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# A Survey of Fish Contamination in Small Wadeable Streams in the Mid-Atlantic Region

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## Abstract

In 1993 and 1994, fish tissue samples were collected from first, second and third order streams in the Mid-Atlantic Region of the United States. The tissue samples were prepared from whole fish from prioritized lists of Small Target Species and Large Target Species. The two types of samples were analyzed for 56 contaminants, of which 22 had median values that were above the detection limits for at least one category of fish. For this report, the data analyses were conducted in order to determine 1) exposure to contaminants, 2) the magnitude of exposure, and 3) the location of the sites which exceeded toxicological benchmark values. All sites from which samples were taken showed exposure to at least one contaminant. In order to determine the magnitude of this exposure, no observed adverse effects level (NOAEL) benchmark values for 16 of the analytes were used. These NOAEL benchmark values are estimates of the greatest concentration of contaminants at which it is unlikely that the belted kingfisher (*Megaceryle alcyon*) would suffer adverse effects from consumption. These NOAEL benchmark values were then compared to the concentration of contaminants found in Small Target Species tissue sampled at each site. Maps were generated which showed the locations of the sites that exceeded the NOAEL benchmark values. Seventy sites (100%) exceeded at least one NOAEL benchmark value and twenty two sites (31.4%) exceeded four or more NOAEL benchmark values. The number of sites exceeding multiple NOAEL benchmark values suggests a comprehensive study of fish tissue contaminants is warranted for the region.





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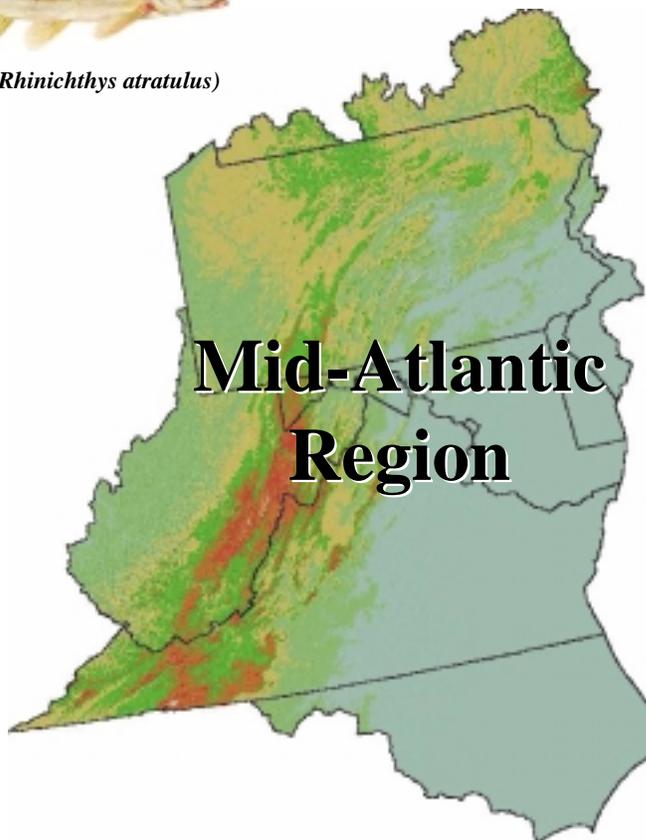
# A Survey of Fish Contamination in Small Wadeable Streams in the Mid-Atlantic Region



**Blacknose Dace** (*Rhinichthys atratulus*)



**Creek Chub** (*Semotilus atromaculatus*)



**White Sucker** (*Catostomus commersoni*)



## Introduction

This report uses contaminant levels in fish tissue samples as indicators of pollutant exposure to the fish themselves and the predators that might eat them. In 1993 and 1994, fish tissue samples were collected from first, second and third order streams in the Mid-Atlantic Region of the United States. These fish tissue samples were analyzed for the concentration of selected metals and organic compounds including mercury, lead, and organochlorides (i.e., PCBs and DDT). The data provide an opportunity to screen for levels of contaminants that may cause adverse effects to fish and wildlife. The objectives of this report are to determine 1) exposure to contaminants, 2) the magnitude of exposure, and 3) the location of the sites which exceeded toxicological benchmark values.

## Background

The analysis of fish tissue samples measures the bioaccumulation of toxic chemicals. Bioaccumulation occurs when organisms incorporate and retain chemicals from the surrounding environment. In aquatic ecosystems, these chemicals are associated with water, sediments, suspended solids and prey organisms. If the incorporation of the chemical outpaces the metabolism or excretion of the chemical, then bioaccumulation occurs. The result is that the

concentration of the chemical inside the organism is greater than it is in the environment. Therefore, tissue analysis can reveal the presence of contaminants that may not be detected otherwise that is, they have such low concentrations in the environment that they cannot be observed through chemical analysis of the water column or sediments (USEPA 1992). When used in combination with other diagnostic indicators (e.g., physical habitat and water chemistry) and response indicators (e.g., fish, benthic macroinvertebrate and algae assemblages), fish tissue analysis can be an effective tool in determining the overall condition of an aquatic ecosystem (USEPA 1995).

Fish tissue studies have traditionally focused on the bioaccumulation of contaminants in large game fish because these fish are more likely to pose health risks to humans (USEPA 1995, 1997). Fish tissue studies have also focused on the bioaccumulation of toxic chemicals in the fillets and livers of fish as well as in the whole fish (USEPA 1995). This study analyzed whole fish of both large and small species and both game and non-game species. While an analysis of the bioaccumulation of toxic chemicals in the fillets of large game fish may give a better indication of the risks to humans from consuming these organisms, whole fish analysis that also includes small non-game fish will give a better indication of the risks to all

potential predators, both humans and non-humans.

From each site that was visited in this study, attempts were made to collect two categories of fish tissue samples. One of these categories (Small Target Species, Table 1) included fish taxa of which the adults are small and the other category (Large Target Species, Table 2) included fish taxa of which the adults are large. The use of smaller fish is advantageous because 1) the common species are more likely to be widely distributed among first to third order streams, 2) their large numbers may make it possible to obtain a more representative sample of bioaccumulation, 3) they are more likely to be preyed upon by piscivorous fish and wildlife and 4) they are less expensive and less time-consuming to process in the field and in the laboratory. The use of larger fish is advantageous because they are longer lived and bioaccumulation can occur over a longer time period. Therefore, there may be an increased likelihood of detecting the presence of contaminants in the ecosystem when using larger fish for tissue analysis. Although it is known that the rates of bioaccumulation vary between species (Rubinstein et al. 1984; Williams and Eddy 1986; USEPA 1992, 1993a), the relationship between large and small fish with respect to bioaccumulation of contaminants is not well understood. The principal factor in determining the rate of bioaccumulation is lipid content (USEPA 1991a, 1997), thus, there may be no relationship between the two fish categories in their rates of bioaccumulation. Therefore, it becomes necessary to analyze the tissue from both fish categories and each category must be measured separately (USEPA 1995). In this study, each tissue sample represents a composite of individuals of a single species rather than a mixture of species found at a site.

**Table 1.** The Small Target Species for the Mid-Atlantic Tissue Analysis in Order of Priority

Priority	Small Target Species
1	Blacknose dace ( <i>Rhinichthys atratulus</i> )
2	Another Dace species ( <i>Rhinichthys</i> spp., <i>Phoxinus</i> spp., <i>Clinostomus</i> spp.)
3	Creek chub ( <i>Semotilus atromaculatus</i> ) or Fallfish ( <i>S. corporalis</i> )
4	Slimy sculpin ( <i>Cottus cognatus</i> ) or Mottled sculpin ( <i>C. bairdi</i> )
5	Central stoneroller ( <i>Campostoma anomalum</i> )
6	A Darter species (F. Percidae)
7	A Shiner species (F. Cyprinidae)

**Table 2.** The Large Target Species for the Mid-Atlantic Tissue Analysis in Order of Priority

Priority	Large Target Species
1	White sucker ( <i>Catostomus commersoni</i> )
2	Northern hogsucker ( <i>Hypentelium nigricans</i> )
3	A Bass species (F. Centrarchidae, <i>Micropterus</i> spp.)
4	A Trout species (F. Salmonidae)
5	A Sunfish species (F. Centrarchidae, <i>Lepomis</i> spp.)
6	Common carp ( <i>Cyprinus carpio</i> )

## Materials and Methods

### Study Area and Sampling Design

The Mid-Atlantic Region is in the United States Environmental Protection Agency's (USEPA's) Region III which encompasses the states of Delaware, Maryland, Pennsylvania, Virginia and West Virginia and the District of Columbia. The majority (63%) of the stream kilometers (km) in the study area are made up of first order streams. Second order streams make up 15%, third order streams make up 11% and fourth order streams make up 11% of the stream km in the study area (USEPA 1994).

The sampling locations were selected using a spatially-constrained, randomized design (Overton et al. 1991; Herlihy et al. in press). The randomization of the site selection increases the likelihood that the level of contamination detected in the sampled sites is representative of the contamination in the overall population of streams (USEPA 1997; Paulsen et al. 1991; Olsen et al. 1999). Site selection was limited to include only wadeable (first, second and third order) streams. USGS topographical maps (1:100,000 scale) were used to establish the random placement of points within the population of streams. These points were used as the middle of each respective reach. USGS maps of a finer resolution (1:24,000) were used by the field crews in order to locate the sites to be sampled. The latitude and longitude of the random points were confirmed by the field crews by global positioning system (GPS) instruments. The locations of sample sites where fish tissue samples were collected are shown in Figure 1.

## **Collection of Samples**

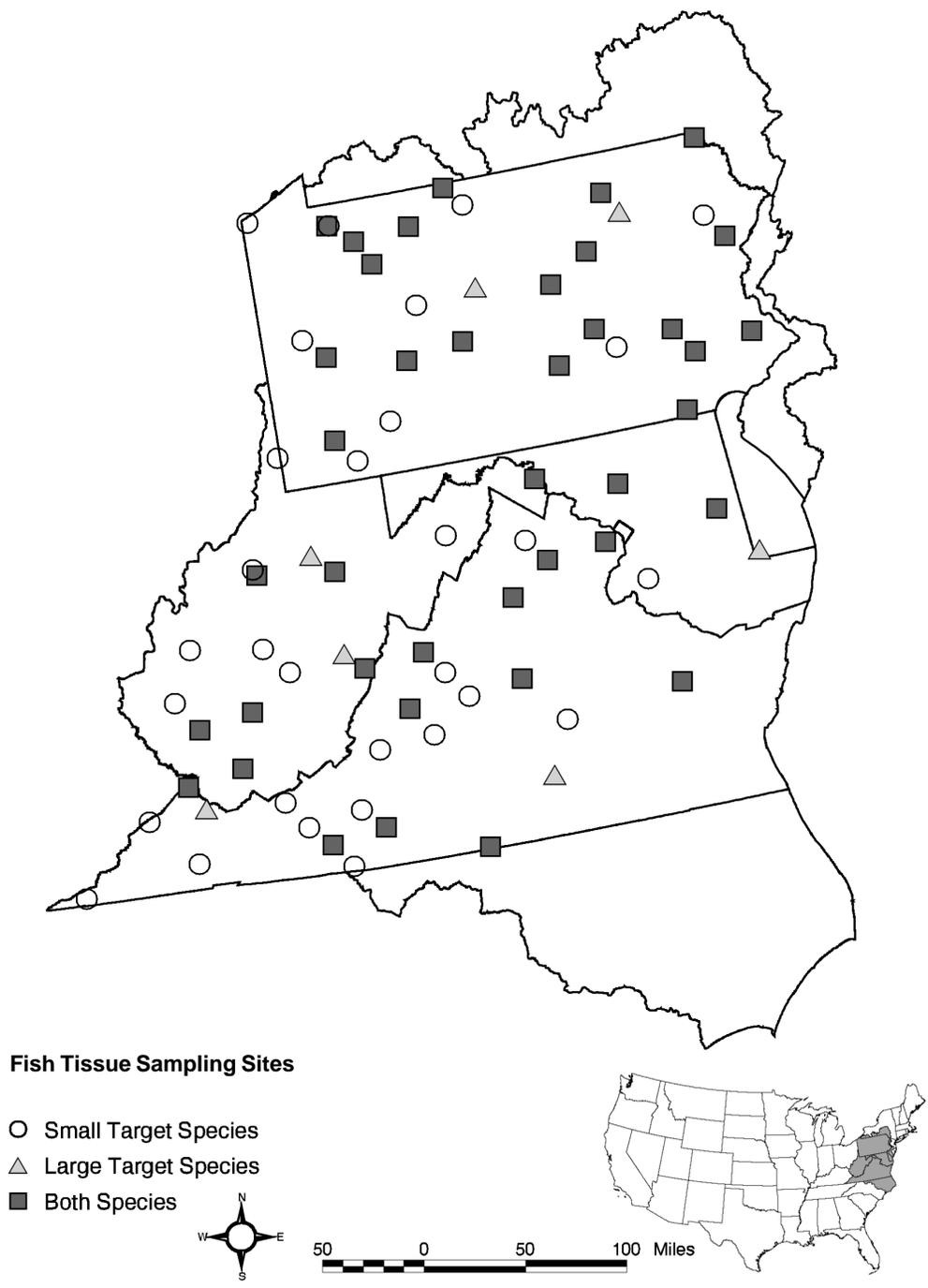
Fish tissue samples were collected as a part of the USEPA's Environmental Monitoring and Assessment Program (EMAP). Fish were collected using pulsed DC backpack electrofishing equipment supplemented by seining. The amount of sampling time and the length of the sample reach used for the sampling of streams were based on the standardized EMAP protocol (USEPA 1997). The length of each reach was 40 times the mean width of the wetted channel at the designated point. The minimum length of any reach was 150 meters (m) and the maximum length was 500 m. Sampling was conducted for a minimum time of 45 minutes and a maximum time of three hours.

Before collection began, two categories of target taxa were established based upon their anticipated distribution in the region. The two

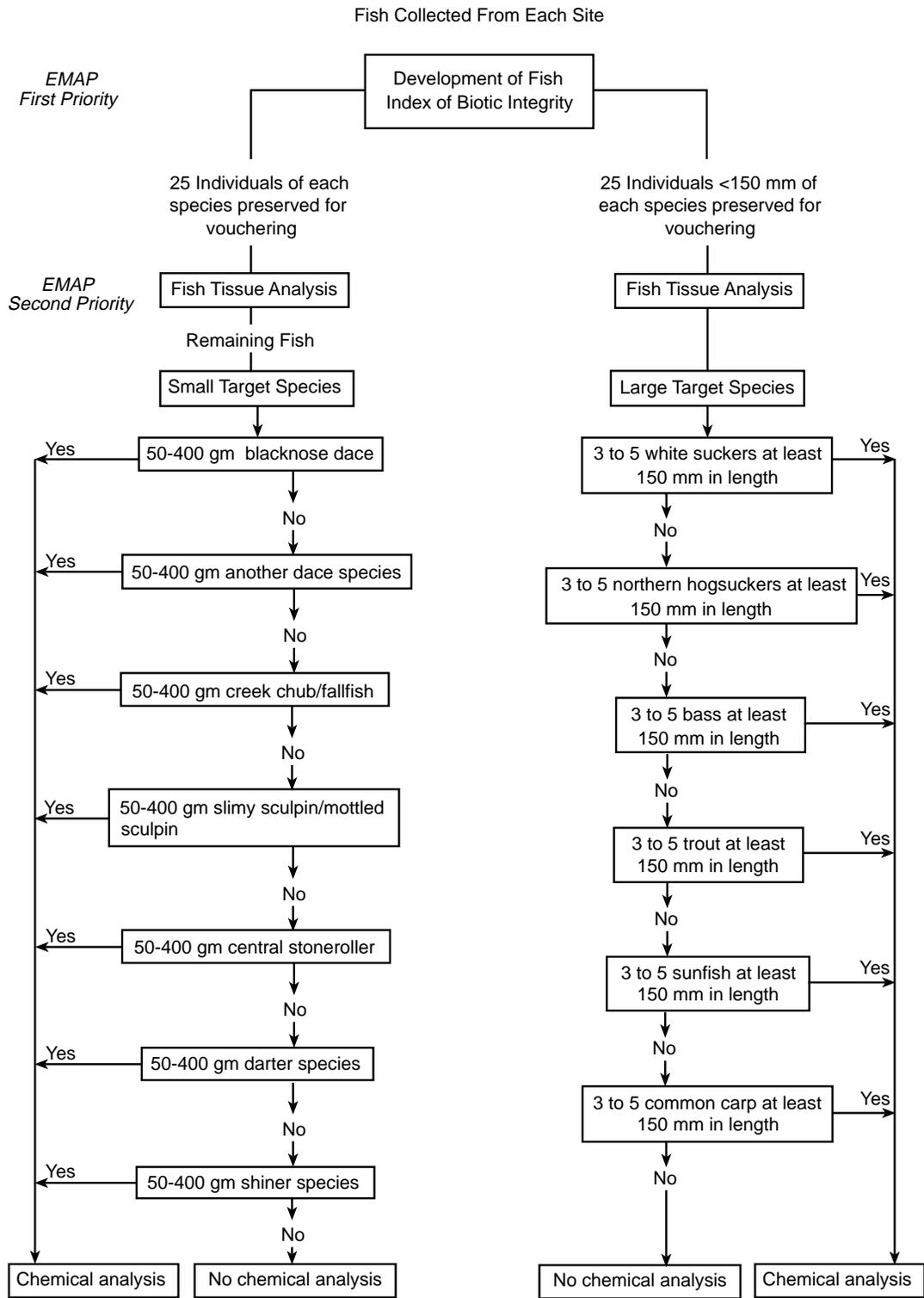
categories of target taxa were Small Target Species (Table 1) and Large Target Species (Table 2). The criteria for establishing the Small Target Species list were that the adults of the species be small (< 100 mm), short-lived, widely distributed and abundant. The criteria for establishing the Large Target Species list were that the adults of the species be large (> 150mm), that the species have a natural history of living more than three years, and that the species be likely to accumulate contaminants under prolonged exposure. The taxa on each list were ranked according to their priority for collection (Tables 1 and 2). The prioritization of the fish was based on their anticipated common occurrence and abundance. An attempt was made to collect one sample from each list at each sampling site. Each sample was made up of multiple individuals of the same species.

The optimum weight for each tissue sample of Small Target Species was 400 grams (g) and the sample could weigh no less than 50 g. The Large Target Species samples were made up of individuals from one category on the Large Target Species list that were at least 150 mm in length. The optimum number of individuals to make up a sample of Large Target Species was five and the minimum number of individuals used to make up a sample was three. There was no weight requirement for the Large Target Species tissue samples.

The primary objective of this field effort was the development of an Index of Biotic Integrity (IBI) for the region (Figure 2). The secondary objective was the assessment of the magnitude of contaminants in fish tissue samples (Figure 2). Therefore, the Small Target Species sample collected for tissue analysis at each site was made up of individuals from the highest ranking category on the Small Target Species list for which there were enough individuals to meet the 50 g minimum requirement after the removal of



**Figure 1.** A map of the fish tissue sample sites in the Mid-Atlantic Region.



**Figure 2.** A graphical representation of the fish collection priorities used in the Mid-Atlantic fish tissue sampling.

25 voucher specimens for the IBI study. Because the individuals from the Large Target Species list that were removed as voucher specimens were less than 150 mm in length and the individuals on the Large Target Species list that were collected for tissue samples were more than 150 mm in length, the vouchering aspect probably had no impact on the collection of these species for tissue analysis. Individuals making up the samples were always from the same species or group of species on the target species lists.

The samples used for tissue analyses consisted of fish with similar lengths. The general criterion used in order for fish to be considered similar in length was that the length of the smallest individual in the composite sample was no less than 75% of the length of the largest individual in the composite sample. If fewer than the acceptable number of Large Target Species of the acceptable size were collected, then smaller individuals were added to the sample. If an acceptable number of Large Target Species was not collected, then only Small Target Species were kept for tissue analysis. Likewise, if too few Small Target Species were collected, then only Large Target Species were kept for tissue analysis. If neither the criteria for Small nor Large Target Species were met, then best professional judgement was used in determining what type of fish tissue sample would be submitted for analysis or if there would be no fish tissue analysis for that particular site.

Fish were collected for tissue analyses from 27 April 1993 to 8 July 1993 and from 18 April 1994 to 24 June 1994. There were 102 sites selected for fish tissue sampling and fish tissue samples were collected at 77 of these sites. There were 70 sites at which Small Target Species fish tissue samples were collected, 47 sites at which Large Target Species tissue samples

were collected. Of these, both Small and Large Target Species tissue samples were collected at 40 sites (Figure 1).

Small Target Species samples were composited and wrapped in aluminum foil in the field. Individuals making up the Large Target Species samples were individually wrapped in aluminum foil. Samples were then placed in a labeled plastic bag which was placed within a second plastic bag. The samples were then sealed with tape and placed on dry ice or in a portable freezer where they were kept frozen until they were shipped to the laboratory via overnight express mail (USEPA 1994).

## **Laboratory Analysis**

The tissue samples were analyzed by a contractor, the Patuxent Analytical Control Facility located in Patuxent, Maryland. Fish samples were held at -20°C until analysis. In the laboratory, the aluminum foil was removed from the fish samples and the outside of each fish was thoroughly washed with distilled water and then weighed. The fish in the samples that contained three to five large fish (i.e., Large Target Species) were weighed individually while the fish in the samples that contained many small fish (i.e., Small Target Species) were weighed together. The total weight and number of fish in each composite sample was recorded. Each composite sample of Small and Large Target Species from each site was analyzed separately. Whole fish were analyzed to determine the overall ecological condition of the streams and the consumption risks to piscivorous wildlife (USEPA 1994).

Laboratory analyses determined the concentrations of a suite of elemental and organic contaminants (Table 3). These analytes were taken from the EMAP Estuary Implementation

**Table 3.** List of Analytes from the Mid-Atlantic Fish Tissue Analysis Study. The Fish Categories for which the Median Analyte Concentrations were above Detection Limits are Noted

Analyte	CAS Number	Category of fish for which the median concentration of the respective analyte was above the detection limit
*	309-00-2	None
#Aluminum	7429-90-5	All
*Arsenic	7440-38-2	None
*BHC - alpha	58-89-9	None
*BHC - beta	58-89-9	None
*BHC - delta	58-89-9	None
*BHC - gamma	58-89-9	None
*Cadmium	7440-43-9	White sucker
Chromium	7440-47-3	All
Copper	7440-50-8	All
2,4'-DDD	53-19-0	All
4,4'-DDD	72-54-8	All
*2,4'-DDE	3424-82-6	None
4,4'-DDE	72-55-9	All
*2,4'-DDT	789-02-6	Small Target Species, Blacknose dace, White sucker
*4,4'-DDT	50-29-3	Large Target Species, White sucker
Dieldrin	60-57-1	All
*Endosulfan-I	959-98-8	None
*Endosulfan-II	33213-65-9	None
*Endrin	72-20-8	None
*Heptachlor	76-44-8	None

\*These compounds were not used in CDFs, histograms or box plots for at least one category of fish because their median values were below detection limits.

#The detected levels of aluminum may have been artificially inflated by the use of aluminum foil in the packaging and storage of samples (See Collection of Samples and Laboratory Analysis Sections).

(continued)

**Table 3.** (Continued)

Analyte	CAS Number	Category of fish for which the median concentration of the respective analyte was above the detection limit
Heptachlor epoxide	1024-57-3	All
*Hexachlorobenzene	118-74-1	Small Target Species, Blacknose dace, White sucker
Iron	7439-89-6	All
*Lead	7439-92-1	None
Mercury	7439-97-6	All
*Mirex	2385-85-5	None
Nickel	7440-02-0	All
trans-Nonachlor	3675-80-5	All
cis-Nonachlor	5103-73-1	All
Oxychlordane	27304-13-8	All
Chlordane (alpha and gamma)	57-74-9	All
*Selenium	7782-49-2	None
Zinc	7440-66-6	All
<b>+PCB Congeners</b>		
2,4-Dichlorobiphenyl, #8	34883-43-7	All
2,2',5-Trichlorobiphenyl, #18	37680-65-2	All
2,4,4'-Trichlorobiphenyl, #28	7012-37-5	All
2,2',3,5'-Tetrachlorobiphenyl, #44	41464-39-5	All
2,2',5,5'-Tetrachlorobiphenyl, #52	35693-99-3	All
2,3',4,4'-Tetrachlorobiphenyl, #66	32598-10-0	All
2,2',4,5,5'-Pentachlorobiphenyl, #101	37680-73-2	All
2,3,4,4',5-Pentachlorobiphenyl, #118	31508-00-6	All

\*These compounds were not used in CDFs, histograms or box plots for at least one category of fish because their median values were below detection limits.

+Laboratory analysis was conducted for each of these PCB congeners. However, the data analysis for this report only considered Total PCBs.

(continued)

**Table 3.** (Continued)

Analyte	CAS Number	Category of fish for which the median concentration of the respective analyte was above the detection limit
<b>+PCB Congeners</b>		
2,2',4,4',5,5'-Hexachlorobiphenyl, #153	35065-27-1	All
2,3,3',4,4'-Pentachlorobiphenyl, #105	32598-14-4	All
2,2',3,4,4',5-Hexachlorobiphenyl, #138	35065-28-2	All
2,2',3,4',5,5',6-Heptachlorobiphenyl, #187	52663-68-0	All
2,2',3,3',4,4'-Hexachlorobiphenyl, #128	38380-07-3	All
2,2',3,4,4',5,5'-Heptachlorobiphenyl, #180	35065-29-3	All
2,2',3,3',4,4',5-Heptachlorobiphenyl, #170	35065-30-6	All
2,2',3,3',4,4',5,6-Octachlorobiphenyl, #195	52663-78-2	All
2,2',3,3',4,4',5,5',6-Nonachlorobiphenyl, #206	40186-72-9	All
Decachlorobiphenyl, #209	2051-24-3	All
3,3',4,4'-Tetrachlorobiphenyl, #77	32598-13-3	All
3,3',4,4',5-Pentachlorobiphenyl, #126	25429-29-2	All
3,3',4,4',5,5'-Hexachlorobiphenyl, #169	32774-16-6	All
Total PCBs	NA	All
+Laboratory analysis was conducted for each of these PCB congeners. However, the data analysis for this report only considered Total PCBs.		

Plan so that this study would be consistent with the EMAP Estuary Fish Tissue Contaminant Program, the EMAP Northeast Lakes Fish Tissue Contaminant Program and the Office of Water's National Contaminant Program. Tissue samples were homogenized with a Teckmar Tissumizer and sub-sampled. Tissue samples were digested by a mixture of sulfuric and nitric acids for mercury determination. For other elemental analyses, tissue samples were either digested with nitric acid or dry ashed in a muffle

furnace. Metals were determined by one of three techniques depending on the element and concentration. Mercury was determined by cold vapor technique (USEPA method 245.6, USEPA, 1991b) atomic absorption spectrometry (AAS), in which stannous chloride was used to reduce HgO. Arsenic, cadmium, selenium and lead were determined by graphite furnace AAS, in which electrical heating was used to produce an atomic cloud. The remaining metals (also cadmium and lead when in high concentration)

were determined by atomic emission spectrometry using an argon plasma.

Extractions of the tissue samples for the analysis of organic contaminants (i.e., polycyclic aromatic hydrocarbons, pesticides and PCBs) were performed using the National Oceanic and Atmospheric Administration (NOAA) Status and Trends method (MacLeod et al. 1985) with minor modification (Brooks et al. 1989; Wade et al. 1988). Briefly, an aliquot of tissue homogenate (1-10 g) was dried with sodium sulfate and extracted with methylene chloride. The tissue extract was purified by silica/aluminum column chromatography and high performance liquid chromatography (HPLC) to isolate the desired organic fraction and to remove interfering lipids. The quantitative analysis was performed by gas chromatography (GC) with mass spectrometer detector (MSD) in single ion monitoring (SIM) mode for polycyclic aromatic hydrocarbons and with electron capture detector (ECD) for pesticides and PCBs. Where known co-elution occurred in GC/ECD (e.g., endosulfan I and PCB congeners 114 and 117), GC with MSD in SIM mode was used.

The Quality Assurance (QA)/Quality Control (QC) for fish tissue analyses used in EMAP for inland surface waters (EMAP-SW) protocols (USEPA 1993b) is based on performance. It uses a list of required elements and limits (USEPA 1993b, 1994) of which a Standard Reference Materials (SRM) is one of the principle elements. This SRM must be made up of a matrix of similar fish tissue, of natural origin and contain several of the indicator values.

## **Data Analysis**

### **Analysis of Data Sets**

For all data analyses, analytes which had concentration values below the detection limits

were given values of 50% of the detection limit. This approach helped reduce either overestimating or underestimating the concentrations of these contaminants.

The analyses of the data from this study were approached in two different ways. One approach to analyzing the data was to consider the Small Target Species and the Large Target Species as groups and the other approach to analyzing the data was to consider each individual species or species group (e.g., creek chub/fallfish) separately. When considering individual species or species groups, separate subsets of the data were created for analysis of the two most common species (i.e., blacknose dace and white sucker). For these subsets, the data used were from the first visit to a site in which that particular species was collected.

White sucker made up a significant portion of the Large Target Species and blacknose dace made up a significant portion of the Small Target Species. The proportions that these individual species contributed to the Large and Small Target Species are shown in Appendices A and B, respectively.

Sites that were visited more than once by the field crews required subsetting of the data for analysis. One subset was created to analyze the Small Target Species data as a group. Among the Small Target Species, there were often two to three different species of fish collected during multiple visits. For those sites that had more than one visit and more than one species collected during those different visits, the sample made up of the highest priority fish species available was used for analysis. If this highest priority fish species was the same for more than one visit, the sample collected during the earliest visit was used. Another subset of data was created to analyze Large Target Species as a group. Because the same Large Target

Species were collected during all visits to the same site, this subset of data included all Large Target Species samples that were collected during the first visit to a site.

## Objectives

The data were analyzed so that three questions could be answered:

- 1) Where were fish exposed to contaminants?
- 2) What was the magnitude of the exposure?
- 3) Where were the sites that exceeded toxicological benchmark values?

## Descriptive Statistics

In order to interpret the data, several descriptive statistics were generated. The proportion of each fish category across the stream orders was described and box plots representing the distribution of analyte levels across stream order for blacknose dace and white sucker were generated. Histograms which show the proportion of white sucker to Large Target Species and the proportion of blacknose dace to Small Target Species with their respective levels of exposure to 22 analytes were also generated. These histograms not only describe the level of exposure for four categories of fish but they also describe the relative contribution of the white sucker to the Large Target Species category and the relative contribution of the blacknose dace to the Small Target Species category.

Empirical cumulative distribution functions (CDFs) were calculated for 22 analytes. A CDF indicates, across the full range of values, the proportion of samples at or below a given value. CDFs are a useful descriptive tool in determining whether most of the values are very low, with a few high values or whether values cover

a broader range. Finally, box plots showing level of analytes detected for each of four categories of fish were generated. Histograms, CDFs and box plots were not generated for analytes which had median values below the detection limits in a particular category of fish. Because of the infrequent detections of these analytes, histograms, CDFs and box plots would provide very little information. Those analytes for which histograms, CDFs and box plots were not generated are summarized in Tables 4 through 7.

## Exposure

The laboratory analyses provided the information necessary to determine that exposure to contaminants had occurred based on the detection of contaminants in the fish tissue samples.

The 90th percentile and 95% confidence intervals were calculated for the contaminant exposure of the most commonly occurring species (blacknose dace) to each of the analytes for which the median values were above the

**Table 4.** Analytes for which the Median Values were Below the Detection Limits in Small Target Species Samples (N=70)

Analyte	75th Percentile	Maximum	Detection Limit
(µg/g)	0.0002	0.0004	0.0002
Arsenic (µg/g)	3.7500	5.1000	3.7500
Cadmium (µg/g)	0.1600	0.7200	0.1000
o,p'-DDE (µg/g)	0.0002	0.0010	0.0002
p,p'-DDT (µg/g)	0.0002	0.0070	0.0002
Endosulfan I (µg/g)	0.0004	0.0021	0.0004
Endosulfan II (µg/g)	0.0004	0.0041	0.0004
Endrin (µg/g)	0.0002	0.0033	0.0002
Heptachlor (µg/g)	0.0002	0.0006	0.0002
BHC - alpha (µg/g)	0.0002	0.0007	0.0002
BHC - beta (µg/g)	0.0002	0.0005	0.0002
BHC - delta (µg/g)	0.0002	0.0007	0.0002
BHC - gamma (µg/g)	0.0002	0.0022	0.0002
Mirex (µg/g)	0.0002	0.0006	0.0002
Lead (µg/g)	1.2500	2.8900	1.2500
Selenium (µg/g)	3.7500	5.5900	3.7500

**Table 5.** Analytes for which the Median Values were Below the Detection Limits in Blacknose Dace Samples (N=33)

Analyte	75th Percentile	Maximum	Detection Limit
(µg/g)	0.0002	0.0004	0.0002
Arsenic (µg/g)	3.7500	4.2800	3.7500
Cadmium (µg/g)	0.1500	0.6400	0.1000
o,p'-DDE (µg/g)	0.0003	0.0010	0.0002
p,p'-DDT (µg/g)	0.0002	0.0029	0.0002
Endosulfan I (µg/g)	0.0004	0.0009	0.0004
Endosulfan II (µg/g)	0.0004	0.0041	0.0004
Endrin (µg/g)	0.0002	0.0008	0.0002
Heptachlor (µg/g)	0.0002	0.0006	0.0002
BHC - alpha (µg/g)	0.0002	0.0007	0.0002
BHC - beta (µg/g)	0.0002	0.0002	0.0002
BHC - delta (µg/g)	0.0002	0.0007	0.0002
BHC - gamma (µg/g)	0.0003	0.0022	0.0002
Mirex (µg/g)	0.0002	0.0003	0.0002
Lead (µg/g)	1.2500	1.2500	1.2500
Selenium (µg/g)	3.7500	5.5300	3.7500

**Table 6.** Analytes for which the Median Values were Below the Detection Limits in Large Target Species Samples (N=47)

Analyte	75th Percentile	Maximum	Detection Limit
(µg/g)	0.0002	0.0007	0.0002
Arsenic (µg/g)	3.7500	7.6700	3.7500
Cadmium (µg/g)	0.1000	0.6700	0.1000
o,p'-DDE (µg/g)	0.0002	0.0011	0.0002
o,p'-DDT (µg/g)	0.0006	0.0073	0.0002
Endosulfan I (µg/g)	0.0004	0.0107	0.0004
Endosulfan II (µg/g)	0.0004	0.0002	0.0004
Endrin (µg/g)	0.0002	0.0037	0.0002
Heptachlor (µg/g)	0.0002	0.0009	0.0002
Hexachloro- benzene (µg/g)	0.0004	0.0014	0.0002
BHC - alpha (µg/g)	0.0002	0.0004	0.0002
BHC - beta (µg/g)	0.0002	0.0002	0.0002
BHC - delta (µg/g)	0.0002	0.0002	0.0002
BHC - gamma (µg/g)	0.0002	0.0012	0.0002
Mirex (µg/g)	0.0002	0.0007	0.0002
Lead (µg/g)	1.2500	2.4200	1.2500
Selenium (µg/g)	3.7500	6.6400	3.7500

**Table 7.** Analytes for which the Median Values were Below the Detection Limits in White Sucker Samples (N=24)

Analyte	75th Percentile	Maximum	Detection Limit
(µg/g)	0.0002	0.0006	0.0002
Arsenic (µg/g)	3.7500	7.6700	3.7500
Cadmium (µg/g)	0.1500	0.6700	0.1000
o,p'-DDE (µg/g)	0.0002	0.0110	0.0002
Endosulfan I (µg/g)	0.0004	0.0031	0.0004
Endosulfan II (µg/g)	0.0004	0.0009	0.0004
Endrin (µg/g)	0.0002	0.0037	0.0002
Heptachlor (µg/g)	0.0002	0.0009	0.0002
BHC - alpha (µg/g)	0.0002	0.0004	0.0002
BHC - beta (µg/g)	0.0002	0.0002	0.0002
BHC - delta (µg/g)	0.0002	0.0002	0.0002
BHC - gamma (µg/g)	0.0004	0.0012	0.0002
Lead (µg/g)	1.2500	2.4200	1.2500
Mirex (µg/g)	0.0002	0.0005	0.0002
Selenium (µg/g)	3.7500	6.6400	3.7500

detection limits. These statistics help to describe the level of exposure to contaminants. In addition, the percentages of sites at which Small Target and/or Large Target Species showed exposure to contaminants above detection limits were calculated.

## Magnitude of Exposure

In order to determine the magnitude of exposure, toxicological benchmarks from Sample et al. (1996) were used. The benchmark values were based on the no observed adverse effects level (NOAEL) for the belted kingfisher (*Megaceryle alcyon*) for food consumption. The NOAEL for the belted kingfisher is the maximum concentration of the contaminant (g contaminant/g fish) that could be found in fish such that the belted kingfisher would be likely to suffer no adverse effects by consuming them. The methods used for the derivation of the NOAEL benchmark values are detailed in Sample et al. (1996). The exceedence of NOAEL benchmark values and the degree to which the NOAEL benchmark values were ex-

ceeded were judged to be indicative of the magnitude of exposure.

The belted kingfisher was chosen to be a representative of the wildlife in the region because it is widely distributed throughout the region, lives near bodies of water and feeds primarily on fish. It is likely that its prey would be near the size of the fish that were on the Small Target Species list (Terres 1980; Peterson and Peterson 1998). Because the sites for this study were chosen randomly, not all sites will be representative of typical belted kingfisher habitat and the fish from those sites, therefore, may not realistically represent a part of a belted kingfisher's diet. However, the NOAEL-based toxicological benchmarks should serve adequately as screening values for determining the magnitude of exposure.

All analytes used in this study (Table 3) for which there were NOAEL benchmark values reported in Sample et al. (1996) were used in data analysis. These analytes include As, Cd, Cr, Cu, Pb, Hg, Ni, Se, Zn, DDT and metabolites, endosulfan, dieldrin, endrin, chlordane, gamma-BHC and total PCBs (Table 8). For cases in which the benchmark values were calculated for a particular form of an element (e.g., Methyl mercury dicyandiamide) and the laboratory analysis for this study yielded only a value for the element (e.g., Mercury), then the lowest available benchmark was used. This was done in order to represent the range of exposure to these 16 contaminants.

For the calculation of these benchmark values, it was assumed that there was no exposure to contaminants by the ingestion of water. The toxicological benchmark values for food were used in order to best estimate the effects of a belted kingfisher eating the fish that were collected from these streams. Because the prey of the belted kingfisher is likely to be small fish, only the data from the Small Target Species were considered.

**Table 8.** Toxicological Benchmark Values for the Belted Kingfisher (Sample et al. 1996)

Chemical	Form Referenced	NOAEL (Food, µg/g)
Arsenic	Copper acetoarsenite	4.9
Cadmium	Cadmium chloride	2.86
Chromium	Cr <sup>3+</sup> as CrK(SO <sub>4</sub> ) <sub>2</sub>	1.97
Copper	Copper oxide	92.7
Mercury	Methyl mercury dicyandiamide	0.013
Nickel	Nickel sulfate	152.74
Lead	Lead acetate	2.23
*Selenium	Selanomethionine	0.789
Zinc	Zinc sulfate	28.6
Dieldrin	n/a	0.152
gamma-BHC	n/a	3.95
DDT & metabolites	n/a	0.006
Chlordane	n/a	4.20
Endosulfan	n/a	19.7
Endrin	n/a	0.020
Total PCBs	Arochlor 1254	0.355

\*The 50% value of the detection limit for Selenium is greater than the reported NOAEL value.

For the magnitude of exposure analyses, six DDT metabolites were summed to obtain a single value for DDT. Endosulfan I and endosulfan II were totaled for total endosulfan. The values for alpha-chlordane, gamma-chlordane, oxychlordane, cis-nonachlor and trans-nonachlor were summed for total chlordane. Before summing, half the detection limit was used for any values that were below the detection

limits. For the contaminants not used in summing, half the detection limit was used if the value was below the detection limit before comparing it to the NOAEL.

### *Location of Sites Exceeding Toxicological Benchmark Values*

The locations of the sites that yielded the Small Target Species tissue samples that exceeded the NOAEL benchmark values were mapped using GIS software. The maps were constructed to illustrate the degree to which the benchmark values were exceeded at each site for each of the selected contaminants and to illustrate the number of benchmark values that were exceeded at each site.

## **Results**

### *Descriptive Statistics*

The database containing the data collected during this study is located at [www.epa.gov/emap/html/data/surfwater/data/mastreams/9396](http://www.epa.gov/emap/html/data/surfwater/data/mastreams/9396). Fish tissue samples were collected at 77 of the 102 sites selected for fish tissue sampling. In 92 visits to these 77 sites, Small Target Species were collected during 83 visits to 70 sites and Large Target Species were collected during 53 visits to 47 sites. Of these, both Small and Large Target Species were collected during 44 visits to 40 sites. The prediction that the Small Target Species would be more widely distributed in first through third order streams within the region is supported by these data.

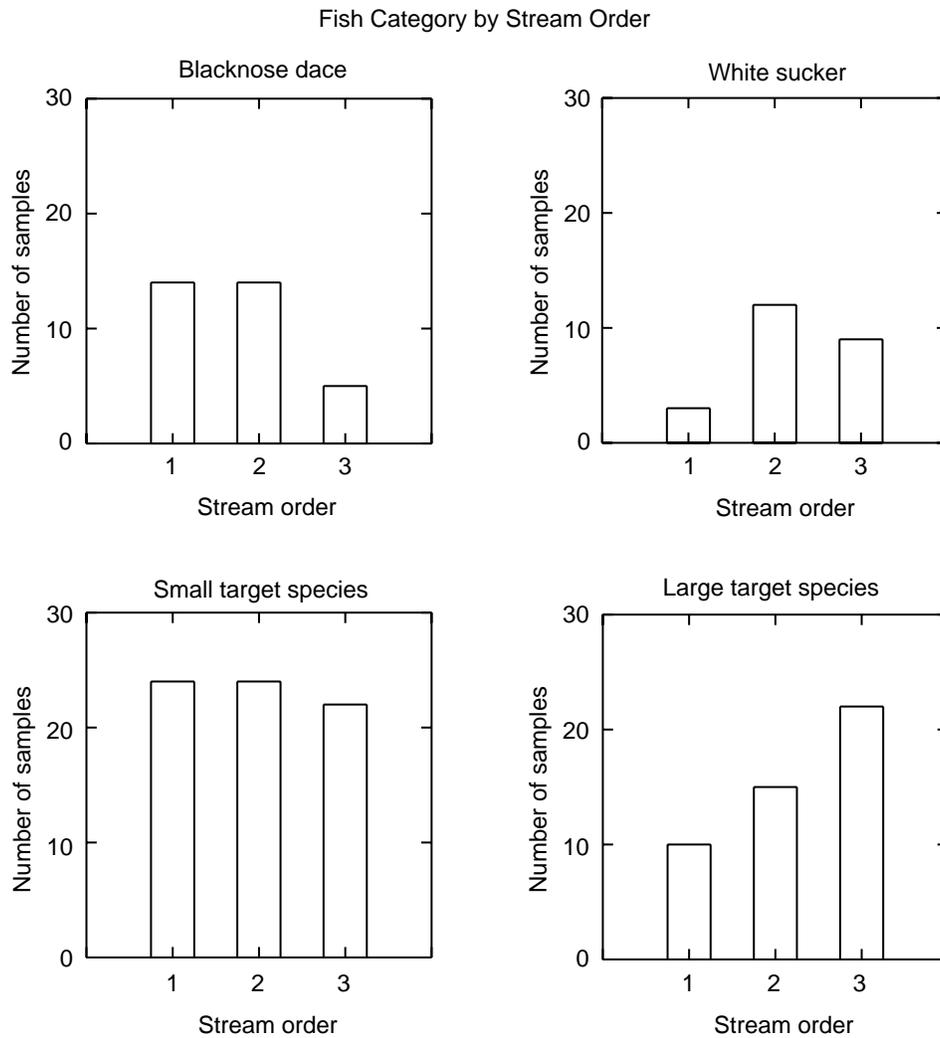
No Small Target Species tissue samples were collected at 32 sites (Table 9). There were no Small Target Species tissue samples collected from 15 of these sites because either the sites were not sampleable (e.g., no water present) or no fish were present in the reach. At 13 of

**Table 9.** A Summary of the Number of Sites Visited, Number of Sites where Tissue Samples were Collected, and the Number of Sites at which no Tissue Samples were taken

	Number of Sites	
	Small Target Species	Large Target Species
Total Sites Visited	102	102
Tissue Sample Collected	70	47
No Fish Collected	15	15
No Target Fish Collected	4	21
Target Fish Collected but No Tissue Sample Available	13	19

the remaining sites, at least one individual of the Small Target Species was caught, but there were either too few fish to take a fish tissue sample or the sample was lost after the fish tissue sample was collected. At four sites, fish were collected but there were no Small Target Species present. No Large Target Species tissue samples were collected at 55 sites (Table 9). There was no Large Target Species tissue samples collected from 15 of these because either the sites were not sampleable or no fish were present in the reach. At 19 of the remaining sites, Large Target Species were caught, but there were either too few fish to take a fish tissue sample or the sample was lost after the fish tissue sample was collected. At the other 21 sites, fish were collected but there were no Large Target Species present.

A series of histograms displays the number of four of the fish categories that were collected in the three stream orders (Figure 3). Note that the Small Target Species were collected in fairly even numbers among the stream orders,



**Figure 3.** The number of blacknose dace, white sucker, small target species and large target species collected for fish tissue analysis by stream order.

however, very few of the Large Target Species were collected in first order streams and the greatest number were collected in third order streams.

Although Small Target Species were approximately evenly distributed among first, second, and third order streams (Figure 3), blacknose dace were more common in first and second order streams. Large Target Species were least common in first order streams (about 20%) and most common in third order streams

(about 45%). However, white sucker samples were collected primarily from second order streams (about 50%), with another large proportion in third order streams and only about 10% in first order streams.

Box plot representations of the distribution of various analytes across the stream orders for blacknose dace and white sucker were developed (Appendix C). For blacknose dace, samples from third order streams generally showed higher variability and often higher me-

dians than samples from first and second order streams. However, some of this variability may be an artifact of a much smaller sample size (n=5) for third order streams. The greatest values for DDT metabolites and organics were usually found in samples from second or third order streams. For white sucker, there were no apparent differences among stream order for pesticides (DDT and metabolites), most organics, total PCBs, or metals. However, chlordane derivatives often showed slightly higher variability among samples from first order sites (n=3).

Two sets of histograms were generated for the analytes for which the median values were above the detection limits. One set of histograms shows the proportion of white sucker to Large Target Species (Appendix A) and the other set shows the proportion of blacknose dace to Small Target Species (Appendix B). These histograms describe the level of exposure of the four most common categories of fish to contaminants.

They also describe the relative contribution of the white sucker to the Large Target Species tissue samples and the relative contribution of the blacknose dace to the Small Target Species tissue samples.

Sets of CDFs were calculated for each of the 22 analytes for which the median values were above the detection limits (Appendix D). Box plot representations of these data are presented in Appendix E. The production of the CDFs provides some key insights into the distribution of the data. For example, the CDFs reveal that all contaminants had distributions which were skewed toward low values or the detection limits. They also illustrate that metals were present in relatively low concentrations at most sites, but with a range of moderate to high values at some sites. Cadmium was present in quantities less than the detection limit for all groups except white sucker, in which concentrations were relatively

high for a large proportion of sites. Some metals (i.e., Fe, Hg, Ni and Zn) had a maximum concentration among blacknose dace which was much lower than it was for the Small Target Species group as a whole. However, this was not true of white suckers in relation to the Large Target Species group. For both Large and Small Target Species, DDT and its metabolites were largely below detection limits for most sites with only a very small number of sites having relatively high concentrations of a given metabolite. The concentration of most organics were below detection limits in most species at over 80% of the sites.

The central part of the distribution of each contaminant, except Zn, was similar among individual species and groups of species (i.e., Large and Small Target Species), but outliers and maximum values varied greatly among the categories depending on the contaminant (Appendix E). Zn values tended to be much greater among Small Target Species than they were among Large Target Species. For the remainder of the analytes, there was no consistency as to whether the Large or Small Target Species had the greatest values for concentrations of contaminants.

## Exposure

Blacknose dace was the most common species in the study. The 90th percentile levels of contaminants were calculated for the blacknose dace (Table 10). This table only includes those analytes for which the median values were above their respective detection limits. Because at least one contaminant was above the detection limit at every site (Tables 11 through 13), exposure occurred at every site. When considering the results of the AI portion of the analysis, it is important to note that these results may be artificially inflated because of the way in which the field samples were processed and stored (see Collection of Samples and Labora-

tory Analysis Sections). It is possible that the use of aluminum foil in the storage of samples affected the results of the Al analysis. The percentage of sites at which exposure occurred for both Small and Large Target Species was calculated for each analyte (Tables 11 and 12, respectively). For visits occurring in both the Large and Small Target Species data sets, the number of sites at which there was exposure for one or both categories of target fish was also calculated (Table 13). For both categories of target species, exposure to most contaminants occurred at a moderate to high percentage of sites. When considering only sites where Small and Large Target species were collected, exposure was fairly consistent between large and small species.

**Table 10.** The 90% Levels of Contaminant Concentrations in Blacknose Dace Tissue Samples (N=33)

Contaminant	90th percentile (µg/g)	95% CI
*Aluminum	180.58	(103.03, 188.27)
Chromium	1.51	(1.36, 1.60)
Copper	1.23	(1.07, 1.47)
Iron	141.57	(98.88, 209.60)
Mercury	0.0763	(0.0582, 0.0993)
Nickel	0.43	(0.350, 0.740)
Zinc	54.19	(47.40, 56.24)
o,p'-DDD	0.0015	(0.0007, 0.0021)
p,p'-DDD	0.0029	(0.0010, 0.0034)
o,p'-DDT	0.0019	(0.0007, 0.0057)
p,p'-DDE	0.0397	(0.0099, 0.0704)
Dieldrin	0.0109	(0.0028, 0.0338)
Heptachlor epoxide	0.0014	(0.0007, 0.0057)
Hexachlorobenzene	0.0006	(0.0004, 0.0010)
alpha-Chlordane	0.0060	(0.0014, 0.0503)
gamma-Chlordane	0.0054	(0.0015, 0.0342)
cis-Nonachlor	0.0038	(0.0014, 0.0435)
trans-Nonachlor	0.0130	(0.0037, 0.1001)
Oxychlordane	0.0033	(0.0012, 0.0371)
Total PCBs	0.1971	(0.0660, 0.4981)

\*The detected levels of aluminum may have been artificially inflated by the use of aluminum foil in the packaging and storage of samples (See Collection of Samples and Laboratory Analysis Sections).

## Magnitude of Exposure

The benchmark toxicological values for the 16 contaminants that were available from Sample et al. (1996) are presented in Table 8. Table 14 shows the percentage of sites in which the NOAEL benchmark values were exceeded by Small Target Species, by factors of 1 or 10, and which NOAEL benchmark values were not exceeded by Small Target Species. Figures 4 through 11 show the locations of the sites that exceeded the benchmark values for As, Cr, Hg, Pb, Se, Zn, DDT and metabolites and Total PCBs. Because the NOAEL benchmark value for Se was less than 50% of the detection limit for Se, then the concentration of Se in the Small Target Species tissue samples exceeds the NOAEL benchmark value at all 70 sites. Thus, the map for Se indicates the sites where NOAEL values were exceeded but were below the detection limit and those sites where NOAEL values were exceeded and were also above the detection limit. Maps were not produced for those analytes whose NOAEL benchmark values were not exceeded at any sites (i.e., Cd, Cu, Ni, chlordane, dieldrin, endosulfan, endrin and gamma-BHC).

## Location of Sites Exceeding Toxicological Benchmark Values

Of the sites from which Small Target Species tissue samples were collected, 70 (100%) exceeded at least one of the 16 NOAEL toxicological benchmark values (Table 15). The location of the sites and the number of NOAEL benchmark values exceeded at those sites are shown in Figure 12. Figure 13 shows the locations of the sites that exceeded the NOAEL benchmark values for both metal and organic contaminants. Note that this map reflects the pervasiveness of DDT and its metabolites. Be-

**Table 11.** Percentage of Sites at which Small Target Species Exhibited Exposure to Contaminants Above Detection Limits (N=70)

Contaminant	% of sites exposed
*Aluminum	100.0
Arsenic	5.7
Cadmium	38.6
Chromium	100.0
Copper	100.0
Lead	51.4
Mercury	84.3
Nickel	70.0
Selenium	4.3
Zinc	100.0
o,p'-DDD	71.4
o,p'-DDE	28.6
o,p'-DDT	62.9
p,p'-DDD	75.7
p,p'-DDT	10.0
p,p'-DDE	100.0
	15.7
Dieldrin	100.0
Endosulfan I	7.1
Endosulfan II	18.6
Endrin	11.4
Heptachlor	14.3
Heptachlor epoxide	65.7
Hexachlorobenzene	81.4
BHC -alpha	12.9
BHC-beta	7.1
BHC-delta	2.9
BHC-gamma	25.7
alpha-Chlordane	77.1
gamma-Chlordane	72.9
cis-Nonachlor	88.6
trans-Nonachlor	100.0
Oxychlordane	90.0
Mirex	11.4

\*The detected levels of aluminum may have been artificially inflated by the use of aluminum foil in the packaging and storage of samples (See Collection of Samples and Laboratory Analysis Sections).

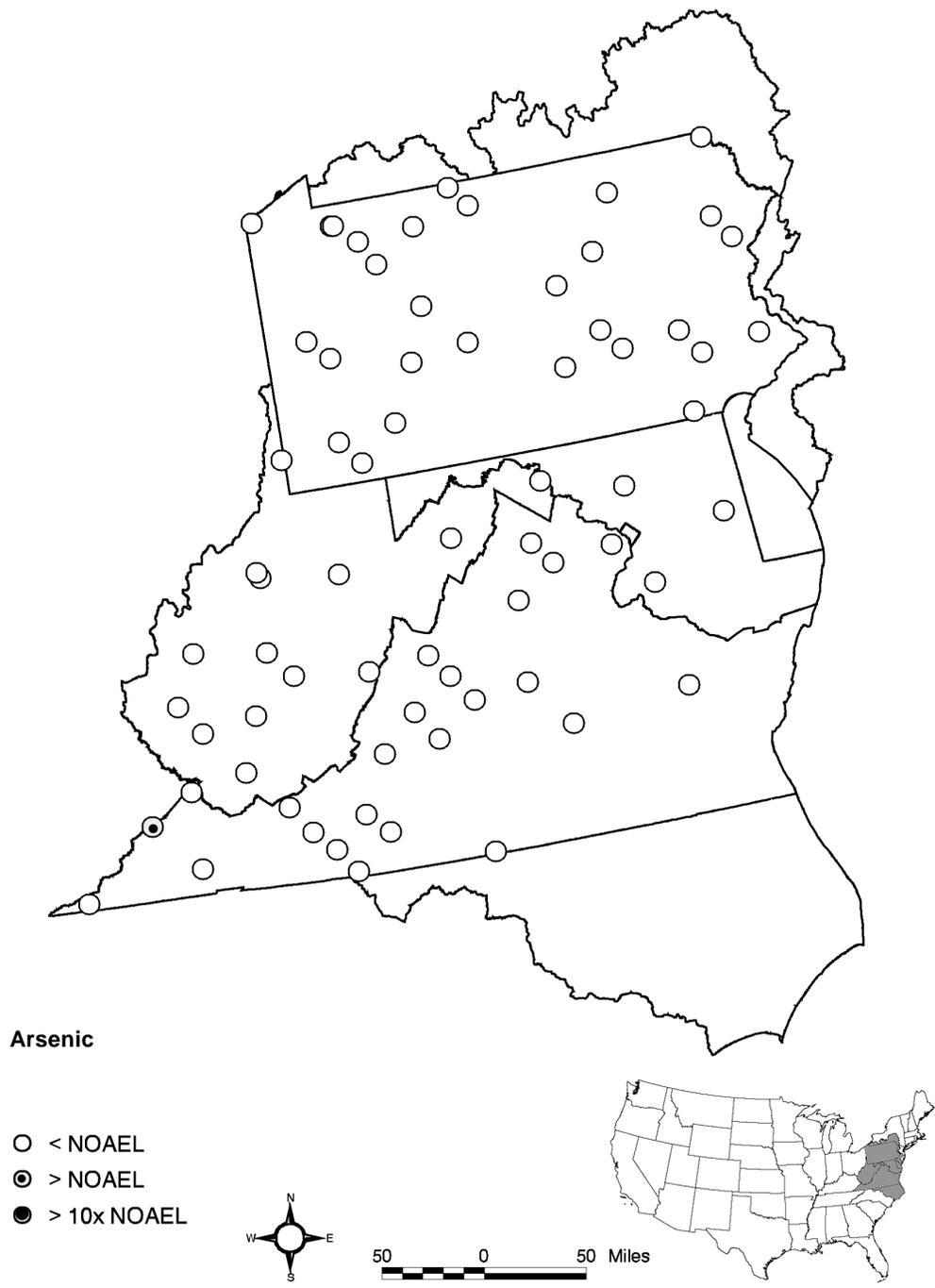
**Table 12.** Percentage of Sites at which Large Target Species Exhibited Exposure to Contaminants Above Detection Limits (N=47)

Contaminant	% of sites exposed
*Aluminum	100.0
Arsenic	2.1
Cadmium	44.7
Chromium	100.0
Copper	100.0
Lead	63.8
Mercury	87.2
Nickel	78.7
Selenium	2.1
Zinc	100.0
o,p'-DDD	61.7
o,p'-DDE	14.9
o,p'-DDT	55.3
p,p'-DDD	78.7
p,p'-DDT	72.3
p,p'-DDE	100.0
	8.5
Dieldrin	93.6
Endosulfan I	6.4
Endosulfan II	19.1
Endrin	4.3
Heptachlor	4.3
Heptachlor epoxide	57.4
Hexachlorobenzene	63.8
BHC -alpha	10.6
BHC-beta	0.0
BHC-delta	0.0
BHC-gamma	23.4
alpha-Chlordane	68.1
gamma-Chlordane	57.4
cis-Nonachlor	87.2
trans-Nonachlor	100.0
Oxychlordane	91.5
Mirex	10.6

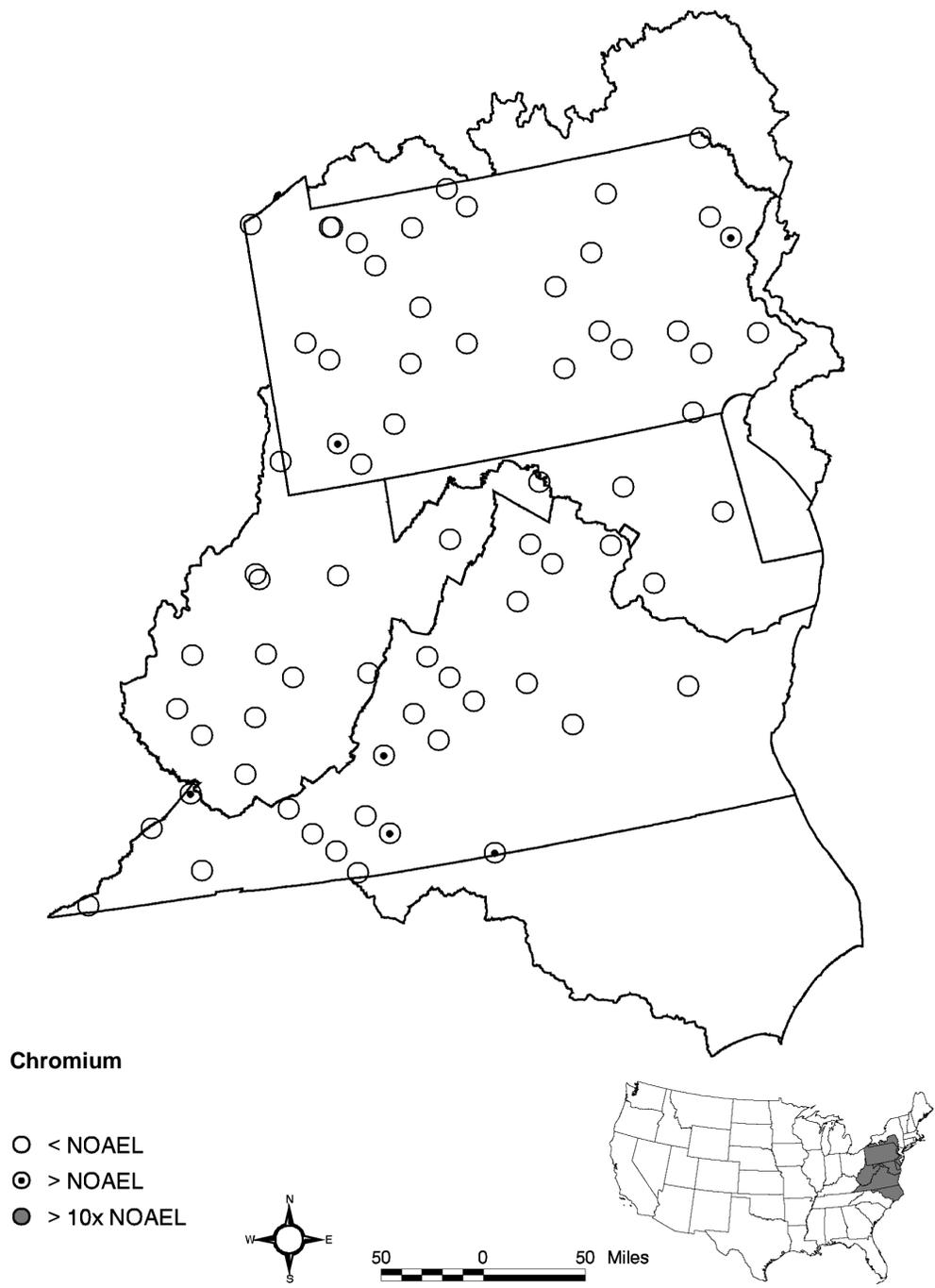
\*The detected levels of aluminum may have been artificially inflated by the use of aluminum foil in the packaging and storage of samples (See Collection of Samples and Laboratory Analysis Sections).

cause both Hg and Se exceed NOAEL values at a large number of sites, they were removed from the data set in order to produce the map shown in Figure 14. There were four sites that

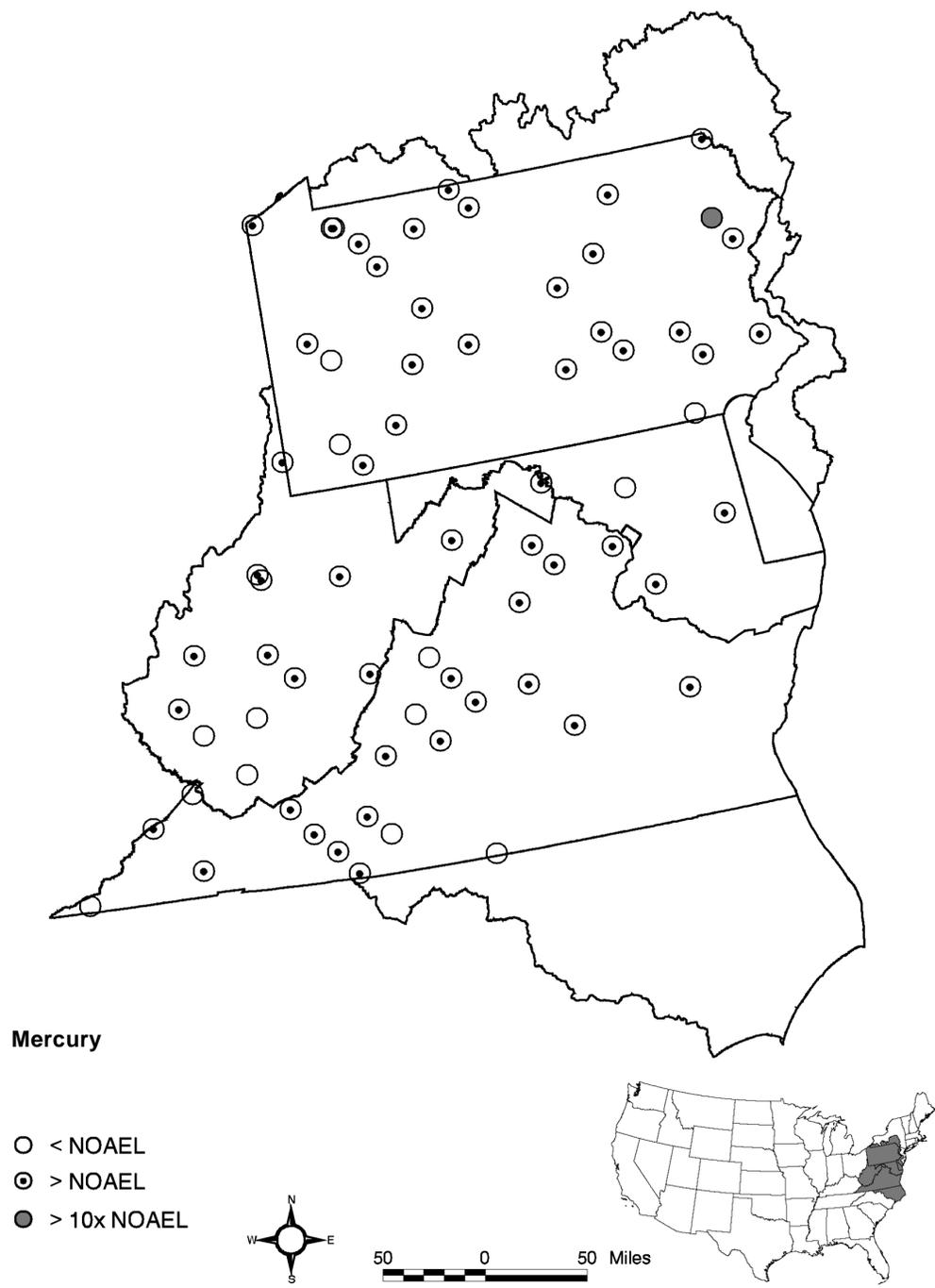
exceeded more than four NOAEL benchmark values. One of these sites was a first order stream, one was a second order stream and two were third order streams (Table 16).



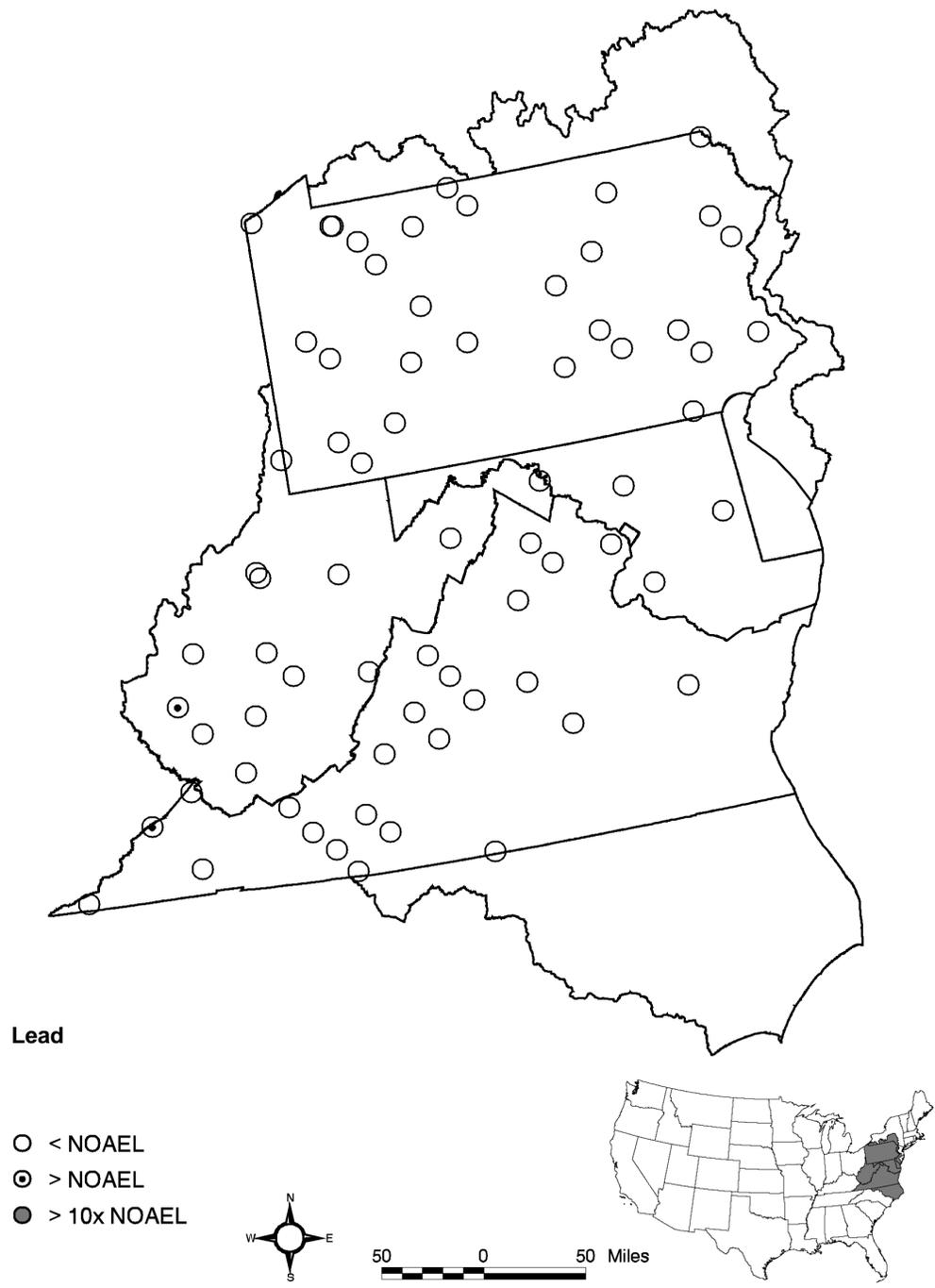
**Figure 4.** The location of the site at which the concentration of arsenic in the small target species tissue sample exceeded the NOAEL benchmark value for the belted kingfisher.



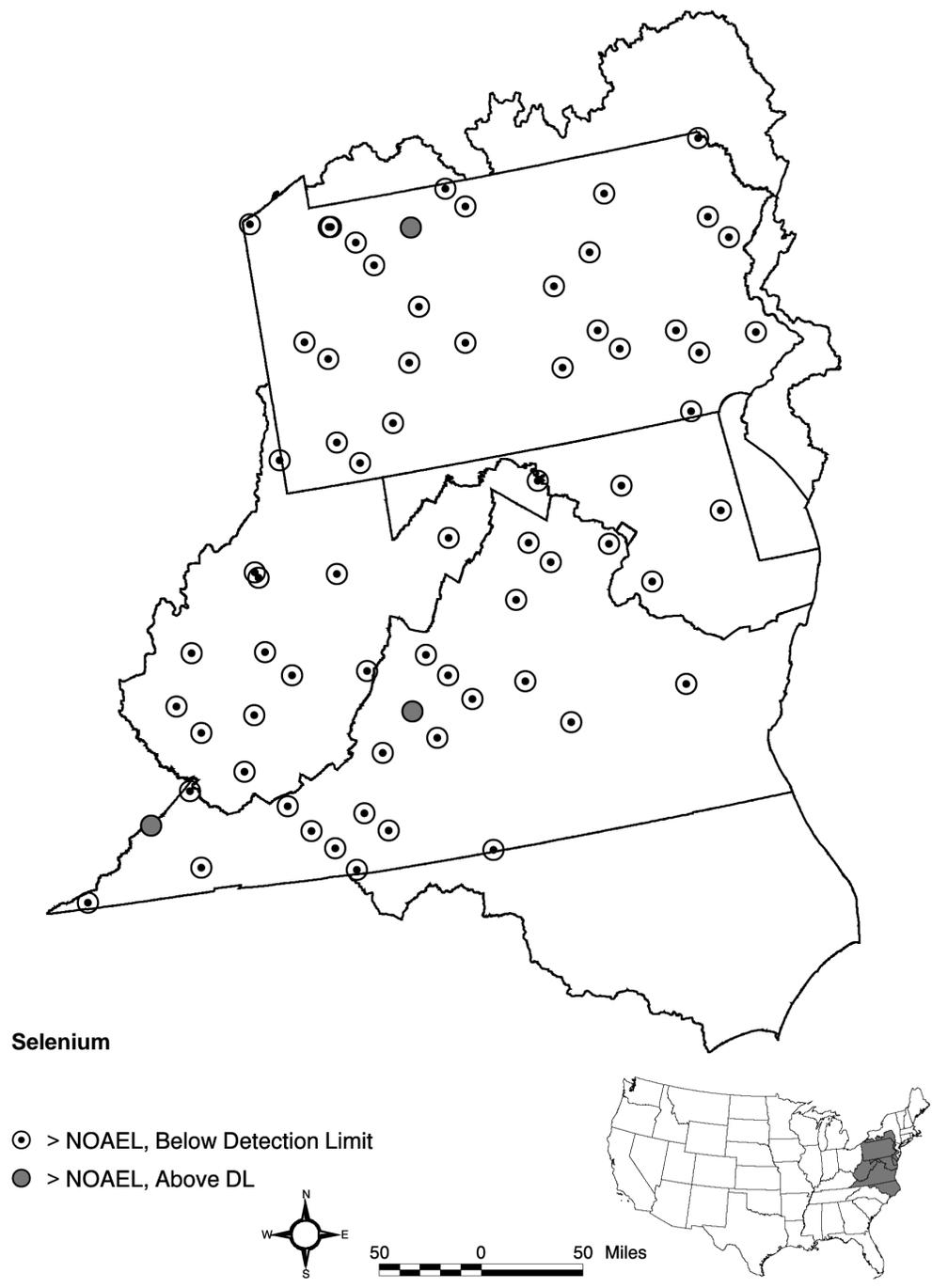
**Figure 5.** The locations of the sites at which the concentrations of chromium in small target species tissue samples exceeded the NOAEL benchmark value for the belted kingfisher.



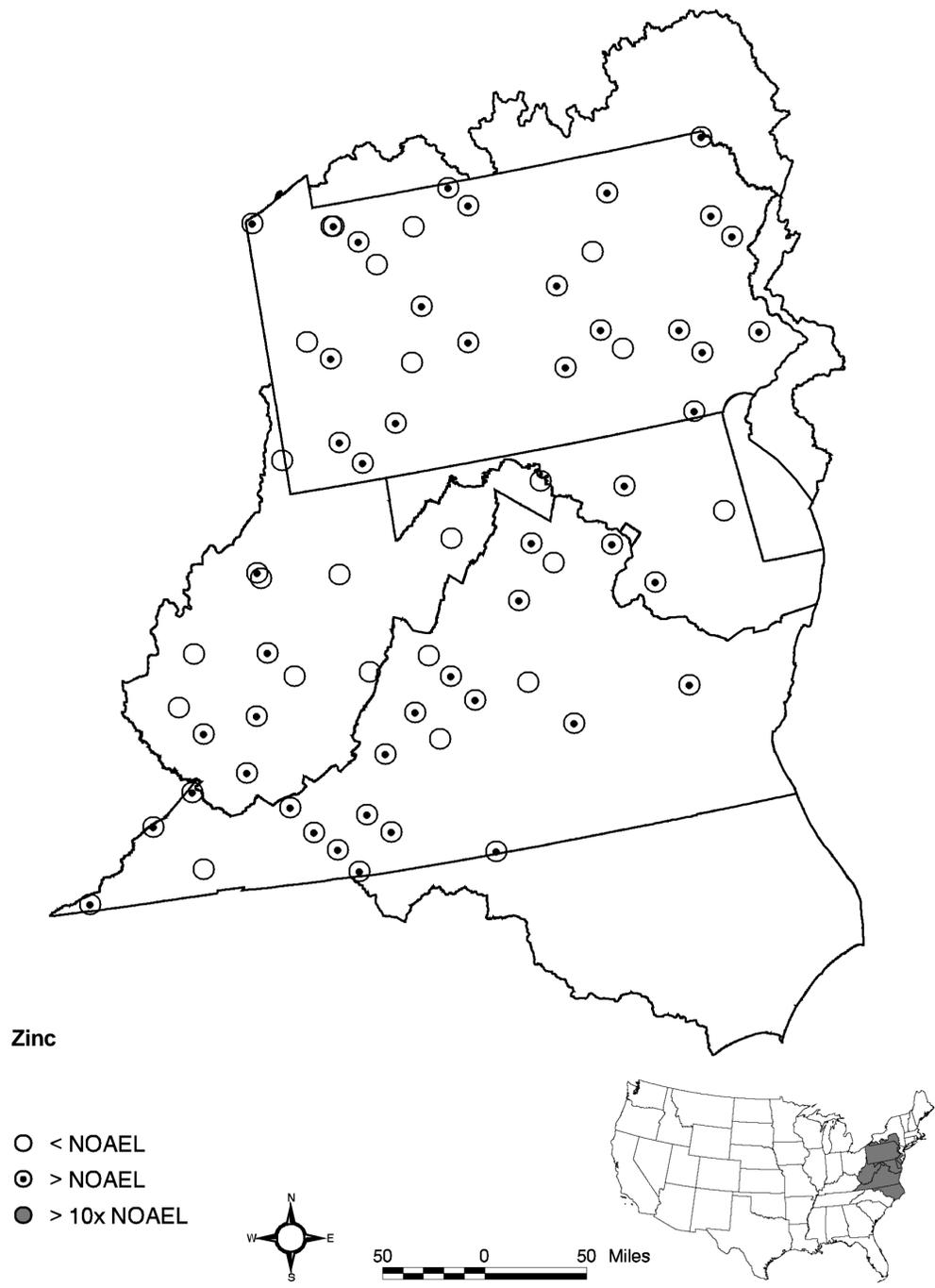
**Figure 6.** The locations of the sites at which the concentrations of mercury in small target species tissue samples exceeded the NOAEL benchmark value for the belted kingfisher.



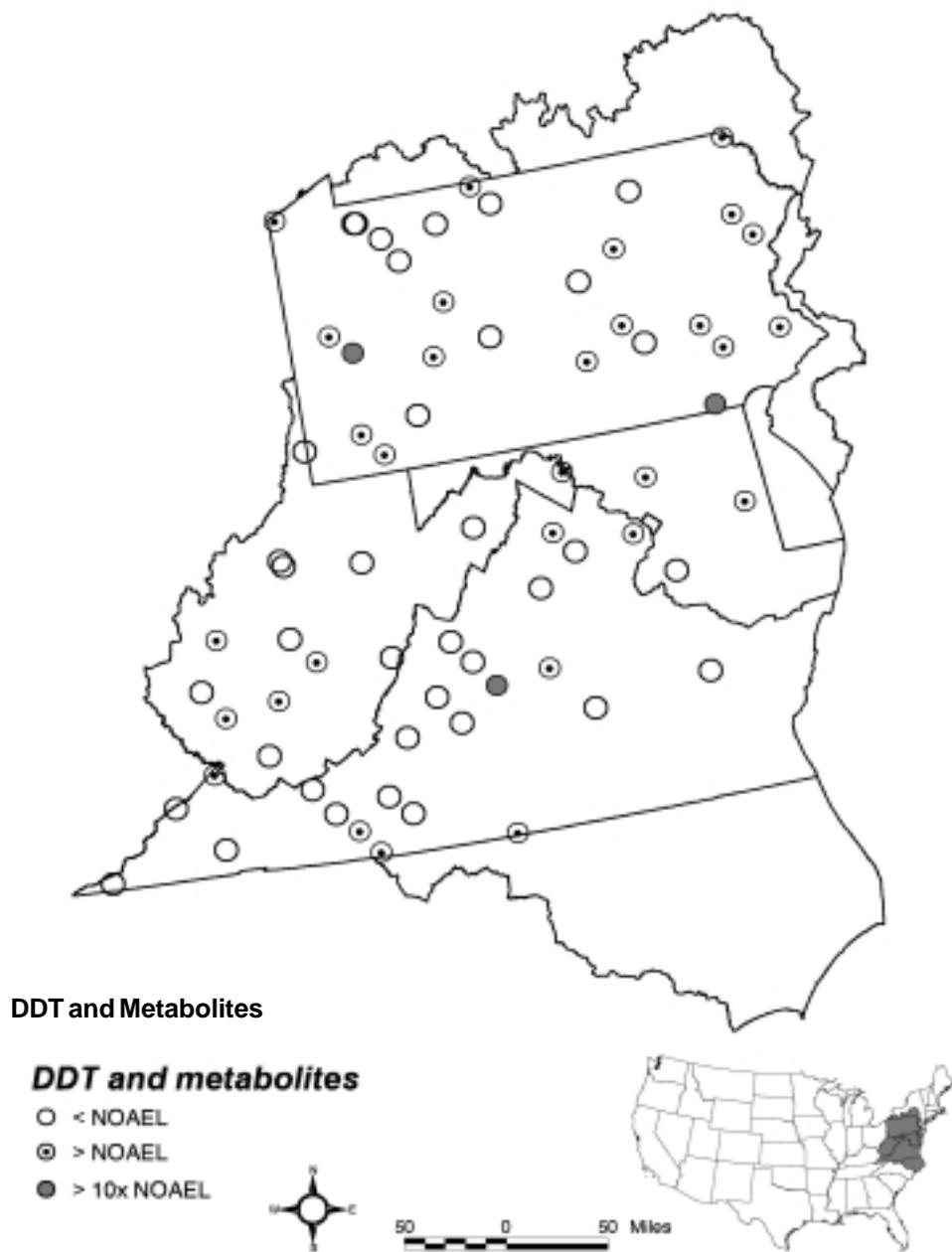
**Figure 7.** The locations of the sites at which the concentrations of lead in small target species tissue samples exceeded the NOAEL benchmark value for the belted kingfisher.



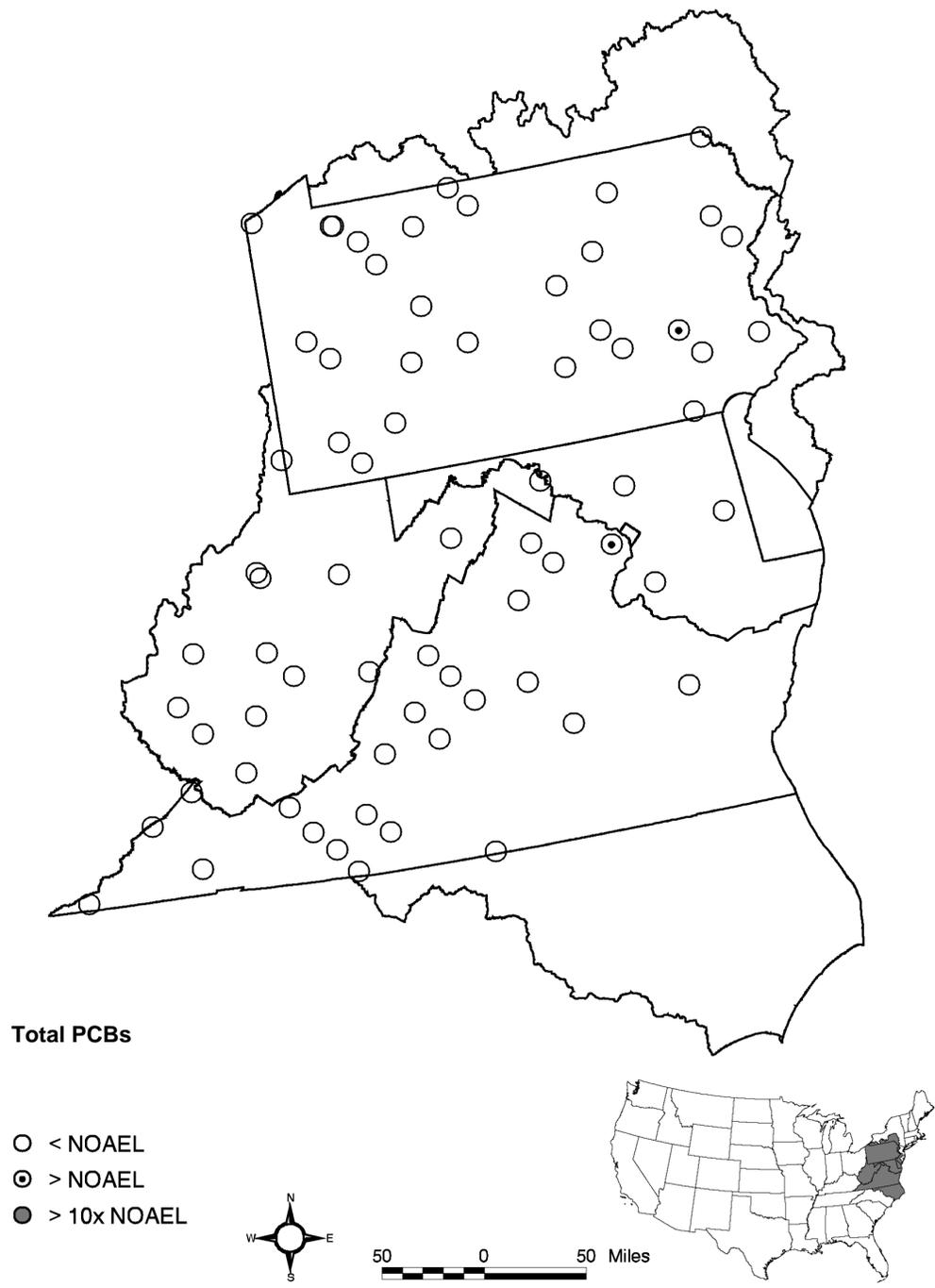
**Figure 8.** The locations of sites at which the concentrations of selenium in small target species tissue samples exceeded the NOAEL benchmark value for the belted kingfisher.



**Figure 9.** The locations of the sites at which the concentrations of zinc in small target species tissue samples exceeded the NOAEL benchmark value for the belted kingfisher.



**Figure 10.** The locations of the sites at which the concentrations of DDT and its metabolites in small target species tissue samples exceeded the NOAEL benchmark value for the belted kingfisher.



**Figure 11.** The locations of the sites at which the concentrations of total PCBs in small target species tissue samples exceeded the NOAEL benchmark value for the belted kingfisher.

**Table 13.** Number of Sites at which Small Target Species, Large Target Species, neither or both Exhibited Exposure to Contaminants Above Detection Limits (N=35)

Contaminant	Both	None	Small	Large
*Aluminum	35	0	0	0
Arsenic	0	34	0	1
Cadmium	10	15	3	7
Chromium	35	0	0	0
Copper	35	0	0	0
Lead	21	9	2	3
Mercury	22	3	2	8
Nickel	24	6	0	5
Selenium	0	32	2	1
Zinc	35	0	0	0
o,p'-DDD	19	7	6	3
o,p'-DDE	4	23	6	2
o,p'-DDT	19	8	7	1
p,p'-DDD	25	3	4	3
p,p'-DDT	3	9	1	22
p,p'-DDE	27	0	6	2
	2	29	3	1
Dieldrin	32	0	3	0
Endosulfan I	2	29	3	1
Endosulfan II	6	27	1	1
Endrin	1	32	2	0
Heptachlor	1	28	6	0
Heptachlor epoxide	19	9	6	1
Hexachlorobenzene	20	4	10	1
BHC-alpha	1	32	1	1
BHC-beta	0	34	1	0
BHC-delta	0	35	0	0
BHC-gamma	7	26	2	0
alpha-Chlordane	23	3	7	2
gamma-Chlordane	22	8	5	0
cis-Nonachlor	30	2	1	2
trans-Nonachlor	35	0	0	0
Oxychlordane	28	2	1	4
Mirex	3	28	2	2

\*The detected levels of aluminum may have been artificially inflated by the use of aluminum foil in the packaging and storage of samples (See Collection of Samples and Laboratory Analysis Sections).

## Discussion and Conclusions

While smaller species of fish are more prevalent in small streams, tissue from small

**Table 14.** Percentage of Sites that were Less than or Exceeded the NOAEL Benchmark Values and the Degree to which they were Exceeded. These Percentages are Based on Small Target Species Tissue Samples (N=70)

Contaminant	<NOAEL	>1x NOAEL	>10x NOAEL
Arsenic	98.6	1.4	0.0
Cadmium	100.0	0.0	0.0
Chromium	91.4	8.6	0.0
Copper	100.0	0.0	0.0
Mercury	18.6	80.0	1.4
Nickel	100.0	0.0	0.0
Lead	97.1	2.9	0.0
*Selenium	0.0	100.0	0.0
Zinc	31.4	68.6	0.0
Chlordane	100.0	0.0	0.0
Dieldrin	100.0	0.0	0.0
DDT & metabolites	52.9	42.9	4.3
Endosulfan	100.0	0.0	0.0
Endrin	100.0	0.0	0.0
gamma-BHC	100.0	0.0	0.0
Total PCBs	97.1	2.9	0.0

\*The 50% value of the detection limit for Selenium is greater than the reported NOAEL value.

fishes has rarely been collected and analyzed for contaminants as an indicator of exposure to fish or their predators. The data presented here demonstrate the usefulness of small fish, as well as larger fish in larger streams, as indicators of exposure to contaminants, especially those contaminants that are persistent and bioaccumulate.

A number of contaminants were measured above detection limits at more than half of the sites that were sampled (Table 3). Among these were Hg, Zn, DDT metabolites, PCBs, dieldrin and chlordane, some of which may be irreversibly accumulating in the ecosystem or have very slow rates of decomposition. A subset of contaminants that were widely distributed also occurred at levels that exceeded NOAEL benchmark values for the belted kingfisher. DDT, Hg and Zn concentrations exceeded NOAEL

**Table 15.** Numbers and Percentages of Sites with Varying Numbers of Contaminants Exceeding the NOAEL Benchmark Values

Number of contaminants exceeding NOAEL	Number of sites	Percentage of sites
0	0	0.0
1	1	1.4
2	15	21.4
3	32	45.7
4	18	25.7
5	4	5.7

benchmark values at greater than 40% of the sites where small target species were collected (Table 14). The widespread occurrences of these contaminants (Figures 12 through 14) suggests the influence of non-point sources of pollution (e.g., agriculture and atmospheric deposition) should be investigated.

The number of sites exceeding NOAEL benchmarks for mercury, DDT and PCB values (Table 14) suggests a comprehensive study of fish tissue contaminants is warranted for the region. While the NOAEL values are very conservative estimations of the effects of a polluted food source on belted kingfishers, they are useful indicators of excess contamination.

Low values for fish contaminants do not necessarily mean absence of contaminants and their sources. Low values of contaminants in fish

tissue can occur when the exposure pathway is incomplete. For instance, it is possible that even when mercury sources are uniformly distributed throughout a region, higher methylation and, hence, higher bioaccumulation may occur in response to the nutrient and dissolved organic carbon (DOC) status of the stream. (Krabbenhof et al. 1999, Krabbenhof and Weiner 1999; Weiner and Krabbenhof 1999; Eisler 2000).

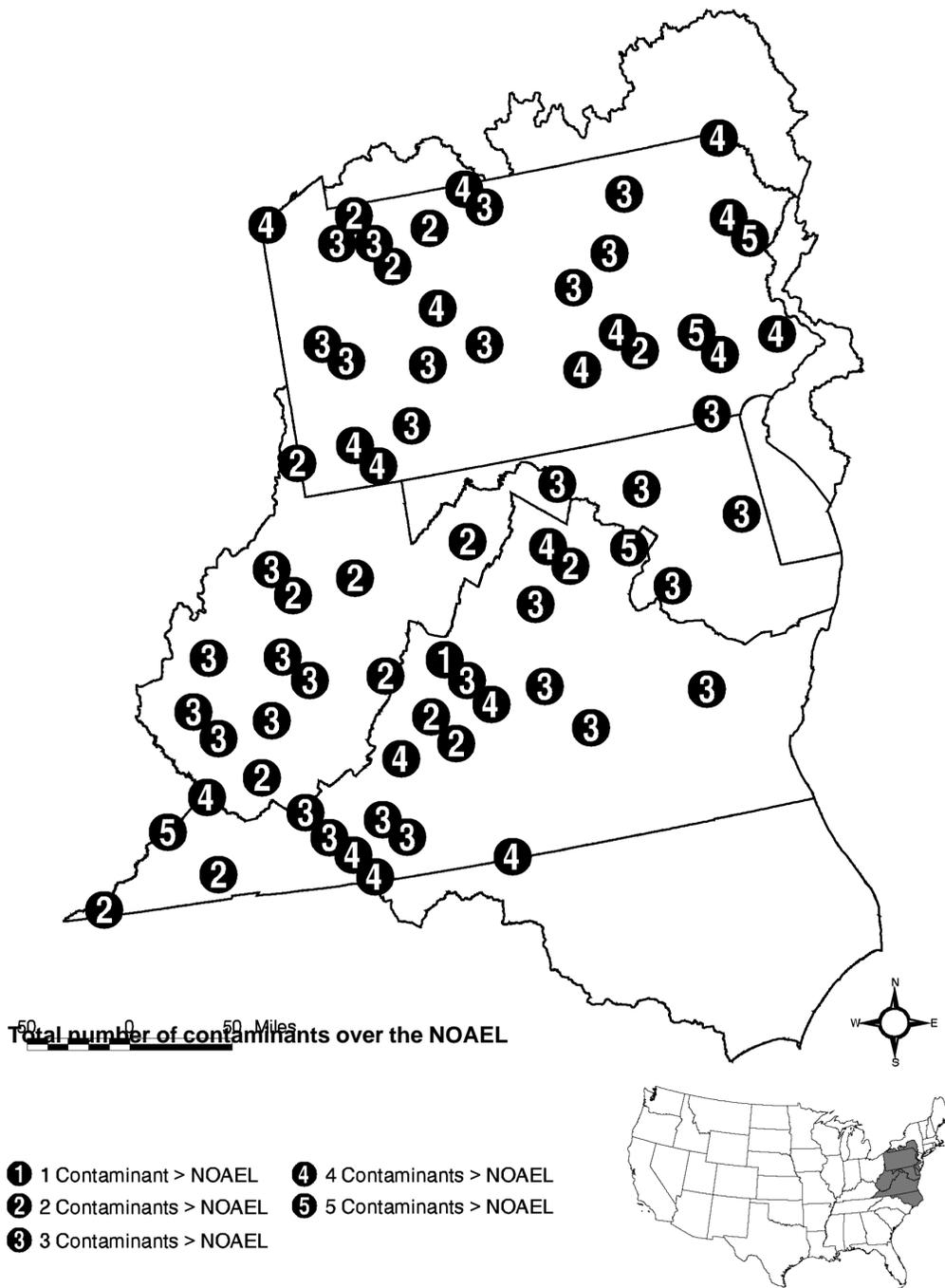
Characterizing the presence of Se is problematic. More than half of the sites did not have values that met or exceeded the detection limit for Se. However, Se is highly toxic to wildlife. In fact, the NOAEL benchmark value for Se was less than half of its detection limit. Thus, no measurements could be reported below the NOAEL. As a precaution and because no screening was possible, Se is reported at or above its NOAEL at every site sampled for small target species. To identify sites with safe values of Se in fish tissues, analytical methods are needed that have detection limits that are at least ten times lower.

In using the information provided in this report, several factors should be kept in mind. One factor is that it is known that different fish species bioaccumulate contaminants at different rates. Rubinstein et al. (1984) demonstrated in a controlled laboratory experiment that three

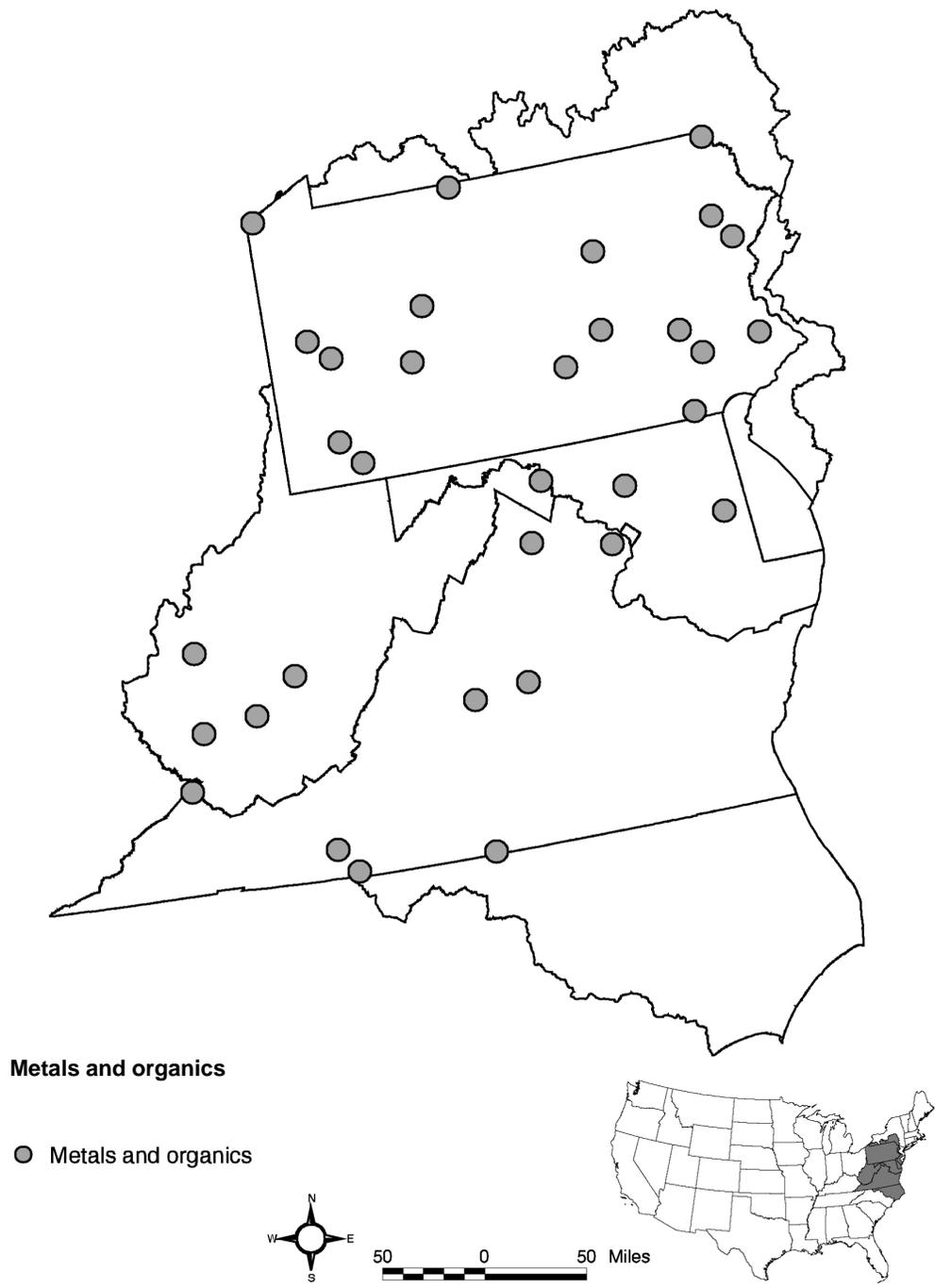
**Table 16.** Sites which Exceeded Five or More NOAEL Benchmark Values with their Respective Stream Orders and Selected Contaminant Levels

No. chemicals over benchmark	Stream order	Arsenic (µg/g)	Chromium (µg/g)	Mercury (µg/g)	Lead (µg/g)	Selenium (µg/g)	Zinc (µg/g)	DDT (µg/g)	Total PCBs (µg/g)
5	1	3.750*	1.130	0.079	1.250*	3.750*	36.430	0.018	0.498
5	2	5.1000	1.190	0.047	2.640	4.880	34.140	0.004	0.088
5	3	3.750*	1.360	0.053	0.080	3.750*	45.930	0.055	0.508
5	3	3.750*	3.030	0.066	0.030*	3.750*	30.700	0.016	0.069

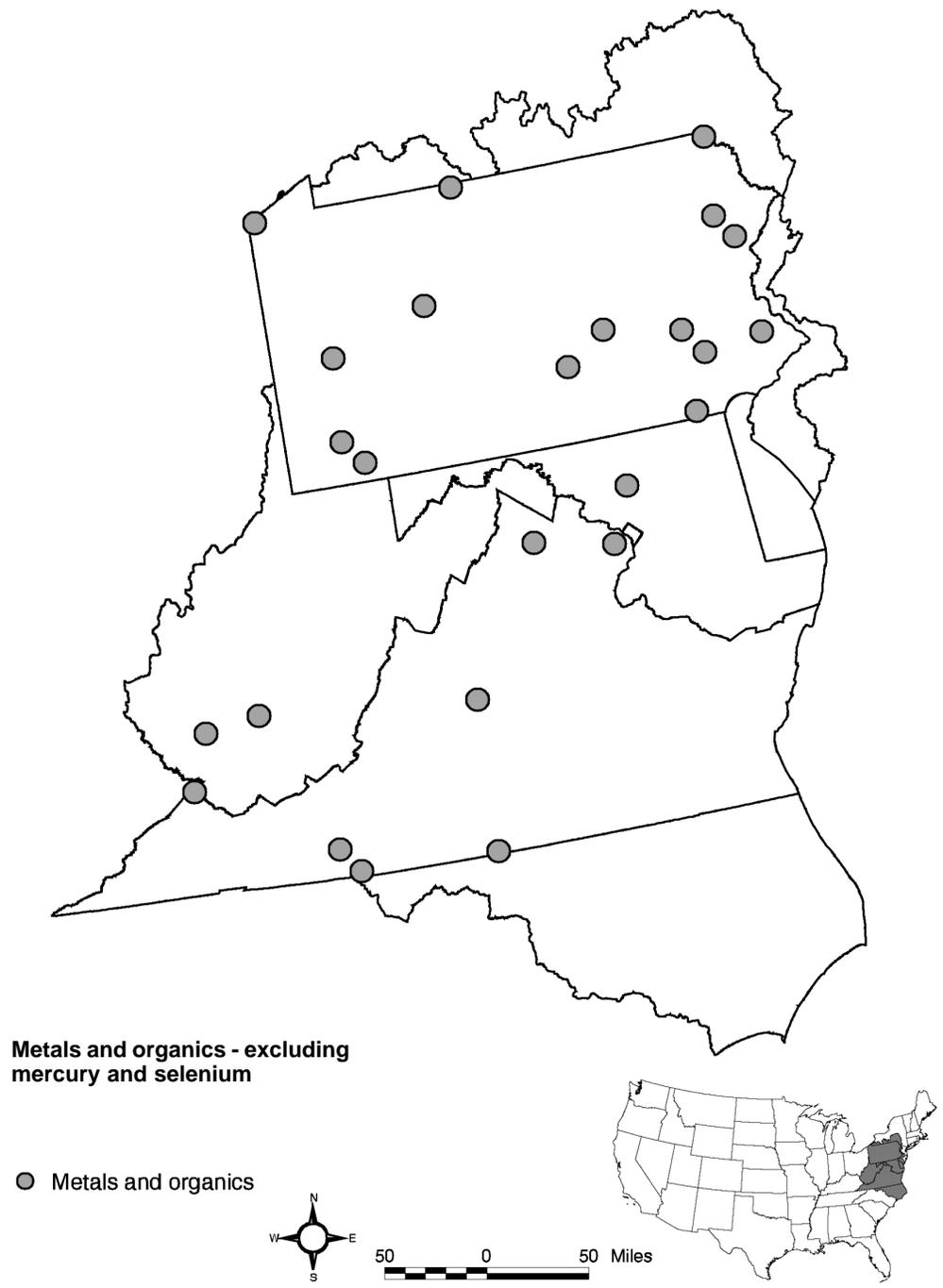
\*The concentration of the contaminant was below the detection limit. The value given is the detection limit.



**Figure 12.** The locations of the sites at which the concentrations of contaminants in small target species tissue samples exceeded at least one NOEL benchmark value and the number of benchmark values that were exceeded.



**Figure 13.** The locations of the sites at which the concentrations of both organic and metal contaminants in small target species tissue samples exceeded at least one NOAEL benchmark value.



**Figure 14.** The locations of the sites at which the concentrations of both organic and metal (excluding Hg and Se) contaminants in small target species tissue samples exceeded at least one NOEL benchmark value.

different fish species bioaccumulated PCBs at different rates. Williams and Eddy (1986) noted that common carp and tench (*Tinca tinca*) had low Cl uptake rates and were more resistant to NO<sub>2</sub> than rainbow trout (*Oncorhynchus mykiss*), perch (*Perca* spp.), and northern pike (*Esox lucius*) which had higher Cl uptake rates. Also, it is generally reported that for hydrophobic chemicals (e.g., chlorinated hydrocarbon pesticides) and mercury, greater bioaccumulation occurs in organisms with higher lipid content. This increases the importance of collecting fish during a season in which reproductive activities, feeding habits or other influences have not affected the lipid content of the sampled organisms (USEPA 1992, 1993a). In a study by the USEPA's National Study of Chemical Residues in Fish (NSCRF), it was found that bottom-feeding fish and game fish bioaccumulated different dioxins, furans and xenobiotic compounds at very different rates (USEPA 1992). Therefore, the white sucker from the Large Target Species list would accumulate chemicals at a very different rate than a species of bass or trout, which are also on the Large Target Species list.

Although it is known that fish bioaccumulate contaminants at different rates, it is not known how the bioaccumulation rates among the species used for this study may differ. The American Fisheries Society's PCB subcommittee advised against assuming that a bioaccumulation factor that was developed for contaminants in one waterbody would be applicable to other waterbodies. The authors state that the amount of bioaccumulation that occurs for a given concentration of a chemical in the water column or in the sediments is usually site-specific and, therefore, should not be inferred to remain the same at other sites (Veith et al., 1979). Thus, it is difficult to accurately compare sites when those comparisons are based

on the contaminant levels found in different species. The life histories of large fish are generally different from the life histories of smaller fish. It would be imprudent to compare sites based on different contaminant levels found in the two target categories of fish or any two species.

Human health studies have taken a different approach to measuring dietary exposure to chemical contaminants (Thomas et al. 1997). In this approach, composited samples that represent actual diet are analyzed for chemical contaminants. Sampling could be adapted for assessments of wildlife that take into account that different species of fish may have different concentrations of contaminants and wildlife ingest a variety of food items. The critical component is obtaining a representative dietary sample. A representative sample would consist of prey items in the proportion likely to be caught by the predator. A simplifying assumption is that predators take prey in the proportion to the occurrence in the total fish assemblage. This approach would permit sites to be compared on the basis of potential exposure of predators to contaminants in fish.

This report describes fish tissue contaminant data collected from randomly-selected sites in the Mid-Atlantic Region. The report is intended to be used to screen exposure levels for fish and wildlife. An alternative approach could have used a subset of the data from the Mid-Atlantic Highlands to represent the proportion of stream miles with various levels of fish tissue contamination. However, this alternative approach was not used so that this report could present all of the data collected in 1993 and 1994, including data from areas outside of the Mid-Atlantic Highlands. These data also warrant further analysis of the associations of fish tissue contaminant levels with habitat and water chemistry factors and with invertebrate and fish assemblages.

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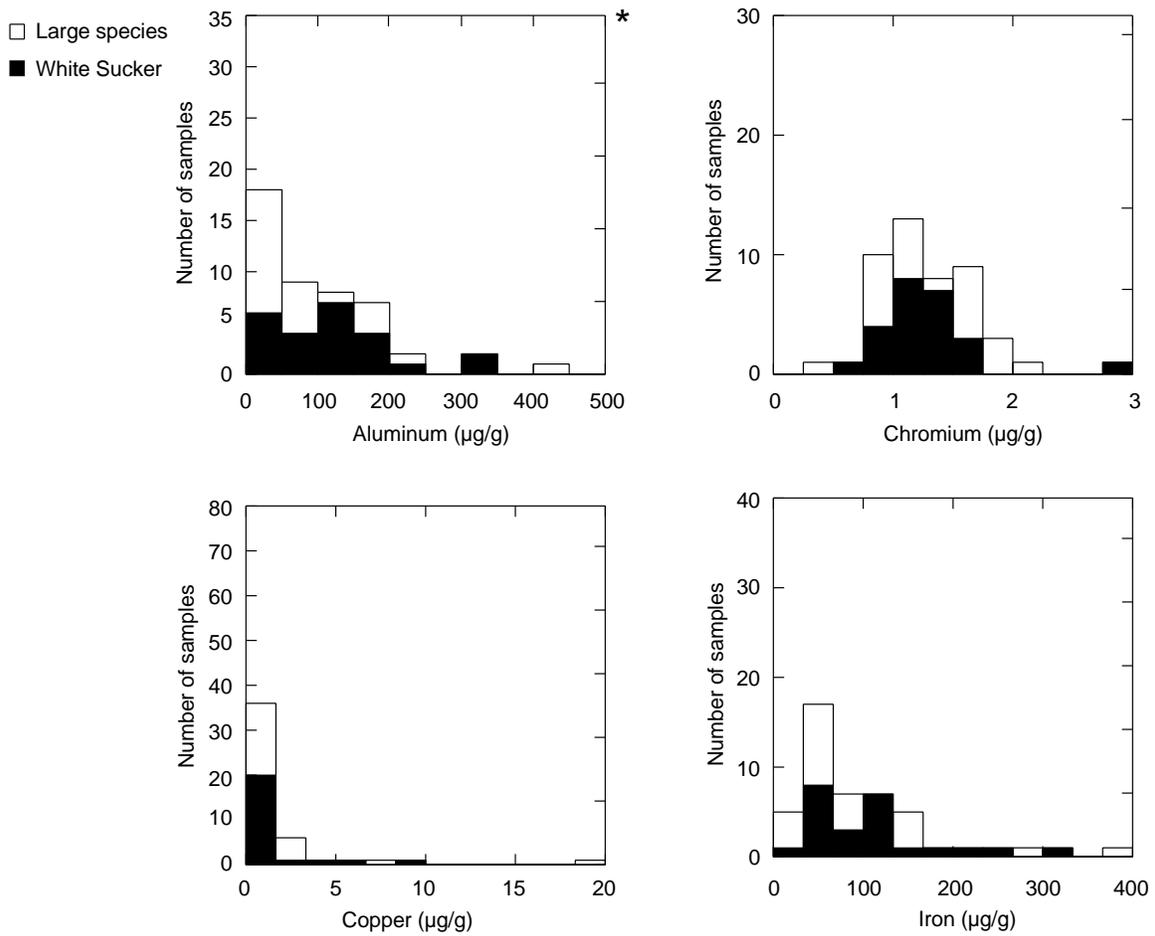
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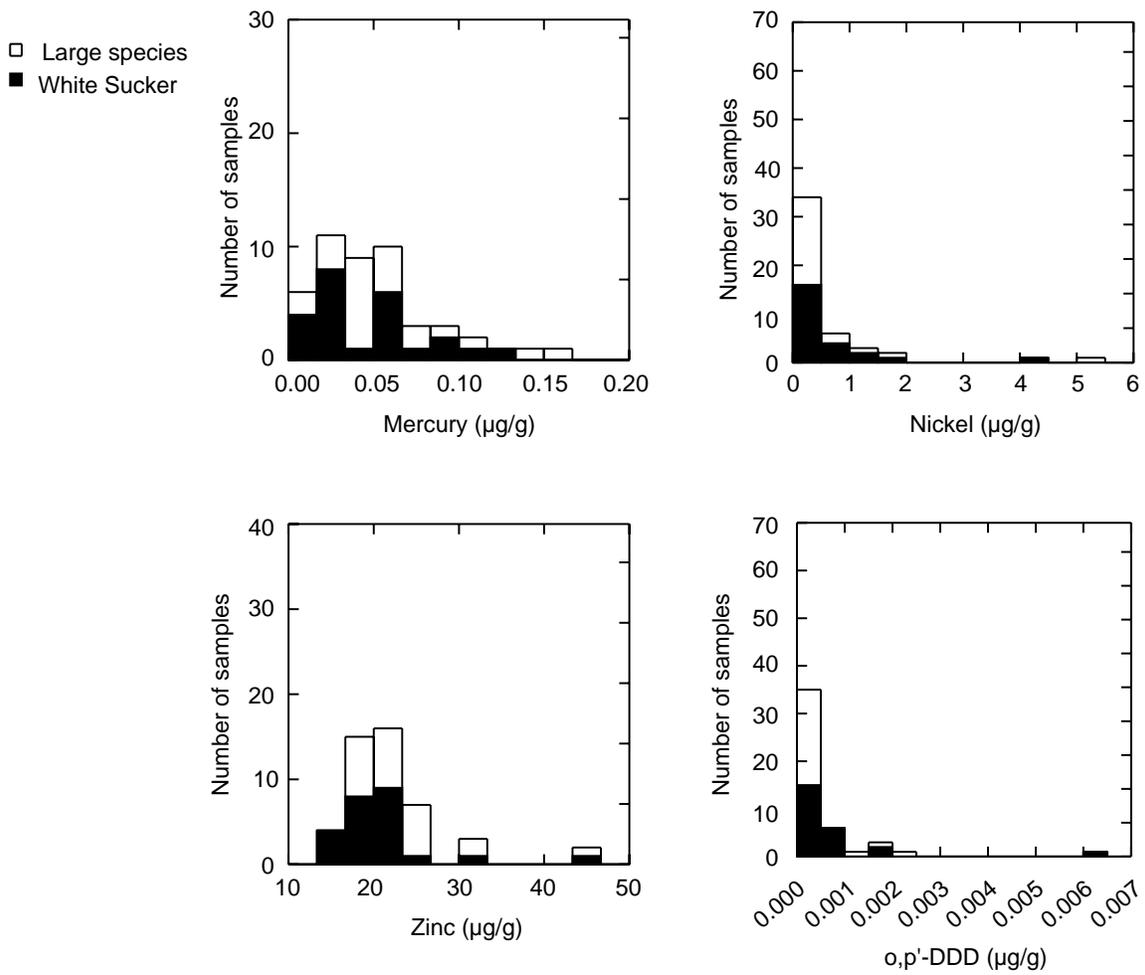
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Mottled Sculpin ( <i>Cottus bairdi</i> ) .....	2, 5
Nickel .....	8, 13, 16-18, 27, A3, B3, C3, C12, D8, E4
NOAA .....	10
NOAEL .....	ii, 12-14, 17, 19-31
Nonachlor .....	8, 13, 17, 18, 27, A6, B6, C9-10, C18-19, D20-21, E7
Oxychlorane .....	8, 13, 17, 18, 27, A6, B6, C10, D22, E2
PCB .....	1, 8-10, 13, 16, 17, 26-28, 32, A4 B4, C10, D23, E2
Congeners .....	8-10, 27
Perch ( <i>Perca</i> spp.) .....	32
Pike, Northern ( <i>Esox lucius</i> ) .....	32
Selenium .....	8, 9, 11-13, 17, 18, 23, 27, 28, 31, C4, C13
Shiner (F. Cyprinidae) .....	2, 5
Slimy Sculpin ( <i>Cottus cognatus</i> ) .....	2, 5
Sunfish (F. Centrarchidae, <i>Lepomis</i> spp.) .....	2, 5
Tench ( <i>Tinca tinca</i> ) .....	32
Trout (F. Salmonidae) .....	2, 5, 32
Rainbow ( <i>Oncorhynchus mykiss</i> ) .....	32
White Sucker ( <i>Catostomus commersoni</i> ) .....	2, 5, 7, 8, 10-12, 15, 16, 32,

**Appendix A**  
**Histogram Representations of the**  
**Proportion of the Large Target Species**  
**Category Made Up of White Sucker for**  
**Selected Analytes**

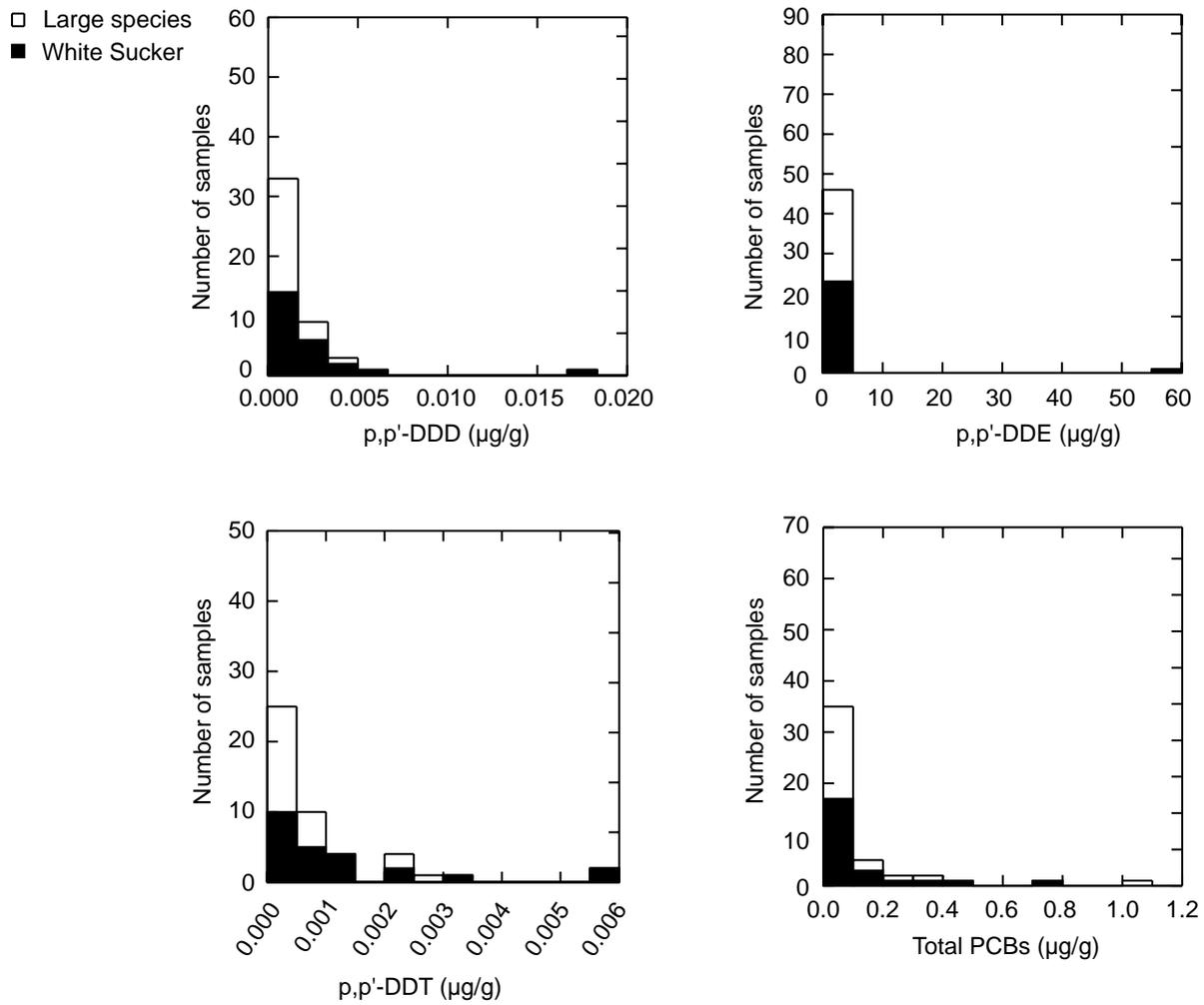


\*The detected levels of aluminum may have been artificially inflated by the use of aluminum foil in the packaging and storage of samples (See Collection of Samples and Laboratory Analysis Sections).

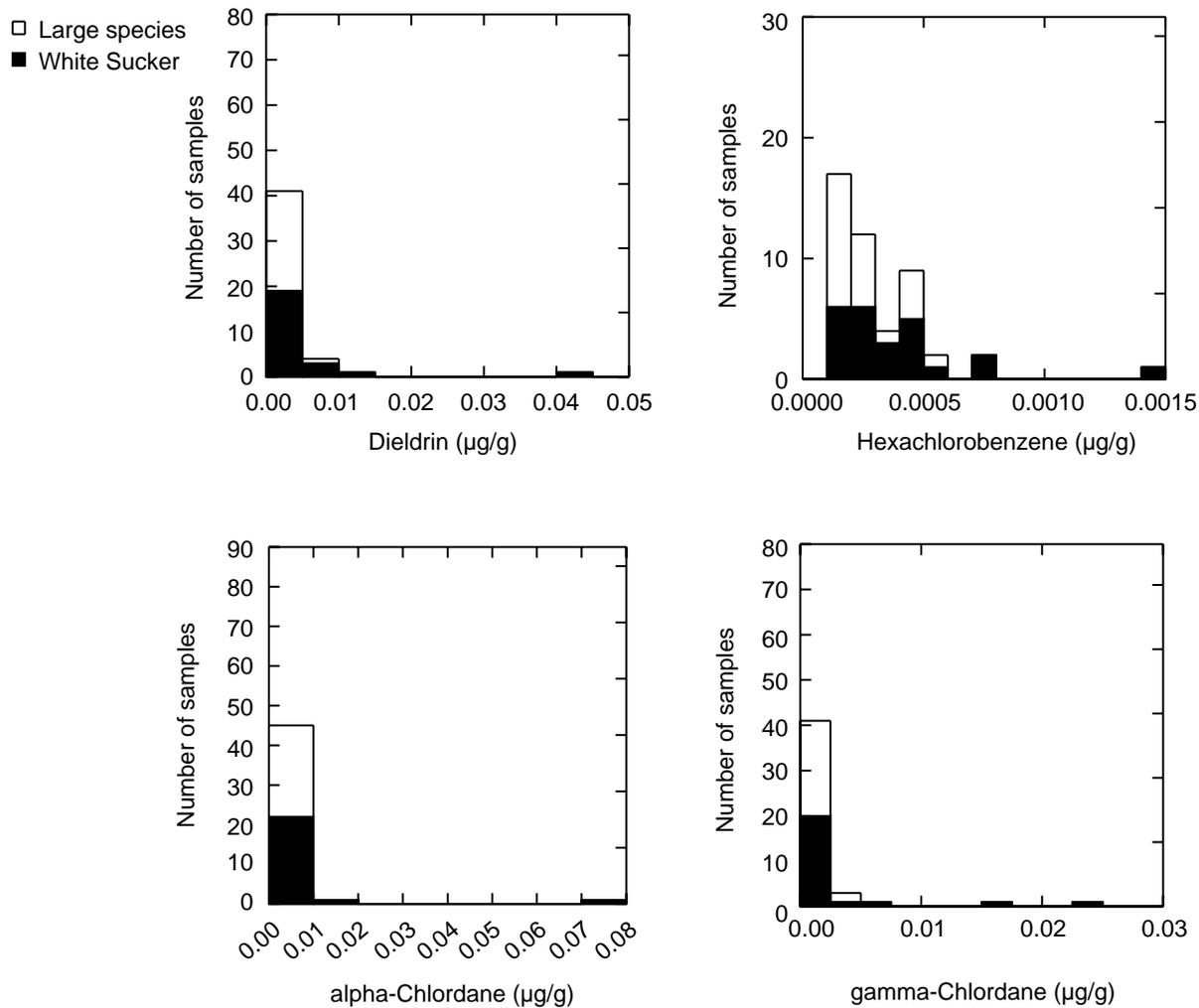
**Figure A-1.** Histogram representations of the proportion of the large target species category made up of white sucker for Al, Cr, Cu and Fe.



**Figure A-2.** Histogram representations of the proportion of the large target species category made up of white sucker for Hg, Ni, Zn, and o-p'-DDD.

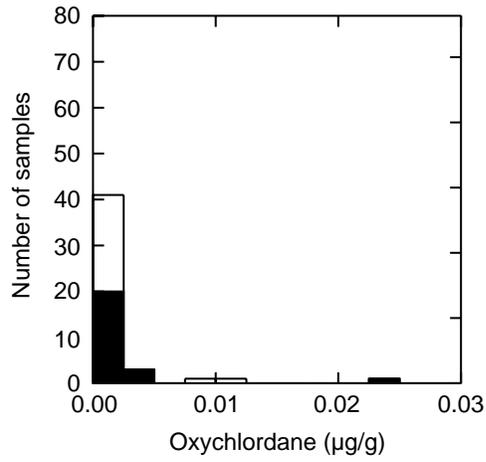
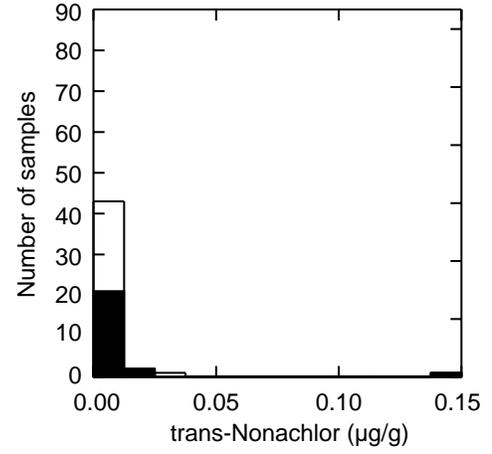
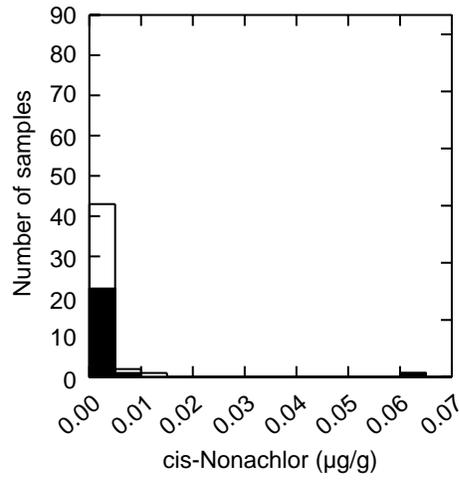


**Figure A-3.** Histogram representations of the proportion of the large target species category made up of white sucker for p,p'-DDD, p,p'-DDE, p,p'-DDT and total PCBs.



**Figure A-4.** Histogram representations of the proportion of the large target species category made up of white sucker for dieldrin, hexachlorobenzene, alpha-chlordane and gamma-chlordane.

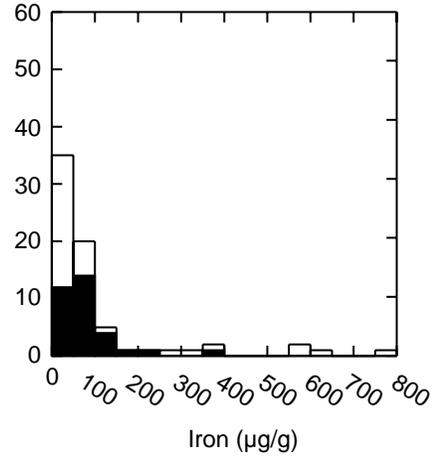
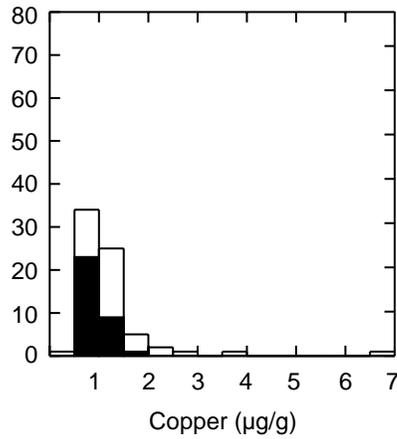
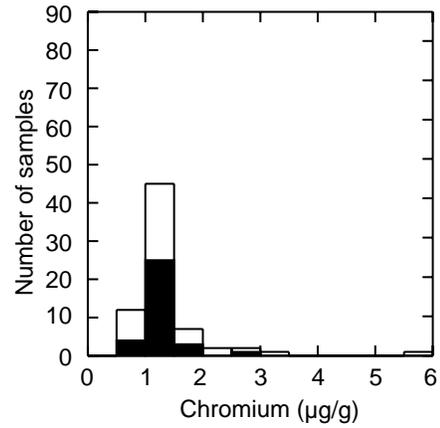
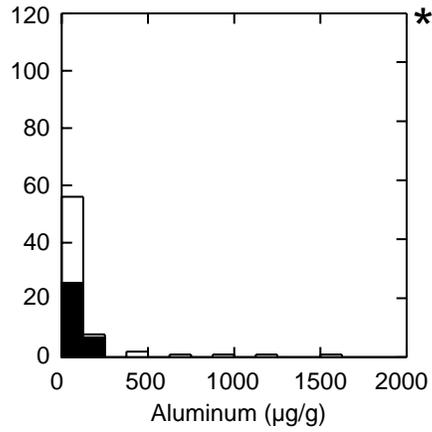
□ Large species  
■ White Sucker



**Figure A-5.** Histogram representations of the proportion of the large target species category made up of white sucker for cis-nonachlor, trans-nonachlor and oxychlordane.

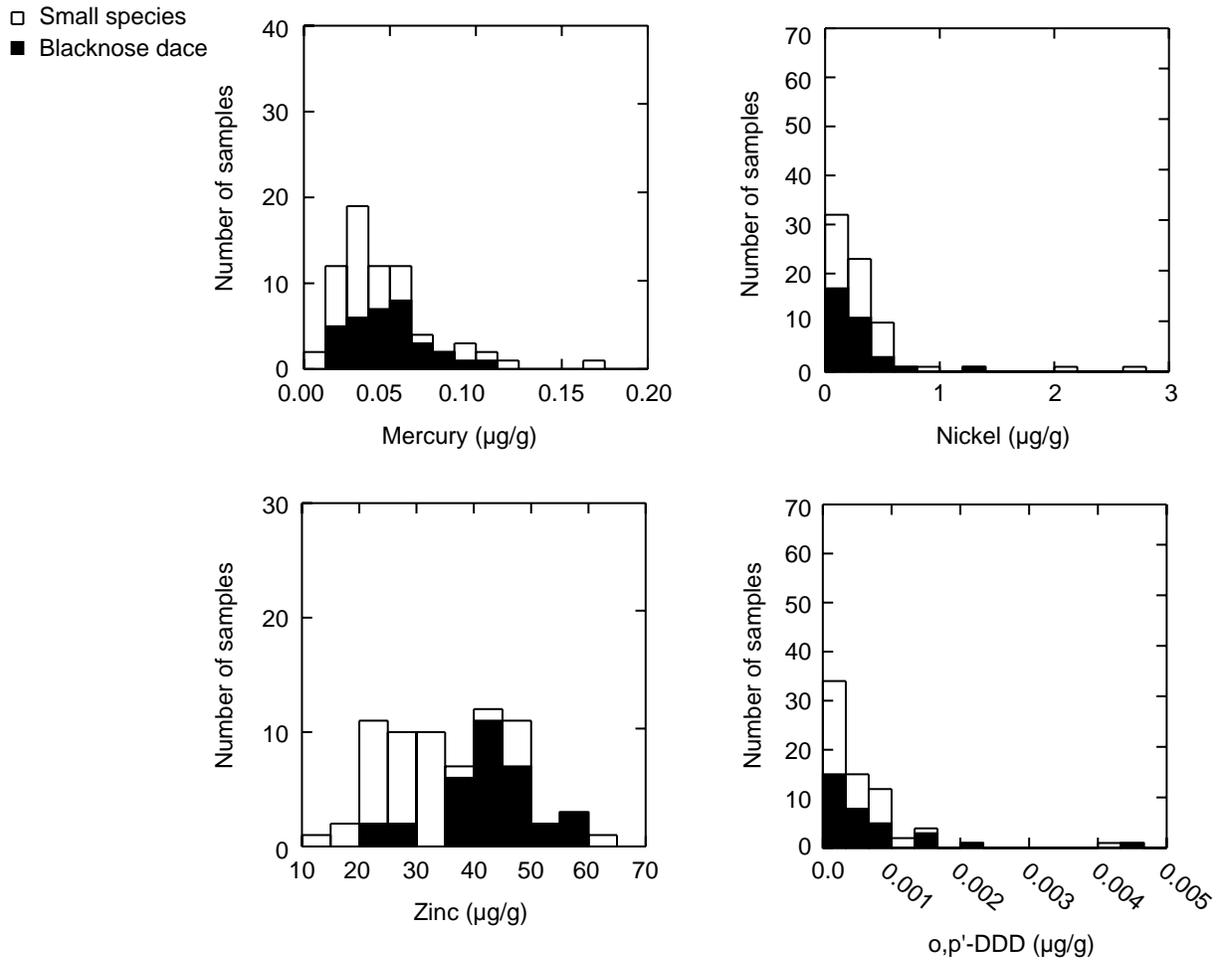
**Appendix B**  
**Histogram Representations of the**  
**Proportion of the Small Target Species**  
**Category Made Up of Blacknose Dace for**  
**Selected Analytes**

□ Small species  
 ■ Blacknose dace



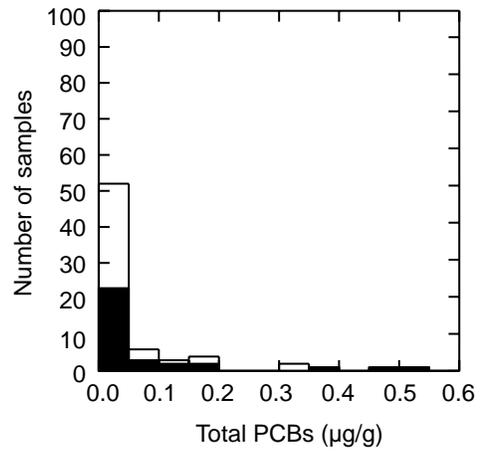
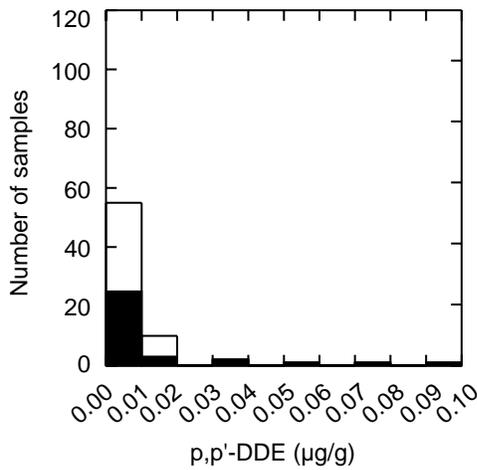
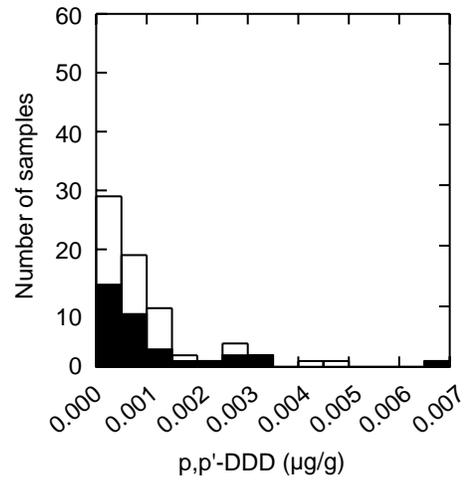
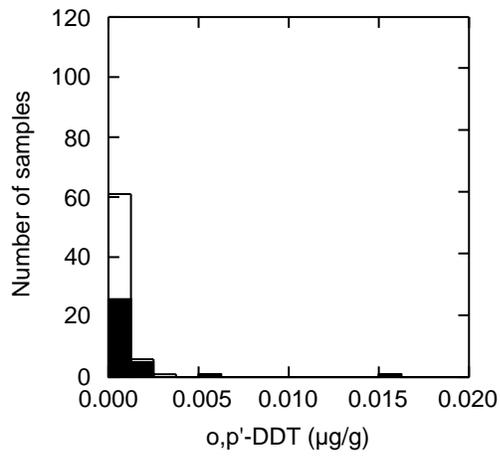
\*The detected levels of aluminum may have been artificially inflated by the use of aluminum foil in the packaging and storage of samples (See Collection of Samples and Laboratory Analysis Sections).

**Figure B-1.** Histogram representations of the proportion of the small target species category made up of blacknose dace for Al, Cr, Cu and Fe.

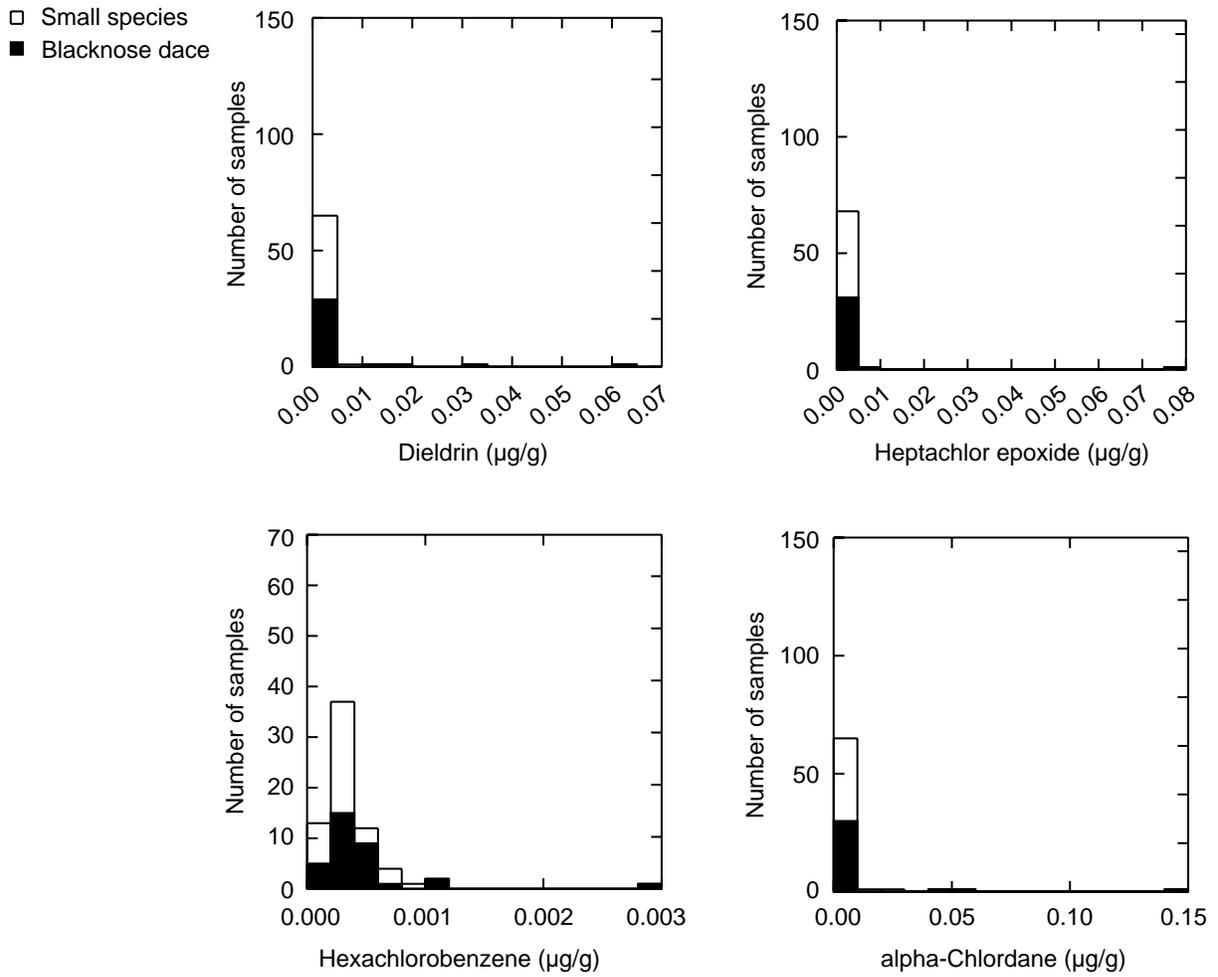


**Figure B-2.** Histogram representations of the proportion of the small target species category made up of blacknose dace for Hg, Ni, Zn and o,p'-DDD.

□ Small species  
 ■ Blacknose dace

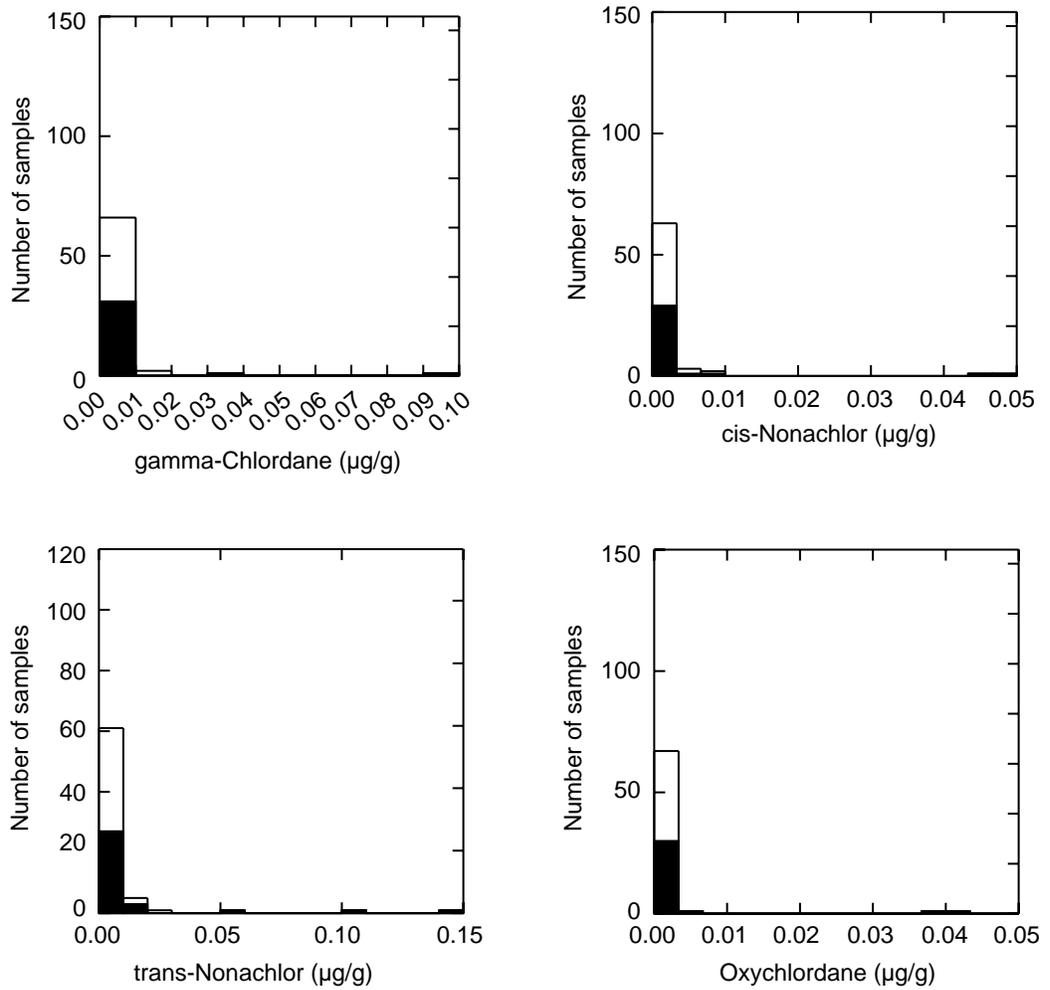


**Figure B-3.** Histogram representations of the proportion of the small target species category made up of blacknose dace for o,p'-DDT, p,p'-DDD, p,p'-DDE and total PCBs.



**Figure B-4.** Histogram representations of the proportion of the small target species category made up of blacknose dace for dieldrin, heptachlor epoxide, hexachlorobenzene and alpha-chlordane.

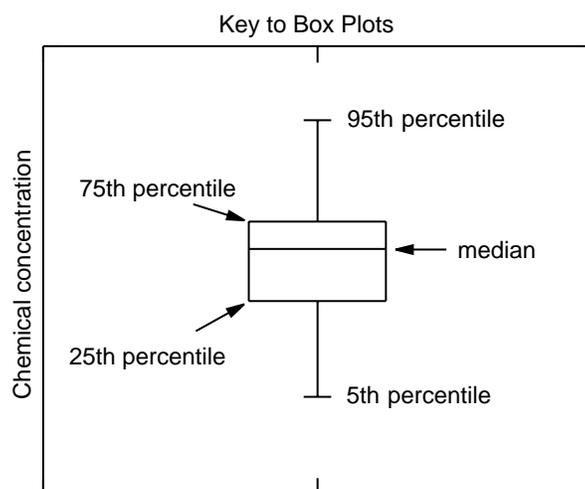
□ Small species  
■ Blacknose dace



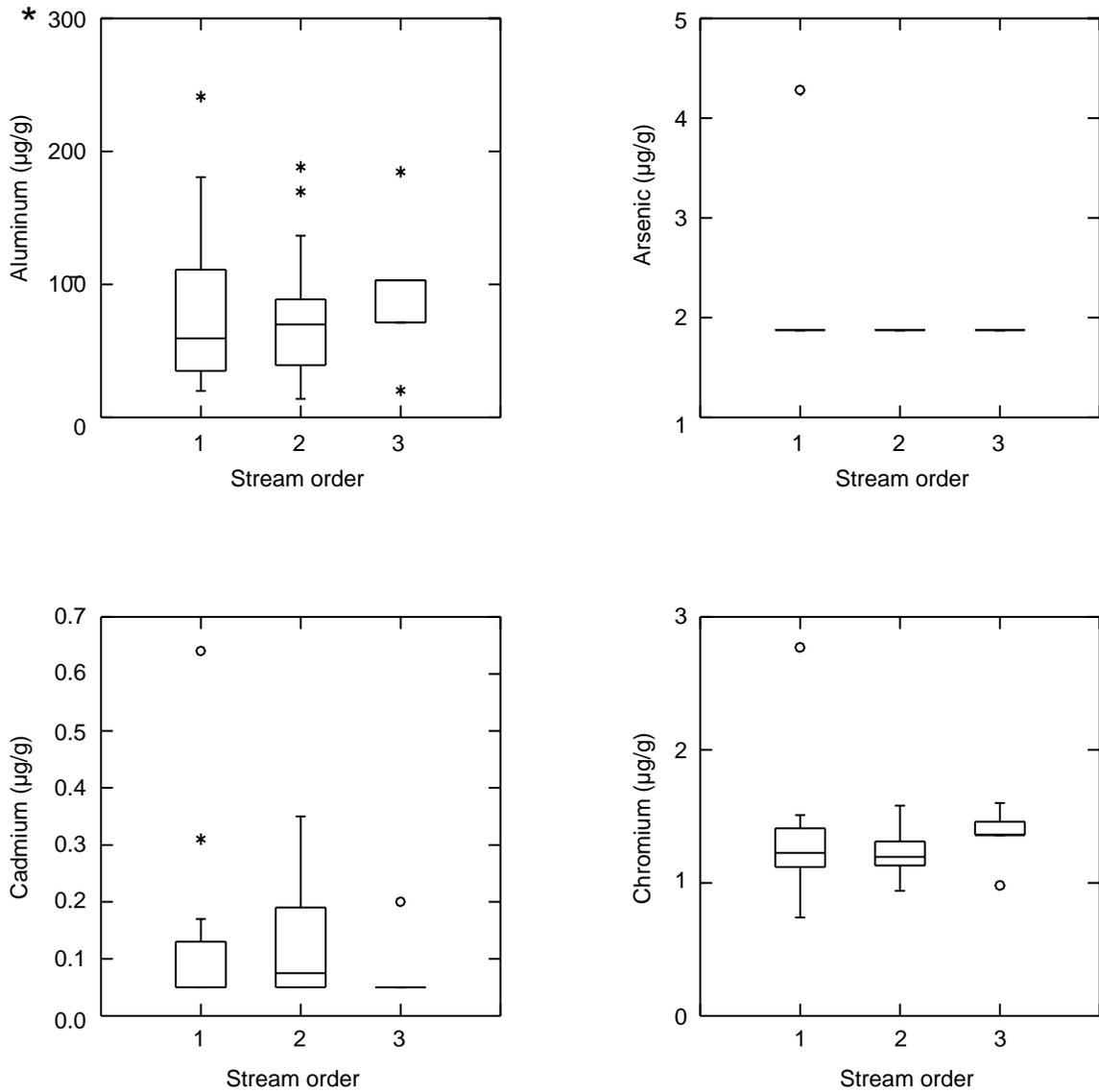
**Figure B-5.** Histogram representations of the proportion of the small target species category made up of blacknose dace for gamma-chlordane, cis-nonachlor, trans-nonachlor and oxychlordane.

## Appendix C

### Box Plots Representing the Distribution of Analyte Data Across Stream Order for Blacknose Dace and White Sucker



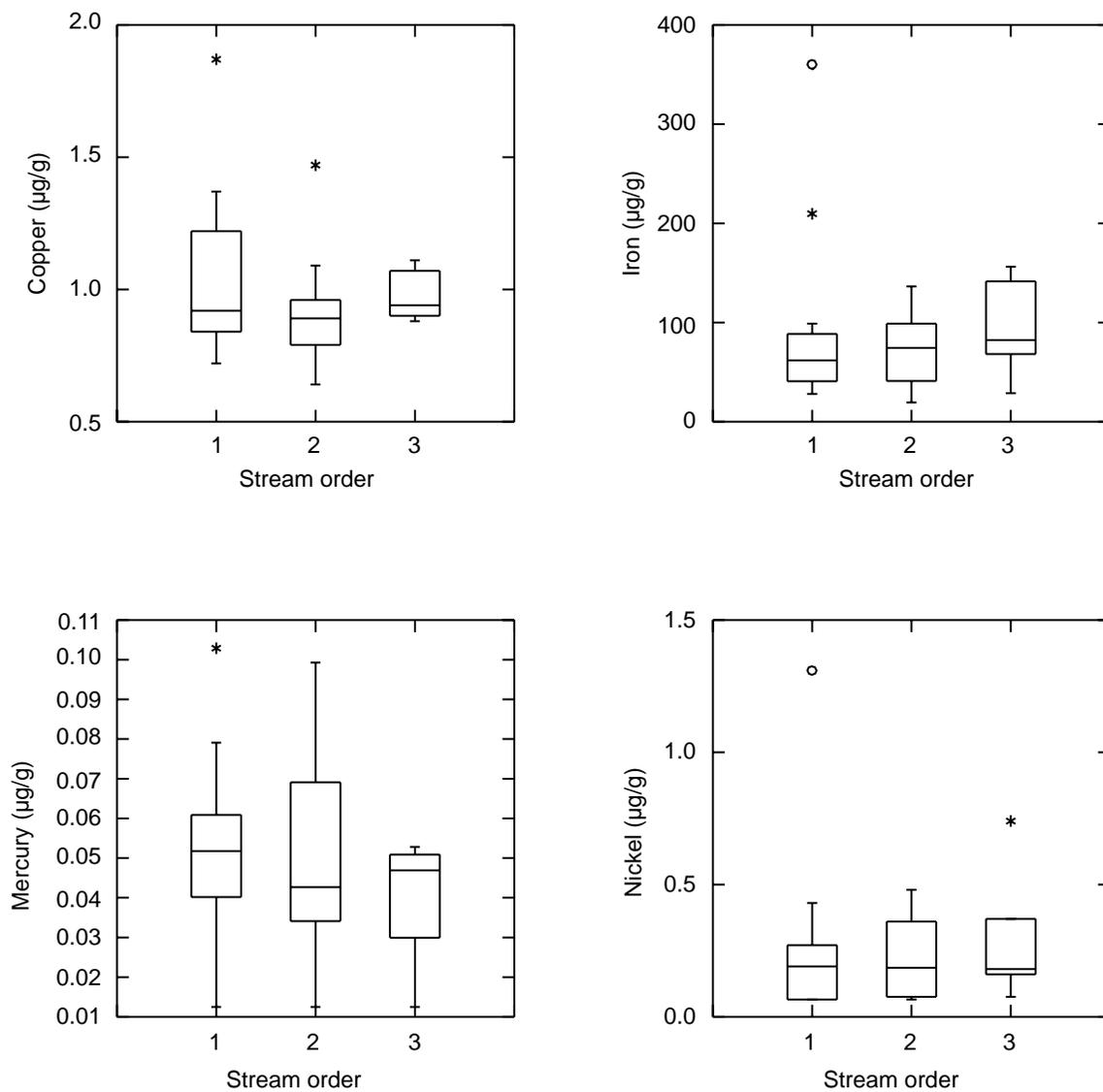
Blacknose Dace



\* The detected levels of aluminum may have been artificially inflated by the use of aluminum foil in the packaging and storage of samples (See Collection of Samples and Laboratory Analysis Sections).

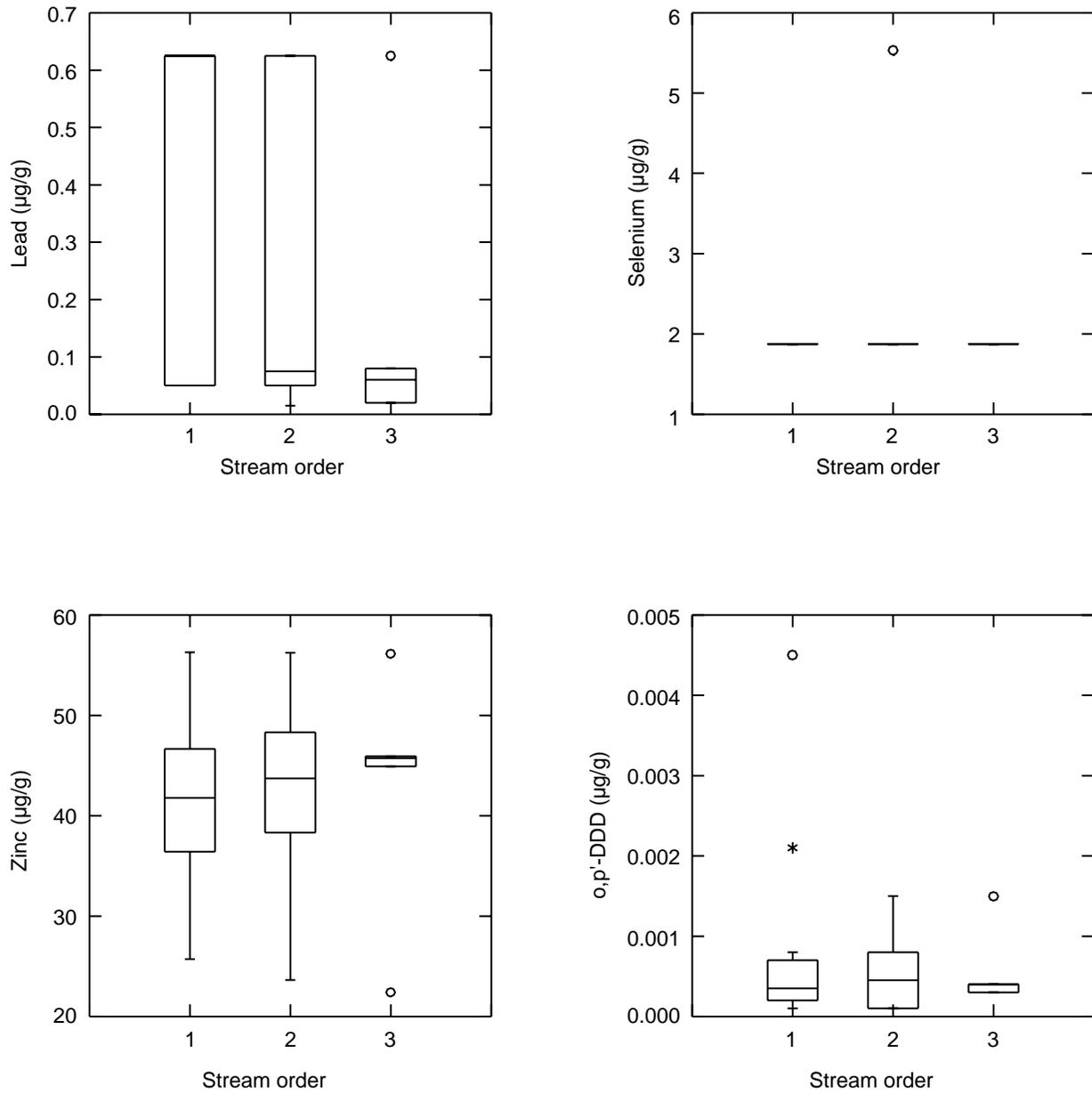
**Figure C-1.** Box plots representing the distribution of Al, As, Cd and Cr data across stream order for blacknose dace.

Blacknose Dace



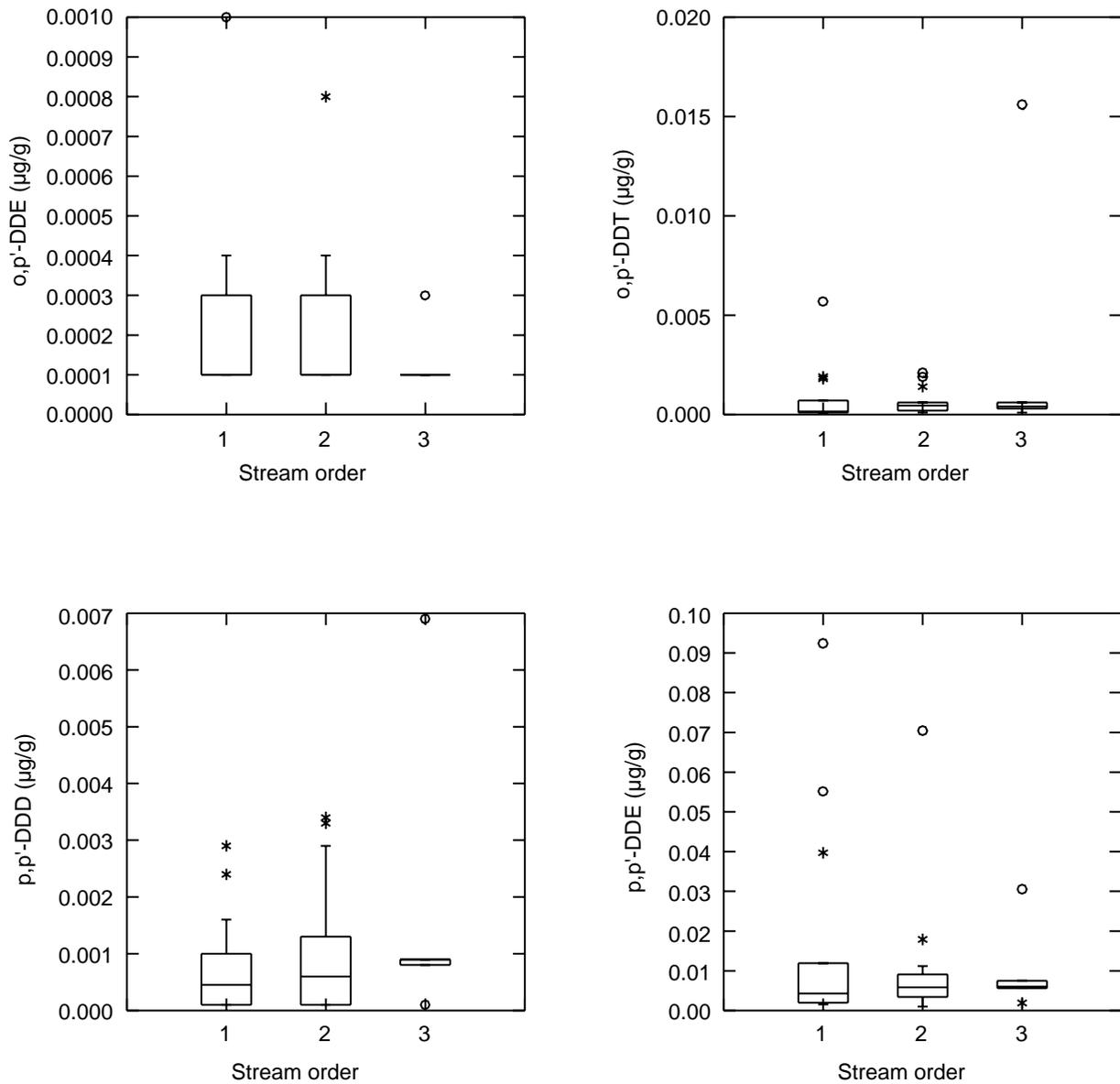
**Figure C-2.** Box plots representing the distribution of Cu, Fe, Hg and Ni data across stream order for blacknose dace.

Blacknose Dace



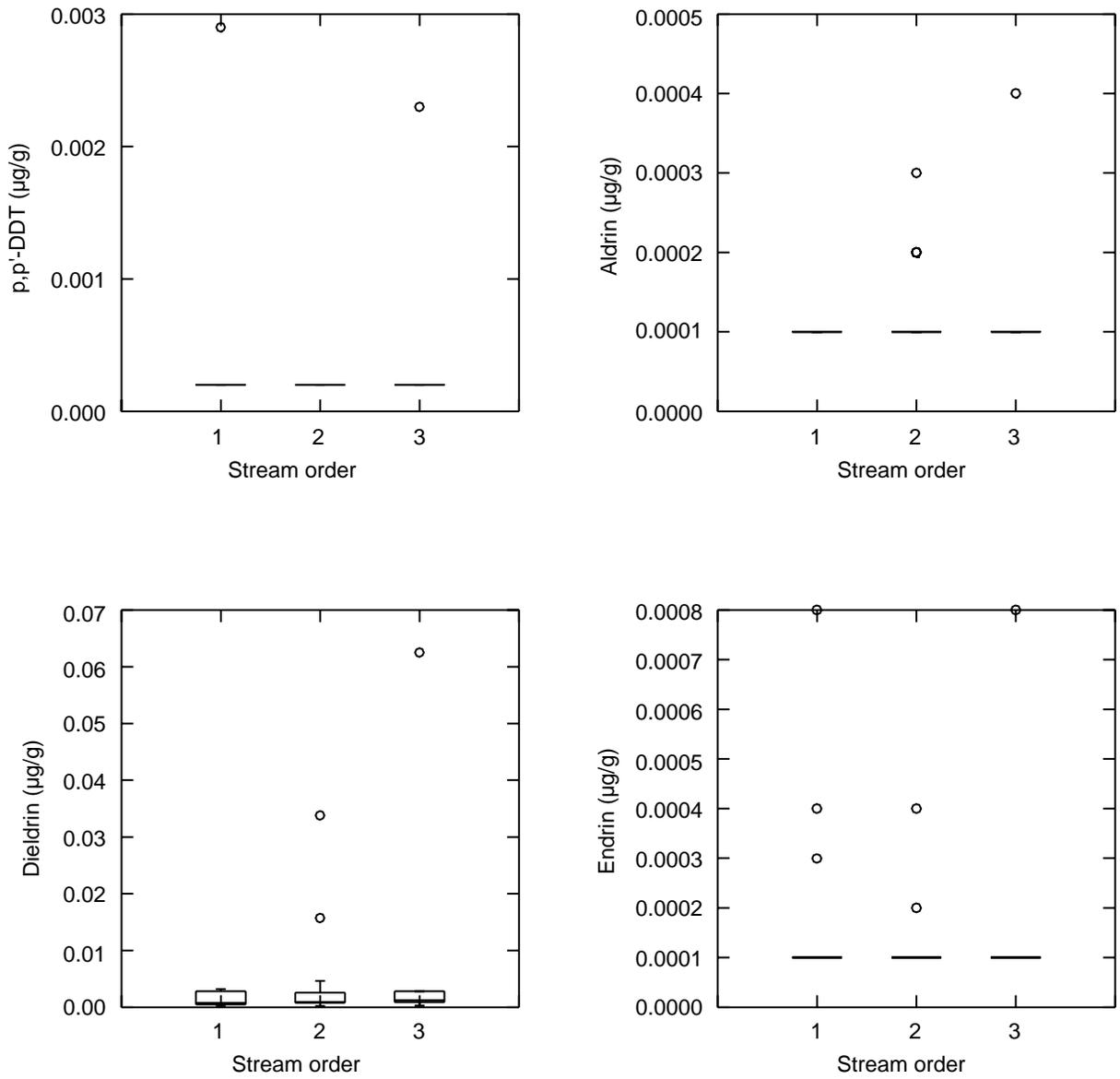
**Figure C-3.** Box plots representing the distribution of Pb, Se, Zn and o,p'-DDD data across stream order for blacknose dace.

Blacknose Dace



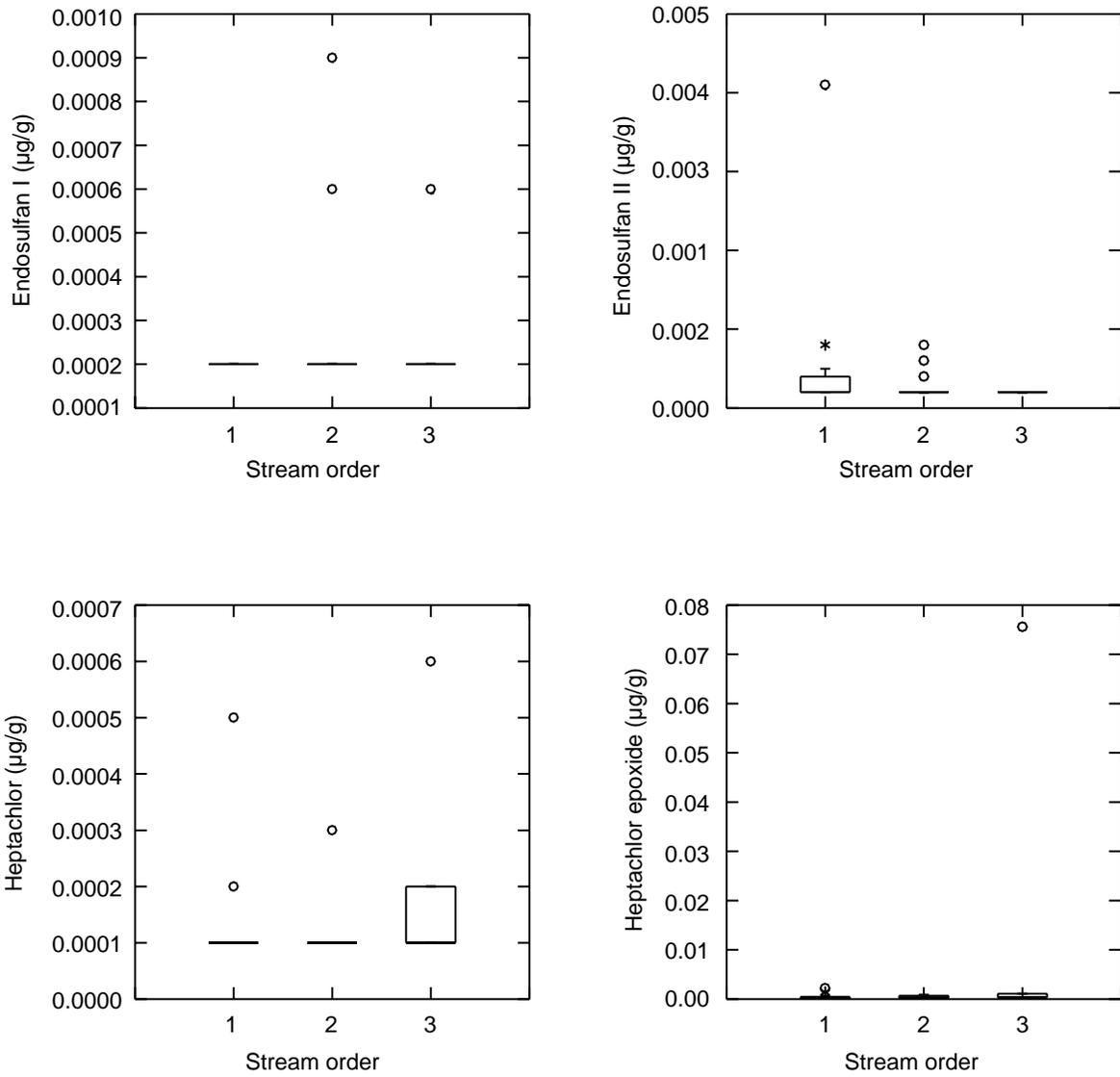
**Figure C-4.** Box plots representing the distribution of o,p'-DDE, o,p'-DDT, p,p'-DDD and p,p'-DDE data across stream order for blacknose dace.

Blacknose Dace



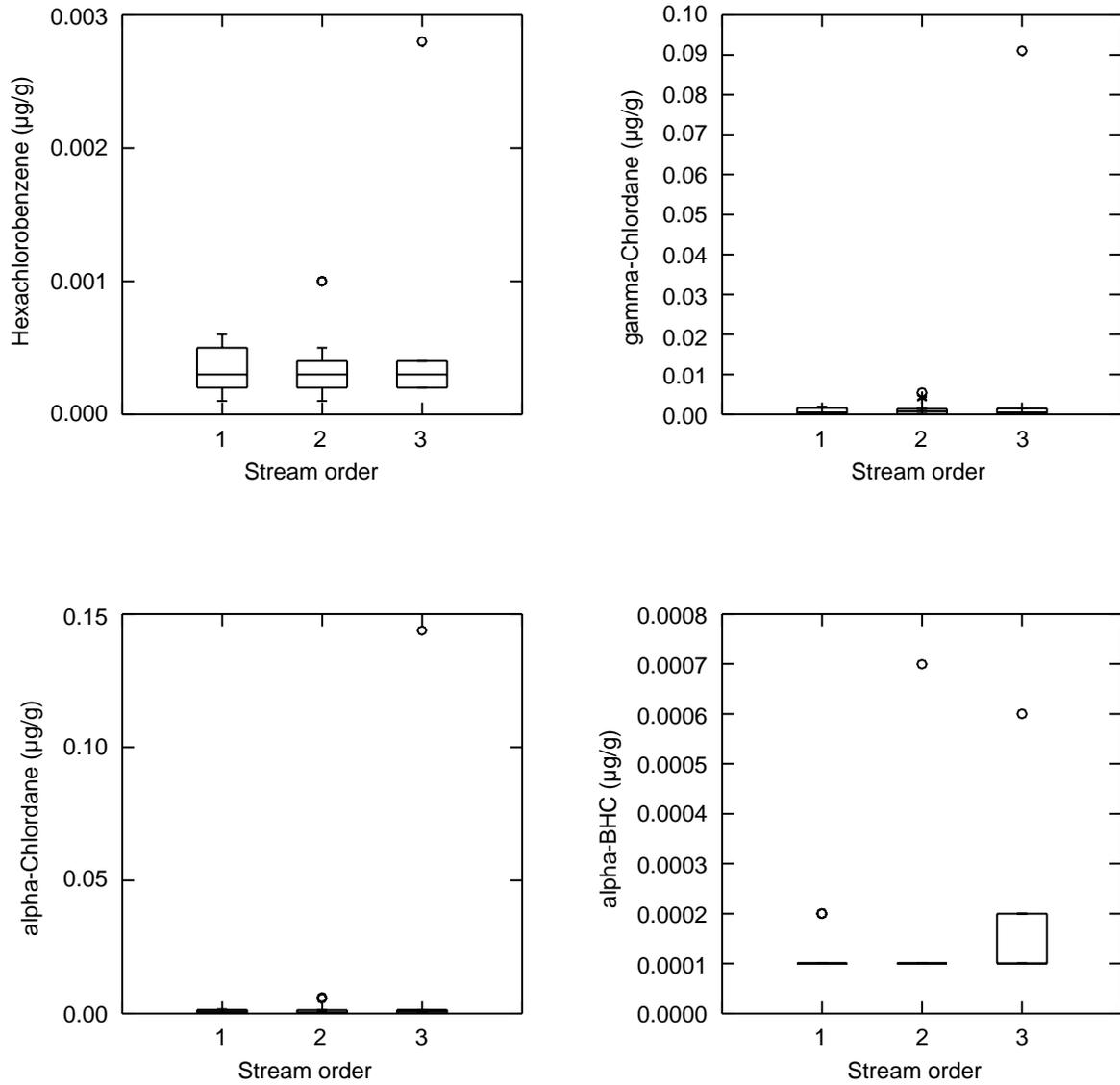
**Figure C-5.** Box plots representing the distribution of p,p'-DDT, aldrin, dieldrin and endrin data across stream order for blacknose dace.

Blacknose Dace



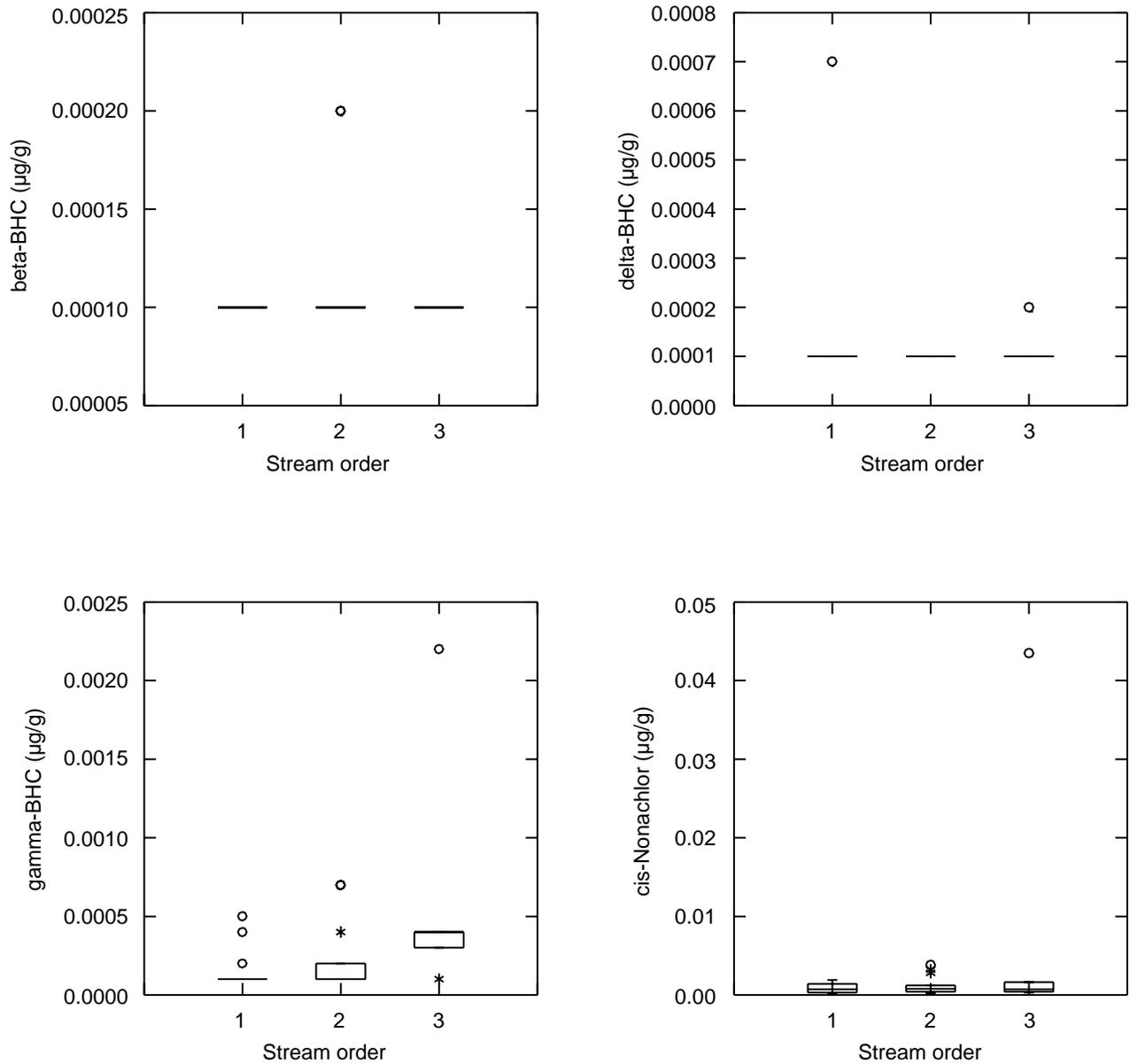
**Figure C-6.** Box plots representing the distribution of endosulfan I, endosulfan II, heptachlor and heptachlor epoxide data across stream order for blacknose dace.

Blacknose Dace



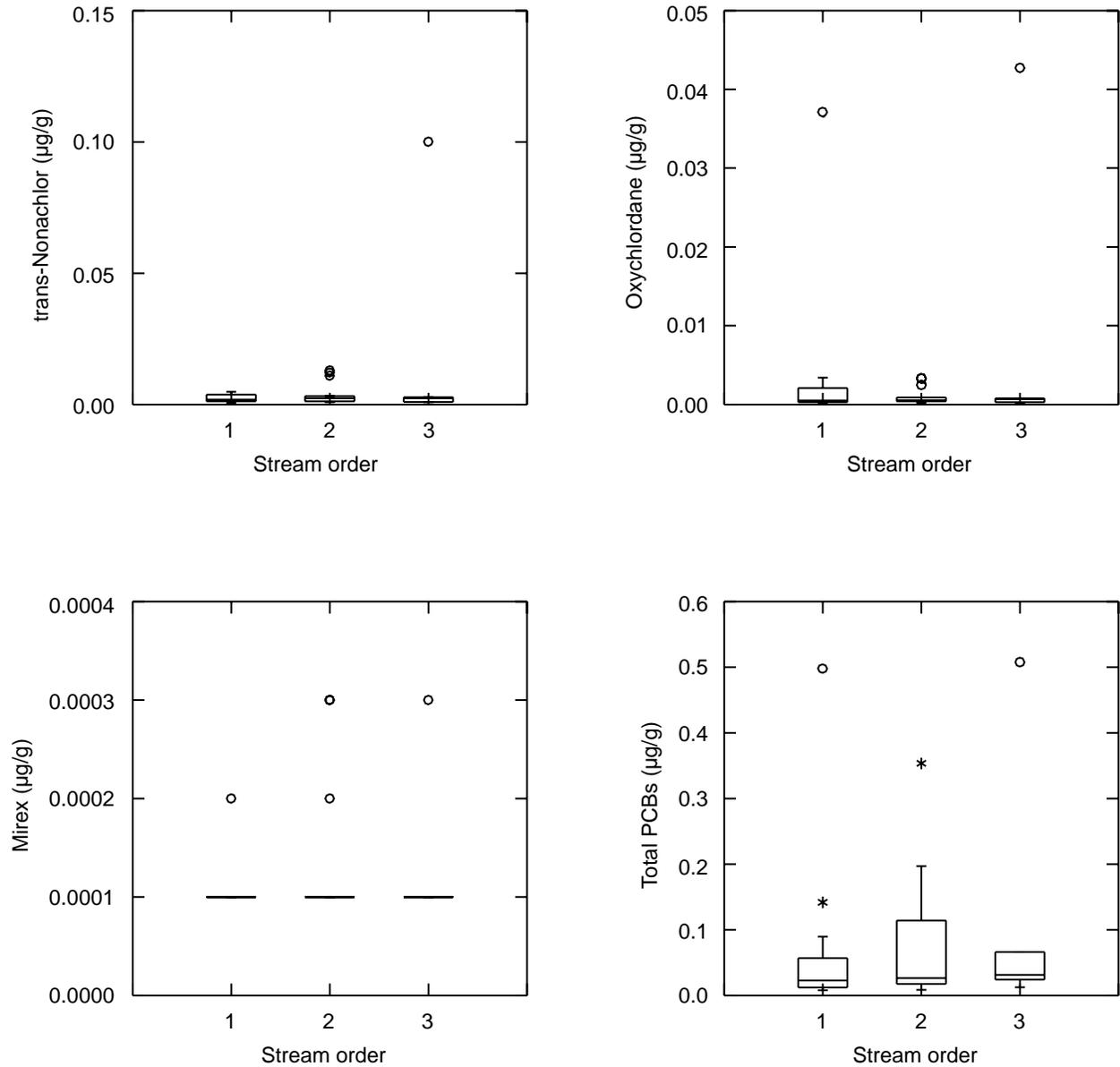
**Figure C-7.** Box plots representing the distribution of hexachlorobenzene, gamma-chlordane, alpha-chlordane and alpha-BHC data across stream order for blacknose dace.

Blacknose Dace



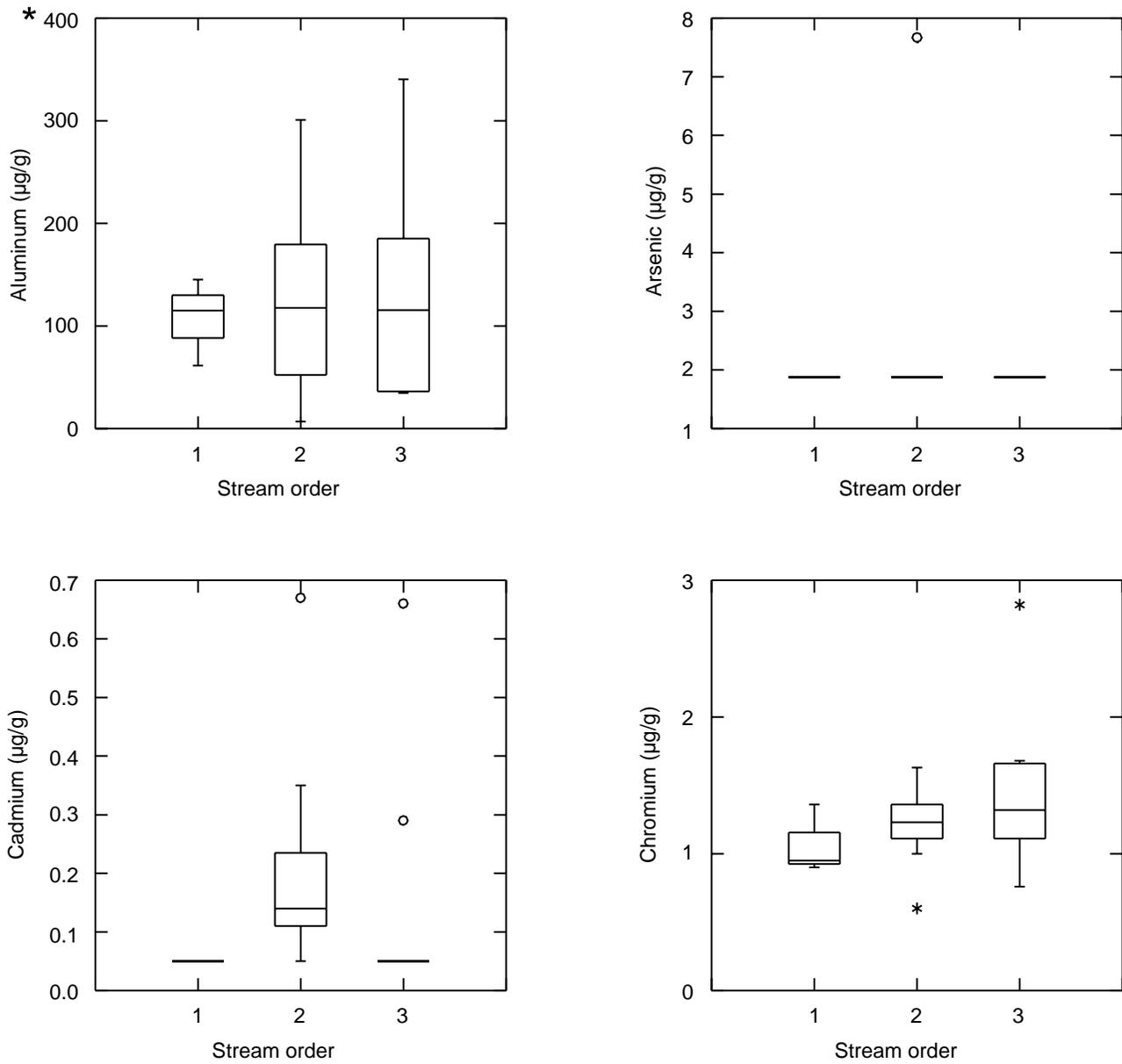
**Figure C-8.** Box plots representing the distribution of beta-BHC, delta-BHC, gamma-BHC and cis-nonachlor data across stream order for blacknose dace.

Blacknose Dace



**Figure C-9.** Box plots representing the distribution of trans-nonachlor, oxychlordane, mirex and total PCB data across stream order for blacknose dace.

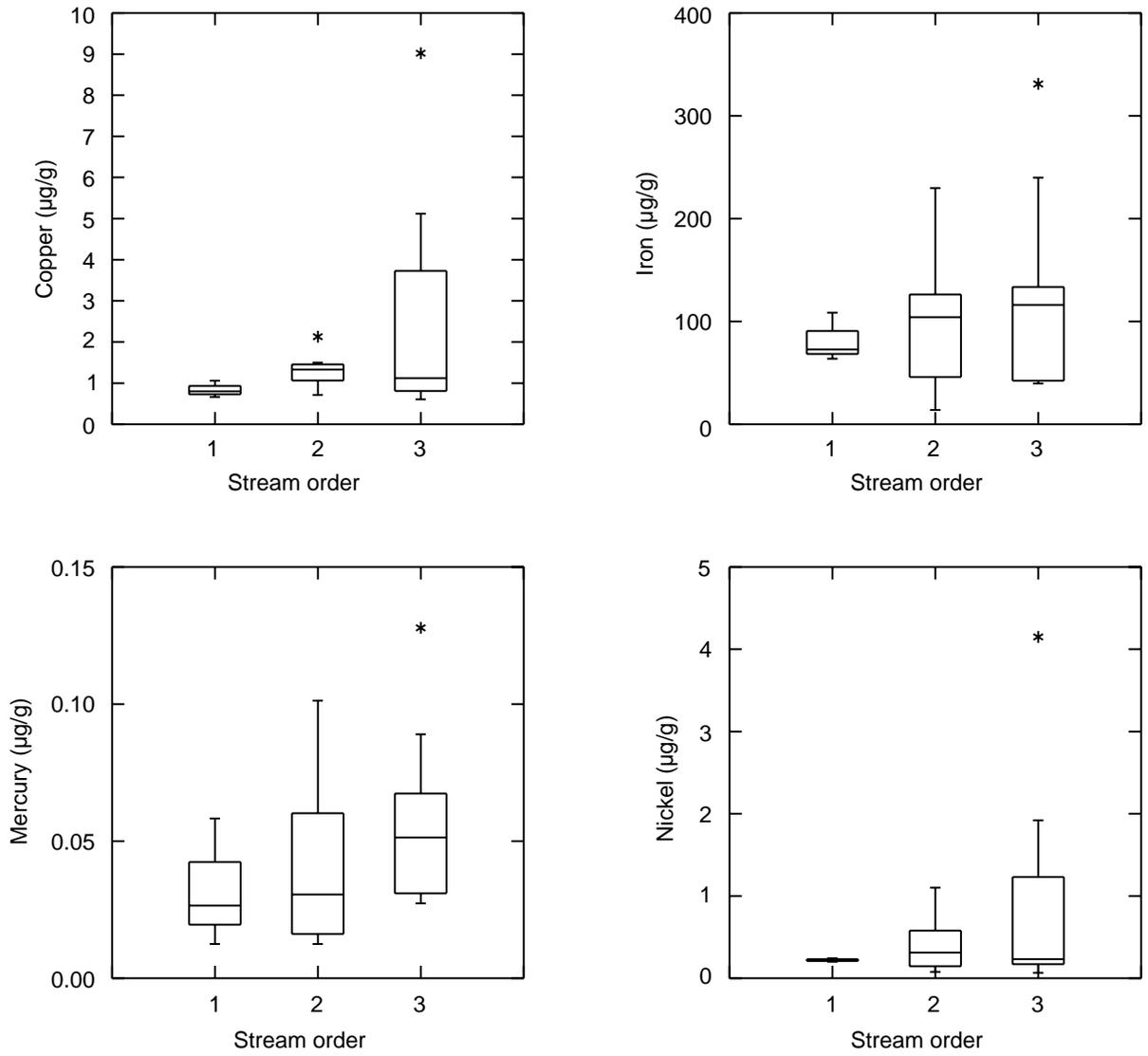
White Sucker



\* The detected levels of aluminum may have been artificially inflated by the use of aluminum foil in the packaging and storage of samples (See Collection of Samples and Laboratory Analysis Sections).

**Figure C-10.** Box plots representing the distribution of Al, As, Cd and Cr data across stream order for white sucker.

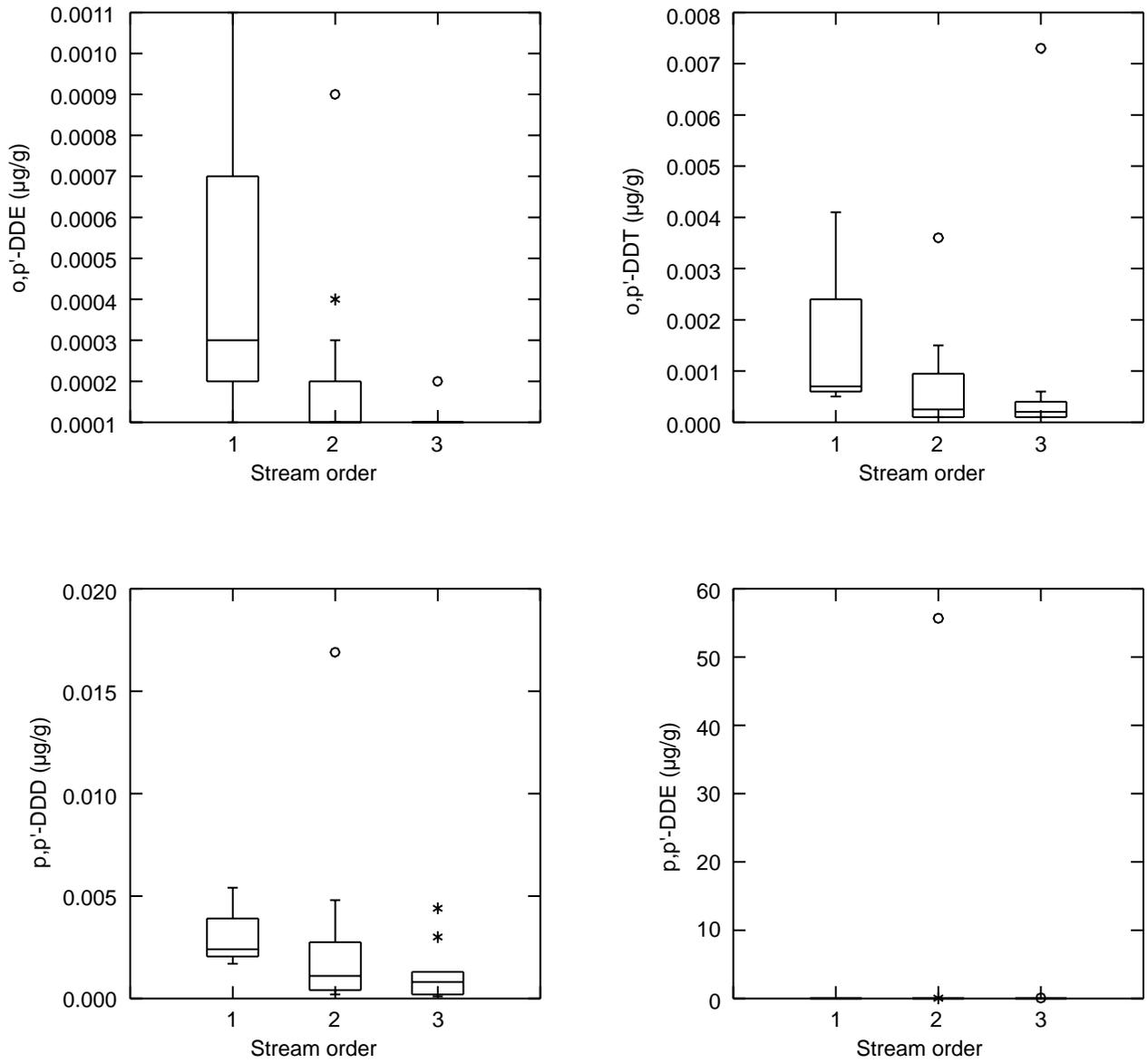
White Sucker



**Figure C-11.** Box plots representing the distribution of Cu, Fe, Hg and Ni data across stream order for white sucker.

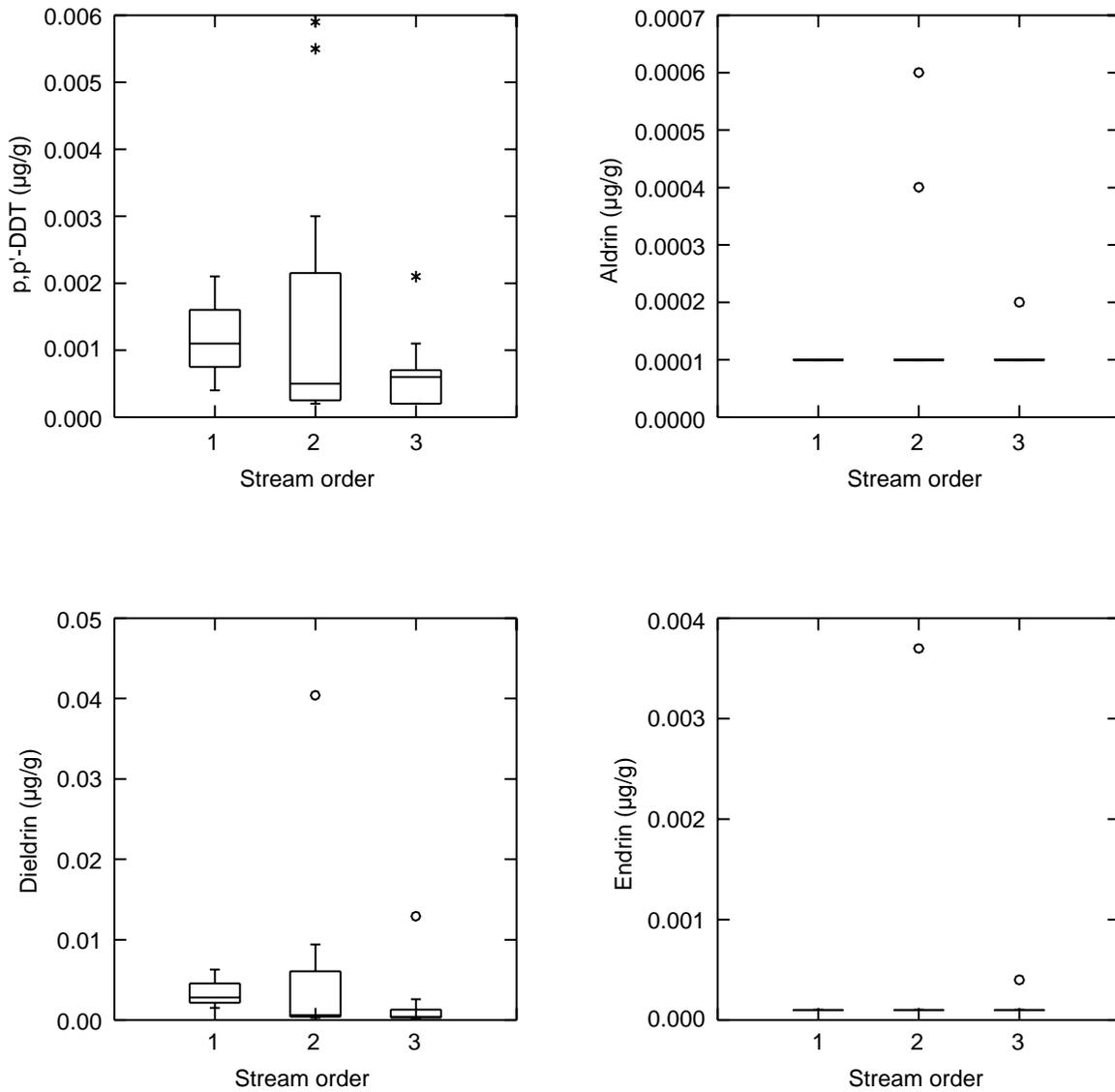
**Figure C-12.** Box plots representing the distribution of Pb, Se, Zn and o,p'-DDD data across stream order for white sucker.

White Sucker



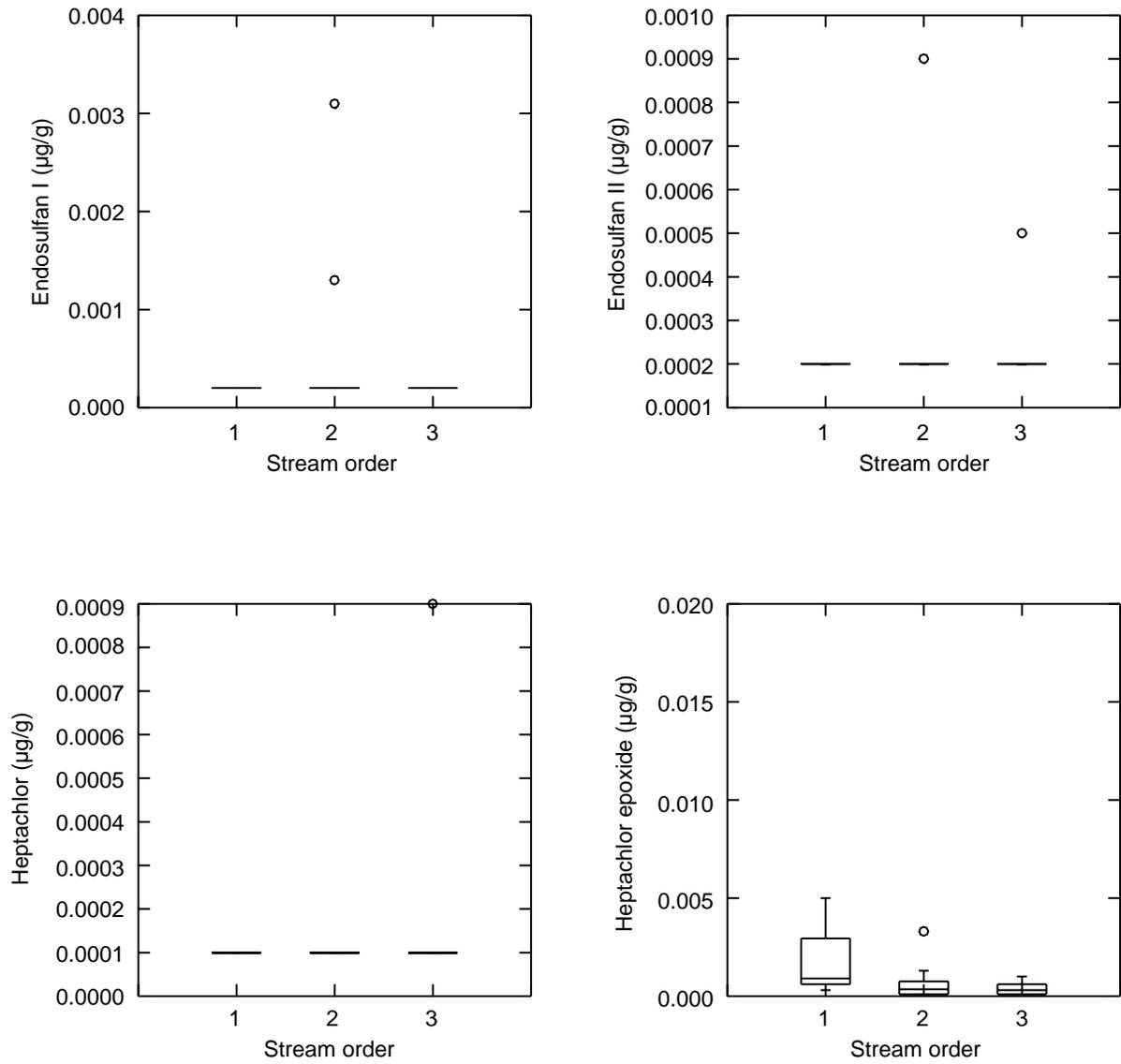
**Figure C-13.** Box plots representing the distribution of o,p'-DDE, o,p'-DDT, p,p'-DDD and p,p'-DDE data across stream order for white sucker.

White Sucker



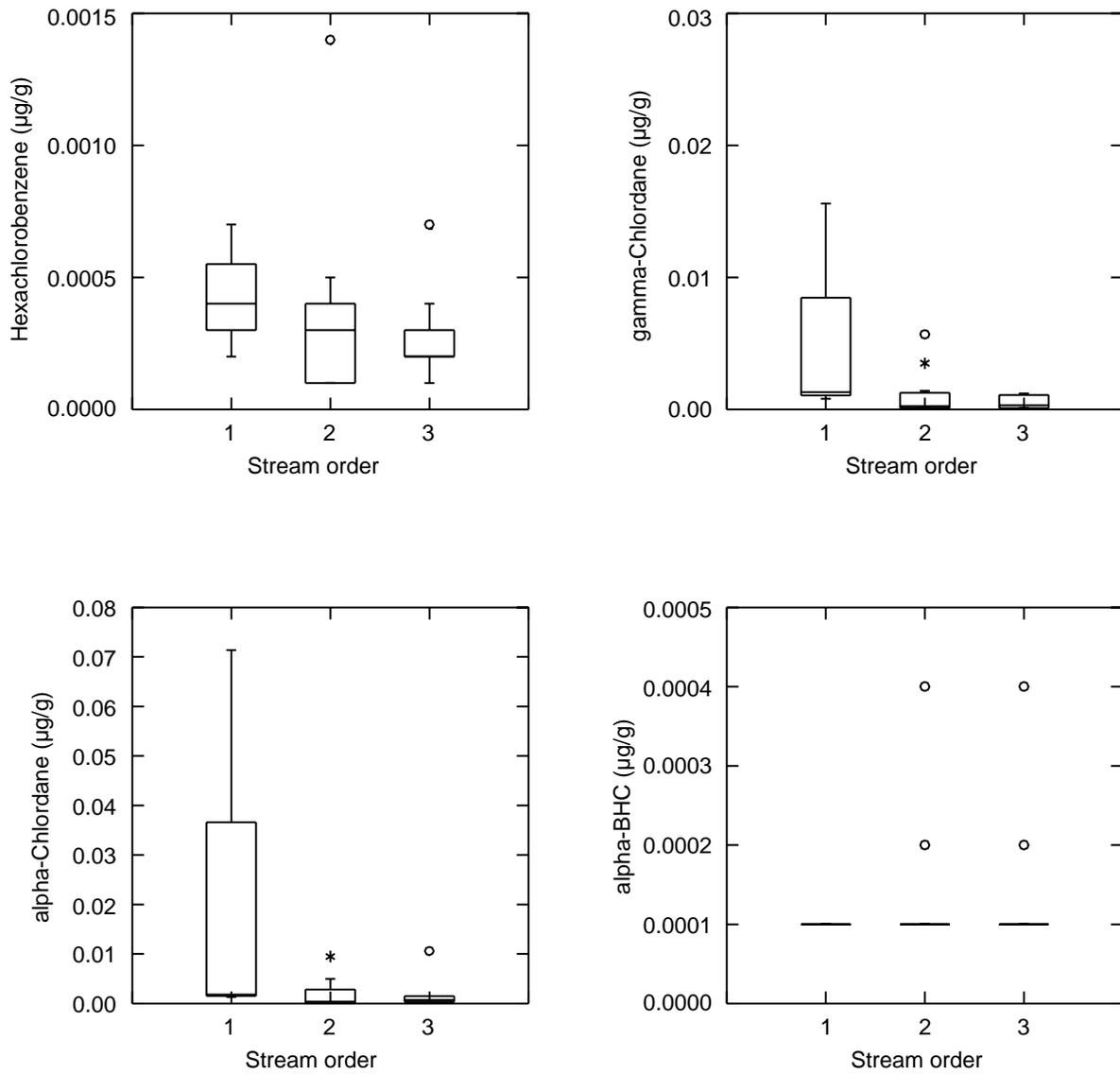
**Figure C-14.** Box plots representing the distribution of p,p'-DDT, aldrin, dieldrin and endrin data across stream order for white sucker.

White Sucker



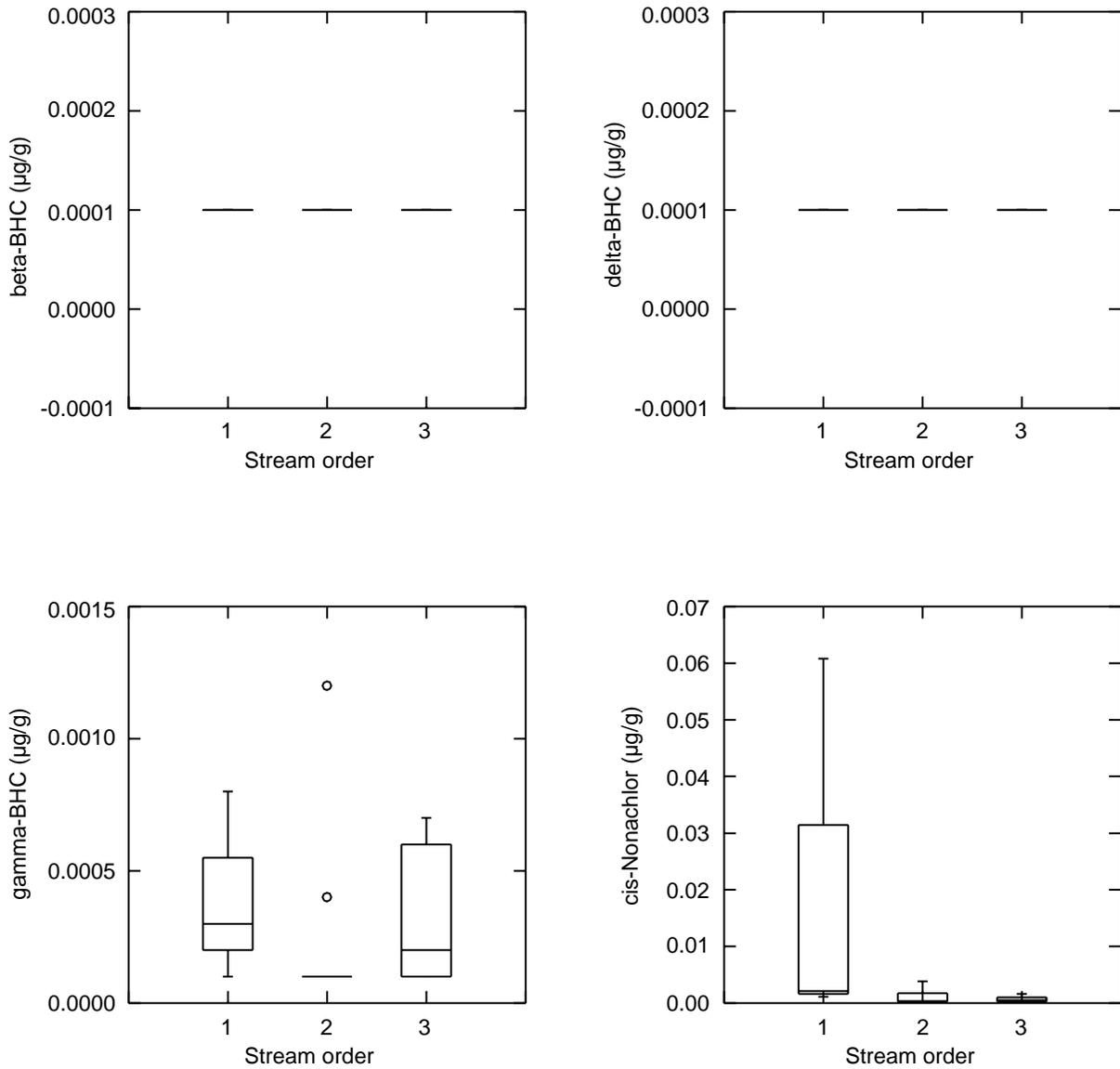
**Figure C-15.** Box plots representing the distribution of endosulfan I, endosulfan II, heptachlor and heptachlor epoxide data across stream order for white sucker.

White Sucker



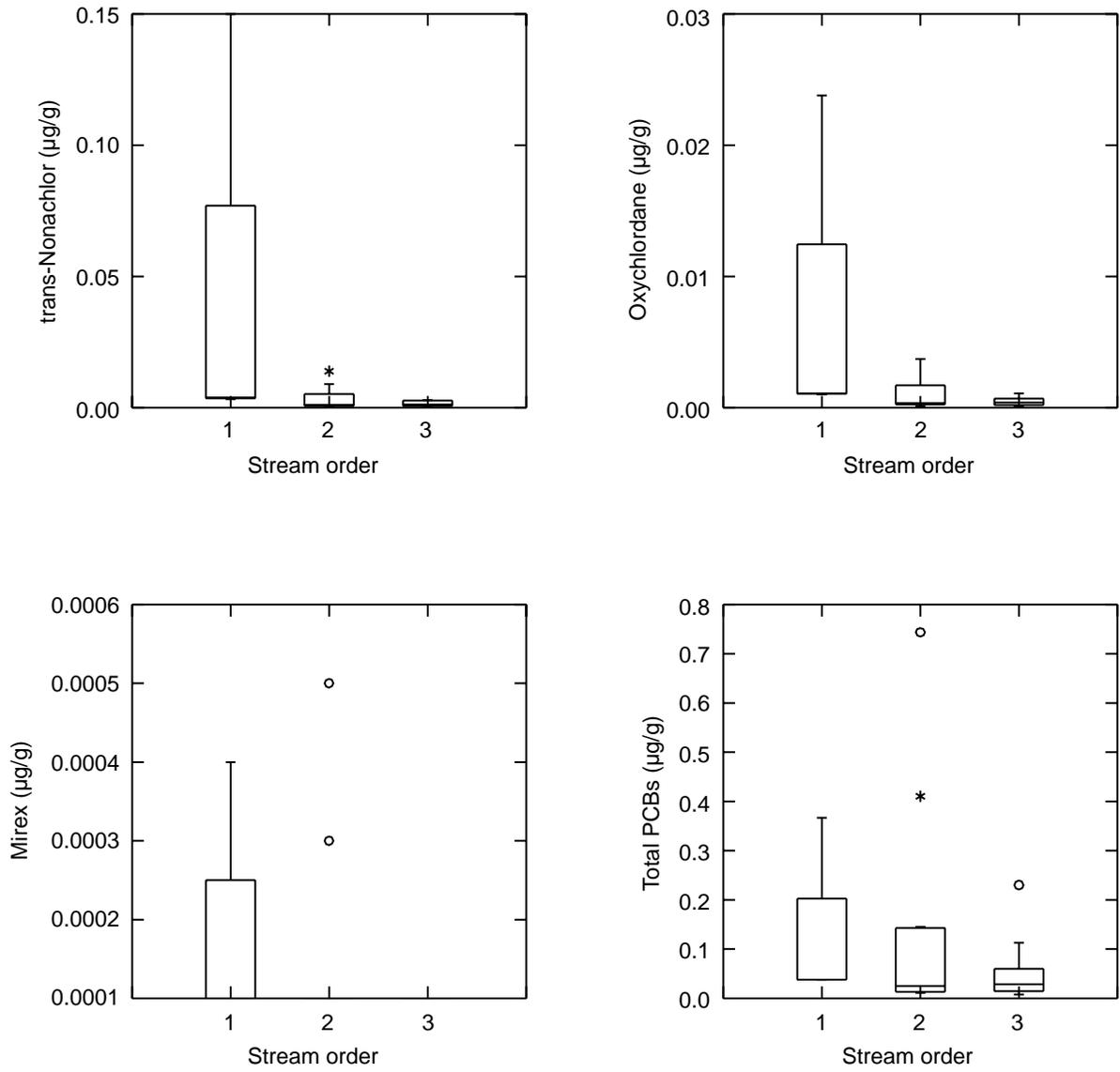
**Figure C-16.** Box plots representing the distribution of hexachlorobenzene, gamma-chlordane, alpha-chlordane and alpha-BHC data across stream order for white sucker.

White Sucker



**Figure C-17.** Box plots representing the distribution of beta-BHC, delta-BHC, gamma-BHC and cis-nonachlor data across stream order for white sucker.

White Sucker



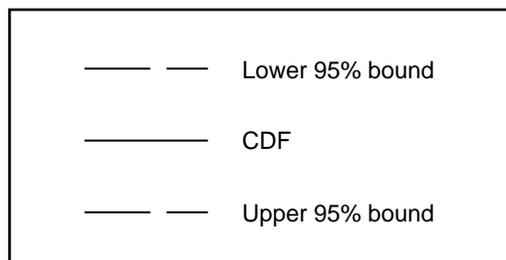
**Figure C-18.** Box plots representing the distribution of beta-BHC, delta-BHC, gamma-BHC and cis-nonachlor data across stream order for white sucker.

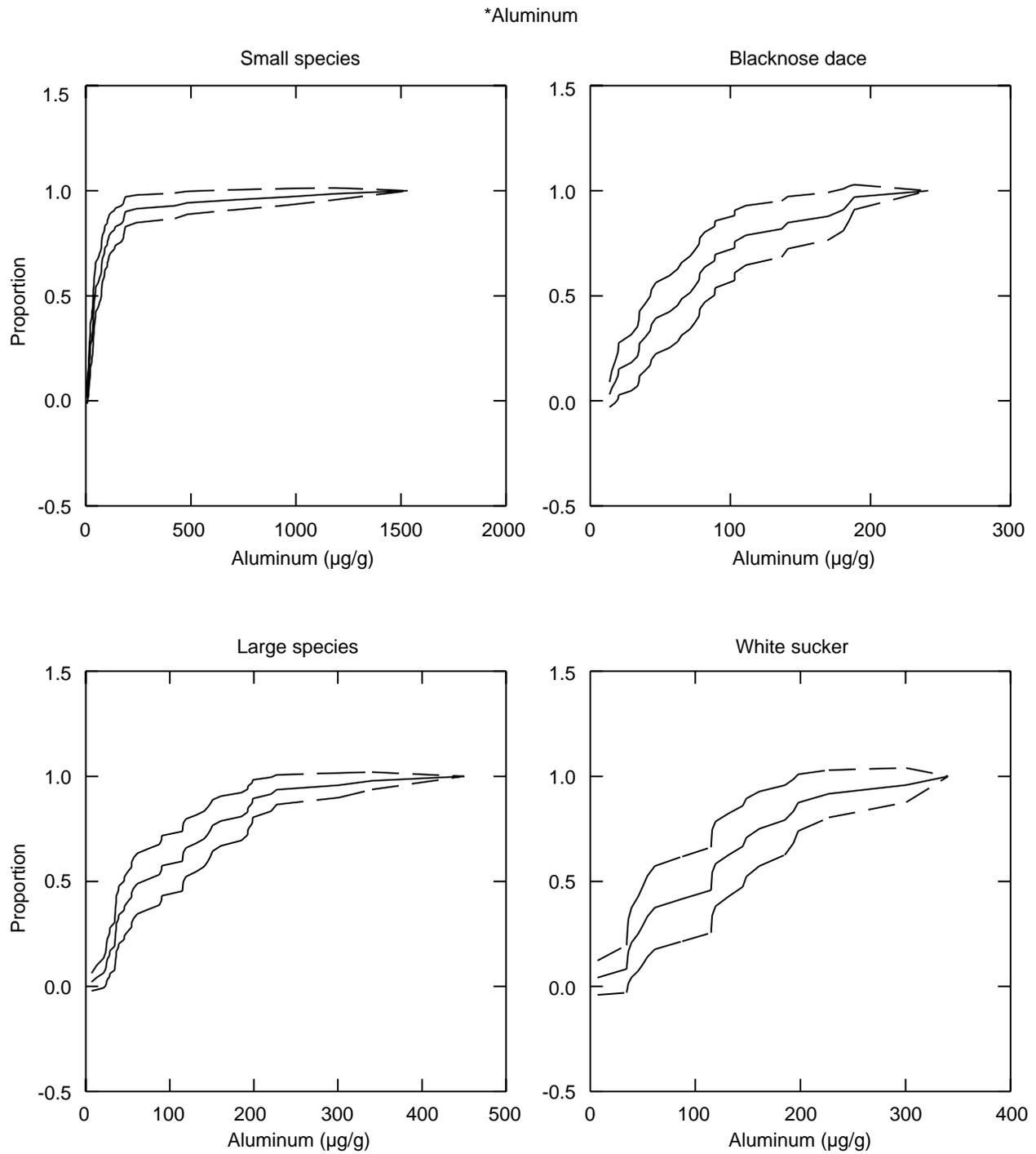
## Appendix D

# Cumulative Distribution Functions (CDFs) Showing the Proportion of the Four Fish Categories that are At or Below Varying Concentrations of Selected Analytes.

If the median value of the analyte was below the detection limit in a category of fish, a CDF was not generated for that category of fish (See Table 3).

Key to CDFs





\*The detected levels of aluminum may have been artificially inflated by the use of aluminum foil in the packaging and storage of samples (See Collection of Samples and Laboratory Analysis Sections).

**Figure D-1.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of Al. Note that the value scales vary among CDFs.

Cadmium

Small species

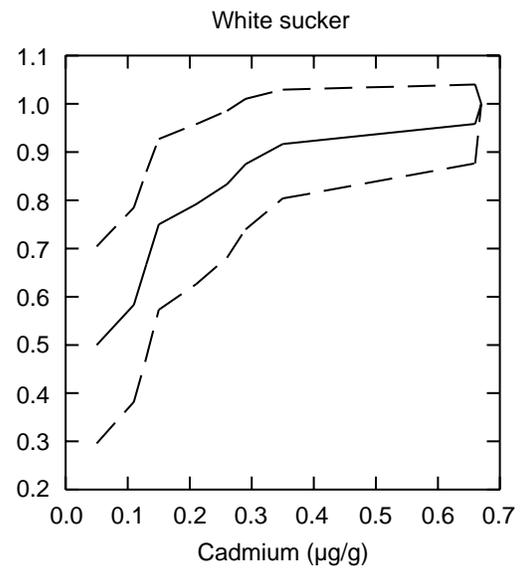
Blacknose dace

Median value was below the detection limit

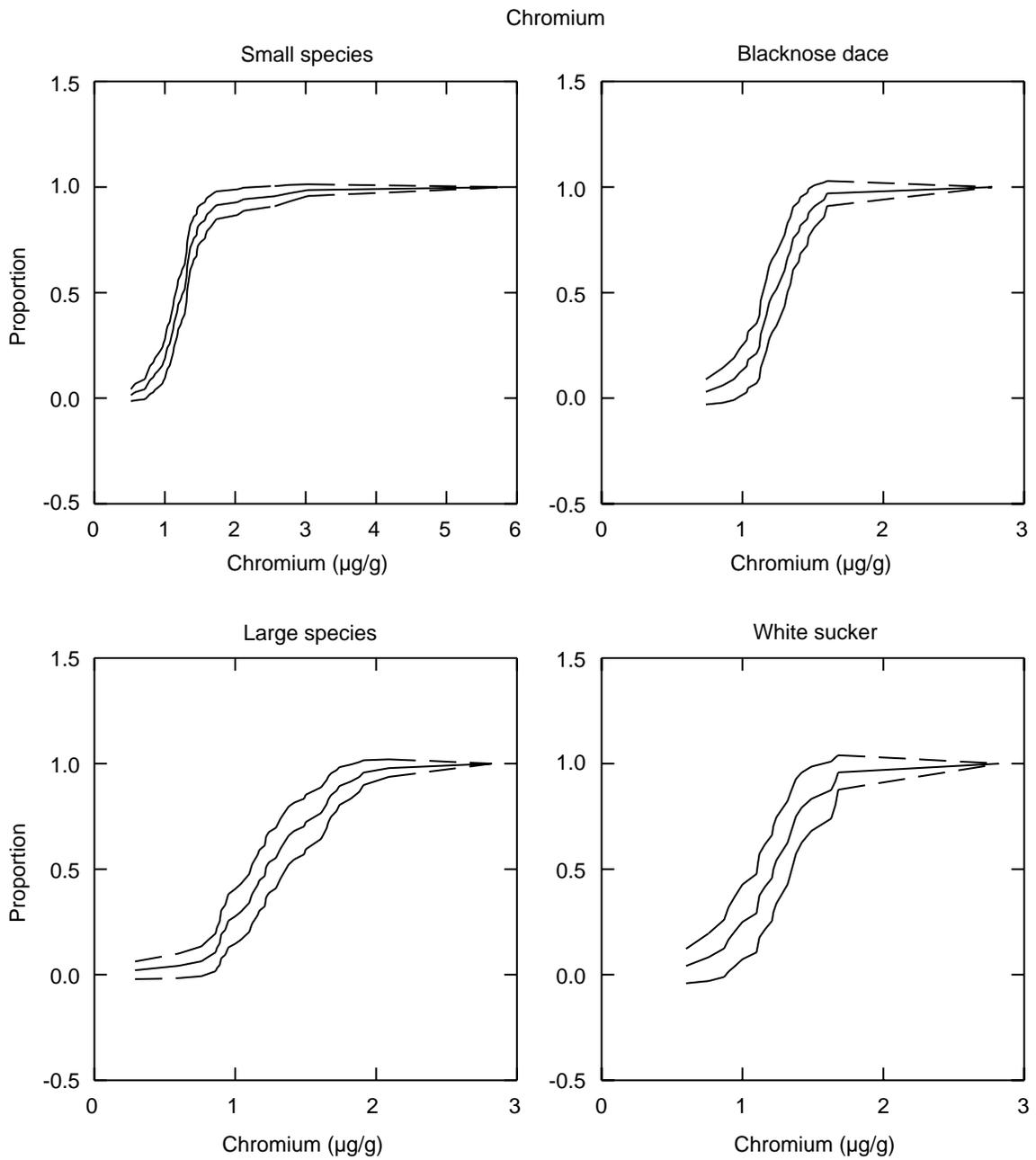
Median value was below the detection limit

Large Species

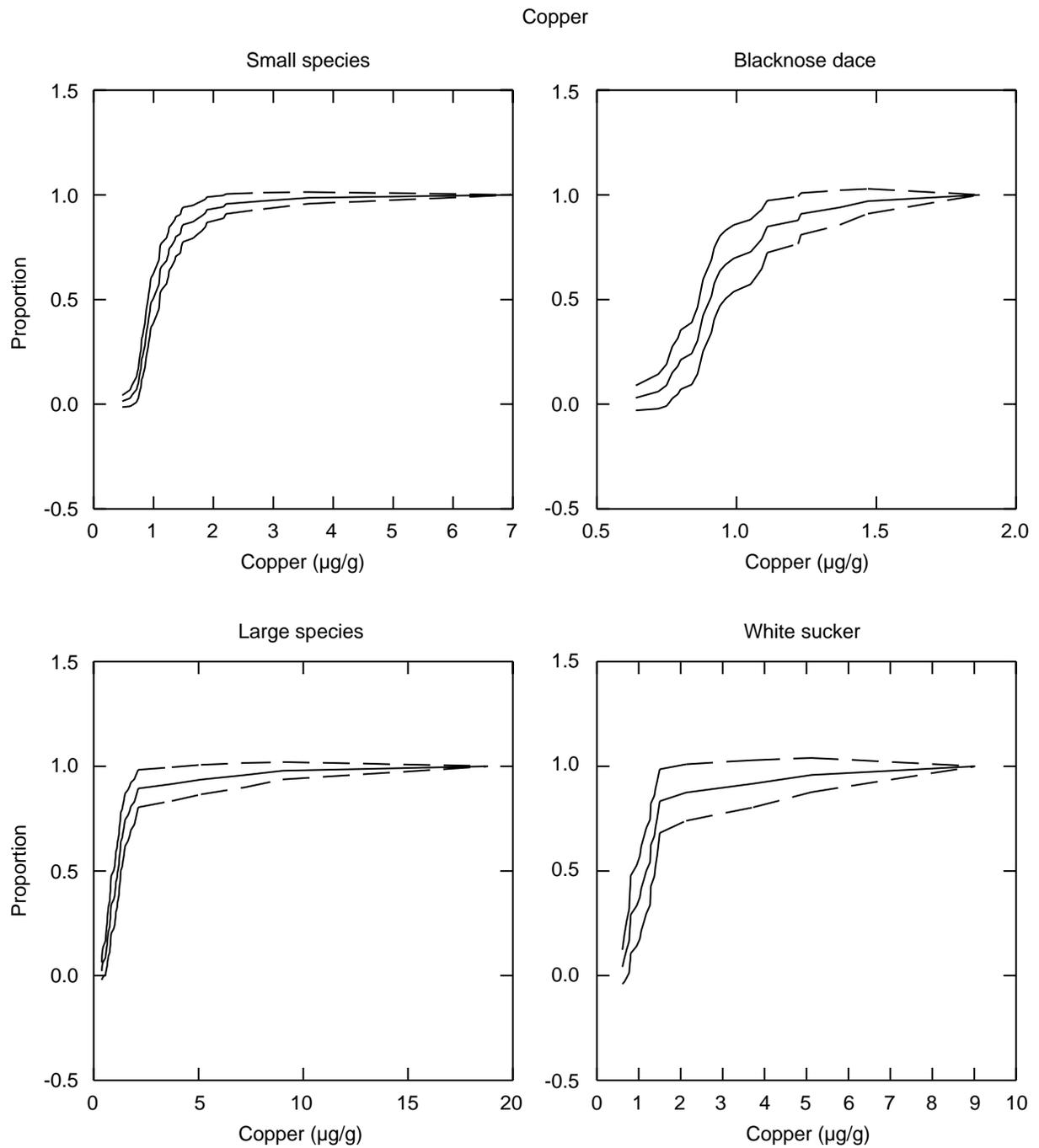
Median value was below the detection limit



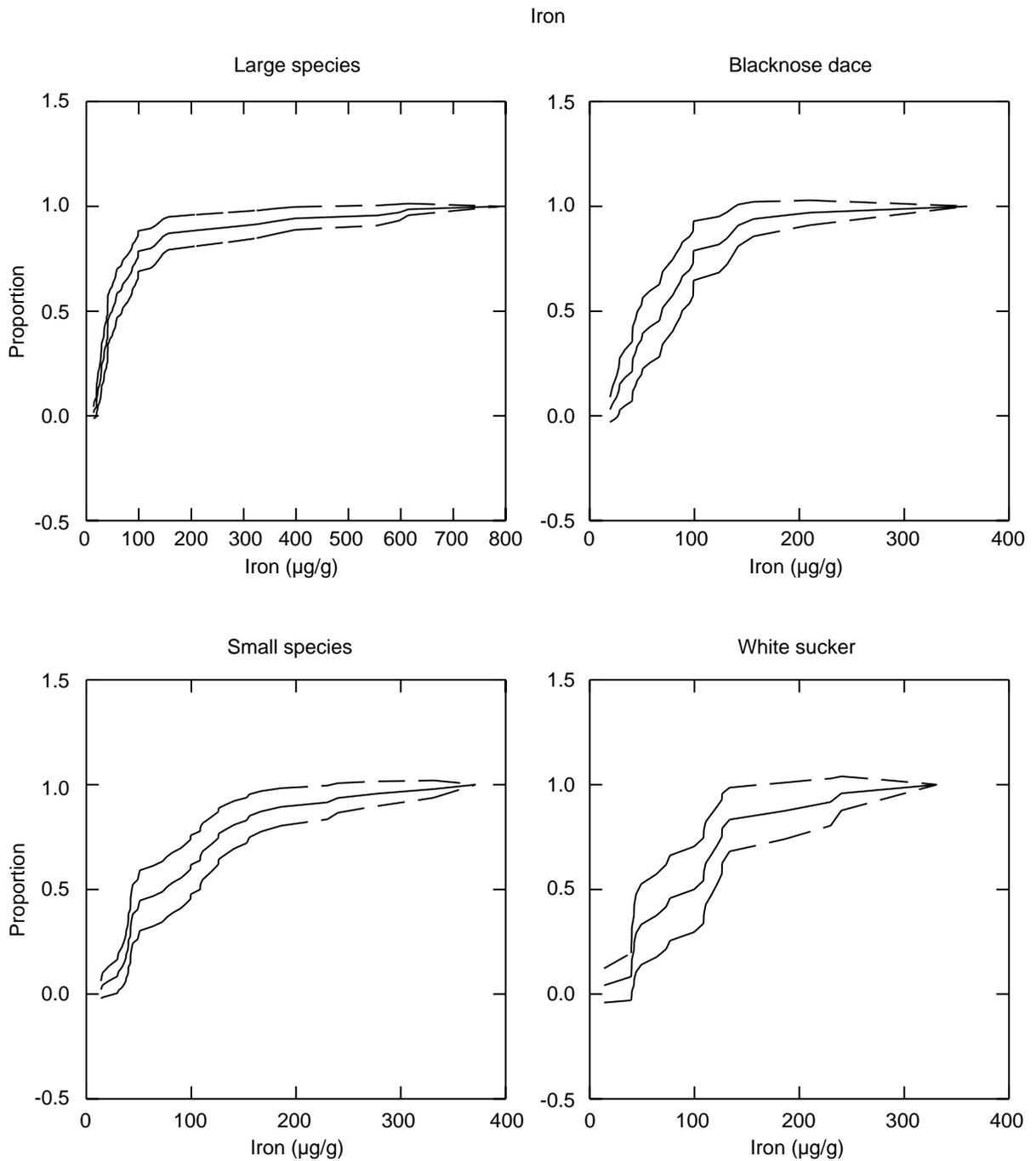
**Figure D-2.** CDF showing the proportion of white sucker that are at or below varying concentrations of cadmium.



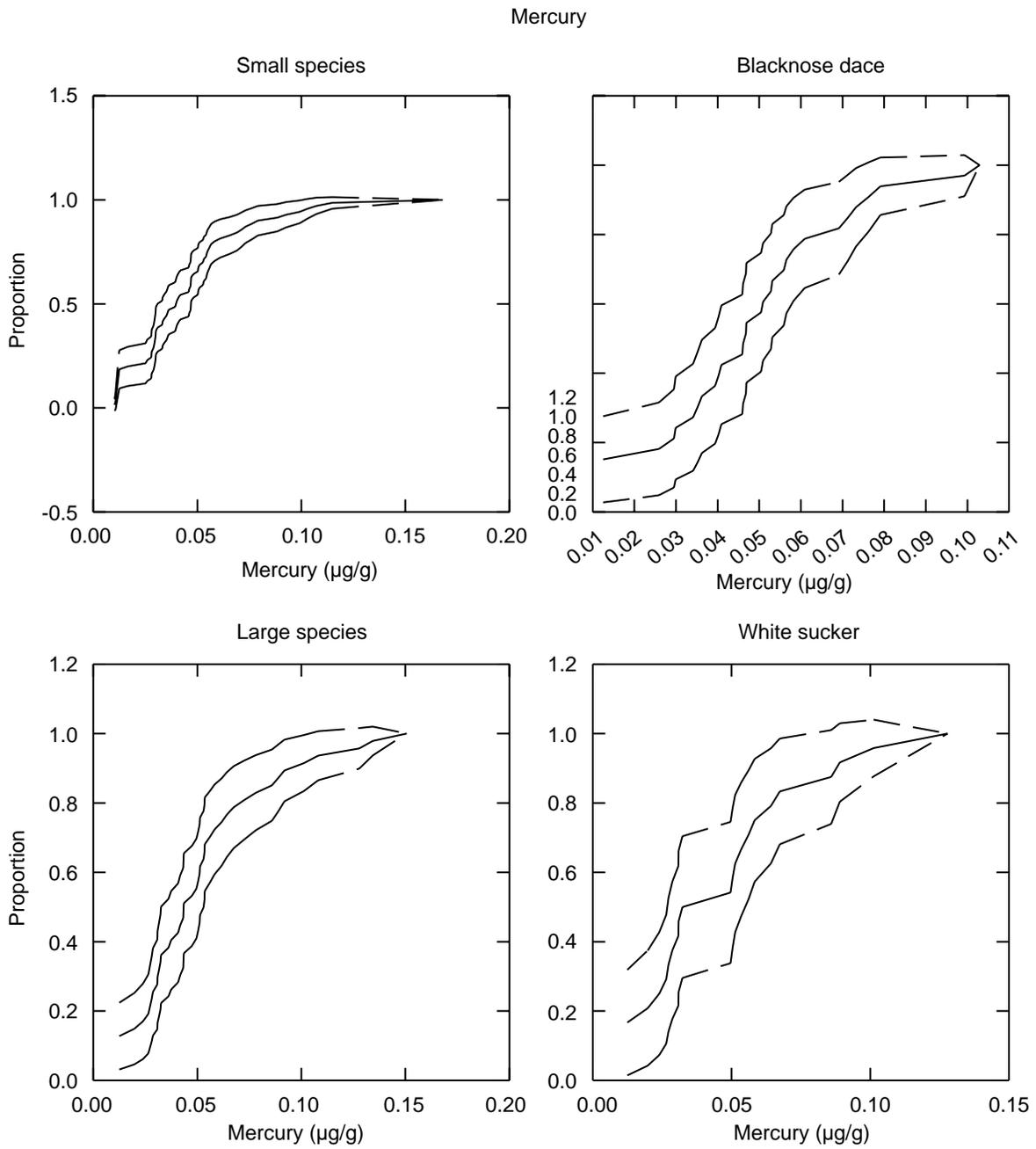
**Figure D-3.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of chromium. Note that the value scales vary among CDFs.



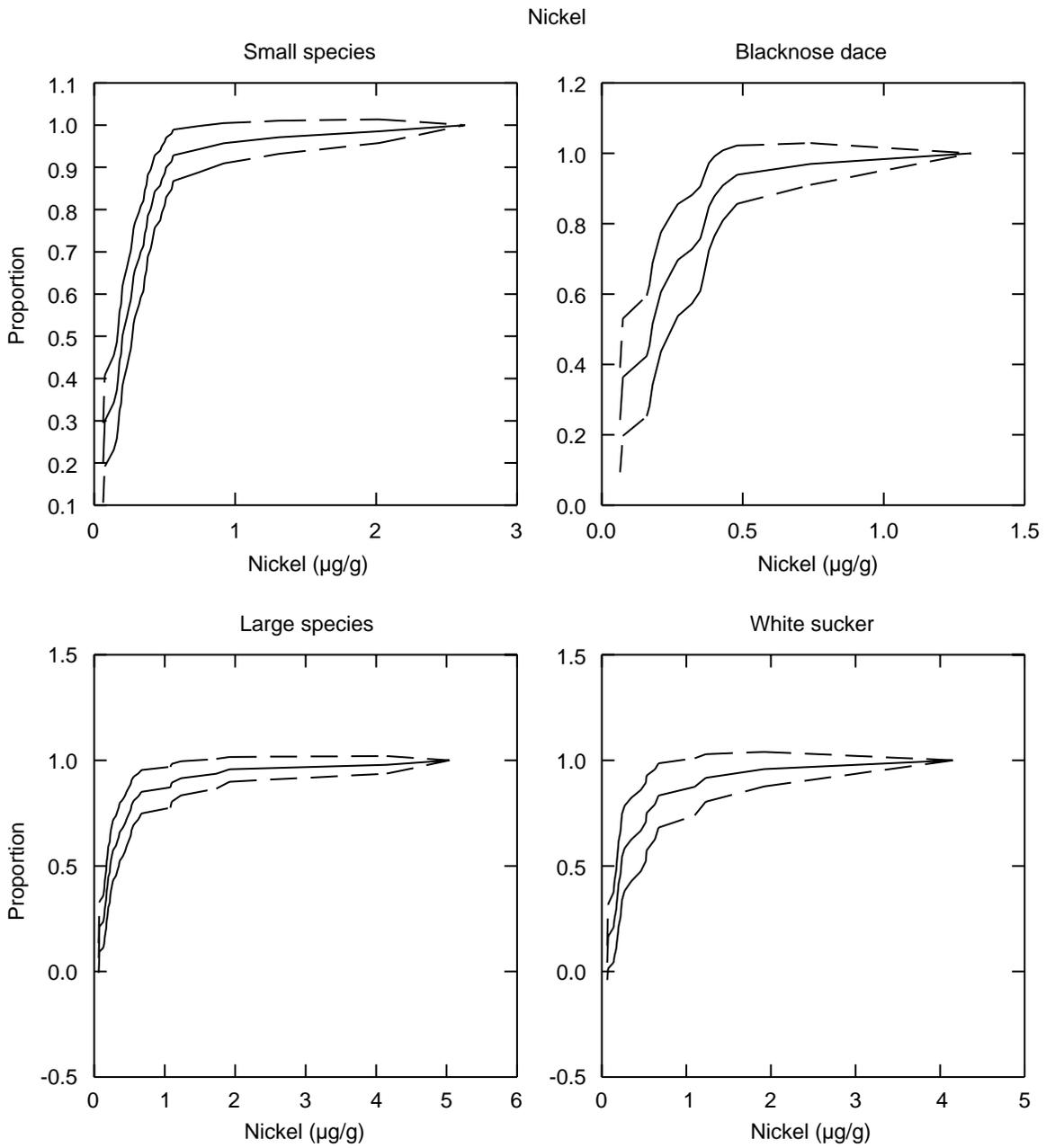
**Figure D-4.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of copper. Note that the value scales vary among CDFs.



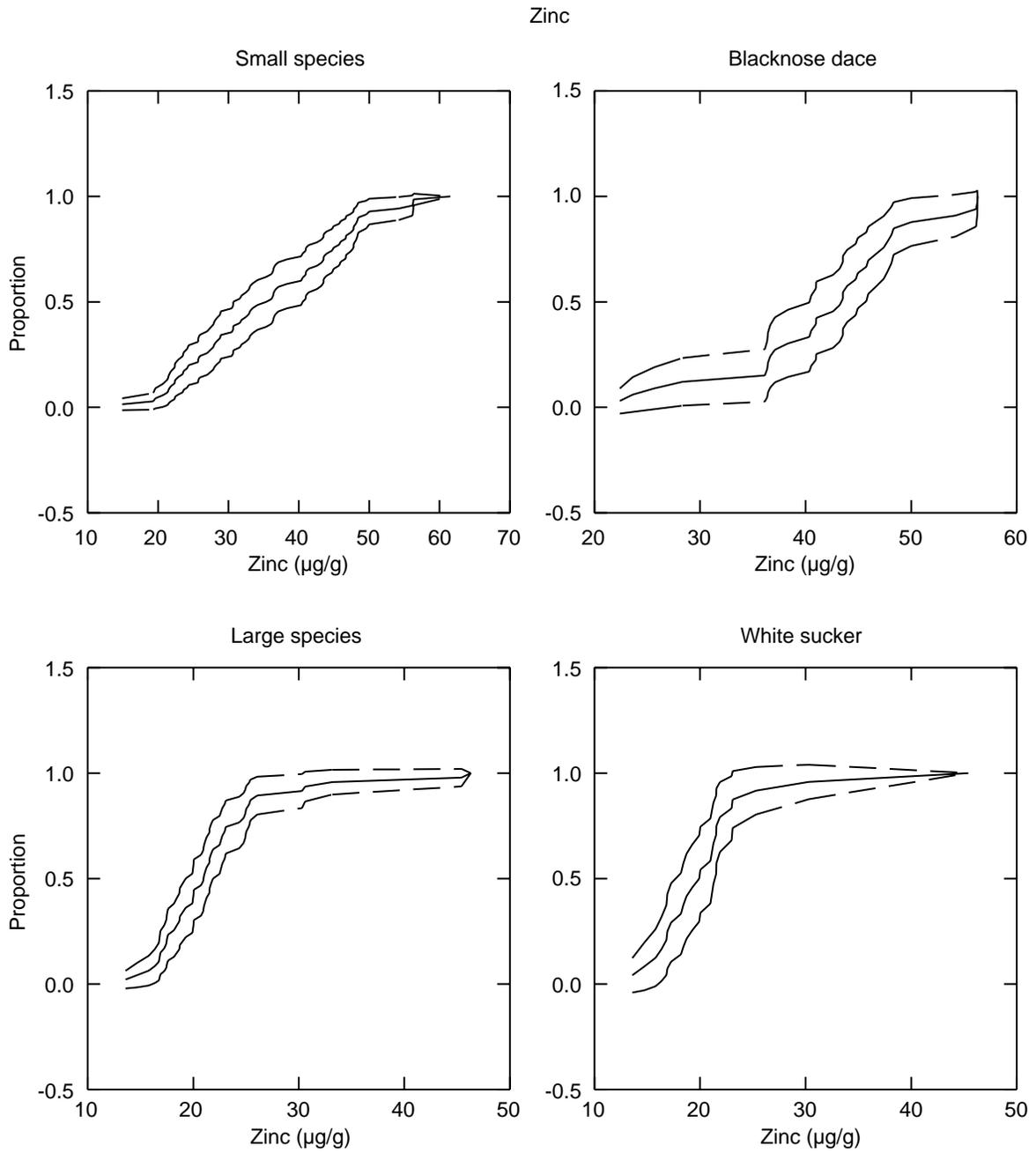
**Figure 5.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of iron. Note that the value scales vary among CDFs.



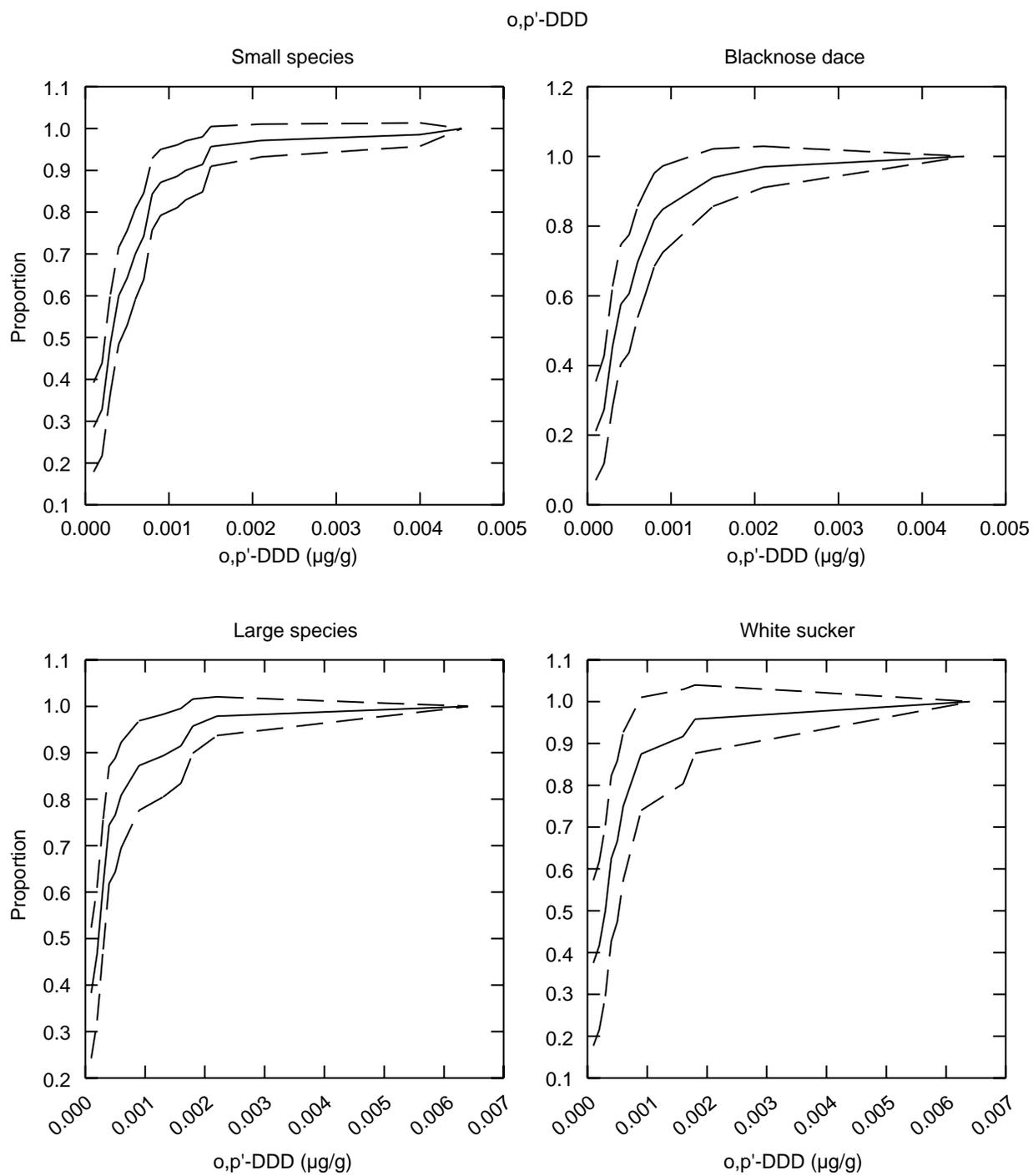
**Figure D-6.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of mercury. Note that the value scales vary among CDFs.



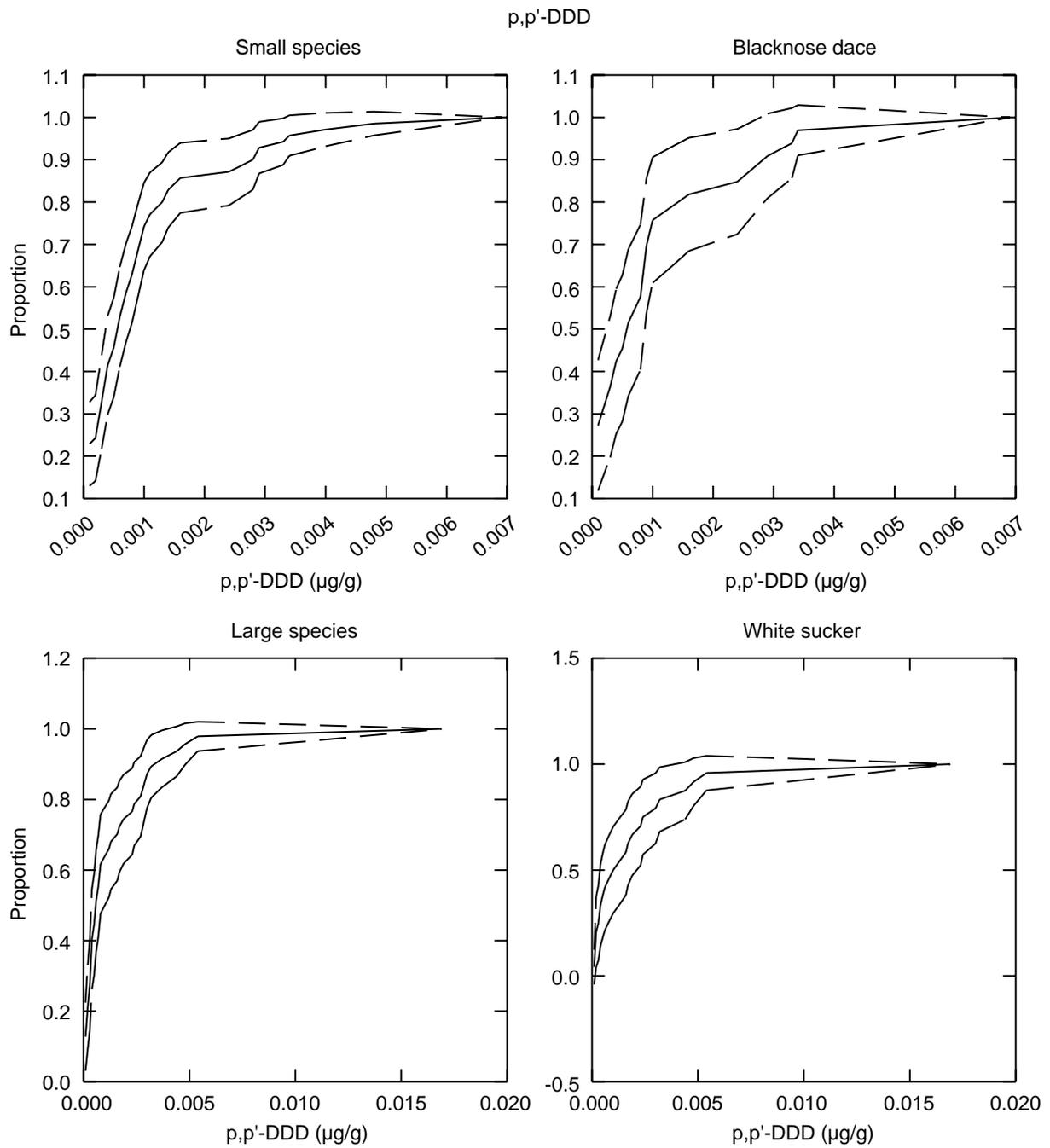
**Figure D-7.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of nickel. Note that the value scales vary among CDFs.



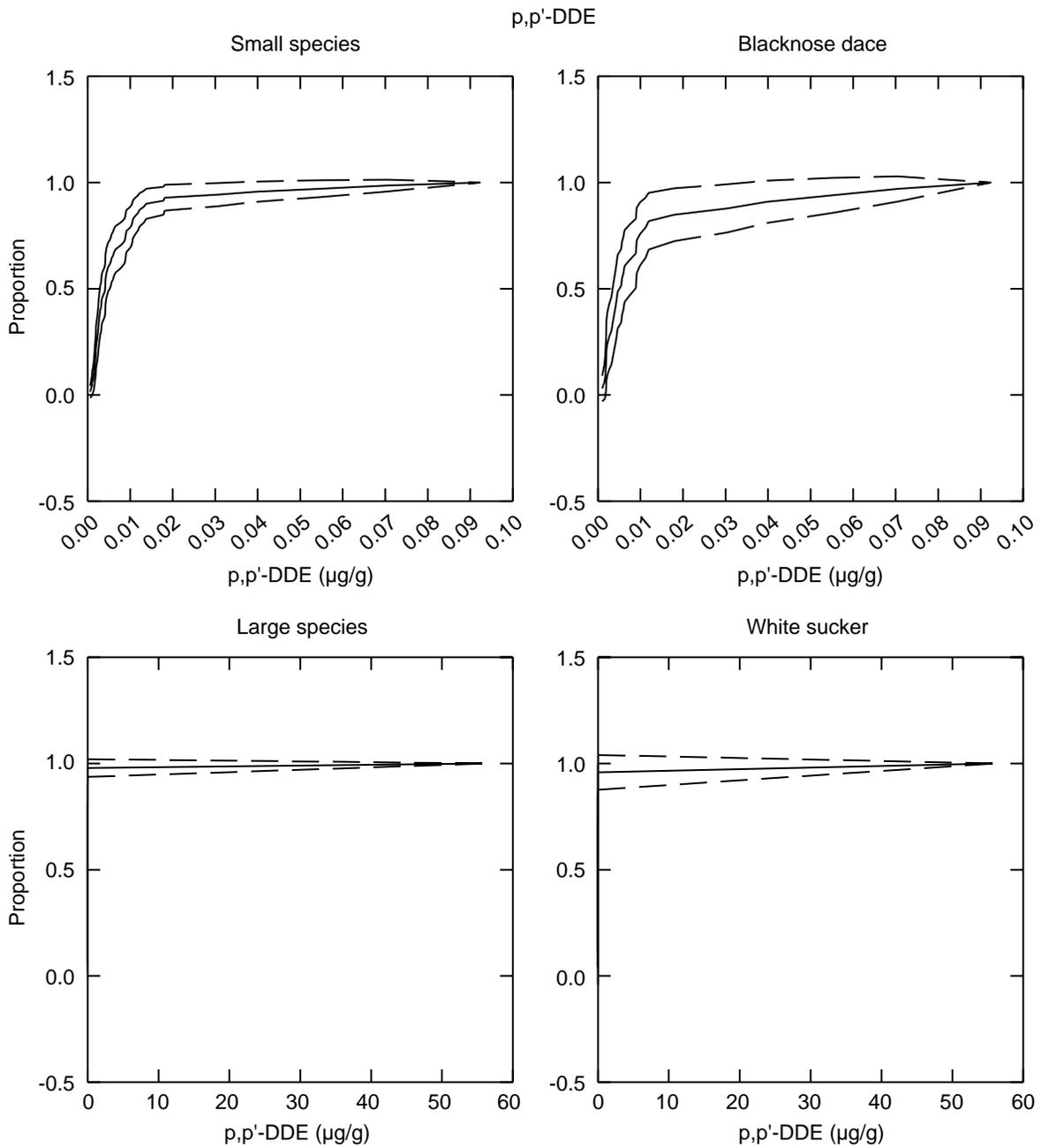
**Figure D-8.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of zinc. Note that the value scales vary among CDFs.



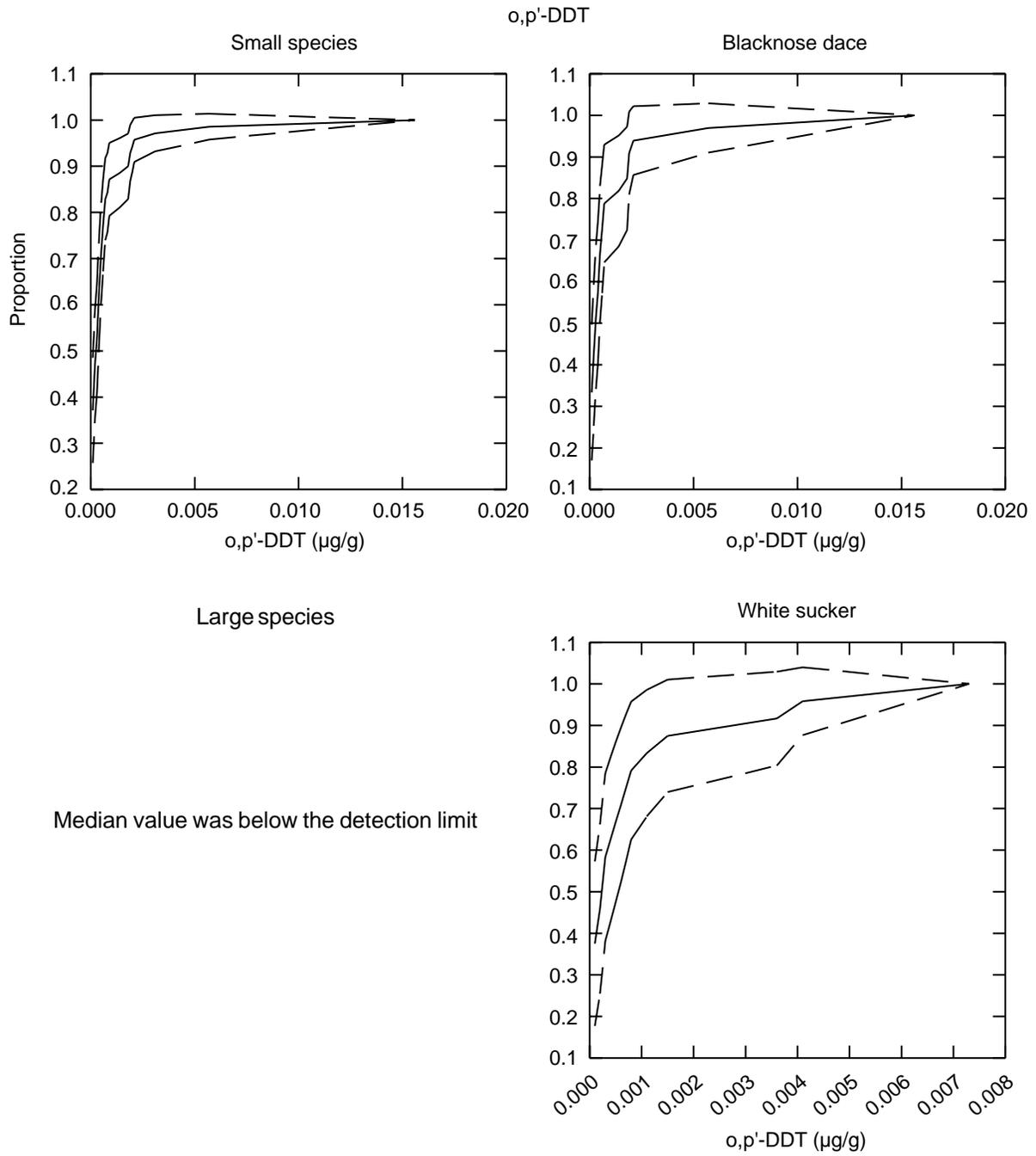
**Figure D-9.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of o,p'-DDD. Note that the value scales vary among CDFs.



**Figure D-10.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of p,p'-DDD. Note that the value scales vary among CDFs.



**Figure D-11.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of p,p'-DDE. Note that the value scales vary among CDFs.



**Figure D-12.** CDFs showing the proportion of three fish categories that are at or below varying concentrations of o,p'-DDT. Note that the value scales vary among CDFs.

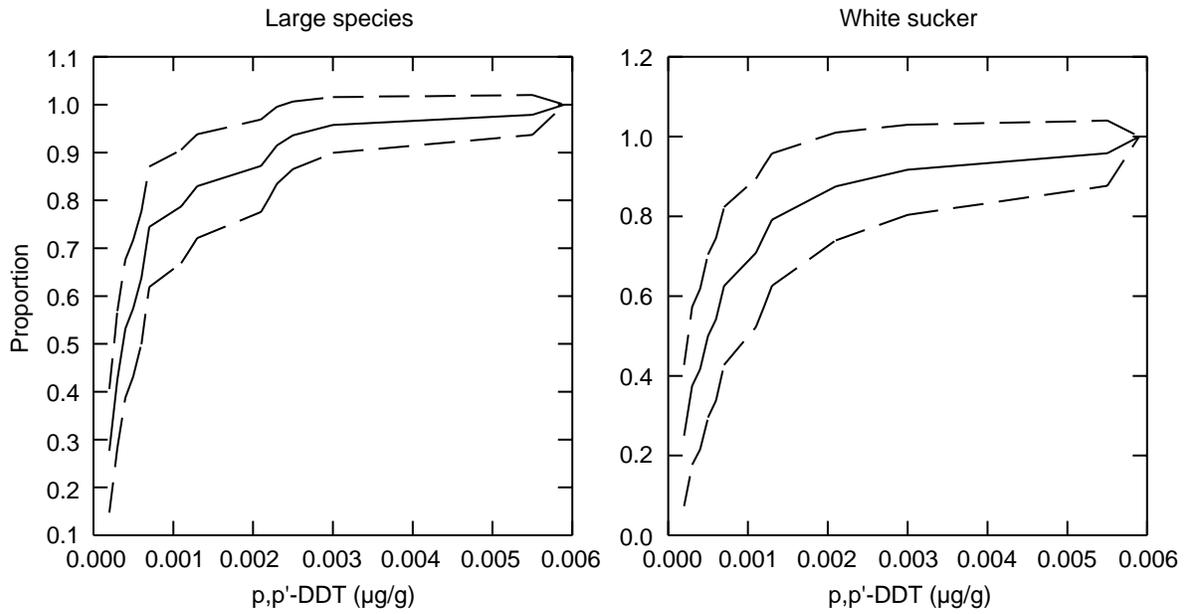
p,p'-DDT

Small species

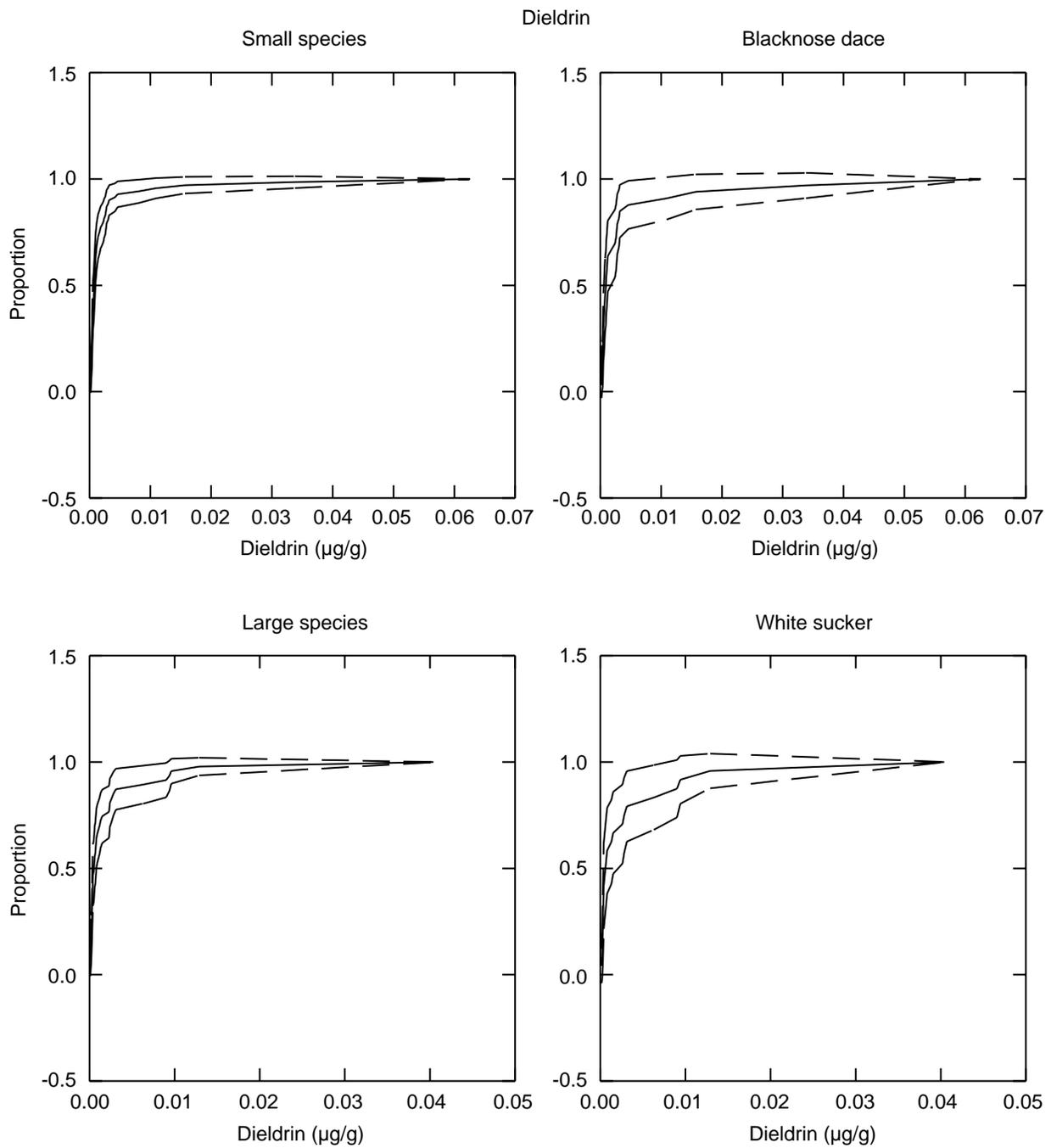
Blacknose dace

Median value was below the detection limit

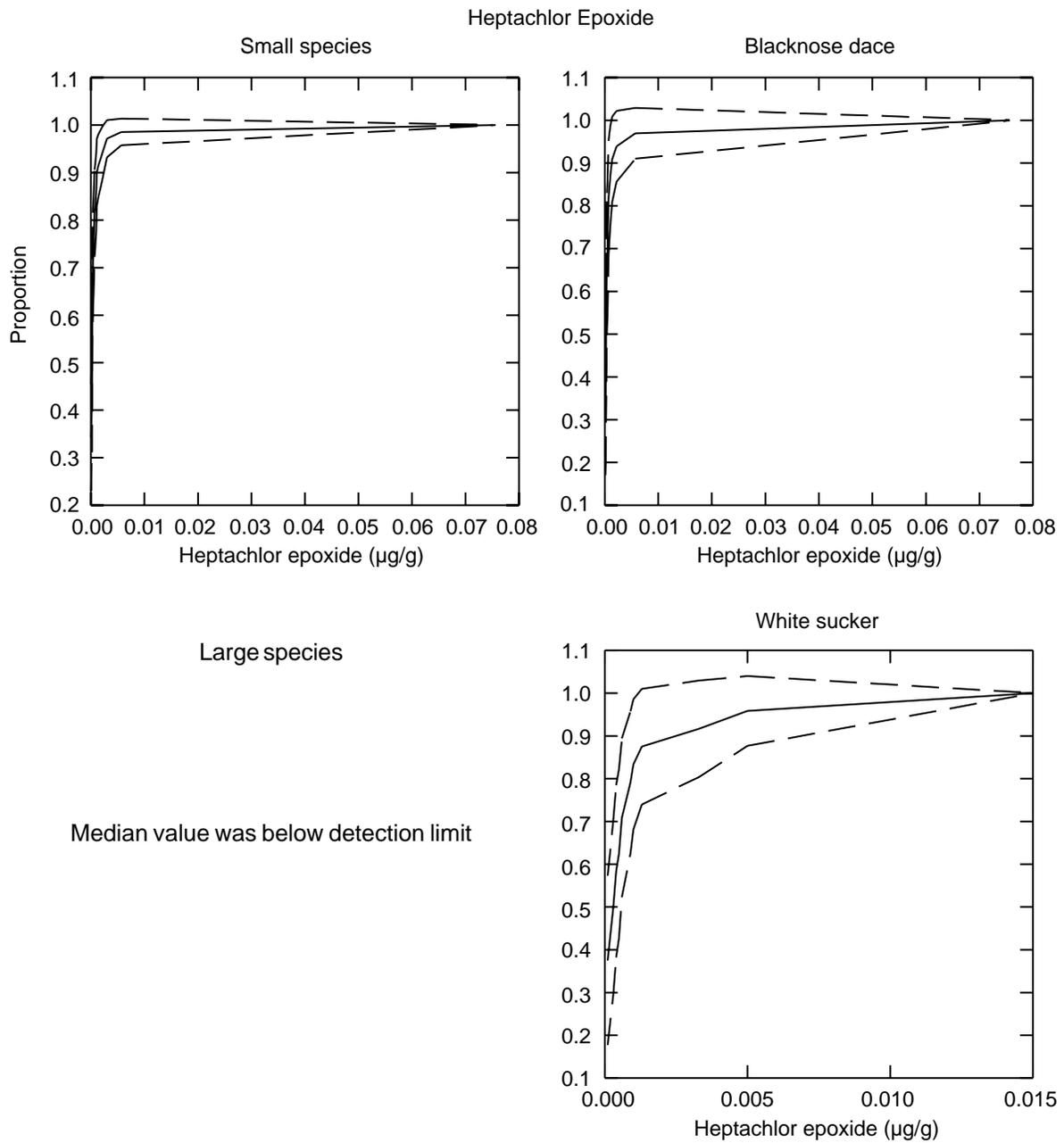
Median value was below the detection limit



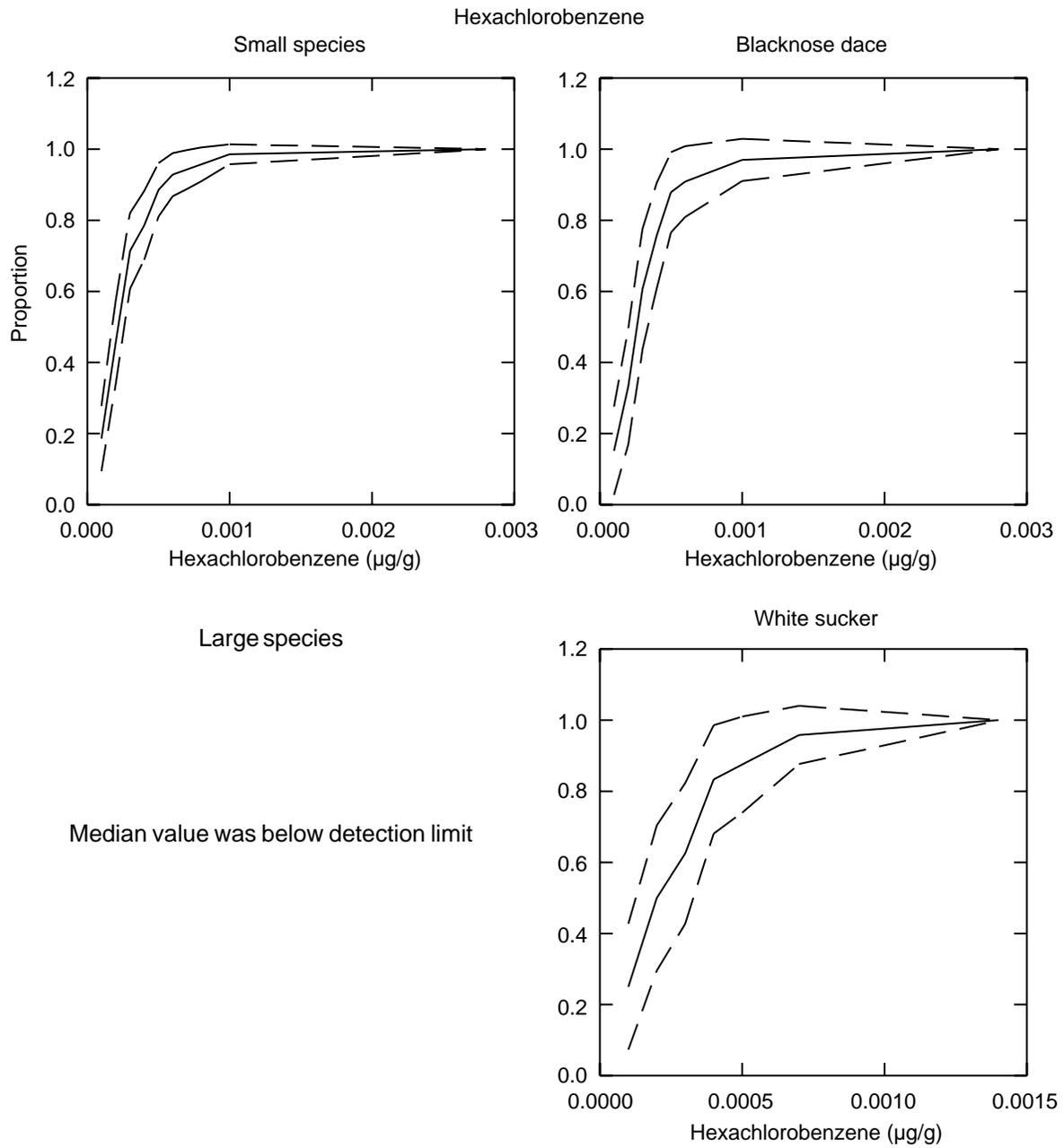
**Figure D-13.** CDFs showing the proportion of two fish categories that are at or below varying concentrations of p,p'-DDT. Note that the value scales vary among CDFs.



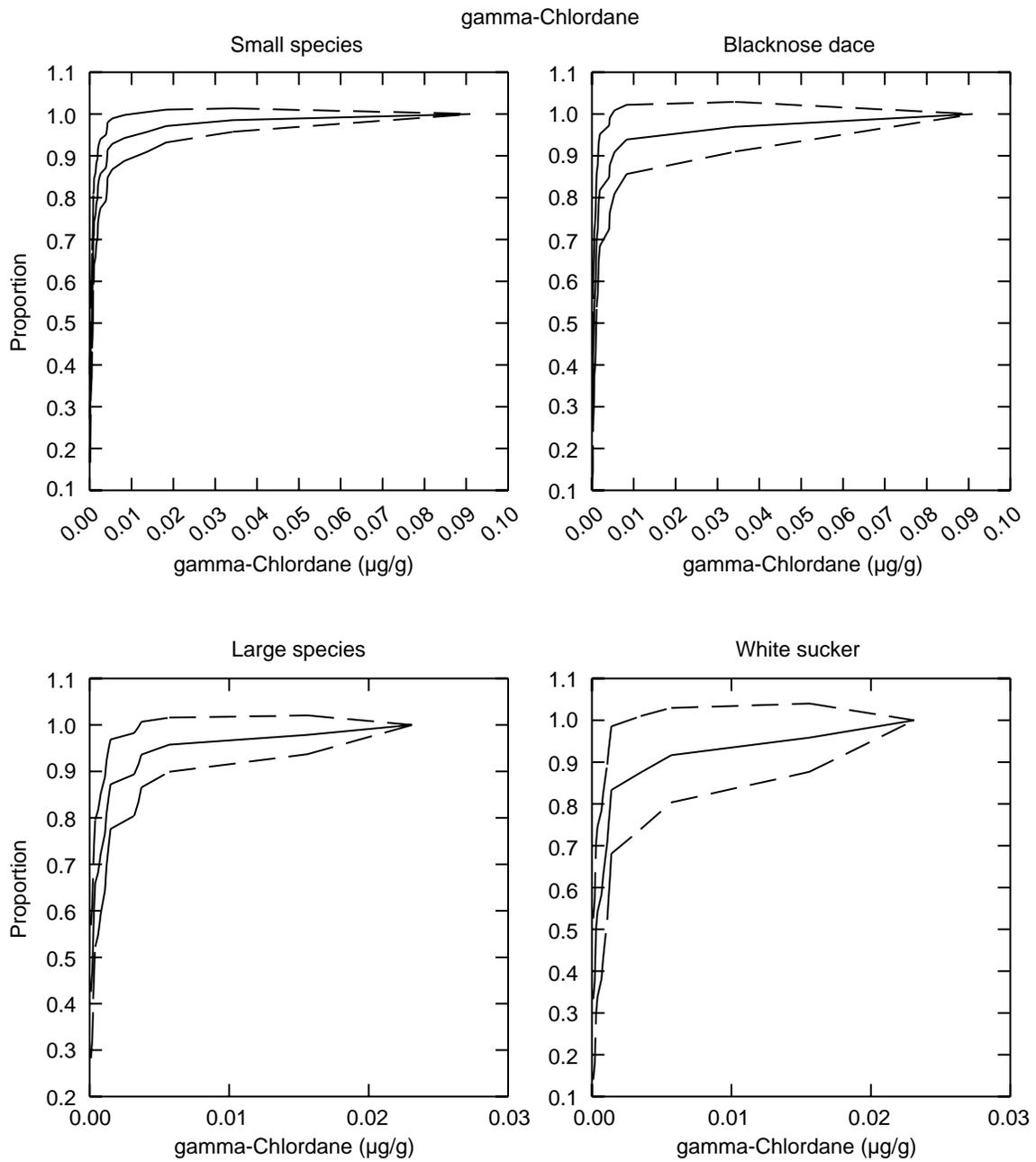
**Figure D-14.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of dieldrin. Note that the value scales vary among CDFs.



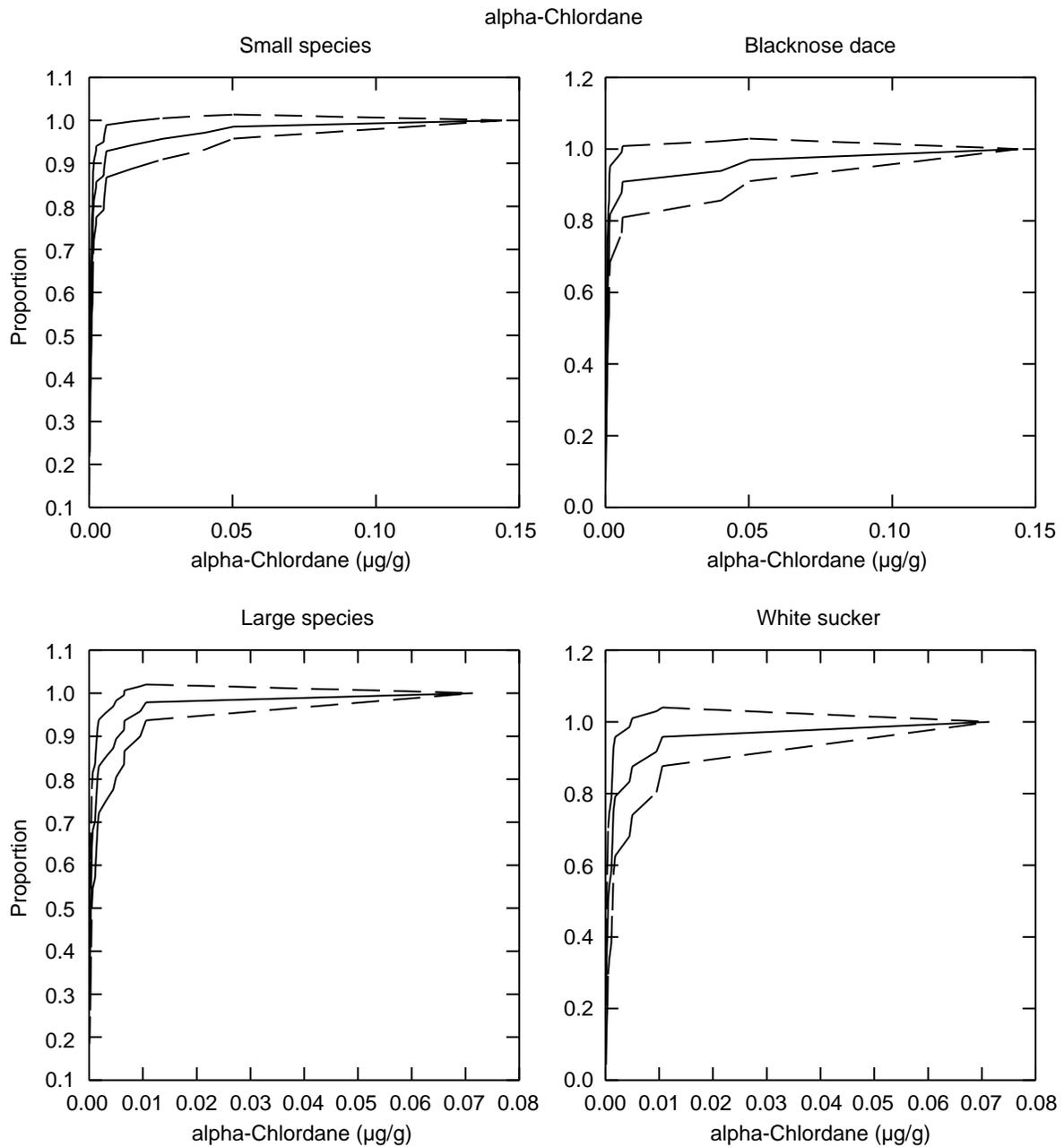
**Figure D-15.** CDFs showing the proportion of three fish categories that are at or below varying concentrations of heptachlor epoxide. Note that the value scales vary among CDFs.



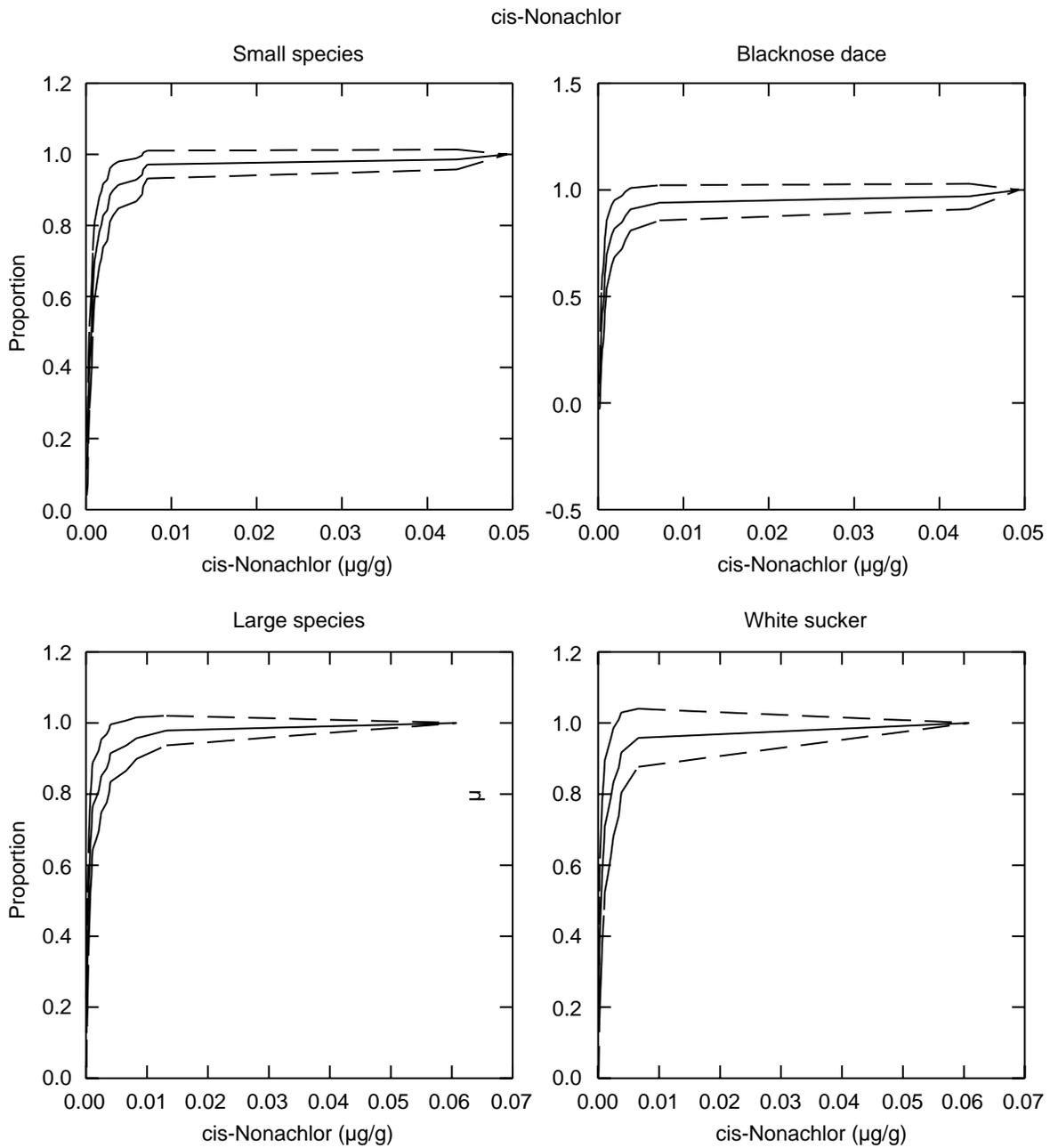
**Figure D-16.** CDFs showing the proportion of three fish categories that are at or below varying concentrations of hexachlorobenzene. Note that the value scales vary among CDFs.



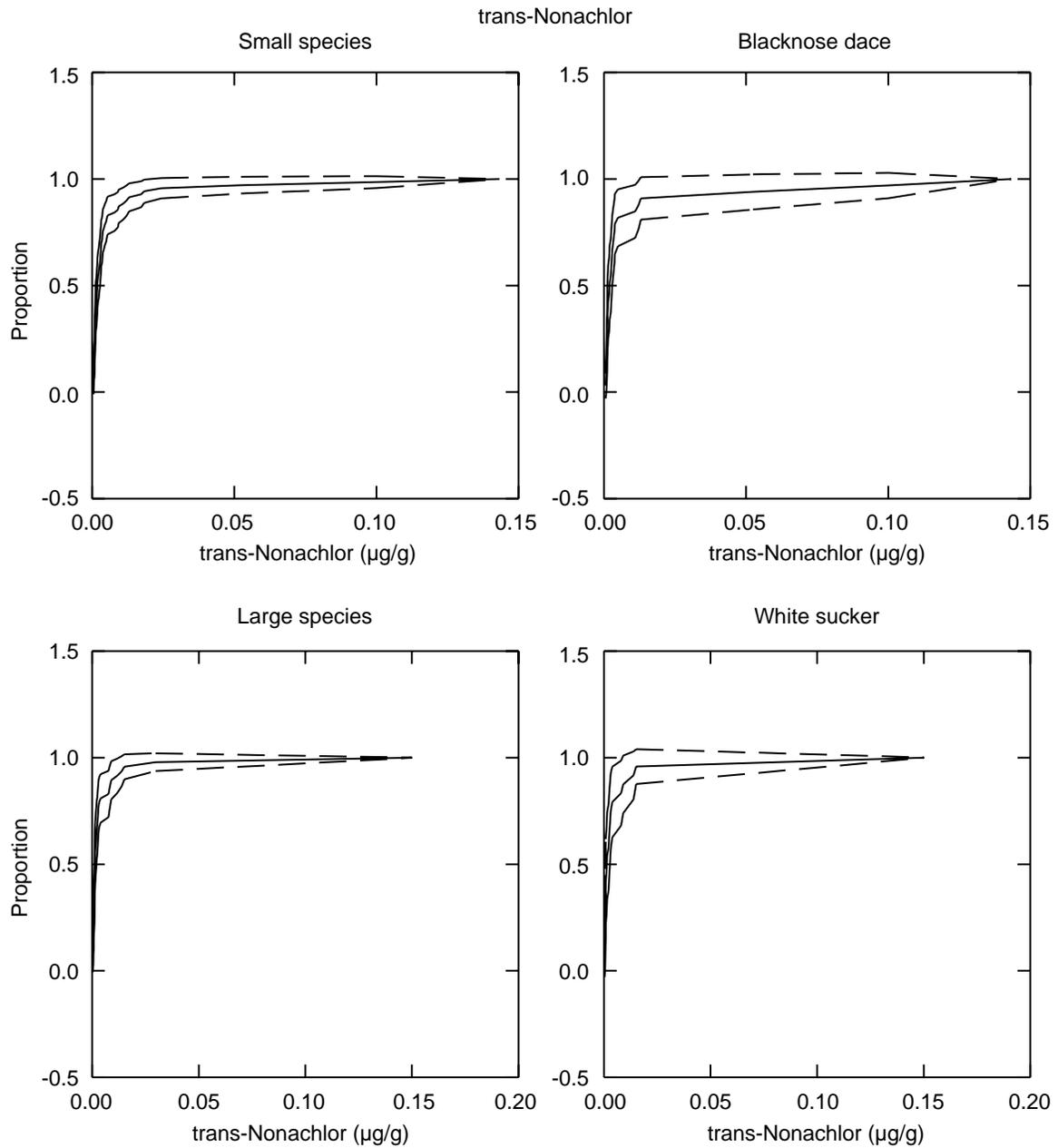
**Figure D-17.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of gamma-chlordane. Note that the value scales vary among CDFs.



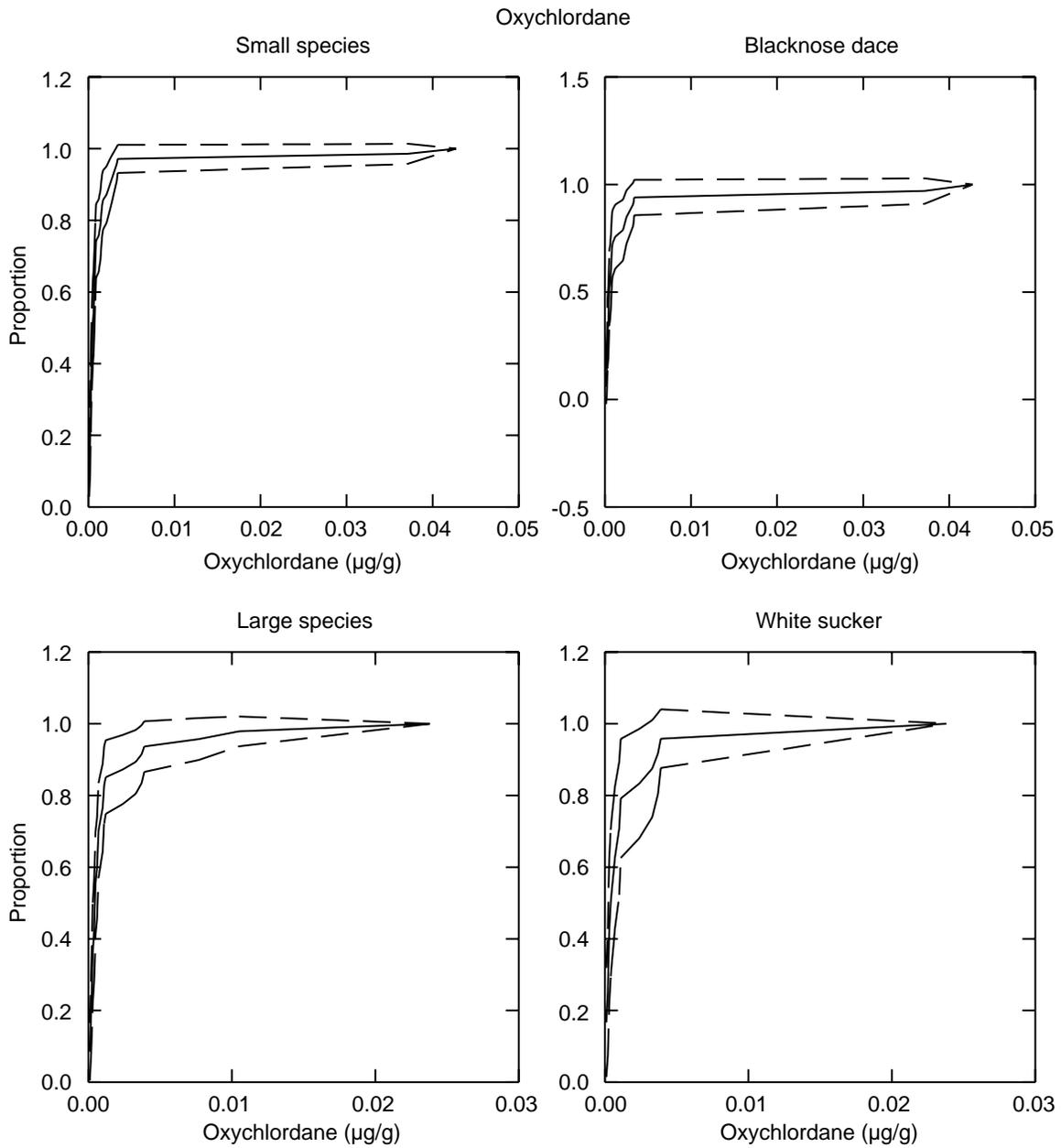
**Figure D-18.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of alpha-chlordane. Note that the value scales vary among CDFs.



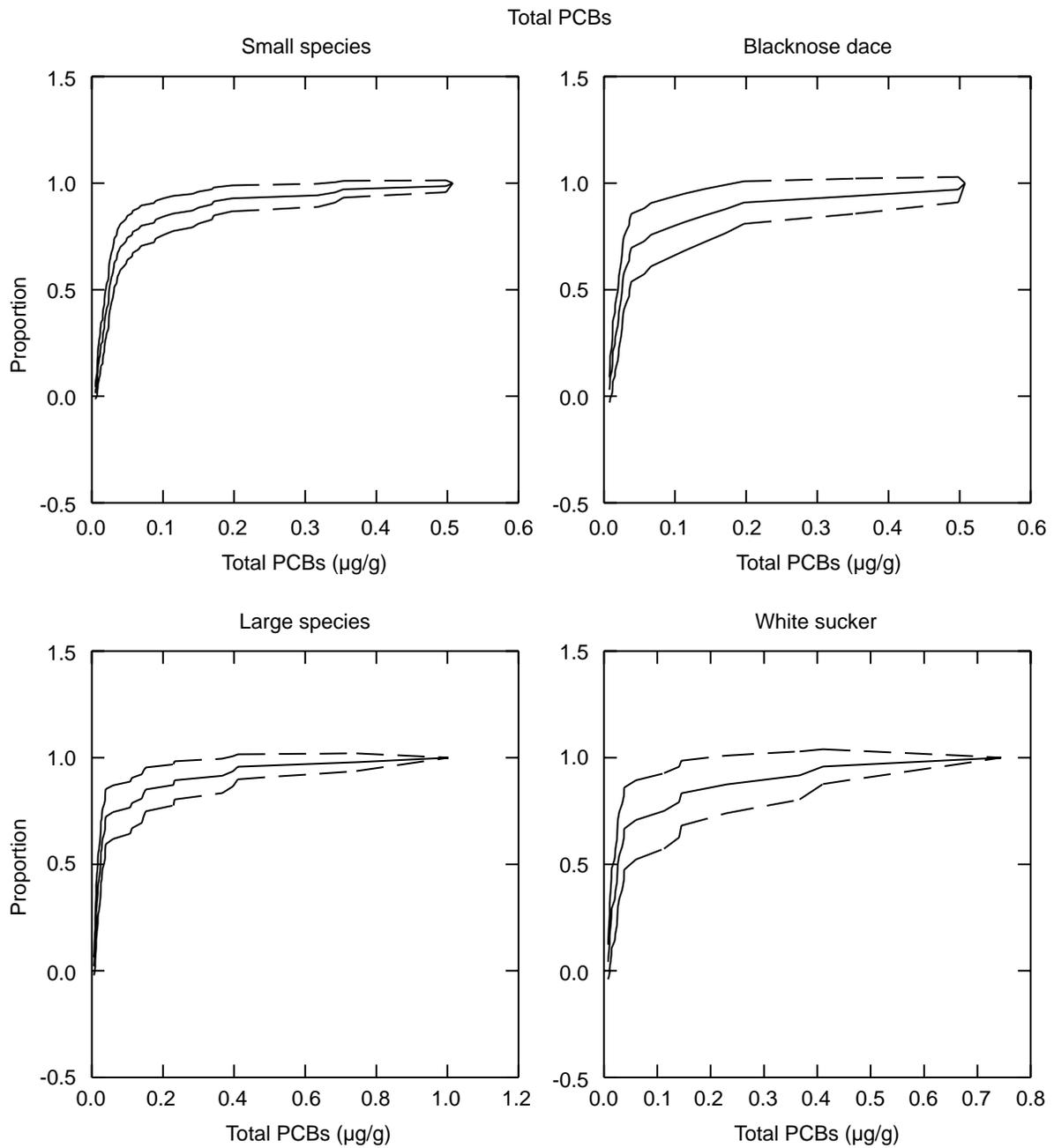
**Figure D-19.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of cis-nonachlor. Note that the value scales vary among CDFs.



**Figure D-20.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of trans-nonachlor. Note that the value scales vary among CDFs.



**Figure D-21.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of oxychlordane. Note that the value scales vary among CDFs.



**Figure D-22.** CDFs showing the proportion of the four fish categories that are at or below varying concentrations of total PCBs. Note that the value scales vary among CDFs.