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CONTAMINATION OF FISH IN STREAMS OF THE MID-ATLANTIC REGION: AN APPROACH TO REGIONAL INDICATOR SELECTION AND WILDLIFE ASSESSMENT

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Abstract—The extent of contamination of fish in the Mid-Atlantic Region was evaluated as part of the U.S. Environmental Protection Agency’s Monitoring and Assessment Program’s regional assessment in 1993 through 1994. Fish assemblages from wadeable streams were dominated by small, short-lived fishes (e.g., minnows, darters, and sculpins) that were more widely distributed and abundant than large fishes typically chosen for tissue contaminant studies (e.g., trout, black bass, sunfish, common carp). Chemical concentrations in whole-fish homogenates exceeded detection limits for mercury, DDT, and polychlorinated biphenyls (PCBs) in 75 to 100% of the stream length assessed using small fishes and 84 to 100% of the stream length assessed using large fishes. Wildlife values (WVs) representing a threshold for toxic effect were developed to allow examination of the spatial extent of potential risk to piscivorous wildlife. For mercury, DDT, dieldrin, and chlordane, estimates of the regional extent of streams where fish contaminant concentrations exceeded the WVs were greater when based on small fishes than on large fishes. However, within the distribution of stream lengths assessed using small and large fishes, the percentage of stream kilometers exceeding the WVs were quite similar. Our data demonstrate that the greater abundance and distribution of small, short-lived fishes provide greater estimates of regional extent of contamination for first- through third-order streams and can be used for regional assessments of potential exposure and effects in wildlife.

Keywords—Fish homogenates Regional contamination indicator Wildlife values Mercury Organics

INTRODUCTION

One goal of the U.S. Environmental Protection Agency’s (U.S. EPA) Environmental Monitoring and Assessment Program (EMAP) [1], was to assess the regional extent of exposure to wildlife and humans from chemical contamination in fish and provide a means of tracking how this exposure changes over time [2]. Historically, fish contaminant surveys focused on large sportfish because they are the species most often consumed by humans [2–8]. When collecting fish for such studies, large carnivorous fish (e.g., black bass [Centrarchidae] and trout [Salmonidae]) or benthivorous fish (e.g., common carp [Cyprinidae] and catfish [Ictaluridae]) have been the species targeted for collection. Exposure assessments of large wild fish (bald eagle and osprey) have also selected top carnivores or benthic fish as target species [9,10]. The major advantage of using larger fish was greater bioaccumulation and thus greater potential sensitivity for detection of contaminants [2]. Voiland et al. [11] observed a correlation between increasing size and contaminant tissue concentration for a number of freshwater fish species. Fatty and/or larger fish contained higher organic contaminant concentrations than leaner, smaller fish, but contaminant concentrations varied among different fish species. Stafford and Haines [4] reported that mercury concentrations increase with fish age or size. Similarly, Peterson et al. [12] found lower concentrations of mercury (Hg) in blacknose dace than in sunfish. However, dace were still considered effective monitors of Hg contamination because they mirrored the sunfish results.

Fish contaminant data such as that collected using the EMAP sampling design can also be useful for formulating and/or conducting an initial tier regional-scale wildlife risk assessment. Consistent with the ecological risk assessment framework, characterization of exposure and effects are necessary components of any risk assessment. If estimates of stream length with contaminated fish derived from EMAP sampling are used as an initial estimate of the exposure of piscivorous wildlife to contaminants, then comparison with a benchmark or criteria representing a threshold for toxic effect could be used to derive a regional characterization of potential risk.

To test the utility of the Mid-Atlantic Region (MAR) whole-fish homogenate contamination data in making regional estimates of the potential for wildlife exposures, tissue-based wildlife values were derived for several of the contaminants of concern, specifically those that are known to bioaccumulate in fish. Currently, there is no nationally consistent or mandated methodology for deriving wildlife criteria for protecting piscivorous wildlife from chemical contaminants. The U.S. EPA developed water quality criteria for the protection of piscivorous wildlife as part of the Great Lakes Water Quality Initiative (GLWQI) [13,14] and the U.S. EPA report on assessing chemical contaminant data [5]. In both efforts, the criteria derived were water based, i.e., the values proposed were expressed as chemical concentrations in water. One of the major uncertainties involved in deriving water-based criteria is the determination and use of bioaccumulation factors to convert dietary concentrations of contaminants associated with toxicity (i.e., toxicity information for mammals and birds is typically reported as concentration in the diet) to water concentrations. Having con-
Fig. 1. Map of sites where fish were and were not collected in the Mid-Atlantic Region of the United States for contaminant analyses (77). Samples were unavailable at 25 sites (open circles) because sites were dry, contained no fish, or yielded insufficient numbers of individuals for a sample.

taminant concentrations measured in whole-fish homogenates, as in this study, obviates the need for bioaccumulation factors to convert dietary intake of contaminants to water concentrations and hence reduces uncertainty associated with the wildlife values (WVs). As with water quality criteria for wildlife, these WVs are intended to be protective. As long as exposure remains below the value, it is unlikely that adverse effects will occur; however, exceeding the WV does not necessarily indicate that the wildlife population will suffer adverse effects.

The objectives of this study were to evaluate a multifish species approach for contaminant sampling, compare the extent of exposure of stream ecosystems with contaminants of concern using small adult fish and large adult fish, and compare regional estimates of wildlife exposure and potential effects using small adult fish and large adult fish.

MATERIALS AND METHODS

Study area and sampling design

The MAR region of the eastern United States encompasses approximately 205,000 km² and extends from the Atlantic coastal plain to the Ohio River and from the Catskill Mountains in New York to the North Carolina–Tennessee–Virginia state borders (USA) (Fig. 1). Small first-order streams make up 70% of the stream kilometers in the region, second-order streams 15%, third-order streams 7%, and fourth-order and higher orders of streams 8%. Stream sample sites were selected using a randomized sampling design with a systematic spatial component [1,15,16]. The sample frame was based on first-through third-order (Strahler) wadeable stream traces present on the digital 1:100,000 scale U.S. Geological Survey topographic maps that were incorporated into U.S. EPA’s River Reach File (Ver 3, www.epa.gov/OST/BASINS/metadata/). We used variable sample probabilities so that roughly equal numbers of first-, second-, and third-order stream sites would be selected because EMAP wanted to be able to make subpopulation estimates for conditions in small versus medium versus large streams. Each sample site had a weighting factor (calculated as the inverse of the selection probability) so that inference to the entire population of streams in the study area could be made using the sample data [16]. In all, we present assemblage data on fish collected at 245 different sites from three different probability monitoring projects (a Regional Environmental Monitoring and Assessment Project, an acid deposition project Temporally Integrated Monitoring Effort and MAR), representative of 186,947 km of wadeable Mid-Atlantic streams. A random subset of 102 sites (Fig. 1) was selected from which to collect fish for contaminant analyses. For this subset, site weights were adjusted for the random subsetting process so that regional steam length estimates could be made. This design allowed estimation of the extent of fish contamination for small streams in the entire MAR, with quantifiable uncertainty of the estimates of stream miles affected [15–18].

Fish species selection

Using regional ichthyological references [19,20], we considered species or species groups for whole-fish tissue sampling that, based on their native range, we expected to be widely distributed, abundant, and representative of communities present in small, wadeable streams in the MAR. We established two categories of fishes, one characterized by small (typically <100 mm), short-lived (2–5 year) adults and one that had large (typically >150 mm) and long-lived (>3 years)
adults. These size criteria were chosen from regional ichthyology references [19,20] and are meant to serve as surrogates for age (because aging fish in the field is not practical). Our expectations were that fish belonging to species that achieve large sizes as adults would exceed minimum size criteria by a particular age as reported in ichthyology references [19,20]. The small species group consisted of blacknose dace (Rhinichthys atratulus), any similar species (Rhinichthys, Phoxinus, or Clinostomus spp.), creek chub or fallfish (Semotilus spp.), slimy or mottled sculpin (Cottus spp.), central stoneroller (Campostoma anomalum), a darter species (Percidae, Etheostoma spp., Percina spp., etc.), or a shiner species (Cyprinidae, Notropis spp.). Large species included white sucker (Catostomus commersoni), northern hogsucker (Hypentelium nigricans), a black bass (Centrarchidae, Micropterus spp.), a trout species (Salmonidae), a sunfish species (Centrarchidae, Lepomis spp.), or common carp (Cyprinus carpio). We prioritized species lists based on the probability that a species would be captured in sufficient numbers to provide a sample for analysis of whole-fish tissue concentrations.

Field collection of samples

Streams were sampled during a 12-week period from April to July, corresponding to spring low-flow conditions. Fish were collected by electroshocking according to standard time (45–180 min) and distance (150–500 m, equivalent to 40× the mean wetted channel width) criteria using pulsed direct-current backpack electroshocking equipment supplemented by seining [21]. Samples for whole-fish homogenate analyses of small and large fishes were obtained from the fish collections where sufficient numbers of individuals and sample weights were available. For small fish species, 20 to 200 individuals were composited to obtain a sample weight between 50 and 400 g. A minimum of three individuals of a large species was kept for whole-fish analysis. Field crews were instructed to save individuals of similar length [21]. As a general rule, the total length of the smallest individual included in the composite was no less than 75% of the total length of the largest individual. Composite samples of small fish species were wrapped in aluminum foil in the field. Large fish species were wrapped individually. Samples were double-bagged in labeled plastic bags and sealed with tape. Samples were placed on dry ice or in a portable freezer as soon as possible after collection and kept frozen until they were shipped via overnight express mail [22,23].

Laboratory analyses

Fish tissue samples were analyzed through a contract with the U.S. Fish and Wildlife Patuxent Analytical Control Facility (Patuxent, MD) that had two laboratories under contract during the course of the study. Both laboratories followed the EMAP-Surface Waters Quality Assurance Project Plan for EMAP-Surface Waters [23,24] and procedures found in Yeardley et al. [2]. The approach taken was one that is performance-based and does not specify a single, standardized method for laboratory analysis of its target analytes. The analytical lab chose any method as long as the required quality assurance/quality control elements were present and the quality control limits were met [23,24]. Some of the key elements of this quality assurance/quality control are a control chart that shows proof of ability to consistently meet standard reference material warning limits of 80 to 120% for organics, 90 to 110% for inorganics, and control limits of 70 to 130% for organics and 85 to 115% for inorganics. For spiked matrix, recoveries >50% was set as a warning limit.

In the laboratory, fish were unwrapped, washed using contaminant-free distilled water, and reweighed prior to homogenization. For samples consisting of many small fish, the total weight and number of fish in the composite sample were recorded. Large fish were weighed individually. If the homogenate was to be refrozen prior to extraction or digestion, the exact amount needed was weighed into individual containers. This procedure was repeated with additional containers for duplicates, splits, or excess homogenate that was to be saved for potential reanalysis or archival purposes. Each laboratory determined the minimum amount of homogenate needed to meet the target detection limits [23]. The detection limits obtained in this study were 0.025 µg/g for mercury and 0.002 µg/g for organics (pesticides and polychlorinated biphenyls [PCBs]). Briefly, the tissue samples (1–10 g wet wt) were homogenized. Contaminant extracts were prepared from the homogenate by adding surrogate standards, Na₂SO₄, and methylene chloride in a centrifuge tube. The homogenate extracts were purified by silica/alumina column chromatography to isolate the aliphatic and polyaromatic hydrocarbons/pesticide/PCB fractions. The polyaromatic hydrocarbons/pesticide/PCB fraction was further purified by high-pressure liquid chromatography to remove interfering lipids. The quantitative analyses were performed by capillary gas chromatography (CGC) with a flame ionization detector for aliphatic hydrocarbons, CGC with electron capture detector for pesticides and PCBs, and a mass spectrometer detector in the single ion mode for aromatic hydrocarbons. There are specific cases where analytes requested for the pesticide and PCB analyses are known to coelute with other analytes in the normal CGC with electron capture. These include the pesticide Endosulfan I and the PCB congeners 114 and 157. In these cases, the samples were analyzed by CGC with a mass spectrometer detector in the single ion mode. For mercury analyses, homogenates were either digested with nitric acid or dry ashed in a furnace. Mercury concentrations were determined by cold vapor atomic absorption spectrometry, in which Sn²⁺ is used to reduce HgO. Where laboratory detection limits differed, the higher of the two detection limits was used when assessing estimates above detection limits [23,24].

Derivation of wildlife values

Wildlife values were derived for chlordane, DDT and its metabolites, dieldrin, endrin, mercury, and PCBs using the approach described in U.S. EPA's GLWQI [13]. In our study, the WVs represent toxicant concentrations in whole fish, rather than in water, that are expected to protect the viability of piscivorous wildlife. The WVs were derived for piscivorous birds and mammals that are likely to experience the highest exposures to bioaccumulative contaminants through the aquatic food web. We selected river otter (Lutra canadensis) and mink (Mustela vison) based on the potential intensity of exposure and knowledge of their current or historical occurrence in the MAR. Based on distribution maps from the U.S. Geological Survey Breeding Bird Survey (http://www.mnp2-pwr-usgs.gov/bbs/), we selected belted kingfisher (Ceryle alcyon) as the representative avian species. The belted kingfisher is a regular resident of riparian zones of small streams in the MAR and feeds almost exclusively on small fish species [25,26].

Exposure parameter values used to calculate WV for river
otter, mink, and belted kingfisher in this study are listed in Appendix 1. Most of the exposure assumptions and parameter values were obtained from U.S. EPA [13,14] with the following exceptions. For all species, we assumed that no contaminant exposure occurred via ingestion of water. This assumption is supported by the GLWQI wherein water ingestion contributed less than 1/10,000 of the total intake of the bioaccumulative compounds 2,3,7,8-tetrachlorodibenzo-p-dioxin, PCBs, DDT, and mercury [13]. All species were assumed to have a dietary composition of 100% fish. This assumption was made to simplify our assessment (i.e., one less term in the exposure equation); however, it is not unreasonable based on known dietary habits for the species selected. The belted kingfisher in almost any habitat feeds exclusively on aquatic prey, predominantly fish (<10 cm in length) from shallow water [26]. In a study of kingfisher diet in Ohio, stonerollers were the most commonly caught food item [26]. River otter feed primarily on fish, usually small fish, but also larger fish (e.g., northern pike, walley, trout) [25]. Mink consume both aquatic and terrestrial prey [25], the proportion of each varying with habitat. The aquatic component often includes nonpiscivorous wetland animals (e.g., muskrats, amphibians, water fowl) as well as fish. The nonfish aquatic species consumed by mink are generally of the same or lower trophic level as the fish consumed. Therefore, while a detailed dietary composition analysis for the mink is beyond the scope of this study, our assumption that mink consumes 100% fish, whether small or large, should err on the conservative side for the bioaccumulative compounds of interest.

The test doses (TDs) used to calculate species-specific wildlife values for the current study were selected based on the criteria described in U.S. EPA [13,14] and best professional judgment. For DDT, mercury, and PCBs, the TDs were those identified or derived in the GLWQI [13]. For chlordane, dieldrin, and endrin, the selection criteria presented in U.S. EPA [14] for measurement endpoint (i.e., reproductive or development success, organismal viability or growth, effect on population dynamics), taxonomic class (i.e., wildlife species preferred over laboratory species), study duration (i.e., subchronic or chronic), and peer review were applied in selecting studies from which a TD could be derived. All TDs were converted to milligrams ingested per kilogram body weight per day according to the procedure described by the U.S. EPA [14]. The TD selected or calculated for each chemical and each representative species is presented in Appendix 2. Uncertainty factors were applied in the WV equation to adjust the TD for interspecies differences in toxicological sensitivity, subchronic to chronic extrapolations, and lowest-observed-adverse-effect level to no-observed-adverse-effect level extrapolations. The scientific basis and selection guidance for the uncertainty factors used has been described in detail previously [14]. The equation (Appendix 3) used to calculate wildlife values is essentially as described by the U.S. EPA [14] except that it does not include an exposure component from ingestion of water and it is expressed in milligrams of chemical per kilogram of fish. This approach results in a tissue-based WV and eliminates the need for bioaccumulation factors. The WV for the contaminants of concern and wildlife species are presented in Table 1.

Statistical analyses

We calculated the percent relative abundance of each species collected at 245 sites in the MAR to evaluate our species selection criteria [27]. We made regional estimates of the extent of fish contamination by extrapolating the results from the sample sites using the site weighting factors derived from the survey probability design as derived by a SAS® program (SAS Institute, Cary, NC, USA). The sum of all the sample site weights gives the total stream length in the study population. Summing the site weights for those sites where whole-fish homogenate concentrations exceeded the various WVs gives the length of stream where WVs were exceeded. Similar estimates were made for the presence/absence of the different fish species in the region. Though different species had widely different ranges of occurrence, all the regional estimates of contamination are expressed as a percentage of the total stream length from which tissue samples were collected (186,947 km). We used linear regression to compare lipid-normalized tissue concentrations of mercury, chlordane, dieldrin, DDT and its metabolites, and PCBs in small fishes with those in large fishes from the same site (n = 40).

RESULTS

Small, short-lived fishes represented 83.6% of all individuals collected in the MAR, while larger, longer lived taxa comprised 16.4%. Cyprinids (Cyprinidae) represented 66% of all individuals collected, sculpins (Cottidae) 12.4%, and darters (Percidae) 1.7% (Fig. 2). Suckers (Catostomidae) were the most common of the large fish species (7.2%), followed by black bass and sunfish (Centrarchidae) species (5.2%) and trout (Salmonidae) (3.2%) (Fig. 2). Carp were collected at only eight sites and comprised less than 1% of the individuals collected. Based on regional estimates obtained from assemblage data [16], blacknose dace (Rhinichthys atratus; ~98,000 km of streams) and creek chub (Semotilus atromaculatus; 69,000 km) have the widest distribution in the region, followed by white sucker (Catostomus commersoni; 54,000 km), bluegill (Lepomis macrochirus; 37,000 km), and brook trout (Salvelinus fontinalis; 33,000 km). Cyprinids (minnows) were present in more than twice the estimated stream kilometers in the MAR than suckers or sunfish (132,000 vs 60,000 km). Large piscivores (smallmouth bass Micropterus dolomieu; rockbass, Ambloplites rupestris; and chain pickerel, Esox niger) were present in less than 16,000 km of the stream length in the MAR.

We obtained fish for contaminant analyses from 77 of the 102 sites for the EMAP-Surface Waters Mid-Atlantic Region Assessment (Table 2). At 25 sites, either no fish were collected (n = 15) or there were insufficient numbers (n = 5) or weight (n = 5) for a sample. Samples of small fish species were collected at 70 sites and large species were collected at 47

### Table 1. Contaminants evaluated in this study with detection limits and wildlife values for protection of piscivorous wildlife. Calculations and assumptions used in determination of wildlife values are presented in Appendices I through III

<table>
<thead>
<tr>
<th>Contaminant</th>
<th>Detection limits</th>
<th>Wildlife values (mg/kg fish)</th>
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</thead>
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<td></td>
<td></td>
<td>Otter</td>
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<tr>
<td>Chlordane</td>
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<td>1.14</td>
</tr>
<tr>
<td>DDT and its metabolites</td>
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<td>0.49</td>
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<tr>
<td>Dieldrin</td>
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</tr>
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<td>PCBs</td>
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<td>0.18</td>
</tr>
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* Polychlorinated biphenyls.
sites. Samples of both small and large species were collected at 40 sites. Species distribution estimates based on small species in the MAR were 70% greater than those of large species (119,663 km vs 70,695 km; Fig. 3, extent) with blacknose dace (30 samples; 62,385 km) and white sucker (24 samples; 38,583 km) constituting most of the collections.

Figure 3 illustrates the actual stream length (km) assessed for contaminants using both small fishes and large fishes. As can be seen, the actual number of stream kilometers in the MAR that contain fish with detectable contaminants is always greater when estimated from small fishes than from large fishes. Likewise, the estimates of stream kilometers with fishes containing contaminants that exceed the kingfisher WV was always greater when small fishes were used to estimate extent. The extent of stream kilometers where fish contaminant concentrations exceeded the otter WV was relatively small overall (maximum = 16.2% for PCBs in large fish). Estimates were similar for small and large fish for mercury (small = 9.4%, large = 12.9%), DDT and its metabolites (small = 0%, large = 1.4%), and dieldrin (small = 0.8%, large = 1.4%), but large fish yielded greater estimates for PCBs (16.2%) than small fish (5.7%).

Estimates of regional extent of contamination expressed as the percent of stream length assessed by small fishes and large fishes are presented in Figure 4. Estimates above detection limits were used as a means to look at the regional distributional patterns of contaminants and as an indicator of chemical condition. Regional estimates of the stream length in the MAR where contaminant concentrations exceeded the detection limits were approximately the same for small as for large fishes for chlordane (96.8 vs 96.1%), dieldrin (100 vs 98.4%), mercury (78.2 vs 84.4%), PCBs (100 vs 100%), and DDT and its metabolites (100 vs 100%). Contamination by parent DDT accounted for 28% (~5,000 km) of the total estimated contamination by DDT and its metabolites (52,789 km). Fifty-two percent of the stream length (97,000 km) had fish in which the concentrations of mercury, PCBs, and DDT exceeded the detection limits for all three analytes. Sites where contaminant concentrations in fish exceeded the detection limits for all of the contaminants represented 46,000 km (25%) of the regional stream length. Estimates of the regional extent of mercury contamination were 15 and 26% of the total stream length when based on white sucker (large fish) and blacknose dace (small fish) tissue concentrations, respectively.

The percent of stream kilometers assessed using small and large fishes, where whole-fish homogenate concentrations of mercury, PCBs, DDT and its metabolites, chlordane, and dieldrin exceed WV's are also shown in Figure 4. The concentration of mercury in small fishes exceeded the kingfisher WV for 72.0% of stream length, the mink WV for 22.7% of stream length, and the otter WV for 9.4% of stream length assessed.
Fig. 4. Estimated percent of stream length (km) with contaminant concentrations exceeding detection limits (A) and wildlife values for kingfisher (B) and otter (C) for small (solid bar) and large (open bar) fish species. Estimates for the extent of contamination by endrin are not presented because it affected less than 1% of the stream length. Regional estimates of contaminants exceeding wildlife values and detection limits are based on weighted probabilities from 102 sites. The estimates are adjusted for sample sizes of the small versus large fish species so that they express the percentage of the length assessed for each group. The total regional stream length assessed was 186,000 km. Refer to Table 1. PCBs = polychlorinated biphenyls.

We obtained similar results for mercury concentrations in large fishes, with 71.2, 26.6, and 13.0% of stream length exceeding WVs for kingfisher, mink, and otter, respectively. The PCB concentrations in both small and large fishes exceeded the mink WV in 13.0% (small) and 20.4% (large) of the stream length, followed by otter (5.7% small; 15.7% large) and kingfisher (1.4% small; 2.2% large). Concentrations of DDT and metabolites exceeded the WV for kingfisher in 21.2 and 26.0% of regional stream length based on small and large fishes, respectively. The concentration DDT and metabolites exceeded WVs for mink and otter in a much smaller proportion of stream miles (1.4% for both) and only in large fishes. Concentrations of chlordane in small and large tissue samples exceeded the WV for kingfisher in approximately the same proportion of stream length (small = 43.9%, large = 46.5%) but were below the WVs for mink and otter throughout the MAR. Dieldrin concentrations exceeded the WV for mink and otter in both fish categories in a small percentage of stream length (small = 1.8% for mink and 0.8% for otter, large = 1.4% for both); neither small or large fishes had dieldrin concentrations that exceeded the WV for kingfisher. Whole-fish concentrations of endrin and hexachlorobenzene did not exceed the WVs for any of the wildlife species, irrespective of the fish category.

Lipid content and lipid-normalized fish contaminant concentrations in small and large fish from the same site (n = 40 sites) are compared in Figure 5. Lipid content in small fish was found to be significantly greater (analyses of variance; $F = 9.98; p = 0.002$) than in large fish. Lipid-normalized concentrations of PCBs, chlordane, and dieldrin in large species were all significantly ($p < 0.01$) and strongly ($r^2 = 0.58–0.78$) related to those from small fish (Fig. 5).

**DISCUSSION**

For regional stream surveys such as EMAP, collection of small, adult fishes may present several potential advantages over the larger species typically targeted in studies of fish contaminants. Small fishes are often widely distributed regionally and more abundant locally than larger fishes, providing samples from a greater proportion of sites and more individuals to form a composite at each site. Larger sample sizes should result in more representative and repeatable characterizations of contaminant load in a stream reach, thereby decreasing sample variance and improving the power to assess status and trends. In addition, we suggest that small adult fish may be more appropriate for assessing potential wildlife exposures to contaminants because they are prey for a greater diversity of fish-eating animals, such as the piscivorous fish, birds, and small mammals in the MAR.

Collections of fish for chemical analyses have been historically driven by concerns for human health and the protection of large avian species. Because most (85%) of the streams in the MAR are classified as first or second order, the fishes most commonly collected for analyses (bass, sunfish, trout, and common carp) represented only 16% of all individuals.
and approximately 37% of the total stream length sampled. In contrast, the small fishes collected during this survey represented 84% of individual fish sampled and 64% of the sampled stream length. Because more individuals of small fish are required to meet criteria for sample weight, contaminant analyses of the smaller fish may better represent the distribution of persistent bioaccumulative chemicals in this region. Indeed, we found that the actual number of stream kilometers in the MAR that contain fish with detectable contaminants is always greater when estimated from small fishes than from large fishes (Table 2; Fig. 3). Thus, by selecting two fish species groups representing the most dominant fish taxa in the region and analyzing whole fish, our current approach provides better assessments of the presence of contaminants of concern and potential exposures for fish-eating wildlife across the region.

Our estimates of the regional stream length that have fish with concentrations of contaminants that exceed detection limits demonstrate how EMAP data may provide valuable insights for regional-scale wildlife exposure assessments. Thus, by selecting two fish species groups representing the most dominant fish taxa in the region and analyzing whole fish, our current approach provides better assessment of the presence of contaminants of concern in fish across the region. Although unlikely, accepting this assumption would provide an upper-bound estimate of exposure and would indicate that wildlife are potentially being exposed, via the diet, to concentrations of mercury, PCBs, DDT and its metabolites, chlordane, and dieldrin that are detectable in fish in greater than 75% of the stream length in the MAR.

Because we did not determine the presence of piscivorous wildlife at the sampling localities, we cannot directly assess contaminant exposures of avian and mammalian wildlife. Examination and quantification of the stream length sampled that are suitable feeding sites for piscivorous wildlife would be a logical next step in conducting a more definitive analysis of wildlife exposure in the MAR. We must also stress that the EMAP sampling design and our current wildlife assessment using EMAP data are not appropriate for identifying and/or assessing hot spots (e.g., sediment deposition areas, Superfund sites) within the region. Assessment of such types of contamination would require more site-specific approaches for problem formulation and sampling design.

By estimating the extent of stream kilometers that had tissue contaminant concentrations that exceeded wildlife values, we found that, for most of the contaminants assessed in this study, small species also presented wildlife with more extensive geographic potential for exposure than large species (Fig. 3). Only for PCBs (otter) and DDT and its metabolites (mink and otter) did large fishes project a greater regional extent of exposure than small species. Interestingly, when the extent was expressed within the fishes distribution (i.e., as percent of stream length assessed; Fig. 4), the estimates of spatial extent of stream length with fish containing contaminants that exceeded WVs using small fish species was in remarkably close concordance with that predicted by large species. Hence, although the small fish clearly show a greater spatial extent of potential wildlife exposure, the percentage of stream kilometers within the distributions of small and large fishes that exceed the WVs are essentially the same. This information has value in defining assumptions and hypotheses during the problem-formulation phase of a regional-scale risk assessment.

In comparing the fish tissue data with the WVs, we are able expand the biological context of the exposures to wildlife that prey on both the small and large fish species. The detection limit-based stream length estimates only establish the potential for exposure and do not tell us anything about effects on exposed wildlife. This information has value in defining assumptions and hypotheses during the problem formulation phase of a regional risk assessment. For example, given that our data show that small fish or large fish indicate essentially the same percentage of stream miles with contamination, future iterations of a regional risk assessment could be more specific and focus on identifying and sampling the types of fish most likely to be consumed by the wildlife of concern. The methodology used to derive the wildlife values is based largely on the methodology used to derive wildlife criteria for the GLWQI. The methodology has been extensively peer reviewed and represents a protective approach commonly used in tier risk analysis. Such protective threshold benchmarks are typically conservative but still have utility in problem formulation and screening exercises and for ranking and prioritizing further study. As is demonstrated by our data, although the percentage of stream length where fishes have measurable concentrations of contaminants is quite high (i.e., >75%), the percent of stream length where the concentrations of contaminants in fish may be expected to have adverse effects on wildlife is substantially lower for all contaminants considered, with the exception of mercury. This type of analysis can be used to focus future risk assessments.

Our analysis also demonstrates which contaminants may be of most concern to specific wildlife species on a regional scale. In planning future regional wildlife risk assessment, our analysis shows that piscivorous birds such as the kingfisher may require a more thorough assessment of persistent bioaccumulative toxicants than mammalian wildlife. Furthermore, there would be little impetus to conduct further regional-scale sampling and analysis of chemicals that were detected but did not exceed the WVs for any of the species of interest (e.g., dieldrin in our study). In contrast, the finding that concentrations of mercury, chlordane, DDT and its metabolites, and PCBs in fish exceeded at least one of the WVs indicates that these compounds should be considered as chemicals of potential ecological concern in the MAR.

CONCLUSIONS

The fish species approach described for the MAR met our expectations for sample availability and our ability to determine the extent of exposure of stream ecosystems to contaminants of concern. Small fish species had a more extensive regional distribution than large fish species and yielded greater regional estimates of the extent of contamination than large fish species typically chosen for human consumption advisories. Because more individuals of small fish species are required to meet criteria for sample weight, contaminant analyses of the smaller fishes provide a robust representation of the distribution of persistent bioaccumulative chemicals in this region. The approach allows assessment of the extent of both potential exposure and effects to piscivorous wildlife. Several contaminants of concern had an extensive regional distribution and exceeded calculated avian and mammalian wildlife values. This information can be used by environmental managers to focus resources to investigate the possibility that there might be atmospheric sources of mercury, chlordane, dieldrin, PCBs, and DDT and its metabolites because these compounds are broadly distributed across the MAR. Further, integrating whole-fish contaminant extent data with wildlife toxicity-based
benchmarks can be useful in prioritizing sites or regions for further investigation or in conducting the problem-formulation phase of risk assessments. This study demonstrates the value of collecting and analyzing both small and large fish when assessing contaminant issues on a regional scale in wadeable systems.

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REFERENCES


APPENDIX 1

Exposure parameter values and trophic level of prey for species potentially at risk from bioaccumulative contaminants in the Mid-Atlantic Region (USA)

<table>
<thead>
<tr>
<th>Species</th>
<th>Adult body weight* (kg)</th>
<th>Ingestion rate (kg/kg⋅d)*</th>
<th>% of Diet</th>
<th>Kilograms fish/day</th>
</tr>
</thead>
<tbody>
<tr>
<td>River otter</td>
<td>7.4</td>
<td>0.17</td>
<td>TL3: 80%</td>
<td>TL3: 0.976</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>TL4: 20%</td>
<td>TL4: 0.244</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total: 1.22</td>
<td></td>
</tr>
<tr>
<td>Mink</td>
<td>0.80</td>
<td>0.23</td>
<td>TL3: 100%</td>
<td>TL3: 0.18</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total: 0.18</td>
<td></td>
</tr>
<tr>
<td>Belted kingfish</td>
<td>0.15</td>
<td>0.45</td>
<td>TL3: 100%</td>
<td>TL3: 0.067</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Total: 0.067</td>
<td></td>
</tr>
</tbody>
</table>

* Adult body weight represents average of male and female values for otter and mink.
  * Ingestion rate represents average of male and female values for otter and mink.
  * Trophic level 3.
  * Trophic level 4.

APPENDIX 2

Test dose and uncertainty factors used for calculating wildlife values*

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Test dose (mg/kg-d)</th>
<th>Reference</th>
<th>Representative species</th>
<th>$UF_a$</th>
<th>$UF_s$</th>
<th>$UF_l$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chlordane</td>
<td>1.875$^e$</td>
<td>[28]</td>
<td>River otter/mink</td>
<td>10</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.020$^d$</td>
<td>[29]</td>
<td>Kingfisher</td>
<td>10</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>DDT and its metabolites</td>
<td>0.800$^c$</td>
<td>[13]</td>
<td>River otter/mink</td>
<td>10</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.027$^c$</td>
<td>[13]</td>
<td>Kingfisher</td>
<td>1</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Dieldrin</td>
<td>0.050$^c$</td>
<td>[30]</td>
<td>River otter/mink</td>
<td>10</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.478$^c$</td>
<td>[31]</td>
<td>Kingfisher</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Endrin</td>
<td>0.025$^c$</td>
<td>U.S. EPA$^d$</td>
<td>River otter/mink</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.300$^c$</td>
<td>[32]</td>
<td>Kingfisher</td>
<td>3</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>PCBs</td>
<td>0.300$^c$</td>
<td>[13]</td>
<td>River otter/mink</td>
<td>1</td>
<td>1</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>1.786$^c$</td>
<td>[13]</td>
<td>Kingfisher</td>
<td>3</td>
<td>1</td>
<td>3</td>
</tr>
<tr>
<td>Mercury</td>
<td>0.165$^c$</td>
<td>[13]</td>
<td>River otter/mink</td>
<td>1</td>
<td>10</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>0.078$^c$</td>
<td>[13]</td>
<td>Kingfisher</td>
<td>3</td>
<td>1</td>
<td>2</td>
</tr>
</tbody>
</table>

* $UF_a = $ uncertainty factor for extrapolating toxicity data across species (unitless);
  * $UF_s = $ uncertainty factor for extrapolating from subchronic to chronic exposures (unitless);
  * $UF_l = $ uncertainty factor for extrapolating from lowest-observable-acute-effect level to no-observable-acute-effect level (unitless);

$^a$ Calculated in U.S. EPA [13].
$^b$ Calculated as in U.S. EPA [14].

APPENDIX 3

Formula for calculation of fish-tissue based wildlife values

$$WV = TD \cdot \frac{1}{\left[ UF_a \cdot UF_s \cdot UF_l \right]} \cdot BW \left[ F_{(species, TL3)} + F_{(species, TL4)} \right]$$

where

- $WV = $ species-specific wildlife value in milligrams of chemical per gram whole fish
- $TD = $ test dose for the test species in milligrams of chemical per kilogram body weight per day (mg/kg-d)
- $UF_a = $ uncertainty factor for extrapolating toxicity data across species (unitless)
- $UF_s = $ uncertainty factor for extrapolating from subchronic to chronic exposures (unitless)
- $UF_l = $ uncertainty factor for extrapolating from lowest-observable-acute-effect level to no-observable-acute-effect level (unitless)
- $BW = $ average body weight for the representative species in kilograms (kg)
- $F_{(species, TL3)} = $ average daily amount of food consumed from trophic level 3 for the representative species in kilograms per day (kg/d).
- $F_{(species, TL4)} = $ average daily amount of food consumed from trophic level 4 for the representative species in kilograms per day (kg/d).