The Atmospheric Release of Mercury from Combustion Processes:An Evaluation of Potential Health Effects

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Hook into Healthy Fish!

Reel in the facts about mercury in fish

Fish are fun to catch and good to eat.
Fish are healthy food — high in protein and low in fat.

But too much of a good thing can be bad for you. All fish contain some mercury. Eating too much contaminated fish can be harmful to you and your child's health.

Keep eating fish.
The benefits outweigh the health risks as long as you follow guidelines on how much fish to eat. These guidelines will help you limit your exposure to mercury while still enjoying healthy meals of fish.

Get more information:

For more information please consult the full fish consumption advisory booklet. This booklet is available at your local DNR office, your local health department, or on the web at: www.dnr.state.wi.us.

WISCONSIN DEPT. OF NATURAL RESOURCES

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► Safe Eating Guidelines

for *most* of Wisconsin's inland (non-Great Lakes) waters.

Women of childbearing years, nursing mothers and all children under 15 may eat:*

1 meal per week	Bluegill, sunfish, black crappie, white crappie, yellow perch or bullheads,
AND	
1 meal per month	Walleye, northern pike, smallmouth bass, largemouth bass, channel catfish, flathead catfish, white sucker, drum, burbot, sauger, sturgeon, carp, white bass, rock bass or other species.*

*Muskies should not be eaten by this group of people due to high mercury content.

Men, and women beyond their childbearing years may eat:

Unlimited amounts	Bluegill, sunfish, black crappie, white crappie, yellow perch, or bullheads,
AND	
1 meal per week	Walleye, northern pike, smallmouth bass, largemouth bass, channel catfish, flathead catfish, or other species.

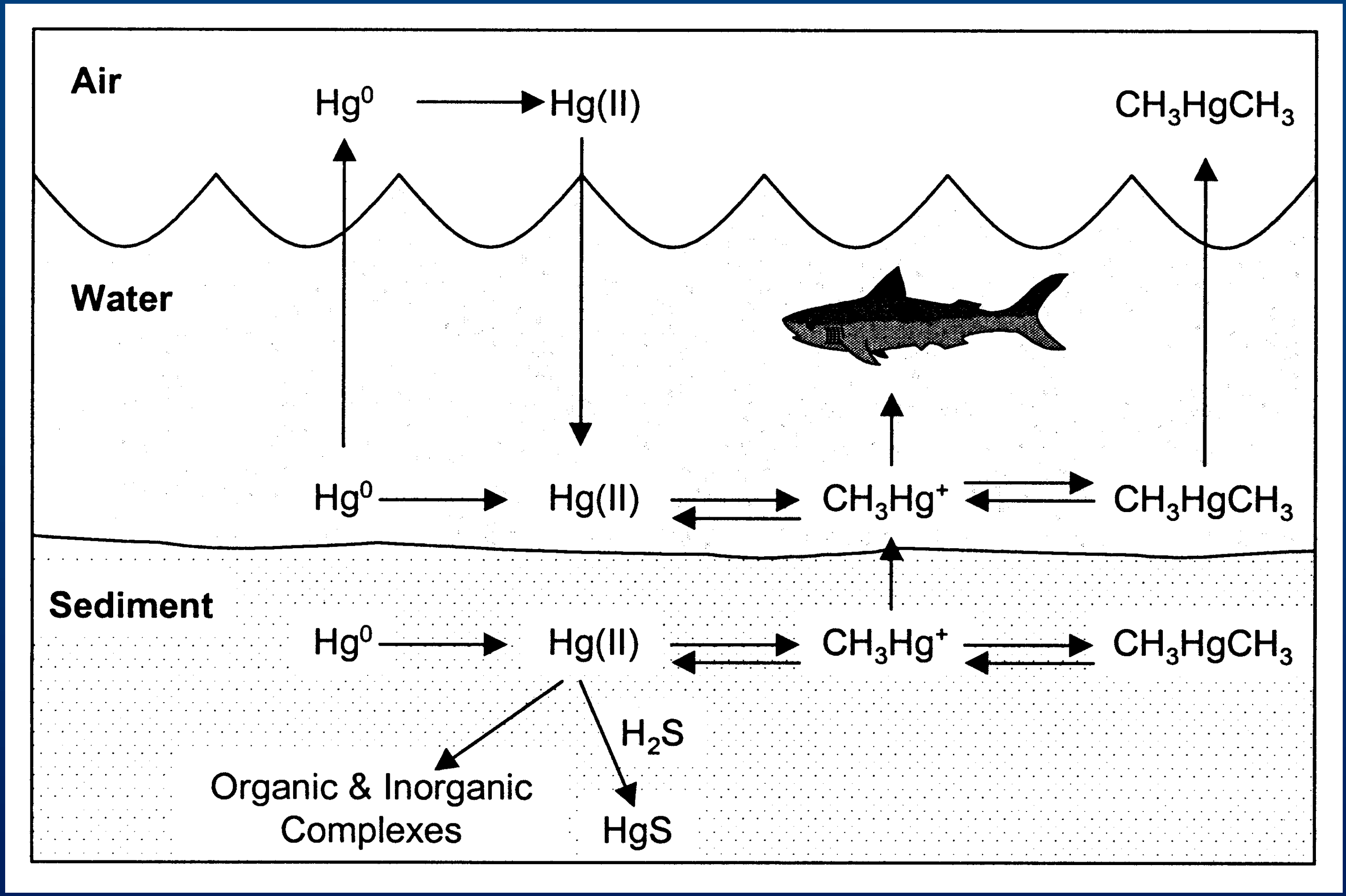
Additional restrictive advice is necessary for some waters where fish have been found to contain higher levels of mercury. These waters are listed on the back of this flyer. Additional specific advice for waters with PCBs and other chemicals, such as the Great Lakes and major rivers, is in the full fish consumption advisory booklet.

SECTION 1

What Do We Know About the Toxicity of Mercury Species Associated with Combustion?

- Elemental Mercury [Hg^0]
- Divalent (Mercuric) Mercury [Hg^{+2}]
- Methylmercury [MeHg]

Cycling of Mercury in Aquatic System



Source: Toxicological Effects of Methylmercury, NRC (2000).

Human Exposure to Mercury: Japan

- Industrial discharge of mercury waste to Minamata Bay between 1953-1960
- Discharged mercury was converted to methylmercury by aquatic organisms
- Surrounding residents subsisted on fish/shellfish caught in the bay
- Approximately 2200 people impacted [12 deaths]

Human Exposures to Mercury: Iraq

- In 1971, 90,000 metric tons of grain treated with methylmercury as a fungicide were distributed throughout the country for planting
- Due to the timing of the distribution, grain was ground into flour and consumed
- Approximately 6530 people impacted [459 deaths]

Effects of High Dose Methylmercury Exposure

- In-Utero Exposure
  - Mental retardation
  - Cerebral palsy
  - Deafness
  - Blindness
  - Dysarthria*

*slurred, slow, difficult speech

Effects of High Dose Methylmercury Exposure

- Adult Exposure
  - Sensory impairment
  - Motor impairment
  - Paresthesia
  - Ataxia
  - Tremors
  - Deafness
  - Difficulty walking

Toxicity of Elemental Mercury [Hg^0]

- Critical organ for toxicity is the brain (kidneys?)
- Inhaled Hg^0 is lipid soluble and readily absorbed into the blood stream where it is converted into Hg^{+2}
- Prior to oxidation, Hg^0 can cross the blood-brain barrier and placenta where it can be oxidized
- Kidneys contain highest concentrations of mercury following Hg^0 exposure
- Although toxicity is dose-dependent, combination of increased excitability, tremors and gingivitis has been characteristic of mercury vapor exposure
- CNS and renal effects are primarily seen in occupational exposures [rare]

Toxicity of Mercuric Mercury [Hg^{+2}]

- Critical organ for toxicity is the kidney
- Due to ionic charge, does not readily cross the blood-brain barrier
- Due to ionic charge, does not readily cross the placenta
- Approximately 50% of a non-toxic dose of Hg^{+2} is found within the kidneys within a few hours of exposure
- Renal toxicity believed to be mediated through binding to sulfhydryl (-SH) groups in enzymes located in the cells lining the proximal tubules
- Some evidence in animals of immunologic glomerular disease which may also exist in humans

Toxicity of Methylmercury [MeHg]

- Critical organ for toxicity is the brain
- Readily crosses the blood-brain barrier
- Readily crosses the placenta
- Accumulates in the brain, slowly converted to Hg^{+2}
- Toxicity believed to be mediated through binding to sulfhydryl groups in critical enzymes
- Unclear if toxicity is from MeHg or Hg^{+2}
- Very young appear to be particularly sensitive

Pharmacokinetic Parameters for Methylmercury

Parameter	Value
Oral Absorption	>95%
Absorbed Dose in Blood	6%
Body Half Life	70-74d

Human Epidemiological Studies: Faroes

- Islands located northwest of Scotland between Iceland and Norway
- Fish- and sea mammal-eating population
- Prospective developmental study involving 900 mother-infant pairs
- Children subjected to standardized neuropsychological tests at age of 7 years
- Subtle dose-related developmental effects complicated by PCB exposures

Human Epidemiological Studies: Seychelles

- Islands located 1,000 miles from Africa in the Indian Ocean
- Fish-eating population
- Prospective developmental study involving 779 mother-infant pairs
- Infants followed from birth to 5.5 yrs and subjected to standardized neuropsychological tests
- Although pilot study indicated mercury-related impairment, main study did not
- Subsequent analyses have suggested an improvement in developmental parameters

Human Epidemiological Studies: New Zealand

- 11,000 mother-infant pairs submitted hair samples and completed diet survey
- 1,000 mothers consumed fish >3 times/wk throughout pregnancy; 73 mothers had hair mercury levels >6ppm
- Developmental studies conducted involving standardized neuropsychological tests at ages 4 and 6-7 yrs
- Exposed children were matched against children from mothers with lower hair mercury
- Dose-related developmental effects observed

USEPA's Reference Dose (RfD)

- An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime
- Developed to protect against ingested contaminants
- Usually based on animal studies
- Expressed as a daily dose (mg/kg body weight/day)

USEPA's Reference Concentration (RfC)

- An estimate (with uncertainty spanning perhaps an order of magnitude) of a daily inhalation exposure to the human population (including sensitive subgroups) that is likely to be without an appreciable risk of deleterious effects during a lifetime
- Developed to protect against inhaled contaminants
- Often based on occupational exposures in humans
- Expressed as an air concentration (mg/m^3)

USEPA's Use of Benchmark Dose to Derive RfD

- NOAEL (No-Observed-Adverse-Effect-Level)

  Exposure level at which no statistically or biologically significant increase in frequency or severity of adverse effects in comparison between exposed population and control group
- BMD (Benchmark Dose)

  Quantitative assessment that uses a curve-fitting procedure to determine a level equivalent to the NOAEL (i.e., estimated dose that corresponds to a specified risk above background risk. USEPA used 5%)
- BMDL (Benchmark Dose Lower Limit)

  Statistical lower limit on a calculated BMD. USEPA used the 95% lower confidence limit

Toxicity Criteria for Mercury Species

Speciation	RfD (mg/kg-d)	RfC (mg/m^3)
Hg^0	*8.6E-5**	3.0E-4**
Hg^{+2}	3.0E-4**	*1.1E-3**
MeHg	1.0E-4**	*3.5E-4**

* Calculated values from HHRAP, USEPA (2005).

** IRIS values USEPA (2005).

Use of Reference Dose to Quantify Health Impacts

$$Hazard\ Quotient(HQ) = \frac{Average\ Daily\ Intake\ (DI)}{Reference\ Dose\ (RfD)}$$

$$DI_{fish} = CR_{fish} \times C_{fish}$$

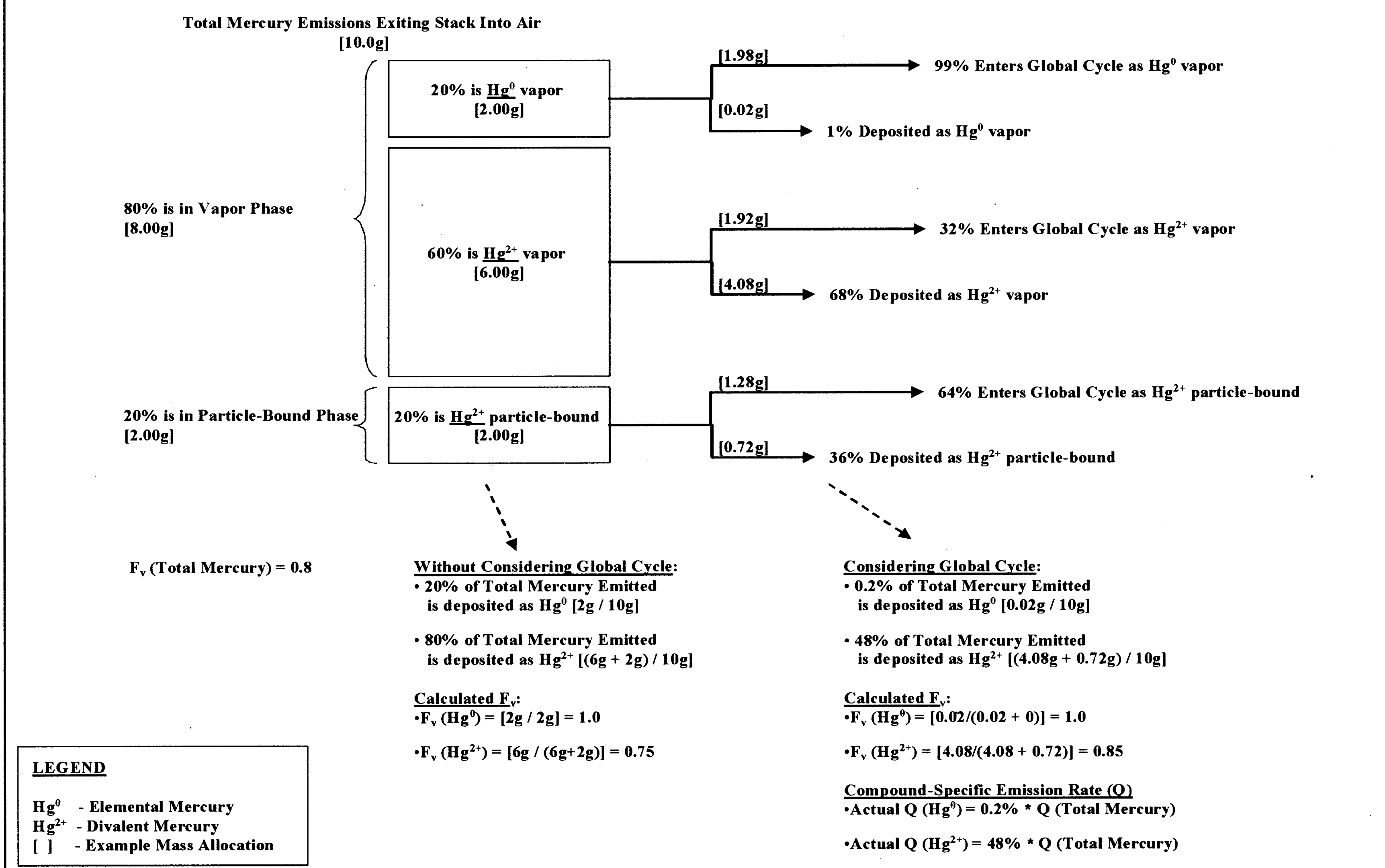
- DI = Daily intake (mg/kg-d)
- CR_{fish} = Daily consumption of fish (kg/kg-d)
- C_{fish} = MeHg concentration in fish (mg/kg)
- RfD = Reference dose (mg/kg-d)

SECTION 2

What Do We Know About the Fate and Transport of Mercury Species Associated with Combustion?

- Elemental Mercury [Hg^0]
- Divalent (Mercuric) Mercury [Hg^{+2}]
- Methylmercury [MeHg]

FIGURE 2-4
PHASE ALLOCATION AND SPECIATION OF MERCURY IN AIR



Source: HHRAP, USEPA (2005).

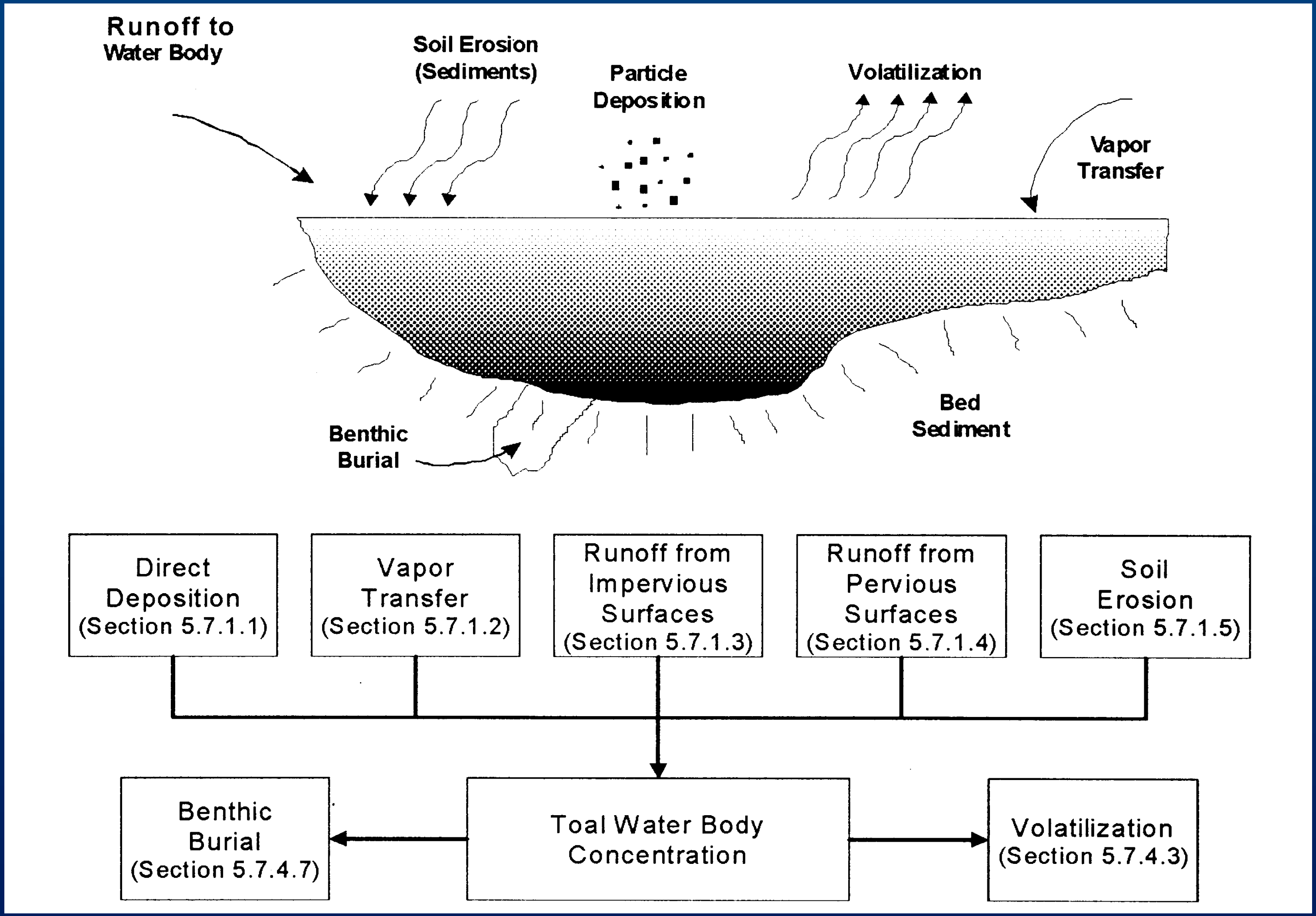
Impact of Mercury Speciation on HHRA

Default Speciation [Assumed 20% Hg^0 and 80% Hg^{+2}]				
Speciation	10g	Local (%)	Local (g)	
Hg^0 Vapor	2g	1	0.02	0.02
Hg^{+2} Vapor	6g	68	4.08	4.80
Hg^{+2} [Particle-Bound]	2g	36	0.72	

Impact of Mercury Speciation on HHRA

Site-Specific Speciation [Assumed 90% Hg^0 and 10% Hg^{+2}]				
Speciation	10g	Local (%)	Local (g)	
Hg^0 Vapor	9g	1	0.09	0.09
Hg^{+2} Vapor	0.75g	68	0.51	0.60
Hg^{+2} [Particle-Bound]	0.25g	36	0.09	

Mercury Loading to Water Bodies



Source: HHRAP, USEPA (2005)

Mercury Loading to Surface Water Bodies

- Direct deposition
- Runoff from impervious surfaces within watershed
- Runoff from pervious surfaces within watershed
- Soil erosion over total watershed
- Direct diffusion (vapor phase) into surface water
- Internal transformation in surface water

Effects of Site Conditions on Methylation

Physical/Chemical Condition	Impact on Methylation
Low Dissolved Oxygen	+
Decreased pH	+ WC / - S
Increased Dissolved Organic Carbon	- WC / + S
Increased Salinity	-
Increased Nutrient Levels	+
Increased Selenium Levels	-
Increased temperature	+
Increased Sulfate Levels	+
Increased Sulfide Levels	+

Source: HHRAP, USEPA (2005)

$$C_{fish_{(MeHg)}} = C_{dw_{(MeHg)}} \times BAF_{fish_{(MeHg)}}$$

Where:

$C_{fish(MeHg)}$ = Concentration of MeHg in fish tissue (mg/kg);

$C_{dw(MeHg)}$ = Dissolved phase concentration of MeHg (mg/L); and

$BAF_{fish(MeHg)}$ = Bioaccumulation factor for MeHg in fish (L/kg).

Variability in Bioaccumulation Factors (BAFs) for Modeling Fish Tissue Methylmercury Concentrations

Classification	Methylmercury BAF_4 (L/kg)			
	GLWQI USEPA, 1995	MSRC USEPA, 1997	HHRAP USEPA, 2005	AWQC USEPA, 2001
Trophic Level 4	1.40E+05	6.80E+06	6.80E+06	2.70E+06
Trophic Level 3	2.79E+04	1.60E+06	--	6.80E+05

Classification of Fish Populations in Ohio River

Parameter	TL 4	<TL 3
Fish Collected (Number as %)	73.9	26.1
Fish Meals Consumed (Number as %)	64.8	35.2

Source: Knuth et al (1993)

Classification of Fish Populations in Wabash River

Parameter	TL 4	<TL 4
Fish Collected (Number as %)	10.8	89.2
Fish Collected (Mass as %)	9.6	90.4

Source: Indiana DNR (1993)

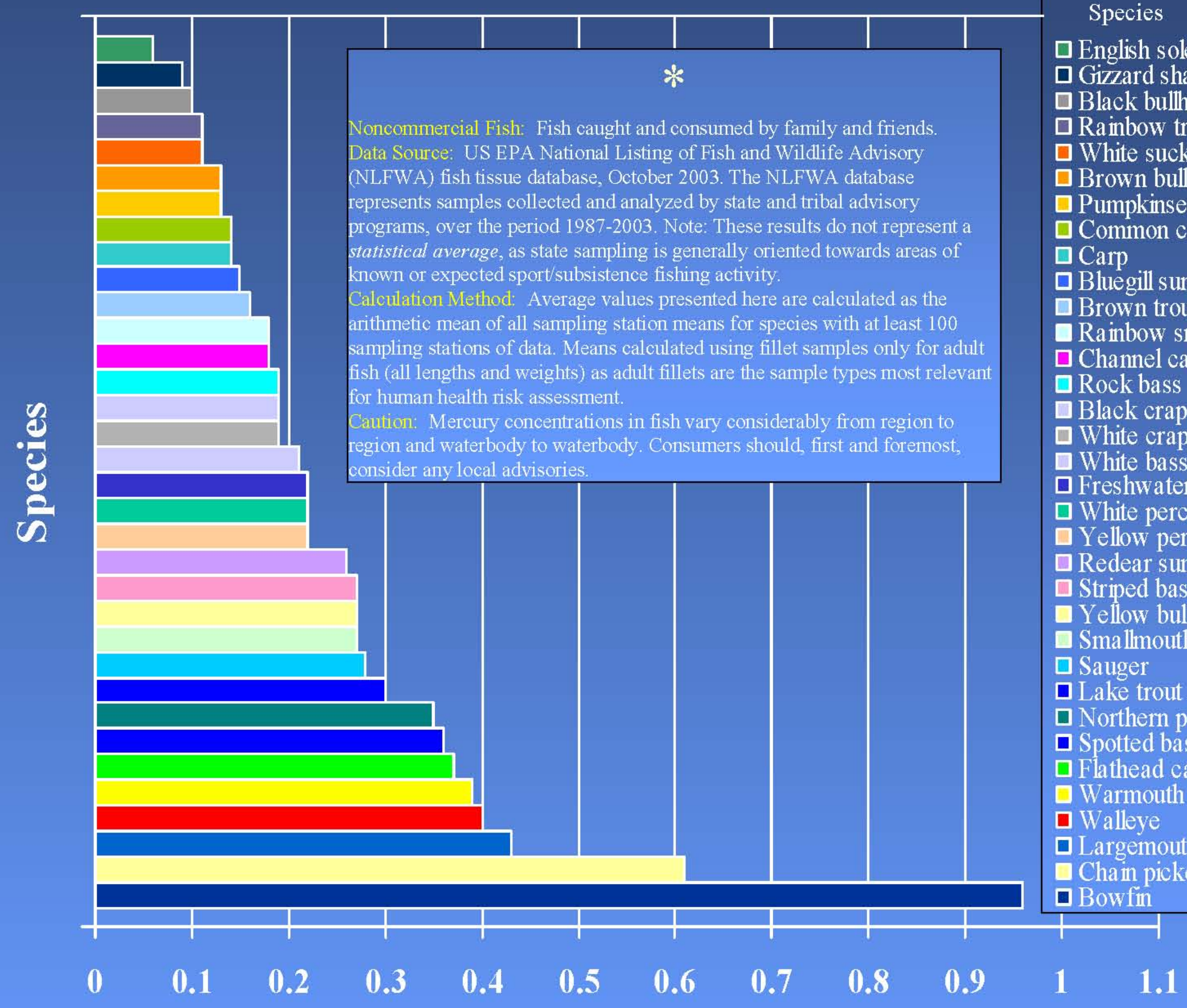
Aquatic Ecosystem-Specific Fish BAFs

Surface Water Classification	Methylmercury BAF (L/kg)	
	BAF_4	BAF_3
Lentic Ecosystem [lake, swamp]	5.74E+06	1.12E+06
Lotic Ecosystem [river]	1.24E+06	5.17E+05
Combined [Draft BAF]	2.70E+06	6.80E+05

Variability in Fish Consumption Values for HHRAs

Regulatory Driver	Fish Consumption (g/day)	
	Adult	Child
USEPA HHRAP [S]	87.5	13.2
Kentucky [S]	149.0	21.0
Kentucky [R]	11.7	1.6
Michigan [R]	15.0	2.1
Pennsylvania [R]	20.9	2.9

Average Tissue Mercury Concentrations in Noncommercial Fish*



Species	No. Sampling Stations	Average Conc. (ppm)
English sole	241	0.06
Gizzard shad	151	0.09
Black bullhead	130	0.10
Rainbow trout	119	0.11
White sucker	714	0.11
Brown bullhead	214	0.13
Pumpkinseed sunfish	107	0.13
Common carp	737	0.14
Carp	426	0.14
Bluegill sunfish	1,062	0.15
Brown trout	131	0.16
Rainbow smelt	116	0.18
Channel catfish	1,213	0.18
Rock bass	376	0.19
Black crappie	652	0.19
White crappie	352	0.19
White bass	212	0.21
Freshwater drum	226	0.22
White perch	133	0.22
Yellow perch	604	0.22
Redear sunfish	215	0.26
Striped bass	146	0.27
Yellow bullhead	185	0.27
Smallmouth bass	738	0.27
Sauger	109	0.28
Lake trout	160	0.30
Northern pike	1,322	0.35
Spotted bass	163	0.36
Flathead catfish	158	0.37
Warmouth sunfish	147	0.39
Walleye	1,520	0.40
Largemouth bass	2,425	0.43
Chain pickerel	250	0.61
Bowfin	358	0.96

*

Noncommercial Fish: Fish caught and consumed by family and friends.
Data Source: US EPA National Listing of Fish and Wildlife Advisory (NLFWA) fish tissue database, October 2003. The NLFWA database represents samples collected and analyzed by state and tribal advisory programs, over the period 1987-2003. Note: These results do not represent a *statistical average*, as state sampling is generally oriented towards areas of known or expected sport/subsistence fishing activity.
Calculation Method: Average values presented here are calculated as the arithmetic mean of all sampling station means for species with at least 100 sampling stations of data. Means calculated using fillet samples only for adult fish (all lengths and weights) as adult fillets are the sample types most relevant for human health risk assessment.
Caution: Mercury concentrations in fish vary considerably from region to region and waterbody to waterbody. Consumers should, first and foremost, consider any local advisories.

EPA National Fish and Wildlife Contamination Program

www.epa.gov/waterscience/fish

Summary and Conclusions

- ☞ Concern associated with the emissions of mercury from combustion units results primarily from impacts on surface water
- ☞ Inorganic mercury in water bodies can be converted to MeHg which readily bioaccumulates through the aquatic food chain
- ☞ Consumers, including man, located at the top of the food chain can be exposed to elevated dietary levels of MeHg
- ☞ Primary concern appears to focus on exposure of the fetus or nursing neonate to MeHg ingested by its mother
- ☞ Epidemiological studies suggest that low level MeHg exposure can have neuropsychological impacts during development

Cautions?

- Fate and transport of mercury species in and around surface water bodies is extremely complex and can be influenced by numerous external factors
- Controversy that subtle developmental impacts resulting from fish ingestion may be offset by nutritional benefits (i.e., Omega-3-FAs)
- High level of uncertainty associated with the prediction of MeHg exposure levels based on stack emissions