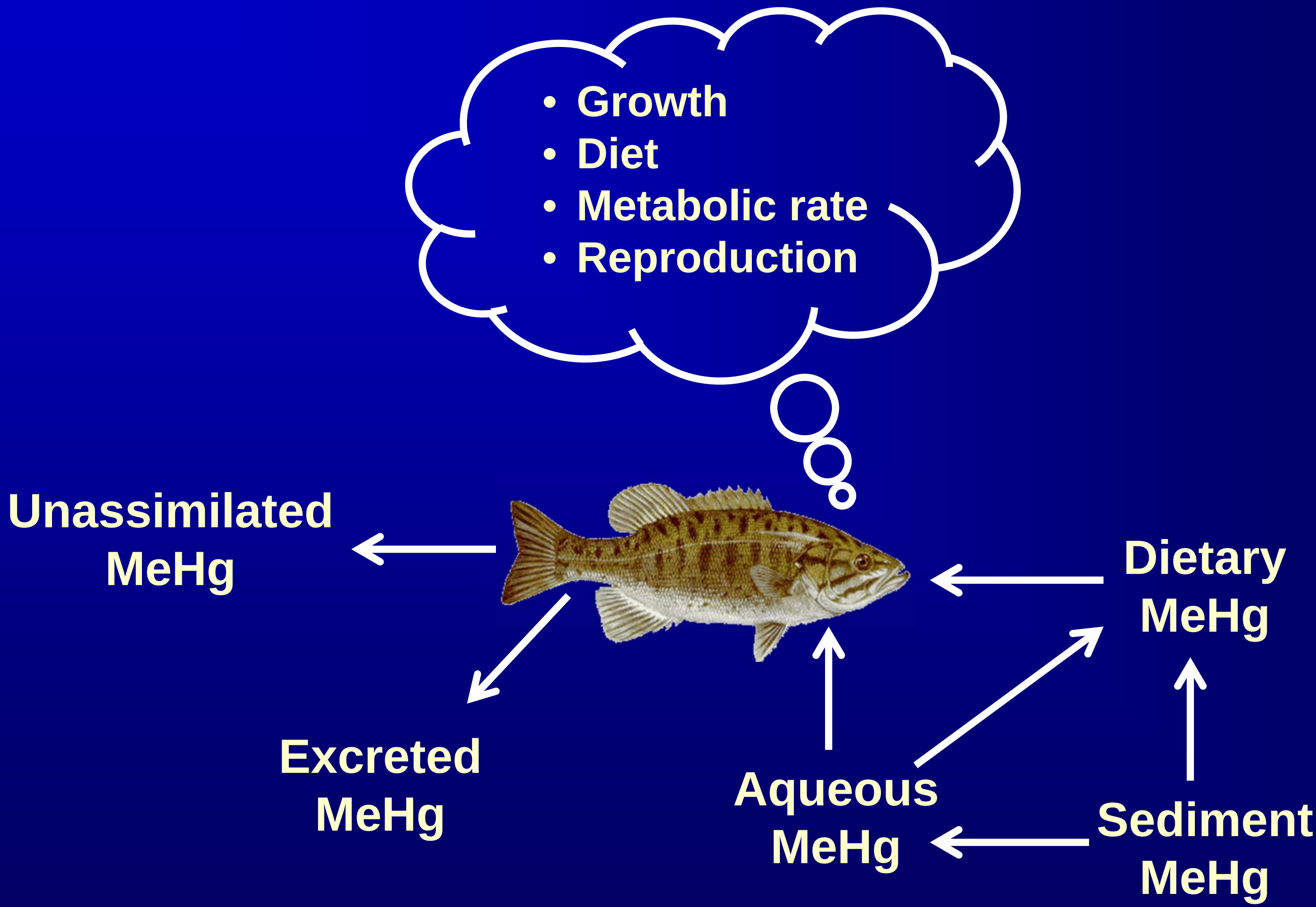
Tasks

- Assess predicted patterns of methylmercury accumulation
- Determine percentage of dietary uptake
- Evaluate predictive ability
- Assess sensitivity to food web structure
- Demonstrate utility for evaluation of remediation options

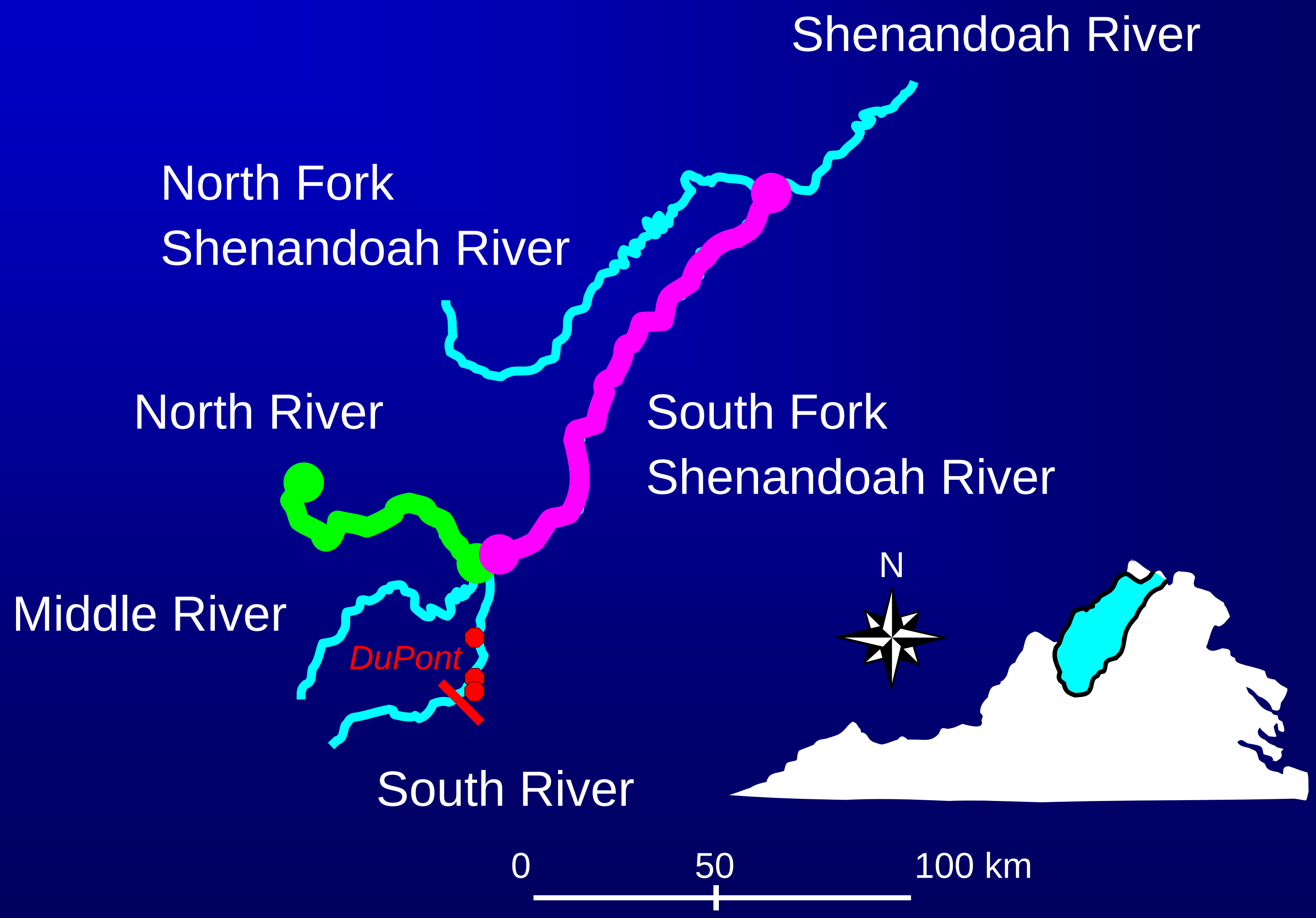
Model Description (BASS)

- Bioaccumulation and Aquatic System Simulator
- Predicts population and bioaccumulation dynamics of age-structured fish communities
- Simulates fish growth using standard mass balance, bioenergetics model
- Operated in Food and Gill Exchange of Toxic Substances mode during this study

BASS Model


• Growth
• Diet
• Metabolic rate
• Reproduction
Unassimilated MeHg
Excreted MeHg
Dietary MeHg
Aqueous MeHg
Sediment MeHg

Study Area and Sites



Simulated Fish Communities

South River	S. F. Shenandoah River	North River
Redbreast sunfish	Redbreast sunfish	Redbreast sunfish
Smallmouth bass	Smallmouth bass	Smallmouth bass
White sucker	White sucker	White sucker
Margined madtom	Margined madtom	Margined madtom
Fantail darter	Satinfin shiner	Comely shiner
Common shiner	Channel catfish	-

www.nativefish.org

www.assabetriver.org

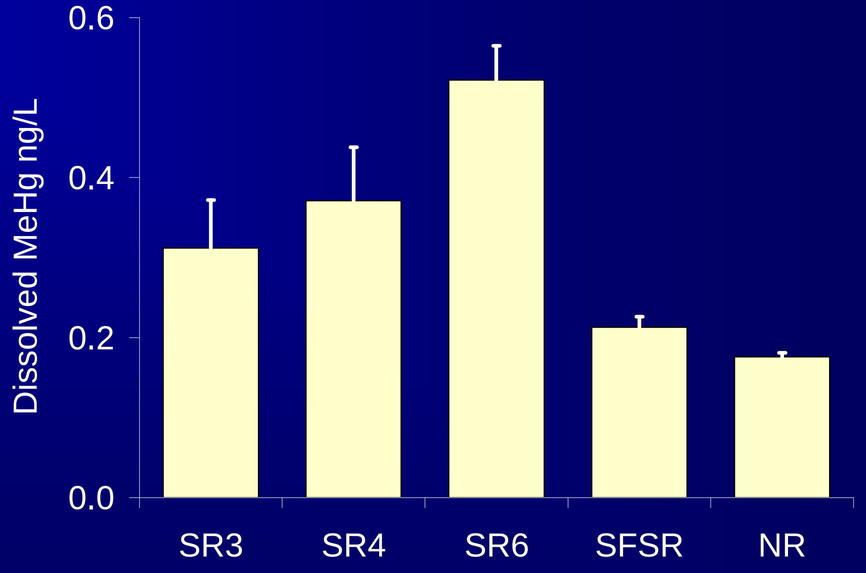
www.nanfa.org

Simulation Control Parameters

- Length of simulation depended on fish age
- January was initial month of simulation
- Water temperature

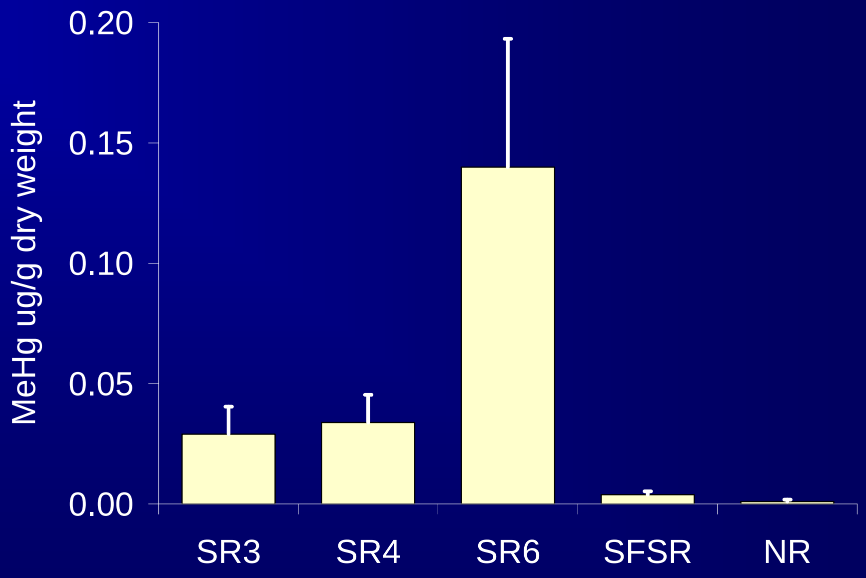
Chemical Parameters
Aqueous Dissolved Methylmercury

- Virginia DEQ data
- Aqueous concentrations dissolved methylmercury
- Chemical equilibrium with benthic sediments



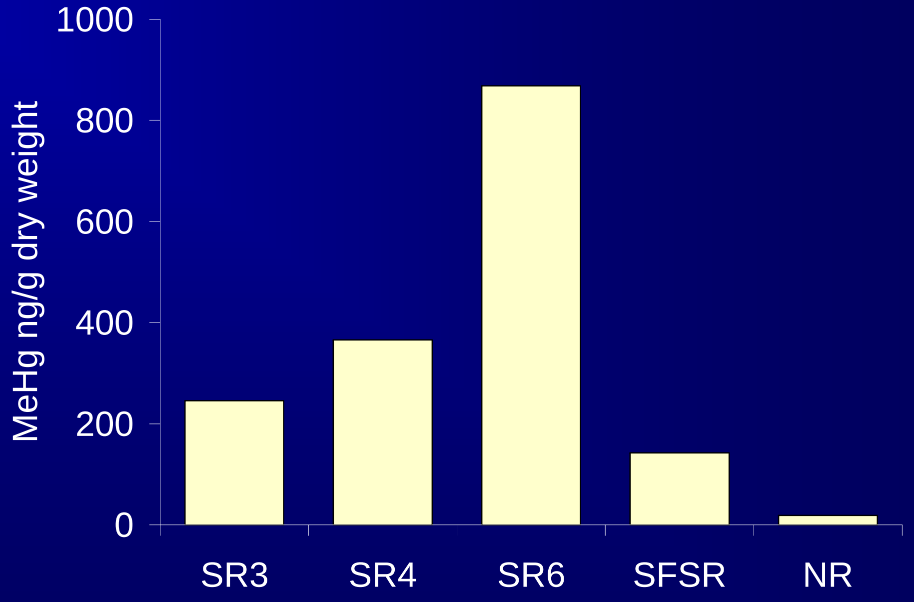
Chemical Parameters
Sediment Methylmercury

- Estimated sediment concentrations using AMRL 1998 report
- Assumed methylmercury percentage of 0.89%



Chemical Parameters
Dietary Methylmercury

- Estimated using objective 2 data
- Determined moisture content by drying
- Chemical equilibrium with aqueous dissolved methylmercury



Fish Parameters
Taxonomic, Recruitment, and Mortality

- Spawning period
- Reproductive biomass investment
- Age-0 live weight
- Maximum life span

Fish Parameters
Morphometry and Composition

- Length weight relationship
- Gill area
- Lamellar length and density
- Interlamellar distance
- Aqueous lipid relationship
- Lipid fraction

www.trc.ucdavis.edu

Fish Parameters
Physiological

- Assimilation efficiencies
- Routine/standard oxygen
- Respiratory quotient
- Specific dynamic action/ingestion ratio
- Standard oxygen consumption

Fish Parameters

Feeding, Ecological, and Initial Conditions

- Average length of prey
- Specific growth rate
- Dietary composition
- Initial age, live body weight, and methylmercury by age class

Model Predictive Ability

- Assessed model predicted and observed concentrations of methylmercury:
  - Graphically
  - Mean absolute % error

Sensitivity to Food Web Structure

- Dietary composition:
  - Channel catfish
- Average length of prey:
  - Smallmouth bass
- Specific growth rate:
  - Redbreast sunfish, smallmouth bass, and white sucker

Example Management Application
Sediment Remediation

- SR6 on South River
- Fish mercury levels related to sediment
- Sediment remediation potential option
- Simulate reductions of 25, 50, and 75%

www.bigeastern.com

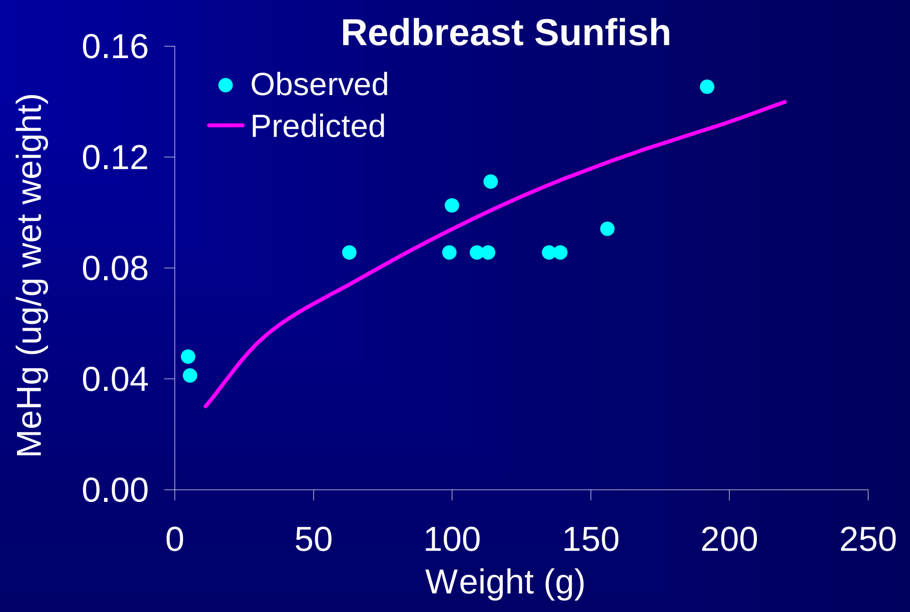
Bioaccumulation Results

- Methylmercury increased with size and age (*P*<0.05)
- Methylmercury highest in smallmouth bass
- Accumulation rates faster in forage fish by size
- Dietary pathways accounted for 87% of methylmercury in contaminated rivers

www.thecontentwell.com

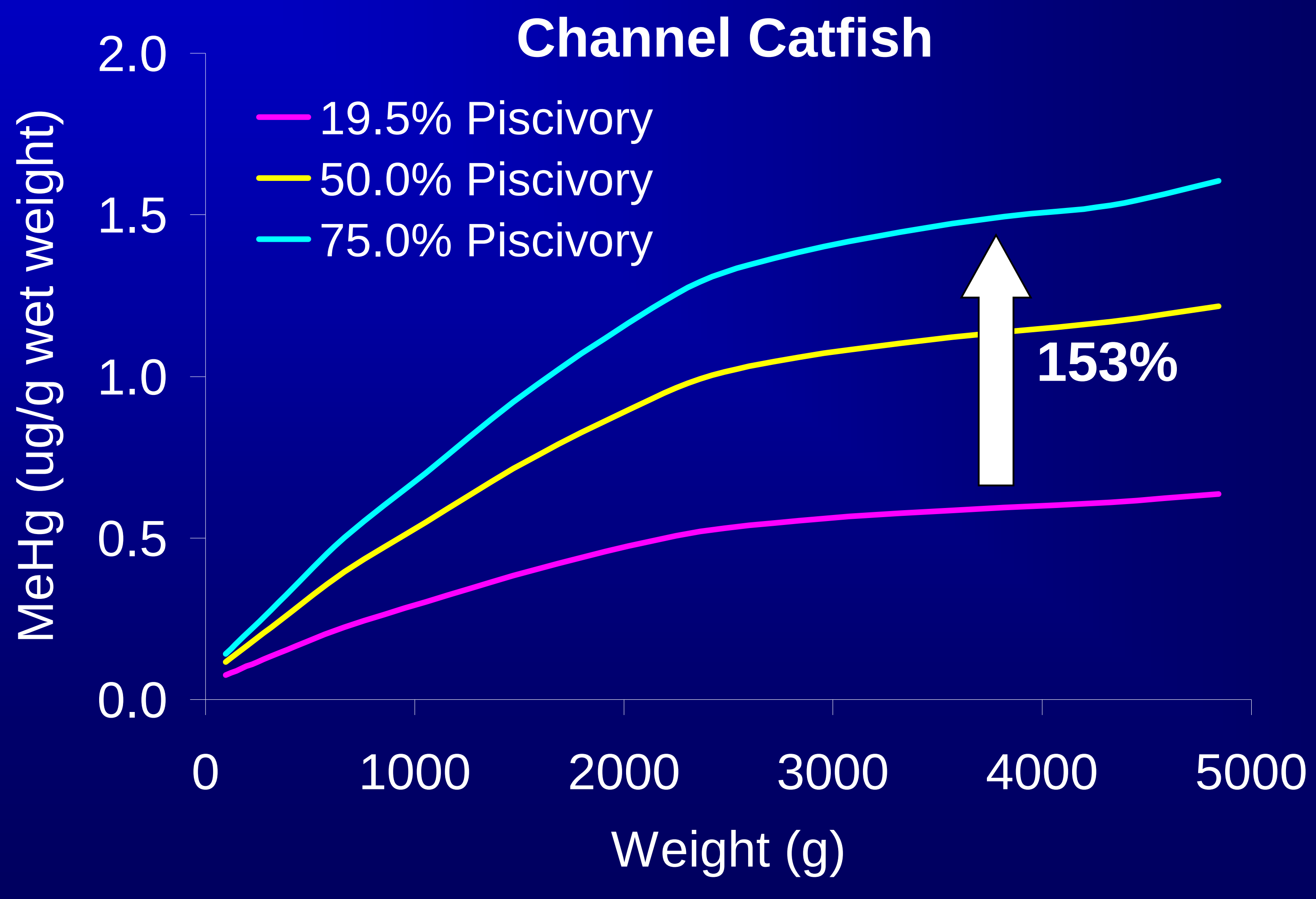
Model Predictive Ability

- Predicted and observed data comparable
- Mean absolute error 52% (17-149%)
- Predicted best for SR4 and S. F. Shen. River
- Predicted best for forage fish



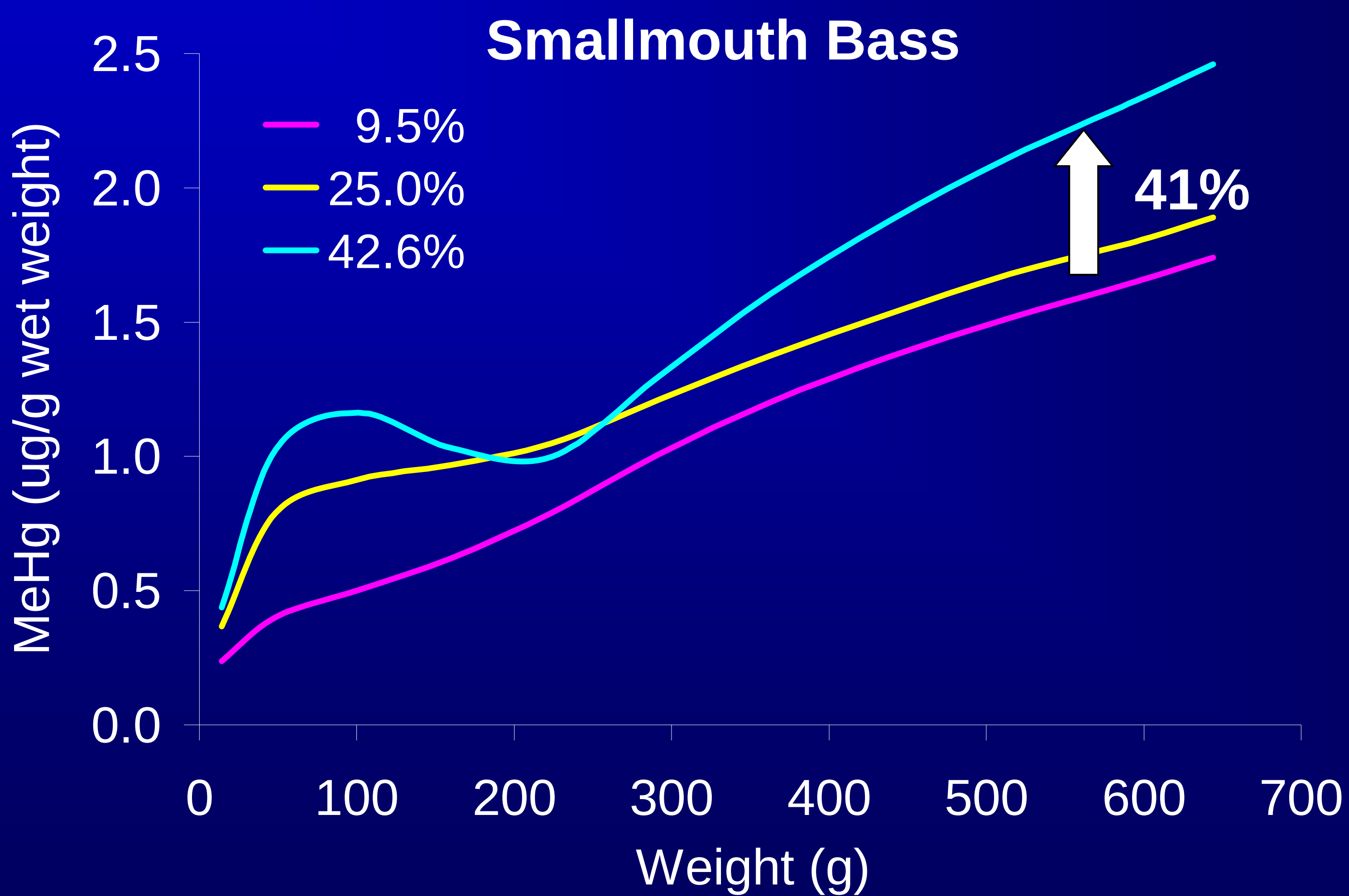
Sensitivity to Food Web Structure

Dietary Composition



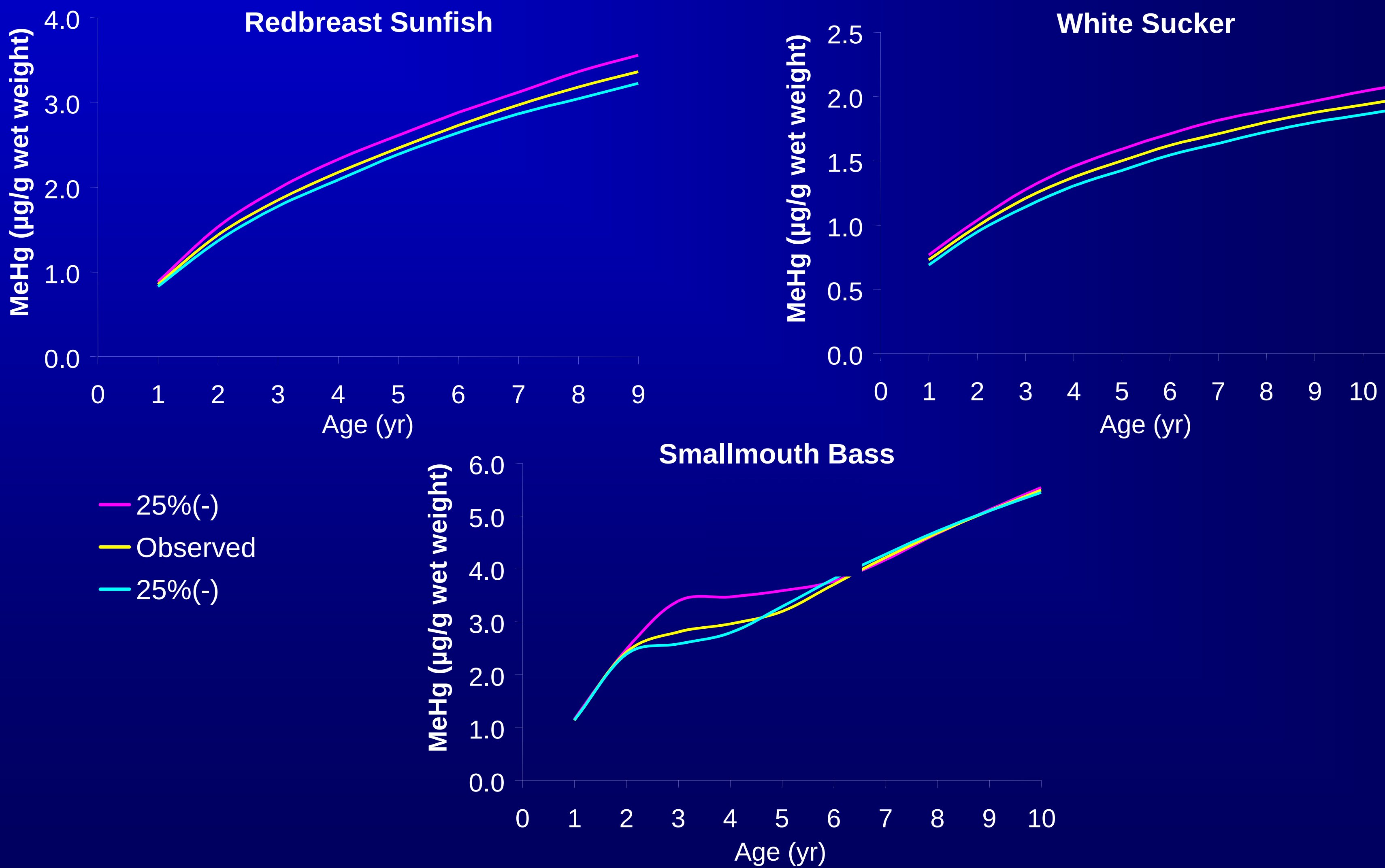
Sensitivity to Food Web Structure

Average Length of Prey



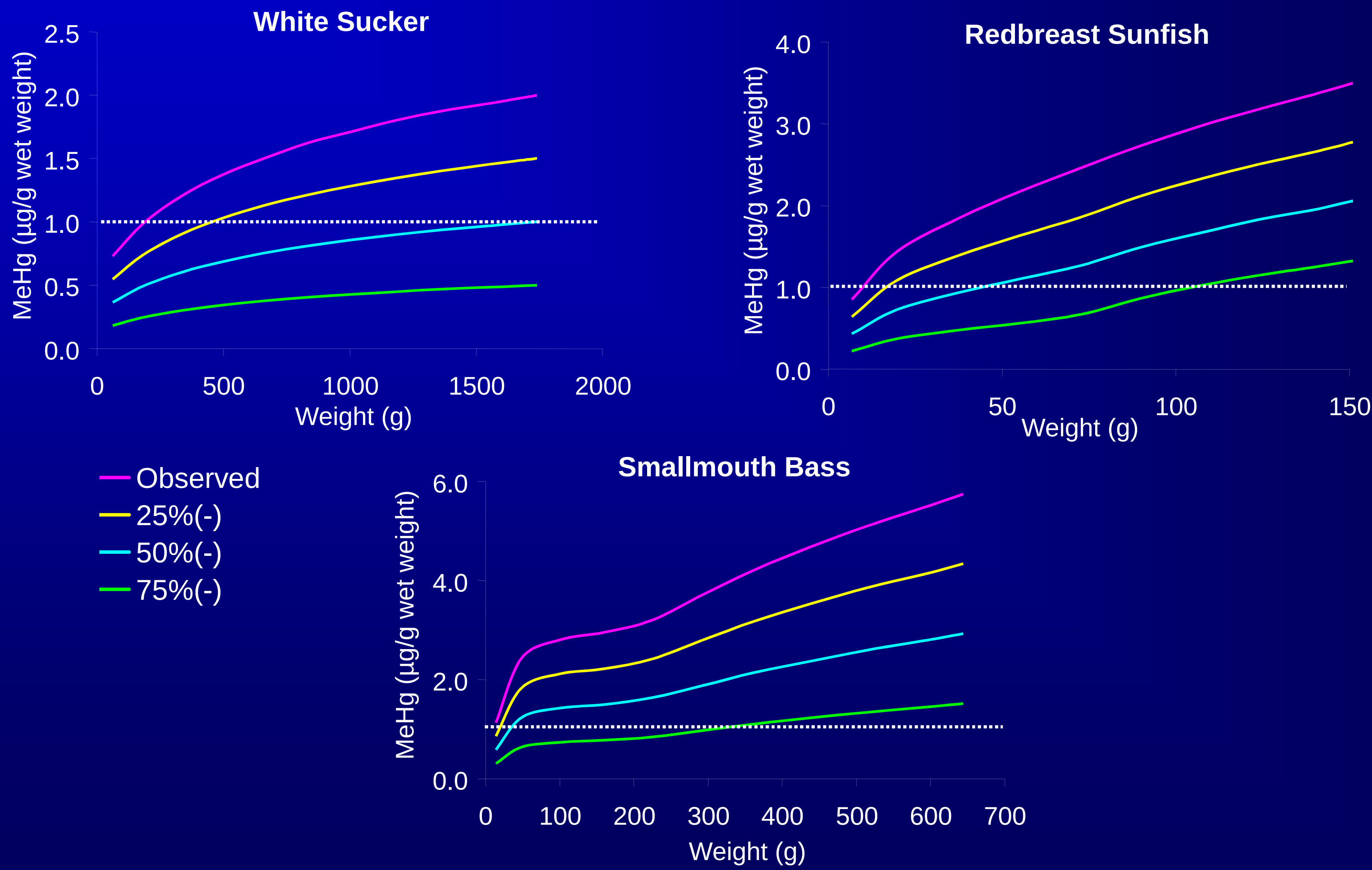
Sensitivity to Food Web Structure

Specific Growth Rate



Example Management Application

Sediment Remediation



Conclusions

- Developed working model for Shenandoah River basin that accurately predicts bioaccumulation
- No set combination of validation techniques
- Food web structure critical to methylmercury bioaccumulation dynamics
- BASS model useful tool for evaluating alternative management options


Objective 4
Bentonville, VA

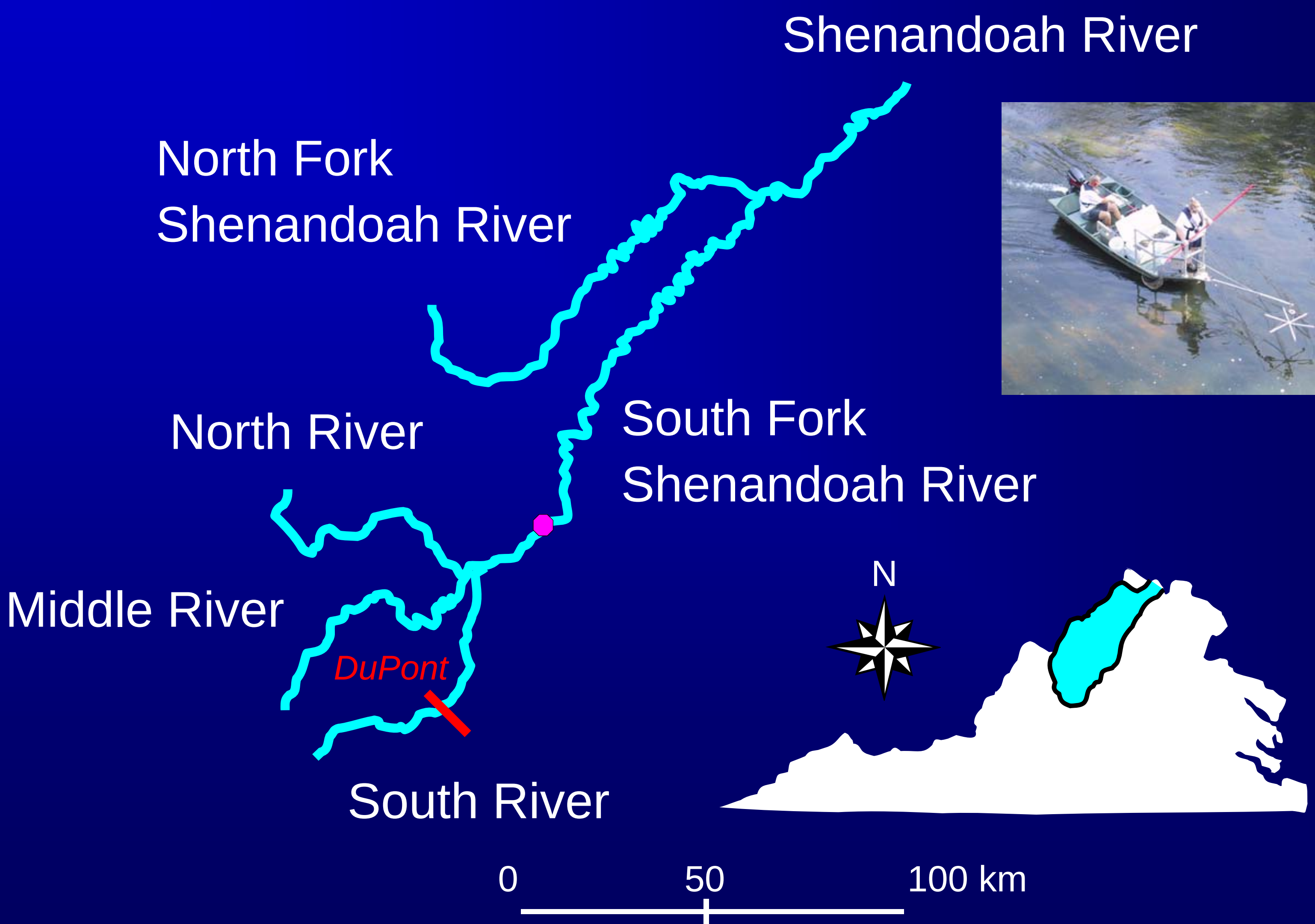
Variability of Mercury in Fish

- Mercury accumulation remains poorly understood
- Understanding intrapopulation variability critical to fisheries management
- No reports of sexual and seasonal variations of mercury in smallmouth bass

Objective 4

Evaluate sexual and seasonal variations of mercury in smallmouth bass

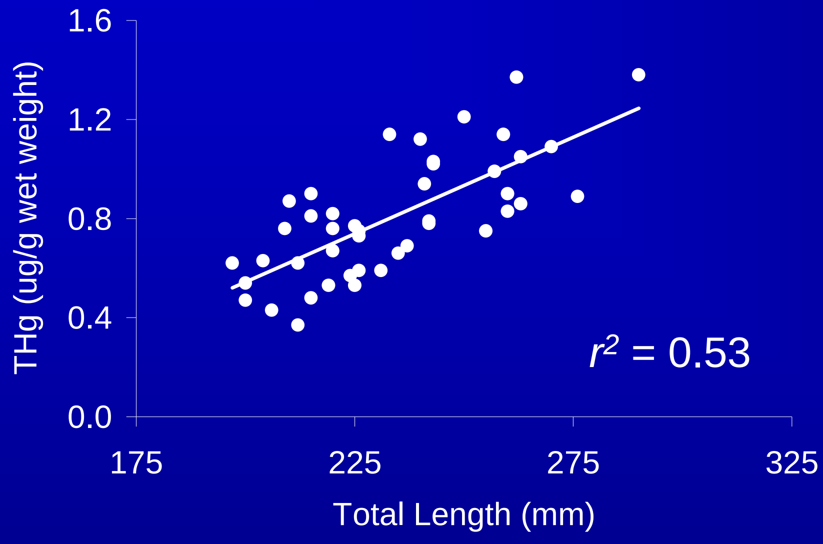
Study Area and Methods

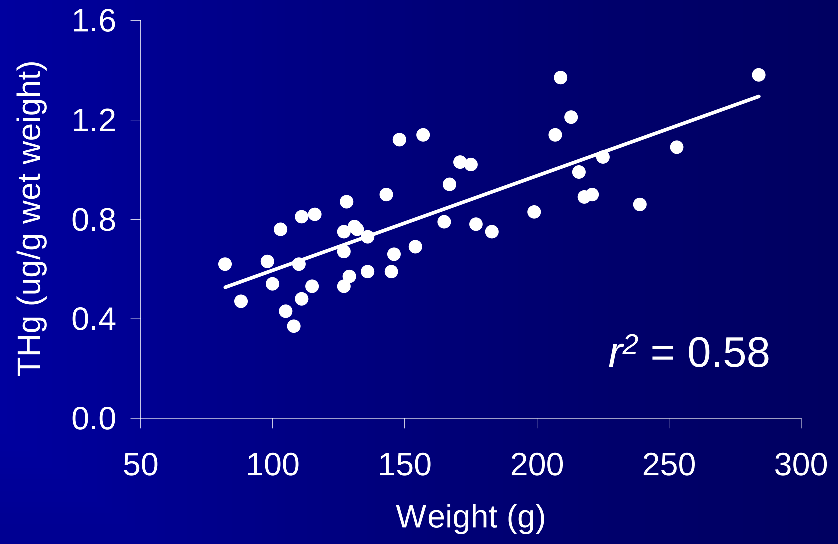


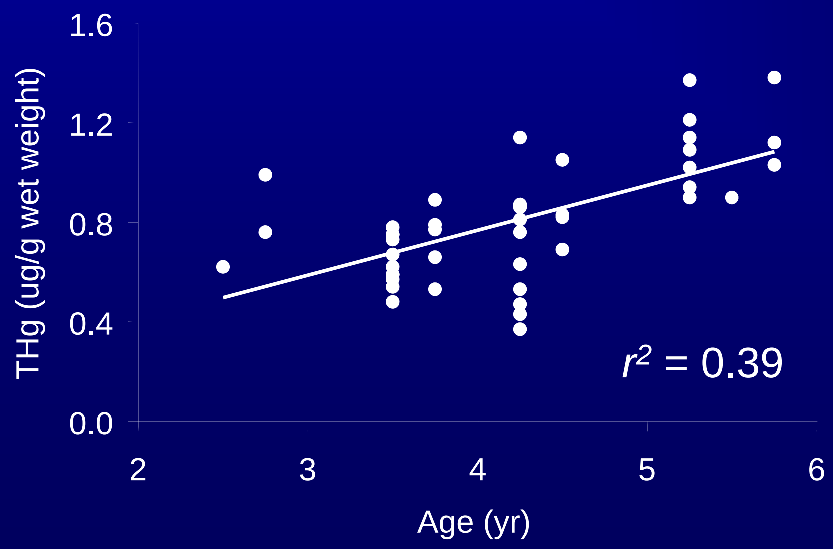
Collection Results

N	TL range (mm)	WT range (g)	Age range (yr)	Mean THg (µg/g)	THg range (µg/g)
			Spring		
8 females	206-270	105-253	4-5	0.94	0.37-1.37
9 males	200-263	88-239	4-5	0.78	0.47-1.14
			Summer		
7 females	197-263	82-221	2-5	0.79	0.62-1.05
10 males	200-255	100-183	3-4	0.65	0.48-0.82
			Fall		
6 females	209-243	103-171	2-5	0.86	0.66-1.12
5 males	225-290	127-284	2-5	0.82	0.30-1.38

Fish Size/Age and Mercury







ANCOVA Summary

Source	Type III sum of squares	Mean square	*F*	*P*
Age	0.594	0.594	12.62	**0.0010**
Sex	0.056	0.056	1.19	0.2820
Season	0.025	0.012	0.27	0.7667
Sex*Season	0.012	0.006	0.13	0.8742
Total Length	1.078	1.078	31.39	**<0.0001**
Sex	0.219	0.219	6.38	**0.0158**
Season	0.220	0.110	3.21	**0.0516**
Sex*Season	0.068	0.034	1.00	0.3775
Weight	1.192	1.192	38.08	**<0.0001**
Sex	0.200	0.200	6.39	**0.0157**
Season	0.118	0.059	1.89	0.1651
Sex*Season	0.091	0.045	1.45	0.2466

Sexual and Seasonal Patterns

- Mercury 10-20% higher in females than males
- Mercury 14-21% higher during spring than summer or fall

www.stewartsguideservice.com

Conclusions

- Sexual variations:
  - Growth dilution
  - Reproductive demands
- Seasonal variations:
  - Methylation rates
  - Food habits
  - Proximate composition of muscle tissue


www.watersheds.org


Management
Recommendations

Recommendations

Food Habits

- Assess size dependent patterns in channel catfish and white sucker
- Compare food habits of selected fish species during normal hydrologic conditions
- Investigate food habits for foundation of mercury bioaccumulation studies
- Research food habits of invertebrates and forage fish to better understand mercury uptake

Recommendations

Mercury in Invertebrates and Fish

- Monitor mercury in aquatic invertebrates or forage fish to track yearly differences in mercury
- Concentrate future monitoring/research in the vicinity of site SR6-Crimora on South River
- Assess concentrations of mercury in detritus
- Research sediment associations

Recommendations

Bioaccumulation Modeling

- Bioaccumulation models
- Couple BASS model to fate and transport model
- Address ecological impacts of remediation option
- Investigate population dynamics
- Make methylmercury focus of future studies

Recommendations

Sexual and Seasonal Differences

- Standardize sampling periods (spring)
- Record sex of fish
- Assess consistency and magnitude of sexual and seasonal variations among other species (e.g., channel catfish)


Questions?