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Mercury Study Report to Congress

Volume V: An Ecological Assessment of Anthropogenic Mercury Emissions in the United States

SAB REVIEW DRAFT

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Office of Air Quality Planning & Standards
and
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LIST OF SYMBOLS, UNITS AND ACRONYMS

ATP	Adenosine triphosphate
AWQC	Ambient Water Quality Criteria
BAF	Bioaccumulation factor
BAF_3	Aquatic life bioaccumulation factor for trophic level 3
BAF_4	Aquatic life bioaccumulation factor for trophic level 4
BCF	Bioconcentration factor
BCF_{IHg}	Total mercury concentration in fish divided by that in water following a waterborne exposure to inorganic mercury
BCF_{MHg}	Total mercury concentration in fish divided by that in water following a waterborne exposure to methylmercury
BSAF	Biota-sediment accumulation factor
BMF	Biomagnification factor
bw	Body weight
CAA	Clean Air Act as Amended in 1990
CAP	Chlor-alkali plant
CMWI	Continuous medical waste incinerator
COMPDEP	Short range air dispersion model for mercury
d	Day
DDE	p,p-Dichlorodiphenyldichloroethylene
DDT	4,4-Dichlorodiphenyltrichloroethane
F_A	Average daily amount of food consumed
FCM	Food chain multiplier
FD_3	Fraction of the diet derived from trophic level 3
FD_4	Fraction of the diet derived from trophic level 4
FDER	Florida Department of Environmental Regulation
GLWQI	Great Lakes Water Quality Initiative
GM	Geometric mean
GSD	Geometric standard deviation
ha	Hectare
Hg^0	Elemental mercury
Hg_2^{2+}	Mercurous ion
Hg^{2+}	Mercury II
$HgBAF_3$	Total mercury in forage fish (trophic level 3) divided by that in water accumulated by all possible routes of exposure
$HgBAF_4$	Total mercury in piscivorous fish (trophic level 4) divided by that in water accumulated by all possible routes of exposure
IEM2	Indirect exposure methodology
IJC	International Joint Commission
IMWI	Intermittent medical waste incinerator
kg	Kilogram
L	Liter
LC_{50}	Lethal concentration (for fifty percent of population)
LCUB	Large coal-fired utility boiler
LMWC	Large municipal waste combustor
LOAEL	Lowest-observed-adverse-effect level
MCUB	Medium coal-fired utility boiler
MCM	Mercury cycling model

LIST OF SYMBOLS, UNITS AND ACRONYMS (continued)

$MeHg_T$	Percent of total mercury in fish tissues existing as the methylated form
$MeHg_W$	Percent of total mercury in water existing as the methylated form
MDNR	Michigan Department of Natural Resources
m	Meter
m^3	Cubic meter
mg	Milligram
MOUB	Medium oil-fired utility boiler
ng	Nanogram
nM	Nanomole
NOAEL	No-observed-adverse-effect level
PCBs	Polychlorinated biphenyls
PCS	Primary copper smelter
pctl	Percentile
pg	Picogram
pH	Logarithm of the reciprocal of the hydrogen ion concentration. A measure of acidity
PLS	Primary lead smelter
PPF	Predator-prey factor
PPF_4	The observed ratio of total mercury concentration at trophic level 4, divided by methylmercury concentrations at trophic level 3
RELMAP	Regional Lagrangian Model of Air Pollution
SAB	Science Advisory Board
SCUB	Small coal-fired utility boiler
SMWC	Small municipal waste combustor
sp.	Species
TL_3	Trophic level 3
TL_3	Trophic level 4
UF_A	Uncertainty factor for species extrapolation
UF_S	Uncertainty factor for use of less than lifetime study
UF_L	Uncertainty factor for use of a lowest adverse effect level
U.S. EPA	U.S. Environmental Protection Agency
µg	Microgram
µM	Micromole
W_A	Average daily volume of water consumed
WC	Wildlife criterion level
WC_f	Final wildlife criterion level
WC_i	Intermediate wildlife criterion level
WC_s	Species-specific wildlife criterion level
WHO	World Health Organization
Wt_A	Average species weight

EXECUTIVE SUMMARY

Section 112(n)(1)(B) of the Clean Air Act (CAA), as amended in 1990, directs the U.S. Environmental Protection Agency (U.S. EPA) to submit to Congress a comprehensive study on emissions of mercury to the air. Volume V, which addresses the ecological exposure and effects assessment for mercury and mercury compounds, is part of a seven-volume report developed by U.S. EPA in response to this directive.

Volume V comprises an ecological assessment for anthropogenic mercury emissions. It follows the format of the U.S. EPA Framework for Ecological Risk Assessment (U.S. EPA 1992a). The first step in the Framework is the problem formulation phase, wherein the potential ecological impacts of mercury are reviewed. This is followed by the presentation of a conceptual model describing how airborne mercury accumulates in aquatic biota, biomagnifies in aquatic food chains and is consumed by wildlife that eat contaminated fish. Subsequent steps in the assessment include an exposure assessment and finally the calculation of criteria for the protection of piscivorous avian and mammalian wildlife.

Scope of the Assessment

The scope of this assessment was limited solely to anthropogenic mercury that is emitted directly to the atmosphere. The origins and extent of these emissions are reviewed in Volume II of this Report. This analysis did not address mercury originating from direct wastewater discharge to water bodies, mining waste or the application of mercurial pesticides. In a number of instances, these and other "point" sources have been related to unacceptably high mercury levels in fish, triggering site-specific fish consumption advisories. Clearly, where such point sources exist, there is a need to address the combined impacts of mercury originating from all sources, including air emissions.

Mercury in the Environment

Wet deposition is thought to be the primary mechanism by which mercury emitted to the atmosphere is transported to surface waters and land, although dry deposition may also contribute substantially. Once deposited, mercury enters aquatic and terrestrial food chains. Mercury concentrations increase at successively higher trophic levels, as a result of bioconcentration (in prey organisms), bioaccumulation and biomagnification. Of the various forms of mercury in the environment, methylmercury has the highest potential for bioaccumulation and biomagnification. Predators at the top of these food chains are potentially at risk from consumption of mercury in contaminated prey. Based on the review of available information, it was concluded that piscivorous (fish-eating) birds and mammals are particularly at risk from airborne mercury emissions. This risk is likely to be greatest in areas that receive high levels of mercury deposition or, because of a strong negative correlation between surface water pH and mercury residues in fish, in regions that contain poorly buffered surface waters.

The assessment endpoint for this ecological assessment is identified as the maintenance of self-sustaining wildlife populations. Measurement endpoints include the growth and survival of individual animals, and reproductive success.

Exposure of Piscivorous Wildlife to Mercury

Exposure was characterized in a progressive manner, with varying reliance on computer models for mercury deposition and fate. The objective of this analysis was to characterize the extent to which piscivorous wildlife are exposed to mercury originating from airborne emissions. Details on exposure assessment inputs, methods and results can be found in Volume III of this Report to Congress. Four general approaches were used, which are described as follows.

1. Estimation of current average exposure to piscivorous wildlife on a nationwide basis.

The first analysis was conducted without computer models. Estimates of current mercury exposure to selected piscivorous wildlife species were calculated as the product of the fish consumption rate and measured mercury concentrations in fish. This analysis was not intended to be a site-specific analysis, but rather to provide national exposure estimates for piscivorous wildlife. This analysis used mean total mercury measurements from a nationwide study of fish residues and published fish consumption data for the selected wildlife species. The relative ranking of exposure in μg/kg bw/d of selected wildlife species was as follows: kingfisher > river otter > osprey = mink ≥ bald eagle.

2. Estimation of mercury levels in fish using measured deposition values and an indirect exposure methodology.

In the second analysis, measured mercury deposition rates were used as inputs to an indirect exposure methodology (IEM2) to estimate mercury concentrations in water, soil and fish. Additional inputs to the IEM2 model include the characteristics of a hypothetical lake and its associated watershed. The analysis was conducted for two such hypothetical lakes, one located in the Western U.S., the other located in the Eastern U.S. Residue values were calculated as the product of predicted mercury concentrations in water and estimated bioaccumulation factor (BAF) values for fish in trophic levels 3 and 4. (An explanation of trophic levels and the assumptions used in this analysis are described in Chapter 4 and Appendix of this volume.) Mercury levels in fish estimated in this manner, summarized in Table ES-1 below, were consistent with measured values from field studies.

Table ES-1
Percentiles of Predicted Methylmercury Concentrations in Fish (μg/g) Based on a Total Mercury Dissolved Water Concentration of 0.7 ng/L

Parameter	Geometric Mean	Percentile of Distribution				
		5th	25th	50th	75th	95th
Trophic 3 BAF	67,000	6,400	25,400	66,200	172,400	684,000
Predicted Fish Concentration (μg/g)	0.05	0.00	0.02	0.05	0.12	0.48
Trophic 4 BAF	335,000	22,700	111,000	336,000	1,000,000	4,700,000
Predicted Fish Concentration (μg/g)	0.23	0.02	0.08	0.24	0.70	3.30

3. Estimation of mercury deposition on a regional scale (40 km grid), and a comparison of these deposition data with species distribution information.

The third type of analysis was carried out on a national scale. A long-range atmospheric transport model (RELMAP) was used in conjunction with the mercury emissions inventory to generate predictions of mercury deposition across the continental U.S. Ecosystems subject to high levels of mercury deposition (e.g., near sources of mercury emissions, in areas with high deposition rates) will be more exposed to mercury than ecosystems with lower levels of mercury deposition. The pattern of mercury deposition nationwide, therefore, will influence which ecoregions and ecosystems might be exposed to hazardous levels of mercury. Thus, predictions of mercury deposition were compared with the locations of major lakes and rivers, national resource lands, threatened and endangered plant species and the distributions of selected piscivorous wildlife species. Additionally, mercury deposition data were superimposed onto a map of surface waters impacted by acid deposition, because it has been shown that low pH values are positively correlated with high levels of mercury in fish. Areas receiving high levels of deposition that also contain large numbers of poorly buffered lakes were designated "regions of concern" (see Figure ES-1). The extent of overlap of selected species distributions with these "regions of concern" was characterized.

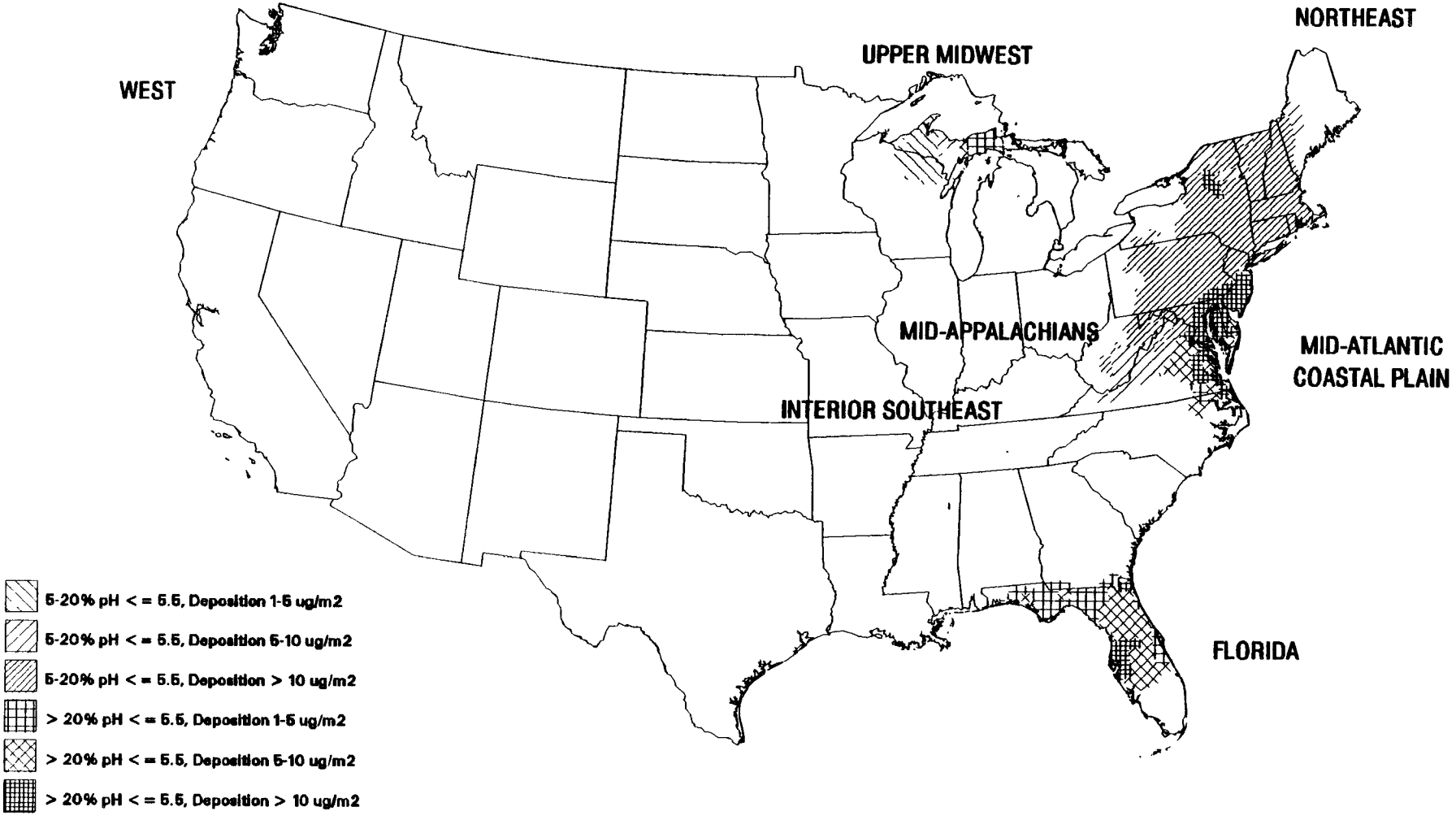
In the case of plant life, analysis was limited to plotting the location of federally threatened or endangered species and indicating where threatened populations coincide with estimated high mercury deposition. Large concentrations of endangered plant populations exposed to high levels of deposition occur in central and southern Florida, along the northeastern coastal region and scattered throughout the Midwest. Mercury has been demonstrated to have adverse impacts on a number of plant species.

Avian wildlife considered in this analysis included piscivorous species with habitats that are widely distributed (kingfishers) and narrowly distributed (bald eagles), as well as birds whose range fell within areas of high mercury deposition (ospreys and common loons). All the birds selected were piscivores that feed at or near the top of aquatic food chains and are therefore at risk from biomagnified mercury. Two of the mammals selected for this analysis (mink and river otters) are piscivorous and widely distributed. The other mammal selected, the Florida panther, is not widely distributed but is listed as an endangered species. The Florida panther lives in an environment known to be contaminated with mercury and preys upon small mammals (such as raccoons) which may contain high tissue burdens of mercury. Results for each avian and mammalian species are summarized in Table ES-2.

Table ES-2
Percent of Species Range Overlapping with Regions of Concern

Species	Percent of Range Impacted
Kingfisher	8%
Bald Eagle	17%
Osprey	13%
Common Loon	23%
Florida Panther	<1%
Mink	9%
River Otter	14%

Figure ES-1
Surface Water and pH ≤ 5.5 and Anthropogenic Mercury Deposition



Approximately 8% of the kingfisher's range occurs within regions of concern. Given this small degree of overlap, mercury does not appear to be a threat to the species nationwide.

Although a recovery in the population of bald eagles in some areas has resulted in a status upgrade from "endangered" to "threatened" in five states (Michigan, Minnesota, Oregon, Washington and Wisconsin) bald eagle populations are still depleted throughout much of their range. Bald eagles can be found seasonally in large numbers in several geographic locations, but most of these individuals are transient, and the overall population is still small. Historically, eagle populations in the U.S. have been adversely impacted by the effects of bioaccumulative contaminants (primarily DDT and perhaps PCBs). Approximately 17% of the bald eagle's range overlaps mercury regions of concern. The risk to eagles posed by mercury appears to be greatest in the Great Lakes region, the northeastern Atlantic states and south Florida.

Nationwide, approximately 13% of the osprey's total range overlaps regions of concern; however, a much larger fraction of the osprey's eastern population occurs within these regions. The osprey diet consists almost exclusively of fish, and they are known to take dead fish from the water surface if the fish are fresh. Their position at the top of the aquatic food chain places ospreys at risk from toxins that bioaccumulate. Osprey populations underwent severe declines during the 1950s through the 1970s; these declines have been linked to exposure to DDT.

Nearly 23% of the loon's range is located in regions of concern (see Figure ES-2). Moreover, nearly all of the loon's range occurs in regions where mercury deposition is predicted. Limited data from the study of mercury point sources showed that loon reproductive success was negatively correlated with exposure to mercury in a significant dose-response relationship. Residue data, combined with field observations, suggest that loon populations in areas of Minnesota and Wisconsin may be adversely impacted by mercury originating from airborne deposition.

The Florida panther, an endangered species, lives in an environment known to be contaminated with mercury and preys upon small mammals (such as raccoons) that may contain high tissue burdens of mercury. Although the panther's range falls outside of identified regions of concern (<1%), the species habitat is contiguous with this region (see Figure ES-3). Measured mercury levels found in Florida panther tissue have approached levels that are frankly toxic in other feline species.

Approximately 9% of the range of mink habitat coincides with regions of concern nationwide. Mink occupy a large geographic area and are common throughout the U.S. In general, mink prey on small mammals for most of the year; however, some populations prey primarily on fish and aquatic birds. Mink that prey on aquatic animals are most at risk from mercury contamination. In addition small predators may be at greater risk than large predators due to higher food consumption rate per unit of body weight.

River otter habitats overlap regions of concern for about 14% of the range for this species nationwide. River otters occupy large areas of the U.S., but their population numbers are thought to be declining in the Midwestern states. The river otter's diet is almost exclusively of aquatic origins and includes fish (primarily), crayfish, amphibians and aquatic insects. The species of fish taken depends on the fish's ability to escape capture. The consumption of large, piscivorous fish puts the river otter at risk from bioaccumulative contaminants such as mercury.

Figure ES-2
Common Loon Range, Surface Water with pH ≤ 5.5, and Anthropogenic Mercury Deposition

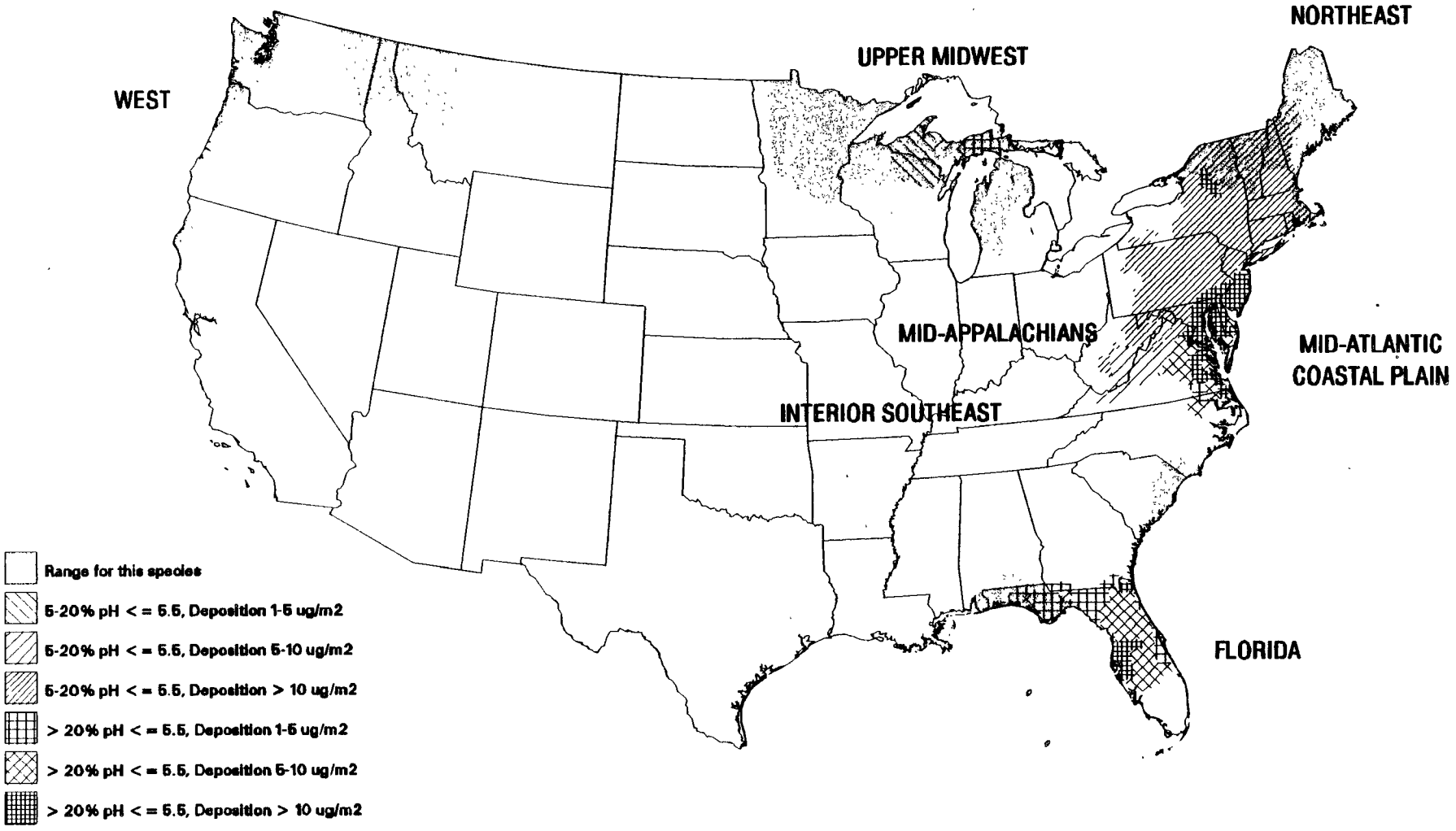
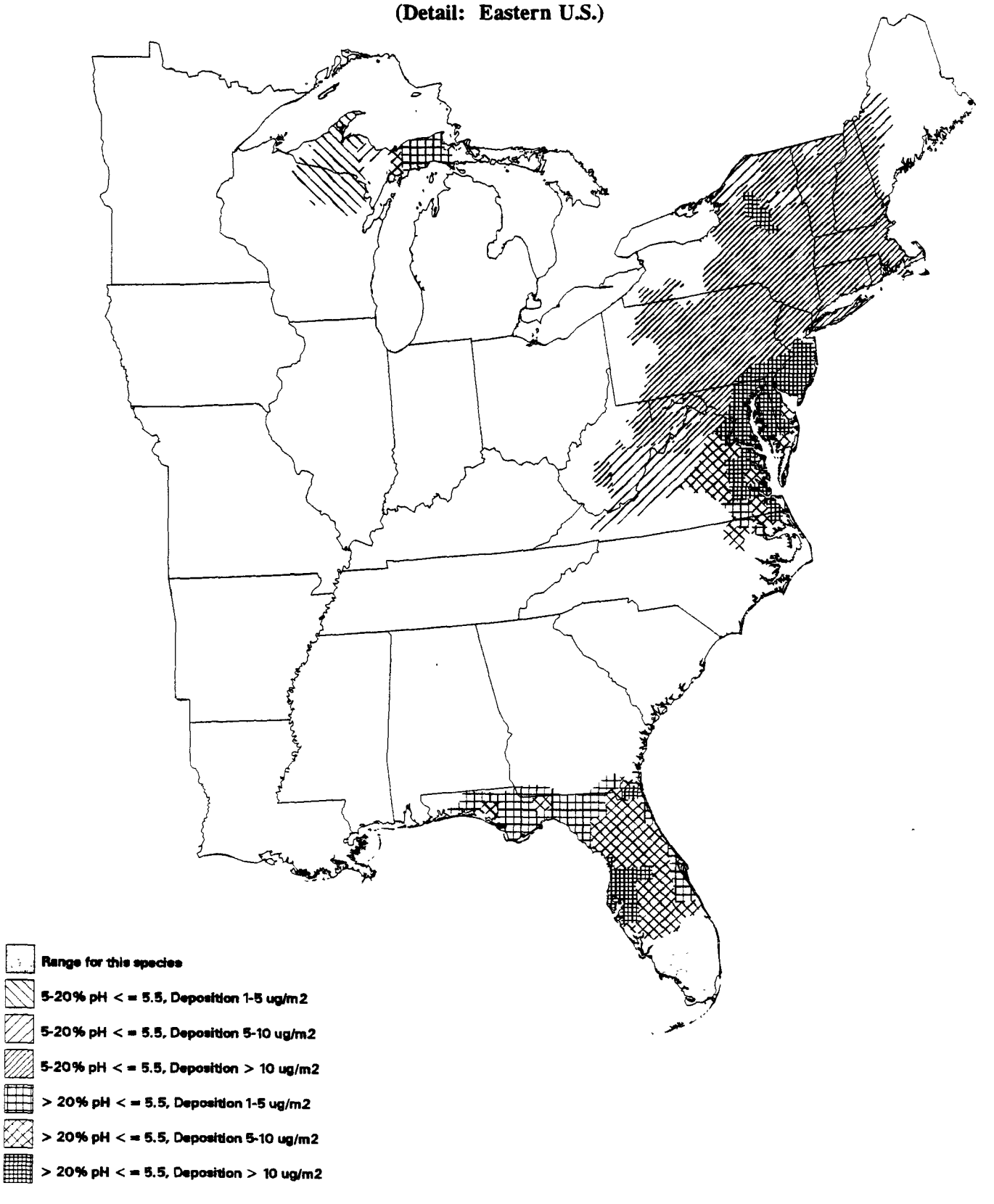


Figure ES-3
Florida Panther Range, Surface Water with pH $\leq$ 5.5,
and Anthropogenic Mercury Deposition
(Detail: Eastern U.S.)



Otter population declines do not overlap to a large extent with regions of concern; however, the area of decline does coincide with RELMAP predictions of high mercury deposition rate.

4. Estimation of mercury deposition on a local scale in areas near emissions point sources.

A final analysis was conducted using a local-scale air dispersion model (COMPDEP), in addition to the long-range transport data and the indirect exposure methodology, to predict mercury concentrations in water and fish under a variety of hypothetical emissions scenarios. COMPDEP simulated mercury deposition originating from model plants representing a range of mercury emissions source classes. The six source categories were selected based on their estimated annual mercury emissions or their potential to be localized point sources of concern. The categories selected were these: municipal waste combustors (MWCs), medical waste incinerators (MWIs), utility boilers, chlor-alkali plants, primary copper smelters and primary lead smelters.

The analysis was conducted for two hypothetical lakes located in the Western and Eastern U.S. The proximity of these lakes to the source was varied to examine the effect of this parameter on model predictions. To account for the long range transport of emitted mercury, the 50th percentile RELMAP atmospheric concentrations and deposition rates were included in the estimates from the local air dispersion model.

These data were used to rank the relative contributions of different emission source types and the exposure of selected wildlife species. It was concluded from this analysis that local emissions sources have the potential to increase significantly the exposure of piscivorous birds and mammals to mercury. The extent of this local contribution depends in turn upon watershed characteristics, facility type, local meteorology, and terrain. The exposure of a given wildlife species is also highly dependent upon the fish bioaccumulation factor, the trophic level(s) at which it feeds and the amount of fish consumed per day.

Effects Assessment for Mercury

Due to the broad range and extent of mercury emissions throughout the United States, many potential ecological effects could have been considered. Neither the available data nor existing methodology supported evaluation of all possible risks.

The ecosystem effects of mercury are incompletely understood. No applicable studies of the effects of mercury on intact ecosystems were found. Characterization of risk for non-human species, thus, did not attempt to quantify effects of mercury on ecosystems, on plant and animal communities or on species diversity. Direct effects of methylmercury on fish and other aquatic biota were not estimated, although there is evidence of adverse impacts on these organisms following point source releases of mercury and in aquatic environments affected by urban runoff.

Data on methylmercury effects suitable for dose-response assessment are limited to what are termed "individual effects" in the U.S. EPA Framework for Ecological Risk Assessment. In general, selections of wildlife species for dose-response assessment were based on the following factors: (1) exposure to bioaccumulative contaminants; (2) relevance to establishing species of concern on a national basis; (3) availability of information with which to calculate criterion values; and (4) evidence for bioaccumulation and/or adverse effects. The species selected were piscivorous birds and mammals. Avian species were the bald eagle (*Haliaeetus leucocephalus*), the osprey (*Pandion haliaetus*) and the belted kingfisher (*Ceryle alcyon*). Mammalian species were the mink (*Mustela vison*) and the river otter (*Lutra canadensis*).

The goal of this assessment was to calculate a water-based wildlife criterion (WC) value that, if not exceeded, would be protective of piscivorous avian and mammalian wildlife. Because this assessment (and the local-scale exposure assessment) depends to a large extent on the assignment of BAFs for mercury in fish at trophic levels 3 and 4, an effort was made to review published field data from which these BAFs could be estimated. A Monte Carlo analysis was then performed to characterize the variability around these estimates.

A WC for mercury was estimated as the ratio of a no-adverse-effect dosing level (NOAEL; in µg/d) to an estimated exposure level (L/d), referenced to a water concentration using a BAF. Individual wildlife criteria are provided in Table ES-3. This approach is similar to that used in non-cancer human health risk assessment and was employed previously to estimate a WC for mercury in the Water Quality Guidance for the Great Lakes System. Species-specific WC values for mercury were estimated for selected avian and mammalian wildlife. A final mammalian WC was then calculated as the lowest mean of WC values for each of the two taxonomic classes (birds and mammals). The final WC for mercury was based on individual WC values calculated for the river otter and mink, and was estimated to be 346 picograms (ng) total mercury/L water. The WC was calculated based on a NOAEL for nervous system damage in mink fed mercury in fish or chow. The avian WC was based on the lowest adverse effect level for behavioral and reproductive effects in three generations of mallard ducks fed mercury in grain. Existing data were not sufficient to calculate a WC for the Florida panther; however, a NOAEL based on laboratory data from domestic cats was identified as 20 µg methylmercury/kg bw/d.

The evaluation of data and calculation of WC in this Report was done in accordance with the methods and assessments published in the Final Water Quality Guidance for the Great Lakes System: Final Rule (U.S. EPA 1995). Availability of additional data led to differences in calculated values of the WC in this Report and those published in the final rule. Differences were the result of three factors. The Report uses more recent data to derive BAF. Second, the final rule appropriately used some region-specific assumptions that were not used in the nationwide assessment in the Report, for example, consumption of herring gulls by eagles. Finally different endpoints were used for the evaluation of mammals because the purposes of the assessments in the Report and final rule were different. In the final rule, a risk-management decision was made to base the wildlife criterion on endpoints likely to influence whole populations (mortality, growth). In this Report a more sensitive endpoint was selected with the goal of assessing the full range of effects of mercury. The difference in the results reflects the amount of discretion allowed under Agency Risk Assessment Guidelines.

Table ES-3
Wildlife Criteria for Mercury

Organism	Wildlife Criterion (pg/L)
Mink	415
River otter	278
Kingfisher	193
Osprey	483
Bald eagle	538

Of the pathways by which ecosystems and components of ecosystems might be exposed to atmospheric mercury, exposure of high trophic level wildlife to mercury in food is particularly important. The trophic level and feeding habits of an animal influence the degree to which that species is exposed to mercury. Mercury biomagnifies in aquatic food chains, with the result that mercury concentrations in tissue increase as trophic levels increase. Predatory animals primarily associated with aquatic food chains accumulate more mercury than those associated with terrestrial food chains. Thus, piscivores and their predators generally have the highest exposure to mercury. Species with high tissue levels of mercury include otter and mink, which are top mammalian predators of aquatic food chains. Top avian predators of aquatic-based food chains include raptors such as the osprey and bald eagle.

Although clear causal links have not been established, mercury originating from airborne deposition may be a contributing factor to population effects on bald eagles, river otters and mink. Stronger evidence is available to support the possibility of toxic effects on the common loon and the Florida panther. Effects of mercury originating from point sources on restricted wildlife populations have been conclusively demonstrated and provide a tissue residue basis for evaluation of risk to other populations.

Information presented in Volume V of this Report suggests that the ecosystems most at risk from mercury releases to air exhibit one or more of the following characteristics:

- They are located in areas where exposure to mercury (e.g., atmospheric deposition of mercury) is high;
- They include surface waters already impacted by acid deposition;
- They possess characteristics other than low pH that result in high levels of bioaccumulation; and/or
- They include sensitive species.

Conclusions

The following conclusions are presented in approximate order of degree of certainty in the conclusion, based on the quality of the underlying database. The conclusions progress from those with greater certainty to those with lesser certainty.

- Inorganic mercury emitted to the atmosphere deposits on watersheds and is translocated to waterbodies. A variable proportion of this mercury is transformed by abiotic and biotic chemical reactions to organic derivatives, including methylmercury. Methylmercury bioaccumulates in individual organisms, biomagnifies in aquatic food chains and is also the most toxic form of mercury to which wildlife are exposed.
- The proportion of total mercury in biota that exists as methylmercury tends to increase with trophic level. Greater than 90% of the mercury contained in freshwater fish exists as methylmercury. Methylmercury accumulates in fish throughout their lifetime, although changes in concentration as a function of time may be complicated by growth dilution and changing dietary habits.

- Piscivorous avian and mammalian wildlife are exposed to mercury primarily through consumption of contaminated fish and accumulate mercury to levels above those in prey items.

- Toxic effects on piscivorous avian and mammalian wildlife due to consumption of contaminated fish have been observed in association with point source releases of mercury to the environment.

- Concentrations of mercury in the tissues of wildlife species have been reported at levels associated with adverse health effects in laboratory studies in the same species.

- Piscivorous birds and mammals receive a greater exposure to mercury than any other known component of aquatic ecosystems.

- Field data are highly suggestive of adverse toxicological effects in common loons due to accumulation of mercury originating from airborne emissions. Field data are also suggestive of adverse toxicological effects in the Florida panther due to mercury; however, this mercury may have originated from both airborne and non-airborne sources. Field data suggest that bald eagles have not suffered adverse toxic effects due to airborne mercury emissions. Field data are insufficient to conclude whether the mink, river otter, or kingfisher have suffered adverse toxic effects due to airborne mercury emissions.

- BAFs for mercury in fish vary widely; however, field data are sufficient to calculate representative means for different trophic levels. The recommended estimates in this Report for BAFs for topic levels 3 and 4 are 66,200 and 335,000, respectively. In general, BAFs for fish sampled from poorly buffered surface waters are higher than those for fish obtained from well buffered surface waters.

- Based upon knowledge of mercury bioaccumulation in fish, and of feeding rates and the identity of prey items consumed by piscivorous wildlife, it is possible to rank the relative exposure of different piscivorous wildlife species. Of the five wildlife species selected for detailed analysis, the relative ranking of exposure to mercury is this: kingfisher > river otter > osprey = mink $\geq$ bald eagle. Existing data are insufficient to estimate the exposure of the Florida panther relative to that of the selected species.

- Local emissions sources (<50 km from receptors) have the potential to increase the exposure of piscivorous wildlife well above that due to remote sources (background).

- Based upon knowledge of mercury exposure to wildlife and its toxicity in long-term feeding studies, criterion values can be calculated for the protection of piscivorous avian and mammalian wildlife. A wildlife criterion value is defined as the concentration of total mercury in water that, if not exceeded, protects avian and mammalian wildlife populations from adverse effects resulting from ingestion of surface waters and from ingestion of aquatic life taken from these surface waters.

- The criterion value protective of piscivorous avian wildlife is 405 pg/L.

- The criterion value protective of piscivorous mammalian wildlife is 346 pg/L.

- Modeled estimates of mercury concentration in fish around hypothetical mercury emissions sources predict exposures at the wildlife WC. The wildlife WC, like the human RfD, is predicted to be a safe dose over a lifetime. It should be noted, however, that the wildlife effects used as the basis for the WC are gross clinical manifestations or death. Expression of subtle adverse effects at these doses cannot be excluded.

There are many uncertainties associated with this analysis, due to an incomplete understanding of the toxicity of mercury and mercury compounds. The sources of uncertainty include the following:

- Variability in the calculated BAFs is a source of uncertainty. BAFs given in this Report relate total mercury in fish (most of which exists as methylmercury) to total mercury in the water column. Methylmercury is the bioaccumulating species of mercury, but existing data are insufficient to estimate BAFs on a methylmercury basis. Methods for the speciation of mercury in environmental samples are rapidly improving but remain difficult to perform. Questions also remain concerning the bioavailability of methylmercury associated with particulate and dissolved organic material. Local biogeochemical factors that determine net methylation rates are not fully understood and are not amenable at this time to generalized modeling.

- The representativeness of field data used in establishing the BAFs is a source of uncertainty. The degree to which the analysis is skewed by the existing data set is unknown. A disproportionate amount of data is from north-central and northeastern lakes. The applicability of these data to a national assessment is not known.

- Limitations of the toxicity database present a source of uncertainty. Few controlled studies of quantifiable effects of mercury exposure in wildlife are available. These are limited to few species, necessitating the use of uncertainty factors in extrapolating to species of interest. The toxic endpoints reported in existing studies can be considered severe, raising questions as to the degree of protection against subtle effects offered by reference doses and water criteria calculated on those endpoints. Use of less than lifetime studies for prediction of effects from lifetime exposure is a source of uncertainty.

- Concern has been raised regarding the possibility of toxic effects in species other than those piscivorous birds and mammals evaluated in this Report. In particular there is considerable uncertainty about mercury effects in biota at trophic levels 1 and 2 in aquatic ecosystems and about effects in terrestrial systems.

- Lack of knowledge of wildlife feeding habits is a source of uncertainty. Existing information frequently is anecdotal or confined to evaluations of a particular locality; the extent to which this information is generalizable is open to question. In some instances wherein feeding habits are relatively well characterized (e.g., Florida panther), the extent of mercury contamination of prey is poorly known (e.g., in raccoons).

- While the methods used to develop wildlife criteria are based on effects in individual organisms, the stated goal of the assessment is to characterize the potential for adverse effects in wildlife populations. Factors that contribute to uncertainty in population-

based assessments include these: variability in the relationship between individuals and populations; variability in fecundity; lack of data on carrying capacity; and relationships of one population, of the same or different species, to another population.

- A focus on populations may not always be appropriate. This could be true for endangered species, which may be highly dependent for the survival of the species on the health of a few individuals. This may also be true for some regional or local populations of widespread species; the local population may be "endangered" and thus dependent on the survival of individuals.

To improve the ecological risk assessment for mercury and mercury compounds, U.S. EPA would need the following:

- Mechanistic research is needed for better understanding of variability of mercury effects. This would include studies on the following: factors determining rates of methylation and demethylation; dietary absorption efficiencies from natural food sources; effects of dietary choice; and bioavailability of methylmercury in the presence of dissolved organic material and other material that could bind mercury.

- Data are needed for better definition of adverse effects on the species that were evaluated in this Report. Information is also lacking on species at trophic levels 1 and 2.

- Efforts to develop and standardize methods for analysis of total mercury and methylmercury in environmental samples (including animal and plant tissue) remain important.

- The current wildlife criteria are based on linear, four-tiered food chains. Research on the appropriateness of this design and information that will improve the model are important.

- Research is needed to reduce uncertainty regarding the accumulation of mercury at lower trophic levels.

- High quality field data will be useful to support the process-based research described above, as well as to determine residue concentrations in fish and other aquatic biota consumed by wildlife.

- There is a need to collect additional natural history data for macroinvetebrates and amphibians. Seasonal and spatial effects on predation should be explored and described.

Based on the extant data and knowledge of developing studies the U.S. EPA predicts the following:

- "Regions of concern" are defined as those geographic areas in the contiguous U.S. that are thought to receive high levels of mercury deposition and that contain relatively large numbers (>5% below pH 5.5) of poorly buffered surface waters. The designation of an area as a region of concern implies an increased risk of mercury toxicity to

wildlife. This designation could be used to define critical habitat, identify wildlife populations potentially at risk and provide a focus for future research.

- Increased deposition will lead to increased levels in fish.
- Increased levels in fish will lead to toxicity in piscivorous birds and mammals.
- These impacts are most likely to occur in areas that receive high levels of deposition and that also contain poorly buffered surface waters.

1. INTRODUCTION

Section 112(n)(1)(B) of the Clean Air Act (CAA), as amended in 1990, requires the U.S. Environmental Protection Agency (U.S. EPA) to submit a study on atmospheric mercury emissions to Congress. The sources of emissions that must be studied include electric utility steam generating units, municipal waste combustion units and other sources, including area sources. Congress directed that the Mercury Study evaluate the rate and mass of mercury emissions, health and environmental effects, technologies to control such emissions and the costs of such controls.

In response to this mandate, U.S. EPA has prepared a seven-volume Mercury Study Report to Congress. The seven volumes are as follows:

I. Executive Summary
II. An Inventory of Anthropogenic Mercury Emissions in the United States
III. An Assessment of Exposure from Anthropogenic Mercury Emissions in the United States
IV. Health Effects of Mercury and Mercury Compounds
V. An Ecological Assessment for Anthropogenic Mercury Emissions in the United States
VI. Characterization of Human Health and Wildlife Risks from Anthropogenic Mercury Emissions in the United States
VII. An Evaluation of Mercury Control Technologies and Costs

This volume (Volume V) comprises an ecological assessment for airborne mercury emissions. It provides an overview of the ecological effects of mercury, uses modeling predictions from Volume III (Exposure Assessment) on airborne mercury concentrations and deposition rates to assess potential ecological exposures, and reviews available toxicity and bioaccumulation data for the purpose of developing a criterion for the protection of sensitive wildlife species.

Volume V is composed of three main sections, organized by a format provided by U.S. EPA's Framework for Ecological Risk Assessment (U.S. EPA, 1992a). Chapter 2 corresponds to the problem formulation phase of the assessment and reviews the potential ecological impacts of mercury. Based upon this information it is concluded that piscivorous avian and mammalian wildlife are potentially at risk due to airborne mercury emissions. A conceptual model is presented to describe how airborne mercury becomes concentrated in aquatic biota which serve in turn as the primary food source for piscivorous wildlife. An exposure analysis is conducted in Chapter 3. Effects are analyzed in Chapter 4, culminating in calculation of a criterion value for protection of piscivorous wildlife. Chapter 5 discusses further research needs. References are provided at the end of the volume. An ecological risk characterization for mercury is developed separately in Volume VI of this Report.

The scope of this assessment is limited to consideration of only that mercury which is emitted directly to the atmosphere. The origins and extent of these emissions are reviewed in Volume II of this Report. This analysis does not address mercury originating from mine leachate, the manufacturing and disposal of batteries, dental amalgam (in municipal wastewater), or the application of mercurial pesticides. In a number of instances, these and other "point" sources have been related to unacceptably high mercury levels in fish, triggering site-specific fish consumption advisories. Clearly, where such point sources exist, there is a need to address the combined impacts of mercury originating from all sources, including air emissions.

The exposure analysis for piscivorous wildlife was designed to address the following questions.

- What is the current degree of exposure of piscivorous avian and mammalian wildlife?
- In what broad geographical areas of the continental United States is there a high probability for co-occurrence of high mercury deposition rates and wildlife species of concern?
- What is the relative increase in exposure that can be anticipated for wildlife species that live in proximity to mercury emissions sources?
- What is the relative ranking of source categories with regard to their contribution to mercury concentrations in fish consumed by piscivorous wildlife?

The first of these questions was addressed by defining in detail what piscivorous wildlife eat and then characterizing the mercury content of these food items. The second question was addressed by superimposing the results of a long-range transport analysis onto wildlife distribution information. The last two questions were addressed by using the results of a local-scale air dispersion model, combined with an indirect exposure methodology, to generate hypothetical exposure scenarios for wildlife. This short-range analysis is analogous to that used in the human health exposure assessment (Volume III). Descriptions of the long- and short-range air dispersion models and the indirect exposure methodology are provided in Appendix D to Volume III.

The goal of the effects analysis was to calculate a water-based wildlife criterion value for mercury which, if not exceeded, would be protective of piscivorous avian and mammalian wildlife. An effort was then made to calculate fish residue concentrations corresponding to this criterion value. These residue values are compared in Volume VI with measured values obtained from environmental sampling efforts.

Owing to its importance for both the ecological and human health assessments, an effort was made to re-evaluate and calculate bioaccumulation factors (BAFs) for mercury in fish and to characterize the uncertainties associated with this estimate. The data and methods used to derive these BAFs are presented in a separate Appendix (Appendix A). A summary of this material is provided in Section 4.1 as an input to the wildlife criterion development effort.

2. PROBLEM FORMULATION

U.S. EPA defines ecological risk assessment as "a process that evaluates the likelihood that adverse ecological effects may occur or are occurring as a result of exposure to one or more stressors" (U.S. EPA, 1992a). A "stressor" is defined as any chemical, biological, or physical entity that causes adverse effects on ecological components, i.e., individuals, populations, communities, or ecosystems. Although ecological risk assessment follows the same basic risk paradigm as the human health risk assessment, there are three key differences between the two types.

- Ecological risk assessment can consider effects on populations, communities and ecosystems in addition to effects on individuals of a single species.
- No single set of ecological values to be protected is applicable in all cases; instead, they must be selected for each assessment based on both scientific and societal merit.
- Nonchemical stressors (e.g., physical disturbances) often need to be evaluated as well as chemical stressors.

The problem formulation phase of an environmental risk assessment consists of three main components: (1) characterizing the stressors, potential exposure pathways, ecosystems potentially at risk, and ecological effects; (2) selecting endpoints (the ecological values to be protected); and (3) developing a conceptual model of the problem (U.S. EPA, 1992a).

Section 2.1 reviews the characteristics of mercury in the environment, including its various chemical forms (speciation), chemical transformations and movement within and between the air, surface water, and soil compartments of the environment (cycling). Section 2.2 identifies the exposure pathways by which plants and animals can be exposed to mercury in both aquatic and terrestrial ecosystems. Section 2.3 provides an overview of what is known about the effects of mercury on organisms, populations, communities and ecosystems. Section 2.4 identifies ecosystems and ecosystem components that are thought to be most at risk from mercury in the environment. Section 2.5 describes the selection of assessment and measurement endpoints for the ecological risk assessment. A conceptual model of mercury fate and effects in the environment is presented in Section 2.6, setting the framework for the risk assessment that follows.

It should be noted that this review of mercury fate and effects is limited to consideration of only terrestrial and freshwater aquatic ecosystems. It is recognized that mercury that deposits in coastal areas can be translocated to estuarine environments, and that biota which inhabit these and nearby marine systems have the potential to be adversely impacted. Presently, however, uncertainties regarding mercury deposition, cycling, and effects in such environments are so great as to preclude even a qualitative risk assessment.

2.1 Stressor Characteristics: Mercury Speciation and Cycling

Mercury in the environment can occur in various physical and chemical forms. Physically, mercury may exist as a gas or liquid, or it may be associated with solid particulates. Chemically, mercury can exist in three oxidation states:

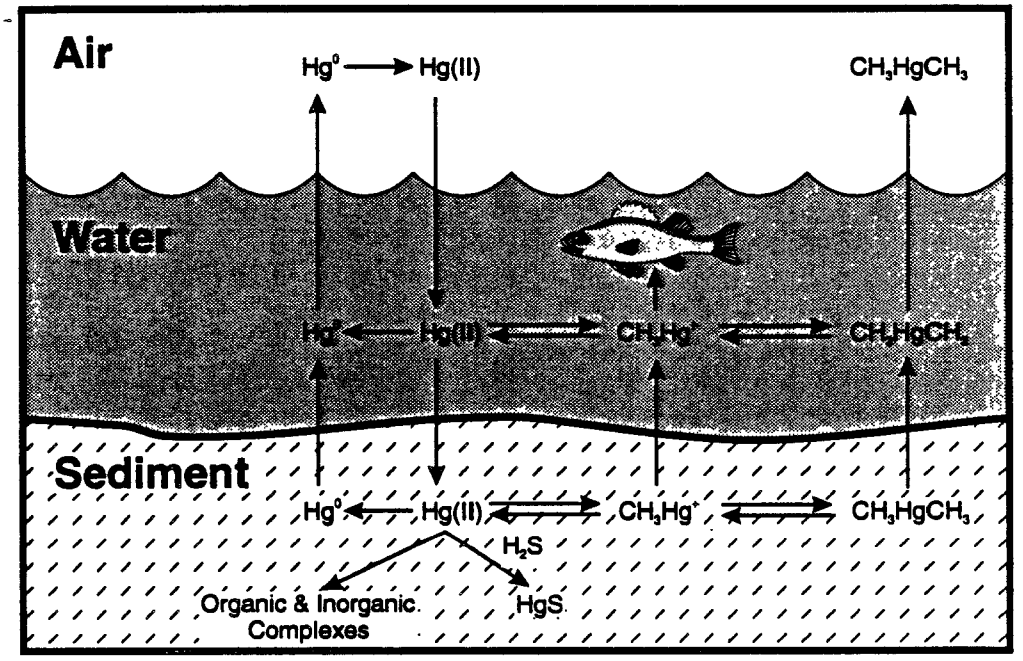
(1) Hg^0 – **elemental mercury**, also called metallic mercury;

(2) Hg_2^{2+} – **mercurous ion** (monovalent mercury, mercury I); or

(3) Hg^{2+} – **mercury II** (mercuric ion, divalent mercury).

Mercury also reacts with other chemicals to form inorganic compounds (e.g., $HgCl_2$ – mercuric chloride) and organic compounds (e.g., CH_3Hg^+ – monomethylmercury, $(CH_3)_2Hg$ – dimethylmercury, C_6H_5HgCl – phenyl mercuric chloride). Figure 2-1 illustrates the major transformations between these different forms in the environment. Dimethylmercury is highly volatile and dissociates to monomethylmercury at neutral or acid pH (pH < 8) (Huckabee et al., 1979). In contrast, monomethylmercury is stable and tends to accumulate in living organisms as described below (Bloom, 1992). Throughout this volume, monomethylmercury is referred to simply as methylmercury.

Figure 2-1
Cycling of Mercury in Freshwater Lakes (adapted from Winfrey and Rudd, 1990)



As discussed in the box below, methylation is an important step in the mercury cycle that strongly influences the ecological fate and effects of mercury. Methylmercury is readily accumulated by fish due, in part, to efficient uptake from dietary sources and to low rates of elimination (Bloom, 1992). It is also the most toxic form of mercury to wildlife (Eisler, 1987).

Mercury cycling and partitioning in the environment are complex phenomena which depend on numerous environmental parameters. The following sections provide a brief overview of mercury speciation and partitioning in the atmosphere, surface water and soil, including information from specific case studies. For a detailed review, see Volume III of this Report to Congress.

FOCUS ON METHYLMERCURY

Methylmercury is the form of mercury of particular concern in ecosystems for three reasons.

(1) All forms of mercury can be methylated by natural processes in the environment.
(2) Methylmercury bioaccumulates and biomagnifies in aquatic food webs at higher rates and to a greater extent than any other form of mercury.
(3) Methylmercury is the most toxic form of mercury.

All forms of mercury discharged into surface waters can be converted to methylmercury by natural processes. In the 1960s, researchers found methylmercury in fish in Swedish lakes, although no discharge of methylmercury had occurred in those lakes (Bakir et al., 1973). Later research determined that the methylation of mercury in sediments by anaerobic sulfur-reducing bacteria was a major source of methylmercury in many aquatic environments (Gilmour and Henry, 1991; Zillioux et al., 1993). Aerobic bacteria and fungi, including yeasts that grow best in acid conditions, also can methylate mercury (Eisler, 1987; Yannai et al., 1991). In addition, fulvic and humic material may abiotically methylate mercury (Nagase et al., 1984; Lee et al., 1985; Weber, 1993). The major site of methylation in aquatic systems is the sediment, but methylation also occurs in the water column (Wright and Hamilton, 1982; Xun et al., 1987; Parks et al., 1989; Bloom and Effler, 1990; Winfrey and Rudd, 1990; Bloom et al., 1991; Gilmour and Henry, 1991; Miskimmin et al., 1992). The rate of mercury methylation varies with microbial activity, mercury loadings, suspended sediment load, nutrient content, pH and redox conditions, temperature, and other variables. The net rate of mercury methylation in an ecosystem is determined by competing rates of methylation and demethylation.

Methylmercury bioaccumulates and biomagnifies in aquatic food webs at higher rates and to a greater extent than any other form of mercury (Watras and Bloom, 1992). "Bioaccumulation" refers to the net uptake of a contaminant from the environment into biological tissue via all pathways. It includes the accumulation that may occur by direct contact of skin or gills with mercury-contaminated water as well as ingestion of mercury-contaminated food. "Biomagnification" refers to the increase in chemical concentration in organisms at successively higher trophic levels in a food chain as a result of the ingestion of contaminated organisms at lower trophic levels. Methylmercury can comprise from 10 percent to over 90 percent of the total mercury in phytoplankton and zooplankton (trophic levels 1 and 2)(May et al., 1987; Watras and Bloom, 1992), but generally comprises over 90 percent of the total mercury in fish (trophic levels 3 and 4)(Huckabee et al., 1979; Grieb et al., 1990; Bloom, 1992; Watras and Bloom, 1992). Fish absorb methylmercury efficiently from dietary sources and store this material in organs and tissues. The biological half-life of methylmercury in fish is difficult to determine but is generally thought to range from months to years.

Methylmercury is the most hazardous form of mercury to birds, mammals, and aquatic organisms due to its high stability and strong affinity for sulfur-containing organic compounds (e.g., proteins). Biological membranes, including the blood-brain barrier and the placenta, that tend to discriminate against other forms of mercury allow relatively easy passage of methylmercury and dissolved mercury vapor (Eisler, 1987). Methylmercury can cause death, neurological disorders, organ damage, impaired immune response, impaired growth and development and reduced reproductive success (Klaassen, 1986). In mammals, fetuses are particularly sensitive to mercury, experiencing deleterious developmental effects when the mothers appear to be unaffected (Clarkson, 1990).

2.1.1 Mercury in Air

In the atmosphere, most mercury (95 to over 99 percent) exists as gaseous Hg^0; the remainder generally is comprised of gaseous methylmercury (~0 to 5 percent) and mercury associated with particulates (Lindqvist, 1991; MDNR, 1993). Gaseous Hg^{2+} also may exist in air, especially near mercury emissions sources. Mercury associated with particulates in air includes Hg^{2+}, thought to occur primarily as mercuric chloride (MDNR, 1993).

The form of mercury in air affects both the rate and mechanism by which it deposits to earth. Hg^{2+} and methylmercury are more likely to be deposited than Hg^{o} because they are more soluble and are scavenged by precipitation more easily. Methylmercury is also thought to be dry-deposited more effectively than Hg^{o}. As a result, although methylmercury and Hg^{2+} generally comprise less than five percent of mercury in the atmosphere, they are thought to comprise a higher proportion of deposited mercury (Lindqvist, 1991).

Wet deposition apparently is the primary mechanism for transporting mercury from the atmosphere to surface waters and land (Lindqvist, 1991). In the Great Lakes area, for example, wet deposition is believed to account for 60 to 70 percent of total mercury deposition. Hg^{2+} is the predominant form in precipitation (MDNR, 1993).

2.1.2 Mercury in Surface Water

Mercury can enter surface water as Hg^{o}, Hg^{2+}, or methylmercury. Once in aquatic systems, mercury can exist in dissolved or particulate forms, and can undergo the following transformations (See Figure 2-1) (Lindqvist et al., 1991; Winfrey and Rudd, 1990).

- Hg^{2+} in surface waters can be reduced to Hg^{o}.
- Volatile Hg^{o} in surface waters can be released to the atmosphere.
- Atmospheric Hg^{o} may be oxidized to form Hg^{2+}, and may be deposited/ redeposited to surface waters.
- Hg^{2+} can be methylated in sediments and the water column to form methylmercury.

Each of these reactions can also occur in the reverse direction. The net rate of production of each mercury species is determined by the balance between forward and reverse reactions.

Estimates of the percent of total mercury in surface waters that exists as methylmercury vary. Generally, methylmercury makes up less than 20 percent of the total mercury in the water column of lakes (Kudo et al., 1982; Parks et al., 1989; Bloom and Effler, 1990). In lakes without point discharges, methylmercury frequently comprises less than ten percent of the total mercury in the water column (Lee and Hultberg, 1990; Lindqvist, 1991; Porcella et al., 1991; Watras and Bloom, 1992).

Contaminated sediments can serve as an important mercury reservoir, with sediment-bound mercury recycling back into the aquatic ecosystem for decades or longer. Biological processes affect this recycling process. For example, bacterial activity affects the transformation of one mercury form to another (e.g., sulfate-reducing bacteria mediate mercury methylation) (Gilmour and Henry, 1991). Benthic invertebrates may take up mercury from sediments, making it available to other aquatic animals through the food chain, and to vertebrates that consume emergent aquatic insects (Hildebrand et al., 1980; Wren and Stephenson, 1991; Dukerschein et al., 1992; Saouter et al., 1993; Suchanek et al., 1993). Physical factors, such as reduced pH, stimulate methylmercury production at the sediment/water interface and thus may accelerate the rate of mercury methylation resulting in increased accumulation by aquatic organisms (Figure 2-1) (Winfrey and Rudd, 1990).

2.1.3 Mercury in Soil

Mercury deposited from the air forms stable complexes with soil particles of high organic or sulfur content and with humic and fulvic acids (Andersson, 1979; WHO, 1989; Johansson et al., 1991). These chemical bonds limit mercury's mobility in soils and its availability for uptake by living organisms. In general, the distribution of mercury in soil is likely to follow the distribution of organic matter. Mercury has a long retention time in soils. As a result, mercury that has accumulated in soils may continue to be released to surface waters for long periods of time, possibly hundreds of years (Johansson et al., 1991)

Hg^{2+} in soils can be transformed to other mercury species. Bacteria and organic substances can reduce Hg^{2+} to Hg^{0}, releasing volatile inorganic mercury to the atmosphere. Alternatively, bacteria and organic substances can methylate mercury, and subsequently demethylate it, depending on environmental conditions (Allard and Arsenie, 1991; Gilmour and Henry, 1991).

2.2 Potential Exposure Pathways

Plants and animals can be exposed to mercury by direct contact with contaminated environmental media or ingestion of mercury-contaminated water and food (Figure 2-2). Mercury deposited in soil can be a source of direct exposure from physical contact (e.g., earthworms, terrestrial plants). Animals also can ingest mercury in soil, either purposefully (e.g., earthworms) or incidentally (e.g., grazers). Mercury in the air can be taken up directly by terrestrial or aquatic emergent plants, or inhaled by terrestrial animals. Mercury in water can be a source of direct exposure to aquatic plants (e.g., algae, seagrasses) and aquatic animals (e.g., zooplankton, fish) and can be ingested by terrestrial animals in drinking water (e.g., moose). Finally, both aquatic and terrestrial animals can be exposed to mercury in contaminated food sources (e.g., fish, piscivorous mammals and birds).

Not all of these potential exposure pathways are equally important, however. The remainder of this section evaluates the likely importance of different routes of exposure consequent to mercury release to air. Section 2.2.1 discusses the fate and bioavailability of mercury in aquatic systems and the pathways by which aquatic plants and animals can be exposed to mercury directly in contaminated water or indirectly through aquatic food webs. Section 2.2.2 provides information on the fate and bioavailability of mercury in terrestrial ecosystems and the pathways by which terrestrial plants and animals can be exposed. Bioaccumulation of mercury in aquatic and terrestrial organisms is discussed further in Section 2.3.1.

2.2.1 Exposure Pathways in Aquatic Systems

Figure 2-3 illustrates the potential distribution of mercury in a water body. As shown, mercury can be present in surface waters in various forms: (1) dissolved in the water; (2) concentrated in the surface microlayer (the uppermost layer of a surface water); (3) attached to seston[1]; (4) in the bottom sediments; and (5) in biota (e.g., fish, macroinvertebrates[2]).

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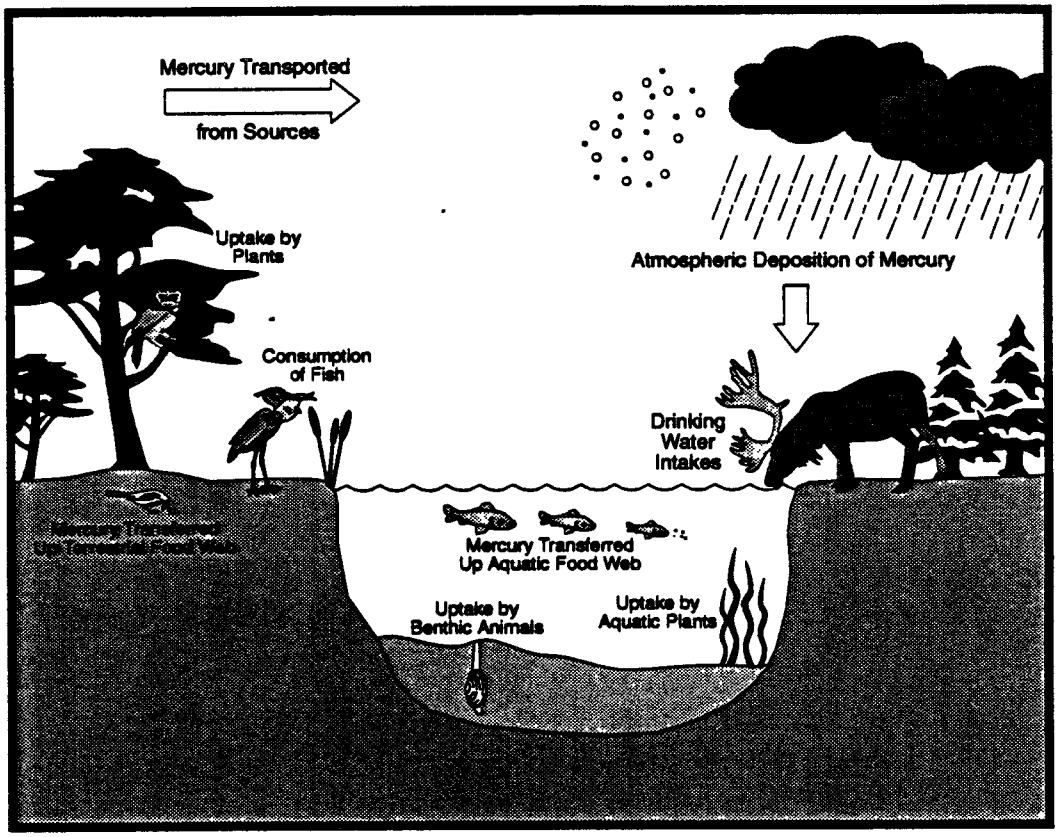
[1] Seston is suspended particulate matter, including detritus (dead organic matter) and plankton (i.e., living plants and animals that passively float or weakly swim in the water column such as algae, water fleas, and copepods).

[2] Macroinvertebrates are invertebrates (i.e., animals without backbones) that are visible to the naked eye, such as worms, clams, snails, insects and insect larvae, and crayfish.

Figure 2-2
Possible Routes of Exposure to Mercury

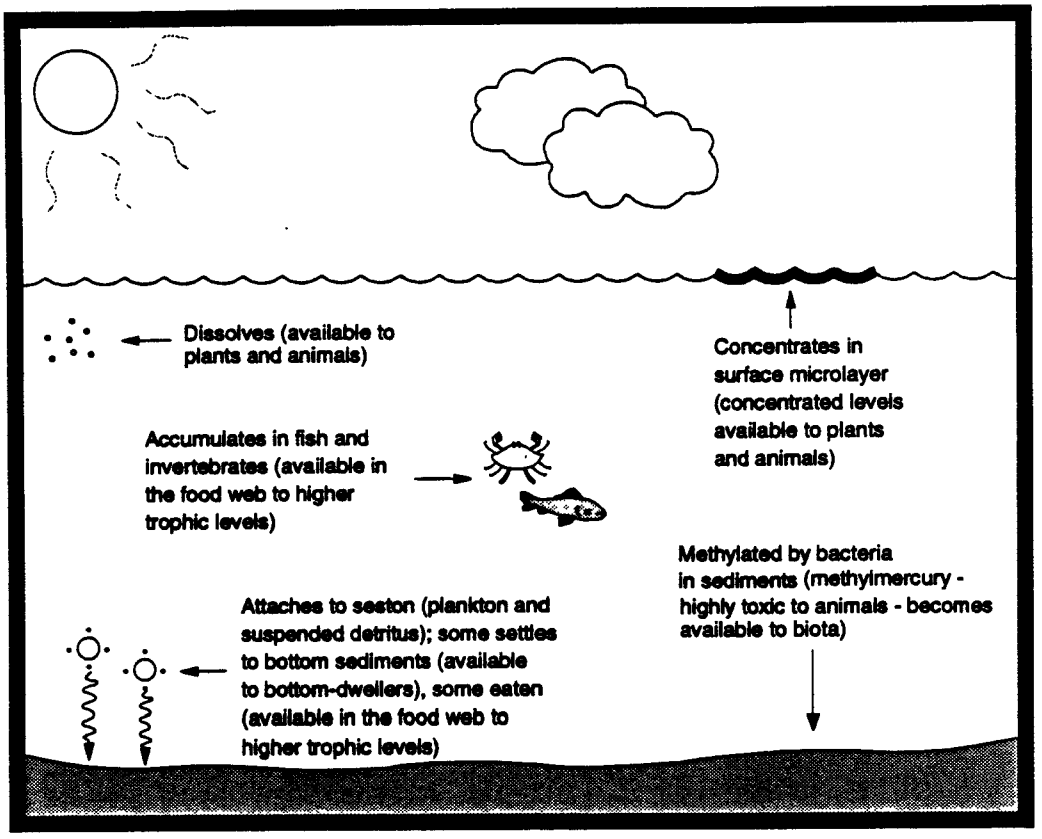


The form and location of mercury in a water body determines its bioavailability. For example, dissolved mercury is available for direct uptake by aquatic plants, fish and invertebrates. Mercury that concentrates in the surface microlayer is available to organisms that live, reproduce, or feed on the surface of water bodies (i.e., neuston). Mercury attached to seston can be ingested by aquatic animals that feed on plankton. Additionally, mercury that has deposited on the accumulated in the sediments is available to benthic (i.e., bottom-dwelling) plants and animals.

Aquatic plants may take up mercury from air, water or sediments (Crowder, 1991). Planktonic plants (i.e., phytoplankton such as algae) are not rooted; therefore, their only route of exposure is uptake from water. Both submerged aquatic vegetation and wetland emergent plants are rooted, however, and can be exposed to mercury in sediments. In locations with mercury-contaminated sediments, mercury levels in aquatic macrophytes[3] have been measured at 0.01 μg/g, indicating that these plants do not strongly accumulate mercury from sediments (Wells et al., 1980; Crowder et al., 1988). The ratio between inorganic and organic mercury varies in plants (Crowder, 1991).

[3] Macrophytes are aquatic plants that are large enough to be visible to the naked eye.

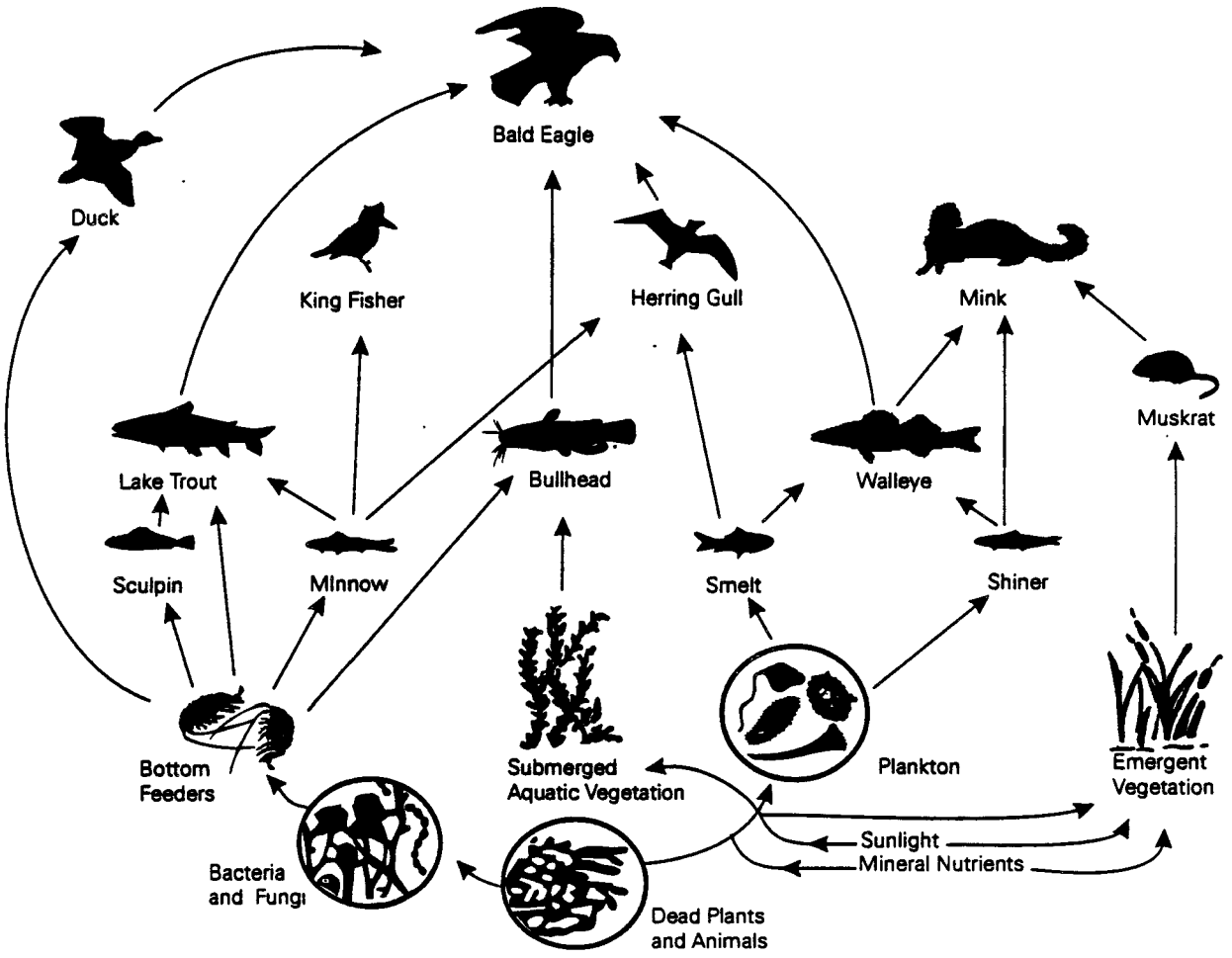
Figure 2-3
Distribution of Mercury in a Water Body



For aquatic animals, the primary exposure routes of concern are direct contact with mercury-contaminated water and sediments, and ingestion of mercury-contaminated food. Fish can absorb mercury through the gills, skin and gastrointestinal tract (U.S. EPA, 1985). These fish then become a source of mercury for piscivorous birds and mammals. Emergent aquatic insects represent another potential source of mercury for insectivorous birds and mammals (Dukerschein et al., 1992; Saouter et al., 1993).

As discussed in more detail in Section 2.3, mercury in aquatic biota tends to occur at higher concentrations in higher trophic levels. An example aquatic food web is shown in Figure 2-4. At the top trophic levels are piscivores, such as humans, bald eagles, cormorants, herring gulls, loons, kingfishers, mergansers, herons, egrets, ospreys, bald eagles, river otters, mink, alligators, snapping turtles and water snakes. The largest of these species (e.g., bald eagle, otter) can prey on fish that occupy high trophic levels, such as trout and salmon, which in turn feed on smaller "forage" fish, such as smelt, alewife, minnow, chub, and sculpin. Smaller piscivorous wildlife (e.g., kingfishers, ospreys, terns) tend to feed on the smaller forage fish, which in turn feed on zooplankton or benthic invertebrates. Zooplankton (e.g., copepods, water fleas) feed on phytoplankton (i.e., microscopic algae), and the smaller benthic invertebrates tend to feed on algae and detritus. Thus mercury can be

Figure 2-4
Example Aquatic Food Web



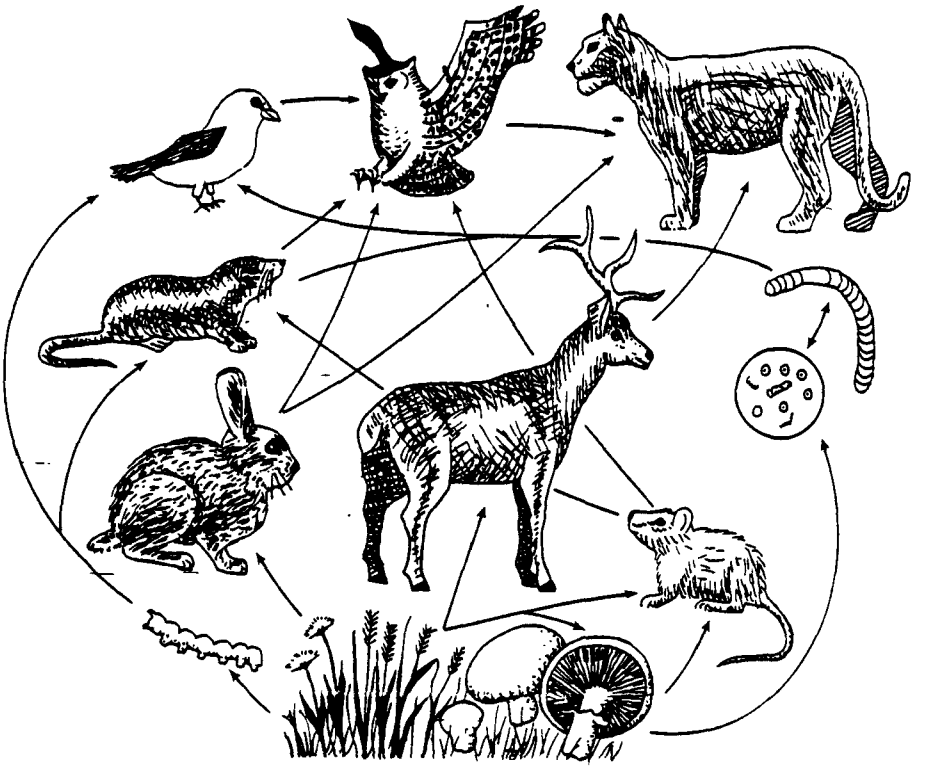
transferred and accumulated through three or four trophic levels to reach the prey of piscivorous wildlife species. In some large lakes, food chains can be even longer.

2.2.2 Exposure Pathways in Terrestrial Systems

Several exposure pathways are possible for both plants and animals in terrestrial systems. The two main pathways by which terrestrial plants can be exposed to mercury are uptake from soils into

the roots and intake from the air via stomata[4] or passive absorption. Potential exposure routes for terrestrial animals include the following: (1) ingestion of mercury-contaminated food; (2) direct contact with a contaminated medium; (3) ingestion of mercury-contaminated drinking water; and (4) inhalation. Food ingestion is of primary concern for vertebrate carnivores (including humans) because mercury accumulates in prey species. Once mercury enters a terrestrial food web, like that shown in Figure 2-5, it can be transferred in increasing concentrations to higher trophic levels (Talmage and Walton, 1993).

Figure 2-5
Example Terrestrial Food Web



2.2.2.1 Terrestrial Plants

Uptake by plants plays a major role in the entry of metals to terrestrial food webs. Mercury uptake by terrestrial vascular plants[5] can occur through the roots and/or through the leaves, by way of stomata and by passive absorption of gaseous mercury (Mosbaek et al., 1988; Crowder, 1991; Maserti and Ferrara, 1991). A vascular plant's uptake of mercury from the soil depends on soil type,

[4] Stomata (plural of stoma) are the minute openings in the epidermis of leaves, stems, or other plant organs that allow gas to diffuse in and out.

[5] Plants with roots, stems, and leaves, such as ferns and seed plants.

decreasing as organic matter, which binds mercury, increases (WHO, 1989). Uptake of mercury through leaves is considered to be a negligible source of mercury for beech and spruce (Schmidt, 1987), but is an important route for pine and herbaceous plants (Mosbaek et al., 1988; Maserti and Ferrara, 1991). Bryophytes and lichens, on the other hand, have no roots and take up metals only from air or water (WHO, 1989; Crowder, 1991). Some species of bryophytes and lichens can bioconcentrate mercury to relatively high levels (e.g., up to 1200 μg/g in *Sphagnum* sp.) (Siegal et al., 1985). Some woody plants (e.g., *Pinus* sp.) also bioconcentrate mercury (Siegal et al., 1987).

2.2.2.2 Terrestrial Animals

Dietary exposure is the primary route of mercury exposure for vertebrate members of terrestrial food webs. Figure 2-5 illustrates a terrestrial food web. Plants are eaten by a wide diversity of herbivorous animals (e.g., grasshoppers, caterpillars, mice, voles, rabbits, deer). Insects, earthworms and other soil macroinvertebrates can accumulate mercury to levels well above those of the soil in which they reside (Siegel et al., 1975; Helmke et al., 1979; Beyer et al., 1985), and are themselves consumed by many species of birds, shrews, snakes, and amphibians. Small mammals, birds, reptiles and amphibians are consumed by larger predators, such as owls, hawks, eagles, mink, wolves, and big cats. Thus mercury can be transferred and accumulated through two or three trophic levels to reach the prey of top carnivores in terrestrial systems.

For these terrestrial animals, exposure to mercury depends largely on the animal's feeding strategy. For example, generalist herbivores (plant-eaters) may be less exposed to mercury than species that are specialized in or restricted to feeding on highly exposed plant species (e.g., reindeer foraging mostly on lichens and bryophytes).

2.2.3 Summary of Aquatic and Terrestrial Exposure Pathways

Food chain transfers of mercury are thought to be the most important exposure pathways in both aquatic and terrestrial ecosystems. Mercury, however, tends to bioaccumulate and biomagnify more strongly in aquatic than in terrestrial ecosystems. Several possible explanations exist to explain this observation. First, the transfer of metals to higher trophic levels depends to some extent on where the metals are stored within prey organisms. Birds and mammals accumulate mercury in their feathers and fur, which are not eaten or are poorly digested. In contrast, most of the mercury in fish is contained in muscle tissue, which is consumed and digested by piscivorous wildlife. In addition, mercury in terrestrial food webs frequently exists in an inorganic form, rather than as methylmercury. Inorganic mercury accumulates to only a limited extent in plants and soil organisms and does not biomagnify in the organisms that feed on them. Finally, aquatic food chains often include more trophic levels than terrestrial food chains. A typical food chain in aquatic systems would consist of phytoplankton/algae/detritus → zooplankton/benthic invertebrates → small forage fish → larger piscivorous fish. Piscivorous birds and mammals would represent the fifth step in the chain. In some cases a sixth step exists, as when a bald eagle consumes a piscivorous herring gull or when a Florida panther consumes a raccoon. A typical food chain in terrestrial systems might be plants → small herbivorous mammals → predatory birds and mammals. Another typical terrestrial food chain would be plants → herbivorous insects → small birds → birds of prey. In these examples, the top predators represent the third and fourth step in the chain (although additional steps are possible), instead of a fifth or sixth level as can be the case for aquatic systems.

2.3 Ecological Effects

This section provides an overview of potential effects of mercury on ecosystems and components of ecosystems. Contaminants such as mercury can affect individual organisms, populations, communities, or ecosystems (Table 2-1). Effects on individuals can be lethal or sublethal, including behavioral, reproductive and developmental effects. Additionally, effects can be immediate, due to acute (short-term) exposures, or may be manifested only after chronic (long-term) exposures.

Table 2-1
Examples of Effects of Contaminants on Ecosystem Components

Component	Examples of Effects
Individual	Change in respiration Change in behavior (e.g., migration, predator-prey interactions) Inhibition or induction of enzymes Increased susceptibility to pathogens Decreased growth Decreased reproduction Death
Population	Decreased genotypic and phenotypic diversity Decreased biomass Increased mortality rate Decreased fecundity rate Decreased recruitment of juveniles Increased frequency of disease Decreased yield Change in age/size class structure Extinction
Community	Decreased species diversity Change in species composition Decreased food web diversity Decreased productivity Increased algal blooms
Ecosystem	Decreased diversity of communities Altered nutrient cycling Decreased resilience

In animals, toxic effects caused by mercury exposure vary depending on a number of factors, including but not limited to these:

- delivered dose (i.e., amount and duration of exposure);
- the form of mercury to which an organism is exposed;
- physical and chemical parameters of the environment (e.g., pH, temperature);
- the extent to which an organism is exposed to other chemicals or non-chemical stressors; and

- the life stage, age, sex, species, and physiological condition of the exposed organisms.

The remainder of this section provides an overview of potential adverse ecological effects of mercury. Section 2.3.1 discusses the bioaccumulation and biomagnification of mercury in food chains, Section 2.3.2 reviews individual-level effects, Section 2.3.3 reviews population-level effects, and Section 2.3.4 reviews effects on communities and ecosystems.

2.3.1 Bioaccumulation of Mercury

As discussed previously, plants and animals may absorb mercury from direct exposure to contaminated media (e.g., water, soil, air). In addition, animals can acquire mercury through ingestion of mercury-contaminated food. These pathways determine how much mercury an organism is exposed to from outside sources. An additional factor that determines the effect of mercury on ecological systems is how much mercury is accumulated by organisms. Mercury accumulation can result in concentrations in exposed plants and animals that are higher than those in surrounding media or in ingested food. This section outlines the basic processes by which mercury accumulates and introduces the different ways that chemical accumulation in biological systems is measured and expressed.

Three separate terms are commonly used to describe the mechanism by which a contaminant accumulates in living tissues. The term "bioconcentration" is used to refer to the uptake of a chemical directly from an organism's surrounding medium (e.g., uptake by a fish from water through the gills and epithelial tissue, or uptake by earthworms from soil through the skin) and does not include the ingestion of contaminated food. The term "bioaccumulation" refers to the net uptake of a contaminant from all possible pathways. It includes the accumulation that may occur by direct exposure to contaminated media as well as exposure from food. The term "biomagnification" refers to the increase in chemical concentration in organisms at successively higher trophic levels as a result of the ingestion of contaminated organisms at lower trophic levels. Mercury is known to bioconcentrate, bioaccumulate and biomagnify. In fact, mercury is one of the few metals that is known to biomagnify in aquatic food webs.

Different numerical factors are used to estimate the extent to which a contaminant bioconcentrates, bioaccumulates and biomagnifies.

- The bioconcentration factor (BCF) is the ratio of a substance's concentration in tissues (generally expressed on a whole-body basis) to its concentration in the surrounding medium (e.g., water, soil) in situations where an organism is exposed through the medium only.

- The bioaccumulation factor (BAF) is the ratio of a substance's concentration in tissue to its concentration in the surrounding medium (e.g., water, soil), in situations where the organism is exposed both directly and through the food web.

- The biota-sediment accumulation factor (BSAF) is a specialized form of the BAF which refers to the chemical concentration in an aquatic organism divided by that in surficial bottom sediments. To date it has been applied only to bioaccumulative organic compounds, but in principal it could be applied to mercury also. When applied to organic compounds, chemical concentrations in tissues and sediment are generally normalized for lipid content and organic carbon content, respectively.

- The predator-prey factor (PPF, also known as the biomagnification factor, or BMF) is the factor by which a substance's concentration in the organisms at one trophic level exceeds the concentration in the next lower trophic level. For example, the PPF for mercury at trophic level 4 equals the observed mercury concentration in trophic level 4 organisms divided by mercury concentration in trophic level 3 organisms.

- The food chain multiplier (FCM) is the factor by which the BAF of a substance at trophic level 2 or higher exceeds the BCF at trophic level 1. Implied by this definition is the assumption that organisms at trophic level 1 are at or near chemical equilibrium with their environment.

BAF, BSAF, PPF and FCM values are trophic-level specific. Depending on environmental levels of mercury, sufficient mercury may accumulate in organisms at one or more trophic levels to produce adverse effects at the individual, population, community or ecosystem level.

Mercury accumulates in an organism when the rate of uptake exceeds the rate of elimination. Although all forms of mercury can accumulate to some degree, methylmercury generally accumulates to a greater extent than other forms of mercury. Methylmercury is absorbed into tissues quickly and becomes sequestered due to covalent reactions with sulfhydryl groups in proteins and other macromolecules. Inorganic mercury can also be absorbed but is generally taken up at a slower rate and with lower efficiency than methylmercury (Eisler, 1987). Elimination of methylmercury takes place very slowly resulting in tissue half-lives (the time required for half of the mercury in the tissue to be eliminated) ranging from months to years (Westermark et al., 1975). Elimination of methylmercury from fish is so slow that long-term reductions of mercury concentrations in fish are often due mainly to growth of the fish. In comparison, other mercury compounds are eliminated relatively quickly resulting in reduced levels of accumulation (Eisler, 1987).

Methylmercury and total mercury concentrations both tend to increase in aquatic organisms as trophic level increases in aquatic food webs. In addition, methylmercury generally comprises a relatively greater percentage of the total mercury content at higher trophic levels (May et al., 1987; Watras and Bloom, 1992). Accordingly, mercury exposure and accumulation is of particular concern for animals at the highest trophic levels in aquatic food webs and for animals that feed on these organisms.

2.3.1.1 Field-derived BAFs, BSAFs, and PPFs

In this section, BAFs for organisms that occupy the base of aquatic food chains are reviewed, along with BSAFs for fish and PPFs for avian and mammalian piscivores. BAFs for earthworms and emergent aquatic insects are also presented because both represent possible vectors for mobilization of sediment-associated mercury and subsequent translocation to wildlife. BAFs derived for fish are discussed in detail in Appendix A. Derivation is summarized in Section 4.1.

The only known data from which to estimate BAFs for phytoplankton were reported by Suchanek et al. (1993) for Clear Lake, California. Averaged across seven sampling sites, the BAF for total mercury was 100,880, which was about 14% greater than the corresponding value for zooplankton from the same system (see below). In contrast, the BAF for methylmercury in phytoplankton was 477,300, which was approximately one-third that for zooplankton (1,273,300).

BAFs published for zooplankton, expressed as ratios of total mercury, range from approximately 35,600 (Sorenson et al., 1990) to 285,200 (Lindqvist, 1991). Intermediate values include those reported by Watras and Bloom (1992), approximately 56,200 for the reference basin, and Suchanek et al. (1993), average of 87,260 across sampling sites. This broad range of values typifies BAF data for aquatic systems generally, and is thought to be due largely to natural variation in the percentage of total mercury that exists as methylmercury, the principal bioaccumulating species. Fewer data exist with which to estimate BAFs for zooplankton on a methylmercury basis. Watras and Bloom (1992) reported a BAF for methylmercury of approximately 1,000,000, which is similar to the value (1,273,300) obtained by Suchanek et al. (1993).

To date, BSAFs for mercury have not been estimated; however, limited data exist that allow such calculations to be made. Hildebrand et al. (1980) observed a linear relationship between mercury in sediment and that in benthic invertebrates. A BSAF of approximately 0.4 is obtained from the slope of this relationship (after expressing benthos data on a dry weight basis). The relationship between mercury in fish (rock bass and hog suckers) and that in sediments was reported by Hildebrand et al. (1980) to be logarithmic. Taking as an average a fish tissue value of 4.0 μg/g (dry weight; converted from 1.0 μg/g wet weight) and solving for the sediment concentration yields a value of 2.78 μg/g. The BSAF is equal to the ratio of fish and sediment values, or approximately 1.4. Data presented by Sorenson et al. (1990) yield BSAFs (dry weight basis) of approximately 2.0 and 10.1 for zooplankton and northern pike, respectively. Data presented by Wren and MacCrimmon (1986) allow BSAFs to be calculated for two Ontario lakes that differ considerably with respect to total mercury residues in biota. In both lakes BSAFs (dry weight basis) appeared to be very similar, ranging from approximately 5.1 (clams) to 24.0 (northern pike) in the less contaminated of the two lakes, and 3.4 (clams) to 27.1 (pike) in the other system. Using the mid-range of values reported by Lindqvist (1991), BSAFs (dry weight) of approximately 2.2, 17.2, 17.7, and 45.7 are obtained for zooplankton, macroinvetebrates, yellow perch (small and large), and northern pike (large and small), respectively. Boyer (1982) reported mercury concentrations in fish and sediments from several locations on the upper Mississippi River. Expressed on a dry weight basis, these data yield BSAFs ranging from 2.5 to greater than 50.

In summary, BSAFs calculated for mercury in aquatic biota ranged from 0.4 to about 50, and appeared to increase with trophic level. In both magnitude and in increase with trophic level, BSAFs for mercury are similar to BSAFs reported for hydrophobic organic compounds (lipid/carbon normalized). It could be hypothesized, therefore, that similar processes are at work. This is unlikely, since bioaccumulation of organic compounds is largely a partitioning process, while for mercury the chemical interactions tend to more specific, often involving the formation of covalent bonds. Because mercury does not partition into lipid, normalization for lipid content makes little sense. The existence of strong relationships between mercury and organic carbon content (see for example Wiener et al., 1982; Lindqvist, 1991) suggests, however, that some type of carbon normalization may be appropriate.

Limited data are available that allow calculation of BAFs for emergent aquatic insects and earthworms. Saouter et al. (1993) exposed mayflies for 10 days to methylmercury in sediment and obtained a BAF (wet weight basis) of 4.0. This value would increase somewhat if it was expressed on a dry weight basis. The concentration of mercury in earthworms collected from an uncontaminated field site was 27.1 times that of soil and 6.9 times that of decaying vegetation (dry weight basis; Siegel et al., 1975). In a 12 wk laboratory exposure, earthworms accumulated an average of 21.3 times the mercury concentration of the soil to which they were exposed (including control and treatment groups; Beyer et al., 1985).

PPFs for piscivorous birds and mammals are difficult to determine accurately because residue data cannot be attributed with any specificity to residues in a particular prey item; feeding observations for the species in question are rarely reported in these studies. PPFs were, therefore, estimated by constructing rough averages of residue values in prey items occupying similar trophic levels. For this analysis, mink, mergansers, and loons were assumed to feed exclusively at trophic level 3. River otters were assumed to feed at trophic levels 3 (80%) and 4 (20%). All PPFs were calculated as the ratio of total mercury concentration in muscle tissue to that in the prey items.

PPFs calculated for piscivorous birds ranged from 1.73 (hooded merganser; Vermeer et al., 1973) to 7.7 (herring gull; Wren et al., 1983). Intermediate values include those estimated for the common merganser (2.51; Vermeer et al., 1973) and loon (6.8; Wren et al., 1983). PPFs for mammals ranged from 1.72 (otter; Wren et al., 1986) to 7.7 (mink; Wren et al., 1983). Kucera (1983) reported that the ratio of mercury concentrations in mink and otter to that in predatory fish in the same region was about 10. Thus, it can be shown that mercury biomagnifies in piscivorous wildlife, although the extent of this biomagnification is less than that typically reported for persistent organic compounds. For example, data reported by Braune and Norstrom (1989) suggest that the PPF for PCBs in piscivorous birds can approach 100. These observations have led to the suggestion that mercury is eliminated by piscivorous wildlife in feathers and fur, and perhaps also via a demethylation pathway (Wren et al., 1986); however, extensive elimination would be expected to result in PPFs of 1 or less.

2.3.1.2 Mercury Residues in Fish

Estimation of an average mercury concentration in freshwater fish at any given trophic level requires the collection of a large number of samples from randomly selected waterbodies. What, in fact, generally exists in the literature is a collection of individual studies which characterize mercury concentrations in a relatively small number of fish from restricted geographical regions. Many of these studies were initiated because of real or suspected problems with mercury in the region of interest. Thus, a sample developed by a compilation of these data may be biased toward the high-end of the distribution of mercury concentrations in fish nationwide.

The most appropriate source for estimating average concentrations of mercury in freshwater fish appears to be a study conducted by U.S. EPA (U.S. EPA, 1992b, Bahnick et al., 1994). This is the only identified nationwide fish collection effort that used consistent sampling and mercury measurement techniques. Samples were obtained from 279 sites across the U.S., based on proximity to suspected point and non-point pollution sources. Additionally, fish were collected from 35 "remote" sites that were thought to provide background pollutant concentrations in fish. Whole-body mercury levels were determined for bottom feeders, and mercury levels in fillets were analyzed for game fish. The maximum mercury level detected was 1.8 μg/g wet weight, and the mean across all fish and all sites was 0.26 μg/g (Table 2-2). The highest values were detected in piscivorous game fish (trophic level 4), including walleye, bass and northern pike. Lower levels were found in herbivores (carp, sucker), omnivores (catfish), and species that prey extensively on insects (trout and crappie). In general, this sampling effort did not address fish that occupy trophic level 3 (forage fish). A "national" average for trophic level 3 fish must, therefore, be estimated by dividing mercury concentrations in piscivorous fish by an appropriate predator-prey factor (PPF). A PPF for trophic level 4 (PPF_4) can be estimated from existing field data. This was done in Appendix A to Volume V, resulting in a mean PPF_4 of about 5. Dividing this value into the mean residue for trophic level 4 fish (0.40 μg/g) yields a value for trophic level 3 fish of 0.08 μg/g.

Table 2-2
Nationwide Average of Mercury Residues in Fish[a]

Fish Species	Mercury Concentration Averaged Across Sampling Sites (μg/g wet weight)
Carp	0.11
Sucker (White, Redhorse and Spotted)	0.167
Catfish (Channel and Flathead)	0.16
Bass (Largmouth, Smallmouth and White)	0.38
Walleye pike	0.52
Northern pike	0.31
Crappie	0.22
Brown Trout	0.14
Mean of All Fish Sampled	0.26

[a] Data from Bahnick et. al., 1994.

The highest mercury concentrations in fish generally occur in the blood, spleen, kidney and liver, and may exceed those in muscle by a factor of 2 - 10 (McKim et al., 1976; Olson et al., 1978, Ribeyre and Boudou, 1984; Boudou and Ribeyre, 1985; Harrison et al., 1990; Niimi and Kissoon, 1994). Owing to the size of these organs relative to that of other tissues, however, most of the mercury contained in a fish at any given time is associated with muscle tissue.

2.3.1.3 Mercury Residues in Avian and Mammalian Wildlife

A large volume of mercury residue data exists for both avian and mammalian wildlife which cannot be directly related to mercury concentrations in water or sediment. Nevertheless, these data are of considerable value because they indicate the range of mercury concentrations that can be expected in animals inhabiting both contaminated and uncontaminated environments. A comparison of these residues with those obtained from laboratory dose-response studies provides additional information, including the extent of difference between "natural background" residues and those which are associated with toxic effects. Emphasis is placed on piscivorous birds and mammals; however, data is also provided for the tree swallow because of its link to aquatic sediments through consumption of emergent insects.

Mercury residues in tissues from birds are given in Table 2-3. The birds represented in this table include animals taken from polluted environments and individuals collected from environments for which there were no known point sources. This table is not intended to be an exhaustive compilation of measured residues, but instead illustrates the range of values encountered in environmental sampling efforts. Residues which, in the opinion of the author of the Report, were associated with toxic effects are noted.

Table 2-3
Mercury Residues in Tissues of Piscivorous Birds

Species	Mercury (µg/g fresh weight)	Tissue	Sampling Location	Comments	Reference
Bald eagle	13.0 - 21.0	feathers	Great Lakes region	adults	1
Bald eagle	3.7 - 20.0	feathers	Great Lakes region	nestlings	1
Common loon	8.7	feathers	Minnesota lakes	adults	2
Common loon	2.7	feathers	Minnesota lakes	juveniles	2
Common loon	11.0 - 18.0	feathers	Wisconsin lakes	adults	3
Common loon	2.0 - 5.0	feathers	Wisconsin lakes	juveniles	3
Wood stork	1.9	feathers	South Florida	juveniles	4
Bald eagle	0.07 - 0.41	eggs	15 States (USA)		5
Common loon	0.40 - 1.10	eggs	Wisconsin lakes		3
Common loon	2.0 - 3.0	eggs	Northwestern Ontario	polluted by point source; LOAEL - reproduction	6
Common tern	3.6	eggs	Northwestern Ontario	polluted by point source; LOAEL - reproduction	7
Herring gull	2.3 - 15.8	eggs	Clay Lake, Ontario	polluted by point source, no adverse effects	8
Wood stork	0.7	eggs	South Florida		9
Tree swallow	0.04 - 0.08	eggs	Lower Great Lakes	consume emergent aquatic insects	10
Common loon	1.6 - 47.7	liver	Northwestern Ontario	LOAEL - reproduction	6

Table 2-3 (continued)
Mercury Residues in Tissue of Piscivorous Birds

Species	Mercury (µg/g fresh weight)	Tissue	Sampling Location	Comments	Reference
Common loon	9.5 - 90.0	liver	Wisconsin lakes	adults found dead	3
Common loon	5.6	liver	Minnesota lakes	adults found injured	2
Common loon	0.2 - 6.9	breast muscle	Northwestern Ontario	polluted by point source	6
Common goldeneye	0.9 - 19.4	breast muscle	Clay Lake, Ontario	polluted by point source	8
Common merganser	4.4 - 13.1	breast muscle	Clay Lake, Ontario	polluted by point source	8
Hooded merganser	3.9 - 17.6	breast muscle	Clay Lake, Ontario	polluted by point source	8
Herring gull	0.7 - 4.0	breast muscle	Tadenac Lake, Ontario		11
Common loon	1.5	breast muscle	Tadenac Lake, Ontario		11

References:

1. Bowerman et al., 1994; range of means across sampling locations.
2. Ensor et al., 1992; mean of birds caught by nightlighting.
3. Belant and Anderson, 1990; range of individual values. Means for feathers (adult and juvenile), eggs and liver were 14.8, 4.0, 0.64 and 40.9, respectively.
4. Burger et al., 1993; mean value.
5. Wiemeyer et al., 1993; range of means across sampling locations (collected after failure to hatch).
6. Barr, 1986; range of individual values. Means for liver and muscle were 13.0 and 2.3, respectively.
7. Fimreite, 1974.
8. Vermeer et al., 1973; range of individual values. Means for goldeneye, common merganser and hooded merganser were 7.8, 6.8 and 12.3, respectively.
9. Fleming et al., 1984; mean value.
10. Bishop et al., 1995; range of individual values, mean = 0.07.
11. Wren et al., 1983; gull data are reported as the range of individual values, mean = 1.7.

Factors contributing to the accumulation of mercury in wild birds are reviewed by Scheuhammer (1987, 1991). Interpretation of residue data is complicated by the likelihood that mercury distribution in tissues varies among species, and perhaps also among individuals of a single species, depending upon age, sex, diet, and other factors. Nevertheless, several generalizations can be attempted. Mercury levels in feathers of birds experimentally dosed with methylmercury generally exceed levels in muscle, liver and kidney by a factor of 4 or more (Heinz, 1976a; Stickel et al., 1977; Finley and Stendell, 1978), and it has been suggested that in free-living birds greater than 50% of the total body burden of mercury may be present in the plumage (Braune and Gaskin, 1987). Natural background levels of mercury in feathers of non-piscivorous raptorial birds are thought to range from 1-5 μg/g (dry weight).

Tissue levels of mercury associated with toxic effects in birds appear to exceed those in birds inhabiting relatively uncontaminated environments by a factor of ten or less. This observation is consistent with data for other environmental media (water, sediments, fish), which evidence similar differences between natural "background" levels of mercury and those which cause significant environmental damage. Owing to their ease of collection, the analysis of bird feathers and eggs has been suggested as a means of identifying species that are at risk due to mercury. This suggestion has particular merit in view of the natural variation in mercury levels in the fish upon which these animals prey. Mercury residues in tissues also tend to integrate variations in mercury loading and elimination due to changes in dietary habits, migration, egg production, etc.

The nature and abundance of mercury residue information for mammals reflects to a large degree the availability of specimens as a byproduct of commercial trapping. Thus, abundant residue data are available for wild muskrat, beaver, fox, weasel, bobcat, marten, fisher, wolf, raccoon, opossum, mink and river otter. Data are also available for a number of game species, including squirrels, rabbits, caribou, moose, deer, elk, mountain goat and bear. An extensive compilation of these data is provided by Wren (1986), along with a review of tissue levels in both wild and laboratory animals that have been associated with toxic effects. Some of the data from this compilation are presented in Table 2-4, as well as more recent information. Emphasis was placed on piscivorous species because of the exposure to these animals from consumption of contaminated fish. Data from beaver and muskrat have also been included, both to provide a general comparison of aquatic-based species, and because in several studies data were available for piscivores and herbivores from the same waterbody. Emphasis was also placed on residues in fur and liver. This was done for two reasons: (1) the highest residues are generally found in the liver and kidney; however, there are more reported values for liver. (2) Fur, like feathers, has been suggested as a way of non-invasively determining the residue status of wild animals and of identifying areas where animals may be at risk due to mercury intoxication. Finally, data from raccoons trapped in South Florida are included in Table 2-4 because they are suspected of contributing to mercury exposure in the Florida panther.

In general, the rank order of mercury residues in tissues from wild mink and otter is liver = kidney > muscle > brain. Levels in fur relative to those in other tissues are variable but in most cases are higher than those in liver. Comparisons between residues in wild animals with those in animals experimentally dosed with mercury appear to be complicated by kinetics-based differences in disposition. Thus, Wobeser et al. (1976b) reported that mercury levels in the fur of experimentally dosed mink were low (1.5 μg/g) relative to concentrations in liver (24.3), kidney (23.1), muscle (16.0) or brain (11.9). A similar pattern of distribution was reported for mink by Aulerich et al. (1974). In contrast, mercury levels in the fur of an individual mink found dying of mercury poisoning were higher than concentrations in any other tissue (Wobeser and Swift, 1976; see Table 2-4). Apparently, the length of time over which a dose is obtained dictates its distribution, with redistribution from well-

Table 2-4
Mercury Residues in Tissues of Piscivorous Mammals

Species	Mercury (µg/g fresh weight)	Tissue	Sampling Location	Comments	Reference
Otter	15.2 - 25.6	fur	Georgia		1
Otter	6.5 (max. = 63.2)	fur	Wisconsin		2
Otter	47.0	fur	Clay Lake, Ontario	polluted by point source; death due to poisoning	3
Mink	10.7 (max. = 17.3)	fur	Georgia		4
Mink	7.6 (max. = 41.2)	fur	Wisconsin		2
Mink	34.9	fur	Saskatchewan	polluted by point source; death due to poisoning	5
Raccoon	4.4	fur	S. Florida		6
Muskrat	0.06	fur	Wisconsin		2
Beaver	0.03	fur	Wisconsin		2
Otter	1.7 - 3.4	liver	Manitoba	males and females	7
Otter	2.4 - 4.5	liver	Winnipeg R.	males and females; polluted by point source	7
Otter	0.3 - 3.0	liver	Louisiana		8
Otter	0.9 - 3.5	liver	Ontario	residues correlated with acidity	9
Otter	96.0	liver	Clay Lake, Ontario	polluted by point source; death due to poisoning	5

Table 2-4 (continued)
Mercury Residues in Tissues of Piscivorous Mammals

Species	Mercury (µg/g fresh weight)	Tissue	Sampling Location	Comments	Reference
Otter	3.3 (max. = 23.6)	liver	Wisconsin		2
Mink	0.4 - 1.7	liver	Manitoba		7
Mink	2.1 (max. = 17.4)	liver	Wisconsin		2
Mink	0.1 - 2.6	liver	Ontario	residues correlated with acidity	9
Mink	58.2	liver	Saskatchewan	polluted by point source; death due to poisoning	5
Raccoon	1.5 - 24.0	liver	S. Florida		10
Muskrat	< 0.02	liver	Wisconsin		2
Beaver	0.04	liver	Wisconsin		2

References:

1. Halbrook, R.S. 1978. Masters thesis. Environmental Pollutants in the River Otter of Georgia. University of Georgia at Athens; range of means across sampling locations.
2. Sheffy and St. Amant, 1982; mean value.
3. Wren, 1985; one individual.
4. Cumbie, 1975; mean value.
5. Wobeser and Swift, 1976; one individual.
6. Bigler et al., 1975; mean value.
7. Kucera, 1983; Manitoba data are reported as the range of means across sampling locations. Data from the Winnipeg river are reported as a mean value.
8. Beck, 1977; range of means across sampling locations.
9. Wren et al., 1986; range of means across sampling locations.
10. Roelke et al., 1991; range of means across sampling locations.

perfused organs (liver, kidney) to storage tissues (fur and muscle) slowly taking place during lifetime exposures. These observations suggest that comparisons between mercury residues in wild and experimental animals should be limited to consideration of well-perfused tissues. Wobeser et al. (1976b) reported that mercury residues in the liver and kidney of mink that died during a 93-day feeding study were 24.3 and 23.1 μg/g, respectively.

Somewhat higher values were reported for mink by Aulerich et al. (1974; 55.6 and 37.7 μg/g), and for otter by O'Connor and Nielson (1980; 39.0 and 33.0 μg/g). Even if comparisons between wild and experimental animals are limited to well-perfused tissues, questions still remain, however. In general, mercury residues in all tissues from wild animals that are suspected to have died from mercury poisoning are about twice those of animals that died from experimental intoxication (Wren, 1985, 1991).

Perhaps the most valid comparison that can be made at this time is that between apparently unaffected wild animals and wild animals that have died from mercury poisoning. An examination of Table 2-4 suggests that mercury residues in tissues from mink and otters from Wisconsin (Sheffy and St. Amant, 1982) approached, and in several cases even exceeded, those of the "naturally" poisoned animals. High mercury residues in fur were also reported for river otters trapped in several locations across Georgia (Halbrook, 1978). The livers of raccoons captured in South Florida are also notably high in mercury content (Roelke et al., 1991).

2.3.2 Individual Effects

Exposure to mercury can cause adverse effects in a wide variety of organisms, including plants, fish and aquatic invertebrates, birds and mammals. In this section, we review information on exposure levels that can cause adverse effects in these groups.

2.3.2.1 Individual Effects on Plants

Effects of mercury on aquatic plants include death and sublethal effects. Sublethal effects include plant senescence, growth inhibition, decreased chlorophyll content, decreased protein and RNA content, inhibited catalase and protease activities, inhibited and abnormal mitotic activity, increased free amino acid content, discoloration of floating leaves, and leaf and root necrosis (Boney, 1971; Stanley, 1974; Muramoto and Oki, 1984; Mhatre and Chaphekar, 1985; Sarkar and Jana, 1986). The level of mercury that results in toxic effects varies greatly among aquatic plants, as illustrated in Table 2-5.

Table 2-5
Toxicity Values for Aquatic Plants

Water Type	Hg^{2+} ($HgCl$ or $HgNO_3$) (μg/L)		Methylmercury (μg/L)	
	Low End	High End	Low End	High End
Fresh Water	53 (alga)	3,400 (submerged aquatic vegetation)	0.8 (alga)	6.0 (alga)
Salt Water	10 (alga)	160 (seaweed)	Not available	Not available

Source: U.S. EPA, 1985.

Mercury can also cause death and sublethal effects in terrestrial plants. Sublethal effects on terrestrial plants include decreased growth, leaf injury, root damage, inhibited root growth and function, hampered nutrient uptake, chlorophyll decline and reduced photosynthesis (Schlegel et al., 1987; Lindqvist, 1991; Godbold, 1991).

Methylmercury is more toxic to terrestrial plants than Hg^{2+}. One to ten nM (nanomolar) mercuric chloride or methyl mercuric chloride (provided in a nutrient solution) can inhibit root elongation in spruce seedlings. However, methyl mercuric chloride has a greater effect than mercuric chloride at the same concentration (Godbold, 1991). Sublethal effects, including decreased transpiration, decreased chlorophyll concentration, partial stomatal closure, and reduced photosynthesis, occurred at nutrient solution concentrations of 10 nM methyl mercuric chloride (Schlegel et al., 1987).

2.3.2.2 Individual Effects on Fish and Aquatic Invertebrates

The toxicity of mercury to fish has been reviewed by Eisler (1987) and more recently by Wiener and Spry (1995). Toxicity varies, depending on the fish's characteristics (e.g., species, life-stage, age, size), environmental factors (e.g., temperature, salinity, dissolved oxygen content, hardness, and the presence of other chemicals) and the form of mercury available. In particular, early life stages (especially of salmonids) exhibit greater sensitivity to elevated metal concentrations than later life stages. The toxicity of Hg^{2+} compounds to salmonids and catfish tends to increase with temperature (see Table 2-6). Organomercury compounds, such as methylmercury, generally are much more acutely toxic than Hg^{2+} to aquatic organisms.

Effects of mercury on fish include death, reduced reproduction, impaired growth and development, behavioral abnormalities, altered blood chemistry, impaired osmoregulation, reduced feeding rates and predatory success, and effects on oxygen exchange. LC_{50} values for fish range from 30 µg/L for guppies to 1,000 µg/L for the Mozambique tilapia (U.S. EPA, 1985). Symptoms of acute mercury poisoning in fish include increased secretion of mucous, flaring of gill opercula, increased respiration rate, loss of equilibrium and sluggishness. Signs of chronic poisoning include emaciation (due to reduced food intake), brain lesions, cataracts, inability to capture food, abnormal motor coordination and various erratic behaviors (e.g., altered feeding behavior) (Weis and Weis, 1989, 1995).

Table 2-6
Mercury Toxicity Increases With Temperature

Temperature (°C)	LC_{50} (µg/l)
Rainbow Trout with HgCl	
5	400
10	280
15	220
Temperature (°C)	LC_{50} (µg/l)
Juvenile Catfish with Phenylmercuric Acetate	
10	1,960
16.5	1,360
24	233

Source: U.S. EPA, 1985.

It is generally thought that toxic effects on fish in the environment are unlikely, except in the case of point source pollution discharges. An accumulating body of evidence, however, suggests that histological changes and effects on behavior, reproduction, and development can occur at water concentrations as low as 0.1 µg/L (Wiener and Spry, 1995), or about two orders of magnitude higher than those in a relatively pristine environment.

Levels of mercury that induce toxic effects in aquatic invertebrate species vary. For Hg^{2+}, acute (LC_{50}) values for invertebrates range from 2.2 µg/L for the cladoceran *Daphnia pulex* to 2,000 µg/L for the larval forms of three insects (U.S. EPA, 1985). Examples of some specific toxicity values for fish and aquatic invertebrates are provided in Table 2-7.

Table 2-7
Toxicity Values for Fish and Aquatic Invertebrates

Organism	Hg^{2+} (HgCl or $HgNO_3$) (µg/L)	Methylmercury (µg/L)
ACUTE (LC_{50})		
Fresh water invertebrates	2.2 (cladoceran) to 2,000 (insect larvae)	Not available
Fresh water fish	30 (guppy) to 1,000 (tilapia)	Not available
Rainbow trout	155 to 420	24 to 84
Fresh water AWQC[a]	2.4 (total mercury)	
Salt water invertebrates	3.5 (mysid) to 400 (soft clam)[b]	Not available
Salt water fish	36 (juvenile spot) to 1,678 (flounder)[c]	51.1 (mummichog)
Salt water AWQC[a]	2.1 (total mercury)	
CHRONIC		
Fresh water invertebrates	0.96 (cladoceran) to 1.287 (cladoceran)	< 0.04 (cladoceran)
Fresh water fish	< 0.23 (minnow) to < 0.26 (minnow)	0.29 (brook trout) to 0.93 (brook trout)
Fresh water AWQC[a]	0.012 (total mercury)	
Salt water invertebrates	1.131 (mysid)	Not available
Salt water AWQC[a]	0.025 (total mercury)	

[a] AWQCs are designed to be protective of the aquatic community as a whole.
[b] As cited in U.S. EPA, 1985, LC_{50}s of 10,000 and 8,700 µg/L for Atlantic clams (*Rangia cuneata*) were reported by Olson and Harrell (1973), but Dillon (1977) reported LC_{50} values of 58 and 122 µg/L for the same clam species.
[c] As cited in U.S. EPA, 1985, an LC_{50} of 2,000 µg/L for mummichogs was reported by Klaunig et al. (1975), but Dorfman (1977) and Eisler and Hennekey (1977) reported LC_{50} values of 800 µg/L or less for the same fish species.

Source: U.S. EPA, 1985 except where otherwise noted.

2.3.2.3 Individual Effects on Birds

Methylmercury has been shown to be more toxic to birds than inorganic mercury. Mercury poisoning in birds is characterized by muscular incoordination, falling, slowness, fluffed feathers, calmness, withdrawal, hyperactivity, hypoactivity and eyelid drooping (reviewed by Eisler, 1987; Fimreite, 1979; Scheuhammer, 1987, 1991). Acute oral toxicity studies using methylmercury yielded LD_{50} values ranging from 2.2 to 23.5 μg/g for mallards (*Anas platyrhynchos*), 11.0 to 27.0 μg/g for quail (*Coturnix*) and 28.3 μg/g for northern bobwhite (*Colinus virginianus*). Some bird kills have occurred, generally due to ingestion of mercury-based fungicides applied to grain. Whole-body residues of mercury in acutely poisoned birds usually exceed 20 μg/g fresh weight and have been found up to 126 μg/g. Mercury levels observed in such cases are generally highest in the brain, followed by the liver, kidney, muscle and carcass.

Sublethal effects of mercury on birds include liver damage, kidney damage, neurobehavioral effects, reduced food consumption, weight loss, spinal cord damage, effects on enzyme systems, reduced cardiovascular function, impaired immune response, reduced muscular coordination, impaired growth and development, altered blood and serum chemistry, and reproductive effects (Eisler, 1987; Scheuhammer, 1987, 1991; MDNR, 1993). Reproductive effects, however, are the primary concern for avian mercury poisoning and can occur at dietary concentrations well below those that cause overt toxicity.

Scheuhammer (1991) concluded that on the basis of laboratory dose-response studies (Heinz, 1976a; Finley and Stendell, 1978) piscivorous birds consuming diets containing >1 μg/g (dry weight) methylmercury in their diet (approximately 0.25 μg/g wet weight) will accumulate >20 μg/g (dry weight) in their feathers. Similar levels in both spiked diets (Heinz, 1974, 1976a,b, 1979) and natural prey sources (Barr, 1986) have been shown to be toxic to birds. Thus, it appears that mercury levels in feathers exceeding 20 μg/g should be interpreted as evidence for possible toxic effects. Eisler (1987) recommended that 5.0 μg/g fresh weight in feathers be used as a criterion for the protection of birds.

Tissue mercury concentrations that are associated with toxicity in birds are remarkably similar despite differences in species, dietary exposure level and length of time necessary to produce the effect (Scheuhammer, 1991). Frank neurological signs are generally associated with brain mercury concentrations of 15 μg/g (wet weight) or higher, and 30 μg/g or more in liver and kidney. Liver mercury concentrations of 2-12 μg/g (wet weight) were associated with reproductive impairment in adult pheasants and mallard ducks (Fimreite, 1971; Heinz, 1976a,b). Mortality was observed in newly hatched ducklings with brain mercury concentrations of 3-7 μg/g (wet weight), while levels four times these values are required to cause mortality in adults (Stoewsand et al., 1974; Finley et al., 1979; Scheuhammer, 1988).

Reproductive impairment has been observed in laboratory studies when mercury concentrations in eggs exceed 0.5 μg/g (Fimreite, 1971; Heinz, 1974, 1976a,b, 1979). Field studies tend to confirm these results. Reproductive impairment in the loon was associated with mercury levels in eggs ranging from 2-3 μg/g (Barr, 1986). Adverse effects on hatching and fledging were observed when mercury concentrations in the eggs of common terns exceeded 3.6 μg/g (Fimreite, 1974). Mercury appeared to be a contributing factor to reduced reproductive success in raptors at some locations (Odsjö, 1982; Evans, 1986). In one study, however, hatching in herring gulls appeared to be unaffected, despite the fact that eggs contained upwards of 10 μg/g of mercury (Vermeer et al., 1973). Lowest-observed-adverse-effect level (LOAEL) and no-observed-adverse-effect level (NOAEL) values for effects of

methylmercury on avian wildlife are derived in Section 4.2.2 of this Report. Possible effects on populations of selected avian species are discussed in Section 2.3.3.

2.3.2.4 Individual Effects on Mammals

Extensive research on the toxicity of mercury to mammals indicates that effects vary depending on the form of mercury ingested or inhaled. Inorganic mercury is corrosive, and acute exposure to humans and other mammals may cause burning, irritation, salivation, vomiting, bloody diarrhea, upper gastrointestinal tract edema, abdominal pain, and hemorrhaging (Klaassen et al., 1986). Ingestion of mercurial salts in large doses may cause kidney damage. The main toxic effects due to ingestion of organic mercurials are neurological effects such as paresthesia, visual disturbances, mental disturbances, hallucinations, ataxia, hearing defects, stupor, coma and death (Klaassen et al., 1986).

The differences between the toxicity of different forms of mercury was exemplified in a study by Aulerich et al.(1974) using mink (*Mustela vison*) given either 5 ppm methylmercury (in food) or 10 ppm mercuric chloride. Mink treated with methylmercury died within 30 days, while those treated with mercuric chloride suffered no ill effects. Methylmercury attacks the central nervous systems in mammalian wildlife as well as in humans. The nervous system of the developing fetus may be particularly vulnerable (Bakir et al., 1973), and concern for these effects tends to drive human health risk assessments for mercury (Clarkson, 1990; reviewed in Volume IV of this Report). Methylmercury ingestion can also cause reduced food intake, weight loss, muscular atrophy and damage to the animal's heart, lungs, liver, kidneys or stomach (Klaassen et al., 1986; MDNR, 1993).

Levels of exposure that induce mercury poisoning in mammals vary among species. For sensitive mammals, effects can occur at a dose of 0.25 μg/g bw/d, or 1.1 μg/g in the diet (Eisler, 1987). Death occurs in sensitive mammal species at 0.1-0.5 μg/g bw/d, or 1.0-5.0 μg/g in the diet. Smaller animals (e.g., minks, monkeys) are generally more susceptible to mercury poisoning than are larger animals (e.g., mule deer, harp seals), perhaps because of differences in elimination rates. Also, smaller mammals eat more per unit body weight than larger mammals and, thus, may be exposed to larger amounts of mercury on a body weight basis. LOAEL and NOAEL values for effects of methylmercury on mammalian wildlife are derived in Section 4.2.2 of this Report.

2.3.3 Population Effects

Mercury contamination has been documented in endangered species such as the Florida panther and the wood stork, as well as in populations of loons, eagles and furbearers such as mink and otters. These species are at high risk of mercury exposure and effects because they either are piscivores or eat piscivores.

2.3.3.1 Loon Populations

It has been suggested by several researchers that loons are at risk from mercury contamination in aquatic food chains. Loons are primarily piscivorous but also consume benthic macroinvertebrates, such as crayfish, when water is too turbid for catching fish (Barr, 1973). Mercury levels in crayfish approach and may even exceed those of prey fish from the same lakes (Barr, 1986). Concern for the loon is due also to the fact that much of its summer range coincides with areas that are known to be susceptible to acid deposition. As noted previously, a negative correlation often exists between the pH of surface water and mercury concentrations in fish.

The most comprehensive study of mercury toxicity in wild loons was conducted by Barr (1986). Loons were collected from three habitats within the Wabigoon River watershed (Ontario, Canada) both above and below a chlor-alkali plant which discharged mercury into the river system. The first habitat (designated C1) consisted of the lakes and river directly downstream of the plant. Habitat C2 did not receive mercury discharges but was accessible to mercury-contaminated fishes which originated in C1. Habitat C3 was upstream from the chlor-alkali plant and received no appreciable mercury from other sources. Contaminated fish were prevented from entering C3 by a waterfall. A nearby habitat (C4), not connected to the other three habitats, received no mercury contamination and served as a control. Human disturbances in all habitats were determined to be minimal, and concentrations of organochlorine contaminants were low (less than 0.02 ppm total for all pesticides, including all DDT metabolites, and 0.04 ppm for PCBs).

Barr (1986) found a strong negative correlation between mercury levels in water and reproductive success in loons as far as 160 km downstream from the mercury source. Mercury in prey fish and invertebrates declined with increasing distance from the mercury source but contaminated fish were able to migrate into the uncontaminated C2 habitat. Mercury levels in loon tissues (eggs, liver, muscle and brain in both adults and chicks) were highest in the C1 habitat but were also elevated in the C2 habitat, presumably because loons were feeding on contaminated prey which migrated from C1. Mercury levels in loons from habitat C3 (upstream from mercury source and inaccessible to contaminated fish) were comparable with levels from the uncontaminated control habitat, C4. With the exception of the liver, most of the mercury in loon tissues was in the form of methylmercury. Mercury in the liver appeared to be inorganic, suggesting the existence of a demethylation pathway. Dose-response relationships appeared to exist between mercury in both prey and various tissues, and reproductive success. For example, reductions in egg laying and in nest site and territorial fidelity were associated with prey containing mean mercury concentrations in the range of 0.3-0.4 μg/kg. Reproductive success was also reduced in loons with brain or egg levels of 2-3 μg/kg, and in loons with liver residues above 13 μg/g. No loons reproduced successfully where prey species contained mercury at levels greater than 0.4 μg/kg.

Ensor et al. (1992) captured 93 loons and collected 128 dead or dying loons from 18 northern and central counties in Minnesota. Feathers were collected from live loons. Feathers and liver tissue were collected from the dead loons. In 22 percent of the liver samples, mercury concentrations exceeded the level (13 μg/g) associated by Barr (1986) with impaired reproduction. Adult loons contained greater concentrations of mercury (8.7 vs. 2.7 μg/g in feathers and 6.6 vs. 1.1 μg/g wet weight liver) than juvenile loons, as expected for a contaminant which bioaccumulates. The mercury in the juvenile loons was considered to be representative of local mercury contamination since all of their food would have been obtained from lakes within Minnesota. Mercury in adult loons was thought to represent contributions from both the summering (Minnesota) and wintering (Gulf of Mexico) grounds.

Ensor et al. (1992) concluded that juvenile loons which died of disease had significantly higher mercury levels in feathers than juvenile loons which died from injury or which were caught alive. Emaciated loons also had significant elevations of mercury in both feathers and liver (significance level not reported). It was not clear whether elevated mercury in emaciated loons resulted from concentration of existing mercury stores while body fat and protein were catabolized or whether mercury contributed to the emaciation. The authors concluded that evidence of adverse impacts on the Minnesota loon population was sufficient to recommend monitoring of loon populations and mercury levels.

Working in north central Wisconsin, Belant and Anderson (1990) collected both live and dead loons and addled eggs from abandoned nests. Mercury residues and 14 organochlorine pesticides were measured in feathers (live and dead loons), brain, muscle, and liver (dead loons). The conclusions reported in this study were similar to those reached by Ensor et al. (1992). Pesticide concentrations in dead loons were relatively low. In contrast, mercury levels in liver (mean concentration of 40.9 μg/kg wet weight) exceeded those reported by Barr (1986) to be associated with reproductive dysfunction.

Scheuhammer and Blancher (1994) reported mercury levels in fish sampled from lakes throughout Ontario, Canada in areas without known point sources of mercury. Up to 30 percent of the lakes contained fish with mercury levels which exceeded 0.3 μg/kg (wet weight), which Barr (1986) had shown previously to be associated with reproductive impairment in loons. The lack of any identified point source of mercury contamination was considered by the authors to be indirect evidence of airborne deposition of mercury over large portions of Ontario.

The viability of loon populations within their traditional habitats in the United States is unclear. None of the studies reviewed was able to demonstrate clear population declines on a regional or national basis. Several well conducted studies have found that substantial numbers of loons sampled contained mercury at or above levels demonstrated to reduce reproductive success. It has also been suggested (but not clearly demonstrated) that sublethal effects of mercury exposure may produce greater susceptibility to environmental stresses including other contaminants. Mercury also may make loons more susceptible to secondary infections, especially during stressful activities such as molting and migration. Investigations in response to a die-off of over 2,500 loons in the Gulf of Mexico in 1983 found that elevated levels of mercury were associated with abnormally high infestations of parasites (Barr, 1986).

2.3.3.2 Eagle Populations

Bald eagles are distributed throughout the United States. Many migrate into the lower forty-eight states only during the winter months; others are resident throughout the year. Bald eagles, like several other avian species, are thought to have been adversely impacted by DDT and its metabolites. Because of their status as a federally listed "threatened" species, the potential for mercury exposure to pose a threat to eagle survival and recovery is a concern.

Researchers have measured mercury residues in bald eagle feathers (U.S. FWS, 1993; Welch, 1994; Bowerman, 1994), eggs (Grier, 1974; Wiemeyer et al., 1984, 1993; Grubb et al., 1990; Anthony et al., 1993) and blood (Anthony et al., 1993; U.S. FWS, 1993; Welch, 1994). Several of these studies have also included analyses of eagle tissue for other contaminants which might threaten eagle reproduction.

Wiemeyer et al. (1984) sampled bald eagle eggs that had failed to hatch from nests located in 14 states between 1969 and 1979; eggs were tested for organochlorine residues and mercury. The highest levels of mercury were detected in eggs from Maine. Eight organic contaminants were significantly, negatively correlated with eggshell thinning, a trait often linked with reproductive failure in birds. When mercury levels were compared with the mean 5-year production rate for eagle nests, a weak negative correlation was suggestive of an adverse effect of mercury. The effect was confounded, however, by the co-occurrence of DDE in many of the eggs with the highest mercury levels. The authors concluded that mercury contamination appears to have the potential for adverse effects on eagle production in only a few of the breeding areas sampled, primarily in Maine.

Continuing the work begun earlier, Wiemeyer et al. (1993) collected eggs that had failed to hatch from 15 states between 1980 and 1984 and analyzed them for organochlorine pesticides, polychlorinated biphenyls (PCBs) and mercury. These data were then combined with the data collected previously (Wiemeyer et al., 1984). As before, DDE was the contaminant most significantly (negatively) correlated with eggshell thinning, with DDD, DDT and PCBs significantly but less strongly correlated. The highest levels of DDE, PCBs and mercury occurred in eggs collected in Maine. Mercury levels in eagle eggs, at or above 0.28 μg/g (wet weight), were significantly correlated with a reduction in mean 5-year production rate for eagle nests. This value compares with a value of 0.5 μg/g derived earlier (Wiemeyer et al., 1984). The authors noted, however, that only three egg samples (all from Maine) contained mercury levels greater than 0.5 μg/g and that these eggs also contained levels of DDE (>6 μg/g) known to reduce eagle productivity. Wiemeyer et al. (1993) concluded that recent data provide even less evidence than previously indicated (Wiemeyer et al., 1984) that contaminants other that DDE are adversely impacting bald eagle productivity. Grubb et al. (1990), Grier (1974) and Anthony et al. (1993) reached similar conclusions on the lack of evidence for an association of mercury levels with reproductive failure in bald eagles.

Bowerman and co-workers (Bowerman, 1993; Bowerman et al. 1994) examined the productivity of bald eagles in six geographic regions, including Lakes Superior, Michigan, Huron, and Erie, and the states of Michigan and Minnesota. Significant negative correlations existed between PCB and p,p'-DDE in plasma and reproductive success. Mercury levels in feathers ranged from 9.0 to 23.4 μg/g; there was no correlation with reproductive success.

Welch (1994) sampled eggs, blood and feathers from Maine bald eagles and analyzed for organochlorine pesticides, PCBs, TCDD equivalents (TCDD-eq) and mercury. Mercury levels in inland eagles were higher than concentrations in eagles inhabiting the coastline. In general, these elevated mercury levels appeared to be related to mercury residues in fish from the two areas. Productivity was also lower for inland eagle nests; however, the correlation of mercury levels in blood and feathers with mean productivity (5 and 15 yr) was not significant.

One of the difficulties in evaluating the effect of mercury on the bald eagle is the co-occurrence of organochlorine compounds such as PCBs, DDE and TCDDs at levels which are known to affect reproduction adversely. Bowerman (1993) pointed out that the effect of the organochlorine contaminants may be masking the effect of mercury. The U.S. Fish and Wildlife Service (1993) also suggested that while mercury was not found in Florida bald eagles at lethal levels, undetected sublethal effects may be adversely affecting eagle reproduction.

2.3.3.3 Wood Stork Populations

Mercury has been detected in feathers of the endangered wood stork, although the levels detected apparently have not caused toxic effects. Young wood storks in Florida had mercury levels of 1.87 μg/g dry weight; higher mercury levels would be expected for adults from the same area (Burger et al., 1993). Fleming et al. (1984) reported mercury levels of 0.66 μg/g wet weight in wood stork eggs, which is somewhat less than Eisler's (1987) recommended criterion of <0.90-2.0 μg/g wet weight in eggs.

2.3.3.4 Furbearer Populations

In one Ontario incident, an eagle was found scavenging on a mercury-poisoned dead otter at Clay Lake (Wren, 1985). Mercury levels in the otter (liver - 96 μg/g; kidneys - 58 μg/g; brain - 30

μg/g) were well above those known to be toxic to otters in laboratory exposures. The primary source of the mercury was a chlor-alkali plant that discharged mercury directly into the river. Although population data were not collected, a Native American had discontinued trapping in the area because furbearers such as otters and mink had disappeared, providing anecdotal evidence of population declines. Because other stressors could also be present (such as hunting pressure and habitat loss or degradation), the role of mercury in contributing to any furbearer population declines is uncertain.

In a separate incident, a mink exhibiting unnatural behavior was collected near the mercury-contaminated Saskatchewan River (Wobeser and Swift, 1976). Subsequent determination of mercury levels in the liver (58 μg/g), kidney (32.9 μg/g), muscle (15.2 μg/g), brain (13.4 μg/g) and fur (34.9 μg/g), combined with clinical and pathologic findings, were deemed sufficient by the authors to conclude that the animal had been poisoned by mercury. Residue levels found in this animal exceeded those determined in laboratory studies to be associated with toxicity. The origins of mercury in this case could not be determined; however, it was suggested that fish from the Saskatchewan contain mercury at concentrations higher than those known to cause toxicity to mink.

In a study of furbearers obtained from trappers (1972-1975) in the Wisconsin River watershed, otters contained the highest tissue mercury levels, followed by minks, raccoons, foxes, muskrats and beavers (Sheffy and St. Amant, 1982).

2.3.3.5 Florida Panther Populations

Mercury is suspected of contributing to population declines of the endangered Florida panther (*Felis concolor coryi*). The Florida Panther Interagency Committee (FPIC, 1989) reported that approximately 100 ppm of mercury was detected in the liver and 130 ppm in the hair of a 4-year-old female panther. The panther, No. 27, had been radio-instrumented since 1988 and was found dead in the eastern part of the Florida Everglades National Park (FPIC, 1989). Relatively high levels of mercury (0.005-20.0 ppm) were detected in archived liver samples from six dead panthers, and levels ranging from 0.02-130.0 ppm have been measured in the hair samples from ten live individuals. Cause of death of the six archived animals was not mentioned in this Report. The FPIC concluded, however, that panther No. 27 died of mercury poisoning.

The most probable source of mercury contamination in Florida panthers is via the food chain. The diet of the Florida panther varies greatly depending on prey availability; however, mercury contamination in raccoons has been documented to occur in a distributional pattern similar to that of Florida panthers (Roelke et al., 1991). The accumulation of mercury in raccoons is thought to be due in turn to consumption of contaminated aquatic life, including invertebrates, fish and amphibians. The panthers most at risk, therefore, appear to be those that consume mercury-contaminated raccoons. Panthers which prey on deer are less exposed to mercury because deer are herbivores and accumulate less mercury. Based upon the findings of the FPIC, habitat modifications have been implemented in the Florida Everglades to increase forage for deer.

In addition to increasing mortality, mercury contamination could decrease reproductive success in the Florida panther. Methylmercury ingested by a pregnant mammal passes through the placenta to the developing fetus, potentially causing abortions, stillbirths, congenital defects and behavioral modifications that result in early neonatal death. Roelke et al. (1991) found a significant inverse correlation between mercury concentrations in mother panthers and survivorship of the young. Because so few Florida panthers remain (only 30 to 50 in the wild) (Jordan, 1990), the possibility

exists that mercury contamination could contribute to the extinction of this endangered species (Roelke et al., 1991).

2.3.4 Communities and Ecosystems

2.3.4.1 Aquatic Communities and Ecosystems

Effects of contaminants on aquatic communities have been investigated by examining functional and structural responses of natural assemblages in laboratory settings to toxic substances added singly or in combination. The species diversity of freshwater and brackish-water microbial communities was reduced by exposure to 40 µg/L of mercuric chloride (Singleton and Guthrie, 1977). Carbon fixation was reduced by 50 percent in freshwater phytoplankton communities exposed to 0.4 µgL of mercuric chloride, but this effect was mitigated by the presence of humus or sediment (Hongve et al., 1980). Mercuric chloride (0.5 µg/L) administered to a marine aquatic community inhibited phytoplankton growth, killed or retarded development in copepods and increased the number of viable bacteria (Kuiper, 1981). The species composition of the phytoplankton also changed, possibly due to selective reduction of predation by the copepods. Bacterial populations may have increased due to increased food supply in the form of dead phytoplankton (Kuiper, 1981).

In general, mercury concentrations (as Hg^{+2}) required to elicit toxic effects on natural aquatic communities exceed those commonly measured in surface waters by two or more orders of magnitude (low ng/L in waters not impacted by point source discharge; Spry and Wiener, 1991; Wiener and Spry, 1995). Studies of the effects of methylmercury on aquatic assemblages were not found, however, and it can be reasonably anticipated that the toxicity of methylmercury to these communities would exceed that of mercuric chloride. Effects of mercury or any other substance at this level of biological organization could potentially have far-reaching impacts on the entire food chain by changing both nutrient and energy fluxes.

Field studies of mercury occurrence and effects at the community level are not available. Moreover, interpreting field studies can be difficult because more than one stressor is often present. For example, high concentrations of toxic substances including mercury have been found in various locations in the Great Lakes, and several species of piscivorous wildlife have suffered or continue to suffer reduced reproductive success and population declines in these areas (e.g., Caspian terns, herring gulls, double-crested cormorants, mink) (Peakall, 1988; Colborn, 1991; Environment Canada, 1991; Gilbertson et al., 1991). Other bioaccumulative contaminants present in high concentrations, such as PCBs, dioxins and DDT/DDE have been implicated as the most likely cause in most reported cases (Colborn, 1991; Gilbertson et al., 1991).

2.3.4.2 Terrestrial Communities and Ecosystems

As noted previously, atmospherically deposited heavy metals such as mercury tend to accumulate in top soils. This results in particularly high exposures in decomposer communities, which play a crucial role within the natural nutrient cycles of terrestrial ecosystems. Mercury forms stable complexes with organic substances of high molecular weight (humic acids) and, thus, exhibits limited mobility within soils, posing a cumulative risk to soil biological activity. Processes that may be affected by heavy metals in the top soil include soil type, litter decomposition, carbon mineralization, nitrogen transformation and enzyme activity. Mercury effects on soil microorganisms vary depending on soil type (Zelles et al., 1986). Mercury generally inhibits ATP, heat production, respiration and iron reduction by soil microorganisms in sandy soils and, to a lesser extent, in clay. At some

intermediate concentrations, however, mercury may stimulate microbial activity in peat (Zelles et al., 1986).

It is difficult to estimate specific toxic levels for microbial-mediated processes and decomposer communities, due to widely differing soil properties and methodological discrepancies in the literature. In a report on mercury in the Swedish environment, Lindqvist (1991) cites a study in which soil microbial activity was significantly reduced at mercury concentrations ranging from 0.06-0.08 μg/g dry weight of humus. The concentration of mercury in forest soils in Sweden is in the range 0.01-0.09 μg/g. In a second cited study, however, the mercury concentration in soil required to reduce soil microbial activity was 50 μg/g. A common effect of metal contamination in soil animal groups is a decrease in species diversity. In some species, susceptibility to metals is thought to be a secondary effect due to differences in food availability rather than metal toxicity per se.

2.3.5 Conclusions

Of the pathways by which ecosystems and components of ecosystems might be exposed to atmospheric mercury, exposure of high trophic level wildlife to mercury in food is particularly important. The trophic level and feeding habits of an animal influence the degree to which that species is exposed to mercury. Mercury biomagnifies in aquatic food chains with the result that tissue concentrations of mercury increase as trophic levels increase. Predatory animals primarily associated with aquatic food chains accumulate more mercury than those associated with terrestrial food chains. Thus, piscivores and other carnivores that prey on piscivores generally have the highest exposure to mercury. In a study of furbearing mammals in Wisconsin, the species with the highest tissue levels of mercury were otter and mink, which are top mammalian predators on aquatic food chains (Sheffy and St. Amant, 1982). Top avian predators of aquatic-based food chains include raptors such as the osprey and bald eagle. Smaller birds feeding at lower levels in aquatic food chains also may be exposed to substantial amounts of mercury because of their high food consumption rate (consumption/d/g of body weight) relative to larger birds.

Although clear causal links have not been established, mercury originating from airborne deposition may be a contributing factor to population effects on bald eagles, river otters and mink. Stronger evidence is available to support the possibility of toxic effects on the common loon and the Florida panther. Effects of mercury originating from point sources on restricted wildlife populations have been conclusively demonstrated and provide a tissue residue basis for evaluation of risk to other populations. Based upon reviews of both laboratory and field data, mercury levels that exceed the following values (in μg/g fresh weight) have been suggested as evidence for possible adverse impacts on avian populations: feathers - 20 μg/g (Scheuhammer, 1991); eggs - 2.0 μg/g (Scheuhammer, 1991; after conversion from dry weight); liver - 5 μg/g (Zillioux et al., 1993). Such criteria must be used with caution, however, as residue thresholds both above and below these values have been reported. Field data for mammals are not as extensive as those for birds; they appear to be in as good agreement with laboratory data. Mercury residues in mink and otter that were thought to have been poisoned by mercury originating from a point source exceeded those seen in dead laboratory animals by a factor of two or more (Wren, 1991; see Section 2.3.2.4). The reason for this variation is not presently known. Additional information is needed before tissue-residue-based criteria for piscivorous mammals can be developed. Criterion values for fish and water that are designed to be protective of piscivorous wildlife are calculated in Section 4.2 of this Volume.

2.4 Ecosystems Potentially at Risk

The information presented in Sections 2.2 and 2.3 suggests that the ecosystems most at risk from mercury releases to air exhibit one or more of the following characteristics:

- They are located in areas where exposure to mercury (e.g., atmospheric deposition of mercury) is high;
- They include surface waters already impacted by acid deposition;
- They possess characteristics other than low pH that result in high levels of bioaccumulation; and/or
- They include sensitive species.

2.4.1 Highly Exposed Areas

Ecosystems subject to high levels of mercury deposition (e.g., near sources of mercury emissions, in areas with high deposition rates) will be more exposed to mercury than ecosystems with lower levels of mercury deposition. The pattern of mercury deposition nationwide, therefore, will influence which ecoregions and ecosystems might be exposed to hazardous levels of mercury.

2.4.2 Lakes and Streams Impacted by Acid Deposition

In many aquatic systems the tendency for mercury to bioaccumulate in fish appears to be inversely correlated with pH and alkalinity (or acid neutralizing capacity) (reviewed by Spry and Wiener, 1991). Thus, fish in acidic lakes (pH 6.0 to 6.5 or less) often have higher body or tissue burdens of mercury than fish in nearby lakes with higher pH. This relationship has been found for a variety of fish species and water bodies, including the following:

- various fish species in 14 lakes and 31 streams in Florida (FDER, 1990);
- yellow perch from lakes in the Upper Michigan peninsula (Grieb et al., 1990);
- yellow perch from seepage lakes in Northern Wisconsin (Cope et al., 1990);
- yellow perch from an experimentally acidified lake in Northern Wisconsin (Wiener et al., 1990);
- yellow perch from Southern Ontario lakes (Suns and Hitchin, 1990);
- walleyes from Wisconsin lakes (Lathrop et al., 1991);
- largemouth bass from 53 lakes in Florida (Lange et al., 1993);
- northern pike from 80 Minnesota lakes (Sorensen et al., 1990); and
- smallmouth bass from Ontario lakes (McMurtry et al., 1989).

The increased accumulation of mercury in low pH lakes appears to be due largely to increased microbial production of methylmercury (Xun et al, 1987; Bloom et al., 1991; Miskimmin et al., 1992), although biogeochemical processes that release mercury from sediments have also been implicated (Rada et al., 1993). The bioavailability of methylmercury is probably also enhanced by decreased levels of calcium, as is typical of such lakes. Exceptions to the general relationship between pH and bioaccumulation of mercury exist, however (Fjeld and Rognerud, 1993).

2.4.3 Factors in Addition to Low pH that Contribute to Increased Bioaccumulation of Mercury in Aquatic Biota

Numerous factors in addition to low pH can influence the bioaccumulation of mercury in aquatic biota. These include length of the aquatic food chain, temperature (Bodaly et al., 1993), and other water chemistry parameters (e.g. dissolved organic material; McMurtry et al., 1989; Nilsson and Hakanson, 1992; Fjeld and Rognerud, 1993). Physical and chemical characteristics of a watershed affect the amount of mercury that is translocated from soils to water bodies (McMurtry et al., 1989, Johnston et al., 1991; Joslin, 1994). Interrelationships between these factors are poorly understood, however, and there is no single factor (including pH) that has been correlated with mercury bioaccumulation in all cases examined.

2.4.4 Sensitive Species

For the purpose of this discussion, sensitive species are defined as those species that are more likely than others to experience adverse effects due to mercury contamination. Such species may or may not be inherently more sensitive on an absorbed dose basis. Sensitive species also may be at risk because they receive high methylmercury exposures due to their position in the food chain, or because their populations are already stressed. In the first category are top-level predators of aquatic-based food webs exposed to high concentrations of mercury in their prey. Examples include raptors (e.g., bald eagles, ospreys) and piscivorous waterbirds (e.g., herons, gulls, terns, cormorants). The second category includes threatened and endangered species, which are species that have already experienced severe population declines and are at risk of further population declines or extinction.

2.5 Endpoint Selection

Endpoints for Ecological Risk Assessment

Assessment endpoint - an explicit expression of the environmental value that is to be protected (U.S. EPA, 1992a).

Measurement endpoint - a measurable ecological characteristic that is related to the valued characteristic chosen as the assessment endpoint. Measurement endpoints are often expressed as the statistical or arithmetic summaries of the observations that comprise the measurement (U.S. EPA, 1992a).

A goal of the problem formulation phase in an ecological risk assessment is to select ecological endpoints that are relevant to decisions to be made. An endpoint is defined as a characteristic of an ecological component (e.g., increased mortality in fish) that may be affected by exposure to a stressor (U.S. EPA, 1992a). Ecological endpoints can be chosen at any level of biological organization, from biochemical and cellular levels through individuals, populations, communities, and ecosystems (U.S. EPA, 1992a).

U.S. EPA distinguishes two types of endpoints for ecological risk assessment purposes: assessment endpoints and measurement endpoints (see text box). Assessment endpoints are explicit expressions of the actual environmental value that is to be protected. Usually the assessment endpoint

cannot be measured directly, so a risk assessor selects a measurement endpoint (or a group of measurement endpoints) that can be related, either quantitatively or qualitatively, to the assessment endpoint (U.S. EPA, 1992a).

Table 2-8 provides examples of ecological assessment and measurement endpoints at various levels of biological organization. In current practice, the most tractable endpoints are at the individual or population level and include mortality, growth and development and reproduction.

Table 2-8
Examples of Assessment and Measurement Endpoints

Level of Organization	Assessment Endpoints	Measurement Endpoints
Ecoregion[a]	Biodiversity Regional production Landscape aesthetics	Habitat area Regional production Other landscape descriptors
Ecosystem	Productive capability Nutrient balance Soil balance	Habitat area Biomass Productivity Nutrient export
Community	Recreational quality Change to less useful/desired type Market/sport value	Species number Species evenness Species diversity Market/sport value Saprobic index
Population	Extinction Abundance Yield/production Frequent gross morbidity Massive mortality Range	Occurrence Numbers/density Age structure Fecundity Yield/production Frequency of gross morbidity Mortality rate
Individual	Survival Growth and development Reproduction Good physical condition	Longevity Growth and development Fecundity Overt symptomology Biomarkers
Abiotic	Habitat quality	Temperature Water flow Soil characteristics Sediment characteristics

Source: Adapted from U.S. EPA, 1989.

[a] An ecoregion is an area (region) of relative homogeneity in ecological systems (based on elevation, soils, latitude, precipitation).

Based on the information provided in Sections 2.1 through 2.4, the ecological components that appear to be most at risk from atmospheric mercury are piscivorous mammals and birds that feed at or near the top of aquatic food chains. This is particularly true of threatened or endangered species that already have suffered severe population declines due to one or more causes. An appropriate assessment endpoint, therefore, would be maintenance of self-sustaining populations of these species. Appropriate measurement endpoints for exposed wildlife species would include growth and survival of adults or other life-stages, and reproductive success. Alternatively, when such data are difficult to collect (or are of questionable utility due to the mode of toxic action), it may be necessary to infer adverse effects on wildlife from laboratory toxicity studies.

2.6 Conceptual Model for Mercury Fate and Effects in the Environment

The final goal of the problem formulation phase in risk assessment is to develop a conceptual model of how the stressor may affect ecological components of the natural environment (U.S. EPA, 1992a). The conceptual model identifies the ecosystem(s) potentially at risk, exposure pathways between sources and receptors and the relationship(s) between (the) measurement and assessment endpoints. A preliminary analysis of the ecosystem, stressor characteristics and ecological effects helps to define possible exposure scenarios; that is, qualitative descriptions of how the stressors co-occur with or contact the various ecological components.

A conceptual model of the ecological effects of airborne mercury emissions can be visualized in Figures 2-1 through 2-5. Mercury is emitted to the atmosphere primarily as the elemental form or as an inorganic ion. Inorganic mercury returns to earth in wet deposition due to its relatively high solubility in water and because it adsorbs to airborne particulates. Elemental mercury has a long half-life in the atmosphere and tends to stay aloft but may react with other chemicals to form inorganic mercury species. Wet deposition containing mercury falls on watersheds or directly on water bodies. Mercury deposited to watersheds is rapidly bound to organic matter and tends to accumulate over time. A portion of this mercury is continually released, however, and is transported in runoff and groundwater to receiving waters such as lakes, streams and wetlands. Biotic and abiotic chemical reactions transform mercury in water and associated sediments to organic derivatives (primarily methylmercury). Organomercurial compounds then accumulate in aquatic food chains, due both to their tendency to become sequestered in tissues and to the efficiency with which they are transferred from one trophic level to another. Eventually, mercury in fish is consumed by piscivorous wildlife, with the resulting potential for adverse toxicological effects. Uptake pathways other than consumption of contaminated prey (e.g., inhalation and drinking of contaminated water) are considered to be of little consequence for piscivorous birds and mammals.

3. EXPOSURE OF PISCIVOROUS AVIAN AND MAMMALIAN WILDLIFE TO AIRBORNE MERCURY

3.1 Objectives and Approach

The objective of this analysis was to characterize the extent to which piscivorous wildlife are exposed to mercury originating from airborne emissions. Four general approaches were used, which may be described as follows.

1. Estimation of current average exposure to piscivorous wildlife on a nationwide basis (Section 3.3).

Estimates of current mercury exposure to selected piscivorous wildlife species were calculated as the product of the fish consumption rate and measured mercury concentrations in fish. This was not intended to be a site-specific analysis, but was instead intended to provide national exposure estimates for piscivorous wildlife based on typical mercury concentrations in fish. This analysis utilized mean total mercury measurements from a nationwide study of fish residues and published fish consumption data for the selected wildlife species.

2. Estimation of mercury levels in fish using measured deposition values and an indirect exposure methodology (Section 3.4).

Mercury levels in fish were estimated by using measured mercury deposition values as inputs to an indirect exposure model (IEM2). Additional inputs to the IEM2 model include the characteristics of a hypothetical lake and its associated watershed. The analysis was conducted for two such lakes, one located in the Western U.S., the other located in the Eastern U.S. Residue values were calculated as the product of predicted mercury concentrations in water and estimated BAF values for fish in trophic levels 3 and 4.

3. Estimation of mercury deposition on a regional scale (40 km grid), and a comparison of these data with species distribution information (Section 3.5).

A long-range atmospheric transport model (RELMAP) was used in conjunction with a mercury emissions inventory to generate predictions of mercury deposition across the continental U.S. This information was then compared with wildlife species distributions to characterize the potential for co-occurrence of high mercury deposition rates and the presence of wildlife species of concern. Additionally, mercury deposition data were superimposed onto a map of surface waters impacted by acid deposition, since it has been shown that low pH values are positively correlated with high levels of mercury in fish.

4. Estimation of mercury deposition on a local scale in areas near emissions point sources (Section 3.6).

A local-scale atmospheric transport model (COMPDEP) was used to simulate mercury deposition originating from six different mercury emissions source classes. The analysis was conducted for two hypothetical lakes located in the Western and Eastern U.S. The proximity of these lakes to the source was varied to examine the effect of this parameter on model predictions. To account for the long-range transport of emitted mercury, the 50th percentile RELMAP atmospheric concentrations and deposition rates were included in the estimates from the local air dispersion model.

3.2 Computer Models

The models used for the wildlife exposure assessment are identical to those used for the human health assessment and are described in detail in Volume III of this Report. Atmospheric transport models were used to simulate the deposition of mercury at two different geographical scales (Table 3-1). A regional-scale analysis was conducted using the Regional Lagrangian Model of Air Pollution (RELMAP). RELMAP calculates annual mean air concentrations and annual mean deposition rates for each cell in a 40 km grid. This analysis covered the 48 contiguous states and was based upon a recent inventory of mercury emissions sources (presented in Volume II of this Report). A local-scale exposure analysis was conducted by using both RELMAP and a local air transport model, COMPDEP, to generate hypothetical exposure scenarios for six source classes. COMPDEP is designed to estimate deposition originating from local point sources (<40 km from the receptor). For this analysis, COMPDEP results were summed with those from the RELMAP analysis, which in this case can be thought of as providing the regional "background" to which local source material was added. Three exposure scenarios were evaluated corresponding to lakes located 2.5, 10, and 25 km from the emissions source. In each case, deposition information was used to estimate mercury concentrations in water, averaged over the entire lake.

Table 3-1
Models Used to Predict Mercury Air Concentrations, Deposition Fluxes and Environmental Concentrations

Model	Description
RELMAP	Predicts average annual atmospheric mercury concentration and wet and dry deposition flux for each 40 km^2 grid in the U.S. due to all anthropocentric sources of mercury in the U.S.
COMPDEP	Predicts average concentration and deposition fluxes within 50 km of emission source.
IEM2	Predicts environmental concentrations based on air concentrations and deposition rates to watershed and water body.

The IEM2 model was used to translate both regional and local-scale mercury deposition estimates into mercury levels in soil, water and biota. Mercury levels in fish were calculated from average water concentrations using estimated BAFs for fish occupying trophic levels 3 and 4. It was assumed throughout the wildlife exposure analysis that 100% of mercury contained in fish exists as methylmercury.

The approach used to characterize mercury exposure to piscivorous wildlife is the same as that used to characterize human exposure to mercury from consumption of contaminated fish (Volume III). The same methodology was used to facilitate comparisons between exposure levels to human and wildlife receptors.

3.3 Current Exposure of Piscivorous Wildlife to Mercury

Three avian species (eagle, kingfisher and osprey) and two mammalian species (otter and mink) were assumed to be exposed to methylmercury through the ingestion of contaminated fish. Fish consumption is thought to be the dominant mercury exposure pathway for piscivores (see Section 2). Consequently, an analysis of these ecological receptors' methylmercury contact rate based on the daily ingestion rate of fish is reasonable and appropriate.

The piscivorous bird's or mammal's mercury contact rate from fish consumption can be estimated as the product of mercury levels in the fish and the daily amount of fish eaten. The trophic level at which piscivores feed significantly impacts their exposure to mercury. Those piscivores consuming a diet primarily consisting of trophic level 3 fish are expected to ingest approximately 5 times less methylmercury per gram of fish eaten than those eating trophic level 4 fish from the same site. This assumed that the predator prey factor for trophic level 3 to 4 fish was approximately 5. Animals consuming a mixture of trophic level 3 and 4 fish would experience (on a per gram of fish basis) an intermediate level exposure. Finally, many top level predators are known to consume a mixture of both aquatic and terrestrially-derived prey. In general, mercury levels in the tissues of terrestrial animals are much lower than those of fish. The simplifying assumption can, therefore, be made that most terrestrially-derived prey contain no mercury. A special case exists, however, when a terrestrial animal (e.g., a raccoon) feeds on aquatic biota and is itself preyed upon by a larger terrestrial animal (e.g., the Florida panther). A similar situation exists when a piscivorous bird (e.g., the herring gull) is consumed by a larger bird (e.g., the bald eagle). In these situations, the potential exists for the top predator to obtain a higher mercury dose than it would otherwise receive from a strictly fish-based diet. The extent of this increase would depend in turn upon the proportion of the diet composed of these mammalian and avian prey items, and the extent to which the prey items themselves accumulate mercury in excess of levels found at trophic levels 3 and 4.

Exposure factors for the present analysis were obtained from two recent compilations of wildlife dietary habits (U.S. EPA, 1993a, 1995a) and are shown in Table 3-2. Bald eagles were assumed to eat fish derived from trophic levels 3 and 4, as well as prey derived from other sources. Expressed as percentages, these prey items were assumed to contribute 74, 18 and 8% of the daily dietary intake. For this Report, dietary items other than fish were assumed to contain no mercury. Eagles are, therefore, expected to experience a greater methylmercury exposure per gram of fish consumed than ospreys and kingfishers, which were assumed to consume only trophic level 3 fish. Part of this increase, however, is offset by the contribution of uncontaminated prey consumed by eagles. Similarly, among the mammals, otters, which were assumed to consume an 80/20 mix of trophic level 3 and 4 fish are expected to have a greater methylmercury exposure per gram of fish consumed than mink, which were assumed to eat only trophic level 3 fish. In addition, 10% of the mink diet was assumed to consist of uncontaminated prey items.

The ratio of grams fish consumed per day to piscivore body weight is also significant in estimating mercury exposure on a g/kg bw/d basis. The greater this ratio, the higher the resulting mercury exposure, assuming that methylmercury concentrations in fish remain constant. For example, osprey and kingfishers each consume trophic level 3 fish only. Kingfishers consume an amount of fish equivalent to about 50% of their body weight each day, while osprey consume roughly 20% of their body weights in fish per day. The resulting average daily intake of methylmercury in μg/g body weight will, therefore, be higher in kingfishers. The source of the measured fish residue data was a study entitled "A National Study of Chemical Residues in Fish" conducted by U.S. EPA (1992b) and also reported in Bahnick et al. (1994). This is the only identified nationwide fish collection effort that

Table 3-2
Exposure Parameters for Mink, Otter, Kingfisher, Osprey, and Eagle

Species	Body Wt. (Wt_A) kg	Ingestion Rate (F_A) kg/d	Drinking Rate (W_A) L/d	Trophic Level of Wildlife Food Source	% Diet at Each Trophic Level
Mink	0.80	0.178	0.081	3	90
Otter	7.40	1.220	0.600	3,4	80,20
Kingfisher	0.15	0.075	0.017	3	100
Osprey	1.50	0.300	0.077	3	100
Eagle	4.60	0.500	0.160	3,4	74,18,8

used consistent sampling and mercury measurement techniques. These data are presented in Table 2-2 (Section 2.3.1.2). Based upon these values, national average methylmercury concentrations in fish tissue were determined to be 0.08 μg/g and 0.40 μg/g for fish occupying trophic levels 3 and 4, respectively. Eagles consume approximately 500 g of food per day (U.S. EPA, 1993a, 1995a), 74% of which (370 g/d) consists of trophic level 3 fish, and 18% of which (90 g/d) consists of trophic level 4 fish. Multiplying these consumption rates by the methylmercury concentrations at trophic levels 3 and 4 and dividing by the average weight of an adult eagle (4.6 kg; U.S. EPA, 1993a, 1995a) yields an average daily exposure of approximately 14 μg methylmercury/kg bw/d. Similar calculations were made for other piscivores in this hypothetical exposure scenario allowing comparisons to be made among species (Table 3-3).

From a modeling standpoint, methylmercury levels in trophic level 3 fish and the mercury concentration in water are irrelevant to a ranking of predator exposure; only the relationship between the methylmercury concentrations in trophic levels 3 and 4 is critical. As noted previously, fish consumption rate expressed per gram of body weight has a large effect on these exposure calculations. Thus, despite consuming a comparatively small amount of the trophic level 3 fish, the kingfisher ranks well above any other birds (or mammals) in this estimated amount of mercury ingested per kg/bw.

Table 3-3
Summary of Sample Calculations of Wildlife Species Methylmercury Exposure From Fish Ingestion, Based on Average Fish Residue Values

Species	Sample Estimated Methylmercury Exposure from Fish Ingestion (μg/kg bw/d)
Kingfisher	40
Otter	24
Osprey	16
Mink	16
Eagle	14

3.4 Exposure Estimates Based on Measured Deposition and an Indirect Exposure Methodology

Published mercury deposition data are insufficient to generate a "national average"

value. An increasing amount of this type of information is being reported, however, and it is possible to use these data to bound an analysis of mercury fate and effects in a hypothetical watershed. For the purposes of this analysis, mercury air concentration, deposition rate and soil concentration (initial condition) were set equal to 1 ng/m^3, 10 µg/m^2/yr, and 50 ng/g, respectively (as total mercury). These values were then used as inputs to an indirect exposure model (IEM2) to predict mercury residues in fish. The scientific basis for these input values is described in Volume III.

IEM2 uses atmospheric chemical loadings to perform mass balances on a watershed soil element and a surface water element. The mass balances are performed for total mercury, which is assumed to speciate into three components: Hg^0, Hg^{2+} and methylmercury. The fraction of mercury in each of these components is specified for the soil and the surface water elements. Loadings and chemical properties are given for the individual mercury components, and the overall mercury transport and loss rates are calculated.

IEM2 first performs a terrestrial mass balance to obtain mercury concentrations in watershed soils. Soil concentrations are used along with vapor concentrations and deposition rates to calculate concentrations in various food plants. These are used, in turn, to calculate concentrations in animals. IEM2 next performs an aquatic mass balance driven by direct atmospheric deposition along with runoff and erosion loads from watershed soils. This analysis was conducted for two hypothetical waterbodies located in the Western U.S. and the Eastern U.S. Predicted mercury concentrations in water, soil and benthic sediments are presented in Table 3-4.

Table 3-4
Mercury Concentrations in Water and Sediment Predicted Using a Mercury Air Concentration of 1 ng/m^3, Deposition Rate of 10 µg/m^2/yr, and Soil Concentration of 50 ng/g

Parameter	Eastern Setting	Western Setting
Total Mercury Water Concentration (ng/L)	1.02	1.00
Percent of Mercury Dissolved (%)	71	77
Predicted Suspended Sediment Concentration (mg/L)	3.17	2.15
Total Mercury Benthic Sediment Concentration (ng/g)	110	118

Mercury residues in fish were estimated by making the simplifying assumption that aquatic food chains can be adequately represented using four trophic levels. Respectively, these trophic levels are the following: level 1 - phytoplankton (algal producers); level 2 - zooplankton (primary herbivorous consumers); level 3 - small forage fish (secondary consumers); and level 4 - larger, piscivorous fish (tertiary consumers). This type of food chain typifies the pelagic assemblages found in large freshwater lakes, and has been used extensively to model bioaccumulation of hydrophobic organic compounds (see for example Thomann, 1989; Clark, 1990; Gobas, 1993). It is recognized, however, that food chain structure can vary considerably among aquatic systems resulting in large differences in bioaccumulation in a given species of fish (Futter, 1994; Cabana et al., 1994). In addition, this simplified structure ignores several important groupings of organisms, including benthic detritivores, macroinvertebrates, generally, and herbivorous fishes.

Methylmercury concentrations in fish were derived from total mercury water concentrations by using BAFs for trophic levels 3 and 4 (Table 3-5). Respectively, these BAFs are 66,200 and 335,000. The BAFs selected for these calculations were estimated from existing field data. A detailed description of their derivation is presented in Appendix A.

Table 3-5
Methylmercury Concentrations in Fish (μg/g) Predicted Using a Mercury Air Concentration of 1 ng/m^3, Deposition Rate of 10 μg/m^2/yr, and Soil Concentration of 50 ng/g

Trophic Level	Predicted Fish Concentration (μg/g)	
	Eastern Site	Western Site
Trophic Level 3 Fish	0.049	0.052
Trophic Level 4 Fish	0.241	0.259

An effort was also made to simulate the variability around these fish residue values (Table 3-6). This was accomplished by using percentile information for the BAF estimates developed in Appendix A (Tables A-9 and A-10). The water concentration used to drive the variability analysis was 0.7 ng/L dissolved total mercury. The results of this analysis demonstrate the large variability in fish residues that may occur at a given water concentration. This variability is due in turn to the large variability in field-derived BAF values.

Table 3-6
Percentiles of Predicted Methylmercury Concentrations in Fish (μg/g) Based on a Total Mercury Dissolved Water Concentration of 0.7 ng/L

Parameter	Geometric Mean	Percentile of Distribution				
		5th	25th	50th	75th	95th
Trophic 3 BAF	67,000	6,400	25,400	66,200	172,400	684,000
Predicted Fish Concentration (μg/g)	0.05	0.00	0.02	0.05	0.12	0.48
Trophic 4 BAF	335,000	22,700	111,000	336,000	1,000,000	4,700,000
Predicted Fish Concentration (μg/g)	0.23	0.02	0.08	0.24	0.70	3.30

3.5 Regional-scale Exposure Estimates

There are many stationary, anthropogenic mercury sources in the U.S., and the impact of these emissions may not be entirely limited to the local area around the facility. To account for impacts of mercury emitted from these non-local sources, the long-range transport of mercury was simulated using the RELMAP model. The RELMAP model was used to predict the average annual atmospheric

mercury concentration and the wet and dry deposition flux for each 40 km^2 grid in the continental U.S. The emission, transport and fate of airborne mercury over the continental U.S. were modeled using meteorologic data for the year of 1989. This year was assumed to be a typical year from an atmospheric dispersion perspective. Inputs to the RELMAP model were obtained from the mercury emissions inventory presented as Volume II of this Report. In all, over 10,000 mercury emitting cells within the U.S. were addressed. A detailed description of the RELMAP model is provided in Appendix D to Volume III.

3.5.1 Analysis of RELMAP Results

In the first stage of analysis, estimated total mercury deposition data were used with ARC/INFO cartography software to generate U.S. map overlays. The overlays can be applied to similar scale maps of natural resources and species distributions or combined with additional data such as acid deposition and alkalinity or pH of surface waters. Figure 3-1 shows RELMAP projections for total (including wet and dry) anthropogenic mercury deposition. Nearly all the land area east of the Mississippi River is projected to receive mercury deposition greater than 5 $\mu g/m^2$. Projections for the highly industrialized northeast and south Florida are projected to receive more than 20 $\mu g/m^2$. RELMAP results are projections that may differ quantitatively from actual sampling data for a given locale. It is anticipated, however, that additional sampling data will confirm the prediction that mercury is deposited in significant quantities over large geographic areas.

Limitations on data precluded a quantitative, nation-wide analysis of the exposure of piscivorous wildlife to mercury. Existing data are sufficient, however, to permit a qualitative analysis. In the case of plant life, analysis was limited to plotting the location of federally threatened or endangered species and indicating where threatened populations coincide with estimated high mercury deposition.

Avian wildlife selected for this analysis included species that are widely distributed (kingfishers) and narrowly distributed (bald eagles), as well as birds whose range fell within areas of high mercury deposition (ospreys and common loons). All the birds selected were piscivores that feed at or near the top of aquatic food chains and are therefore at risk from biomagnified mercury.

Two of the mammals selected for this analysis (mink and river otters) are piscivorous and widely distributed. The other mammal selected, the Florida panther, is not widely distributed but is listed as an endangered species. The Florida panther lives in an environment known to be contaminated with mercury and preys upon small mammals (such as raccoons) which may contain high tissue burdens of mercury.

The maps and map overlays that follow were used to examine in a qualitative fashion the potential for anthropogenic mercury to impact representative piscivorous species in a variety of ecosystems. Animal distribution information was obtained from the Nature Conservancy (1994)

3.5.2 Locations of Socially Valued Environmental Resources

Major freshwater lakes and river systems potentially affected by atmospheric mercury deposition are illustrated in Figure 3-2. Most of the freshwater located in the lower 48 states occurs in areas where mercury deposition is predicted to be high. Because mercury accumulates in sediments, it is anticipated that significant mercury inputs to surface waters will continue for a long period of time

Figure 3-1
Total Anthropogenic Mercury Deposition

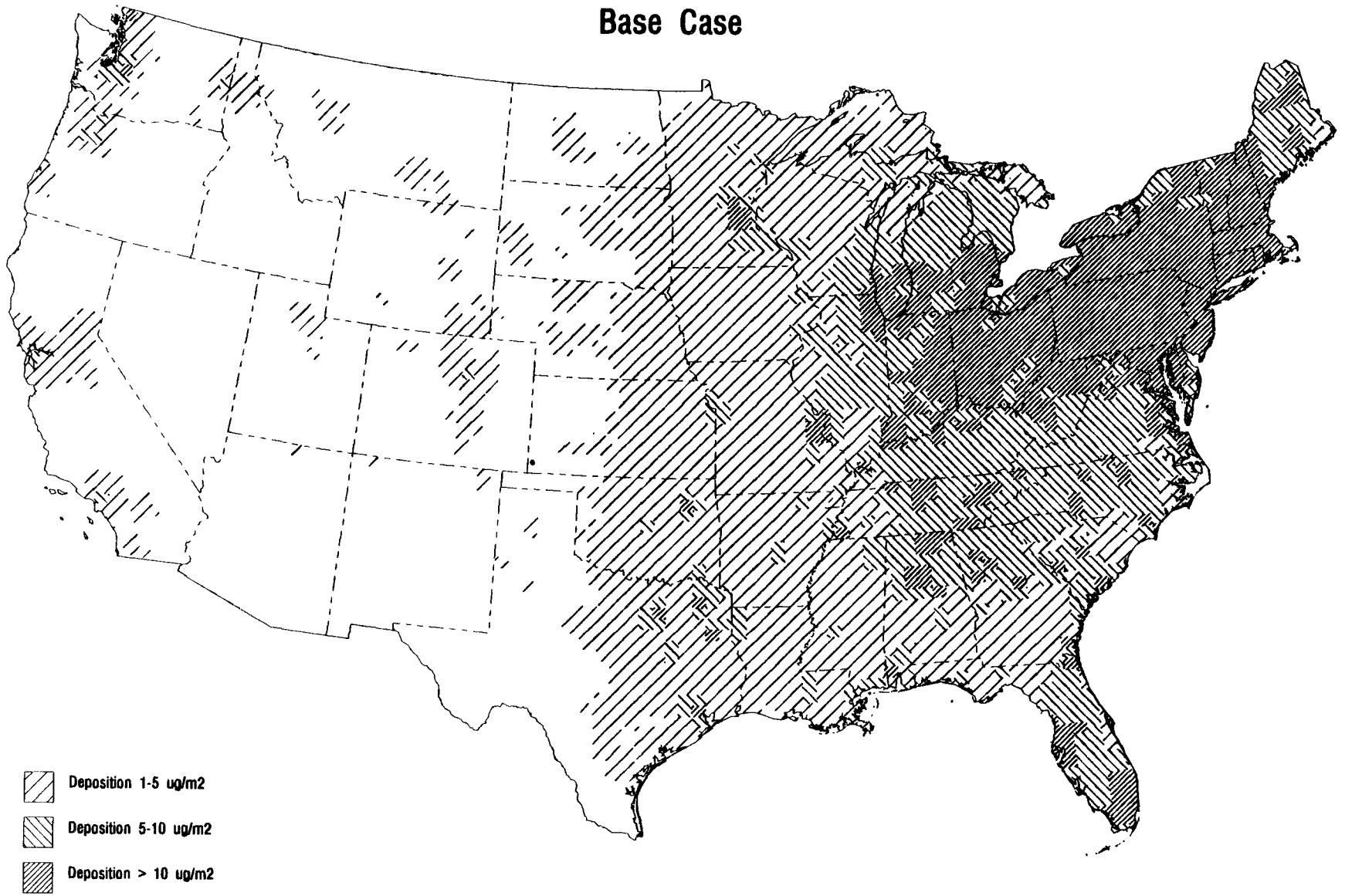
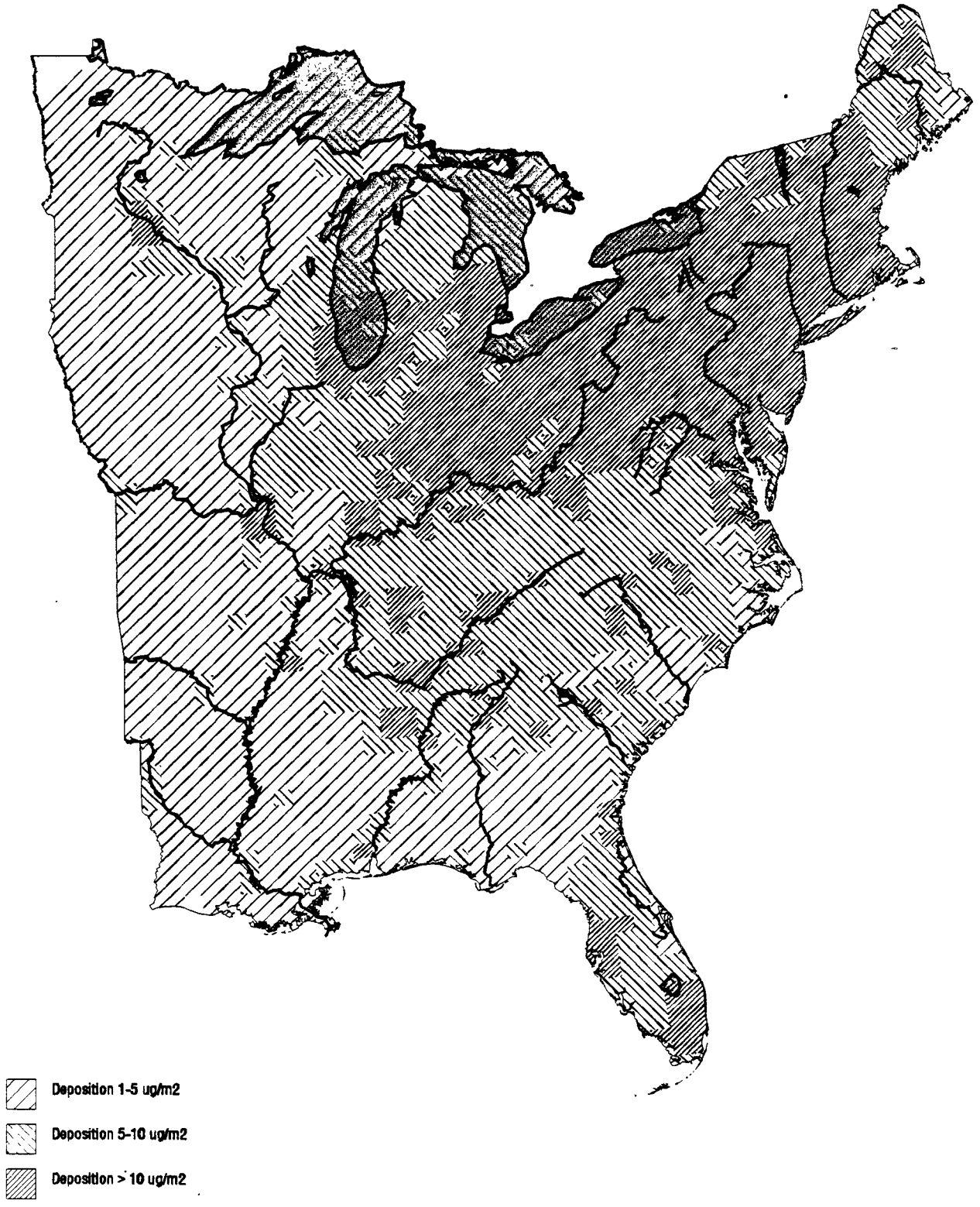


Figure 3-2
Major Rivers and Lakes



even if atmospheric deposition is substantially reduced. The Great Lakes are particularly vulnerable because of the length of time necessary to replenish contaminated water with clean fresh water.

Figure 3-3 shows the location of national resource lands, which include national parks and monuments, national forests, wildlife refuges and Native American reservation lands. The area of national resource lands that are predicted to have high mercury deposition is relatively small when compared with the total area of national resource lands, most of which are located in the western states. The small size of eastern resources makes them especially vulnerable to the effects of mercury because depleted wildlife populations cannot easily be repopulated from less-impacted adjoining regions. Increasingly, natural areas may become "islands" surrounded by development. The loss of biodiversity is an important problem that could be exacerbated by the added stress of mercury toxicity.

3.5.3 Airborne Deposition Overlay with Threatened and Endangered Plants

Figure 3-4 shows the geographic locations of populations of threatened and endangered plant species overlaid with RELMAP's predicted mercury deposition. Large concentrations of endangered plant populations exposed to high levels of deposition occur in central and southern Florida, along the northeastern coastal region and scattered throughout the midwest. Mercury has been demonstrated to have adverse impacts on a number of plant species (see Section 2).

3.5.4 Regions of Concern Defined by High Mercury Deposition Coincident with Acidic Surface Water

Figure 3-5 overlays airborne deposition predictions and areas where surface water pH is 5.5 or lower (NAPAP, 1990). All areas where >5% of surface waters are at or below pH 5.5 are subsequently referred to as "regions of concern". This distinction is based on the observation that mercury concentrations in fish flesh have been positively correlated with low pH. Designation of a particular area as a region of concern implies an increased risk of mercury toxicity to wildlife. Regions of concern could be used to define critical habitat, predict potentially endangered species, and may be useful to identify future research needs.

3.5.5 Regions of Concern Overlay with Wildlife Species Distribution Maps

Figure 3-6 shows the range of kingfisher habitat and areas where this habitat overlaps with regions of concern. Kingfishers are piscivorous, consuming fish primarily from trophic level 3. Approximately 8% of the kingfisher's range occurs within regions of concern and mercury does not appear to be a threat to the species nationwide.

Figure 3-7 overlays the range of bald eagle habitat onto regions of concern. Although a recovery in the population of bald eagles in the lower 48 states has resulted in a status upgrade from "endangered" to "threatened", bald eagle populations are still depleted throughout this range. Bald eagles can be found seasonally in large numbers in several geographic locations, but most of these individuals are transient, and the overall population is still small. Historically, eagle populations in the lower 48 states have been adversely impacted by the effects of bioaccumulative contaminants (primarily DDT and perhaps also PCBs). Approximately 17% of the bald eagle's range overlaps regions of concern. The risk to eagles posed by mercury appears to be greatest in the Great Lakes region, the northeastern Atlantic states and south Florida.

Figure 3-3
National Resource Lands

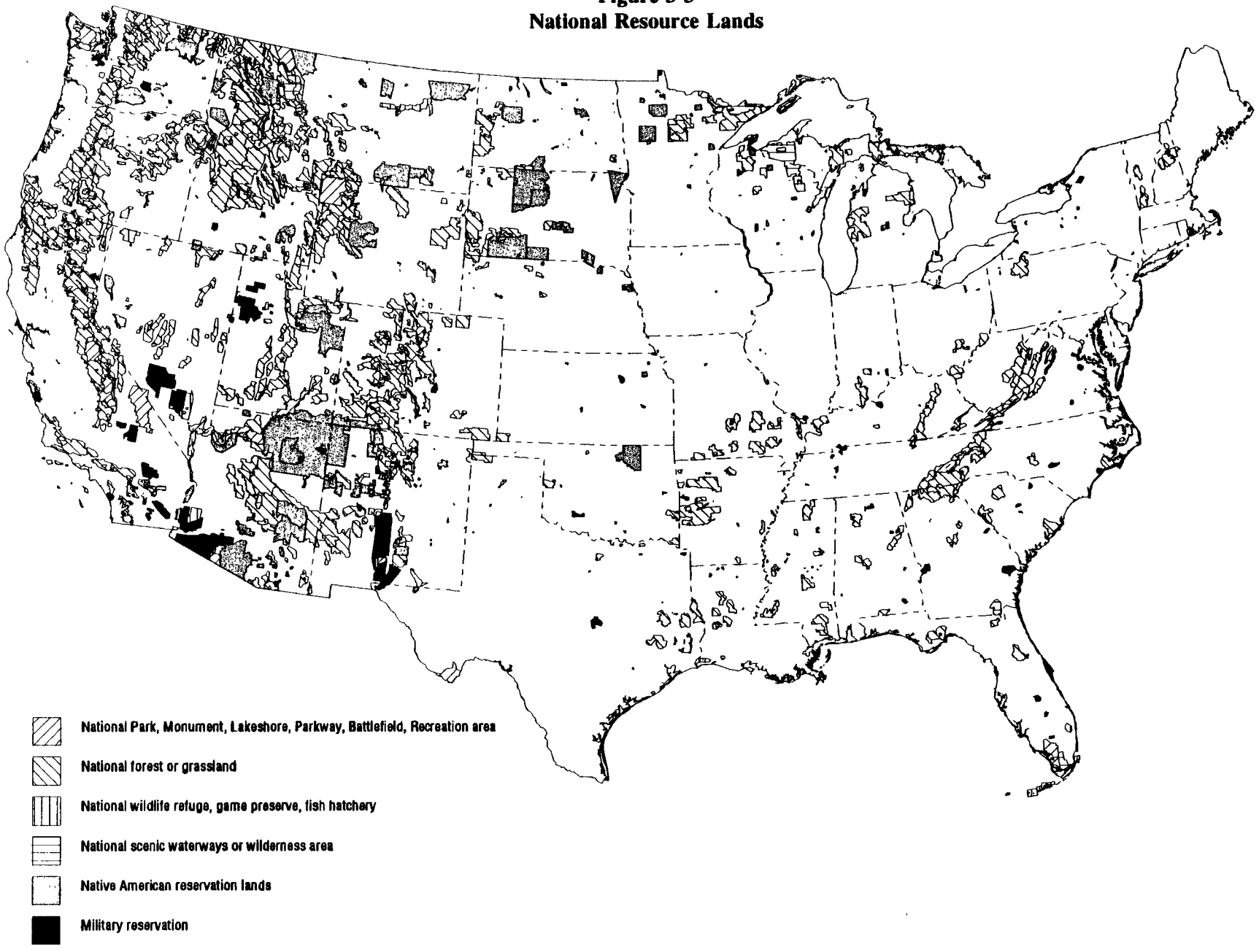


Figure 3-4
Threatened and Endangered Plan Species and anthropogenic Mercury Deposition

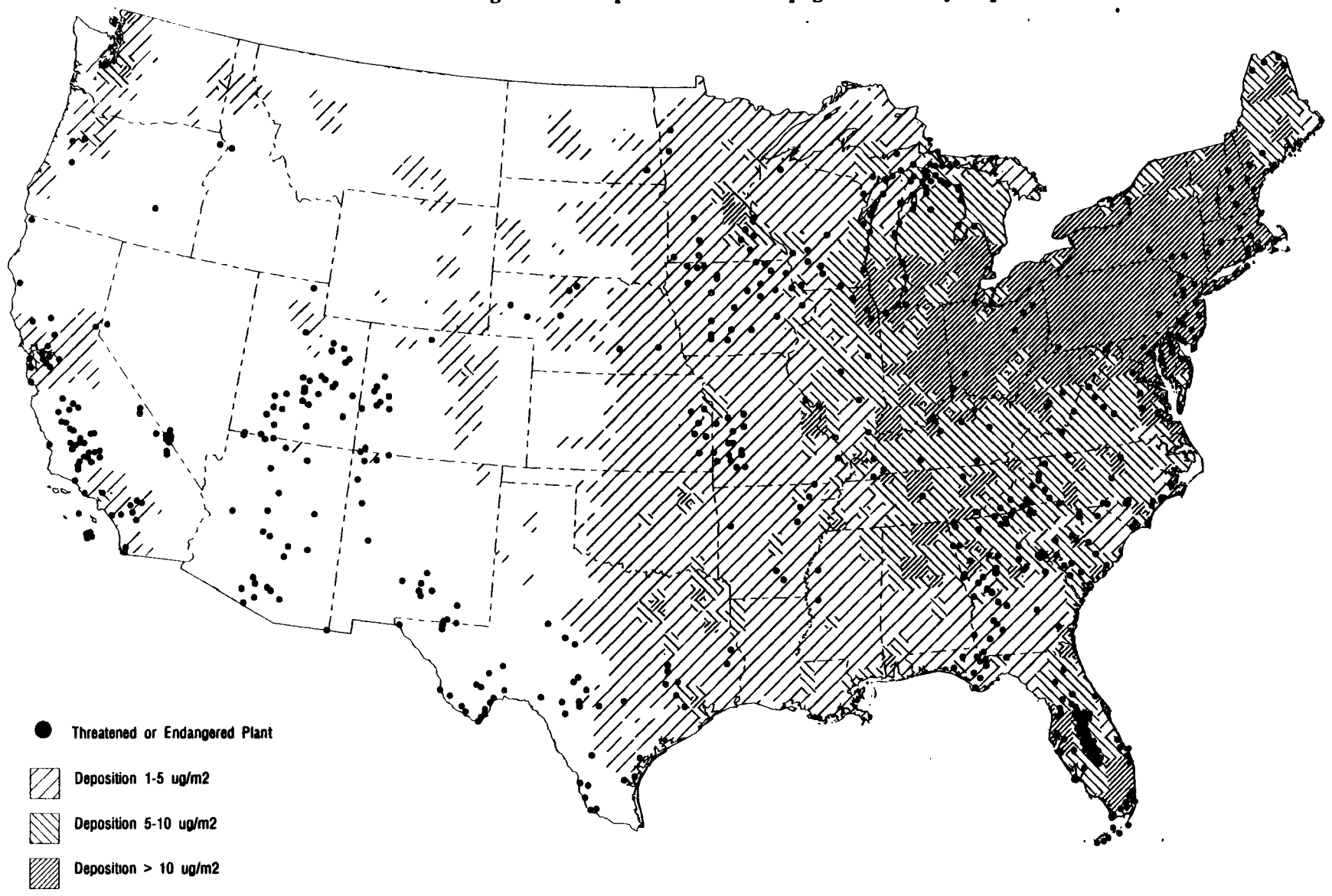


Figure 3-5
Surface Water and pH≤ 5.5 and Anthropogenic Mercury Deposition

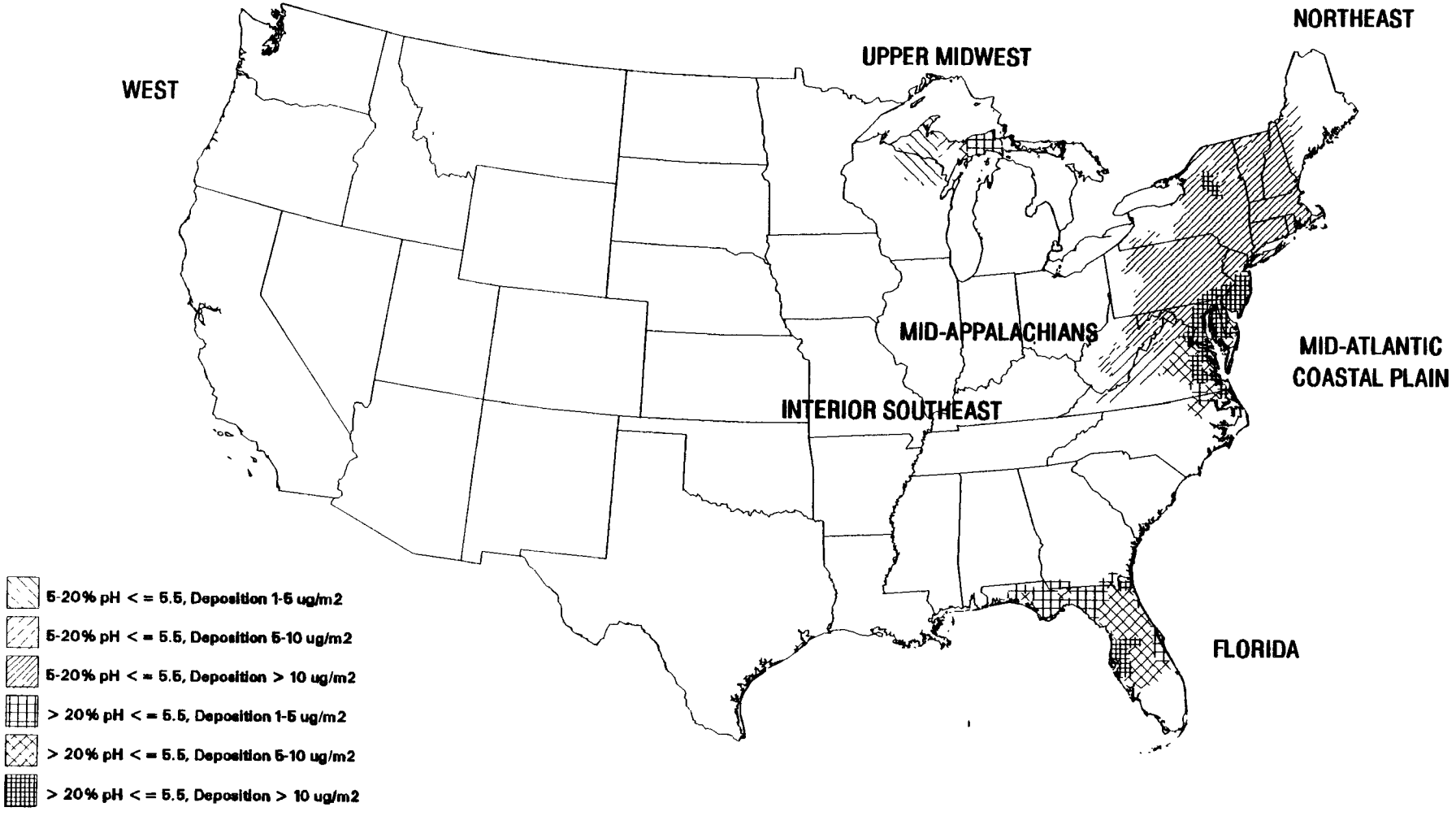


Figure 3-6
Kingfisher Range, Surface Water with pH $\leq$ 5.5, and Anthropogenic Mercury Deposition

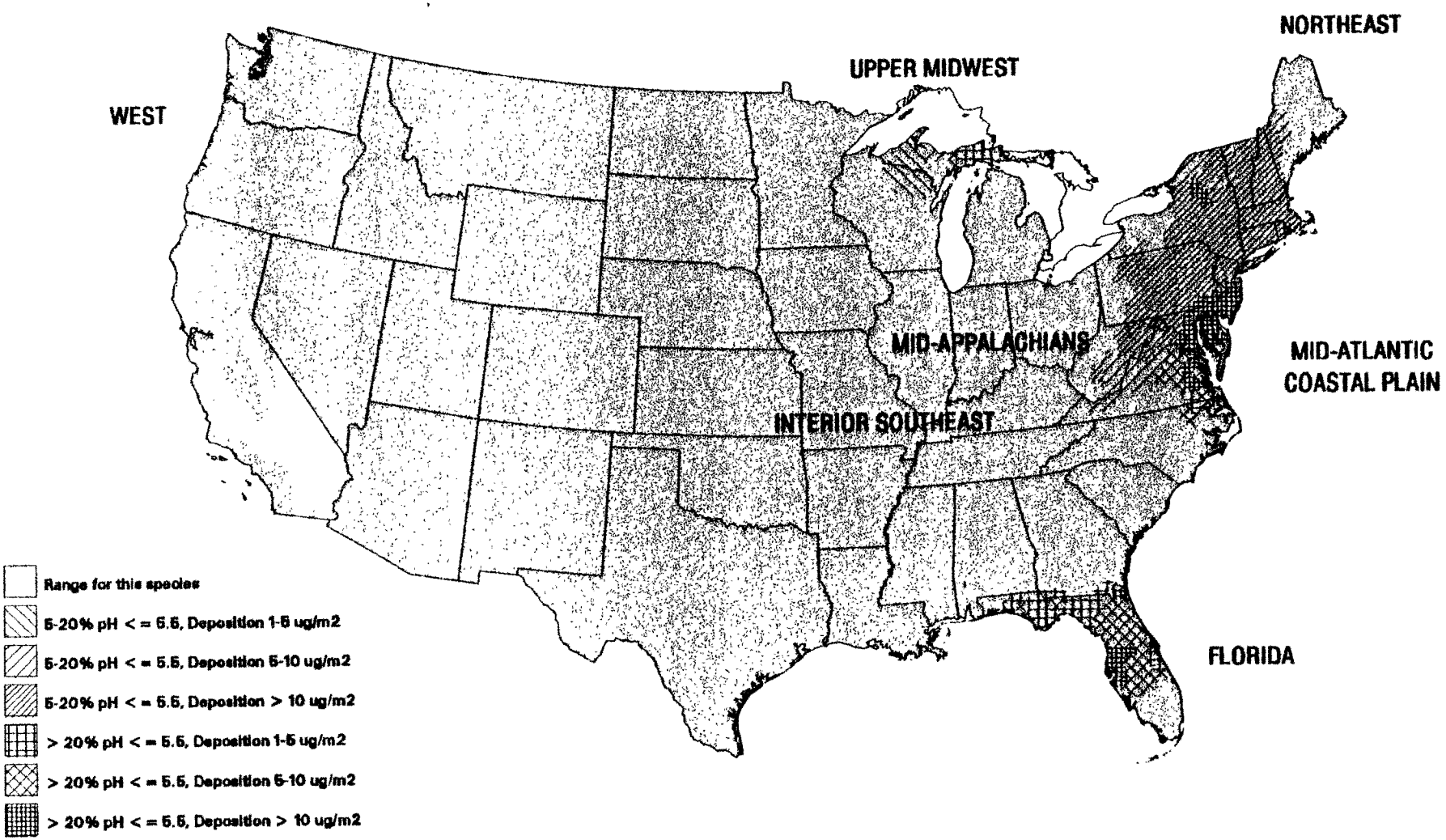


Figure 3-7
Bald Eagle Range, Surface Water with pH $\leq$ 5.5, and Anthropogenic Mercury Deposition

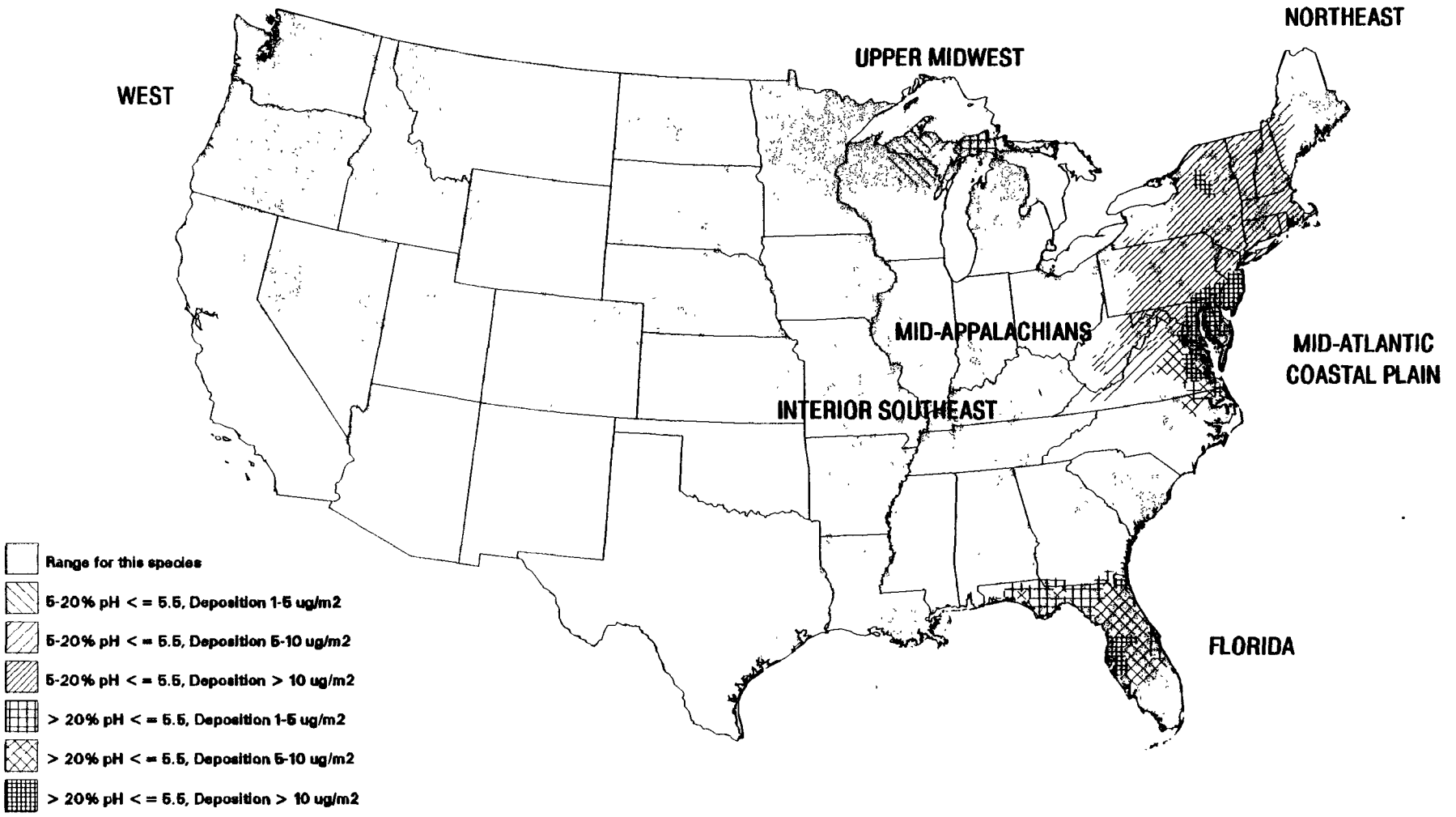


Figure 3-8 indicates where the range of osprey coincides with regions of concern. Nationwide, approximately 13% of the osprey's range overlaps these regions; however, a much larger fraction of the osprey's eastern population occurs within these regions. The osprey diet consists almost exclusively of fish, and they are known to take dead fish from the water surface if they are fresh. Their position at the top of the aquatic food chain places ospreys at risk from toxins that bioaccumulate. Osprey populations underwent a severe declines during the 1950s through the 1970s which has been linked to exposure to DDT.

Figure 3-9 depicts areas where the range of the common loon coincides with regions of concern. Nearly 23% of the loon's range is located in regions of concern. Moreover, nearly all of the loon's range occurs in regions where mercury deposition is predicted to be high (Figure 3-1). Limited data from the study of a mercury point source showed that loon reproductive success was negatively correlated with exposure to mercury in a significant dose-response relationship (Section 2.3.3). Residue data, combined with field observations, suggest that loon populations in areas of Minnesota and Wisconsin may be adversely impacted by mercury originating from airborne deposition.

Figure 3-10 shows the Florida panther's range. Although the panther's range falls outside of identified regions of concern (<1%), the species habitat is contiguous with this region. Section 2.3.3 describes data which establish a link between mercury exposure and adverse impacts on the Florida panther. Mercury levels found in Florida panther tissue approach levels that are frankly toxic in other feline species. The State of Florida has taken measures to reduce the risk to panthers posed by mercury. Existing plans include modification of surface vegetation to increase the number of deer available as prey in order to reduce the reliance of panthers on raccoons. As indicated previously, raccoons frequently feed at or near the top of aquatic food chains and can accumulate substantial tissue burdens of mercury.

Figure 3-11 gives the range of the mink where this habitat coincides with regions of concern (approximately 9% of the range, nationwide). Mink occupy a large geographic area and are common throughout this range, although rarely observed because of their nocturnal habits. In general, mink prey on small mammals for most of the year; however, some populations prey primarily on fish and aquatic birds. Mink that prey on aquatic animals are most at risk from mercury contamination. In additional small mammalian and avian predators may be a greater risk than large predators due to higher food consumption rate per unit of body weight (Section 2.3.2).

Figure 3-12 shows the range of the river otter where this habitat coincides with regions of concern (approximately 14% of the range, nationwide). River otters occupy large areas of the United States, but their population numbers are thought to be declining in the midwestern states. The river otter's diet is almost exclusively of aquatic origins and includes fish (primarily), crayfish, amphibians and aquatic insects. The species of fish taken depends on the fish's ability to escape capture. The consumption of large, piscivorous fish puts the river otter at risk from bioaccumulative contaminants such as mercury. Otter population declines do not overlap to a large extent with regions of concern; however, the area of decline does coincide with RELMAP predictions of high mercury deposition rate (Figure 3-1).

Figure 3-8
Osprey Range, Surface Water with pH ≤ 5.5,
and Anthropogenic Mercury Deposition
(Detail: Eastern U.S.)

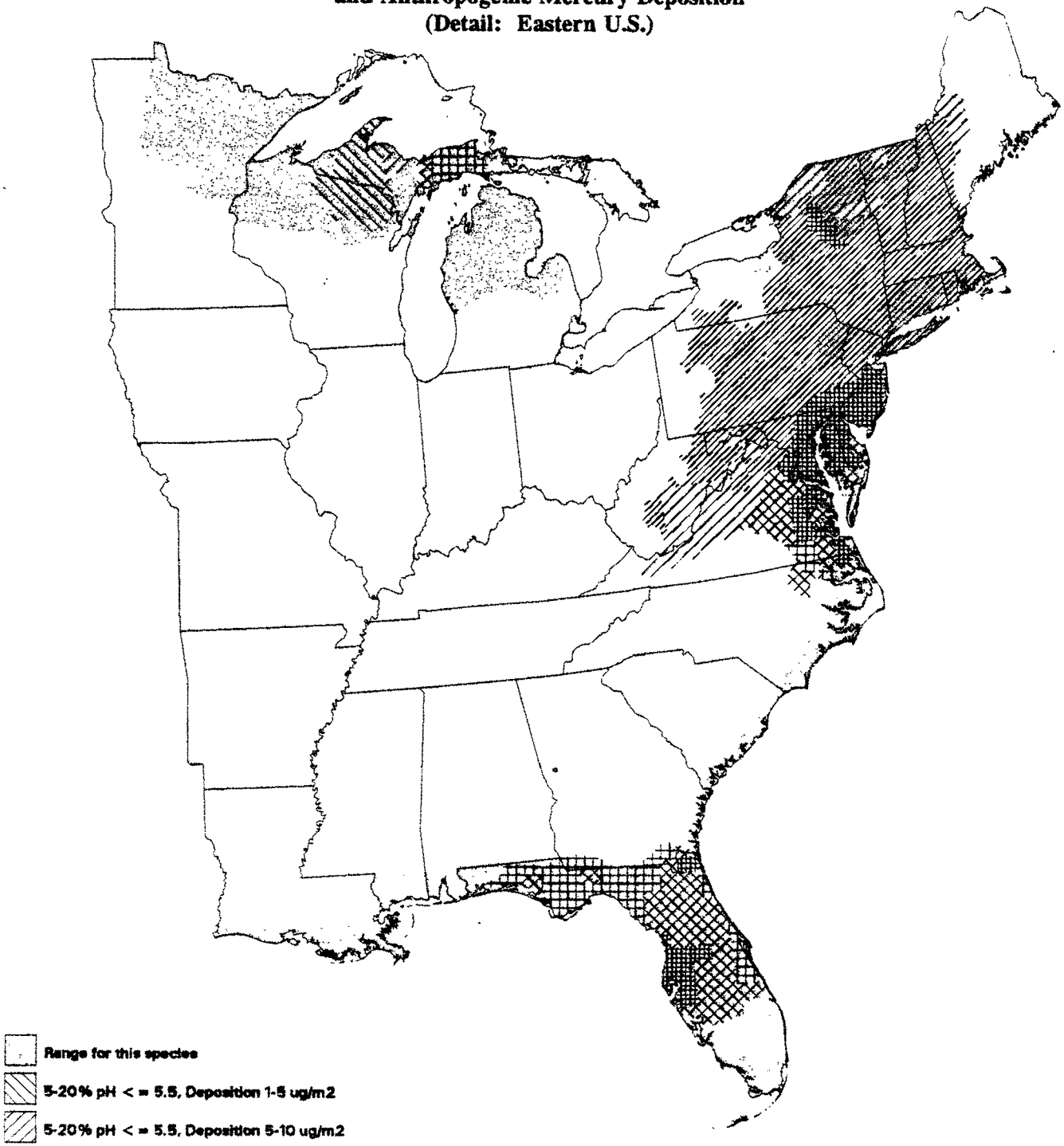


Figure 3-9
Common Loon Range, Surface Water with pH $\leq$ 5.5, and Anthropogenic Mercury Deposition

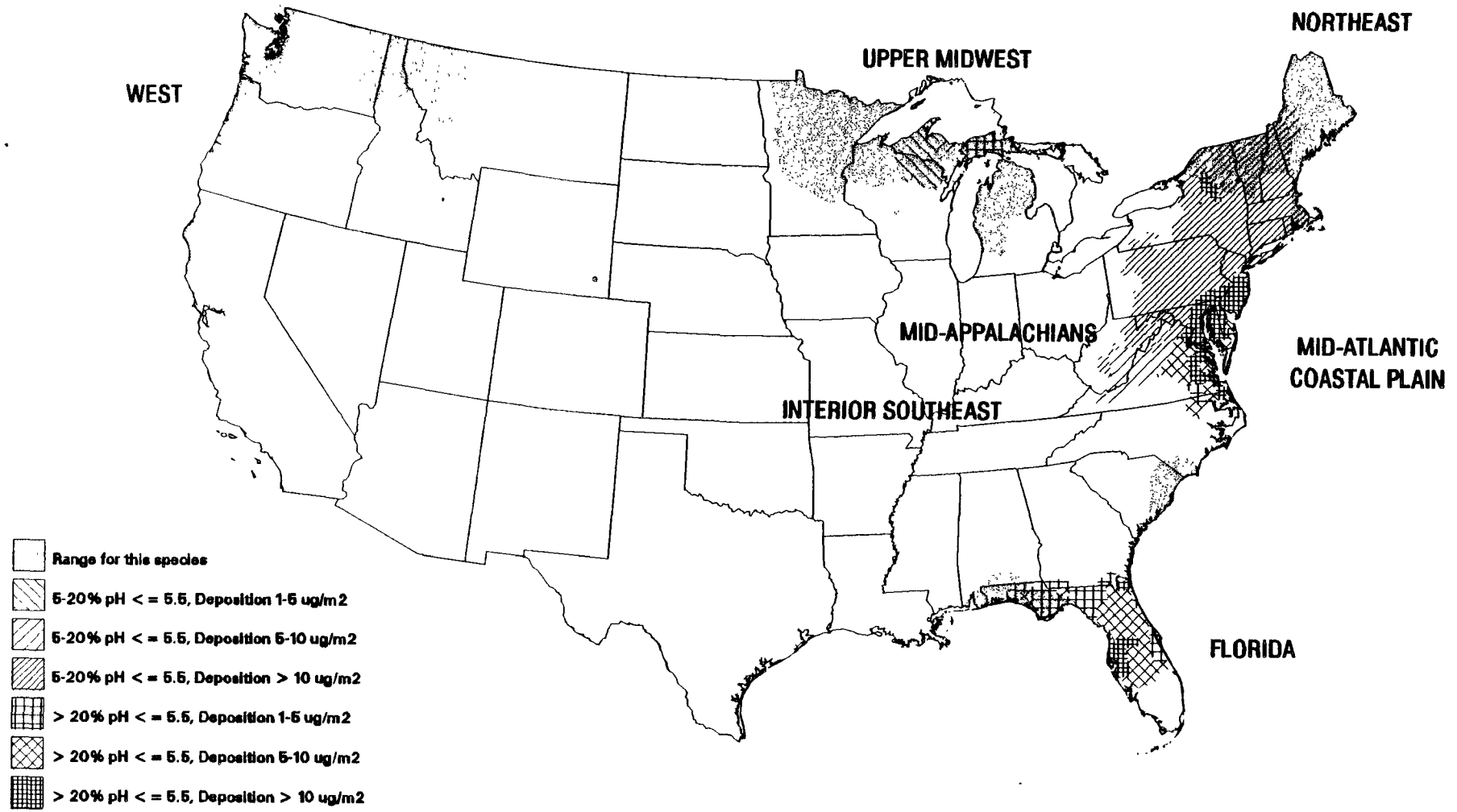


Figure 3-10
Florida Panther Range, Surface Water with pH $\leq$ 5.5,
and Anthropogenic Mercury Deposition
(Detail: Eastern U.S.)

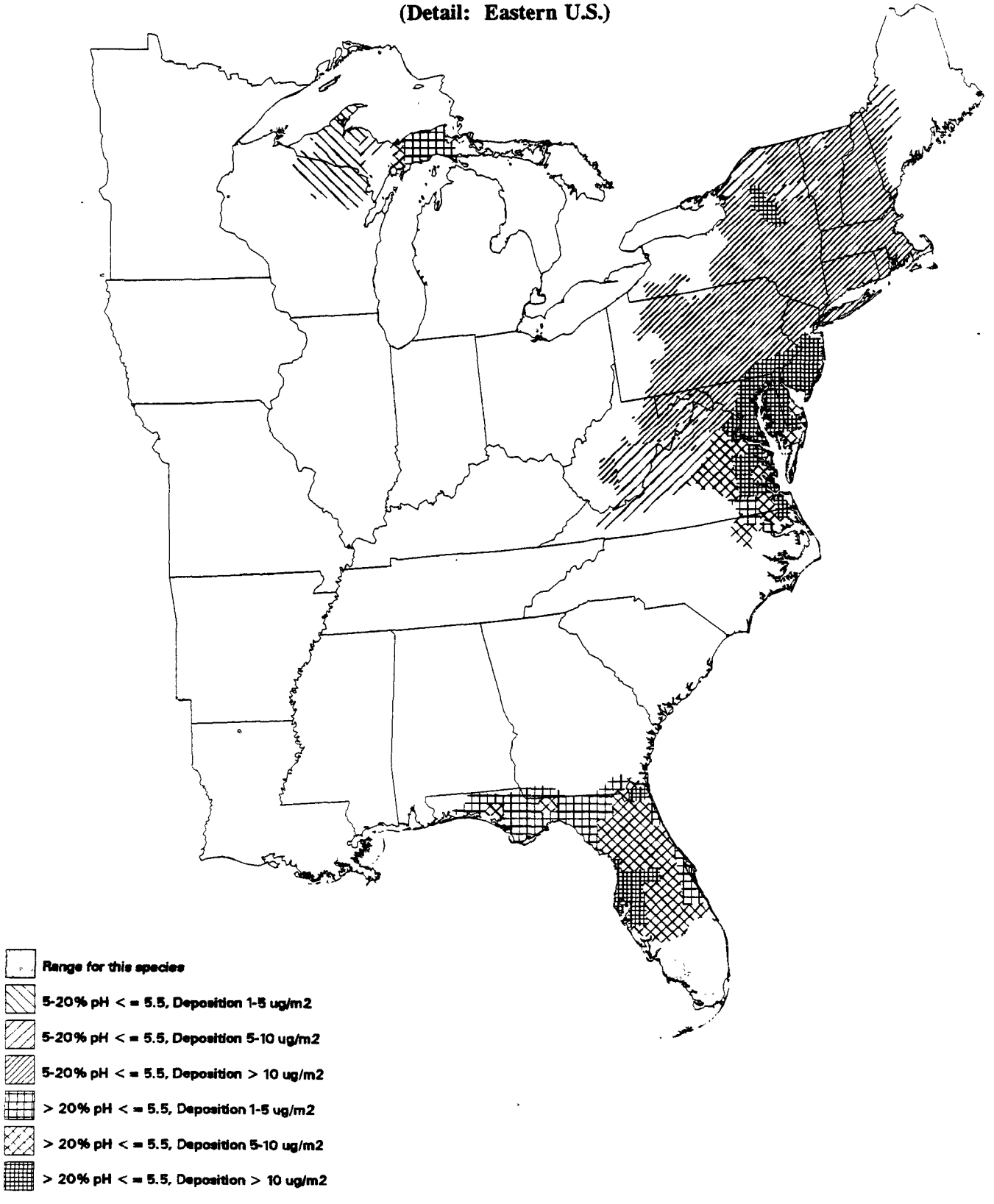


Figure 3-11
Mink Range, Surface Water with pH ≤5.5, and Anthropogenic Mercury Deposition

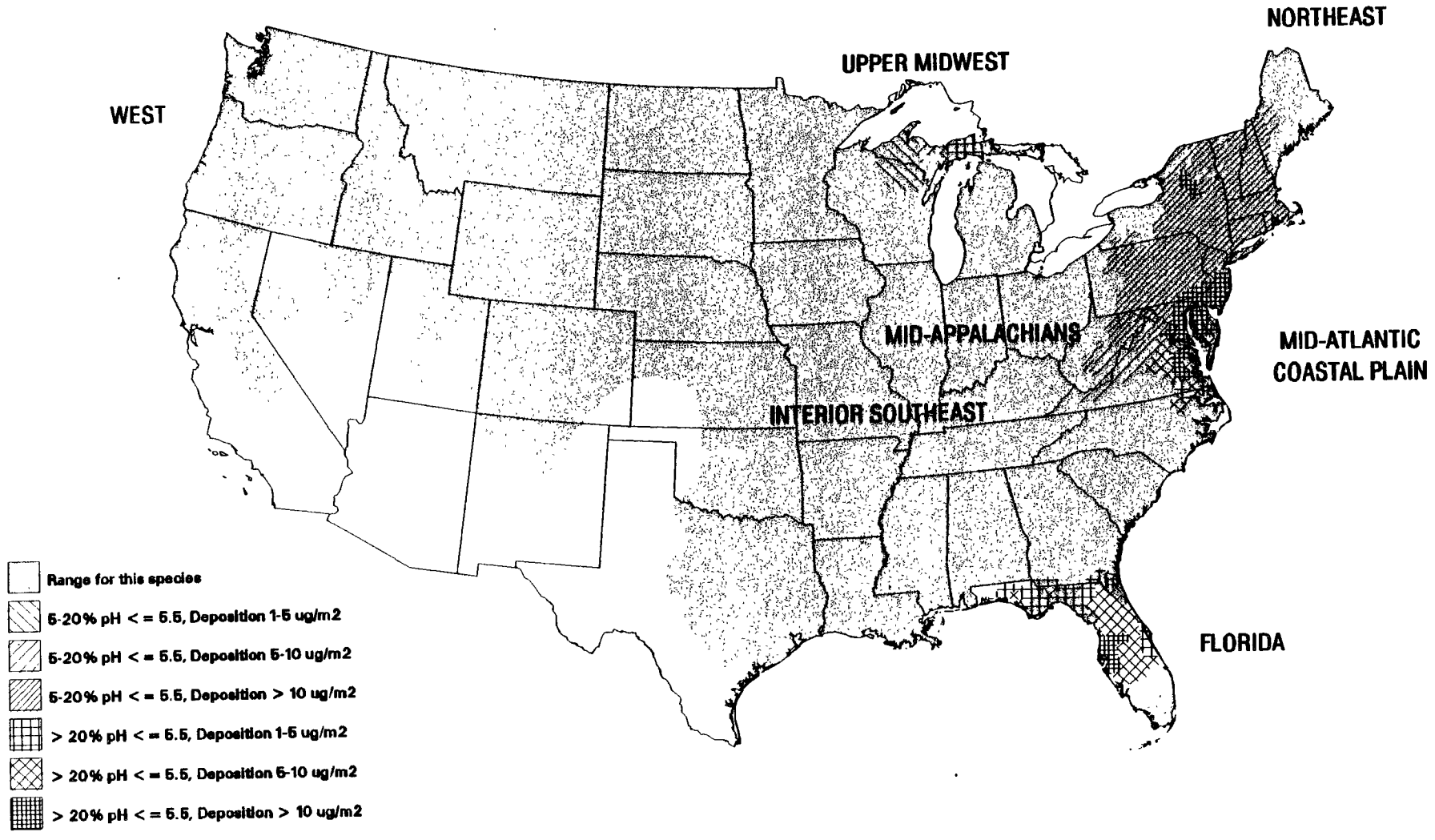
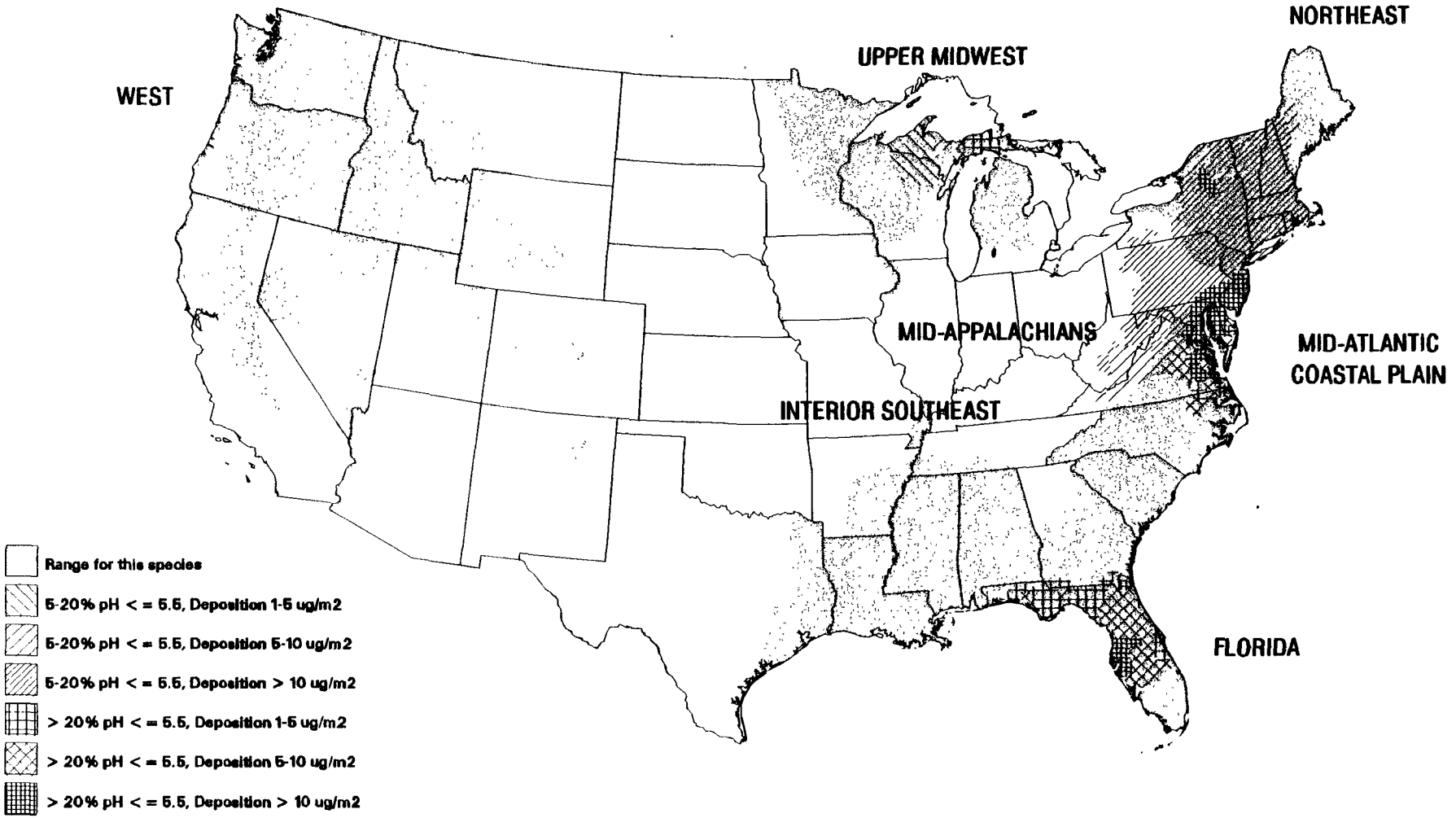


Figure 3-12
River Otter Range, Surface Water with pH ≤5.5, and Anthropogenic Mercury Deposition



3.6 Local-scale Exposure Estimates

3.6.1 Approach and Assumptions

The goal of the local scale analysis was to evaluate the extent to which local mercury emissions sources have the potential to create locally elevated mercury exposures for piscivorous wildlife receptors. Air concentrations and deposition rates due to a single local source were predicted using the COMPDEP model, specifically modified to model the atmospheric transport of mercury. For the purposes of this study, hypothetical sources were assumed to contribute mercury in addition to that simulated by RELMAP. Details of the local-scale modeling exercise are presented in Volume III of this Report.

Model plants (hypothetical mercury emitters) representing six source classes were developed to represent a range of mercury emissions sources. The source categories were selected for the indirect exposure analysis based on their estimated annual mercury emissions or their potential to be localized point sources of concern. The categories selected were these: municipal waste combustors (MWCs), medical waste incinerators (MWIs), utility boilers, chlor-alkali plants, primary copper smelters, and primary lead smelters. Table 3-7 shows the process parameters assumed for each of these facilities.

Table 3-7
Process Parameters for the Model Plants Considered in the Local Impact Analysis

MODEL PLANT	Plant Size	Stack Ht.(ft)	Stack Diam (ft)	Baseline Hg Emission Rate (kg/yr)	Speciation % (Hg^0/Hg^{2+}/ methylmercury)	Exit Vel. (m/sec)	Exit Temperature (F)
Large MWC	2250 tons/d	230	9.5	1330	20/60/20	21.9	285
Small MWC	200 tons/d	140	5	170	20/60/20	21.9	375
Continuous MWI	1500 lb/hr capacity (1000 lb/hr actual)	40	2.7	80	20/60/20	7.3	1500
Intermittent MWI	200 lb/hr capacity (133 lb/hr actual)	40	1.2	2.4	20/60/20	7.3	1500
Large Coal-fired Utility Boiler	975 Megawatts	732	27	230	50/30/20	31.1	273
Medium Coal-fired Utility Boiler	375 Megawatts	465	18	90	50/30/20	26.7	275
Small Coal-fired Utility Boiler	100 Megawatts	266	12	10	50/30/20	6.6	295
Medium Oil-fired Utility Boiler	285 Megawatts	290	14	2	50/30/20	20.7	322
Chlor-alkali plant	300 tons chlorine/d	10	0.5	380	70/30/0	0.1	Ambient
Primary Copper Smelter	180 tons Cu/d	505	15	5360	85/10/5	6	430
Primary Lead Smelter	304 tons lead/d	350	20	2680	85/10/5	2.8	347

The model plants were placed in hypothetical sites assumed to lie in the eastern and western U.S. The hypothetical sites were assumed to have flat terrain. Emitted mercury is thought to influence both local and regional atmospheric concentrations and deposition. To account for the long range transport of emitted mercury, the 50th percentile RELMAP atmospheric concentrations and deposition rates were included in the estimates from the local air dispersion model. Model simulations were generated for the same hypothetical watersheds and waterbodies described previously. These waterbodies were assumed to be located 2.5, 10 and 25 Km from the sources.

COMPDEP uses hourly meteorological data to estimate hourly air concentrations and deposition fluxes within 50 km of a point source. For each hour, general plume characteristics are estimated based on the source parameters (gas exit velocity, temperature, stack diameter, stack height, wind speed at stack top, atmospheric stability conditions) for that hour. COMPDEP was run using five years of actual meteorological data. The average values for air concentration and deposition rates were then used as inputs for to IEM2 model. These values were assumed to be representative for 30 years, the assumed typical lifetime of a facility. During this 30-year period, the mercury concentration in soil was allowed to build up, taking into account loss processes such as leaching, runoff and erosion. Simulated values at the end of the 30-year period were then used as input to the water portion of the IEM2 model to calculate steady-state water concentrations. Finally, the estimated water concentrations were used to predict methylmercury concentrations in fish that occupy trophic levels 3 and 4. This was accomplished by multiplying the predicted total mercury dissolved water concentration by the BAF at each trophic level. Wildlife receptors were assumed to ingest the fish at rates given previously (Table 3-2).

3.6.2 Results of Local-scale Exposure Analysis

High rates of mercury deposition were associated with proximity to industrial sources emitting substantial levels of divalent mercury (Tables 3-8 and 3-9). Additional factors that contributed to high local deposition rates include low stack height and slow stack exit gas velocities. In general, total mercury concentrations in lake waters located 2.5 km from the source were much higher than levels predicted at 10 or 25 km. This was due primarily to the dilution of the mercury emissions in the atmosphere. Mercury concentrations in fish (hence the mercury exposure to piscivores) were proportional to dissolved mercury levels in the local waters. At 10 and 25 km the water concentrations and, thus, the predicted levels in fish, are elevated relative to levels predicted when only remote sites are modeled (i.e., RELMAP predictions). When the two hypothetical locations were compared (western and eastern), higher mercury concentrations were predicted to occur in the environmental media at the eastern location. This was due primarily to higher levels of precipitation at the eastern site, which tends to remove mercury from the atmosphere. In this modeling effort, mercury deposition patterns dominate soil, water and fish mercury concentrations. Although (as described in Volume III) watershed characteristics influence model simulations, the facility type, local meteorology and terrain are generally more important for predicting local dissolved mercury concentrations in water.

Table 3-8
Predicted Intakes for Wildlife Receptors for the Eastern Site

Eastern Site	Surface Water Concentration (ng/L)	Fish Methylmercury Concentrations (µg/g)		Predicted Methylmercury Intake (µg/g bw/d)				
		Tier 3	Tier 4	Bald Eagle	Osprey	Kingfisher	River Otter	Mink
Resource Plus Local Source Deposition	1.022	0.049	0.242	0.009	0.010	0.024	0.014	0.010
2.5 km								
Large MWC	23.539	1.122	5.575	0.199	0.224	0.561	0.332	0.225
Small MWC	3.692	0.176	0.874	0.031	0.035	0.088	0.052	0.035
Continuous MWI	2.291	0.109	0.543	0.019	0.022	0.055	0.032	0.022
Intermittent MWI	0.080	0.004	0.019	0.001	0.001	0.002	0.001	0.001
Large Coal-fired Utility Boiler	0.572	0.027	0.136	0.005	0.005	0.014	0.008	0.005
Medium Coal-fired Utility Boiler	0.451	0.022	0.107	0.004	0.004	0.011	0.006	0.004
Small Coal-fired Utility Boiler	0.081	0.004	0.019	0.001	0.001	0.002	0.001	0.001
Medium Oil-fired Utility Boiler	0.014	0.001	0.003	0.000	0.000	0.000	0.000	0.000
Chlor-alkali plant	8.990	0.428	2.129	0.076	0.086	0.214	0.127	0.086
Primary Copper Smelter	1.307	0.062	0.309	0.011	0.012	0.031	0.018	0.012
Primary Lead Smelter	7.195	0.343	1.704	0.061	0.069	0.171	0.101	0.069
10 km								
Large MWC	3.015	0.144	0.714	0.026	0.029	0.072	0.042	0.029
Small MWC	0.527	0.025	0.125	0.004	0.005	0.013	0.007	0.005
Continuous MWI	0.362	0.017	0.086	0.003	0.003	0.009	0.005	0.003
Intermittent MWI	0.012	0.001	0.003	0.000	0.000	0.000	0.000	0.000
Large Coal-fired Utility Boiler	0.107	0.005	0.025	0.001	0.001	0.003	0.002	0.001
Medium Coal-fired Utility Boiler	0.074	0.004	0.017	0.001	0.001	0.002	0.001	0.001
Small Coal-fired Utility Boiler	0.013	0.001	0.003	0.000	0.000	0.000	0.000	0.000
Medium Oil-fired Utility Boiler	0.002	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Chlor-alkali plant	0.968	0.046	0.229	0.008	0.009	0.023	0.014	0.009
Primary Copper Smelter	0.210	0.010	0.050	0.002	0.002	0.005	0.003	0.002
Primary Lead Smelter	1.178	0.056	0.279	0.010	0.011	0.028	0.017	0.011
25 km								
Large MWC	0.666	0.032	0.158	0.006	0.006	0.016	0.009	0.006
Small MWC	0.134	0.006	0.032	0.001	0.001	0.003	0.002	0.001
Continuous MWI	0.090	0.004	0.021	0.001	0.001	0.002	0.001	0.001
Intermittent MWI	0.003	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Large Coal-fired Utility Boiler	0.021	0.001	0.005	0.000	0.000	0.001	0.000	0.000
Medium Coal-fired Utility Boiler	0.016	0.001	0.004	0.000	0.000	0.000	0.000	0.000
Small Coal-fired Utility Boiler	0.003	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Medium Oil-fired Utility Boiler	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Chlor-alkali plant	0.209	0.010	0.050	0.002	0.002	0.005	0.003	0.002
Primary Copper Smelter	0.051	0.002	0.012	0.000	0.000	0.001	0.001	0.000
Primary Lead Smelter	0.295	0.014	0.070	0.002	0.003	0.007	0.004	0.003

Table 3-9
Predicted Intakes for Wildlife Receptors for the Western Site

Western Site	Surface Water Concentration (ng/L)	Fish Methylmercury Concentrations (µg/g)		Predicted Methylmercury Intake (µg/g bw/d)				
		Tier 3	Tier 4	Bald Eagle	Osprey	Kingfisher	River Otter	Mink
Regional Plus Local Source Deposition	1.002	0.052	0.259	0.009	0.010	0.026	0.015	0.010
2.5 km								
Large MWC	8.818	0.458	2.279	0.081	0.092	0.229	0.136	0.092
Small MWC	1.672	0.087	0.432	0.015	0.017	0.043	0.026	0.017
Continuous MWI	1.558	0.081	0.403	0.014	0.016	0.040	0.024	0.016
Intermittent MWI	0.060	0.003	0.016	0.001	0.001	0.002	0.001	0.001
Large Coal-fired Utility Boiler	0.223	0.012	0.058	0.002	0.002	0.006	0.003	0.002
Medium Coal-fired Utility Boiler	0.157	0.008	0.041	0.001	0.002	0.004	0.002	0.002
Small Coal-fired Utility Boiler	0.032	0.002	0.008	0.000	0.000	0.001	0.000	0.000
Medium Oil-fired Utility Boiler	0.005	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Chlor-alkali plant	8.185	0.426	2.115	0.076	0.085	0.213	0.126	0.085
Primary Copper Smelter	0.438	0.023	0.113	0.004	0.005	0.011	0.007	0.005
Primary Lead Smelter	2.627	0.137	0.679	0.024	0.027	0.068	0.040	0.027
10 km								
Large MWC	2.095	0.109	0.541	0.019	0.022	0.054	0.032	0.022
Small MWC	0.417	0.022	0.108	0.004	0.004	0.011	0.006	0.004
Continuous MWI	0.323	0.017	0.084	0.003	0.003	0.008	0.005	0.003
Intermittent MWI	0.010	0.001	0.003	0.000	0.000	0.000	0.000	0.000
Large Coal-fired Utility Boiler	0.066	0.003	0.017	0.001	0.001	0.002	0.001	0.001
Medium Coal-fired Utility Boiler	0.039	0.002	0.010	0.000	0.000	0.001	0.001	0.000
Small Coal-fired Utility Boiler	0.008	0.000	0.002	0.000	0.000	0.000	0.000	0.000
Medium Oil-fired Utility Boiler	0.001	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Chlor-alkali plant	1.007	0.052	0.260	0.009	0.010	0.026	0.015	0.010
Primary Copper Smelter	0.109	0.006	0.028	0.001	0.001	0.003	0.002	0.001
Primary Lead Smelter	0.651	0.034	0.168	0.006	0.007	0.017	0.010	0.007
25 km								
Large MWC	0.776	0.040	0.201	0.007	0.008	0.020	0.012	0.008
Small MWC	0.149	0.008	0.038	0.001	0.002	0.004	0.002	0.002
Continuous MWI	0.095	0.005	0.025	0.001	0.001	0.002	0.001	0.001
Intermittent MWI	0.003	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Large Coal-fired Utility Boiler	0.021	0.001	0.005	0.000	0.000	0.001	0.000	0.000
Medium Coal-fired Utility Boiler	0.012	0.001	0.003	0.000	0.000	0.000	0.000	0.000
Small Coal-fired Utility Boiler	0.003	0.000	0.001	0.000	0.000	0.000	0.000	0.000
Medium Oil-fired Utility Boiler	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Chlor-alkali plant	0.263	0.014	0.068	0.002	0.003	0.007	0.004	0.003
Primary Copper Smelter	0.039	0.002	0.010	0.000	0.000	0.001	0.001	0.000
Primary Lead Smelter	0.235	0.012	0.061	0.002	0.002	0.006	0.004	0.002

4. EFFECT OF AIRBORNE MERCURY ON PISCIVOROUS AVIAN AND MAMMALIAN WILDLIFE

As described in Section 2 of this volume, mercury bioconcentrates, bioaccumulates and biomagnifies in aquatic food chains. These processes result in mercury residues in fish that are much higher than concentrations in the water in which they live, thereby providing an enriched contaminant source for piscivorous avian and mammalian wildlife. Section 4.2 presents derivation of a wildlife criterion level (WC) for mercury that is protective of piscivorous wildlife. This WC is defined as the concentration of mercury in water that, if not exceeded, protects avian and mammalian wildlife populations from adverse effects resulting from ingestion of surface waters and from ingestion of aquatic life taken from these surface waters. The health of wildlife populations may, therefore, be considered the assessment endpoint of concern.

Calculation of a WC for mercury is based upon the use of a wildlife reference dose approach, combined with knowledge of the extent to which mercury becomes concentrated in aquatic food chains. The methods used to calculate this criterion value are based on those described in the Proposed Great Lakes Water Quality Guidance for the Great Lakes Water Quality Initiative (U.S. EPA, 1993c) and implemented in the final Water Quality Guidance for the Great Lakes System (U.S. EPA, 1995b), henceforth referred to as the "Proposed Guidance" and "Final Guidance," respectively. This approach yields a single measurement endpoint, which is the total mercury concentration in water that is believed to be protective of piscivorous wildlife. It should be noted, however, that this endpoint can be related to total mercury residues in fish through the use of bioaccumulation factors (BAFs).

BAFs for trophic levels 3 and 4 (forage fish and larger, piscivorous fish, respectively) are estimated in Appendix A. It is recognized that there is considerable natural variability with respect to the accumulation of mercury in aquatic food chains, which contributes in turn to variability in trophic relationships and BAFs. In addition, there is a lack of understanding of fundamental processes that contribute to methylation of mercury and subsequent bioaccumulation in aquatic organisms. Additional uncertainty derives from ongoing improvements in sampling technique and analytical methodology.

Tempering these uncertainties is a large and growing volume of both laboratory and field data for mercury. From the perspective of WC development, field data are of particular interest. The Proposed Guidance (or GLWQI) provides that when sufficient field data are available, field-derived BAFs should take precedence over values estimated from laboratory studies or by employing empirical relationships (e.g., correlation with chemical hydrophobicity). It was thought that when sufficient field data exist, field-derived BAFs represent the best obtainable estimate of mercury bioaccumulation by fish. An effort was made, therefore, to collect both field and laboratory data and to characterize the variation arising from the aforementioned sources and incorporate it into the analysis by using a Monte Carlo simulation approach. The results of this effort are summarized in Section 4.1.

4.1 Bioaccumulation Factors (BAFs) for Magnification of Methylmercury in the Aquatic Food Chain

4.1.1 Definition of BAFs and Overview

The bioaccumulation factor (BAF) for any given trophic level is defined as the ratio of the total mercury concentration in fish flesh divided by the concentration of total dissolved mercury in the water column. The BAF represents the accumulation of mercury in fish of a specific trophic level

from both water intake and predation on contaminated organisms. The BAF is a principal input variable in the Indirect Exposure Model (see Volume III) and is used to link estimates of mercury deposition to exposure levels for fish-consuming species.

In this Report BAFs are estimated for trophic level 3 (foraging fish) and trophic level 4 (piscivorous fish) designated as BAF_3 and BAF_4, respectively. BAF_4 is estimated by three different methods and BAF_3 by two. The result, or output, of each estimation is a distribution of BAF values, each associated with some degree of likelihood. The three methods by which BAF_4 is estimated are the GLWQI method, the BAF × PPF method and the field-derived method from measured BAFs at trophic level 4. BAF_3 is estimated by the GLWQI method and directly from measured BAFs at trophic level 3. Each of these methods is described in detail in Appendix A and summarized in Section 4.1.3. BAF_4 is intended to be representative of the random selection of a trophic level 4 fish from a random lake in a random geographical location. It is meant to be used to estimate the concentration of methylmercury in such a randomly-selected fish when multiplied by the total dissolved mercury (inorganic and organic combined) concentration in the water column. BAF_3 performs the same function for trophic level 3 fish.

The general approach used in this analysis is estimation of BAFs using probabilistic Monte Carlo simulation methods as described in Appendix A. This approach was taken to allow quantitative expression of the overall variability surrounding the various estimates of the BAFs and to determine the relative sensitivity of the estimates to specific individual variables.

4.1.2 BAF Estimation Methods

GLWQI Method

The GLWQI method is essentially the same as that in the Proposed Guidance (U.S. EPA, 1993c). The formula is given in equation 1.

$$BAF_n = BCF_{Hg} \times FCM_n \quad (1)$$

where

- n is the trophic level for which the BAF is estimated,
- BCF_{Hg} is the weighted-average bioconcentration factor (BCF) for total mercury at trophic level 1 and
- FCM_n is the food-chain multiplier representing the cumulative biomagnification of mercury from trophic level 2 to trophic level n, n=[3,4].

The formula for BCF_{Hg} is given in equation 2.

$$BCF_{Hg} = (BCF_{mHg} \times MeHg_W) + (BCF_{iHg} \times (1 - MeHg_W)) \quad (2)$$

where

- BCF_{mHg} is the bioconcentration factor for methylmercury at trophic level 1,
- BCF_{iHg} is the bioconcentration factor for inorganic mercury at trophic level 1 and

$MeHg_W$ is the fraction of total mercury in the water column that is in the methyl form.

The formulas for FCM_3 and FCM_4 are given in equations 3 and 4, respectively.

$$FCM_3 = PPF_2 \times PPF_3 \quad (3)$$

$$FCM_4 = PPF_2 \times PPF_3 \times PPF_4 \quad (4)$$

where

PPF_2 is the predator-prey factor at trophic level 2 representing the biomagnification of mercury in zooplankton as a result of feeding on contaminated phytoplankton,

PPF_3 is the same for trophic level 3 fish feeding on contaminated organisms and

PPF_4 is the same for trophic level 4 fish feeding on trophic level 3 fish.

Distributions were assigned to each of the variables in equations 1-4 based on data available in the published literature. The basis and description of the distribution for each variable are described in Appendix A. The nominal values for some of the variables are not the same as presented in the Proposed Guidance (U.S. EPA, 1993c) because of differing assumptions and different approaches to data analysis. The differences in the input variables do not result in significant differences in the BAFs estimated by the Monte Carlo simulations and the BAFs calculated in the Proposed Guidance.

BAF × PPF Method

The formula for the calculation of BAF_4 by this method is given in equation 5.

$$BAF_4 = BAF_3 \times PPF_4 \quad (5)$$

where

BAF_3 is the field-measurement-derived distribution for the BAF at trophic level 3 and

PPF_4 is the same as for the GLWQI method.

Field-derived Method

This method estimates BAF_3 and BAF_4 directly from measurements of BAFs in field studies. The derivation of the BAF distributions is described in Appendix A.

4.1.3 Results of BAF Simulations and Recommended Values

Results of the Monte Carlo simulations for each of the methods are given in Table 4-1, which shows representative statistics for each BAF output distribution. All of the statistics are given as the geometric equivalents (antilogs) of the actual values generated by the simulations. There is a large variance in the distributions, which cannot be separated into variability in BAFs and uncertainty in their estimation. In the absence of appropriate local data, it is recommended to use the geometric mean values in Table 4-1. BAFs derived from data collected at the site of concern are preferred to the estimated values in Table 4-1.

Table 4-1
Summary of Bioaccumulation Factors for Trophic Levels 3 and 4
(mean, 5%, and 95% values)

	BAF_3		BAF_4		
Recommended	66,200		335,000		
Method	Field-derived	GLWQI	BAF_3 x PPF_4	Field-derived	GLWQI
Geometric Mean	66,200	25,200	335,000	400,000	136,000
5th pctl	6,400	2,310	22,700	23,600	8,760
95th pctl	684,000	308,000	4,700,000	6,780,000	2,070,000
GSD[a]	4.14	4.41	5.05	5.59	5.25

[a] Geometric Standard Deviation

The selection of the $BAF_3 \times PPF_4$ as the recommended approach is based on several considerations. Although the mean values of all three BAF_4 simulations agree within a factor of 3, the GLWQI results stand somewhat apart. The mean value of 136,000 for the GLWQI method falls at the 30th and 35th percentile of the BAF_4 distributions for the field-derived and BAF x PPF methods, respectively. The GLWQI method is also more complex with more variables and assumptions than the other two approaches. The BAF x PPF and field-derived methods represent a consolidation of earlier stages of the GLWQI method and should give more accurate results than the GLWQI method provided that the data defining the distributions are at least as good as the data defining the GLWQI variables. Five studies are available for defining BAF_3; however, three of the critical variables in the GLWQI method are based on only one or two studies. In addition the field measurements for BAF_3 and PPF_4 apply directly to variables, while the BCFs in the GLWQI approach do not. That is, the measurements are taken directly from fish at the appropriate trophic levels for BAF_3 and PPF_4; BCF_{mHg} and BCF_{iHg} apply to phytoplankton (trophic level 1) but are estimated from measurements in trophic level 3 fish. The $BAF_3 \times PPF_4$ approach is also less variable than either of the other two methods, as indicated by the geometric standard deviation (Table 4-1).

4.1.4 Sensitivity Analysis

Sensitivity analyses were conducted to examine the effect of changes in assumptions. Three factors have been studied in this analysis: sensitivity of output to individual input variables, PPF_4 disaggregation and correlation of input variables.

The relative contribution of each input variable to the variance of the output distribution was determined for the BAF x PPF method. BAF_3 and PPF_4 contribute 64% and 36% to the variance of BAF_4, respectively. Acquisition of additional data for the determination of BAF_3 is expected to decrease the uncertainty of BAF_4. Refinements to the PPF_4 distribution, however, will have a significant impact on the mean value of BAF_4 for application in specific scenarios.

Different species of piscivores are likely to feed on a restricted fish size range; alternate PPF_4 distributions were, thus, constructed from restricted ranges of the data to represent specific fish size (age) distributions. The distributions represent three ranges of fish sizes, described in Appendix A. Because of the limited amount of data, these distributions are hypothetical, in part. The alternate PPF_4 distributions do have potential significance in real-world scenarios, however. The mid and high PPF_4 distributions, for example, represent estimates of PPF_4 for standardized (two- to four-year-old fish) and older tier 4 fish (eg.,large pike), respectively. These estimates could apply to situations where the size of the consumed fish is known to be at one end of the distribution. The mean estimates of BAF_4 vary from 150,000 to 900,000 using the alternate PPF_4 distributions.

The BAF_4 simulation based on the BAF × PPF method assumes that the input variables are independent. Both BAF_3 and PPF_4, however, depend on the concentration of methylmercury in trophic level 3 fish (BAF_3 is directly dependently, and PPF_4 is inversely dependent). The assumption of independence, in this case, increases variability in the output distribution. Simulations were run with varying assumptions of correlation between the two variables; the details are presented in Appendix A. The results of the simulations show that a moderately strong correlation (50%) between BAF_3 and PPF_4 would have a significant effect on the spread of the output, reducing it by a factor of 3.5. If the correlation were weaker (10%), the spread of the distribution would be reduced by only 22%.

4.1.5 Uncertainty and Variability

Generally, in the representation of the input and output distributions, there are no distinctions as to size or species of fish, location or type of lake (eutrophic or oligotrophic), water column pH, absolute mercury concentrations (in fish or water) or relative methylmercury concen-trations in the water column. The available data are insufficient to make these distinctions. Field data are heavily biased towards northern (oligotrophic) lakes and somewhat towards smaller (younger) fish.

There is no distinction between variability and uncertainty in the BAF_4 distributions. That is, the variability in the output distributions reflects both naturally variable processes and the uncertainty around those processes. For example, the BAF_4 distributions include variability in the BAF associated with variations in fish size combined with the variability associated with methylmercury-generating processes in the water column and the measurement uncertainties associated with both factors.

The large amount of variability evidenced by the data and reflected in the BAF distributions arises from several identifiable but, as yet, unquantified sources. A primary source of variability in both BAF_3 and PPF_4 is the dependence of methylmercury bioaccumulation on the age of the fish. Although the age of fish is probably a major contributor to the variance of PPF_4, the influence of age on BAF_3 is probably much less. Because the value BAF_4 is more dependent on the magnitude of BAF_3 than on PPF_4 the total reduction in variability of the BAF_4 by accounting for fish age may not be large. A second source of variability is seasonal variation of total dissolved mercury in the water column. While the concentration of methylmercury in fish flesh is presumably a function of the varying water concentration, specific values for BAF_3 are generally calculated from single representative values.

Perhaps the greatest source of variability is that of model uncertainty; that is, uncertainty introduced by failure of the model to account for significant real-world processes. The simple linear BAF model relating methylmercury in fish to total mercury in water masks a number of nonlinear processes leading to the formation of bioavailable methylmercury in the water column. Much of the

variability in field data applicable to the estimation of mercury BAFs can be attributed to differences between individual organisms and between aquatic systems. For example, in lake surveys conducted within a relatively restricted geographic region, large differences can exist between lakes with respect to mercury concentrations in a given species of fish (see for example Cope et al., 1990; Grieb et al., 1990; Sorenson et al., 1990; Jackson, 1991; Lange et al., 1993). These observations have led to the suggestion that much of the variability in fish mercury levels is due to differences in local bio-geochemistry processes that determine the percentage of total mercury that exists as the methylated form. In addition, it has been repeatedly shown that mercury in fish accumulates throughout the lifetime of the individual (Scott and Armstrong, 1972; MacCrimmon et al., 1983; Wren et al., 1983; Mathers and Johansen, 1985; Skurdal et al., 1985, Wren and MacCrimmon, 1986; Sorenson et al., 1990; Jackson, 1991; Gutenmann et al., 1992; Glass et al., 1993, Suchanek et al., 1993; Lange et al., 1993). Reported BAF values for a given species may therefore vary as a function of the ages of the animals examined. As a result, some researchers have suggested that comparisons between lakes should be made using "standardized" fish values (that is, a value for a hypothetical 1 kg northern pike), typically derived by linear regression of residue data collected from individuals of varying size and/or age (Wren and MacCrimmon, 1986; Sorenson et al., 1990; Meili et al., 1991).

4.1.6 Conclusions

BAFs derived from adequate data collected at the site of concern should be used in lieu of the estimated values presented in this Report. The criteria for defining the adequacy of data are discussed in the Data Quality Objectives section of Appendix A. When such values are not available, the use of the geometric mean values from the BAF_3 and BAF_4 output distributions generated from the field-derived BAF_3 and PPF_4 distributions is the recommended approach. Use of the geometric mean, rather than the arithmetic mean, is a consequence of the assumption that BAFs are distributed in nature as the logarithm of the observed value. The recommended approach is more direct and less variable than the GLWQI method and involves fewer assumptions. Direct application of the field-derived BAF_4 distribution is not recommended because of the current data limitations. The recommendation as to the use of the (geometric) mean value of these distributions is based on the inability to distinguish among various sources of uncertainty and variability in the output distributions, with consequent problems of interpretation of specific percentiles. Because the exposure concern is for repeated ingestion of contaminated fish, the mean, rather than the median, is the appropriate value. The median is only useful if the concern was the random selection of a single fish. In this case, the mean and median values are virtually identical for both distributions because of the choice of the form of the input distributions.

Reducing the uncertainty in the BAFs generated by these methods will require the collection of more data representative of the critical factors underlying the observed variability, and the inclusion of additional terms to explicitly model those factors. For example, the inclusion of an age/size regression term should account for a substantial portion of the variability in both BAF_3 and PPF_4. Of longer-term significance is the modeling of factors representing the methylmercury-generating processes in the water column, itself, such as those in the Mercury Cycling Model (Hudson et al., 1994).

4.2 Calculation of a Criterion Value for Protection of Piscivorous Wildlife

4.2.1 Procedure Used to Develop Criterion Values for Wildlife in the Water Quality Guidance for the Great Lakes System

The WC for mercury is defined as the concentration of total mercury in surface water that, if not exceeded, protects both avian and mammalian wildlife that use the water as a drinking or foraging source. Thus, the WC is the highest aqueous concentration of mercury that causes no significant reduction in growth, reproduction, viability or usefulness (in a commercial or recreational sense) of a population of animals exposed over multiple generations. For the purpose of this analysis, the term "aqueous concentration" refers to the total concentration of all mercury species in filtered water, including both freely dissolved forms and mercury that is associated with dissolved organic material.

The equation used in this analysis to calculate a WC for mercury is identical to that described in the Proposed Guidance (U.S. EPA, 1993c) and implemented in the final Water Quality Guidance for the Great Lakes System (U.S. EPA, 1995b):

$$WC = \frac{(TD \times [1/UF]) \times Wt_A}{W_A + [(FD_3)(F_A \times BAF_3) + (FD_4)(F_A \times BAF_4)]}$$

where,

WC	=	wildlife criterion value (pg/L; after converting from µg/L)
Wt_A	=	average species weight (g)
W_A	=	average daily volume of water consumed (L/d)
F_A	=	average daily amount of food consumed (g/d)
FD_3	=	fraction of the diet derived from trophic level 3
FD_4	=	fraction of the diet derived from trophic level 4
BAF_3	=	aquatic life bioaccumulation factor for trophic level 3 (L/g; methylmercury concentration in fish/total mercury in water)
BAF_4	=	aquatic life bioaccumulation factor for trophic level 4 (L/g; methylmercury concentration in fish/total mercury in water)
TD	=	tested dose (µg/g bw/d)
UF	=	uncertainty factor

In the equation used in this Report the term F (defined in the GLWQI as the food ingestion rate of prey for a tropic level) is broken into the terms F_A and F_D above. The UF considers uncertainty in three areas described below.

A similar equation was first used by the State of Wisconsin to set Wild and Domestic Animal Criteria (State of Wisconsin, 1989). The entire approach, including both the equation and data requirements for its parameterization, was later modified by U.S. EPA for incorporation into the Proposed Guidance (U.S. EPA, 1993c) and Final Guidance (U.S. EPA, 1995b). The method, in its current form, was reviewed in 1992 at a workshop entitled the National Wildlife Criteria

Methodologies Meeting, sponsored by U.S. EPA (U.S. EPA, 1994). Subsequently, it was used to develop interim Tier I WC for four compounds (PCBs, DDT, dieldrin, and mercury) in the Great Lakes Basin (U.S. EPA, 1993b). These criteria have received public comment. The method has been reviewed by the Science Advisory Board (SAB) on two occasions, most recently in June of 1994. Detailed descriptions of the method, including comparisons with other proposed methods for setting wildlife criterion values, are presented in U.S. EPA (1993c, 1994).

An examination of this equation reveals both a hazard and an exposure component. The GLWQI equation includes a term TD for "tested dose". In this Report, data were reviewed to ascertain an appropriate NOAEL, which was used for the TD. In the absence of a NOAEL, a LOAEL was used with the addition of an appropriate factor (UF_L) to indicate uncertainty around the toxic threshold. An uncertainty factor (UF_A) may be used to provide a margin of safety when applying data from a species other than the species of concern. A third uncertainty factor (UF_S) may be used to extrapolate from subchronic to chronic exposures. Additional adjustments may be warranted by toxicokinetic or toxicodynamic considerations. Collectively, the application of the UF to the TD results in the estimation of a "reference dose" for subsequent calculation of WC.

The WC for mercury is expressed as the total mercury concentration in filtered water. It is recognized that methylmercury is the form of mercury that bioaccumulates in fish. Few laboratories, however, currently possess the analytical capability to speciate mercury in water from natural sources (presently, the different forms of methylmercury tend to be operationally defined; e.g., freely dissolved, weakly bound and strongly bound). In the future, as analytical capabilities improve and a basic understanding of methylmercury formation and behavior is acquired, it may be advisable to calculate WC values based on methylmercury concentrations.

A WC for mercury was calculated in the Proposed Guidance using fixed values for all parameters in the equation. Species-specific WC values (WC_s) were calculated for each of the wildlife species of concern (eagle, herring gull, kingfisher, mink, otter). Intermediate WC values (WC_i) were then obtained for avian and mammalian wildlife by calculating the geometric mean of values for contributing species. The final WC (WC_f) was set equal to the lowest of the two resulting intermediate values and, for mercury, was driven by the calculations for avian species.

The WC_f for mercury derived in the Proposed Guidance is 1300 pg/L. A comparison of the GLWQI criteria for birds and mammals with those derived in this Report is found in Section 4.2.9.

For the present analysis, it was decided to consider some of the same wildlife species considered in the Proposed Guidance. Herring gulls, which are indigenous to the Great Lakes region, were not evaluated in this Report. The avian wildlife for which WC values were calculated are the bald eagle (*Haliaeetus leucocephalus*), osprey (*Pandion haliaetus*) and belted kingfisher (*Ceryle alcyon*). The mammalian wildlife for which WC are calculated are the mink (*Mustela vison*) and river otter (*Lutra canadensis*). Each of these species was originally selected after consideration of the following: (1) their exposure to bioaccumulative contaminants; (2) relevance to Great Lakes ecosystems; (3) availability of information with which to calculate criterion values; and (4) evidence for accumulation and/or adverse effects.

It was recognized that several other wildlife species would satisfy most or all of the selection criteria presented in the GLWQI. Notable examples include the herring gull (*Larus argentatus*), Forster's tern (*Sterna forsteri*), double-breasted cormorant (*Phalacrocorax auritus*), wood stork (*Mycteria americana*), raccoon (*Procyon lotor*), snapping turtle (*Chelydra serpentina*), and American

alligator (*Alligator mississippiensis*). Exposure factors for a large number of wildlife species are available in a recently published handbook (U.S. EPA, 1993a). A critical evaluation of these data as they pertain to the development of WC is also available (U.S. EPA, 1995a). Allometric equations may also be used to calculate both feeding and drinking requirements (see for example, Calder and Braun, 1983; Nagy, 1987). In time, the inclusion of other species, including both amphibians and reptiles, may be appropriate, particularly if an effort is made to calculate WC_f on a regional basis, or if the species used in the present analysis are not representative of the ecosystem of concern. The present analysis is intended, however, to be national in scope. Each of the species selected in the Proposed Guidance is distributed over large portions of the country (see species distributions, Section 3.2), and in these locations each species is closely tied to water resources via aquatic food chains.

4.2.2 Exposure Parameters

Exposure parameters for the present analysis are shown in Table 4-2. The scientific basis for these parameters is reviewed elsewhere (U.S. EPA 1993a, 1995a). For this analysis, it was assumed that prey not attributed to trophic levels 3 and 4 were derived from non-aquatic origins and do not contain mercury. Were these prey to contain mercury, WC values calculated for the relevant species would decrease. BAFs for trophic levels 3 and 4 were assigned the values recommended in Section 4.1.6.

Table 4-2
Exposure Parameters for Mink, Otter, Kingfisher, Osprey, and Eagle

Species	Body Wt. (WtA) kg	Ingestion Rate (F_A) kg/d	Drinking Rate (W_A) L/d	Trophic Level of Wildlife Food Source	% Diet at Each Trophic Level
Mink	0.80	0.178	0.081	3	90
Otter	7.40	1.220	0.600	3,4	80,20
Kingfisher	0.15	0.075	0.017	3	100
Osprey	1.50	0.300	0.077	3	100
Eagle	4.60	0.500	0.160	3,4	74,18

4.2.3 Health Endpoints for Avian Wildlife

Most studies of chronic exposure to birds involve feeding grain contaminated with a mercurial compound applied to the feed grain. Exposure of birds to mercury commonly occurs when they feed on seed grain that has been treated with mercurials as a preservative (Eisler, 1987). Fimreite (1970) identified a LOAEL of 1.1 µg/g/d for growth inhibition in leghorn cockerel chicks (*Gallus*) based upon 6 µg/g methylmercury dicyandiamide in the feed. Fimreite (1971) also identified a LOAEL for reproductive effects (reduced survival, reduced egg production, defective shells) of 0.18 µg/g/d in ring-necked pheasant (*Phasianus colchicus*) fed seed treated with methylmercury dicyandiamide. Scott (1977) identified a LOAEL for reproductive effects (reduced fertility, reduced egg number, reduced survival, defective shells) of 4.9 µg/g/d in domestic chickens.

The most comprehensive studies of the effect of mercury on birds were conducted by Heinz and co-workers. Heinz (1974, 1975, 1976a,b, 1979) assessed the effects of dietary methylmercury dicyandiamide (0, 0.5 and 3.0 ppm as elemental mercury) over three generations of mallard ducks. Treatment groups were housed in separate wire pens and fed dry duck mash treated with methylmercury dicyandiamide. In the first generation, treatment began in adult ducks. Subsequent generations received treatment beginning at nine days of age.

Initially, Heinz (1974) identified a NOAEL of 0.5 ppm based upon reproductive effects in a 21 week study. In a later study, reproduction in first and second generation ducks was evaluated (Heinz, 1976a,b), and the NOAEL for the first generation was again determined to be 0.5 ppm. The second generation, however, suffered adverse reproductive effects including eggs laid outside the nest box ($p<0.05$), reduced number of ducklings surviving to one week of age ($p<0.05$), and reduced growth of ducklings ($p<0.05$) at the 0.5 ppm dose. Consequently, the LOAEL for reproductive effects for the second generation was 0.5 ppm with no NOAEL identified. A third generation of mallards also demonstrated adverse reproductive effects at 0.5 ppm mercury in the diet. Effects observed included reduced number of sound eggs laid per day ($p<0.01$) and thinner egg shells ($p<0.05$).

Heinz (1975, 1979) also examined behavioral effects of mercury exposure in the approach response of chicks to maternal calls and avoidance of frightening stimuli. In third generation ducklings there was a reduction in response rate and speed of response to maternal calls ($p<0.01$). When data were pooled from all studies and subject to analysis of variance (ANOVA) with multiple comparisons, alterations of behavior were observed in the lowest dose groups in all generations. These alterations included reduction in the number of ducklings which approached maternal calls ($p<0.01$) and an increase in the distance traveled to avoid a threatening stimulus ($p<0.05$). In summary, no NOAEL could be determined for behavioral effects, and the NOAEL for reproductive effects could only be demonstrated for the first generation.

For the determination of an appropriate LOAEL, it was concluded that effects observed in second and third generation ducks at 0.5 ppm should not be discounted. It seems likely that the effects observed in the second and third generations were a result of the earlier onset of dosing (adult onset versus onset as ducklings). For this reason, 0.5 ppm was selected as a LOAEL for mallard ducks. Assuming a feeding rate of 128 mg/g/d for adult mallards, the LOAEL for reproduction and behavior is 0.064 μg Hg/g/d.

4.2.4 Health Endpoints for Mammalian Wildlife

River otters (*Lutra canadensis*) fed 2 ppm methylmercury (0.09 μg/g) for six months suffered from anorexia and ataxia (O'Connor and Nielson, 1981). In mink, 27 ppm of dietary phenylmercuric chloride caused lethality in 40% of the males and 31% of the females within six weeks of exposure (Borst and Lieshout, 1977).

Wobeser et al. (1976a,b) studied the effects of dietary consumption of methylmercury on ranch mink. There were two parts to this study, which together formed the basis of Wobeser's dissertation research (Wobeser, 1973). In the first part (Wobeser et al., 1976a), 25 adult female mink and their litters were divided into three groups: Group I contained five females and 19 kits (control); Group II contained 10 females and 34 kits (50% fish diet); and Group III contained 10 females and 29 kits (75% fish diet). The ration was prepared using mercury-contaminated freshwater drum from Lake Winnipeg, Manitoba; mercury in fish tissue was assumed for the purposes of the present analysis to consist primarily of methylmercury. The fish was supplied in a ground, frozen form and was then

mixed with cereal and uncontaminated chow to a desired composition of 50 or 75 kg fish/100 kg of food. All mink were fed once daily in slight excess of consumption. The three exposure groups were observed for 145 days. Assuming a food consumption rate of 0.16 g/g/d (appropriate to captive animals; Bleavins and Aulerich, 1981) and an average weight of 0.8 kg for the mink, these treatments corresponded to dosing levels of approximately 35 and 55 μg/kg bw/d. One female and 3-6 kits were euthanized every 15 (treatment) or 30 (control) days. Complete necropsies were then performed. No clinical signs of disease were observed in any of the mink within the experimental period, and no mortality or growth impairment occurred which could be attributed to the feeding of mercury-contaminated fish.

In a second experiment (Wobeser et al., 1976b), 30 adult female mink were assigned to one of six groups of five animals each. The animals were fed chow spiked with methylmercuric chloride at 0.0 (control), 1.1, 1.8, 4.8, 8.3, or 15.0 μg/g (by analysis), corresponding to dosing levels of 180, 290, 770, 1330, and 2400 μg/kg bw/d. Two mink from each group were allowed to die of intoxication or were euthanized after 93 days (the end of the experiment). Animals were necropsied and the tissues analyzed for mercury content. All animals in the control group remained clinically normal, and the only clinical sign in the 1.1 μg/g dose group was a slight tendency for two of the animals to move more slowly than the others during the last few days of the experiment. Anorexia, posterior ataxia and lateral recumbency were observed in the other four dose groups. Death occurred within 26-36 days at 4.8 μg/g, and within 19-26 days at 8.3 μg/g. Histopathological abnormalities were seen at 1.1 μg/g, including pale, yellow livers, lesions in the central nervous system, and axonal degeneration.

Based upon a review of the Wobeser studies (Wobeser, 1973; Wobeser et al., 1976a,b) it can be concluded that the LOAEL for subchronic exposure of mink to methylmercury is 180 μg/kg bw/d (1.1 μg/g dose group), using nerve tissue lesions as an effects endpoint. The NOAEL derived from these studies is 55 μg/kg bw/d. Importantly, it was Wobeser's opinion that had the studies been carried out for a longer duration, nervous tissue damage observed in the 1.1 μg/g dose group would have become manifested as impaired motor function.

Charbonneau et al. (1974) fed random-bred domestic cats (*Felis domesticus*) 3, 8.4, 20, 46, 74 or 176 μg/kg/d of mercury, either as methylmercuric chloride in food or as methylmercury-contaminated fish, 7 d/week for 2 years. Clinical examinations of the animals were conducted periodically. Neurological examinations, using a modification of the method of McGrath (1960) were conducted prior to the test, monthly throughout the test and more frequently as clinical signs of methylmercury toxicosis became apparent. Neurological impairment, including hindrance of the hopping reaction and hypalgesia, was observed in animals exposed to 46, 74, or 176 μg/kg/d, regardless of whether casts were fed contaminated fish or spiked food. No treatment-related effects were observed in three lower dosage groups. Overt signs of toxicity, including ataxia, loss of balance and motor incoordination, were observed in animals fed 74 or 176 μg/kg/d. These findings suggest that 20 μg/kg/d is the NOAEL and 46 μg/kg/d is the LOAEL for chronic dietary exposure to methylmercury in domestic cats. Charbonneau et al. (1974) also concluded that there was no difference in the toxicity or bioavailability between naturally contaminated fish and fish spiked with methylmercuric chloride.

4.2.5 Summary of Health Endpoints for Avian and Mammalian Wildlife

The avian chronic TD value was derived from studies by Heinz (1975, 1976a,b, 1979) in which three generations of mallard ducks (*Anas platyrhynchos*) were dosed with methylmercury dicyandiamide (0, 0.5 and 3.0 ppm). The lowest dose, 0.5 ppm (64 μg/kg bw/d), resulted in adverse

effects on reproduction and behavior and was designated as a chronic LOAEL. As no NOAEL was reported, a UF_L of 3 was used according to methodology described in U.S. EPA (1995b).

The mammalian chronic NOAEL was derived from studies of subchronic exposure by Wobeser (1973, 1976a,b) in which mink were dosed with mercury in the form of mercury-contaminated fish (0.22 and 0.33 ppm, naturally incorporated into fish; 1.1, 1.8, 4.8, 8.3 and 15.0 ppm spiked into the diet). Effects observed included histopathologic lesions in nerve tissue at 1.1 ppm and higher doses. Anorexia, ataxia and death occurred at 1.8 ppm and higher doses. The dose of 0.33 ppm (55 µg/kg bw/d) was selected as the NOAEL for subchronic exposure. As this was a less than lifetime study, a UF_S of 10 was applied to the TD or NOAEL. The subchronic NOAEL/UF_S is 5.5 µg/kg bw/d, which is approximately one-fourth the chronic NOAEL (20 µg/kg/d) estimated from long-term feeding studies with domestic cats (Charbonneau et al., 1974).

Based on the information above, the TDs used for calculation of a WC for mercury were these:

For avian wildlife - A LOAEL of 64 µg/kg bw/d, with a UF_L of 3; and

For mammalian wildlife - A NOAEL of 55 µg/kg bw/d, with a UF_S of 10.

4.2.6 Calculation of Wildlife Criterion Values

WC values were calculated for each of the wildlife species of concern using exposure parameters values recommended in previous sections. UF_As were employed as recommended in the GLWQI to extrapolate from test species to the species of interest. Because the mammalian TD (NOAEL) was derived from studies with mink, the UF_A for species extrapolation of the mink WC was set equal to 1.0. Otter were considered sufficiently similar to mink so that a UF_A of 1 was also considered appropriate. A UF_A of 3 was used for extrapolation of mallard data to the kingfisher, eagle, and osprey. Calculations of WC values for each of the selected species follow.

For the mink:

$$WC_S = \frac{(TD \times [1/(UF_A \times UF_S \times UF_L)]) \times Wt_A}{W_A + [(0.9)(F_A \times BAF_3)]}$$

$$WC_S = \frac{(0.055\ mg/kg/d \times [1/(1 \times 10 \times 1)] \times 0.8\ kg}{0.081\ L/d + [(0.9)\ (0.178\ kg/d \times 66{,}200)]}$$

$$WC_S = 415\ pg/L$$

For the otter:

$$WC_S = \frac{(TD \times [1/(UF_A \times UF_S \times UF_L)] \times Wt_A}{W_A + [(0.8)(F_A \times BAF_3) + (0.2)(F_A \times BAF_4)]}$$

$$WC_S = \frac{(0.055\ mg/kg/d \times [1/(1 \times 10 \times 1)] \times 7.4\ kg}{0.60\ L/d + [(0.8)(1.22\ kg/d \times 66{,}200) + (0.2)(1.22\ kg/d \times 335{,}000)]}$$

$$WC_S = 278\ pg/L$$

For the kingfisher:

$$WC_S = \frac{(TD \times [1/(UF_A \times UF_S \times UF_L)] \times Wt_A}{W_A + [(1.0)(F_A \times BAF_3)]}$$

$$WC_S = \frac{(0.064\ mg/kg/d \times [1/(3 \times 1 \times 3)] \times 0.15\ kg}{0.017 + [(1.0)(0.075 \times 66{,}200)]}$$

$$WC_S = 193\ pg/L$$

For the osprey:

$$WC_S = \frac{(TD \times [1/(UF_A \times UF_S \times UF_L)] \times Wt_A}{W_A + [(1.0)(F_A \times BAF_3)]}$$

$$WC_S = \frac{(0.064\ mg/kg/d \times [1/(3 \times 1 \times 3)] \times 1.5\ kg}{0.077\ L/d + [(1.0)(0.3\ kg/d \times 66{,}200)]}$$

$$WC_S = 483\ pg/L$$

For the bald eagle:

$$WC_S = \frac{(TD \times [1/(UF_A \times UF_S \times UF_L)] \times Wt_A}{W_A + [(0.74)(F_A \times BAF_3) + (0.18)(F_A \times BAF_4]}$$

$$WC_S = \frac{(0.064\ mg/kg/d \times [1/(3 \times 1 \times 3)] \times 4.6\ kg}{0.16\ L/d + [(0.74)(0.5\ kg/d \times 66{,}200) + (0.18)(0.5\ kg/d \times 335{,}000)]}$$

$$WC_S = 538\ pg/L$$

The mean of the two WC_s values calculated for mammals is 346 pg/L. The mean of the three avian values is 405 pg/L. The lowest of these is the WC_i calculated for avian species.

Therefore, the WC_f for mercury is 346 pg/L.

4.2.7 Calculation of Mercury Residues in Fish Corresponding to the Wildlife Criterion Value

The WC for mercury can be used to calculate corresponding mercury residues in fish through the use of appropriate BAFs. Using the BAFs presented in Section 4.1, a WC of 346 pg/L corresponds to methylmercury concentrations in fish of 0.023 µg/g and 0.116 µg/g for trophic levels 3 and 4, respectively.

4.2.8 Calculation of a Wildlife Criterion for the Florida Panther

Estimates of the NOAEL and LOAEL in domestic cats were not intended for use in the derivation of a WC for Florida panthers, but were presented instead to provide a comparison with other mammals. The chronic NOAEL for cats (20 µg/kg/d) is close to that for mammals generally (5.5 µg/kg/d; that is, the subchronic NOAEL of 55 µg/kg/d divided by a UF_S of 10). Cats do not, therefore, appear to be uniquely sensitive or insensitive to the toxic effects of mercury.

Derivation of a WC to protect the panther is complicated by possibility that prey items (e.g., the raccoon) accumulate mercury to an even greater extent than the fish represented by trophic level 4. Other prey (e.g., deer) probably contain relatively lower levels of mercury. Calculation of a WC protective of the panther, therefore, requires collection of additional information on the diet of this species and mercury residues contained therein. These residues would then have to be related back to corresponding levels in water through the use of PPFs (e.g., raccoon/fish or other aquatic biota) and BAFs (aquatic biota/water). Existing data are insufficient to support such an analysis but could be collected and developed for this purpose.

4.2.9 Comparison of GLWQI Criteria with WC Derived in this Report

The evaluation of data and calculation of WC in this Report was done in accordance with the methods and assessments published in the draft GLWQI (U.S. EPA 1993a). Availability of additional

data and differences in interpretation of those data led to differences in the calculated values of the WC in this Report and those published in the final GLWQI (U.S. EPA 1995b). Both evaluations employed the same methodology as described in Section 4.2.1. Both used the same studies as the basis for WC calculation: for birds, the three generation reproduction study in mallards (Heinz, 1974, 1975, 1976a,b, 1979); and for mammals the subchronic dietary studies in mink (Wobeser et al., 1976a,b). In addition to these studies, the authors of this Report were able to obtain Wobeser's dissertation (Wobeser, 1973); this provided some additional information, which was augmented by discussions with the author.

Table 4-3 presents a comparison between the WC calculated in the GLWQI (U.S.EPA, 1995b) and this Report. All of the WC calculated in this Report are lower (more conservative) than those published in the GLWQI. All species-specific WC, however, differ less than an order of magnitude from one another. Range in differences is from nearly four-fold lower for the WC.

Table 4-3
Species-specific Wildlife Criteria Calculated in the Great Lakes Water Quality Initiative (GLWQI)[a] and in the Mercury Study Report to Congress

Species	Wildlife Criterion (pg/L)	
	GLWQI	Mercury Study Report to Congress
Mink	2880	415
Otter	1930	278
Kingfisher	1040	193
Osprey	Not done	483
Eagle	1920	538

[a] U.S.EPA, 1995b

In the evaluation of effects in birds, both the GLWQI and this Report identified a LOAEL for reproductive effects in the second generation of mallards exposed to 0.5 ppm mercury in diet (Heinz 1976b, 1979). In the GLWQI this LOAEL was adjusted to 0.078 mg/kg bw/d by applying an average food ingestion rate for treated mallards of 0.156 kg/kg-d. This Report converted the LOAEL to 0.064 mg/kg bw/d by application of an assumed feeding rate for adult mallards of 0.128 kg/kg-d. In calculating the wildlife reference dose, the GLWQI used a UF_A of 3 and a UF_L of 2. This Report used a UF_A of 3 and a UF_L of 3 (see Section 4.5.2 for a discussion of UF_L).

In the effects assessment for piscivorous mammals both the GLWQI and this Report used data on mink administered mercury in the diet. The GLWQI identified a NOAEL of 1.1 ppm. At this dietary exposure there were changes in the liver, lesions in the central nervous system and axonal degeneration; moreover, two of the animals in this treatment group were observed at the end of treatment to move slowly by comparison to other mink. The study authors reported their opinion that mink treated at 1.1 ppm in the diet for longer than the study would be expected to show clinical signs of nervous system damage. Animals treated at the next dose, 1.8 ppm, were observed with anorexia,

ataxia and increased mortality. Based on these considerations, this Report considered 1.1 ppm to be LOAEL, and as described in Section 4.2.4, used data from the first part of the study to identify a NOAEL of 0.33 ppm. This Report used data from Wobeser (1973) to establish the weights of female mink and kits used in this part of the study; this resulted in slight differences in conversion of dose in ppm diet to µg/kg bw/d.

In assessment of exposure to birds through consumption of prey, the GLWQI made assumptions that were appropriate the Great Lakes region. In particular the GLWQI assumed that mercury contaminated herring gulls constitutes 6% of the diet of bald eagles. As this Report is a nationwide assessment, use of this region-specific assumption was not considered appropriate; eagles were assumed to consume non-fish prey, with no mercury contamination, as 9% of the total diet. The largest numerical difference in exposure assessment between the GLWQI and this Report is in the use of BAF. The GLWQI used a BAF of 27,000 for trophic level 3 and a BAF of 140,000 for trophic level 4. Derivation of the BAF_3 of 66,200 and BAF_4 of 335,000 used in this Report is described in Section 4.1.

Thus, the differences between the wildlife criterion in the Guidance and in this Report are a result of three factors. First, and with the greatest numerical impact, this Report uses more recent data to derive BAFs. The Supplementary Information Document to the final Water Quality Guidance for the Great Lakes System noted that the preliminary report containing these data was available but was not used because it had not been completed at the time the final guidance was published (U.S. EPA 1995b, p. 144). Second, the Guidance appropriately used some region-specific assumptions that were not used in this nationwide assessment (e.g., consumption of herring gulls by eagles). Finally, different endpoints were used because the purposes of the assessments were different. In the Guidance wildlife methodology, a risk-management decision was made to base the wildlife criterion on endpoints likely to influence wildlife populations (e.g., reproductive/developmental, mortality, growth). In this Report, a more sensitive endpoint was selected with the goal of assessing the full range of effects of mercury. The difference in the results reflects the amount of discretion allowed under the Agency Risk Assessment Guidelines.

4.3 Uncertainty Analysis

A formal analysis of uncertainty around the WC estimate was not attempted. Such an analysis would require specification of numeric distributions for each of the parameters in the equation. While theoretically possible, this approach is of questionable value since the overall analysis is intended to be protective of that subset of each species which feeds extensively at the top of aquatic food chains. Thus, incorporation of data reflecting the range of dietary items upon which the bald eagle feeds would tend to generate an extremely broad range of WC values for this species. In addition, data for several of the parameters in the equation, in particular the NOAEL and UF estimates, are presently sufficient only to generate point estimates.

A restricted uncertainty analysis involving only incorporation of numeric distributions for each of the BAF estimates could be accomplished using existing data, but would probably not be useful. As noted previously, BAF distributions generated by Monte Carlo analysis of field data are thought to reflect real, naturally-derived variation in mercury bioaccumulation and biomagnification. Despite the relative abundance of such data, BAFs expressed on a total mercury basis remain difficult to interpret. Because methylmercury is the form of mercury accumulating in fish, WC distributions based on the distribution of methylmercury BAFs are more likely to yield information of value to risk assessors.

4.4 Sensitivity Analysis

In a sensitivity analysis, an attempt is made to characterize the extent to which a calculated value (e.g., a WC value) changes with changes in the parameters upon which its calculation depends. Examination of the equation for calculation of WC values suggests that a proportional relationship exists between the WC and the NOAEL, UF or Wt_A. The relationships between the WC and parameters that appear in the denominator are not as apparent and must be explored by varying these parameters one-by-one in systematic fashion. The analysis is also complicated by the variable relationship that exists between FD_3 and FD_4. In the otter and eagle, FD_3 and FD_4 tend to be reciprocal (although in the eagle these values do not add up to 1.0). In the mink, however, FD_3 is assigned a value of less than 1.0 and the remainder of the diet is assumed to consist of prey that are not aquatic in origin and are not contaminated with mercury.

Nevertheless, general conclusions can be reached regarding the sensitivity of WC estimates to changes in these parameters. These can be described as follows:

- A decrease in any parameter that appears in the denominator will have a larger effect on WC than an equivalent percentage-wise increase.

- When BAF_3 appears alone in the denominator, a percentage-wise increase in BAF_3 or FD_3 will cause a less than proportional decrease in the WC; conversely a decrease in BAF_3 or FD_3 will cause a greater than proportion increase the WC.

- When both BAF_3 and BAF_4 appear in the denominator, an equivalent percentage-wise change in BAF_4 (and by extension PPF_4) has a greater impact on the WC than a change in BAF_3, but in either case the effect is less than proportional.

- If BAF_3 and BAF_4 are both allowed to change (holding PPF_4 constant), a percentage-wise increase in BAF_3 (and by extension BAF_4) will have a less than proportional effect on WC, while a decrease in BAF_3 will have a greater than proportional impact.

- Under all circumstances, a percentage-wise increase in F_A will cause a less than proportional decrease in WC, while a decrease in F_A will cause a greater than proportional increase in WC.

- Owing to its small contribution to the analysis as a whole, large changes in W_A have a very small impact on WC.

With the exception of F_A, it is not possible to conclude that for all species the WC is most sensitive to one or the other of the parameters in the denominator of the equation. For species that feed at one trophic level, all parameters other than F_A have the potential to change WC in a proportional or greater than proportional manner. For species that feed at two trophic levels, the BAF at the lower trophic level becomes relatively less important, but it may still have a large impact on WC if the percentage of the diet represented by this lower trophic level is large (e.g., in the mink).

4.5 Uncertainties Associated with the GLWQI Methodology

Efforts to develop WC for the protection of piscivorous wildlife are relatively recent in origin, and the methods employed for this purpose continue to undergo modification and refinement. Owing

to the complexity of natural systems, uncertainties associated with the development of WC are to be expected. Additional uncertainties derive from the relative scarcity of wildlife toxicity information and the necessity of extrapolating individual-based effects to higher levels of biological organization (e.g., populations).

Uncertainties associated with the GLWQI methodology have been reviewed elsewhere (U.S. EPA, 1994). It is not our intent to repeat this information, but instead to focus on those areas which are especially pertinent to the development of a WC for mercury. These are listed below in no particular order.

4.5.1 Limitations of the Toxicity Database

Substantial uncertainties underlie most of the toxicity data for mercury in wildlife. Comparison of NOAELs and LOAELs between species requires adoption of unproven assump-tions about the uptake, distribution, elimination, and toxic effects of mercury. Conclusions based upon extrapolation from one species to another are, therefore, tenuous and result in the use of uncertainty factors for species extrapolation. Additional uncertainties derive from the necessity of extrapolating from LOAELs to NOAELs, and from subchronic endpoints to chronic endpoints. In some instances there may also be a need to account for the possibility that test results do not adequately protect the most sensitive individuals. This may be particularly germane to the case of the Florida panther, when there is concern for individual animals).

Existing epidemiological data are complicated by the possibility that "naturally incorporated" mercury is accompanied by other contaminants which are exerting some or all of the observed effect. Ideally, it is desirable to compare the effects of mercury that has been incorporated naturally with effects that are due to mercury that has been spiked into a prepared diet. By spiking mercury into the diet, the researcher can better control the dose to the animal. The bioavailability of mercury in such a formulation may be very different from that which exists naturally. Charbonneau et al. (1976) has demonstrated that the bioavailability and toxicity of methylmercury to cats is equivalent whether given in contaminated fish or spiked in the diet.

Despite a lack of toxicity information and problems concerning its interpretation, estimated NOAELs for piscivorous birds and mammals are very similar (55 µg/kg/d for mammals versus 21 µg/kg/d for birds). Moreover, the existence of toxicity information for the mink eliminates the need to incorporate additional uncertainty factors into the analysis. Unfortunately, similar data for piscivorous birds do not exist.

EPA cannot test all wildlife species of interest. The use of uncertainty factors for species extrapolation is likely, therefore, to continue. Existing information can be used, however, to suggest which species should be singled out for testing. Information of this type is reviewed in this document in several locations and includes species distribution, natural history considerations and exposure factors. Properly applied, species sensitivity factors probably represent a relatively small source of error in the calculation of WC values.

Finally, comparisons between wildlife and human NOAELs are complicated by differences in the ability of a given study to reveal an adverse effect when it occurs. For wildlife, most of the endpoints selected can be considered severely adverse or frank effects. Very few studies to date have been designed to study subtle adverse effects or precursors to adverse effects in wildlife. Developmental neurotoxicity endpoints are of particular interest because of their demonstrated

sensitivity in humans. The question arises, therefore: what would the LOAEL or NOAEL for a given wildlife species have been had the researcher been looking for (or was able to detect) these more subtle effects? One possible approach to this question is to examine the results of studies in which both frank and more subtle effects were observed and determine the corresponding difference between dosage levels.

Clearly, more research of this type is needed. The available data do, however, suggest that uncertainty factors presently employed to derive chronic reference doses for birds and mammals are unlikely to be greatly underprotective or overprotective, and are, therefore, reasonable.

4.5.2 LOAEL-to-NOAEL Uncertainty Factor UF_L

In determining the WC for mercury exposure in wildlife, a NOAEL is preferred as the value to be used as the term TD. The WC can be considered a wildlife Reference Dose (RfD) with an adjustment for exposure assumptions. As is the case for human health RfDs, the wildlife RfD is an attempt to estimate a threshold dose for adverse effects and then to determine a level below that threshold dose. It is assumed that daily consumption of an amount of material below the threshold for adverse effects should be without ill effect.

In cases where studies do not identify a NOAEL, the data are examined to identify a lowest-observed-adverse-effect level (LOAEL) to be used in estimating the RfD. A UF_L of 3 or 10 (based on EPA Reference Dose methodology) is typically applied when a LOAEL is used in the absence of a NOAEL.

In determining the RfD for human exposure to methylmercury, a large number of laboratory animal studies on methylmercury toxicity were summarized as supporting data. Results from many of those studies permitted estimation of both a LOAEL and a NOAEL. Those studies were examined in an effort to determine the most appropriate UF_L for wildlife exposure to mercury.

The studies examined are summarized in Volume IV of this Report. Nineteen studies were selected as being the most relevant and appropriate for determining a UF_L. Selection criteria included the following:

- methylmercury toxicity to nonhuman mammals;
- oral exposure (with preference given to dosing in food or drinking water); and
- chronic or subchronic exposure durations (with exceptions for reproductive and developmental toxicity where such distinctions are less relevant).

Cancer and genotoxic endpoints were not included because tumors are not often reported in wildlife toxicity studies. Endpoints included in the analysis (Table 4-4) included lethality, neurotoxicity, renal toxicity, gastrointestinal toxicity, immunotoxicity, developmental toxicity and reproductive toxicity. Data abstracted from the studies include the species and sex of the test subjects, toxicologic endpoint, LOAEL, NOAEL and the ratio between them. The LOAEL:NOAEL ratios were not segregated by endpoint because there were an insufficient number of studies at most endpoints to determine statistical significance.

Table 4-4
Analysis of LOAEL-to-NOAEL Uncertainty Factor

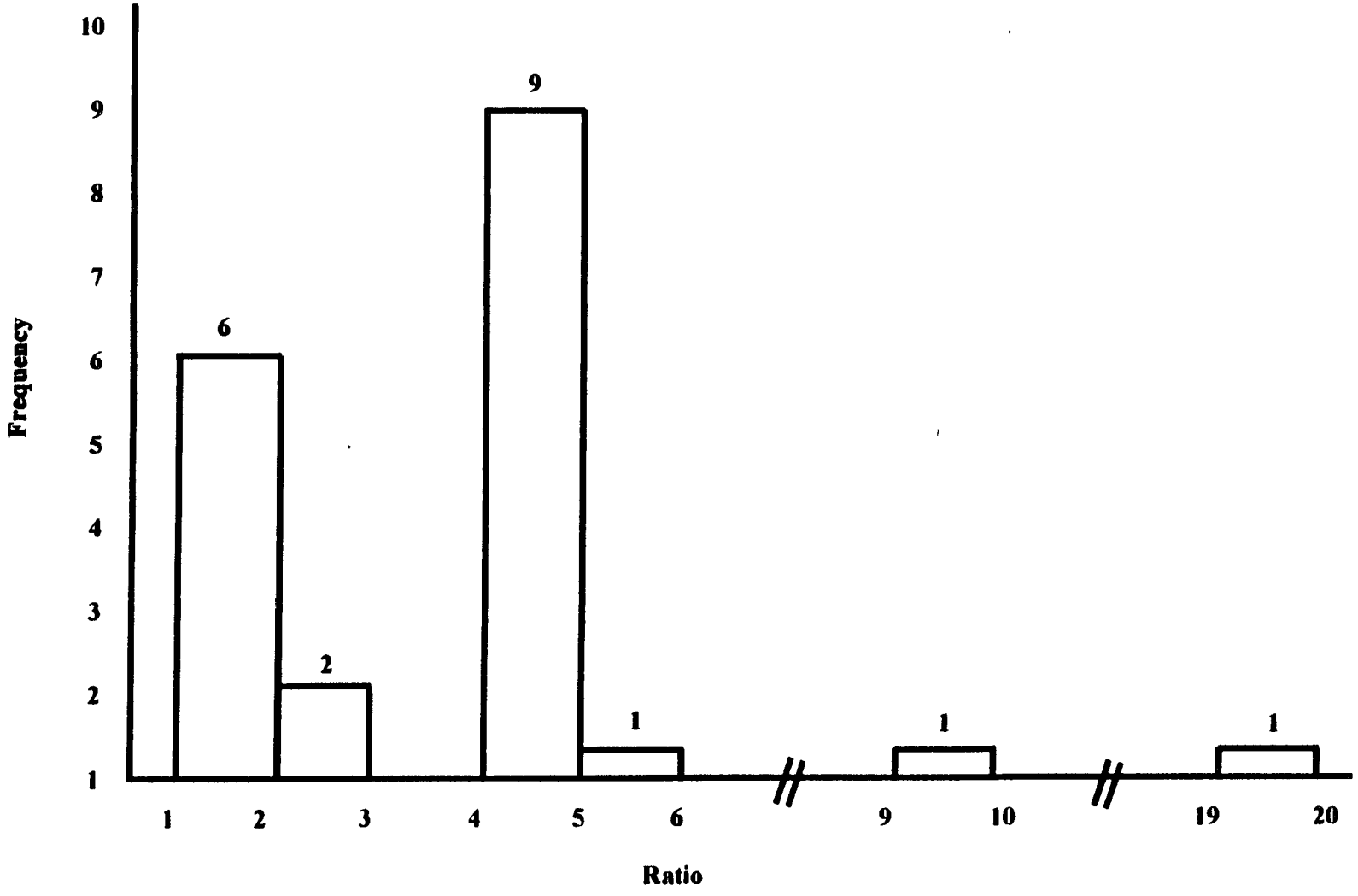
Endpoint Species and Sex		LOAEL (mg/kg/day)	NOAEL (mg/kg/day)	RATIO LOAEL:NOAEL	Study
Lethality					
B6C3F1 Mouse	M	0.69	0.60	1.15	Mitsumori et al., 1990
Neurotoxicity					
Rat (Wistar)	M & F	0.25	0.05	5.0	Munro et al., 1980
Cat	sex NS	0.046	0.020	2.3	Charbonneau et al., 1976
Monkey *(Macaca fasicularis)*	M & F	0.03	0.02	1.5	Sato and Ikuta, 1975
Monkey *(Macaca artoides* and *M. nemestrina)*	M & F	0.5	0.4	1.25	Evans et al., 1977
Renal Toxicity					
Mouse (ICR)	M F	0.72 0.62	0.15 0.11	4.8 5.6	Hirano et al., 1986
Mouse (B6C3F1)	M F	0.14 0.6	0.03 0.13	4.7 4.6	Mitsumori et al., 1990
Gastrointestinal Toxicity					
Mouse (B6C3F1)	M	0.69	0.14	4.9	Mitsumori et al., 1990
Immunotoxicity					
Rabbit (New Zealand White)	M & F	0.4	0.04	10.0	Koller et al., 1977
Developmental Toxicity					
Rat (Charles River)	F	4.0	0.2	20.0	Nolen et al., 1972
Rat (Wistar)	F	0.25	0.05	5.0	Khera and Tabacova, 1973
Rat (Charles River)	F	1.4	0.7	2.0	Fowler and Woods, 1977
Rat (Wistar)	offspring of both sexes	0.6	0.2	3.0	Schreiner et al., 1986

Table 4-4 (continued)
Analysis of LOAEL to NOAEL Uncertainty Factor

Endpoint Species and Sex		LOAEL (mg/kg/day)	NOAEL (mg/kg/day)	RATIO LOAEL:NOAEL	Study
Reproductive Toxicity					
Rat (Wistar)	M	0.5	0.1	5.0	Khera, 1973
Mouse (ICR)	M	0.72	0.15	4.8	Hirano et al., 1986
Mouse (B6C3F1)	M	0.68	0.14	4.9	Mitsumori et al., 1990
Monkey *(Macaca facicularis)*	M	0.065	0.047	1.4	Mohamed et al., 1987
Monkey *(M. facicularis)*	F	0.06	0.04	1.5	Burbacher et al., 1988

NS - Not stated.

Figure 4-1
LOAEL-to-NOAEL Ratio Distribution



The ratios of LOAEL-to-NOAELs for laboratory animal studies are plotted versus frequency in Figure 4-1. These ratios can be thought of as the reduction in the LOAEL necessary to estimate the corresponding NOAEL. Figure 4-1 illustrates that the majority of ratios lie between one and two (n=6) and between four and five (n=9). Only one ratio of the 19 plotted was greater than 10. A ratio of five indicates that the NOAEL observed following exposure to methylmercury is 5-fold less than the corresponding LOAEL. These data imply that most ratios between LOAELs and their corresponding NOAELs will be less than 10.

A similar analysis of animal toxicity data (Weil and McCollister, 1963) was provided by Dourson and Stara (1983). None of the LOAEL-to-NOAEL ratios from studies of 52 chemical substances exceeded 10. Only two of the 52 ratios exceeded five. The Dourson and Stara (1983) analysis has been cited in support of the use of a variable UF_L of as much as 10 in deriving reference doses for humans. Dourson and Stara (1983) recommended the application of a relatively large UF_L when estimating a NOAEL from a LOAEL for a severe or frank toxicological effect. Conversely, a low UF could be applied when the toxicological effect was considered to be relatively mild.

The analysis by Dourson and Stara (1983) and the analysis reported here support the UF_L of two selected for derivation of the avian wildlife criterion in the Great Lakes Water Quality Initiative (U.S. EPA, 1993b). The UF_L of three was selected by the authors of this Report for use with the avian LOAEL from the same data (Heinz, 1975, 1976a,b, 1979) as a reasonable compromise between UF ratios of two and five. Given the substantial uncertainties in all the values used to calculate the wildlife criteria for mercury exposure, neither two nor three can be considered to be the only correct value.

The distribution of LOAEL:NOAEL ratios around two and five primarily reflect the dose spacing selected for the study designs. Two-fold, 5-fold and 10-fold spacing are common in experiments of this type. The most appropriate interpretation of the ratios reported here and by Dourson and Stara (1983) is that the threshold for the toxicologic effects, defined by each study, lies within the bounds of the experimentally derived LOAEL divided by an UF and that most of the effects thresholds will be encompassed by using an UF_L of 10 or less. It is also likely that the most appropriate UF_L will vary with the toxicological endpoint selected. For studies that identify only a LOAEL, the principal assumption is that the next lower dose, had it been tested, would be a NOAEL. This assumption is best applied to studies that identify a LOAEL for mild effects. LOAELs for severe or frank effects (which are generally no used for human health risk assessment) require a high degree of professional judgment in applying an UF_L.

4.5.3 Validity of BCF/BAF Paradigm

A significant shortcoming of the WC for mercury calculated in the GLWQI is its reliance upon BCF values determined in the laboratory. This methodology is based on a bioaccumulation paradigm (steady-state BCF x FCM) that was developed for neutral hydrophobic organic compounds and that may be inappropriate for application to mercury.

Field studies indicate that many, if not most fish, accumulate mercury throughout their lives, often in a nearly linear fashion with age (see for example: Scott and Armstrong, 1972; MacCrimmon et al., 1983; Wren et al., 1983; Mathers and Johansen, 1985; Skurdal et al., 1985; Wren and MacCrimmon, 1986; Sorenson et al., 1990; Jackson, 1991; Gutenmann et al., 1992; Glass et al., 1993; Suchanek, 1993; Lange et al., 1993). Moreover, most of the mercury accumulated by fish at trophic levels 3 and 4 is thought to be taken up from dietary sources. Thus, particularly for long-lived

piscivorous fish, a relatively short (one year or less) waterborne exposure cannot duplicate the extent of accumulation that takes place in nature. In addition, the relationship between a concentration of an applied mercury species in the laboratory and the concentrations of multiple species present in the environment (some of which may not be bioavailable) is completely unknown.

The apparent progress to "steady-state" observed in several chronic laboratory studies (see McKim et al., 1976) should not be misinterpreted as an actual steady-state condition, but instead probably reflects growth dilution with rapidly growing fish. Such growth dilution will tend to depress BCF values during the period of rapid growth, but as the growth rate slows continued accumulation of mercury would result in an increase in whole-body concentration with age.

In the present analysis, BAF values for trophic levels 3 and 4 were estimated using field residue data. Uncertainties remain, however, with respect to the naturally-derived variability that exists around these estimates. A growing body of information suggests that much of this variability can be attributed to site-specific factors that control the net rate of mercury methylation, but numerous additional factors may influence the extent to which mercury accumulates and biomagnifies in aquatic food webs.

4.5.4 Selection of Species of Concern

The species identified for the present analysis were selected because they were considered likely to be exposed not because of their inherent sensitivity to mercury. Lacking toxicity information, little guidance is available concerning which wildlife species are most sensitive to mercury. In addition, there are problems associated with any comparison of laboratory and field data. For example, laboratory data suggest that mercury residues in eggs exceeding 0.5 μg/g are associated with impaired reproduction in mallard ducks (Heintz, 1974, 1976a,b, 1979) and ring-necked pheasant (Fimreite, 1971). In contrast, reproduction in herring gulls appears to be unaffected even when egg residues exceed 10 μg/g (Vermeer et al., 1973). Taken alone, these data suggest that mallards and pheasant are more sensitive to the toxic effects of mercury than are gulls. This may in fact be true; however, such comparisons are complicated by the presence/absence of additional stressors such as confinement, handling, and weather, differences between natural and prepared diets, and the interplay between "inherited" (egg) residues and that which the chick consumes. Toxicity can be difficult to observe in a field study, even when it is occurring due to any number of factors. Nest predation is one such example: in 18 of 38 nests under study by Vermeer et al. (1973) hatching success could not be evaluated for one reason or another. Moreover, it is possible that in gulls the most sensitive endpoint for mercury toxicity is not reproduction but some other effect such as neurological impairment.

Clearly, exposure and sensitivity are related. If, for example, a species was, on a delivered dose basis, 10 times more sensitive than the eagle, but because of its dietary habits received less than 10% of the dose, it would not be expected to show adverse effects at water concentrations protective of the eagle. Pharmacokinetic considerations may also be important. Thus, it has been suggested that birds eliminate a substantial amount of mercury through incorporation into plumage. The frequency and extent to which birds moult may, therefore, impact their apparent sensitivity in an environmental setting. It has also been suggested that some birds and mammals demethylate, or otherwise eliminate mercury by some route other than in hair or plumage (see Wren et al., 1986 for a discussion of these data). Enhanced elimination would be particularly important if it represented an adaptive strategy for piscivorous species. The need for toxicity information has already been noted. As such information becomes available it may be necessary to revise the WC for mercury.

There is a need also to consider animals other than birds and mammals. In particular, there is a need to characterize the exposure of carnivorous reptiles such as the alligator which is known to consume considerable quantities of fish and which also feeds on animals (e.g., raccoon) which themselves feed on aquatic biota and are known to accumulate mercury (Roelke et al., 1991).

4.5.5 Trophic Levels at Which Wildlife Feed

The dietary preferences of the wildlife species identified for this analysis are shown in Table 4-2. Justification for these assignments can be found in two recent U.S. EPA publications that were developed for the purpose of supporting WC calculations (U.S. EPA 1993a, 1995a). It can be expected, however, that representatives of the same species will be exposed to different levels of mercury due to different feeding habits and/or differences in the availability of specific prey items. For example, bald eagles living on the shores of the Great Lakes may consume significant numbers of herring gulls (Kozie and Anderson, 1991). Since the gulls themselves are piscivores, feeding primarily at trophic level 3, it has been argued that when an eagle consumes a gull it is feeding at trophic level 4 or higher; the gull/forage fish PPF is thought to be about 10, while the PPF for fish at trophic level 4 is believed to be approximately 5 (U.S. EPA, 1995a). Eagles living in other parts of the country, or migrating into an area during a particular time of year, may consume relatively few fish, feeding instead on carrion, including rabbits, squirrels, and dead domestic livestock such as pigs and chickens (Harper et al., 1988). Other populations, however, are critically dependent upon the seasonal availability of fish, particularly spawning salmonids.

The feeding habits of bald eagles are reviewed extensively elsewhere (U.S. EPA, 1993a, 1995a). The intent of this discussion is not to characterize the food preferences of the eagle, but instead to demonstrate how difficult it is to characterize wildlife feeding habits on a nationwide, year-around basis. For some species, such as the kingfisher and river otter, it can be reasonably assumed that fish always comprise a high percentage of the diet. For others, such as the eagle and mink, considerable variations in diet are likely to exist. Still others, such as the Florida panther, consume prey (e.g., the raccoon) which, as a species, consume variable amounts of aquatic biota, but which in south Florida are thought to represent a close link to the aquatic food chain.

Since mercury bioaccumulation is largely a problem associated with aquatic ecosystems, it is reasonable to focus attention on populations of selected wildlife species whose feeding habits are tied to these systems. Existing data permit a general treatment of mercury exposure and effects on such populations. A more accurate characterization of the risk posed by mercury to a specific group of animals occupying a given location will depend upon the collection of necessary supporting information such as food habits, migratory behavior, breeding biology, and mercury residues in preferred prey items.

4.5.6 Variability in BAFs at each Trophic Level

A concern related to the issue of feeding preference is the possibility that trophic levels presently assigned to the wildlife species in this analysis overestimate the actual extent to which they are exposed to mercury. This is because BAFs are developed to represent the average value for a trophic level, when in fact piscivorous birds and mammals are more likely to target prey at the lower end of the size (age) distribution. Thus, eagles are more likely to consume a 1 kg northern pike than a 10 kg individual, yet both are represented in the BAF for trophic level 4. Similarly, kingfishers are probably limited to smaller representatives of trophic level 3 than would be true of an osprey. The reason that these differences are important is that mercury tends to accumulate throughout the life of

an individual fish with the result that concentrations in an older individual at a given trophic level may far exceed those in a younger individual.

The need in this study to apply BAF estimates on a nationwide basis precludes further refinement. It may, however, be possible to explore this issue by using the Monte Carlo method to analyze individual datasets. Specifically, it would be of interest to determine whether percentile information from the Monte Carlo distributions can be related to fish of known size. Eventually, it may be possible to use this or another approach to refine BAF estimates for mercury.

4.5.7 Natural History Considerations

Natural exposures are likely to vary in both spatial and temporal domains. This is particularly true of species that migrate, including the bald eagle, osprey and belted kingfisher. The necessity of incorporating this type of information and the means by which this can be accomplished are open questions.

4.5.8 Individuals Versus Populations

The methods used to develop a WC for mercury are based on effects data from individual organisms. The stated assessment endpoint for this analysis, however, is the health of wildlife populations. The relationship between individuals and populations is likely to vary with the species and a large number of environmental factors (e.g., availability of food in a given breeding season). For a given population, the loss of a significant number of individuals may have little effect, particularly if environmental factors (like carrying capacity) limit population size. For other populations, in particular those with low fecundity, loss of a relatively few individuals could have a large impact. Clearly, there is a need to be able to extrapolate toxic effects on individuals to effects on populations. Unfortunately, this type of analysis is complicated by numerous factors (such as relationship of one population to other populations) and is essentially impossible to apply on a national scale.

Finally, a focus on populations may not always be appropriate, particularly when endangered species are involved. The same may also be true when various factors contribute to the possibility of regional effects. For example, 95% of eagles nationwide might be protected by a WC for avian species, but in a given region mortality could approach 100% if low pH of surface waters contribute to higher than average accumulation of mercury in the aquatic food chain.

4.5.9 Species Versus Taxa

The WC developed for mercury in birds was calculated as the geometric mean of values for three species. Similarly, the geometric mean of values for two species was used to represent all mammals. This approach is reasonable if the WC calculated for each species within a taxa are similar, but would fail to protect species for which the WC value is much lower than the others with which it was averaged. In the latter case, averaging would effectively lead to protection to <100% of all species.

In the present analysis, WC values calculated for eagles, osprey and kingfisher were within a factor of three of one another. WC values for mink and otter agreed to within a factor of about two. As additional data are gathered, there is a need to identify species which, by virtue of sensitivity

and/or exposure, are particularly vulnerable to mercury. Decisions could then be made concerning the advisability of special measures to insure their protection.

4.5.10 Discussion of Uncertainties Associated with the GLWQI Methodology

The existing limited data suggest that BAF values represent the most important source of uncertainty in present efforts to calculate water-based WC values, although a lack of toxicity information and incomplete knowledge of what wildlife eat contribute substantially. Considerable progress has been made in understanding and predicting how lakewater characteristics (e.g., pH, temperature,dissolved organic carbon) affect methylation rates, and in time it may be possible to adjust BAF predictions as needed to represent surface waters of concern. The prospect for continuing uncertainty surrounding these estimates argues, however, for adoption of a residue-based approach; that is, the use of measured mercury residues in fish and wildlife to identify populations at risk.

It is important to recognize that BAF values are calculated as the ratio of a tissue concentration and a water concentration. Emphasis has been placed on problems associated with obtaining the numerator in this equation. Considerable uncertainty, however, also exists with respect to the denominator. In several instances it has been shown that with improved analytical methods, mercury levels in a given water body tend to come "down", resulting in an increase in the apparent BAF. This "decline" is usually not thought to be real but instead reflects improvements in sampling technique and analytical methods.

It is also unclear which of the mercury species are bioaccumlative and should, therefore, appear in the denominator. Presently, the denominator in most studies consists of total amount of mercury in filtered water. It is more likely that there may be multiple "pools" of mercury, each of which is bioavailable to varying degrees. In this regard it is important to realize that even in highly polluted systems >99% of all methylmercury is complexed, either in biomass, or with dissolved organic material, particulate material and sediments.

An effort was made to treat the uncertainty in BAF estimates by using a Monte Carlo simulation approach. The advantage of this approach is that it explicitly treats known variation in these parameters thereby providing for the statistical possibility of a high or low end result. In addition, the distributions themselves follow from the processes at work. As more information about mercury is obtained, the distributions themselves can be improved. One example of this relationship has already been discussed; namely, the fact that a skewed BAF distribution for trophic level 4 would tend to follow from random sampling of a fish population due to the relative scarcity of the oldest individuals. An additional example is the highly skewed distribution of methylmercury values as a percent of total, which can be adequately represented as a beta distribution. With respect to the definition of these distributions, it is important to recall the possibility of regional bias introduced previously. Thus, it could be argued that FCMs based on regression of data for a large number of lakes should be given greater weight (perhaps equal to the number of lakes) than data from a single location. This, however, would only serve to increase the degree of regional bias that is already present.

5. CONCLUSIONS

The following conclusions are presented in approximate order of degree of certainty in the conclusion, based on the quality of the underlying database. The conclusions progress from those with greater certainty to those with lesser certainty.

- Mercury emitted to the atmosphere deposits on watersheds and is translocated to waterbodies. A variable proportion of this mercury is transformed by abiotic and biotic chemical reactions to organic derivatives, including methylmercury. Methylmercury bioaccumulates in individual organisms, biomagnifies in aquatic food chains and is also the most toxic form of mercury to which wildlife are exposed.

- The proportion of total mercury in biota that exists as methylmercury tends to increase with trophic level. Greater than 90% of the mercury contained in freshwater fish exists as methylmercury. Methylmercury accumulates in fish throughout their lifetime, although changes in concentration as a function of time may be complicated by growth dilution and changing dietary habits.

- Piscivorous avian and mammalian wildlife are exposed to mercury primarily through consumption of contaminated fish and accumulate mercury to levels above those in prey items.

- Toxic effects on piscivorous avian and mammalian wildlife due to consumption of contaminated fish have been observed in association with point source releases of mercury to the environment.

- Concentrations of mercury in the tissues of wildlife species have been reported at levels associated with adverse health effects in laboratory studies in the same species.

- Piscivorous birds and mammals receive a greater exposure to mercury than any other known component of aquatic ecosystems.

- Field data are highly suggestive of adverse toxicological effects in common loons due to accumulation of mercury originating from airborne emissions. Field data are also suggestive of adverse toxicological effects in the Florida panther due to mercury; however, this mercury may have originated from both airborne and non-airborne sources. Field data suggest that bald eagles have not suffered adverse toxic effects due to airborne mercury emissions. Field data are insufficient to conclude whether the mink, otter, or kingfisher have suffered adverse toxic effects due to airborne mercury emissions.

- BAFs for mercury in fish vary widely; however, field data are sufficient to calculate representative means for different trophic levels. The recommended estimates in this Report for BAFs for topic levels 3 and 4 are 66,200 and 335,000, respectively. In general, BAFs for fish sampled from poorly buffered surface waters are higher than those for fish obtained from well buffered surface waters.

- Based upon knowledge of mercury bioaccumulation in fish, and of feeding rates and the identity of prey items consumed by piscivorous wildlife, it is possible to rank the relative exposure of different piscivorous wildlife species. Of the five wildlife species selected for detailed analysis, the relative ranking of exposure to mercury is this: kingfisher > otter >

osprey = mink $\geq$ bald eagle. Existing data are insufficient to estimate the exposure of the Florida panther relative to that of the selected species.

- Local emissions sources (<50 km from receptors) have the potential to increase the exposure of piscivorous wildlife well above that due to sources located more than 50 km from the receptors (i.e., "remote" sources).

- Based upon knowledge of mercury exposure to wildlife and its toxicity in long-term feeding studies, criterion values can be calculated for the protection of piscivorous avian and mammalian wildlife. A wildlife criterion value is defined as the concentration of total mercury in water which, if not exceeded, protects avian and mammalian wildlife populations from adverse effects resulting from ingestion of surface waters and from ingestion of aquatic life taken from these surface waters.

- The criterion value protective of piscivorous avian wildlife is 405 pg/L.

- The criterion value protective of piscivorous mammalian wildlife is 346 pg/L.

- Modeled estimates of mercury concentration in fish around hypothetical mercury emissions sources predict exposures at the wildlife WC. The wildlife WC, like the human RfD, is predicted to be a safe dose over a lifetime. It should be noted, however, that the wildlife effects used as the basis for the WC are gross clinical manifestations or death. Expression of subtle adverse effects at these doses cannot be excluded.

There are many uncertainties associated with this analysis, due to an incomplete understanding of the toxicity of mercury and mercury compounds. The sources of uncertainty include the following:

- Variability in the calculated BAFs is a source of uncertainty. BAFs given in this Report relate total mercury in fish (most of which exists as methylmercury) to total mercury in the water column. Methylmercury is the bioaccumulating species, but existing data are insufficient to estimate BAFs on a methylmercury basis. Methods for the speciation of mercury in environmental samples are rapidly improving but remain difficult to perform. Questions also remain concerning the bioavailability of methylmercury associated with particulate and dissolved organic material. Local biogeochemical factors that determine net methylation rates are not fully understood and are not amenable at this time to generalized modeling.

- The representativeness of field data used in establishing the BAFs is a source of uncertainty. The degree to which the analysis is skewed by the existing data set is unknown. A disproportionate amount of data is from north-central and northeastern lakes. The applicability of these data to a national assessment is not known.

- Limitations of the toxicity database present a source of uncertainty. Few controlled studies of quantifiable effects of mercury exposure in wildlife are available. These are limited to few species, necessitating the use of uncertainty factors in extrapolating to species of interest. The toxic endpoints reported in existing studies can be considered severe, raising questions as to the degree of protection against subtle effects offered by reference doses and water criteria calculated on those endpoints. Use of less than lifetime studies for prediction of effects from lifetime exposure is a source of uncertainty.

- Concern has been raised regarding the possibility of toxic effects in species other than those piscivorous birds and mammals evaluated in this Report. In particular there is considerable uncertainty about mercury effects in biota at trophic levels 1 and 2 in aquatic ecosystems and about effects in terrestrial systems.

- Lack of knowledge of wildlife feeding habits is a source of uncertainty. Existing information frequently is anecdotal or confined to evaluations of a particular locality; the extent to which this information is generalizable is open to question. In some instances wherein feeding habits are relatively well characterized (e.g., Florida panther), the extent of mercury contamination of prey is poorly known (e.g., in raccoons).

- While the methods used to develop wildlife criteria are based on effects in individual organisms, the stated goal of the assessment is to characterize the potential for adverse effects in wildlife populations. Factors which contribute to uncertainty in population-based assessments include these: variability in the relationship between individuals and populations; variability in fecundity; lack of data on carrying capacity; and relationships of one population, of the same or different species, to another population.

- A focus on populations may not always be appropriate. This could be true for endangered species, which may be highly dependent for the survival of the species on the health of a few individuals. This may also be true for some regional or local populations of widespread species; the local population may be "endangered" and, thus, dependent on the survival of individuals.

To improve the ecological risk assessment for mercury and mercury compounds, U.S. EPA would need the following:

- Mechanistic research is needed for better understanding of variability of mercury effects. This would include studies on the following: factors determining rates of methylation and demethylation; dietary absorption efficiencies from natural food sources; effects of dietary choice; and bioavailability of methylmercury in the presence of dissolved organic material and other material which could bind mercury.

- Data are needed for better definition of adverse effects on the species which were evaluated in this Report. Information is also lacking on species at trophic levels 1 and 2.

- Efforts to develop and standardize methods for analysis of total mercury and methylmercury in environmental samples (including animal and plant tissue) remain important.

- The current wildlife criteria are based on linear, four-tiered food chains. Research on the appropriateness of this design and information which will improve the model are important.

- Research is needed to reduce uncertainty regarding the accumulation of mercury at lower trophic levels.

- High quality field data will be useful to support the process-based research described above, as well as to determine residue concentrations in fish and other aquatic biota consumed by wildlife.

Based on the extant data and knowledge of developing studies, the U.S. EPA predicts the following:

- "Regions of concern" are defined as those geographic areas in the contiguous U.S. that are thought to receive high levels of mercury deposition and that contain relatively large numbers (>5% below pH 5.5) of poorly buffered surface waters. The designation of an area as a region of concern implies an increased risk of mercury toxicity to wildlife. This designation could be used to define critical habitat, identify wildlife populations potentially at risk, and provide a focus for future research.

- Increased deposition will lead to increased levels in fish.

- Increased levels in fish will lead to toxicity in piscivorous birds and mammals.

- These impacts are most likely to occur in areas that receive high levels of deposition and that also contain poorly buffered surface waters.

6. RESEARCH NEEDS

Mercury is unusual among environmental contaminants in that levels that are likely to cause significant environmental damage exceed those thought to be present "naturally" by less than two (and perhaps closer to one) order(s) of magnitude. Conservative use of uncertainty factors can, therefore, lead to calculation of WC or other similar criterion values that are lower than mercury residues actually measured in the environment. With this in mind, there are two general areas within which research progress must be made if environmental assessments are to be improved. The first area pertains to basic information on the fate and effects of mercury in the environment, which would result in reduced use of uncertainty factors and ensure that WC, BAFs, and other estimates, are based on a mechanistic understanding of the relevant processes. The second area is an improvement in the ability to detect ecological damage when it is in fact occurring. The present assessment of the "ecological impacts" of anthropogenic mercury emissions is largely limited to consideration of toxic effects on individuals. Models that would permit extrapolation of these results to populations (the simplest extrapolation of individual-based information) do not exist for most species. Further extrapolation to communities and ecosystems is presently out of the question.

Throughout this assessment, uncertainties, discussed above and elsewhere in the text, have limited the scope of possible conclusions. Although lack of sufficient data is a limiting factor in all phases of this assessment, a number of research needs have emerged as being especially important. These are described below and are presented in no particular order.

6.1 Process-based Research

Mechanistic information is needed to understand the variability that presently typifies the mercury literature. This research includes laboratory and field studies to identify the determinants of mercury accumulation in aquatic food chains and kinetic information that would allow researchers to describe the dynamics of these systems. Areas of uncertainty include these: (1) factors that determine net rates of methylation and demethylation; (2) dietary absorption efficiency from natural food sources; (3) effect of dietary choice; and (4) bioavailability of methylmercury in the presence of dissolved organic material and other potential ligands.

In time it is anticipated that this information can be used to develop process-based models for mercury bioaccumulation in fish and other aquatic biota. Significant progress in this direction is represented by the Mercury Cycling Model (MCM), presently being developed and evaluated by the Electric Power Research Institute (Hudson et al., 1994).

6.2 Wildlife Toxicity Data

There is a need to reduce the present reliance on a relatively few toxicity studies for WC development. Additional data are needed for wildlife that constitute the most exposed organisms in various parts of the country (e.g., the Florida panther). There is also a critical requirement for toxicity data that can be related to effects on populations (see Table 2-1), including effects on organisms that comprise the lower trophic levels.

6.3 Improved Analytical Methods

Efforts to develop and standardize methods for analysis of total mercury and methylmercury in environmental samples should be continued. Such methods must recognize the importance of contamination, both during the collection of such samples and during their analysis. It is particularly

important that mercury measurements, which are at present operationally defined (e.g., "soluble", "adsorbed to organic material"), be made in such a way that mercury residues in fish can be correlated with the bioavailable mercury pool.

As validated methods become available, it is important to analyze for both total and methylmercury whenever possible so that differences between aquatic systems can be definitively linked to differences in methylmercury levels. Analyzing the two mercury species together will contribute to an understanding of existing data, most of which is reported as total mercury. It is also anticipated that developing BAFs in terms of methylmercury will reduce the variability that currently exists around BAF estimates based on total mercury.

6.4 Complexity of Aquatic Food Webs

Present efforts to develop WC values for mercury are based on linear, four-tiered food chain models. Research is needed to determine the appropriateness of this simple paradigm and to develop alternatives if field data suggest otherwise. Of particular interest is whether zooplankton and phytoplankton should be modeled as two different trophic levels. Current information for detritivores and benthic invertebrates is extremely limited, even though their importance in mobilizing hydrophobic organic contaminants has been demonstrated.

6.5 Accumulation in Trophic Levels 1 and 2

Ongoing efforts to understand mercury bioaccumulation in aquatic systems continue to be focused on trophic levels 3 and 4, despite the fact that uncertainties in PPFs are relatively small. Additional emphasis should be placed on research at the lower trophic levels. In particular, there is a need to understand the determinants of mercury accumulation in phytoplankton and zooplankton, and how rapid changes in plankton biomass impact these values.

6.6 Field Residue Data

High-quality field data are needed to support process-based research efforts and to determine residue concentrations in the fish and other aquatic biota that wildlife eat. Whenever possible, it is desirable to collect residue data at all trophic levels and to analyze mercury levels in the abiotic compartments of a system (eg., water and sediments). It is particularly important that such measurements be made in a broader array of aquatic ecosystem types (including both lakes and rivers) so that a better understanding of mercury cycling and accumulation can be obtained.

Residue data from wildlife are also needed to identify populations that are being adversely impacted or are potentially at risk. Feathers and fur hold considerable promise in this regard because of the potential for "non-invasive" determination of mercury residues. Laboratory research is required, however, to allow interpretation of these data. Factors such as age, sex, and time to last moult are likely to result in variability among individuals of a single population, and need to be understood. Sampling efforts should be targeted on areas receiving high levels of mercury deposition and/or regions containing large numbers of poorly buffered surface waters, as discussed throughout this Report.

6.7 Natural History Data

The development of WC requires knowledge of what wildlife eat. Fish sampling efforts are frequently focused on species that are relevant to human consumers but that may be of little significance to wildlife. There is an additional need to collect information for macroinvertebrates and amphibians. Seasonal and spatial effects on predation should be explored and methods developed to describe this information adequately. Additional life history data is needed to characterize fully the nature and extent of exposure to mercury. Complicating factors must be considered, including migratory behaviors and sex-specific differences in distribution and resource allocation. It is particularly important that information be collected to support the development of predictive population models for sensitive species.

7. REFERENCES

Allard, B. and I. Arsenie (1991). Abiotic reduction of mercury by humic substances in aquatic system - An important process for the mercury cycle. *Water Air Soil Pollut.* 56:457-464.

Andersson, A. (1979). Mercury in soils. In: *The Biogeochemistry of Mercury in the Environment.* J.O. Nriagu (Ed.), Elsevier/North Holland Biomedical Press, Amsterdam, The Netherlands, pp. 79-106.

Anthony, R.G., M.G. Garrett and C.A. Schuler (1993). Environmental contaminants in bald eagles in the Columbia River estuary. *J. Wildl. Manage.* 57:10-19.

Aulerich, R.J., R.K. Ringer and S. Iwamoto (1974). Effects of dietary mercury in mink. *Arch. Environ. Contam. Toxicol.* 2(1):43-51.

Bahnick, D., C. Sauer, B. Butterworth and D. Kuehl (1994). A national study of mercury contamination in fish. *Chemosphere* 29:537-546.

Bakir, F., S.F. Damluji, L. Amin-Zaki, M. Murtadha, A. Khalidi, N.Y. Al-Rawi, S. Tikriti, and H.E. Dhahir (1973). Methylmercury poisoning in Iraq. *Science* 181: 230-240.

Barr, J.F. (1973). Feeding biology of the common loon (*Gavia immer*) in oligotrophic lakes of the Canadian Shield. Ph.D. dissertation, University of Guelph, Canada.

Barr, J.F. (1986). Population dynamics of the common loon (*Gavia immer*) associated with mercury-contaminated waters in northwestern Ontario. Occasional Paper No. 56, Canadian Wildlife Service.

Beck, D.L. (1977). Pesticide and heavy metal residues in Louisiana river otter. M.S. thesis, University of Texas, Houston, TX.

Belant, J.L. and R.K Anderson (1990). Environmental contaminants in common loons from northern Wisconsin. *Pass. Pigeon* 52:306-310.

Beyer, W.N., E. Cromartie and G.B. Moment (1985). Accumulation of methylmercury in the earthworm, *Eisenia foetida*, and its effect on regeneration. *Bull. Environ. Contam. Toxicol.* 35:157-162.

Bigler, W.J., R.H. Jenkins, R.M. Cumbie, G.L. Hoff and E. Prather (1975). Wildlife and environmental health. Raccoons as indicators of zoonoses and pollutants in southeastern U.S.A. *J. Amer. Med. Assoc.* 167:592-597.

Bishop, C.A., M.D. Koster, A.A. Chek, D.J.T. Hussell and K. Jock (1995). Chlorinated hydrocarbons and mercury in sediments, red-winged blackbirds (*Agelaius phoeniceus*) and tree swallows (*Tachycineta biocolor*) from wetlands in the Great Lakes-St. Lawrence River basin. *Environ. Toxicol. Chem.* 14:491-501.

Bleavins, M.R. and R.J. Aulerich (1981). Feed consumption and food passage in mink (*Mustela vison*) and European ferrets (*Mustela putorius furo*). *Lab. Animal Sci.* 31:268-269.

Bloom, N.S (1992). On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can. J. Fish. Aquat. Sci.* 49:1010-1017.

Bloom, N.S. and S.W. Effler (1990). Seasonal variability in the mercury speciation of Onondaga Lake (New York). *Water Air Soil Pollut.* 53:251-265.

Bloom, N.S., C.J. Watras and J.P. Hurley (1991). Impact of acidification on the methylmercury cycle of remote seepage lakes. *Water Air Soil Pollut.* 56:477-491.

Bodaly, R.A., J.W.M. Rudd, R.J.P. Fudge and C.A. Kelly (1993). Mercury concentrations in fish related to size of remote Canadian shield lakes. *Can. J. Fish. Aquat. Sci.* 50:980-987.

Boney, A.D. (1971). Sub-lethal effects of mercury on marine algae. *Mar. Pollut. Bull.* 2:69-71.

Borst, H.A. and C.G. Lieshout (1977). Phenylmercuric acetate intoxication in mink. *Tijdschr. Diergeneesk* 102:495-503.

Boudou, A. and F. Ribeyre (1985). Experimental study of trophic contamination of *Salmo gairdneri* by two mercury compounds - $HgCl_2$ and CH_3HgCl - analysis at the organism and organ levels. *Water Air Soil Pollut.* 26:137-148.

Bowerman, W.W. IV (1993). Regulation of bald eagle (*Haliaeetus leucocephalus*) productivity in the Great Lakes basin: An ecological and toxicological approach. Ph.D. dissertation, Michigan State University, East Lansing, MI.

Bowerman, W.W. IV., E.D. Evans, J.P. Giesy and S. Postupalsky (1994). Using feathers to assess risk of mercury and selenium to bald eagle reproduction in the Great Lakes region. *Arch. Environ. Contam. Toxicol.* 27:294-298.

Boyer, H.A. (1982). Trace elements in the water, sediments, and fish of the upper Mississippi River, twin cities metropolitan area. In: *Contaminants in the Upper Mississippi River.* J.G. Wiener, R.V. Anderson and D.R. McConville (Eds.). Butterworth Publishers, Boston, MA, pp. 195-230.

Braune, B.M. and D.E. Gaskin (1987). Mercury levels in Bonaparte's gulls (*Larus philadelphia*) during autumn molt in the Quoddy region, New Brunswick, Canada. *Arch. Environ. Contam. Toxicol.* 16:539-549.

Braune, B.M. and R.J. Norstrom (1989). Dynamics of organochlorine compounds in herring gulls: III. Tissue distribution and bioaccumulation in Lake Ontario gulls. *Environ. Toxicol. Chem.* 8:957-968.

Burbacher, T.M., M.K. Mohamed and N.K. Mottett. 1988. Methylmercury effects on reproduction and offspring size at birth. *Reprod. Toxicol.* 1(4):267-278.

Burger, J., J.A. Rodgers, Jr. and M. Gochfeld (1993). Heavy metal and selenium levels in endangered wood storks *Mycteria americana* from nesting colonies in Florida and Costa Rica. *Arch. Environ. Contam. Toxicol.* 24:417-420.

Cabana, G., A. Tremblay, J. Kalff and J.B. Rasmussen (1994). Pelagic food chain structure in Ontario lakes: a determinant of mercury levels in lake trout (*Salvelinus namaycush*). *Can. J. Fish. Aquat. Sci.* 51:381-389.

Calder, W.A. and E.J. Braun (1983). Scaling of osmotic regulation in mammals and birds. *Am. J. Physiol.* 244:R601-R606.

Charbonneau, S.M., I.C. Munro, E.A. Nera, R.F. Willes, T. Kuiper-Goodman, F. Iverson, C.A. Moodie, D.R. Stoltz, F.A.J. Armstrong, J.F. Uthe, H.C. Grice (1974). Subacute toxicities of methylmercury in the adult cat. Toxic. Appl. Pharm. 27:569-581.

Charbonneau, S.M., I.C. Munro, E.A. Nera, F.A.J. Armstrong, R.F. Willes, F. Bryce and R.F. Nelson (1976). Chronic toxicity of methylmercury in the adult cat. Interim report. *Toxicol.* 5:337-349.

Clark, K.E., F.A.P.C. Gobas and D. Mackay (1990). Model of organic chemical uptake and clearance by fish from food and water. *Environ. Sci. Technol.* 24:1203-1213.

Clarkson, T.W. (1990). Human health risks from methylmercury in fish. *Environ. Toxicol. Chem.* 9:957-961.

Colborn, T.I. (1991). Epidemiology of Great Lakes bald eagles. *J. Environ. Health Toxicol.* 4:395-453.

Cope, W.G., J.G. Wiener and R.G. Rada (1990). Mercury accumulation in yellow perch in Wisconsin seepage lakes: Relation to lake characteristics. *Environ. Toxicol. Chem.* 9:931-940.

Crowder, A. (1991). Acidification, metals and macrophytes. *Environ. Pollut.* 71:171-203.

Crowder, A.A., W. Dushenko and J. Grieg (1988). Metal contamination of wetland food chains in the Bay of Quinte, Ontario. Environment Ontario, Nov. 28-29, 1988. Toronto, Canada, pp. 133-153.

Cumbie, P.M. (1975). Mercury levels in Georgia otter, mink, and freshwater fish. *Bull. Environ. Contam. Toxicol.* 14:193-196.

Dillon, T.M. (1977). Mercury and the estuarine marsh clam, *Rangia cuneata* Gray. I. Toxicity. *Arch. Environ. Contam. Toxicol.* 6:249-255.

Dorfman, D. (1977). Tolerance of *Fundulus heteroclitus* to different metals in salt waters. *Bull. New Jersey Acad. Sci.* 22:21.

Dourson, M.L. and J.F. Stara (1983). Regulatory history and experimental support of uncertainty (safety) factors. *Reg. Toxicol. Pharmacol.* 3:224-238.

Dukerschein, J.T., J.G. Wiener, R.G. Rada and M.T. Steingraeber (1992). Cadmium and mercury in emergent mayflies (*Hexagenia bilineata*) from the upper Mississippi River. *Arch. Environ. Contam. Toxicol.* 23:109-116.

Eisler, R. (1987). Mercury hazards to fish, wildlife, and invertebrates: A synoptic review. Publication No. 85 (1.10), U.S. Fish and Wildlife Service, Department of the Interior, Washington, DC.

Eisler, R. and R.J. Hennekey (1977). Acute toxicities of Cd^{+2}, Cr^{+6}, Hg^{+2}, Ni^{+2}, and Zn^{+2} to estuarine macrofauna. *Arch. Environ. Contam. Toxicol.* 6:315-323.

Ensor, K.L., D.D. Helwig and L.C. Wemmer (1992). Environmental mercury and lead in Minnesota common loons (*Gavia immer*). Minnesota Pollution Control Agency, Water Quality Division, St. Paul, MN.

Environment Canada (1991). Toxic chemicals in the Great Lakes and associated effects: Volume I - Contaminant levels and trends. Department of Fisheries and Oceans, Health and Welfare Canada, Toronto, Canada.

Evans, R.D. (1986). Sources of mercury contamination in the sediments of small headwater lakes in south-central Ontario, Canada. *Arch. Environ. Contam. Toxicol.* 15:505-512.

Evans, H.L., R. Garman and B. Weiss. 1977. Methylmercury: Exposure duration and regional distribution as determinants of neurotoxicity in nonhuman primates. *Toxicol. Appl. Pharmacol.* 41:15-33.

Fimreite, N. (1970). Effects of methylmercury treated feed on the mortality and growth of leghorn cockerels. *Can. J. Anim. Sci.* 50:387-389.

Fimreite, N. (1971). Effects of methylmercury on ring-necked pheasants. Canadian Wildlife Service Occasional Paper Number 9. Department of the Environment. 39 pp.

Fimreite, N. (1974). Mercury contamination of aquatic birds in northwestern Ontario. *J. Wildl. Manage.* 38:120-131.

Fimreite, N. (1979). Accumulation and effects of mercury on birds. In: *The Biogeochemistry of Mercury in the Environment.* J.O. Nriagu (Ed.), Elsevier/North-Holland Biomedical Press, Amsterdam, The Netherlands, pp. 601-628.

Finley, M.T. and R.C. Stendell (1978). Survival and reproductive success of black ducks fed methyl mercury. *Environ. Pollu.* 16:51-64.

Finley, M.T., W.H. Stickel and R.E. Christensen (1979). Mercury residues in tissues of dead and surviving birds fed methylmercury. *Bull. Environ. Contam. Toxicol.* 21:105-110.

Fjeld, E. and S. Rognerud (1993). Use of path analysis to investigate mercury accumulation in brown trout (*Salmo trutta*) in Norway and the influence of environmental factors. *Can. J. Fish. Aquat. Sci.* 50:1158-1167.

Fleming, W.J., J.A. Rodgers, J.A., Jr., and C.J. Stafford, C.J. (1984). Contaminants in wood stork eggs and their effects on reproduction, Florida, 1982. *Colonial Waterbirds* 7:88-93.

Florida Department of Environmental Regulation (FDER, 1990). Mercury, largemouth bass, and water quality: A preliminary report. Department of Environmental Regulation, Florida.

Florida Panther Interagency Committee (FPIC, 1989). Mercury contamination in Florida panthers. Status Report of the Technical Subcommittee.

Fowler, B.A. and J.S. Woods. 1977. The transplacental toxicity of methylmercury to fetal rat liver mitochondria. *Lab. Invest.* 36:122-130.

Futter, M.N. (1994). Pelagic food-web structure influences probability of mercury contamination in lake trout (*Salvelinus namaycush*). *Sci. Tot. Environ.* 145:7-12.

Gilbertson, M., T. Kubiak, J. Ludwig and G. Fox (1991). Great Lakes embryo mortality, edema, and deformities syndrome (GLEMEDS) in colonial fish-eating birds: Similarity to chick-edema disease. *J. Toxicol. Environ. Health* 33:455-520.

Gilmour, C.C. and E.A. Henry (1991). Mercury methylation in aquatic systems affected by acid deposition. *Environ. Pollut.* 71:131-169.

Glass, G.E., J.A. Sorensen, K.W. Schmidt, J.K. Huber and G.R. Rapp, Jr. (1993). Mercury sources and distribution in Minnesota's aquatic resources: Precipitation, surface water, sediments, plants, plankton, and fish. Final report to Minnesota Pollution Control Agency and Legislative Commission on Minnesota Resources, 1989-1991 (Contract Nos. 831479 and WQ/PDS020).

Gobas, F.A.P.C. (1993). A model for predicting the bioaccumulation of hydrophobic organic chemicals in aquatic food webs: Application to Lake Ontario. *Ecol. Model.* 69:1-17.

Godbold, D.L. (1991). Mercury-induced root damage in spruce seedlings. *Water Air Soil Pollut.* 56:823-831.

Grieb, T.M., C.T. Driscoll, S.P. Gloss, C.L. Schofield, G.L. Bowie and D.B. Porcella (1990). Factors affecting mercury accumulation in fish in the upper Michigan peninsula. *Environ. Toxicol. Chem.* 9:919-930.

Grier, J.W. (1974). Reproduction, organochlorines, and mercury in northwestern Ontario bald eagles. *Can. Field Nat.* 88:469-475.

Grubb, T.G., S.N. Wiemeyer and L.F. Kiff (1990). Eggshell thinning and contaminant levels in bald eagle eggs from Arizona, 1977 to 1985. *The Southwestern Naturalist* 35:298-301.

Gutenmann, W.H., J.G. Ebel, Jr., H.T. Kuntz, K.S. Yourstone and D.J. Lisk (1992). Residues of p,p'-DDE and mercury in lake trout as a function of age. *Arch. Environ. Contam. Toxicol.* 22:452-455.

Halbrook, R.S. (1978). Environmental pollutants in the river otter of Georgia. M.S. thesis, University of Georgia, Athens, GA.

Harper, R.G., D.S. Hopkins and T.C. Dunstan (1988). Nonfish prey of wintering bald eagles in Illinois. *Wilson Bull.* 100:688-690.

Harrison, S.E., J.F. Klaverkamp and R.H. Hesslein (1990). Fates of metal radiotracers added to a whole lake: accumulation in fathead minnow (*Pimephales promelas*) and lake trout (*Salvelinus namaycush*). *Water Air Soil Pollut.* 52:277-293.

Heinz, G.H. (1974). Effects of low dietary levels of methylmercury on mallard reproduction. *Bull. Environ. Contam. Toxicol.* 11:386-392.

Heinz, G.H. (1975). Effects of methylmercury on approach and avoidance behavior of mallard ducklings. *Bull. Environ. Contam. Toxicol.* 13:554-564.

Heinz, G.H. (1976a). Methylmercury: Second-year feeding effects on mallard reproduction and duckling behavior. *J. Wildl. Manag.* 40(1):82-90.

Heinz, G.H. (1976b). Methylmercury: Second-generation reproductive and behavioral effects on mallard ducks. *J Wildl. Manag.* 40(4):710-715.

Heinz, G.H. (1979). Methylmercury: Reproductive and behavioral effects on three generations of Mallard ducks. *J. Wildl. Manage.* 43:394-401.

Helmke, P.A., W.P. Robarge, R.L. Korotev and P.J. Schomberg (1979). Effects of soil-applied sewage sludge on concentrations of elements in earthworms. *J. Environ. Qual.* 8:322-327.

Hildebrand, S.G., R.H. Strand and J.W. Huckabee (1980). Mercury accumulation in fish and invertebrates of the North Fork Holston River, Virginia and Tennessee. *J. Environ. Qual.* 9:393-400.

Hirano, M., K. Mitsumori, K. Maita, et al. 1986. Further carcinogenicity study on methylmercury chloride in ICR mice. *Jap. J. Vet. Sci.* 48(1):127-135.

Hongve, D., O.K. Skogheim, A. Hindar and H. Abrahamsen (1980). Effects of heavy metals in combination with NTA, humic acid, and suspended sediment on natural phytoplankton photosynthesis. *Bull. Environ. Contam. Toxicol.* 25:594-600.

Huckabee, J.W., J.W. Elwood and S.G. Hildebrand (1979). Accumulation of mercury in freshwater biota. In: *The Biogeochemistry of Mercury in the Environment.* J.O. Nriagu (Ed.), Elsevier/North Holland Biomedical Press, Amsterdam, The Netherlands, pp. 277-302.

Hudson, R.J.M., S.A. Gherini, C.J. Watras, and D.B. Porcella (1994). Modelling the biogeochemical cycle of mercury in lakes: the mercury cycling model (MCM) and its application to the MTL study lakes. In: *Mercury Pollution: Integration and Synthesis.* C.J. Watras and J.W. Huckabee (Eds.), Lewis Publishers, Boca Raton, FL, pp. 473-523.

Jackson, T.A. (1991). Biological and environmental control of mercury accumulation by fish in lakes and reservoirs of northern Manitoba, Canada. *Can. J. Fish. Aquat. Sci.* 48:2449-2470.

Johansson, K., M. Aastrup, A. Andersson, L. Bringmark and A. Iverfeldt (1991). Mercury in Swedish forest soils and waters - Assessment of critical load. *Water Air Soil Pollut.* 56:267-281.

Johnston, T.A., R.A. Bodaly and J.A. Mathias (1991). Predicting fish mercury levels from physical characteristics of boreal reservoirs. *Can. J. Fish. Aquat. Sci.* 48:1468-1475.

Jordan, D. (1990). Mercury contamination: Another threat to the Florida panther. *Fish and Wildlife Service Endangered Species Technical Bulletin* 15(2):1.

Joslin, J.D. (1994). Regional differences in mercury levels in aquatic ecosystems: A discussion of possible causal factors with implications for the Tennessee River system and the northern hemisphere. *Environ. Manage.* 18:559-567.

Khera, S. 1973. Reproductive capability of male rats and mice treated with methyl mercury. *Toxicol. Appl. Pharm.* 24:167-177.

Khera, K.S. and S.A. Tabacova. 1973. Effects of methylmercuric chloride on the progeny of mice and rats treated before or during gestation. *Food. Cosmet. Toxicol.* 11:245-254.

Klaassen, C.D., M.O. Amdur and J. Doull (1986). *Casarett and Doull's Toxicology: The Basic Science of Poisons.* MacMillan Publishing Company, New York, NY.

Klaunig, J., S. Koepp, and M. McCormick (1975). Acute toxicity of a native mummichog population (*Fundulus heteroclitus*) to mercury. *Bull. Environ. Contam. Toxicol.* 14:534-536.

Koller, L.D., J.H. Exon and B. Arbogast. 1977. Methylmercury: Effect on serum enzymes and humoral antibody. *Journal of Toxicology and Environmental Health* 2:1115-1123.

Kozie, K.D. and R.K. Anderson (1991). Productivity, diet, and environmental contaminants in bald eagles nesting near the Wisconsin shoreline of Lake Superior. *Arch. Environ. Contam. Toxicol.* 20:41-48.

Kucera, E. (1983). Mink and otters as indicators of mercury in Manitoba waters. *Can. J. Zool.* 61:2250-2256.

Kudo, A., H. Nagase and Y. Ose (1982). Proportion of methylmercury to the total amount of mercury in river waters in Canada and Japan. *Water Res.* 16:1011-1015.

Kuiper, J. (1981). Fate and effects of mercury in marine plankton communities in experimental enclosures. *Ecotoxicol. Environ. Safety* 5:106-134.

Lange, T.R., H.E. Royals and L.L. Connor (1993). Influence of water chemistry on mercury concentration in largemouth bass from Florida lakes. *Trans. Am. Fish. Soc.* 122:74-84.

Lathrop, R.C., P.W. Rasmussen and D.R. Knauer (1991). Mercury concentrations in walleyes from Wisconsin (USA) lakes. *Water Air Soil Pollut.* 56:295-307.

Lee, Y.H., H. Hultberg and I. Andersson (1985). Catalytic effect of various metal ions on the methylation of mercury in the presence of humic substances. *Water Air Soil Pollut.* 25:391-400.

Lee, Y.H. and H. Hultberg (1990). Methylmercury in some Swedish surface waters. *Environ. Sci. Technol.* 9:833-841.

Lindqvist, O. (1991). Mercury in the Swedish environment. Recent research on causes, consequences and corrective measures. *Water Air Soil Pollut.* 55:1-261.

MacCrimmon, H.R., C.D. Wren and B.L. Gots (1983). Mercury uptake by lake trout, *Salvelinus namaycush*, relative to age, growth, and diet in Tadenac Lake with comparative data from other precambrian shield lakes. *Can. J. Fish. Aquat. Sci.* 40:114-120.

Maserti, B.E. and R. Ferrara (1991). Mercury in plants, soil and atmosphere near a chlor-alkali complex. *Water Air Soil Pollut.* 56:15-20.

Mathers, R.A. and P.H. Johansen (1985). The effects of feeding ecology on mercury accumulation in walleye (*Stizostedion vitreum*) and pike (*Esox lucius*) in Lake Simcoe. *Can. J. Zool.* 63:2006-2012.

May, K., M. Stoeppler and K. Reisinger (1987). Studies in the ratio total mercury/methylmercury in the aquatic food chain. *Tox. Environ. Chem.* 13:153-159.

McGrath, J.T. (1960). *Neurological Examination of the Dog with Clinicopathological Observations. 2nd ed.* Lea and Febiger, Philadelphia, PA.

McKim, J.M., G.F. Olson, G.W. Holcombe and E.P. Hunt (1976). Long-term effects of methylmercuric chloride on three generations of brook trout (*Salvelinus fontinalis*): Toxicity, accumulation, distribution, and elimination. *J. Fish. Res. Bd. Can.* 33:2726-2739.

McMurtry, M.J., D.L. Wales, W.A. Schneider, G.L. Beggs and P.E. Diamond (1989). Relationship of mercury concentrations in lake trout (*Salvelinus namaycush*) and smallmouth bass (*Micropterus dolomieui*) to the physical and chemical characteristics of Ontario lakes. *Can. J. Fish. Aquat. Sci.* 46:426-434.

Meili, M., A. Iverfeldt and L. Hakanson (1991). Mercury in the surface water of Swedish forest lakes - concentrations, speciation and controlling factors. *Water Air Soil Pollut.* 56:439-453.

Mhatre, G.N. and S.B. Chaphekar (1985). The effect of mercury on some aquatic plants. *Environ. Pollut.* 39:297-216.

Michigan Department of Natural Resources (MDNR, 1993). Mercury in Michigan's environment: Environmental and human health concerns. A science report to Governor John Engler. R.D. Sills, Michigan Environmental Science Board, Lansing, MI.

Miskimmin, B.M., J.W.M. Rudd and C.A. Kelly (1992). Influence of dissolved organic carbon, pH and microbial respiration rates on mercury methylation and demethylation in lake water. *Can. J. Fish. Aquat. Sci.* 49:17-22.

Mitsumori, K., M. Hirano, H. Ueda, et al. 1990. Chronic toxicity and carcinogenicity of methylmercury chloride in B6C3F1 mice. *Fundamental and Applied Toxicology* 14:179-190.

Mohamed, M., T. Burbacher and N. Mottet. 1987. Effects of methyl mercury on testicular functions in Macaca fascicularis monkeys. *Pharmacol. Toxicol.* 60(1):29-36.

Mosbaek, H., J.C. Tjell and T. Sevel (1988). Plant uptake of airborne mercury in background areas. *Chemosphere* 17:1227-1236.

Munro, I.C., E.A. Nera, S.M. Charbonneau, et al. 1980. Chronic toxicity of methylmercury in the rat. *J. Environ. Path. Toxicol.* 3:437-447.

Muramoto, S. and Y. Oki (1984). Influence of anionic surface-active agents on the uptake of heavy metals by water hyacinth (*Eichornia crassipes*). *Bull. Environ. Contam. Toxicol.* 33:444-450.

Nagase, H., Y. Ose, T. Sato and T. Ishikawa (1984). Mercury methylation by compounds in humic material. *Sci. Tot. Environ.* 32:147-156.

Nagy, K.A. (1987). Field metabolic rate and food requirement scaling in mammals and birds. *Ecol. Monogr.* 57:111-128.

National Acid Precipitation Assessment Program (NAPAP, 1990). Acidic deposition: State of science and technology, volume II, aquatic pocesses and effects. National Acid Precipitation Program, Washington, D.C.

Nature Conservancy (1994). Heritage database. Eastern Heritage Task Force, Boston, MA. Developed under U.S. EPA appropriation 683\40108 for the Office of Air Quality Planning and Standards, Emissions Standards Division, Research Triangle Park, NC.

Niimi, A.J. and G.P. Kissoon (1994). Evaluation of the critical body burden concept based on inorganic and organic mercury toxicity to rainbow trout (*Oncorhynchus mykiss*). *Arch. Environ. Contam. Toxicol.* 26:169-178.

Nilsson, A. and L. Hakanson (1992). Relationships between mercury in lake water, water color and mercury in fish. *Hydrobiologia* 235/236:675-683.

Nolen, G.A., E.V. Buchler, R.G. Geil, et al. 1972. Effects of trisodium nitrotriacetate on cadmium and methylmercury toxicity and teratogenicity in rats. *Toxicol. Appl. Pharmacol.* 23:222-237.

O'Connor, D.J. and S.W. Nielsen (1980). Environmental survey of methylmercury levels in wild mink (*Mustela vison*) and otter (*Lutra canadensis*) from the northeastern United States and experimental pathology of methylmercurialism in the otter. *Worldwide Furbearer Conference Proceedings*, pp. 1728-1745.

Odsjö, T. (1982). Eggshell thinning and levels of DDT, PCB and mercury in the eggs of osprey (*Pandion haliaetus L.*) and marsh harrier (*Circus aeruginosus L.*) in relation to their breeding success and population status in Sweden. Ph.D. dissertation, University of Stockholm, Sweden.

Olson, K.R. and R.C. Harrel (1973). Effect of salinity on acute toxicity of mercury, copper, and chromium for *Rangia cuneata* (Pelecypoda, Mactridae). *Contrib. Mar. Sci.* 17:9-13.

Olson, K.R., K.S. Squibb and R.J. Cousins (1978). Tissue uptake, subcellular distribution, and metabolism of $^{14}CH_3HgCl$ and $CH_3{}^{203}HgCl$ by rainbow trout, *Salmo gairdneri. J. Fish. Res. Bd. Can.* 35:381-390.

Parks, J.W., A. Lutz and J.A. Sutton (1989). Water column methylmercury in the Wabigoon/English River-Lake system: Factors controlling concentrations, speciation, and net production. *Can. J. Fish. Aquat. Sci.* 46:2184-2202.

Peakall, D.B. (1988). Known effects of pollutants on fish-eating birds in the Great Lakes of North America. In: *Toxic Contamination in Large Lakes. Vol. I: Chronic Effects of Toxic Contaminants in Large Lakes.* N.W. Schmidtke (Ed.), Lewis Publishers, Inc., Chelsea, MI, pp. 39-54.

Porcella, D.B., C.J. Watras and N.S. Bloom (1991). Mercury species in lake water. In: The deposition and fate of trace metals in our environment. Gen. Tech. Rep. NC-150, S. Verry and S.J. Vermette, U.S. Dept. Agric., Forest Service, North Central Forest Exp. Station, St. Paul, MN, pp. 127-138.

Rada, R.G., D.E. Powell and J.G. Wiener (1993). Whole-lake burdens and spatial distribution of mercury in surficial sediments in Wisconsin seepage lakes. *Can. J. Fish. Aquat. Sci.* 50:865-873.

Ribeyre, R. and A. Boudou (1984). Bioaccumulation et repartition tissulaire du mercure - $HgCl_2$ et CH_3HgCl - chez *Salmo gairdneri* apres contamination par voie directe. *Water Air Soil Pollut.* 23:169-186.

Roelke, M.E., D.P. Schultz, C.F. Facemire, S.F. Sundlof and H.E. Royals (1991). Mercury contamination in Florida panthers. A report of the Florida Panther Technical Subcommittee to the Florida Panther Interagency Committee.

Saouter, E., L. Hare, P.G.C. Campbell, A. Boudou and F. Ribeyre (1993). Mercury accumulation in the burrowing mayfly (*Hexagenia rigida*) (ephemeroptera) exposed to CH_3HgCl or $HgCl_2$ in water and sediment. *Water Res.* 27:1041-1048.

Sarkar, A. and S. Jana (1986). Heavy metal pollutant tolerance of *Azolla pinnata*. *Water Air Soil Pollut.* 27:15-18.

Sato, T. and F. Ikuta (1975). Long-term studies on the neurotoxicity of small amount of methylmercury in monkeys (first report). In: Tsubaki T, ed. Studies on the Health Effects of Alkylmercury in Japan. Japan: Environment Agency, 63-70.

Scheuhammer, A.M. (1987). The chronic toxicity of aluminum, cadmium, mercury, and lead in birds: A review. *Environ. Pollut.* 46:263-295.

Scheuhammer, A.M. (1988). Chronic dietary toxicity of methylmercury in the zebra finch, *Poephila guttata*. *Bull. Environ. Contam. Toxicol.* 40:123-130.

Scheuhammer, A.M. (1991). Effects of acidification on the availability of toxic metals and calcium to wild birds and mammals. *Environ. Pollut.* 71:329-375.

Scheuhammer, A.M. and P.J. Blancher (1994). Potential risk to common loons (*Gavia immer*) from methylmercury exposure in acidified lakes. *Hydrobiologia* 279-289:445-455.

Schlegel, H., D.L. Godbold and A. Huttermann (1987). Whole plant aspects of heavy metal induced changes in CO_2 uptake and water relations of spruce (*Picea abies*) seedlings. *Physiol. Plant.* 69:265-270.

Schmidt, M. (1987). Atmosphärischer eintrag und interner umsatz von schwermetallen in waldökosystemen. ber. forschungszentr. Waldökosys./Waldst. A 34/37; Göttingen.

Schreiner, G., B. Ulbrich and R. Bass. 1986. Testing strategies in behavioral teratology: II. Discrimination learning. *Neurobehav. Toxicol. Teratol.* 8:567-572.

Scott, M.L. (1977). Effects of PCBs, DDT, and mercury compounds in chickens and Japanese quail. *Fed. Proc.* 36:1888-1893.

Scott, D.P. and F.A.J. Armstrong (1972). Mercury concentration in relation to size in several species of freshwater fishes from Manitoba and Northwestern Ontario. *J. Fish. Res. Bd. Can.* 29:1685-1690.

Sheffy, T.B. and J.R. St. Amant (1982). Mercury burdens in furbearers in Wisconsin. *J. Wildl. Manage.* 46:1117-1120.

Siegel, S.M., B.Z. Siegel, N. Puerner and T. Speitel (1975). Water and soil biotic relations in mercury distribution. *Water Air Soil Pollut.* 4:9-18.

Siegel, S.M., B.Z. Siegel, C. Lipp, A. Kruckeberg, G.H.N. Towers and H. Warren (1985). Indicator plant-soil mercury patterns in a mercury-rich mining area of British Columbia. *Water Air Soil Pollut.* 25:73-85.

Siegel, S.M., B.Z. Siegel, C. Barghigiani, K. Aratani, P. Penny and D. Penny (1987). A contribution to the environmental biology of mercury accumulation in plants. *Water Air Soil Pollut.* 33:65-72.

Singleton, F.L. and R.K. Guthrie (1977). Aquatic bacterial populations and heavy metals - I. Composition of aquatic bacteria in the presence of copper and mercury salts. *Water Res.* 11:639-642.

Skurdal, J., T. Qvenild and O.K. Skogheim (1985). Mercury accumulation in five species of freshwater fish in Lake Tyrifjorden, southeast Norway, with emphasis on their suitability as test organisms. *Environ. Biol. Fish.* 14:233-237.

Sorensen, J.A., G.E. Glass, K.W. Schmidt, J.K. Huber and G.R. Rapp, Jr. (1990). Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton, and fish of eighty northern Minnesota lakes. *Environ. Sci. Technol.* 24:1716-1727.

Spry, D.J. and J.G. Wiener (1991). Metal bioavailability and toxicity to fish in low-alkalinity lakes: A critical review. *Environ. Pollut.* 71:243-304.

Stanley, R.A. (1974). Toxicity of heavy metals and salts to Eurasian watermilfoil (*Myriophyllum spicatum* L.). *Arch. Environ. Contam. Toxicol.* 2:331-341.

State of Wisconsin (1989). Technical support document for NR 105, 1988. Wisconsin Administrative Code NR 105.07, 1989.

Stickel, L.F., W.H. Stickel, M.A.R. McLane and M. Bruns (1977). Prolonged retention of methyl mercury by mallard drakes. *Bull. Environ. Contam. Toxicol.* 18:393-400.

Stoewsand, G.S., C.A. Bache and D.J. Lisk (1974). Dietary selenium protection of methylmercury intoxication of Japanese quail. *Bull. Environ. Contam. Toxicol.* 11:152-156.

Suchanek, T.H., P.J. Richerson, L.A. Woodward, D.G. Slotton, L.J. Holts and C.E.E. Woodmansee (1993). A survey and evaluation of mercury in: sediment, water, plankton, periphyton, benthic invertebrates and fishes within the aquatic ecosystem of Clear Lake, California. Preliminary Report, Prepared for the U.S. Environmental Protection Agency, Region 9: Superfund Program, by the Institute of Ecology, University of California at Davis, Davis, CA.

Suns, K. and G. Hitchin (1990). Interrelationships between mercury levels in yearling yellow perch, fish condition and water quality. *Water Air Soil Pollut.* 50:255-265.

Talmage S.S. and B.T. Walton (1993). Food chain transfer and potential renal toxicity of mercury to small mammals as a contaminated terrestrial field site. *Ecotoxicol.* 2:243-256.

Thomann, R.V. (1989). Bioaccumulation model for organic chemical distribution in aquatic food chains. *Environ. Sci. Technol.* 23:699-707.

U.S. Environmental Protection Agency (U.S. EPA, 1985). Ambient water quality criteria for mercury - 1984. EPA/440/5-84/026. Office of Water, Washington, D.C.

U.S. Environmental Protection Agency (U.S. EPA, 1989). Ecological assessment of hazardous waste sites: A field and laboratory reference. Corvallis, Oregon: Environmental Research Laboratory. EPA/600/3-89/013.

U.S. Environmental Protection Agency (U.S. EPA, 1992a). Peer review workshop on a framework for ecological risk assessment. Risk assessment forum. EPA/625/3-91/002.

U.S. Environmental Protection Agency (U.S. EPA, 1992b). A national study of chemical residues in fish. EPA 823/R-92/008. Office of Water Regulations and Standards, Washington, D.C.

U.S. Environmental Protection Agency (U.S. EPA, 1993a). Wildlife exposure factors handbook. EPA/600/R-93/187a. U.S. EPA Office of Research and Development, Washington, DC.

U.S. Environmental Protection Agency (U.S. EPA, 1993b). Great Lakes water quality initiative criteria documents for the protection of wildlife (proposed) DDT; Mercury; 2,3,7,8-TCDD; PCBs. EPA/822/R-93/006. U.S. EPA Office of Science and Technology, Washington, DC.

U.S. Environmental Protection Agency (U.S. EPA, 1993c). Water quality guidance for the Great Lakes system and correction: Proposed rules. *Fed. Regist.* 58(72):20802-21047 (April 16, 1993).

U.S. Environmental Protection Agency (U.S. EPA, 1994). Draft proceedings of the national wildlife criteria methodologies meeting, April 13-16, 1992, Charlottesville, VA. U.S. EPA Office of Water and Office of Science and Technology, Washington, DC.

U.S. Environmental Protection Agency (U.S. EPA, 1995a). Trophic level and exposure analyses for selected piscivorous birds and mammals. Volume I. Analysis for species of the Great Lakes Basin (Draft). U.S. EPA Office of Science and Technology, Washington, DC.

U.S. Environmental Protection Agency (U.S. EPA, 1995b). Final water quality guidance for the Great Lakes system: Final Rule. *Fed. Regist.* 60(56):15366-15425 (March 23, 1995).

U.S. Fish and Wildlife Service (U.S. FWS, 1993). Mercury contamination in tissues of Florida bald eagles. Final Project Report. Prepared for the U.S. Fish and Wildlife Service, Department of the Interior, Washington, DC. (December, 1993)

Vermeer, K., F.A.J. Armstrong and D.R.M. Hatch (1973). Mercury in aquatic birds at Clay Lake, Western Ontario. *J. Wildl. Manage.* 37:58-61.

Watras, C.J. and N.S. Bloom (1992). Mercury and methylmercury in individual zooplankton: Implications for bioaccumulation. *Limnol. Oceanogr.* 37:1313-1318.

Weber, J.H. (1993). Review of possible paths for abiotic methylation of mercury (II) in the aquatic environment. *Chemosphere* 26:2063.

Weil, C.S. and D.D. McCollister (1963). Relationship between short- and long-term feeding studies in designing an effective toxicity test. *Agric. Food Chem.* 11:486-491.

Weis, J.S. and P. Weis (1989). Tolerance and stress in a polluted environment. *BioScience* 39:89-95.

Weis, J.S. and P. Weis (1995). Effects of embryonic exposure to methylmercury on larval prey-capture ability in the mummichog, *Fundulus heteroclitus*. *Env. Toxicol. Chem.* 14:153-156.

Welch, L.J. (1994). Contaminant burdens and reproductive rates of bald eagles breeding in Maine. Ph.D. dissertation, University of Maine, Orono, ME.

Wells, J.R., P.B. Kaufman and J.D. Jones (1980). Heavy metal contents in some macrophytes from Saginaw Bay (Lake Huron, USA). *Aquat. Bot.* 9:185-193.

Westermark, T., T. Odsjö, T. and A.G. Johnels (1975). Mercury in bird feathers before and after the Swedish ban on alkyl mercury in agriculture. *Ambio* 4:87-97.

Wiemeyer, S.N., T.G. Lamont, C.M. Bunck, C.R. Sindelar, F.J. Gramlich, J.D. Fraser and M.A. Byrd (1984). Organochlorine pesticide, polychlorobiphenyl, and mercury residues in bald eagle eggs - 1969-1979 - and their relationships to shell thinning and reproduction. *Arch. Environ. Contam. Toxicol.* 13:529-549.

Wiemeyer, S.N., D.M. Bunck and C.J. Stafford (1993). Environmental contaminants in bald eagle eggs - 1980-1984 - and further interpretations of relationships to productivity and shell thickness. *Arch. Environ. Contam. Toxicol.* 24:213-227.

Wiener, J.G., G.A. Jackson, T.W. May and B.P. Cole (1982). Longitudinal distribution of trace elements (As, Cd, Cr, Hg, Pb, and Se) in fishes and sediments in the upper Mississippi River. In: *Contaminants in the Upper Mississippi River.* J.G. Wiener, R.V. Anderson and D.R. McConville (Eds.). Butterworth Publishers, Boston, MA. p. 139-170.

Wiener, J.G.; R.E. Martini, T.B. Sheffy and G.E. Glass (1990). Factors influencing mercury concentrations in walleyes in northern Wisconsin lakes. *Trans. Amer. Fish. Soc.* 119:862-870.

Wiener, J.G. and D.J. Spry (1995). Toxicological significance of mercury in freshwater fish. In: *Interpreting Environmental Contaminants in Animal Tissues.* G. Heinz and N. Beyer (eds.), Lewis Publishers, Chelsea, MI. (in press).

Winfrey, M.R. and J.W.M. Rudd (1990). Review - Environmental factors affecting the formation of methylmercury in low pH lakes. *Environ. Toxicol. Chem.* 9:853-869.

Wobeser, G. (1973). Aquatic mercury pollution: studies of its occurrence and pathologic effects on fish and mink. Ph.D. dissertation, University of Saskatchewan, Saskatoon, Saskatchewan, Canada.

Wobeser, G. and M. Swift III (1976). Mercury poisoning in a wild mink. *J. Wildl. Diseas.* 12:335-340.

Wobeser, G., N.D. Nielsen and B. Schiefer (1976a). Mercury and mink I: The use of mercury contaminated fish as a food for ranch mink. *Can. J. Comp. Med.* 40:30-33.

Wobeser, G., N.D. Nielsen and B. Schiefer (1976b). Mercury and mink II: Experimental methyl mercury intoxication. *Can. J. Comp. Med.* 40:34-45.

World Health Organization (WHO, 1989). Environmental health criteria 86: Mercury - environmental aspects.

Wren, C.D. (1985). Probable case of mercury poisoning in a wild otter, *Lutra canadensis*, in northwestern Ontario. *Can. Field Nat.* 99:112-114.

Wren, C.D. (1986). A review of metal accumulation and toxicity in wild mammals. I. Mercury. *Environ. Res.* 40:210-244.

Wren, C.D. (1991). Cause-effect linkages between chemicals and populations of mink (*Mustela vison*) and otter (*Lutra canadensis*) in the Great Lakes basin. *J. Toxicol. Environ. Health* 33:549-585.

Wren, C.D., H.R. MacCrimmon and B.R. Loescher (1983). Examination of bioaccumulation and biomagnification of metals in a precambrian shield lake. *Water Air Soil Pollut.* 19:277-291.

Wren, C.D. and H.R. MacCrimmon (1986). Comparative bioaccumulation of mercury in two adjacent freshwater ecosystems. *Water Res.* 20:763-769.

Wren, C.D., P.M. Stokes and K.L. Fischer (1986). Mercury levels in Ontario mink and otter relative to food levels and environmental acidification. *Can. J. Zool.* 64:2854-2859.

Wren, C.D. and G.L. Stephenson (1991). The effect of acidification on the accumulation and toxicity of metals to freshwater invertebrates. *Environ. Pollu.* 71:205-241.

Wright, D.R. and R.D. Hamilton (1982). Release of methyl mercury from sediments: effects of mercury concentration, low temperature, and nutrient addition. *Can. J. Fish Aquat. Sci.* 39:1459-1466.

Xun, L., N.E.R. Campbell and J.W.M. Rudd (1987). Measurements of specific rates of net methyl mercury production in the water column and surface sediments of acidified and circumneutral lakes. *Can. J. Fish. Aquat. Sci.* 44:750-757.

Yannai, S., I. Berdicevsky and L. Duek (1991). Transformations of inorganic mercury by *Candida albicans* and *Saccharomyces cerevisiae*. *Appl. Environ. Micro.* 57:245-247.

Zelles, L., I. Scheunert and F. Korte (1986). Comparison of methods to test chemicals for side effects on soil microorganisms. *Ecotoxicol. Environ. Safety* 12:53-69.

Zillioux, E.J., D.B. Porcella and J.M. Benoit (1993). Mercury cycling and effects in freshwater wetland ecosystems. *Environ. Toxicol. Chem.* 12:2245-2264.

APPENDIX A

ESTIMATION OF BIOACCUMULATION FACTORS FOR MERCURY IN FISH

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A.1 Introduction

This appendix describes efforts to estimate bioaccumulation factors (BAFs) for mercury in fish. Following the food chain structure described in Section 3.3 of Volume V, BAFs were estimated for fish that occupy trophic levels 3 and 4. These values are referred to as BAF_3 and BAF_4, respectively. These BAFs serve as inputs to the calculation of wildlife criterion values (WC) and are also used to characterize human exposure from consumption of contaminated fish. Emphasis was placed on evaluating uncertainties associated with these values.

Measures of mercury accumulation that are not treated in this appendix include the following: (1) BAFs for trophic levels 1 and 2; (2) biota-sediment bioaccumulation factors (BSAFs) for trophic levels 1 - 4; and (3) predator-prey factors (PPFs) for piscivorous wildlife (that is, the concentration of mercury in piscivorous birds and mammals divided by that of their prey). Information on these parameters, including summaries of field data from which estimated values can be derived, can be found in Section 2.3.1 of Volume V.

For the purposes of this analysis, BAFs for mercury are defined as the concentration of methylmercury in whole fish divided by the concentration of total mercury in filtered water. This definition is used so that reference dose values (RfDs) for methylmercury fed to wildlife can be related directly to water concentration. A more common definition of BAF is the total concentration in fish divided by the total concentration in water; the degree of error introduced by the definition used in this Report is minimal, as it is generally agreed that 95% or more of the total mercury in fish is methylmercury (Bloom, 1994).

The methods used to derive BAFs in the Great Lakes Water Quality Initiative (GLWQI) served as a starting point for the present analysis. The analysis was then extended to include an examination of field data from which BAFs could be estimated. It was recognized that considerable natural variability exists with respect of the accumulation of mercury in aquatic food chains. An effort was, therefore, made to incorporate this variability into the analysis. This was accomplished by using a Monte Carlo simulation approach. The Monte Carlo simulation method is described in Section A.2.2. Important modeling assumptions were evaluated by performing a sensitivity analysis, the results of which are presented in Section A.3.6.

A.2 Monte Carlo Analysis

A.2.1 Sources of Uncertainty and Their Treatment

Models of environmental phenomena must deal with two basic sources of uncertainty. The first is uncertainty arising from natural variability, such as the size of individuals in a population. The second is uncertainty around the value of a parameter or variable when it is known that there is a single value. These two sources of uncertainty are formally referred to as "variability" and "uncertainty". There is no attempt in the current analysis to separate variability and uncertainty fully in the current analysis. In this appendix the term "variability" is used in a general context, comprising both variability and uncertainty. The term "variable" is used to describe model variables treated as random variates, while the term "parameter" refers to a fixed parameter of the mathematical form of a specific distribution.

In dealing with the issue of uncertainty, it is important to distinguish between qualitative and quantitative models. A qualitative analysis can only make descriptive value judgment statements about the magnitude of the uncertainty or about the general confidence in the model output, such as "high", "medium" or "low" and cannot address the statistical properties of the model. A quantitative analysis allows for a more precise expression of the overall variability, is essential for comparing the results of

different models and is necessary to determine which of the input parameters have the greatest effect on the model output. The latter procedure, called a sensitivity analysis, allows the model developers to focus future efforts on the most important aspects of the model and gives the risk assessor or risk manager valuable perspective for interpreting the results.

A.2.2 Probabilistic Simulation Using the Monte Carlo Method

There are a number of methods for expressing uncertainty in a quantitative fashion, the discussion of which is beyond the scope of this document; see Morgan and Henrion (1990) for a description of these techniques. A Monte Carlo simulation approach was used as a means of treating the variability in the input variables (Rubinstein, 1981). The Monte Carlo method is an iterative random sampling technique that mathematically combines specified distributions (rather than single numbers) and allows for the propagation of variability in each input variable throughout the model; that is, the variability in each input will be reflected in the output. Implicit in this treatment is the assumption that all parameters vary independently of one another. Thus, during a single iteration, a "high" value for one variable is equally likely to be combined with a "high" or "low" value of a second variable.

In a probabilistic Monte Carlo approach, a distribution for each variable in a mathematical equation is prescribed. The equation is then repeatedly evaluated by random drawing of a value from each distribution for each iteration and placing the result in the output distribution. The process is typically repeated 10,000 times or more and produces a distribution of values that can be described in terms of percentiles. The focus of this analysis was on the 50^{th} percentile and the spread of the distribution between the 5^{th} and 95^{th} percentiles. The central tendency (median or mean) of the output distribution is primarily dependent on the median values of the input distributions. The spread of the output distribution will be determined by the spread of each of the input distributions and by the nature of the mathematical operation applied to each input.

Calculation of a WC value requires that a single BAF value be established for each trophic level contributing to the analysis. The same is true for estimating human exposure due to ingestion of contaminated fish. It should be noted, however, that the Monte Carlo approach yields both a mean and distribution of BAF values. Although mean values were used for the calculation of WC values, it is useful to characterize the statistical variation about this mean as it may reflect actual variation in natural systems. The possible significance of these distributions is discussed in Volume VI.

A.2.3 Selection of Distributions for Input Variables

Input distributions were based on an analysis of published data and data from two unpublished reports (see Section A.3.1., Data Quality Objectives). In general, an empirical distribution representing both the central tendency and the extremes of the given data was determined. It was decided to represent the actual input distributions in parameterized form for this analysis. That is, formal analytic distributions that are expressed by a mathematical equation (with specific defining parameters) were assigned to the inputs rather than using the empirical data. This decision was based on the general scarcity of data and on theoretical considerations. The particular set of parameters chosen for each of the variables is only one choice of a number of possible choices. The choice of the form, location and scale for each of the variables is largely a matter of judgment.

The general form of the distribution, whether normal, lognormal, beta, or otherwise, was determined by examination of the shape of a histogram (distribution) of empirical the data and by consideration of the underlying biological and physical processes.

Generally speaking, distributions are characterized by location and scale parameters. The location of a distribution is its central tendency, either the mean, median or mode. The mean is the average of all possible values. The median is the value below which 50% of all possible values fall. The mode is the value that occurs most frequently. The scale parameter generally represents the spread of the distribution. The standard deviation (s.d.) is the scale parameter for the normal and lognormal distributions, which are both open-ended; that is, they have no absolute limits. For closed-end distributions, such as the triangular and beta, scale is represented by the smallest and largest values that the function can take on. For any given variable, extreme values are generally considered to be less likely than values near the median. In these cases distributions with higher probabilility densities in the middle than in the tails (either end of the distribution) is assigned. All distributional forms except the uniform belong to this class. In some cases, when this assumption is unwarranted, a uniform distribution, in which all values are equally likely, was assigned.

Many of the variables reflect underlying exponential processes and are distributed as the logarithm of the nominal values. Hereafter, such variables will be denoted as being distributed in log space. In these cases, and when the empirical data suggest such a distribution, a lognormal or log-uniform distribution was chosen to represent the variable. Triangular or beta distributions were used when a judgement was made that the value of the variable will fall within identifiable absolute limits. A triangular distribution, which requires fewer assumptions than a beta, could be used in those cases where a beta is assigned. The beta distribution, however, allows for greater uncertainty in the central tendency and is an appropriate alternative for nonsymmetrical triangular distributions (Evans et al., 1993). The standard beta variate, with limits of 0 and 1 and a range of shapes, is an appropriate choice for modeling fractions and percentiles.

Determination of the distribution parameters focuses on identifying the median and extreme percentiles. The location parameter was estimated from the data. Scale was determined as a function of the number of observations and the observed extreme values. The empirically-determined percentiles corresponding to the lowest and highest observations, determined by dividing the rank order of the observation by n + 1 (where n is the total number of observations), were preserved in the mathematically defined distribution whenever possible. Calculating the percentiles on the basis of n + 1, rather than n, allows for possibility of obtaining more extreme values in larger sample sizes.

The fundamental data unit in all analyses was defined as the study. That is, each published study was treated as an independent unit. High and low values from each study were included in the empirical distribution if reported. Otherwise, the study was represented by the reported mean value.

Monte Carlo simulations were performed on Intel® 486 DX2/66 CPUs in Crystal Ball® (version 3.0) for Excel® (version 4.0) and in S-PLUS® in the MS Windows® (version 3.1) environment.

A.3 Estimation of BAFs for Mercury

BAF values for mercury in aquatic food chains were calculated in three different ways. The first method of calculation was identical to that used to support WC development in the GLWQI (U.S. EPA, 1995) and involved multiplication of a weighted bioconcentration factor (BCF) by appropriate food chain multipliers (FCMs). This method yields BAFs for trophic levels 3 and 4. The second method involved estimation of a BAF for trophic level 3 from field data, which was then multiplied by a predator-prey factor (PPF) for trophic level 4 to yield a BAF for trophic level 4. A BAF for trophic level 4 was also directly estimated from field data. The results of all three analyses were then compared.

It is recognized that other, more detailed approaches have been proposed to estimate BAFs for mercury in aquatic food chains (e.g., the mercury cycling model (MCM), developed by the Electric

Power Research Institute; Hudson et al., 1994). Such approaches were considered to be inappropriate, however, in view of the general lack of understanding of mercury accumulation and the broad geographical focus of this Report. In particular, it was determined that models requiring calibration to specified food chains and lake water characteristics were unlikely to yield information that could be applied with confidence to a different food chain, or in a lake with different biogeochemical characteristics. Instead, the decision was made to accept that considerable variability exists in mercury bioaccumulation in fish and to employ statistical methods that treat this variability quantitatively.

A.3.1 Data Quality Objectives

Preference was given to data published in the peer-reviewed literature. In some instances, due to advances in analytical methods, preference was also given to the most recently published values. An attempt was made to characterize the data as necessary to permit comparisons to be made between studies. For example, mean values were estimated, even if the original authors did not do so. Every effort was made to report BAFs in terms of both the age and/or size of the fish involved and the mercury species. In general, BAFs are expressed in the literature as total mercury in fish divided by total mercury in filtered water from which the fish were obtained. Exceptions to this rule were noted where they occured and were included only if they provided other pertinent information (such as, a predator-prey factor for two adjacent trophic levels).

Field data from two unpublished reports were also included (Suchanek et al., 1993; Parsons and Bigham, 1994). Both of these studies are notable for their extent and quality and include data collected from organisms in all four trophic levels.

A.3.2 Estimation of BAFs For Mercury Using Methods Presented in Proposed Guidance for the Great Lakes Water Quality Initiative

A.3.2.1 BAFs Published in the Proposed Guidance (GLWQI)

BAFs for mercury were estimated to support the development of WC values in the GLWQI (U.S. EPA, 1993). The approach and assumptions used in these calculations were subsequently modified to incorporate new information (U.S. EPA, 1995). The following is a description of the modified approach.

BAFs were calculated in support of the GLWQI to relate methylmercury concentrations in fish to total mercury concentrations in filtered water. The formula for the calculation of the BAF for trophic level 4 (BAF_4) is given in equation 1.

$$BAF_4 = BCF_{Hg} \times FCM_4 \times MeHg_T \quad (1)$$

where

BCF_{Hg} is the weighted-average bioconcentration factor (BCF) for total mercury at trophic level 1 and

FCM_4 is the food-chain multiplier representing the cumulative biomagnification of mercury from trophic level 2 to trophic level 4.

$MeHg_T$ is the fraction of total mercury in fish flesh that is in the methylated form.

The formula for calculating BCF_{Hg} is given in equation 2.

$$BCF_{Hg} = (BCF_{MHg} \times MeHg_W) + (BCF_{iHg} \times (1 - MeHg_W)) \quad (2)$$

where

BCF_{MHg} is the bioconcentration factor for methylmercury at trophic level 1,
BCF_{IHg} is the bioconcentration factor for inorganic mercury at trophic level 1 and
$MeHg_W$ is the fraction of total mercury in the water column that is in the methylated form.

The formula for FCM_4 is given in equation 3.

$$FCM_4 = PPF_2 \times PPF_3 \times PPF_4 \quad (3)$$

where

PPF_2 is the predator-prey factor at trophic level 2 representing the biomagnification of mercury in zooplankton as a result of feeding on contaminated phytoplankton,
PPF_3 is the predator-prey factor for forage fish feeding on contaminated zooplankton, and
PPF_4 is the predator-prey factor piscivorous fish feeding on forage fish.

The estimated BAFs for trophic levels 3 and 4 are as follows:

BAF for trophic level 4 = 140,000
BAF for trophic level 3 = 27,900

Several assumptions were made to permit estimation of these values. These assumptions include the following.

1. 17% of total mercury in the water column exists as methylmercury.
2. 97.5% of total mercury in fish exists as methylmercury.
3. The predator-prey factors (PPFs) for trophic levels 2, 3 and 4 are 2.00, 1.26 and 5.00, respectively. Thus, the FCM for trophic level 2 is 2.0, that for trophic level 3 is 2.0 x 1.26, or 2.52, and that for trophic level 4 is 2.0 x 1.26 x 5.0, or 12.6.
4. The mercury concentration at trophic level 1 is determined by the extent to which mercury bioconcentrates during an aqueous exposure.
5. The BCF for inorganic mercury in aquatic biota is 2,998.
6. The BCF for methylmercury in aquatic biota is 52,175.

BAFs for mercury at trophic levels 3 and 4 were then determined as follows.

1. A weighted BCF for total mercury (inorganic and methyl) at trophic level 1 was calculated, based on the assumption that 17% of the total mercury in water exists as the methylated form, and 83% as the inorganic form.
2. The weighted BCF for total mercury at trophic level 1 was multiplied by FCMs for trophic levels 2, 3 and 4 to obtain BAFs for total mercury.
3. BAFs for total mercury were multiplied by 0.975 to obtain BAFs for methylmercury in fish.

A.3.2.2 Inputs and Assumptions for the Present Analysis

In the present analysis, data used to calculate BAFs for the GLWQI were combined with additional information from both published and unpublished sources. Input variable distributions are presented individually along with the data from which they were derived. In addition, several of the assumptions made to support the WC calcuation in the GLWQI were evaluated in light of recent findings.

Mercury Speciation in Water

Variable: $MeHg_W$
Definition: Percent of total mercury in water existing as the methylated form
Units: %

Technical Basis:

Kudo et al. (1982) reported that methylmercury in water from two Japanese rivers constituted "around 30%" of total mercury (range of 26% to 46%). Similar levels were found in three rivers in Canada and Japan. The two Japanese rivers were known to be polluted by mercury from point source discharges.

A value of < 10% was reported by Parks et al. (1989) at sampling sites downstream of a chlor-alkali plant on the Wabigoon-English River Lake system.

Organomercury as a percentage of total mercury was reported to range from 1 to 89% in twelve lakes and eight rivers located throughout the United States (Gill and Bruland, 1990). Particulate mercury comprised a high, but variable (10% - 92%), percentage of the total mercury present but was not divided into mercury species.

Bloom and Effler (1990) reported that methylmercury constituted from 3.6% to 27.3% of total mercury in samples from Onondaga Lake in New York State, which is known to have been polluted with mercury by a chlor-alkali plant. Values are for unfiltered water, although values for filtered water are also available and yield similar or higher percentages for methylmercury. Data varied considerably with season and depth indicating the presence of a dynamic system. Additional data from other sources were presented for comparison, but they were not presented in a manner that allows calculation of maximum values. Based upon these data, it appears that methylmercury as a percent of total mercury ranges up to 10% in both polluted and pristine waters.

Based upon their analysis of surface waters from Sweden, Lee and Hultberg (1990) concluded that the percentage of organic-bound mercury that is methylmercury is relatively low (6% to 13%). The percentage of total mercury existing as methylmercury in these water samples varied from 3.6% to 5.3%.

Methylmercury constituted from 5% to 12% of total mercury in surface water samples obtained from Little Rock Lake (Watras and Bloom, 1992). The lower figure corresponds to an untreated reference basin, the higher figure to an experimentally acidified treatment basin.

Summary:

Speciation data for mercury in water remain relatively scarce, and comparisons are difficult to make because the different mercury species tend to be operationally defined. This reflects the fact that methods for measuring the different mercury species and the interpretation of these values are in a state of evolution. This, in turn, impacts the derivation of BAF values for methylmercury, since it is not always clear which of these operationally defined measurements be used in calculation.

Speciation data from Gill and Bruland (1990) suggest that the range of possible methylmercury values may be large, although there is a question of how much organomercury exists as the methylated form. Gill and Bruland (1990) assumed that virtually all the organic mercury fraction is methylmercury. Actual measurements of methylmercury in this fraction range from 6-56% (Lee and Hultberg, 1990; Meili et al., 1991). In a majority of published studies, methylmercury as a percentage

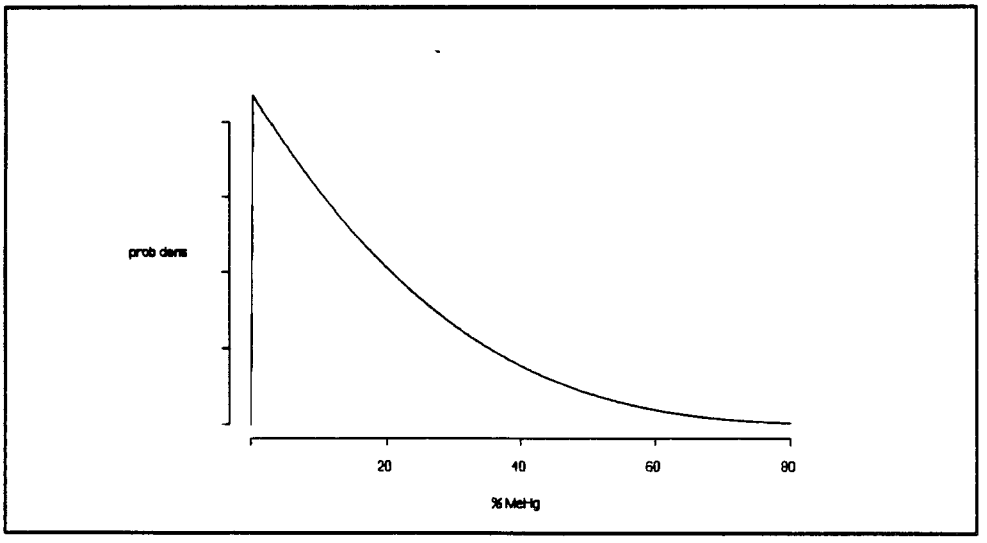
of total mercury in water is reported to range from 5% to 15%. Thus for many systems, the figure (17%) used in the GLWQI may be too high. It may also be important to distinguish between surface and subsurface waters. Measurements made by Bloom and Effler (1990) suggest that methylmercury levels in surface waters may be considerably lower than those at depth and would, therefore, not accurately reflect the situation that exists throughout a water body.

The values defining the empirical distribution for $MeHg_W$ are given in Table A-1. The beta distribution was chosen as best representative of this highly skewed closed-end distribution. The probability density function is graphically illustrated in Figure A-1. Figure A-1 plots probability density on the y-axis against the the values of $MeHg_W$ (in %) on the x-axis.

Table A-1
Methylmercury as a Percentage of Total Mercury in Water

Values	Reference
3.6, 5.3	Lee and Hultberg, 1990
5, 12	Watras and Bloom, 1992
8, 10	Parks et al., 1989
3.6, 27.3	Bloom and Effler, 1990
3.5, 50	Gill and Bruland, 1990
26, 46	Kudo et al., 1982
26, 51	Meili et al., 1991

Figure A-1
Input Distribution for $MeHg_W$



Variable: $MeHg_T$
Definition: Percentage of total mercury in fish tissues existing as the methylated form.
Units: %

Technical Basis:

Based upon their review of data obtained in earlier studies, Huckabee et al. (1979) concluded that methylmercury constitutes from 80% to 95% of total mercury in fish.

Hildebrand et al. (1980) obtained an average value of 91.7% in muscle from 86 rock bass and hog suckers (range from 78.9% to 103.8%). The authors also cite numerous older references corroborating this value.

Values ranging from 59% to 96% were reported by Cappon and Smith (1981) in muscle tissue from seven species of freshwater fish, including walleye and northern pike, small and largemouth bass, yellow perch, bullhead and muskellunge; however, the mean of these values tended toward the high end of the range. Literature cited by the authors suggests that methylmercury values in marine fish tend to vary somewhat more (38.4% - 92.9%, with numerous values around 60%) than in their freshwater counterparts; total mercury concentrations were similar. Additional data cited from several sources suggest that methylmercury comprises > 95% of the total in northern pike from Finland and Sweden.

Paasivirta et al. (1981) reported values ranging from 82% to 84% in muscle tissue from northern pike.

Methylmercury as a percentage of total mercury was reported to range from 79.2% to 94.8% in pike and roach from four lakes in Finland (Paasivirta et al., 1983).

Baluja et al. (1983) reported values ranging from 75% to 94% in sand smelt, carp and eel, with the mean tending toward the high end of the range.

Values ranging from 62.9% to 79.2% were measured by Cappon (1984) in muscle tissues from coho and chinook salmon, and brown and lake trout from Lake Ontario.

Methylmercury was reported to comprise 99% of total mercury in muscle tissue of yellow perch, northern pike and white suckers from lakes in northern Wisconsin and the upper peninsula of Michigan (Grieb et al., 1990).

Jackson (1991) reported that methylmercury constitutes 80% to 90% of total mercury in muscle tissue from several species of fish in lakes and reservoirs in Manitoba.

Bloom (1992) reported that virtually all (>95%) of the mercury in muscle tissues from largemouth bass, yellow perch, northern pike and white suckers existed as methylmercury. The author suggested that lower values reported in earlier literature are probably erroneous due to inadequate sampling and analytical techniques.

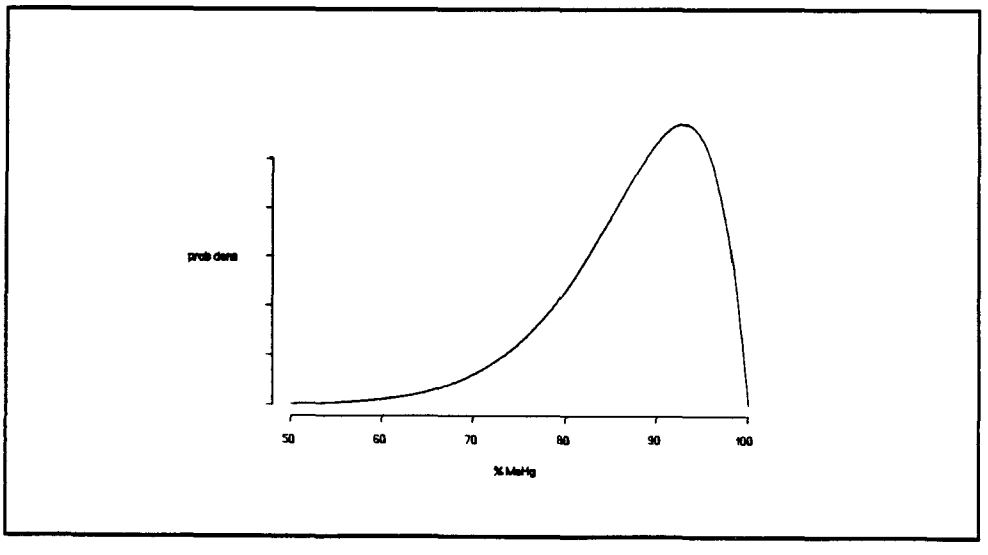
Summary:

Because of continued refinement in mercury analysis methods, more confidence should be placed in recent values (see Bloom (1992) for a discussion of factors that can result in lower estimates than are actually present). Collectively, the most recent values suggest that the percentage of mercury in fish that exists as the methylated form is close to and perhaps even exceeds 95%. Minor differences in reported values may be due the different types of samples evaluated (e.g., whole fish vs. skin-on fillets vs. skin-off fillets) but are unlikely to be important in the calculation of a BAF. The values used to define $MeHg_T$ are given in Table A-2. The beta distribution was chosen as best representative of this highly skewed closed-end distribution. The probability density function for this distribution is shown in Figure A-2.

Table A-2
Methylmercury as a Percentage of Total Mercury in Fish

Value	Reference
71	Cappon, 1984
83	Paasivirta et al., 1981
85	Jackson, 1991
87	Cappon and Smith, 1981
87	Paasivirta et al., 1983
90	Baluja et al., 1983
92	Hildebrand et al., 1980
95	Bloom, 1992
99	Grieb et al., 1990

Figure A-2
Input Distribution for $MeHg_T$



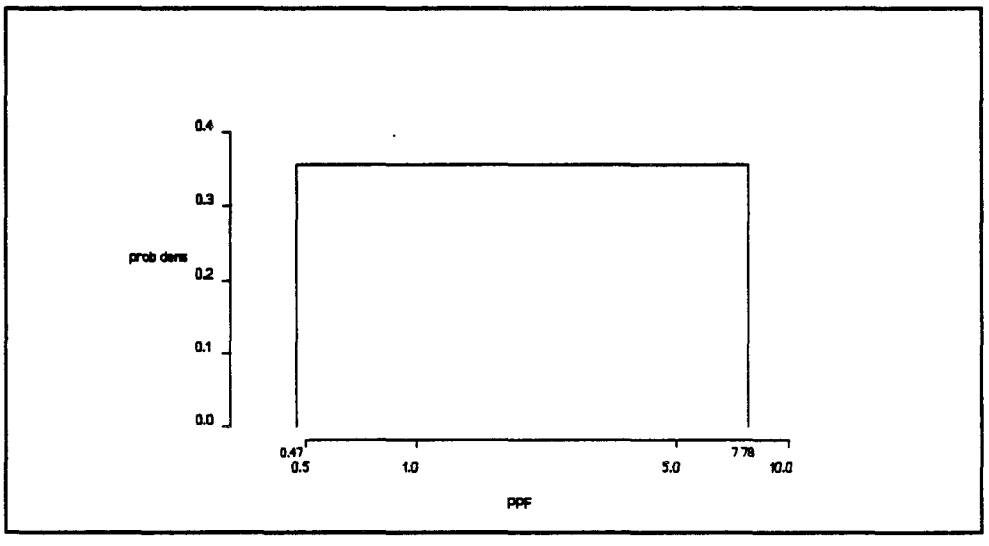
Predator-Prey Factor for Trophic Level 2

Variable: PPF_2
Definition: Factor by which mercury concentrations in trophic level 2 organisms exceed those in trophic level 1 organisms upon which they prey.
Units: Unitless

Technical Basis:

Estimates of PPF_2 and PPF_3 used to derive BAFs in the GLWQI were based on a single study (Watras and Bloom, 1992) in which the concentration of total mercury was measured in phytoplankton (trophic level 1), zooplankton (trophic level 2) and age-1 (year old) yellow perch (trophic level 3). For the present analysis, a distribution of PPF_2 values was developed based on the logs (base 10) of single high and low values of 1.2 and 3.07, defining the 33rd and 67th percentiles, respectively. These values were calculated from the reported low and high Hg concentrations of 36 and 92 µg/g, respectively, in zooplankton divided by the single reported value of 30 µg/g in phytoplankton (Watras and Bloom, 1992). The uniform distribution was chosen because there is no reason to believe that either of the reported values for zooplankton are more likely to occur. The probability density function for PPF_2 is shown in Figure A-3.

Figure A-3.
Input Distribution for PPF_2



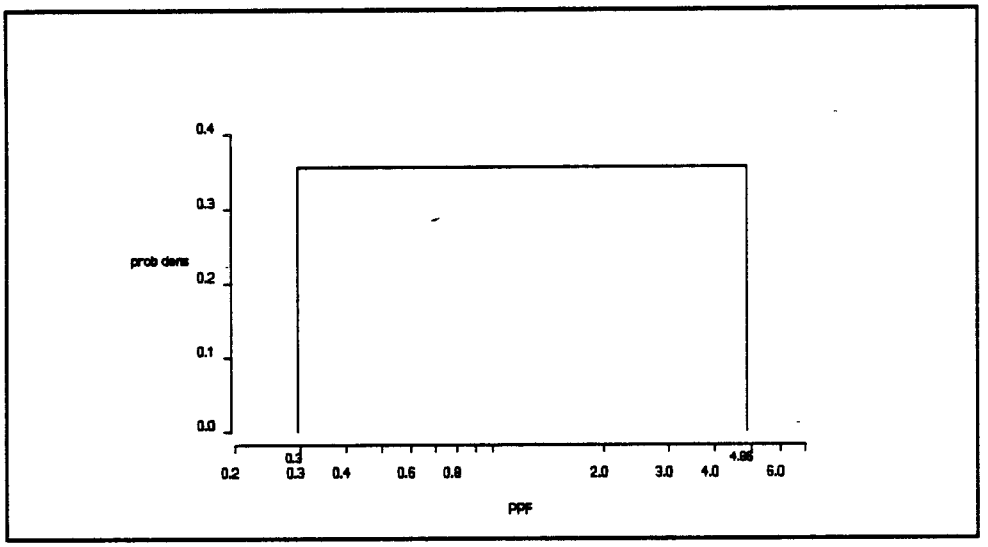
Predator-Prey Factor for Trophic Level 3

Variable: PPF_3
Definition: Factor by which mercury concentrations in trophic level 3 organisms exceed those in trophic level 2 organisms upon which they prey.
Units: Unitless

Technical Basis:

A single value of about 1.2 was calculated for PPF_3 from Figure 3 in Watras and Bloom (1992), by dividing the visually-interpolated BCF for yellow perch by that for zooplankton. The form and relative scale of this distribution was assumed to be same as that for PPF_2. The probability density function for PPF_3 is shown in Figure A-4.

Figure A-4.
Input Distribution for PPF_3



Predator-Prey Factor for Trophic Level 4

Variable: PPF_4
Definition: Factor by which mercury concentrations in trophic level 4 organisms exceed those in trophic level 3 organisms upon which they prey.
Units: Unitless

Technical Basis:

PPF_4s ranging from 2.4 to 7.5 were estimated for "standardized" lake trout (60 cm) and rainbow smelt (15 cm) from nine Ontario lakes (MacCrimmon et al., 1983). Values from very old (20+ years) lake trout from Tadenac Lake exceeded those of age 2+ year-old rainbow smelt by a factor of 12.3. Levels in trout appeared to increase dramatically when they became large enough (about 6 years old) to switch from a diet of benthic invertebrates to smelt.

PPF_4s ranging from 1.2 to 8.4 were calculated from data reported by Wren et al. (1983). These estimates were computed by dividing the average values for three predators (smallmouth bass, northern pike, and lake trout) by average values for two forage fish (bluntnose minnow and rainbow smelt). The maximum value was obtained by dividing the value for pike by that for minnows.

Data presented by Mathers and Johansen (1985) were used to calculate PPF_4s of 5.9 and 4.9 for northern pike and walleye, respectively. Each value was calculated by dividing the mercury residue in eight-year-old fish by the weighted average mercury content of the diet for each species.

Corresponding values for four-year-old fish were 2.8 and 2.2, respectively. Values for both species tended to increase with fish age and in some very old walleye exceeded 10.0.

PPF_4s ranging from 2.7 to 15.1 were computed by dividing the average mercury residues in two predators (northern pike and brown trout) by average values for two forage fish (whitefish and smelt) (Skurdal et al., 1985). The maximum value was obtained by dividing the mercury level in brown trout by that in whitefish; however, brown trout were reported to leave this lake system to forage in the ocean, thus complicating the comparison. The maximum PPF_4 for pike was 4.46 (pike ÷ whitefish).

PPF_4s from 3.0 to 3.2 were calculated from data presented by Wren and MacCrimmon (1986). Concentrations in "standardized" northern pike were divided by those in "standardized" yellow perch. The range represents values calculated for two adjacent freshwater systems.

A PPF_4 of 2.5 was obtained from average values for 1+ year-old pike and 1+ year-old yellow perch collected from several locations on the English/Wabigoon system (Parks, 1988). This value may be lower than others calculated for similar systems due to the small size of the pike sampled (mean = 26 cm).

A PPF of 6.3 was calculated from data presented by Cope et al. (1990). Data for age 5 walleye were regressed against data from age 2 yellow perch. All fish were collected from northern Wisconsin seepage lakes. The PPF was calculated from the regression equation for a perch containing 0.1 micrograms/g of total mercury. It should be noted that in this study mercury levels in muscle from walleye were compared with whole-body levels in perch.

Data collected by Sorenson (1990) from northern Minnesota lakes suggest that the PPF across two trophic levels (1 kg northern pike to zooplankton) is approximately 5. Assuming the same increase between trophic levels, the increase from trophic level 3 to trophic level 4 would be 2.25.

Residue data given by Jackson (1991) was used to calculate PPF_4s ranging from 5.2 (average of walleye and pike/shiners) to 15.5. Estimates were computed for two lakes in Manitoba by dividing the average values for two predators (northern pike and walleye) by average values for two forage fish (yellow perch and spottail shiners). The maximum value of 15.5 was obtained by dividing the value for pike by that for perch. The maximum value for walleye was 12.0 (walleye ÷ perch).

A value of 6.8 was obtained by regressing data for 1 kg northern pike against that from 8 to 10 cm yellow perch (Lindqvist, 1991). The data are from 43 lakes and are remarkable for the consistency of the relationship.

A PPF_4 of 7.4 was calculated by comparing 1 kg northern pike with 5 to 10 g yellow perch (Meili et al., 1991).

Average concentrations of total mercury were calculated for largemouth bass and shiners in Clear Lake, California (Suchanek, 1993). The PPF_4 estimated from these data was 5.4. Interestingly, chemical analysis on the same samples suggests that the PPF_4 for methylmercury is considerably higher (17.7). The reason for this discrepancy is not presently known.

Summary:

Predator-prey factors reflecting the increase in mercury concentration between trophic levels 3 and 4 range from 1.2 to 15.1; the mean is close to 5.0. Interpretation of predator-prey factors is complicated by the fact that piscivorous fish accumulate mercury throughout their lifetime; thus, calculation of this value for a given species and system depends to a large extent upon the age of the

fish sampled. In addition, it is well known that the diet of a piscivorous fish changes with age, tending in many cases to be dominated by invertebrates until fish reach a critical size that allows them to prey efficiently upon small fish. In general, therefore, the mercury concentration in prey of a piscivorous fish can be expected to increase with the age or size of the predator. Additional considerations, including sexual reproduction, prey selection and availability and seasonal changes in bioenergetics due to changes in water temperature are also likely to be important determinants of bioaccumulation.

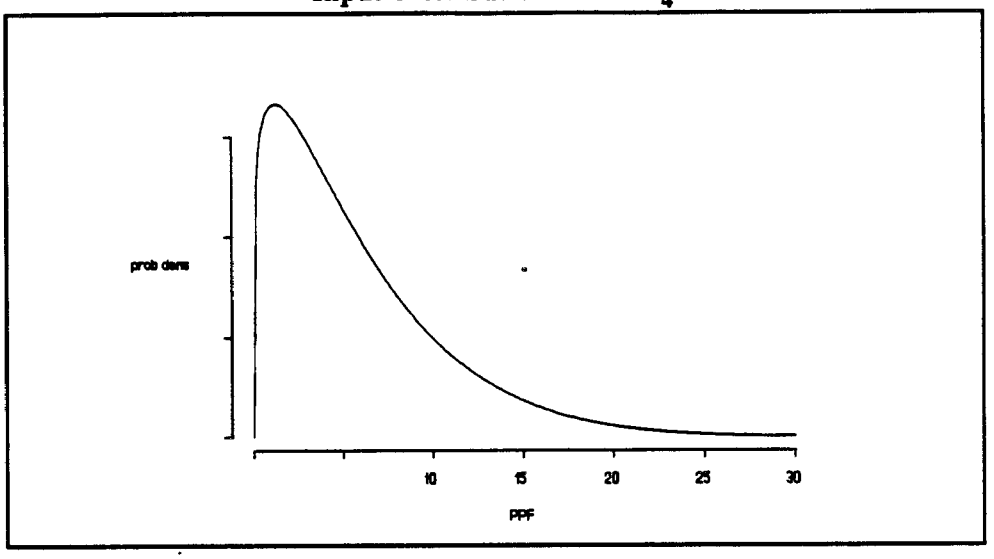
Overall, it can be shown that for many, if not most, piscivorous fish, mercury concentrations increase in a nearly linear fashion with age. For a given system, therefore, it may be possible to extrapolate data for small predators to larger members of the same species. Furthermore, the statistical distribution of BAFs determined from a random sampling of a population of predators would be expected to reflect the relative abundance of the different size classes and would have an upper limit reflecting the fact that fish have finite life spans.

The values defining the empirical distribution for PPF_4 are given in Table A-3. Five of the twelve studies permitted a calculation of both low and high values; the high values pertain to older fish. Both the low and high values from these studies were included in the analysis along with average values reported in the other seven studies. The PPF, being a ratio of two positive values, cannot be lower than 0. The distribution was truncated at the practical minimum of 1 because fish do not appear to be capable of eliminating mercury at any appreciable rate. The probability density function for this distribution is shown in Figure A-5. The beta function was chosen because the distribution is bounded at the lower end, and the general shape of the distribution matches that of the empirical distribution more closely than a lognormal form does. The upper limit of 54 was not predetermined but is a result of preserving the empirically-determined percentiles of the maximum observed values (15.1-15.5 at the 91st percentile) in the closed-form (beta) representation.

Table A-3
Predator-Prey Factor for Trophic Level 4

Value	Reference
2.25	Sorenson et al., 1990
2.5	Parks, 1988
3.1	Wren and MacCrimmon, 1986
2.7, 15.1	Skurdal et al., 1985
2.2, 11	Mathers and Johansen, 1985
2.4, 12.3	MacCrimmon et al., 1983
1.2, 8.4	Wren et al., 1983
5.4	Suchanek et al., 1993
6.3	Cope et al., 1990
6.8	Lindqvist, 1991
7.4	Meili et al., 1991
4.5, 15.5	Jackson, 1991

Figure A-5
Input Distribution for PPF_4



Bioconcentration Factor for Inorganic Mercury in Fish

Variable: BCF_{IHg}
Definition: Total mercury concentration in fish divided by that in water following a waterborne exposure to inorganic mercury.
Units: Unitless

Technical Basis:

Snarski and Olson (1982) reported a BCF of 4994 for fathead minnows exposed to mercuric chloride for 287 days.

A BCF of 1800 was measured in rainbow trout fry exposed to mercuric chloride for 60 days (Boudou and Ribeyre, 1984).

Ribeyre and Boudou (1984) obtained a BCF of 7000 in rainbow trout exposed to mercuric chloride for 30 days.

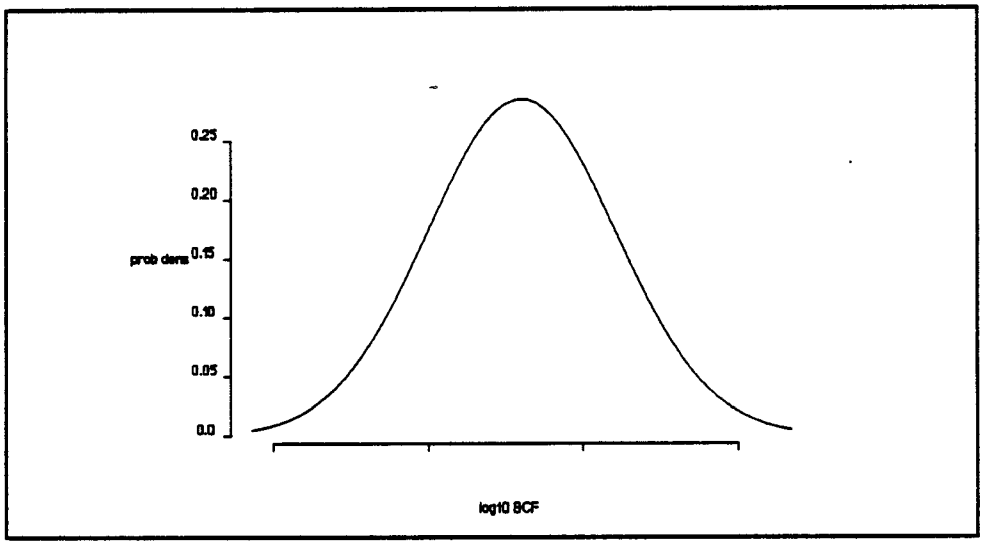
Summary:

Laboratory exposures (water-only) conducted using small fish yielded values ranging from 1,800 to 7,000. The BCF used to support BAF development in the GLWQI was based on two of the three values listed above (Snarski and Olson (1982) and Boudou and Ribeyre (1984)). Importantly, the data collected in these studies did not permit an evaluation of progress to chemical steady-state. It is possible, therefore, that if exposure times were extended the fish would have continued to accumulate mercury, thereby resulting in higher BCF values. In addition, exposures conducted with fast-growing fish have the potential to yield concentration estimates that are lower than those which would have been observed in fish that were not growing, due to the effect of growth dilution. The values defining the empirical distribution for BCF_{IHg} are given in Table A-4. These values are assumed to be distributed in log space and are assigned a lognormal distribution. The probability density function for this distribution is shown in Figure A-6.

Table A-4
Bioconcentration Factor for Inorganic Mercury in Fish

Value	Reference
1,800	Boudou and Ribeyre, 1984
4,994	Snarski and Olson, 1982
7,000	Ribeyre and Boudou, 1984

Figure A-6.
Input Distribution for BCF_{IHg}



Bioconcentration Factor for Methylmercury in Fish

Variable: BCF_{MHg}
Definition: Total mercury concentration in fish divided by that in water following a waterborne exposure to methylmercury.
Units: Unitless

Technical Basis:

BCFs ranging from 44,130 to 84,670 were reported by Olson et al. (1975) in fathead minnows exposed to methyl mercuric chloride for 336 days. Interestingly, BCF values appeared to vary inversely with test concentration.

McKim et al. (1976) obtained BCFs ranging from 10,000 to 33,333 in brook trout exposed to methyl mercuric chloride for 273 days. Methylmercury concentrations in muscle were essentially the same as those in whole body and were directly proportional to water concentration. A kinetic analysis showed that although mercury concentration in tissues tended toward a "steady-state" value, the total amount in tissues continued to increase. Progress to "steady-state", therefore, reflected growth dilution

more than an actual decline in uptake. In fact, uptake remained constant or increased throughout the exposures.

Ribeyre and Boudou (1984) reported a BCF of 36,000 in rainbow trout exposed to methyl mercuric chloride for 30 days. A somewhat lower BCF of 11,000 was reported by Boudou and Ribeyre in rainbow trout fry exposed for 60 days, possibly due to growth dilution in the smaller, faster growing fish.

A BCF of 85,700 was reported for rainbow trout exposed for 75 days (Niimi and Lowe-Jinde, 1984).

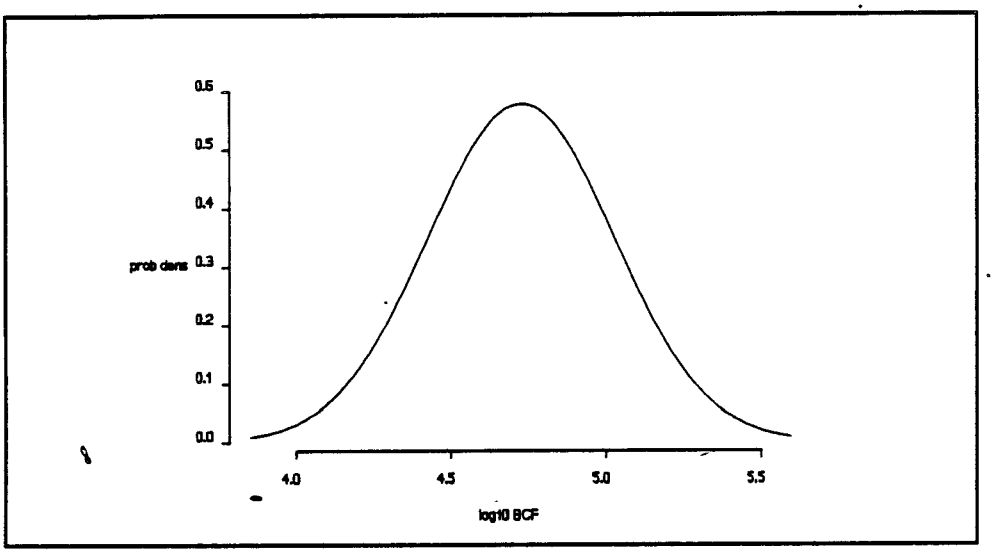
Summary:

BCF values reported in the literature range from 11,000 to approximately 86,000. It has been argued that because the BCF appears to vary inversely with water concentration, priority should be given in each study to the BCF calculated for the lowest level tested. This is reasonable, since, in general, laboratory exposure concentrations tend to be higher than those measured in the environment. For this reason, it has also been suggested that a regression equation be applied to extrapolate to an "environmentally relevant" value. Existing data are not sufficient, however, to support such an extrapolation due both to a lack of data and to differences in exposure duration, species, etc. There is also a question as to whether chemical steady-state conditions ever occurs in fish exposed in a laboratory setting. Data collected from the two studies of longest duration (McKim et al. (1976) and Olson et al. (1975)) suggest that the appearance of a constant concentration during the latter phase of each study was due to growth dilution and not to a steady-state condition. The values defining the empirical distribution for BCF_{MHg} are given in Table A-5. These values were assumed to be distributed in log space and are assigned a lognormal distribution. The probability density function for this distribution is shown in Figure A-7.

Table A-5
Bioconcentration Factor for Methylmercury in Fish

Value	Reference
11,000	Boudou and Ribeyre, 1984
33,333	McKim et al., 1976
36,000	Ribeyre and Boudou, 1984
84,670	Olson et al., 1975
85,700	Niimi and Lowe-Jinde, 1984

Figure A-7
Input Distribution for BCF_{MHg}



Geometric Increase in Food Chain Multiplier

A geometric increase in the food chain multiplier occurs when the predator-prey factors at each trophic level are approximately equal. This assumption was part of the original set of assumptions made to calculate a BAF for mercury in the GLWQI (U.S. EPA, 1993), but was later dropped in favor of incorporating measured PPFs (U.S. EPA, 1995). An attempt was made to evaluate the validity of this assumption on the basis of existing literature.

Technical Basis:

Lindqvist (1991) reported that mercury concentrations in pike (trophic level 4) were 6.8 times those in perch (trophic level 3) and 25 times those in zooplankton (trophic level 2). Predator-prey factors of 6.8 for trophic level 4 and 3.7 for trophic level 3 were calculated from this study.

Data presented by Jackson (1991) suggested that methylmercury concentrations in walleye and pike were about 5.2 times those of shiners, while total mercury concentrations in shiners were about twice those of zooplankton.

Data published by Watras and Bloom (1992) suggested that the PPF between trophic levels 1 and 2 was approximately two, while total mercury concentrations in age-1 yellow perch were only slightly higher (approximately 1.25 times) than those in zooplankton.

Total mercury data from Clear Lake, CA (Suchanek et al., 1993) suggested that the PPF for trophic level 4 (largemouth bass) was 5.4, while that for trophic level 3 (silversides) was about 3.6. In contrast, residue concentrations in zooplankton (trophic level 2) were similar to or perhaps even slightly lower than those in phytoplankton (trophic level 1) suggesting a PPF for trophic level 2 of approximately 1.0. A separate analysis of methylmercury residues suggested that PPFs increased from about 2.2 between trophic levels 1 and 2, to about 20 between trophic levels 3 and 4. This resulted in an exponential increase in the food chain multiplier and was apparently due to differences in the percentage of total mercury existing as methylmercury at each trophic level. In general, the percentage

of total mercury existing as methylmercury increased with trophic level, ranging from about 50% at trophic level 1, to 100% at trophic levels 3 and 4.

PPFs reported by Parsons and Bigham (1994) declined with successively higher trophic level; the PPF between trophic levels 1 and 2 was approximately 8.0, that between trophic levels 2 and 3 was approximately 5.8, while that between trophic levels 3 and 4 was about 1.8.

Summary:

The few data that can be used to evaluate this assumption do not support a scientific consensus. In some systems the PPF for both total and methylmercury appears to increase with trophic level (eg., Lindqvist, 1991; Jackson, 1991; Suchanek et al., 1993), while in others the PPF tends to decrease (Watras and Bloom, 1992; Parsons and Bigham, 1994).

Each of the studies examined supports the conclusion that mercury is biomagnified in aquatic food chains. There is considerable uncertainty, however, concerning the extent to which this occurs, particularly at the lower trophic levels. This uncertainty has a large potential to impact subsequent calculation of BAFs due to the multiplicative manner in which PPFs are used.

A.3.2.3 Results of Monte Carlo Analysis of GLWQI Methodology

The distribution for BAF_3 generated from the Monte Carlo simulation of the GLWQI methodology is shown in Figure A-8, with selected statistics given in Table A-6. The direct output of the distribution is given as the log (base 10) of the statistic because the distribution is based on the logarithms of the original observations. The quantities in the 'Value' column are the antilogs of the distribution output.

Figure A-8
Distribution of BAF_3 Values from the Monte Carlo Simulation of the GLWQI Methodology

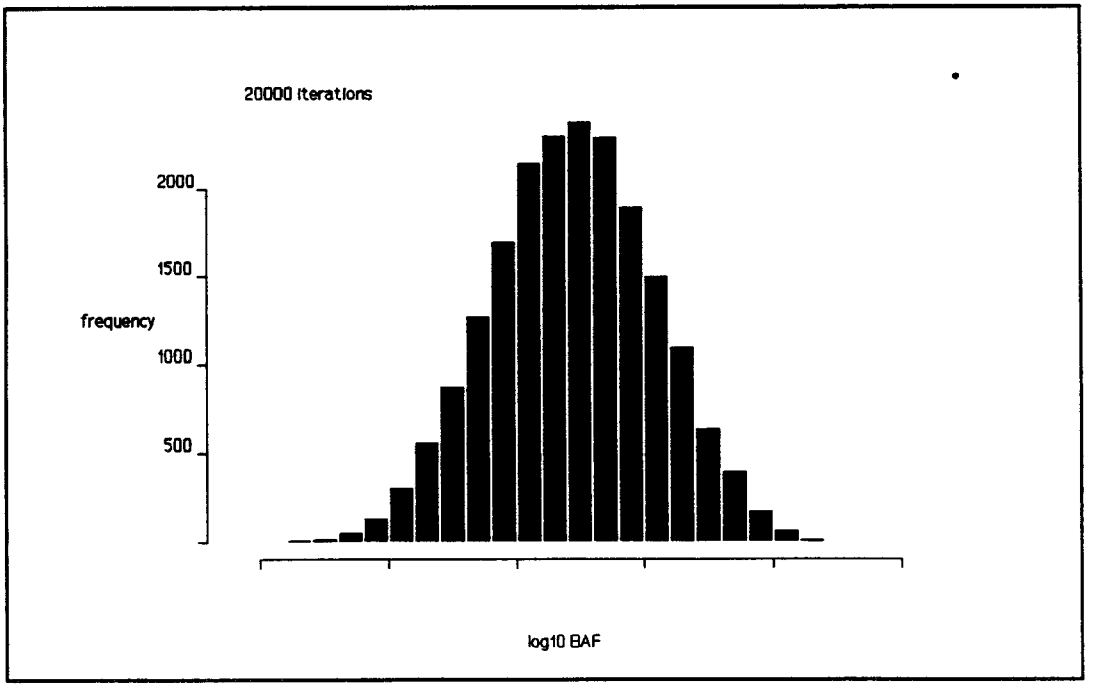


Table A-6
Statistics for BAF_3 Calculated Using the GLWQI Methodology

Statistic	Value (log10)	Value
Mean	4.437	27,360 (GM)
Standard Deviation	0.644	4.41 (GSD)
Percentiles:		
5th	3.363	2,307
25th	4.000	10,040
50th	4.446	27,930
75th	4.879	75,750
95th	5.488	307,530

GM = geometric mean; GSD = geometric standard deviation

The distribution for BAF_4 generated from the GLWQI methodology is shown in Figure A-9, with selected statistics given in Table A-7. The direct output of the distribution is given as the log (base 10) of the statistic as the distribution is based on the logarithms of the original observations. The quantities in the 'Value' column are the antilogs of the distribution output.

Figure A-9
Distribution of BAF_4 Values from the Monte Carlo Simulation of the GLWQI Methodology

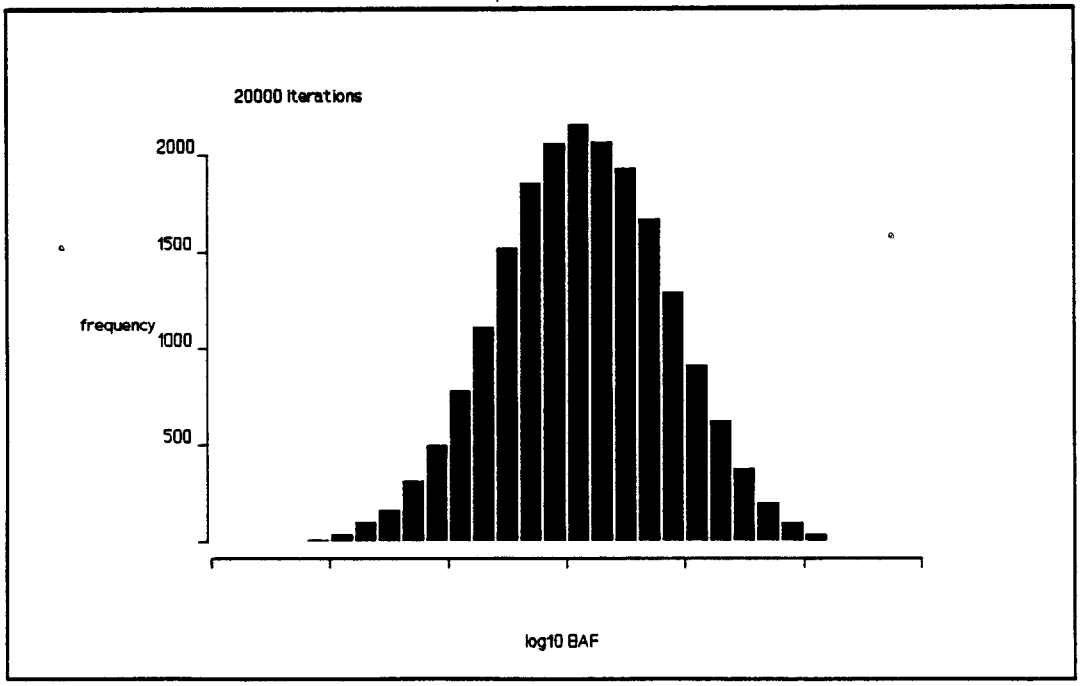


Table A-7
Statistics for BAF_4 from the GLI Approach

Statistic	Value (log10)	Value
Mean	5.134	136,070 (GM)
Standard Deviation	0.720	5.25 (GSD)
Percentiles:		
5th	3.942	8,757
25th	4.647	44,330
50th	5.135	136,540
75th	5.635	431,750
95th	6.316	2,069,200

GM = geometric mean; GSD = geometric standard deviation

A.3.3 Estimation of a BAF_4 for Mercury Using Measured Values for Trophic Level 3 and a Field-Derived Food Chain Multiplier

In this analysis a BAF for trophic level 4 was calculated using a BAF value derived from field data for trophic level 3 and published predator-prey factors for trophic level 4. The distribution of BAFs for trophic level 3 is presented with the data from which it was derived. The distribution of predator-prey factors for trophic level 4 was defined previously in Section A.3.2.2. In contrast to the GLWQI methodology, the simplifying assumption was made that 100% of total mercury in fish exists as methylmercury. This decision was based upon a review of published (see Section A.3.2.2) and unpublished data (Bloom, 1994). Here, as is the case throughout the document, BAF_3 and BAF_4 refer to the concentrations of methylmercury in fish divided by the concentration of total mercury in filtered water.

A.3.3.1 Bioaccumulation Factors Determined From Field Data - Total Mercury in Forage Fish

Variable: BAF_3
Definition: Methylmercury in forage fish (trophic level 3) divided by total mercury in filtered water, accumulated by all possible routes of exposure.
Units: Unitless.

Technical Basis:

BAF_3s ranging from 25,000 to 68,000 were reported by Glass et al. (1993) for yellow perch ranging in size from 3.8 to 10.5 cm. Data were obtained from 215 individuals collected from Crane and Sand Point Lakes (MN) and were averaged across season and site. BAF_3s ranging from 1,400 to 35,000 were measured in a variety of forage fish collected from the St. Louis River estuary. These data were not included in the analysis, however, because high mercury levels in the estuary (due to an emissions point source) were thought to result in anomalously low BAF_3 estimates.

Watras and Bloom (1992) reported BAF_3s for year-1 yellow perch ranging from approximately 63,000 to 250,000. The fish were collected from Little Rock Lake (WI), which has been the subject

of investigations concerning the effects of experimental acidification. The lower figure corresponds to perch collected from the reference basin (pH of 6.1), while the higher value is for fish collected from the acidified basin (pH of 4.7). Most fish will not survive if pH is reduced to a value much less than that of the acidified basin of Little Rock Lake. Lakes approaching this value, and which contain viable populations of perch and other fish, are common in areas that are impacted by acid precipitation, including large portions of the upper midwest and northeast. Such fish populations are likely to contribute substantially to the diet of piscivorous wildlife living in these areas. The entire range of values reported in this study is, therefore, relevant to the present analysis.

Yellow perch (5 to 10 g) collected from 25 lakes in Sweden were shown to have BAF_3s ranging from 17,000 to about 65,000 (mean 40,400; Mieli et al., 1991). These estimates were obtained by dividing minimum and maximum residue values by the mean water value. Water samples, however, do not appear to have been filtered before analysis. The total mercury value for water, therefore, includes an unknown quantity of mercury adsorbed to particulate matter. If the samples had been filtered, it is likely that total mercury concentrations in water would have declined, resulting in correspondingly higher BAF_3 values.

Parsons and Bigham (1994) reported BAF_3s of approximately 28,300, 31,500, and 178,000 for bluegill, gizzard shad and white perch collected from Onondaga Lake (NY). It can be argued that large white perch occupy a trophic position intermediate to levels 3 and 4. Unfortunately, the sizes of the fish sampled were not given. Lacking this information, it was assumed that the animals from which these values were derived represent the complete range of reported year classes (bluegill and shad - 0 to 5 years; white perch - 0 to 7 years). The extent of the error introduced by including both large and small individuals is, therefore, assumed to be small.

BAF_3s determined for silversides from Clear Lake (CA) ranged from 83,000 to 483,000 (mean of 208,400; Suchanek et al., 1993). Silversides are almost entirely planktivorous and form the forage base for the piscivores (e.g., largemouth bass) in this system.

Summary:

Because of recent advances in analytical techniques for measurement of mercury in natural waters, consideration was given only to those values reported since 1990. BAFs calculated in earlier literature tend to be lower due to higher reported water concentrations; see for example, Parks (1988). BAFs for forage fish (trophic level 3) ranged from 10,000 to nearly 500,000. This range brackets the BAF_3 derived for the GLWQI (27,900; U.S. EPA, 1995), although in three out of five systems the GLWQI estimate appears to be low.

In defining the distribution, the log transformations of the data points were used because the untransformed data are highly skewed to the right, and the underlying physical and biological processes are more likely to be multiplicative than additive. The values defining the empirical distribution for BAF_3 are given in Table A-8 and are the limits of the ranges given under Technical Basis above. These values are assumed to be distributed in log space and are assigned a lognormal distribution. The probability density function for BAF_3 derived from field data is shown in Figure A-10, with selected statistics given in Table A-9. The direct output of the distribution is given as the log (base 10) of the statistic as the distribution is based on the logarithms of the original observations. The quantities in the 'Value' column are the antilogs of the distribution output.

Table A-8
Bioaccumulation Factor for Methylmercury in Trophic Level 3 Fish

Values	Reference
25,000; 68,000	Glass et al., 1993
63,000; 250,000	Watras and Bloom, 1992
17,000; 65,000	Mieli et al., 1991
28,300; 178,000	Parsons and Bigham, 1994
83,000; 483,000	Suchanek et al., 1993

Figure A-10
Distribution of Field-derived BAF_3 Values

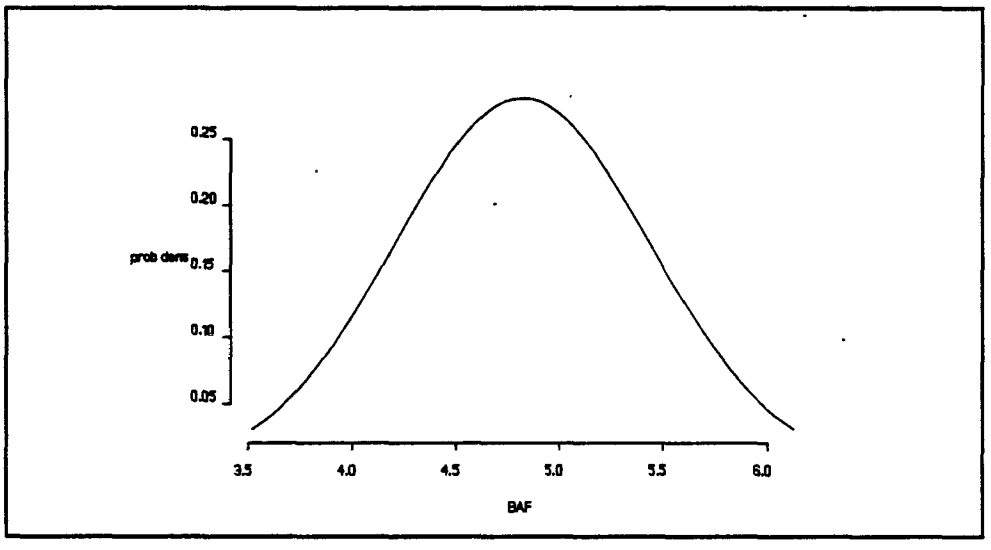


Table A-9
Statistics for Field-derived BAF_3

Statistic	Value (log10)	Value
Mean	4.820	66,170 (GM)
Standard Deviation	0.617	4.14 (GSD)
Percentiles:		
5th	3.806	6,400
25th	4.405	25,390
50th	4.820	66,170
75th	5.237	172,400
95th	5.835	684,000

GM = geometric mean; GSD = geometric standard deviation

A.3.3.2 Results of Monte Carlo Analysis Using Field-derived BAF_3 and PPF_4 Estimates

The formula for the calculation of BAF_4 by this method is given in equation 4.

$$BAF_4 = BAF_3 \times PPF_4 \quad (4)$$

where

BAF_3 is the field-derived distribution for the BAF at trophic level 3
PPF_4 is the predator-prey factor at trophic level 4 representing the biomagnification of mercury in piscivorous fish feeding on forage fish

The distribution of BAFs calculated by Monte Carlo simulation using field-derived BAF_3 values and PPF_4 estimates is shown in Figure A-11. Table A-10 shows selected statistics from this distribution. Results are expressed both as the logarithms (base 10) of the value and the BAF value itself.

Figure A-11
Distribution of BAF_4 Values Output from the Monte Carlo Simulation of the Product of BAF_3 and PPF_4

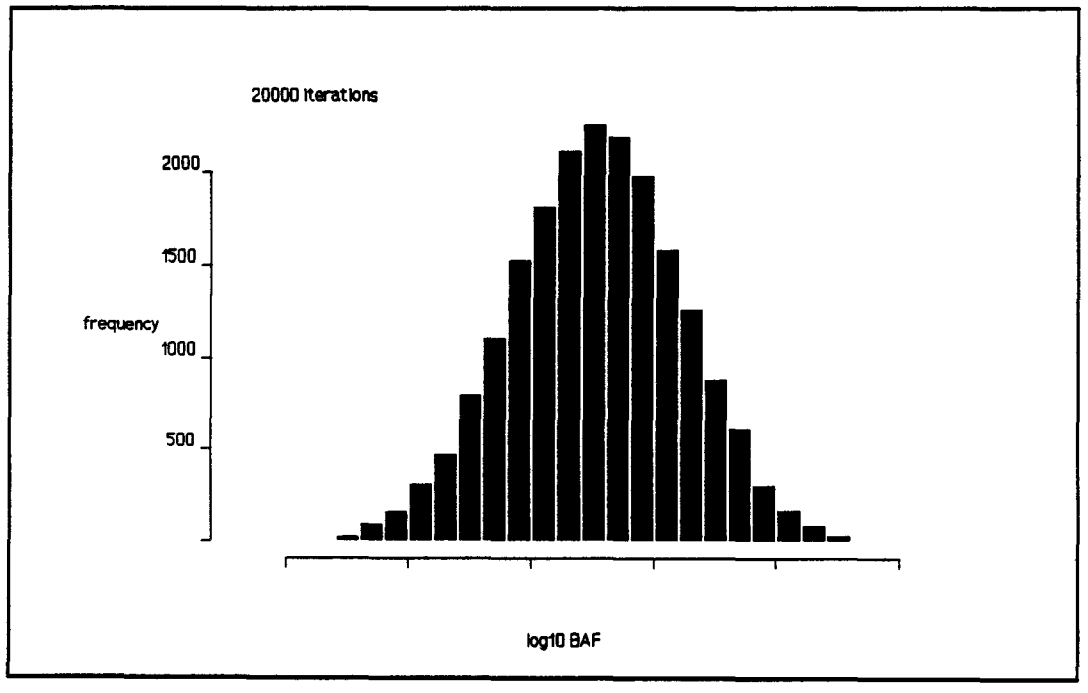


Table A-10
Statistics for BAF_4 based on BAF_3 and PPF_4

Statistic	Value (log10)	Value
Mean	5.525	335,000 (GM)
Standard Deviation	0.703	5.053 (GSD)
Percentiles:		
5th	4.356	22,700
25th	5.046	111,000
50th	5.526	336,000
75th	6.001	1,000,000
95th	6.672	4,700,000

GM = geometric mean; GSD = geometric standard deviation

A.3.4 Specification of a Distribution for BAF_4 Directly from Field Data

A.3.4.1 Bioaccumulation Factors Determined From Field Data - Total Mercury in Piscivorous Fish

Variable: BAF_4
Definition: Methylmercury in piscivorous fish (trophic level 4) divided by that in water, accumulated by all possible routes of exposure.
Units: Unitless.

Technical Basis:

Mercury concentrations in standardized (1 kg) northern pike collected from 25 lakes in Sweden were reported by Meili et al. (1991). These data were divided by the mean concentration of total mercury in water to obtain BAF_4s ranging from 128,000 to approximately 425,500 (mean of 297,900). As noted in the discussion of BAF_3 values, water samples analyzed for these calculations do not appear to have been filtered. BAF_4s calculated on a dissolved total mercury basis are, therefore, likely to be higher.

BAF_4s reported by Suchanek et al. (1993) for largemouth bass ranged from 440,000 to nearly 2,900,000 (mean of 1,161,000). The ages of the bass analyzed were not given; however, their weights were listed (ranging from 340 g to 4.44 kg) and suggest that a broad range of year classes was represented.

Mercury residues were computed by Sorenson et al. (1990) for 65 standardized (1 kg) pike collected from lakes located throughout northern Minnesota. Dividing by the average mercury level in water from these study sites yielded BAF_4s ranging from 56,700 to 615,400 (mean of 178,100).

BAF_4s of 123,900 and 249,300 were reported by Parsons and Bigham (1994) for smallmouth bass and walleye from Onondaga Lake (NY). These estimates were obtained from adult fish representing a broad range of age classes (walleye - 4 to 10, bass - 4 to 11). Ranges for individual species were not given.

Summary:

BAFs for piscivorous fish (trophic level 4) range from 130,000 to nearly 3,000,000 and, thus, bracket the BAF_4 derived for the GLWQI (140,000; U.S. EPA, 1995); in three out of four systems the GLWQI estimate appears to be low.

Even though data for trophic level 4 are few, support for these numbers is provided by combining observations for trophic level 3 and the PPF for trophic level 4. Thus, taking 70,000 as an estimate for tropic level 3 and multiplying by a PPF_4 of 5.0 yields an estimated BAF for trophic level 4 of 350,000.

Additional support for BAFs in this range is provided by measured BAFs for methylmercury in fish and water. For example, Jackson (1991) reported methylmercury BAFs ranging from 3,000,000 to greater than 9,000,000 in walleye from northern Manitoba. Similarly, Parsons and Bigham (1994) reported a BAF for methylmercury in walleye of approximately 5,500,000. Dividing these values by 20 (a reasonable figure if about 5% of total mercury in water is assumed to be methylated) yields BAFs ranging from 150,000 to 450,000.

The values defining the empirical distribution for BAF_4 are given in Table A-11 and are the limits of the ranges given under Technical Basis above. These values are assumed to be distributed in log space and are assigned a lognormal distribution. The probability density function for this distribution is shown in Figure A-12. Statistics and percentiles derived from this distribution are given in Table A-12. Results are expressed both as the logarithms (base 10) of the value and the BAF value itself.

Table A-11
Bioaccumulation Factors for Methylmercury in Trophic Level 4 Fish

Value	Reference
128,000; 425,000	Meili et al., 1991
123,900; 249,300	Parsons and Bigham, 1994
56,700; 615,400	Sorenson et al., 1990
440,000; 2,900,000	Suchanek et al., 1993

Figure A-12
Distribution of Field-Derived BAF_4 Values

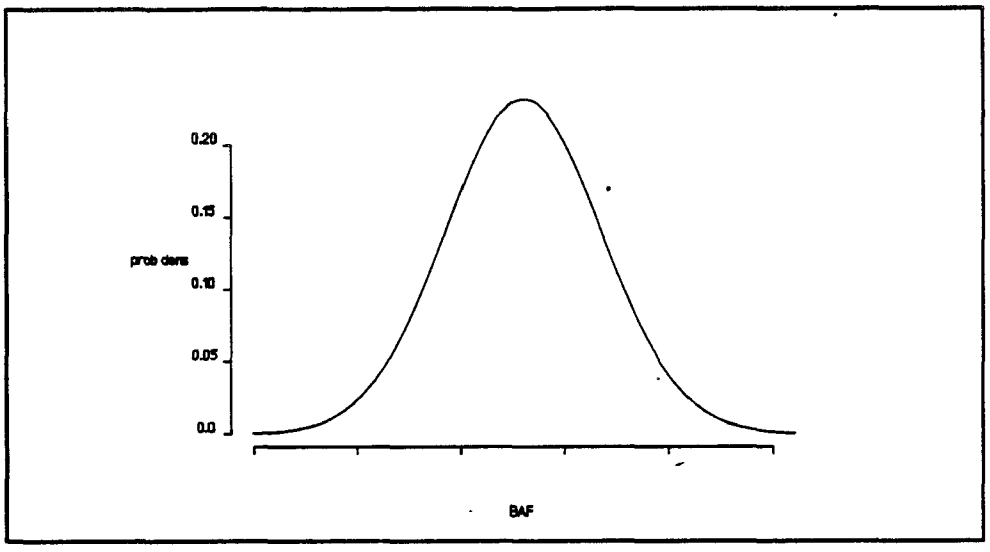


Table A-12
Statistics for Field-Derived BAF_4

Statistic	Value (log10)	Value
Mean	5.602	400,000 (GM)
Standard Deviation	0.747	5.585 (GSD)
Percentiles:		
5th	4.374	23,600
25th	5.099	125,000
50th	5.602	400,000
75th	6.106	1,280,000
95th	6.831	6,780,000

GM = geometric mean; GSD = geometric standard deviation

A.3.5 Selection of Bioaccumulation Factors for Trophic Levels 3 and 4

Bioaccumulation factors calculated using each of the three previously described methods are given in Table A-13. Field data for trophic levels 3 and 4 yield mean BAF_4 estimates that differ by less than 20%, while methods employed in the GLWQI yield a mean BAF_4 value that is between one-half and one-third of those derived from field data. No attempt was made to estimate a BAF for trophic level 3 from field data for trophic level 4.

It should be noted that throughout this discussion most of the BAF estimates reported to date originate from studies of similar types of freshwater systems; that is, those that are at risk due to acid deposition and that, by virtue of average temperature, etc., support similar fish assemblages (typically northern pike, walleye, yellow perch, spottail shiners). This has the potential for two problems of interpretation.

1) Because data from the reported systems tend to be similar, relationships could be overlooked that would be important under a different set of circumstances.

2) The relative abundance of these data introduce a regional bias into any type of analysis that is intended for nationwide application.

In this regard, data from Suchanek et al. (1993) are notable because they suggest that in Clear Lake (CA), BAFs for trophic levels 3 and 4 are considerably higher than those reported by other authors for yellow perch, walleye, and northern pike. Clear Lake is warm, highly eutrophic and receives considerable agricultural runoff from nearby orchards and vineyards. Lacking any corroborating information, it is not possible to determine how representative the Clear Lake data are of warm water systems generally. Clearly, however, there is a need for additional residue data collected from a broader spectrum of freshwater systems.

Table A-13
Summary of Bioaccumulation Factors for Trophic Levels 3 and 4
(mean, 5% and 95% values)

Trophic Level	BAF_3		BAF_4		
Recommended	66,200		335,000		
Method	Field-derived	GLWQI	BAF_3 x PPF_4	Field-derived	GLWQI
Mean	66,200	25,200	335,000	400,000	136,000
5^{th} pctl	6,400	2,310	22,700	23,600	8,760
95^{th} pctl	684,000	308,000	4,700,000	6,780,000	2,070,000

In the Proposed Guidance to the GLWQI it is stated that field-derived BAFs should take precedence over values estimated using laboratory data, when such data are deemed to be sufficient (U.S. EPA, 1993; p. 20859). Based upon a review of the foregoing analyses, it was judged that BAFs calculated from existing field data are more accurate and reflect better the true level of natural variability than BAFs calculated using the GLWQI methodology. Specifically, the recommendation that field data for trophic levels 3 and 4 (ie., the BAF_3 x PPF_4 method) be used to estimate BAFs for fish was based on the following considerations. The GLWQI method involves several variables and is dependent upon a number of assumptions, some of which are poorly supported. The direct application of field data to the estimation of BAF_4 yields a value similar to the BAF_3 x PPF_4 method, but it results in wide variability about the mean, due to the small number of measured values, one of which (Suchanek et al., 1993) appears as a relative outlier. The BAF_3 x PPF_4 approach results in an intermediate degree of variability about the mean BAF_4 estimate, and the inclusion of PPF_4 allows for a better representation of fish size (age) distribution.

The mean BAF values estimated using the BAF_3 x PPF_4 method were, therefore, recommended in this Report for subsequent calculation of a WC for mercury (Volume V) and for an evaluation of human exposure due to consumption of contaminated fish (Volume III). These BAFs are the following.

For trophic level 3, the BAF for mercury was estimated to be 66,200 L/kg.

For trophic level 4, the BAF for mercury was estimated to be 335,000 L/kg.

A.3.6 Sensitivity Analysis

Sensitivity analyses examining the effect of changes in assumptions have been conducted. Three factors have been varied in this analysis: (1) dependency of one input variable on another; (2) distributional assumptions for BAF_3; and (3) disaggregation of PPF_4.

A.3.6.1 Sensitivity of Output to Correlation of Input Variables (Dependency of on Variable on Another Variable)

Sensitivity analyses of the dependence of the variance (spread) of BAF_4 have been performed with varying assumptions about the correlations between input variables. Both BAF_3 and PPF_4 depend on the concentration of methylmercury in trophic level 3 fish ($[MeHg_3]$). The BAF_3 is directly proportional to $[MeHg_3]$, and PPF_4 is inversely proportional to $[MeHg_3]$. The equation for BAF_4, which is the product of BAF_3 and PPF_4, thus, has the same term in the numerator and denominator, the variance or which will be counted twice. As a result, the apparent variance of the BAF_4 simulation will be inflated unless the correlation is taken into account. This can be accomplished by inversely correlating BAF_3 and PPF_4 in the Monte Carlo simulation. The magnitude of the correlation depends on the data overlap (defining each variable) and the extent of the contribution of $[MeHg_3]$ to the overall variance of each variable (BAF_3 and PPF_4). BAF_3 and PPF_4 are based on the same data for 3 out of 9 and 2 out of 17 data points, respectively (Meili et al., 1991, and Suchanek et al., 1993 studies). Assuming that the two implicit variables in each of BAF_3 and PPF_4 contribute equally to the variance, and that each data point contributes equally to the variance of the simulated distribution, the overall correlation is unlikely to be greater (more negative) than -0.25, and very likely to be less. The standard simulation assumed no correlation.

Table A-14 shows the effect of different correlation assumptions on the spread of the BAF_4 distribution and on the relative contributions of each variable to the overall variance. The results of the simulations show that a moderately strong correlation (50%) between BAF_3 and PPF_4 would have a significant effect on the spread of the output, reducing it by a factor of 3.6. If the correlation were weaker (10%), the spread of the distribution would be reduced by only 30%.

Table A-14
Sensitivity of BAF_4 Estimate to Correlation of Input Variables

Correlation	5^{th}	95^{th}	$\log_{10}$ span	Contribution to variance	
				BAF_3	PPF_4
none	22,700	4,700,000	2.32	64%	36%
-0.1	25,800	4,210,000	2.21	67%	33%
-0.25	30,500	3,430,000	2.05	74%	26%
-0.5	42,300	2,570,000	1.78	94%	6%

A.3.6.2 Simulation of BAF_4 With Disaggregated PPF_4 Distributions

Alternate PPF_4 distributions were constructed from restricted ranges of the data to represent specific fish size (age) distributions. The distribution definitions are the following:

Name: mid predator-prey factor for trophic level 4
Label: PPF_{4M}
Form: Uniform {min = 2.5, max = 7.5}
Basis: Standardized pike/yellow perch ratios; n = 4
Description: PPF_{4M} is based on four data points representing two- to four-year-old pike. This distribution is meant to represent a more homogeneous sample of average size trophic level 4 fish. The form of the distribution reflects the lack of information pertaining to the estimation of the relative probability of any given value in this range. The median of the distribution corresponds to the median of the four data points. The tails were unweighted.

Name: low predator-prey factor for trophic level 4
Label: PPF_{4L}
Form: Uniform {min = 1, max = 4}
Basis: Lowest six values for PPF_4
Description: PPF_{4L} is based on the smallest values for PPF_4 representing smaller tier 4 fish. The rationale is the same as for PPF_{4M}.

Name: high predator-prey factor for trophic level 4
Label: PPF_{4H}
Form: Uniform {min = 11, max = 17}
Basis: Highest four values for PPF_4
Description: PPF_{4H} is based on the values reported for older (larger) tier 4 fish for PPF_4. The rationale is the same as for PPF_{4M}.

Table A-15 shows the results of BAF_4 Monte Carlo simulations with alternate PPF_4 distributions. These simulations represent scenarios in which the consumption patterns of the final consumer can be more narrowly defined in terms of fish size. No correlation between BAF_3 and each of the alternate PPF_4s was assumed for these simulations. The corresponding percentile of the standard BAF_3 output distribution is given for the median values of the alternate scenarios.

Table A-15
BAF_4 Simulations with Alternate PPF_4 Distributions

Distribution	Percentiles		
	5th	50th	95th
low PPF_4	13,460	151,500 (31st)	1,590,000
mid PPF_4	27,790	308,100 (48th)	3,297,000
high PPF_4	85,160	904,800 (73rd)	9,106,000

A.3.7 Interpretation and Discussion of Sensitivity Analysis

The BAF_4 output distribution attempted to simulate the selection of a random tier 4 fish from a random lake in a random location. It is meant to be used to estimate the concentration of methylmercury in such a randomly-selected fish when multiplied by the total mercury (inorganic and organic combined) concentration in filtered water. The BAF_3 performs the same function for trophic level 3 fish. Because of the large variance in the distributions, and due to lack of a distinction between variability and uncertainty, the recommendation was to apply the mean values from each distribution in the appropriate situations.

Except as discussed below, there were no distinctions, for either distribution, as to size of fish, lake trophic status, lake pH, absolute mercury concentrations (in fish or water) or relative methylmercury concentrations in the water column. The data, however, are heavily biased towards northern oligotrophic lakes and somewhat towards smaller (younger) fish. There was also no distinction made between variability and uncertainty in the BAF_3 and BAF_4 distributions. Thus, it cannot be determined where natural variability stops and uncertainty starts; the percentiles of the distribution cannot be interpreted as the likelihood of the true mean value. The bounding distributions are meant to give a rough idea of uncertainty in the mean itself but are hypothetical in part. The actual distribution of the mean is unknown. The bounding distributions do have potential significance in real-world scenarios, however. The mid and high PPF_4 distributions, for example, represent estimates of PPF_4 for standardized two- to four-year-old and older tier 4 fish (eg., large pike), respectively. These estimates could be applied in situations where the size of the consumed fish is known to be at one end of the distribution; for example with recreational anglers, who tend to catch larger individuals within a given population.

The large amount of variability evidenced by the data and reflected in the output distributions arises from several identifiable but, as yet, unquantified sources. A primary source of variability in both BAF_3 and PPF_4 is the dependence of methylmercury bioaccumulation on the age of the fish. For example, it has been repeatedly shown that mercury in fish accumulates throughout the lifetime of the individual (Scott and Armstrong, 1972; MacCrimmon et al., 1983; Wren et al., 1983; Mathers and Johansen, 1985; Skurdal et al., 1985, Wren and MacCrimmon, 1986; Sorenson et al., 1990; Jackson, 1991; Gutenmann et al., 1992; Glass et al., 1993, Suchanek et al., 1993; Lange et al., 1993). Reported BAF values for a given species may, therefore, vary as a function of the ages of the animals examined. As a result, some researchers have suggested that comparisons between lakes should be made using "standardized" fish values (for example, a value for a hypothetical 1 kg northern pike), typically derived by linear regression of residue data collected from individuals of varying size and/or age (Wren and MacCrimmon, 1986; Sorenson et al., 1990; Meili et al., 1991).

Although the fish age factor is probably a major contributor to the variance of PPF_4, the influence of this factor on BAF_3 is probably much less. Because of the lesser sensitivity of BAF_4 to PPF_4 than to BAF_3, the total reduction in variability of the BAF_4 by accounting for fish age may not be large.

Perhaps the greatest source of variability is that of model uncertainty; that is, uncertainty introduced by failure of the model to account for significant real-world processes. The simple linear BAF model relating methylmercury in fish to total mercury in water masks a number of nonlinear processes leading to the formation of bioavailable methylmercury in the water column. Much of the variability in field data applicable to the estimation of mercury BAFs can be attributed to differences between aquatic systems. For example, in lake surveys conducted within a relatively restricted geographic region, large differences can exist between lakes with respect to mercury concentrations in a given species of fish (see for example Cope et al., 1990; Grieb et al., 1990; Sorenson et al., 1990; Jackson, 1991; Lange et al., 1993). These observations have led to the suggestion that much of this variability is due to differences in within-lake processes that determine the percentage of total mercury that exists as the methylated form. Limited data also suggest that within a given water body concentrations of methylmercury are likely to vary with depth and season. Unfortunately, while the concentration of methylmercury in fish flesh is presumably a function of these varying concentrations, published BAFs are generally estimated from a small number of measured water values, the representativeness of which is poorly known.

A.4 References

Baluja, G., L.M. Hernandez, J. Gonzalez and R. Clavero (1983). Mercury distribution in an ecosystem of the "Parque Nacional de Donana," Spain. *Bull. Environ. Contam. Toxicol.* 30:544-551.

Bloom, N.S (1992). On the chemical form of mercury in edible fish and marine invertebrate tissue. *Can. J. Fish. Aquat. Sci.* 49:1010-1017.

Bloom, N.S. (1994). Considerations in the Analysis of Water and Fish for Mercury. Presented at the National Forum on Mercury in Fish, New Orleans, LA, September 27, 1994.

Bloom, N.S. and S.W. Effler (1990). Seasonal variability in the mercury speciation of Onondaga Lake (New York). *Water Air Soil Pollu.* 53:251-265.

Boudou A. and F. Ribeyre (1984). Influence of exposure length on the direct bioaccumulation of two mercury compounds by *Salmo gairdneri* (fry) and the relationship between organism weight and mercury concentrations. *Water Res.* 18:81-86.

Cappon, C.J. (1984). Content and chemical form of mercury and selenium in Lake Ontario salmon and trout. *J. Great Lakes Res.* 10:429-434.

Cappon, C.J. and J.C. Smith (1981). Mercury and selenium content and chemical form in fish muscle. *Arch. Environ. Contam. Toxicol.* 10:305-319.

Cope, W.G., J.G. Wiener and R.G. Rada (1990). Mercury accumulation in yellow perch in Wisconsin seepage lakes: Relation to lake characteristics. *Environ. Toxicol. Chem.* 9:931-940.

Evans, M., N. Hastings and B. Peacock (1993). *Statistical Distributions.* 2nd Edition. John Wiley and Sons, Inc., New York, NY, pp. 42-44.

Gill, G.A. and K.W. Bruland (1990). Mercury speciation in surface freshwater systems in California and other areas. *Environ. Sci. Technol.* 24:1392-1400.

Glass, G.E., J.A. Sorensen, K.W. Schmidt, J.K. Huber and G.R. Rapp, Jr. (1993). Mercury sources and distribution in Minnesota's aquatic resources: Precipitation, surface water, sediments, plants, plankton, and fish. Final report to Minnesota Pollution Control Agency and Legislative Commission on Minnesota Resources, 1989-1991 (Contract Nos. 831479 and WQ/PDS020).

Grieb, T.M., C.T. Driscoll, S.P. Gloss, C.L. Schofield, G.L. Bowie and D.B. Porcella (1990). Factors affecting mercury accumulation in fish in the upper Michigan peninsula. *Environ. Toxicol. Chem.* 9:919-930.

Gutenmann, W.H., J.G. Ebel, Jr., H.T. Kuntz, K.S. Yourstone and D.J. Lisk (1992). Residues of p,p'-DDE and mercury in lake trout as a function of age. *Arch. Environ. Contam. Toxicol.* 22:452-455.

Hildebrand, S.G., R.H. Strand and J.W. Huckabee (1980). Mercury accumulation in fish and invertebrates of the North Fork Holston River, Virginia and Tennessee. *J. Environ. Qual.* 9:393- 400.

Huckabee, J.W., J.W. Elwood and S.G. Hildebrand (1979). Accumulation of mercury in freshwater biota. In: *The Biogeochemistry of Mercury in the Environment.* J.O. Nriagu (Ed.), Elsevier/North Holland Biomedical Press, Amsterdam, The Netherlands, pp. 277-302.

Hudson, R.J.M, S.A. Gherini, C.J. Watras and D.B. Porcella (1994). Modeling the biogeochemical cycle of mercury in lakes: the mercury cycling model (MCM) and its application to the MTL study lakes. In: *Mercury Pollution, Integration and Synthesis*. C.J. Watras and J.W. Huckabee (Eds.), Lewis Publishers, Boca Raton, FL, pp. 473-523.

Jackson, T.A. (1991). Biological and environmental control of mercury accumulation by fish in lakes and reservoirs of northern Manitoba, Canada. *Can. J. Fish. Aquat. Sci.* 48:2449-2470.

Kudo, A., H. Nagase and Y. Ose (1982). Proportion of methylmercury to the total amount of mercury in river waters in Canada and Japan. *Water Res.* 16:1011-1015.

Lange, T.R., H.E. Royals and L.L. Connor (1993). Influence of water chemistry on mercury concentration in largemouth bass from Florida lakes. *Trans. Am. Fish. Soc.* 122:74-84.

Lee, Y.H. and H. Hultberg (1990). Methylmercury in some Swedish surface waters. *Environ. Sci. Technol.* 9:833-841.

Lindqvist, O. (1991). Mercury in forest lake ecosystems - Bioavailability, bioaccumulation and biomagnification. *Water Air Soil Pollu.* 55:131-157.

MacCrimmon, H.R., C.D. Wren and B.L. Gots (1983). Mercury uptake by lake trout, *Salvelinus namaycush*, relative to age, growth, and diet in Tadenac Lake with comparative data from other precambrian shield lakes. *Can. J. Fish. Aquat. Sci.* 40:114-120.

Mathers, R.A. and P.H. Johansen (1985). The effects of feeding ecology on mercury accumulation in walleye (*Stizostedion vitreum*) and pike (*Esox lucius*) in Lake Simcoe. *Can. J. Zool.* 63:2006-2012.

McKim, J.M., G.F. Olson, G.W. Holcombe and E.P. Hunt (1976). Long-term effects of methylmercuric chloride on three generations of brook trout (*Salvelinus fontinalis*): Toxicity, accumulation, distribution, and elimination. *J. Fish. Res. Bd. Can.* 33:2726-2739.

Meili, M., A. Iverfeldt and L. Hakanson (1991). Mercury in the surface water of Swedish forest lakes - Concentrations, speciation, and controlling factors. *Water Air Soil Pollu.* 56:439-453.

Morgan, M.G. and M. Henrion (1990). *Uncertainty*. Cambridge University Press, Cambridge, England.

Niimi, A.J. and L. Lowe-Jinde (1984). Differential blood cell ratios of rainbow trout (*Salmo gairdneri*) exposed to methylmercury and chlorobenzenes. *Arch. Environ. Contam. Toxicol.* 13:303-311.

Olson, G.F., D.I. Mount, V.M. Snarski and T.W. Thorslund (1975). Mercury residues in fathead minnows, *Pimephales promelas* Rafinesque, chronically exposed to methylmercury in water. *Bull. Environ. Contam. Toxicol.* 14:129-134.

Paasivirta, J., J. Sarkka, K. Surma-Aho, T. Humppi, T. Kuokkanen and M. Marttinen (1983). Food chain enrichment of organochlorine compounds and mercury in clean and polluted lakes of Finland. *Chemosphere* 12:239-252.

Paasivirta, J., J. Sarkka, M. Aho, K. Surma-Aho, J. Tarhanen and A. Roos (1981). Recent trends of biocides in pikes of the Lake Paijanne. *Chemosphere* 10:405-414.

Parks, J.W. (1988). Selected ecosystem relationships in the mercury contaminated Wabigoon-English River system, Canada, and their underlying causes. *Water Air Soil Pollu.* 42:267-279.

Parks, J.W., A. Lutz and J.A. Sutton (1989). Water column methylmercury in the Wabigoon/English River-Lake system: Factors controlling concentrations, speciation, and net production. *Can. J. Fish. Aquat. Sci.* 46:2184-2202.

Parsons, A. and G. Bigham (1994). Comments on the Proposed Water Quality Guidance for the Great Lakes System. Report presented to the U.S. EPA Great Lakes Task Force, Washington, DC. PTI Environmental Services , Waltham, MA.

Ribeyre, F. and A. Boudou (1984). Bioaccumulation et repartition tissulaire du mercure - $HgCl_2$ et CH_3HgCl - chez *Salmo gairdneri* apres contamination par voie directe. *Water Air Soil Pollu.* 23:169-186.

Rubinstein, R.Y. (1981). *Simulation and the Monte Carlo Method.* John Wiley and Sons, Inc., New York, NY.

Scott, D.P. and F.A.J. Armstrong (1972). Mercury concentration in relation to size in several species of freshwater fishes from Manitoba and Northwestern Ontario. *J. Fish. Res. Bd. Can.* 29:1685-1690.

Skurdal, J., T. Qvenild and O.K. Skogheim (1985). Mercury accumulation in five species of freshwater fish in Lake Tyrifjorden, southeast Norway, with emphasis on their suitability as test organisms. *Environ. Biol. Fish.* 14:233-237.

Snarski, V.M. and G.F. Olson (1982). Chronic toxicity and bioaccumulation of mercuric chloride in the fathead minnow (*Pimephales promelas*). *Aquat. Toxicol.* 2:143-156.

Sorensen, J.A., G.E. Glass, K.W. Schmidt, J.K. Huber and G.R. Rapp, Jr. (1990). Airborne mercury deposition and watershed characteristics in relation to mercury concentrations in water, sediments, plankton, and fish of eighty northern Minnesota lakes. *Environ. Sci. Technol.* 24:1716-1727.

Suchanek, T.H., P.J. Richerson, L.A. Woodward, D.G. Slotton, L.J. Holts and C.E.E. Woodmansee (1993). A survey and evaluation of mercury. In: Sediment, water, plankton, periphyton, benthic invertebrates and fishes within the aquatic ecosystem of Clear Lake, California. Preliminary lake study report prepared for the U.S. Environmental Protection Agency, Region 9, Superfund Program.

U.S. Environmental Protection Agency (1993). Water Quality Guidance for the Great Lakes System and Correction; Proposed Rules. *Fed. Regist.* 58(72):20802-21047 (April 16, 1993).

U.S. Environmental Protection Agency (1995). Great Lakes Water Quality Initiative Technical Support Document for the Procedure to Determine Bioaccumulation Factors. EPA-820-B-95-005. U.S. EPA, Office of Water, Washington, D.C.

Watras, C.J. and N.S. Bloom (1992). Mercury and methylmercury in individual zooplankton: Implications for bioaccumulation. *Limnol. Oceanogr.* 37:1313-1318.

Wren, C.D. and H.R. MacCrimmon (1986). Comparative bioaccumulation of mercury in two adjacent freshwater ecosystems. *Nat. Resour.* 20:763-769.

Wren, C.D., H.R. MacCrimmon and B.R. Loescher (1983). Examination of bioaccumulation and biomagnification of metals in a precambrian shield lake. *Water Air Soil Pollu.* 19:277-291.

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16. ABSTRACT
In this volume of the draft Mercury Study Report to Congress an ecological assessment for anthropogenic mercury emissions is developed. The assessment follows the U.S.EPA Framework for Ecological Assessment: problem formulation; presentation of a conceptual model describing airborne mercury accumulation in aquatic biota, biomagnification in the aquatic food chain; and analysis of exposure of wildlife species to methylmercury through consumption of fish and shellfish. Exposures of wildlife species to methylmercury through the aquatic food chain are compared with toxicity data calculated in the development of criteria for the protection of fish-eating avian and mammalian wildlife. Descriptions of mercury impacts on biota are provided in the problem formulation chapter. Estimates are provided of mercury deposition on a local scale in areas near emissions point sources. The distributions of selected fish-consuming wildlife species are overlaid with predicted high mercury areas of high concern (e.g., areas with low-pH surface water) and compared with predicted deposition of anthropogenic mercury emissions. This volume of the draft Report analyzes sources of variability and uncertainty in these estimates and identifies data that would strengthen the certainty of these findings.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Mercury; Methylmercury; Mercury Poisoning; Animals, wild; Wildlife; Bioaccumulate; Aquatic food chain; Fishes, poisonous; Neurotoxin; Piscivorous; Toxicology; Indirect exposure..	Air Pollution Control	

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