MISSOURI
DEPARTMENT OF
NATURAL RESOURCES

Intent to Initiate Triennial Review of Missouri Water Quality Standards

PUBLIC COMMENTS

Public Notice
January 2 through March 2, 2019

Missouri Department of Natural Resources
Water Protection Program
PO Box 176
Jefferson City, MO 65102-0176
800-361-4827 / 573-751-1300

INTRODUCTION

The Missouri Department of Natural Resources made available for public comment the *Intent to Initiate Triennial Review of Missouri Water Quality Standards.* The public notice period was from January 2, 2019 through March 2, 2019. All original comments are included here in their entirety.

Comments were received from the following groups or individuals:

Blue Springs, Missouri Public Works Department
Heuser, Jeanne
Kennett Board of Public Works
McClure Engineering Company
Missouri Coalition for the Environment
National Waste and Recycling Association
Newman, Comley & Ruth P.C.

Blue Springs, Missouri
Public Works Department

March 1, 2019

Attn: Angela Falls
Water Quality Standards Coordinator
Water Protection Program
Missouri Department of Natural Resources
P.O. Box 176, Jefferson City, MO 65102

<<Sent Via E-mail>>

Re: Site-specific criteria for dissolved oxygen for City of Blue Springs and Sni-a-Bar Creek

Ms. Falls,

The City of Blue Springs (City) fully supports including site-specific dissolved oxygen criteria for the City and Sni-a-Bar Creek in the upcoming triennial review rule package. The City also thanks the Missouri Department of Natural Resources (MDNR) for having the opportunity to present on this issue before the Water Protection Forum on December 11, 2018. As you are aware, time-limited site-specific dissolved oxygen criteria (SSDOC) expired on October 31, 2014. It is important for the City and the Department to find a permanent solution for this issue. To this end, the City intends to submit a report summarizing additional data collection efforts in support of permanent SSDOC in the near future.

Please contact me if you have any questions or would like to discuss these matters further.

Sincerely,

Christopher G. Sandie, P.E.
Director of Public Works

Memorandum

TO: WQS Coordinator, Missouri Department of Natural Resources, Water Protection Program

FROM: Jeanne Heuser, Jamestown, MO

RE: Water Quality Standards Triennial Review Topics for Consideration

DATE: March 2, 2019

- **Ammonia as Nitrogen**

USEPA published the updated national water quality criteria (WQC) for ammonia in 2013 based on the high sensitivity of mussels and snails. On August 22, 2014, DNR published a fact sheet on ammonia criteria (Galbraith 2014), which did not have a firm target date for new standards development although stakeholder discussions apparently began. The fact sheet stated, "Part of the consideration during these discussions will include an evaluation of actual species of mussels native to Missouri and their sensitivity to ammonia."

Perhaps such an evaluation has been completed as shown in the 2017 study by researchers at the USGS in Columbia (Wang, et al. 2017). The study states, "Use of toxicity data from fatmucket, in conjunction with the available USEPA ICE models, should provide good estimates of risk to mussels regardless of their taxonomic classification for the purpose of deriving WQC or other environmental guidance values and conducting risk assessment."

There is an additional study since the previous stakeholder discussions that might provide some insight into WQC. Researchers created a model to evaluate a "mussel mortality threshold" (Bril, et al. 2017) and reported that the "model suggests the mortality threshold for juvenile *Lampsilis* species could be exceeded at low mussel biomass if exposed for even a short time to the highly elevated total N loadings endemic to the agricultural Midwest."

It is my understanding the science behind the USEPA mussel criteria is almost 20-years old and is well known and accepted. In addition, there are advancements in meeting ammonia limits since the 2013 USEPA WQC publication. I believe it is time to finalize the development of WQC for ammonia as nitrogen. It seems a collaboration with the researchers at the USGS Columbia Environmental Research Center with their extensive experience in mussel toxicity would be advantageous to accomplish the task.

- **Nutrient Criteria for Classified Rivers and Streams**
- **Human Health Protection 304(a)**

I believe it is essential to begin developing WQC for these two complex topics; a target date needs to be set, and a plan developed for moving forward.

References

Bril, JS, K Langenfeld, CL Just, SN Spak, and TJ Newton. 2017. "Simulated Mussel Mortality Thresholds as a Function of Mussel Biomass and Nutrient Loading." *PeerJ 5:e2838.* doi:10.7717/peerj.2838.

Galbraith, Ed. 2014. *Ammonia Criteria: New EPA Recommended Criteria.* Missouri Department of Natural Resources. https://dnr.mo.gov/pubs/pub2481.htm.

Wang, N, CH Ivey, CG Ingersoll, WG Brumbaugh, D Alvarez, EJ Hammer, CR Bauer, T Augspurger, S Raimondo, and MC Barnhart. 2017. "Acute Sensitivity of a Broad Range of Freshwater Mussels to Chemicals with Different Modes of Toxic Action." *Environmental Toxicology and Chemistry*, Vol. 36, No. 1: 786-796.

Simulated mussel mortality thresholds as a function of mussel biomass and nutrient loading

Jeremy S. Bril[1], Kathryn Langenfeld[1], Craig L. Just[1], Scott N. Spak[1] and Teresa J. Newton[2]

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ABSTRACT

A freshwater "mussel mortality threshold" was explored as a function of porewater ammonium (NH_4^+) concentration, mussel biomass, and total nitrogen (N) utilizing a numerical model calibrated with data from mesocosms with and without mussels. A mortality threshold of 2 mg-N L^{-1} porewater NH_4^+ was selected based on a study that estimated 100% mortality of juvenile *Lampsilis* mussels exposed to 1.9 mg-N L^{-1} NH_4^+ in equilibrium with 0.18 mg-N L^{-1} NH_3. At the highest simulated mussel biomass (560 g m^{-2}) and the lowest simulated influent water "food" concentration (0.1 mg-N L^{-1}), the porewater NH_4^+ concentration after a 2,160 h timespan without mussels was 0.5 mg-N L^{-1} compared to 2.25 mg-N L^{-1} with mussels. Continuing these simulations while varying mussel biomass and N content yielded a mortality threshold contour that was essentially linear which contradicted the non-linear and non-monotonic relationship suggested by *Strayer (2014)*. Our model suggests that mussels spatially focus nutrients from the overlying water to the sediments as evidenced by elevated porewater NH_4^+ in mesocosms with mussels. However, our previous work and the model utilized here show elevated concentrations of nitrite and nitrate in overlying waters as an indirect consequence of mussel activity. Even when the simulated overlying water food availability was quite low, the mortality threshold was reached at a mussel biomass of about 480 g m^{-2}. At a food concentration of 10 mg-N L^{-1}, the mortality threshold was reached at a biomass of about 250 g m^{-2}. Our model suggests the mortality threshold for juvenile *Lampsilis* species could be exceeded at low mussel biomass if exposed for even a short time to the highly elevated total N loadings endemic to the agricultural Midwest.

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Additional Information and Declarations can be found on page 13

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Keywords Native freshwater mussels, Ammonia mortality thresholds, Nutrients, Numerical modeling

INTRODUCTION

Native freshwater mussels are large (25–200+ mm in length), long-lived (>25 y) invertebrates that transfer nutrients from the overlying water to sediments through filter feeding (*Christian et al., 2005*). These benthic, burrowing, and suspension-feeding bivalves stimulate production across multiple trophic levels (*Vaughn, Nichols & Spooner, 2008*); the

biomass of healthy mussel beds can exceed the biomass of all benthic organisms by an order of magnitude (*Negus, 1966*; *Layzer Gordon & Anderson, 1993*). There are billions of mussels within the Upper Mississippi River (UMR) and the filtration capacity in a 480 km segment (about 13% of the river length), as a percentage of river discharge, is estimated to be up to 1.4% at high flows, up to 4.4% at moderate flows, and up to 12.2% during low flows (*Newton et al., 2011*). Collectively, these mussels filter over 14 billion gallons of water, remove tons of particulate organic matter from the overlying water, and deposit tons of ammonium (NH_4^+), associated ammonia (NH_3), and carbon at the sediment-water interface each day.

Our previous work showed that native freshwater mussels directly elevate NH_4^+ and indirectly elevate nitrate (NO_3^-) and nitrite (NO_2^-) concentrations in lab-based mesocosms (*Bril et al., 2014*). The increase in NH_4^+ concentrations by mussels has been associated with ingestion of food (e.g., algae, phytoplankton, bacteria, and fungi), digestion, and subsequent NH_4^+ excretion (*Thorp et al., 1998*; *Vaughn, Nichols & Spooner, 2008*). However, the dynamics among food, mussels, NH_4^+, and, more broadly the nitrogen (N) cycle, especially given increasing anthropogenic releases of nutrients to mussel habitats, remain poorly understood (*Strayer, 2014*). The negative aspects of increased nutrient loading are most frequently reported, but an increase in nutrients to some level, may favor growth and fecundity and may increase populations of host fish (*Strayer, 2014*). However, there is likely a threshold, such that extreme eutrophication may have negative consequences for mussels, perhaps by decreasing the fatty acid content of food (*Muller-Navarra et al., 2004*; *Basen Martin-Creuzburg & Rothhaupt , 2011*) and/or by increasing levels of toxic *Microcystis* algae (*Bontes et al., 2007*). These realities led us to examine where the biogeochemical boundaries and thresholds are that indicate healthy versus unhealthy outcomes for freshwater mussels as a function of variable nutrient loadings and mussel biomass. A hypothetical relationship between mussel abundance and nutrient loading has been proposed by *Strayer (2014)* (Fig. 1), that postulates thresholds for minimum food, NH_3 toxicity, interstitial hypoxia and toxic or poor algae quality. Strayer concluded that "it would be useful to identify early warning signs that the 'death threshold' is about to be crossed." Thus, the objective of our study was to develop a numerical model to conceptualize this "mortality threshold" as governed by mussel biomass and nutrient loading.

Little is known about minimum food thresholds (let alone food quality guidelines) for mussels and, in the current era of increasing nutrient loadings, this concept will likely become less relevant over time (*Bergstrom & Jansson, 2006*; *Strayer, 2014*). Therefore, we chose elevated porewater NH_4^+ concentration as an easily measured indicator of potential mortality thresholds for mussels. This is biologically relevant because native freshwater mussels have been shown to be some of the most sensitive organisms tested for NH_3 toxicity associated with equilibrium concentrations of NH_4^+ (*Augspurger et al., 2003*; *Newton & Bartsch, 2007*). A fraction of the toxic biological response, regardless of species, is almost certainly caused by NH_3 in equilibrium with NH_4^+. Therefore, NH_4^+ concentration is an acceptable surrogate for total ammonia nitrogen only when the temperature and pH of the aquatic habitat is known. The deposition of NH_4^+ and other reduced N species by

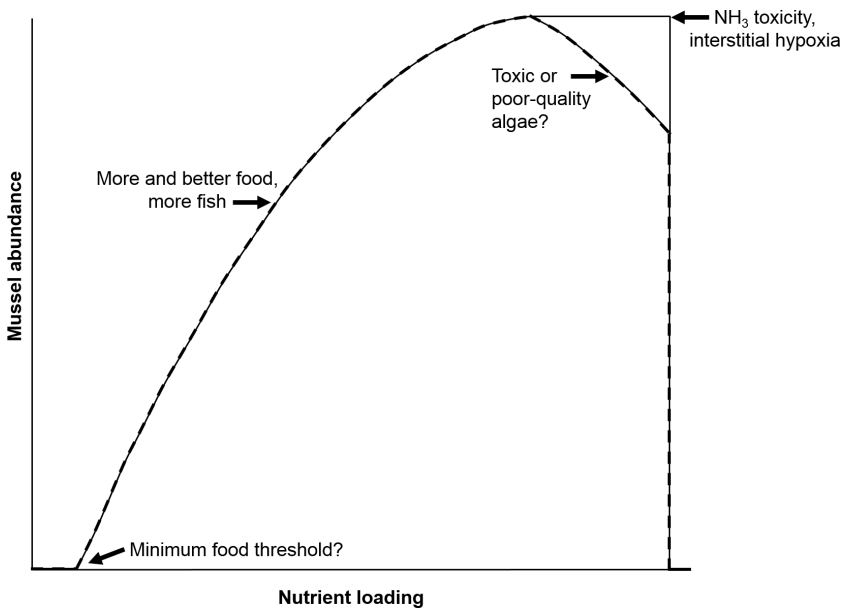

Figure 1 Hypothetical relationship between nutrient loading and mussel abundance. Concepts of minimum food threshold, ammonia toxicity, etc. are postulated to define the displayed curve. Adapted from *Strayer (2014)*.

mussels comes mostly in the form of feces and pseudofeces (*Vaughn, Gido & Spooner, 2004*; *Lauringson et al., 2007*; *Christian, Crump & Berg, 2008*; *Gergs, Rinke & Rothhaupt, 2009*). About 90% of the food taken in by mussels is excreted (*Christian, Crump & Berg, 2008*), which emphasizes the importance of knowing food concentrations, especially as a function of N content, when predicting associated porewater NH_4^+ concentrations.

This study focuses on an intensively sampled 10-d data set that was used to evaluate the ability of our numerical model to simulate food, NH_4^+, NO_2^-, NO_3^-, organic N (org N), and total N concentrations in the overlying water and porewater of continuous-flow laboratory mesocosms. The model was calibrated using literature values and water chemistry measurements from a separate, 7-d mesocosm sampling period reported in our previous work (*Bril et al., 2014*). The mussel species *Amblema plicata* and *Lampsilis cardium* were selected due to their abundance in the Iowa River (*Zohrer, 2006*) and throughout the UMR Basin (*Newton et al., 2011*), where N runoff from industrial agriculture severely impacts the aquatic N cycle. This research is novel in that a multi-rate nitrification/denitrification model was developed, calibrated, and evaluated with sensor-based, highly time-resolved data from mesocosms containing mussels. To our knowledge, this is the first use of such a model to simulate various "mortality threshold" scenarios for mussels.

MATERIALS AND METHODS

Mesocosm setup

Four 140 L, flow-through mesocosms (Fig. 2) continuously received untreated Iowa River water during the 107-d experiment, which culminated in an intensive 10-d water chemistry sampling period. Two mesocosms contained mussels collected from the Iowa

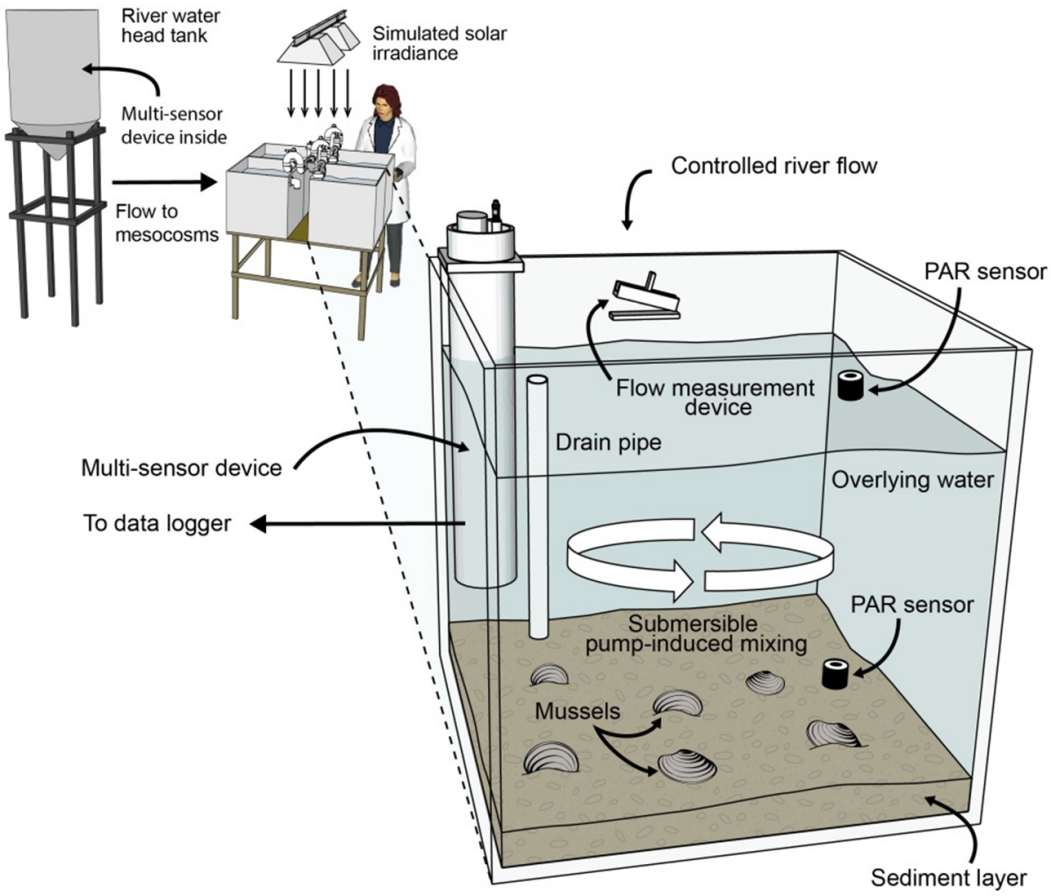

Figure 2 Schematic diagram of the flow-through, 4-mesocosm system, which was continuously fed Iowa River water (monitored with a multisensor device), contained a sand and river-sediment bottom layer and was irradiated with simulated sunlight (12 h daily). Each mesocosm was equipped with a constant head inlet, a flow measurement device, a recirculating pump, photosynthetically active radiation (PAR) sensors, and a multisensor, water-chemistry device. Two mesocosms contained mussels, and 2 contained no mussels.

River and two were without mussels (control). Twelve adult *A. plicata* and 13 adult *L. cardium* were placed in one mesocosm and 13 *A. plicata* and 12 *L. cardium* were placed in another mesocosm. This approximates a density of 70 mussels m^{-2}, which although high, is still a realistic density in some reaches of the UMR (*Newton et al., 2011*). Across both mesocosms, shell length (±1 standard deviation) was 95 ± 20 mm in *A. plicata* and 120 ± 25 mm in *L. cardium*. Initially, all mesocosms contained 8 cm of purchased sand substrate, but particulate deposition from the river water altered this composition over time. A gravity-fed, constant head system provided a controllable flow rate between 9 and 55 L h^{-1}. The flow rate during the 10-d intensive sampling period was 8.5 L h^{-1} (16 h hydraulic residence time). Complete mixing in each mesocosm was provided by 1,500 L h^{-1} submersible pumps, and two 1,000-watt solar simulators provided illumination on a 12:12 h light–dark cycle. Additional details regarding the mussel mesocosm system are available elsewhere (*Bril et al., 2014*).

Mesocosm sampling and analyses

Data from a 10-d intensive sampling period (days 97–107 of the 107-d experiment) were used for model evaluation. We intentionally delayed the start of the intensive sampling by 97 days so that the mussels could acclimate and bacteria responsible for nitrification and denitrification could establish. Electronic water chemistry sensors (model DS5; Hach Chemical Company, Loveland, CO, USA) were used to measure highly time-resolved (30-min) water chemistry data in the overlying water of each mesocosm and in the influent head tank. The sensors measured chlorophyll *a* (chl-*a*), NH_4^+, NO_3^-, pH, and temperature. Custom-made flow measurement devices with magnetic reed switches were used to quantify influent flow. Photosynthetically active radiation (PAR) sensors (model SQ-120; Apogee Instruments, Logan, Utah) were used to measure solar irradiance at the substrate and water surface of each mesocosm. All measurements obtained by the sensors were collected and stored using two data loggers. The model inputs for influent river temperature, food, NH_4^+, NO_2^-, NO_3^- and org N (Fig. 3) were measured values from within the river water head tank during the 10-d sampling period.

Discrete water chemistry samples were collected and analyzed at five time points during the 10-d sampling period from the overlying water and porewater of each mesocosm and from the influent head tank. The discrete samples were analyzed for chl-*a*, NH_4^+, NO_2^-, NO_3^-, org N, and total N. Chl-*a* was measured by fluorescence. Measured chl-*a* concentrations ($\mu g\ L^{-1}$) were converted to "food" biomass ($mg\ L^{-1}$) based on literature values for phytoplankton chl-*a* content (*Kasprzak et al., 2008*). The fraction of nitrogen in food biomass ($mg\text{-}N\ L^{-1}$) was calculated using the empirical formula $C_{106}H_{263}O_{110}N_{16}P$ (*Chapra, 1997*). NH_4^+ was determined using the Salicylate Method, and NO_3^- was determined using the Dimethylphenol Method (*APHA, 1996*). NO_2^- was measured using the Diazotization Method, and total N was measured using the Persulfate Digestion Method (*APHA, 1996*). Sample measurements for org N were estimated by subtracting the sum of NH_4^+, NO_3^-, and NO_2^- from the total N measurements. A more detailed description of the mesocosm sampling and analysis setup is available (*Bril et al., 2014*).

Model calibration and sensitivity analyses

Seven days of the 107-d experiment were intensively sampled and previously reported (*Bril et al., 2014*) for food, NH_4^+, NO_2^-, NO_3^-, org N, and temperature; these values were used as model calibration inputs. Linear interpolation between discrete samples was used where 30-min measurements were unavailable (org N, NO_2^-, and total N), and ranges for unmeasured model variables (e.g., nitrification rate, denitrification rate) were obtained from the literature (Table 1). The model, created in Stella (version 8.0, ISEE Systems, Inc., Lebanon, New Hampshire), was initially calibrated using the no-mussel control data, then refined using data from mesocosms containing mussels to properly parameterize clearance and excretion rates (*Bayne, Hawkins & Navarro, 1987*; *Englund & Heino, 1994*; *Haag, 2012*). The optimized values used in the model calibration are given in Table 1. The optimized calibration values were determined by comparing model outputs to sensor

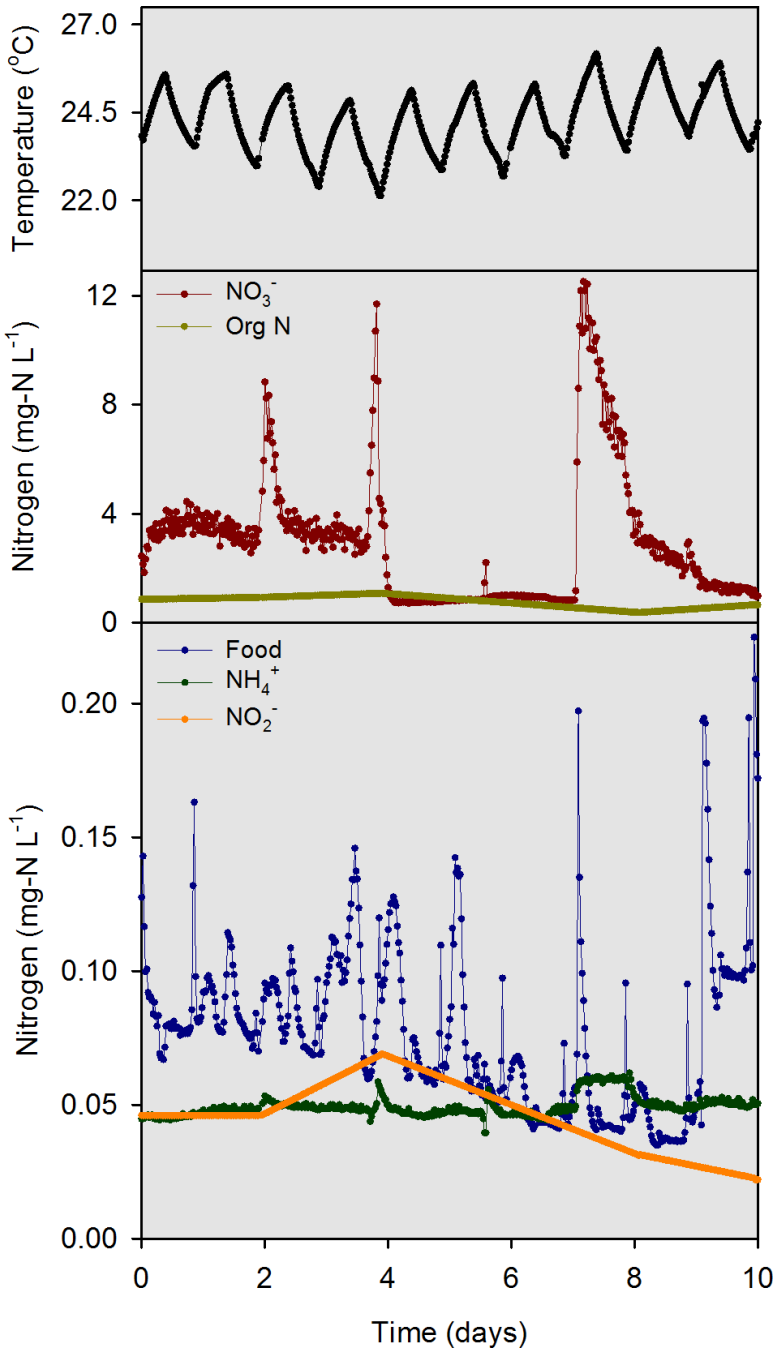

Figure 3 **Model input data for temperature, food (converted from chl *a* data), NH_4^+, NO_2^-, NO_3^-, and org N as measured in the river water head tank during the 10-d model evaluation period.**

and discrete sample measurements and then minimizing normalized mean error and maximizing R^2 values (Table 2).

Sensitivity analyses were conducted to identify the most important variables contributing to net system dynamic concentration response. A single variable sensitivity analysis was completed by adjusting the model variables based on a range of literature values (Table 1).

Table 1 Model calibration values.

Variable	Description	Literature range	Calibration
H	Water depth (m)	–	0.406
$k_{ai}(T)$	NH_4^+ to NO_2^- nitrification rate (h^{-1})	–	0.12
k_{am}	Half-saturation constant for NH_4^+ preference (mg-N L^{-1})	0.001–0.05 (*Chapra, 1997*)	0.05
$k_d(T)$	Food death rate (h^{-1})	0.0021–0.0104 (*Schnoor, 1996*)	0.002
$k_{dn}(T)$	Denitrification rate (h^{-1})	0.0005–0.0996 (*Richardson et al., 2004*)	0.0005
$k_{g,T}$	Food growth rate (h^{-1})	0.0417–0.0833 (*Schnoor, 1996*)	0.025
$k_{hn}(T)$	Org N hydrolysis rate (h^{-1})	0.00004–0.0083 (*Schnoor, 1996*)	0.00004
$k_{ig}(T)$	NO_2^- to N_2 gas denitrification rate (h^{-1})	–	0.0005
$k_{in}(T)$	NO_2^- to NO_3^- nitrification rate (h^{-1})	–	0.21
$k_n(T)$	Nitrification rate (h^{-1})	0.0001–0.21 (*Strauss et al., 2004*)	0.1
$k_{ni}(T)$	NO_3^- to NO_2^- denitrification rate (h^{-1})	–	0.0005
$k_{ra}(T)$	Food respiration/excretion rate (h^{-1})	0.0004–0.0208 (*Chapra, 1997*)	0.004
k_{sn}	Nitrogen half-saturation constant (mg-N L^{-1})	0.005–0.02 (*Chapra, 1997*)	0.02
k_{sp}	Phosphorus half-saturation constant (mg-P L^{-1})	0.001–0.005 (*Chapra, 1997*)	0.005
M_b	Mussel biomass (g)	–	200
M_{cl}	Mussel clearance rate (h^{-1} g^{-1} mussel biomass)	0.000007–0.00786 (*Silverman et al., 1997*; *Spooner & Vaughn, 2008*; *Newton et al., 2011*)	0.002[a], 0.0005[b]
M_{ex}	Mussel excretion rate (mg-N L^{-1} h^{-1} g^{-1} mussel biomass)	0.0001–0.00083 (*Baker & Hornbach, 2000*; *Baker & Hornbach, 2001*; *Christian et al., 2008*; *Spooner & Vaughn, 2008*)	0.00009[a], 0.000075[b]
p	Phosphorus concentration (mg-P L^{-1})	0.04–1.31 (*Espinosa-Villegas et al., 2004*)	0.3
T	Temperature (°C)	5–25 (*Espinosa-Villegas et al., 2004*)	Variable
$V_{s,a}$	Food + settling rate (m h^{-1})	0–0.083 (*Schnoor, 1996*)	0.001
$V_{s,o}$	Org N settling rate (m h^{-1})	0–0.083 (*Schnoor, 1996*)	0.001
τ	Hydraulic retention time (h)	–	2.5
φ_L	Light attenuation factor	0–1 (*Steele, 1965*)	Variable

Notes.
[a]Value used when food concentration > 0.1 mg-N L^{-1}, and hydraulic retention time < 12 h.
[b]Value used when food concentration ≤ 0.1 mg-N L^{-1}, and hydraulic retention time < 12 h.

When such information was unavailable, the value of the variable used in model calibration was adjusted by ±50%. Ten sensitivity model runs were completed for each variable using values obtained by sampling the range of literature values (or ±50% adjustments) at 10 equal intervals. The sensitivity analysis was considered for the normalized sensitivity coefficient (*Fasham, Ducklow & McKelvie , 1990*) (NSC):

$$\mathrm{NSC} = \left(\frac{\frac{\varphi}{\varphi_0}}{\frac{P}{P_0}} \right) \frac{P_0}{\varphi_0} \tag{1}$$

where, φ = mean value of a parameter (e.g., NH_4^+, NO_3^-) over the simulation period for the sensitivity run (mg-N L^{-1}), φ_o = mean value of a parameter over the simulation period for the calibrated model (mg-N L^{-1}), P = value of model variable in sensitivity run, and P_o = value of model variable in calibrated model. The NSC values for each sensitivity run were averaged to determine a net NSC for each model variable.

Table 2 Model performance statistics.

Measurement type	Parameter	Concentration (mg-N L^{-1})				Mean bias (mg-N L^{-1})	Mean error (mg-N L^{-1})	NMB	NME	R^2	RMSE
		Observed		Simulated							
		Mean	SD	Mean	SD						
7-d model calibration											
Sensor	Food	0.07	0.03	0.07	0.04	0.004	0.013	5.2%	20%	0.81	0.018
	NH_4^+	0.09	0.01	0.09	0.01	−0.001	0.005	−1.3%	6%	0.33	0.006
	NO_3^-	0.62	0.11	0.62	0.10	0.0001	0.024	0.02%	4%	0.94	0.030
Discrete sample	Food	0.07	0.03	0.07	0.03	−0.007	0.037	−9.9%	51%	0.01	0.045
	NH_4^+	0.09	0.02	0.09	0.01	−0.002	0.012	−2.4%	13%	0.10	0.015
	NO_3^-	0.61	0.14	0.61	0.11	0.004	0.034	0.6%	6%	0.91	0.048
	Org N	0.49	0.13	0.49	0.15	0.002	0.118	0.3%	24%	0.19	0.142
	NO_2^-	0.05	0.01	0.04	0.01	−0.002	0.006	−5.2%	12%	0.37	0.006
	Total N	1.2	0.18	1.2	0.19	−0.00004	0.111	−0.003%	9%	0.54	0.133
10-d model evaluation											
Sensor	Food[a]	0.08	0.03	0.08	0.03	−0.013	0.013	−17.1%	17.1%	0.85	0.016
	NH_4^+	0.03	0.002	0.03	0.002	0.0003	0.001	1.0%	7.7%	0.35	0.001
Discrete sample	NO_3^-	3.5	1.8	3.0	1.3	−0.513	0.549	−14.5%	15.5%	0.93	0.817
	Food	0.03	0.02	0.09	0.04	0.064	0.065	250%	260%	0.51	0.080
	NH_4^+	0.04	0.01	0.03	0.002	−0.004	0.011	−11%	28%	0.06	0.014
	NO_3^-	4.3	2.5	3.5	1.5	−0.874	0.938	−20%	22%	0.98	1.391
	Org N	0.79	0.14	0.77	0.24	−0.027	0.090	−3.4%	11%	0.78	0.121
	NO_2^-	0.03	0.01	0.03	0.005	0.001	0.006	3.1%	19%	0.62	0.006
	Total N	5.2	2.5	4.3	1.5	−0.903	0.954	−17%	18%	0.96	1.296

Notes.
[a]25 day moving average.
SD, Standard deviation; NMB, Normalized mean bias; NME, Normalized mean error; RMSE, Root mean square error.

Mussel mortality threshold simulations

Based on 28-day laboratory toxicity tests with juvenile fat mucket mussels (*Lampsilis siliquoidea*), *Wang et al. (2011)* reported that 100% mortality occurred at 2.08 mg L^{-1} total ammonia nitrogen (TAN). Given the pH (8.2) and temperature (20 °C) of that study, of the 2.08 mg L^{-1}TAN, about 1.9 mg-N L^{-1} would be in the NH_4^+ form and about 0.18 mg-N L^{-1} would be in the NH_3 form. Given that our models were developed at a similar pH (8.2) and temperature (24 °C) to the *Wang et al. (2011)* study, we selected 2.0 mg-N L^{-1} NH_4^+ in porewater as a surrogate mortality threshold for *Lampsilis* mussels. Furthermore, the US Environmental Protection Agency (EPA) determined species mean chronic values of NH_3 for *Lampsilis siliquoidea* and *L. fasciola* to calculate a geometric mean chronic NH_3 value of 2.1 mg-N L^{-1} for the genus *Lampsilis* (*US Environmental Protection Agency, 2013*).

The average measured porewater concentrations for NH_4^+, NO_3^-, NO_2^-, org N, and food during the 10-d evaluation period (3.9, 0.2, 0.06, 5, and 0.1 mg-N L^{-1}, respectively) were used as initial conditions for porewater in the model. The average overlying water concentrations for the same variables were 0.05, 5, 0.05, 2.8, and 0.1 mg-N L^{-1}, respectively, and the "river water" inputs for 90-d model simulations were initially set to these values.

The mussel density in our mesocosms was converted to estimated biomass (g m^{-2}) using the allometric function, $M = aL^b$, where M is tissue dry mass (g) and L is length (mm) and with values for "a" and "b" for *A. plicata* taken from the literature (*Newton et al., 2011*). The resulting mass of 6.0 g $mussel^{-1}$ was multiplied by 35 mussels m^{-2} (half the population) to determine an estimated biomass of 210 g m^{-2} for *A. plicata*. In the absence of allometric data for *L. cardium*, the tissue dry mass was assumed to be 10 g $mussel^{-1}$(167% of *A. plicata*), and when multiplied by 35 mussels m^{-2} resulted in a biomass of 350 g m^{-2}. Adding these values gave a maximum biomass of 560 g m^{-2}, which was used as the upper bound for the simulations. To simulate changes in porewater NH_4^+ concentration as a function of mussel biomass and food availability, mussel biomass was varied at zero, 140, 280, 420 and 560 g m^{-2} while the N content of food was varied at zero, 0.1, 1, 5 and 10 mg-N L^{-1}.

RESULTS AND DISCUSSION

Model Evaluation

For the river water head tank (pH 8.2), a combination of sensor data (temperature, NO_3^-, "food," and NH_4^+) and interpolated discrete data (org N and NO_2^-) were collected and used as input to the numerical model on a 30 min time step (Fig. 3). For overlying water in mesocosms, the "food" sensor data were converted to a 25-d moving average (Fig. 4A) to condition the inherently noisy signal to enable visual comparison to the model output. The discrete sample results for NO_2^- concentrations in the overlying water were similar in magnitude, but did not agree closely with the model output (Fig. 4B). The model output for NH_4^+ and NO_3^- concentrations (Figs. 4C and 4D) compared well with the sensor measurements. Overall, the model was capable of outputting results that accurately predicted the concentrations, and most of the dynamics, of the major N species at a 30 min time interval for the 10-d evaluation period.

The model was evaluated quantitatively using the standard deviation (SD) of the measured data variable compared to the root mean square error (RMSE) of the model output. If the RMSE was less than half the SD, the model output for that variable was deemed "accurate" (*Singh et al., 2005*; *Moriasi et al., 2007*). For comparative purposes, values for the mean bias, mean error, normalized mean bias, normalized mean error, and R^2 are reported along with the SD and RMSE for food, NH_4^+, NO_2^-, NO_3^-, org N, and total N for the 7-d model calibration and 10-d evaluation periods (Table 2). The RMSE to SD ratio was $\leq$0.5 for the sensor-measured data for food, NH_4^+ and NO_3^- for the 10-d evaluation period. The model evaluation based on discrete sample data yielded mixed results with RMSE to SD ratios of 0.55, 0.60, and 0.52 for NO_3^-, NO_2^- and total N, respectively. The RMSE to SD ratios for food, NH_4^+, and org N were 4.0, 1.4, and 0.86 for the discrete sample data, respectively. The lower accuracy determinations based on discrete sample data were likely a function of the small sample sizes, as compared to sensor measurements, and the low concentrations of food and NH_4^+ which challenged the analytical limits of quantitation for these variables.

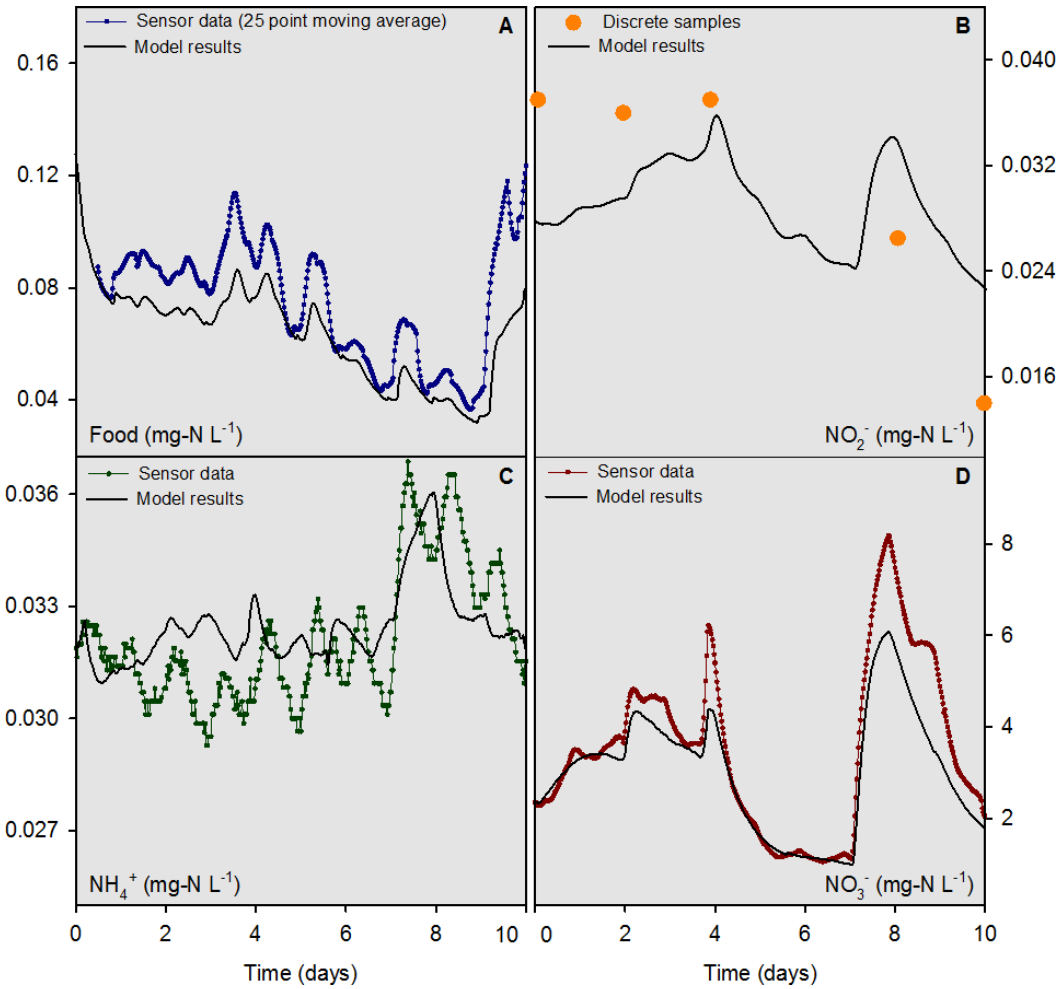

Figure 4 **Overlying water sensor data and discrete sample results from the mesocosms containing mussels compared to model outputs for food, NH_4^+, NO_2^-, and NO_3^- for the 10-d model evaluation period.**

Sensitivity analysis

The modeled nitrogen species were collectively most sensitive to changes in temperature, hydraulic retention time, and mussel biomass (Table 3). Temperature was expected to be an influential variable since the majority of the first-order rate expressions are temperature dependent. Hydraulic retention time was also expected to be influential since the influent river water has a major impact on mesocosm water chemistry in a continuous-flow system. Mussel biomass was an unexpectedly sensitive model variable. However, given the influence of mussels on food, NH_4^+, NO_2^-, and NO_3^- concentrations shown in our previous work (*Bril et al., 2014*), this result, in hindsight, should have been anticipated.

Mussel mortality threshold simulations

At the highest simulated mussel biomass (555 g m^{-2}) and the lowest simulated influent water food concentration (0.1 mg-N L^{-1}), the porewater NH_4^+ concentration after a 2,160 h timespan in the absence of mussels, was 0.5 mg-N L^{-1} compared to 2.3 mg-N L^{-1} in the

Table 3 **Most influential variables for simulated parameters (in decreasing order).**

Food	NH_4^+	NO_2^-	NO_3^-	Org N	Total N
Temperature	Mussel excretion rate	NH_4^+ to NO_2^- rate	Temperature	Water depth	Temperature
Mussel biomass	Mussel biomass	NO_2^- to NO_3^- rate	Hydraulic retention time	Org N settling rate	Mussel biomass
Hydraulic retention time	Nitrification rate	Temperature	Nitrification rate	Hydraulic retention time	Mussel excretion rate

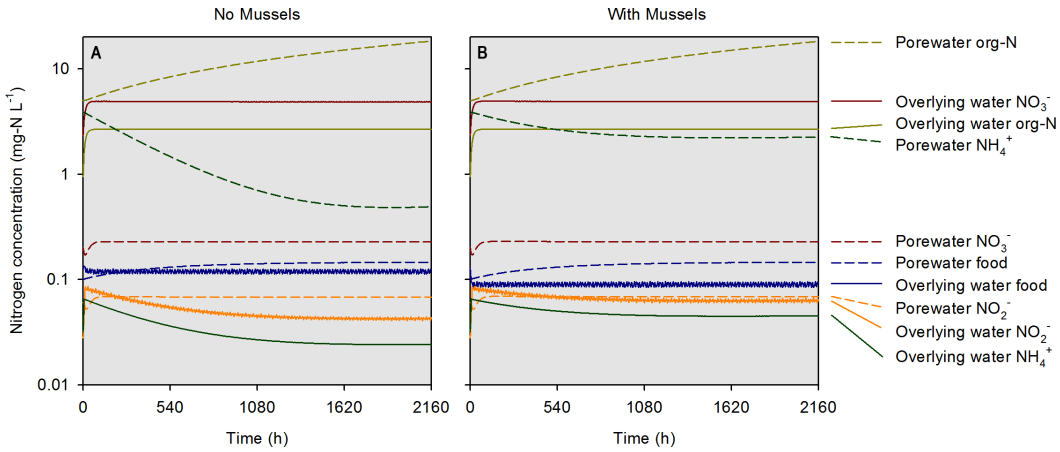

Figure 5 **Simulated concentrations of various nitrogen-containing species over a 2,160 h (90 d) timespan in the absence and presence of mussels at a specific biomass (560 g m^{-2}).** Modeled constituents in porewater and overlying water are shown by dashed and solid lines, respectively.

presence of mussels (Fig. 5). The food concentration in mesocosms without mussels was visibly higher than in mescocosms with mussels while NH_4^+ and NO_2^- concentrations in overlying water were lower in the absence of mussels. Mortality threshold contours were estimated by varying mussel biomass and N concentration in the model (Fig. 6). Even when the simulated overlying water food availability was low, the mortality threshold was reached at a mussel biomass of about 480 g m^{-2}. At a food concentration of 10 mg-N L^{-1} the mortality threshold was reached at a biomass of about 250 g m^{-2}.

In eastern Iowa, the median total N concentration in rivers and streams is commonly >10 mg-N L^{-1} (*Kalkhoff et al., 2000*), which can place juvenile freshwater mussels at particular risk to ammonia toxicity. Minnesota has a draft criterion for aquatic life of 4.9 mg-N L^{-1} total N, which was exceeded in 68% of samples collected in a study of Iowa waters between 2004 and 2008 (*Garrett, 2012*). The US EPA national recommended final acute ambient water quality criterion (AWQC) for protecting freshwater organisms from potential effects of ammonia is 17 mg-N L^{-1} and the final chronic AWQC for ammonia is 1.9 mg-N L^{-1} at pH 7.0 and 20 °C (*US Environmental Protection Agency, 2013*). At a total N concentration of 10 mg L^{-1}, our model predicts the mortality threshold to be reached when mussel biomass is about 400 g m^{-2}. However, the maximum total N concentration measured between 2004 and 2008 was 37.8 mg-N L^{-1} (*Garrett, 2012*). Our model suggests

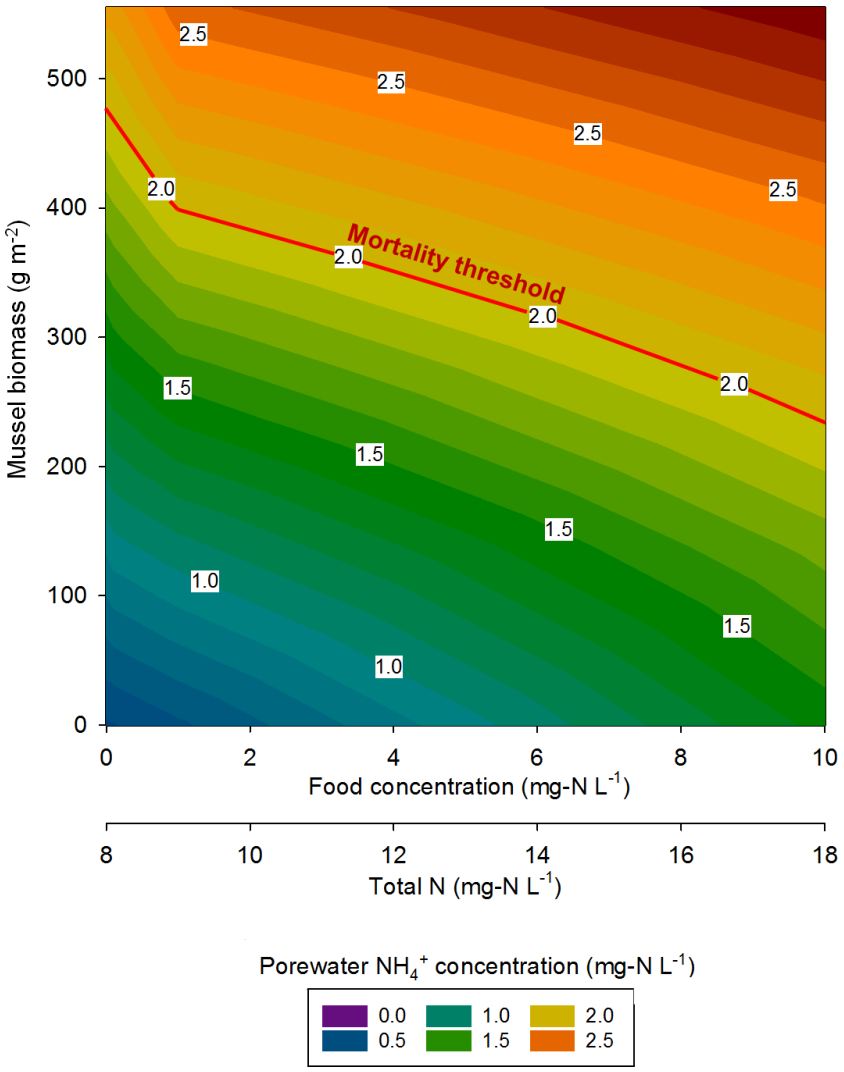

Figure 6 **The mussel mortality threshold, defined as a porewater NH_4^+ concentration of ≥2 mg-N L^{-1} as a function of mussel biomass, overlying water food concentration, and overlying water total N concentration.**

the mortality threshold for juvenile *Lampsilis* could be exceeded at low mussel biomass if even a short exposure occurs at such a high total N concentration.

Reflecting on the relationships between nutrients and freshwater mussels conceptualized by *Strayer (2014)*, we concur that high nutrient loads (particularly N in the agricultural Midwest) are a threat to the well-being of mussels. Conversely, our model predicts a somewhat linear mortality threshold relationship as mussel biomass and total N are varied, whereas Strayer stated this relationship would probably be non-linear and non-monotonic. In agreement with Strayer, our model suggests that mussels spatially focus nutrients from the overlying water to the sediments as evidenced by elevated porewater NH_4^+ in mescosms with mussels. However, our previous work (*Bril et al., 2014*), and the model developed here, show elevated concentrations of NO_2^- and NO_3^- in overlying waters as an indirect

consequence of mussel activity. This still represents a spatial focusing of nutrients by mussels, but the impact is not seen in the sediment alone.

CONCLUSIONS

The concept of a variable "mussel mortality threshold" as a function of mussel biomass and nutrient loading was successfully explored using a numerical model calibrated with data from mesocosms with and without mussels. With a threshold porewater NH_4^+ value of 2 mg-N L^{-1}, mussel mortality was predicted to occur well within the range of documented total N concentrations in eastern Iowa rivers and streams and at biologically relevant mussel biomasses. The model could be used as a screening tool to determine when mussel populations might be at risk due to high levels of chronic and acute nutrient loadings.

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ADDITIONAL INFORMATION AND DECLARATIONS

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Competing Interests

The authors declare there are no competing interests.

Author Contributions

- Jeremy S. Bril and Kathryn Langenfeld conceived and designed the experiments, performed the experiments, analyzed the data, wrote the paper, prepared figures and/or tables, reviewed drafts of the paper.
- Craig L. Just conceived and designed the experiments, analyzed the data, contributed reagents/materials/analysis tools, wrote the paper, prepared figures and/or tables, reviewed drafts of the paper.
- Scott N. Spak and Teresa J. Newton conceived and designed the experiments, analyzed the data, contributed reagents/materials/analysis tools, wrote the paper, reviewed drafts of the paper.

Data Availability

The following information was supplied regarding data availability:

The raw data used to run one model simulation is in Figs. 3 and 4. The model equations are in the Supplemental Information.

Supplemental Information

Supplemental information for this article can be found online at http://dx.doi.org/10.7717/peerj.2838#supplemental-information.

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ACUTE SENSITIVITY OF A BROAD RANGE OF FRESHWATER MUSSELS TO CHEMICALS WITH DIFFERENT MODES OF TOXIC ACTION

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Abstract: Freshwater mussels, one of the most imperiled groups of animals in the world, are generally underrepresented in toxicity databases used for the development of ambient water quality criteria and other environmental guidance values. Acute 96-h toxicity tests were conducted to evaluate the sensitivity of 5 species of juvenile mussels from 2 families and 4 tribes to 10 chemicals (ammonia, metals, major ions, and organic compounds) and to screen 10 additional chemicals (mainly organic compounds) with a commonly tested mussel species, fatmucket (*Lampsilis siliquoidea*). In the multi-species study, median effect concentrations (EC50s) among the 5 species differed by a factor of $\leq$2 for chloride, potassium, sulfate, and zinc; a factor of $\leq$5 for ammonia, chromium, copper, and nickel; and factors of 6 and 12 for metolachlor and alachlor, respectively, indicating that mussels representing different families or tribes had similar sensitivity to most of the tested chemicals, regardless of modes of action. There was a strong linear relationship between EC50s for fatmucket and the other 4 mussel species across the 10 chemicals ($r^2 = 0.97$, slope close to 1.0), indicating that fatmucket was similar to other mussel species; thus, this commonly tested species can be a good surrogate for protecting other mussels in acute exposures. The sensitivity of juvenile fatmucket among different populations or cultured from larvae of wild adults and captive-cultured adults was also similar in acute exposures to copper or chloride, indicating captive-cultured adult mussels can reliably be used to reproduce juveniles for toxicity testing. In compiled databases for all freshwater species, 1 or more mussel species were among the 4 most sensitive species for alachlor, ammonia, chloride, potassium, sulfate, copper, nickel, and zinc; therefore, the development of water quality criteria and other environmental guidance values for these chemicals should reflect the sensitivity of mussels. In contrast, the EC50s of fatmucket tested in the single-species study were in the high percentiles (>75th) of species sensitivity distributions for 6 of 7 organic chemicals, indicating mussels might be relatively insensitive to organic chemicals in acute exposures. *Environ Toxicol Chem* 2017;36:786–796. Published 2016 Wiley Periodicals, Inc. on behalf of SETAC. This article is a US government work and, as such, is in the public domain in the United States of America.

Keywords: Juvenile mussels Acute toxicity Water quality criteria Water quality guidelines Species sensitivity distribution

INTRODUCTION

Freshwater mussels (order Unionoida) are one of the most imperiled groups of animals, and environmental contamination has been identified as a causal or contributing factor to the decline of mussel populations [1–4]. Previous studies indicate that freshwater mussels are more sensitive than commonly tested organisms to some chemicals (e.g., copper, ammonia, and chloride [5–11]). However, mussels are generally underrepresented in toxicity databases used for the development of water quality criteria, standards, and other environmental guidance values [6,7,12,13]. In addition, the limited mussel data available have been generated mostly from toxicity tests with a few species of the taxonomic tribe Lampsilini [5–16]. Studies with broader phylogenetic representation are needed to understand the range of sensitivity among freshwater mussels, compare the overall sensitivity of mussels to other freshwater species, and evaluate the degree to which existing or proposed environmental guidance values are protective of mussels.

Freshwater mussels are a taxonomically diverse group of bivalve mollusks with a complex reproductive cycle. Approximately 300 species in the order Unionoida historically occur in North America. These species are classified in 2 families, with 5 in the family Margaritiferidae and the rest in the family Unionidae. Unionidae include 2 subfamilies, the Unioninae and the Ambleminae. Subfamily Unioninae includes the tribe Anodontini, and subfamily Ambleminae includes tribes Lampsilini, Amblemini, Pleurobemini, Quadrulini, and Gonideini [17]. Ambleminae includes 250 North American species and 37 genera, which represent 85% of North American species and 75% of North American genera of Unionoida [17,18]. Most freshwater mussels have a reproductive cycle involving a parasitic stage on fish. Sperm released by a male enters a female through the incurrent siphon, and fertilized eggs develop to larvae called glochidia, which mature in specialized chambers (marsupia) of the mussel gills. Glochidia are released into the water and must attach to the gills or fins of a suitable host fish. After 1 wk to several weeks of the parasitic stage, glochidia transform to juvenile mussels, detach from the fish, and drop to the stream or lake bottom to begin the free-living juvenile stage.

The primary objectives of the present study were, first, to compare the sensitivity of 5 phylogenetically diverse species of mussels in acute exposures to 10 chemicals with different modes of toxic action (multi-species study) and, second, to screen 10

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additional chemicals with a commonly tested mussel species (single-species study). For the multi-species study, the family Margaritiferidae was represented by western pearlshell (*Margaritifera falcata*), which is native to the western United States, and the family Unionidae was represented by threeridge (*Amblema plicata*; Amblemini), paper pondshell (*Utterbackia imbecillis*; Anodontini), fatmucket (*Lampsilis siliquoidea*; Lampsilini), and washboard (*Megalonaias nervosa*; Quadrulini), which are distributed widely in the Midwest and the Southeast of the United States. These mussels include 2 life-history strategies [4]: 2 short-term brooders and 3 long-term brooders (Table 1). Fatmucket was selected for the single-species study with 10 additional chemicals because it has been used widely in previous toxicity tests in the United States and Canada [5–7,11,13,14]. In addition, the sensitivity of the commonly tested fatmucket among different populations was evaluated in acute exposures to 2 commonly used reference toxicants (copper and sodium chloride).

The 10 chemicals selected for the multi-species study were 2 organic compounds used as herbicides (alachlor and metolachlor), ammonia, 3 major ions (potassium, chloride, and sulfate), and 4 metals (chromium [VI], copper, nickel, and zinc; Table 2). These chemicals were selected based on interest of the US Environmental Protection Agency (USEPA) in developing or updating ambient water quality criteria, the availability of toxicity data for non-mollusk species (e.g., at least 10 species) in the USEPA Interspecies Correlation Estimation (ICE) database [19,20], the high sensitivity of mollusks that are not mussels, different chemical classes and modes of toxicity action [21], and environmental relevance. The 10 chemicals for the single-species study (Table 2) were selected based on the same approach for chemical selection in the multi-species study except that no or few toxicity data from mussels were available for these chemicals. The chemicals used in the single-species study included 7 organic compounds used as pesticides (2,4-dichlorophenoxyacetic acid, 4-nonylphenol, azoxystrobin, bifenthrin, carbaryl, malathion, and molinate), arsenic (V), calcium chloride, and aluminum.

Two air-breathing freshwater snail species (*Physa gyrina* and *Lymnaea stagnalis*) and 3 commonly tested invertebrates (amphipod *Hyalella azteca*, and cladocerans *Ceriodaphnia dubia* and *Daphnia magna*) were also tested in acute exposures with the 10 chemicals used in the multi-species study following ASTM International standard methods [22]. The methods and results for the acute exposures with the snails and other invertebrates are reported in a companion paper Ivey et al. [23] in this issue. However, the toxicity data from these non-mussel species were included in toxicity databases compiled in the present study to compare the mussel sensitivity with that of other freshwater species.

MATERIALS AND METHODS

Acute 96-h toxicity tests with newly transformed (6 d to 10 d old) juvenile mussels were conducted following ASTM International standard methods [24]. Conditions for conducting the toxicity tests are summarized in Supplemental Data, Table S1.

Test organisms

Gravid female mussels brooding mature glochidia (larval mussels) were collected during early season of glochidia release between 2012 and 2015 from Missouri, USA (fatmucket, paper pondshell); Wisconsin, USA (threeridge, washboard); and California, USA (western pearlshell; Table 1). Mussels at all collection sites were abundant and apparently healthy, and reproduction and recent recruitment were evident. For toxicity tests to evaluate the sensitivity among different populations of fatmucket, adult mussels were obtained from 2 wild populations and 1 captive population in May 2014: a population from Silver Fork of Perche Creek, Boone County, Missouri (this population has been used routinely in previous toxicity studies [6–10]); a population from the Bourbeuse River, Gasconade County, Missouri; and a captive population at the Kansas City Zoo (Kansas City, MO, USA). Mussels in the captive population were 4 yr old and were derived from glochidia obtained from 6 females collected from the Silver Fork of Perche Creek.

The collected female paper pondshell, fatmucket, and western pearlshell were transferred to culture facilities at Missouri State University (Springfield, MO, USA), and female threeridge and washboard were transferred to Genoa National Fish Hatchery (Genoa, WI, USA). The adult mussels were held at 10 °C to 12 °C and fed commercially available cultured algae (*Nannochloropsis* and Shellfish Diet; Reed Mariculture). The culture water used at Missouri State University was filtered (10 μm) river water collected from James River, Greene County, Missouri, with a hardness 160 mg/L as $CaCO_3$ and pH 8.1; the culture water used in the Genoa National Fish Hatchery was well water with a hardness 200 mg/L as $CaCO_3$ and pH 7.5. To culture juvenile mussels, roughly equal numbers of glochidia were removed from each of at least 3 adult mussels (Table 1). The viability of glochidia isolated from each adult mussel was tested with a subsample using the closing response to sodium chloride [24]. The viability of glochidia from all samples exceeded 90%. The glochidia isolated from the adult mussels were pooled and placed on hatchery-reared fish for metamorphosis. The number of adult mussels used for

Table 1. Gravid female mussels and host fish for juvenile mussel culture

Family (Tribe)	Species	Reproduction	Collection location	No. of mussels for a batch culture	Host fish
Unionidae (Amblemini)	Threeridge (*Amblema plicata*)	Short-term brooder	Mississippi River, Prairie du Chien, WI, USA	4 or 8	Largemouth bass (*Micropterus salmoides*)
Unionidae (Anodontini)	Paper pondshell (*Utterbackia imbecillis*)	Long-term brooder	Kansas City Zoo, Kansas City, MO, USA	3	Bluegill (*Lepomis macrochirus*)
Unionidae (Lampsilini)	Fatmucket (*Lampsilis siliquoidea*)	Long-term brooder	Perche Creek, Boone County, MO, USA[a]	3 or 5	Largemouth bass (*Micropterus salmoides*)
Unionidae (Quadrulini)	Washboard (*Megalonaias nervosa*)	Long-term brooder	Mississippi River, Crawford County, WI, USA	15	Channel catfish (*Ictalurus punctatus*)
Margaritiferidae	Western pearlshell (*Margaritifera falcata*)	Short-term brooder	South Fork Eel River, Mendocino County, CA, USA	7 or 8	Rainbow trout (*Oncorhynchus mykiss*)

[a]Two other populations of fatmucket were collected from Bourbeuse River (Gasconade County, MO, USA) and Kansas City Zoo (Kansas City, MO, USA) for reference toxicant (sodium chloride and copper) tests to determine the sensitivity among three populations (details in text).

Table 2. Chemicals and modes of toxic action in two studies[a]

Toxicant	Chemical formula	Purity (%)	Broad MOA[b]	Specific MOA[b]
Multi-species study				
Alachlor	$C_{14}H_{20}ClNO_2$	99.2	Narcosis	Nonpolar
Metolachlor	$C_{15}H_{22}ClNO_2$	97.6	Narcosis	Nonpolar
Ammonia	NH_4Cl	99.5	Lono/Osmoregulatory/Circulatory impairment	Other osmoregulatory impairment
Potassium	KCl	99.7	Lono/Osmoregulatory/Circulatory impairment	Other osmoregulatory impairment
Chloride	NaCl	100	Lono/Osmoregulatory/Circulatory impairment	Other osmoregulatory impairment
Sulfate	Na_2SO_4	100	Lono/Osmoregulatory/Circulatory impairment	Other osmoregulatory impairment
Chromium (VI)	CrO_3	98	Lono/Osmoregulatory/Circulatory impairment	Metallic iono/osmoregulatory impairment
Copper	$CuSO_4 \cdot 5H_2O$	99	Lono/Osmoregulatory/Circulatory impairment	Metallic iono/osmoregulatory impairment
Nickel	$NiCl_2$	100	Lono/Osmoregulatory/Circulatory impairment	Metallic iono/osmoregulatory impairment
Zinc	$ZnCl_2$	98	Lono/Osmoregulatory/Circulatory impairment	Metallic iono/osmoregulatory impairment
Single-species study				
2,4-dichlorophenoxyacetic acid	$C_8H_6Cl_2O_3$	97	Narcosis	Nonpolar
4-nonylphenol	$C_{15}H_{24}O$	100	Narcosis	Polar
Azoxystrobin	$C_{22}H_{17}N_3O_5$	100	Narcosis	Ester
Bifenthrin	$C_{23}H_{22}ClF_3O_2$	100	Neurotoxicity	Pyrethroid sodium channel modulation
Carbaryl	$C_{12}H_{11}NO_2$	97	Acetylcholinesterase inhibition	Carbamate
Malathion	$C_{10}H_{19}O_6PS_2$	100	Acetylcholinesterase inhibition	Organophosphate
Molinate	$C_9H_{17}NOS$	100	Narcosis	Nonpolar
Arsenic (V)	$Na_2HAsO_4 \cdot 7H_2O$	98	Electron transport inhibition	Arsenical respiratory inhibition
Calcium chloride	$CaCl_2$	98	Uncertain	Uncertain
Aluminum	$AlCl_3$	99	Lono/Osmoregulatory/Circulatory impairment	Metallic iono/osmoregulatory impairment

[a]All chemicals were obtained from Sigma-Aldrich, except ammonia chloride and potassium chloride (obtained from Fisher Scientific).
[b]Mode of action (MOA) determined from Barron et al. [21].

glochidia sampling and the viability of glochidia met the recommendations in ASTM International methods [24]. The host fish (Table 1) were maintained at 20 °C to 22 °C (except for western pearlshell at 13 °C to 15 °C) in a recirculating system equipped for recovery of juveniles. Juvenile mussels were recovered 2 wk (5 wk for western pearlshell) after fish infestation. Juvenile mussels recovered from the host fish during the 2-d peak of recovery were shipped overnight to the US Geological Survey, Columbia Environmental Research Center (Columbia, MO) for toxicity testing.

The newly transformed juvenile mussels (generally <5 d old) were acclimated to test water and temperature in 1-L glass beakers with gentle aeration through a glass pipette or in a recirculating bucket [25] for at least 2 d before the start of a test. Approximately 25% of the water in the containers was gradually replaced with test water twice daily. The juvenile mussels were fed an algal mixture (*Nannochloropsis* concentrate and Shellfish Diet; Reed Mariculture [7]) during the acclimation period twice daily in the morning and afternoon, with an algal density of 5 nL cell volume/mL to 10 nL cell volume/mL after each feeding.

Test water and exposure concentrations

Test water (control water) was prepared by diluting Columbia Environmental Research Center well water of hardness 300 mg/L as $CaCO_3$ with deionized water to a hardness of 100 mg/L as $CaCO_3$. The formula, purity, source, and modes of toxic action of test chemicals are listed in Table 2. For each chemical, 5 concentrations plus a control were tested. Test concentrations were chosen based on results of previous acute toxicity tests with juvenile mussels. When a prediction of toxicity for a particular chemical was not available for mussels, an initial 96-h range-finding test was first conducted with a limited number of mussels (5 to 10) and replicates (1 or 2) in a control and 5 concentrations of the test chemical that differed by a dilution factor of up to 10.

Toxicity tests were conducted under static-renewal conditions, with the exception that ammonia toxicity tests were conducted under flow-through conditions to maintain constant concentrations over 96-h exposures [8]. For static-renewal toxicity tests, a solution of the highest exposure concentration was prepared 4 h to 24 h before the start of a test by adding either a certain amount of chemical (e.g., NaCl, KCl, and Na_2SO_4) or a certain volume of stock solution (metals and organic chemicals) into 1000 mL or 2000 mL of control water in a glass jar. One-half of the solution was then used for 50% dilutions to create other solutions of lower concentrations. The control water and solutions were held in the dark at 4 °C and warmed to test temperature in water baths for use at the beginning of a test and for water renewal. Triethylene glycol (Sigma-Aldrich) was used as solvent to prepare stock solutions of organic chemicals, with the exceptions of carbaryl and bifenthrin, for which acetone (Sigma-Aldrich) was used. The solvent concentration in test solutions was kept to a minimum and did not exceed 0.5 mL/L [24]. A dilution-water control and a solvent control containing the highest concentration of the solvent in test solutions were included in tests with organic chemicals. Ammonia toxicity tests were conducted in an intermittent flow-through proportional diluter system [8]. The diluter delivered 5 ammonia concentrations with a 50% dilution series plus a control. Ammonium chloride (NH_4Cl; Table 2) was used to prepare an ammonia stock solution in a 2000-mL volumetric flask. The pH in the stock solution was adjusted to a pH of 8.0 (close to the pH in the control water) by adding <1 mL of a solution of ammonium hydroxide (NH_4OH; 30% purity; Fisher Scientific). The stock solution was delivered with each cycle of the diluter system by Hamilton syringe pump (Hamilton).

Toxicity testing

At the beginning of each static-renewal test, 5 juvenile mussels were impartially transferred into each of 4 separate 50-mL replicate glass beakers containing 30 mL of water. Test beakers were held in a plastic container (30 cm × 18 cm × 10 cm) with a cover to reduce evaporation. The containers were held in a water bath at 23 ± 1 °C (or 20 ± 1 °C for western pearlshell, a western US resident species that inhabits cooler water). Water temperature was monitored daily. Ambient

laboratory light was 400 lux to 500 lux with 16:8-h light:dark photoperiod. Test organisms were not fed during 96-h exposures. Approximately 75% of the water in each replicate beaker was removed and renewed after 48 h. At the end of exposures, mussels in each beaker were examined under a dissecting microscope. The endpoint was mortality (empty shell with little or no tissue) plus immobility (no foot or shell movement within a 5-min observation period). The test acceptability criterion was ≥90% control survival [24].

For the flow-through ammonia toxicity tests conducted in the diluter, 10 mussels were impartially transferred into each of 4 replicate exposure units at the beginning of exposures. The exposure unit consisted of an inner chamber and an outer beaker [10]. The inner chamber was a 160-mL glass tube with stainless-steel screen (254-μm opening) at the bottom, used to facilitate retrieval of small juvenile mussels at the end of the acute exposure. Two glass rods were attached to the top of the inner chamber to keep the chamber suspended in a 300-mL glass outer beaker. The outer beaker had a 2.5-cm hole in the side covered with a stainless-steel screen (279-μm opening) and contained 200 mL of water. The diluter system delivered 125 mL of test solution into each inner chamber once every 4 h. The excess water flowed out through the side screen of the outer beaker. At the end of exposures, mussels in each inner chamber were rinsed into a glass tray with control water, and recovered and transferred into a 50-mL glass beaker containing 20 mL of the test solution; survival was determined under a dissecting microscope. Other test conditions and test acceptability criteria were the same as those described previously for the static-renewal tests.

Water quality and chemical analysis

Dissolved oxygen, pH, conductivity, hardness, and alkalinity were measured using standard methods [26] on composite water samples collected from the replicates in the control, medium, and high exposure concentrations at the beginning and the end of each test. Water samples for major cations (calcium, potassium, magnesium, and sodium), major anions (chloride and sulfate), and dissolved organic carbon (DOC) were periodically collected from control water. Major cations were analyzed by inductively coupled plasma–mass spectrometry (ELAN DRC-e; PerkinElmer) according to USEPA method 6020B [27], and major anions were analyzed by ion chromatography (ICS-1100; Dionex) according to USEPA method 9056A [28]. Samples for the analysis of DOC were filtered through 0.45 μm polyethersulfone membranes and measured by a total organic carbon analyzer (Model TOC-L CSH; Shimadzu Scientific Instruments) according to USEPA method 415.3 [29].

Water samples for the analyses of toxicants were collected in all exposure concentrations generally at the beginning of metal exposures, and at the beginning and the end of exposures to other chemicals for which the stability of concentration over 96-h exposure was uncertain (Supplemental Data, Tables S4 and S5). Water samples for metal analysis were drawn from mid-depth of each exposure chamber with an all-polypropylene syringe fitted with a tetra-fluoroethylene sipper straw. The sample was then dispensed through a 0.45-μm pore size polyethesulfone membrane filter into an acid-cleaned polyethylene bottle, except the sample for analysis of total aluminum, which was not filtered. Each 20-mL sample was stabilized within 24 h by adding 0.2 mL of concentrated nitric acid. Concentrations of the metals were determined by inductively coupled plasma–mass spectrometry according to USEPA method 6020B [27]. Chloride and sulfate were analyzed by the ion chromatography described previously or by a Hach HQ440d benchtop dual input, multi-parameter meter (Hach). In 2 chloride toxicity tests conducted earlier with threeridge and washboard, chloride concentrations were not measured. Rather, salinity and conductivity were measured in all exposure concentrations at the beginning and the end of each test to confirm the chloride concentrations (Supplemental Data, Table S4-4). Total ammonia nitrogen (N) was determined by a Hach HQ440d benchtop meter with a PHC301 Re-fillable pH Electrode. The meter was calibrated before measuring samples with 1.0 mg N/L and 10 mg N/L calibration standards. The method detection limit was 0.03 mg N/L.

Water samples for analysis of organic chemicals were extracted using Oasis HLB solid phase extraction cartridges (60 mg, 3 cc; Waters Corp). The cartridges were conditioned using ethyl acetate and methanol followed by deionized water prior to the drop-wise addition of the 10-mL water samples. The cartridges were then dried under nitrogen or by pulling laboratory air through for 5 min, placed in plastic bags and stored at –20 °C until extraction. Chemicals were eluted from the cartridges using 80:20 (v/v) dichloromethane:methyl-*tert*-butyl ether (alachlor, carbaryl, malathion, and metolachlor), methanol (2,4-dichlorophenoxyacetic acid and 4-nonylphenol), and ethyl acetate (azoxystrobin, bifenthrin, and molinate) prior to analysis. Analyses for alachlor, carbaryl, malathion, and metolachlor were conducted using an Agilent 6890 gas chromatograph with a 5973N mass selective detector. Analyses for 2,4-dichlorophenoxyacetic acid and 4-nonylphenol were conducted using liquid chromatography with photodiode array detection (Surveyor system; Thermo-Finnigan). Analyses for azoxystrobin, bifenthrin, and molinate were conducted using an Agilent 7890A gas chromatograph with a 5975C mass selective detector. Additional details of the extraction and analysis methods can be found in Alvarez et al. [30] and Hladik et al. [31].

Analyses of tested chemicals were performed by chemistry laboratories at the Columbia Environmental Research Center and US Geological Survey (Sacramento, CA), following internal standard operating procedures and quality assurance/quality control protocols. Established laboratory quality assurance/quality control procedures and sample types (second source calibration verification, laboratory spikes, duplicates, reference/laboratory control materials) were used to verify instrument performance, accuracy, and precision throughout the analyses. These established procedures were in place to ensure method performance and instrumental suitability. Results from each laboratory underwent data quality review prior to use in the present study.

Data analysis

Median effect concentrations (EC50s) based on mortality plus immobility of juvenile mussels were estimated with the Toxicity Response Relationship Analysis Program (TRAP; Ver 1.30a [32]), using the tolerance distribution analysis with the Gaussian (normal) distribution model and with log-transformed exposure concentrations. When the data did not meet the requirements of the TRAP (least 2 partial responses), either a Spearman-Karber or a trimmed Spearman-Karber method was used following the flowchart for EC50 determination recommended by the USEPA [33] using TOXSTAT® software (Ver 3.5; Western EcoSystems Technology).

To compare the relative sensitivity of mussels with other freshwater species, toxicity databases were compiled by adding

the mussel toxicity data from the present study to additional databases, including the USEPA ICE database [19,20] for alachlor, metolachlor, chloride (as NaCl), potassium (as KCl), calcium chloride, 2,4-dichlorophenoxyacetic acid, 4-nonylpgenol, azoxystrobin, bifenthrin, malathion, molinate, chromium (VI), and nickel; the databases used to derive USEPA water quality criteria for arsenic (V) [34], ammonia [35], copper [36], and carbaryl [37]; the database used to update water quality criteria for aluminum (D. Eignor, USEPA, Washington, DC, unpublished data); a zinc database [38]; a sulfate database representing a hardness range of 80 mg/L to 120 mg/L [16]; and the toxicity data from the companion study with the 2 snails and 3 other invertebrates (Ivey et al. [23] in this issue) and unpublished toxicity data from acute toxicity tests conducted at the Columbia Environmental Research Center that met ASTM International test acceptability criteria, such as >90% control survival. Toxicity data for nickel and zinc were normalized to a hardness of 50 mg/L as $CaCO_3$ using the equations in the USEPA water quality criteria for nickel or zinc [34], and copper data were normalized using a biotic ligand model [36]. Ammonia data were normalized to total ammonia-nitrogen at pH 7 and 20°C [35]. Aluminum data in a pH range of 6.5 to 9.0 were normalized to a hardness of 100 mg/L as $CaCO_3$ (D. Eignor, USEPA, Washington, DC, draft update water quality criteria for aluminum). Because sodium chloride toxicity typically decreases with increasing water hardness [11,39,40], the chloride data were compiled in a hardness range of 80 mg/L to 180 mg/L.

RESULTS AND DISCUSSION

Water quality

Water quality characteristics are summarized in Supplemental Data, Tables S2 and S3. The concentrations of dissolved oxygen ranged from 7 mg/L to 9 mg/L. Mean measured water quality characteristics were similar to nominal values of the diluted well water with hardness of 100 mg/L as $CaCO_3$, alkalinity of 90 mg/L as $CaCO_3$, conductivity of 250 μS/cm, and pH of 8.2 (Supplemental Data, Tables S2 and S3), with a few exceptions. Higher alkalinity of 131 mg/L to 168 mg/L was observed in high exposure concentrations in the toxicity tests with 2,4-dichlorophenoxyacetic acid, arsenic (V), and aluminum, probably because of the addition of a large amount of the tested chemical or the counterion of chemicals (i.e., up to 800 mg/L 2,4-dichlorophenoxyacetic acid, 1020 mg/L sodium arsenate dibasic heptahydrate, or 360 mg/L aluminum chloride). In addition, as expected, the conductivity increased with increasing exposure concentrations of ammonium chloride, potassium chloride, sodium chloride, and sodium sulfate. Measured conductivity values at different exposure concentrations for these chemicals are presented in Supplemental Data, Tables S4-3 to S4-6. Mean major ions and DOC measured periodically in the control water were 26 mg Ca/L, 9.0 mg mg/L, 9.0 mg Na/L, 0.9 mg K/L, 11 mg Cl/L, 20 mg SO_4/L, and 0.5 mg/L DOC, which were similar to those reported in previous studies with the diluted well water [16,41].

Chemical analysis

Mean measured concentrations of inorganic chemicals typically differed less than 20% from nominal concentrations, whereas measured concentrations of most organic chemicals were 20% to 50% lower than nominal concentrations (Supplemental Data, Tables S4 and S5). Measured concentrations of organic chemicals were generally consistent at the beginning and end of a test, except that the concentrations of carbaryl and malathion decreased substantially at the end of testing (Supplemental Data, Table S5). The EC50s were calculated based on measured concentrations or on nominal concentrations adjusted by measured concentrations in some of organic chemical tests where not all concentrations were measured (Supplemental Data, Tables S4 and S5). Nominal concentrations were used for the EC50 calculation in 2 chloride tests with threeridge and washboard where chloride concentrations were not measured. Mean measured salinity and conductivity values were relatively consistent with the nominal NaCl concentrations (Supplemental Data, Table S4-4), confirming that the chloride concentrations were close to the nominal concentrations. Nominal concentrations were also used to calculate EC50s in 2 organic chemical tests (threeridge–alachlor test and fatmucket–carbaryl test) because the measured concentrations showed high, unexplained variability (1 measured concentration was similar to the nominal but another measured concentration was much different from the nominal; Supplemental Data, Tables S4-1 and S5) and the nominal concentrations represented our best estimate of actual exposure concentrations. Detailed information on the concentrations used for EC50 calculation is provided in Supplemental Data, Tables S4 and S5.

Toxicity tests with the 5 mussel species and 10 chemicals in the multi-species study

Toxicity data. In the multi-species study, 60 acute toxicity tests were completed with 5 mussels and 10 chemicals (Table 3). A test was repeated (if a new batch of mussels was available) when an EC50 could not be estimated because more than 50% mortality was observed in all exposure concentrations (fatmucket–potassium test and western pearlshell–potassium test; Table 3) or because there were no partial kills (fatmucket–nickel test). The EC50s for chloride and copper from the tests with fatmucket from different populations are also reported in Table 3 (test number 1 for the Silver Fork population, test number 2 for the Bourbeuse River population, and test number 3 for the Kansas City Zoo population). Ammonia toxicity was not tested with fatmucket in the present study because fatmucket has been intensively tested at the Columbia Environmental Research Center in previous ammonia studies [6,8,10]. Two ammonia EC50 values for fatmucket, obtained previously with similar test conditions (e.g., flow-through testing) and with the same life stage (newly transformed mussels) are included in Table 3 for the purpose of comparison among the 5 species.

Survival was ≥90% in the dilution water controls in 56 of the 60 tests, and survival in the solvent controls was ≥90% in all organic chemical tests (Supplemental Data, Tables S4 and S5) and met the test acceptability criterion of ≥90% control survival [24]. The control survival in 4 tests with threeridge (alachlor, metolachlor, sulfate, and chromium tests) ranged from 75% to 88% (Supplemental Data, Table S4-1,2,6,7) and did not meet the test acceptability criterion of ≥90% control survival. However, the control survival in the other 6 chemical tests, which were conducted concurrently with the alachlor, metolachlor, sulfate, and chromium tests using same batch of threeridge juveniles, was above 90%, ranging from 92% to 100% (Supplemental Data, Table S4-3,4,5,8,9,10), and an overall control survival for all 10 chemical tests was 90% (total of 44 control replicates, including solvent control). Furthermore, another copper toxicity test was conducted with a different batch of threeridge (Supplemental Data, Table S4-8), and the copper EC50s between the 2 threeridge tests were

Table 3. Acute median effect concentrations (EC50s) and 95% confidence limits (CLs; in parenthesis) for 10 chemicals in the multi-species study with 5 species of mussels representing different tribes or families of freshwater mussels

		EC50 (95% CL)				
Toxicant (Test no.)	Unit	Threeridge	Paper pondshell	Fatmucket	Washboard	Western pearlshell
Alachlor	mg/L	1.2 (0.8–1.8)[a]	6.7 (5.6–7.9)	2.7 (2.5–2.8)	5.7 (5.0–6.4)[b]	15 (12–20)
Metolachlor	mg/L	4.6 (3.0–7.1)[a]	15 (12–18)	20 (16–26)	6.8 (6.6–7.1)	29 (27–31)
Ammonia (total)	mg/L	1.5 (1.1–2.0)	2.1 (1.4–3.0)	5.2[c]/11[c]	5.1 (4.7–5.5)	8.0 (7.7–8.4)
Chloride (1)[d]	mg/L	1038 (808–1333)	1657 (1346–2039)	1897 (1850–1945)	1398 (1169–1670)	1576 (1391–1786)
Chloride (2)	mg/L	—[e]	—	1944 (1773–2131)	—	—
Chloride (3)	mg/L	—	—	2246 (2211–2281)	—	—
Chloride (4)	mg/L	—	—	1893 (1751–2045)[f]	—	—
Chloride (5)	mg/L	—	—	2092 (1910–2290)[f]	—	—
Potassium (1)[d]	mg/L	31 (17–57)	38 (35–42)	<56	48 (41–56)	<56
Potassium (2)	mg/L	—	—	46 (38–54)	—	38 (37–39)
Sulfate[d]	mg/L	1338 (no CL)[a,g]	2709 (2548–2880)	2325 (2176–2485)	2279 (2206–2355)	1378 (1335–1422)
Chromium (VI)	μg/L	233 (179–303)[a]	213 (187–242)	266 (224–316)	138 (132–144)	624 (603–647)
Copper (1)	μg/L	11 (10–12)	13 (11–15)	48 (40–57)	25 (24–26)	36 (35–38)
Copper (2)	μg/L	10 (8.2–13)	—	35 (30–42)	—	—
Copper (3)	μg/L	—	—	55 (47–64)	—	—
Nickel (1)	μg/L	234 (207–264)	676 (648–705)	506 [350–731][h]	173 (165–181)	269 (259–280)
Nickel (2)	μg/L	—	—	350 (298–411)	—	—
Nickel (3)	μg/L	—	—	445 (429–461)	—	—
Zinc	μg/L	299 (205–438)	520 (446–606)	576 (507–654)	566 (532–602)	447 (397–502)

[a]The EC50 should be used with caution due to low (<90%) control survival. See text for details.
[b]Only 45% mortality was observed in the highest test concentration (Supplemental Data, Table S4-1).
[c]Values for fatmucket were from a previous study at pH 8.1 and 20 °C [8] (see details in text).
[d]Chloride was tested as sodium chloride, potassium as potassium chloride, and sulfate as sodium sulfate (details in Table 2).
[e]A dash (—) indicates that the chemical was not tested with that species.
[f]Exposure solutions were prepared with a 30% series dilution (rather than 50% dilution in other tests).
[g]No CL could be calculated due to inadequate partial effects (Supplemental Data, Table S4-6).
[h]An EC50 could not be calculated due to no partial mortality (Supplemental Data, Table S4-9). The geometric mean of the bracketing concentrations with 0% and 100% mortality was calculated to obtain an estimated EC50. The 0% and 100% effect concentrations are provided in bracket as [0–100% effect concentration].

almost identical (Table 3). Therefore, the EC50s from the 4 tests with lower control survival were included in Table 3 with a footnote denoting that the control survival was less than 90%. When using the overall control survival data to recalculate the EC50s for the 4 tests, the EC50s would be slightly lower than those reported in Table 3: 1.1 mg/L (0.7–1.8 mg/L) alachlor, 4.4 mg/L (2.9–6.6 mg/L) metolachlor, 1017 mg/L (834–1241 mg/L) sulfate, and 206 μg/L (156–273 μg/L) chromium (VI).

Sensitivity comparisons among the 5 mussel species. The EC50s of the 5 mussel species ranged from 1.2 mg/L to 15 mg/L alachlor, 4.6 mg/L to 29 mg/L metolachlor, 1.5 mg/L to 8.0 mg/L total ammonia, 1038 mg/L to 2246 mg/L chloride, 31 mg/L to 48 mg/L potassium, 1338 mg/L to 2709 mg/L sulfate, 138 μg/L to 624 μg/L chromium, 10 μg/L to 55 μg/L copper, 173 μg/L to 676 μg/L nickel, and 299 μg/L to 576 μg/L zinc (Table 3). No single tested species had lower or higher EC50s than other species across all 10 chemicals. However, threeridge had the lowest EC50s for 8 of the 10 chemicals, and western pearlshell had the highest EC50s for 4 of the 10 chemicals. The EC50s for each chemical among the 5 species differed by a factor of ≤ 2 for chloride, potassium, sulfate, and zinc; a factor of ≤ 5 for ammonia, chromium, copper, and nickel; and factors of 6 and 12 for metolachlor and alachlor, respectively. In most cases, the 95% confidence limits for each chemical overlapped among the 5 mussel species. The results indicate that the mussels across different families or tribes had similar sensitivity to most of the tested chemicals, regardless of modes of action.

Sensitivity comparisons within a mussel species from the same population or from different populations. The EC50s for a single species in the repeated tests were similar (Table 3). Specifically, the EC50s for a species differed within a factor of 1.1 to 1.4 in the tests with 2 or 3 different batches of juveniles from the same population (i.e., fatmucket–chloride tests 1, 4 and 5; fatmucket–potassium test; threeridge–copper test; fatmucket–nickel test; Table 3). The low variability in EC50 among tests in a single laboratory was consistent with a previous study, in which the differences in EC50s in repeated copper tests with juvenile fatmucket from 1 population were within a factor of 1.4 [42]. The EC50s for chloride or copper among different populations of fatmucket were also similar, within a factor of 1.2 for chloride and 1.6 for copper (Table 3; test number 1 for fatmucket from the Silver Fork, test number 2 for fatmucket from the Bourbeuse River, and test number 3 for fatmucket from the Kansas City Zoo). The results indicate that the sensitivity of juvenile fatmucket among different populations was similar in acute exposures to copper or chloride. Importantly, the sensitivity of juvenile fatmucket cultured from larvae of wild adults was similar to the sensitivity of juveniles cultured from larvae of captive-cultured adults (Kansas City Zoo). This result shows that captive-cultured adult mussels can reliably be used to reproduce juveniles for toxicity testing.

Sensitivity comparisons between fatmucket and other mussels. The sensitivity of the commonly tested fatmucket was compared to the other 4 mussels across the 10 chemicals with a regression plot. A strong linear relationship was obtained between EC50s for fatmucket and the other mussel species ($r^2 = 0.97$), and the slope of the regression was close to 1.0 (Figure 1). Over 73% of EC50s for the other 4 species were within 2-fold of EC50s for fatmucket. The results indicate that the toxicity of these chemicals to different species of mussels can be predicted with fatmucket toxicity data. Raimondo et al. [20] developed a toxicity database, including preliminary data from the present study, to examine the variability in sensitivity among mussels, cladocerans, and fish to chemicals with different modes of action. Their study demonstrated that

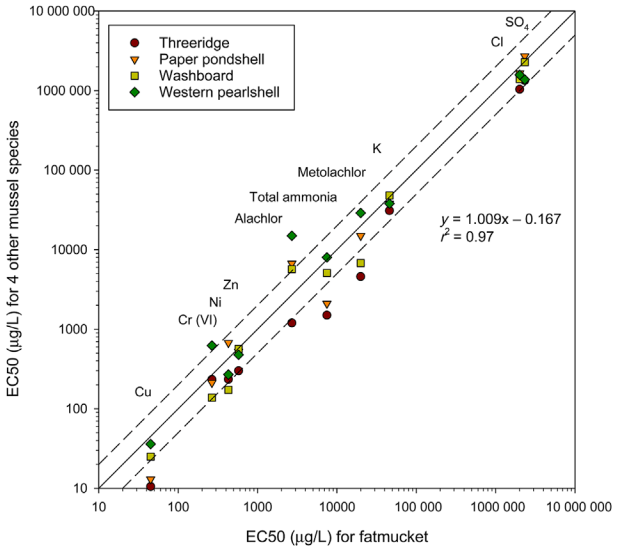

Figure 1. Relationship between the median effect concentrations (EC50s) from a commonly tested mussel (fatmucket) and the EC50s from 4 other mussels in acute 96-h exposures with the 10 chemicals for the multi-species study. The solid line indicates the 1:1 line of perfect agreement, and dashed lines indicate 1:2 and 2:1 lines (i.e., bounds for EC50s from the 4 mussel species being within 2-fold of EC50s from fatmucket). For repeat tests with a chemical (Table 3), a geometric mean of EC50s was used. The results of linear regression analysis (SigmaPlot, Ver 13.0; Systat Software) are also shown.

71% to 79% of EC50s for the most commonly tested mussel species (fatmucket, paper pondshell, or rainbow mussel *Villosa iris*) were within 2-fold of EC50s for up to 10 other mussel species; however, only 34% to 37% of EC50s for commonly tested cladocerans (*D. magna* and *C. dubia*) and 16% to 23% of commonly tested fish (*Oncorhynchus mykiss*, *Pimephales promelas*, and *Lepomis macrochirus*) were within 2-fold of EC50s for mussels [20].

Species sensitivity comparisons among mussels and other freshwater organisms. In the companion study (Ivey et al. [23] in this issue), the freshwater snail species (*P. gyrina* and *L. stagnalis*) and commonly tested amphipod (*H. azteca*) and cladocerans (*C. dubia* and *D. magna*) were tested in acute exposures to the 10 chemicals used in the multi-species study with the 5 mussels. Compared with the 5 mussels tested in the present study, the 2 snails had greater EC50s for ammonia, potassium, sulfate, and chromium but had similar EC50s for the other 6 chemicals. For the 10 chemicals, the EC50s for *C. dubia* were similar to or less than the EC50s for *D. magna, H. azteca,* and the 2 snails. However, *C. dubia* had substantially greater EC50s for ammonia and potassium compared with the 5 mussels. The results indicate that *C. dubia* may sufficiently represent sensitivity of the snails to the 10 chemicals but may not adequately represent the sensitivity of mussels to some chemicals. In the expanded database with more chemicals and mussel species, Raimondo et al. [20] found that, in general, *C. dubia* was less sensitive than mussels.

Species mean acute values (calculated as geometric mean of EC50s for a test species) for all freshwater species in the compiled toxicity databases were ranked and plotted in cumulative distribution for the 10 chemicals tested in the present study (Figure 2). The ranges of ranked SMAVs for mussels in different families or tribes were relatively narrow, generally within the lower 50th percentile of the species sensitivity distributions for the tested chemicals, except for the 2 organic chemicals (alachlor and metolachlor; Figure 2). One or more mussel species were among the 4 most sensitive species in the databases for 8 of the 10 chemicals tested in the multi-species study. Of the 6 tested chemicals for which the USEPA has water quality criteria [43], most species mean acute values for chloride or nickel from mussels and some species mean acute values for ammonia, copper, or zinc from mussels were similar to or less than the final acute value used to derive the USEPA acute criterion (Figure 2). These results indicate that mussels representing different tribes or families had similar sensitivity to inorganic chemicals across different modes of toxic action whereas the sensitivity to organic chemicals was relatively variable among mussels, and the water quality criteria development for alachlor, chloride, potassium, sulfate, copper, nickel, and zinc should reflect the sensitivity of mussels to these chemicals. The USEPA uses the genus level sensitivity distribution approach to develop acute water quality criterion, which is typically based on laboratory toxicity data from a suite of aquatic organisms that are assumed to represent the sensitivity of untested species (i.e., minimum data requirement of 8 different families [44]). Because of the high sensitivity of mussels to numerous chemicals across different modes of action, water quality criteria that better protect freshwater organisms may be obtained if the minimum data requirement for deriving water quality criteria were updated to include native mussels as a required family.

The USEPA updated the ammonia water quality criteria in 2013, and the acute criterion is 1.4-fold lower than the previous acute criterion, primarily because of the inclusion of mussel toxicity data [35]. In the 2013 water quality criteria, the 10 lowest species mean acute values, 7 lowest genus mean acute values, and 2 lowest species mean chronic values are for mussels. It is reasonable to expect some of the approximately 270 US native species of mussels that were not included in that dataset may be equally or more sensitive. A few mussel species, including threeridge from the present study, had ammonia EC50s below the 2013 water quality criteria final acute value (Figure 2). This and other information on mussel sensitivity to ammonia may be utilized to develop site-specific environmental guidance values and to provide enhanced conservation of especially vulnerable or important populations and/or communities of mussels. Another approach may be the development of taxon-specific criteria. Conceptually, a taxon-specific criterion could be derived to protect a species, genus, or family that is not adequately protected by general national aquatic life water quality criteria. Taxon-specific criteria would provide probabilistic estimates of hazard based on the subset of data most relevant to individual taxa of conservation concern. A mussel-specific ammonia criterion would complement the general national water quality criteria, which are derived to be protective of a large number of taxa but not meant to protect all species, by providing a technically sound risk management option for water quality managers' consideration when developing state or tribal water quality standards.

Toxicity tests with fatmucket and 10 additional chemicals in the single-species study

Ten additional chemicals were tested with fatmucket in the single-species study. Mean survival was >90% in the controls, including the solvent controls in organic chemical tests, and met the test acceptability criterion of ≥90% control survival [24]. Survival was >80% in all treatments at the end of exposures to 2,4-dichlorophenoxyacetic acid, bifenthrin, carbaryl, and aluminum (Supplemental Data, Table S5), even though the

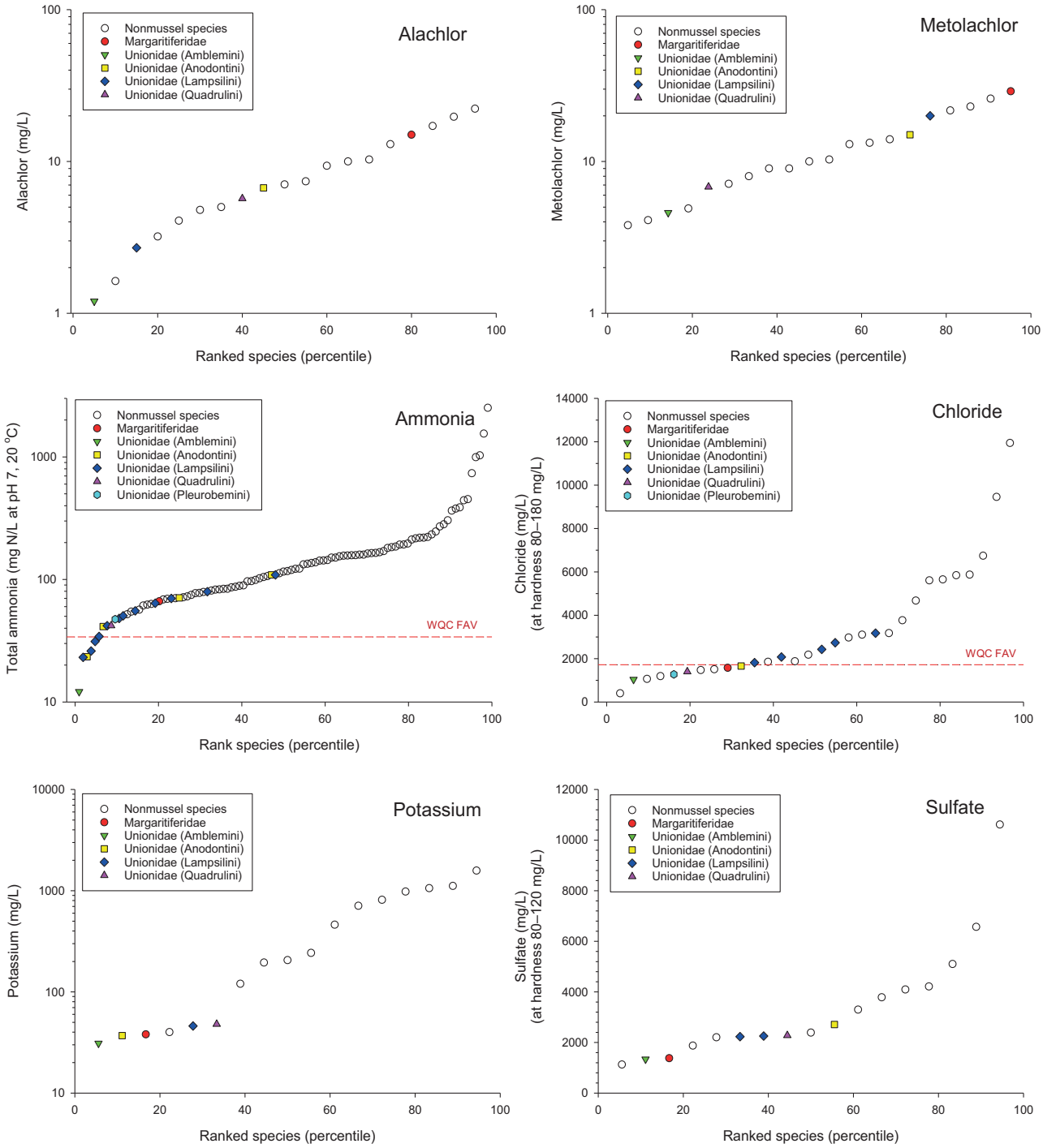

Figure 2. Ranked freshwater species mean acute values in compiled databases, with addition of species mean acute values for freshwater mussels of different tribes or families tested in the present study. Dashed line indicates the final acute value (FAV) in the US Environmental Protection Agency ambient water quality criteria (WQC).

high nominal concentrations of the 3 organic chemicals were close to solubility and a large amount of aluminum floc was observed on the bottom of test beakers in the high and medium-high concentrations.

The EC50s for the 10 chemicals tested in the single-species study with fatmucket and the percentiles of the species mean acute values for fatmucket in the species sensitivity distribution for all freshwater species are presented in Table 4. The EC50s for fatmucket were in the higher percentiles (≥45th) of the species sensitivity distribution, except for 4-nonylphenol in the 27th percentile. There were limited mussel data for chemicals tested in the single-species study. The EC50 of 23 mg/L malathion for fatmucket tested in the present study was close to the low range of 96-h EC50s from 24 mg/L to 219 mg/L for juveniles of 6 other mussel species tested in a previous study [45]. Milam et al. [46] conducted acute toxicity tests with glochidia of 6 mussel species in 24-h exposures that included 3 organic chemicals tested in the present study with juvenile fatmucket. The EC50s of >311 mg/L 2,4- dichlorophenoxyacetic acid, 0.099 mg/L 4-nonylphenol, and >8.0 mg/L carbaryl for juvenile fatmucket tested in the present study were within the 24-h EC50 ranges of 82 mg/L to 437 mg/L 2,4- dichlorophenoxyacetic acid, 0.057 mg/L to 1.19 mg/L 4-nonylphenol, and 3.1 mg/L to 43 mg/L carbaryl for glochidia of the 6 mussel

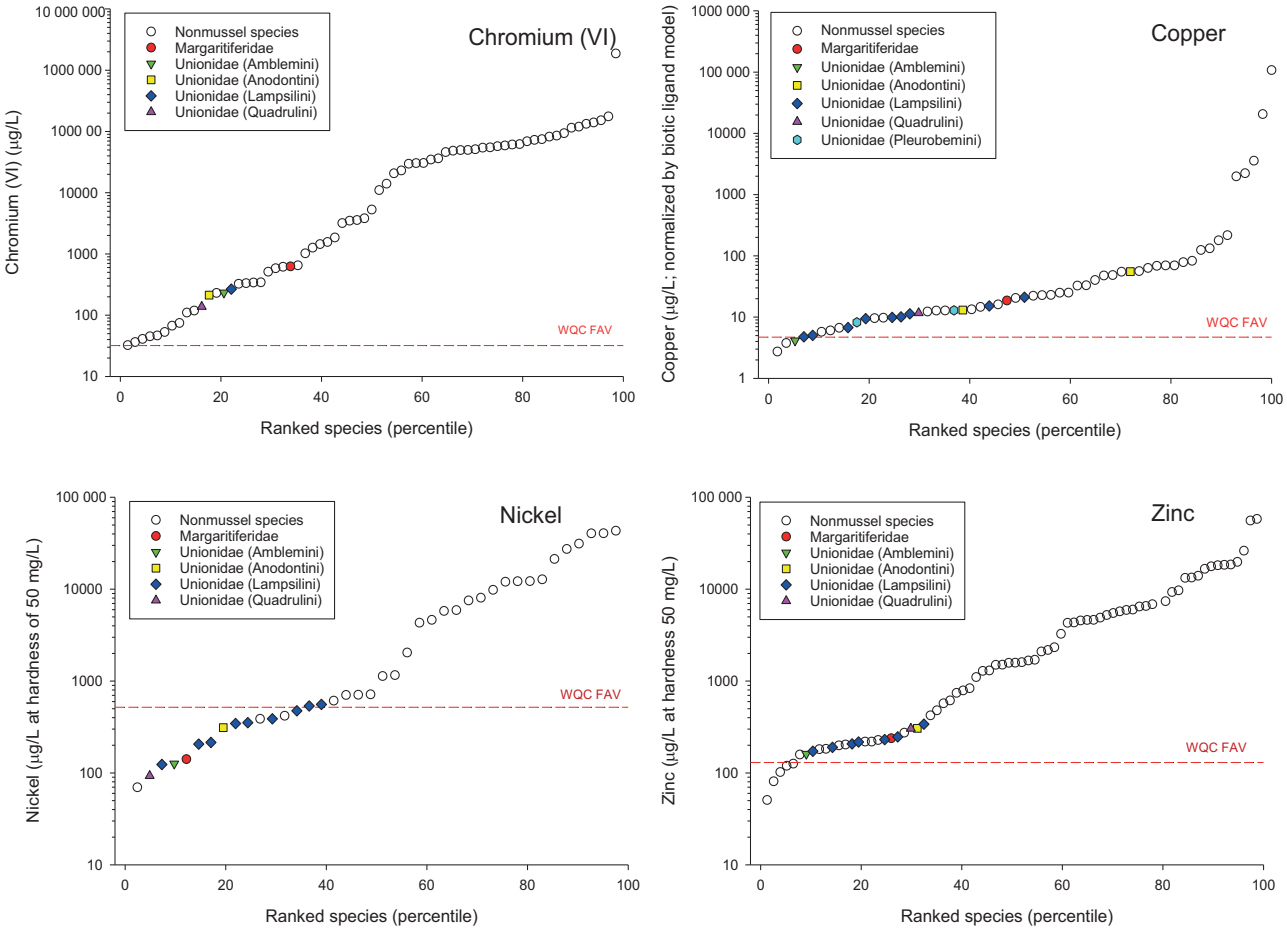

Figure 2. (*Continued*)

species [46], respectively. Of the 3 tested chemicals (carbaryl, arsenic [V], and aluminum) for which the USEPA has water quality criteria, the species mean acute values for fatmucket tested in the present study and other mussel species tested in previous studies [45,46] were far above the final acute values (Table 4). The results indicate that mussels tested were not sensitive to the chemicals tested in the single-species study, except 4-nonylphenol. Notably, 7 of the 10 chemicals tested in the single-species study were organic chemicals (Table 4). The mussels appeared to be less sensitive to organic chemicals. The relative (to other taxa) insensitivity of mussels to other organic contaminants has been reported previously [47].

The demonstrated sensitivity of mussels to a diversity of inorganic toxicants makes ensuring mussels are represented in

Table 4. Acute median effect concentrations (EC50s) and 95% confidence limits (CLs; in parentheses) for 10 chemicals in the single-species study with fatmucket (*Lampsilis siliquoidea*)[a]

Toxicant	EC50 (95% CL) (mg/L)	FAV (mg/L)	SSD percentile
2,4-dichlorophenoxyacetic acid	>311	NA	76 ($n=24$)
4-nonylphenol	0.099 (0.096–0.102)	0.056	27 ($n=29$)
Azoxystrobin	0.725 (0.697–0.754)	NA	83 ($n=5$)
Bifenthrin	>0.0267	NA	86 ($n=6$)
Carbaryl	>8.0	0.004	77 ($n=61$)
Malathion	23 [16–33][b]	NA	82 ($n=75$)
Molinate	53 (51–55)	NA	94 ($n=17$)
Arsenic (V)	117 (113–122)[c]	0.68	62 ($n=12$)
Calcium chloride	5383 [3862–7502][b]	NA	45 ($n=10$)
Aluminum (total)	>54	1.5[d]	72 ($n=17$)

[a]Final acute values (FAVs) in the US national ambient water quality criteria and a percentile of EC50 for fatmucket in the species sensitivity distribution (SSD) for all freshwater species are presented.
[b]An EC50 could not be calculated because of no partial mortality (Supplemental Data, Table S5). The geometric mean of the bracketing concentrations with 0% and 100% mortality was calculated to obtain an estimated EC50. The 0% and 100% effect concentrations are provided in bracket as [0–100% effect concentration].
[c]The effect concentration was calculated in terms of assayed arsenic concentration.
[d]The FAV in draft updated water quality criteria for aluminum at hardness 100 mg/L and pH range of 6.5 to 9.0 (D. Eignor, US Environmental Protection Agency, Washington, DC, unpublished data).
NA = not applicable.

water quality criteria development or other hazard assessments critical for the protection of mussels. As mentioned previously, direct testing of mussels is recommended when deriving estimates of protective concentrations for inorganic constituents because mussels have been demonstrated to be among the most sensitive forms of aquatic life to some metals and common ions. Where direct testing of the taxa is not feasible, extrapolation approaches such as the USEPA ICE models can provide estimated values that represent inherent taxa sensitivity. The ICE models are log-linear relationships of acute sensitivity between a surrogate species and predicted taxa of interest and can be used to estimate toxicity to the predicted taxa (species, genus, family) from measured toxicity of the surrogate [19]. The ICE models rely on an existing database of diverse species and chemicals, such as that used to develop species sensitivity distributions in the present study. Previous versions of the USEPA web-based ICE application had limited predictions to freshwater mussels because of limited measured data. A recent study expanded the database for freshwater mussels and provided additional guidance on inclusion of the mussel data into ICE models [20].

CONCLUSIONS

The present study confirms findings from previous studies that mussels are generally sensitive to ammonia, metals, and ion constituents, but are not generally among the most sensitive organisms for organic chemicals (including various pesticides) in acute exposures. Furthermore, mussels representing different families or tribes had similar sensitivity to most tested chemicals regardless of modes of toxic action. The sensitivity of the commonly tested fatmucket was similar to other mussel species tested. In addition, the sensitivity of juvenile fatmucket among different populations or cultured from larvae of wild adults and captive-cultured adults was also similar in acute exposures to copper or chloride. Use of toxicity data from fatmucket, in conjunction with the available USEPA ICE models, should provide good estimates of risk to mussels regardless of their taxonomic classification for the purpose of deriving water quality criteria or other environmental guidance values and conducting risk assessments.

In compiled toxicity databases for freshwater organisms, mussels were among the more sensitive species to alachlor, ammonia, chloride, potassium, sulfate, copper, nickel, and zinc. Therefore, the development of water quality criteria and other environmental guidance values for these chemicals should reflect the sensitivity of mussels. Including a native mussel as a required family in the minimum data requirement for deriving water quality criteria [44] should be considered in any water quality criteria developments or updates. Further studies are warranted to evaluate chronic sensitivity of mussels across phylogenetically diverse species in longer-term (e.g., 28 d to 90 d) exposures to chemicals with different modes of toxic action and to derive or update water quality criteria and other guidance to protect these long-lived mussels from long-term exposures.

Supplemental Data—The Supplemental Data are available on the Wiley Online Library at DOI: 10.1002/etc.3642.

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Disclaimer—The views expressed herein do not necessarily represent the views of the US Environmental Protection Agency and the US Fish and Wildlife Service. Any use of trade, firm, or product names is for descriptive purposes only and does not imply endorsement by the US Government.

Data Availability—Data, associated metadata, and calculation tools are available from the corresponding author (nwang@usgs.gov).

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Kennett Board Of Public Works

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February 28, 2019

Missouri WQS Triennial Review
Attn: WQS Coordinator, Department of Natural Resources
P.O. Box 176
Jefferson City, MO 65102-0176

Dear Water Quality Standards Coordinator,

The City of Kennett submits the following comments in response to the Missouri Department of Natural Resources, Water Protection Program's Public Notice of Intent to Initiate Triennial Review of Missouri Water Quality Standards. The City requests that the Department include regional dissolved oxygen criteria and revised aquatic life uses for hydrologically modified streams in the Bootheel region in the next Triennial Review.

Missouri is a diverse state, with varying environmental conditions across regions. This is predominantly evident in the Bootheel region, where hydrologically modified drainage ditches created for the Little River Drainage District in 1914 face naturally occurring low dissolved oxygen. The City is acutely aware of this at Buffalo Ditch. While conditions in the Bootheel make naturally occurring low dissolved oxygen common, that is not true of other parts of the State. Therefore, the City urges the Department to adopt rules that take into account these regional differences.

The current regulations do not address naturally occurring low dissolved oxygen in the Bootheel and the City supports the Department adopting rules that establish regional dissolved oxygen criteria. This is a sound scientific approach for protecting aquatic life in the Bootheel region. This recognizes that regional differences have a profound impact on dissolved oxygen levels and a stream's ability to support aquatic life. The low-lying drained swamp lands that are characteristic of the Bootheel region can never support the levels of dissolved oxygen or aquatic

life found in other regions of the state. This is evident by the fact that area reference streams, which represent the least disturbed conditions, fail to meet Missouri's existing dissolved oxygen criteria. The regional dissolved oxygen approach will allow the state to account for these regional differences in developing appropriate and attainable stream criteria.

The City appreciates the Department's consideration of its comments. Attached to this letter are reports providing additional data regarding low dissolved oxygen in the Bootheel region. Please let the City know if the Department needs any additional information.

Sincerely,

David Wilkins

David Wilkins

CC: Ed Galbraith, Department of Natural Resources
Chris Wieberg, Department of Natural Resources

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308 South Airport Road
Pearl, MS 39208–6649
e-mail: dc ms@usgs.gov
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National NAWQA Program:

Chief, NAWQA Program
U.S. Geological Survey
Water Resources Division
12201 Sunrise Valley Drive, M.S. 413
Reston, VA 20192
http://water.usgs.gov/nawqa/

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River Basin Assessments

Albemarle–Pamlico Drainage Basin (Circular 1157)
Allegheny and Monongahela River Basins (Circular 1202)
Apalachicola–Chattahoochee–Flint River Basin (Circular 1164)
Central Arizona Basins (Circular 1213)
Central Columbia Plateau (Circular 1144)
Central Nebraska Basins (Circular 1163)
Connecticut, Housatonic, and Thames River Basins (Circular 1155)
Eastern Iowa Basins (Circular 1210)
Georgia-Florida Coastal Plain (Circular 1151)
Hudson River Basin (Circular 1165)
Kanawha–New River Basins (Circular 1204)
Lake Erie–Lake Saint Clair Drainages (Circular 1203)
Las Vegas Valley Area and the Carson and Truckee River Basins (Circular 1170)
Lower Illinois River Basin (Circular 1209)
Long Island–New Jersey Coastal Drainages (Circular 1201)
Lower Susquehanna River Basin (Circular 1168)
Ozark Plateaus (Circular 1158)
Potomac River Basin (Circular 1166)
Puget Sound Basin (Circular 1216)
Red River of the North Basin (Circular 1169)
Rio Grande Valley (Circular 1162)
Sacramento River Basin (Circular 1215)
San Joaquin–Tulare Basins (Circular 1159)
Santee River Basin and Coastal Drainages (Circular 1206)
South-Central Texas (Circular 1212)
South Platte River Basin (Circular 1167)
Southern Florida (Circular 1207)
Trinity River Basin (Circular 1171)
Upper Colorado River Basin (Circular 1214)
Upper Mississippi River Basin (Circular 1211)
Upper Snake River Basin (Circular 1160)
Upper Tennessee River Basin (Circular 1205)
Western Lake Michigan Drainages (Circular 1156)
White River Basin (Circular 1150)
Willamette Basin (Circular 1161)

National Assessments

The Quality of Our Nation's Waters—Nutrients and Pesticides (Circular 1225)

Front cover: Photograph of the Black Swamp, Cache River Basin, near Gregory, Arkansas.

Back cover: Left, cotton grows on the banks of bayous in the Yazoo Basin; center, many of the rivers in the bootheel of Missouri have been channelized; right, soybeans are a major crop in the Mississippi Embayment Study Unit.

Photographs in this report were all taken by members of the MISE NAWQA Study Unit, U.S. Geological Survey.

Water Quality in the Mississippi Embayment, Mississippi, Louisiana, Arkansas, Missouri, Tennessee, and Kentucky,1995–98

By Barbara A. Kleiss, Richard H. Coupe, Gerard J. Gonthier, *and* Billy G. Justus

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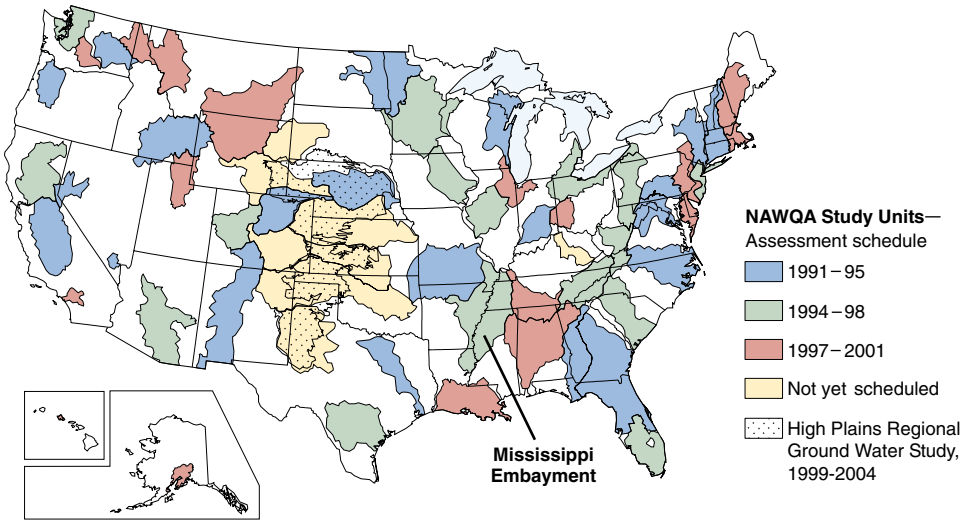
THIS REPORT summarizes major findings about water quality in the Mississippi Embayment that emerged from an assessment conducted between 1995 and 1998 by the U.S. Geological Survey (USGS) National Water-Quality Assessment (NAWQA) Program. Water quality is discussed in terms of local and regional issues and compared to conditions found in all 36 NAWQA study areas, called Study Units, assessed to date. Findings are also explained in the context of selected national benchmarks, such as those for drinking-water quality and the protection of aquatic organisms. The NAWQA Program was not intended to assess the quality of the Nation's drinking water, such as by monitoring water from household taps. Rather, the assessments focus on the quality of the resource itself, thereby complementing many ongoing Federal, State, and local drinking-water monitoring programs. The comparisons made in this report to drinking-water standards and guidelines are only in the context of the available untreated resource. Finally, this report includes information about the status of aquatic communities and the condition of in-stream habitats as elements of a complete water-quality assessment.

Many topics covered in this report reflect the concerns of officials of State and Federal agencies, water-resource managers, and members of stakeholder groups who provided advice and input during the Mississippi Embayment assessment. Basin residents who wish to know more about water quality in the areas where they live will find this report informative as well.



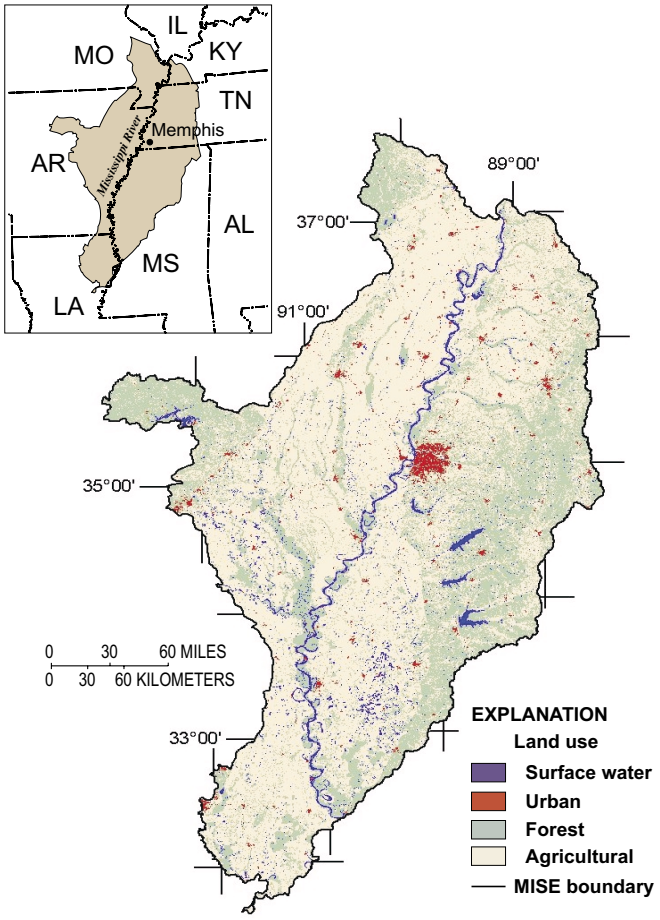
THE NAWQA PROGRAM seeks to improve scientific and public understanding of water quality in the Nation's major river basins and ground-water systems. Better understanding facilitates effective resource managment, accurate identification of water-quality priorities, and successful development of strategies that protect and restore water quality. Guided by a nationally consistent study design and shaped by ongoing communication with local, State, and Federal agencies, NAWQA assessments support the investigation of local issues and trends while providing a firm foundation for understanding water quality at regional and national scales. The ability to integrate local and national scales of data collection and analysis is a unique feature of the USGS NAWQA Program.

The Mississippi Embayment is one of 51 water-quality assessments initiated since 1991, when the U.S. Congress appropriated funds for the USGS to begin the NAWQA Program. As indicated on the map, 36 assessments have been completed, and 15 more assessments will conclude in 2001. Collectively, these assessments cover about one-half of the land area of the United States and include water resources that are available to more than 60 percent of the U.S. population.

Stream and River Highlights

The climate, rainfall, soil type, and surficial geology of the Mississippi Embayment (MISE) Study Unit strongly influence land use in the basin and subsequently influence water quality. About 62 percent of the Study Unit is used for agriculture. In areas of intensive row-crop production, as much as 90 percent of the land is used for agriculture. This influence from agricultural land use, with additional contributions from urban areas, has resulted in streams that often have high turbidities, mixtures of pesticides, and degraded riparian habitat. Biological communities in the streams commonly are stressed. However, human activities on the Earth's surface seem to have a limited effect on the ground-water resources, which supply the vast majority of the region's drinking water.

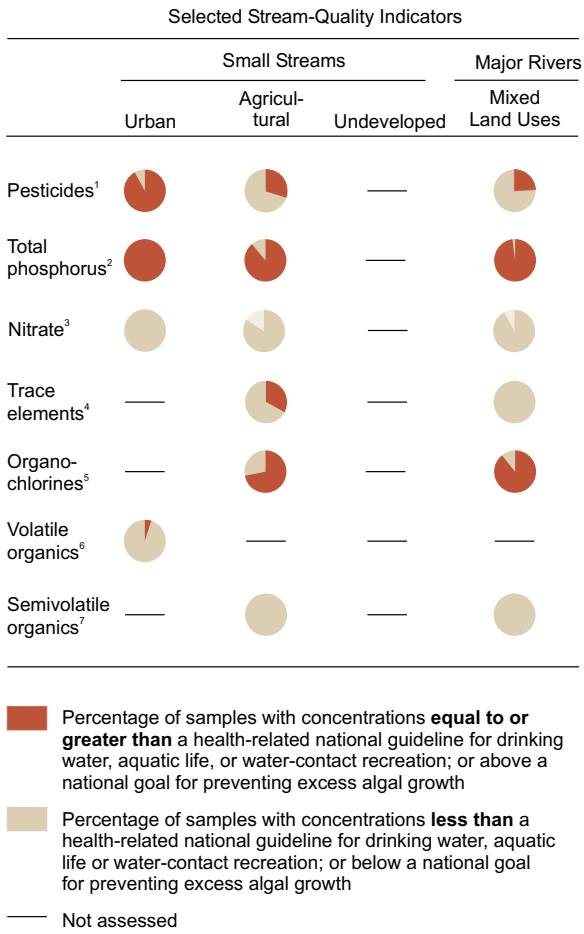
- Herbicides frequently were detected in streams draining agricultural or mixed land-use basins; insecticides were detected less often. Pesticides in over 60 percent of samples collected from these streams exceeded aquatic-life guidelines. Insecticides frequently were detected in samples from the urban stream; diazinon and chlorpyrifos were detected in every sample, usually in concentrations above aquatic-life guidelines.
- Nitrogen concentrations in the MISE generally were in the middle range of the national data, whereas total phosphorus concentrations were in the 67th to 93d percentile. The phosphorus concentrations in the Study Unit probably were related to many factors, such as rainfall amounts, soils, and artificial drainage of agricultural fields. No sample exceeded the guidelines and standards for nitrate or ammonia, but most exceeded the U.S. Environmental Protection Agency's (USEPA) goal of 0.1 mg/L (milligram per liter) of phosphorus for the prevention of plant nuisances in streams.
- Although the sale of the organochlorine insecticide DDT was discontinued in 1972, DDT and metabolites (chemicals resulting from the breakdown of DDT) were widespread within the MISE. DDT, or one of its metabolites, was found in every fish tissue sample collected and was found in 67 percent of the streambed-sediment samples. Detectable levels of a metabolite of DDT were measured in 14 percent of surface-water samples.
- Although volatile and semivolatile organic compounds often were detected in urban stream water and in bed sediment, they were rarely at levels of concern.
- Aquatic organisms present in the MISE streams were typical of those found in impacted or degraded streams. Fish communities in most of the streams were dominated by fish tolerant of poor water quality conditions. The aquatic insects and algal communities generally were tolerant of turbid, silty conditions.
- Methyl parathion, a metabolite of DDT, and several other pesticides were detected in air and rain samples collected in an agricultural area and in the urban area of Jackson, Mississippi.



The Mississippi Embayment (MISE) Study Unit is an approximately 49,800-square-mile area in the six States of Arkansas, Kentucky, Louisiana, Mississippi, Missouri, and Tennessee. Land use in the MISE is principally agricultural. Approximately 62 percent of the study area is agricultural, 33 percent is forested, and 5 percent represents other land uses. The land use in some of the smaller drainage basins sampled is greater than 90 percent agricultural.

Major Influences on Streams and Rivers

- Runoff from agricultural and urban areas
- Drainage modifications and channelization of streams
- Modification or elimination of riparian habitat



[1] Insecticides, herbicides, and pesticide metabolites, sampled in water.
[2] Total phosphorus, sampled in water.
[3] Nitrate (as nitrogen), sampled in water.
[4] Arsenic, mercury, and metals sampled in sediment.
[5] DDT and PCBs sampled in fish tissue.
[6] Solvents, refrigerants, fumigants, and gasoline compounds sampled in water.
[7] By-products of fossil-fuel combustion; components of coal and crude oil sampled in sediment.

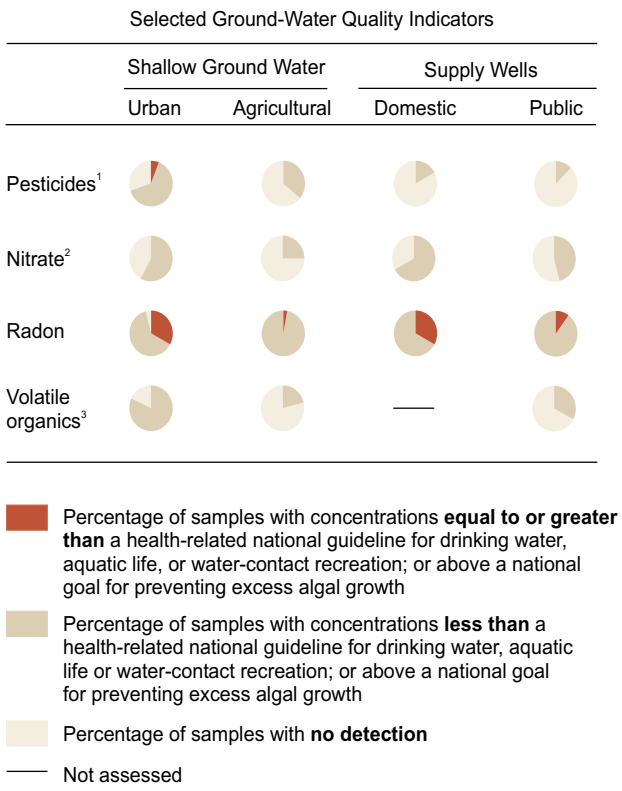
Ground-Water Highlights

Ground-water quality in the Mississippi Embayment Study Unit generally is very good. Ground water in the deep Tertiary aquifers, which supply most of the region's drinking water, generally is isolated from surface activities by thick "confining layers" of clays. Surface activities influence ground water where shallow deposits cover the hills in the eastern part of the Study Unit and in the Memphis shallow aquifers more than in the deeper aquifers. The abundant ground water in the alluvial aquifer of the Mississippi River valley is near the land surface but is covered by dense clays.

- Pesticides, such as atrazine, simazine, and metolachlor, were detected most frequently in the ground water in the shallow deposits that cover the hills in the eastern part of the Study Unit and in ground water underlying urban areas. Bentazon, molinate, and fluometuron were the pesticides most frequently detected in the alluvial aquifer. Atrazine and dieldrin were detected one time each in shallow urban wells at levels above the drinking-water standards and guidelines.
- Nutrient concentrations in the ground water in the MISE generally were low. All nitrate concentrations were below the USEPA drinking-water standard of 10 mg/L.
- Radon is naturally occurring and was detected in almost every well sampled. Concentrations above the USEPA-proposed drinking water standard of 300 picocuries per liter were found in water from only 16 of 109 wells. These levels are low, relative to levels detected in other NAWQA Study Units.
- Volatile organic compounds (VOCs) were detected in ground water throughout the Study Unit; however, concentrations were well within drinking-water standards. The most frequently detected VOCs were 1,2,4-trimethylbenzene and carbon disulfide.

Major Influences on Ground Water

- Ground water is commonly protected from surface activities by thick, regional clay layers.



[1] Insecticides, herbicides, and pesticide metabolites, sampled in water.
[2] Nitrate (as nitrogen), sampled in water.
[3] Solvents, refrigerants, fumigants, and gasoline compounds sampled in water.

In 1821, while painting a peregrine falcon, John James Audubon described the Yazoo River, the largest river wholly contained within the Mississippi Embayment Study Unit, as "a beautiful stream of transparent water, covered by thousands of geese and ducks and filled with fish" (Smith, 1954). Since that time, the bottomland hardwood forests that covered the Mississippi River Alluvial Plain have been cleared for agricultural use of the rich alluvial soils for the production of cotton, soybeans, rice, and corn. This clearing of the land has exposed the fine alluvial soils to erosion. Over time, the clays, along with nutrients and agricultural chemicals sorbed to the clay surfaces, were washed into the rivers and streams, thus greatly changing the water quality of the area.

John James Audubon's painting of the peregrine falcon that he worked on while visiting the Yazoo River area in 1821.
(Reprinted courtesy of the National Audubon Society.)

Physiography and Ecoregions

Within the Mississippi Embayment (MISE) Study Unit, the surficial geology is the underlying controlling factor for the physiography, land use, biological communities, and water quality of the area. Therefore, the areas defined as physiographic regions (Fenneman, 1938) strongly correspond to the related ecoregions defined by Omernik in 1987 (fig. 1).

Much of the Mississippi Embayment Study Unit was bottomland hardwood forests and wetlands well into the 20th century.

About 57 percent of the MISE Study Unit lies within the Mississippi Alluvial Plain physiographic province and ecoregion. This area has been dominated by the flow and flooding of the Mississippi River during the past 2 million years or more. The Mississippi Alluvial Plain is an area of little topographic relief with an average slope of about 0.5 foot per mile toward the Gulf of Mexico. One of the distinct features of the alluvial plain is the formation of natural levees along the banks of the rivers, and the associated backswamp deposits that are dominated by dense alluvial clays and historically have supported extensive wetland areas. These clays have created low permeability soils, which limit the ability of rainwater to infiltrate the ground surface and may cause runoff from agricultural fields to rapidly enter rivers and streams. These clays also seem to limit the susceptibility of the ground water to surface activities in intense agricultural areas.

Thirty-five percent of the remainder of the Study Unit lies in the Gulf Coastal Plains physiographic province, which includes the area identified as the Mississippi Valley Loess Plains and Southeastern Plains ecoregions (fig. 1). The Gulf Coastal Plains are separated from the eastern edge of the Mississippi Alluvial Plain by the Loess Hills, which extend most of the length of the Study Unit. These hills are made of windblown silts, rise a few hundred feet above the Mississippi Alluvial Plain, and average about 15 miles in width. The remaining part of the Gulf Coastal Plains uplands and Southeastern Plains ecoregion generally is rolling to hilly with low to moderate topographic relief. The soils are composed, in part, of silts and are more permeable than the alluvial clays; there are indications that this allows for the downward infiltration of precipitation. This may partly protect the streams and rivers from compounds carried in runoff but may make the ground water slightly more susceptible to surface contamination. These coarser soils on steeper slopes are more erodible than alluvial soils, and large amounts of soil from the Gulf Coastal Plains uplands have

eroded into the Mississippi Alluvial Plain.

In the west, the Study Unit abuts small areas of the Ozark Highlands. Limited sampling was done in these areas during this project.

The land surface generally slopes toward the Mississippi River from both the eastern and western sides of the Study Unit and to the south toward the Gulf of Mexico. Thus, nearly all of the activities in this Study Unit that influence water quality ultimately influence the water quality of the Mississippi River and the Gulf of Mexico.

Geology

The Mississippi Alluvial Plain is in the northern part of the Mississippi Embayment, a geologic structural trough in which the underlying crust of the Earth forms a deep valley. Large rivers, such as the Mississippi, Arkansas, and Ohio Rivers, have flowed through this region, carved the surface, and deposited clay, silt, sand, and gravel, collectively called alluvium. During the past 2 million years, up to 300 feet of alluvium has filled this valley. The alluvium can be grouped into three major units: the Pleistocene Prairie Complex, Pleistocene valley trains, and the Holocene alluvium (see fig. 7 for map; Autin and others, 1991; Saucier, 1994).

The Prairie Complex is older than the Pleistocene valley trains and the Holocene alluvium. Saucier (1994) suggested that the Prairie Complex was deposited between about 120,000 years ago and the time of the greatest extent of the last glacier, about 18,000 years ago. The Pleistocene valley trains were mostly deposited during two time periods, between about 60,000 and 25,000 years ago and during the waning phase of the latest glacial period between 18,000 and 10,000 years ago. Glacial outwash (melting) flowing from north to south provided enough energy to cause a braided stream depositional environment to form in the Lower Mississippi River Valley during this time. By about 9,000 years ago, the rate of glacial outwash in the Lower Mississippi River Valley declined, and valley train deposi-

During much of the growing season, rice crops are flooded with water withdrawn from the alluvial aquifer.

Cotton is still "king" in many areas of the Mississippi Embayment. Cotton requires extensive use of agricultural chemicals for successful cultivation.

Ground water is used to maintain more than 100,000 acres of catfish ponds in the MISE Study Unit.

Figure 1. Boundaries for Fenneman's (1938) physiographic regions are very similar to Omernik's Level III ecoregions (1987), at least in part because the surficial geology is a controlling factor in the MISE Study Unit. The only major metropolitan area in the Study Unit is Memphis, Tennessee. The area has many rivers, as well as several large river systems, including the Yazoo and St. Francis Rivers and parts of the White and Arkansas Rivers. Major crops include soybeans, cotton, rice, and corn. Catfish farms are a major component of the landscape as well as a principal user of ground water.

tion ceased. The braided stream depositional process of the Pleistocene epoch was replaced by the lower energy meander stream depositional process of the Holocene epoch near major rivers, such as the Mississippi and Arkansas Rivers. (See fig. 2 for more explanation.) Autin and others (1991) reported that the depositional transition from Pleistocene valley trains (braided streams) to Holocene alluvium (meander streams) started near Baton Rouge, Louisiana, around 12,000 years ago and migrated northward to near Cairo, Illinois, by 9,000 years ago.

The Pleistocene valley train deposits generally have a coarser grain size than the Holocene alluvium. Also, water well drillers' logs indicate that the clay and silt layer near the surface is thicker in the Holocene alluvium, whereas the underlying sand and gravel layer (alluvial aquifer) is thicker in the Pleistocene valley train deposits.

Hydrogeology

Two principal aquifer systems provide drinking-water supplies in the Mississippi Embayment—the Tertiary and the alluvial aquifers (fig. 3).

Tertiary Aquifers

The geologic groups associated with the deep Tertiary aquifers are the Midway, Wilcox, Claiborne, and the Jackson groups. The deep Tertiary aquifers sampled in this study are thick sand deposits within the Wilcox and Claiborne groups. The names of the aquifers, from youngest to oldest, include the Cockfield, Sparta, Winona-Tallahatta, Memphis, Meridian-upper Wilcox, and Wilcox.

Figure 2. Although the photograph on the left was recently taken of a stream in the Western United States, its braided condition is representative of what streams in the Mississippi Valley may have looked like during the Pleistocene geologic period. These high-energy systems allow sand and gravel carried by the stream to be deposited in the flood plain. The photograph on the right depicts a classic meandering stream. Streams like this are low-energy systems and primarily deposit clay, silt, and fine sand in the flood plains adjacent to the streams. This depositional pattern is present today and has been the dominant form of deposition in the Lower Mississippi River Valley during the last 9,000 to 12,000 years. These differences in depositional environments appear to influence the chemistry of the ground water, the bioaccumulation of pesticides, and biological communities.

The natural regional flow of ground water in the Mississippi Embayment in the Tertiary aquifers is from the outcrop areas in the upper Gulf Coastal Plain, laterally along the aquifers toward the embayment axis, and then upward through overlying confining units and aquifers to the surface of the Mississippi Alluvial Plain (Grubb, 1986; Ackerman, 1989). Pumping in the deep Tertiary aquifers has caused recharge rates to increase in the outcrop and production areas of the aquifer (Williamson and others, 1990).

Alluvial Aquifers

The Mississippi River confining unit is composed of the upper silt and clay of the Quaternary allu-

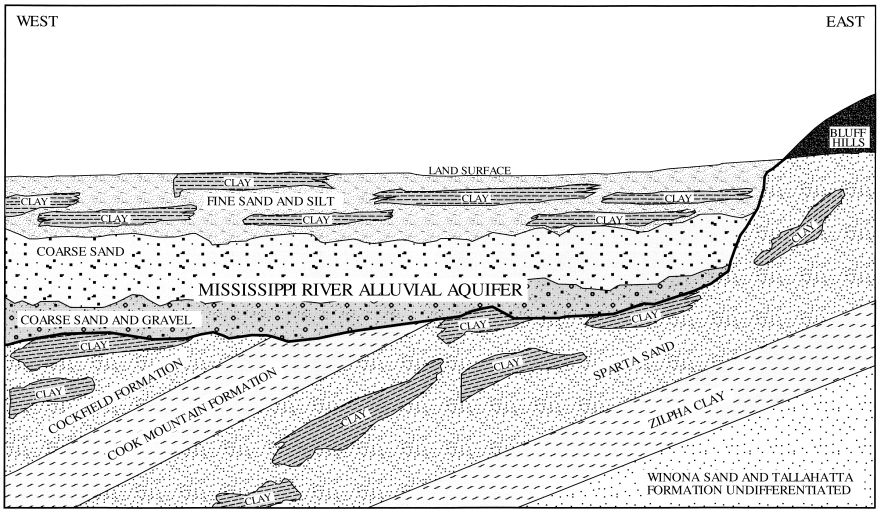


Figure 3. Generalized geohydrologic section of the Mississippi River alluvial aquifer and underlying Tertiary aquifers (from Arthur, 1994).

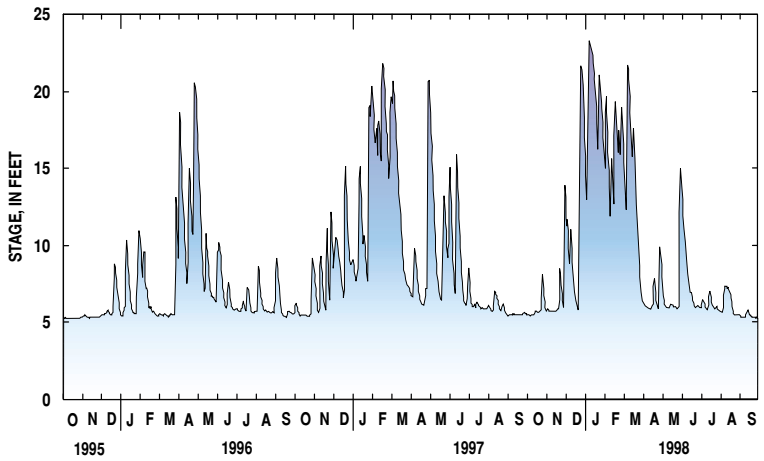


Figure 4. This hydrograph is representative of streams in the Mississippi Alluvial Plain. Often streams in this Study Unit flood rapidly, remain at high levels for long periods, and have very low streamflows in the fall. During the years of this project, 1996 was drier than usual, and 1997 and 1998 were wetter than usual.

vium, whereas the Mississippi River alluvial aquifer is composed of the lower sand and gravel of the Quaternary alluvium (Boswell and others, 1968; Ackerman, 1989). Overlying silt and clay of the confining unit impedes recharge into the alluvial aquifer. Confining unit thickness generally ranges from 10 to 50 feet and generally increases from north to south within the MISE Study Unit. The thickness of the alluvial aquifer ranges from 60 to 140 feet. Wells screened in the alluvial aquifer typically yield between 1,000 and 2,000 gallons per minute (Whitfield, 1975). Prior to development, ground-water flow is believed to have been generally from the older adjacent and underlying aquifers toward the alluvial aquifer (Williamson and others, 1990).

Climate

Climate in the MISE Study Unit varies from humid, temperate in the northern part to humid, subtropical in the southern part. This warm climate results in a long growing season and few killing frosts, which influences the types of crops that can be grown and the amount of pesticides that generally are applied. Mean annual precipitation ranges from about 48 inches per year in the northern part of the Study Unit to 56 inches per year in the southern part. Precipitation generally is greatest in April and least in October but is distributed fairly evenly throughout the year. This causes minor drought conditions to occur frequently during the summer, when the evapotranspiration rate is higher than the precipitation rate. These conditions also result in streams which flood rapidly, remain at high levels for long periods of time, and have low flows in the fall (fig. 4).

Water Use

In general, about three times as much ground water is used compared to surface water in the MISE Study Unit (fig. 5). During the summer months, both ground and surface water are used for irrigating crops. Most (in excess of 7 billion gallons per day) of the irrigation water is withdrawn from the alluvial aquifer. This aquifer is also used for domestic drinking water, aquaculture (primarily for catfish ponds), power production, and other commercial and industrial needs. Ground water, primarily from the Tertiary aquifers, is used for public supply. The principal use of surface water is for power production where it is used for cooling water for electric power generation. The second largest use of surface water is for irrigation.

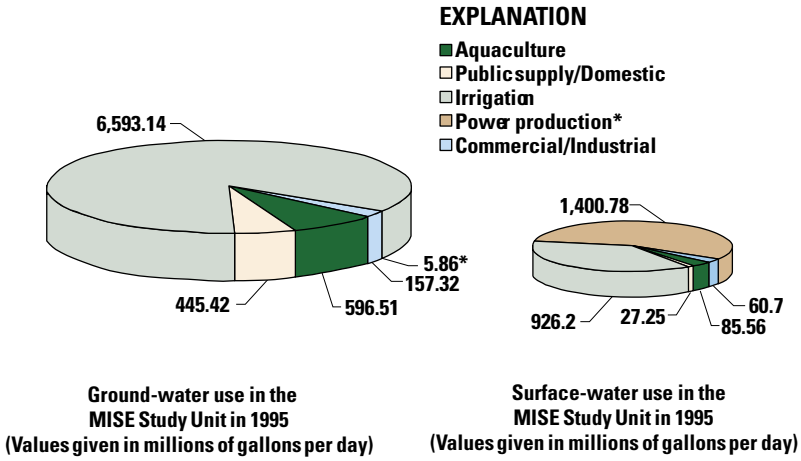


Figure 5. Ground-water use in the Mississippi Embayment (MISE) Study Unit is dominated by irrigation usage. Surface water is also used for irrigation, but more is used for cooling water for electrical power production.

Nutrient Contributions to the Mississippi River System

Although nitrogen and phosphorus, as well as silica and other nutrients, are natural and important parts of a healthy ecosystem, severe water-quality problems can arise if an ecosystem becomes enriched, or overloaded, with nutrients. In recent years, scientists have become aware of a large area of low dissolved oxygen that develops off the coast of Louisiana and Texas each summer. The extent and duration of this area of low dissolved oxygen has been related to the amount of nutrients, especially nitrogen, and freshwater flowing from the Mississippi River into the Gulf of Mexico (Goolsby and others, 1999). The proximity of the MISE Study Unit to the Gulf and the use of nitrogen fertilizer in the agricultural areas of the Study Unit, especially the Yazoo River Basin, have led to speculation that the surface waters of the Study Unit may be contributing a disproportionate amount of nitrogen and phosphorus to the Mississippi River and ultimately to the Gulf of Mexico.

In the MISE Study Unit investigations have shown that concentrations of nutrients (except total phosphorus) are higher in the Mississippi River at Vicksburg, Mississippi than near the mouth of the Yazoo River (table 1). The annual load of nitrogen and phosphorus from the Yazoo River for the 1996–97 calendar years, while significant, was only a small percentage of the load carried by the Mississippi River (Coupe, 1998).

Water-Quality Standards

Concentrations of nitrogen and phosphorus were measured from weekly to at least monthly at nine stream-sampling sites in the MISE Study Unit. Nitrate concentrations never exceeded the drinking-water standard of 10 mg/L in any sample, and ammonia concentrations did not exceed aquatic-life guidelines. However, the USEPA goal of 0.1 mg/L or less total phosphorus for streams not entering reservoirs was exceeded in every sample from the urban stream and in more than 50 percent of the samples from five streams located in the Mississippi Alluvial Plain. Samples from the streams located in the Gulf Plains exceeded the recommended goal of 0.1 mg/L or less total phosphorus in less than 50 percent of the samples.

The Yazoo River, the river with the largest drainage area wholly contained in the Mississippi Embayment Study Unit, enters the Mississippi River just north of these bridges at Vicksburg, Mississippi.

Comparison of Nitrogen and Phosphorus in Streams in the Mississippi River Basin

The yield of nitrogen (mass per unit area), from streams in the MISE Study Unit during 1995–96 was compared to the average yield during 1980–96 from streams in

Table 1. Concentrations of nutrients near the mouth of the Yazoo River compared to the Mississippi River at Vicksburg, Mississippi.

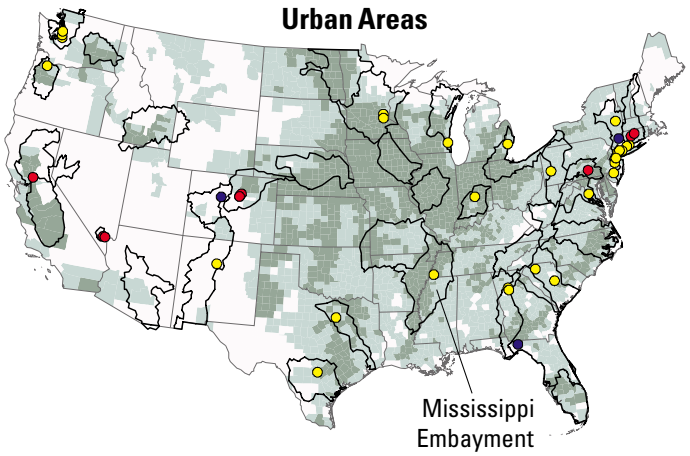
[Concentrations are in milligrams per liter]

Constituent	Site	Year	Maximum	Minimum	Mean
Total nitrogen	Yazoo River	1996–97	3.3	0.57	1.3
	Mississippi River	1984–93	3.8	1.1	2.3
Nitrate as N	Yazoo River	1996–97	1.2	0.16	0.45
	Mississippi River	1984–93	2.7	0.70	1.5
Total phosphorus	Yazoo River	1996–97	0.89	0.12	0.26
	Mississippi River	1984–93	0.38	0.04	0.16
Orthophosphate as P	Yazoo River	1996–97	0.10	0.01	0.043
	Mississippi River	1984–93	0.13	0.02	0.058

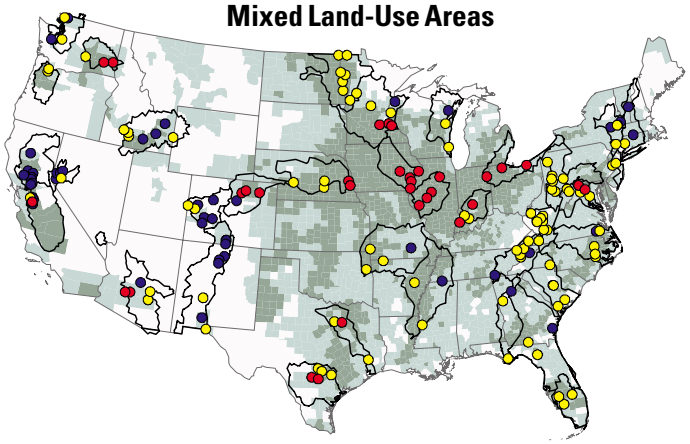
National Comparison of Total Nitrogen in Streams

TOTAL NITROGEN IN STREAMS

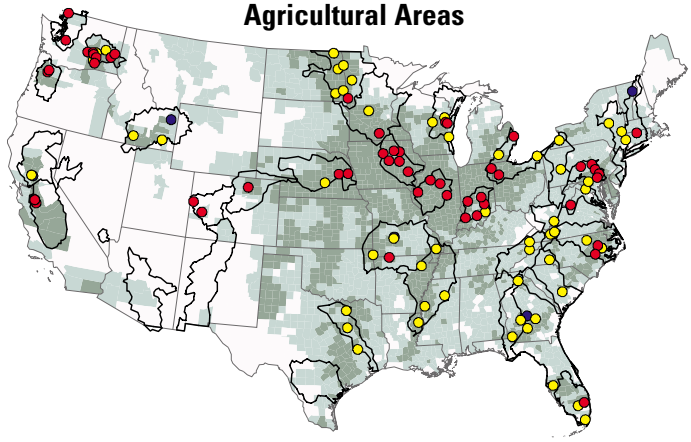
Urban Areas



Mixed Land-Use Areas



Agricultural Areas



Nitrogen is a natural and important component of a healthy stream; however, too much nitrogen can lead to degraded stream-water quality, affecting both the aquatic ecosystem and its use as a recreational or drinking-water source for humans. The sources of nitrogen in surface water are many and include atmospheric deposition, municipal and industrial wastewater, and fixation of nitrogen from the atmosphere by plants and some species of algae.

By far, the biggest source of nitrogen in an agricultural setting, such as the Mississippi Embayment (MISE) Study Unit, is from the application of fertilizer to crops. For most of the Study Unit, the average annual total nitrogen input from fertilizer, manure, and the atmosphere combined is greater than 25 pounds per acre. Most of the agriculturally productive Midwest receives the same amount.

The average annual concentration of total nitrogen from agricultural and mixed land-use streams in the MISE Study Unit is in the medium range, whereas nationally, most streams that drain areas with greater than 25 pounds per acre of nitrogen input are in the high range. The lower concentrations of total nitrogen in the MISE Study Unit may be due to the milder climate that increases microbial activity in the winter and to the increased uptake of nitrogen by vegetation during the longer growing season.

Nationally, the average annual total nitrogen concentrations in urban streams, including the one urban site in the Mississippi Embayment Study Unit, tend to fall into the “medium” classification.

EXPLANATION

Average annual concentration of total nitrogen—
in milligrams per liter

- Highest (greater than 2.9)
- Medium (0.64 to 2.9)
- Lowest (less than 0.64)

Average annual total nitrogen input —
in pounds per acre, by county, for 1995–98.
Inputs are from fertilizer, manure, and the atmosphere

- Greater than 25 pounds per acre
- 6 to 25 pounds per acre
- Less than 6 pounds per acre

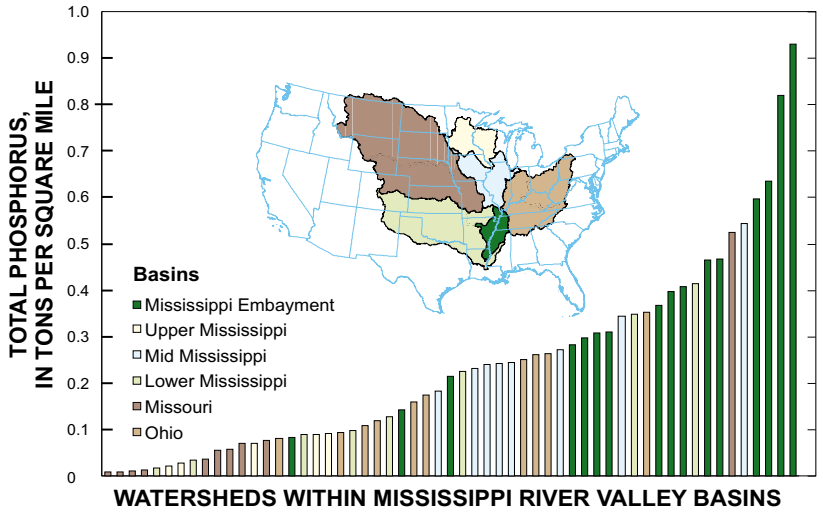
the Mississippi River Basin. These data indicate that the yield of nitrogen from the MISE Study Unit was less than the average yield from streams in intensive agricultural areas of the Midwest, but more than from streams in the drier West or in the less agricultural Upper Mississippi River Basin. The flow-weighted mean total nitrogen concentrations for streams in the MISE Study Unit were generally in the 50th to 60th percentile for all data collected in the national NAWQA Program (372 steam sites). The exception was the mean nitrogen concentration at the smallest mixed land-use site which was near the 20th percentile, nationally.

The yields of total phosphorus generally were higher in the MISE Study Unit than from most other areas in the Mississippi River Basin, and the percentile ranking of the flow-weighted mean total phosphorus concentration generally was quite high (67th to 93d). Again, the exception was the smallest mixed land-use site, where the mean total phosphorus concentration was near the 40th percentile. These high phosphorus yields were somewhat unexpected, as the soils in the MISE Study Unit, while fertile, do not contain excessive amounts of phosphorus. Also, phosphorus is used less as a fertilizer in the MISE Study Unit than in many parts of the Midwest (Battaglin and Goolsby, 1995), and due to the rural nature of the MISE, there are few significant point sources. One hypothesis for the high yields and concentrations of phosphorus in the MISE involves a combination of factors, such as soils, rainfall, and agricultural drainage. The sediment in the rivers of the MISE Study Unit is composed of fine, clay-sized particles to which phosphorus can sorb. Heavy rainfalls in the Study Unit increase the potential for erosion and the movement of these fine clay-sized particles from agricultural fields into the streams. Additionally, because of the large amount of rain, the tight clays that decrease infiltration of water, and the relatively flat terrain, much of the Study Unit has artificial drainage to expedite the movement of water. Most of this artificial drainage is surface drainage, which has been shown to decrease nitrate concentrations but to increase total phosphorus concentrations.

The Effects of Land Use and Geology on Nutrient Concen3rations and Yields

Generally, total nitrogen and phosphorus concentrations and yields were higher in streams with predominantly agricultural land use in the Mississippi Alluvial Plain, but the highest nutrient concentrations and yields were from the urban stream. However, one stream located in the Gulf Plains in an area with no urban land use and only a moderate amount of agricultural land use had comparatively high total nitrogen and phosphorus yields. The high yields in this stream are reflective of the steep topography of the area and channelization of the stream for flood-control purposes.

Nutrient Yields from MISE Watersheds



Phosphorus yields from watersheds within the MISE Study Unit were the highest in the Mississippi River Basin (represented by the dark green bars). These high phosphorus yields probably are related to several factors such as soils, amounts of rainfall, and artificial drainage of agricultural fields. In contrast, total nitrogen yields in streams in the Mississippi Embayment were less than those from the agriculturally productive Midwest, but more than those in the drier western part of the basin or the cooler Upper Mississippi River Basin, and about the same as streams in the Ohio River Basin. (Data from Goolsby and others, 1999.)

More details on nutrients in the Yazoo River can be found in the report:
Coupe, R.H., 1998, Concentrations and loads of nitrogen and phosphorus in the Yazoo River, northwestern Mississippi, 1996–97: U.S. Geological Survey Water-Resources Investigations Report 98–4219, 17 p.

The report also can be downloaded at:
http://ms.water.usgs.gov/misenawqa//

Pesticides Commonly Found in Mississippi Embayment Surface Water

The occurrence and temporal distribution of more than 80 pesticides and pesticide metabolites were determined at five stream-sampling sites from 1996 to 1998 in the MISE Study Unit. More than 230 stream samples were collected and analyzed. The five rivers sampled included three rivers with small, primarily agricultural watersheds; one river with a small, urban watershed; and one large river (the Yazoo River) with mixed land use (row-crop agriculture, forest, pasture, and a small amount of urban). Pesticides, usually herbicides, frequently were detected in water samples from all five rivers sampled. Aquatic-life guidelines were frequently exceeded in the urban stream and occasionally exceeded in all of the rivers sampled in the MISE Study Unit.

Water samples are filtered and processed in a mobile laboratory immediately after sample collection.

Agricultural Streams

The pesticides detected in the rivers that drain the agricultural watersheds in the MISE Study Unit showed distinct seasonal patterns that corresponded to the type of crops grown in the basin and the use of pesticides on those crops. For instance, the highest concentration of the pre-emergent herbicide atrazine frequently was found early in the growing season (April-May) corresponding to its application prior to the planting of corn and grain sorghum (fig. 6). The highest concentrations of herbicides that are used on other crops (cotton and rice) with later planting dates, or herbicides that are used after the crop has emerged from the ground, such as fluometuron and molinate, were detected later in the growing season (June–July). The concentrations of most of these herbicides were well below any acute toxicity; however, the long-term effects of chronic exposure to low levels of multiple herbicides are not well known.

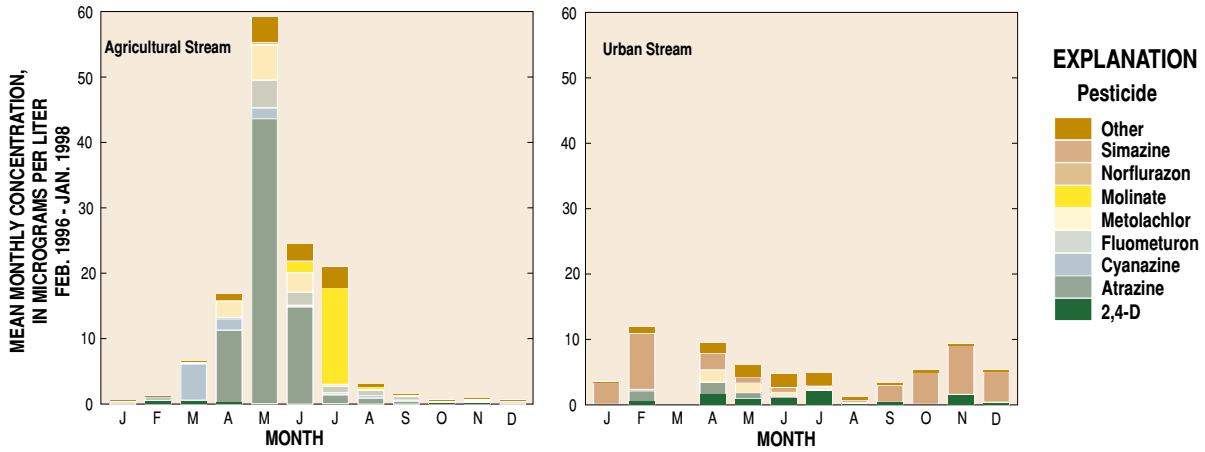
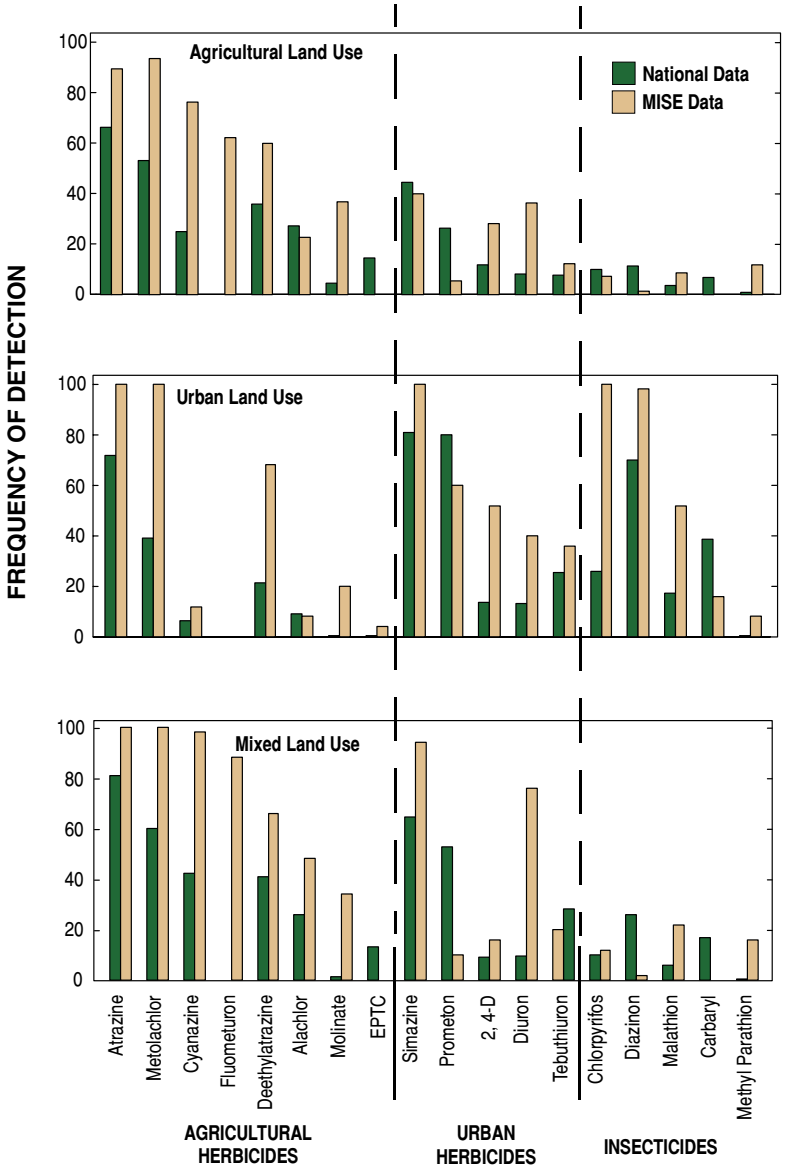


Figure 6. Herbicides in agricultural streams in the Mississippi Embayment Study Unit had higher concentrations, showed clear seasonal patterns, and contained different compounds than herbicides in urban streams. The urban stream samples were dominated by simazine, a turf grass herbicide. Concentrations of herbicides in the urban stream remained fairly constant throughout the year, whereas agricultural sites had concentrations that peaked in the spring shortly after application. Agricultural sites also were dominated by different herbicides (in this case atrazine).

Pesticides in Streams Across the United States



This diagram shows the top 15 pesticides most frequently detected in surface water at NAWQA Study Units throughout the United States and detections in surface water of the Mississippi Embayment (MISE Study Unit). Three pesticides used heavily in the Study Unit—fluometuron, methyl parathion, and molinate—but not used extensively throughout the United States, also are included for comparison. Few areas of the United States are as suited to agriculture as the Mississippi River Alluvial Plain in the MISE Study Unit. The combination of rich alluvial soils; a long, hot, growing season; flat terrain; and plentiful rainfall make agriculture the dominant economic force in the Study Unit. These same conditions also increase the weed and insect pressure and subsequently lead to an intensive use of pesticides to encourage profitable farming. In general, the frequency of detection of pesticides in surface waters of the MISE Study Unit exceed the national average.

Urban Stream

The type, amounts, and timing of the occurrence of pesticides in the stream draining an urban watershed are much different from those in the agricultural streams (fig. 6). The herbicides most frequently occurring in the urban stream such as atrazine, 2,4–D, simazine, and prometon, are those used in lawn care and in the maintenance of rights-of-way. The urban stream was also the only stream with frequent occurrences of insecticides: chlorpyrifos and diazinon were detected in every urban stream sample collected and exceeded the aquatic-life guidelines in 12 of 25 and 24 of 25 samples, respectively.

Many pesticides are applied by aircraft in the Study Unit.

DDT Metabolites in Surface Water

Although DDT strongly sorbs to sediments rather than readily dissolving in water, detectable levels of DDE, a metabolite of DDT, were found in 14 percent of the filtered stream-water samples analyzed.

More details on pesticides in streams in the MISE can be found in the report:
Coupe, R.H., 2000, Occurrence of pesticides in five rivers of the Mississippi Embayment Study Unit, 1996–98: U.S. Geological Survey Water-Resources Investigations Report 99–4159, 69 p.

The report also can be downloaded at:
http://ms.water.usgs.gov/misenawqa/

Tertiary Aquifers Have High-Quality Drinking Water

During the spring of 1996, water samples were collected from 30 public-supply wells in the deep Tertiary aquifers in the MISE Study Unit. The most significant finding from this part of the study is that all of the samples analyzed from these public-supply wells met all existing drinking-water standards and guidelines. Concentrations of most of the constituents measured that could adversely affect water quality, including nutrients, pesticides, radon, and volatile organic compounds, were below drinking-water standards and guidelines.

The Deep Tertiary Aquifers

The deep Tertiary aquifers underlie about 80 percent of the MISE Study Unit. Much of the population in this part of the country depends on these aquifers for drinking water. Wells sampled range in depth from 208 to 1,460 feet below the ground surface.

Ground-water samples commonly were collected from municipal drinking-water facilities, such as the one pictured above.

Sample Results

Water from wells in the deep Tertiary aquifers had low nutrient concentrations. The highest nutrient concentration measured in a sample was 3.8 mg/L of nitrite plus nitrate nitrogen, which is less than half the drinking-water guideline of 10 mg/L. Pesticides were detected in water from only one of the wells. Water from the shallowest well sampled had a 0.16-µg/L (microgram per liter) concentration of the herbicide bromacil and a 0.004-µg/L concentration of deethylatrazine, a metabolite of the herbicide atrazine. Volatile organic compounds (VOCs) are compounds that have a high vapor pressure relative to their water solubility and include such things as components of gasoline and organic solvents. VOCs were detected frequently in the MISE, but concentrations were far below drinking-water guidelines. Samples from 26 of the 30 public-supply wells had at least one VOC detection. The VOCs most commonly detected were methylethylketone and 1,2,4-trimethylbenzene, detected in 23 and 7 percent of the wells, respectively. Nutrients, pesticides, and VOCs generally enter the ground water from surface contamination; however, public-supply wells were generally deep enough to avoid elevated levels of these compounds.

Radon in water from the public-supply wells ranged from 54 to 270 picocuries per liter; none exceeded guidelines. Radon levels found in the ground water in the MISE were the second lowest of the 16 Study Units sampled during 1996–98.

Ground-water sample preparation occurred inside plastic enclosures in order to minimize sample contamination from chemicals in the atmosphere.

Few Pesticides Detected in Memphis Shallow Aquifers

In addition to the Tertiary aquifers, 32 shallow monitoring wells (not public-supply, drinking-water wells) were sampled in the shallow aquifers near Memphis, Tennessee. Results were similar to those from the deep Tertiary aquifer study except that pesticides were more frequently detected and radon concentrations were higher. An atrazine concentration of 3.14 µg/L was measured in one well, which narrowly exceeded the drinking-water guideline of 3.0 µg/L, and dieldrin was measured above the drinking-water guideline of 0.02 µg/L in another well.

More details on ground-water quality in the deep Tertiary aquifers can be found in the report:

Gonthier, G.J., 2000, Water quality in the deep Tertiary aquifers of the Mississippi Embayment, 1996: U.S. Geological Survey Water-Resources Investigations Report 99–4131, 91 p.

The report also can be downloaded at: http://ms.water.usgs.gov/misenawqa/

Water-Quality Differences in Geological Subunits of the Alluvial Aquifer

Previous researchers have studied the alluvial aquifer as a single Quaternary feature (Grubb, 1986; Ackerman, 1989). However, during this NAWQA investigation, the results of the water-chemistry studies were examined by dividing the area into different major geologic units, two of which are the Pleistocene valley trains and the Holocene alluvium (Saucier, 1994). The data collected suggest that the differences in the geology influence the chemical makeup of the ground water in the alluvial aquifer.

The Alluvial Aquifer

The alluvial aquifer is a large, underground, water-bearing layer of sand and gravel in the Lower Mississippi River Valley (fig. 7). Water use from the alluvial aquifer is enormous; pumpage from the aquifer is about 7 billion gallons per day (Mesko and others, 1990). Most of the water pumped from the alluvial aquifer is used to irrigate crops or to maintain aquaculture, but the ground water also is used for public supply and industry.

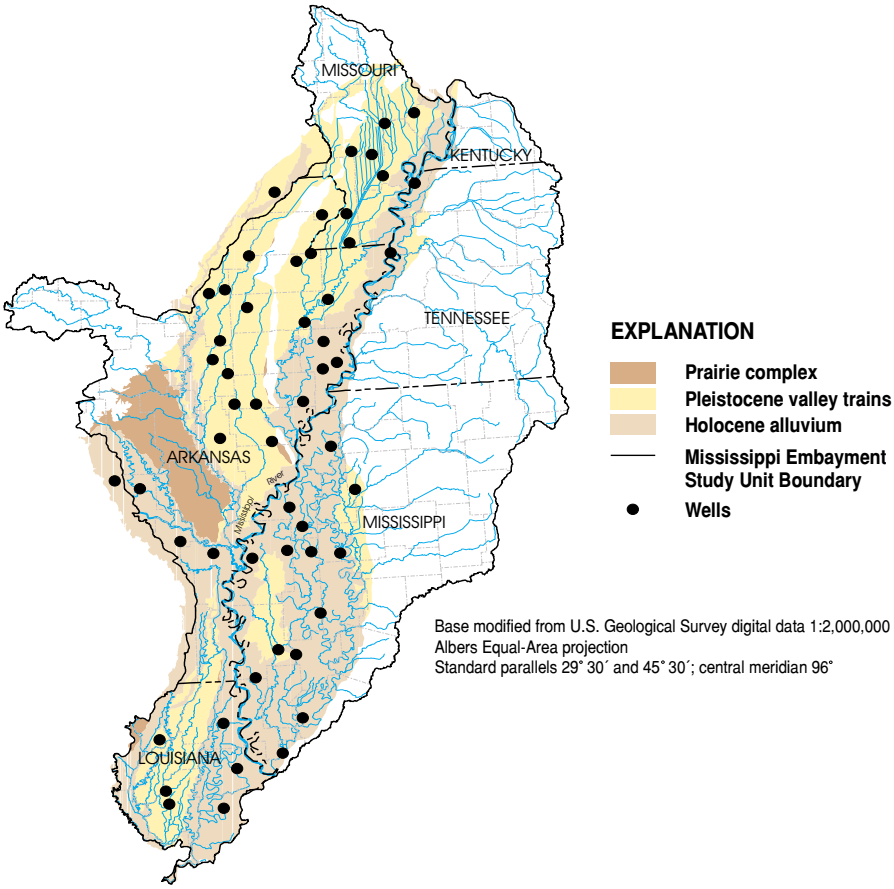


Figure 7. The colored part of this map depicts the areal extent of the three main geologic subunits of the alluvial aquifer and the location of the 54 wells that were sampled as part of this study. Statistically significant differences exist in the nutrient, carbon, and metal chemistry of the water sampled in wells located in the Pleistocene valley trains as compared to the Holocene alluvium, demonstrating the effect of geology on other components of the environment.

Many of the water samples collected from the alluvial aquifer were taken from irrigation wells in agricultural areas.

Water-Chemistry Analysis Results

Twenty-nine wells in the Pleistocene valley trains and 25 wells in the Holocene alluvium were sampled during the summer of 1998. At least one pesticide was detected in water from 19 of the 54 wells, but none of the concentrations were above drinking-water standards or guidelines. The most frequently detected pesticide was bentazon, an herbicide used to control weeds in soybean fields. Other pesticides detected in the alluvial aquifer in very low concentrations were molinate, fluometuron, 2,4–D, fenuron, atrazine, deethylatrazine, metolachlor, propanil, and *p,p´*DDE. At least one VOC was detected in water from 25 of 46 wells; 1,2,4-trimethylbenzene was detected most frequently. However, all of the VOC concentrations were well below drinking-water standards or guidelines.

Pleistocene Valley Trains and the Holocene Alluvium

The two subunits of the alluvial aquifer, the Pleistocene valley trains and the Holocene alluvium, have different lithological charac-

teristics. The Pleistocene valley trains generally have coarser grain sizes than the Holocene alluvium, whereas the Holocene alluvium has a thicker clay and silt surficial unit. These characteristics indicate that ground-water flow may be more active in the Pleistocene valley trains.

Results of the ground-water chemistry showed that sulfate, pH, tritium, chloride, and radon-222 were present in higher concentrations in water from wells in the Pleistocene valley trains, whereas dissolved organic carbon, iron, ammonia, fluoride, potassium, bicarbonate, magnesium, radium-226, barium, calcium, chromium, and dissolved solids were present in higher concentrations in water from wells in the Holocene alluvium. Examples of some of these differences are shown in figure 8. Water in the Holocene alluvium tends to be older than water in the Pleistocene valley trains; that is, it has been underground longer. This increases possible contact with buried organics, resulting in less dissolved oxygen, which could influence concentrations of other chemical constituents.

Arsenic Concentrations

Arsenic, a compound that has been implicated in causing several cancers, was found at concentrations that exceeded current drinking-water guidelines in water from only one irrigation well that pumped water from the alluvial aquifer. However, concentrations at several other wells were high enough to justify additional testing if proposals to lower the standards are promulgated.

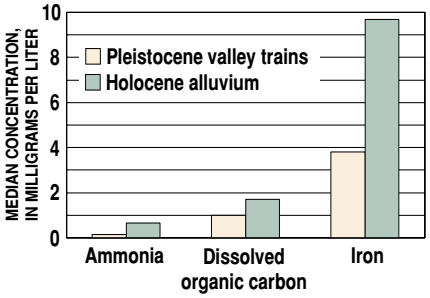
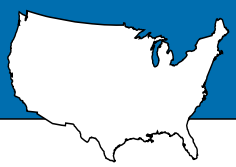


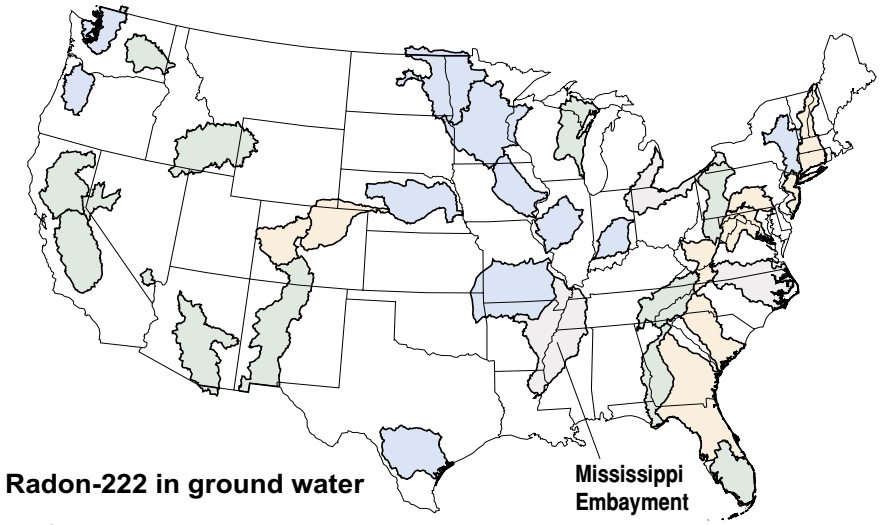
Figure 8. This graph shows some of the differences in chemistry in water from the Pleistocene valley trains and from the Holocene alluvium for a few selected constituents. Water from the wells in the Holocene deposits tended to be older and had lower oxygen levels. Low dissolved-oxygen concentrations in ground water may be associated with the presence of ammonia, dissolved organic carbon, and iron.

Radon Levels in Ground Water Low in Mississippi Embayment Study Unit



Radon is a colorless, odorless, radioactive gas that forms naturally in rocks and soils as an intermediate product in the radioactive decay of uranium-238. According to the U.S. Environmental Protection Agency, breathing radon in indoor air is the second leading cause of lung cancer in the United States. Radon can enter homes from soil or bedrock through cracks in basements or foundations, or it can be released from water during bathing, cooking, or showering.

Radon is highest in areas where there are uranium-rich metamorphic and igneous rocks. Because the MISE Study Unit is located in an area of thick alluvial soils that have few rocks, the radon levels in the ground water are some of the lowest reported by the NAWQA Program.



Aquatic Communities Show Environmental Stress

A combination of natural and anthropogenic (human-related) factors results in stream conditions that stress aquatic communities in the Mississippi Embayment Study Unit. The streams have naturally low gradients that result in sluggish flows and slow rates of reaeration (the ability of oxygen to enter the water). Also, the streams, in their natural conditions, have an abundance of streamside vegetation and swamps, resulting in an abundance of organic material in the water. This organic material is a good source of food for invertebrates (aquatic insects, crayfish, and freshwater shrimp) that inhabit the streams, but decay of the organic material and seasonally high water temperatures contribute to low dissolved-oxygen concentrations. The combination of low flow, high organic concentrations, and high temperatures results in a natural environment in which the organisms are often stressed by low dissolved-oxygen concentrations.

These natural conditions are coupled with many anthropogenic conditions in the area. These include stream channelization, which can eliminate riparian vegetation and degrade stream habitat; agricultural runoff into streams, which adds sediments, pesticides, and fertilizers to the aquatic environment; and the decline in the base flow of the streams due to ground-water withdrawal, which reduces the quantity of water available for organisms. This combination of natural and anthropogenic conditions affects each of the major biotic communities differently.

Algae

As a result of the dominant agricultural land use, fine alluvial soils, and limited vegetation in streamside or riparian areas, most of the streams in the MISE Study Unit are very turbid. Turbidity refers to the reduced clarity of surface water due to particles (usually sediment) suspended in the water. Many of the streams within the MISE also have moderately high phosphorus levels, which encourage algal growth. However, the algal growth in the streams is often more limited by the inability of light to penetrate the turbid waters, than by lack of nutrients. One indication of this can be seen in the Algal Siltation Index on page 17. This index uses the relative abundance of diatom species, which are able to move and avoid being buried under large amounts of sediment, as an indication of stream-water quality. Levels of this index are high in agricultural areas of the MISE and moderate in mixed land-use areas.

Aquatic Invertebrates

Aquatic invertebrates in the MISE are influenced by habitat quantity and quality as well as by water chemistry. Often, the loss of stream and riparian habitat in the MISE is associated with stream channelization, where streams have been cleared, ditched, and straightened to facilitate the movement of floodwaters. These activities also result in the loss of microhabitats that are essential to aquatic invertebrates for food sources and refuge. Lower numbers of invertebrate taxa were found at sites that had

Streams in the Mississippi Embayment Study Unit have small changes in elevation from their headwaters to the mouth of the stream. This makes them very slow moving and generally contributes to low oxygen concentrations in the streams. The natural streams commonly have swamps adjacent to them, resulting in water stained with organics, ample habitat, and difficult sampling conditions, as shown above. The many channelized streams in the area (see upper left photograph) have commonly lost all of their riparian vegetation, and the streams have little habitat for aquatic organisms.

Some of the samples for both algae and invertebrates were collected by scraping organisms off submerged sticks in the streams. These sticks are commonly some of the best remaining habitats in many streams and rivers in the Mississippi Embayment Study Unit.

A prime habitat for invertebrates in the Mississippi Embayment Study Unit is this "undercut bank" where insects and other organisms hide in the roots and sticks. This habitat is removed or disturbed by channelization of streams and rivers or other habitat alterations.

lower habitat quality (fig. 9). Other factors, including turbidity, low dissolved-oxygen concentrations, and the introduction of contaminants to the water, also affect invertebrate communities.

When compared to samples collected in other NAWQA Study Units across the United States (p. 17), invertebrate communities in MISE agricultural areas have low numbers of species and high proportions of tolerant organisms.

Fish

The condition of the fish communities in the MISE Study Unit was related to both water quality and land-use activities. The best quality fish communities occurred where instream variables such as turbidity, total ammonia, the average number of herbicides detected, and total DDT in fish tissue were lowest. As shown in figure 10, the number of bass, an important game fish in the MISE, was highest at the sites where the turbidity was lowest. The condition of the fish communities also was correlated to landscape-level variables such as insecticide application rates and soil permeability.

When compared to fish communities collected at NAWQA Study Units across the Nation (p. 17), the MISE had more fish that are omnivores (that is, fish that eat whatever is available and therefore are more tolerant than fish that have more restrictive diets) and more fish that are considered tolerant of poor water-quality conditions. However, there were fewer anomolies (sores, parasites and other abnormalities on the fish) and non-native fish found in the MISE than in other locations. This resulted in an overall national fish ranking of MISE agricultural streams slightly below the midpoint between the most degraded and least degraded streams in the NAWQA Program, whereas mixed land-use streams ranged from good to less than average.

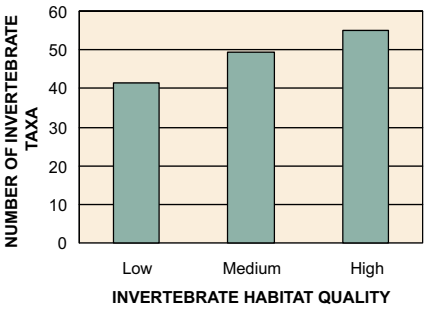


Figure 9. The number of invertebrate taxa increased as the quality of the invertebrate habitat increased in MISE streams.

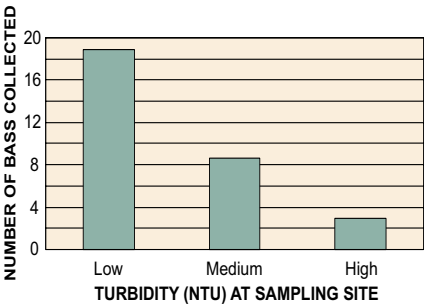
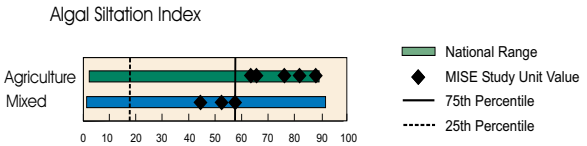


Figure 10. The number of bass collected at a stream site was highest in those streams where the turbidity was the lowest.

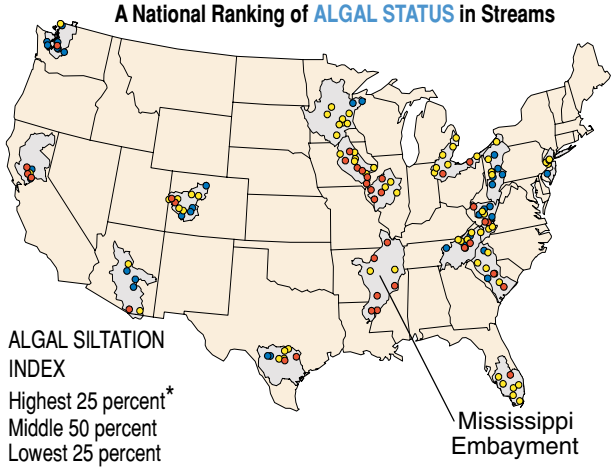
Comparison of Mississippi Embayment Aquatic Communities to National Results

Algal Siltation Index

Algae collected at the 8 MISE basic fixed ecology sites were compared to algae at 140 other NAWQA sites by use of the Siltation Index (Bahls and others, 1992). This index is the relative abundance of motile diatoms, the species *Navicula*, *Nitzschia*, *Cylindrotheca*, and *Surirella* in a diatom count. These diatoms are able to move through silt particles and are associated with fine sediments. Because they are able to avoid being buried, they are considered more tolerant of sedimentation than other diatoms. Generally, this index tends to be higher for streams in agricultural basins. Relative to this index, all of the MISE agricultural sites fall into the most-degraded category for streams along with one of the mixed land-use sites, whereas the other two sites fall into the middle 50 percent.

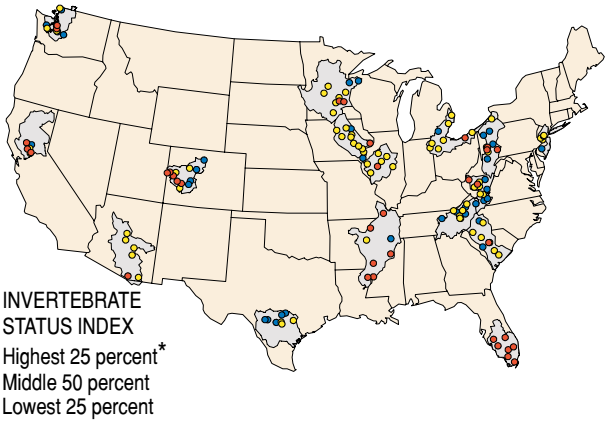


A National Ranking of ALGAL STATUS in Streams



* Higher values suggest a more degraded stream site

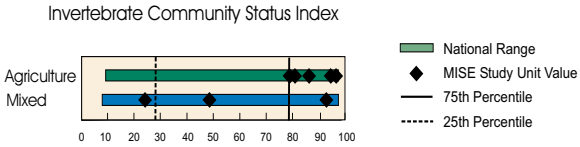
A National Ranking of INVERTEBRATE STATUS in Streams



* Higher values suggest a more degraded stream site

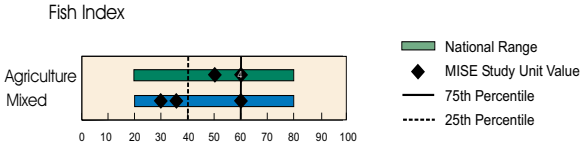
Invertebrate Community Status Index

To compare the invertebrate communities at MISE ecological basic fixed sites to national sites, a multimetric index called the Invertebrate Community Status Index was developed. The index combines 11 metrics, including ones that address taxa richness and diversity, richness of mayflies, stoneflies, and caddisflies, and tolerance metrics. Relative to this index, MISE agricultural streams are all ranked within the 25-percent most-degraded category for streams, whereas the mixed land-use streams have one site that falls into each category. Across the United States, both agricultural and urban sites tend to fall into the more degraded category.

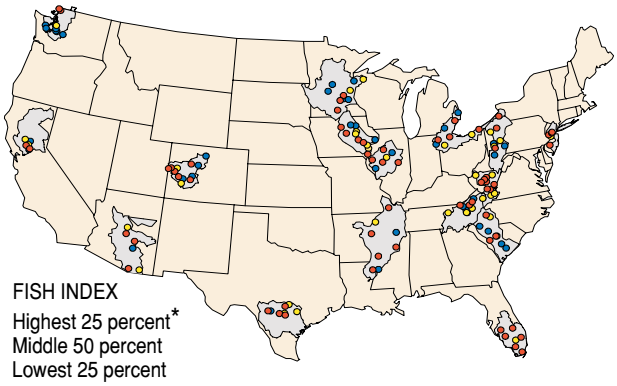


Fish Community Index

Similar in concept to the invertebrates, a multimetric fish index was developed to facilitate the comparison of fish communities across the United States. This index included four metrics: the percentage of tolerant individuals, the percentage of omnivorous individuals, the percentage of non-native individuals, and the percentage of individuals with anomalies. In all four metrics, a high percentage of individuals with the characteristic is typical of degraded sites. Agricultural sites in the MISE Study Unit generally fell at the boundary between the most-degraded category and the middle 50 percent (four sites are represented by the symbol at the 60-percent point). The mixed land-use sites ranged from the least-degraded category to the highly degraded category.



A National Ranking of FISH STATUS in Streams



* Higher values suggest a more degraded stream site

Organochlorine Pesticides Persist in Fish Tissue

During the 1950s and 1960s, organochlorine pesticides were heavily used in the MISE Study Unit to control insects, particularly those associated with the cultivation of cotton. One of the most widely used organochlorine insecticides was DDT. In 1972, the sale of DDT was discontinued, and the use of most of the persistent organochlorine pesticides was discontinued during the 1970s. Nearly 30 years later, however, DDT or its metabolites were detected in fish tissue from all 41 sites sampled in the Study Unit. Thirty of these sites have total DDT levels in excess of the 0.2-mg/kg (milligram per kilogram) or 200 µg/kg (micrograms per kilogram) criterion set by the State of New York for the protection of fish-eating wildlife (Newell and others, 1987).

Although somewhat less prevalent and at lower concentrations, other organochlorine compounds also were detected in fish, including chlordane (at 33 percent of the sites), dieldrin (79 percent), heptachlor (7 percent), mirex (29 percent), and toxaphene (56 percent).

Most of the rivers in the MISE Study Unit were too deep to wade, so boat-mounted electroshocking equipment was used to collect fish (usually common carp) for tissue analysis.

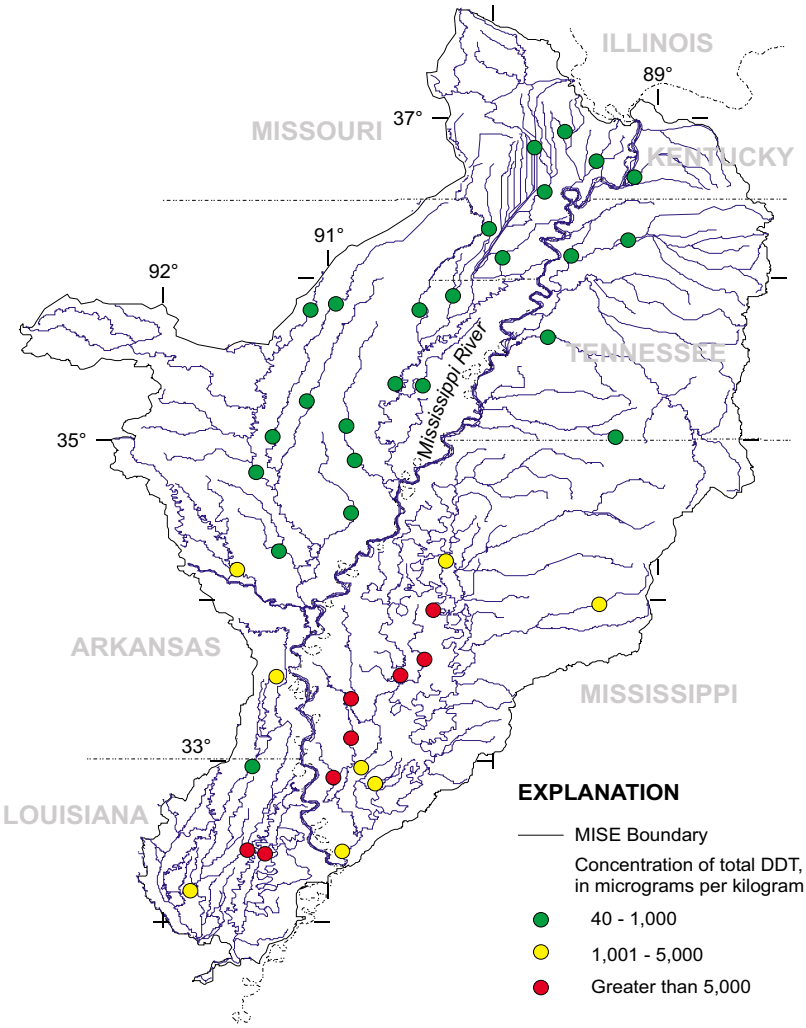


Figure 11. The concentrations of organochlorine pesticides were measured in fish tissue collected at 41 sites in the MISE Study Unit. Total DDT, an insecticide that has not been sold in the United States since 1972, was detected at all sites and occurs in concentrations that are of possible human health concern at some sites.

Of the 506 sites sampled thus far in the National Water-Quality Assessment Program, the highest concentrations of total DDT and toxaphene were found in fish collected in the Mississippi Embayment Study Unit (see pages 33 and 34 in Appendix A).

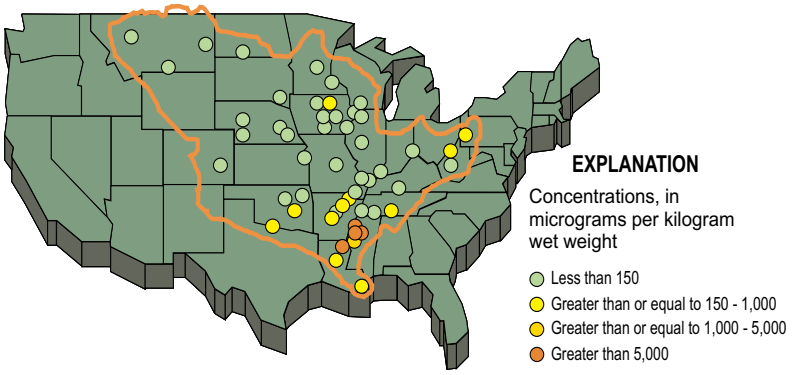
Distribution of Concentrations of DDT Within the Mississippi Embayment Study Unit

Although DDT was detected in fish tissue at every sampling site, tissue samples from sites in the southern part of the Study Unit (fig. 11) had much higher concentrations of total DDT. On a national scale, Nowell and others, (1999) presented a positive correlation between median total DDT concentrations in whole fish and agricultural use of DDT in 1966. In the MISE, however, there seem to be additional factors influencing the persistence of DDT in fish tissue. Fish tissue data were compared to dozens of land-use and water-chemistry variables. Good correla-

tions can be made between total DDT concentrations and dissolved ammonia, nitrate, total phosphorus, and turbidity. The correlations with land-use variables, such as the percentage of the basin in agricultural production or the percentage of the basin in which cotton is grown, are much weaker, suggesting that factors in addition to land use and pesticide use are contributing to the distribution of DDT.

A relation exists between the concentrations of DDT in fish tissue and the geology of the area. Total DDT concentrations are much higher at sites in the Holocene alluvium than in the Pleistocene valley trains (fig. 12). The soils and geologic deposits in the Holocene alluvium are largely composed of dense clays that may cause agricultural runoff from these areas to enter the streams directly rather than infiltrate through the soils. Also, DDT tends to sorb onto clay particles and may be carried into streams attached to these particles. Once in the stream, the cohesive nature of clay tends to prevent the material from moving downstream. These combined mechanisms may cause greater amounts of DDT to be in streams and available to organisms in Holocene areas than in streams in the Pleistocene valley trains.

DDT in Fish Tissue in the Mississippi River Valley



Fish collected in 1995 during an interdisciplinary USGS study found that the highest total DDT levels in the Mississippi River Valley were measured in the MISE Study Unit. Information about study methods can be found in Schmitt and Dethloff (2000).

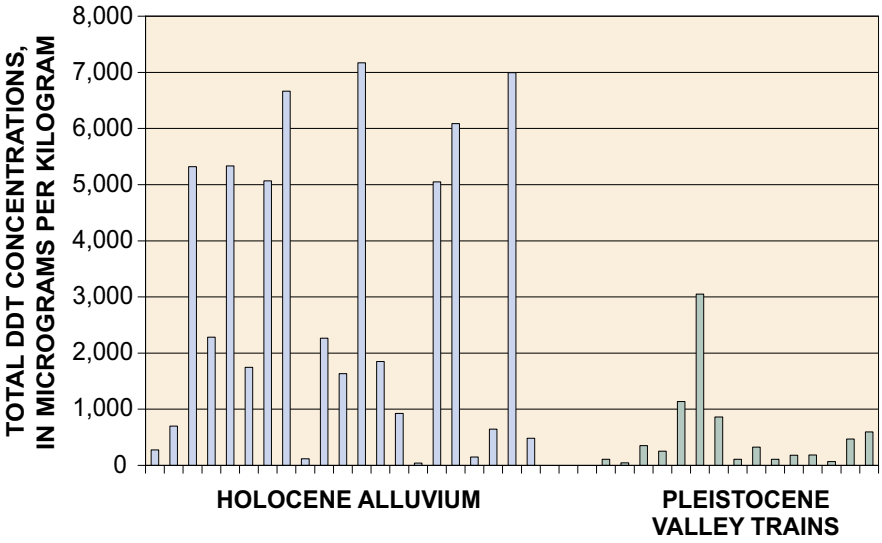


Figure 12. The concentration of total DDT in fish tissue is higher at Holocene alluvium sampling sites than at sites in the Pleistocene valley trains. The mean concentration for the Holocene sites is 2,895 micrograms per kilogram, while the mean concentration for the Pleistocene sites is 522 micrograms per kilogram.

Total DDT concentrations were detected in streambed sediments at all 15 sites measured. However, the concentrations in the sediments were many times lower than those in fish tissue.

Human Health Considerations

Because the NAWQA sampling was designed to measure the occurrence and distribution of compounds in the environment rather than address human health issues, whole fish (usually common carp) rather than fish fillets or other edible fish parts were analyzed for organochlorine compounds. However, the high concentrations of organochlorines that were detected at some of the sites in the MISE Study Unit suggest the need for further investigation. In the years since the sale of DDT and toxaphene has been discontinued, concerns have been raised about not only the toxicity of the pesticides but also the carcinogenic nature of organochlorine compounds.

Pesticides in Air and Rain Samples from Agricultural and Urban Sites

During the 1995 growing season, weekly air and rain samples were collected from two sites in Mississippi and analyzed for 49 pesticides and pesticide metabolites. The two sites represented an agricultural area and an urban area. Every air and rain sample had detectable levels of multiple pesticides; the pesticides detected and the frequency of detection varied between the two sites and were related to the types of pesticides used nearby. However, long-range transport appears to have an effect, as some pesticides that are not registered for use in an urban setting were found in air and rain samples at the urban site. These findings demonstrate that small amounts of pesticides can be transported through the atmosphere and deposited into aquatic and terrestrial ecosystems at a substantial distance from their point of use.

Pesticides in the Air

Pesticides can enter the atmosphere through volatilization, wind erosion of soil particles to which pesticides are attached, and direct spraying into the atmosphere during pesticide application.

Seasonal distribution of pesticides at the agricultural site is related to local application times of individual compounds. At the start of the study in April, the herbicides pendimethalin and trifluralin were the pesticides found in the highest concentrations in the air. In May, the two pesticides with the highest measured concentrations were the herbicides propanil and thiobencarb, which typically are used on rice. By August, the insecticide methyl parathion was detected in the highest concentration of any of the pesticides in the air at the agricultural site.

In contrast, diazinon was detected in the highest concentration in the air at the urban site. Chlorpyrifos also was detected frequently, and carbaryl, methyl parathion, and trifluralin were found less often. Although most of these compounds are used commonly in residential settings for such purposes as termite control, methyl parathion is used only for insect control in agricultural settings, thus suggesting the long distance atmospheric transport of this compound.

The yellow polyurethane foam plug was used to collect pesticides distributed into the gas phase of the atmosphere.

Pesticides in the Rain

Once in the atmosphere, pesticides can be degraded, transported, and (or) redeposited. Deposition can be either wet, as with rain or snow, or dry, as with gaseous sorption and particle fallout.

The urban atmospheric sampling site on the left is in a residential area in southern Jackson, Mississippi, a metropolitan area of about 400,000 people. The site is more than 10 miles from the nearest agricultural field. The agricultural site on the right is located in the center of a catfish pond complex in Sharkey County, Mississippi. This site was selected to measure pesticides in the atmosphere in an area with minimal influence of direct application of pesticides to nearby fields. The nearest agricultural field is about one-half mile away, and the major crops grown in this area are soybeans, cotton, corn, and rice.

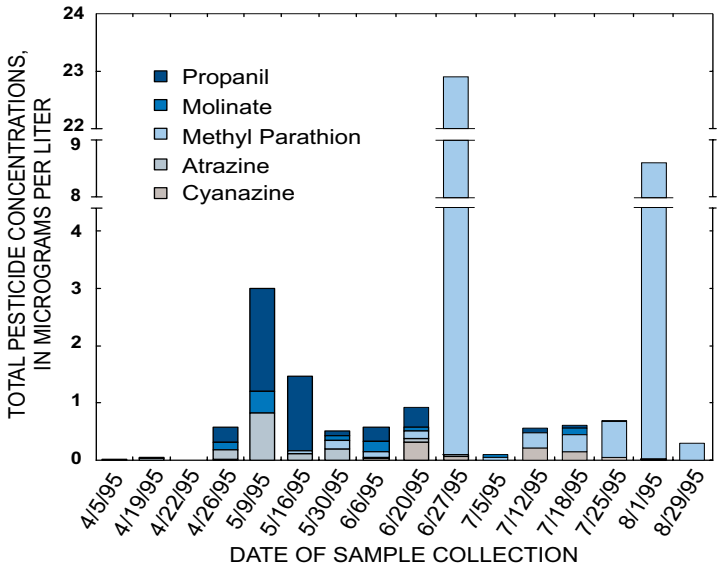


Figure 13. Pesticide concentrations in rainfall samples collected at an agricultural site in Mississippi during the 1995 growing season. In the spring, atrazine and propanil were detected in higher concentrations, but by summer the dominant pesticide measured was methyl parathion.

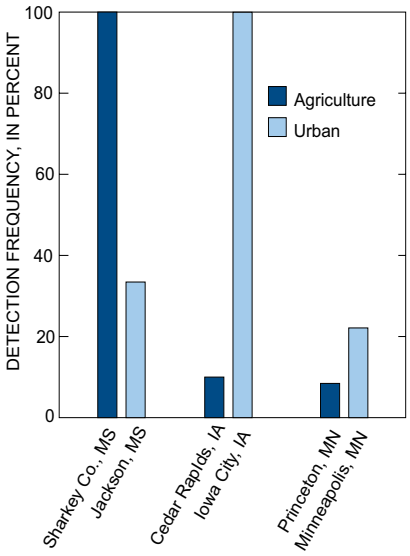
The concentrations of selected pesticides detected in rainfall samples from the agricultural site are shown in figure 13. The pesticides detected in the highest concentrations during the early part of the growing season were the herbicides atrazine, used on corn and grain sorghum, and propanil, used mainly on rice. Later in the growing season, the pesticide found in the highest concentrations was the insecticide methyl parathion.

The pesticides detected in rainfall samples from the urban site—atrazine, carbaryl, methyl parathion, and propanil—were similar to those found at the agricultural site, but the concentrations were much lower. Because methyl parathion and propanil do not have legal urban uses, it is assumed that these pesticides were transported in the atmosphere from their application areas. Methyl parathion and propanil are the first and sixth most heavily used agricultural pesticides in Mississippi.

Metabolites of DDT in the Air

In order to fully understand the fate, transport, and environmental effects of a pesticide, major metabolites of the pesticide commonly are included in the sampling program. One of the major metabolites of the organochlorine insecticide DDT is *p,p´*-DDE. In 1971, Stanley and others (1971) detected *p,p´*-DDE in the air at an agricultural site near Stoneville, Miss. (about 60 miles north of the Sharkey County site) in concentrations ranging from 2.6 to 7.1 ng/m^3 (nanograms per cubic meter). Twenty-four years later, the range of *p,p´*-DDE in air samples from the agricultural site ranged from 0.13 to 1.1 ng/m^3, lower than reported by Stanley and others (1971) but still significant considering that there is no current use of DDT in the area. These results indicate that a persistent metabolite of *p,p´*- DDT was still measurable in the air more than two decades after the sale of DDT was discontinued in the United States.

DDT Metabolites in the Air Across Mid-America



The air concentrations of *p,p´*-DDE, a metabolite of DDT, were determined at paired urban and agricultural sites in Mississippi, Iowa, and Minnesota (Foreman and others, 2000). The agricultural site in Mississippi and the urban site in Iowa had detectable levels of *p,p´*-DDE in every sample. Approximately 10 to 30 percent of the samples collected at the other sites had detectable levels of *p,p´*-DDE. It is likely that these concentrations of *p,p´*-DDE are from past local use of DDT. However, DDT is still being used in other parts of the world, and it is possible that some proportion of this *p,p´*-DDE originated elsewhere and was transported in the atmosphere.

More details on pesticides in the atmosphere can be found in the paper:
Coupe, R.H., Manning, M.A., Foreman, W.T., Goolsby, D.A., and Majewski, M.S., 2000, Occurrence of pesticides in urban and agricultural areas of Mississippi, April–September 1995: Science of the Total Environment, v. 248, no. 2–3, p. 227.

The paper also can be downloaded at:
http://ms.water.usgs.gov/misenawqa/

Integration of Biological, Geological, and Chemical Data Improves Understanding of Aquatic Systems

One of the most significant advances in the aquatic sciences during the last century is the growing understanding that aquatic systems, such as lakes and rivers, are profoundly influenced by the biological, chemical, and physical aspects of the drainage basin in which the water body is located (Wetzel, 1983). Although the conceptual framework for these ideas is decades old, scientists are still developing the technologies and accumulating the data bases necessary to more fully understand the relations between a body of water, the biotic components within it, and the chemical and physical influences of the drainage basin.

In the NAWQA Program, researchers often collect biological, geological, and chemical information from the same stream sites and analyze land use from the corresponding drainage basins. This information presents an opportunity to examine biogeochemical relations within the watersheds. This interdisciplinary approach has yielded at least three broad findings in the MISE Study Unit. Three findings, which need to be examined in more detail to guide scientific understanding and management in this region, are: (1) DDT and its metabolites remain detectable in many parts of the environment; (2) numerous interrelations exist between the biological, geological, and chemical components of the MISE Study Unit; and (3) evidence exists that the geology of the Study Unit exerts an influence on many aspects of the environment.

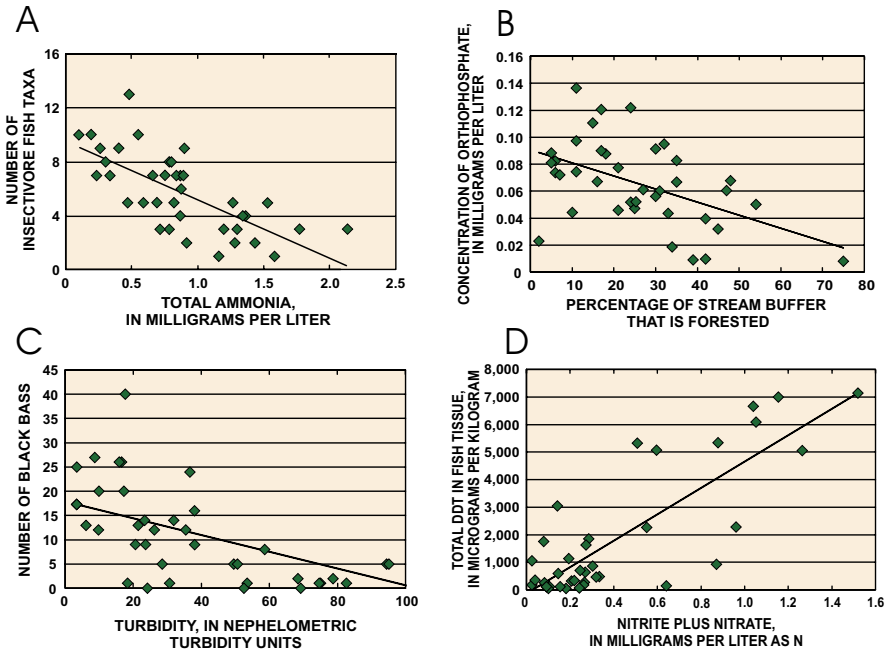


Figure 14. There are numerous interrelations among stream biology, basin geology, stream chemistry, and land use in the Mississippi Embayment Study Unit. The lines in these graphs represent linear relations between some of the variables.

DDT and Its Metabolites Are Present Throughout the Environment

Nearly 30 years after the sale of DDT was discontinued, the pesticide and its metabolites were detected in all parts of the MISE Study Unit environment. While residual total DDT is found throughout the world, the concentrations in the MISE are among the highest in the United States. (See water, fish tissue, and bed sediment sections of the national comparison tables on pages 31, 33, and 34 for a comparison of MISE results to other NAWQA Study Units in the United States.) A metabolite of DDT, DDE persists in various concentrations in many different parts of the MISE environment, including the air, water, streambed sediment, and fish tissue, generating interesting questions about its transport, accumulation, and persistence.

Biological and Chemical Relations

The MISE Study Unit has numerous complex interrelations among stream biology, basin geology, stream chemistry and land use. Some of these interrelations are illustrated by a variety of linear relations among biological, geological, and chemical components of 36 stream sites and their drainage basins in the MISE Study Unit (fig. 14). Figures 14A and 14C illustrate how differences in stream chemistry can affect biological communities in the stream. Figure 14A shows that the number of insectivore fish taxa decreases as total ammonia increases, whereas figure 14C

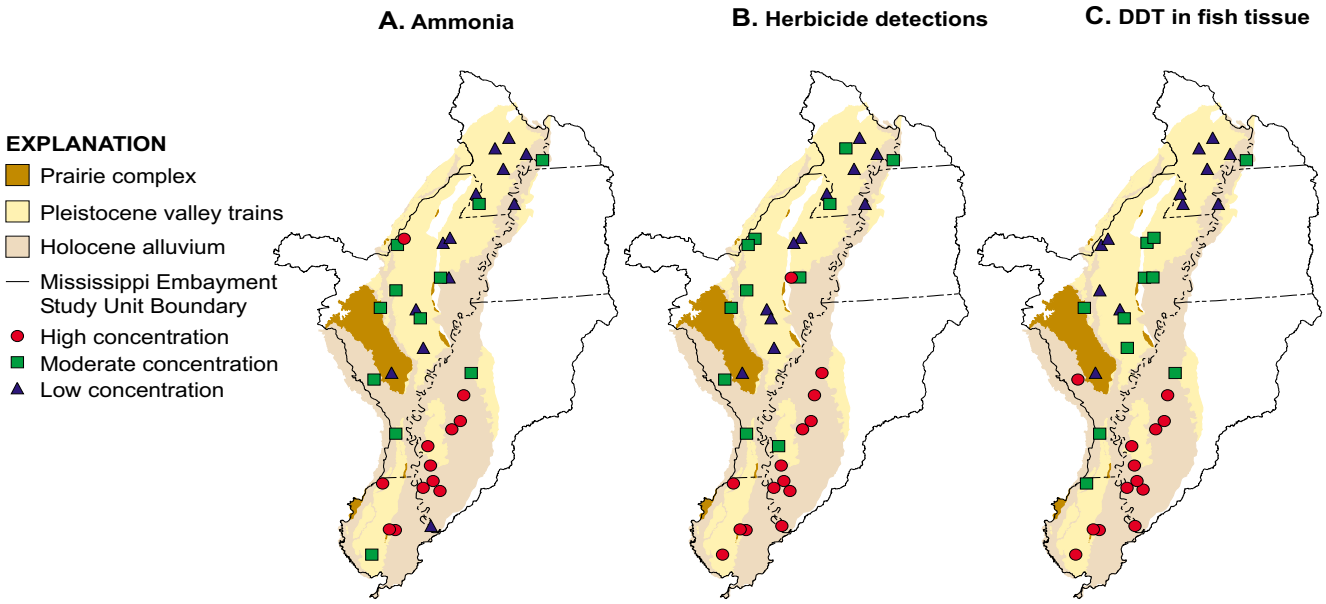


Figure 15. Several variables in the MISE Study Unit vary spatially and correspond generally to the Quaternary geology of the Mississippi Alluvial Plain. Soils formed from the Holocene alluvium tend to be dense, thick clays, whereas the Pleistocene features tend to have soils that have more silts and sands. These soils influence permeability and runoff, which in turn, appear to affect the amount and persistence of agricultural chemicals in the streams.

shows that the number of black bass decreases as turbidity increases. Figures 14B and 14D show how factors in the drainage area, but not in the stream, can influence the stream. Figure 14B shows that as the percentage of forested stream buffer (the area within 60 meters of the streams) increases, concentrations of orthophosphate in the stream decrease, indicating the value of vegetated stream buffers in minimizing the amount of runoff entering streams and rivers. Finally, figure 14D illustrates that as the concentration of dissolved nitrite plus nitrate increases, the amount of total DDT in fish tissue increases, suggesting that conditions that facilitate agricultural runoff affect nutrient levels in the streams and the long-term bioaccumulation of organochlorine pesticides in fish tissue.

The sum of these various relations shows the complexity of the system, underscores the need for multidisciplinary studies in order to thoroughly understand the Mississippi Embayment Study Unit, and discourages simplistic, one-dimensional management solutions.

Geology Influences Many Variables

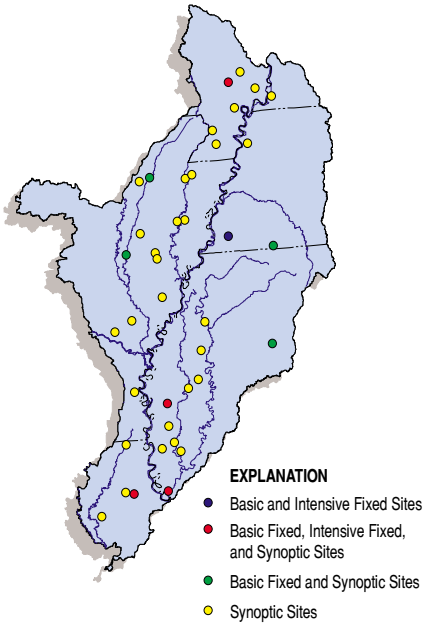
Within the Mississippi Embayment Study Unit, the geology of the land surface appears to exert an overarching influence on many components of the environment. The dense, tight clays of the Holocene alluvium dictate the types of crops grown and cause high runoff potential in the area. These factors help to determine the types of agricultural chemicals that are applied and the amounts of these chemicals that are transported into rivers and streams. Once in the streams, the clays tend to cause chemicals sorbed to sediments to remain locally in the bed sediment rather than to be washed downstream. Sites where high concentrations of ammonia were found are clustered in the Holocene alluvium (fig. 15A), whereas similar clusters occurred for the number of herbicides detected in the water (fig. 15B) and the amount of total DDT found in fish tissue (fig. 15C). In turn, many biological metrics were lower at sites located in the Holocene alluvium, and differences in ground-water chemistry were detected (pages 13 and 14).

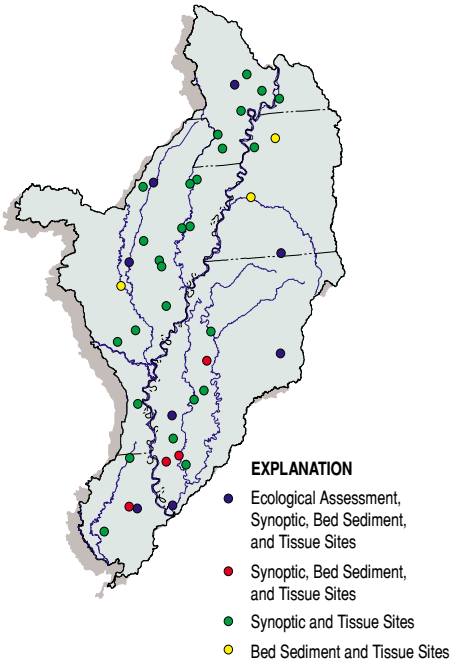
This information reaffirms that a better understanding of the underlying geology of the Earth itself is needed to fully understand the effects of human activities on the environment.

Carp used for tissue analysis.

Stream Chemistry

The stream-chemistry network was designed to measure the effects of land use (primarily cropland) on stream quality and to integrate the effects of multiple land uses and hydrogeologic settings on water quality. Data from the Basic Fixed Sites were used to examine differences in water quality from one basin to another. Data from Intensive Fixed Sites, which were sampled more often, were used to examine seasonal changes in stream quality and to calculate fluxes from the basin. Also, detailed data on pesticides dissolved in the water were collected at intensive sites. A synoptic study was conducted to measure a selected set of constituents at 38 sites in the Study Unit in order to better understand spatial differences among the basins and to compare water chemistry to biological and landscape parameters.



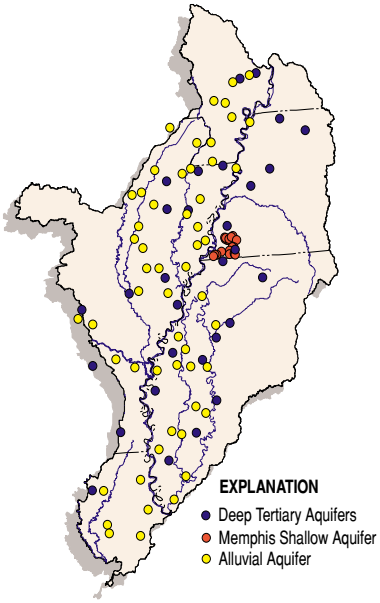


Stream Ecology

Ecological assessments were done annually at the basic and intensive stream-chemistry sites. The objective of these studies was to investigate biological, chemical, and physical data as multiple lines of evidence to assess water quality. Some of the assessments examined multiple reaches of a stream to determine spatial variations in the community structure of the aquatic organisms. Synoptic studies were designed to examine spatial variability in biological communities in the Study Unit and to relate this variability to stream chemistry and landscape variables. Early in the project, bed sediment and fish tissue were sampled at a subset of sites; later in the project, fish tissue was sampled for organochlorine concentrations at all of the synoptic sites.

Ground-Water Chemistry

Three surveys examined the effects of land use on ground water in different aquifer settings. The deep Tertiary aquifers are the deepest aquifers studied and the ones that provide drinking water to the greatest number of people in the Study Unit. The Memphis shallow aquifer survey was designed to assess the ground-water quality in commercial and residential areas. The alluvial aquifer survey examined ground-water quality from a shallow aquifer that is heavily used for agriculture.



SUMMARY OF DATA COLLECTION IN THE MISSISSIPPI EMBAYMENT STUDY UNIT, 1995–98

Study component	What data were collected and why	Types of sites sampled	Number of sites	Sampling frequency and period
Stream Chemistry				
Basic Fixed Sites	Continuous streamflow, nutrients, major ions, organic carbon, suspended sediment, and physical parameters were measured to describe concentrations and seasonal variations.	Sites were selected to represent the range of ecoregions, physiographic regions, and land uses present in the Study Unit.	9	Samples were collected monthly February 1996 – January 1998.
Intensive Fixed Sites	In addition to the above list of data collected at the Basic Fixed Sites, information on 82 dissolved pesticides was collected to determine concentrations, seasonal variations, and loads. Volatile organic compounds also were measured at the urban site.	Three of the sites were located at streams that drained intensive agricultural areas but were dominated by different crop types. One site was a large river site with mixed land use. The remaining site was located in a rapidly growing urban area.	5	Sampling frequency ranged from biweekly during the growing season to weekly throughout the remainder of the period February 1996 – January 1998.
Synoptic Sites—Water Chemistry	Nutrients, pesticides, and physical properties were measured to broaden the spatial coverage of water-quality information in the Study Unit.	Synoptic sites were selected in an effort to sample streams that drained all major crop types grown in the Study Unit.	38	Samples were collected once during May, July, and August 1997.
Stream Ecology				
Ecological Assessment Sites	Fish, macroinvertebrate, algae, and habitat data were collected to examine relations among the biological community and water chemistry, land use, and physical components of the landscape and drainage basin.	Sites were selected to represent the range of ecoregions, physiographic regions, and land uses present in the Study Unit.	8	Samples were collected once during low-flow conditions in the summers of 1996–98; at two sites, three reaches were sampled in 1996.
Synoptic Sites—Ecology	Fish, macroinvertebrate, habitat, and streamflow data were collected once at a larger number of sites to develop a better understanding of the spatial aspects of aquatic communities in the Study Unit.	Synoptic sites were selected in an effort to sample streams that drained all major crop types grown in the Study Unit.	38	Samples were collected July–September 1997 for macroinvertebrates; July–September 1998 for fish.
Contaminants in Bed Sediments	Total PCB's, organochlorine pesticides, semivolatile organic compounds, and trace elements were measured in order to determine the occurrence and distribution of contaminants in stream sediments.	Sites were selected to represent the range of ecoregions, physiographic regions, and land uses present in the Study Unit.	15	Samples were collected during August and September 1995.
Contaminants in Fish Tissue	Organochlorine pesticides were measured in whole fish, and trace elements were measured in fish liver.	Sites were selected in an effort to sample streams that drained all major crop types grown in the Study Unit.	41 (pesticides) 15 (trace elements)	Samples were collected during late summer low-flow conditions in 1995–98.
Ground-Water Chemistry				
Deep Tertiary Aquifers	Nutrients, major ions, pesticides, volatile organic compounds, radioisotopes, stable isotopes, and physical parameters were measured to determine overall water quality in a deep aquifer used for drinking water.	Public-supply wells screened in the deep Tertiary aquifers (Claiborne and Wilcox Groups) were sampled.	30	Samples were collected once during April and May 1996.
Memphis Shallow Aquifers	Nutrients, major ions, trace elements, pesticides, volatile organic compounds, radioisotopes, stable isotopes, and physical parameters were measured to determine overall water quality in shallow aquifers in a rapidly developing urban area.	Twenty-four monitoring wells screened in the shallow water-table aquifer and eight monitoring wells screened in the upper part of the Memphis aquifer were sampled.	32	Samples were collected once during April and May 1997.
Alluvial Aquifer	Nutrients, major ions, trace elements, pesticides, volatile organic compounds, radioisotopes, stable isotopes, and physical parameters were measured to determine overall water quality in an aquifer largely used for agricultural irrigation, but also for public supply and industry.	Twenty-five irrigation wells screened in the Holocene alluvium and 29 irrigation wells screened in the Pleistocene valley trains were sampled.	54	Samples were collected once during the summer of 1998.
Special Studies				
Pesticides in the Atmosphere	Pesticides were measured in the air and in the rain.	Two sites were sampled–one in an agricultural area in Sharkey County, Miss., and one in an urban area in Jackson, Miss.	2	Samples were collected April–September 1995.
Pesticides in Fish Tissue in the Mississippi River	Organochlorine pesticides in whole fish (common carp) were measured to determine if pesticides leaving the Yazoo River Basin could be detected in fish in the Mississippi River.	Four sites were selected within an area 100 miles upstream and another four sites were selected 100 miles downstream from the confluence of the Yazoo River and the Mississippi River.	8	Samples were collected once during November 1997.

Algae - Chlorophyll-bearing nonvascular, primarily aquatic species that have no true roots, stems, or leaves; most algae are microscopic, but some species can be as large as vascular plants.

Alluvial aquifer - A water-bearing deposit of unconsolidated material (sand and gravel) left behind by a river or other flowing water.

Alluvium - Deposits of clay, silt, sand, gravel or other particulate rock material left by a river in a streambed, on a flood plain, delta, or at the base of a mountain.

Aquatic-life criteria - Water-quality guidelines for protection of aquatic life. Often refers to U.S. Environmental Protection Agency water-quality criteria for protection of aquatic organisms. See also Water-quality guidelines, Water-quality criteria, and Freshwater chronic criteria.

Aquifer - A water-bearing layer of soil, sand, gravel, or rock that will yield usable quantities of water to a well.

Atmospheric deposition - The transfer of substances from the air to the surface of the Earth, either in wet form (rain, fog, snow, dew, frost, hail) or in dry form (gases, aerosols, particles).

Basic Fixed Sites - Sites on streams at which streamflow is measured and samples are collected for temperature, salinity, suspended sediment, major ions and metals, nutrients, and organic carbon to assess the broad-scale spatial and temporal character and transport of inorganic constituents of streamwater in relation to hydrologic conditions and environmental settings.

Bed sediment - The material that temporarily is stationary in the bottom of a stream or other watercourse.

Bioaccumulation - The biological sequestering of a substance at a higher concentration than that at which it occurs in the surrounding environment or medium. Also, the process whereby a substance enters organisms through the gills, epithelia tissues, dietary, or other sources.

Biota - Living organisms.

Channelization - Modification of a stream, typically by straightening the channel, to provide more uniform flow; often done for flood control or for improved agricultural drainage or irrigation.

Community - In ecology, the species that interact in a common area.

Concentration - The amount or mass of a substance present in a given volume or mass of sample. Usually expressed as microgram per liter (water sample) or microgram per kilogram (sediment or tissue sample).

Criterion - A standard rule or test on which a judgment or decision can be based.

Degradation products - Compounds resulting from transformation of an organic substance through chemical, photochemical, and/or biochemical reactions.

Detection limit - The minimum concentration of a substance that can be identified, measured, and reported within 99 percent confidence that the analyte concentration is greater than zero; determined from analysis of a sample in a given matrix containing the analyte.

DDT - Dichloro-diphenyl-trichloroethane. An organochlorine insecticide no longer registered for use in the United States.

Dissolved solids - Amount of minerals, such as salt, that are dissolved in water; amount of dissolved solids is an indicator of salinity or hardness.

Drainage area - The drainage area of a stream at a specified location is that area, measured in a horizontal plane, which is enclosed by a drainage divide.

Drinking-water standard or guideline - A threshold concentration in a public drinking-water supply, designed to protect human health. As defined here, standards are U.S. Environmental Protection Agency regulations that specify the maximum contamination levels for public water systems required to protect the public welfare; guidelines have no regulatory status and are issued in an advisory capacity.

Ecosystem - The interacting populations of plants, animals, and microorganisms occupying an area, plus their physical environment.

Eutrophication - The process by which water becomes enriched with plant nutrients, most commonly phosphorus and nitrogen.

Fixed Sites - NAWQA's most comprehensive monitoring sites. See also Basic Fixed Sites and Intensive Fixed Sites.

Ground water - In general, any water that exists beneath the land surface, but more commonly applied to water in fully saturated soils and geologic formations.

Habitat - The part of the physical environment where plants and animals live.

Herbicide - A chemical or other agent applied for the purpose of killing undesirable plants. See also Pesticide.

Holocene - A subdivision of geologic time which began at the end of the Pleistocene (approximately 9,000 to 11,000 years ago) and extends to the present.

Human health advisory - Guidance provided by U.S. Environmental Protection Agency, State agencies or scientific organizations, in the absence of regulatory limits, to describe acceptable contaminant levels in drinking water or edible fish.

Intensive Fixed Sites - Basic Fixed Sites with increased sampling frequency during selected seasonal periods and analysis of dissolved pesticides for 1 year. Most NAWQA Study Units have one to two integrator Intensive Fixed Sites and one to four indicator Intensive Fixed Sites.

Load - General term that refers to a material or constituent in solution, in suspension, or in transport; usually expressed in terms of mass or volume.

Loess - Homogeneous, fine-grained sediment made up primarily of silt and clay, and deposited over a wide area (probably by wind).

Maximum contaminant level (MCL) - Maximum permissible level of a contaminant in water that is delivered to any user of a public water system. MCLs are enforceable standards established by the U.S. Environmental Protection Agency.

Median - The middle or central value in a distribution of data ranked in order of magnitude. The median is also known as the 50th percentile.

Metabolite- A compound derived by chemical, biological, or physical action upon a pesticide. The breakdown is a natural process which may result in a more toxic or a less toxic compound and a more persistent or less persistent compound.

Method detection limit - The minimum concentration of a substance that can be accurately identified and measured with present laboratory technologies.

Micrograms per liter (µg/L) - A unit expressing the concentration of constituents in solution as weight (micrograms) of solute per unit volume (liter) of water; equivalent to one part per billion in most streamwater and ground water. One thousand micrograms per liter equals 1 mg/L.

Minimum reporting level (MRL) - The smallest measured concentration of a constituent that may be reliably reported using a given analytical method. In many cases, the MRL is used when documentation for the method detection limit is not available.

Nitrate - An ion consisting of nitrogen and oxygen (NO3-). Nitrate is a plant nutrient and is very mobile in soils.

Nonpoint source - A pollution source that cannot be defined as originating from discrete points such as pipe discharge. Areas of fertilizer and pesticide applications, atmospheric deposition, manure, and natural inputs from plants and trees are types of nonpoint source pollution.

Nutrient - Element or compound essential for animal and plant growth. Common nutrients in fertilizer include nitrogen, phosphorus, and potassium.

Organochlorine insecticide - A class of organic insecticides containing a high percentage of chlorine. Includes dichlorodiphenylethanes (such as DDT), chlorinated cyclodienes (such as chlordane), and chlorinated benzenes (such as lindane). Most organochlorine insecticides were banned because of their carcinogenicity, tendency to bioaccumulate, and toxicity to wildlife.

Periphyton - Organisms that grow on underwater surfaces; periphyton include algae, bacteria, fungi, protozoa, and other organisms.

Phosphorus - A nutrient essential for growth that can play a key role in stimulating aquatic growth in lakes and streams.

Physiography - A description of the surface features of the Earth, with an emphasis on the origin of landforms.

Pleistocene - A subdivision of geologic time which began about 2 million years ago and ended at the beginning of the Holocene epoch, approximately 9,000 to 11,000 years ago.

Quaternary - A subdivision of geologic time which began about 2 million years ago and extends to the present. The Quaternary period is further divided into two epochs, the Pleistocene and the Holocene.

Recharge - Water that infiltrates the ground and reaches the saturated zone.

Sediment quality guideline - Threshold concentration above which there is a high probability of adverse effects on aquatic life from sediment contamination, determined using modified USEPA (1996) procedures.

Semivolatile organic compound (SVOC) - Operationally defined as a group of synthetic organic compounds that are solvent-extractable and can be determined by gas chromatography/mass spectrometry. SVOCs include phenols, phthalates, and polycyclic aromatic hydrocarbons (PAHs).

Species diversity - An ecological concept that incorporates both the number of species in a particular sampling area and the evenness with which individuals are distributed among the various species.

Species (taxa) richness - The number of species (taxa) present in a defined area or sampling unit.

Stream reach - A continuous part of a stream between two specified points.

Study Unit - A major hydrologic system of the United States in which NAWQA studies are focused. Study Units are geographically defined by a combination of ground- and surface-water features and generally encompass more than 4,000 square miles of land area.

Study-Unit Survey - Broad assessment of the water-quality conditions of the major aquifer systems of each Study Unit. The Study-Unit Survey relies primarily on sampling existing wells and, wherever possible, on existing data collected by other agencies and programs. Typically, 20 to 30 wells are sampled in each of three to five aquifer subunits.

Synoptic sites - Sites sampled during a short-term investigation of specific water-quality conditions during selected seasonal or hydrologic conditions to provide improved spatial resolution for critical water-quality conditions.

Taxon (plural taxa) - Any identifiable group of taxonomically related organisms.

Total DDT - The sum of DDT and its metabolites (breakdown products), including DDD and DDE.

Trace element - An element found in only minor amounts (concentrations less than 1.0 milligram per liter) in water or sediment; includes arsenic, cadmium, chromium, copper, lead, mercury, nickel, and zinc.

Triazine herbicide - A class of herbicides containing a symmetrical triazine ring (a nitrogen-heterocyclic ring composed of three nitrogens and three carbons in an alternating sequence). Examples include atrazine, propazine, and simazine.

Turbidity - Reduced clarity of surface water because of suspended particles, usually sediment.

Volatile organic compounds (VOCs) - Organic chemicals that have a high vapor pressure relative to their water solubility. VOCs include components of gasoline, fuel oils, and lubricants, as well as organic solvents, fumigants, some inert ingredients in pesticides, and some by-products of chlorine disinfection.

Water-quality criteria - Specific levels of water quality which, if reached, are expected to render a body of water unsuitable for its designated use. Commonly refers to water-quality criteria established by the U.S. Environmental Protection Agency. Water-quality criteria are based on specific levels of pollutants that would make the water harmful if used for drinking, swimming, farming, fish production, or industrial processes.

Water-quality guidelines - Specific levels of water quality which, if reached, may adversely affect human health or aquatic life. These are nonenforceable guidelines issued by a governmental agency or other institution.

Water-quality standards - State-adopted and U.S. Environmental Protection Agency-approved ambient standards for water bodies. Standards include the use of the water body and the water-quality criteria that must be met to protect the designated use or uses.

Water year - The continuous 12-month period, October 1 through September 30, in U.S. Geological Survey reports dealing with the surface-water supply. The water year is designated by the calendar year in which it ends and which includes 9 of the 12 months. Thus, the year ending September 30, 1980, is referred to as the water year 1980.

Wetlands - Ecosystems whose soil is saturated for long periods seasonally or continuously, including marshes, swamps, and ephemeral ponds.

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APPENDIX—WATER-QUALITY DATA FROM THE MISSISSIPPI EMBAYMENT IN A NATIONAL CONTEXT

For a complete view of Mississippi Embayment data and for additional information about specific benchmarks used, visit our Web site at http://water.usgs.gov/nawqa/. Also visit the NAWQA Data Warehouse for access to NAWQA data sets at http://water.usgs.gov/nawqa/data.

This appendix is a summary of chemical concentrations and biological indicators assessed in the Mississippi Embayment. Selected results for this Study Unit are graphically compared to results from as many as 36 NAWQA Study Units investigated from 1991 to 1998 and to national water-quality benchmarks for human health, aquatic life, or fish-eating wildlife. The chemical and biological indicators shown were selected on the basis of frequent detection, detection at concentrations above a national benchmark, or regulatory or scientific importance. The graphs illustrate how conditions associated with each land use sampled in the Mississippi Embayment compare to results from across the Nation, and how conditions compare among the several land uses. Graphs for chemicals show only detected concentrations and, thus, care must be taken to evaluate detection frequencies in addition to concentrations when comparing study-unit and national results. For example, fluometuron concentrations in Mississippi Embayment agricultural streams were similar to the national distribution, but the detection frequency was much higher (63 percent compared to 8 percent).

CHEMICALS IN WATER

Concentrations and detection frequencies, Mississippi Embayment, 1995–98—Detection sensitivity varies among chemicals and, thus, frequencies are not directly comparable among chemicals

- ◆ Detected concentration in Study Unit
- 66 38 Frequencies of detection, in percent. Detection frequencies were not censored at any common reporting limit. The left-hand column is the study-unit frequency and the right-hand column is the national frequency
- -- Not measured or sample size less than two
- *12* Study-unit sample size. For ground water, the number of samples is equal to the number of wells sampled

National ranges of detected concentrations, by land use, in 36 NAWQA Study Units, 1991–98—Ranges include only samples in which a chemical was detected

- Streams in agricultural areas
- Streams in urban areas
- Streams and rivers draining mixed land uses
- Shallow ground water in agricultural areas
- Shallow ground water in urban areas
- Major aquifers

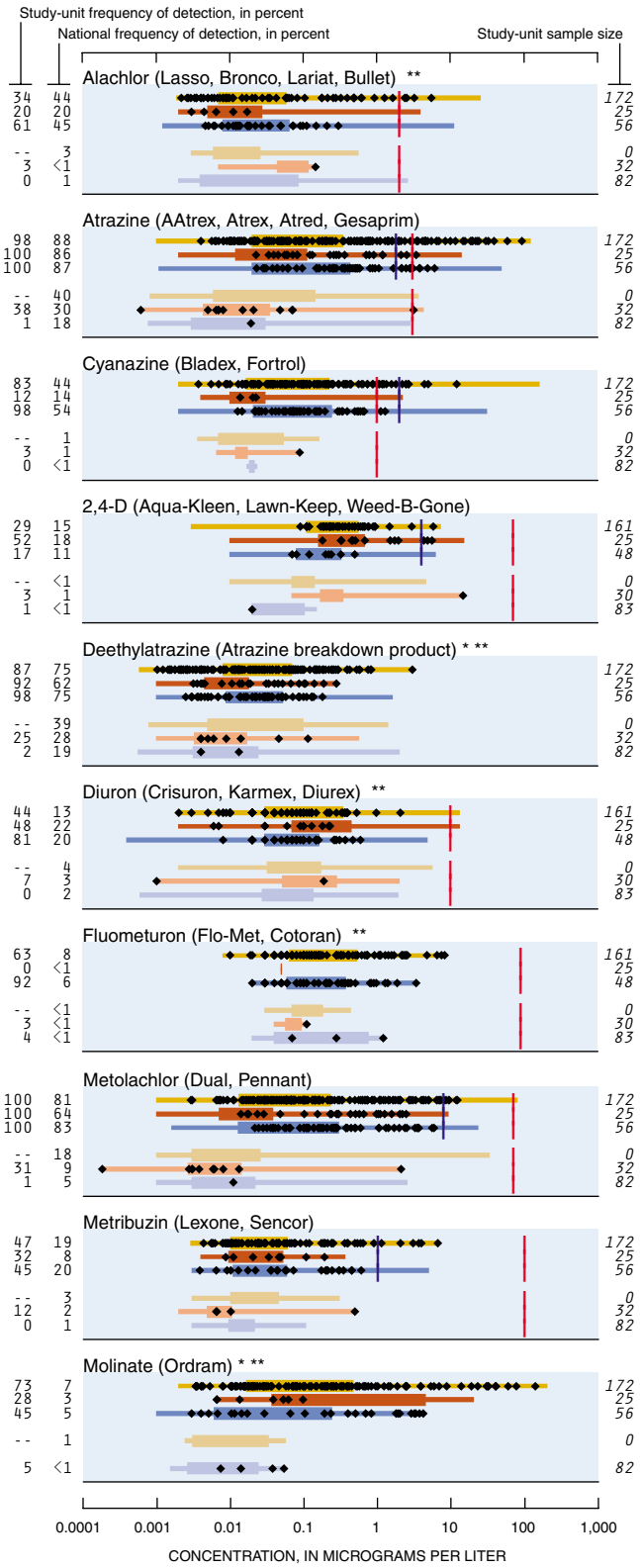
Lowest 25 percent | Middle 50 percent | Highest 25 percent

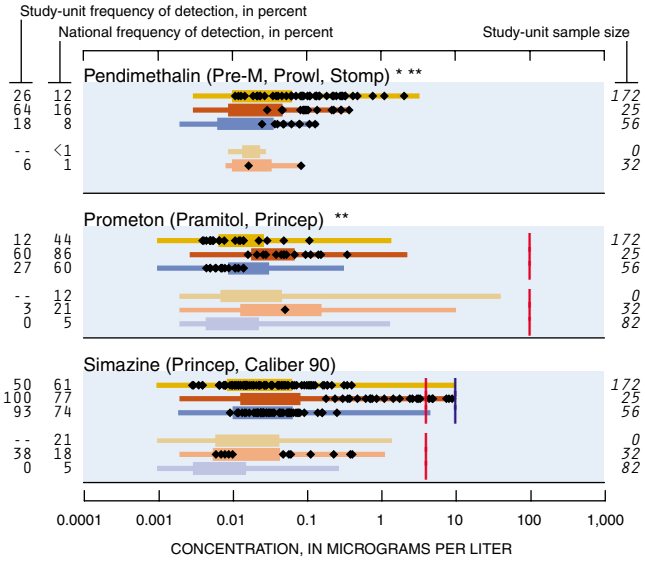
National water-quality benchmarks

National benchmarks include standards and guidelines related to drinking-water quality, criteria for protecting the health of aquatic life, and a goal for preventing stream eutrophication due to phosphorus. Sources include the U.S. Environmental Protection Agency and the Canadian Council of Ministers of the Environment

- | Drinking-water quality (applies to ground water and surface water)
- | Protection of aquatic life (applies to surface water only)
- | Prevention of eutrophication in streams not flowing directly into lakes or impoundments
- * No benchmark for drinking-water quality
- ** No benchmark for protection of aquatic life

Pesticides in water—Herbicides

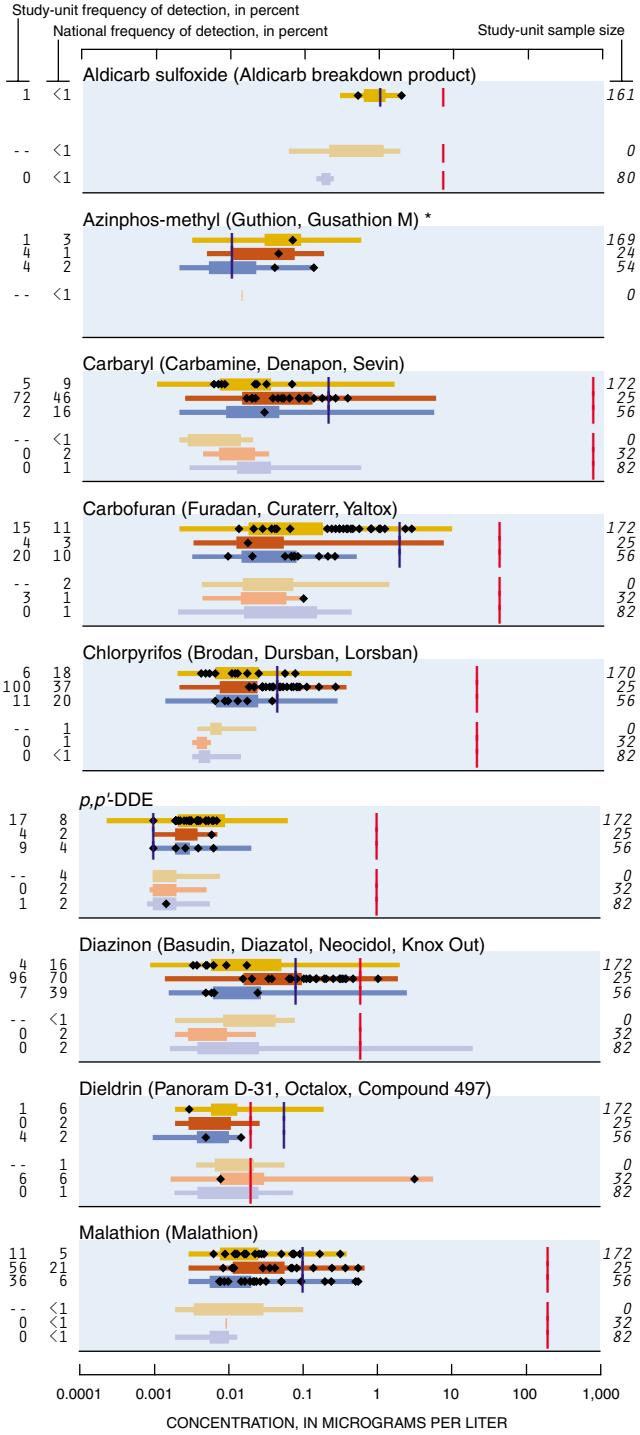




Other herbicides detected
Acetochlor (Harness Plus, Surpass) * **
Acifluorfen (Blazer, Tackle 2S) **
Benfluralin (Balan, Benefin, Bonalan) * **
Bentazon (Basagran, Bentazone) **
Bromacil (Hyvar X, Urox B, Bromax)
Bromoxynil (Buctril, Brominal) *
2,4-DB (Butyrac, Butoxone, Embutox Plus, Embutone) * **
DCPA (Dacthal, chlorthal-dimethyl) * **
Dacthal mono-acid (Dacthal breakdown product) * **
Dicamba (Banvel, Dianat, Scotts Proturf)
Dichlorprop (2,4-DP, Seritox 50, Lentemul) * **
Dinoseb (Dinosebe)
EPTC (Eptam, Farmarox, Alirox) * **
Fenuron (Fenulon, Fenidim) * **
Linuron (Lorox, Linex, Sarclex, Linurex, Afalon) *
MCPA (Rhomene, Rhonox, Chiptox)
Napropamide (Devrinol) * **
Neburon (Neburea, Neburyl, Noruben) * **
Norflurazon (Evital, Predict, Solicam, Zorial) * **
Pebulate (Tillam, PEBC) * **
Picloram (Grazon, Tordon)
Pronamide (Kerb, Propyzamid) **
Propachlor (Ramrod, Satecid) **
Propanil (Stam, Stampede, Wham) * **
Tebuthiuron (Spike, Tebusan)
Terbacil (Sinbar) **
Thiobencarb (Bolero, Saturn, Benthiocarb) * **
Triclopyr (Garlon, Grandstand, Redeem, Remedy) * **
Trifluralin (Treflan, Gowan, Tri-4, Trific)

Herbicides not detected
Butylate (Sutan +, Genate Plus, Butilate) **
Chloramben (Amiben, Amilon-WP, Vegiben) **
Clopyralid (Stinger, Lontrel, Transline) * **
2,6-Diethylaniline (Alachlor breakdown product) * **
Ethalfluralin (Sonalan, Curbit) * **
MCPB (Thistrol) * **
Oryzalin (Surflan, Dirimal) * **
Propham (Tuberite) **
2,4,5-T **
2,4,5-TP (Silvex, Fenoprop) **
0Triallate (Far-Go, Avadex BW, Tri-allate) *

Pesticides in water—Insecticides



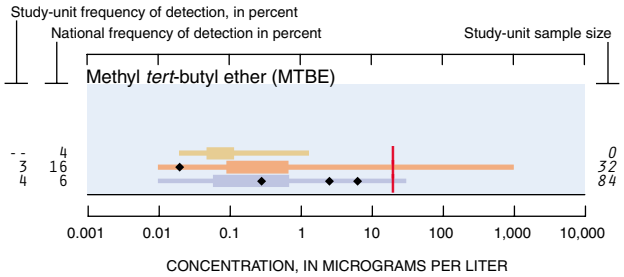
Other insecticides detected
Disulfoton (Disyston, Di-Syston) **
Methomyl (Lanox, Lannate, Acinate) **
Methyl parathion (Penncap-M, Folidol-M) **
Propargite (Comite, Omite, Ornamite) * **

Insecticides not detected
Aldicarb (Temik, Ambush, Pounce)
Aldicarb sulfone (Standak, aldoxycarb)
Ethoprop (Mocap, Ethoprophos) * **

Fonofos (Dyfonate, Capfos, Cudgel, Tycap) **
alpha-HCH (alpha-BHC, alpha-lindane) **
gamma-HCH (Lindane, gamma-BHC)
3-Hydroxycarbofuran (Carbofuran breakdown product) * **
Methiocarb (Slug-Geta, Grandslam, Mesurol) * **
Oxamyl (Vydate L, Pratt) **
Parathion (Roethyl-P, Alkron, Panthion, Phoskil) *
cis-Permethrin (Ambush, Astro, Pounce) * **
Phorate (Thimet, Granutox, Geomet, Rampart) * **
Propoxur (Baygon, Blattanex, Unden, Proprotox) * **
Terbufos (Contraven, Counter, Pilarfox) **

Volatile organic compounds (VOCs) in ground water

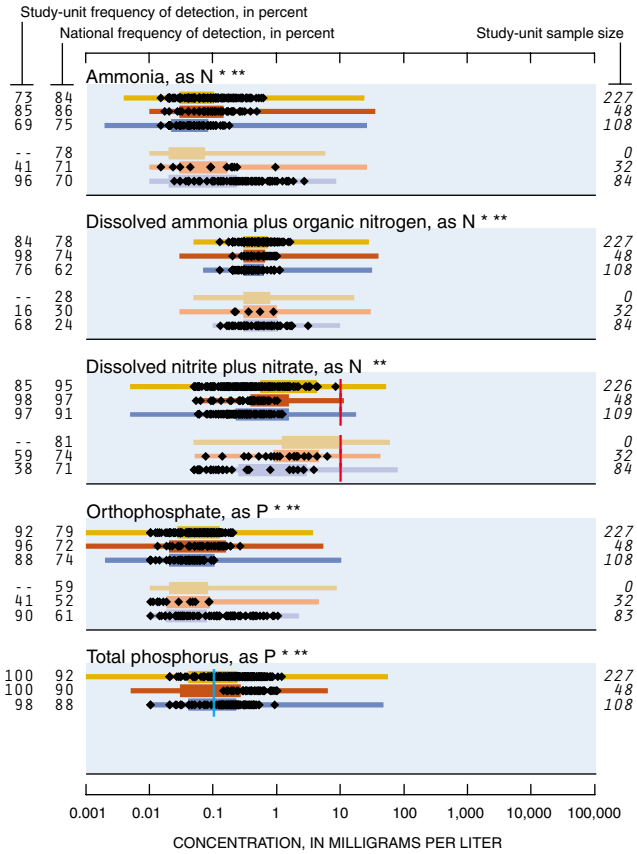
These graphs represent data from 16 Study Units, sampled from 1996 to 1998



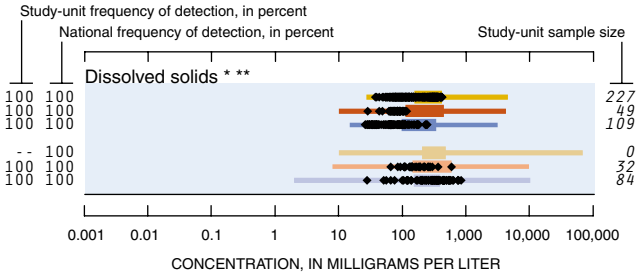
Other VOCs detected
tert-Amylmethylether (*tert*-amyl methyl ether (TAME)) *
Benzene
Bromodichloromethane (Dichlorobromomethane)
2-Butanone (Methyl ethyl ketone (MEK)) *
Carbon disulfide *
Chlorobenzene (Monochlorobenzene)
Chloroethane (Ethyl chloride) *
Chloromethane (Methyl chloride)
1,4-Dichlorobenzene (*p*-Dichlorobenzene)
Dichlorodifluoromethane (CFC 12, Freon 12)
1,2-Dichloroethane (Ethylene dichloride)
1,1-Dichloroethane (Ethylidene dichloride) *
1,1-Dichloroethene (Vinylidene chloride)
trans-1,2-Dichloroethene ((E)-1,2-Dichlorothene)
cis-1,2-Dichloroethene ((Z)-1,2-Dichloroethene)
Dichloromethane (Methylene chloride)
Diethyl ether (Ethyl ether) *
Diisopropyl ether (Diisopropylether (DIPE)) *
1,2-Dimethylbenzene (*o*-Xylene)
1,3 & 1,4-Dimethylbenzene (*m*-&*p* -Xylene)
1-4-Epoxy butane (Tetrahydrofuran, Diethylene oxide) *
Ethenylbenzene (Styrene)
1-Ethyl-2-methylbenzene (2-Ethyltoluene) *
Ethylbenzene (Phenylethane)
4-Methyl-2-pentanone (Methyl isobutyl ketone (MIBK)) *
Methylbenzene (Toluene)
2-Propanone (Acetone) *
Tetrachloroethene (Perchloroethene)
1,1,1-Trichloroethane (Methylchloroform)
Trichloroethene (TCE)
Trichlorofluoromethane (CFC 11, Freon 11)
Trichloromethane (Chloroform)
1,2,3-Trimethylbenzene (Hemimellitene) *
1,2,4-Trimethylbenzene (Pseudocumene) *
1,3,5-Trimethylbenzene (Mesitylene) *

VOCs not detected
Bromobenzene (Phenyl bromide) *
Bromochloromethane (Methylene chlorobromide)
Bromoethene (Vinyl bromide) *
Bromomethane (Methyl bromide)
n-Butylbenzene (1-Phenylbutane) *
sec-Butylbenzene *
tert-Butylbenzene *
3-Chloro-1-propene (3-Chloropropene) *
1-Chloro-2-methylbenzene (*o*-Chlorotoluene)
1-Chloro-4-methylbenzene (*p*-Chlorotoluene)
Chlorodibromomethane (Dibromochloromethane)
Chloroethene (Vinyl chloride)
1,2-Dibromo-3-chloropropane (DBCP, Nemagon)
1,2-Dibromoethane (Ethylene dibromide, EDB)
Dibromomethane (Methylene dibromide) *
trans-1,4-Dichloro-2-butene ((Z)-1,4-Dichloro-2-butene) *
1,2-Dichlorobenzene (*o*-Dichlorobenzene)
1,3-Dichlorobenzene (*m*-Dichlorobenzene)
1,2-Dichloropropane (Propylene dichloride)
2,2-Dichloropropane *
1,3-Dichloropropane (Trimethylene dichloride) *
trans-1,3-Dichloropropene ((E)-1,3-Dichloropropene)
cis-1,3-Dichloropropene ((Z)-1,3-Dichloropropene)
1,1-Dichloropropene *
Ethyl methacrylate *
Ethyl *tert*-butyl ether (Ethyl-*t*-butyl ether (ETBE)) *
Hexachlorobutadiene
1,1,1,2,2,2-Hexachloroethane (Hexachloroethane)
2-Hexanone (Methyl butyl ketone (MBK)) *
Iodomethane (Methyl iodide) *
Isopropylbenzene (Cumene) *
p-Isopropyltoluene (*p*-Cymene) *
Methyl acrylonitrile *
Methyl-2-methacrylate (Methyl methacrylate) *
Methyl-2-propenoate (Methyl acrylate) *
Naphthalene
2-Propenenitrile (Acrylonitrile)
n-Propylbenzene (Isocumene) *
1,1,2,2-Tetrachloroethane *
1,1,1,2-Tetrachloroethane
Tetrachloromethane (Carbon tetrachloride)
1,2,3,4-Tetramethylbenzene (Prehnitene) *
1,2,3,5-Tetramethylbenzene (Isodurene) *
Tribromomethane (Bromoform)
1,1,2-Trichloro-1,2,2-trifluoroethane (Freon 113) *
1,2,4-Trichlorobenzene
1,2,3-Trichlorobenzene *
1,1,2-Trichloroethane (Vinyl trichloride)
1,2,3-Trichloropropane (Allyl trichloride)

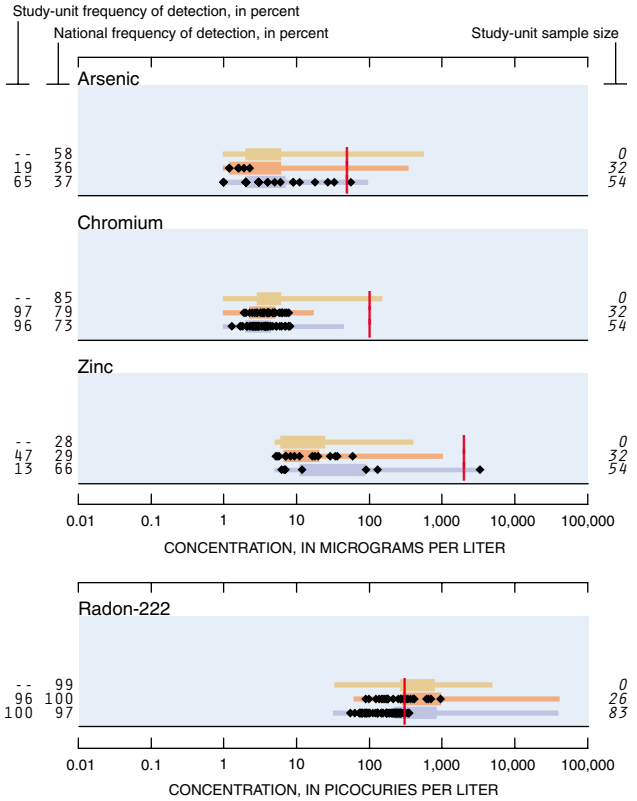
Nutrients in water



Dissolved solids in water



Trace elements in ground water



Other trace elements detected
Selenium
Uranium

Trace elements not detected
Cadmium
Lead

CHEMICALS IN FISH TISSUE AND BED SEDIMENT

Concentrations and detection frequencies, Mississippi Embayment, 1995–98—Detection sensitivity varies among chemicals and, thus, frequencies are not directly comparable among chemicals. Study-unit frequencies of detection are based on small sample sizes; the applicable sample size is specified in each graph

◆ Detected concentration in Study Unit

66 38 Frequencies of detection, in percent. Detection frequencies were not censored at any common reporting limit. The left-hand column is the study-unit frequency and the right-hand column is the national frequency

-- Not measured or sample size less than two

12 Study-unit sample size

National ranges of concentrations detected, by land use, in 36 NAWQA Study Units, 1991–98—Ranges include only samples in which a chemical was detected

Fish tissue from streams in agricultural areas
Fish tissue from streams in urban areas
Fish tissue from streams draining mixed land uses
Sediment from streams in agricultural areas
Sediment from streams in urban areas
Sediment from streams draining mixed land uses

Lowest 25 percent | Middle 50 percent | Highest 25 percent

National benchmarks for fish tissue and bed sediment

National benchmarks include standards and guidelines related to criteria for protection of the health of fish-eating wildlife and aquatic organisms. Sources include the U.S. Environmental Protection Agency, other Federal and State agencies, and the Canadian Council of Ministers of the Environment

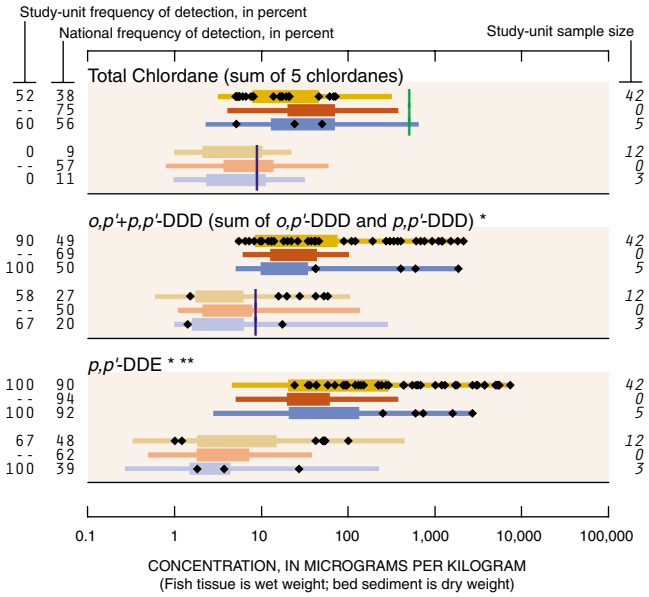
Protection of fish-eating wildlife (applies to fish tissue)

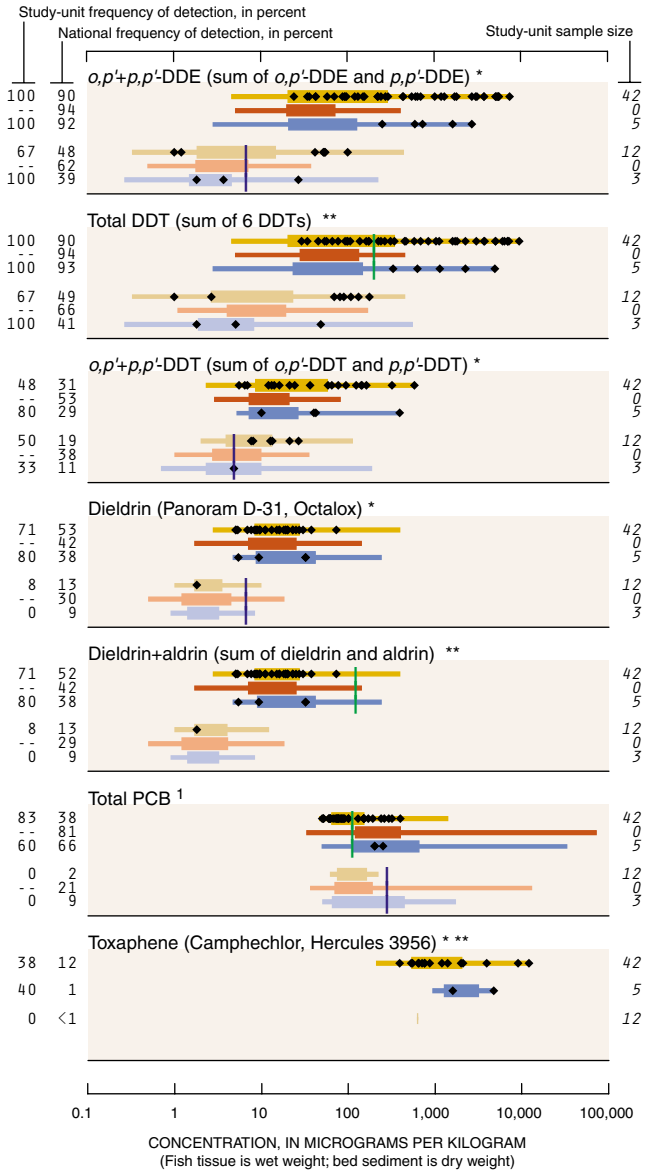
Protection of aquatic life (applies to bed sediment)

* No benchmark for protection of fish-eating wildlife

** No benchmark for protection of aquatic life

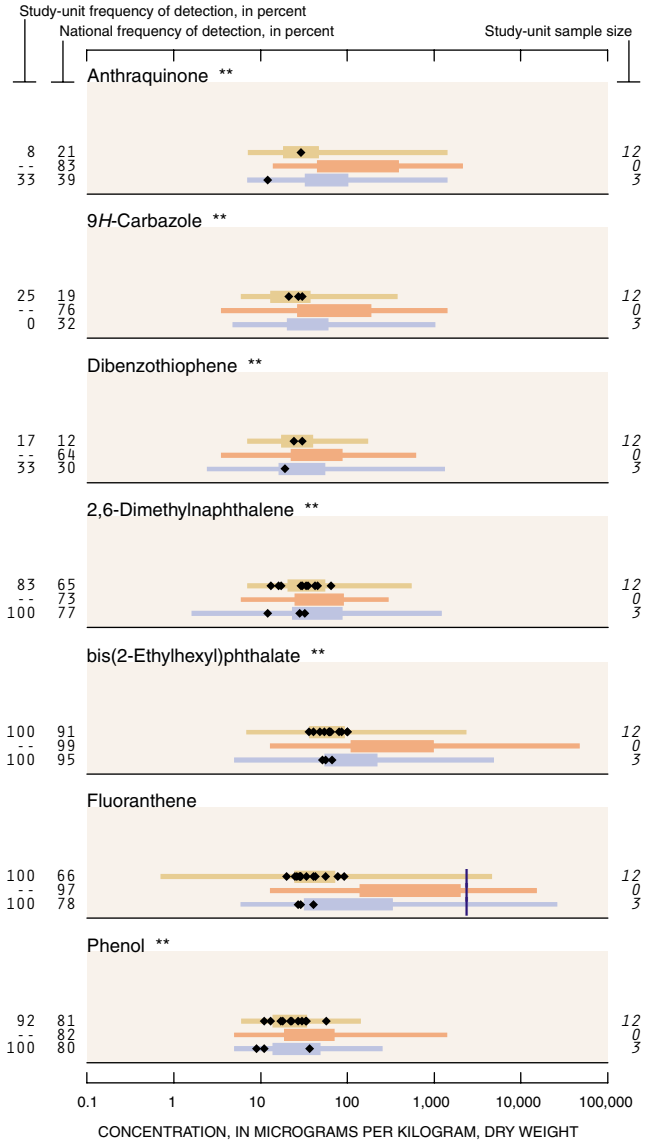
Organochlorines in fish tissue (whole body) and bed sediment





[1] The national detection frequencies for total PCB in sediment are biased low because about 30 percent of samples nationally had elevated detection levels compared to this Study Unit. See http://water.usgs.gov/nawqa/ for additional information.

Semivolatile organic compounds (SVOCs) in bed sediment



Other organochlorines detected

Total-HCH (sum of alpha-HCH, beta-HCH, gamma-HCH, and delta-HCH) **
Heptachlor+heptachlor epoxide (sum of heptachlor and heptachlor epoxide) **
Hexachlorobenzene (HCB) **
Mirex (Dechlorane) **
Pentachloroanisole (PCA) * **
Toxaphene (Camphechlor, Hercules 3956) * **

Organochlorines not detected

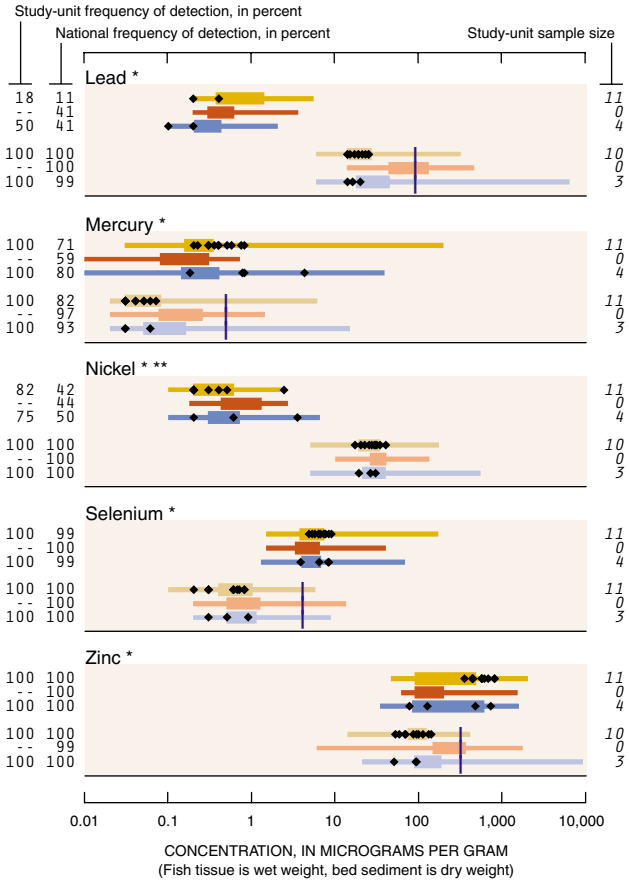
Chloroneb (Chloronebe, Demosan) * **
DCPA (Dacthal, chlorthal-dimethyl) * **
Endosulfan I (alpha-Endosulfan, Thiodan) * **
Endrin (Endrine)
gamma-HCH (Lindane, gamma-BHC, Gammexane) *
Heptachlor epoxide (Heptachlor breakdown product) *
Isodrin (Isodrine, Compound 711) * **
p,p'-Methoxychlor (Marlate, methoxychlore) * **
o,p'-Methoxychlor * **
cis-Permethrin (Ambush, Astro, Pounce) * **
trans-Permethrin (Ambush, Astro, Pounce) * **

Other SVOCs detected

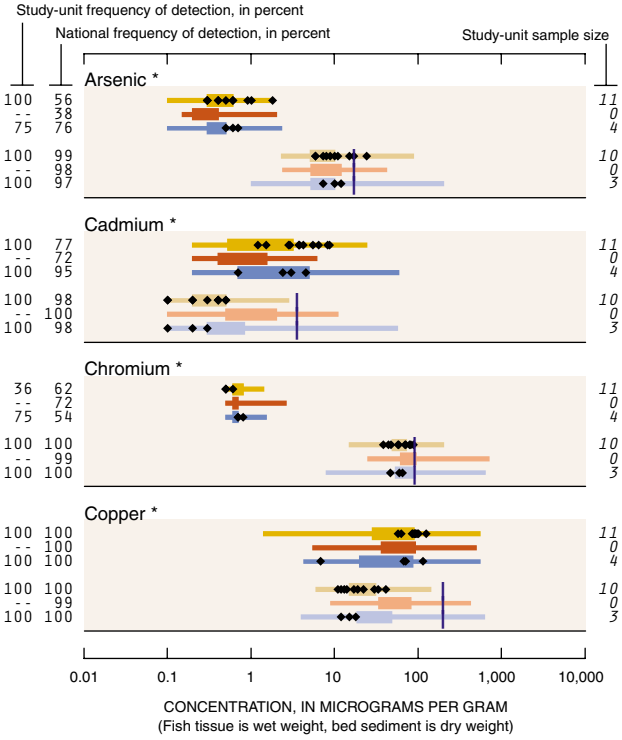
Acenaphthene
Acenaphthylene
Acridine **
Anthracene
Benz[*a*]anthracene
Benzo[*a*]pyrene
Benzo[*b*]fluoranthene **
Benzo[*ghi*]perylene **
Benzo[*k*]fluoranthene **
2,2-Biquinoline **
Butylbenzylphthalate **
Chrysene
p-Cresol **
Di-*n*-butylphthalate **
Di-*n*-octylphthalate **
Diethylphthalate **
1,6-Dimethylnaphthalene **
Dimethylphthalate **
9*H*-Fluorene (Fluorene)
Indeno[1,2,3-*cd*]pyrene **

Isoquinoline **
2-Methylanthracene **
4,5-Methylenephenanthrene **
1-Methylphenanthrene **
1-Methylpyrene **
Naphthalene
Phenanthrene
Pyrene

SVOCs not detected
C8-Alkylphenol **
Azobenzene **
Benzo[*c*]cinnoline **
4-Bromophenyl-phenylether **
4-Chloro-3-methylphenol **
bis(2-Chloroethoxy)methane **
2-Chloronaphthalene **
2-Chlorophenol **
4-Chlorophenyl-phenylether **
Dibenz[*a,h*]anthracene
1,2-Dichlorobenzene (*o*-Dichlorobenzene) **
1,3-Dichlorobenzene (*m*-Dichlorobenzene) **
1,4-Dichlorobenzene (*p*-Dichlorobenzene) **
1,2-Dimethylnaphthalene **
3,5-Dimethylphenol **
2,4-Dinitrotoluene **
2-Ethylnaphthalene **
Isophorone **
1-Methyl-9*H*-fluorene **
Nitrobenzene **
N-Nitrosodi-*n*-propylamine **
N-Nitrosodiphenylamine **
Pentachloronitrobenzene **
Phenanthridine **
Quinoline **
1,2,4-Trichlorobenzene **
2,3,6-Trimethylnaphthalene **



Trace elements in fish tissue (livers) and bed sediment



BIOLOGICAL INDICATORS

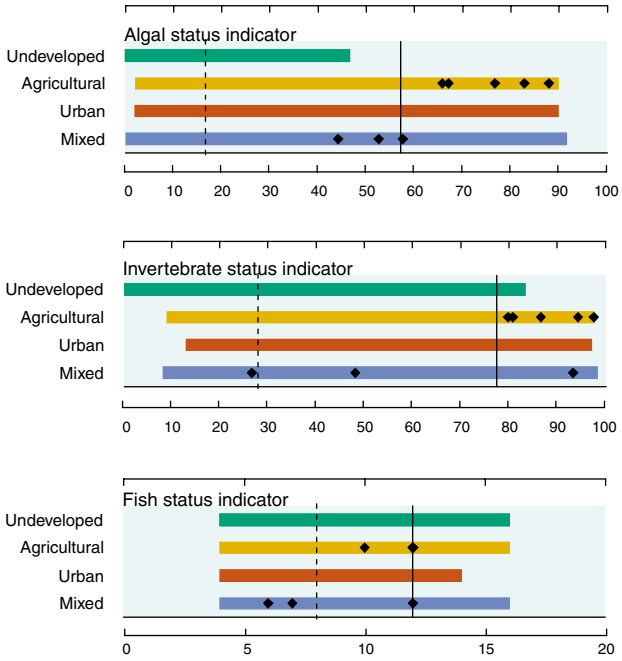
Higher national scores suggest habitat disturbance, water-quality degradation, or naturally harsh conditions. The status of algae, invertebrates (insects, worms, and clams), and fish provide a record of water-quality and stream conditions that water-chemistry indicators may not reveal. **Algal status** focuses on the changes in the percentage of certain algae in response to increasing siltation, and it often correlates with higher nutrient concentrations in some regions. **Invertebrate status** averages 11 metrics that summarize changes in richness, tolerance, trophic conditions, and dominance associated with water-quality degradation. **Fish status** sums the scores of four fish metrics (percent tolerant, omnivorous, non-native individuals, and percent individuals with external anomalies) that increase in association with water-quality degradation

Biological indicator value, Mississippi Embayment, by land use, 1995–98

◆ Biological status assessed at a site

National ranges of biological indicators, in 16 NAWQA Study Units, 1994–98

- Streams in undeveloped areas
- Streams in agricultural areas
- Streams in urban areas
- Streams in mixed-land-use areas
- 75th percentile
- 25th percentile



A COORDINATED EFFORT

Coordination with agencies and organizations in the Mississippi Embayment was integral to the success of this water-quality assessment. We thank those who served as members of our liaison committee.

Federal Agencies
U.S. Army Corps of Engineers
U.S. Department of Agriculture
U.S. Environmental Protection Agency
U.S. Fish and Wildlife Service
U.S. Forest Service
U.S. Geological Survey, BRD

State Agencies
Mississippi Department of Environmental Quality
Mississippi Department of Wildlife, Fisheries, and Parks

Local Agencies
Delta Council
Yazoo-Mississippi Delta Joint Water Management District

Universities
Arkansas State University
Mississippi State University
University of Arkansas
University of Mississippi

Other public and private organizations
Wolf River Conservancy

We thank the following individuals, agencies, and organizations for contributing to the success of this study.

- Chip Bray, Al Gibson, David Loch, Michael Beiser, and David Singleton (Mississippi Department of Environmental Quality), and Charles Knight (Mississippi Department of Wildlife, Fisheries and Parks) for help with biological field work
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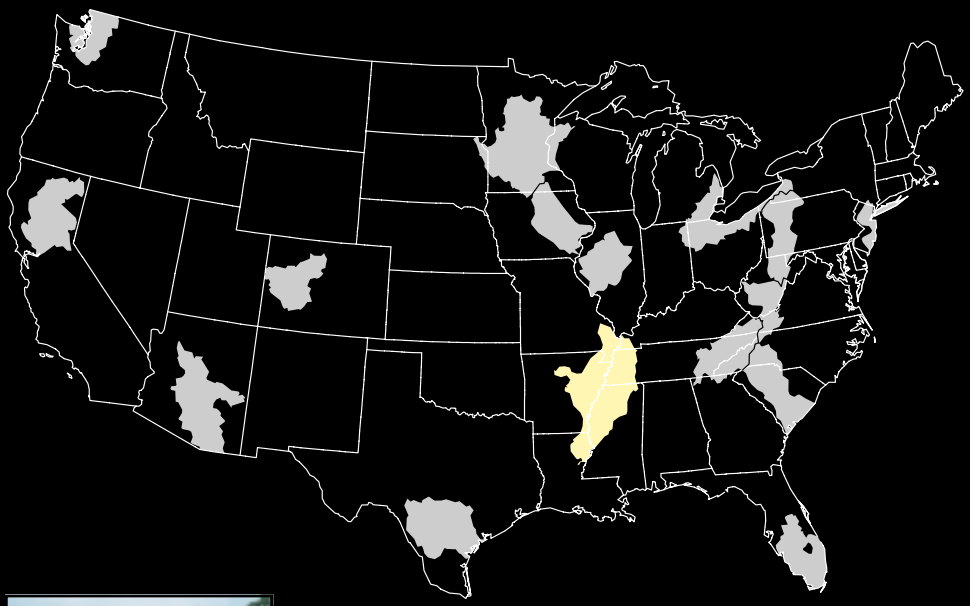
- Brian Hughes and Larry Slack (USGS), Henry Folmar and Richard Ingram (Mississippi Department of Environmental Quality), and Bruce Reid (The National Audubon Society) for providing technical review of the report and Carol Moss, Rebecca Deckard, Sandra Cooper and Mary Kidd (USGS) for editorial input
- Michael Wade and Lance Cooper for graphics and layout for this report
- Todd Slack, Stephen Ross, and Neil Douglas for verifying and vouchering fish specimens
- Michael Thurman (USGS, Kansas District) for contributing analyses of selected pesticides
- USGS employees Michael Manning, Brian Caskey, Robert Joseph, Charles Lee, Darryl Wilson, Susan McIntosh, Desmond Funchess, Paul Floyd, John Storm, Kenny Burks, David Massingill, Bobby Richards, Larry Thomas, Lisa Zimmerman, Jim Alvis, Allen Roberts, Rachel Pike, Jennifer Mahaney, Shane Stocks, Michelle Wates, Fred Morris III, John Ewing, Eric Strom, Wade Bryant, Anuba Dayama, Jan Jones, Tony Schrader, Marsha Gipson, Larry Remsing, Terry Holland, Dwight Lasker, Phil Stephens, Aaron Pugh and others for assisting with collection and compilation of data

NAWQA

National Water-Quality Assessment (NAWQA) Program
Mississippi Embayment



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9 780607 954142

Kleiss and others— Water Quality in the Mississippi Embayment
U.S. Geological Survey Circular 1208

Falls, Angela

To: Water Quality Standards
Subject: RE: Missouri WQS Triennial Review

From: Philip Wilson [mailto:PWilson@mecresults.com]
Sent: Saturday, March 02, 2019 11:57 AM
To: Water Quality Standards
Cc: clarencegas@centurytel.net
Subject: Missouri WQS Triennial Review

I would like to comment on development and incorporation by reference use attainability analyses (UAA) protocols for the recreational and aquatic life protection designated uses. The Department listed updating or revising designated uses on streams with recreational UAAs as well as developing a protocol for aquatic life protection. Both would provide important tools for facilities to use when seeking ways to ensure they are in compliance with environmental requirements, especially facilities located on newly classified streams high in the watershed.

References and explanations of procedures in the existing recreational UAA protocol need to be revised to fit current understanding of waters of the state. Consideration should also be given to the fact that many of the now classified streams are little more than stormwater drainage channels that only convey water to named creeks during wet weather periods, even when a wastewater facility discharges into the waterway in question. Perhaps provisions should allow the person conducting the UAA to stop at the point it is evident the use cannot be attained – as in the case of there being no water in the waterway during base flow conditions.

An aquatic life UAA protocol would be very helpful in determining when the various categories of aquatic life protection uses outlined in 10 CSR 20-7.031(1)(C)1 should be applied to many of the newly classified streams. As was discussed regarding recreational uses, many of the newly classified waterways do not maintain flow in any way that would allow aquatic life to flourish. So, as the Department considers development of the UAA protocol, provisions should be given that allow for a streamlined analysis when there is no water in the waterway during base flow conditions.

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SCHOOL OF LAW

Interdisciplinary Environmental Clinic

March 1, 2019

WQS Coordinator
Missouri Department of Natural Resources Water Protection Program
P.O. Box 176
Jefferson City, MO 65102-0176
Email: wqs@dnr.mo.gov

Re: Missouri's Triennial Review

Dear WQS Coordinator:

The Washington University Interdisciplinary Environmental Clinic (IEC) is providing this letter on behalf of the Missouri Coalition for the Environment (MCE), an independent environmental advocacy group. Founded in 1969, MCE has been actively advocating for Missouri to meet the CWA's fishable/swimmable standard since approximately the year 2000.

MCE requests that DNR consider several key issues in its triennial review process. Specifically, the MCE requests that the DNR protect for fishable/swimmable uses for all waters of the United States within Missouri, including wetlands, small streams, and headwaters, as well as waters already determined to be waters of the United States. MCE also requests that DNR develop nutrient criteria for lakes to protect drinking water and recreational uses, develop nutrient criteria for Missouri's classified streams and rivers to protect all uses, and update its ammonia standards to meet EPA's most recent recommendations.

The importance of these issues, particularly the classification of wetlands and updating the ammonia standards, was highlighted by the Triennial Review Survey Results that were distributed at the February 13, 2019 Water Quality Forum Meeting.[1] The survey asked respondents to categorize 11 environmental issues on a scale ranging from "Very Important" to "Unimportant." "Wetland Classification and Uses" received the second-most "Very Important" votes, while "Mussel Ammonia" received the fourth-most "Very Important" votes. We urge you to include these issues in the next Triennial Review.

A. MCE Requests That Missouri Comply With Federal Law and Add Additional Waters, Particularly Wetlands and Small Streams, to its List of Classified Waters

As you are aware, the Clean Water Act (CWA), passed in 1972, contains the explicit goal of making the nation's waters fishable and swimmable by 1983 and the elimination of "the

1 Triennial Review Survey Results, MDNR. Provided at the Water Quality Forum meeting on February 13, 2019.

discharge of pollutants into navigable waters."[2] Under the CWA, each state also retains the authority to promulgate its own water quality standards,[3] which, at a minimum, must meet those imposed by the CWA itself.[4]

The CWA defines as jurisdictional "waters of the United States," including tributaries, ponds, lakes, and wetlands.[5] Likewise, the River and Harbors Act ("RHA") regulations define "waters of the United States" to include "all waters which are currently used, or were used in the past, or may be susceptible to use in interstate or foreign commerce, including all waters which are subject to the ebb and flow of the tide...includ[ing] wetlands...intrastate lakes, rivers, streams..."[6]

However, as MCE has reminded MDNR on many occasions, Missouri's classification system does not fully conform to the requirements of the CWA. In Missouri, bodies of water are characterized as either classified or unclassified. Classified waterbodies are protected for the fishable/swimmable uses by numeric water quality standards while unclassified waterbodies are not assigned uses and are protected only by narrative criteria. Unless a state can show that the fishable/swimmable level is unattainable, these waters of the U.S. must be protected by numeric criteria to guarantee that the fishable/swimmable uses are achieved. No such showing has been made for Missouri's unclassified waters.

While MCE acknowledges that MDNR's 2013 rule amendments classified an additional 90,000 miles of streams, there are still significant miles of unclassified streams and many acres of unclassified wetlands. Under the 2013 Amendment, rivers and streams that are not represented by flow lines on the United States Geological Survey ("USGS") 1:100,000 National Hydrography Dataset ("NHD") map, and lakes, ponds, and impoundments that do not intersect a flow line on the map, are not assigned default fishable/swimmable uses.[7] This standard leaves at least 63,245 miles of streams, 91,036 acres of lakes and reservoirs, and 988,325 acres of wetlands unprotected by the Clean Water Act.[8]

Moreover, studies and surveys have identified numerous streams, headwaters, and wetlands that are absent from this map.[9] In 2015, MCE submitted a petition asking MNDR to classify

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2 33 U.S.C. § 1251.
3 33 U.S.C. § 1313
4 *Id.*
5 40 C.F.R. § 230.3(o)
6 33 C.F.R. Part 328.3.
7 10 CSR 20-7.031(2); 10 CSR 20-7.031(1)(P).
8 *See* 10 CSR 20-7.031(1)(P). The 100K rule uses the Missouri Use Designation Dataset ("MUDD"), a digital geospatial dataset used in conjunction with GIS and maintained by MDNR. This dataset documents the names and locations of the state's rivers, streams, lakes and reservoirs that have been assigned designated uses. MCE has taken the 1:24,000 NHD map and compared it to the MUDD to determine the miles of water bodies that were represented on the NHD map but not on the MUDD.
9 Judy L. Meyer et al., *Where Rivers are Born: The Scientific Imperative for Defending Small Streams and Wetlands*, AMERICAN RIVERS AND SIERRA CLUB, at 7 (Feb. 2007), *available at* http://www.americanrivers.org/assets/pdfs/reports-and-publications/WhereRiversAreBorn1d811.pdf.

unclassified waters that the Army Corps of Engineers had already determined to be waters of the United States as part of jurisdictional determinations, as well as waters that are similarly situated in the same watershed as those jurisdictional waters. This petition described several waters that were currently unclassified but were required to be classified under the CWA. Those waters should be included as well.

Although the waters of the U.S. regulations are in a state of flux, as a matter of law in Missouri, states are required to protect wetlands as waters of the United States and classify them under the CWA when the wetland "possess[es] a significant nexus to waters that are or were navigable in fact or that could reasonably be so made."[10] Missouri's unclassified wetlands, streams, and lakes have a significant nexus to the health of the classified downstream waters. Further, despite any potential shifts at the federal regulatory level, the science supports inclusion of wetlands, small streams, and headwaters. The latest comprehensive technical review of peer-reviewed scientific literature, *Connectivity of Streams & Wetlands to Downstream Waters: a Review & Synthesis of the Scientific Evidence*,[11] was developed in 2015 by the U.S. EPA and U.S. Army Corps of Engineers. The report summarizes scientific understanding about the connectivity and mechanisms by which streams and wetlands affect the physical, chemical, and biological integrity of downstream waters, and reflects the current scientific understanding of the connectivity of streams to downstream waters.

Wetlands, which may be geographically located well outside of river or floodplain areas, can affect larger water systems.[12] The report found that wetlands are often hydrologically connected to streams, rivers, lakes, or other water bodies, and that spatial proximity is only one determinant of the magnitude of the effect that wetlands have on these bodies of waters. Wetlands can act as either sources or sinks for their connected waters. Wetlands can also modify the water quality of downstream waters, even without direct surface water connections.[13]

In addition, "[t]he scientific literature unequivocally demonstrates that streams, individually or cumulatively, exert a strong influence on the integrity of downstream waters, and that" *all* tributary streams, including perennial, intermittent, and ephemeral streams, are physically, chemically, and biologically connected to downstream rivers via channels and associated alluvial deposits where water and other materials are concentrated, mixed, transformed, and transported.[14] The composition of stream water has a substantial influence on water quality in rivers, and there are compelling links between the chemical composition of streams and the composition of downstream rivers, as sediments generally carry contaminants from streams to

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10 *United States v. Bailey*, 571 F.3d 791, 798 (8th Cir. 2009) (citing *Rapanos v. United States*, 547 U.S. 715, 779 (2006) (Kennedy, J., concurring)).
11 U.S. EPA. Connectivity of Streams and Wetlands to Downstream Waters: A Review and Synthesis of the Scientific Evidence (Final Report). U.S. Environmental Protection Agency, Washington, DC, EPA/600/R-14/475F, 2015. pg. ES-1.
12 *Id.*, pgs. ES-11-12; pgs. 4-21-30.
13 *Id.*, pgs. ES-11-12; pgs. 4-21-30.
14 *Id.*, pg ES-2. (emphasis added).

rivers.[15]

The CWA requires that the state review its water quality standards at least once every three years, a process which has come to be known as triennial review ("The State shall from time to time, but at least once every 3 years, hold public hearings for the purpose of reviewing applicable water quality standards…and, as appropriate, modifying and adopting standards.")[16] As the Triennial Review comes around once again, MCE asks MDNR to bring Missouri law into alignment with the CWA and assign uses to all waters of the U.S. within Missouri's borders. In particular, MCE asks MDNR to assign uses to Missouri's jurisdictional wetlands, to its small streams and headwaters, and to waterbodies which have already been determined to be waters of the U.S.

B. Missouri Should Review and Update its Water Quality Criteria for Nutrients

MCE believes that Missouri's newly-enacted lake nutrient criteria protecting the aquatic life use are insufficient and will not protect Missouri's waters from excess nutrient pollution for any other use. MCE requests that during this triennial review, MDNR will consider updating its current criteria in order to protect the condition of Missouri's water and the health of its residents. Specifically, MCE requests that DNR develop nutrient criteria for lakes to protect drinking water and recreational uses.

Nitrogen and phosphorus pollution, known collectively as nutrient pollution, pose serious environmental and human health problems in waters of the United States. MCE recognizes that creating nutrient criteria is challenging, as nitrogen and phosphorus are naturally present in aquatic ecosystems. However, protective criteria are essential for preventing significant environmental degradation. Protecting Missouri's water from excessive nutrient pollution is a priority to MCE due to the plethora of negative human health and environmental impacts nutrients pose.

1. MDNR Should Have Numeric Criteria for the Protection of Drinking Water Use

MCE believes that the nutrients standards recently approved by EPA do not protect the "most sensitive use" of a water body, as they are required to do. Although MDNR has insisted that its aquatic life standards will also protect the drinking water use, that assertion is not supported by any evidence. In its response to comments dated January 2018, MDNR claimed that the criteria for aquatic life were more protective than the criteria for drinking water, yet data for the Plains regions shows that the threshold criterion for protection of aquatic life was actually 5 µg/L higher than for drinking water supply.[17] Arguing that 25 µg/L is almost as good as 20 µg/L is not

15 *Id.*, pgs. 3-21-37
16 40 C.F.R. § 131.20

17 MDNR "Rationale for Missouri Lake Numeric Nutrient Criteria," December 2017, p.4

based in science and is unsupported by the record of MDNR's criteria development process.

Although MDNR has stated that further studies are necessary before drinking water standards can be derived, the facts suggest otherwise. Until early fall 2017, MDNR's proposed nutrients standards included numeric drinking water criteria. The 2017 "Rationale for Missouri Numeric Nutrient Criteria for Lakes" proposed a numeric drinking water criterion of 25 µg/L for all ecoregions.[18] EPA also developed numeric standards that would protect the drinking water use in its notice of proposed rulemaking dated December 15, 2017. There is no need for further studies, and development of numeric criteria to protect the drinking water use in Missouri's lakes should be part of the upcoming Triennial Review.

MCE's concern over the lack of drinking water criteria in the current rule stems from potential risks to human health. MDNR has previously acknowledged that many Missouri residents rely on drinking water from lakes and that nutrient loading can impact drinking water and, thus, human health.[19] Cyanobacteria blooms resulting from nutrient enrichment can pose a threat to human health by producing dangerous toxins that end up in drinking water.

MDNR chose to rely on the less protective value without evidence that it is actually protective of drinking water, thus endangering the health and safety of Missouri's residents.

2. Nutrient Standards For Lakes Should Include Numeric Criteria to Protect Recreational Uses

In addition to lacking numeric criteria sufficient to protect the drinking water use, the current rule lacks criteria for whole body contact recreation. MDNR has indicated that the information will continue to develop. Putting off the legal requirement to include the most sensitive use because creating numeric criteria is hard is irresponsible as science is always changing. And it is not as though the task is impossible based on the scientific evidence now available. When the current criteria were under development, EPA proposed an "alternative 1" which contained numeric criteria for recreation, proving that criteria development is possible.[20]

Establishing protective numeric criteria is essential for the future protection of Missouri's water, as current narrative standards do not translate into nutrient effluent limitations. Section 301(b)(1)(C) of the CWA requires permitting authorities to include effluent limits as needed to

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18 MDNR, "Rationale for Missouri Numeric Nutrient Criteria for Lakes", 2017, pg 4.

19 MDNR "Draft Regulatory Impact Report (RIR) 10 CSR 20-7.031 Water Quality Standards," September 25, 2017, p.14

20 Water Quality Standards for the State of Missouri's Lakes and Reservoirs, 82 Fed. Reg. 61,213 Dec. 27, 2017.

meet water quality standards.[21] The permitting approach is clearly established in federal regulations as well as the EPA's NPDES Permit Writers' Manual. Permits are necessary to prevent degradation of existing water quality by limiting nitrogen and phosphorus discharges into the waterbody. MDNR's "Nutrient Criteria Implementation Plan" does not include any plan or indication or translating screening values to effluent limits.[22]

MCE requests that MDNR update the numeric criteria for the protection of aquatic life and develop numeric criteria for drinking water and recreation using EPA guidelines. EPA recommends a variety of approaches to developing numeric criteria such as the reference condition approach, empirical stressor-response models and mechanistic water quality models.

C. Missouri Should Develop Nutrient Criteria for Classified Rivers and Streams

MCE is further concerned with the lack of any nutrient criteria for streams and rivers. Currently the 115,732 miles of Missouri's classified flowing waters are without any numeric nutrient criteria at all. MDNR began the process of developing criteria in 2009, but "suspended" meetings in order to come up with "scientifically defendable and sufficiently protective" recommendations.[23] No such recommendations have been made, and Missouri is currently without criteria for streams.

MCE requests that MDNR develop nutrient criteria for Missouri's classified streams and rivers using one of the three suggested methods in EPA's "Nutrient Criteria Technical Guidance Manual: Rivers and Streams." The recommended methods include using previously published criteria, reference reaches or predictive relationships to develop nutrient criteria for rivers and streams.[24]

We recommend that MDNR look to Wisconsin as an example of sufficient and effective nutrient criteria. Wisconsin has numeric total phosphorus criteria for aquatic life, recreation and human health. Wisconsin's numeric criteria are translated to WPDES permits for points sources.

D. Missouri Must Update its Ammonia Criteria in Order to Reflect EPA's Most Recent Recommendations

Finally, MCE requests that MDNR updates Missouri's ammonia water quality criteria during this triennial review process.

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21 33 U.S.C. § 1311.

22 MDNR, "Nutrient Criteria Implementation Plan", July 2018.
23 MDNR, "Nutrient Criteria for Water Bodies", https://dnr.mo.gov/env/wpp/wqstandards/wq_nutrient-criteria.htm
24 Nutrient Criteria Technical Guidance Manual Rivers and Streams, U.S Environmental Protection Agency, July 2000, p. 94-100.

Ammonia is a form of nitrogen that exists in all discharges from domestic wastewater treatment systems as well as in aquatic environments and has the capability to cause direct toxic effects on aquatic life. The degree of ammonia toxicity depends on its chemical form as well as the water's pH and temperature. Un-ionized ammonia crosses fish gills and causes cellular damage. The state supports robust mussel and snail populations. Missouri's species include Unionid Mussels and Non-Pulmonate snails, which are considered sensitive species in regards to ammonia levels. Ammonia is known to leads to slower growth and lower reproduction in these species.[25]
Its effect on the central nervous system of fish can cause convulsions and death.[26]

EPA published national recommended ambient water quality criteria in 2013 for the protection of aquatic life. The EPA guidelines reflect the latest scientific knowledge to be compliant with section 303(a) of the Clean Water Act. EPA prefers the use of site-specific criteria reflecting localized conditions but suggests the use of their proposed criteria when that information is not available.[27] The recommended water quality criteria are found in the table below.[28]

Criterion Duration	1999 Criteria	2009 Draft Updated Criteria	2013 Final Updated Criteria
Acute (1-hour average)	24	19	17
Chronic (30-day rolling average)	4.5*	0.91*	1.9*
*Not to exceed 2.5 times the criterion continuous concentration as a 4-day average within a 30-day period.			
Criteria frequency: Not to be exceeded more than once in three years on average.			

In 2014, MDNR responded to EPA's new recommended criteria acknowledging the state's specific sensitivity to ammonia. MDNR stated that the department had "initiated stakeholder discussions" but that there was "no firm target date for starting the rulemaking to adopt new standards."[29]

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25 Lisa Foersom Huff, U.S EPA Office of Water, Ohio Water Environment Association Government Affairs Specialty Workshop, March 2014.
26 A Literature Review of Effects of Ammonia on Fish, The Nature Conservancy, Nov 2010.
27 Grubbs, Geoffrey. 2001. Development and Adoption of Nutrient Criteria into Water Quality Standards. WQSP–01–01. Policy memorandum signed on November 14, 2001, by Geoffrey Grubbs, Director, Office of Science and Technology, U.S. Environmental Protection Agency, Washington, DC.
28 Notice of Final Aquatic Life Ambient Water Quality Criteria for Ammonia- Freshwater, U.S Environmental Protection Agency, August 2013.
29 Ed Galbraith, Ammonia Criteria: New EPA Recommended Criteria, MDNR, Feb 2014.

It is time to set a target date. MDNR should update its standards to reflect EPA's most recent recommendations and scientific knowledge in order to comply with EPA guidelines.

Conclusion

In conclusion, MCE requests that the DNR protect all waters of the United States within Missouri, including wetlands, small streams and headwaters, as well as waters already determined to be waters of the United States, under the fishable/swimmable standard. The MCE also requests that the DNR develop nutrient criteria for lakes to protect drinking water and recreational uses, develop nutrient criteria for Missouri's classified streams and rivers to protect all uses, and update its ammonia standards to meet the EPA's most recent recommendations.

Sincerely,

Elizabeth J. Hubertz

cc: Maisah Khan

National Waste & Recycling Association℠
Collect. Recycle. Innovate.

Missouri Chapter

February 22, 2019

WQS Coordinator
Missouri Department of Natural Resources
Water Protection Program
P.O. Box 176
Jefferson City, MO 65102-0176

VIA email: wqs@dnr.mo.gov

Attention: MDNR Triennial Water Quality Review Committee

Re: Comments requested by the public to assist in MDNR Triennial Water Quality Review, MDNR's proposed rule 10 CSR 20-7.031

The Missouri Chapter of the National Waste and Recycling Association (NWRA) respectfully submits these comments regarding the MDNR Triennial Water Quality Review:

Please find attached the comments submitted by NWRA on November 16, 2017 during the last Triennial Review. The technical aspects of these comments are believed to still be applicable during this review.

Secondly, NWRA believes that any new regulations or determinations should be developed to be applicable to the unique characteristics of the state of Missouri. Whether that be naturally-occurring water quality characteristics or societal factors, many aspects are unique to Missouri that may not be applicable in other states.

The National Waste & Recycling Association is the trade association representing the private sector solid waste and recycling businesses in Missouri and across the country. NWRA and its members are dedicated to the safe, economic and efficient management of the waste and recycling streams and welcome the opportunity to be involved in this important process.

Respectfully,

Dave Overfelt,
Missouri Chapter, NWRA

Cc: Peggy Macenas, NWRA Midwest Region.

Attachments: Tech Memo 11.16.17

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Technical Memorandum

Date: November 16, 2017

To: Cassidy Luebbering

From: Nick Muenks, Tom Wallace and Kurt Schaefer

Subject: Missouri's Proposed 304(a) Criteria Adoption: Review and Recommendations

SUMMARY AND REQUEST SUPPORTED BY ANALYSIS BELOW

Final adoption of MDNR's proposed rule 10 CSR 20-7.031, to the extent it adopts USEPA's "one size fits all" Sect. 304(a) Water Quality Standards as discussed more fully below, is arbitrary, capricious, an abdication of MDNR's statutory obligations under Chapter 644, RSMo, to develop criteria specific to Missouri, and a violation of the directive from Governor Greitens to not impose further unnecessary regulatory burden on Missouri individuals and businesses.

As stated in detail below, the adoption in this rule of certain USEPA Sect. 303(a) Water Quality Criteria and how such criteria are to be applied will not only be a substantial increase in regulatory burden on Missouri business and industry, it would make Missouri's rule the most stringent and restrictive regulation of all the fifty states in the US.

Contrary to MDNR's stated position for Water Protection Program Rule Development that "Under Gov. Greitens' leadership, all state agencies are working to reduce regulations or other government processes that unnecessarily burden individuals and businesses while doing little to protect or improve public health, safety and our natural resources," this rule is a blind adoption of impractical USEPA Water Quality Criteria which are not tailored to Missouri and which no other state has fully adopted. MDNR has not engaged in any meaningful analysis of how the substantially increased regulatory burden from this rule will impact Missouri individuals and businesses nor human health and the environment.

MDNR's Draft Regulatory Impact Report (RIR), 10 CSR 20-7.031 Water Quality Standards, Public Notice September 25 – November 24, 2017, states that "Missouri is adopting these federal criteria without modification, and any environmental and economic costs and benefits are determined by the actions at the federal level, and not at the state level." Yet, MDNR also admits that while not knowing the impact, the state action that it is taking in adopting the rule will impact

at least "2,676 site-specific permits, 1,388 general permits, 774 storm water permits, and 3 underground injection permits." To the extent that MDNR acknowledges that some facilities may experience increased operational costs from the adoption of this rule, it concludes that "the data to estimate these costs do not exist at this time." Additionally, MDNR's Public Notice of Updated Regulatory Impact Report for 10 CSR 20-7.031, Water Quality Standards, Sept. 25, 2017 – Nov. 24, 2017, states that at least 477 permits will have more stringent standards. Yet, there is no analysis of the cost of compliance to these permittees, no analysis of whether technology even exits for such compliance, or whether requiring compliance will have an appreciable benefit justifying the cost.

The adoption of specific USEPA 304(a) Water Quality Criteria and how those criteria are applied, as stated more fully below, should be withdrawn from the draft rule and subjected to further public comment and agency analysis in order for MDNR and those impacted to fully understand the costs and any potential benefit caused by the increased regulatory burden, and to allow for development of Missouri-specific criteria. MDNR is under no legal time constraint to adopt the proposed criteria discussed below. Withdrawing those portions of the proposed rule would allow for a more reasoned and participatory process of Missouri-specific criteria development.

INTRODUCTION

The Missouri Department of Natural Resources (MDNR) is finalizing the most recent triennial review of Missouri's Water Quality Standards (MDNR 2017a). The proposed Water Quality Standards Rule Regulatory Impact Report (RIR, MDNR 2017b) was placed on public notice September 25, 2017 and will remain on public notice until November 24, 2017. Public comments related to the proposed Water Quality Standards Rule (proposed Rule, MDNR 2017c) must be received by November 28, 2017. Within the proposed Rule, MDNR is intending to adopt the United States Environmental Protection Agency's (USEPA's) recommended national criteria (also known as 304(a) criteria) except those for aluminum, cadmium, manganese, ammonia, and bacteria/pathogens. Missouri is deferring these criteria updates to the next triennial review.

This memorandum is intended to:

- Provide background information related to Section 304(a) of the Clean Water Act (CWA);
- Identify a subset of more stringent proposed 304(a) criteria to assess potential implications of the boarder list of chemicals to National Pollutant Discharge Elimination System (NPDES) permitees.
- Describe surrounding states' adoption of USEPA's recommended national criteria;
- Bring forth concerns with the development and applicability of the proposed criteria which may affect NPDES permit holders with related permit conditions; and
- Provide recommendations to address these concerns.

This memorandum is not intended to be a comprehensive review of all regulatory implications associated with the proposed changes to Missouri's water quality standards.

BACKGROUND

Section 304 of the CWA (33 USC 1314) directs USEPA to develop and/or revise national ambient water quality criteria that reflect the latest scientific knowledge. Section 303 of the CWA (33 USC 1313) directs states to conduct a review of their water quality standards at least once every three years (triennial review). During this review, Section 303 (a)(2) (33 USC 1313) instructs the states to adopt new or revised criteria published under Section 304(a). States may adopt USEPA's recommended national criteria, modify them, or develop state-specific criteria that are based on scientifically defensible methods. For example, the Florida Department of Environmental Protection developed state-specific human health criteria for several parameters based on fish/water consumption and demographics more applicable to Florida than USEPA's default criteria (FDEP 2017). USEPA must review and approve any new water quality standards adopted by a state prior to being used for CWA purposes and has yet to take action in this instance.

USEPA's recommended ambient water quality criteria include values for the protection of aquatic life (USEPA 2016) and values for the protection of human health (USEPA 2015a). The criteria for aquatic life protection are recommended to protect aquatic organisms from acute and chronic toxicity associated with a pollutant. These criteria have been periodically updated over the last 30 years, with the most recent revisions published in 2016 (cadmium and selenium). Many of the revisions to the national aquatic life protection criteria were published in 1986 (Gold Book) and 1995 (numerous metals updates) and remain the most recent updates for most chemical pollutants. Missouri adopted many of the toxic metals criteria revisions in 2005 and has since made no major revisions to the State's water quality criteria for aquatic life protection. Recommended national criteria for human health protection are risk-based and developed to protect humans from toxics accumulation through consumption of water and/or aquatic organisms. USEPA revised the 304(a) criteria for human health protection in 2015 (USEPA 2015a). The 2015 human health protection revisions included updates to 94 chemical pollutants.

The Intent to Initiate Triennial Review (MDNR 2015a) presented at the April 9, 2014 Water Quality Standards Work Group meeting indicated MDNR planned to update 304(a) criteria during the 2015 review. In December of 2015, MDNR presented the 304(a) criteria updates (MDNR 2015b) during a public meeting. Water quality standards stakeholder meeting have taken place periodically since that time. The 304(a) criteria updates are included in the current water quality standards amendment but should be deferred to a future rulemaking.

The proposed water quality standards amendment also includes other important changes (MDNR 2017b, MDNR 2017c), which are supported and should move forward. Most of these changes were developed with significant input from regulated stakeholders throughout Missouri.

1) Numeric Nutrient Criteria for Lakes: Lakes across Missouri are proposed to have numeric chlorophyll criteria based on ecoregional values and screening values, rather than numeric criteria, for nutrients. These criteria were developed using Missouri-specific lake chlorophyll and nutrient data. Currently EPA is under consent order to promulgate Lake Nutrient Criteria if Missouri has not adopted their own by January 2018. It's important these criteria are adopted in December 2017 by the Clean Water Commission to avoid EPA setting criteria for Missouri Lakes, which are likely to be more stringent than the currently proposed criteria. These criteria have gone through significant stakeholder review over the last two years and have the support of both point and non-point source stakeholder groups.
2) Incorporation of the "Waters of the state" definition into the Water Quality Standards by reference to the state statute at Section, 644.016, RSMo.
3) Mixing Zones: Clarifies physical dimensions and requirements and allows for site-specific mixing zone determinations at stream flows which are greater than 20 cubic feet per second as requested by stakeholders.
4) Hardness: Changes the hardness derivation methodology from the 25th percentile to the 50th percentile. Hardness is a key element in calculating hardness dependent metals criteria such as cadmium, chromium (III), copper, lead, nickel, silver and zinc. This change was requested by stakeholders.
5) pH: Clarifies that the criteria for pH are considered a 4-day average and therefore represent a chronic condition.
6) General criteria revisions include language to clarify acute toxicity may be allowed in zones of initial dilution and chronic toxicity allowed in mixing zones. Also, the rule was expanded to ensure protection of downstream uses as required by the CWA.
7) Antidegradation language was modified to reference the updated Antidegradation Implementation Procedure which addresses EPA's concerns with the "de minimis" provisions.
8) Water Quality Standards Variances: Incorporates "Missouri Multiple Discharger Variance Framework from the Water Quality Standards of Total Ammonia Nitrogen, CWC-MDV-1-17". This framework will allow small municipal discharges a variance from ammonia criteria under certain conditions and was developed with stakeholder input.
9) Other revisions to the Rule included removal of expired site-specific criteria and updates to the Losing streams and Missouri Use Designation Dataset GIS layers.

POTENTIAL 304(a) CRITERIA CHANGES RELATED TO NPDES PERMITEE

Our review of the proposed 304(a) criteria spreadsheets provided by MDNR (MDNR 2017d) indicated that approximately 54 chemicals will have more stringent criteria if adopted. A subset of those 304(a) parameters were assessed for this evaluation, referred to herein as parameters of concern (POCs) and include: 2,4,5-trichlorophenol, 2,4,6-trichlorophenol, antimony, arsenic, barium, benzene, cyanide (amenable to chlorination), ethylbenzene, thallium, toluene, trichloroethylene and vinyl chloride (Table 1). Decreases in the criteria (indicating they are more stringent) for these POCs range from 20% (cyanide) to over 99% (arsenic). The MDNR spreadsheet indicated a 7% decrease from the existing most restrictive criteria for antimony, however, the decrease in the human health protection (HHP) criteria is over 99%. Proposed 304(a) criteria for chloride are lower than the current water quality standards criteria and affect a large number of permitees; however, the proposed decrease is marginal (8.0%). Table 1 outlines the POCs current and proposed 304(a) criteria for aquatic life protection and HHP designated uses. The proposed HHP criteria are further segmented into two categories, "Organism+Water" and "Organism Only". As proposed, Missouri's water quality criteria for HHP "Organism+Water" (MDNR 2017c) may be interpreted as applicable to most all waters of the State, regardless if the waterbody is designated for drinking water use or not. There are no proposed changes to the drinking water source or groundwater use criteria for select POCs (Table 1).

TABLE 1 – Current and Proposed Water Quality Criteria for Select POCs.

304(a) Chemical Pollutants	Current Criteria			Proposed Criteria				No Change	Percent Reduction of Most Restrictive Criteria
	Aquatic Life Protection Criteria		Human Health-Fish Protection Criteria	Aquatic Life Protection Criteria		Human Health Protection Criteria		Drinking Water Supply and Groundwater Criteria	
	Acute	Chronic		Acute	Chronic	Organism + Water	Organism Only		
2,4,5-trichlorophenol	--	--	9,800	--	--	300	600	2,600	88
2,4,6-trichlorophenol	--	--	6.5	--	--	1.5	2.8	2	25
Antimony	--	--	4,300	--	--	5.6	640	6	7
Arsenic	--	20	--	340	150	0.018	0.14	50	99+
Barium	--	--	-	--	--	--	1,000	2,000	50
Benzene	--	--	71	--	--	2.1	58	5	58
Cyanide (amenable to chlorination)	22	5	--	22	5.2	4	400	--	20
Ethylbenzene	--	320	--	--	--	68	130	700	79
Thallium	--	--	6.3	--	--	0.24	0.47	50	88
Toluene	--	--	200,000	--	--	57	520	1,000	94
Trichloroethylene	--	--	80	--	--	0.6	7	5	88
Vinyl chloride	--	--	525	--	--	0.022	1.6	2	94

Note: All criteria values are presented in micrograms per liter (µg/L); "--"= no applicable criteria.

The number of facilities identified as having some type of monitoring requirements for selected 304(a) POCs are provided in Table 2 (MDNR 2017b). Monitoring is often required to assess the presence of a pollutant and its reasonable potential to cause or contribute to an excursion of water quality criteria. Future effluent limitations and/or benchmarks may be adjusted or placed in permits if the results of past or future monitoring indicates there is a reasonable potential to cause or contribute to exceedances of a water quality criterion in the receiving waterbody.

TABLE 2 –Number Facilities with 304(a) POCs.

304(a) POCs	Number of NPDES Permits Containing the POC
2,4,5-trichlorophenol	1
2,4,6-trichlorophenol	14
Antimony	41
Arsenic	85
Barium	33
Benzene	61
Cyanide (amenable to chlorination)	50
Ethylbenzene	302
Thallium	44
Toluene	59
Trichloroethylene	10
Vinyl chloride	7

Numeric effluent limits can be established for many of these POCs as technology-based effluent limits (TBELs) in accordance with 40 CFR effluent limit guidelines or as water quality-based effluent limits (WQBELs) using data collected by the permitee for NPDES discharge monitoring. The more stringent of these two will be used to establish effluent limits, when applicable. WQBELs are often more stringent than TBELs and reductions in water quality criteria will likely lead to new or more stringent WQBELs being established during permit renewal.

If a permitted outfall consists of only stormwater, a benchmark may be implemented at the MDNR permit writer's discretion. Benchmarks are not effluent limits but require the facility to monitor for that pollutant. A benchmark exceedance is not a permit violation; however, failure to take corrective actions or implement effective controls is a violation of the permit. During the permit renewal process, more stringent water quality criteria may result in findings of reasonable potential and the establishment effluent limits in place of benchmarks.

TABLE 3 – Current Examples of MDNR Benchmark Values for 304(a) POCs.

304(a) POC	Value (µg/L)	Derivation of Benchmark
Arsenic	33	Permit writer Best Professional Judgement calculation*
Benzene	71	Human Health Protection (HHP) criteria
Ethylbenzene	320	AQL chronic criteria
Thallium	6.3	HHP criteria

Note: "*"= Calculation based on aquatic life (AQL) protection chronic criterion and default limit calculation assumptions.

SURROUNDING STATES' ADOPTION OF USEPA'S NATIONAL RECOMMENDED CRITERIA

A review of the status of adoption of national 304(a) criteria in surrounding states was conducted. Water quality standards for USEPA Region 5 (Illinois, Indiana, Michigan, Minnesota, Ohio and Wisconsin), USEPA Region 6 (Arkansas, Louisiana, New Mexico, Oklahoma and Texas), USEPA Region 7 (Kansas, Nebraska and Iowa), USEPA Region 3 (Maryland), and USEPA Region 4 (Kentucky, and Tennessee) were reviewed for select POCs HHP criteria (Table 4, Appendix A). These states have adopted the 304(a), at least in part, though none to the degree of Missouri's proposed adoption. Of the 18 states included in this review, Missouri would be the only state to adopt USEPA's recommended HHP criteria for 2,4,5 trichlorophenol, cyanide (Organism+Water only), ethylbenzene, and toluene. The subsection "Assigning HHP Organism+Water Criteria to Water Bodies Designated for WWH" (below) provides additional information on how surrounding states have applied "Organism Only" and "Organism+Water" HHP Criteria to waterbody designated uses.

TABLE 4 – Summary of Human Health Protection Criteria in Selected States.

State	2,4,5-trichlorophenol		2,4,6-trichlorophenol		Antimony		Arsenic		Barium		Benzene		Cyanide*		Ethylbenzene		Thallium		Toluene		Trichloroethylene		Vinyl chloride		Carcinogenicity**
	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	
Missouri Current	S	--	S	--	S		--	--	NA	--	S	--	--	--	--	--	S	--	S	--	S	--	S	--	10^{-6}
Missouri Proposed	X	X	X	X	X	X	X	X	NA	X	X	X	X	X	X	X	X	X	X	X	X	X	X	X	10^{-6}
Iowa	--	--	--	--	X	X	S	X	NA	X	X	S	X	S	S	S	X	X	S	S	S	S	S	S	10^{-5}
Kansas	S	--	X	--	X	--	X	--	NA	--	X	--	S	--	S	--	S	--	S	--	S	--	S	--	10^{-6}
Nebraska	--	--	X	X	--	--	S	--	NA	--	X	--	--	S	S	S	X	X	S	--	S	--	S	S	10^{-5}
Illinois	--	--	--	--	--	--	--	--	NA	--	S	--	--	--	--	--	--	--	--	--	--	--	--	--	10^{-6}
Indiana	--	S	S	X	S	S	X	X	NA	--	X	X	--	--	S	S	S	S	S	S	S	S	S	S	10^{-5}
Michigan	--	--	S	S	X	X	S	S	NA	S	X	X	S	S	S	S	S	S	S	S	S	S	S		10^{-5}
Minnesota	--	--	X	--	X	X	S	--	NA	--	X	--	--	--	--	--	X	--	--	--	X	--	X	--	10^{-5}
Ohio	S	--	S	--	S	--	--	--	NA	--	S	--	S	--	S	--	--	--	S	--	S	--	S	--	10^{-5}

Notes: "O" = Organism, "O+W" = Organism+Water; "X"= has a state standard in accordance with USEPA's 304(a) criteria; "S"= has a state standard other than USEPA's 304(a) criteria; "*"= amenable to chlorination; "**"=where applicable.

TABLE 4 – Summary of Human Health Protection Criteria in Selected States.

State	2,4,5-trichlorophenol		2,4,6-trichlorophenol		Antimony		Arsenic		Barium		Benzene		Cyanide*		Ethylbenzene		Thallium		Toluene		Trichloroethylene		Vinyl chloride		Carcinogenicity**
	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	O	O + W	
Wisconsin	S	S	S	S	X	X	S	S	NA	--	X	X	--	--	S	S	--	--	S	S	S	X	X	X	10^{-5}
Arkansas	--	--	--	--	--	--	--	--	NA	--	--	--	--	--	--	--	--	--	--	--	--	--	--	--	10^{-5}
Louisiana	--	--	--	--	--	--	--	S	NA	--	X	X	S	S	S	S	--	--	S	S	S	S	X	S	10^{-6}
New Mexico	--	--	X	--	X	--	S	--	NA		X	--	X		S		X		S		X	--	S	--	10^{-5}
Oklahoma	--	--	--	--	--	--	S	--	NA	--	X	S	--	--	S	S	X	X	S	S	--	--	--	--	10^{-5}
Texas	S	S	--	--	S	S	--	S	NA	S	X	X	--	S	S	S	X	X	--	S	S	X	S	S	10^{-5}
Kentucky	S	--	X	--	X	--	--	--	NA	--	X	--	X	--	S	--	X	--	S	--	S	--	S	--	10^{-6}
Maryland	--	--	X	X	X	X	X	X	NA	X	X	S	X	S	S	S	X	X	S	S	S	S	S	S	10^{-5}
Tennessee	S	S	X	X	X	X	S	S	NA	--	X	S	X	S	S	S	X	X	S	S	S	S	S	S	10^{-5}
Total X	1	1	8	5	10	7	4	4	0	3	15	6	6	1	1	1	10	7	1	1	3	2	4	2	NA
Total S	4	3	4	0	3	2	7	4	0	1	1	1	1	5	13	9	3	1	13	8	12	5	11	6	

Notes: "O" = Organism, "O+W" = Organism+Water; "**X**"= has a state standard in accordance with USEPA's 304(a) criteria; "S"= has a state standard other than USEPA's 304(a) criteria; "*"= amenable to chlorination; "**"=where applicable.

CONCERNS WITH THE DEVELOPMENT AND APPLICABILITY OF PROPOSED CRITERIA

USEPA updated the Human Health Ambient Water Quality Criteria document in 2015 (USEPA 2015b). This update revised 94 existing criteria to reflect the latest scientific information and exposure factors. These criteria were updated and developed following USEPA's methodology for deriving human health criteria (USEPA 2000). The following assumptions, consumption rates, bioaccumulation factors, health toxicity values, and relative source contribution were revised:

- Default body weights were revised from 70 kilograms (kg) to 80 kg;
- Drinking water consumptions rates increased from 2.0 liters per day to 2.4 (90th percentile for adults);
- Fish consumption rates increased from 17.5 grams (g) to 22.0 g per day (90th percentile for adults);
- Bioaccumulation factors for three aquatic organism trophic levels were considered;
- All toxicological effects values were considered; and
- The allotment of exposure from water sources (relative source contribution) were revised and range from 20 to 80 percent.

Without development of state-specific criteria, conservative assumptions are applied in development of the human health ambient water quality criteria. These assumptions can make the criteria unnecessarily stringent, including:

- Fish consumption rates in smaller streams lack trophic level assumptions used in development of national criteria.
- There is no consideration for varying bio-uptake factors for waterbodies of varying sizes.
- Updates to USEPAs default assumptions for body weight, fish consumption, and water ingestion may not represent state-specific values.
- Several POCs may occur naturally at higher background concentrations than proposed HHP criteria.

USEPA also acknowledged several POCs have outstanding technical issues in the science documents and therefore they did not update human health criteria in 2015. POCs with technical issues are discussed in sections below.

Assigning HHP Organism+Water Criteria to Water Bodies Designated for WWH

The proposed amendment to the Water Quality Standards (10 CSR 20-7.031) (SOS 2017) does not clearly state how and to what designated uses the 304(a) criteria for Human Health Protection (HHP) "Organism+Water" and "Organism Only" will be applied. Tables G and H, as proposed in the Rule, include HHP under the designated use for aquatic life protection (warm water habitat,

WWH). Essentially, all classified lakes and streams in Missouri are designated for WWH; therefore, HHP criteria would apply to all classified Missouri waterbodies. Table A-1 (Criteria for Designated Uses and Health Advisory Levels) of the proposed Rule includes both Organism Only and Organism+Water HHP criteria for numerous pollutants. The Organism Only criteria are calculated based on the presumption that the designated waterbody is used as a fishery. The Organism+Water criteria are calculated based on the presumption that the designated waterbody is used as both a fishery and a primary source of drinking water. The resulting concentrations for Organism+Water criteria are therefore appreciably more restrictive than the Organism Only criteria due to the assumed compounded exposure to a pollutant through both fish and water consumption.

Assigning the more restrictive Organism+Water criteria to all WWH water bodies appears to be a misapplication of the Organism+Water criteria. The wide majority of classified Missouri waterbodies are not designated for the DWS use and, with a high level of certainty, would not conceivably be used as a longer-term drinking water source. Our review of HHP criteria in numerous other states indicated that in all cases where Organism+Water criteria were applied, they were only applied when the designated uses for a waterbody included DWS (Table 5).

TABLE 5 – Review of State Designated Uses for Waterbodies where HHP Criteria Apply.

State	Human Health (HH) Standards Applied for:	
	Organism Only	*Organism+Water*
Iowa	HH	HH + DWS
Kansas	Food Procurement designated use	--
Nebraska	AQL	DWS
Illinois	All waters outside mixing zone	--
Indiana	All waters outside mixing zone	Point of public water intake
Michigan	All waters	DWS
Minnesota	AQL and REC	--
Ohio	AQL	--
Wisconsin	All waters	DWS
Arkansas	All waters	--
Louisiana	Fish and Wildlife designated use	DWS
New Mexico	AQL	--
Oklahoma	Fishery designation	DWS
Texas	Fishery designation	DWS + Fishery designated use
Kentucky	All waters outside mixing zone	--
Maryland	Both AQL + REC	REC, AQL and DWS
Tennessee	REC	REC+ DWS

Notes: "HH"= Human Health designated use; "DWS" = Drinking Water Supply designated use; "AQL"= Aquatic Life designated use; "REC'= Recreational Use designation; "--" = State has not adopted Organism+Water Criteria.

Applying Organism+Water criteria to all tributaries of DWS waterbodies would negate consideration of downstream dilution and decomposition, especially for remote reaches of tributaries to waterbodies designated for DWS. A permitted discharge to a remote reach of a tributary to a DWS waterbody would presumably be required to comply with HHP Organism+Water criteria applicable only to a waterbody designated for DWS, which may be many miles downstream from the NDPES discharge. Negating the dilution and decomposition of pollutants between the point of discharge and the first DWS waterbody would, in such a case, be an overly-conservative application of the HHP Organism+Water criteria. In other states, such as Texas, the statutes clarify the point at which these criteria apply: Protected Zones for drinking water supplies extend three linear miles upstream from water supply intake.

In their response to technical comments on the 2015 HHP Criteria update, USEPA responded to a public comment regarding water consumption rates by stating that "....drinking water is a designated use for surface waters under the CWA and, therefore, criteria are needed to assure that this designated use can be protected and maintained..." (USEPA 2015c). Also, USEPA's methodology for deriving HHP states that the HHP Organism Only criteria "applies in those cases where the designated uses of a waterbody include supporting fishable uses....but not as a drinking water supply source..." (USEPA 2000a). By inference, these references demonstrate USEPA's intention to apply the Organism+Water HHP criteria to waterbodies formally designated for the DWS use.

Applying the Organism+Water HHP criteria to waters designated for the DWS use would align with the exposure and risk assumptions included in the HHP Organism+Water criteria methodology. Applying the Organism+Water HHP criteria to all classified waterbodies would place a substantial and unwarranted burden on NPDES permittees and is not consistent with the previously referenced USEPA guidance or the practices of numerous other states.

Adopting HHP Criteria for Pollutants Identified by USEPA as having Technical Issues

Adoption of the recommended 304(a) human health protection criteria will result in more stringent criteria for some pollutants which USEPA describes as having "outstanding technical issues" (USEPA 2015b). These pollutants include; antimony, arsenic, asbestos, barium, beryllium, cadmium, chromium (III or VI), copper, manganese, methylmercury, nickel, nitrates, nitrosamines, N-nitrosodibutylamine, N-nitrosodiethylamine, N-nitrosopyrrolidine, N-nitrosodimethylamine, N-nitrosodi-n-propylamine, N-nitrosodiphenylamine, polychlorinated biphenyls (PCBs), selenium, thallium, zinc, or 2,3,7,8-TCDD (dioxin). In their 2015 Human Health Ambient Water Quality Criteria Update, USEPA did not update the human health criteria for these pollutants and referred to issues with toxicity and bioaccumulation factors (USEPA 2014). We are not aware of USEPA's progress to address these technical issues, but the Agency's

acknowledgement of the issues warrants MDNR's further review of the basis for which these criteria were developed before adopting them for Missouri.

Practical Quantification and Method Detection Limits vs. Criteria Values.

The proposed 304(a) criteria may be lower than current analytical procedures are able to measure with reasonable certainty. Advances in analytical capabilities are generally not keeping up with the development of more stringent water quality criteria. Criteria for protection of human health consider the risks of consumption of a constituent over a given period. As such, criteria values are calculated based on various assumptions such as body weight, consumption rates, health toxicity values and bioaccumulation factors, resulting in criteria values that are much lower than current laboratory tests can accurately measure.

The ability of laboratories to quantify analytes at sufficient levels for comparison to water quality criteria or permit limits can dramatically impact the certainty of regulatory compliance. The Method Detection Limit (MDL) and other reporting parameters that can be achieved by various laboratories needs to be considered when promulgating criteria. The MDL is below the point of calibration and is the minimum concentration that can be measured and reported with 99% confidence that the analyte concentration is greater than zero. The Code of Federal Regulations (40 CFR 136) establishes the statistical approach used for developing an MDL, which are generally developed through interlaboratory studies. Individual laboratories may have slightly different MDLs due to instrumentation accuracy and operator experience. As analyte concentrations approach the MDL, the certainty of the analyte concentration decreases. To address this, laboratories also develop practical quantitation limits (PQLs, also known a Reporting Limits or RLs), which are concentrations the laboratory has much greater certainty and are within the limits of precision and accuracy. There is no regulation which governs the development of PQLs, but it is generally between 3 and 10 times greater than the MDL. The PQL value represents the lowest concentration the laboratory is confident it can quantify. To adequately evaluate compliance with water quality criteria or NPDES permit limits, it is recommended the PQL be below the criterion or permit limit. However, this is often not the case and permittees must rely on more uncertain quantification at or near the MDL.

As previously mentioned, several of the existing laboratory methods are not able to adequately quantify pollutant concentrations for risk-based criteria. Proposed HHP criteria of select POCs that are below typical PQLs include 2,4,6-tricholorophenol, arsenic, amenable cyanide, thallium, and vinyl chloride (Table 6). The remaining POCs have PQLs lower than the proposed HHP criteria. A comparison of the PQLs provided by PACE Analytical Services indicate that the most restrictive proposed criteria for arsenic and thallium are well below both the MDLs and PQLs. The most restrictive proposed criterion for trichloroethylene is slightly higher than PACE's PQL. Appendix A to 40 CFR 136, provides MDLs for the analysis of purgeable halocarbons (2,4,6

trichlorophenol and vinyl chloride). PQLs for these analytes were estimated using three times the MDLs. Based on this assumption, the PQL is slightly above the proposed criterion for 2,4,6 trichlorophenol. Both the PQL and MDL for vinyl chloride are much higher than the most stringent proposed criterion. Cyanide amenable to chlorination (cyanide) is typically analyzed using Standard Method 4500-CN-G. There is no published MDL associated with this method; however, based on the performance of the MDNR's Environmental Services Program Laboratory (MDNR 2015c), an MDL of 3 µg /L and a PQL of 10 µg/L was determined to be practical. This PQL is higher than the most restrictive proposed criterion for cyanide while the MDL is only slightly below the proposed criterion.

TABLE 6 –POCs Currently with Insufficient Laboratory Quantification Limits.

304(a) POC	MDL (µg/L)	PQL (µg/L)	Most Restrictive Proposed MO Criterion (µg/L)
Arsenic[a]	3.22	10	0.018
Thallium[a]	1.61	10	0.24
Trichloroethylene[a]	0.15	0.5	0.6
2,4,6-trichlorophenol[b]	0.64	1.92	1.5
Vinyl chloride[b]	0.18	0.54	0.022
Cyanide (amenable to chlorination)[c]	3.0	10	4.0

Notes: "a"= Pace Analytical Services MDL and PQL; "b"= Method 601 MDL and Estimated PQL (3 x MDL); "c"= SM 4500-CN⁻ G – MDL and PQL as determined by MDNR ESP Laboratory

According to MDNR's current permitting policy, effluent limits below the PQL of an USEPA approved method are set at the method minimum level (ML). The ML is a value derived by multiplying the MDL by 3.18. The 3.18 multiplier was derived from USEPA guidance "Determining Compliance with Water Quality Based Effluent Limits Below Quantification in the Absence of Promulgated Minimum Levels" (1995). Typically, a ML that is approximately equal to the PQL is considered "valid and appropriate" (MDNR 2015c). For example, the PQL and the ML for cyanide (amenable to chlorination) are both 10 µg/L. The use of an ML as a compliance value may result in overly conservative effluent limits. Therefore, sample results less than the ML are considered in compliance with the permit requirements and sample results at or above the ML are considered a permit violation.

RECOMMENDATIONS TO ADDRESS CONCERNS IN THE DRAFT RULE PERTAINING TO CRITERIA REVISIONS

General Recommendations

1) The draft rule should be modified to clearly indicate that HHP Organism+Water criteria are only assigned to waterbodies designated as both human health protection and drinking water supply.

    a. By inference, USEPA references demonstrate the agency's intention to apply the Organism+Water HHP criteria to only waterbodies designated for DWS use.
    b. Applying the Organism+Water HHP criteria to waters designated for the DWS aligns with the exposure values used in the methodology for developing HHP Organism+Water criteria.
    c. Substantial and unwarranted economic burden will be placed on NPDES permittees if Organism+Water HHP criteria are applied to all classified waterbodies designated as warm water habitat (WWH), which is not consistent with USEPA guidance or criteria adopted by numerous other states.

2) MDNR should postpone adoption of HHP criteria for pollutants that USEPA identified as having outstanding technical issues related to toxicity and bioaccumulation factors, which include; antimony, arsenic, barium and thallium.

    a. If adopted, the proposed criteria may result in widespread exceedances of water quality standards and lead to erroneous water quality impairments.
        i. For example, Missouri River arsenic data collected by USGS at Hermann, MO has a geometric mean value of 2.3 µg/L compared to the proposed Organism+Water HHP criterion of 0.018 µg/L.
    b. Only technically defensible criteria should be adopted.

3) MDNR should specify the use of a method PQL or ML for compliance assessments when criteria are below laboratory PQL and/or MDL.

    a. Several proposed criteria have values below the MDL and/or the PQL. MDNR should use the PQL or ML when evaluating data compliance with limits, benchmarks, and monitoring only results.
    b. Due to the level of uncertainty of concentrations measured between the MDL and PQL, MDNR should consider a confidence interval at the PQL when evaluating data compliance with limits, benchmarks, and monitoring only results.

4) MDNR should consider what other states have done in the selection of human health risk factors and the development of state-specific criteria values.

    a. Exposure factors used by USEPA may not represent Missouri-specific factors.
    b. USEPA allows flexibility adopting the 304(a) criteria. States may:
        i. adopt USEPA's recommended criteria;
        ii. adopt criteria modified to reflect site-specific (i.e., state-specific) conditions such as relative source contributions, carcinogenic risk factors, bioaccumulation factors, fish consumption, water intake rates, bio-uptake factors, etc. (e.g., FDEP 2017);
        iii. adopt criteria derived using other scientifically defensible methods; or
        iv. develop narrative criteria in place of numeric criteria (40 CFR 131.11)
    c. This review indicates Missouri is proposing more restrictive criteria than most other states.

Parameter Specific Recommendations

1) MDNR should reevaluate adoption of **2,4,5-trichlorophenol** criteria based on precedent in other states (e.g., USEPA Regions 5, 6, 7, Tennessee, Kentucky and Maryland) and Organism+Water criteria should only apply to those waterbodies with DWS use.
    a. USEPA updated these 304(a) criteria in 2015. None of the 18 reviewed states have adopted USEPA's default criteria but some have alternative criteria. Those that have gone through recent rulemaking (e.g., 2016, 2017) did not adopt the updated USEPA default criteria.
    b. Missouri's proposed criteria are significantly lower than criteria adopted by other states. Missouri should explore why other states did not adopt USEPA's default criteria.
    c. Missouri should establish state-specific criteria if merited.
    d. USEPA's criteria document infers that Organism+Water HHP criteria should apply only to waterbodies designated for DWS use.
    e. Surrounding states apply Organism+Water HHP criteria only to waterbodies designated for DWS use.

2) MDNR should provide assurance that permit limitations for **2,4,6-trichlorophenol** will be established at the method PQL and Organism+Water criteria should only apply to those waterbodies with DWS use.
    a. Proposed HHP criteria are below current laboratory quantification capabilities.
    b. USEPA's criteria document infers that Organism+Water HHP criteria should apply only to waterbodies designated for DWS use.

c. Surrounding states apply Organism+Water HHP criteria only to waterbodies designated for DWS use.

3) MDNR should not adopt proposed **antimony** HHP criteria at this time.
   a. USEPA acknowledges outstanding technical issues in the science documents and opted not to update human health criteria in 2015.
   b. The existing 304(a) HHP criteria for antimony were last updated in 1980 and include assumptions which are not consistent with current science.

4) MDNR should not adopt proposed **arsenic** HHP criteria at this time.
   a. Background concentrations in samples from the Missouri River at Hermann, MO have a geometric mean of 2.3 µg/L (higher than the proposed arsenic HHP criteria).
   b. USEPA acknowledges outstanding technical issues in the science documents and opted not to update human health criteria in 2015.
   c. The existing 304(a) criteria for arsenic were last updated in 1992 and include assumptions which are not consistent with current science.

5) MDNR should not adopt **barium** HHP criteria at this time.
   a. USEPA acknowledges outstanding technical issues in the science documents and opted not to update human health criteria in 2015.
   b. Background concentrations range from 66 to 818 µg/L in samples collected from the Missouri River at Hermann, MO.
   c. The existing 304(a) HHP criteria for barium were last updated in 1986 and include assumptions which are not consistent with current science.

6) As with all POC's, MDNR should assign **benzene** Organism+Water criteria to only those waterbodies with DWS use.
   a. USEPA's criteria document infers that Organism+Water HHP criteria should apply only to waterbodies designated for DWS use.
   b. Surrounding states apply Organism+Water HHP criteria only to waterbodies designated for DWS use.

7) As with all POCs, MDNR should assign **cyanide (amenable to chlorination)** Organism+Water criteria to only those waterbodies with DWS use and give assurance that permit limitations will remain set at the method PQL or ML.
   a. USEPA's criteria document infers that Organism+Water HHP criteria should apply only to waterbodies designated for DWS use.
   b. Surrounding states apply Organism+Water HHP criteria only to waterbodies designated for DWS use.
   c. Current HHP criteria are below laboratory quantification capabilities.

d. Proposed HHP criteria are below laboratory quantification capabilities.
e. Other states that have gone through recent rulemaking have not adopted these criteria.

8) MDNR should reevaluate adoption of **ethylbenzene** proposed 304(a) criteria based on precedent in other states (all USEPA Region 5, 6, 7 states along with Tennessee, Kentucky, and Maryland).
   a. USEPA updated these 304(a) criteria in 2015. None of the 18 reviewed states have adopted USEPA's default criteria but some have alternative criteria. Those that have gone through recent rulemaking (e.g., 2016, 2017) did not adopt the updated USEPA default criteria.
   b. Missouri's proposed criteria are significantly lower than criteria adopted by other states. Missouri should explore why other states did not adopt USEPA's default criteria.
   c. Missouri should establish state-specific criteria if merited.

9) MDNR should not adopt **thallium** HHP criteria at this time.
   a. Proposed HHP criteria are below laboratory quantification capabilities.
   b. USEPA acknowledges outstanding technical issues in the science documents and opted not to update thallium human health criteria in 2015.

10) MDNR should reevaluate adoption of **toluene** criteria based on precedent set by the 18 other states reviewed (all USEPA Region 5, 6, 7 states along with Tennessee, Kentucky, and Maryland).
   a. USEPA updated these 304(a) criteria in 2015. None of the 18 reviewed states have adopted USEPA's default criteria but some have alternative criteria. Those that have gone through recent rulemaking (e.g., 2016, 2017) did not adopt the updated USEPA default criteria.
   b. Missouri's proposed criteria are significantly lower than criteria adopted by other states. Missouri should explore why other states did not adopt USEPA's default criteria.
   c. Missouri should establish state-specific criteria if merited.

11) As with all POC's, MDNR should assign **trichloroethylene** Organism+Water criteria to only those waterbodies with DWS use and give assurance that permit limitations will remain set at the method PQL or ML.
   a. Proposed HHP criteria are below laboratory quantification capabilities.
   b. USEPA's criteria document infers that Organism+Water HHP criteria should apply only to waterbodies designated for DWS use.

c. Surrounding states apply Organism+Water HHP criteria only to waterbodies designated for DWS use.

12) MDNR should reevaluate adoption of **vinyl chloride** criteria based on precedent in other states (USEPA Region 5, 6, 7 states along with Kentucky, Tennessee, and Maryland). Also, as with all POC's, MDNR should assign **vinyl chloride** Organism+Water criteria to only those waterbodies with DWS use and give assurance that permit limitations will be set at the method PQL or ML.
    a. Missouri's proposed criteria are significantly lower than other states evaluated.
    b. Of other state's criteria reviewed for this memo, only Louisiana has adopted these criteria. The other states have not adopted or have adopted criteria at a lower carcinogenic risk factor (i.e., 10^{-5}).
    c. Proposed HHP criteria are below laboratory quantification capabilities.
    d. USEPA's criteria document infers that Organism+Water HHP criteria should apply only to waterbodies designated for DWS use.
    e. Surrounding states apply Organism+Water HHP criteria only to waterbodies designated for DWS use.

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February 19, 2019

VIA EMAIL

Chris Wieberg
Water Protection Program
Missouri Department of Natural Resources
chris.wieberg@dnr.mo.gov

RE: Triennial Review

Dear Chris:

The purpose of this letter is to formally notify the MDNR that the City of Bolivar will be seeking a variance to the water quality standards and the wasteload allocations set forth in the EPA nutrient TMDL. I am providing you this notice pursuant to the department's public notice requesting items to include in the next triennial review.

Sincerely,

NEWMAN, COMLEY & RUTH, P.C.

By: Robert J. Brundage

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ec: Tracy Slagle, City of Bolivar