United States
Environmental Protection
Agency

Office of Science and
Technology (WH-551)
Washington, D.C. 20460

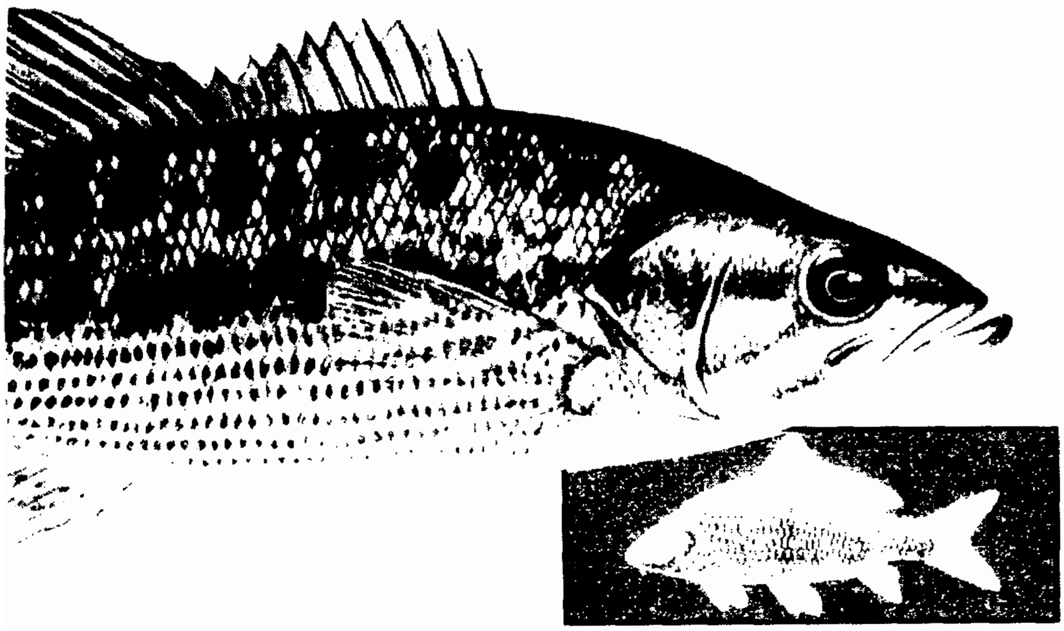
EPA 823-R-92-008a
September 1992

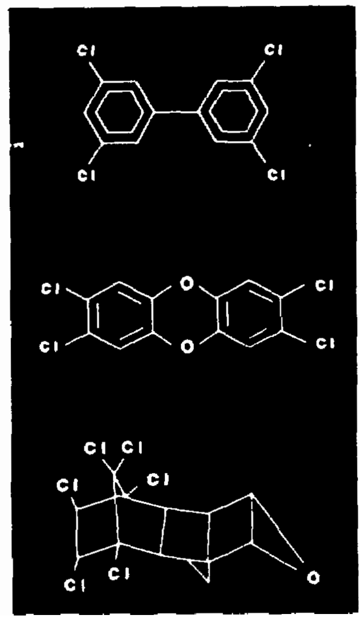
Water

EPA

NATIONAL STUDY OF CHEMICAL RESIDUES IN FISH

Volume I





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National Study of Chemical Residues in Fish

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Office of Science and Technology
Standards and Applied Science Division
U.S. Environmental Protection Agency
401 M Street, SW
Washington, DC 20460

Note

This is the third printing (September 1993) of the *National Study of Chemical Residues in Fish.* All revisions listed on the errata sheet from the first printing have been incorporated into the text of Volumes I and II where appropriate.

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Acknowledgments

This report was prepared under EPA Contract No. 68-C9-0013. EPA Work Assignment Managers for the National Study of Chemical Residues in Fish (NSCRF) were Ruth Yender, Stephen Kroner, Richard Healy, Rod Frederick, Elizabeth Southerland, and Ryan Childs. This study required extensive effort and coordination of many people from EPA Headquarters, EPA Regions, and States. Planning and continuing oversight of the study were provided by the National Bioaccumulation Work Group identified below. EPA staff involved in the planning and initial phase of the study included Martin Brossman, Stephen Kroner, Alec McBride, and Charles Delos.

Samples were collected by staff from EPA Regions and State agencies. The tissue preparation and chemical analyses were performed by staff, identified below, at EPA's laboratory in Duluth, Minnesota. This work was done under the direction of Nelson Thomas and Brian Butterworth. Assistance in methods selection and QA review was provided by Robert Kleopfer and Douglas Kuehl of EPA. Staff from the EPA Duluth laboratory also provided material for the methods section and QA/QC sections of the report. Data evaluations and preparation of the report were accomplished by the NBS Work Group, and their contractors. In addition, staff from other offices within EPA provided information for the chemical profiles, in particular, the Office of Pesticide Programs, Office of Toxic Substances, and Office of Drinking Water. Staff from these and other EPA offices reviewed the report and provided valuable comments, which have been incorporated into the report.

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Executive Summary

This study, previously referred to as the National Bioaccumulation Study, or NBS, is a one-time screening investigation to determine the prevalence of selected bioaccumulative pollutants in fish and to identify correlations with sources of these pollutants. In addition, estimates were made of human health risks for those pollutants studied for which cancer potency factors and/or reference doses have been established. Human health risks were not estimated for dioxins and furans since the potency of these pollutants is the subject of an EPA review.

The study began in 1986 as an outgrowth of the U.S. Environmental Protection Agency's (EPA's) National Dioxin Study, a nationwide investigation of 2,3,7,8 tetrachlorodibenzo-p-dioxin (2,3,7,8 TCDD) contamination of soil, water, sediment, air, and fish. Some of the highest concentrations of 2,3,7,8 TCDD in the National Dioxin Study were detected in fish. EPA's concern that there may be other toxic pollutants bioaccumulating in fish was the primary reason for initiating the National Study of Chemical Residues in Fish. Additionally, this study is considered to be part of a response to a petition from the Environmental Defense Fund and the National Wildlife Federation in which EPA committed to conducting an aquatic monitoring survey of the occurrence of chlorinated dibenzodioxins and chlorinated dibenzofurans. Aquatic biota are being used frequently to determine whether substances are bioaccumulating, to detect acutely toxic conditions, and to detect stresses such as sublethal toxicity, particularly due to interactions among chemicals.

STUDY DESIGN AND APPROACH

The study design and approach for the National Study of Chemical Residues in Fish (NSCRF) focused on pollutant selection, field sampling procedures, analytical protocols (including Quality Assurance/Quality Control), and site selection. Chemicals were selected for analysis based on the potential of the compound to bioaccumulate in fish, the potential for human health effects, the persistence of the chemical in the environment, and the ability to detect the compound in fish tissue. An initial list of 403 pollutants was screened, resulting in a final list of 60 compounds for analysis. These compounds included 15 dioxins and furans, 10 polychlorinated biphenyls (PCBs), 21 pesticides/herbicides, mercury, biphenyl, and 12 other organic compounds.

Field sampling protocols called for the collection of three to five adult fish of the same species and of similar size at each site. Information about the samples was recorded, including the number of samples per composite and sampling date. Age and sex of the fish were not determined. Weight of the sample used for analysis and percent lipid were determined in the laboratory. Lengths and weights of the individual fish were not usually available. Sampling was not conducted during spawning or seasonal migration runs.

At most locations, both a composite sample of a bottom-feeding fish species and a composite sample of a game fish species were collected. Although 119 species were collected, most of the fish samples belonged to 14 different species; carp were the most frequently collected bottom feeder and largemouth bass were the most frequently collected game fish (Table 1). In a few cases, shellfish were collected instead of fish.

TABLE 1
Most Frequently Collected Fish Species

Species	Number of Sites Where Collected
Bottom Feeder Species	
Carp	135
White Sucker	32
Channel Catfish	30
Redhorse Sucker	16
Spotted Sucker	10
Game Species	
Largemouth Bass	83
Smallmouth Bass	26
Walleye	22
Brown Trout	10
White Bass	10
Northern Pike	8
Flathead Catfish	8
White Crappie	7
Bluefish	5

Fish samples were analyzed at EPA's Environmental Research Laboratory (ERL) in Duluth, Minnesota. In general, the bottom feeders were analyzed as whole-body samples to determine the occurrence of the study chemicals and the game fish were analyzed as fillets to indicate the potential for risks to human health from fish consumption. Selected bottom feeders of the type often used for human consumption were analyzed as fillets at a small number of sites and used to evaluate human health risks. To analyze fish for the 15 dioxins and furans, ERL-Duluth refined and expanded the method for dioxin (i.e., 2,3,7,8 TCDD) analysis developed as part of EPA's National Dioxin Study. For 44 of the remaining 45 compounds, ERL-Duluth developed an analytical method specifically for this study. The remaining study compound, mercury, was analyzed using EPA's standard analytical techniques.

Sites were selected for the study by EPA Regional and State staff. Sites consisted of 314 locations thought to be influenced by a variety of point and nonpoint sources (referred to as targeted sites), 39 locations from the USGS National Stream Quality Accounting Network (NASQAN), and 35 sites representative of background levels (Figure 1). Targeted sites included locations near pulp and paper mills, refineries using the catalytic reforming process, Superfund sites, former wood preserving operations, other industrial sites, publicly owned treatment works (POTWs), and agricultural and urban areas. Because the study was initiated as a follow-up to the National Dioxin Study, many of the targeted sites selected were those thought to be producers of dioxins (e.g., pulp and paper mills using chlorine for bleaching).

RESULTS

Prevalence and Concentration

Many of the investigated pollutants were frequently detected in the fish samples from the targeted sites. Seven of the 15 dioxin/furan compounds and 15 of the other 45 compounds were detected at over 50 percent of the sites (Tables 2 and 3). The two most frequently detected dioxin and furan compounds were both found at 89 percent of the sites; these compounds are 1,2,3,4,6,7,8 heptachlorodibenzodioxin (HpCDD) and 2,3,7,8 tetrachlorodibenzofuran (TCDF). These compounds were also detected at the highest concentrations; HpCDD at 249 picograms per gram (pg/g) or 249 parts per trillion by wet weight (ppt) and TCDF at 404 parts per trillion (ppt). The average concentrations of these two compounds were substantially lower at 10.5 and 13.6 ppt, respectively. The dioxin compound considered to be the most toxic, 2,3,7,8 tetrachlorodibenzo-p-dioxin (TCDD), was found at 70 percent of the sites at a maximum concentration of 204 ppt and an average concentration of 6.89 ppt. Only two of the 15 dioxin/furan compounds analyzed were detected at fewer than 20 percent of the sites.

Toxicity equivalent concentrations (TECs) of dioxins/furans were calculated to facilitate comparison of fish tissue contamination among sites. TEC represents a toxicity weighted total concentration of all individual congeners using 2,3,7,8, TCDD as the reference compound. EPA's interim method was used to determine TEC (Barnes, et. al., 1989). This is referred to in the report as the Toxicity Equivalency Concentration (TEC) value, sometimes called TEQ (toxicity equivalents).

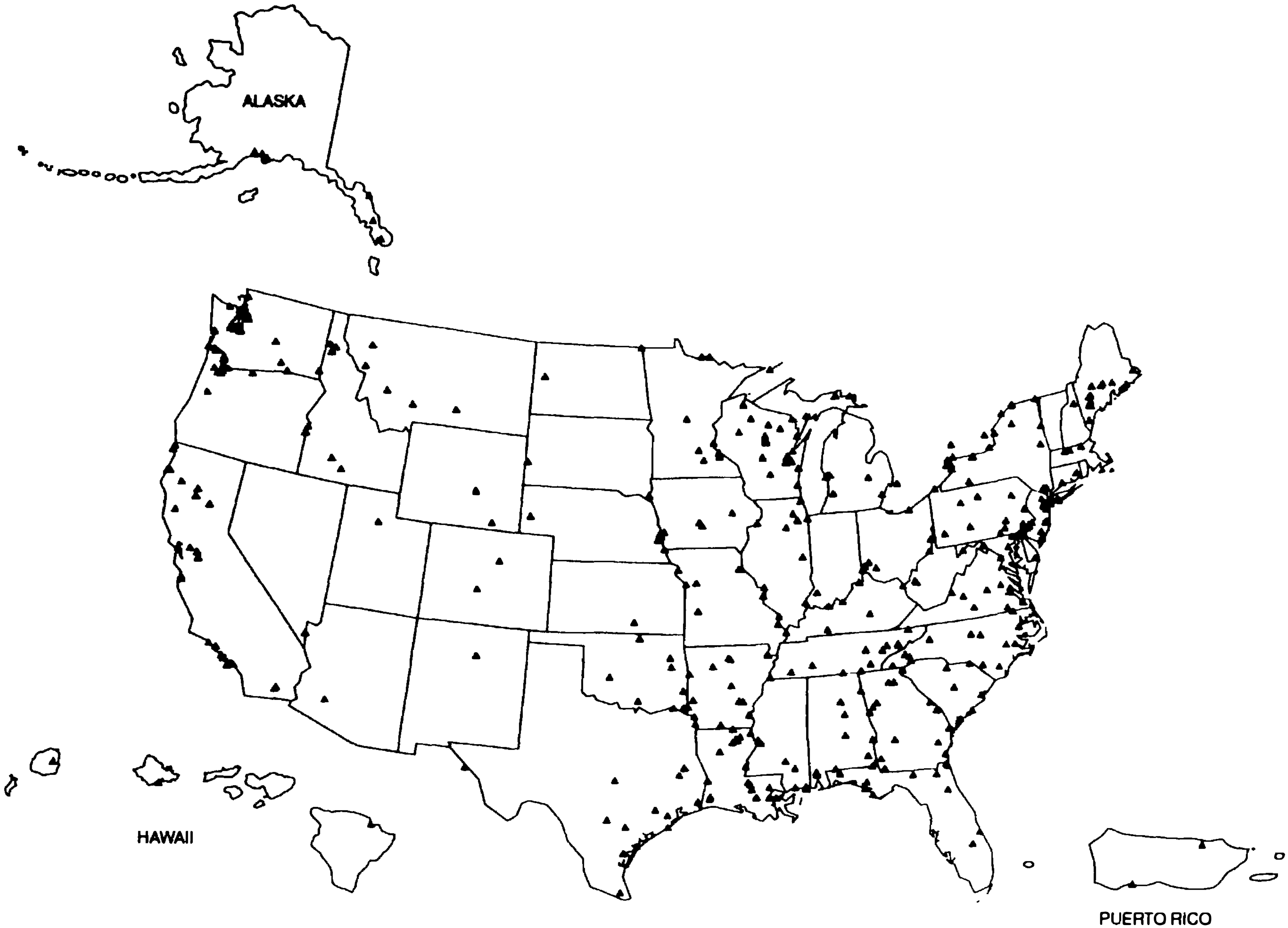


Figure 1. Location of bioaccumulation study sampling sites.

TABLE 2
Summary of Prevalence and Concentration for Dioxins and Furans

Chemical	Percent of Sites Detected	Concentration pg/g or ppt by wet weight: Max	Mean	Median
Dioxins				
1,2,3,4,6,7,8 HpCDD	89	249	10.5	2.83
2,3,7,8 TCDD	70	204	6.89	1.38
1,2,3,6,7,8 HxCDD	69	101	4.30	1.32
1,2,3,7,8 PeCDD	54	54.0	2.38	0.93
1,2,3,7,8,9 HxCDD	38	24.8	1.16	0.69
1,2,3,4,7,8 HxCDD	32	37.6	1.67	1.24
Furans				
2,3,7,8 TCDF	89	404	13.6	2.97
2,3,4,7,8 PeCDF	64	56.4	3.06	0.75
1,2,3,4,6,7,8 HpCDF	54	58.3	1.91	0.72
1,2,3,7,8 PeCDF	47	120.0	1.71	0.45
1,2,3,4,7,8 HxCDF	42	45.3	2.35	1.42
2,3,4,6,7,8 HxCDF	32	19.3	1.24	0.98
1,2,3,6,7,8 HxCDF	21	30.9	1.74	1.42
1,2,3,4,7,8,9 HpCDF	4	2.57	1.24	1.30
1,2,3,7,8,9 HxCDF	1	0.96	1.22	1.38
TEC*	N/A	213	11.1	2.80

* TEC represents the sum of toxicity-weighted concentrations of all dioxins and furans relative to 2,3,7,8 TCDD.

TABLE 3
Summary of Prevalence and Concentration for 45* Other Bioaccumulative Compounds

Chemical	Percent of Sites Detected	Concentration ng/g or ppb by wet weight Max	Mean	Median
DDE	99	14000	295	58.8
Mercury	92	1800	260	170
Biphenyl	94	131	2.7	0.64
Total PCBs	91	124000	1890	209
Nonachlor, trans	77	477	31.2	9.22
Chlordane, cis	64	378	21.0	3.66
Pentachloroanisole	64	647	10.8	0.92
Chlordane, trans	61	310	16.7	2.68
Dieldrin	60	450	28.1	4.16
Alpha-BHC	55	44.4	2.41	0.72
1,2,4 Trichlorobenzene	53	265	3.10	0.64
Hexachlorobenzene	46	913	5.80	ND
Gamma-BHC	42	83.3	2.70	ND
1,2,3 Trichlorobenzene	43	69.0	1.27	ND
Mirex	38	225	3.86	ND
Nonachlor, cis	35	127	8.77	ND
Oxychlordane	27	243	4.75	ND
Chlorpyrifos	26	344	4.09	ND
Pentachlorobenzene	22	125	1.18	ND
Heptachlor Epoxide	16	63.2	2.19	ND
Dicofol	16	74.3	0.98	ND
1,2,3,4 Tetrachlorobenzene	13	76.7	0.47	ND
Trifluralin	12	458	5.98	ND
1,3,5 Trichlorobenzene	11	14.9	0.12	ND
Endrin	11	162	1.69	ND
1,2,3,5 TECB	9	28.3	0.34	ND
Octachlorostyrene	9	138	1.71	ND
1,2,4,5 TECB	9	28.3	0.33	ND
Methoxychlor	7	393	1.32	ND
Isopropalin	4	37.5	0.46	ND
Nitrofen	3	17.9	0.17	ND
Hexachlorobutadiene	3	164	0.57	ND
Heptachlor	2	76.2	0.35	ND
Perthane	1	5.12	0.03	ND
Pentachloronitrobenzene	1	15.5	0.09	ND
Diphenyl Disulfide	1	3.24	0.02	ND

* The number of compounds shown here is 36; the difference is the result of grouping 3 individual PCB compounds with 1 to 10 chlorines. Five of the PCBs were found at concentrations above 50 percent; the remainder were found between 3 and 35 percent.

In general, the maximum and average concentrations for the other 45 compounds are 1,000 to 10,000 times greater than those for dioxins and furans (Table 3). Of these 45 compounds, the most frequently detected pollutant was DDE, found at over 98 percent of all sites sampled. This compound is a metabolic breakdown product of DDT, which was a widely used pesticide and is extremely persistent in the environment. Other compounds detected at more than 90 percent of the sites were mercury, total PCBs, and biphenyl. The high prevalence of mercury results partly from its many industrial uses including use in batteries, vapor lamps, and thermostats; as a fungicide in some exterior water-based paints; and as a cathode in the electrolytic production of chlorine and caustics. Mercury also occurs in the natural environment in both inorganic and organic compounds and is discharged to the atmosphere from natural processes (e.g., degassing of volcanos) and from the burning of fossil fuels. As with DDT, PCBs are very persistent in the environment and, until 1977 when they were essentially banned, were widely used as dielectric fluids in transformers and capacitors. Total PCBs in this study refers to the sum of the concentrations of compounds with 1 to 10 chlorines. Concentrations of specific Aroclors or mono-ortho substituted compounds were not determined in this study. The high number of low-concentration biphenyl samples (88 percent below 2.5 ppb) most likely results from degradation of PCBs. The high-concentration samples appear to be associated with various industrial uses such as heat transfer fluid, dye carriers, and hydraulic fluid.

PCBs were detected at the highest concentration, with a maximum value of 124,000 nanograms per gram (ng/g) or 124,000 parts per billion by wet weight (ppb), and an average concentration of 1,890 ppb. The next highest compound was DDE, with a maximum and average concentration of 14,000 ppb and 295 ppb, respectively. All of the remaining 34 compounds were found at much lower concentrations than DDE.

Prevalence was compared with the most recent (1984) results from the National Contaminant Biomonitoring Program (NCBP), which was formerly part of the National Pesticide Monitoring Program. The NCBP was initiated in 1964 to determine how organochlorine compound levels vary over geographic regions and change over time. In this program, fish were sampled at 112 sites throughout the United States and these samples were analyzed for 19 organochlorine chemicals and 7 metals. The NSCRF analyzed 15 of these 19 organochlorine compounds and mercury. In the NSCRF, 11 compounds were found at greater than 50 percent of the sites. Eight of these were also analyzed in the NCBP, and seven compounds were found at greater than 50 percent of the sites. The results from these two studies track closely for the common pollutants analyzed.

Source Correlation Analysis

Concentration comparisons between selected source categories were made using various statistical tools including a box and whisker plot. The categories used were background sites, sites selected from the USGS NASQAN network, sites near Superfund locationse sites near pulp and paper mills that use chlorine for bleaching, sites near other types of pulp and paper mills, sites near former or existing wood preserving plants, sites near industrial or urban areas, sites near industrial areas that include refineries with catalytic reforming operations, sites that could be influenced by runoff from agricultural areas, and sites near POTWs. These categories were selected based on probable sources of pollutants. Background sites were selected to provide a comparison with areas relatively free of point and nonpoint source pollution. Sites where multiple source categories could have affected fish contamination levels were not used for the box plots or other statistical tests. For example, sites in the chlorine paper mill category that were also near Superfund sites, other paper mills, or reefineries were not used for the dioxin/furan box plots.

Pulp and paper mills using chlorine to bleach pulp appeared to be the dominant source of 2,3,7,8 TCDD and 2,3,7,8 TCDF. Statistical comparison, using Kruskal-Wallis tests and Mann-Whitney U tests show that sites near pulp and paper mills using chlorine have significantly higher concentrations of 2,3,7,8 TCDD than all other source categories. These statistical tests also show the same results for 2,3,7,8 TCDF with the exception that fish contamination levels near sites in the Superfund category marginally met the statistical test criteria for being similar. Analysis of the five sites with the highest 2,3,7,8 TCDD and 2,3,7,8 TCDF concentrations also show that pulp and paper mills using chlorine are dominant sources of these compounds at four of these sites.

Statistical correlation analyses were less definitive for the other dioxins/furans in that results showed no dominant source for any of these chemicals (i.e., a source from which fish contamination levels were significantly higher than all other sources). A review of dioxin/furan data limited to median concentrations alone shows that Superfund sites are highest for penta-furans, paper mills using chlorine are highest for penta- and hexa-dioxins, and refinery/other industry sites are highest for hexa-furans.

Results for the other 45 chemicals studied also showed no single dominant source for any of these chemicals. Although these compounds showed no dominant source, a number of observations can be made from review of the data. Two such examples involve pesticides and PCBs. A comparison of 15 agricultural and 20 background sites for 10 of the pesticides evaluated showed no significant differences between these categories. This same comparison for four other pesticides (DDE, nonachlor, chlordane, and gamma-BHC (lindane)) showed that fish contamination levels were significantly higher at sites near agricultural sources. The median PCB concentration for the 20 background sites was below detection compared with values of 213 to 525 ppb for industrial/urban sites, paper mills using chlorine, refinery/other industry sites, nonchlorine paper mills, and Superfund sites.

HUMAN HEALTH RISK ESTIMATES

Potential upper-bound human cancer risk from consumption of fish was estimated using fillet samples for 14 compounds for which cancer potency factors are available (Table 4). Human health risks were not calculated for dioxins/furans, due to the current review of the potency of these chemicals. Most of the fillets were game fish, but fillets from a few bottom feeders that are consumed by humans were also included. Fillet data were available at 182 sites for mercury and 106 sites for the remaining chemicals. The risk estimates were performed using standard EPA risk assessment procedures and assumed lifetime exposure. Upper-bound cancer potency factors, and fish consumption rates of 6.5, 30, and 140 g/day were used.

The highest estimated lifetime human cancer risk levels are associated with total PCBs. The cancer risk exceeded 10^{-4} at 42 sites for total PCBs for a fish consumption rate of 6.5 g/day (Table 4). The second highest cancer risk was associated with dieldrin where six sites had estimated cancer risks greater than 10^{-4} for a 6.5-g/day fish consumption rate.

Potential noncarcinogenic effects on human health were estimated for the 21 compounds for which reference dose (RfD) values were available. Hazard indices based on a fish consumption rate of 6.5 g/day exceeded a value of 1 (meaning adverse health effects may occur) at a small number of sites due to total PCBs, mirex, and combined chlordane when the maximum fillet concentrations were used in the analysis. No indices were exceeded when the mean or median concentrations were used. Combined chlordane is the sum of the concentrations of cis- and trans- chlordane, cis- and trans-nonachlor, and oxychlordane.

STUDY LIMITATIONS

The risks presented in this report represent a national screening assessment and not a detailed local assessment of risks to specific populations. Such detailed risk assessments would consider the number of people exposed and incorporate local consumption rates and patterns. Furthermore, a detailed assessment would require a greater number of fish samples per site than collected for this screening study. Additionally, this study does not address all the bioaccumulative pollutants that may be present in surface waters.

One of the original intents of the NSCRF was to further investigate dioxin/furan concentrations in fish; consequently, the selection of sites was biased toward sites where these compounds might be found. The intent of the source correlations was to identify potential sources, in addition to pulp and paper mills using chlorine, for either dioxins/furans or the other study compounds.

TABLE S-3
Number of Sites with Estimated Upper-Bound Risks

TARGETED SITES

Chemical	No. of Sites with Fillet Data	RISK LEVEL (Cumulative) 10-6 (>1 in 1,000,000)	10-5 (>1 in 100,000)	10-4 (>1 in 10,000)	10-3 (>1 in 1,000)
PCBs	106	89	79	42	10
Dieldrin	106	53	31	6	0
Combined Chlordane	106	44	10	0	0
DDE	106	40	10	0	0
Heptachlor Epoxide	106	9	2	0	0
Alpha-BHC	106	11	1	0	0
Mirex	106	8	2	0	0
HCB	106	5	0	0	0
Gamma-BHC	106	0	0	0	0
Heptachlor	106	0	0	0	0
Dicofol	106	0	0	0	0
Hexachlorobutadiene	106	0	0	0	0
Pentachloroanisole	106	0	0	0	0
Trifluralin	106	0	0	0	0

BACKGROUND SITES

Chemical	No. of Sites with Fillet Data	10-6 (>1 in 1,000,000)	10-5 (>1 in 100,000)	10-4 (>1 in 10,000)	10-3 (>1 in 1,000)
PCBs	4	1	1	0	0
DDE	4	1	0	0	0

Basis:
1) Used EPA (i.e., upper-bound) cancer potency factors.
2) Used consumption rate of 6.5 grams/day.
3) Used average fillet concentrations at the few sites with multiple samples.

Combined chlordane is the sum of cis- and trans-chlordane isomers, cis- and trans-nonachlor isomers, and oxychlordane.

Chapter 1 - Introduction

BACKGROUND

This report presents the results of the U.S. Environmental Protection Agency's (EPA's) National Study of Chemical Residues in Fish (NSCRF), previously referred to as the National Bioaccumulation Study (NBS). The study was initiated in 1986 as an outgrowth of EPA's National Dioxin Study. The National Dioxin Study was a 2-year, nationwide investigation of 2,3,7,8 tetrachlorodibenzo-p-dioxin (2,3,7,8 TCDD) contamination in soil, water, sediment, air, and fish. Some of the highest concentrations of 2,3,7,8 TCDD discovered in the environment during that effort were detected in fish. EPA's concern that there may be other pollutants with properties similar to 2,3,7,8 TCDD bioaccumulating in fish was a primary reason for initiating the NSCRF. Additionally, in response to a petition from the Environmental Defense Fund and the National Wildlife Federation, EPA committed to conducting an aquatic monitoring survey of the occurrence of chlorinated dibenzodioxins and chlorinated dibenzofurans. Aquatic biota are frequently being used to determine whether substances are bioaccumulating, to detect acutely toxic conditions, and to detect stresses such as sublethal toxicity, particularly due to interactions among chemicals.

The objectives of this one-time screening investigation were to determine the prevalence of selected bioaccumulative pollutants in fish and to identify correlations with sources of these pollutants. In addition, estimates were made of human health risks for those pollutants studied for which cancer potency factors and/or reference doses have been established. Human health risks were not estimated for dioxins and furans since the potency of these pollutants is the subject of an EPA review.

Bioaccumulation is the uptake and retention of chemicals by living organisms. Aquatic organisms such as fish are exposed to pollutants through contaminated water, sediment, and food. A pollutant bioaccumulates if the rate of intake into the living organism is greater than the rate of excretion or metabolism. This results in an increase in the tissue concentration relative to the exposure concentration in the ambient environment. Consequently, analysis of fish tissue can reveal the presence of pollutants in waterbodies that may escape detection through routine monitoring of water alone. Contaminants detected in fish not only indicate pollution impact on aquatic life and other wildlife (i.e., through biomagnification up the food chain), but also can represent a significant route of human exposure to toxic chemicals through consumption of fish and shellfish.

GENERAL APPROACH

Composite fish samples were collected primarily in 1987 at 388 locations nationwide and analyzed for concentrations of 60 contaminants by EPA's Environmental Research Laboratory (ERL) in Duluth, Minnesota. EPA's Office of Science and Technology personnel, Regional Coordinators, and State personnel selected the sampling sites. Locations selected included targeted sites near potential point and nonpoint pollution sources; background sites in areas relatively free of pollution sources; and a small subset of sites selected from the U.S. Geological Survey's (USGS)

National Stream Quality Accounting Network (NASQAN) for nationwide coverage. Targeted sites included areas near significant industrial, urban, or agricultural activities. Over 100 sampling sites near pulp and paper mills using chlorine to bleach pulp were added to the study after results of the National Dioxin Study indicated a correlation between 2,3,7,8 TCDD occurrence in fish and proximity to pulp and paper mill discharges. Some samples collected from the National Dioxin Study sites were reanalyzed as part of this study to obtain information on concentrations of pollutants other than 2,3,7,8 TCDD.

EPA Regional Coordinators managed the collection of composite samples, accomplished primarily by State agencies. In general, a representative bottom-feeding species, whole-body composite sample was collected and analyzed for each site to determine general occurrence of each contaminant in any portion of the fish. A representative game fish fillet composite sample was analyzed at a limited number of the study sites, usually where whole-body concentrations were high, to indicate the potential risk to human health from consumption of the edible portion. A few bottom-feeding species composite samples were also analyzed as fillets and used to estimate human health risks.

Target analytes were selected on the basis of their potential to bioaccumulate, human toxicity, and analytical feasibility. Hundreds of potential chemicals of concern were screened for inclusion in the study. The final list of 60 contaminants included 15 chlorinated dibenzodioxins and dibenzofurans and 45 other xenobiotic chemicals, primarily polychlorinated biphenyls. and chlorinated organic pesticides. The final list did not represent a comprehensive list of all bioaccumulative pollutants of concern.

Three methods were employed for laboratory analyses. ERL-Duluth refined and expanded the method for dioxin analysis developed for the National Dioxin Study to include 14 polychlorinated dibenzodioxins and polychlorinated dibenzofurans in addition to 2,3,7,8 TCDD. ERL-Duluth developed a second method specifically for this study to measure concentrations of 44 of the other xenobiotic study analytes. Mercury was analyzed separately from the other study chemicals using EPA's standard analytical techniques.

Chapter 2 - Study Design and Approach

This chapter provides an overview of the development of the design and analytical approach for this national study of chemical residues in fish. Prior to undertaking the study, a Work/Quality Assurance Project Plan (U.S. EPA, 1986a) was prepared that described the overall goals for the study, the data quality objectives, and the Quality Assurance/Quality Control (QA/QC) procedures to meet the objectives. This study, to a large extent, built upon experience gained during the multimedia EPA National Dioxin Study (U.S. EPA, 1987b), which investigated contamination from 2,3,7,8 tetrachlorodibenzo-p-dioxin (2,3,7,8 TCDD). Unlike the National Dioxin Study, however, this study was intended to screen for a wider range of chemicals with high potential to bioaccumulate in fish (or shellfish) tissue. Consequently, new or modified analytical methods had to be developed. ERL-Duluth was responsible for developing and verifying the analytical methods, determining compliance with precision and accuracy targets, and achieving minimum detection limits to meet the objectives of the study.

POLLUTANT SELECTION SCREENING PROCESS

A screening process was undertaken by EPA to select the pollutants for the study. Four hundred and three chemicals were initially identified as candidate study compounds. Sources from which these chemicals were identified included:

1. List of priority pollutants. Priority pollutants are the 126 pollutants derived from the 65 classes of compounds listed in Clean Water Act section 307(a).[1] Some of the priority pollutants were included on the screening list for this study based on their potential human health or aquatic life effects and exposure potential (Tobin, 1984).

2. Pesticides detected in effluents from pesticide manufacturing plants (Dorman, 1985).

3. The Carcinogen Assessment Group's (CAG's) List of Chemicals Having Substantial Evidence of Carcinogenicity (U.S. EPA, 1980b).

4. Semivolatile organic compounds identified by the Office of Toxic Substances in 1980 to be in human adipose tissue (U.S. EPA, 1980c).

5. Chemicals considered by the International Agency for Research on Cancer (IARC) to have substantial evidence of carcinogenicity (evaluated after CAG 1980 list was completed).

6. National Toxicology Program (NTP) chemicals classified as carcinogens in Annual Reports on Carcinogens (NTP, 1982a,b).

[1] Specific pollutants are listed in 44 FR 34393 (1979), as amended by 46 FR 2266 (1981), and 46 FR 10723 (1981).

7. Clean Water Act 4(c) Program pollutants, other than priority pollutants, identified in industrial and POTW effluents as nonbiodegradable.

8. Additional suggestions from Agency experts.

The resulting list of candidate chemicals was first screened for bioaccumulation potential. Compounds with calculated or experimental Bioconcentration Factors (BCFs) greater than 300 were selected because they have greater potential to bioaccumulate and because the projected human exposure from fish consumption would be greater than the projected exposure from drinking water. The list of chemicals was further screened based on human toxicity, exposure potential, persistence in the aquatic environment, and biochemical fate in fish. For example, compounds that are quickly hydrolyzed or metabolized were identified and eliminated from further consideration. Finally, screening of the remaining chemicals was undertaken with regard to analytical feasibility by chemists at ERL-Duluth. Chemicals presenting significant analytical difficulties, such as not being amenable to generalized isolation procedures, were removed from the list. For example, low recovery from the silica gel column eliminated chlorbenzilate, triphenyl phosphate, and trichloronate. Kepone was deleted due to inconsistent mass spectral response.

A final list of 15 dioxin and furan congeners and 45 other xenobiotic chemicals resulted from the screening process (Table 2-1). The 2,3,7,8 substituted dioxins and furans were selected for analysis due to their toxicity. For these analytes, maximum target detection levels were determined based on potential fish tissue concentration levels of concern, i.e., those associated with a given level of toxicity (10^{-6} risk of cancer). The latter were derived following Agency guidelines (U.S. EPA, 1986a).

FIELD SAMPLING PROCEDURES

Sample Collection

The EPA Regional Offices were responsible for the collection of the fish samples and for transport to ERL-Duluth for analysis. Procedures for sample fish collection, handling, preservation, and transport were described in the Work/Quality Assurance Project Plan (U.S. EPA, 1986a, 1984) and are noted below. Two composite fish samples per site were collected, where possible:

1. A representative bottom-feeding fish composite to be analyzed whole, as an overall indication of pollutant levels at each site.

2. A representative game fish composite to be analyzed as a fillet to provide an indication of potential human health risk from consumption of fish.

Approximately three to five adult fish of similar size and from the same species were collected for each composite at a given site allowing for a minimum sample size of 500 grams. All fish in the composite sample were obtained from the same site. The fish species targeted for sampling were considered to be good bioaccumulators and/or were routinely consumed by humans. For bottom-feeding fish, target fish in order of preference were 1) carp, 2) channel catfish, and 3) white sucker. Suggested target species for game fish included 1) white bass, 2) northern pike, 3) walleye, 4) smallmouth bass, 5) largemouth bass, and 6) crappie. (A

TABLE E-1
List of Target Analytes

DIOXINS

2,3,7,8 Tetrachlorodibenzodioxin (TCDD)
1,2,3,7,8 Pentachlorodibenzodioxin (PeCDD)
1,2,3,6,7,8 Hexachlorodibenzodioxin (HxCDD)
1,2,3,7,8,9 Hexachlorodibenzodioxin(HxCDD)
1,2,3,4,7,8 Hexachlorodibenzodioxin(HxCDD)
1,2,3,4,6,7,8 Heptachlorodibenzodioxin(HpCDD)

FURANS

2,3,7,8 Tetrachlorodibenzofuran (TCDF)
1,2,3,7,8 Pentachlorodibenzofuran (PeCDF)
2,3,4,7,8 Pentachlorodibenzofuran (PeCDF)
1,2,3,6,7,8 Hexachlorodibenzofuran (HxCDF)
1,2,3,7,8,9 Hexachlorodibenzofuran (HxCDF)
1,2,3,4,7,8 Hexachlorodibenzofuran (HxCDF)
2,3,4,6,7,8 Hexachlorodibenzofuran (HxCDF)
1,2,3,4,6,7,8 Heptachlorodibenzofuran (HpCDF)
1,2,3,4,7,8,9 Heptachlorodibenzofuran (HpCDF)

OTHER XENOBIOTICS

Biphenyl
Chlordane, cis
Chlordane, trans
Chlorpyrifos
p,p'-DDE
Dicofol
Dieldrin
Diphenyl Disulfide
Endrin
Heptachlor
Heptachlor epoxide
Hexachlorobenzene
Hexachlorobutadiene
alpha-BHC
gamma-BHC (lindane)
Isopropalin
Mercury
Methoxychlor
Mirex
Nitrofen
Nonachlor, cis
Nonachlor, trans
Octachlorostyrene
Oxychlordane
Pentachloroanisole
Pentachlorobenzene
Pentachloronitrobenzene
Perthane
Polychlorinated Biphenyls
(Mono-Decachlorinated)
1,2,4,5 Tetrachlorobenzene
1,2,3,4 Tetrachlorobenzene
1,2,3,5 Tetrachlorobenzene
1,2,3 Trichlorobenzene
1,2,4 Trichlorobenzene
1,3,5 Trichlorobenzene
Trifluralin

summary of the types of fish actually collected and analyzed and a comparison of the observed fish tissue concentrations detected are included in Chapter 5, "Fish Species Summary and Analysis.")

Sample Handling/Preparation

After collection, the fish were individually wrapped in aluminum foil, labeled, dry-iced, and shipped frozen to Duluth. Chain-of-custody procedures were followed for each sample using a centralized sample control system. Once fish samples were received by ERL-Duluth, the staff completed the chain-of-custody forms and placed the frozen samples in a freezer. Fish tissue was ground frozen and homogenized in a stainless steel meat grinder. For whole-fish samples (e.g., bottom feeders), the entire fish including organs and muscle tissue was ground. For game fish, fillets with the skin off were prepared and then ground. Most filleting (skin-off) was done at ERL-Duluth. All equipment and the stainless steel table were cleaned after each use. The ground tissue was stored at -20°C until extracted.

Fish Length and Weight Data

Length and weight data for individual fish in the bioaccumulation data set were not usually available. Information on the number of samples per composite and sampling date was recorded, along with the weight of the sample and percent lipid (see Appendix D, Vol. II). Age and sex were not determined for this study. To minimize potential differences, fish were not collected during or soon after spawning or during seasonal migration. The dates of sample collection are included in Appendix D, Vol. II. In future studies, it is recommended that length and weight data be obtained for all samples and that enough samples be aged to develop age vs. length and weight relationships. In some cases, only mean lengths and weights were available for the fish from which fillet and whole-body samples were prepared for analysis. A preliminary review of the data indicated that some samples consisted of individual specimens with widely differing lengths and weights. This probably resulted from limited availability of fish. Assuming that length and weight are a reasonable indicator of age for most fish species, then the likely use of different age fish could bias some of the various bioaccumulation study analyses. In general, it may be assumed that older fish would have had a longer exposure to contaminants either through direct contact with substrates (e.g., demersal species) or as predators, having consumed large quantities of contaminated prey. Changes in metabolism related to age and other age-dependent factors may also affect tissue contaminant levels. In general, samples prepared for tissue analyses requiring multiple specimens should, to the extent possible, include only those fish which are essentially the same length and weight and, hence, approximate age.

ANALYTICAL PROTOCOLS

Three analytical procedures were employed during the laboratory analysis of the sample composites. The summaries that follow have been abstracted from U.S. EPA, 1990b, EPA/600/3-90/022 (PCDD/PCDF); U.S. EPA, 1990c, EPA/600/3-90/023 (xenobiotic chemical contaminants); and U.S. EPA, 1989a (mercury).

Dioxins/Furans

A schematic of the analytical procedures used for the tissue extraction of polychlorinated dibenzodioxins and polychlorinated dibenzofurans (PCDD/PCDF) is shown in Figure 2-1. Specific details of the analytical procedures used are provided in U.S. EPA, 1990b (included in Appendix A). After spiking a dry tissue sample with internal standard solutions, the sample was extracted with a mixture of hexane and methylene chloride and the eluent was collected in a Kuderna-Danish (KD) apparatus. The internal standards added at this point consisted of 11 different ^{13}C labeled compounds and four PCDD/PCDF compounds (see Solutions A and B in Table 2-2.). The KD apparatus was then placed in a 60°C water bath under a dry carbon filtered air flow. After the solvent had evaporated, the lower tube and contents were weighed. The lipid was then quantitatively transferred to an acid-celite macro-column, and the lower empty tube and contents were weighed. The percent lipid was calculated based on the difference in weights. The acid-celite column was eluted with benzene/hexane. Isooctane was added and the sample volume reduced for transfer to the activated florisil/sodium sulfate column. The column was eluted with methylene chloride and hexane and the eluate discarded. The column was then washed with methylene chloride, which flowed directly onto a carbon silica gel column for PCDD/PCDF isolation. Benzene/methylene chloride was added to the carbon column, and then the carbon column was inverted. The PCDD/PCDF were eluted with toluene and another internal standard, Solution C in Table 2-2, prior to gas chromatography/mass spectrometry (GC/MS) analysis.

During the course of this study, changes were made to the PCDD/PCDF methodology. In 1987, toluene was replaced with tridecane as the solvent for the standard PCDD/PCDF recovery and calibration solutions. The new standards included more compounds than the original set. In addition, the procedure for determining the minimum level of detection was modified to better reflect actual instrumental analysis. Consequently, results generated after July 1987 reflect a minimum level of detection (MLD) defined as the concentration predicted from the ratio of the baseline noise area to the labeled internal standard area plus three times the standard error of the estimate from the weighted initial calibration curve. Before this procedure, the MLD was determined according to the Analytical Procedures and Quality Assurance Plan for the Analysis of 2,3,7,8 TCDD in Tier 3-7 Samples of the U.S. Environmental Protection Agency National Dioxin Study (EPA/600/3-85-019).

Prior to the addition of the florisil column in July 1988, polychlorinated diphenylethers interfered with the quantification of some of the biosignificant furans (2,3,4,7,8 PeCDF; 1,2,3,4,6,7 HxCDF; 1,2,3,4,7,8 HxCDF; and 2,3,4,6,7,8 HxCDF). The reported values for these compounds may have been overestimated due to the interference. The samples with interferences were flagged in the data reports with a comment. In addition, a flag has been added to the data tables indicating that 1,2,3,4,7,8 HxCDF coelutes with 1,2,3,4,6,7 HxCDF on the GC column (DB5 30M).

All GC/MS analyses were done using high-resolution GC/high-resolution MS (HRGC/HRMS). Before the analyses, each sample was spiked with a standard solution and the sample volume adjusted to 20 µL with tridecane. Sample analyses were done in sets of twelve consisting of:

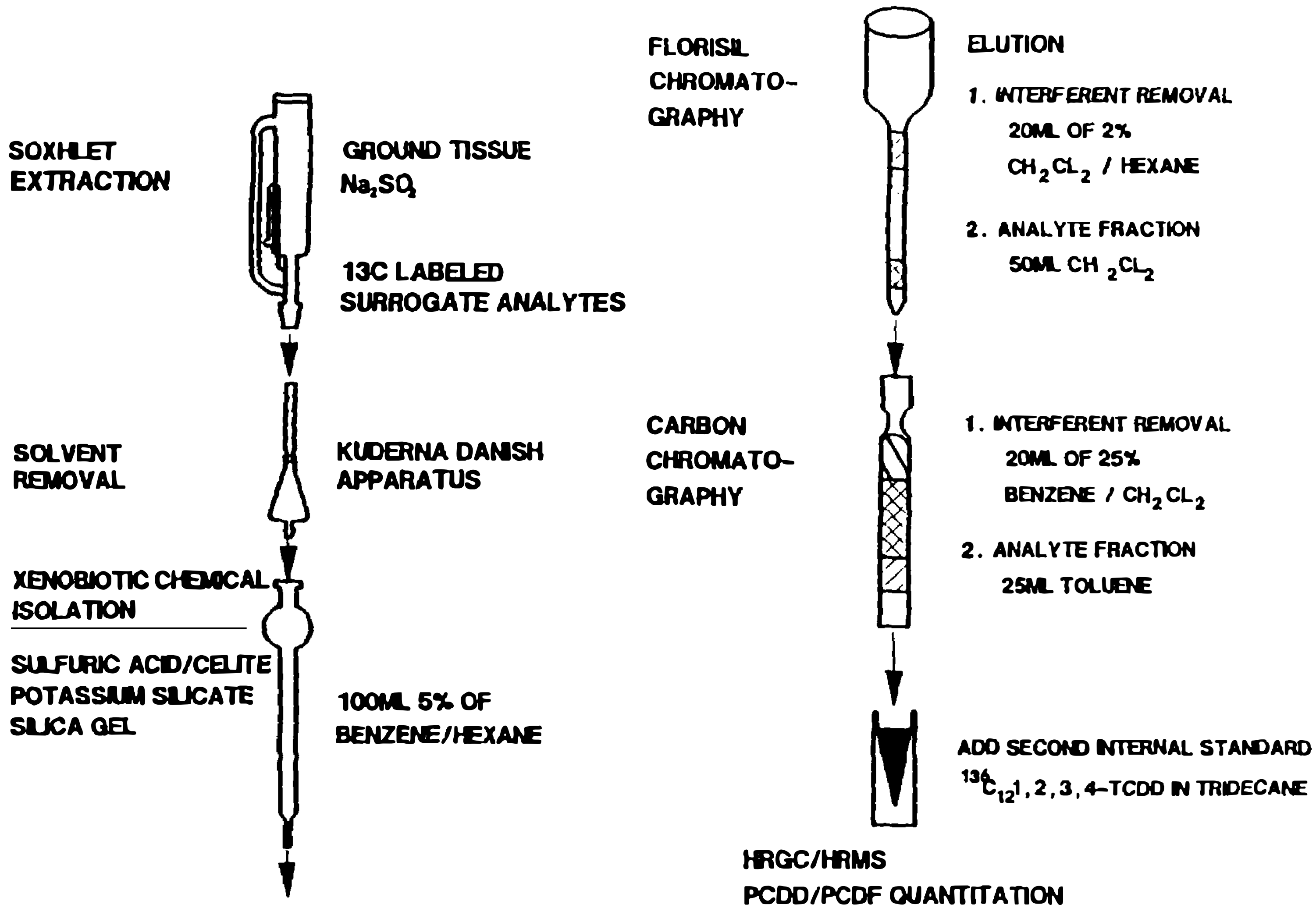


Figure 2-1. Schematic of laboratory procedures for dioxins and furans.

TABLE 2-2. Internal Standard Solutions Used for PCDD/PCDF Analyses

Compound	Concentration in Solution (pg/μL)	Concentration in tissue (pg/g*)
	Internal Standard Solution A. (100μL)	
$^{37}Cl_4$ 2,3,7,8 TCDD	2.0	10.0
$^{13}C_{12}$ 2,3,7,8 TCDD	5.0	25.0
$^{13}C_{12}$ 2,3,7,8 TCDF	5.0	25.0
$^{13}C_{12}$ 1,2,3,7,8 PeCDD	5.0	25.0
$^{13}C_{12}$ 1,2,3,7,8 PeCDF	5.0	25.0
$^{13}C_{12}$ 1,2,3,4,7,8 HxCDD	12.5	62.5
$^{13}C_{12}$ 1,2,3,4,7,8 HxCDF	12.5	62.5
$^{13}C_{12}$ 1,2,3,4,6,7,8 HpCDD	12.5	62.5
$^{13}C_{12}$ 1,2,3,4,6,7,8 HpCDF	12.5	62.5
$^{13}C_{12}$ OCDD	25.0	125.0
$^{37}Cl_4$ 2,3,7,8 TCDF	2.0	10.0
	Internal Standard Solution B.	
1,2,3,4 TCDD	1.0	5.0
1,2,4,7,8 PeCDD	1.0	5.0
1,2,3,4 TCDF	1.0	5.0
1,2,3,6,7 PeCDF	1.0	5.0
	Internal Standard Solution C.	
$^{13}C_{12}$ 1,2,3,4 TCDD	50.0	50.0

*Assumes a 20-g sample.
Reference: U.S. EPA, 1990b.

Surrogate Standard and Internal Standard Solutions Used for Other Xenobiotic Compound Analyses

Compound	Concentration (μg/mL)
	Surrogate Standard Solution A (25μL)
Iodobenzene	125
1-Iodonaphthalene	125
4,4'-Diiodobiphenyl	125
	Internal Standard Solution (10μL)
Biphenyl-D_{10}	50
Phenanthrene-D_{10}	75
Chrysene-D_{12}	75

1. One method blank;

2. One additional fortified matrix (blank) spiked with native analytes;

3. One detection limit verification sample—an environmental sample with a detectable amount of native analyte (determined from a previous analysis), spiked with native analytes, and analyzed with the next sample set (used for only the first three sample sets of a matrix type to establish that the calculated MLD was achievable);

4. One duplicate sample; and

5. Eight (if detection limit verification sample used) or nine environmental samples.

Quantification of analytes was accomplished by assigning isomer identification, integrating the area of mass-specific GC peaks, and calculating an analyte concentration based upon an ion relative response factor between the analyte and the appropriate standard. For the tetrachloro- to heptachloro-congeners/isomers of PCDD/PCDF, analytical results were reported as concentration in picograms per gram (pg/g) (ppt wet weight) for each GC peak in a congener class by making the assumption that the response for the molecular ion of all isomers in that class was equal to the response observed for the isomer for which ERL-Duluth had a standard. Target MLD are noted below:

TCDD, TCDF	1 pg/g
PeCDD, PeCDF	2 pg/g
HxCDD, HxCDF	4 pg/g
HpCDD, HpCDF	10 pg/g

The specific detection limits for each sample with concentrations below detection were recorded in the data base (see Appendix D, Volume II). The actual detection limits achieved were often lower than the above targeted values.

Other Xenobiotic Chemicals

A schematic of the analytical procedures used for the tissue extraction of the other xenobiotic chemicals is shown in Figure 2-2. More specific details are provided in U.S. EPA, 1990c, included in Appendix A. Before extraction, each sample was fortified with a surrogate standard solution (Table 2-2) to evaluate the recovery of target analytes. To isolate the xenobiotic chemical contaminants, a gel permeation chromatography (GPC) system was first used to remove fish lipid interferences. Then a Kontes column packed with silica gel was used to remove naturally occurring cholesterol and fatty acids. Finally, the samples were spiked with an internal standard solution, also listed in Table 2-2, used to quantify target analytes before GC/MS analysis.

In August 1988, two important changes were made in the xenobiotics methodology. The amount of silica gel used was doubled, and the maximum amount of lipid placed on the GPC system was decreased from 1.0 g to 0.8 g. These changes were made to obtain better recovery of the target analytes and to decrease interferences. The quantitative results (concentrations) obtained with the two methods were comparable.

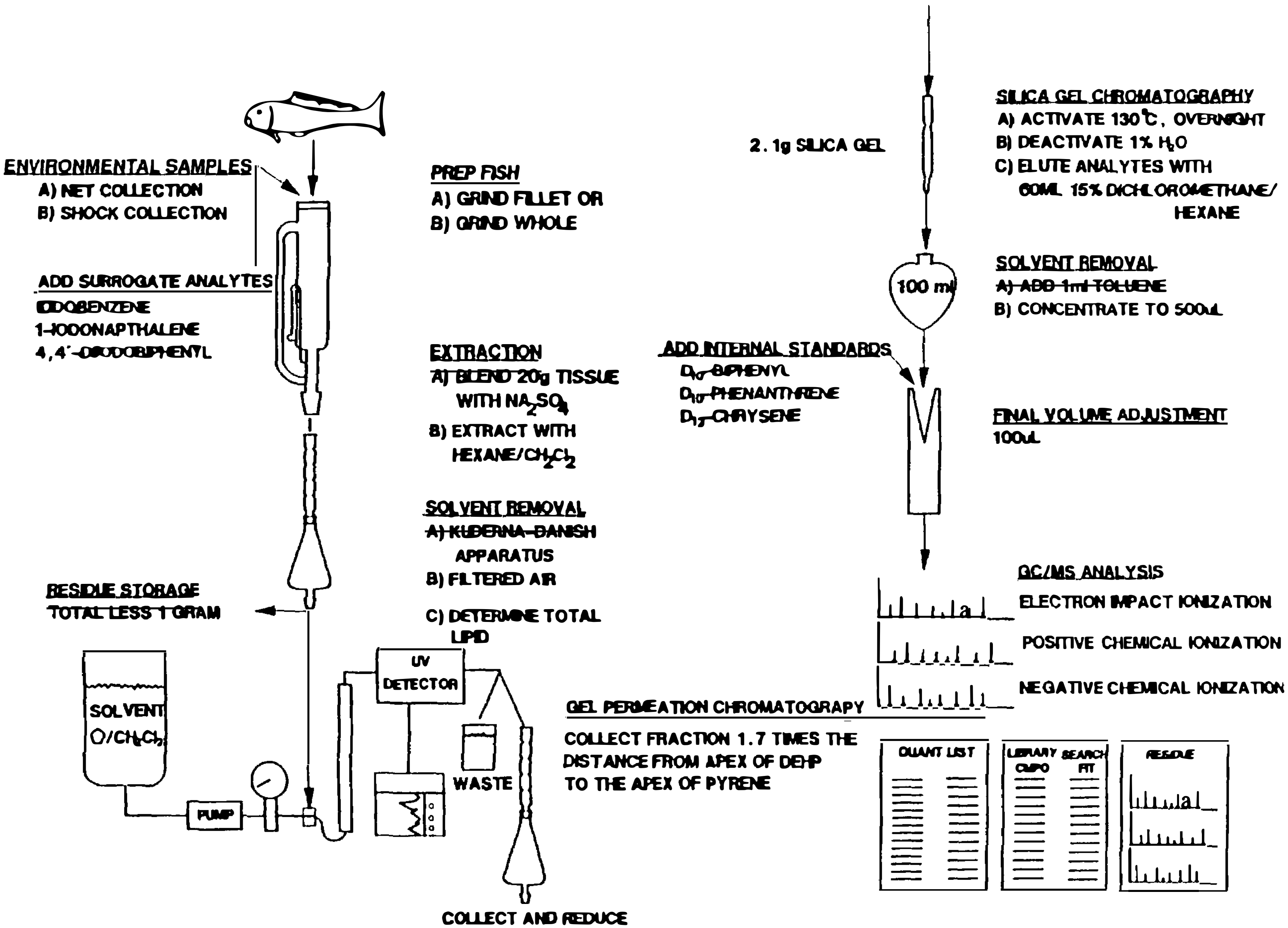


Figure 2-2. Schematic of laboratory analytical procedure for other xenobiotic chemicals.

Samples were analyzed by GC/MS as referenced in U.S. EPA, 1990c. The positive identification of analytes using the MS was based upon a reverse library search threshold value and relative retention time: quantification was based on the response factors relative to one of three internal standards. Sample analyses were done in sets of 12 consisting of:

1. One method blank,

2. One additional fortified matrix (blank) spiked with one of eight mixtures of the target analytes,

3. One duplicate sample, and

4. Nine environmental samples.

All target xenobiotic analytes were quantified as unique values (ng/g-ppb wet weight), except PCBs, which were reported by total congener at each degree of chlorination. Specific detection limits were not determined for individual samples so they have been operationally set at zero. Target quantitation limits for these analytes were:

Target Analytes (except PCBs)		2.5	ng/g
Polychlorinated Biphenyls			
Level of Chlorination:	1-3	1.25	ng/g
	4-6	2.50	ng/g
	7-8	3.75	ng/g
	9-10	6.25	ng/g

Mercury

A schematic of the equipment arrangement for mercury analyses is shown in Figure 2-3. More specific details are provided in Olson et al., 1975; Horwitz, 1983; APHA, 1985; and Glass et al., 1990. The analytical procedure for mercury was based on a standard flameless atomic absorption method. Fish tissue samples were digested in a mixture of nitric acid, sulfuric acid, potassium permanganate, and potassium persulfate as the digestion reagent. The resulting solution was treated with a sodium chloride-hydroxylamine sulfate solution and aqueous stannous chloride. Liberated mercury was measured using an atomic absorption spectrophotometer equipped with a cold mercury vapor apparatus. Data for mercury are reported as microgram per gram (µg/g)(ppm wet weight). The detection limit for mercury was 0.05 µg/g for samples analyzed prior to 1990 and 0.0013 µg/g for the 195 samples analyzed in 1990. The sample size was decreased from 1.0 g to 0.2 g to obtain results within the instrument's calibration range established at the lower detection limit.

Quality Assurance/Quality Control (QA/QC)

Specific laboratory QA procedures were established by ERL-Duluth, and are summarized in Appendix A, Table A-1. The PCDD/PCDF QA requirements for accuracy, method efficiency, precision, and signal quality (signal-to-noise [S/N] ratio) are shown in Appendix A, Table A-2. Limits for recovery of standards were also set. Values that were below 40 percent recovery were

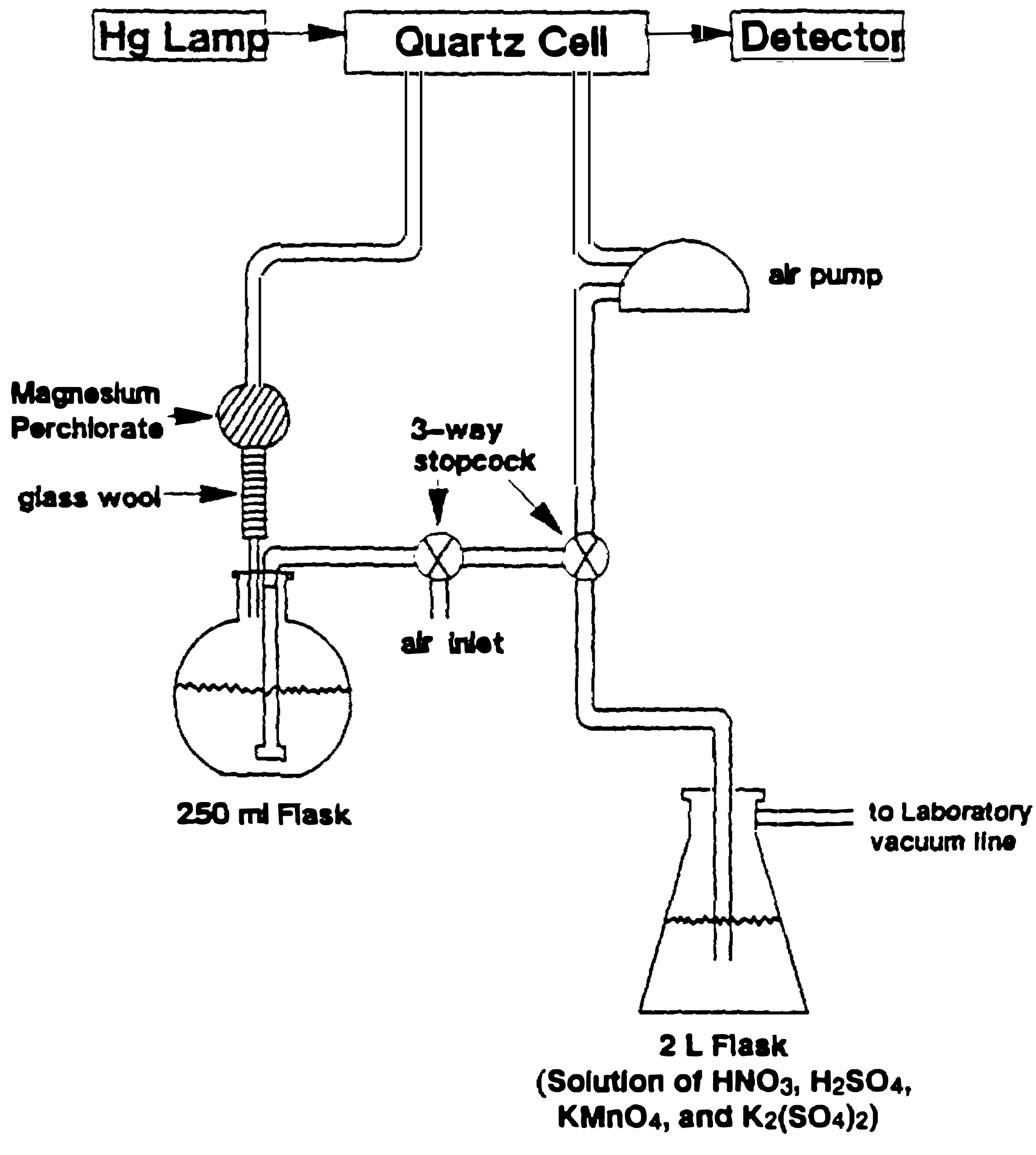


Figure 2-3. Schematic of laboratory analytical procedure for mercury.

flagged with a QR designation in the data base. These values represent minimum concentrations and are included with the data but were not used in the data analyses.

Xenobiotic and mercury data QA requirements are listed in Appendix A, Table A-4 and Appendix A, Table A-7. If more than 20% of the analytes were outside the QA for accuracy and precision, the sample set was reanalyzed. QC charts were maintained by the laboratory for each analyte displaying quantitative bias and precision. Bias and precision were calculated at the completion of the study and are presented in Appendix A. For QA factors outside of the above criteria (Appendix A for xenobiotics), corrective actions were undertaken (e.g., adjust GC or MS parameters, flush/replace GC column, clean MS, reextract and reanalyze samples). An overall data completeness criterion of 80 percent was set for the study. As discussed in Appendix A, this criterion was met.

General guidance for data quality including QA/QC requirements was provided in the Work/Quality Assurance Project Plan (U.S. EPA, 1986a). As stated in this Project Plan:

"The expected quality of the data will be specified in terms of precision, bias, and detection limits. In general, the bias requirements will be 30% (i.e., the reported values will be within 30% of the true values) and the precision requirement will be 50% .... The detection limit for fish will be based on consideration of levels of concern...."

The target for completeness of the data was originally set at 80 percent in the study workplan. This target was the minimum percent of verified data as a percent of total reported data. In fact, this target was exceeded. For the dioxin/furan analyses 96 percent of all analyses met QA/QC criteria. Those analyses which did not are flagged with "QR" in the database (Vol. II, Appendix D) and were not used for any data analyses. All other data met the QA/QC criteria, i.e., the percent of total reported data classified as valid.

Specific protocols were developed in this study for controlling data quality and ensuring data comparability, including:

1. Standardized written sampling and analytical procedures,

2. Standardized handling and shipping procedures,

3. The use of blanks (reagent and field),

4. The use of fortified samples to control accuracy and internal standards to quantify target analytes,

5. Specified calibration procedures to control accuracy and verify detection limits,

6. Replicate analyses to evaluate laboratory precision, and

7. Standardized data reduction and validation procedures.

Procedures for documentation, data reduction and validation, and reporting were specified in the Analytical Procedures and Quality Assurance Plan Manuals (U.S. EPA, 1990b, 1990c, 1989a).

SITE SELECTION

Fish collected from 388 unique sites were analyzed for this study (Figure 2-4). The types of sites sampled included targeted sites near potential point and nonpoint sources (shown separately in Figure 2-5), background sites (shown separately in Figure 2-6), and a subset of sites from the USGS NASQAN (shown separately in Figure 2-7):

Type of Site	Number Sampled
Targeted Sites	314
Background Sites	35
USGS NASQAN Sites (Subset)	39
TOTAL	388

A subset of samples that had been collected at 103 sites during the National Dioxin Study (U.S. EPA, 1987b), and that had been analyzed for 2,3,7,8 TCDD only, were reanalyzed for the other study dioxin/furan congeners and xenobiotic compounds. These sites have episode numbers from 1994 to 2776. The new sites have episode numbers beginning with 3000.

Targeted sites were selected by EPA Regional and State staff based on proximity to potential sources (Figure 2-5). Fish and other aquatic biota were sampled near industrial dischargers, urban areas, or agricultural runoff areas. The number of sites was not allocated equally among types of sources. Some of the targeted sites were selected based on potential chlorinated dioxin and furan contamination, including areas near pulp and paper mills (mills that use chlorine to bleach pulp and other types of mills), wood preservers, users of such contaminated products as polychlorinated phenols and phenoxides, PCB dischargers, organic chemical and pesticide manufacturers, and combustion sources (sewage sludge incinerators, municipal incinerators). Two reasons for selecting these types of sites were:

1. The major sources of chlorinated dioxins and furans are suspected to be similar to the sources of 2,3,7,8 TCDD investigated in the National Dioxin Study, and

2. Certain organic chemicals and pesticide compounds (primarily polychlorinated phenols and polychlorinated phenoxides) had been identified as having chlorinated dioxin or furan contamination. In addition, several PCB mixtures had been reported to contain furan contamination.

More sites with potential dioxin/furan contamination were selected than for other compound groups to follow up the results of the National Dioxin Study. Some targeted sites were also selected for sampling based on the potential for hexachlorobenzene (HCB) contamination. Potential sources of HCB include fugitive emissions from manufacturing plants, impurities in pesticides (e.g., pentachloronitrobenzene [PCNB], dacthal, chlorothalonil, picloram), and previous application of HCB as a fungicide. Production facilities for certain chemicals (e.g., chlorobenzenes, carbon tetrachloride, chlorine) are known to generate HCB as a contaminant (U.S. EPA, 1986a). The ten largest direct dischargers (by production volume) of the chemicals of concern were recommended

Figure 2-4. Location of bioaccumulation study sampling sites.

Figure 2-5. Location of targeted sites.

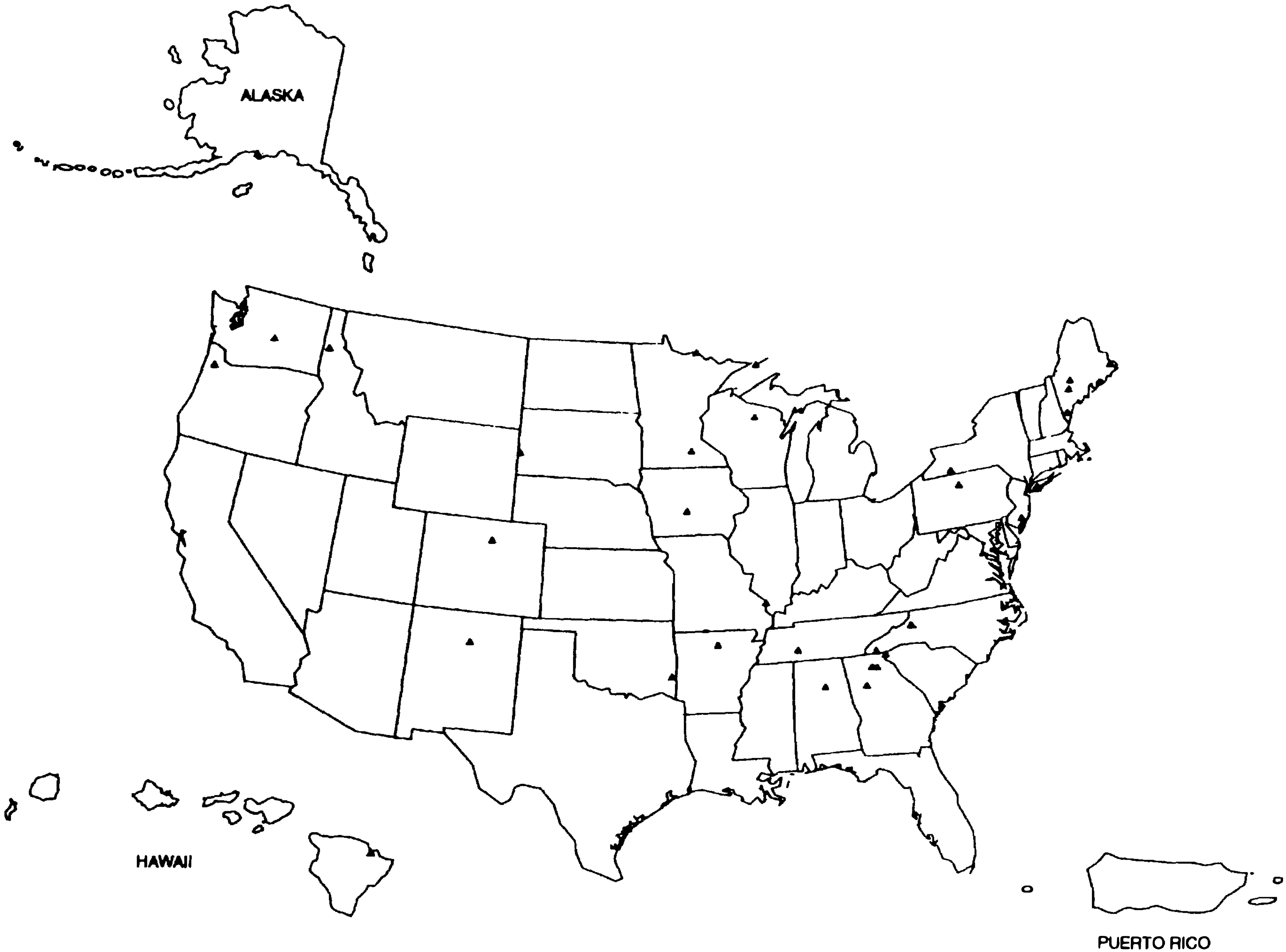


Figure 2-6. Location of sites representing background conditions.

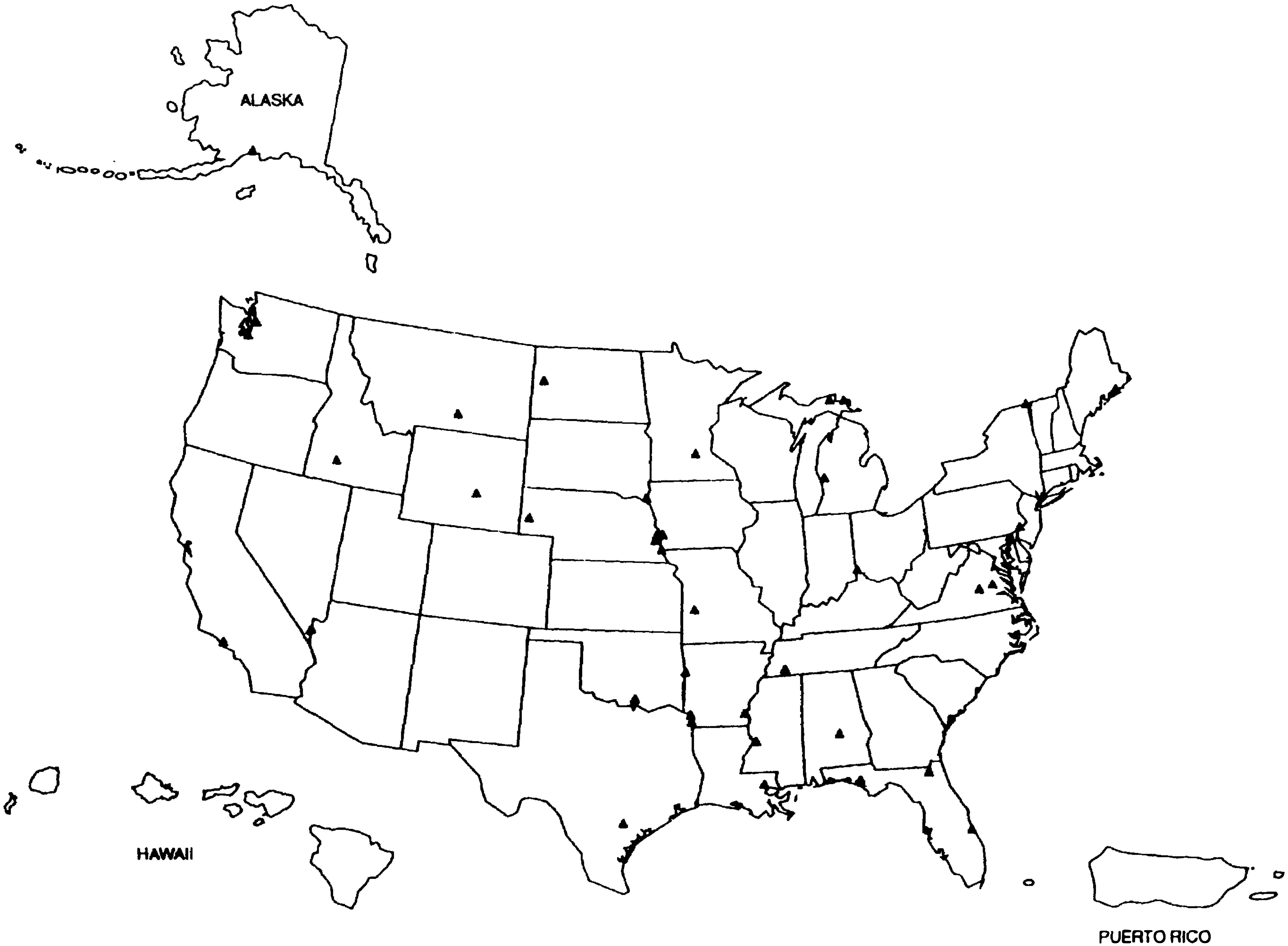


Figure 2-7. Location of sites selected from a subset of the USGS NASQAN Network.

for sampling. In addition, a site within each of the 10 U.S. counties with the highest combined applications of the pesticides PCNB, picloram, and chlorothalonil (Resources for the Future, 1986) were selected by the EPA Regions and targeted for sampling.

The following categories were used for targeted sites: background, paper mills using chlorine, other types of pulp and paper mills, wood preserving plants, refineries/other industries, Superfund sites, industry/urban, agriculture, and POTW. The two broad categories, industry/urban and refineries/other industries, were used to accommodate the sites having multiple point sources.

Background sites, shown in Figure 2-6, were selected by EPA Regional and State staff in areas generally free of influence from industrial releases, urban activities, or agricultural runoff. Results from these background sites were to be compared with concentrations of pollutants found in samples from the targeted, potentially more polluted sites.

A subset of sites were selected based upon hydrologic subdivision of major river basins, from the USGS NASQAN sites for nationwide coverage (Figure 2-7). The sampled sites were intended to represent a larger number of sites from the network.

Chapter 3 - Dioxin and Furan Results and Analysis

This chapter presents the results from analysis of fillet and whole-body samples for dioxin and furan compounds. The first section contains a summary of the prevalence and concentration of all dioxins and furans analyzed, as well as a summary of theToxicity Equivalency Concentration (i.e., a toxicity-weighted concentration of all dioxins and furans). Additional information presented in this chapter consists of a geographical distribution summary and a source correlation analysis. The latter analysis identifies point and nonpoint sources in the vicinity of the highest concentration fish samples and compares concentrations between various site categories.

Chemical profile data for dioxins and furans can be found in Appendix C, Volume II. These data include physical/chemical properties, sources, standards and criteria, and human health effects. The raw concentration data, specific detection limits for dioxin/furan congeners, and location information on the fish samples and other sampling data including sample weight, percent lipid, number of fish per composite, and date of sample collection are included in Appendix D, Volume II. The number of samples taken and analyzed by site can be determined by counting the samples for a given site (episode number) in the data tables (Appendix D, Volume II). The number of fish in each composite sample is provided in Appendix D-6 (Volume II). Other values for a given site can be reviewed by identifying the episode number for the site from the site matrix (Table B-3, Appendix B, in Volume I or Table D-1, Appendix D, in Volume II) and then looking at the data in the raw data tables (Appendix D, Volume II).

PREVALENCE AND CONCENTRATION SUMMARY

Six dioxin congeners and nine furan congeners were measured in the fish tissue and shellfish samples. Summary data regarding the prevalence and concentration of these 15 compounds can be found on Table 3-1 and Figure 3-1. Mean concentrations were calculated using one-half of the detection limit for tissue concentrations below detection. The total number of sites sampled and the percent of sites where at least one sample had a detected concentration are also shown. Each of the dioxin congeners was detected in samples ranging from 32 percent (1,2,3,4,7,8 HxCDD) to 89 percent (1,2,3,4,6,7,8 HpCDD) of the sites (Figure 3-1). The occurrence of furans by site showed more variability, ranging from 1 percent (1,2,3,7,8,9 HxCDF) to 89 percent (2,3,7,8 TCDF). The dioxins and furans detected in samples from more than 50 percent of the sites included:

Compound	Percent of Sites Detected
1,2,3,4,6,7,8 HpCDD	89
2,3,7,8 TCDF	89
2,3,7,8 TCDD	70
1,2,3,6,7,8 HxCDD	69
2,3,4,7,8 PeCDF	64
1,2,3,4,6,7,8 HpCDF	54
1,2,3,7,8 PeCDD	54

TABLE 3-1
Summary of Dioxins/Furans Detected in Fish Tissue

Chemical	Percent of Sites Where Detected	Max*	Mean*	Standard Deviation	Median*	Total Number of Sites	D
2378 TCDF	89.4	403.9	13.61	40.11	2.97	388	7
1234678 HpCDD	89.0	249.1	10.52	25.30	2.83	354	6
2378 TCDD	70.3	203.6	6.89	19.41	1.38	388	1
123678 HxCDD	68.8	100.9	4.30	9.25	1.32	375	4
23478 PeCDF	64.8	56.37	3.06	6.47	0.75	387	9
1234678 HpCDF	53.8	58.3	1.91	4.41	0.72	353	14
12378 PeCDD	53.5	53.95	2.38	4.34	0.93	385	2
12378 PeCDF	47.3	120.3	1.71	7.69	0.45	387	8
123478 HxCDF	42.0	45.33	2.35	4.53	1.42	379	10
123789 HxCDD	37.9	24.76	1.16	1.74	0.69	375	5
123478 HxCDD	32.3	37.56	1.67	2.39	1.24	375	3
234678 HxCDF	31.7	19.80	1.24	1.51	0.98	379	13
123678 HxCDF	20.8	30.86	1.74	2.34	1.42	379	11
1234789 HpCDF	4.0	2.57**	1.24	0.33	1.3	353	15
123789 HxCDF	1.3	0.96**	1.22	0.41	1.38	379	12
TEC	N/A	213.05	11.08	23.77	2.8	388	

* Concentrations are picograms per gram (pg/g) or parts per trillion (ppt) by wet weight. The mean, median, and standard deviation were calculated using one-half the detection limit for samples which were below the detection limit. In cases where multiple samples were analyzed per site, the value used represents the highest concentration.

**Detection limits were higher than the few quantified values for 1,2,3,4,7,8,9 HpCDF and 1,2,3,7,8,9 HxCDF. Maximum values listed are measured values.

TEC = Toxicity equivalency concentration based on method of Barnes et al., 1989.

Note: D is designation of chemical on histogram (Figure 3-1) of the percent of sites with concentrations above detection.

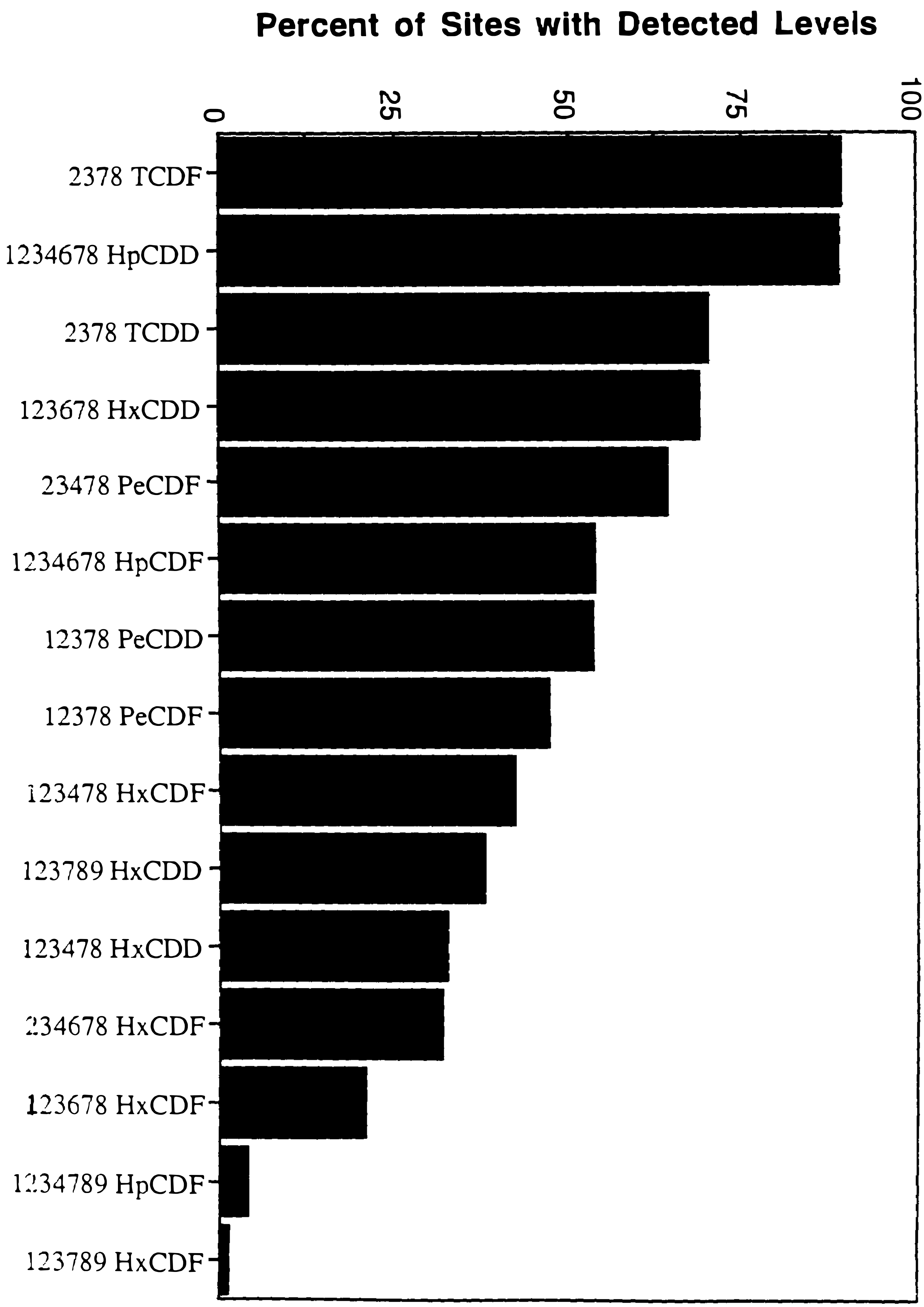


Figure 3-1. Summary of dioxins/furans detected in fish.

The maximum levels of the four most frequently detected compounds and 1,2,3,7,8 PeCDF were greater than 100 ppte The highest mean and median concentrations were for 2,3,7,8 TCDF at 13.6 and 2.97 ppt, respectively.

The lower median value reflects the lognormal type distribution as shown in the cumulative frequency distributions for the six dioxins (Figure 3-2) and for selected furans (Figure 3-3). These graphs were prepared using the maximum detected value at each site. When the duplicate sample value was higher than the original sample, the duplicate value was used. In a similar manner, values for samples from duplicate sites (i.e., resampled locations) were compared and the maximum measured value used. The graphs show that the dioxins 2,3,7,8 TCDD and 1,2,3,4,6,7,8 HpCDD were present at higher concentrations than the other dioxin congeners. For 2,3,7,8 TCDD, 18 percent of the sites had measured concentrations greater than 7 pg/g. A similar pattern was observed for the furans, although the maximum concentration for 2,3,7,8 TCDF was considerably higher than any of the other furan congeners, and this was the only furan congener with a median concentration greater than 2 pg/g.

Toxicity Equivalency Concentration (TEC)

Toxicity equivalent concentrations (TECs) of dioxins/furans were calculated to facilitate comparison of fish tissue contamination among sites. TEC represents a toxicity weighted total concentration of all individual congeners using 2,3,7,8, TCDD as the reference compound. EPA's interim method was used to determine TEC (Barnes, et. al., 1989). This is referred to as the Toxicity Equivalency Concentration (TEC) value, sometimes called TEQ (toxicity equivalents). The TEC method was developed under an international project and advocated by EPA. Under this method, 2,3,7,8 TCDD is used as the reference toxicity compound with all other dioxins and furans compared to this compound through the use of a Toxicity Equivalency Factor (TEF). The factors for determining the relative toxicities are shown in Table 3-2. Octa-dioxins and furans were not analyzed because at the time this study began in 1986, the TEFs were zero for these congeners. Under the 1989 interim method, the TEF was increased to 0.001. Consequently, TEC values may be underreported for samples collected at sites with sources of octa-dioxins, e.g., wood preservers.

The largest TEF used to compute TEC is for 2,3,7,8 TCDD (a value of 1). The next largest factor is for the 2,3,7,8 PeCDDs (i.e., penta-dioxins that have a chlorine atom in each of the 2,3,7,8 molecular positions and the fifth chlorine atom is in any of the remaining positions) and 2,3,4,7,8 PeCDF (both 0.5). The compound 2,3,7,8 TCDF has a TEF of 0.1, but because it is frequently detected it is a significant contributor to the TEC values. The cumulative frequency distribution of TEC values shows that these values exceeded 1 pg/g in at least one sample at 70 percent of the sites (Figure 3-4). The proportion of the TEC contributed by 2,3,7,8 TCDD using the 1989 interim method is over 50 percent in 50 percent of the samples (Figure 3-5a). Four compounds (2,3,7,8 TCDD; 2,3,7,8 TCDF; 1,2,3,7,8 PeCDD; and 2,3,4,7,8 PeCDF) account for a little more than 80 percent of the TEC in three-fourths of the samples (Figure 3-5b). Levels of hepta- and hexa-dioxins, detected in a high percentage of study samples, have gained significance because the factors for these compounds, though low relative to the tetra- and penta-dioxins, have increased from 0.001 under the U.S. EPA's 1987 method to 0.01 for the 2,3,7,8 HpCDDs under the 1989 method and from 0.04 to 0.1 for 2,3,7,8 HxCDDs.

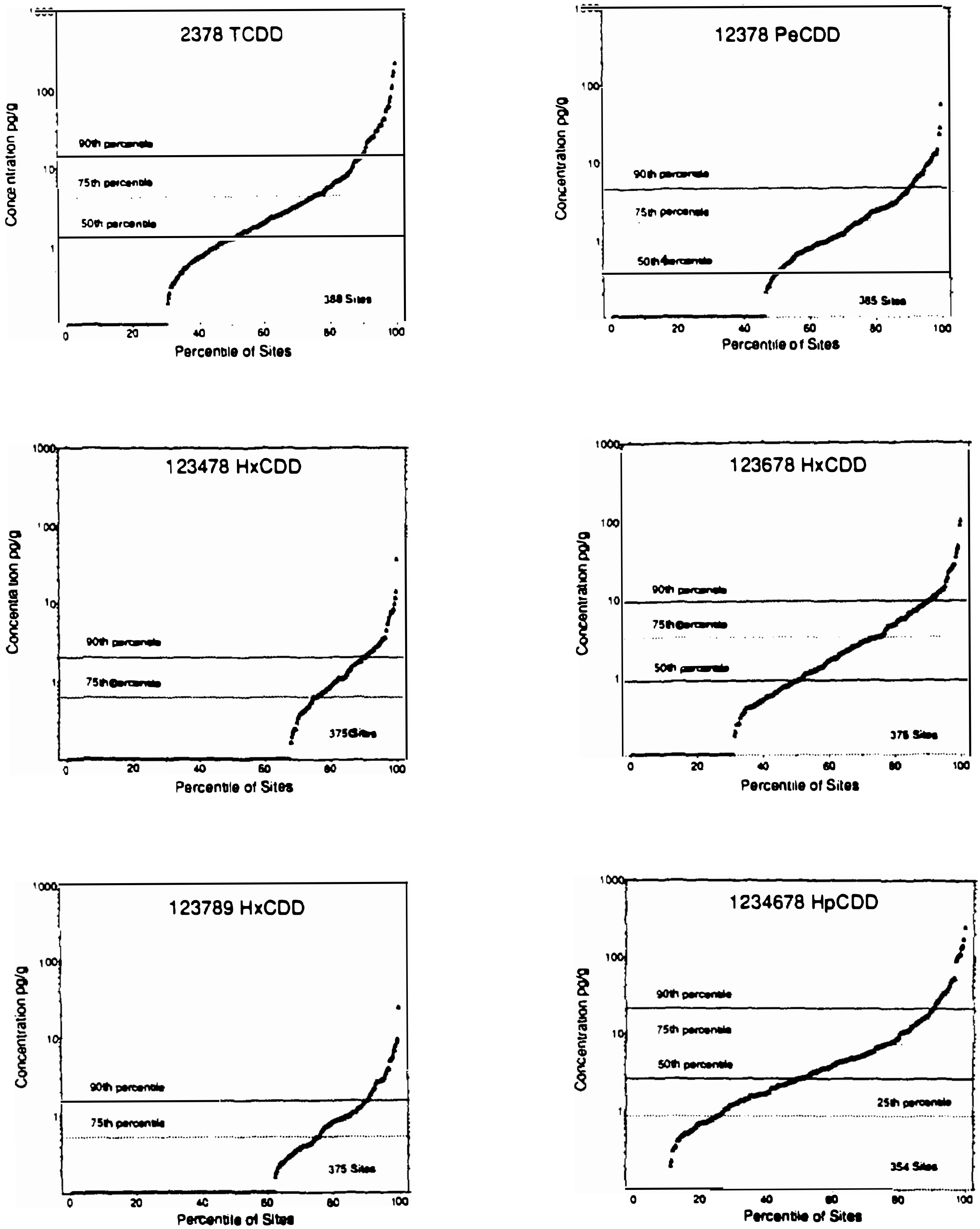


Figure 3-2. Cumulative frequency diagrams of concentrations of six dioxin congeners in fish tissue. Points display values above detection. The bars along the x axis indicate values below detection (ND). The total number of sites is also listed on the graph. Concentrations used are maximum values at each site.

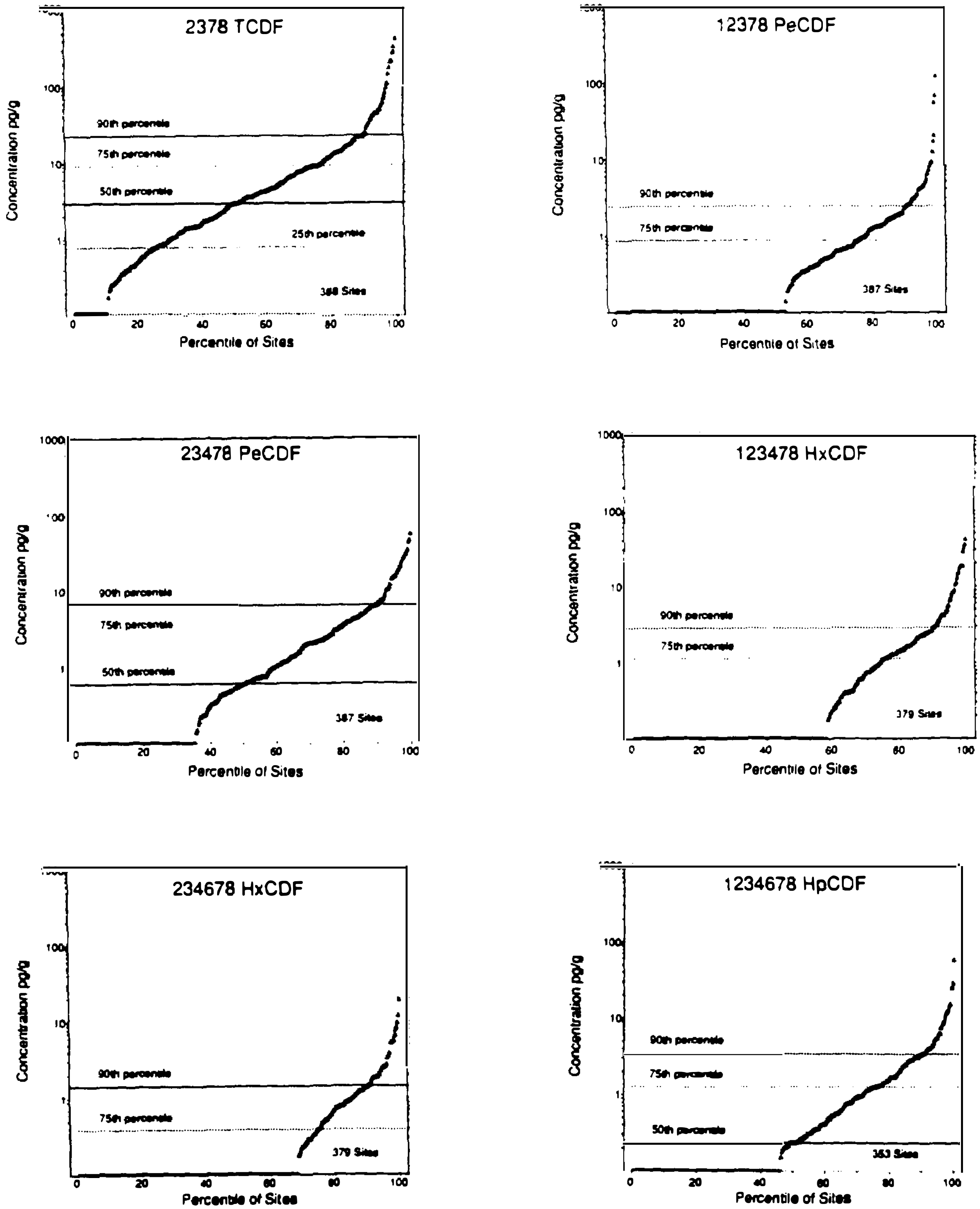


Figure 3-3. Cumulative frequency diagrams of concentrations of six furan congeners in fish tissue. Points display values above detection. The bars along the x axis indicate values below detection (ND). The total number of sites is also listed on the graph. Concentrations used are maximum values at each site.

TABLE 3-2
1989 Toxicity Equivalency Factors

Compound	TEFs/89
Mono-, Di-, and Tri-CDDs	0
2,3,7,8 TCDD	1
Other TCDDs	0
2,3,7,8 PeCDD	0.5
Other PeCDDs	0
2,3,7,8 HxCDDs	0.1
Other HxCDDS	0
2,3,7,8 HpCDD	0.01
Other HpCDDs	0
OCDD	0.001
Mono-, Di-, and Tri-CDFs	0
2,3,7,8 TCDF	0.1
Other TCDFs	0
1,2,3,7,8 PeCDF	0.05
2,3,4,7,8 PeCDF	0.5
Other PeCDFs	0
2,3,7,8 HxCDFs	0.1
Other HxCDFs	0
2,3,7,8 HpCDFs	0.01
Other HpCDFs	0
OCDF	0.001

Reference: Barnes et al., 1989.

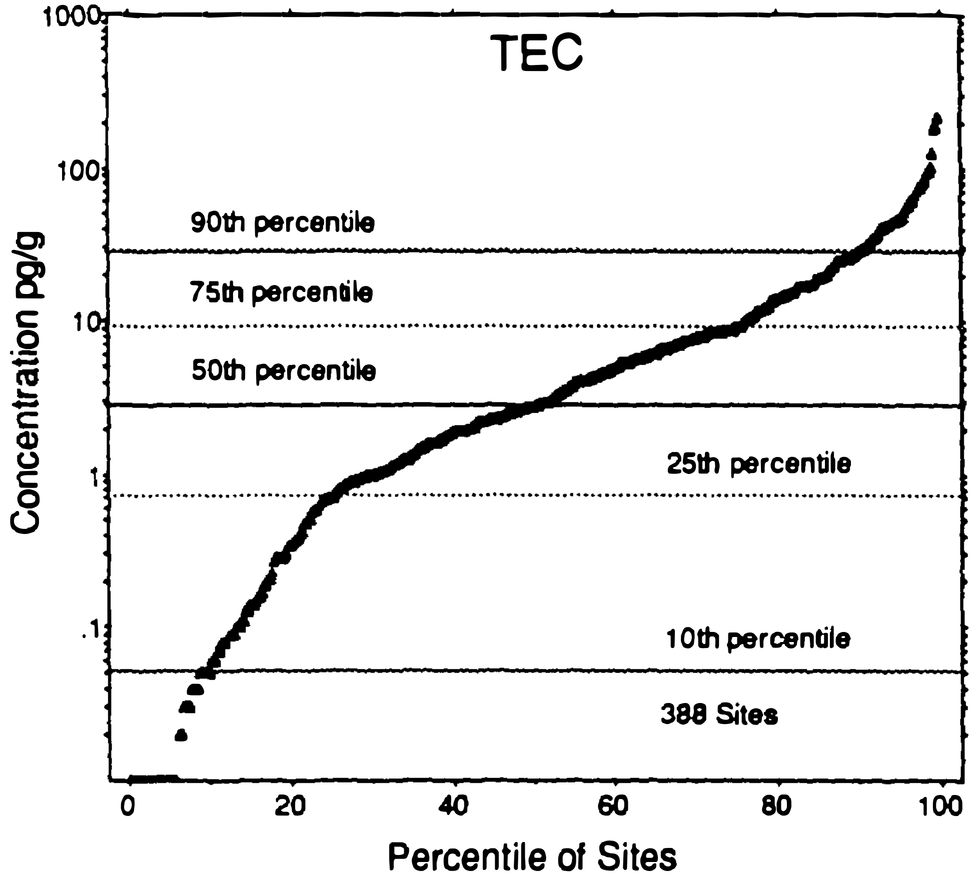


Figure 3-4. Cumulative frequency distribution of maximum calculated TEC values in fish tissue by percentile of sites. Bar on x-axis indicates sites where concentrations of PDCC/PCDF congeners were below detection for all samples from those sites.

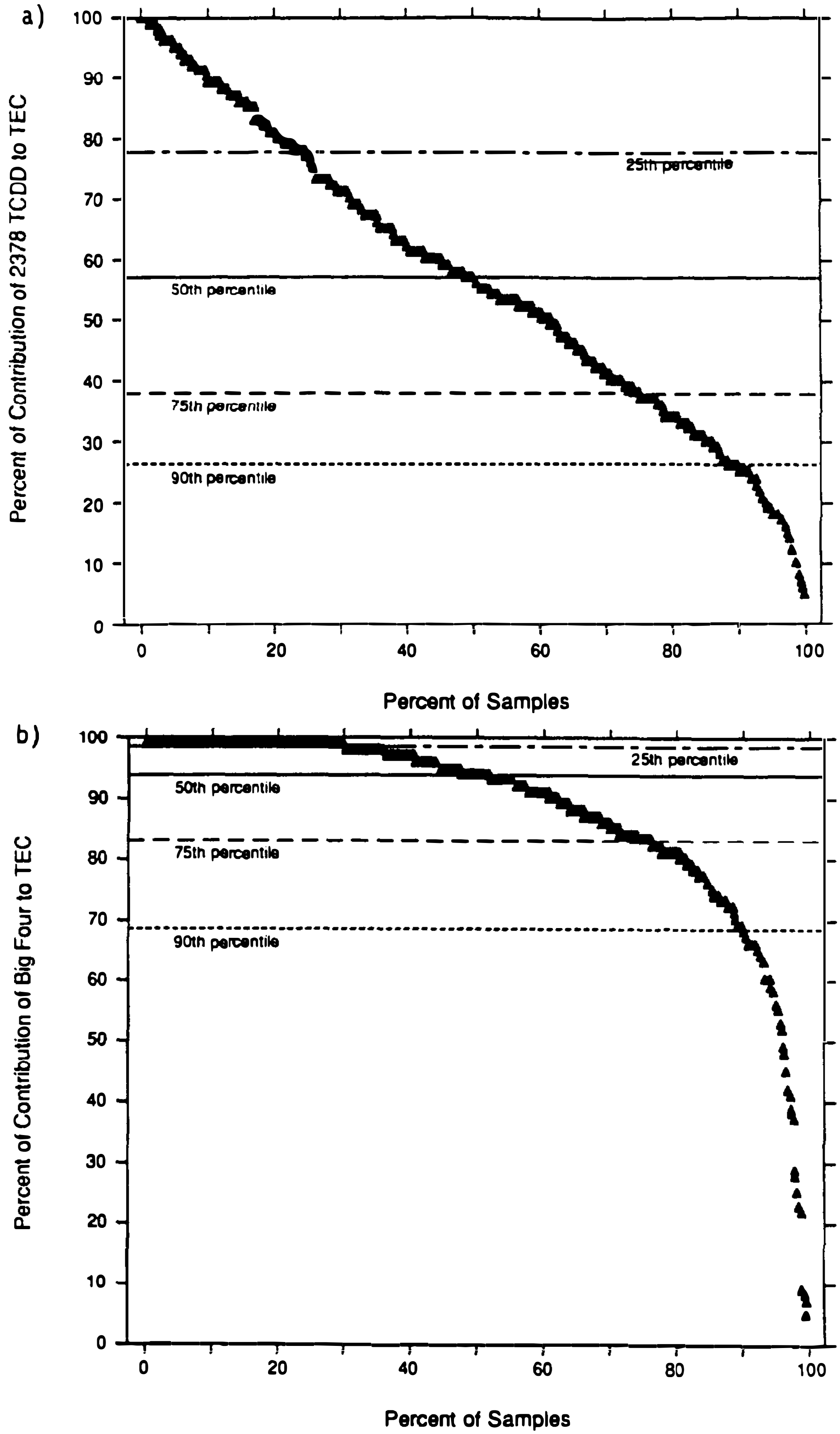


Figure 3-5. Toxicity Equivalency Concentrations (TEC) based on Barnes et al., 1989 method, a) the percent TEC contributed by 2,3,7,8, TCDD, and b) the percent of TEC contributed by 2,3,7,8, TCDD; 2,3,7,8 TCDF: 1,2,3,7,8 PeCDD and 1,2,3,7,8, PeCDF. (Values below the detection have been deleted from the plots.)

Comparison of TCDD and Other Dioxin/Furan Compounds

A comparison by site was made to determine whether any correlations existed between 2,3,7,8 TCDD and detectable levels of the other congeners. This comparison indicated that in most cases detected levels of other dioxin/furan isomers did not occur without detectable levels of 2,3,7,8 TCDD. The principal exception occurred for four congeners, penta-dioxins and furans and 2,3,7,8, TCDF, in less than 15 percent of the samples. Correlation plots of 2,3,7,8 TCDD versus 2,3,7,8 TCDF in the same sample were made to see whether there was a quantitative relationship between these congeners. No such predictive relationships were found based on linear or higher order regressions for these or the other congeners.

GEOGRAPHICAL DISTRIBUTION

The geographical distribution of dioxin and furan levels in fish tissue from the sites sampled is indicated on maps of the continental United States, Alaska, Hawaii, and Puerto Rico, showing the ranges of observed concentrations by site for 2,3,7,8 TCDD, for 2,3,7,8 TCDF, and for TEC. (Concentration ranges for these and all other maps were selected to identify locations with the higher concentrations and for ease of presentation. The first concentration range usually represents values up to the limit of quantification.) The maps depict the maximum values measured at a given location among all species sampled. In most cases, this was a whole-body sample. The maximum fillet concentration was used where no whole-body concentrations were available or where the highest value at a site was a fillet value. The number of cases where fillet data were used as the maximum value is shown on the maps. The specific type of sample at a particular site can be determined using the episode number from the site matrix (Appendix B-3) and the data tables in Appendix D.

Comparison of the maps for 2,3,7,8 TCDD (Figure 3-6) and 2,3,7,8 TCDF (Figure 3-7) shows that both are detected at many of the same sites. For example, Ship Creek in Anchorage near a former salvage yard with PCB contamination, now a Superfund site, had a 2,3,7,8 TCDF concentration of 3.1 pg/g, 2,3,7,8 TCDD of 0.51 pg/g, and TEC of 0.91 pg/g. However, 2,3,7,8 TCDF was detected at high concentrations at more sites. The percent of sites greater than 10 pg/g was 13 percent for 2,3,7,8 TCDD and 23 percent for 2,3,7,8 TCDF. Comparison of the map for 2,3,7,8 TCDD and TEC shows a similar pattern, and that there are some sites where the TEC value is greater than 1 pg/g due to the presence of additional congeners (Figure 3-8).

SOURCE CORRELATION ANALYSIS

Sources Located Near Highest Concentrations

Information on the types of point and nonpoint sources in the vicinity of each site was obtained from the selection criteria in the original study workplan, from the sample collection forms, and from information provided by EPA Headquarters, Regional Coordinators, and State staff involved in collecting the samples. Using these descriptions, a site matrix was prepared showing whether the site had been designated as a targeted site or a background site, or was one of the sites that had been selected from the USGS NASQAN (Appendix B-3). For targeted sites, the matrix indicates the predominant types of sources present and other available information.

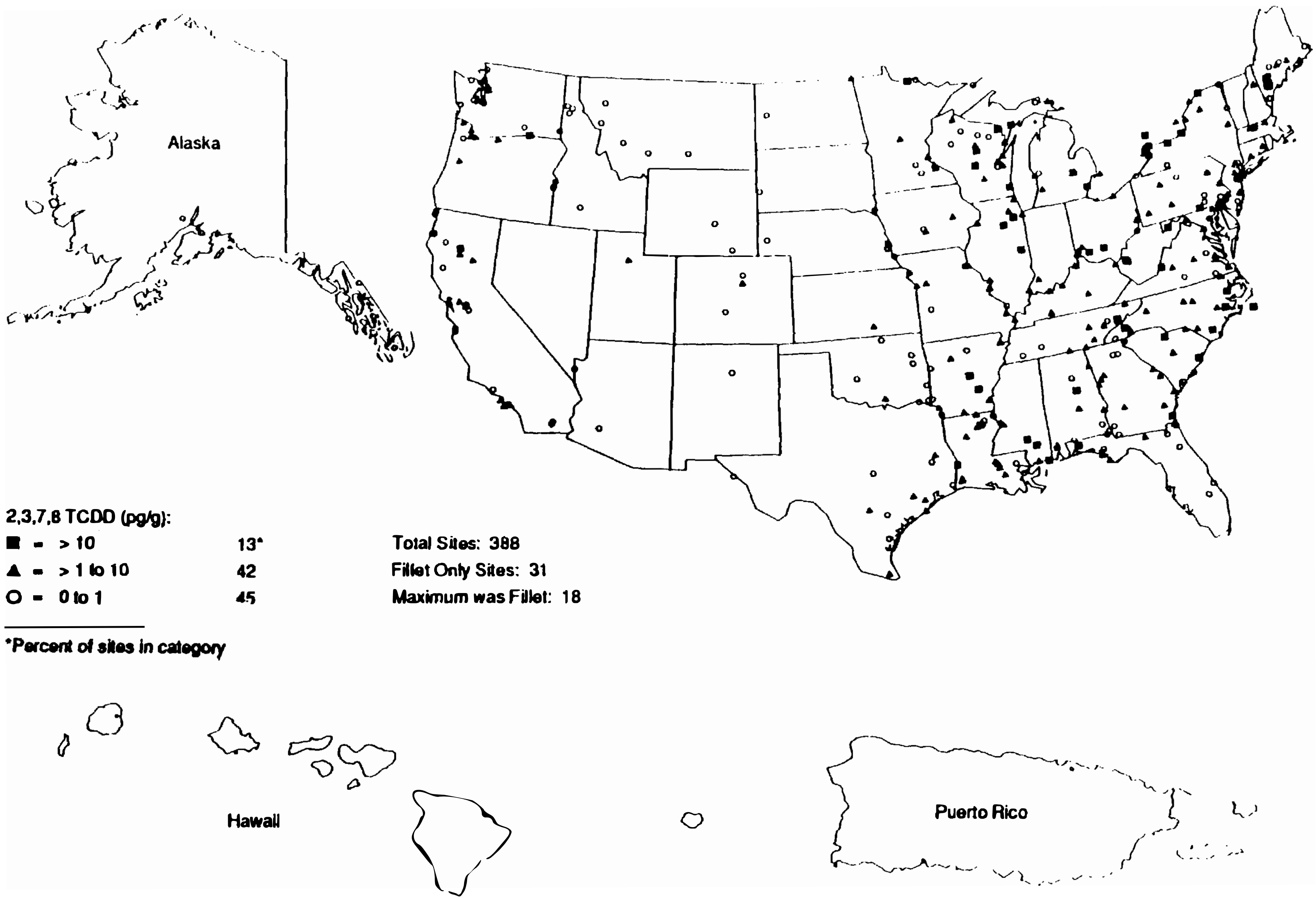


Figure 3-6. Map showing geographical distribution of various concentration ranges of 2,3,7,8 TCDD in fish tissue.

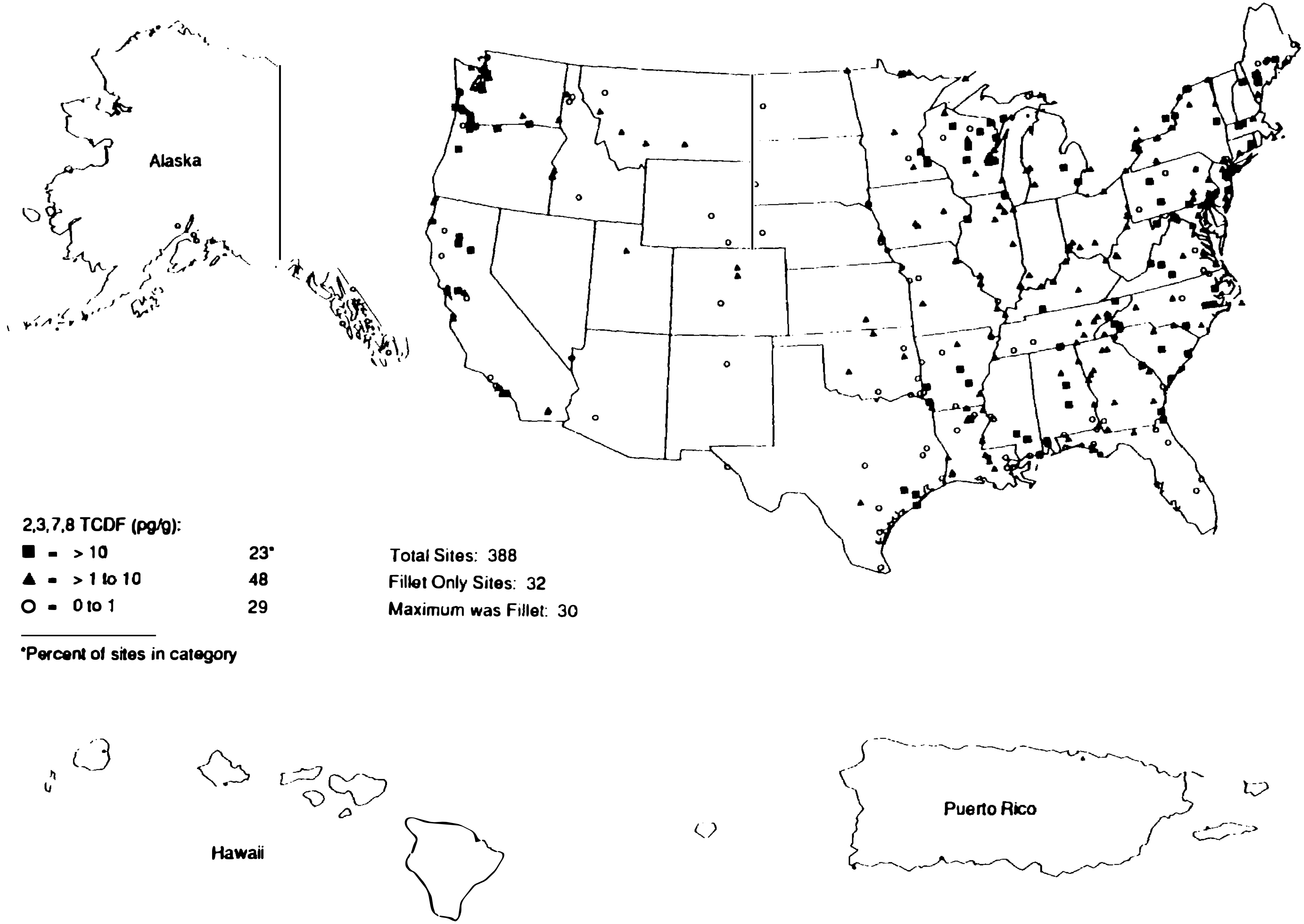


Figure 3-7. Map showing geographical distribution of various concentration ranges of 2,3,7,8 TCDF in fish tissue.

Figure 3-8. Map showing geographical distribution of various concentration ranges of TEC in fish tissue.

Tetra-Dioxins/Furans

The sites with the top 10 percentile concentrations (39 out of 388) were identified for each of the dioxin and furan congeners studied. Sites near paper and pulp mills using chlorine for bleaching accounted for 28 out of the top 39 sites for 2,3,7,8 TCDD and 31 out of the top 39 sites for 2,3,7,8 TCDF. For both 2,3,7,8 TCDD and 2,3,7,8 TCDF, four of the top five sites are located near pulp and paper mills using chlorine. The fifth and highest concentration site (3078) for 2,3,7,8 TCDD is located near a Superfund site with known dioxin contamination. The fifth and highest concentration site (3162) for 2,3,7,8 TCDF is located in a heavily industrialized area with a pulp and paper mill and a Superfund site in the vicinity. The top five sites for both compounds are shown below:

2,3,7,8 TCDD

Conc. pg/g (ppt)	Episode Number	Type of Sample	Location
203.6	3078	WB Sm Buffalo	Bayou Meto, Jacksonville, AR
160.4	3425	WB Carp	Wham Brake, Swartz, LA
143.3	3346	WB Creek Chubsucker	Roanoke R., Plymouth, NC
104.1	3348	WB Blue Catfish	Sampit R., Georgetown, SC
98.9	3340	WB Channel Catfish	Leaf R., New Augusta, MS

2,3,7,8 TCDF

Conc. pg/g(ppt)	Episode Number	Type of Sample	Location
403.9	3162	Hepatopancreas crab	Hylebos Waterway, Tacoma, WA
320.7	3221	WB Carp	Columbia R., Walla Walla, WA
273.8	3395	WB Redhorse Sucker	Neuse R., New Bern, NC
261.3	3087	WB Carp	Wham Brake, Swartz, LA
207.5	2721	WB Sucker	Androscoggin R., Turner Falls, ME

The above sites with the highest 2,3,7,8 TCDD concentrations also had the highest TEC values. Other sources near the remaining top 10 percentile sites included historical PCB contamination, chemical manufacturing plants, automobile manufacturing, a refinery, and an incinerator.

Penta-Dioxins/Furans

The sites with the highest 10 percentile concentrations for 1,2,3,7,8 PeCDD were near a variety of sources. Sites near paper mills using chlorine for bleaching accounted for 13 out of the 39 sites. Sites near Superfund waste disposal areas accounted for 8 sites, 4 were former wood preserving plants, 2 had PCB contamination, 1 had dioxin contamination, and 1 was a former dump with an unknown mixture of chemicals. Six of the sites were located near chemical manufacturing plants. The top 5 out of 385 sites are listed below:

1,2,3,7,8 PeCDD

Conc. pg/g (ppt)	Episode Number	Type of Sample	Location
53.9	3355	WB Carp	Old Mormon Slough, Stockton, CA
27.2	3098	WB White Sucker	Red Clay Cr., Ashland, DE
22.4	3141	WB Carp	Milwaukee R., Milwaukee, WI
15.9	3162	Hepatopancreas Crab	Hylebos Waterway, Tacoma, WA
14.3	2290	WB Spotted Sucker	Savannah R., Augusta, GA

The highest concentration was from a site located on the San Joaquin River system near a former wood preserving plant, now a Superfund site. This site also had the highest concentrations of four other dioxin/furan congeners (1,2,3,4,7,8 HxCDD; 1,2,3,7,8,9 HxCDD; 1,2,3,4,6,7,8 HpCDD; and 1,2,3,4,7,8,9 HpCDF) and was one of the top five sites for three other congeners (1,2,3,6,7,8 HxCDD; 1,2,3,6,7,8 HxCDF; and 1,2,3,4,6,7,8 HpCDF). Of the next four sites, one is near a dump, one is near a highly industrialized area with known PCB contamination, and two are near paper mills. High levels of other congeners were detected at these locations as well.

The top 10 percentile sites out of 387 for the PeCDFs included those near paper mills using chlorine for bleaching (19 out of 39 for 1,2,3,7,8 PeCDF and 9 out of 34 for 2,3,4,7,8 PeCDF), chemical/pesticide manufacturing plants, Superfund sites, and refineries (although other industries were often present). As shown below, three of the top five sites for both of these congeners are the same (3162, 3163, and 3085).

1,2,3,7,8 PeCDF

Con. pg/g(ppt)	Episode Number	Type of Sample	Location
120.3	3162	Hepatopancreas Crab	Hylebos Waterway, Tacoma, WA
68.4	3163	Hepatopancreas Crab	Commencement Bay, Tacoma, WA
54.3	3206	Crayfish	Willamette R., Portland, OR
20.3	3085	PF Back Drum	Brazos R. Freeport, TX
17.2	2290	WB Spotted Sucker	Savannah R., Augusta, GA

2,3,4,7,8 PeCDF

Conc. pg/g (ppt)	Episode Number	Type of Sample	Location
56.37	3162	Hepatopancreas Crab	Hylebos Waterway, Tacoma. WA
45.51	3085	WB Sea Catfish	Brazos River, Freeport, TX
42.58	3299	WB White Sucker	Niagara River, N. Tonawanda, NY
34.48	3163	Hepatopancreas Crab	Commencement Bay, Tacoma, WA
33.25	3086	WB Catfish	Bayou D'Inde, Sulfur, LA

The two sites near Tacoma are in a heavily industrialized area with paper mills, refineries, and other industries that have been designated as one Superfund site. This site also had the highest concentration of 2,3,7,8 TCDF and of two hexa-furans. The Brazos River site is close to the outfall of a pesticide manufacturing plant. The other two sites listed are also near chemical manufacturing plants.

Hexa- and Hepta-Dioxins/Furans

The major sources near the top 10 percentile sites for the hexa- and hepta-dioxins included wood preserving plants, paper mills, Superfund sites, and chemical manufacturing plants. Three of the top five sites (3355, 3167, and 3185) are near wood preserving plants or former plants, one is near multiple urban/industrial sources (3444) and the remainder are near paper mills (Table 3-3).

The major sources at the top 10 percentile sites for the hexa- and hepta-furans were similar to the hexa-dioxins, except that HCB contamination appears to be an important potential source for HxCDFs. Several of the sites had high levels of more than one congener. The top five sites out of 379 listed in Table 3-4 for 1,2,3,7,8,9 HxCDF were the only ones with detectable levels of this compound. Only 14 sites out of 353 had detectable levels of 1,2,3,4,7,8,9 HpCDF. The most common sources near the sites with detectable concentrations of HxCDFs and HpCDFs were paper mills using chlorine for bleaching, Superfund sites, and chemical manufacturing sites.

TABLE S-3
Location of Maximum Measured HxCDD and HpCDD Concentrations in Fish Tissue

Compound	Maximum Concentration pg/g	Episode Number	Type of Fish	Location
123478 HxCDD				
(375 sites)*	37.6	3355	WB Carp	Old Mormon Slough, Stockton, CA
	14.3	3167	WP Bluegill	Medlins Pond, Morrisville, NC
	11.6	2304	WB Carp	Alabama R., Claiborne, AL
	9.9	3092	WB Carp	Dugdemona R., Hodge, LA
	8.7	3444	WB Carp	Nonconnah Creek, Memphis, TN
123678 HxCDD				
(375 sites)	100.9	2290	WB Spotted Sucker	Savannah R., Augusta, GA
	89.1	3355	WB Carp	Old Mormon Slough, Stockton, CA
	50.8	3185	WB Channel Catfish	Bernard Bayou, Gulfport, MS
	47.3	3377	WB Carp	Chattahoochee R., Franklin, GA
	41.9	3376	WB Carp	Chattahoochee R., Whitesburg, GA
123789 HxCDD				
(375 sites)	24.8	3355	WB Carp	Old Mormon Slough, Stockton, CA
	9.5	3185	WB Channel Catfish	Bernard Bayou, Gulfport, MS
	8.5	3167	WP Bluegill	Medlins Pond, Morrisville, NC
	7.8	3377	WB Carp	Chattahoochee R., Franklin, GA
	6.8	3098	WB White Sucker	Red Clay Cr., Ashland, DE
1234678 HpCDD				
(354 sites)	249.1	3355	WB Carp	Old Mormon Slough, Stockton, CA
	171.0	3377	WB Carp	Chattahoochee R., Franklin, GA
	150.8	3444	WB Carp	Nonconnah Creek, Memphis, TN
	141.2	2290	WB Spotted Sucker	Savannah R., Augusta, GA
	138.1	3376	WB Carp	Chattahoochee R., Whitesburg, GA

* Number shown is total number of sites.
WB = whole-body bottom-feeding composite sample.
PF = predator fillet composite sample.
WP = whole-body predator composite sample.

TABLE 3-4
Location of Maximum Measured HxCDF and HpCDF Concentrations in Fish Tissue

Compound	Maximum Concentration pg/g	Episode Number	Type of Fish		Location
123478 HxCDF (379 sites)*	45.3	3162		Hepatopancreas Crab	Hylebos Waterway, Tacoma, WA
	37.9	3297	WB	Carp	Niagara R., Niagara Falls, NY
	34.3	2410	WB	Carp	Rouge R., River Rouge, MI
	30.8	3299	WB	White Sucker	Niagara R., N. Tonawanda, NY
	20.0	3086	WB	Catfish	Bayou D'Inde, Sulfur, LA
123678 HxCDF (379 sites)	30.9	3162		Hepatopancreas Crab	Hylebos Waterway, Tacoma, WA
	16.2	3085	WB	Sea Catfish	Brazos R., Freeport, TX
	14.0	3301	WB	Carp	Eighteen Mile Cr., Olcott, NY
	13.8	3297	WB	Carp	Niagara R., Niagara Falls, NY
	13.1	3355	WB	Carp	Old Mormon Slough, Stockton, CA
123789 HxCDF (377 sites)	0.96	3085	WB	Sea Catfish	Brazos R., Freeport, TX
	0.51	3150	WB	White Sucker	Otter R., Baldwinville, MA
	0.44	3112	WB	Carp	Mississippi R., Little Falls, MN
	0.41	3107	WB	Carp	Wisconsin R., Brokaw, WI
	0.23	3206		Crayfish	Willamette R., Portland, OR
234678 HxCDF (379 sites)	19.3	3167	WP	Bluegill	Medlins Pond. Morrisville, NC
	11.8	3185	WB	Channel Catfish	Bernard Bayou, Gulfport, MS
	9.6	2290	WB	Spotted Sucker	Savannah R., Augusta, GA
	8.4	2225	WB	Shorthead Redhorse	James R., Glasgow, VA
	7.8	2383	WB	Carp	Des Plaines R., Lockport, IL
1234678 HpCDF (353 sites)	58.3	3167	WP	Bluegill	Medlins Pond, Morrisville, NC
	29.4	3185	WB	Channel Catfish	Bernard Bayou, Gulfport, MS
	25.7	3086	WB	Catfish	Bayou D'Inde, Sulfur, LA
	25.4	3355	WB	Carp	Old Mormon Slough, Stockton, CA
	16.4	3377	WB	Carp	Chattahoochee R., Franklin, GA
1234789 HpCDF (353 sites)	2.57	3355	WB	Carp	Old Mormon Slough, Stockton, CA
	1.76	3206		Crayfish	Willamette R., Portland, OR
	1.26	3085	WB	Sea Catfish	Brazos R., Freeport, TX
	0.97	3377	WB	Carp	Chattahoochee R., Franklin, GA
	0.91	3376	WB	Carp	Chattahoochee R., Whitesburg, GA

* Number shown is total number of sites.
WB = whole-body bottom-feeding composite sample.
PF = predator fillet composite sample.
WP = whole-body predator composite sample.

Concentration Comparison Between Site Categories

Description of Categories

The point and nonpoint source categories used for the dioxin/furan comparisons were background sites (B); sites selected from the USGS NASQAN (NSQ); Superfund sites (NPL); sites near pulp and paper mills that use chlorine for bleaching (PPC); sites near other types of pulp and paper mills (PPNC); sites near former or existing wood preserving plants (WP); sites near industrial or urban areas (IND/URB); sites near industrial areas that include refineries with catalytic reforming operations (R/I); sites that could be influenced by runoff from agricultural areas (AGRI); and sites near publicly owned treatment works (POTWs). The two broad categories, industry/urban and refineries/other industry, resulted from a substantial number of sites having multiple point sources. With the exception of background and NASQAN sites, categories were established based on probable sources of various pollutants including dioxins, furans, and pesticides. Background sites were selected to provide a comparison with areas relatively free of point and nonpoint source pollution; however, some background sites do have other source categories present. NASQAN sites were selected to evaluate the geographic extent and prevalence of fish contamination throughout the country rather than to identify specific sources of this contamination.

Sites would, in general, be included in statistical tests (described below) only if a single potential source of contamination existed at the site. The intent was to determine whether concentrations would differ at sites with different sources. Multiple sources were excluded so as not to infer a correlation with a given source when in fact the high contamination levels were due to the contribution of another type of source. The number of sites per category varied for dioxins/furans and other xenobiotics. Two categories (POTWs and agricultural areas) would not, as data on these sites confirm, be expected to significantly impact overall dioxin/furan contamination of fish. Accordingly, the presence of these categories would not preclude a site from being designated as a single category site for purposes of statistical analysis for dioxins/furans. For xenobiotics, no such "override" was included in the analysis of data.

Below is a listing of the number of sites included in each category for dioxins/furans. A similar table is presented in Chapter 4 for xenobiotics. Category data were not available for each site.

Category	Abbreviation	Number of Sites
Background	B	34
USGS/NASQAN	NSQ	40
Paper Mills using Chlorine	PPC	78
Other Types of Pulp and Paper Mills	PPNC	27
Wood Preserving Plants	WP	11
Refineries/Other Industries	R/I	20
NPL (Superfund Sites)	NPL	7
Industry/Urban	IND/URB	106
Agriculture	AGRI	19
Publicly Owned Treatment Works (POTW)	POTW	11

Statistical Comparison Tests

To compare observed concentrations between site categories, box and whisker plots were prepared for the tetra- and penta-dioxins individually and for total hexa-dioxins and total hexa-furans and TEC values. A schematic box and whisker plot is shown in Figure 3-9. The box shows the spread of the data between the 25th percentile and the 75th percentile. The line inside the box represents the median concentration. The "whiskers" or lines extend down to the 10th percentile and up to the 90th percentile. The circles above or below the line represent the extreme upper and lower 10 percent of the data. The maximum value of all samples at each site, including the duplicates, was used. For dioxins/furans, values below detection have been replaced by one-half the detection limit prior to determining the maximum value except for total HxCDDs and total HxCDFs. For these plots the values below detection were assigned a value of zero because detection limits were often high. The summary statistics for each category are shown beneath the plot.

Because the data sets consist of highly-skewed non-normal distributions, nonparametric statistical methods were used to test the significance of the results. The Kruskal-Wallis test is a one-way nonparametric analysis of variance used to determine whether concentrations from three or more categories are from different populations or whether the observed differences could be due to random variations of the parameters. The test is based on a comparison of ranks (order of the observations, i.e., highest = 1, next highest = 2, etc.). The results are presented as an H statistic and a probability (p) that the sets of samples are from the same population (null hypothesis). This value p is then compared to a critical level. For this study a level of significance of 0.05 was used. If the p values for a comparison of categories are less than 0.05, the two categories are considered to be significantly different. This test is analogous to the F test for parametric data, but less powerful. The Kruskal-Wallis test is preferred over a test using only the median, because it considers the distribution of the data as well as the median.

The Mann-Whitney U test is a nonparametric equivalent of the "t" test. The U test is also based on ranks. This statistic was used to test for significant differences in concentrations between two categories (e.g., background sites and agricultural sites). The U statistic is calculated and the probability that the two sets of samples are from the same population is tabulated. A critical level of 0.05 was used as the level of significance in this study. If the probability for a two-way comparison was less than 0.05, the null hypothesis was rejected (i.e., the two categories being compared are significantly different).

Site Category Comparisons

Tetra-Dioxins/Furans

Pulp and paper mills using chlorine appear to be the dominant source of 2,3,7,8 TCDD. The paper mills using chlorine had the highest median concentration (5.66 pg/g) compared to 1.82 pg/g for refinery/other industry sites and 1.27 pg/g for Superfund sites (Figure 3-10). Statistical comparisons based on the Mann-Whitney U tests (Table 3-5) showed that pulp and paper mills using chlorine had significantly higher concentrations than other paper mills, wood preserving operations, Superfund sites, industry/urban sites, or refineries/other industries. As would be expected, the box

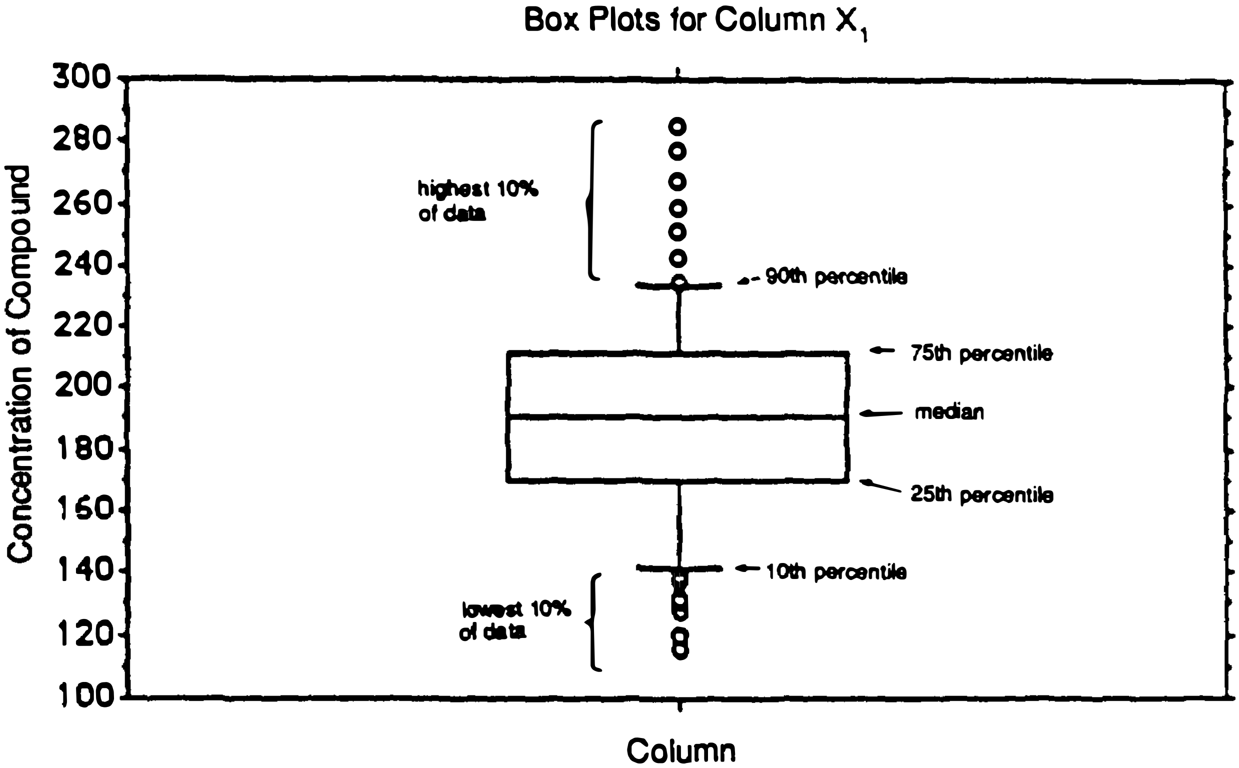
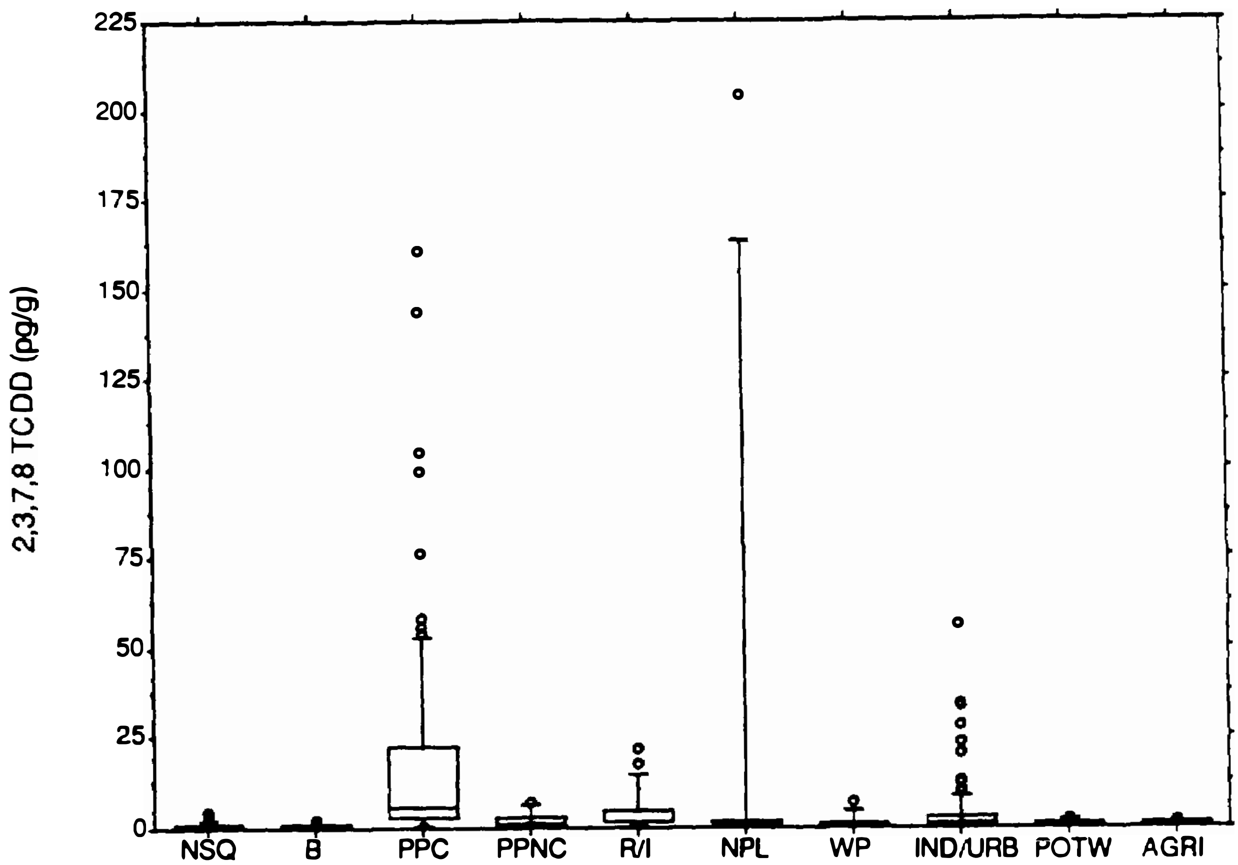


Figure 3-9. Example box plot with explanation of features.



Summary Table for 2,3,7,8 TCDD Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	40	0.17- 4.73	1.02	1.02	0.65
Background (B)	34	0.060 2.26	0.56	0.38	0.50
Paper Mills Using Cl (PPC)	78	0.55 - 160.4	19.02	30.64	5.66
Other Paper Mills (PPNC)	27	0.48 - 7.15	2.17	2.21	1.09
Refinery/Other Industry (R/I)	20	0.50 - 21.55	4.38	5.88	1.82
Superfund Sites (NPL)	7	0.62 - 203.6	30.02	76.54	1.27
Wood Preservers (WP)	11	0.21 - 7.30	1.40	2.08	0.56
Industrial/Urban Sites (IND/URB)	105	0.10 - 56.34	4.04	8.05	1.40
POTW	8	0.18 -2.24	0.90	0.76	0.63
Agricultural (AGRI)	17	0.20 - 1.78	0.75	0.39	0.58

n = number of sites in category. Maximum value at each site was used. One-half the detection limit was used for values below detection. Sites were assigned to only one category.

Figure 3-10. Box and whisker plot for 2,3,7,8 TCDD concentrations in fish tissue.

Table 3.5
Mann-Whitney U Test Results for Dioxins Furan Comparing Selected Source Categories

Chemical	Kruskal-Wallis: All Groups Except NSQ	Kruskal-Wallis: IND/URB,R/I, NPL, PPC, PPNC, WP	Mann-Whitney: PPC, B	PPC, WP	PPC, PPNC	PPC, R/I	PPC, NPL	PPC, IND/ URB	PPC POTW	PPC, AG
2,3,7,8-TCDD	.0001	.0001	.0001	.0001	.0001	.0032	.0348	.0001	.0001	.0001
2,3,7,8-TCDF	.0001	.0001	.0001	.0001	.0001	.0001	.0531	.0001	.0001	.0001
2,3,4,7,8-PeCDF	.0001	.0003	.0001	.0004	.0099	.0881	.3538	.4096	.0002	.0001
1,2,3,7,8-PeCDF	.0001	.0352	.0001	.0252	.0779	.3733	.5650	.2948	.0065	.0005
1,2,3,7,8-PeCDD	.0001	.0871	.0001	.0274	.1021	.4890	.9809	.1389	.0225	.0025
HxCDDs	.0001	.3496	.0001	.1299	.6976	.7377	.7311	.0493	.0003	.0044
HxCDFs	.0013	.4981	.0007	.7553	.1166	.2724	.8479	.9612	.0220	.0249
TEC	.0001	.0001	.0001	.0003	.0001	.0400	.1692	.0001	.0001	.0001

Chemical	Mann-Whitney: WP,B	WP, PPNC	WP, R/I	WP, NPL	WP, IND/ URB	WP, POTW	WP, AG
2,3,7,8-TCDD	.0961	.1567	.0132	.0515	.0102	.8365	.8878
2,3,7,8-TCDF	.1956	.0021	.0118	.0098	.0002	.4090	.1263
2,3,4,7,8-PeCDF	.1780	.1303	.0002	.0032	.0053	.4328	.6381
1,2,3,7,8-PeCDF	.3485	.2337	.0036	.0236	.0077	.2831	.4517
1,2,3,7,8-PeCDD	.7760	.2337	.0219	.1473	.0846	.2831	.9250
HxCDDs	.0617	.3424	.2477	.2976	.5406	.0265	.5885
HxCDFs	.1115	.5302	.4090	.8919	.7808	.1604	.2690
TEC	.1696	.0974	.0287	.0774	.0215	.5633	.9250

Values shown are two-tail probabilities that groups are different. The critical level was set at 0.05. If $p<0.05$, the categories were considered to be significantly different.

Site Categories:

IND/URB	=	Industry and/or Urban	NSQ	=	National ambient stream monitoring network. (This designation is independent of source categories.)
AG	=	Agriculture	WP	=	Wood preserving related activities
B	=	Background	PPC	=	Paper and pulp mills using chlorine for bleaching
NPL	=	National Priority List (Superfund site)	PPNC	=	Other paper and pulp mills including deinking plants
POTW	=	Publicly Owned Treatment Works (sewage)			
R/I	=	Refines using catalytic reforming process and other industry			

plot for combined dioxins/furans based on TEC values (Figure 3-11) also shows that pulp and paper mills using chlorine have the highest median concentration.

The highest median concentration of 2,3,7,8 TCDF was 14.0 pg/g at pulp and paper mills using chlorine (Figure 3-12). The next highest median values were 3.6 pg/g for other pulp and paper mill sites and 3.5 pg/g for Superfund sites. Pulp and paper mills using chlorine also had a substantially higher mean concentration of 2,3,7,8 TCDF than any of the other categories, 39.2 pg/g, compared to 7.2 pg/g for the next highest category, Superfund sites. The Mann-Whitney U tests showed that with the exception of Superfund sites, pulp and paper mills using chlorine had significantly higher concentrations of 2,3,7,8 TCDF than other categories. A Mann-Whitney U comparison of pulp and paper mills using chlorine with Superfund sites results in a value that only slightly exceeds the 0.05 critical value. The similarities between the categories are due in part to the fact that there are only a few (i.e., 7) Superfund sites used in the analysis.

Penta-Dioxins/Furans

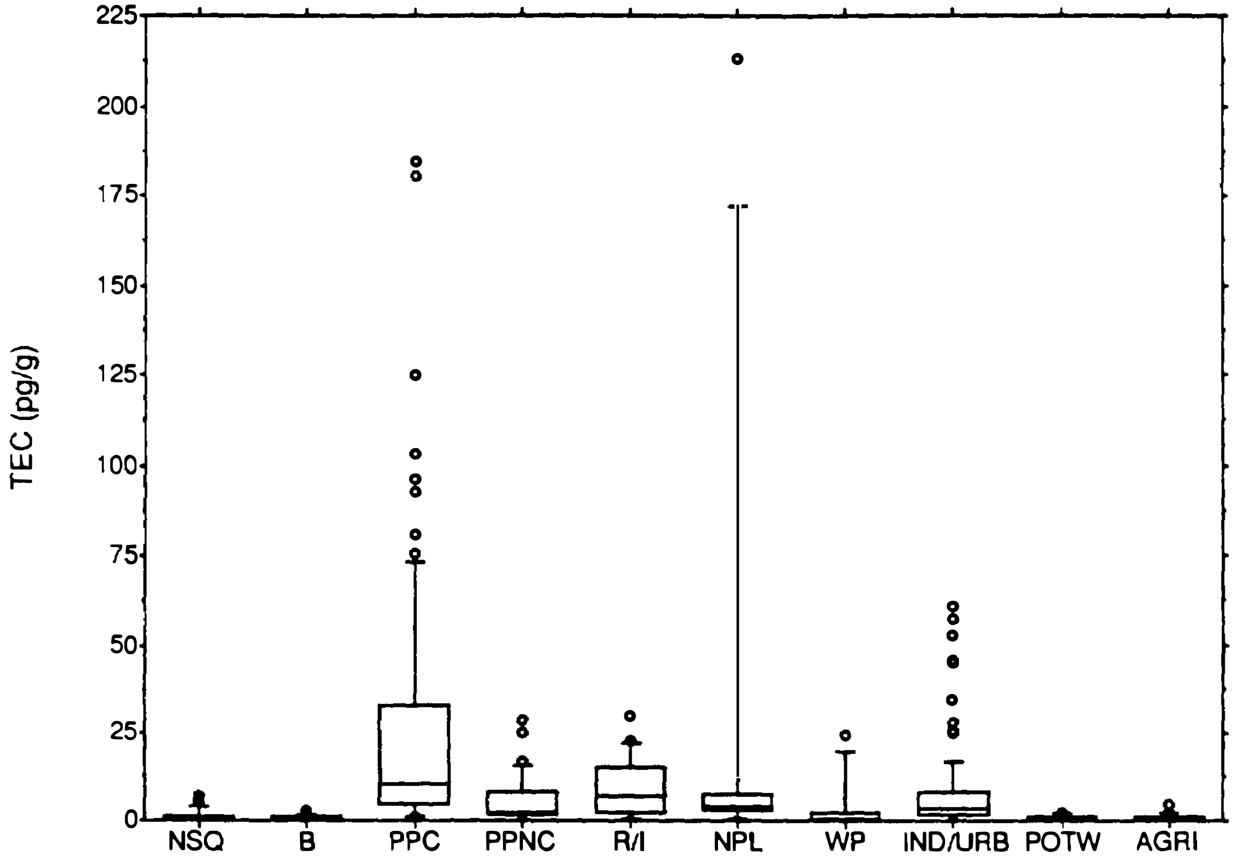
For 1,2,3,7,8 pentachlorodibenzodioxin (1,2,3,7,8 PeCDD), there were several significant sources of contamination, including pulp and paper mills, Superfund sites, industry/urban sites, and refinery/other industry sites (Figure 3-13). The highest median was for paper mills using chlorine at 1.52 pg/g; refinery/other industry had the next highest at 1.35 pg/g followed by 1.09 pg/g for industrial/urban. The highest concentration (27.5 pg/g) was found in the industrial/urban category with the highest mean (3.3 pg/g) found in the refinery/other industry category. Mann-Whitney U tests comparing pulp and paper mills using chlorine with Superfund sites, other paper mills, refinery/other industry sites, and industry/urban sites showed no significant differences (Table 3-5).

For both 1,2,3,7,8 and 2,3,4,7,8 penta-furans, the highest median concentration was found at Superfund sites (Figures 3-14 and 3-15). A review of the median values for other categories indicates that there is no dominant source for either of these penta-furan congeners. This observation is confirmed by the Kruskal-Wallis test for 1,2,3,7,8 PeCDF and by the Mann-Whitney U tests for 2,3,4,7,8 PeCDF (Table 3-5).

Hexa-Dioxins/Furans

For hexa-dioxins the highest median concentration, 3.19 pg/g, occurred at paper mills using chlorine. Median values (Figure 3-16) for the next two highest source categories (refinery/other industry and Superfund sites) were approximately the same at 1.97 and 1.94 pg/g, respectively. A Kruskal-Wallis test (Table 3-5) for paper mills, refinery/other industry sties, industrial/urban sites, Superfund sites, and wood preservers showed that none of the sources was significantly different from the others with regard to fish contamination. Values below detection were set at zero for the hexa-dioxin and hexa-furan box plots because the detection limits were often higher than the measured concentrations.

For hexa-furans, the source category with the highest median concentration is refinery/other industry (Figure 3-17). This category is followed by industrial/urban and Superfund sites. The Kruskal-Wallis test (Table 3-5) shows that no single category is significantly different from all others with regard to hexa-furan fish contamination.

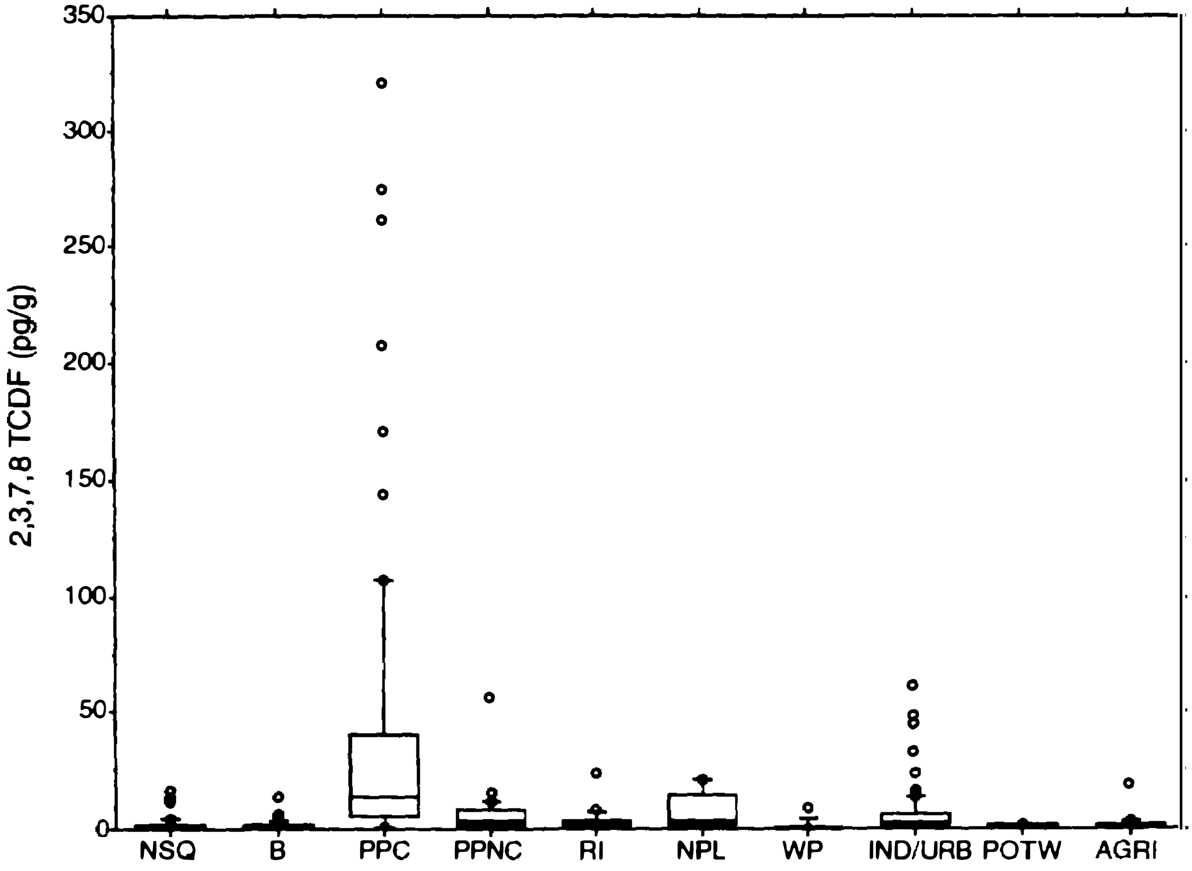


Summary Table for TEC Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	40	ND- 7.18	1.12	1.87	0.16
Background (B)	34	ND- 3.02	0.59	0.9	0.21
Paper Mills Using Cl (PPC)	78	0.4- 184.24	25.84	36.90	10.62
Other Paper Mills (PPNC)	27	ND- 28.9	5.70	7.50	2.39
Refinery/Other Industry(R/I)	20	ND- 30.22	8.89	8.64	6.81
Superfund Sites (NPL)	7	0.13- 213.05	33.86	79.06	4.36
Wood Preservers (WP)	11	0.01-24.84	4.34	8.36	0.43
Industrial/Urban Sites (IND/URB)	105	ND- 61a07	7.79	12.54	3.26
POTW	8	0.03- 2.24	0.70	0.92	0.12
Agricultural (AGRI)	17	ND- 4.44	1.02	1.19	0.79

ND = TEC value not determined because all values below detection. Maximum value at each site was used. Sites were assigned to only one category.

Figure 3-11. Box and whisker plot for TEC concentrations in fish tissue.

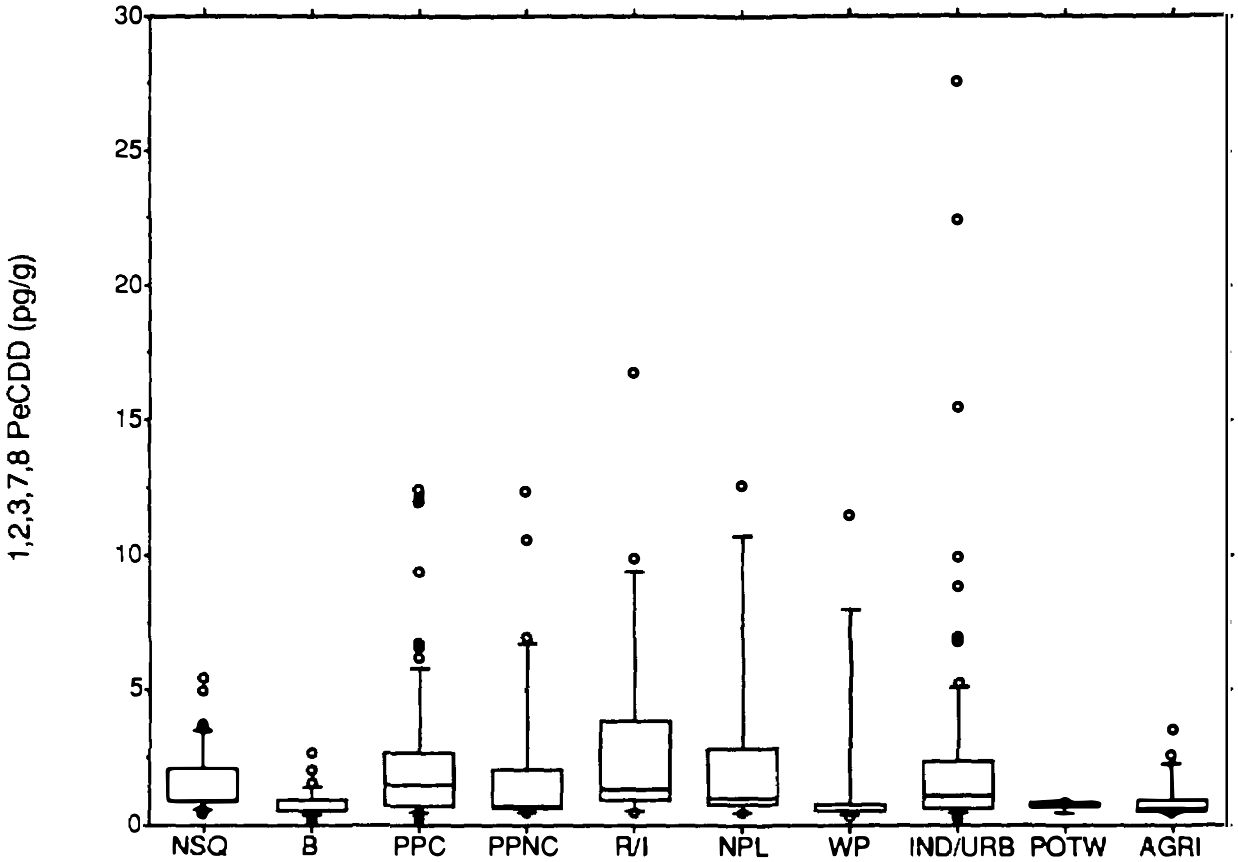


Summary Table for 2,3,7,8 TCDF Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	40	0.19 - 16.61	2.11	3.66	0.68
Background (B)	34	0.10 - 13.73	1.61	2.51	0.90
Paper Mills Using Cl (PPC)	78	0.26 - 320.69	39.20	66.18	14.04
Other Paper Mills (PPNC)	27	0.25 - 55.75	6.42	10.72	3.61
Refinery/Other Industry (R/I)	20	0.24 - 23.36	3.62	5.16	1.91
Superfund Sites (NPL)	7	0.56 - 21..23	7.23	8.62	3.48
Wood Preservers (WP)	10	0.18 - 8.84	1.31	2.54	0.39
Industrial/Urban Sites (IND/URB)	105	0.24 - 61.58	5.93	9.49	2.90
POTW	8	0.24 - 2.00	0.94	0.72	0.79
Agricultural (AGRI)	17	0.19 - 19.28	2.21	4.52	0.84

n = number of sites in category. Maximum value at each site was used. One-half the detection limit was used for values below detection. Sites were assigned to only one category.

Figure 3-12. Box and whisker plot for 2,3,7,8 TCDF concentrations in fish tissue.

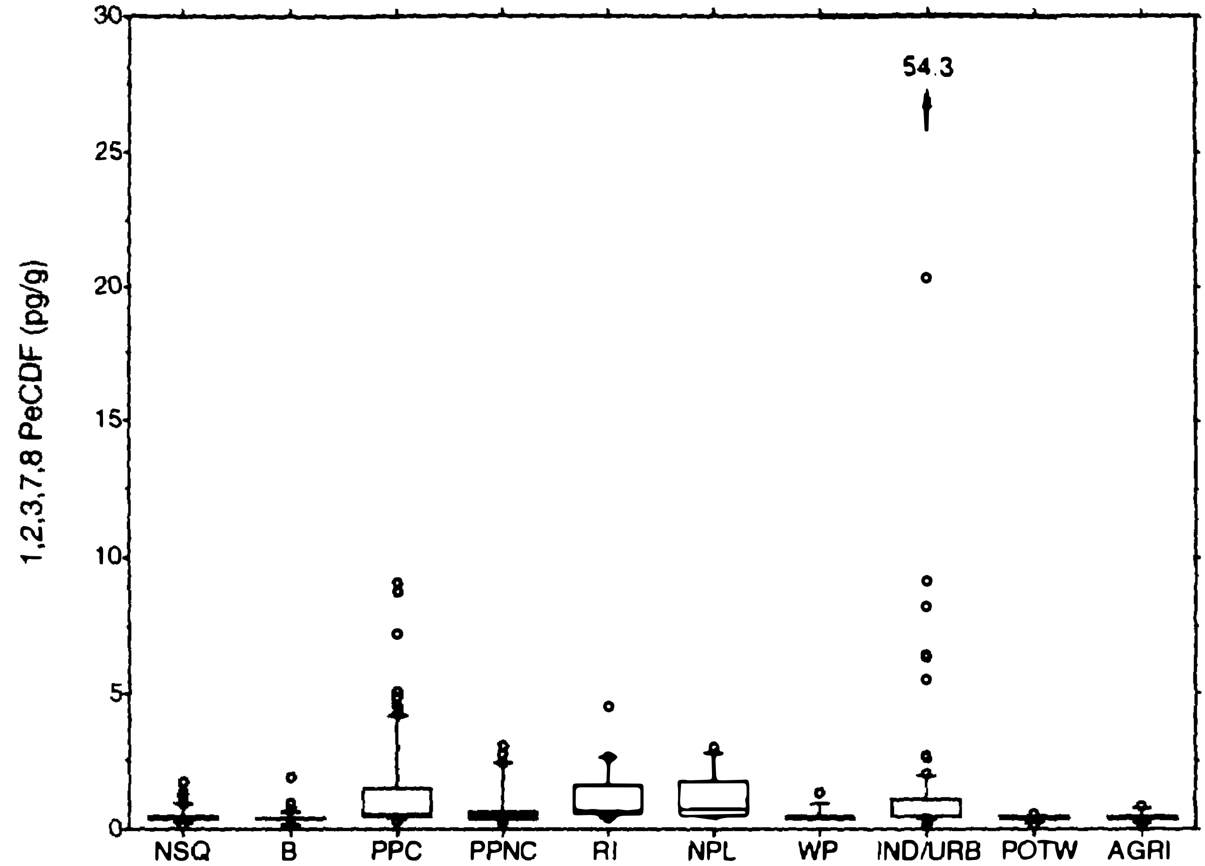


Summary Table for 1,2,3,7,8 PeCDD Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	0.36-5.41	1.53	1.24	0.90
Background (B)	33	0.15-2.67	0.77	0.54	0.54
Paper Mills Using Cl (PPC)	78	0.25-12.48	2.37	2.72	1.52
Other Paper Mills (PPNC)	27	0.45-12.38	2.22	3.19	0.68
Refinery/Other Industry (R/I)	20	0.46-16.80	3.28	4.17	1.35
Superfund Sites (NPL)	7	0.46-12.62	3.01	4.34	1.00
Wood Preservers (WP)	11	0.28-11.50	2.01	3.51	0.52
Industrial/Urban Sites (IND/URB)	105	0.20-27.56	2.32	3.93	1.09
POTW	8	0.46-0.88	0.75	0.185	0.84
Agricultural (AGRI)	17	0.46-3.54	0.92	0.84	0.62

n = number of sites in category. Maximum value at each site was used. One-half the detection limit was used for values below detection. Sites were assigned to only one category.

Figure 3-13. Box and whisker plot for 1,2,3,7,8 PeCDD concentrations in fish tissue.

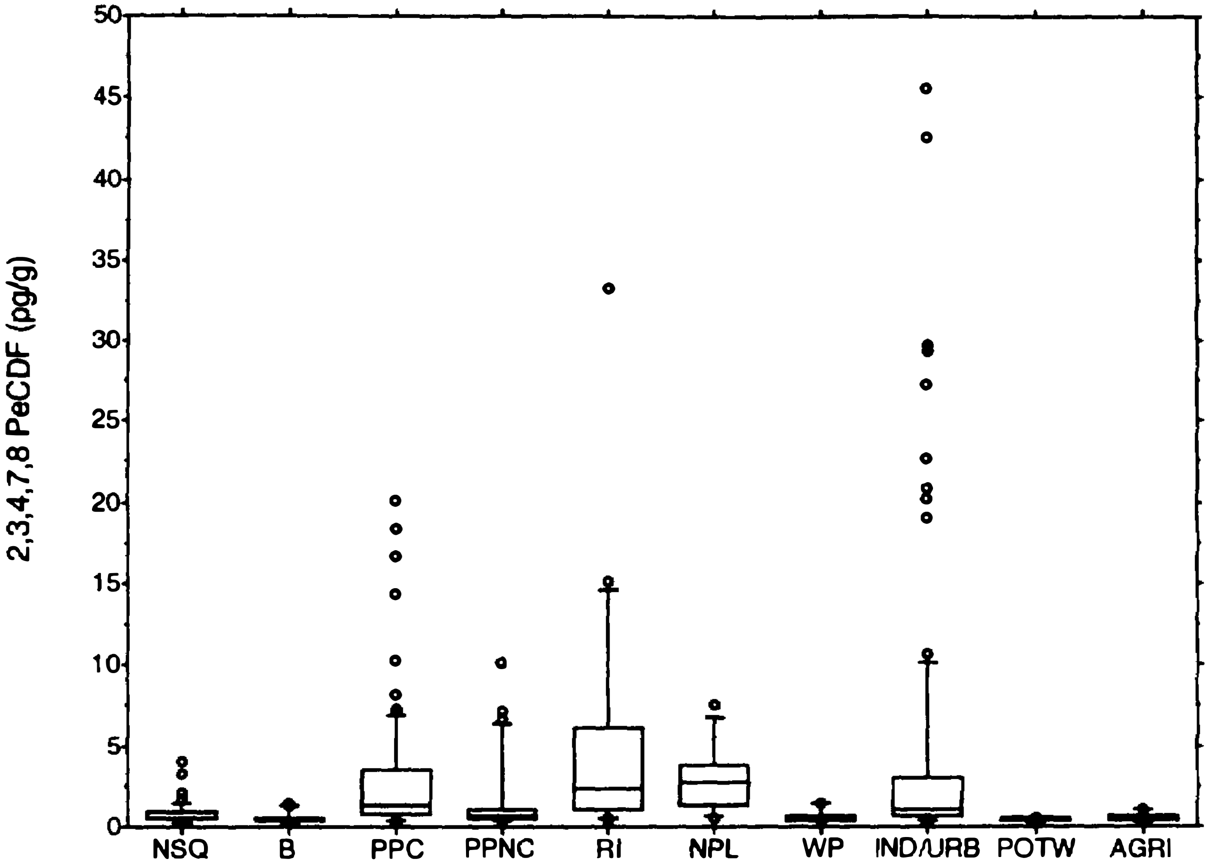


Summary Table for 1,2,3,7,8 PeCDF Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	40	0.16 - 1.69	0.48	0.33	0.39
Background (B)	34	0.10 - 1.90	0.43	0.31	0.39
Paper Mills Using Cl (PPC)	78	0.30 - 9.08	1.43	1.88	0.58
Other Paper Mills (PPNC)	27	0.22 - 3.09	0.80	0.83	0.40
Refinery/Other Industry (R/I)	20	0.38 - 4.47	1.18	1.07	0.66
Superfund Sites (NPL)	7	0.39 - 2.96	1.18	0.97	0.71
Wood Preservers (WP)	10	0.39 - 1.3	0.51	0.28	0.39
Industrial/Urban Sites (IND/URB)	104	0.13 - 54.32	1.73	5.74	0.50
POTW	8	0.16 - 0.51	0.38	0.10	0.38
Agricultural (AGRI)	7	0.20 - 0.89	0.43	0.18	0.38

n = number of sites in category. Maximum value at each site was used. One-half the detection limit was used for values below detection. Sites were assigned to only one category.

Figure 3-14. Box and whisker plot for 1,2,3,7,8 PeCDF concentrations on fish tissue.

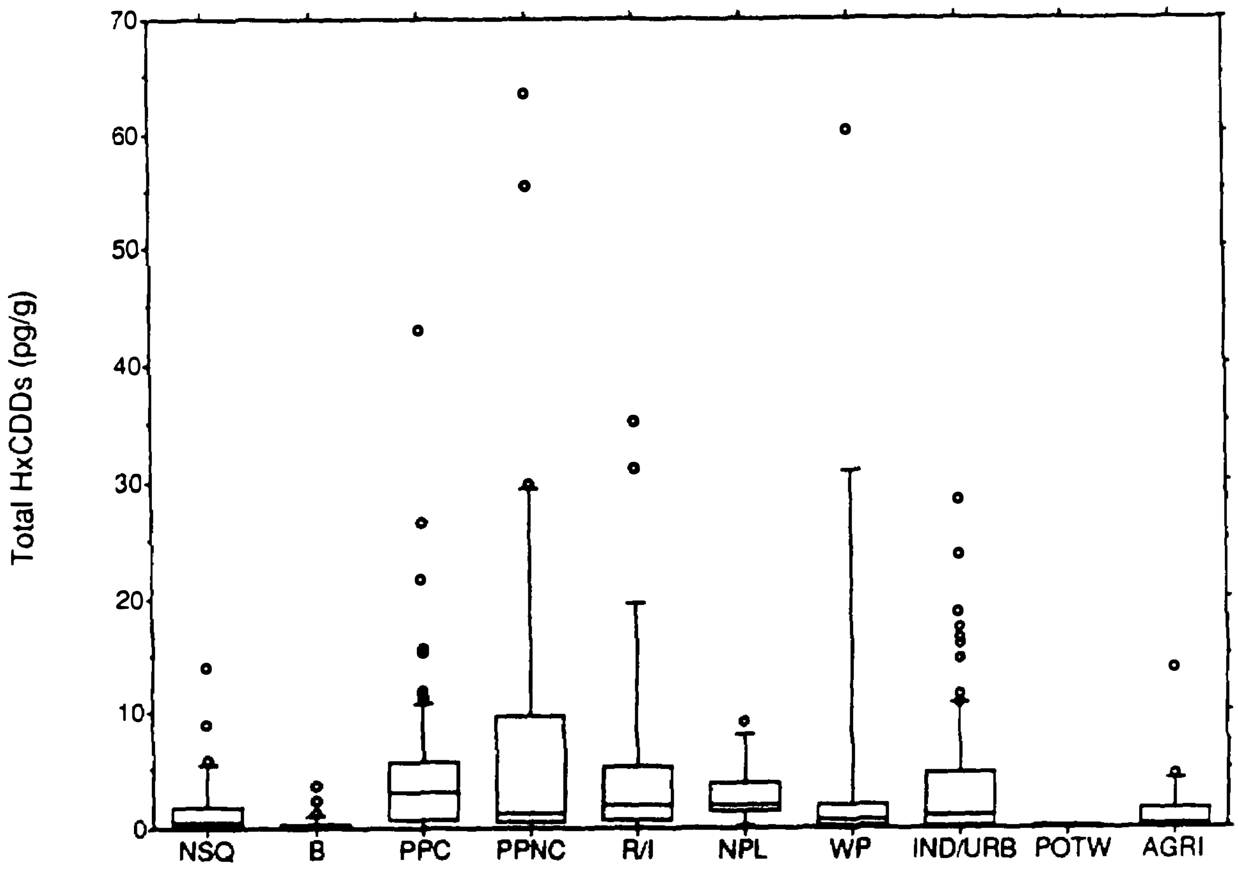


Summary Table for 2,3,4,7,8 PeCDF Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	40	0.16 - 4.11	0.78	0.79	0.46
Background (B)	34	0.10 - 1.39	0.50	0.36	0.42
Paper Mills Using Cl (PPC)	78	0.25 - 20.14	2.92	4.04	1.37
Other Paper Mills (PPNC)	27	0.40 - 10.21	1.71	2.55	0.59
Refinery/Other Industry (R/I)	20	0.42 - 33.25	5.44	7.86	2.32
Superfund Sites (NPL)	7	0.48 - 7.53	2.93	2.37	2.73
Wood Preservers (WP)	10	0.42 - 1.43	0.63	0.40	0.42
Industrial/Urban Sites (IND/URB)	104	0.13 - 45.51	4.09	8.27	0.98
POTW	8	0.16 - 0.59	0.42	0.13	0.44
Agricultural (AGRI)	17	0.15 - 1.02	0.53	0.26	0.42

n = number of sites in category. Maximum value at each site was used. One-half the detection limit was used for values below detection.

Figure 3-15. Box and whisker plot for 2,3,4,7,8 PeCDF concentrations in fish tissue.

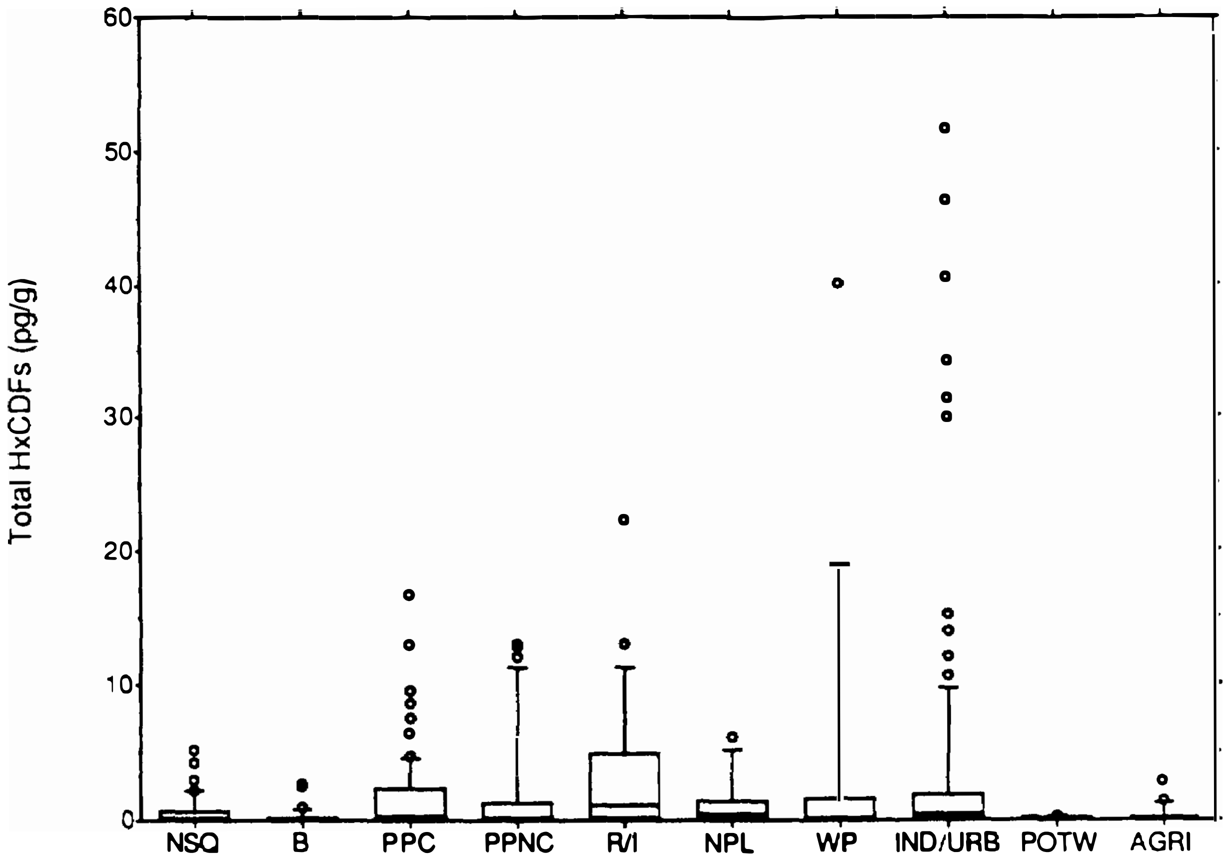


Summary Table for Total HxCDDs Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	37	ND -13.91	1.73	2.94	0.51
Background (B)	30	ND - 3.57	0.39	0.80	ND
Paper Mills Using Cl (PPC)	78	ND - 42.98	4.68	6.66	3.09
Other Paper Mills (PPNC)	27	ND0 63.35	9.23	16.77	1.25
Refinery/Other Industry(R/I)	20	ND - 35.17	5.54	9.75	1.97
Superfund Sites (NPL)	7	ND - 9.07	2.96	2.99	1.94
Wood Preservers (WP)	11	ND -60.10	7.04	17.90	0.71
Industrial/Urban Sites (IND/URB)	100	ND0 28.4	3.60	5.49	1.14
POTW	7	ND	ND	ND	ND
Agricultural (AGRI)	17	ND - 13.79	1.63	3.38	0.44

n = number of sites in category. Maximum value at each site was used. Sites were assigned to only one category. ND0 limit of detection, here set at 0.0.

Figure 3-16. Box and whisker plot for total HxCDDs concentrations in fish tissue.



Summary Table for Total HxCDFs Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND- 5.11	0.58	1.21	ND
Background (B)	29	ND- 2.59	0.22	0.66	ND
Paper Mills Using Cl (PPC)	78	ND- 16.75	1.74	3.11	0.34
Other Paper Mills (PPNC)	27	ND- 12.93	1.94	4.16	ND
Refinery/Other Industry(R/I)	20	ND- 22.46	3.69	5.76	1.05
Superfund Sites (NPL)	7	ND - 6.08	1.22	2.22	0.41
Wood Preservers (WP)	11	ND - 40.1	4.42	11.92	ND
Industrial/Urban Sites (IND/URB)	103	ND- 51.76	3.67	9.49	0.48
POTW	8	ND -0.35	0.04	0.12	ND
Agricultural (AGRI)	17	ND- 3.01	0.31	0.78	ND

n = number of sites in category. Maximum value at each site was used. Sites were assigned to only one category. ND = limit of detection, here set at 0.0.

Figure 3-17. **Box and whisker plot for total HxCDFs concentrations in fish tissue.**

Chapter 4 - Other Xenobiotic Compound Results and Analysis

This chapter presents results for all study compounds other than dioxins and furans. For ease of presentation these other study compounds are referred to as "other xenobiotics" or simply "xenobiotics." The term *xenobiotic* means a compound that does not naturally occur in living organisms, in this case, fish. In addition to an overall summary, the discussion of results for xenobiotic compounds is contained in three sections—xenobiotics detected in samples from greater than 50 percent of the sites, between 10 and 50 percent of the sites, and less than 10 percent of the sites. Within each of the three principal sections, information is provided, as appropriate, on high concentration sources, geographical distribution, and source correlation analysis.

Chemical profile data and information for all of the 45 xenobiotics is presented in Appendix C, Volume II. This information includes physical/chemical properties, standards and criteria, chemical uses, and health effects. Concentration data for individual fish samples, as well as information on where the samples were collected, can be found in Appendix D, Volume II. The number of samples taken and analyzed by site can be determined by counting the samples for a given site (episode number) in the data tables (Appendix D, Volume II). The number of fish in each composite sample is provided in Appendix D-6 (Volume II). Other values for a given site can be reviewed by identifying the episode number for the site from the site matrix (Table B-3, Appendix B, in Volume I or Table D-1, Appendix D, in Volume II) and then looking at the data in the raw data tables (Appendix D, Volume II).

PREVALENCE AND CONCENTRATION SUMMARY

A total of 45 compounds were measured in the fish tissue samples; these compounds include 34 organic compounds, PCBs with 1 to 10 substituted chlorines, and mercury. Summary data regarding the prevalence and concentration of these compounds can be found on Table 4-1 and Figure 4-1. Six pesticides, PCBs, three other industrial organic chemicals, and mercury were detected at more than 50 percent of the sites. All the compounds were detected in samples from at least one site. The compounds detected at more than 50 percent of the sites, at 10 to 50 percent of the sites, and at less than 10 percent of the sites are as follows:

TABLE 4-1
Summary of Xenobiotic Compounds in Fish Tissue

Chemical	Percent of Sites Where Detected	Max*	Mean*	Standard Deviation	Median*	Total Number of Sites	D
			(Units are ng/g)				
p,pDDE	98.6	14028	295.28	972.66	58.25	362	26
Mercury	92.2	1770	260	0.28	170	374	36
Total PCBs	91.4	124192	1897.88	755728	208.78	362	35
Biphenyl	93.9	131	2.71	10.4	0.64	362	7
Nonachlor, Trans	77.1	477	31.24	56.92	9.22	362	25
Chlordane, cis	64.1	378	21.05	42.76	3.66	362	24
Pentachloroanisole	64.4	647	10.77	52.06	0.92	362	13
Chlordane, Trans	61.0	310	16.68	36.74	2.68	362	23
Dieldrin	60.2	450	28.14	58.37	4.16	362	27
Alpha-BHC	55.0	44.4	2.41	4.53	0.72	362	11
124 Trichlorobenzene	53.3	264.8	3.10	1991	0.14	362	2
Hexachlorobenzene	45.9	913	5.80	4979	ND	362	12
Gamma-BHC	42.3	83.3	2.70	7.07	ND	362	14
123 Trichlorobenzene	42.5	69	1.27	5.57	ND	362	3
Mirex	37.8	225	3.86	17.74	ND	362	34
Nonachlor, cis	35.1	127	8.77	17.94	ND	362	31
Oxychlordane	27.3	243	4.75	17.76	ND	362	22
Chlorpyrifos	26.2	344	4.09	20.16	ND	362	18
Pentachlorobenzene	22.1	125	1.98	7.9	ND	362	9
Heptachlor Epoxide	15.7	63.2	2.19	7.36	ND	362	21
Dicofol	15.5	74.3	0.98	5.18	ND	362	33
1234 Tetrachlorobenzene	13.0	76.65	0.47	4.23	ND	362	8
Trifluralin	11.8	458	5.98	32.01	ND	362	10
135 Trichlorobenzene	11.0	14.9	0.12	0.95	ND	362	1
Endrin	10.50	162	1.69	11.22	ND	362	29
1235 TECB	9.40	28.3	0.34	2.1	ND	362	6
Octachlorostyrene	9.9	138	1.71	9.9	ND	362	20
1245 TECB	9.1	28.3	0.33	2.09	ND	362	5
Methoxychlor	7.2	393	1.32	20.68	ND	362	32
Isopropalin	3.9	37.5	0.46	2.96	ND	362	19
Nitrofen	2.8	17.9	0.17	1442	ND	362	28
Hexachlorobutadiene	2.8	164	0.57	8.72	ND	362	4
Heptachlor	2.21	76.2	0.35	4.2	ND	362	17
Perthane	1.4	5.12	0.03	0.35	ND	362	30
Pentachloronitrobenzene	1.1	15.5	0.09	1.1	ND	362	15
Diphenyl Disulfide	0.6	3.24	0.02	0.22	ND	362	16

Note: D is designation of chemical on histogram (Figure 4-1)

In cases where multiple samples were analyzed per site, the value used represents the highest concentration.

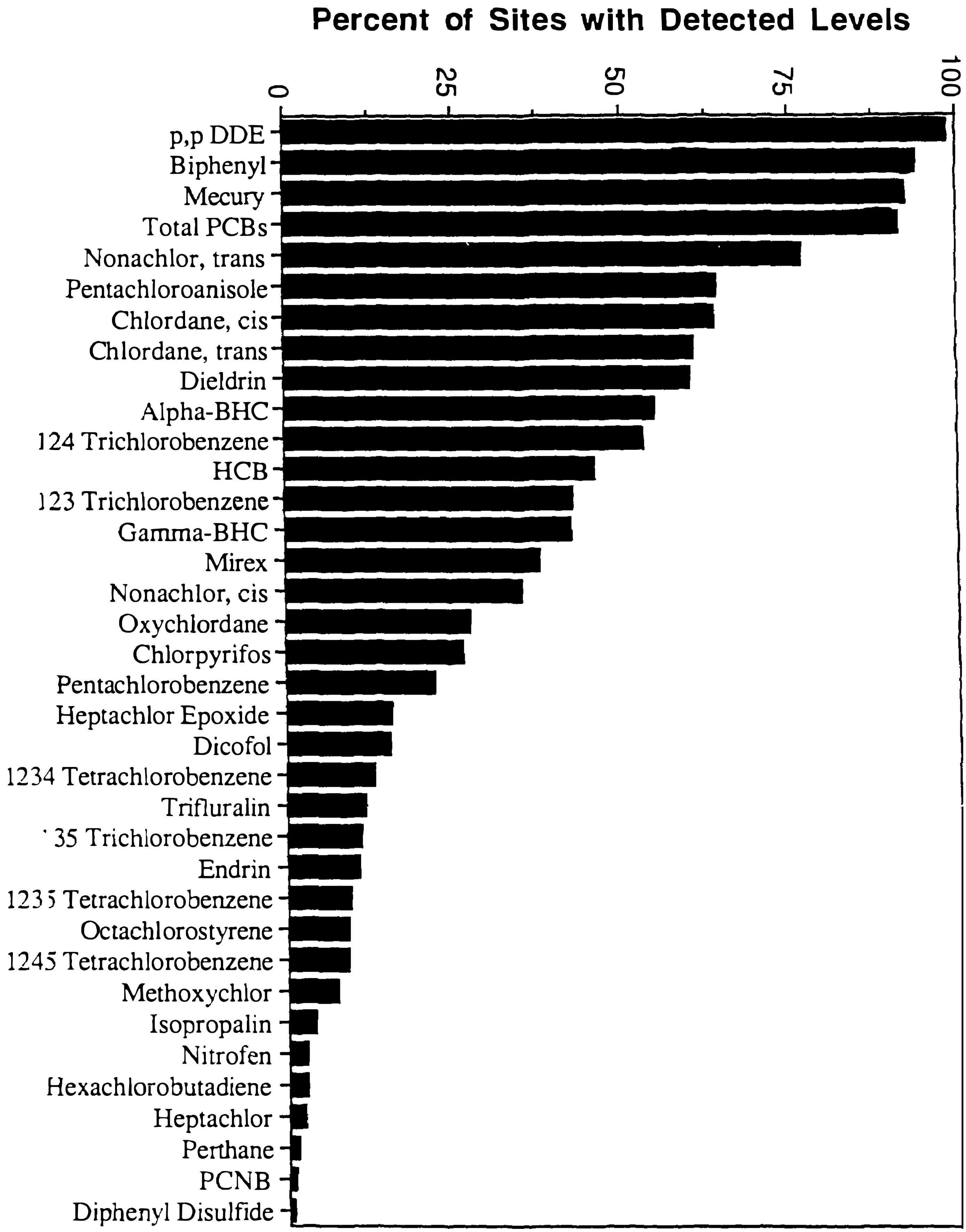


Figure 4-1. Summary of other xenobiotic compounds detected in fish tissue.

More than 50 Percent of the Sites	10 to 50 Percent of the Sites	Less Than 10 Percent of the Sites
Total PCBs	Hexachlorobenzene	Octachlorostyrene
Biphenyl	1,2,3 Trichlorobenzene	1,2,4,5 Tetrachlorobenzene
Mercury	Pentachlorobenzene	1,2,3,5 Tetrachlorobenzene
Pentachloroanisole	1,2,3,4 Tetrachlorobenzene	Hexachlorobutadiene
1,2,4 Trichlorobenzene	1,3,5 Trichlorobenzene	Diphenyl Disulfide
Pesticides:	Pesticides/Herbicides:	Pesticides/Herbicides:
DDE	gamma-BHC[1]	Methoxychlor
trans-Nonachlor	Mirex	Isopropalin
cis-Chlordane	cis-Nonachlor	Nitrofen
trans-Chlordane	Oxychlordane	Heptachlor
Dieldrin	Chlorpyrifos	Perthane
alpha-BHC[1]	Heptachlor Epoxide	Pentachloronitrobenzene
	Trifluralin	
	Dicofol	
	Endrin	

Mean fish tissue concentrations were highest for total PCBs and p,p′-DDE at 1890 and 295 ng/g, respectively (Table 4-1). These two compounds were also detected at over 90 percent of the sampled sites. Mean concentrations of trans-nonachlor and dieldrin were the next highest at 31 and 28 ng/g, respectively. These compounds were also found at a large number of sites, 77 and 60 percent of the sampled sites, respectively. Biphenyl was detected at a large percentage of sites (91 percent), but the levels at most sites were low. Only 12 percent of the sites had biphenyl concentrations above the quantitation level (2.5 ng/g).

As previously discussed in Chapter 3 for dioxins/furans, point and nonpoint sources were divided into nine categories plus NASQAN sites for geographic coverage throughout the country. Below is a listing of the number of sites included in each category for xenobiotics. The number of sites for xenobiotics will be different from the number of sites for dioxins/furans for reasons presented in Chapter 3, as well as the fact that not all xenobiotics were analyzed at all sites.

[1] Alpha-BHC and gamma-BHC (or Lindane) are formally known as α-hexachlorocyclohexane and γ-hexachlorocyclohexane, respectively. The former chemical designations are used in this document.

Number Category	Abbreviation	Number of Sites
Background	B	22
USGS&NASQAN	NSQ	40
Paper Mills using Chlorine	PPC	42
Other types of Pulp and Paper Mills	PPNC	17
Wood Preserving Plants	WP	11
Refineries/Other Industries	R/I	5
NPL (Superfund Sites)	NPL	6
Industry/Urban	IND/URB	35
Agriculture	AGRI	19
POTW	POTW	8

COMPOUNDS DETECTED AT MORE THAN 50 PERCENT OF THE SITES[2]

Total PCBs

Total PCBs were detected at over 91 percent of the sites sampled with the median value of 208.78 ng/g (Figure 4-2a). Twenty-six percent of the sites had fish tissue concentrations greater than 1000 ng/g (Figure 4-2b). A major use of PCBs has been as dielectric fluids in transformers, capacitors, and electromagnets. Prior to 1974, PCBs were also used as plasticizers, lubricants, ink carriers, and gasket seals. PCB production in the United States stopped after 1977, and uses since then have been limited mostly to small, totally enclosed electrical systems in restricted access areas. PCBs can reach water bodies by runoff from PCB spills or electrical equipment fires, or runoff/seepage from disposal sites containing PCB-contaminated soils and equipment.

Summary statistics for the PCB congeners with 1 to 10 substituted chlorines show that the median fish tissue concentration was highest for hexachlorobiphenyl followed by pentachlorobiphenyl (Table 4-2). Total PCBs in this study refers to the sum of the concentrations of compounds with 1 to 10 chlorines. Concentrations of specific Aroclor or mono-ortho substituted compounds were not determined in this study. PCBs were detected in all parts of the country with the highest levels detected in industrial regions. The prevalence of PCBs is consistent with their high bioaccumulation potential and persistence in the environment. The sites with the five highest concentrations are listed below:

[2] Four chemicals found at less than 50 percent of the sites are presented in this section to facilitate their discussion. These are gamma-BHC; 1,2,3 trichlorobenzene; cis-nonachlor; and oxychlordane.

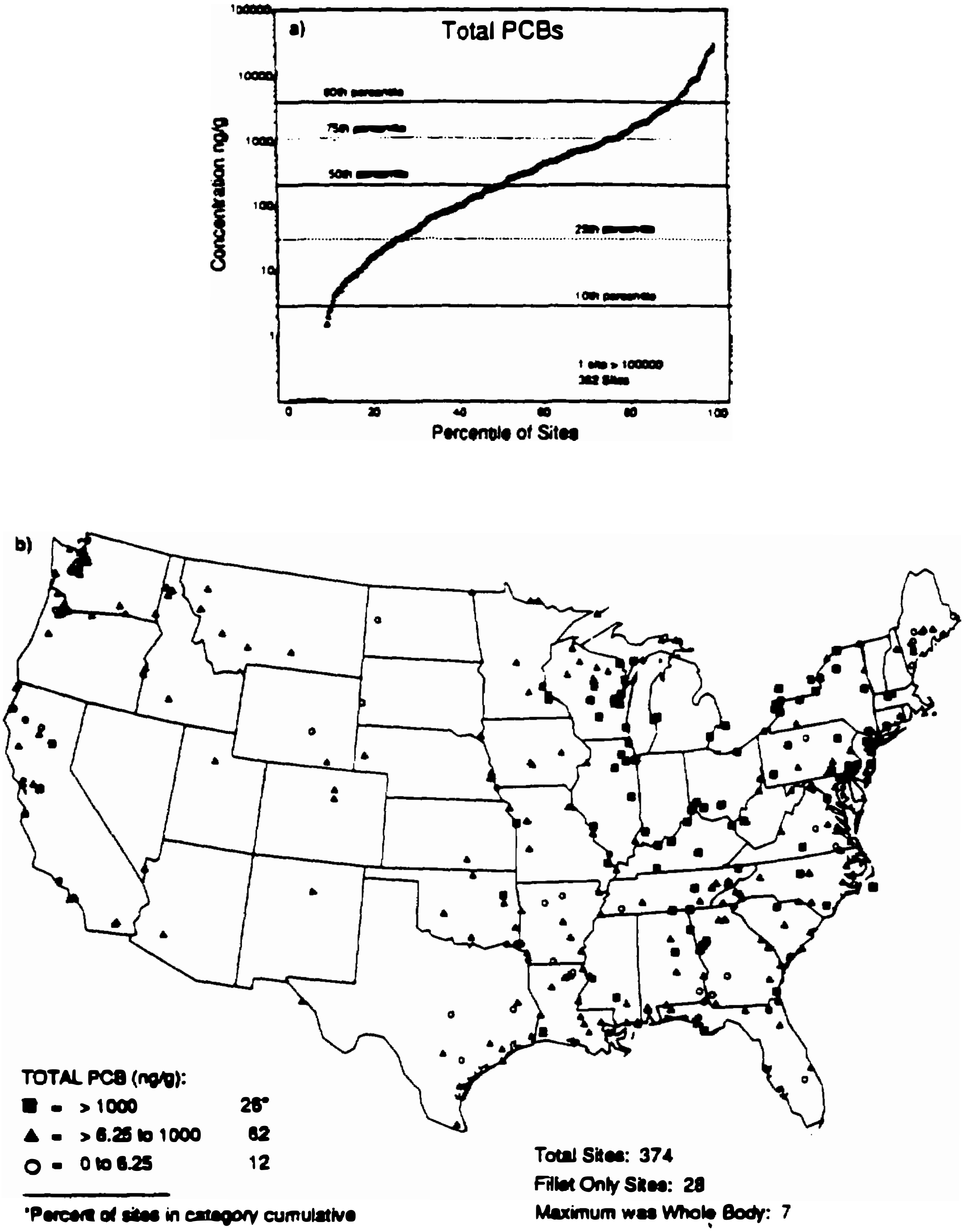


Figure 4-2. **Total PCBs: a) cumulative frequency distribution and b) map of geographical distribution of various concentration ranges in fish tissue.**

TABLE 4-2
Summary of PCBs in Fish Tissue

Chemical	Percent of Sites Where Detected	Max*	Mean*	Standard Deviation	Median*	Total Number of Sites
Total Hexachlorobiphenyl	88.7	8862	355.93	867.13	76.85	362
Total Pentachlorobiphenyl	86.7	29578	564.70	1993.521	72.4	362
Total Tetrachlorobiphenyl	72.4	60764	696.23	3647.97	23.09	362
Total Heptachlorobiphenyl	69.1	1850	96.71	209.98	16.85	362
Total Trichlorobiphenyl	57.5	18344	149.80	1024.59	2.09	362
Total Octachlorobiphenyl	34.8	593	17.37	52	ND	362
Total Dichlorobiphenyl	30.7	5072	21.43	267.74	ND	362
Total Monochlorobiphenyl	13.8	235	1.22	12.56	ND	362
Total Decachlorobiphenyl	3.3	29.5	0.44	3.08	ND	362
Total Nonachlorobiphenyl	9.7	413	3.04	25	ND	362
Total PCBs	91.4		1897.88	7557.8	208.78	362

*Concentrations are nanograms per gram (ng/g) or parts per billion (ppb) by wet weight. In cases where multiple samples were analyzed per site, the value used represents the highest concentration.

PCBs

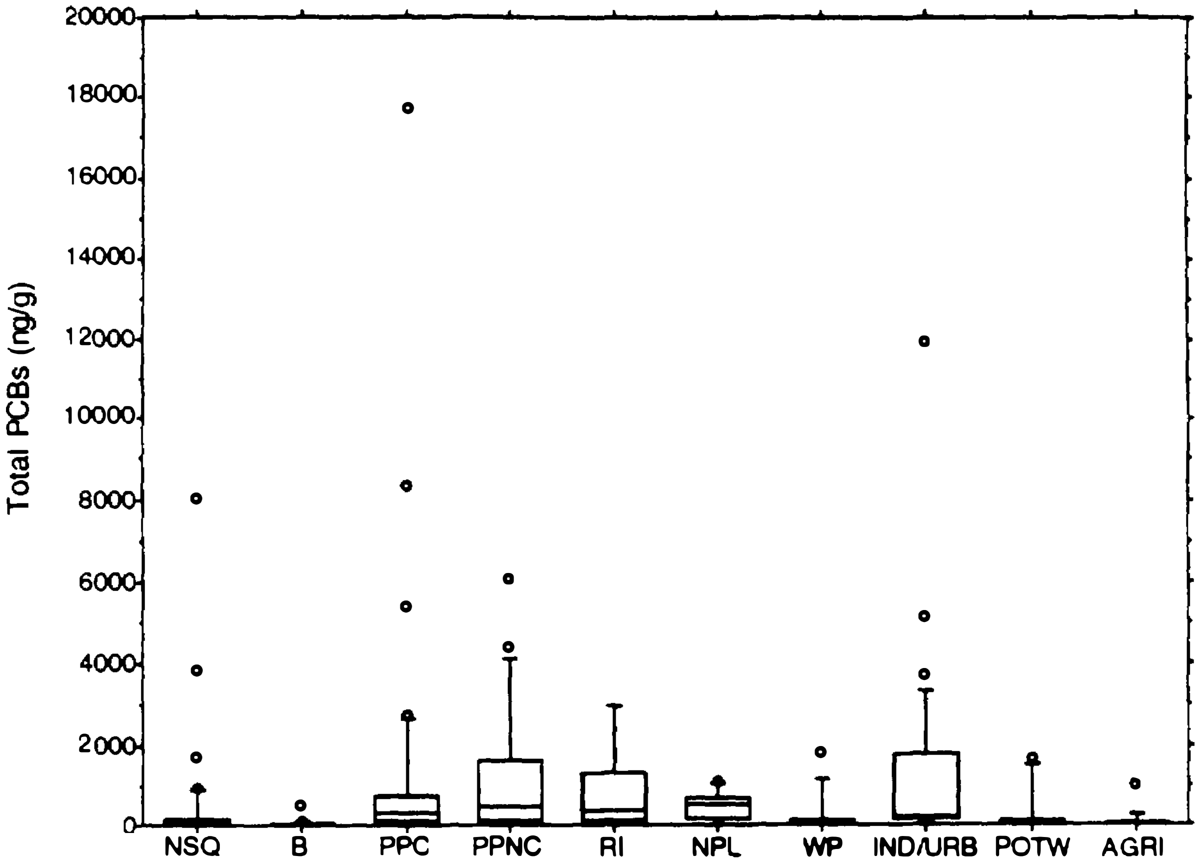
Conc. ng/g	Episode Number	Type of Fish	Location
124192	3259	WB Sucker	Hudson R., Fort Miller, NY
29130	2429	WB Carp	Fox R., Depere Dam, WI
25240	3134	WB Sucker	Manitowoc R., Chilton, WI
24ld8	3182	WB Carp	Mud R., Russellville, KY
23809	3142	WB Carp	Sheboygan R., Kohler, WI

PCB contamination from past spills occurred in the vicinity of the first two sites and the last site. Fish samples with the next three highest PCB concentrations were collected at locations near various industrial and other source categories. It is not apparent from available information which, if any, of these sources can be identified as the cause of each of the next three highest PCB concentrations. Sources in the vicinity of these samples include a metal plating shop, a rendering plant, an incinerator, a water softening plant, a window manufacturing facility with wood treatment operations, and agriculture croplands.

The top 10 percentile sites (36 out of 362) included three additional sites on the Fox River and one additional site on the Hudson River. Historical PCB contamination was present at 12 of the top 10 percentile sites including five Superfund sites. The remaining top 10 percentile sites were located near industrial facilities including chemical and automobile manufacturing plants, foundries, refineries, and paper mills. Two of the sites in the top 10 percentile were located near plants with PCB discharge limits in their NPDES permits (one on the Grass River in New York and one on the Raquette River in New York). The box plot confirms that high concentrations of PCBs were associated with paper mills, refinery/other industry sites, Superfund sites, and industrial/urban areas (Figure 4-3). The two highest median concentrations were 525 ng/g for Superfund sites and 349 ng/g for refinery/other industry sites. The Kruskal-Wallis test (Table 4-3) showed that no dominant source existed.

Biphenyl

Biphenyl was detected at a large percentage of the sites (91e4 percent), but the concentrations at most sites were low. Eighty-eight percent of the sites had concentrations below 2.5 ng/g (Figure 4-4a). Biphenyl is used in the manufacture of PCBs and is also a breakdown product of PCBs. Biphenyl is also produced during the manufacturing of benzene and has other industrial uses as well. The sites with the five highest concentrations are listed below:



Summary Table for Total PCBs Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND - 7977	449.1	1408.9	24.8
Background (B)	20	ND.- 480	46.9	108.7	ND
Paper Mills Using Cl (PPC)	39	ND - 17723	1247.0	3147.5	293.2
Other Paper Mills (PPNC)	17	ND.- 6061	1225.1	1739.5	483.7
Refinery/Other Industry (R/I)	5	ND.- 2974	833.5	1230.5	349.3
Superfund Sites (NPL)	6	2.51 - 1075	49180	390.5	525.2
Wood Preservers (WP)	10	ND.- 1804	260.6	561.4	38.6
Industrial/Urban Sites (IND/URB)	31	2.54 - 12027	1277.9	2374.9	213.2
POTW	6	ND - 1677	302.4	674.3	22.2
Agricultural (AGRI)	15	ND.- 1064	97.4	274.1	8.6

n = number of sites in category. ND's set at zero. Maximum concentrations at sites were used.

Figure 4-3. Box and whisker plot for total PCBs in fish tissue.

TABLE 4.3
Results of Statistical Tests for Selected Xenobiotics and Mercury

Chemical	Kruskal-Wallis: All Groups Except NSQ	Kruskal-Wallis: All Groups Except NSQ, B	Kruskal-Wallis: NPL, IND	Mann-Whitney: PPC, IND	Mann-Whitney: PPNC, IND	Mann-Whitney: WP, IND	Mann-Whitney: B, IND	Mann-Whitney: AG, IND	Mann-Whitney: POTW, IND	Mann-Whitney: RI,B	Mann-Whitney: RI, AG	Mann-Whitney: R/I, POTW	Mann-Whitney: R/I IND
Pentachloobenzene	.7614	.6393	.8529	.1954	.6821	.2246	.1995	.4121	.3227	.2088	.2949	.2733	.4368
1,2,3,4-Tetrachlorobenzene	.8587	.7880	.7417	.8872	.3214	.9516	.7723	.5980	.7108	.2923	.1904	.2733	.2254
1,3,5-Trichlorobenzene	.9600	.9283	.9180	.3206	.8886	.3624	.5243	.2917	4583	.6836	.5127	.5839	.9818
Total PCBs	.0001	.0012	.8368	.3848	.9914	0099	.0001	.0001	.0210	.0324	.0887	.2012	.9453
Biphenyl	6338	.8390	.7417	.8685	.8716	.3164	.0842	.2275	.5640	.9458	.8273	.6481	.2723
Mercury	.0222	.0203	.3706	.5909	.8297	.0177	.0489	.0975	.0017	.6256	.5705	.0828	.0470
1,2,4-Trichlorobenzene	.0645	.0550	.9016	.0228	.7876	0709	.1590	.2759	.7262	.2623	.3827	.7150	.8369
Hexachlorobenzene	.0970	.1176	.4836	.0164	.1996	.0210	.0167	.4968	.0580	.0832	.4581	.1207	.8014
1,2,3-Trichlorobenzene	.3530	.2819	.3127	.4214	.0519	.4038	.8094	.8697	.2840	.6836	.7600	.2733	.7837
Pentachloranisole	.0473	.1979	.6356	.4079	.1036	.2486	.0613	.2321	.7262	.1968	.2752	.8551	.6974

Chemical	Kruskal-Wallis: PPC, PPNC R/I, NPL, IND	Mann-Whitney: WP, PPC	Mann-Whitney: WP, PPNC	Mann-Whitney: PPC, PPNC	Mann-Whitney: POTW, PPC	Mann-Whitney: POTW, NPL	Mann-Whitney: POTW, R/I	Mann-Whitney: POTW, WP
Total PCBs	.9058	—	—	—	—	—	—	—
Pentachloranisole	—	.1881	.0350	.2256	—	—	—	—
Mercury	—	—	—	—	.0158	.1093	.0828	.0562

Values shown are two-tail probabilities that groups are different. The critical level was set at 0.05. If $p<0.05$, the categories were considered to be significantly different.

Site Categories:

IND/URB	=	Industry and/or Urban
AG	=	Agriculture
B	=	Background
NPL	=	National Priority List (Superfund site)
POTW	=	Publicly Owned Treatment Works (sewage)
R/I	=	Refineries using catalytic reforming process and other industry
NSQ	=	National ambient stream quality monitoring network. (This designation is independent of source categories.)
WP	=	Wood preserving related activities
PPC	=	Paper and pulp mills using chlorine for bleaching
PPNC	=	Other paper and pulp mills including deinking plants

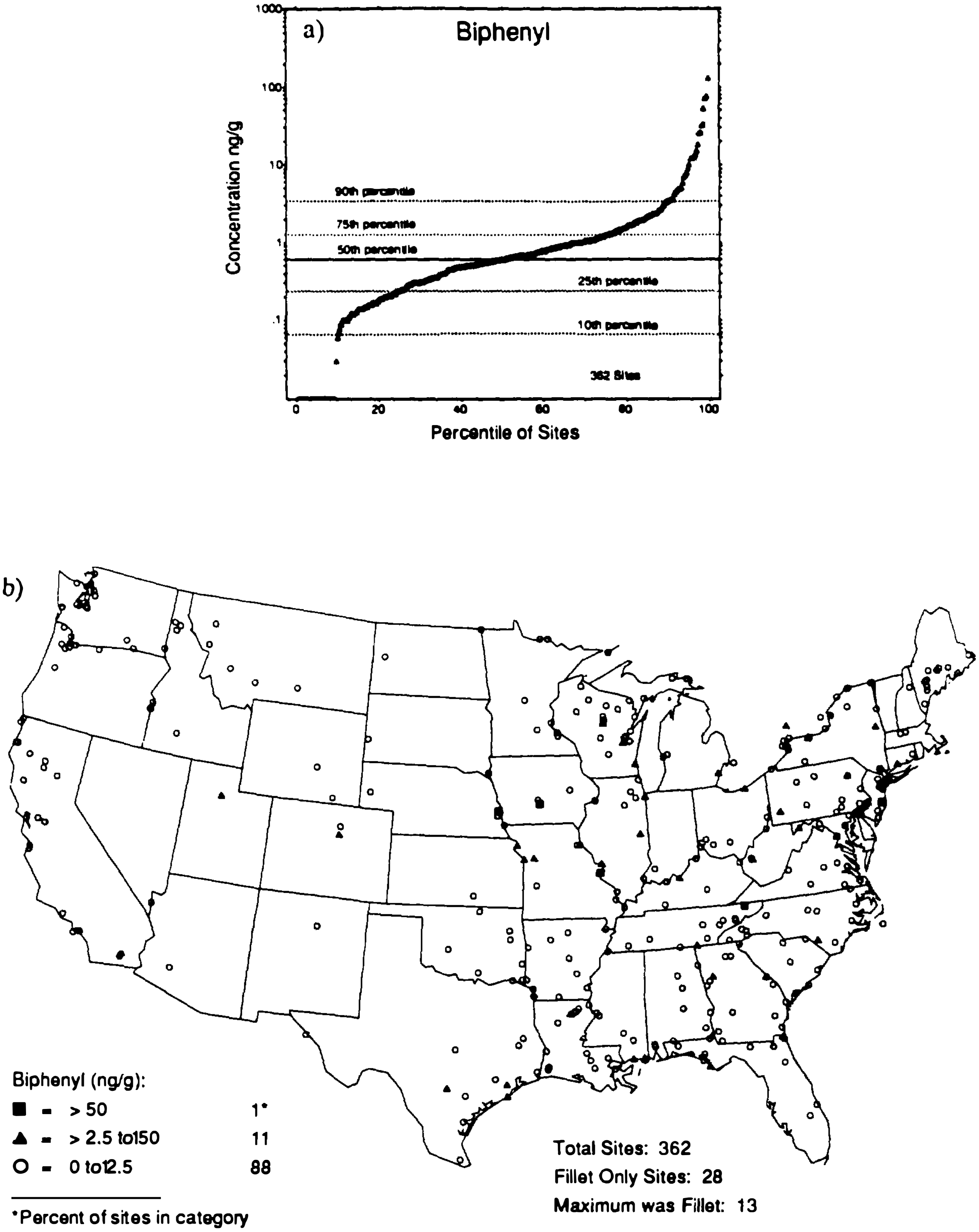


Figure 4-4. Biphenyl: a) cumulative frequency distribution and b) map of geographical distribution of various concentration ranges in fish tissue.

Biphenyl

Conc. ng/g	Episode Number	Type of Sample	Location
13[illegible].7	2654	WB Carp	Toms River, NJ
75.6	3042	WB Carp	Missouri R., Omaha, NE
70.6	3403	WB River Carpsucker	Holston R., S. Fork, Kingsport, TN
70.2	3038	WB Carp	Des Moines R., Des Moines, IA
53.8	3115	PF Catfish	Mississippi R., E. St. Louis (Sauget), IL

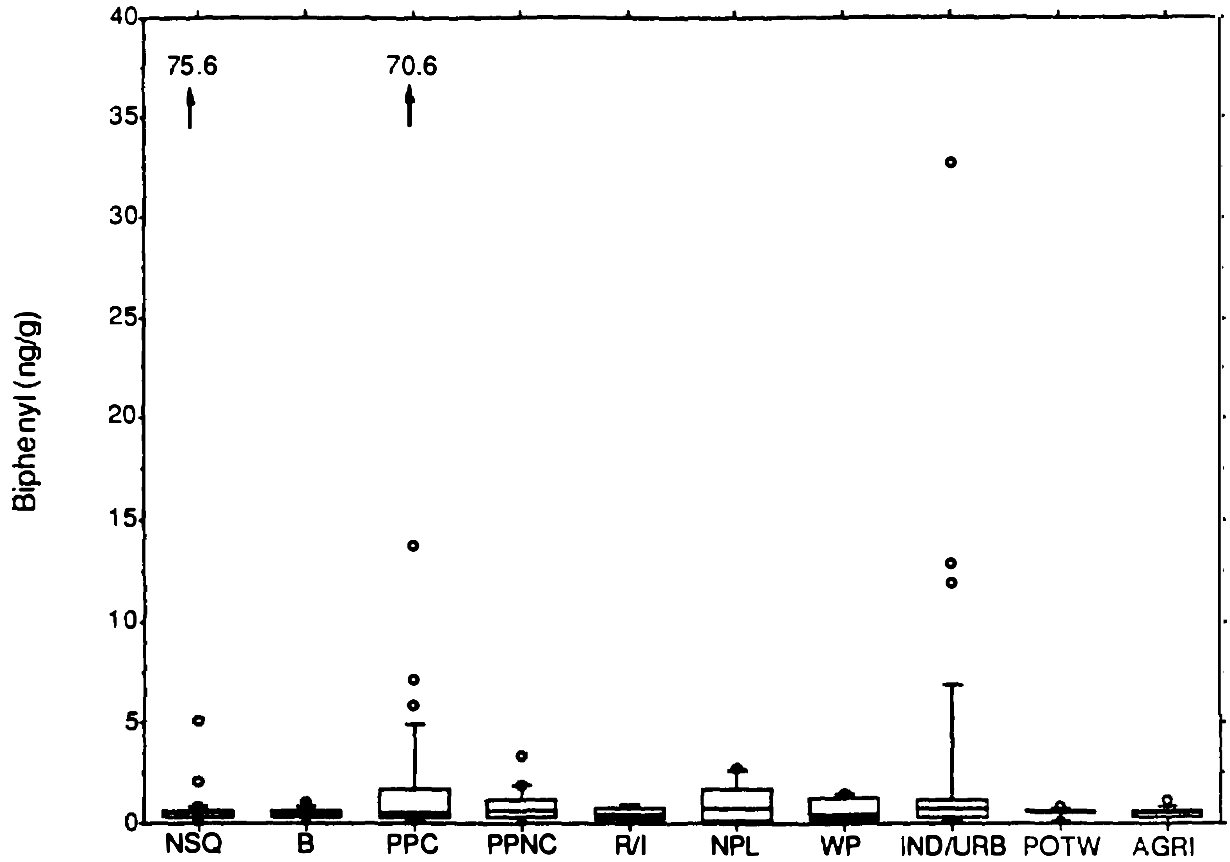
These five sites are near chemical manufacturing plants as were 24 of the top 36 sites representing the highest 10 percentile. The remaining sites were near Superfund sites or paper mills. The overall geographic distribution of biphenyl concentrations and the cumulative frequency distribution show that high concentrations (>50 ng/g) were detected mostly in the Midwest and Northeast (Figure 4-4b).

A comparison of source categories for biphenyl (Figure 4-5) shows that Superfund sites had the highest median concentration, 0.76 ng/g. A Kruskal-Wallis test for all categories except NASQAN and background showed that no significant differences between categories existed (Table 4-3).

Mercury

Mercury was detected in at least one sample from 92 percent of the sites. Mercury has been used in making batteries, lamps, thermostats, and other electrical devices and as a fungicide in latex and exterior water-based paints. Effective August 1990, mercury was banned from interior paint. Mercury is present in soil as a component of a number of minerals (e.g., cinnabar, HgS). It is also discharged to the atmosphere from natural degassing processes and from the burning of fossil fuels. Mercury compounds occur in both organic and inorganic forms. In fish tissue it is nearly all in the organic form, methylmercury. The measured mercury concentrations were usually higher in the fillet samples than in the whole-body samples. This is because, unlike the other organic chemicals studied, organic mercury compounds are taken up and stored in muscle tissue rather than the lipid. There were, however, 15 sites where the concentration in a whole-body sample was higher than that in a fillet sample from the same site. This disparity may have been due to a number of factors, including species variability, stomach content (which may include significant quantities of contaminated sediment ingested during feeding), and other variables.

The measured concentrations ranged up to 1.77 µg/g with 2 percent of the sites greater than 1 µg/g (Figure 4-6a); most of the higher concentrations were in the Northeast (Figure 4-6b). The highest concentration was on the Wisconsin River near Boom Bay at Rhinelander, Wisconsin. The sites with the five highest concentrations are given below:

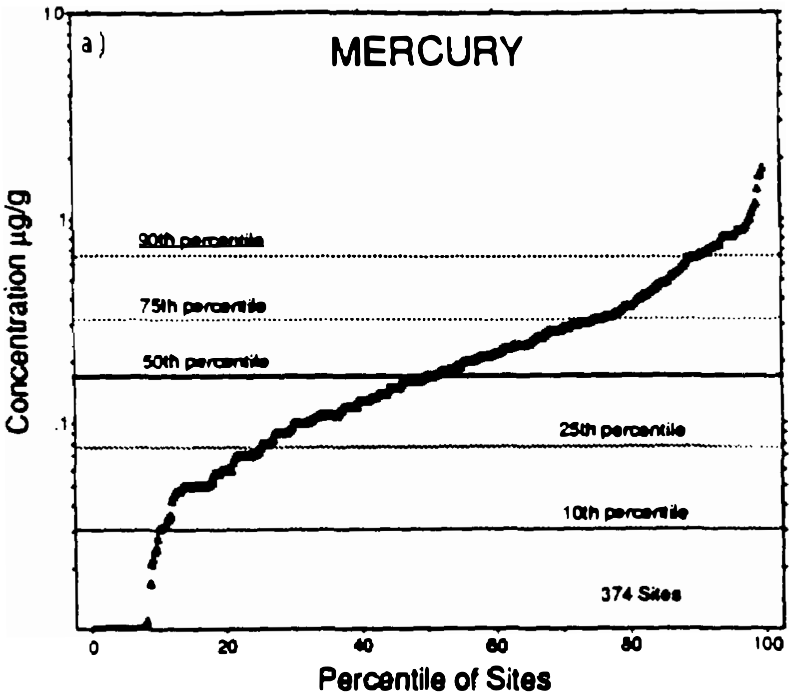


Summary Table for Biphenyl Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND-75.6	2.51	12.04	0.49
Background (B)	20	ND-1.04	0.42	0.30	0.38
Paper Mills Using Cl (PPC)	39	ND-70.6	3.18	11.36	0.54
Other Paper Mills (PPNC)	17	ND-3.35	0.87	0.87	0.61
Refineries/Other Industry (R/I)	5	ND-0.98	0.44	0.40	0.43
Superfund Sites (NPL)	6	ND-2.7	0.97	1.09	0.76
Wood Preservers (WP)	10	ND-1.5	0.60	0.60	0.45
Industrial/Urban Sites (IND/URB)	31	ND-32.8	2.56	6.38	0.68
POTW	6	0.1 -0.79	0.55	0.24	0.63
Agricultural (AGRI)	15	ND-1.11	0.48	0.31	0.53

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-5. Box and whisker plot for biphenyl in fish tissue.



b)

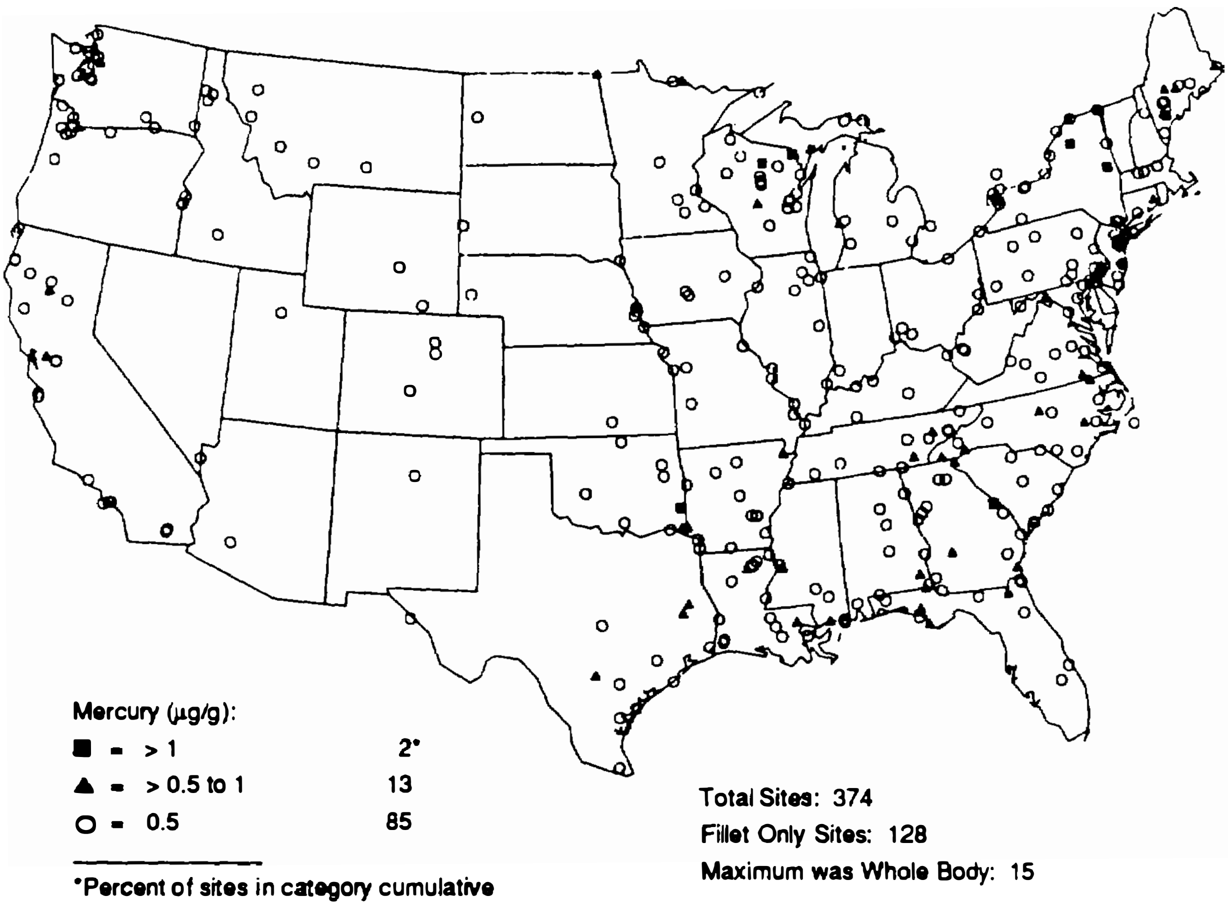


Figure 4-6. Mercury: a) cumulative frequency distribution and b) map of geographical distribution of various concentration ranges in fish tissue.

Mercury

Conc. µg/g(ppm)	Episode Number	Type of Sample	Location
1.77	2397	PF Walleye	Wisc. R/Boom Bay, Rhinelander, WI
1.66	3259	PF Lm Bass	Hudson R., Fort Miller, NY
1.63	2027	PF&Lm Bass	Kiamichi R., Big Cedar, OK
1.40	3122	WB Carp	Menominee R., Quinnesac, MI
1.13	2290	PF&Lm Bass	Savannah R., Augusta, GA

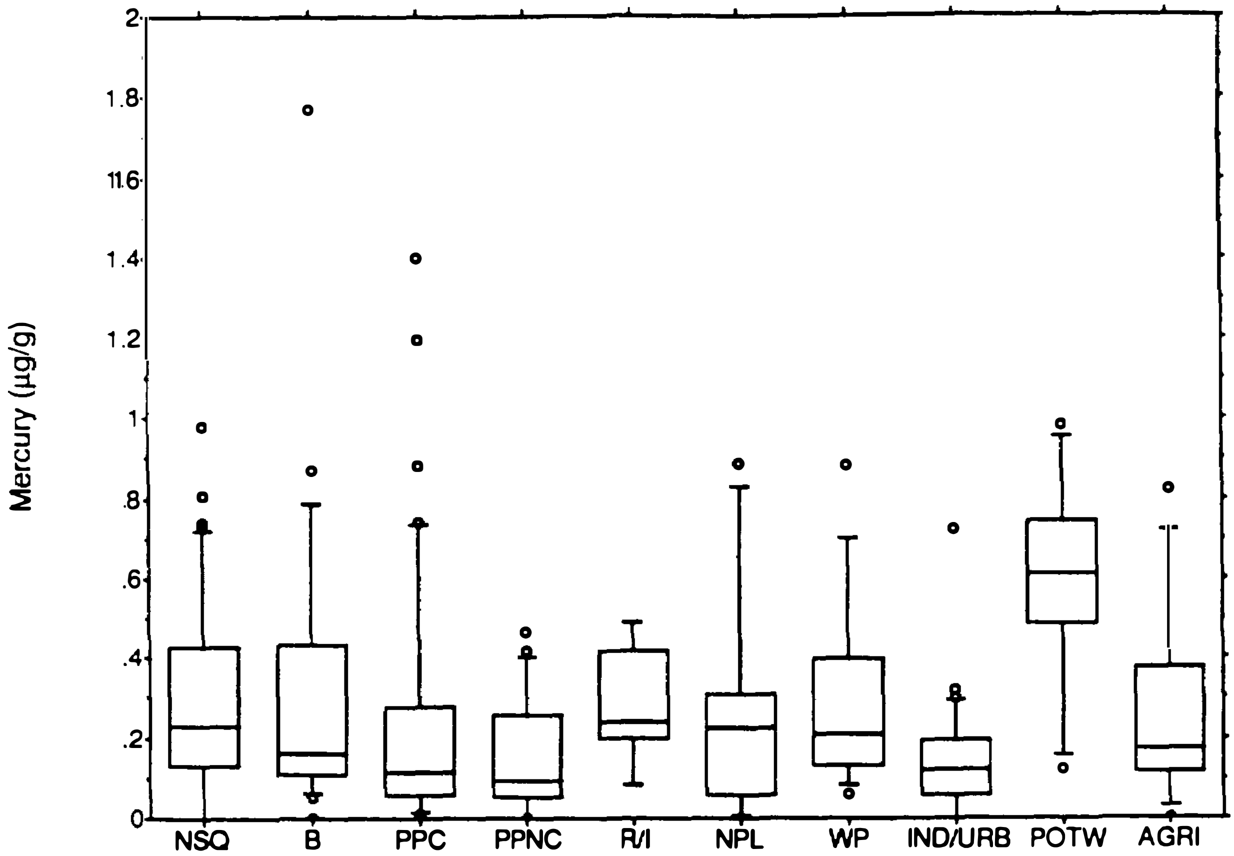
The fish sample with the highest concentration was found at a site designated as background. The site with the third highest concentration was designated as background and agriculture. Additional investigation at these sites is needed to determine sources of mercury contamination. Industrial facilities located in the vicinity of the other three top five sites include pulp and paper mills, a pesticide manufacturing plant, and a textiles facility.

Ten of the sites with the highest 10 percentile concentrations were near paper mills. Four were near Superfund sites, and most of the remaining were from industrial areas. Sources could not be identified at all of these sites. Five sites considered to represent background conditions and six NASQAN sites were included in the top 10 percentile sites.

The box plot for mercury shows that the highest median concentration (0.61 µg/g) was for POTWs (Figure 4-7). The remaining median values had a relatively small range with the lowest being background at 0.09 µg/g and the highest being refinery/other industry at 0.24 µg/g.

Pentachloranisole

Pentachloroanisole was detected in at least one sample from 65 percent of the sites with the median concentration of the sites at 0.9 ng/g (Figure 4-8a). The majority of the higher concentration sites (greater than 2.5 ng/g) are in the eastern part of the country (Figure 4-8b). This compound is a metabolic breakdown product of pentachlorophenol (PCP). PCA is retained in the fish and is therefore easier to measure. The primary uses of PCP are for treating telephone poles, fence posts, and railroad ties. This compound is also used as an antimicrobial agent in pulp and paper manufacturing, to control slimes in cooling towers, and to make anti-fouling paint. Prior to 1984, it was used in the production of the pesticide sodium pentachlorophenate and as a herbicide. The sites with the five highest concentrations out of 362 are listed below.



Summary Table for Mercury Box Plot

Site Category	n	Concentration Range µg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND.- 0.98	0.29	0.25	0.23
Background (B)	21	ND.- 1.77	0.34	0.40	0.16
Paper Mills Using Cl (PPC)	40	ND.- 1.4	0.26	0.33	0.12
Other Paper Mills (PPNC)	17	ND.- 0.46	0.16	0.15	0.09
Refinery/Other Industry (R/I)	5	0.08 - 0.49	0.29	0.16	0.24
Superfund Sites (NPL)	6	ND.- 0.89	0.28	0.32	0.22
Wood Preservers (WP)	11	0.06.- 0.88	0.31	0.24	0.21
Industrial/Urban Sites (IND/URB)	33	ND.- 0.72	0.15	0.14	0.12
POTW	6	0.12.- 0.98	0.59	0.30	0.61
Agricultural (AGRI)	15	ND.- 0.82	0.27	0.24	0.17

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-7. Box and whisker plot for mercury in fish tissue.

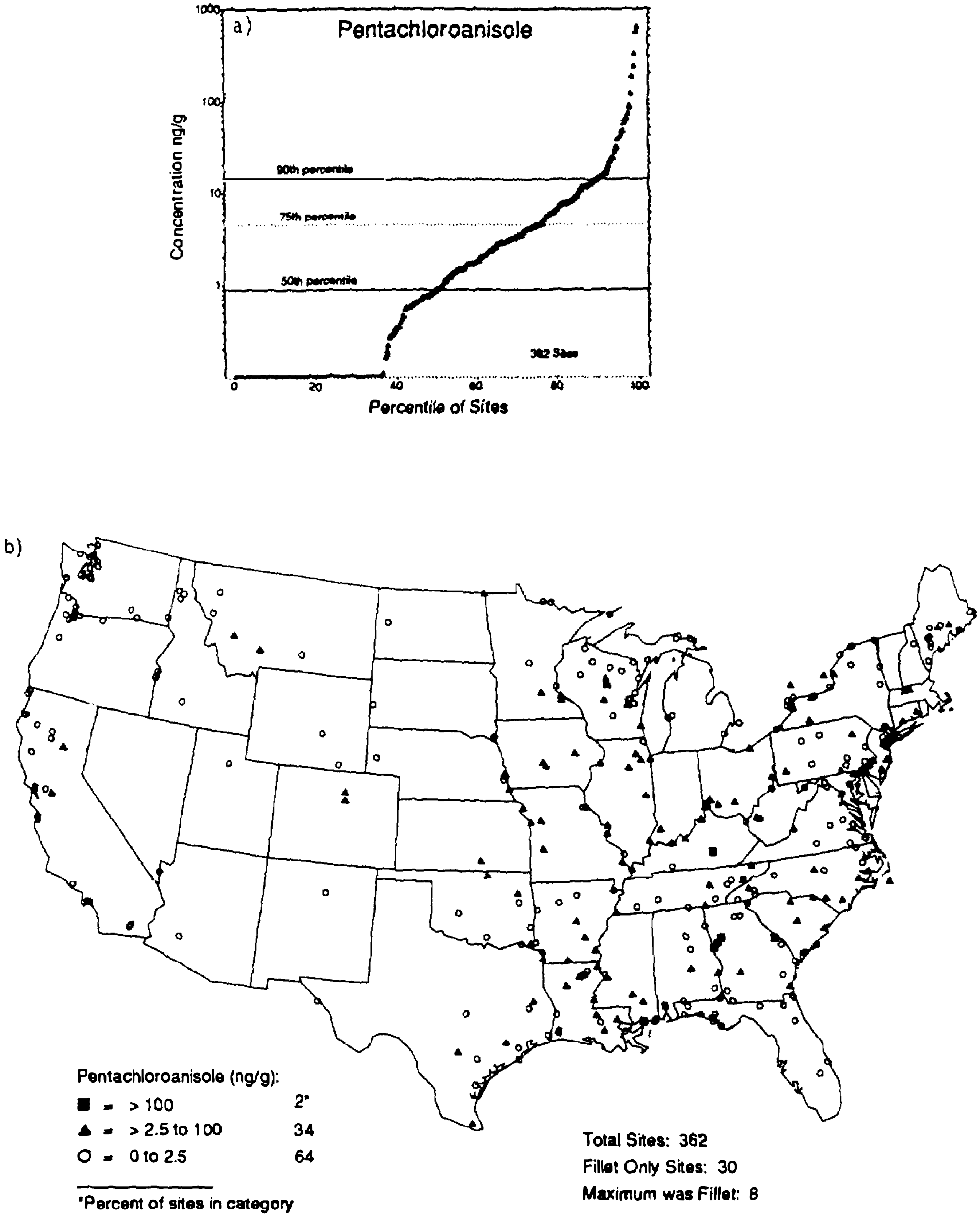


Figure 4-8. Pentachloroanisole: a) cumulative frequency distribution and b) map of geographical distribution of various concentration ranges in fish tissue.

Pentachloroanisole

Conc. ng/g	Episode Number	Type of Fish	Location
647	3375	WB Carp	Chattahoochee R., Austell, GA
570	3185	WB Channel Catfish	Bernard Bayou, Gulfport, MS
334	3376	WB Carp	Chattahoochee R., Whitesburg, GA
240	2618	WB Quillback	Hamilton Canal, Hamilton, OH
187	3377	WB Carp	Chattahoochee R., Franklin, GA

A wood treatment plant and Superfund site with solvents present are located near the Bernard Bayou site. The Hamilton Canal site is near a paper mill and Superfund site. The other three top five sites are located near paper mill operations. Eight of the top 36 sites (highest 10 percentile) were located near Superfund sites of which four were related to wood preserving. Paper mills were located near 17 of the top 36 sites.

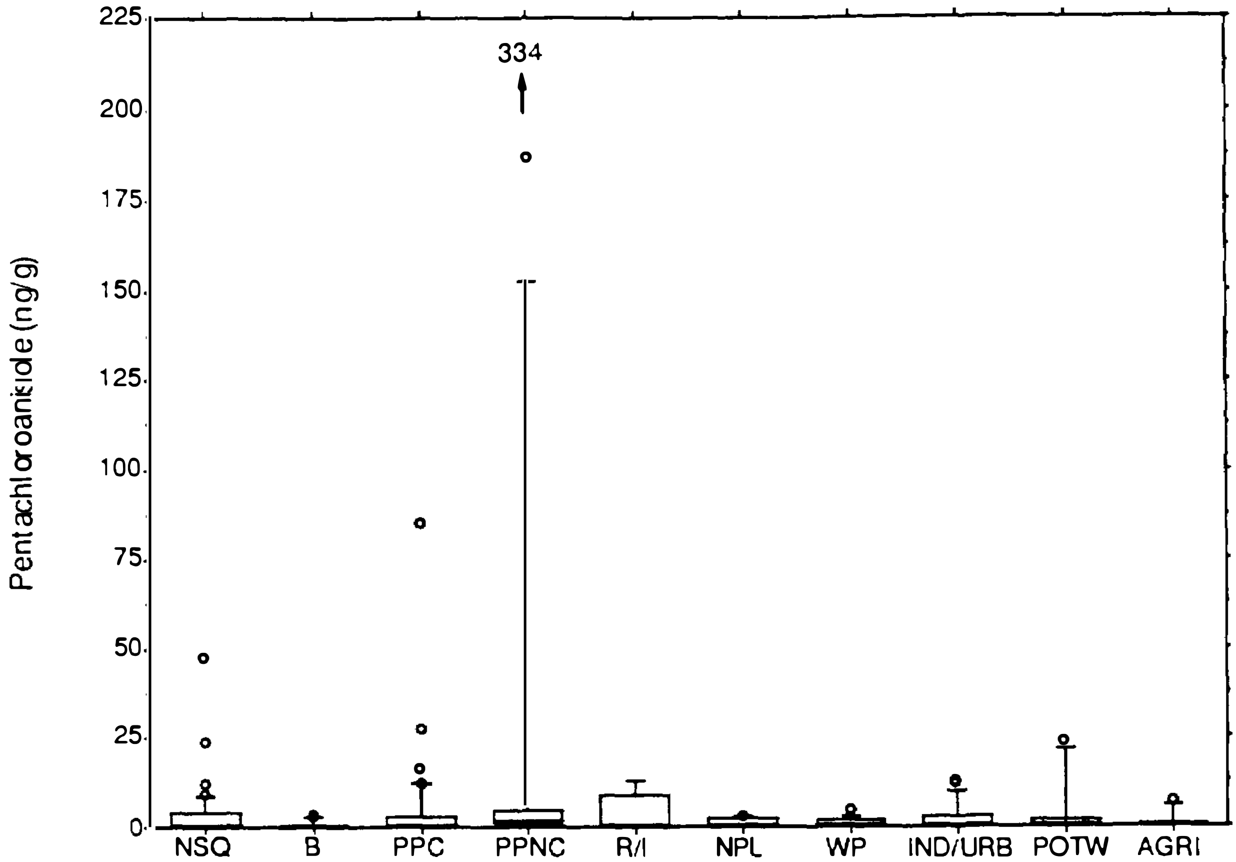
The box plot for pentachloroanisole shows that the highest median concentration was 1.7 ng/g for nonchlorine paper mills (Figure 4-9). The second highest median concentration was for sites near pulp and paper mills that use chlorine in the bleaching process (0.8 ng/g).

1,2,3 and 1,2,4 Trichlorobenzene

The compounds 1,2,3 trichlorobenzene and 1,2,4 trichlorobenzene (TCB) were detected in at least one sample at 42 percent and 53 percent of the sites, respectively. The median concentrations, however, were low (below detection for 1,2,3 TCB and 0.14 ng/g for 1,2,4 TCB) (Figure 4-10a,b). The two compounds are used in a variety of industrial applications including 1,2,4 TCB as a solvent and dielectric fluid and 1,2,3 TCB as a coolant in electrical installations, in the production of dyes, and in products to control termites. The sites with concentrations above 2.5 ng/g are located for the most part near industrial organic chemical manufacturing plants. The five sites with the highest concentrations out of 362 sites are as follows:

1,2,3 TCB

Conc. ng/g	Episode Number	Type of Fish	Location
69.0	2056	WB Carp	Ohio R., West Point, KY
54.9	3097	PF Brown Bullhead	Red Lion Cr., Tybouts Corner, DE
30.2	3164	WB Carp	Haw R., Saxapahaw, NC
26.8	3376	WB Carp	Chattahoochee R., Whitesburg, GA
24.8	2341	WB Carpsucker	Ohio R., Markland, KY



Summary Table for Pentachloroanisole Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND - 46.8	3.75	8.48	0.33
Background (B)	20	ND - 3.33	0.59	1.14	ND
Paper Mills Using Cl (PPC)	39	ND - 85.1	5.46	14.32	0.77
Other Paper Mills (PPNC)	17	ND - 334	33.10	89.53	1.67
Refinery/Other Industry (R/I)	5	ND - 13.2	4.21	5.97	0.32
Superfund Sites (NPL)	6	ND - 2.99	1.00	1.39	0.22
Wood Preservers (WP)	10	ND - 4.47	0.86	1.46	ND
Industrial/Urban Sites (IND/URB)	31	ND - 13	2.44	3.88	0.42
POTW	6	ND - 24.20	4.42	9.72	0.16
Agricultural (AGRI)	15	ND - 7.31	1.18	2.34	ND

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-9. Box and whisker plot for pentachloroanisole in fish tissue.

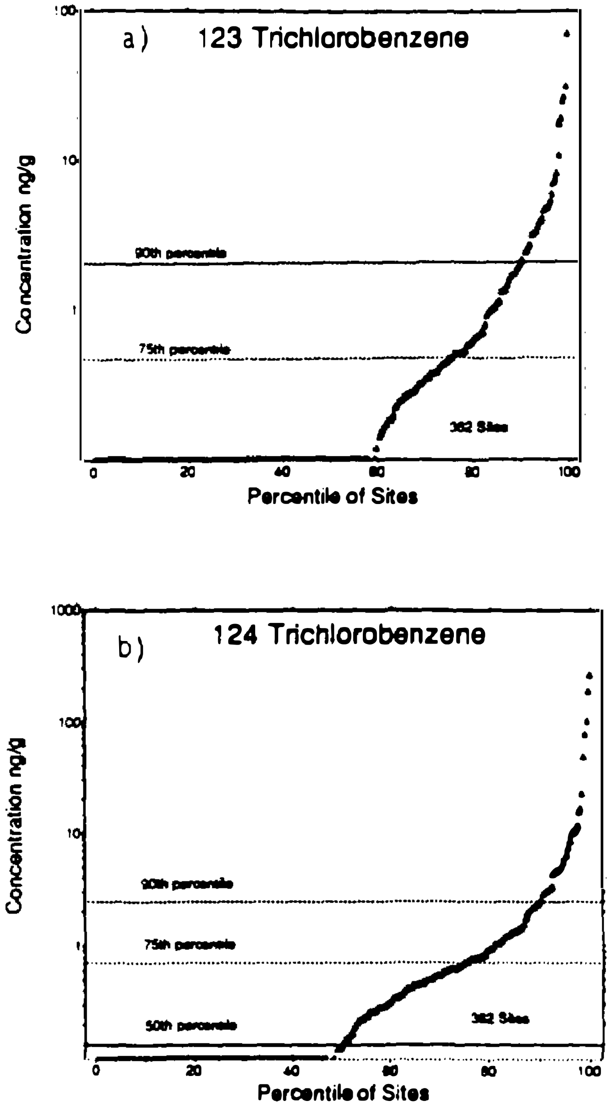


Figure 4-10. Cumulative frequency distributions of a) 1,2,3 trichlorobenzene and b) 1,2,4 trichlorobenzene in fish tissue. (Maximum concentration at each site was used. The bar along the x-axis indicated values below the detection.)

1,2,4 TCB

Conc. ng/g	Episode Number	Type of Fish	Location
264.8	2654	WB Carp	Toms R., NJ
191	2056	WB Carp	Ohio R., West Point, KY
104	2290	WB Spotted Sucker	Savannah R., Augusta, GA
103.8	3097	PF Brown Bullhead	Red Lion Cr., Tybouts Corner, DE
80.4	3410	WB Redhorse Sucker	Rochester Embayment, Rochester, NY

Two of the sites are the same for both 1,2,3, TCB and 1,2,4 TCB. Of the other eight sites shown above, three are near Superfund sites with chlorobenzene contamination (3181, 3097, 2654). Two sites are near paper mills (3376, 2290), one is near a chemical manufacturing plant (3410), and the remaining two are near agricultural/rural areas. For 1,2,4 TCB, nine of the highest 36 sites were near Superfund sites. Chemical manufacturing facilities are near 12 of the sites and paper mills near another six sites. Distribution of 1,2,3 TCB and 1,2,4 TCB is shown in Figures 4-11 a,b. The highest mean concentration for 1,2,3 TCB is 2.2 ng/g from nonchlorine paper mills and for 1,2,4 TCB is 3.2 ng/g for sites in the industrial/urban category (Figures 4-12 and 4-13).

Pesticides/Herbicides

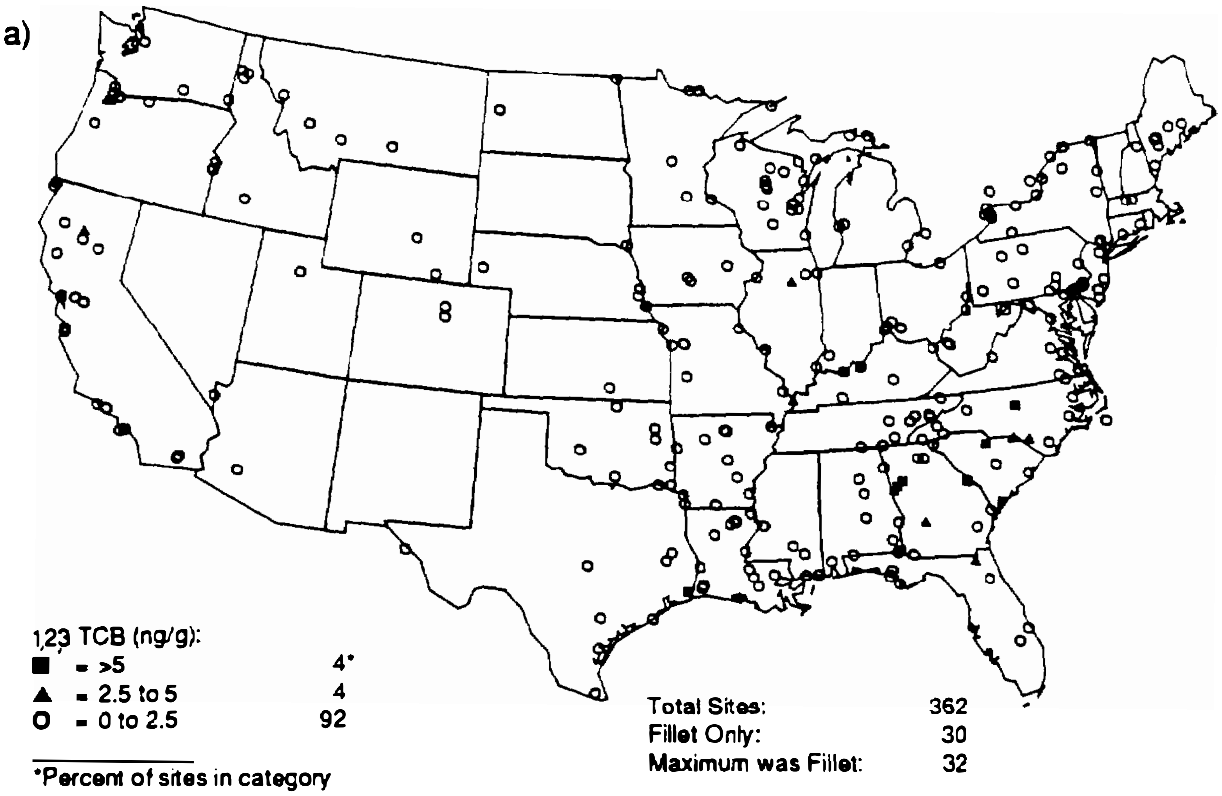
DDE

The most frequently detected xenobiotic compound was p,p′ -DDE at 98.6 percent of the sampled sites (Figure 4-14a). DDE is a metabolic breakdown product of the widely-used pesticide DDT. The geographic distribution of fish tissue concentrations (Figure 4-14b) shows the widespread occurrence of DDE, which is consistent with historic pesticide use patterns of DDT (see profile in Appendix C). The prevalence of DDE at a large number of sites, even though use of DDT was banned in 1972, is consistent with its persistence in the aquatic environment and its high bioaccumulation potential. The concentrations of DDE found at the top 5 out of 362 sites sampled are listed below:

p,p′ -DDE

Conc. ng/g	Episode Number	Type of Fish	Location
14028	3315	WB Carp	Union Canal, Lebanon, PA
8708	3282	WB Carp	Alamo R., Calipatria, CA
3221	3084	WB Channel Catfish	Arroyo Colorado, Harlingen, TX
3214	3212	WB Carp	Owyhee R., Owyhee, OR
2493	3231	WB Carp	Yakima R., Richland, WA

a)



b)

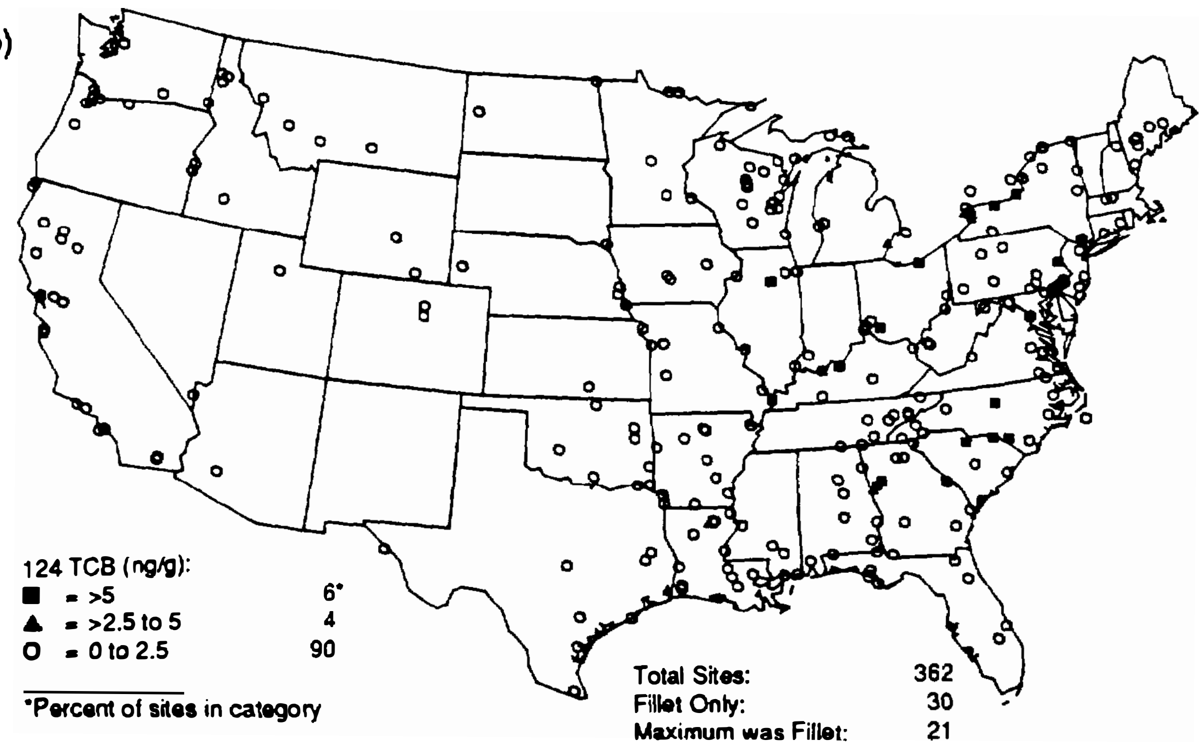
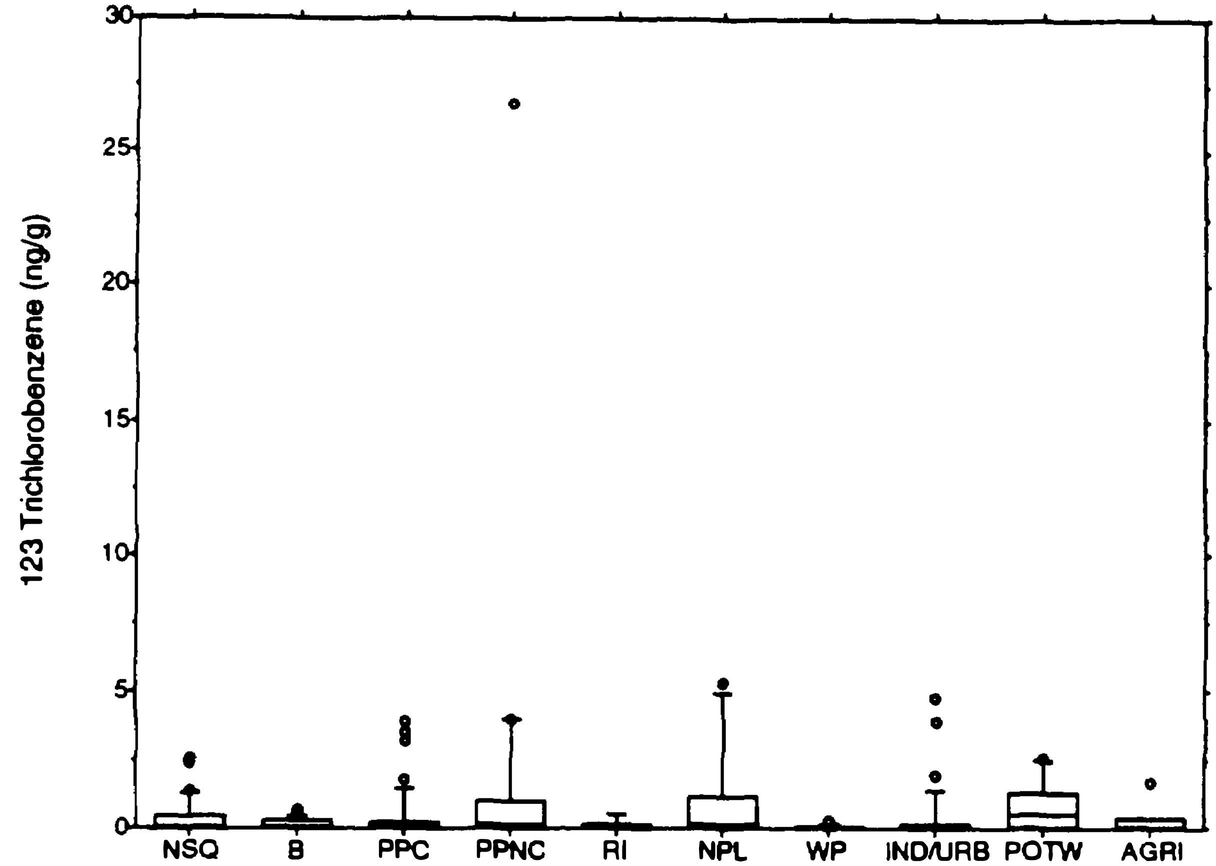


Figure 4-11. Map of geographical distribution of various concentration ranges for a) 1,2,3 trichlorobenzene and b) 1,2,4 trichlorobenzene in fish tissue.

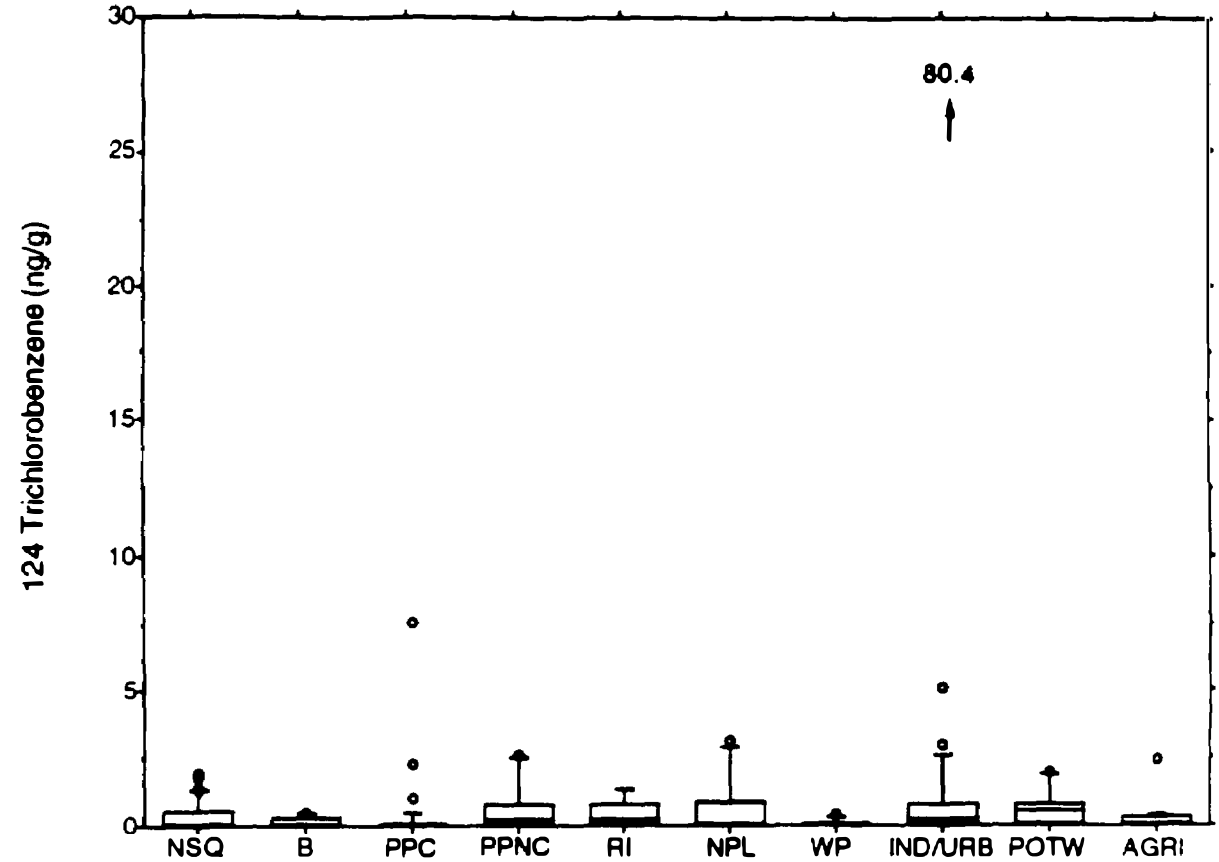


Summary Table for 1,2,3-Trichlorobenzene Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND - 2.6	0.39	0.67	ND
Background (B)	20	ND - 0.69	0.14	0.22	ND
Paper Mills Using Cl (PPC)	39	ND - 3.92	0.42	0.98	ND
Other Paper Mills (PPNC)	17	ND - 26.8	2.25	6.46	0.16
Refinery/Other Industry (R/I)	5	ND - 0.51	0.10	0.23	ND
Superfund Sites (NPL)	6	ND.- 5.34	1.13	2.11	0.16
Wood Preservers (WP)	10	ND - 0.29	0.03	0.09	ND
Industrial/Urban Sites (IND/URB)	31	ND - 4.77	0.43	1.12	ND
POTW	6	ND.- 2.60	0.83	1.05	0.51
Agricultural (AGRI)	15	ND.- 1.71	0.21	0.45	ND

n = number of sites in category. ND's set at 0. Maximum concentrations at sites were used.

Figure 4-12. Box and whisker plot for 1,2,3 tricholorbenzene in fish tissue.



Summary Table for 1,2,4-Trichlorobenzene Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND.- 1.97	0.36	0.55	ND
Background (B)	20	ND.- 0.47	0.17	0.19	0.08
Paper Mills Using Cl (PPC)	39	ND.- 7.58	0.33	1.26	ND
Other Paper Mills (PPNC)	17	ND.- 16.1	1.44	3.86	0.24
Refinery/Other Industry (R/I)	5	ND.- 1.36	0.44	0.56	0.22
Superfund Sites (NPL)	6	ND.- 3.12	0.70	1.23	0.12
Wood Preservers (WP)	10	ND - 0.42	0.07	0.14	ND
Industrial/Urban Sites (IND/URB)	31	ND.- 80.4	3.24	14.36	0.20
POTW	6	ND.- 1.97	0.64	0.73	0.54
Agricultural (AGRI)	15	ND.- 2.46	0.28	0.62	0.09

n = number of sites in category. ND's set at 0. Maximum concentrations at sites were used.

Figure 4-13. Box and whisker plot for 1,2,4 trichlorobenzene in fish tissue.

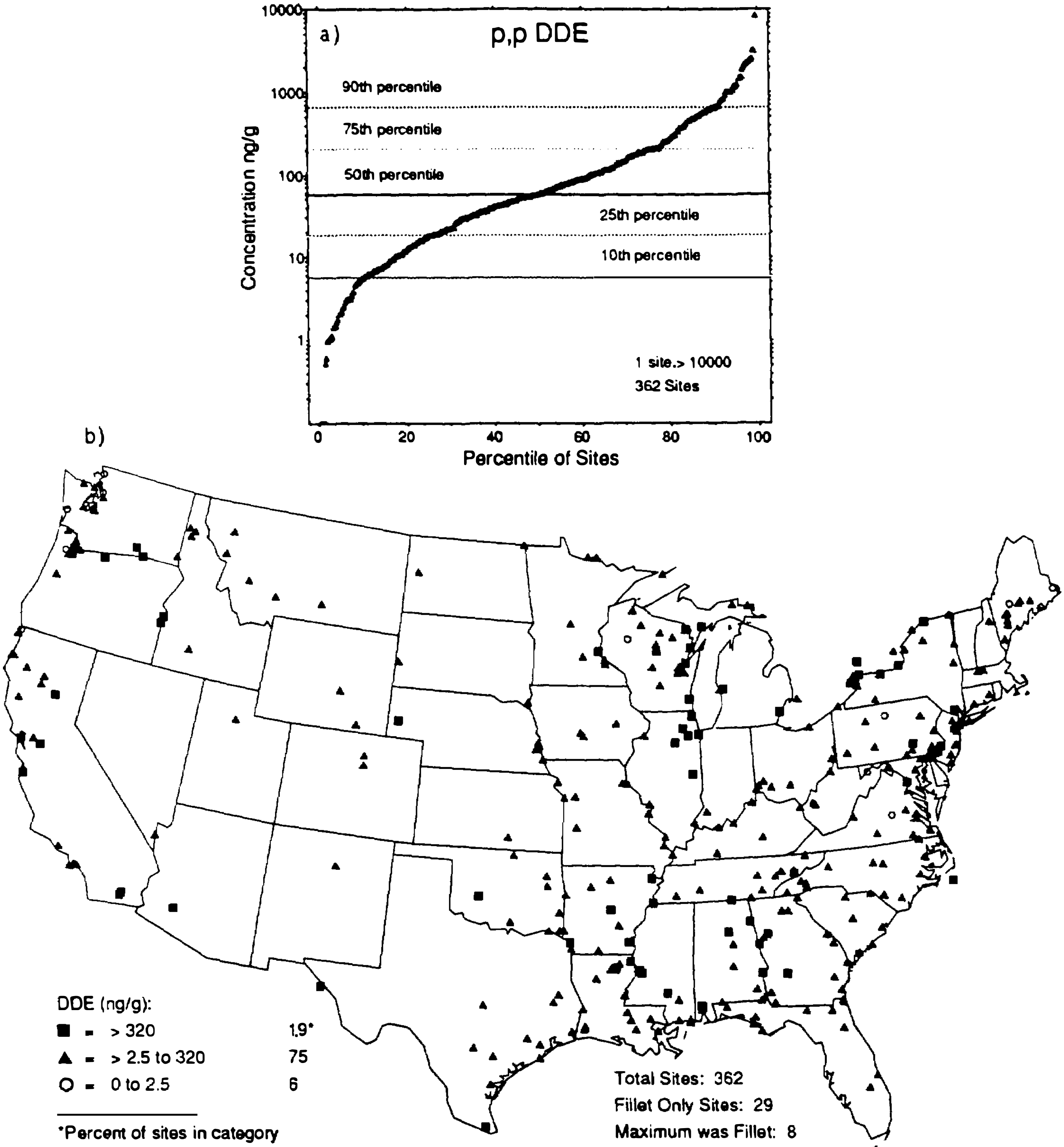


Figure 4-14. p,p'-DDE: a) cumulative frequency distribution and b) map of geographical distribution of various concentration ranges in fish tissue.

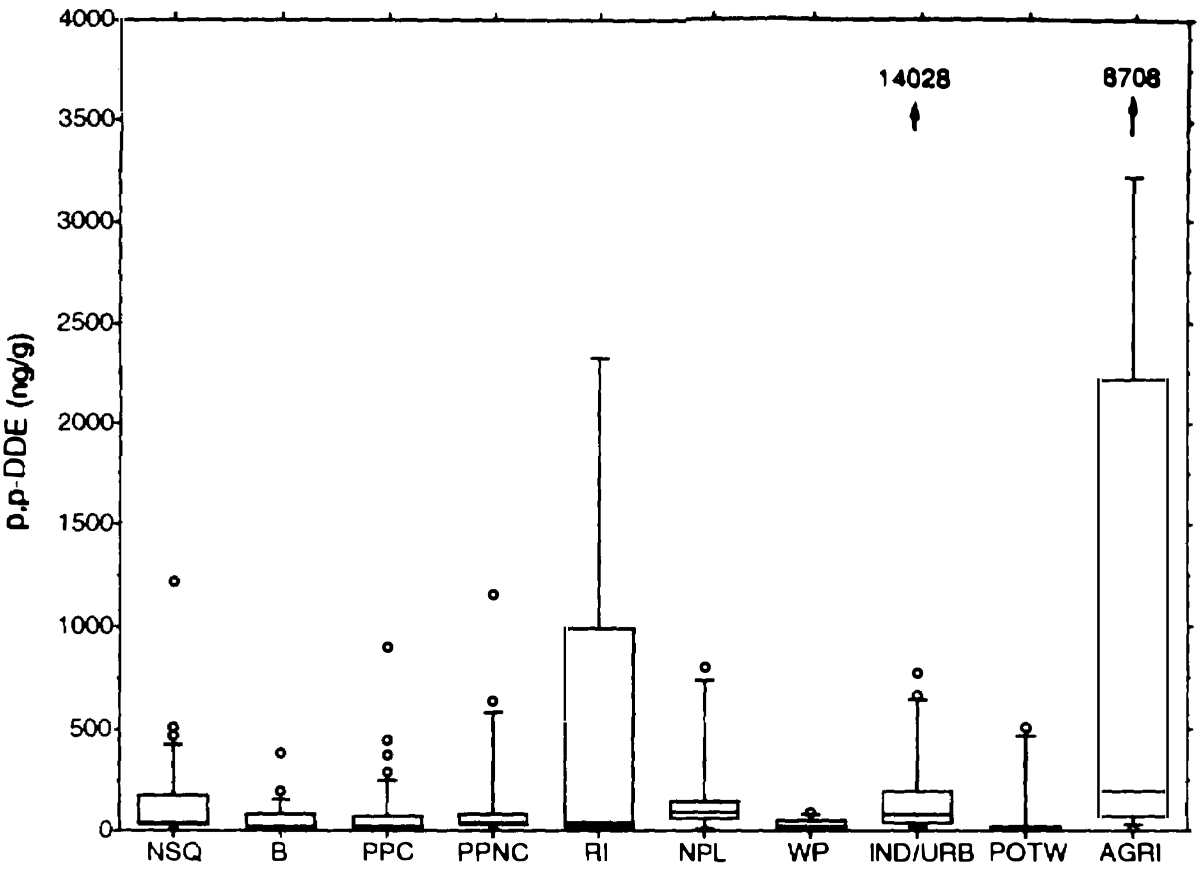
The maximum DDE concentration was found in a whole-body carp sample from Union Canal at Lebanon, Pennsylvania, near pesticide manufacturing plants. The other four sites are located in agricultural areas.

Six of the highest 10 percentile sites (36 out of 362 sites) were also located in agricultural areas without industrial activities. Five of the sites were near Superfund sites. Most of the remaining sites were located in industrial areas. The box plot (Figure 4-15) shows that the highest median concentration was 201 ng/g for agricultural areas. Kruskal-Wallis tests (Table 4-4) comparing agricultural sites with Superfund and industrial/urban sites showed no significant differences with regard to fish contamination levels.

Chlordane and Related Compounds (Nonachlor and Oxychlordane)

The next most frequently detected pesticides were chlordane and the compounds related to chlordane. Chlordane, itself, is a chlorinated hydrocarbon that occurs in two forms—cis and trans. The cis-isomer was detected at about 3 percent more sites than the trans-isomer (Figure 4-16 a,b, c). Prior to 1987, this compound was widely used for termite and ant control and for agricultural uses such as dipping nonfood roots and tops. Also, prior to 1980 it was used to control insects on a variety of crops including corn, grapes, and strawberries. At present, it can be used only for subsurface termite control. Related compounds are cis- and trans-nonachlor and oxychlordane. Nonachlor is a component of chlordane (trans can be 7 to 10 percent in technical-grade chlordane (Takamiya, 1987)) as well as an impurity of heptachlor. Trans-nonachlor was detected at 77 percent of the sites, whereas cis-nonachlor was detected at only 35 percent of the sites (Figure 4-17 a,b, c). Oxychlordane is a metabolic breakdown product of chlordane. Oxychlordane was detected at 27 percent of the sites (Figure 4-16d). Nonachlor and chlordane have a high potential for bioaccumulation, while oxychlordane has a lower potential. The total chlordane and total nonachlor concentrations were compared for the same sample and found to be correlated based on a linear function (r^2 = 0.7) but not as strongly as cis- versus trans-chlordane (r^2 = 0.89). Total chlordane is the sum of the cis- and trans-chlordane isomer concentrations measured in the same sample. Total nonachlor is the sum of the cis- and trans-nonachlor isomers. The correlations are consistent with the multiple sources of nonachlor. Comparing the geographic distribution of the two compounds (Figure 4-18a,b) shows that most of the sites with high levels of total nonachlor (greater than 100 ng/g) also have a high level of chlordane.

The maximum concentrations at the top five sites for each of these compounds were detected near industrial areas and Superfund sites (Table 4-5). The Monongahela River at Clairton, Pennsylvania, an industrial area with manufacturing plants of inorganic chemicals and pesticides, had the highest concentrations of total, cis-, and trans-chlordane and total and trans- nonachlor. This site also had high concentrations of oxychlordane and cis-nonachlor. The highest concentrations of cis-nonachlor and oxychlordane were also in industrial areas, Lake Michigan at Waukegan, Illinois, and Peshtigo River Harbor, Peshtigo, Wisconsin, respectively. The remaining sites were located near various industrial areas involving the production of inorganic and organic chemicals, and pesticides. Sources for the top 10 percentile sites were predominantly industrial areas near chemical manufacturing plants (17 out of 36). Superfund sites were near 10 of the 36 sites. All of these sites were located in areas with nearby industrial activities. The highest median concentrations for chlordane were near Superfund sites and industry/urban areas (Figure 4-19). For total nonachlor



Summary Table for p,p'DDE Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	1.09 - 1223	136.18	226.21	46.90
Background (B)	20	ND.- 384	56.28	93.42	11.68
Paper Mills Using Cl (PPC)	39	1.0 - 895	87.27	167.67	22.20
Other Paper Mills (PPNC)	17	0.9 - 1157	161.94	306.58	42.50
Refinery/Other Industry (R/I)	5	5.9 - 2329	586.87	1000.14	41.50
Superfund Sites (NPL)	6	1.5 - 805	200.17	300.35	97.95
Wood Preservers (WP)	10	1.65 - 91.5	33.13	32.7	16.85
Industrial/Urban Sites (IND/URB)	31	7.23 - 14028	602.34	2499.49	78.80
POTW	6	2.49 - 516	98.16	204.84	17.40
Agricultural (AGRI)	15	13.1 - 8708	1526.89	2313.13	201.00

n = number of sites in category. ND's set at 0. Maximum concentrations at sites were used.

Figure 4-15. Box and whisker plot for p,p'-DDE in fish tissue.

Table 4.4
Results of Statistical Tests for Selected Xenobiotics (Pesticides/Herbicides)

	Kruskal-Wallis		Mann-Whitney				
Chemical	All Groups Except NSQ	Ind/URB NPL, AG	B,PPC,PPNC WP,POTW	AG IND, URB	AG, NPL	AG,B	IND, B
Total Nonachlor	.0071	.7565	.1946	.5346	.5593	.0183	.0013
Trifluralin	.4822	.1363	.9870	.0809	.1021	.0956	.8926
Mirex	.6451	.8643	.3180	.6477	.6128	.4334	.7212
Heptachlor Epoxide	.9599	.7704	.9899	.6144	.8153	.8415	.7576
Dieldrin	.0891	.6856	.4053	.5269	.4835	.3861	.0176
Endrin	.8983	.5777	.7063	.6732	.5858	.8415	.8020
Chlorpyrifos	.4019	.5426	.4757	.6990	.4835	.5938	.2242
Alpha-BHC	.0905	.4388	.1437	.3989	.2129	.1880	.0087
Isopropalin	.9951	.7358	.9920	.4821	1.000	1.000	.4403
Total Chlordane	.0047	.6774	.2289	.6144	.3185	.0164	.0036
p,p' DDE	.0001	.1074	.5430	.0403	.1857	.0002	.0017
Gamma BHC	.0417	.3614	.0184	.2657	.6404	.1615	.0056
Dicofol	.6233	.2085	.8068	.0893	.2429	.2861	.4635
Oxychlordane	.2994	.7081	.9567	.4748	1.000	.6892	.1708

Values shown are two-tail probabilities that groups are different. The critical level was set at 0.05. If p<0.05, the categories were considered to be significantly different.

Site Categories:

IND/URB = Industry and/or urban
AG = Agriculture
B = Background
NPL = National Priority List (Superfund site)
POTW = Publicly Owned Treatment Works (sewage)
R/I = Refines using catalytic reforming process and other industry
NSQ = National Ambient Stream Quality monitoring network. (This designation is independent of source categories.)
WP = Wood preserving related activities
PPC = Paper and pulp mills using chlorine for bleaching
PPNC = Other paper and pulp mills including deinking plants

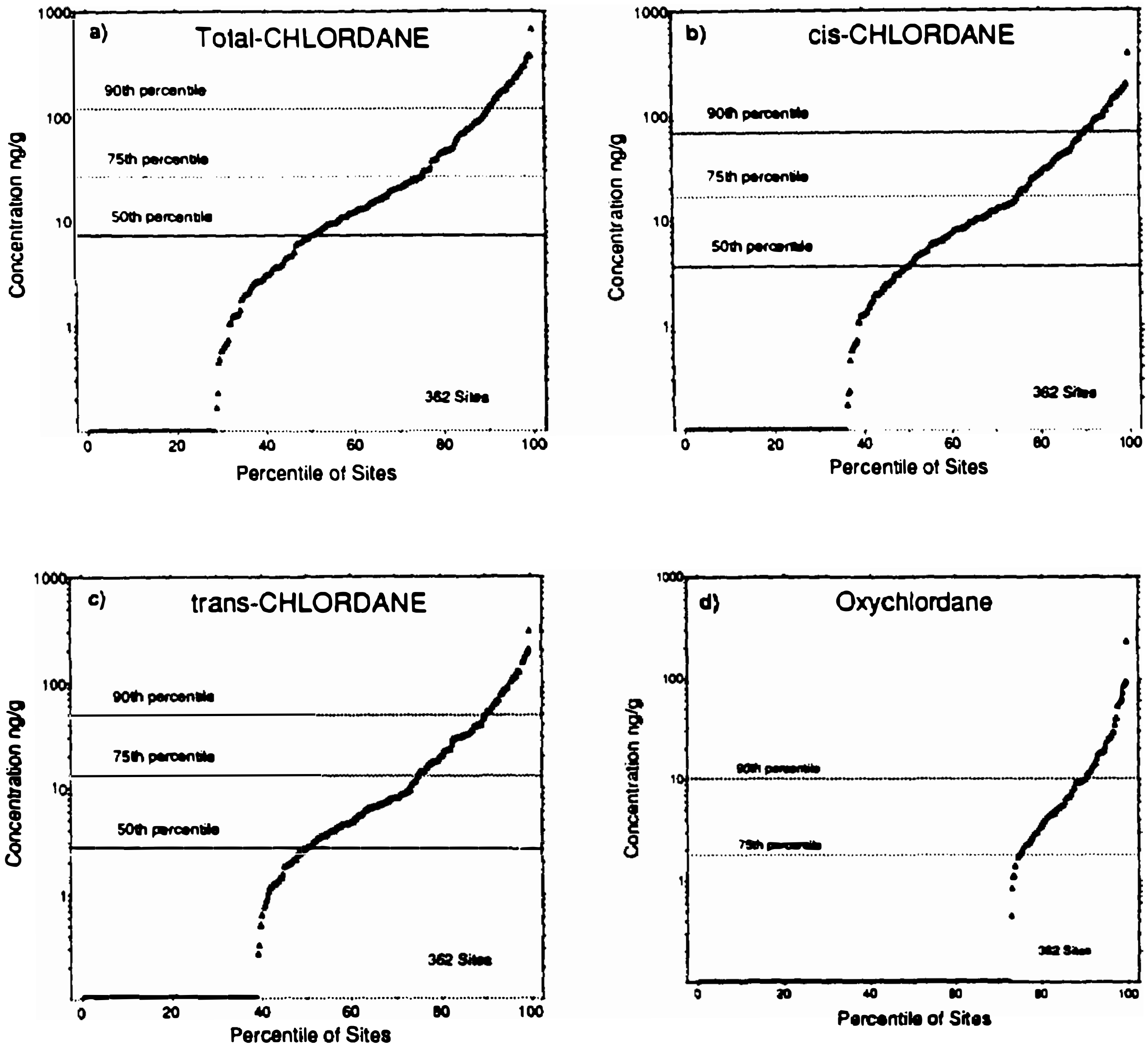
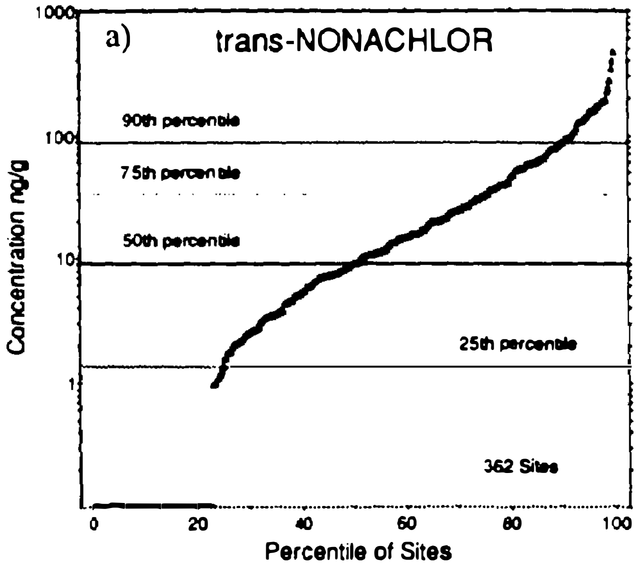
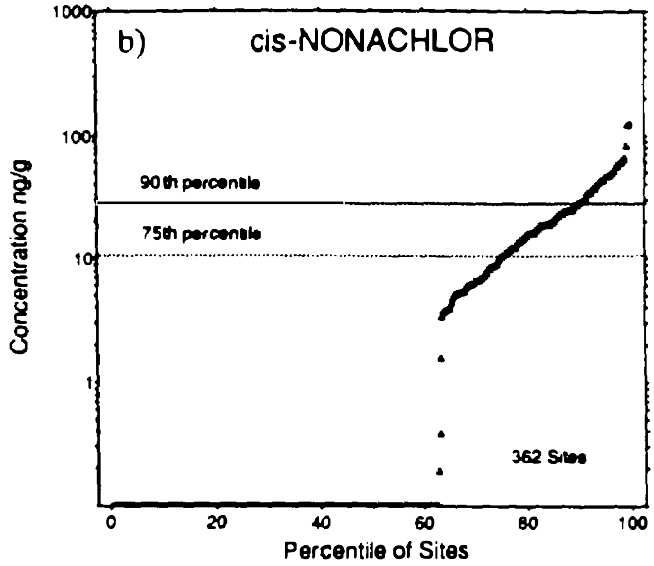


Figure 4-16. Cumulative frequency distribution of a) total chlordane, b) cis-chlordane, c) trans-chlordane and d) oxychlordane. (Maximum concentration at each site was used. The bar along the x-axis indicated values below the detection.)





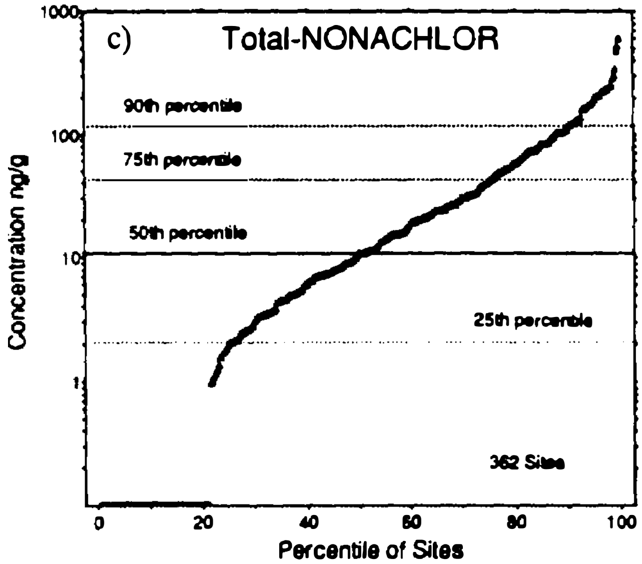


Figure 4-17. Cumulative frequency distribution of a) trans-nonachlor b) cis-nonachlor, and c) total nonachlor. (Maximum concentration at each site was used. Bar at x-axis represents sites with levels below detection.)

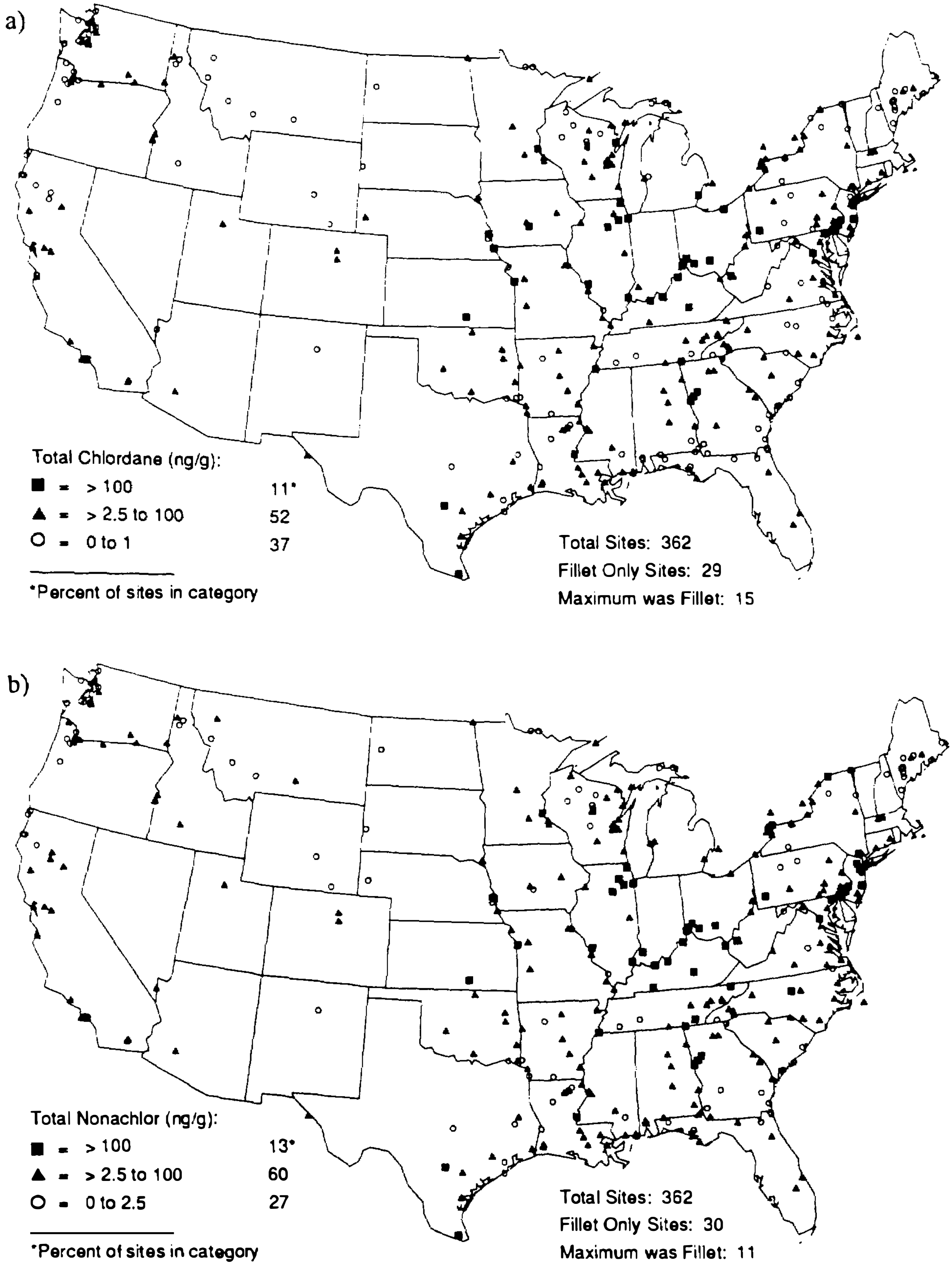
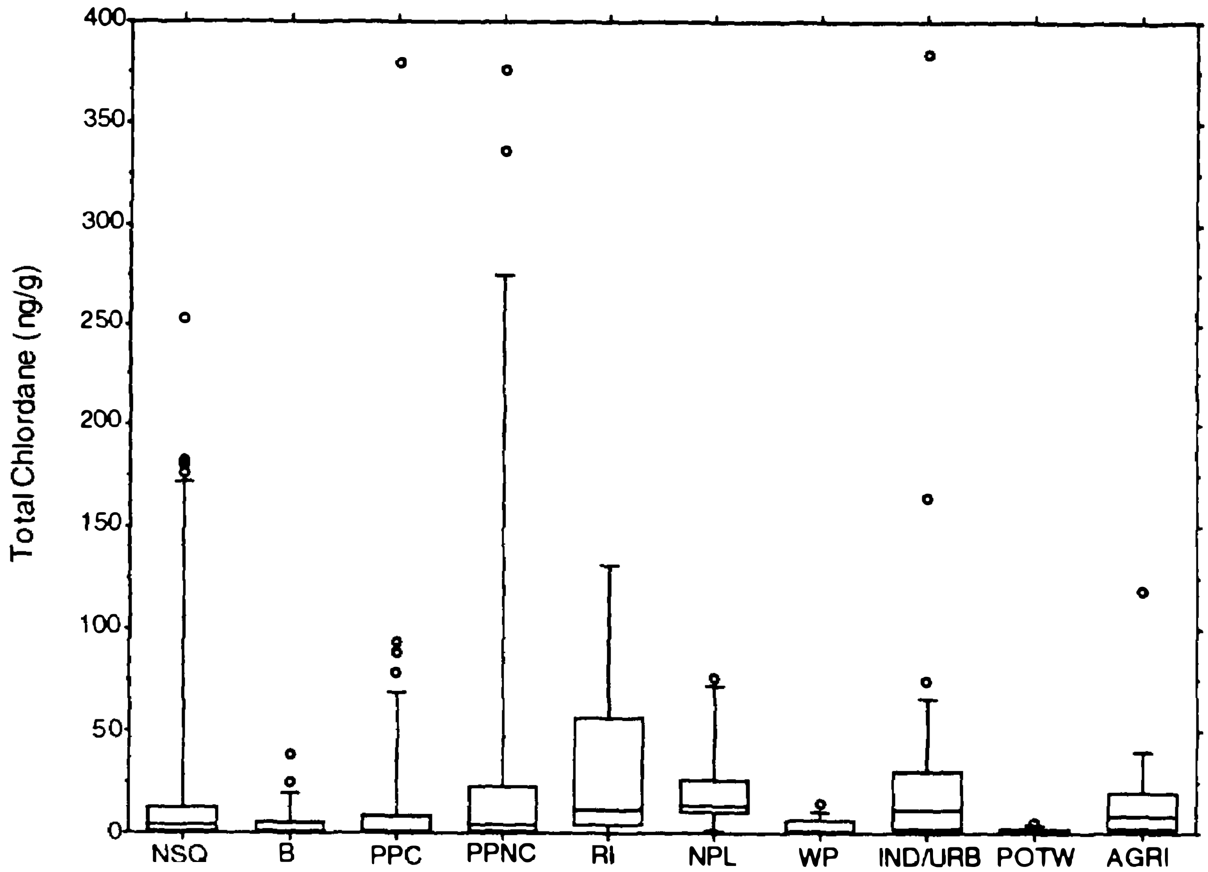


Figure 4-18. Map of geographical distribution of various concentration ranges for a) total chlordane and b) total nonachlor in fish tissue.

TABLE 4-5
Sites With Highest Concentrations Of Chlordane Related Compounds

Chemical	Maximum Concentration ng/g	Episode Number	Type of Fish	Location
Total Chlordane				
	688	2215	WB Carp	Monongahela, Clairton, PA
	384	3045	WBeCarp	Missouri R., Kansas City, MO
	379	3435	WB Bigmouth Buffalo	Mississippi R., Natchez, MS
	376	3376	WB Carp	Chattahoochee R., Whitesburg, GA
	369	3048	WBeCarp	Mississippi R., West Alton, MO
cis-Chlordane				
	378	2215	WB Carp	Monongahela R., Clairton, PA
	200	3048	WBeCarp	Mississippi R., West Alton, MO
	196	3045	WBeCarp	Missouri R., Kansas City, MO
	185	3376	WB Carp	Chattahoochee R., Whitesburg, GA
	179	2383	WB Carp	Des Plaines R., Lockport, IL
trans-Chlordane				
	310	2215	WB Carp	Monongahela R., Clairton, PA
	206	3435	WB Bigmouth Buffalo	Mississippi R., Natchez, MS
	191	3376	WB Carp	Chattahoochee R., Whitesburg, GA
	188	3045	WB Carp	Missouri R., Kansas City, MO
	182	2190	WB Carp	Nishnabotna R., Hamburg, IA
Oxychlordane				
	243	2427	WB Carp	Peshtigo R. Harbor, Peshtigo, WI
	96.2	2618	WB Carp	Hamilton Canal, Hamilton, OH
	91.4	2215	WBeCarp	Monongahela R., Clairton, PA
	87.2	3117	PF Lake Trout	Lake Michigan, Waukegan, IL
	77	2439	WB Carp	Great Miami R., New Baltimore, OH
Total Nonachlor				
	601	2215	WB Carp	Monongahela R., Clairton, PA
	521	3377	WBeCarp	Chattahoochee R., Franklin, GA
	477	3117	PF Lake Trout	Lake Michigan, Waukegan, IL
	340.9	2394	WB Carp	Great Miami R., Franklin, OH
	299	3181	WB Carp	Ohio R., West Point, KY
cis-Nonachlor				
	127	3117	PF Lake Trout	Lake Michigan, Waukegan, IL
	124	2215	WBeCarp	Monongahela R., Clairton, PA
	123	3377	WB Carp	Chattahoochee R., Franklin,GA
	83.2	3285	Stingray	Colorado Lagoon, Long Beach, CA
	65.7	2383	WBeCarp	Des Moines R., Lockport, IL
trans-Nonachlor				
	477	2215	WB Carp	Monongahela R., Clairton, PA
	398	3377	WBeCarp	Chattahoochee R., Franklin, GA
	350	3117	PF Lake Trout	Lake Michigan, Waukegan, IL
	279	2394	WB Carp	Great Miami R., Franklin, OH
	242	3181	WB Carp	Ohio R., West Point, KY

Total number of sites for each chemical was 362.



Summary Table for Total Chlordane Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND - 251.7	31.80	64.97	3.66
Background (B)	20	ND - 38.3	5.20	10.30	ND
Paper Mills Using Cl (PPC)	39	ND - 379	20.54	63.90	ND
Other Paper Mills (PPNC)	17	ND - 376	48.73	116.27	4.52
Refinery/Other Industry (R/I)	5	ND - 131.5	35.45	55.00	11.2
Superfund Sites (NPL)	6	ND - 76.60	23.25	27.53	13.42
Wood Preservers (WP)	10	ND - 14.23	3.0	4.69	0.62
Industrial/Urban Sites (IND/URB)	31	ND - 384	32.80	73.25	11.29
POTW	6	ND - 4.86	1.42	1.95	0.63
Agricultural (AGRI)	15	ND - 120.4	17.20	30.68	7.85

n = number of sites in category. ND's set at 0. Maximum concentrations at sites were used.

Figure 4-19. Box and whisker plot for total chlordane in fish tissue.

(Figure 4-20) the highest median concentrations were near refinery/other industry sites and industry/urban sites. The only median concentration above the detection limit for oxychlordane was near refinery/other industry sites (Figure 4-21). A single dominant source was not observed for either compound based on Kruskal-Wallis tests (Table 4-4).

Dieldrin

Dieldrin, an organochlorine pesticide widely used prior to 1974, was detected at 60 percent of the 362 sites, (Figure 4-22a). The cumulative frequency distribution shows 9 percent of the sites with a concentration above 100 ng/g (Figure 4-22b). The top 5 out of 362 sites for dieldrin are listed below:

Dieldrin

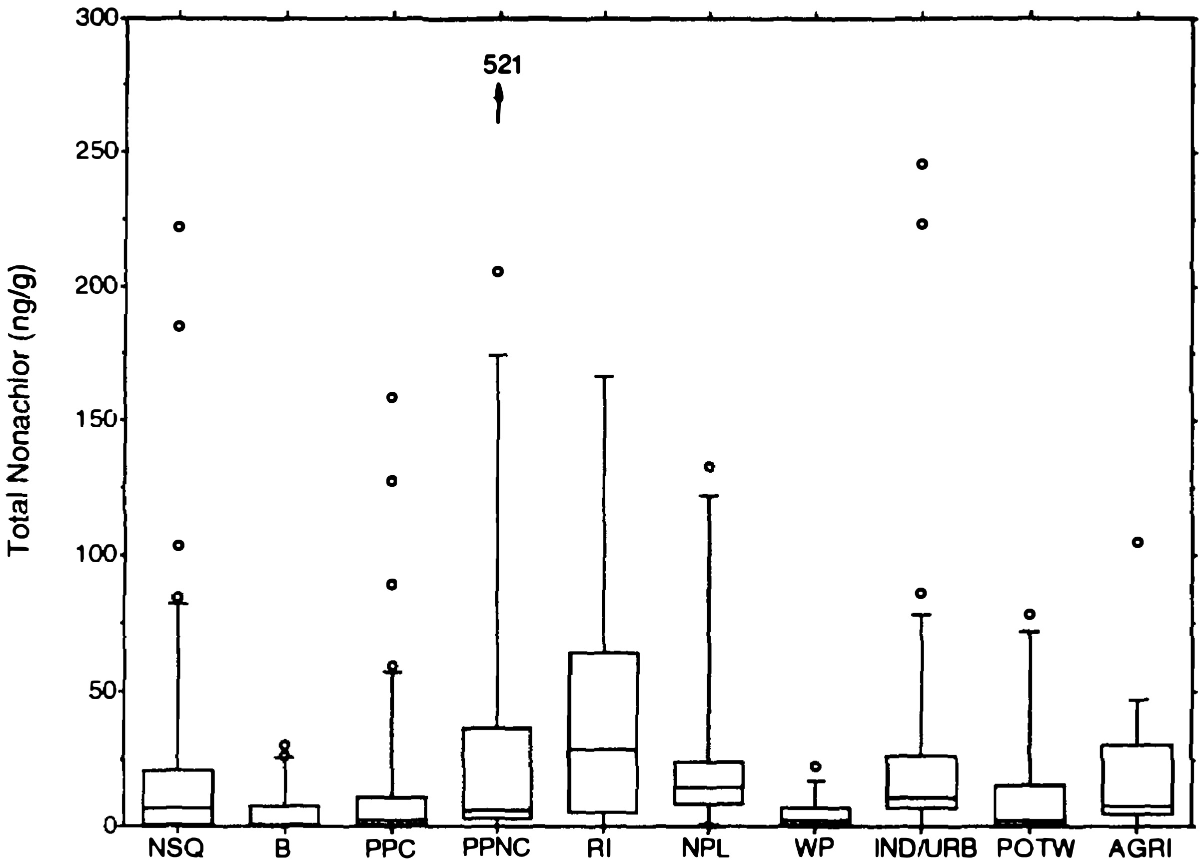
Conc. ng/g	Episode Number	Type of Fish	Location
450	3161	WB Sucker	Cobbs Cr., Philadelphia, PA
405	3117	PF Lake Trout	Lake Michigan, Waukegan, IL
323	3036	WB Carp	Nishnabotna R., Hamburg, IA
312	2199	WB Bigmouth Buffalo	Missouri R., Lexington, MO
260	3272	WB White Surfperch	Lauritzen Canal, Richmond, CA

The first two sites are near Superfund sites in industrial areas. The next two sites are located in agricultural areas. The fifth site is located at a former pesticide packaging plant.

The highest median for dieldrin (13.0 ng/g) was for locations near Superfund sites and the next highest for sites near industrial/urban areas (9.9 ng/g) (Figure 4-23).

alpha/gamma-BHC

Prior to 1977, alpha-BHC was a component of technical grade gamma-BHC, or lindane. Lindane is an insecticide/acaricide which has been used to treat seeds, hardwood lumber, and livestock and also to control soil pests for tobacco, fruit, and vegetable crops. The five sites with the highest concentrations of 362 sites for alpha- and gamma-BHC are listed below.

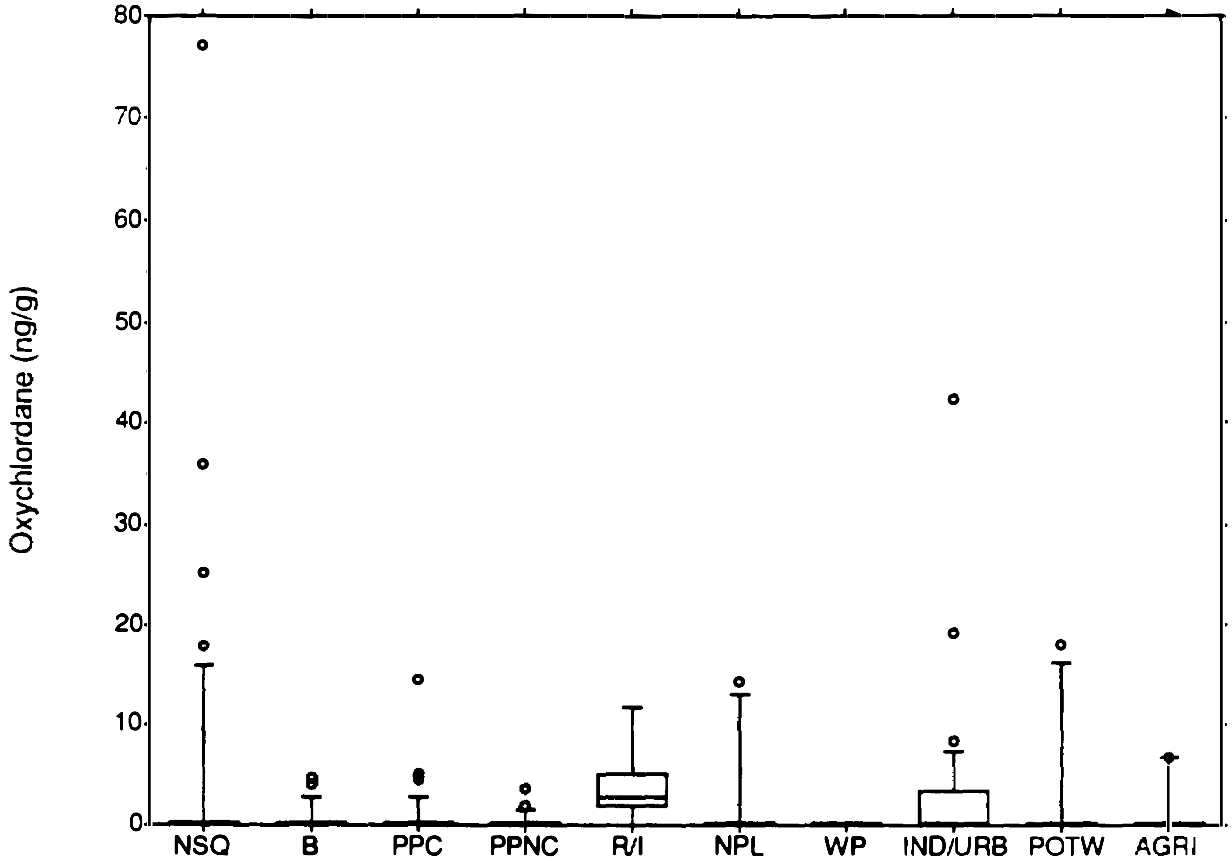


Summary Table for Total Nonachlor Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND - 221.3	26.26	49.28	7.07
Background (B)	20	ND.- 30.4	5.68	9.84	ND
Paper Mills Using Cl (PPC)	39	ND.- 159.3	17.70	36.10	2.29
Other Paper Mills (PPNC)	17	ND.- 521	54.00	130.03	6.59
Refinery/Other Industry (R/I)	5	ND - 166.6	46.48	68.47	28.76
Superfund Sites (NPL)	6	ND.- 132.9	32.35	49.92	14.7
Wood Preservers (WP)	10	ND.- 22.52	5.07	7.15	2.01
Industrial/Urban Sites (IND/URB)	31	ND.- 245	32.45	50.08	11.3
POTW	6	ND - 78.2	16.49	30.77	2.72
Agricultural (AGRI)	15	ND - 105.0	19.88	27.75	7.87

n = number of sites in category. ND's set at 0. Maximum concentrations at sites were used.

Figure 4-20. Box and whisker plot for total nonachlor in fish tissue.

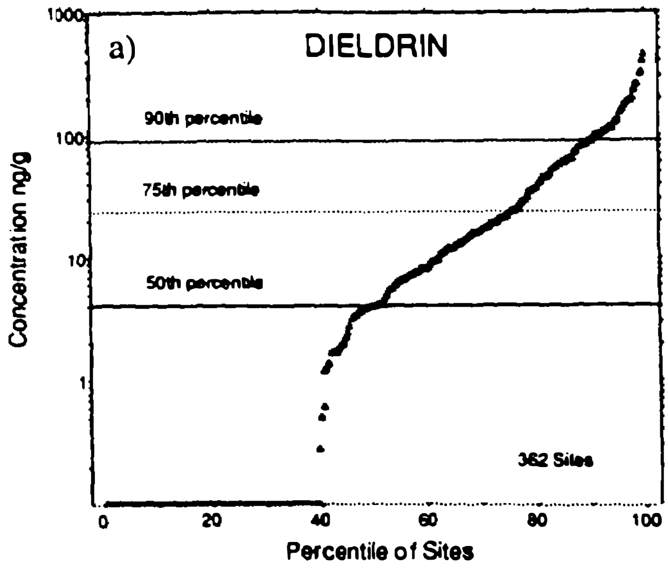


Summary Table for Oxychlordane Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND.- 77.0	4.67	14.1.1	ND
Background (B)	20	ND.- 4.64	0.50	1.34	ND
Paper Mills Using Cl (PPC)	39	ND - 14.4	0.73	2.59	ND
Other Paper Mills (PPNC)	17	ND - 3.48	0.34	0.92	ND
Refinery/Other Industry (R/I)	5	ND.- 11.7	3.87	4.52	2.62
Superfund Sites (NPL)	6	ND - 14.3	2.38	5.84	ND
Wood Preservers (WP)	10	ND	ND	ND	ND
Industrial/Urban Sites (IND/URB)	31	ND.- 42.3	3.34	8.25	ND
POTW	6	ND.- 17.9	2.98	7.31	ND
Agricultural (AGRI)	15	ND - 6.75	2.62	0.68	ND

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-21. Box and whisker plot for oxychlordane in fish tissue.



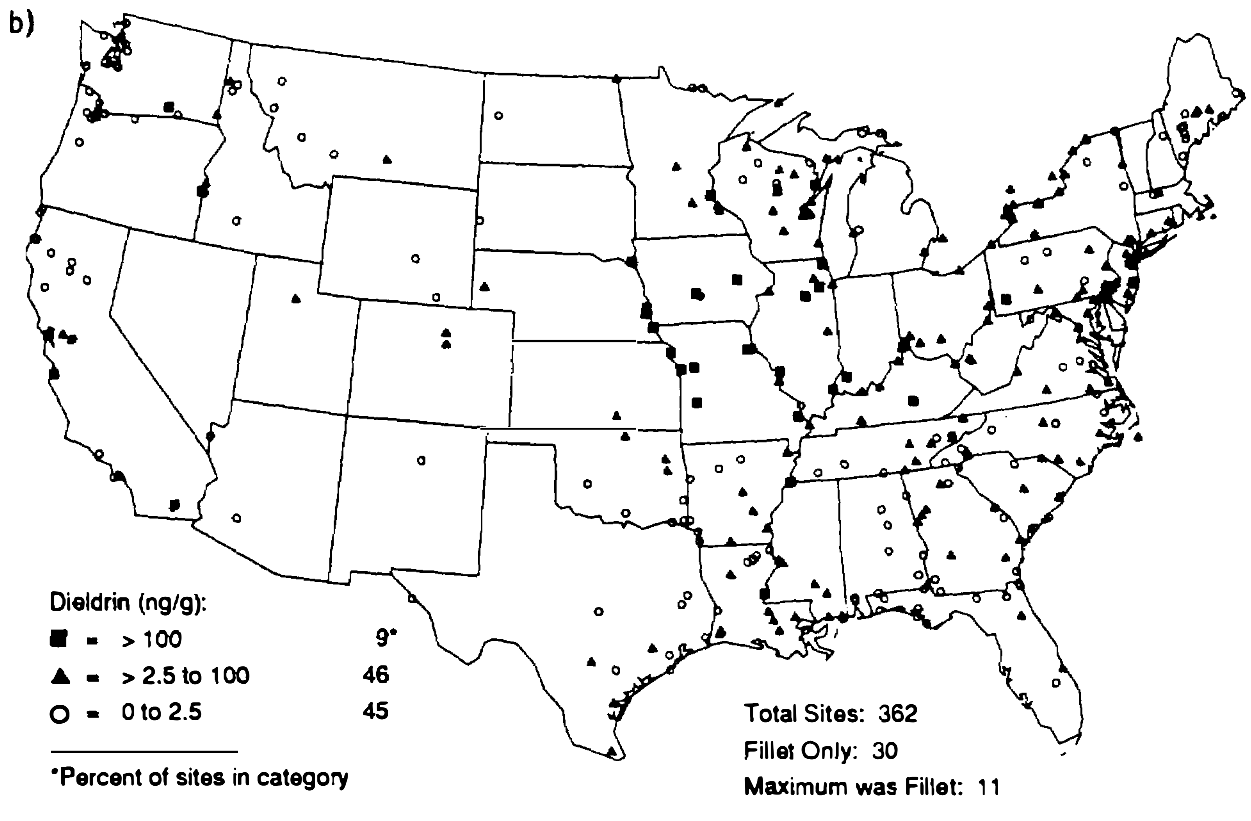
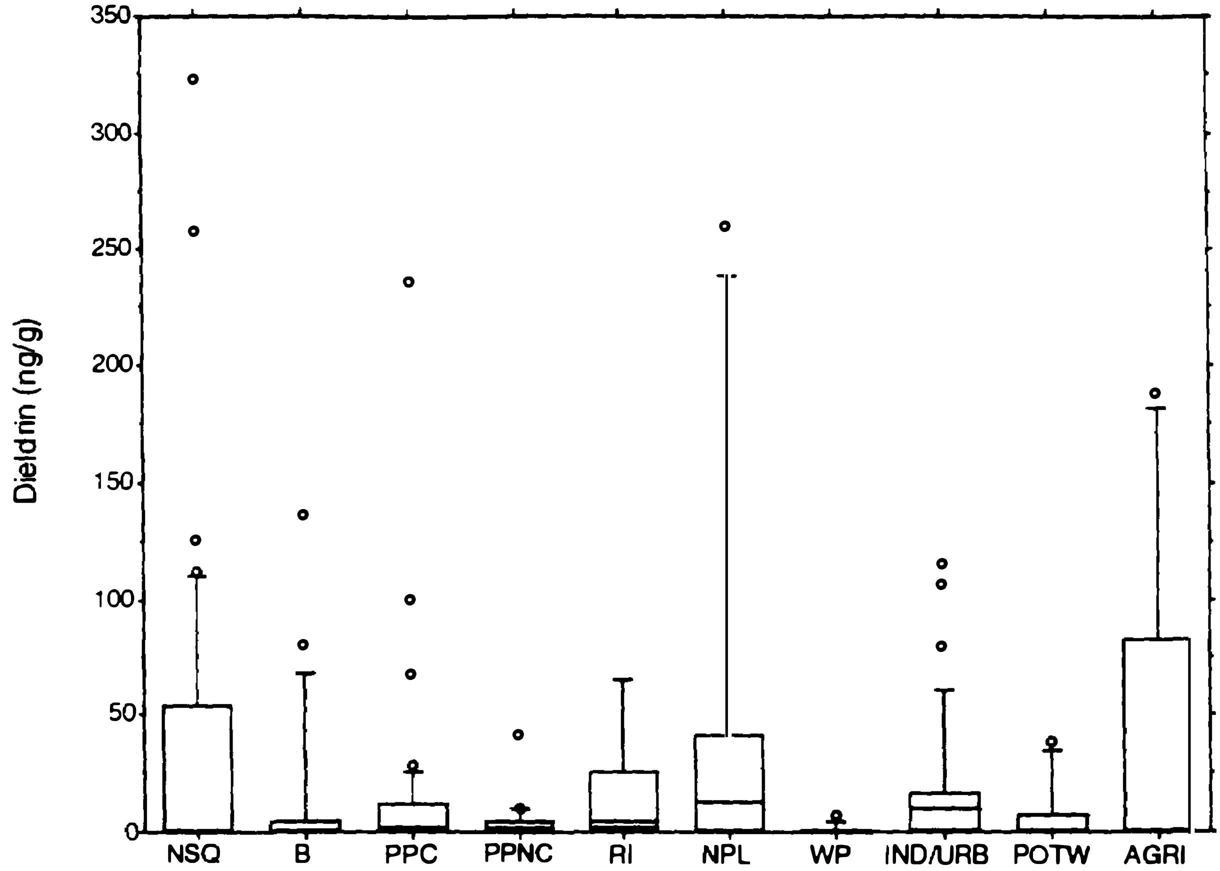


Figure 4-22. Dieldrin: a) cumulative frequency distribution and b) map of geographical distribution of various concentrations in fish tissue.



Summary Table for Dieldrin Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND - 323	35.46	71..16	ND
Background (B)	20	ND - 136	14 .31	35.45	ND
Paper Mills Using Cl (PPC)	39	ND - 236	14.86	41.18	1.40
Other Paper Mills (PPNC)	17	ND.- 41.5	4.90	9.94	1.84
Refinery/Other Industry (R/I)	5	ND.- 64.9	16.64	27.40	4.18
Superfund Sites (NPL)	6	ND.- 260	54.55	101..77	13.05
Wood Preservers (WP)	10	ND.- 7.73	0.97	2.45	ND
Industrial/Urban Sites (IND/URB)	31	ND.- 116	18.48	29.71	9.96
POTW	6	NDa 38.2	7.86	15.16	0.64
Agricultural (AGRI)	15	ND - 188	43.94	69.37	ND

n = number of sites in category. ND's set at 0. Maximum concentrations at sites were used.

Figure 4-23. Box and whisker plot for dieldrin in fish tissue.

alpha-BHC

Conc. ng/g	Episode Number	Type of Fish	Location
44.4	3098	WB White Sucker	Red Clay Cr., Ashland, DE
29.0	2427	WB Carp	Peshtigo R. Harbor, Peshtigo, WI
20.8	2410	WB Carp	Rouge R., River Rouge, MI
19.3	2383	WB Carp	Des Plaines R., Lockport, IL
18.6	2056	WX&Carp	Ohio R., West Point, KY

gamma-BHC (Lindane)

Conc. ng/g	Episode Number	Type of Fish	Location
83.3	3042	WB Carp	Missouri R., Omaha, NE
44.5	2416	WB Carp	Cuyahoga R., Cleveland, OH
38.8	3098	PF American Eel	Red Clay Cr., Ashland, DE
27.4	2439	WB Carp	Great Miami R., New Baltimore, OH
25.7	3342	WB Spotted Sucker	Lumber R., Lumberton, NC

Five of these sites are near chemical manufacturing plants (2383, 2410, 2416, 3042, and 3181). Paper mills were located near three of the sites (2427, 2439, and 3342). The remaining site is in an agricultural area where mushroom farming is done, which uses large quantities of pesticides.

Fifty-five percent of these sites were above detection for alpha-BHC, while only 42 percent of the sites were above detection for gamma-BHC (Figure 4-24a,b). The box plots for alpha-BHC and gamma-BHC are shown in Figures 4-25 and 4-26, respectively. A geographical distribution of various concentration ranges of alpha- and gamma-BHC is shown in Figure 4-27a,b.

COMPOUNDS DETECTED AT BETWEEN 10 AND 50 PERCENT OF THE SITES[3]

Hexachlorobenzene

Hexachlorobenzene (HCB) was one of the original targeted compounds because it may contain dioxin and is toxic itself. HCB can be produced in a number of ways: as a by-product of chlorinated solvent manufacturing; from incineration of municipal waste; from chlorination of wastewater; and as a breakdown product of lindane. It is also an impurity in other currently registered pesticides, (e.g., pentachloronitrobenzene (PCNB)) and in pentachlorophenol (see profile

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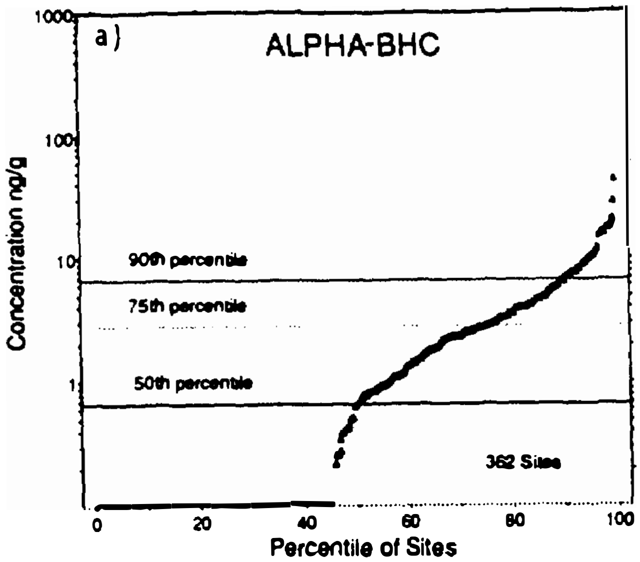
[3] Five chemicals found at less than 10 percent of the sites are presented here for ease of discussion. These are 1,2,3,5 and 1,2,4,5 trichlorobenzene; methoxychlor; isopropalin; and perthane. One chemical, heptachlor epoxide, found at 16 percent of the sites, is presented in the next section with heptachlor.



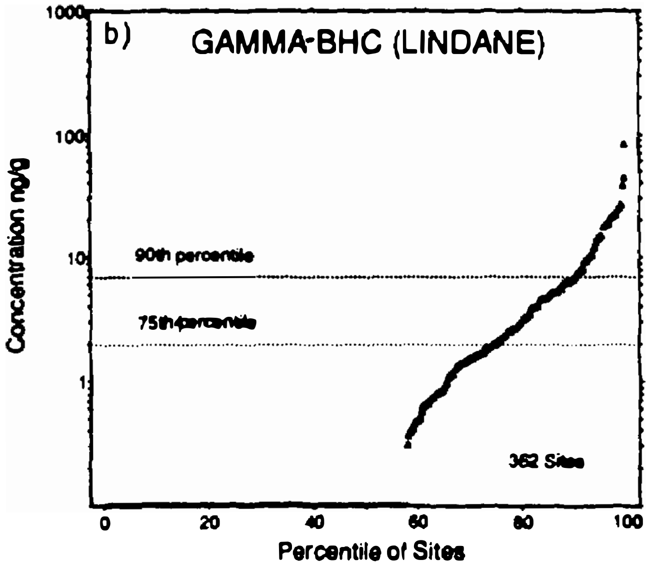
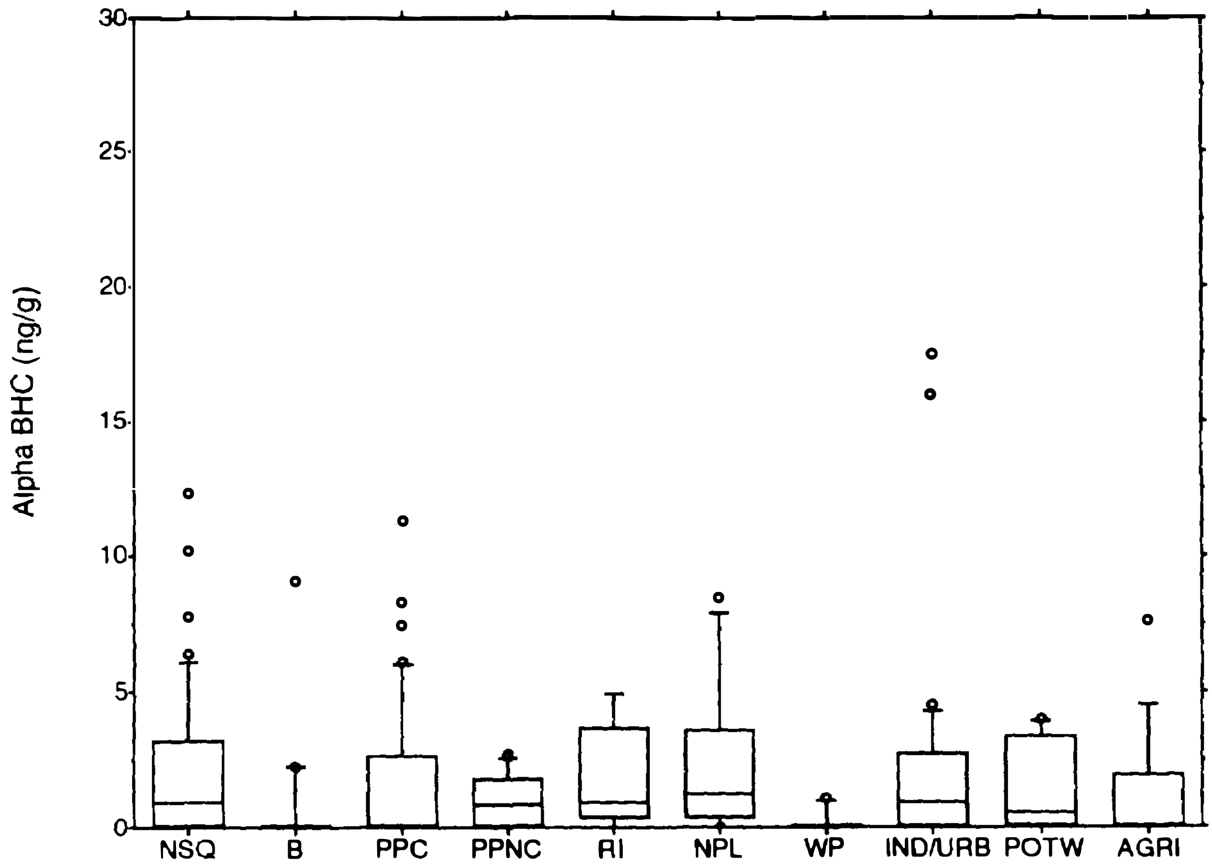


Figure 4-24. Cumulative frequency distribution of a) alpha-BHC and b) gamma-BHC (lindane) in fish tissue.

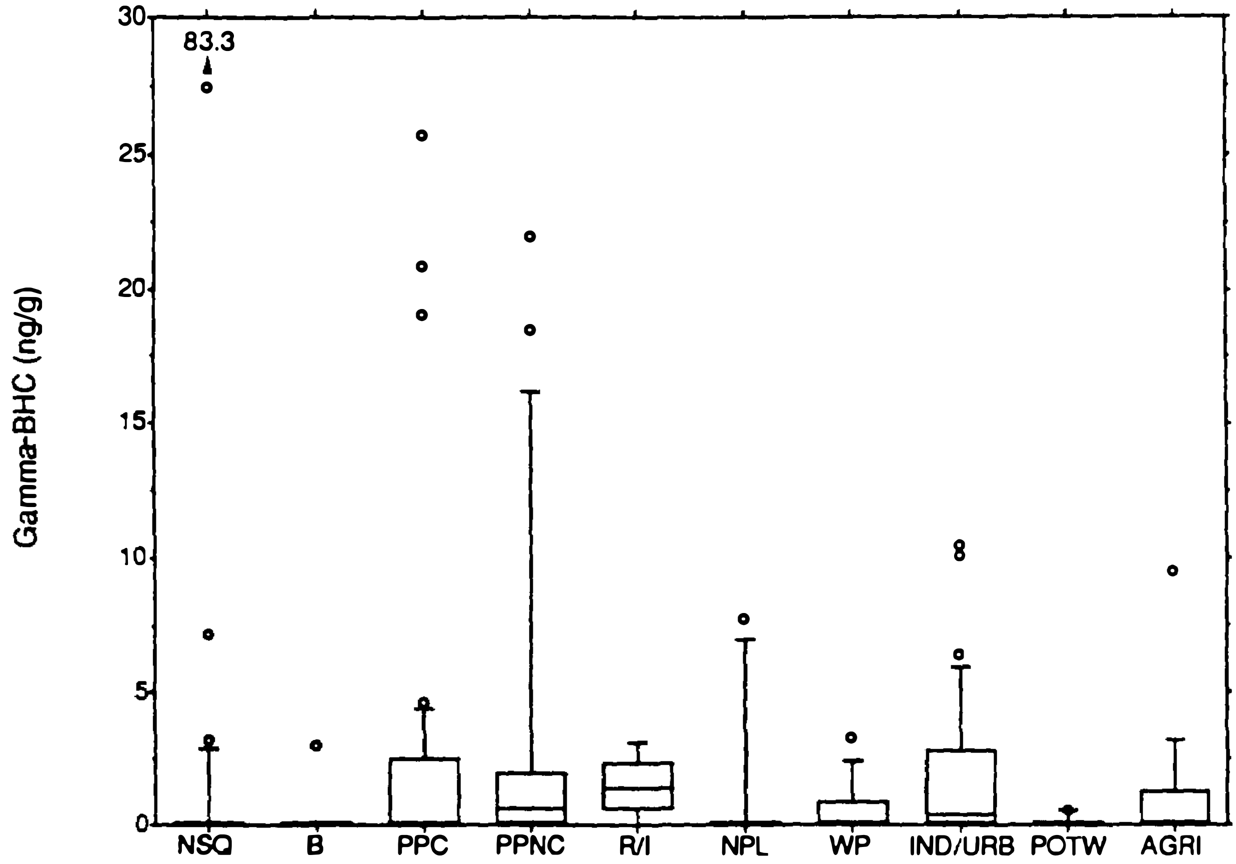


Summary Table for Alpha-BHC Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND - 12.30	1.98	2.98	0.93
Background (B)	20	ND - 9.08	0.72	2.09	ND
Paper Mills Using Cl (PPC)	39	ND.- 11.30	1.74	2.75	ND
Other Paper Mills (PPNC)	17	ND - 2.77	0.99	0.99	0.85
Refinery/Other Industry (R/I)	5	ND.- 4.97	1.92	2.1.1	0.96
Superfund Sites (NPL)	6	ND - 8.43	2.49	3.18	1.26
Wood Preservers (WP)	10	ND.- 1.08	0.21	0.44	ND
Industrial/Urban Sites (IND/URB)	31	ND - 17.48	2.20	4.11	0.91
POTW	6	ND - 3.98	1.41	1.82	0.56
Agricultural (AGRI)	15	ND - 7.56	1.32	2.19	ND

n = number of sites in category. ND's set at zero. Maximum concentrations at sites were used.

Figure 4-25. Box and whisker plot for alpha-BHC in fish tissue.



Summary Table for Gamma-BHC Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND.- 83.3	3.25	13.91	ND
Background (B)	20	ND - 2.97	0.15	0.66	ND
Paper Mills Using Cl (PPC)	39	ND.- 25.7	2.66	5.85	ND
Other Paper Mills (PPNC)	17	ND.- 21.9	3.33	6.60	0.63
Refinery/Other Industry (R/I)	5	ND - 3.1	1.49	1.21	1.41
Superfund Sites (NPL)	6	ND - 7.8	1.30	3.18	ND
Wood Preservers (WP)	10	ND - 3.3	0.57	1.09	ND
Industrial/Urban Sites (IND/URB)	31	NDa 10.5	1.99	2.97	0.37
POTW	6	ND.- 0.58	0.10	0.24	ND
Agricultural (AGRI)	15	ND - 9.6	1.15	2.52	ND

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-26. Box and whisker plot for gamma-BHC in fish tissue.

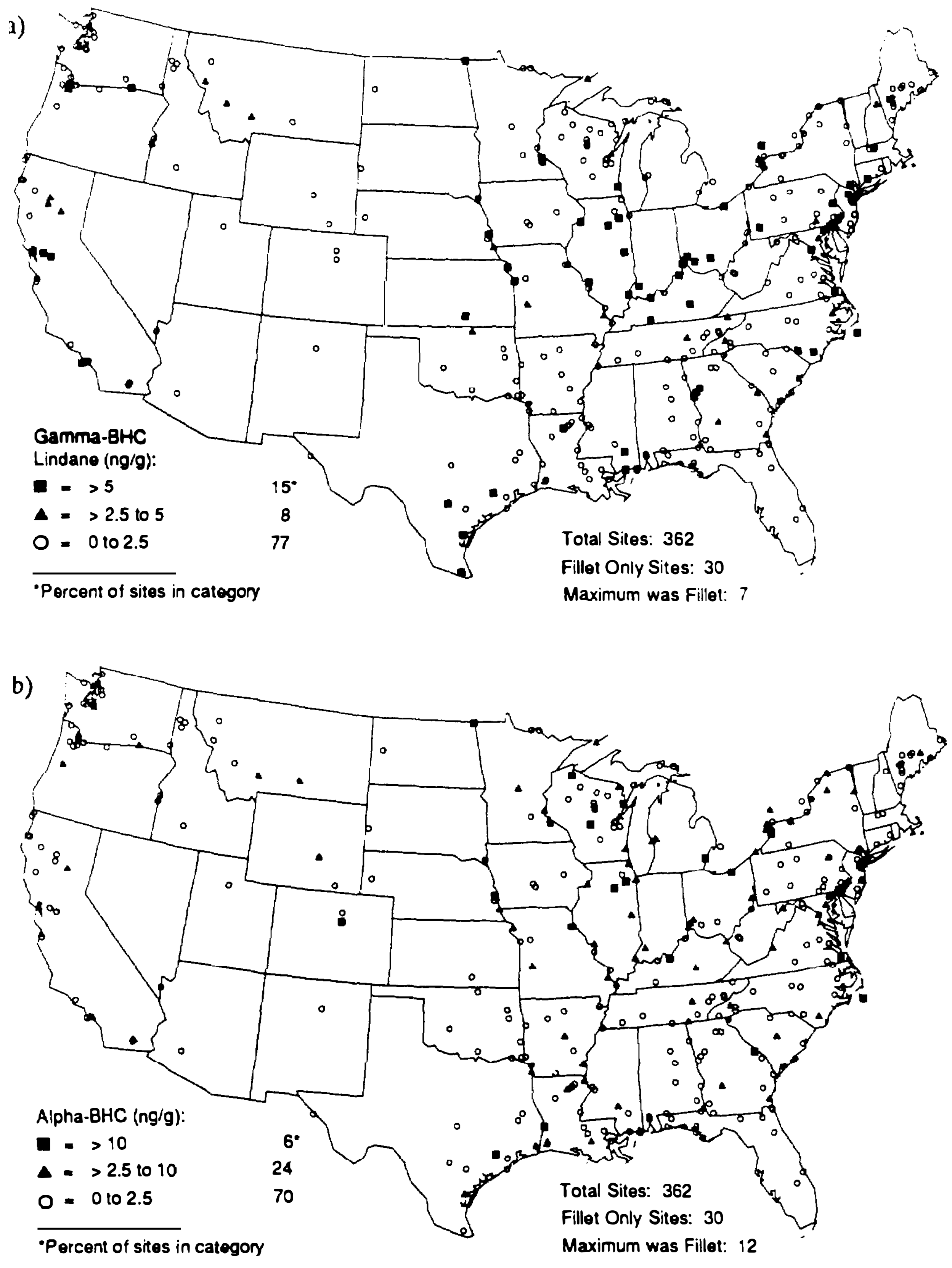


Figure 4-27. Map of geographical distribution of various concentration ranges for a) gamma-BHC (lindane) and b) alpha-BHC in fish tissue.

in Appendix C). The compound is not readily affected by transformation processes (e.g., hydrolysis) and has a high potential for bioaccumulation. Given this variety of sources, it is not surprising that the compound was found at sites located in nearly all parts of the country (Figure 4-28a). HCB was detected at 46 percent of the sites (Figure 4-28b), though the median concentration was below the detection limit. Pentachlorobenzene is also an impurity in PCNB and was found in detectable quantities at some of the same locations as discussed later in this chapter. Sites with the five highest concentrations out of 362 sites are listed below:

Hexachlorobenzene

Conc. ng/g	Episode Number	Type of Sample	Location
913	3085	WB Sea Catfish	Brazos R., Freeport, TX
202	3086	WB Catfish	Bayou D'Inde, Sulfur, LA
93.7	2532	WB Carp	Mississippi R., St. Francisville, LA
85.5	2376	WB White Sucker	Quinipiac R., North Haven, CT
75	3063	WB Sea Catfish	Calcasieu R., Moss Lake, LA

The first two sites are near pesticide manufacturing plants and the remaining sites are near manufacturing plants for other types of chemicals. At the Quinipiac River site, there is also a Superfund site known to have solvent contamination. The predominant sources for the top 10 percentile sites (36 out of 362) were pesticide/chemical manufacturing plants and Superfund sites. Six sites originally selected because of organic chemical manufacturing plants were included in the top 10 percentile sites. Two agricultural sites where pesticides are extensively used were included in the top 10 percentile sites (one at Calipatria, California, and one at Gila Bend, Arizona). A statistical comparison (Kruskal-Wallis test, Table 4-3) of all the various source categories (Figure 4-29) shows that no significant differences exist between any of the categories regarding fish contamination levels.

Pentachlorobenzene

Pentachlorobenzene is an impurity in pentachloronitrobenzene and the sites with the highest concentrations of pentachlorobenzene are mostly in Texas and Louisiana (Figure 4-30a). It was detected at 22 percent of the sites (Figure 4-30b). The top five sites are listed below.

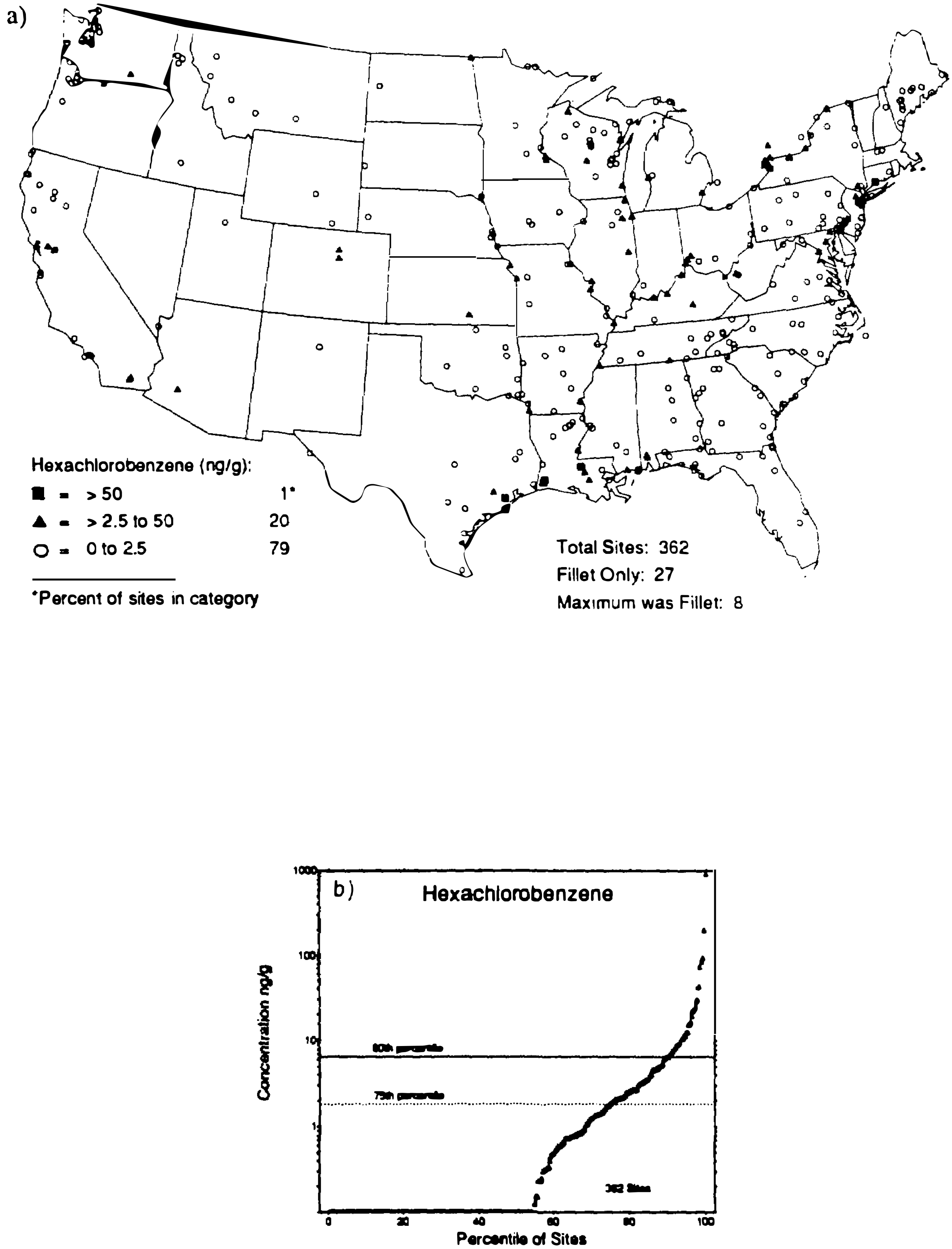
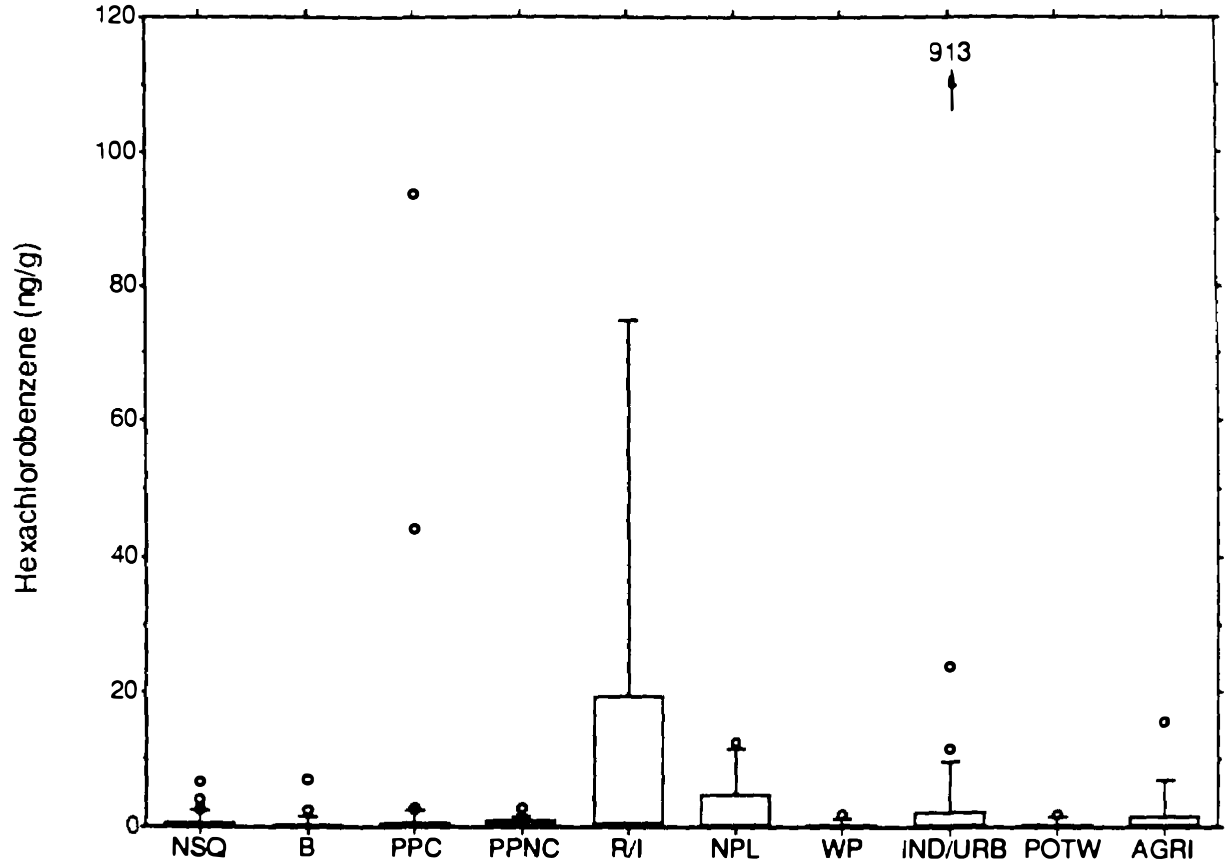


Figure 4-28. Hexachlorobenzene: a) map of geographical distribution of various concentration ranges and b) cumulative frequency distribution in fish tissue.



Summary Table for Hexachlorobenzene Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND.- 6.49	0.63	1.35	ND
Background (B)	20	ND.- 6.88	0.60	1.59	ND
Paper Mills Using Cl (PPC)	39	ND.- 93.7	3.90	16.35	ND
Other Paper Mills (PPNC)	17	ND - 2.7	0.54	0.77	ND
Refinery/Other Industry (R/I)	5	ND.- 75	15.39	33.33	0.73
Superfund Sites (NPL)	6	ND.- 12.5	2.89	5.09	ND
Wood Preservers (WP)	10	ND - 1.89	0.24	0.60	ND
Industrial/Urban Sites (IND/URB)	31	ND - 913	31.56	163.6	0.33
POTW	6	ND -1.76	0.29	0.72	ND
Agricultural (AGRI)	15	ND - 15.6	2.08	4.26	0.09

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-29. Box and whisker plot for hexachlorobenzene in fish tissue.

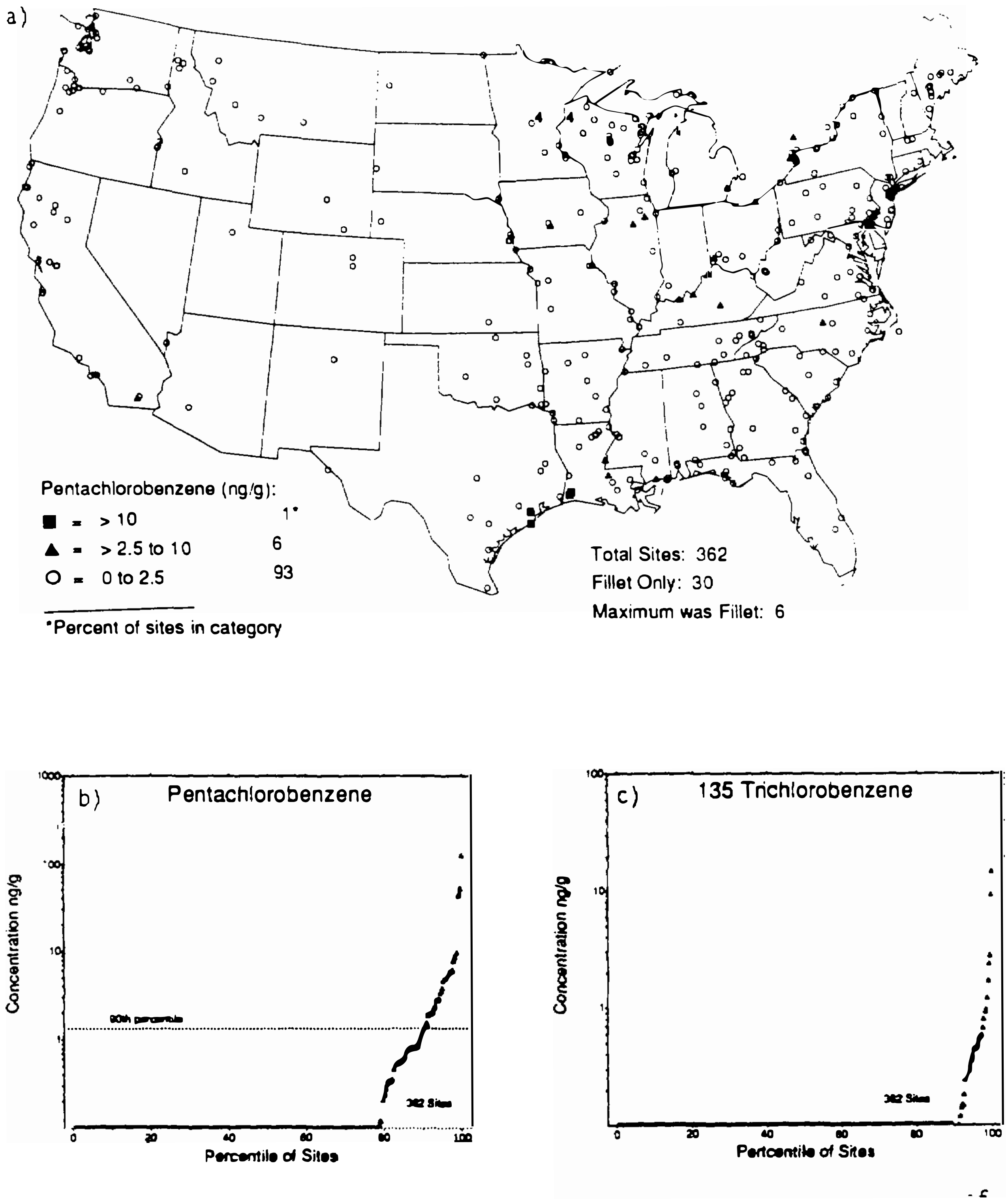


Figure 4-30. Pentachlorobenzene: a) map of geographical distribution of various concentration ranges and b) cumulative frequency distribution in fish tissue. c) Cumulative frequency distribution of 1,3,5 trichlorobenzene in fish tissue.

Pentachlorobenzene

Conc. ng/g	Episode Number	Type of Sample	Location
125	3086	WB Catfish	Bayou D'Inde, Sulfur, LA
51a)	3063	PF Spotted Sea Trout	Calcasieu R., Moss Lake, LA
46.3	3097	WB Carp	Red Lion Cr., Tybouts Corner, DE
42.6	3085	WB Sea Catfish	Brazos R., Freeport, TX
9.6	2532	WB Carp	Mississippi R., St. Francisville, LA

Four of these sites are near chemical manufacturing plants and the other site (3097) is a Superfund site with HCB contamination. In the top 10 percentile of the sites, 22 of the 36 sites out of 362 were near chemical manufacturing plants and nine were near Superfund sites of which four had HCB contamination. The box plot (Figure 4-31) shows that none of the source categories have median concentrations above detection.

1,3,5 Trichlorobenzene

The compound 1,3,5 trichlorobenzene (TCB) is used as a solvent for dyes and in the manufacturing of other organic compounds. Though detected at 11 percent of the sites, the compound 1,3,5 trichlorobenzene was detected above the quantitation limit at only three sites (Figure 4-30c). These sites are listed below:

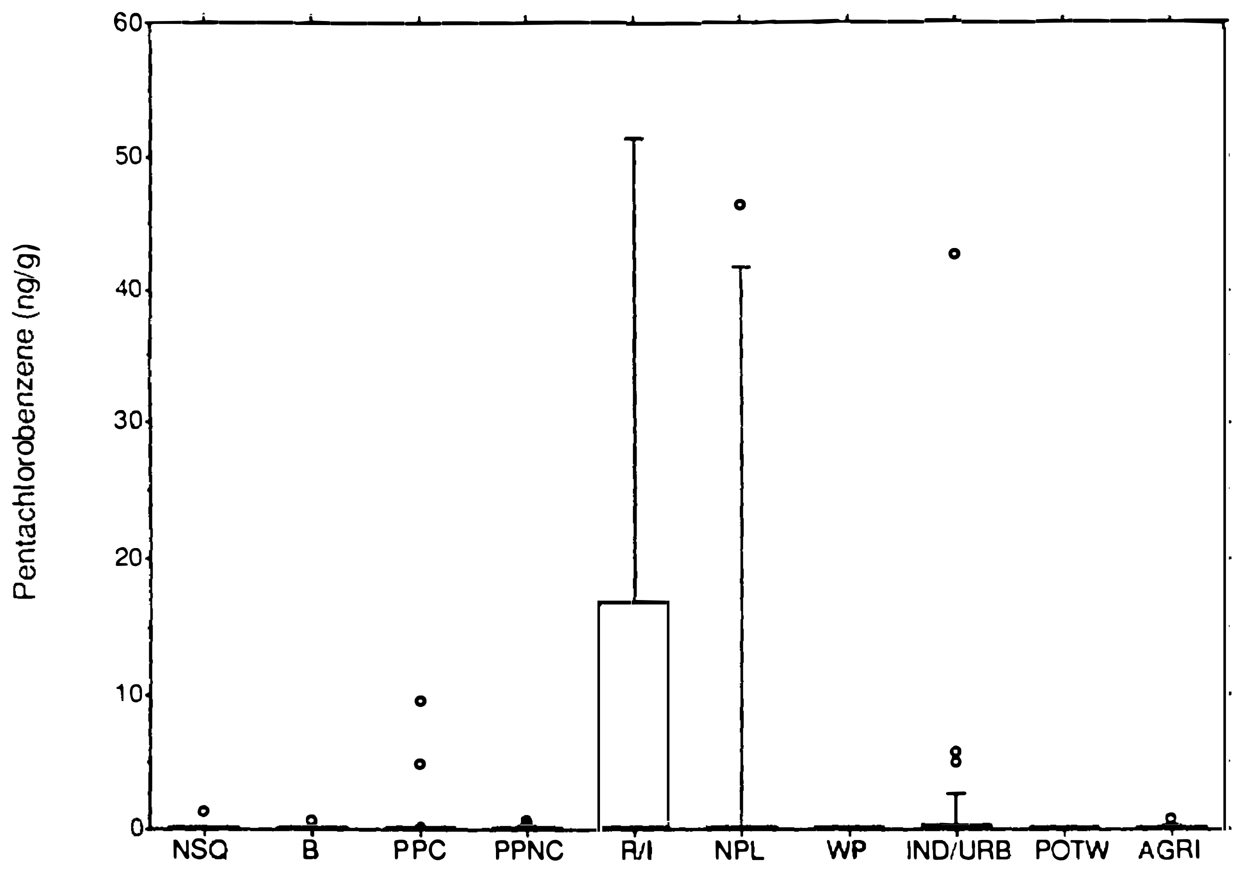
1,3,5 TCB

Conc. ng/g	Episode Number	Type of Sample	Location
14.9	3403	WB River Carpsucker	So. Fork of Holston R., Kingsport, TN
9.2	2290	WB Spotted Sucker	Savannah River, Augusta, GA
2.77	2056	WB Carp	Ohio River, West Point, KY

Sites 3403 and 2290 are near paper mills. The latter site also has other industrial/urban sources nearby. Site 2056 is near a Superfund site known to be contaminated with PCBs, dioxins, furans, and solvents. The median concentration of all source categories was below detection (Figure 4-32).

Tetrachlorobenzenes

Cumulative frequency distributions of the tetrachlorobenzenes (TECB) show that these compounds were detected at less than 15 percent of the sites (Figure 4-33a,b,c). The tetrachlorobenzenes are moderately to highly volatile and, as a result, may be higher than reported because the analytical procedures for this study included an evaporation step. The chemical 1,2,4,5 tetrachlorobenzene is used in the manufacturing of 2,4,5 T (2,4,5 trichlorophenoxyacetic acid), a

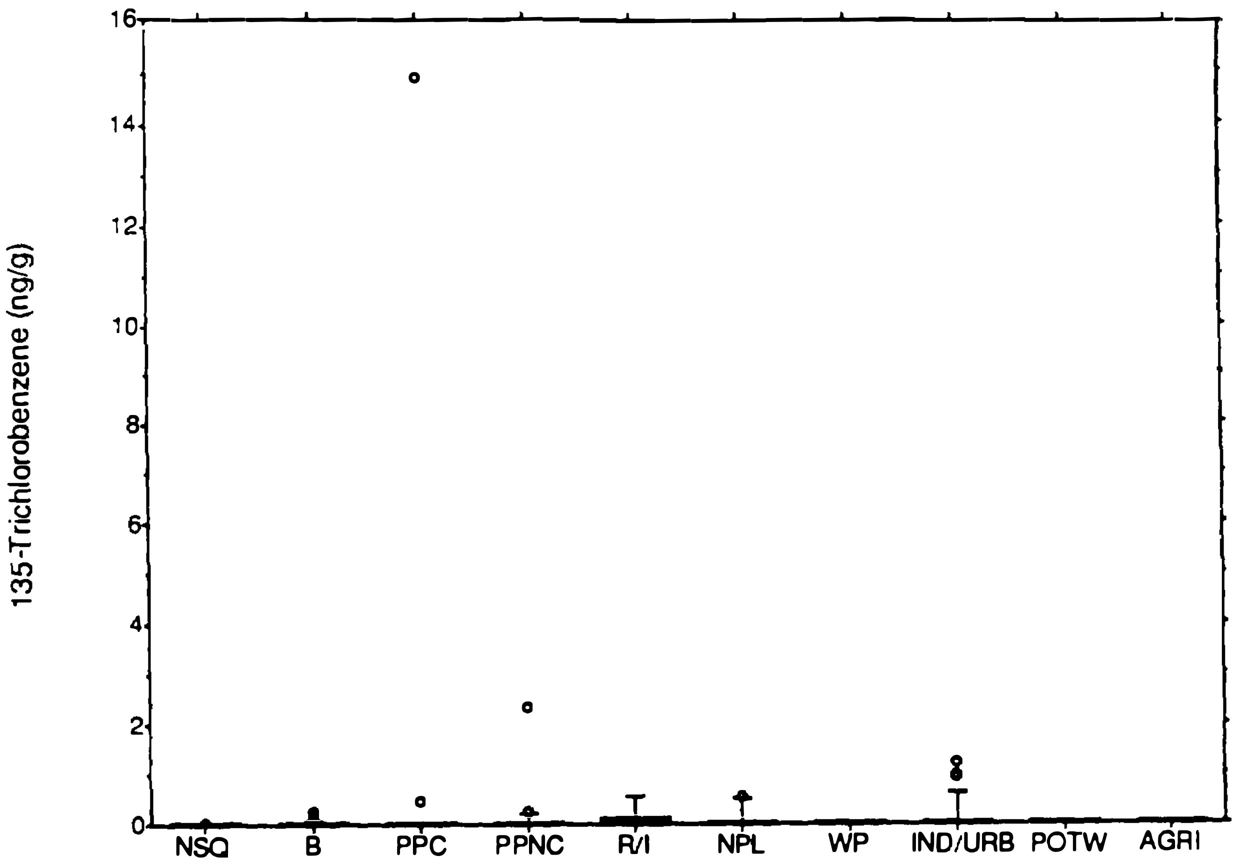


Summary Table for Pentachlorobenzene Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND - 1.26	0.03	0.20	ND
Background (B)	20	ND.- 0.6	0.03	0.13	ND
Paper Mills Using Cl (PPC)	39	ND.- 9.61	0.38	1.71	ND
Other Paper Mills (PPNC)	17	ND - 0.57	0.08	0.17	ND
Refinery/Other Industry (R/I)	5	ND.- 51e4	11.36	22.50	ND
Superfund Sites (NPL)	6	ND.- 46.3	7.72	18.90	ND
Wood Preservers (WP)	10	ND	ND	ND	ND
Industrial/Urban Sites (IND/URB)	31	ND.- 42.6	1.84	7.68	ND
POTW	6	ND	ND	ND	ND
Agricultural (AGRI)	15	NDs 0.75	0.07	0.20	ND

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-31. Box and whisker plot for pentachlorobenzene in fish tissue.



Summary Table for 1,3,5-Trichlorobenzene Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND - 0.06	0.002	0.01	ND
Background (B)	20	ND - 0.24	0.02	0.06	ND
Paper Mills Using Cl (PPC)	39	ND - 14.9	0.40	2.38	ND
Other Paper Mills (PPNC)	17	ND - 2.35	0.16	0.57	ND
Refineries (RFNY)	5	ND - 0.54	0.11	0.24	ND
Superfund Sites (NPL)	6	ND.- 0.55	0.09	0.22	ND
Wood Preservers (WP)	10	ND	ND	ND	ND
Industrial/Urban Sites (IND/URB)	31	ND - 1.20	0.13	0.32	ND
POTW	6	ND	ND	ND	ND
Agricultural (AGRI)	15	ND	ND	ND	ND

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-32. Box and whisker plot for 1,3,5 trichlorobenzene in fish tissue.

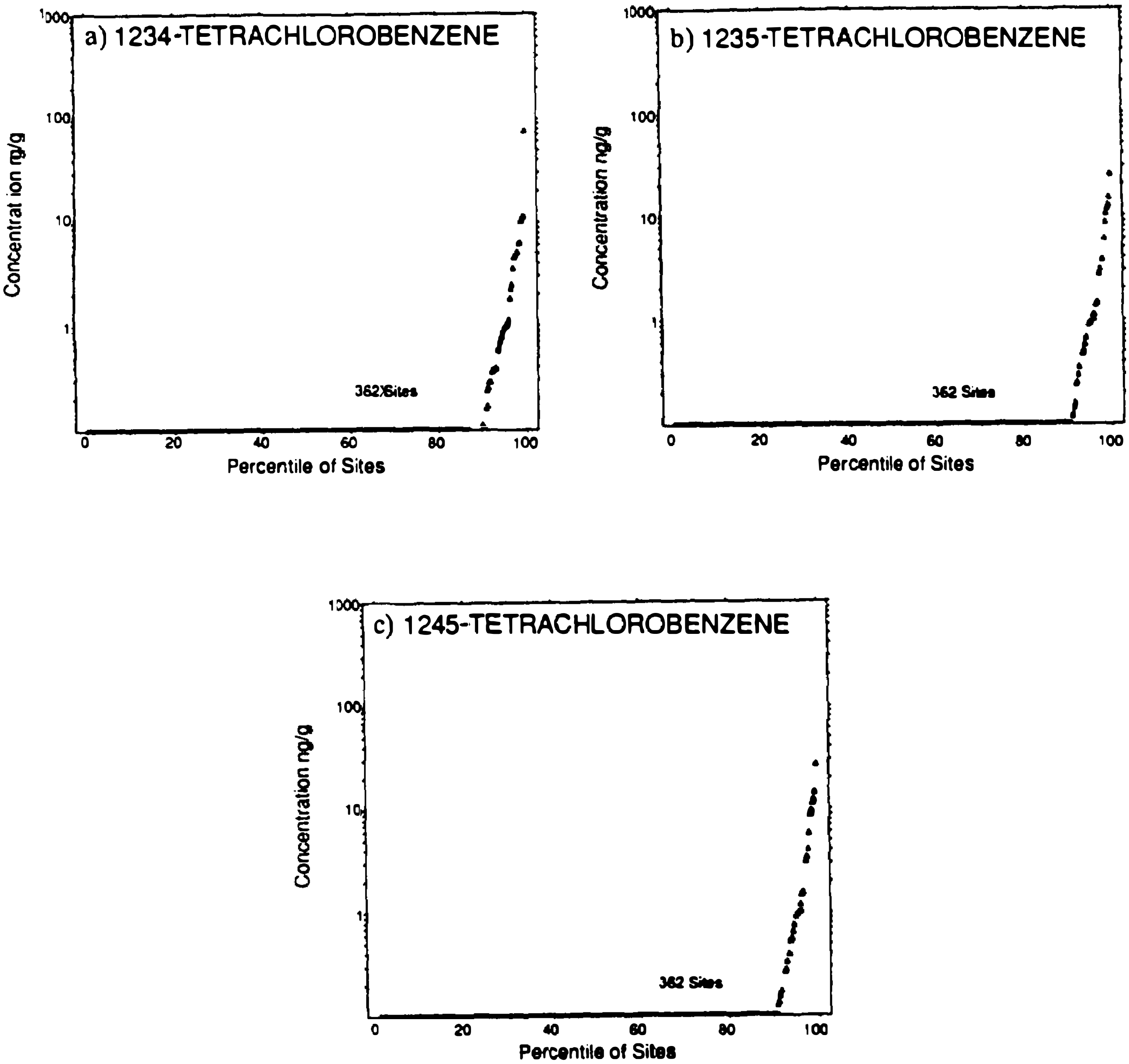


Figure 4-33. Cumulative frequency distribution of a) 1,2,3,4 tetrachlorobenzene, b) 1,2,3,5 tetrachlorobenzene and c) 1,2,4,5 tetrachlorobenzene in fish tissue.

primary component of the defoliant Agent Orange used in Vietnam. It has also been used as a precursor for the manufacture of other organic chemicals and in the dye industry. The 1,2,3,4 isomer is a component of dielectric fluids, and was the most commonly detected of the three isomers (13 percent of the sites versus 9.4 percent for 1,2,3,5 TECB and 9.1 percent for 1,2,4,5 TECB). Median concentrations were below detection for all three of these compounds. Geographic distributions of TECB concentrations are shown in Figure 4-34a,b,c.

The sites with the top five concentrations out of 362 were the same for 1,2,3,5 and 1,2,4,5 TECB as follows:

1,2,3,5 and 1,2,4,5 TECB

Conc. ng/g	Episode Number	Type of Sample	Location
28.3	3097	PF Brown Bullhead	Red Lion Creek, Tybouts Corner, DE
15.3	2056	WB Carp	Ohio River, West Point, KY
12.9	2341	WB Carpsucker	Ohio River, Markland, KY
12.0	2290	WB Spotted Sucker	Savannah River, Augusta, GA
10.7	3086	PF Red Drum	Bayou D'Inde, Sulfur, LA

The first two sampling locations are near Superfund sites, and the others are near chemical plants (2341 and 3086) and paper mills (2290).

The top five sites for 1,2,3,4 TECB are shown below. The first three are the same as described above for 1,2,3,5 and 1,2,4,5 TECB. Site 3096 is located near a refinery, industrial chemical facilities, and a POTW. Site 3094 is near chemical manufacturing plants and a POTW. Median values from all source categories were below detection (Figure 4-35).

1,2,3,4 TECB

Conc. ng/g	Episode Number	Type of Sample	Location
76.65	3097	PF Brown Bullhead	Red Lion Creek, Tybouts Corner, DE
11.50	2056	WB Carp	Ohio River, West Point, KY
11.3	2341	WB Carpsucker	Ohio River, Markland, KY
10.6	3096	WB Channel Catfish	Delaware River, Eddystone, PA
10.4	3094	BF Channel Catfish	Delaware River, Torresdale, PA

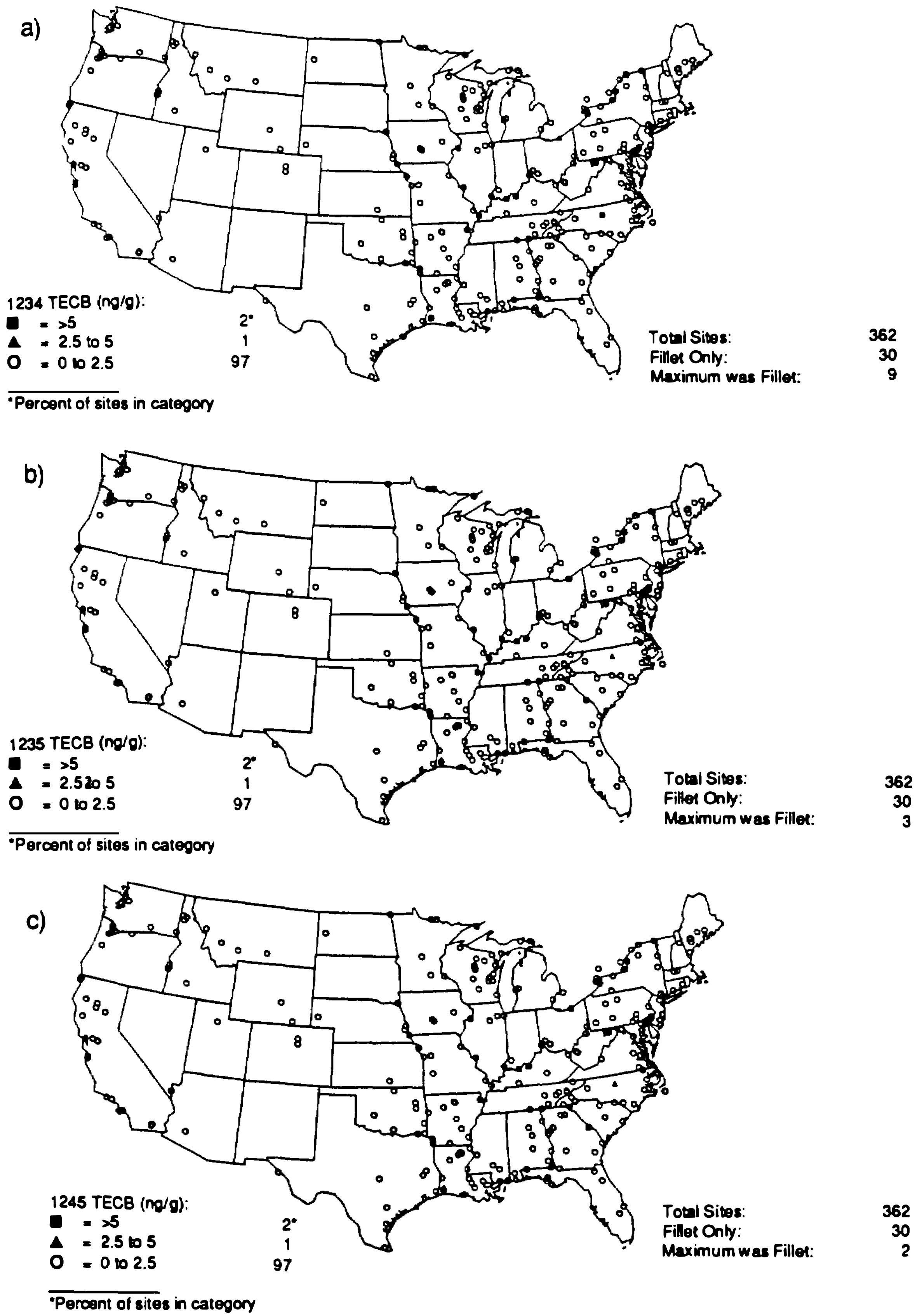
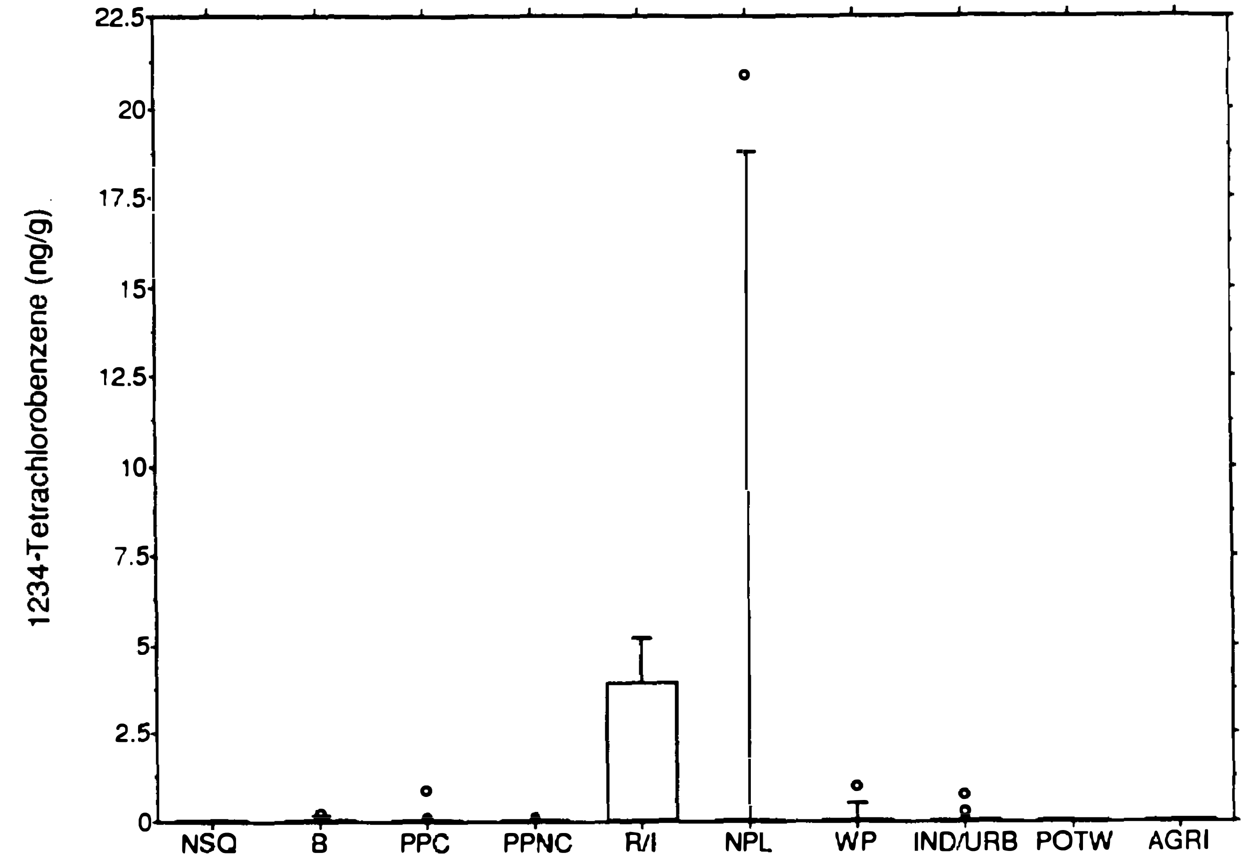


Figure 4-34. Map of geographical distribution of various concentration ranges for a) 1,2,3,4 tetrachlorobenzene, b) 1,2,3,5 tetrachlorobenzene, and c) 1,2,4,5 tetrachlorobenzene in fish tissue.



Summary Table for 1,2,3,4-Tetrachlorobenzene Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND	ND	ND	ND
Background (B)	20	ND - 0.25	0.03	0.08	ND
Paper Mills Using Cl (PPC)	39	ND.- 0.88	0.03	0.14	ND
Other Paper Mills (PPNC)	17	ND - 0.11	0.02	0.03	ND
Refinery/Other Industry (R/I)	5	ND - 5.21	1.74	2.46	ND
Superfund Sites (NPL)	6	ND.-20.92	3.49	8.54	ND
Wood Preservers (WP)	10	ND - 1.01	0.10	0.32	ND
Industrial/Urban Sites (IND/URB)	31	ND - 0.76	0.04	0.14	ND
POTW	6	ND	ND	ND	ND
Agricultural (AGRI)	15	ND	ND	ND	ND

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-35. Box and whisker plot for 1,2,3,4 tetrachlorobenzene in fish tissue.

Pesticides/Herbicides

Mirex, Chlorpyrifos, Dicofol, Methoxychlor, and Perthane

Mirex was used primarily to control fire ants in the Southeast between 1962 and 1975 (NAS, 1978). Mirex has also been used on pineapple mealy bugs in Hawaii and as a fire retardant in plastics and other products. Mirex was detected at 38 percent of the sites primarily in the Southeast and the Great Lakes region (Figure 4-36a). The chemical was produced at plants located along the Niagara River, and it occurred at high levels in this area as shown below:

Mirex

Conc. ng/g	Episode Number	Type of Sample	Location
225	2328	PF Chinook Salmon	Lake Ontario, Olcott, NY
137	3305	WB Channel Catfish	Racquette R., Massena, NY
131	2329	PF Brown Trout	Lake Ontario, Rochester, NY
85.4	3412	WB Carp	Oswego Harbor, Oswego, NY
73.7	3301	WB Carp	Eighteen Mile Cr., Olcott, NY

The box and whisker plot (Figure 4-37) shows that the highest concentration was found in the industrial/urban category. The only median value above detection was for sites in the refinery/other industry category.

Chlorpyrifos, an organophosphate insecticide, was originally developed in the 1960's to replace organochlorine pesticides such as DDT. It is used on cotton, peanuts, sorghum, and a variety of fruits and vegetables, as well as for control of termites and household pests. For chlorpyrifos, over 70 percent of fish concentrations at all sites were below detection (Figure 4-36b). The geographic distribution map shows that the few sites with relatively high concentrations (above 50 ng/g) are scattered throughout the East and Midwest and in California (Figure 4-38). The highest concentrations were observed at sites near agricultural facilities. The top 5 out of 362 sites are listed below:

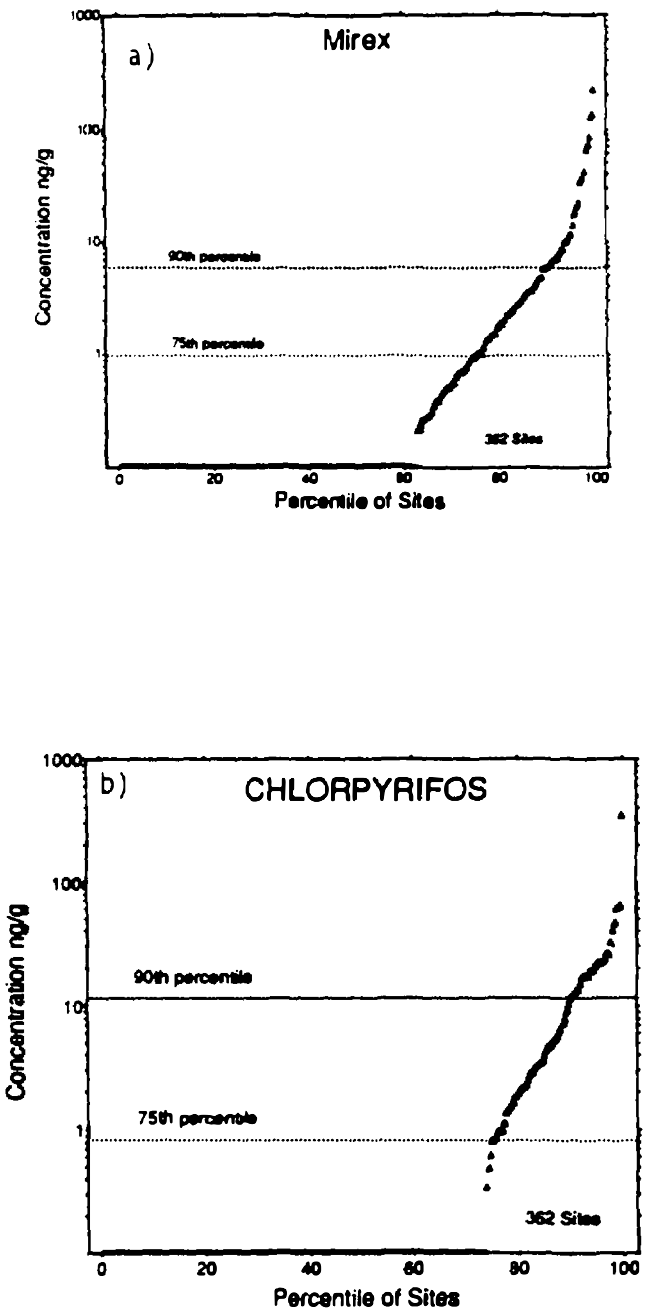
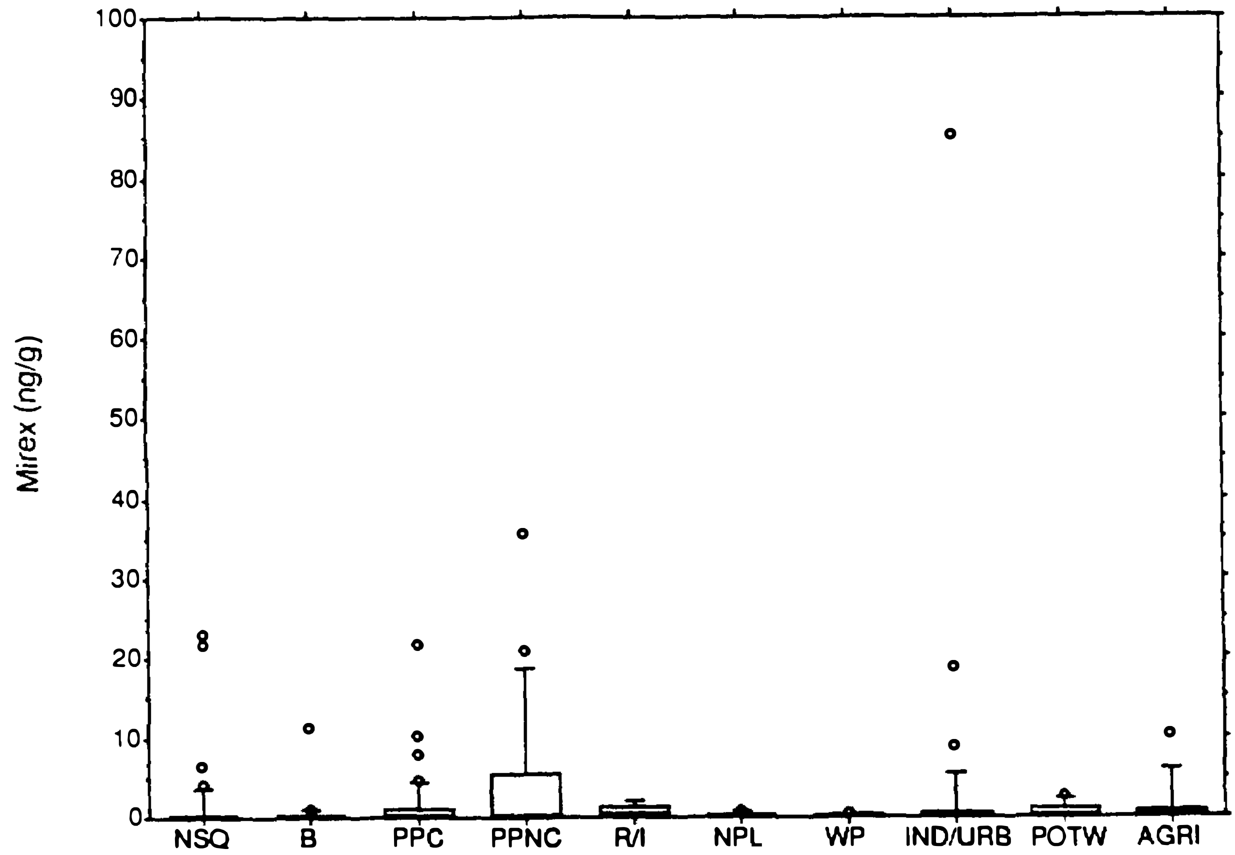


Figure 4-36. Cumulative frequency distribution of a) mirex and b) chlorpyrifos in fish tissue.



Summary Table for Mirex Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND-23.1	1.6	5.0	ND
Background (B)	20	ND-11.3	0.7	2.5	ND
Paper Mills Using Cl (PPC)	39	ND-21a6	1.6	4.0	ND
Other Paper Mills (PPNC)	17	ND-35.5	4.9	9.6	ND
Refineries/Other Industry (R/I)	5	ND-2.0	0.8	0.9	0.7
Superfund Sites (NPL)	6	ND-0.8	0.2	0.3	ND
Wood Preservers (WP)	10	ND-0.5	0.1	0.2	ND
Industrial/Urban Sites (IND/URB)	31	ND-85.4	3.9	15.6	ND
POTW	6	ND-2.6	0.6	1.1	ND
Agricultural (AGRI)	15	ND-10.4	1.3	3.0	ND

n = number of sites in category. ND's set at 0. Maximum concentrations at each site were used.

Figure 4-37. Box and whisker plot for mirex in fish tissue.

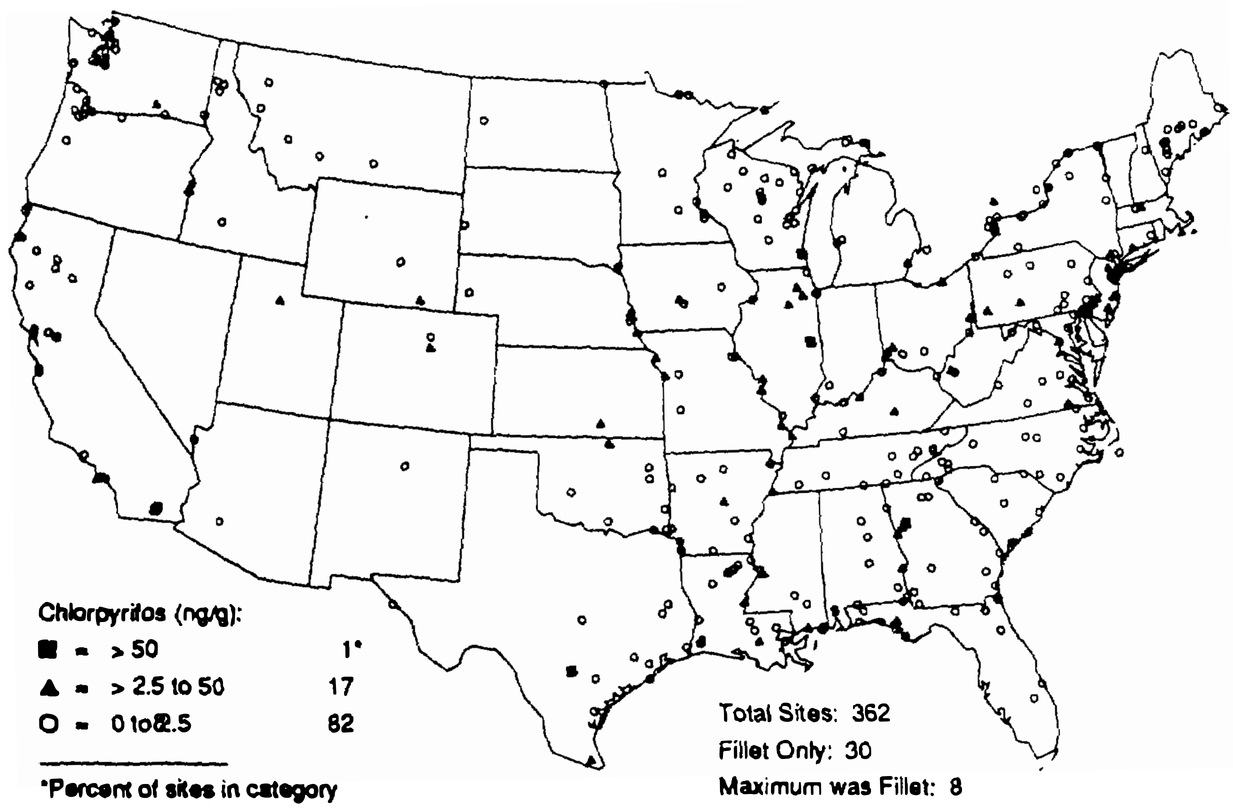


Figure 4-38. Map of geographical distribution of various concentration ranges for chlorpyrifos in fish tissue.

Chlorpyrifos

Conc. ng/g	Episode Number	Type of Sample	Location
344	3282	WB Carp	Alamo R., Calipatria, CA
64.5	3375	WB Carp	Chattahoochee R., Austell, GA
63.7	3071	WB Carp	San Antonio R., Elmendorf, TX
62.7	3141	PF Northern Pike	Milwaukee R., Milwaukee, WI
61.7	3283	WB Carp	New R., Westmoreland, CA

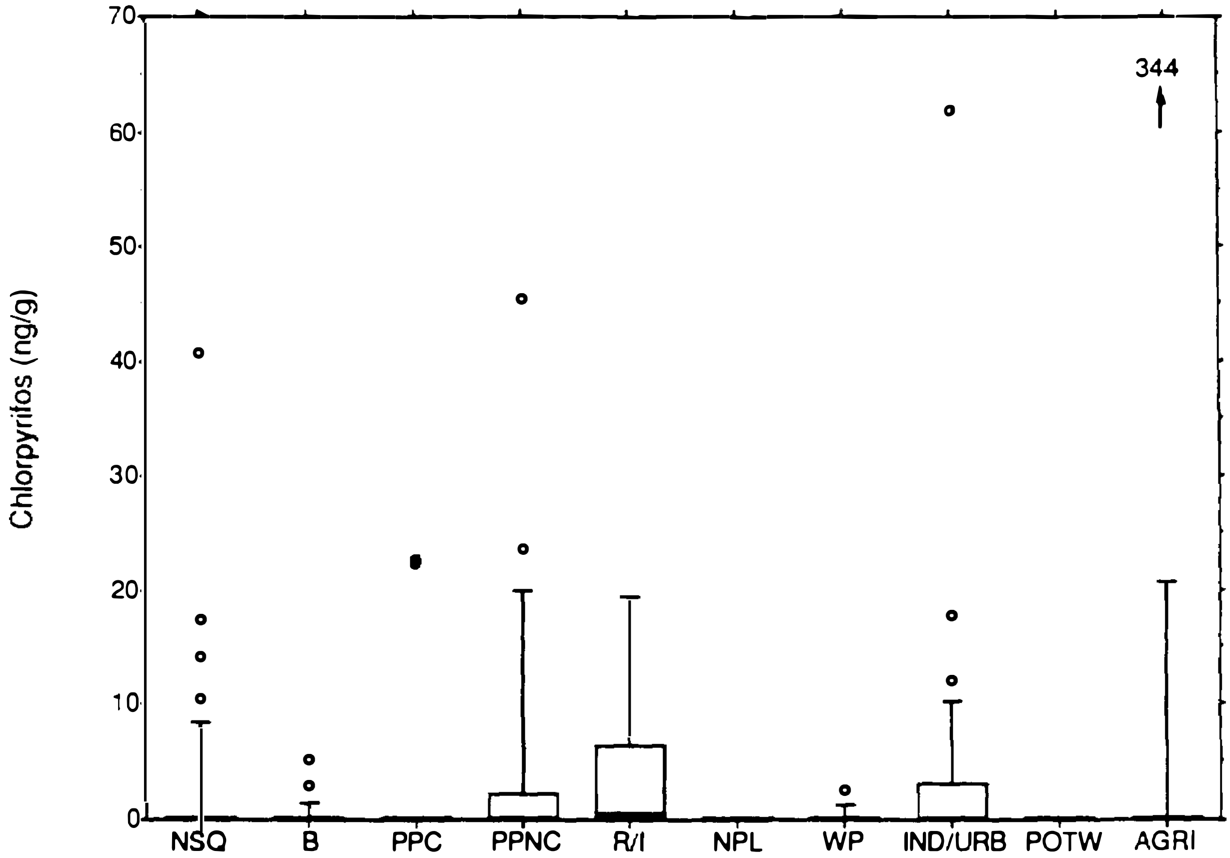
Three of the sites are located in agricultural areas, while the remaining sites (3071 and 3141) are located in urban areas with a variety of nearby industrial sources. The box and whisker plot also shows that the highest mean concentration was for sites in the agricultural category (Figure 4-39).

Dicofol, methoxychlor, and perthane are pesticides similar in structure to DDT, but less persistent. Dicofol and methoxychlor are active ingredients of currently registered pesticides. These three pesticides were detected at less than 16 percent of the sites versus 99 percent of the sites for DDE, the metabolic breakdown product of DDT (Figure 4-40a,b,c). Dicofol is primarily used to control mites on cotton and citrus crops. Other crops to which it has been applied include apples, pears, apricots, cherries, and vegetables. It is also used on turf and shade trees. Methoxychlor, also similar to DDT, has not been widely used since 1982. Prior to that time, it had been applied to a wide variety of fruit, vegetable, and forage crops and had been used to control mosquitos and flies in homes and businesses. Methoxychlor has a lower bioaccumulation factor than dicofol and was detected at fewer sites (7 percent versus 15.5 percent). Dicofol and methoxychlor concentrations were greater than the quantification limit of 2.5 ng/g in samples from 7 and 5 percent of the sites, respectively (see Figure 4-41a,b). Most of the sites appear to be in agricultural areas where citrus and other fruits and vegetables are grown. The box plot for dicofol is shown in Figure 4-42. The highest mean concentration of all the categories was for sites near agricultural areas (2.7 ng/g).

The highest five concentrations of dicofol and methoxychlor are listed below:

Dicofol

Conc. ng/g	Episode Number	Type of Sample	Location
74.3	3355	WB Carp	Old Mormon Slough, Stockton, CA
36.0	3252	WB Sucker	Boise River, Parma, ID
21.1	3198	WB Sucker	South Platte River, Denver, CO
18.4	3208	WB Sucker	Malheur River, Ontario, OR
14.9	3117	PF Lake Trout	Lake Michigan, Waukegan, IL



Summary Table for Chlorpyrifos Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND-40.8	2.34	7.43	ND
Background (B)	20	ND-5.13	0.40	1.29	ND
Paper Mills Using Cl (PPC)	39	ND-22.6	1.15	5.02	ND
Other Paper Mills (PPNC)	17	ND-45.6	4.71	11.98	ND
Refineries/Other Industry (R/I)	5	ND-19.4	4.40	8.43	0.48
Superfund Sites (NPL)	6	ND	ND	ND	ND
Wood Preservers (WP)	10	ND-2.51	0.25	0.79	ND
Industrial/Urban Sites (IND/URB)	31	ND-61..7	3.89	11.50	ND
POTW	6	ND	ND	ND	ND
Agricultural (AGRI)	15	ND-344	24.46	88.56	ND

n = number of sites in category. ND's set at 0.
Maximum value at each site was used.

Figure 4-39. Box and whisker plot for chlorpyrifos in fish tissue.

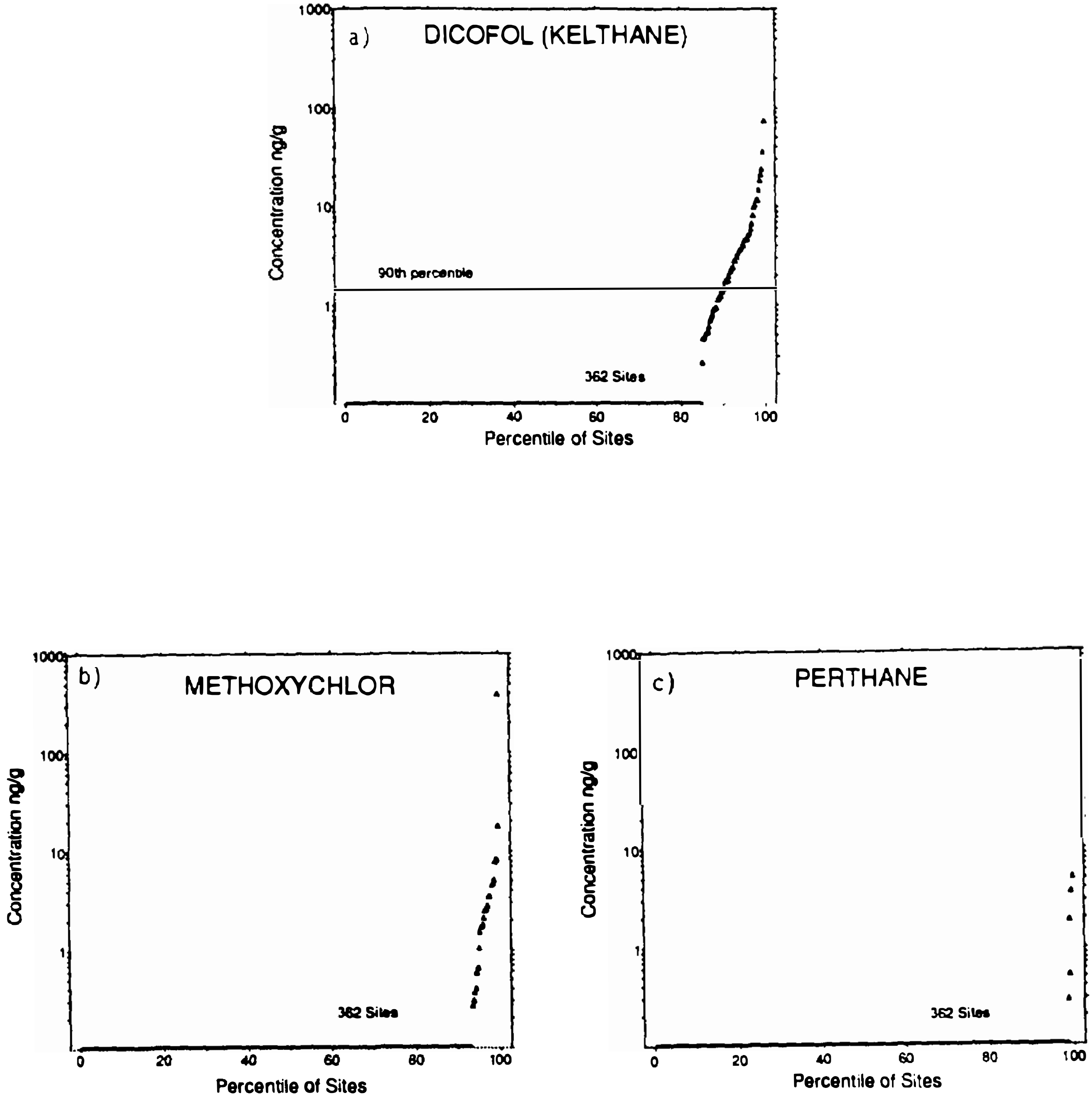


Figure 4-40. Cumulative frequency distribution of a) dicofol (kelthane), b) methoxychlor, and c) perthane in fish tissue.

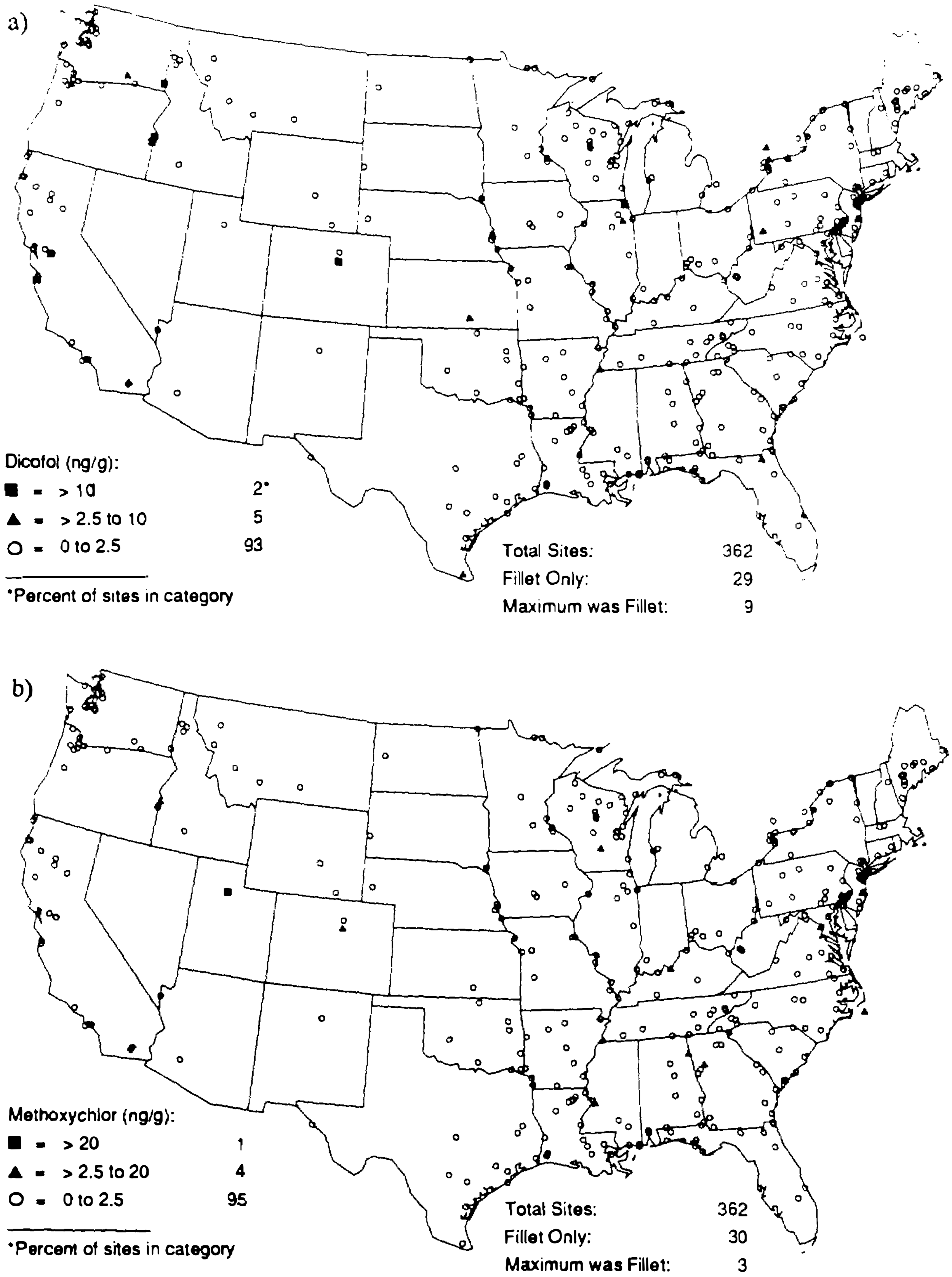
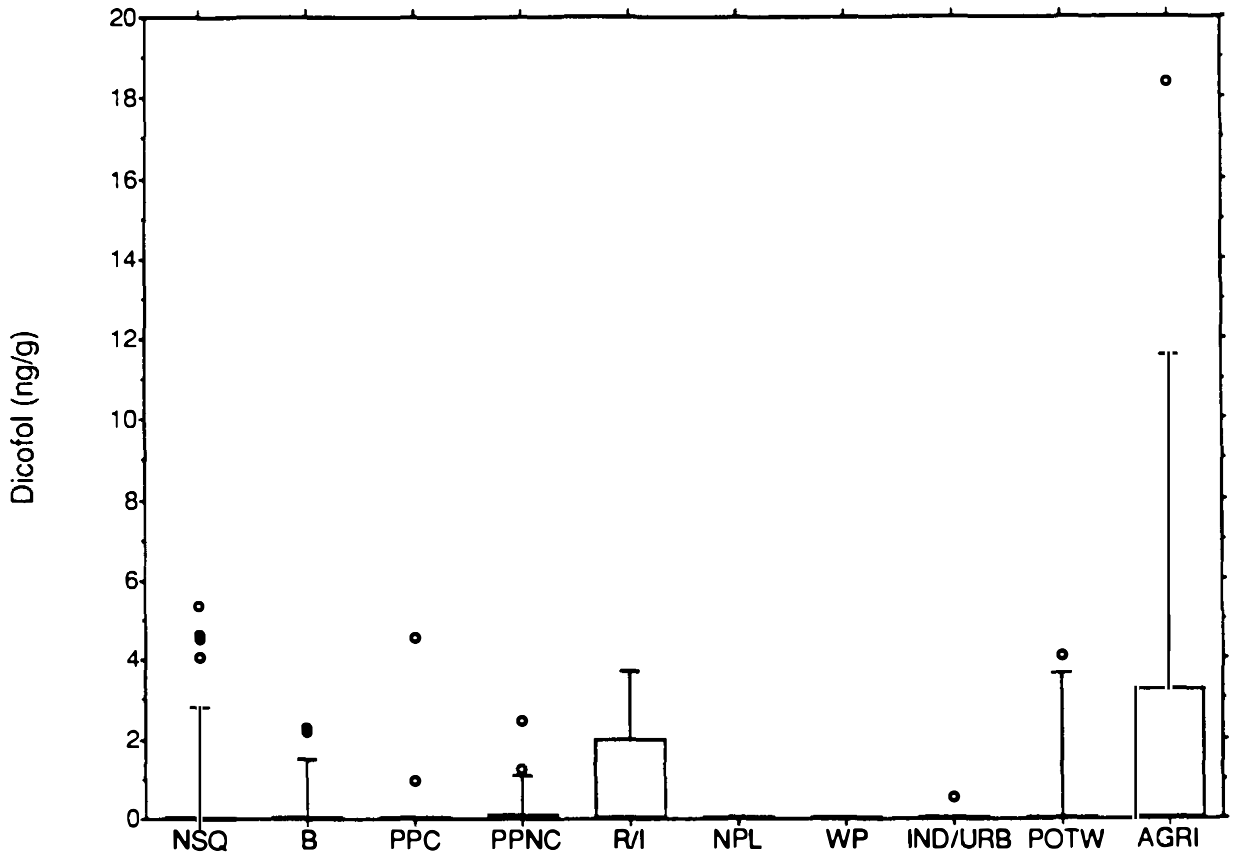


Figure 4-41. Map of geographical distribution of various concentration ranges for a) dicofol and b) methoxychlor in fish tissue.



Summary Table for Dicofol Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND-5.37	0.54	1.44	ND
Background (B)	20	ND-2.29	0.27	0.70	ND
Paper Mills Using Cl (PPC)	39	ND-4.53	0.14	0.74	ND
Other Paper Mills (PPNC)	17	ND-2.44	0.28	0.65	ND
Refineries/Other Industry (R/I)	5	ND-3.69	1.02	1.61	ND
Superfund Sites (NPL)	6	ND	ND	ND	ND
Wood Preservers (WP)	10	ND	ND	ND	ND
Industrial/Urban Sites (IND/URB)	31	ND-0.50	0.02	0.09	ND
POTW	6	ND-4.09	0.68	1.67	ND
Agricultural (AGRI)	15	ND-18.40	2.66	5.41	ND

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-42. Box and whisker plot for dicofol in fish tissue.

Methoxychlor

Conc. ng/g	Episode Number	Type of Sample	Location
393.	3195	WB Chub	Jordan River, Salt Lake City, UT
17.9	3375	WB Carp	Chattahoochee River, Austell, GA
8.22	2056	WB Carp	Ohio River, West Point, KY
8.[illegible]5	3172	WB Carp	Coosa River, AL/GA State Line
7.7[illegible]	3144	WB Carp	Fox River, Portage, WI

The two highest concentrations (3355 and 3195) were found near Superfund sites. The Stockton, California, site is also influenced by agricultural runoff. Two additional locations were near Superfund sources which could be identified as the cause for the high concentrations. Agricultural areas and pesticide manufacturing plants were also near sites in the top 10 percentile.

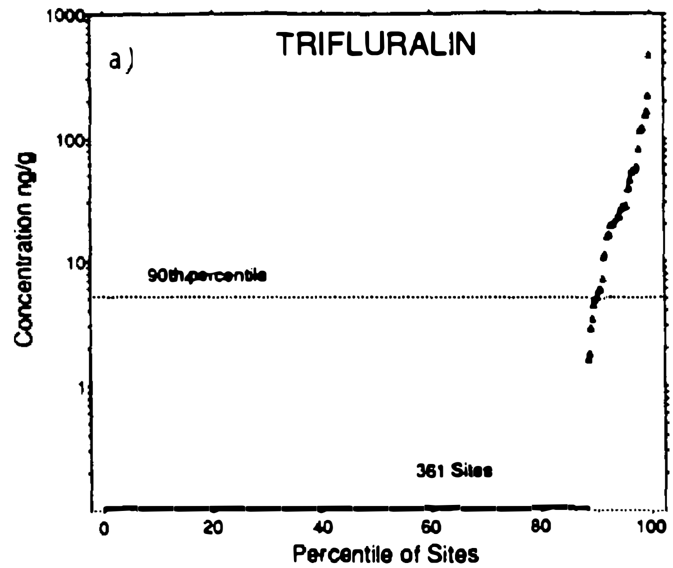
Perthane was detected above the quantitation limit in only one sample—a whole body catfish from the Delaware River at Torresdale, Pennsylvania (3094) where this compound was manufactured. Prior to 1980, perthane was used as an insecticide on fruit and vegetable crops and to protect woolens against moths and beetles.

Trifluralin and Isopropalin

Trifluralin and isopropalin, both currently registered dinitroaniline herbicides, were found above the quantitation limit at 11 and 3 percent of the sites, respectively (Figure 4-43a,b). The largest quantities of trifluralin are used primarily on soybeans, cotton, peanuts, wheat, and barley. The States with the highest uses are Arkansas, Illinois, Iowa, Minnesota, Missouri, North Dakota, South Carolina, Tennessee, and Texas (Resources for the Future, 1986). With a few exceptions, the sites with the highest concentrations were located in these States. Three of the sites on the Missouri River in Nebraska and Kansas were located near pesticide manufacturing plants (Figure 4-44a,b). Trifluralin has a low leaching potential from soils due to its strong capacity for sorption. Isopropalin is less persistent in the aquatic environment due to its greater volatility. Isopropalin was also used on fewer crops, primarily tobacco, peppers, and tomatoes, and therefore would be expected to be less prevalent. At present, the only currently registered use is for tobacco. Box plots for trifluralin and isopropalin show that all median values for the categories were below detection (Figures 4-45 and 4-46, respectively).

Endrin

Endrin is an organochlorine pesticide and a contaminant of dieldrin. Endrin was detected in at least one sample from 10.5 percent of the sites (Figure 4-47a). Endrin is less persistent in the environment than dieldrin and has a lower bioconcentration factor. Endrin was used on tobacco crops prior to cancellation of this use in 1964. Until 1979 it was used mostly to control bollworms on cotton in the Southeast. Other past uses included controlling termites, mice, and rodents, and treatment for a variety of grains and other crops. In 1984, all registered uses of endrin were



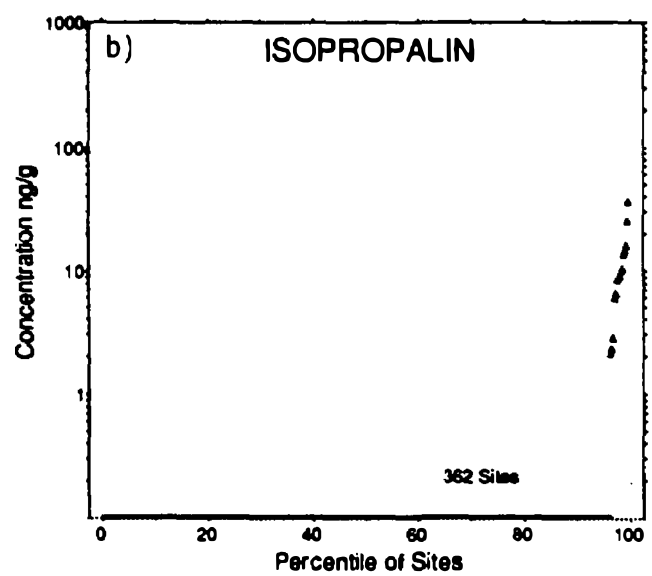
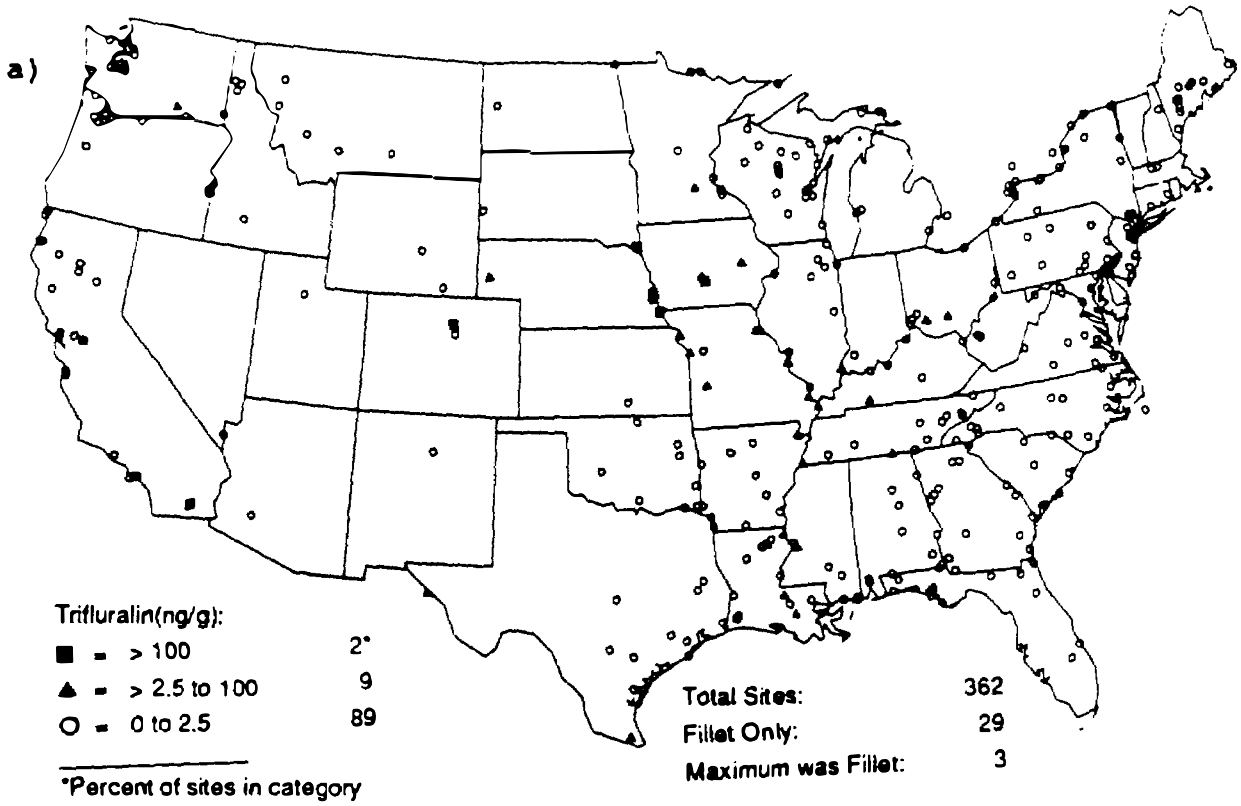


Figure 4-43. Cumulative frequency distribution of a) trifluralin and b) isopropalin in fish tissue.



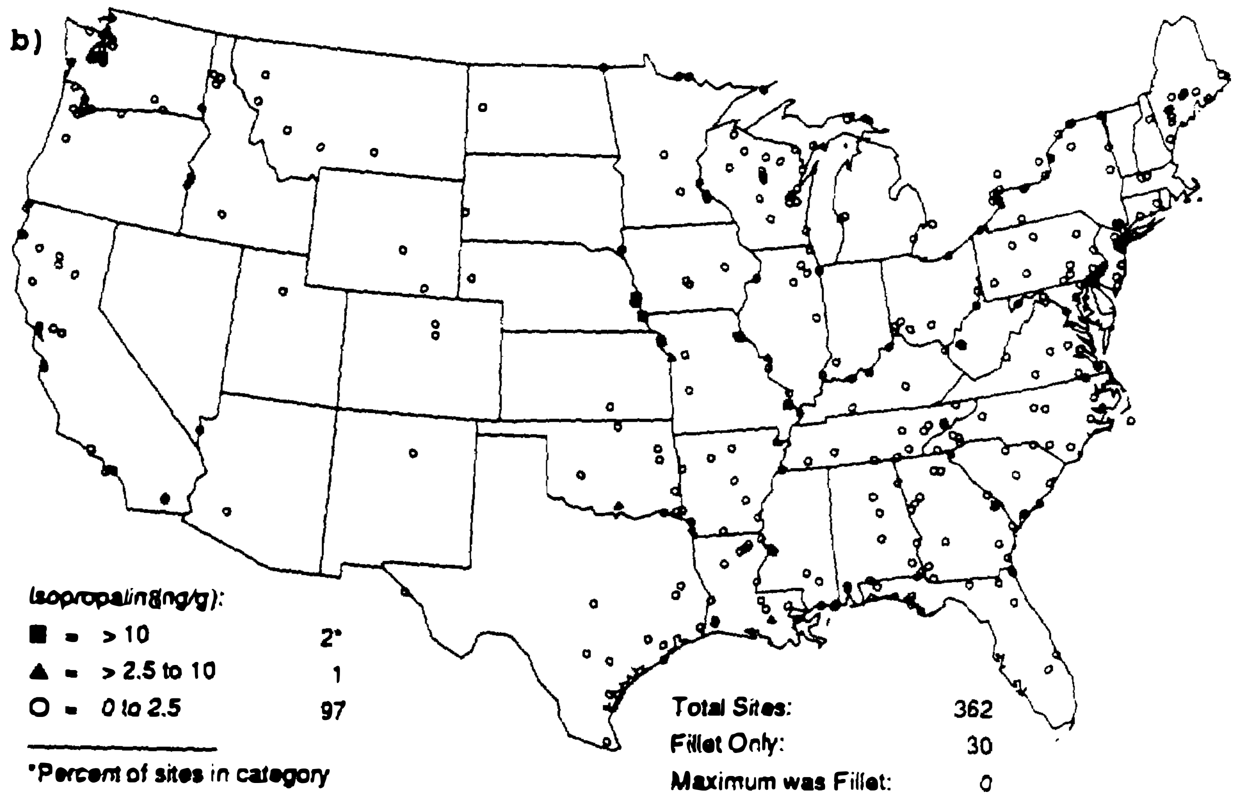
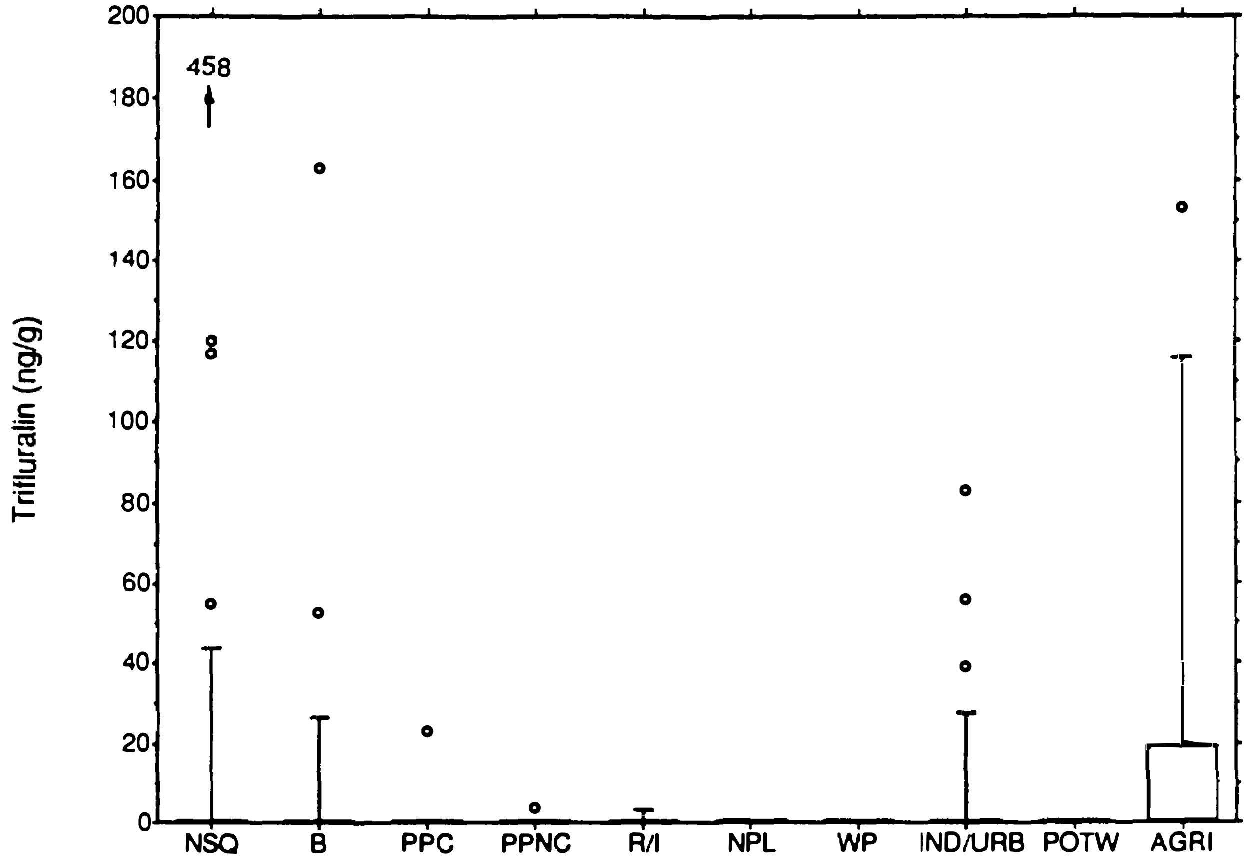


Figure 4-44. Map of geographical distribution of various concentration ranges for a) trifluralin and b) isopropalin in fish tissue.

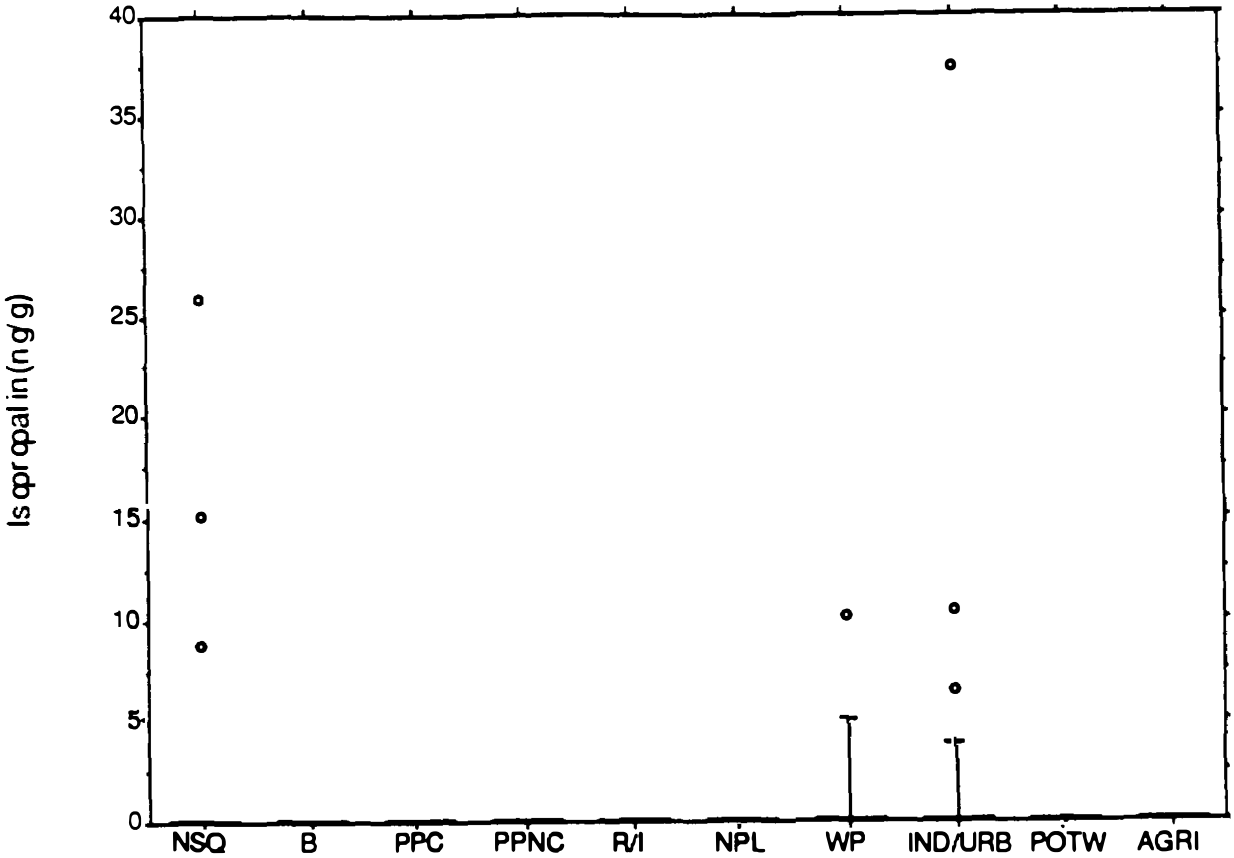


Summary Table for Trifluralin Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND-458	20.92	77.01	ND
Background (B)	20	ND-163	10.80	37.73	ND
Paper Mills Using Cl (PPC)	39	ND-23.1	0.59	3.70	ND
Other Paper Mills (PPNC)	17	ND-3.4	0.20	0.82	ND
Refineries (RFNY)	5	ND.- 2.9	0.58	1.30	ND
Superfund Sites (NPL)	6	ND	ND	ND	ND
Wood Preservers (WP)	10	ND	ND	ND	ND
Industrial/Urban Sites (IND/URB)	31	ND-82.8	6.37	18.83	ND
POTW	6	ND	ND	ND	ND
Agricultural (AGRI)	15	ND-153	23.35	46.52	ND

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-45. Box and whisker plot for trifluralin in fish tissue.

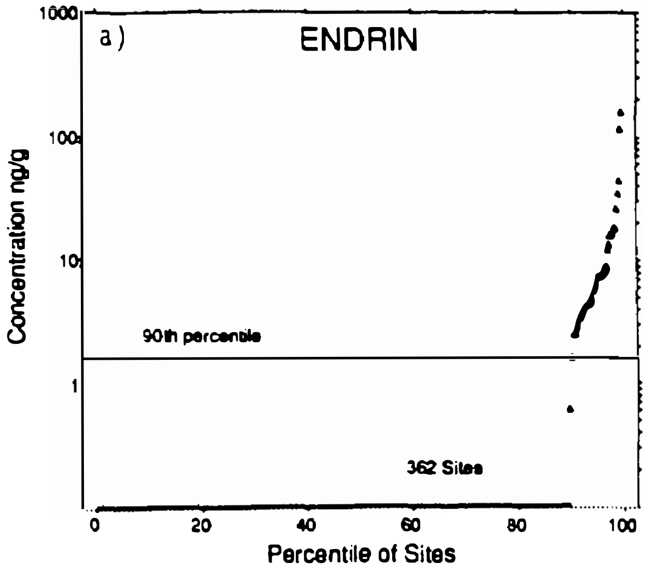


Summary Table for Isopropalin Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND-25.9	1.27	4.89	ND
Background (B)	20	ND	ND	ND	ND
Paper Mills Using Cl (PPC)	39	ND	ND	ND	ND
Other Paper Mills (PPNC)	17	ND	ND	ND	ND
Refinery/Other Industry(R/I)	5	ND	ND	ND	ND
Superfund Sites (NPL)	6	ND	ND	ND	ND
Wood Preservers (WP)	10	ND-10.2	1.02	3.23	ND
Industrial/Urban Sites (IND/URB)	31	ND-37.5	1.83	6.98	ND
POTW	6	ND	ND	ND	ND
Agricultural (AGRI)	15	ND	ND	ND	ND

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-46. Box and whisker plot for isopropalin in fish tissue.



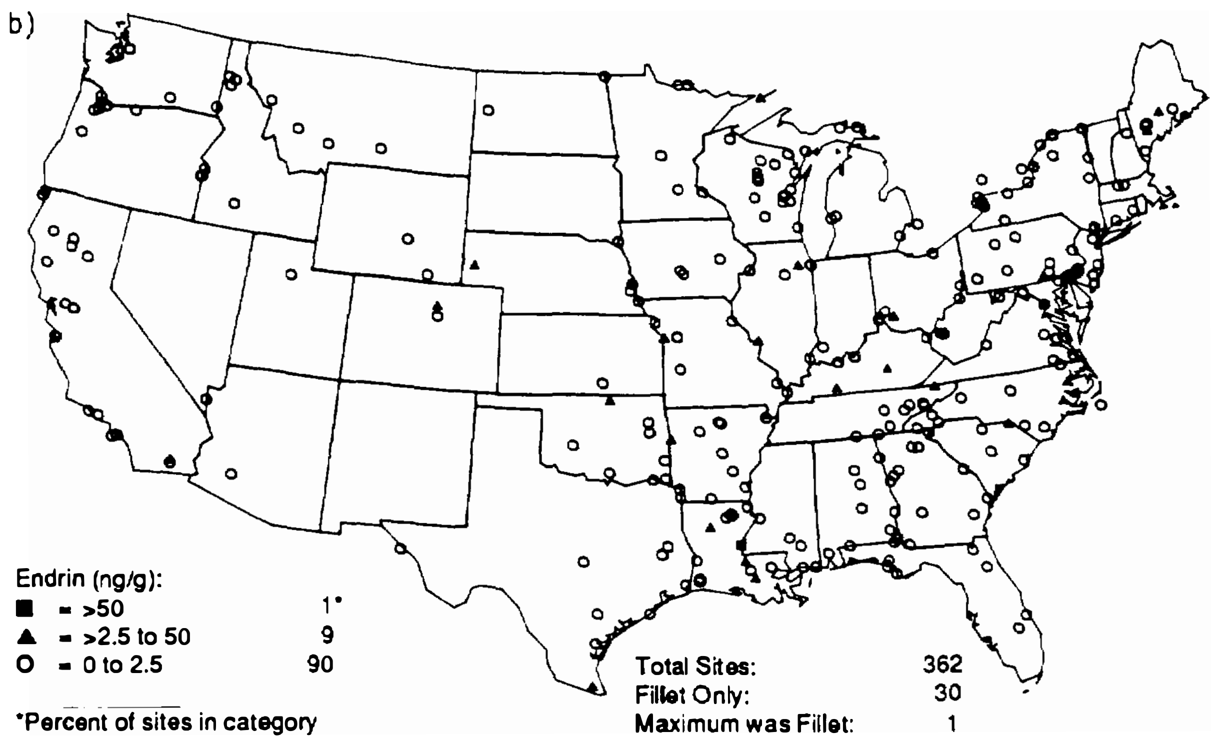


Figure 4-47. Endrin: a) cumulative frequency distribution and b) map of geographical distribution of various concentration ranges in fish tissue.

voluntarily canceled. The geographic distribution of sites is shown in Figure 4-47b. The box plot (Figure 4-48) shows that median concentrations for all source categories were below detection.

COMPOUNDS DETECTED AT LESS THAN 10 PERCENT OF THE SITES[4]

Octachlorostyrene

Octachlorostyrene is not intentionally produced. It can be formed as a by-product of the electrolytic production of chlorine using graphite anodes and coal tar pitch and the electrolytic production of magnesium. The sites where it occurred at levels above quantification (2.5 ng/g) are located in areas where industrial organic chemicals are manufactured. It was detected at only 9 percent of the sites (Figure 4-49a).

Hexachlorobutadiene

Hexachlorobutadiene is a by-product of the carbon disulfide process for the manufacture of the solvent carbon tetrachloride. It was detected in at least one sample from three percent of the sites (Figure 4-49b). Concentrations were above 2.5 ng/g at only four sites. The top five sites (all of which are near organic chemical manufacturing plants) are listed below:

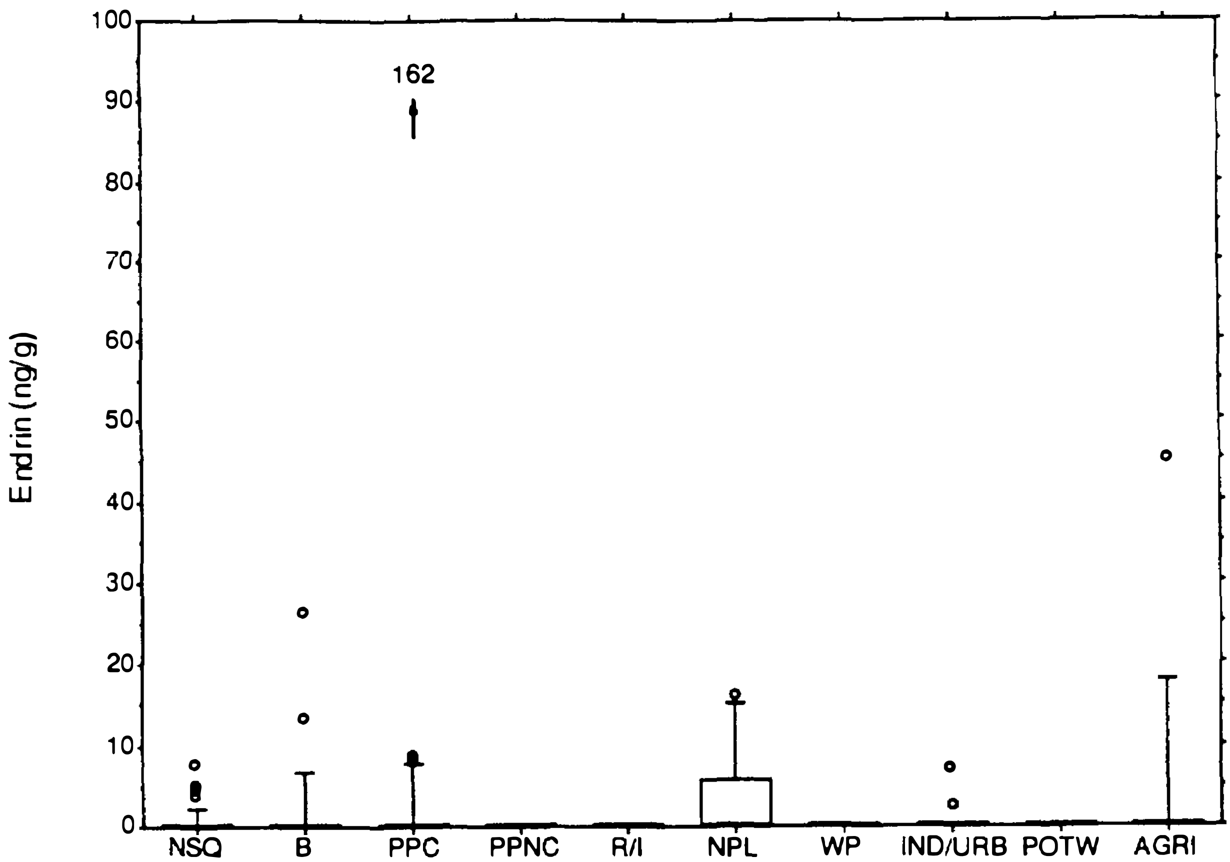
Hexachlorobutadiene

Conc. ng/g	Episode Number	Type of Sample	Location
164.00	3063	WB Sea Catfish	Calcasieu R., Moss Lake, LA
23.00	3085	WB Sea Catfish	Brazos R., Freeport, TX
10.50	3115	PF Catfish	Mississippi R., E. St. Louis (Sauget), IL
2.54	3065	WB Flathead Catfish	Mississippi R., Baton Rouge, LA
2.37	3086	WB Catfish	Bayou D'Inde, Sulfur, LA

Diphenyl Disulfide

Diphenyl disulfide was detected at only two sites (Figure 4-49c). This compound is used in small amounts in the pharmaceutical industry, in the vulcanizing of rubber, and as a flavoring agent.

4 Some chemicals found at less than 10 percent were presented elsewhere for ease of discussion. See footnotes 2, page 57, and 3, page 91.



Summary Table for Endrin Box Plot

Site Category	n	Concentration Range ng/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND-7.5	0.53	1.65	ND
Background (B)	20	ND-26.5	2.00	6.50	ND
Paper Mills Using Cl (PPC)	39	ND-162	5.22	25.90	ND
Other Paper Mills (PPNC)	17	ND	ND	ND	ND
Refinery/Other Industry(R/I)	5	ND	ND	ND	ND
Superfund Sites (NPL)	6	ND-16.2	3.64	6.55	ND
Wood Preservers (WP)	10	ND	ND	ND	ND
Industrial/Urban Sites (IND/URB)	31	ND-7.37	0.32	1.38	ND
POTW	6	ND	ND	ND	ND
Agricultural (AGRI)	15	ND-45.4	4.23	12.30	ND

n = number of sites in category. ND's set at 0.
Maximum concentrations at sites were used.

Figure 4-48. Box and whisker plot for endrin in fish tissue.

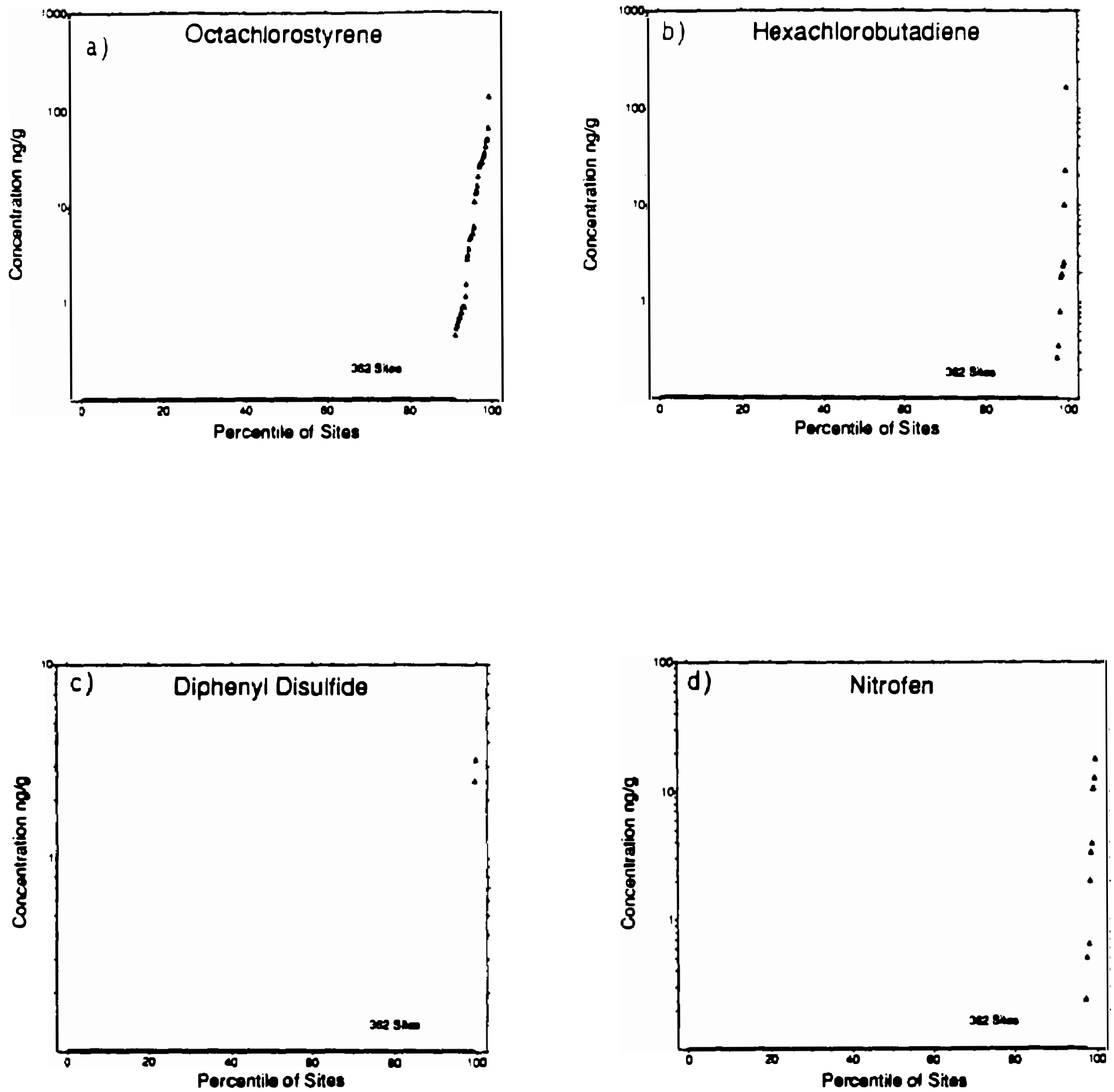


Figure 4-49. Cumulative frequency distribution of a) octachlorostyrene, b) hexachlorobutadiene, c) diphenyl disulfide, and d) nitrofen in fish tissue.

Pesticides/Herbicides

Nitrofen

Nitrofen is a selective herbicide that has not been used in the United States since 1984. Prior to that time it was used to control weeds in vegetables including sugar beets, rice, and on cereal grains. It can biodegrade and undergo photolysis so this chemical is less persistent than a compound such as DDT, and was detected at only 2.8 percent of the sites (Figure 4-49d). This compound was above the quantitation limit at the following sites:

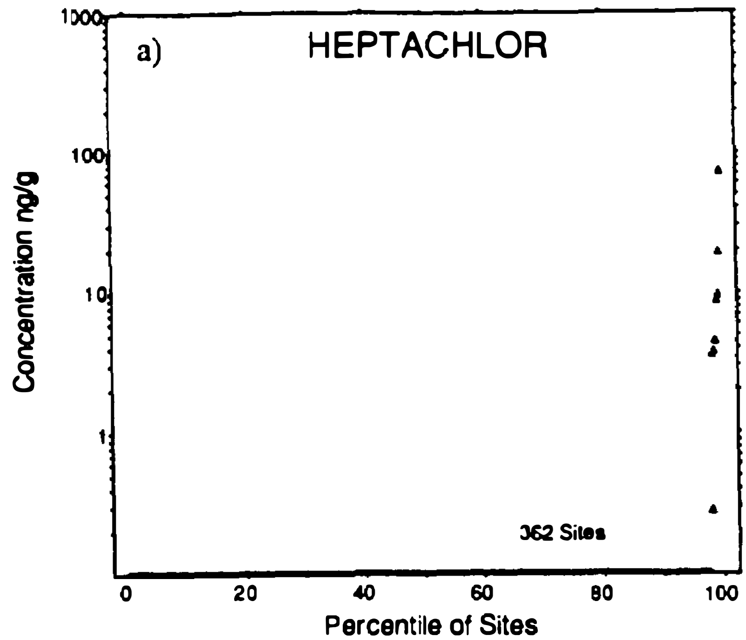
Nitrofen

Conc. ng/g	Episode Number	Type of Sample	Location
17.9	3354	WB Carp	New Mormon Slough, Stockton, CA
12.8	3300	WB White Sucker	Niagara River Delta, Porter, NY
10.4	2654	WB Carp	Toms River, NJ
10.6	3302	WB White Sucker	Niagara River, Lewiston, NY
3.95	3288	PF Squawfish	Blanco Drain, Salinas, CA

The site with the highest concentration is located near a Superfund site, as is the Toms River, New Jersey, site. The Stockton, California, site is also influenced by agricultural runoff. The Niagara River sites are near chemical manufacturing facilities and agricultural areas. The Blanco Drain is located in an agricultural irrigated area where pesticides are used extensively.

Heptachlor and Heptachlor Epoxide

Heptachlor is an insecticide that has been used to control fire ants in southern States and soil insects on corn. Its uses were limited in 1983 to subsurface termite control and dipping of nonfood roots and tops. Massachusetts, Minnesota, and New York allow no uses. It is also a contaminant of chlordane, which is widely used for termite control, especially in urban areas. Heptachlor is moderately volatile and can also be transformed by other environmental processes including hydrolysis and photolysis. It is metabolically converted to heptachlor epoxide, which bioaccumulates to a greater extent than heptachlor and is less affected by transformation processes. Heptachlor epoxide was detected in samples from more sites and, in general, at higher concentrations than heptachlor (Figure 4-50a,b). Thirteen percent of the sites had maximum concentrations over 2.5 ng/g for heptachlor epoxide, but only 3 percent for heptachlor. Heptachlor epoxide was found at higher concentrations in the Midwest, particularly in the Mississippi River system (Figure 4-51). The box plot for heptachlor epoxide shows that median concentrations for all categories were below detection (Figure 4-52).



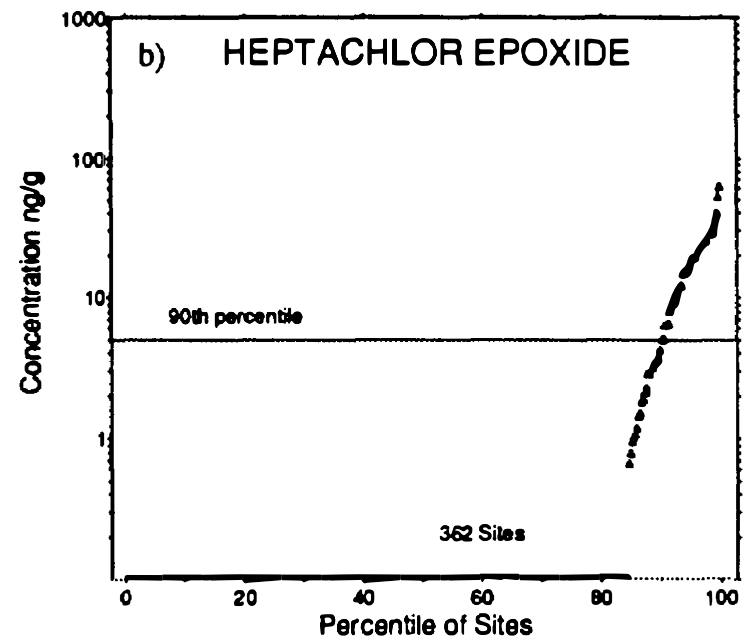
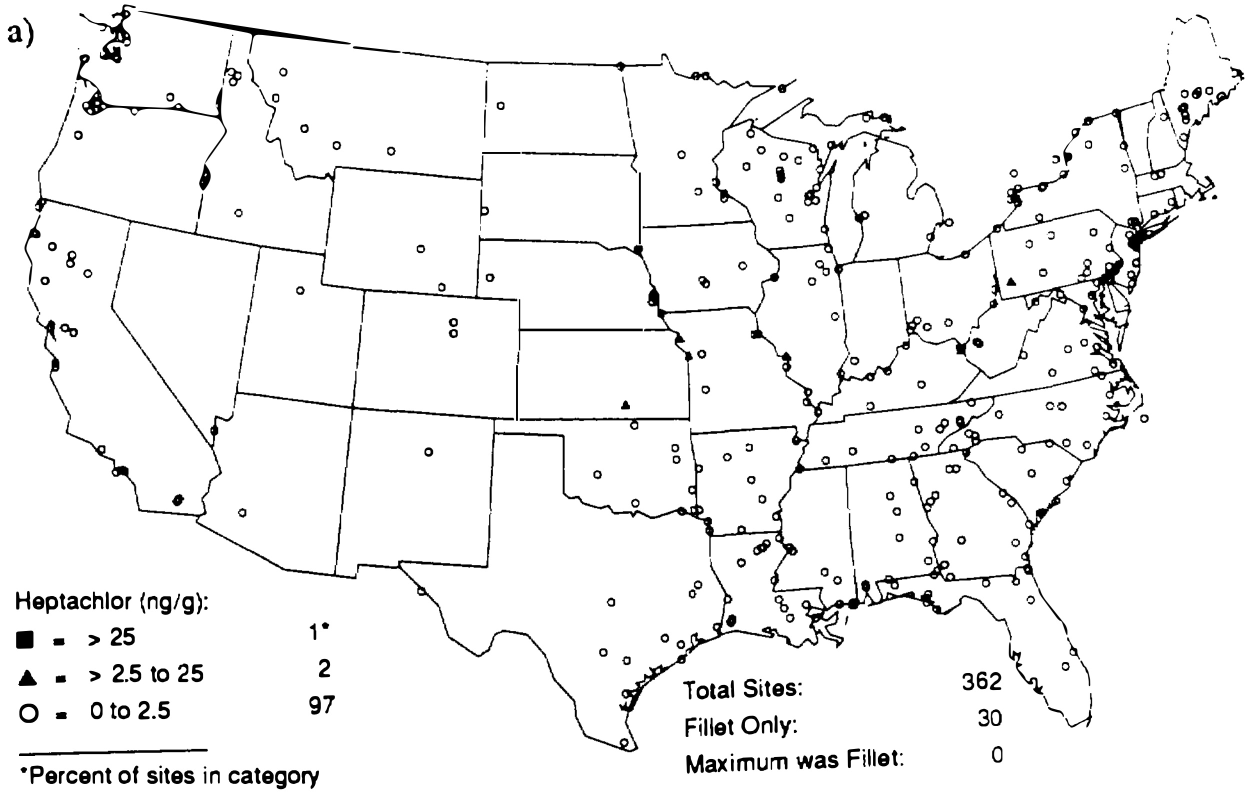


Figure 4-50. Cumulative frequency distribution of a) heptachlor and b) heptachlor epoxide in fish tissue. (Maximum concentration at each site was used. Bar on x-axis represents sites below detection.)



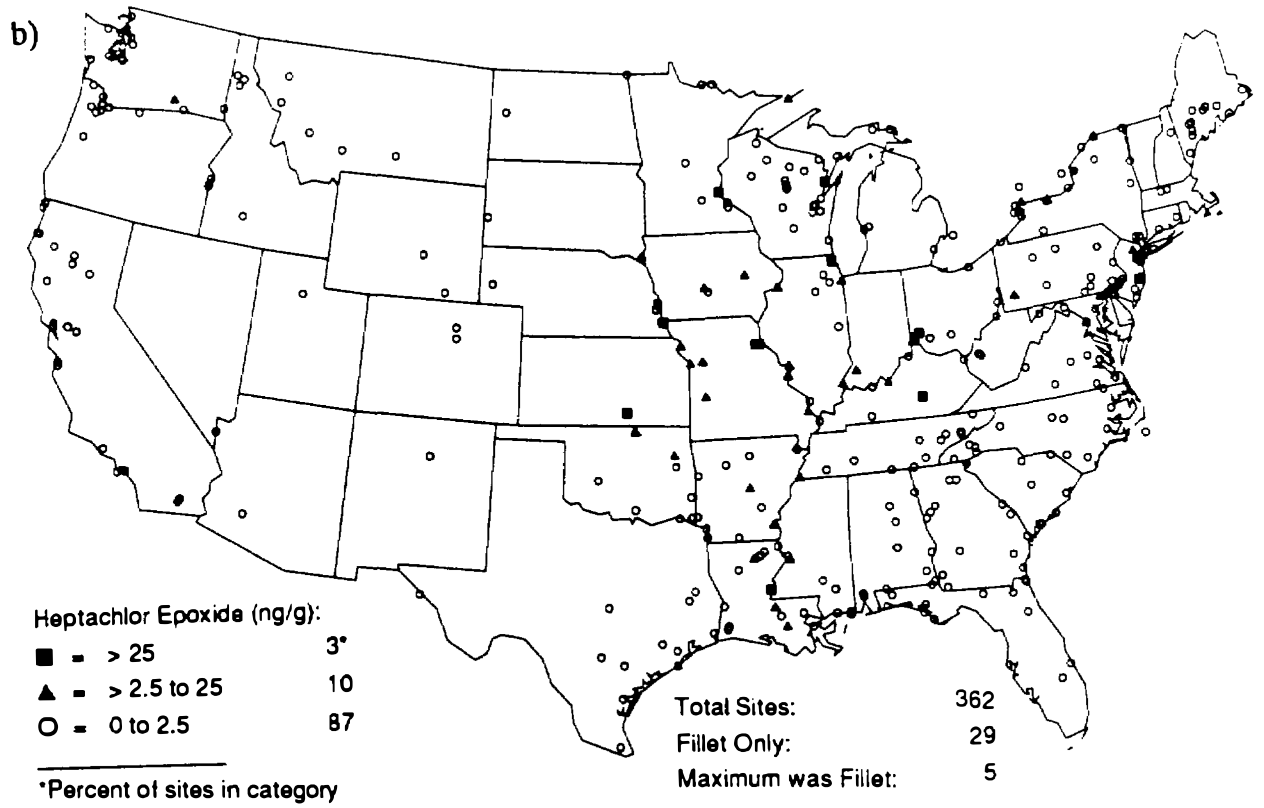
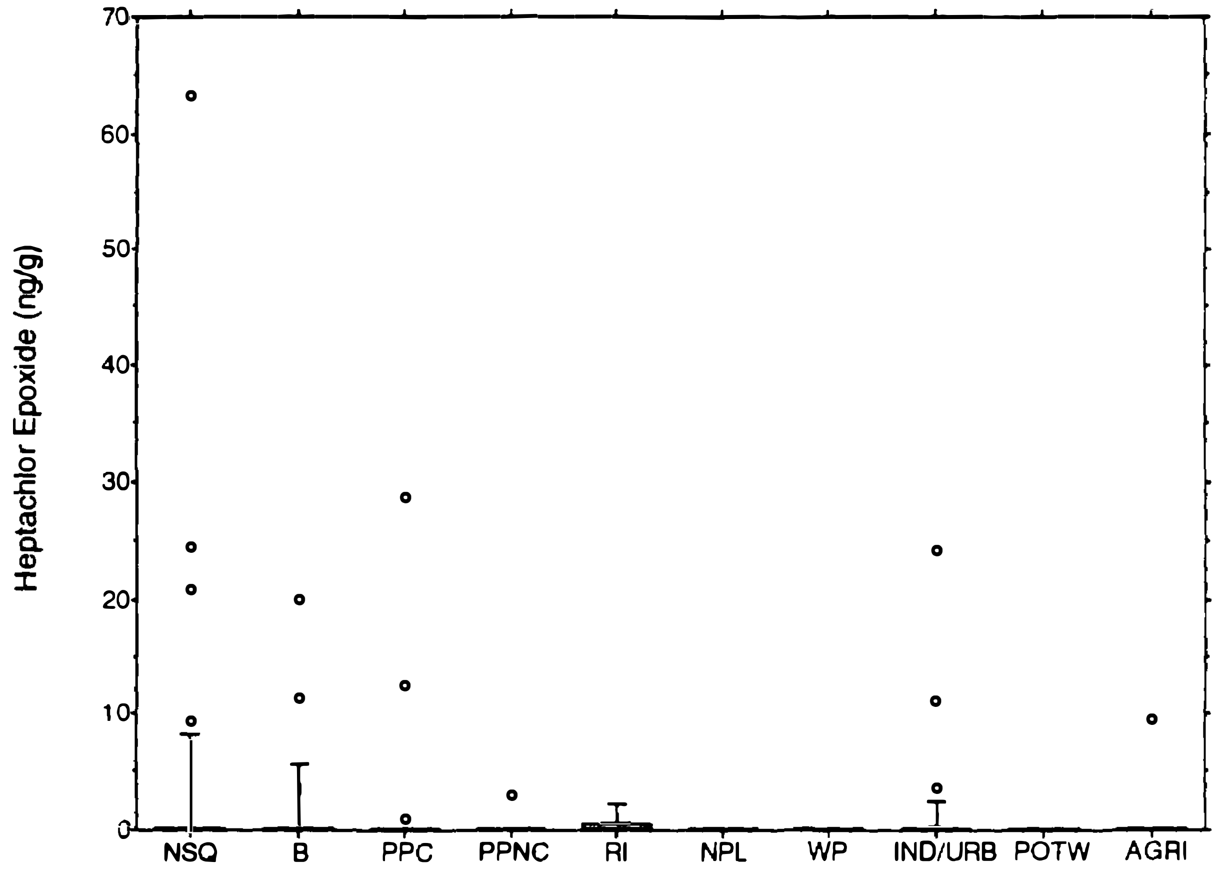


Figure 4-51. Map of geographical distribution of various concentration ranges for a) heptachlor and b) heptachlor epoxide in fish tissue.



Summary Table for Heptachlor Epoxide Box Plot

Site Category	n	Concentration Range pg/g	Mean	Stan. Dev.	Median
NASQAN (NSQ)	39	ND.- 63.2	3.3	11.2	ND
Background (B)	20	ND.- 19.9	1.6	5.0	ND
Paper Mills Using Cl (PPC)	39	ND.- 28.7	1.1	5.0	ND
Other Paper Mills (PPNC)	17	ND.- 2.9	0.2	0.7	ND
Refinery/Other Industry (R/I)	5	ND.- 2.3	0.5	1	ND
Superfund Sites (NPL)	6	ND	ND	ND	ND
Wood Preservers (WP)	10	ND	ND	ND	ND
Industrial/Urban Sites (IND/URB)	31	ND.- 24.1	1.3	4.7	ND
POTW	6	ND	ND	ND	ND
Agricultural (AGRI)	15	ND - 9.3	0.6	2.4	ND

n = number of sites in category. ND's set at 0. Maximum concentrations at sites were used.

Figure 4-52. Box and whisker plot for heptachlor epoxide in fish tissue.

Pentachloronitrobenzene

Pentachloronitrobenzene (PCNB) is used as a soil fungicide, a seed dressing agent for peanuts, to control stem and root rot on flowers and vegetables, and to minimize mold growth on cotton and turf. PCNB was detected at four sites (Figure 4-53a,b). The highest concentration of PCNB was found in a whole-body carp sample from the Missouri River at St. Joseph (3044) located near an agricultural chemical manufacturing plant, and the next highest was a whole-body carp sample from the Scioto River at Chillicothe, Ohio (3132) near pesticide and inorganic chemical manufacturing plants and a Superfund site.

COMPARISON WITH NATIONAL CONTAMINANT BIOMONITORING PROGRAM

The National Contaminant Biomonitoring Program (NCBP), formerly part of the National Pesticide Monitoring Program, is an ongoing study begun in 1964 to determine how organochlorine pollutant levels vary over geographic regions and change over time. Fish have been monitored since 1967 and the latest analyses were performed in 1984 for 19 organochlorine compounds and 7 metals (cadmium, lead, mercury, arsenic, copper, selenium, and zinc). Fifteen of the organochlorine compounds and mercury were also analyzed in the NSCRF.

The 1984 NCBP sampled 112 sites for organic chemicals and 109 sites for metals. The monitoring sites were selected to represent watersheds, and included all of the major river basins in the continental United States. Only 11 sites were common to both the NCBP and NSCRF studies. Composite samples consisted of five fish and were collected at each site for three fish species–two bottom feeder species and one predator species.

A total of 15 organic compounds and mercury were measured in both studies. In the NSCRF, 11 compounds were found at greater than 50 percent of the sites. Eight of these compounds were analyzed in the NCBP: p,p'-DDE, PCBs, dieldrin, cis- and trans-chlordane, pentachloroanisole, trans-nonachlor and alpha-BHC. All of these compounds, except alpha-BHC, were found at greater than 50 percent of the sites in the NCBP. Several other pesticides were found at higher concentrations in the NCBP including dieldrin, endrin, gamma-BHC, and chlordane-related compounds. This is consistent with the larger proportion of sites near agricultural areas in the NCBP. Additionally, the percent occurrence for p,p'-DDE and PCBs in both studies is very close. The percent occurrences for DDE were 99 in the NSCRF and 98 in the NCBP, and 91 for PCBs in both studies. Mercury was similar, found in samples from 92 percent of the sites in the NSCRF and 100 percent of the sites in the NCBP. These results highlight the ubiquitous extent of these three compounds.

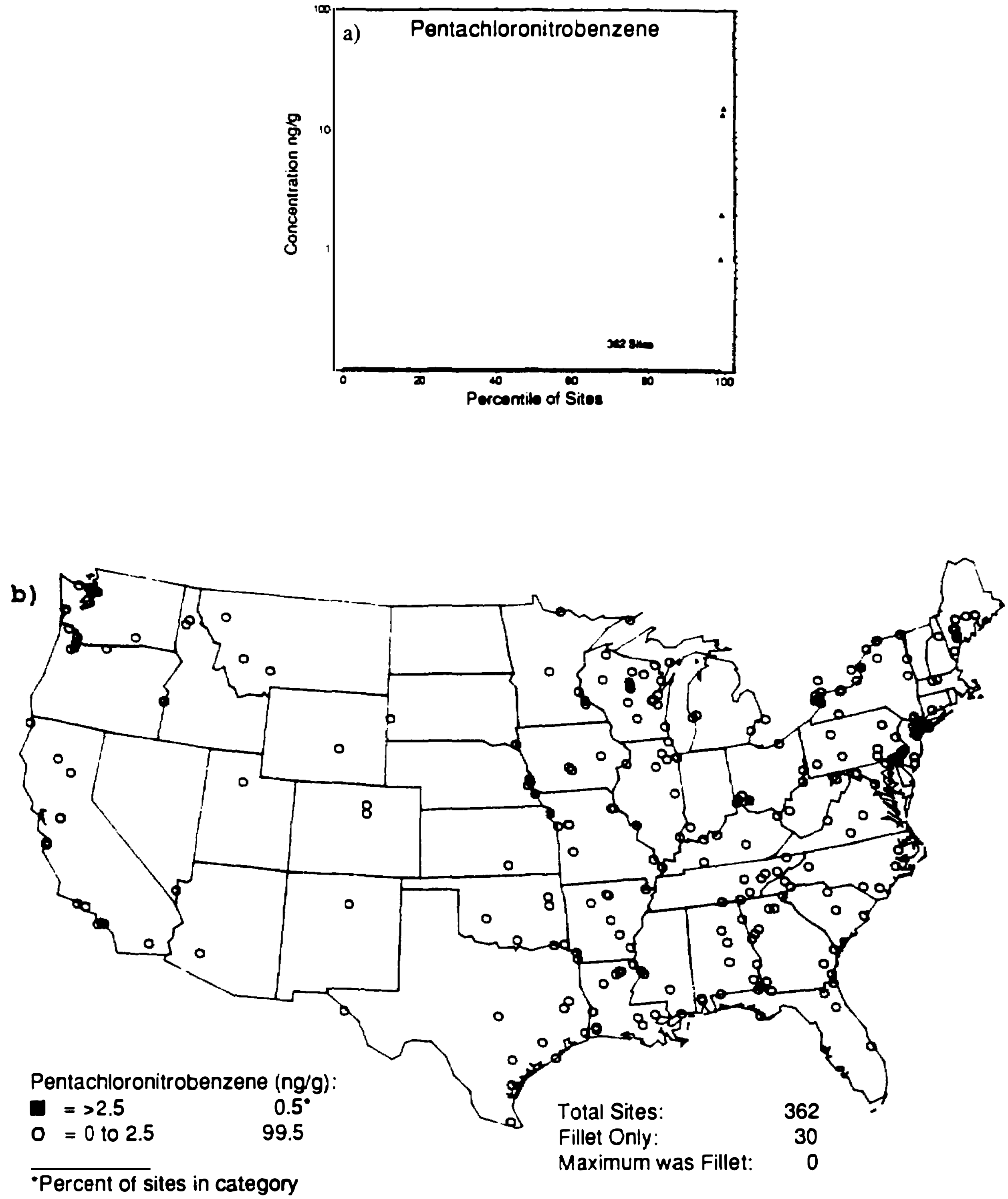


Figure 4-53. Pentachloronitrobenzene: a) cumulative frequency distribution and b) map of geographical distribution of various concentration ranges in fish tissue.

Chapter 5 - Fish Species Summary and Analysis

This chapter provides biological information on the various fish species sampled as well as a summary of average fish tissue concentration data by type of fish species. At most of the sampled sites, few, if any, different types of species were collected. As a consequence, only limited bioaccumulation or other comparions can be made between fish species for a given sampling site. Nevertheless, the tables showing the concentration of chemicals by fish species may provide a good basis for follow-up studies or as a supplement to other fish contamination studies. Additionally, the information on fish feeding strategies may prove useful in developing future source correlation studies.

SUMMARY OF FISH SPECIES SAMPLED

Though protocols were established to minimize fish sample variables among sites, over 119 different species representing 33 taxonomic families of fish were collected for this study. Freshwater, estuarine, and marine samples were included. Table 5-1 lists the species by scientific and common name and shows the number of sites at which they were sampled. This table also shows feeding strategy and indicates whether the fish is found in a freshwater and/or marine environment. Sampling locations were shown earlier in Figure 2-4. Tissue concentrations have been measured in catadromous species (e.g., American eel, Anguilla rostrata); anadromous species (e.g., salmon, Onchorhynchus); and freshwater, estuarine, and marine species, in addition to exotic introduced species such as Tilapia. In addition, 17 samples of shellfish were collected, which are described at the end of this section.

The 14 most frequently sampled species were as follows:

Bottom Feeder Species	Number of Sites Where Sampled
Carp	135
White Sucker	32
Channel Catfish	30
Redhorse Sucker	16
Spotted Sucker	10

Game Species	Number of Sites Where Sampled
Largemouth Bass	83
Smallmouth Bass	26
Walleye	22
Brown Trout	10
White Bass	10
Northern Pike	8
Flathead Catfish	8
White Crappie	7
Bluefish	5

TABLE 5-1
Distribution and Feeding Strategy for Fish Species Collected

Scientific Name	Common Name	Range[1]	Feeding Strategy[2]	No. of Sites[3]
Class - Chondrichthyes				
Order - Squaliformes				
Family - Carcharhinidae				
Triakis semifasciata	Leopard Shark	M	P	1
Order - Rajiformes				
Family - Rajidae				
Raia binoculata	Big Skate	M	B	1
Family - Dasyatidae				
Dasyatis (species unknown)	Stingray	M	P	1
Order - Chimaeriformes				
Family - Chimaeridae				
Hydrolagus colliei	Spotted Ratfish	M	P	1
Class - Osteichthyes				
Order - Acipenseriformes				
Family - Acipenseridae				
Acipenser transmontanus	White Sturgeon	Both	P	4
Order - Semionotiformes				
Family.- Lepisosteidae				
Lepisosteus osseus	Longnose Gar	F	P	1
Lepisosteus platostomus	Shortnose Gar	F	P	1
Order - Amiiformes				
Family.- Amiidae				
Amia calva	Bowfin	F	P (Pisc.)	2
Order - Anquilliformes				
Family - Anquillidae				
Anguilla rostrata	American Eel	Both	P	1
Order - Clupeiformes				
Family - Clupeidae				
Alosa sapidissima	American Shad	Both	P	1
Dorosoma cepedianum	Gizzard Shad	Both	P (Filter Feeder)	1

[1] Estuarine/Marine: M = Marine; F = Freshwater; [I] = Introduced
[2] P = Predator; B = Bottom Feeder
[3] Number of sites where fish were collected and analyzed

SOURCE: AFS. 1980

Pisc. = Piscivorous; Omni. = Omnivorous

TABLE 5-1 (CONT.)

Scientific Name	Common Name	Range[1]	Feeding Strategy[2]	No. of Sites[3]
Order - Osteoglossiformes				
Family - Hiodontidae				
Hiodon alosoides	Goldeye	F	P	1
Order - Salmoniformes				
Family - Salmonidae				
Coregonus clupeaformis	Lake Whitefish	Both	P	1
Oncorhynchus gorbuscha	Pink Salmon	Both	P	1
Oncorhynchus kisutch	Coho Salmon	Both	P (Pisc.)	1
Oncorhynchus mykiss	Rainbow Trout	Both	P (Fish, Insects, Algae)	7
Oncorhynchus tshawytscha	Chinook Salmon	Both	P (Pisc.)	1
Prosopium williamsoni	Mountain Whitefish	F	P (Aq. Insects)	1
Salmo clarki	Cutthroat Trout	Both	P	1
Salmo salar	Atlantic Salmon	Both	P (Pisc.)	2
Salmo trutta	Brown Trout	Both[I]	P (Pisc.)	10
Salvelinus fontinalis	Brook Trout	Both	P	2
Salvelinus malma	Dolly Varden	Both	P	2
Salvelinus namaycush	Lake Trout	F	P (Pisc.)	1
Family - Osmeridae				
Hypomesus pretiosus	Surf Smelt	Both	B	1
Family - Esocidae				
Esox lucius	Northern Pike	F	P (Pisc.)	8
Esox niger	Chain Pickerel	F	P	4
Esox spp.	Pickerel; Pike	F	P	1
Order - Cypriniformes				
Family - Cyprinidae				
Acrocheilus alutaceus	Chiselmouth	F	B	1
Carassius auratus	Goldfish	F[I]	B	1
Ctenopharyngodon idella	Grass Carp	F[I]	B	1
Cyprinus carpio	Common Carp	F[I]	B (Omni.)	135
Gila spp.	Chub	F	B	1
Orthodon microlepidotus	Sacramento Blackfish	F	B	1
Ptychocheilus	Squawfish	F	B (Pisc.)	9
Family - Catostomidae				
Carpiodes carpio	River Carpsucker	F	B	4
Carpiodes cyprinus	Quillback	F	B	1
Catostomus catostomus	Longnose Sucker	F	B	2
Catostomus columbianus	Bridgelip Sucker	F	B	3
Catostomus commersoni	White Sucker	F	B (Omni.)	32
Catostomus macrocheilus	Largescale Sucker	F	B	2
Catostomus occidentalis	Sacramento Sucker	F	B	3
	Sucker (unspecified)	-	-	32

[1] Estuarine/Marine: M = Marine; F = Freshwater; [I] = Introduced
[2] P = Predator; B = Bottom Feeder
[3] Number of sites where fish were collected and analyzed

SOURCE: AFS, 1980

Pisc. = Piscivorous; Omni. = Omnivorous

TABLE 5-1 (CONT.)

Scientific Name	Common Name	Range [1]	Feeding Strategy [2]	No. of Sites [3]
Erimyzon oblongus	Creek Chubsucker	F	B	1
Erimyzon sucetta	Lake Chubsucker	F	B	1
Hypentelium nigricans	Northern Hog Sucker	F	B	1
Ictiobus bubalus	Smallmouth Buffalo	F	B	5
Ictiobus cyprinellus	Bigmouth Buffalo	F	B (Zooplankton & Crust.)	4
Ictiobus niger	Black Buffalo	F	B	1
Minytrema melanops	Spotted Sucker	F	B (Zooplankton Insect Larvae/Plants)	10
Moxostoma anisurum	Silver Redhorse	F	B (Aq. Insects)	1
Moxostoma congestum	Gray Redhorse	F	B (Aq. Insects)	1
Moxostoma duquesnei	Black Redhorse	F	B (Aq. Insects)	1
Moxostoma erythrurum	Golden Redhorse	F	B (Aq. Insects)	1
Moxostoma macrolepidotum	Shorthead Redhorse	F	B (Aq. Insects)	1
Moxostoma poecilurum	Blacktail Redhorse	F	B (Aq. Insects)	1
Moxostoma	Redhorse Sucker	F	B (Aq. Insects)	16
Order - Siluriformes				
Family - Ictaluridae				
Ictalurus catus	White Catfish	F	B	4
Ictalurus furcatus	Blue Catfish	F	B (Omni.)	6
Ictalurus melas	Black Bullhead	F	B (Omni.)	2
Ictalurus natalis	Yellow Bullhead	F	B (Omni.)	1
Ictalurus nebulosus	Brown Bullhead	F	B (Omni.)	4
Ictalurus punctatus	Channel Catfish	F	B (Omni.)	30
Pylodictis olivaris	Flathead Catfish	F	P (Pisc.)	8
	Catfish (unspecified)	-	-	11
Family - Ariidae				
Arius felis	Hardhead Catfish	Both	B	7
Order - Gadiformes				
Family - Gadidae				
Gadus morhua	Atlantic Cod	M	P	1
Order - Perciformes				
Family - Percichthyidae				
Morone americana	White Perch	Both	P	4
Morone chrysops	White Bass	F	P (Fish & Insects)	10
Morone saxatilis	Striped Bass	Both	P	1
	Bass (unspecified)	-	-	3

[1] Estuarine/Marine: M = Marine; F = Freshwater; [I] = Introduced
[2] P = Predator; B = Bottom Feeder
[3] Number of sites where fish were collected and analyzed

SOURCE: AFS. 1980

Pisc. = Piscivorous; Omni. = Omnivorous

TABLE 5-1 (CONT.)

Scientific Name	Common Name	Range [1]	Feeding Strategy [2]	No. of Sites [3]
Family - Centrarchidae				
Ambloplites rupestris	Rock Bass	F	P	4
Lepomis auritus	Redbreast Sunfish	F	P	2
Lepomis cyanellus	Green Sunfish	F	P	2
Lepomis gibbosus	Pumpkinseed	F	P	1
Lepomis gulosus	Warmouth	F	P	1
Lepomis macrochirus	Bluegill	F	P (Insects)	4
Lepomis megalotis	Longear Sunfish	F	P	1
Lepomis microlophus	Redear Sunfish	F	P (Mollusks)	1
Micropterus coosae	Redeye Bass	F	P	1
Micropterus dolomieui	Smallmouth Bass	F	P (Pisc.)	26
Micropterus notius	Suwannee Bass	F	P	1
Micropterus punctulatus	Spotted Bass	F	P	3
Micropterus salmoides	Largemouth Bass	F	P	83
Pomoxis annularis	White Crappie	F	P (Pisc.)	7
Pomoxis nigromaculatus	Black Crappie	F	P (Pisc.)	4
	Crappie (unspecified)	-	-	3
Family - Percidae				
Perca flavescens	Yellow Perch	F	P	1
Stizostedion canadense	Sauger	F	P	3
Stizostedion vitreum vitreum	Walleye	F	P (Pisc.)	22
Family - Pomatomidae				
Pomatomus saltatrix	Bluefish	M	P (Pisc.)	5
Family - Carangidae				
Caranx bartholomaei	Yellow Jack	M	P	1
Caranx hippos	Crevalle Jack	M	P	1
Caranx ignoblis	Papio	M	P	1
Family - Lutjanidae				
Lutjanus campechanus	Red Snapper	M	P	2
Family - Sparidae				
Archosargus probato -cephalus	Sheepshead	M	P	2
Family - Sciaenidae				
Aplodinotus grunniens	Freshwater Drum	F	P (Mollusks & Fish)	3
Cynoscion nebulosus	Spotted Seatrout	Both	P	3
Cynoscion regalis	Weakfish	M	P	3
Equetus punctatus	Spotted Drum	M	P	1
Leiostomus xanthurus	Spot	Both	P	3

[1] Estuarine/Marine: M = Marine: F = Freshwater: (I)& Introduced
[2] P = Predator: B = Bottom Feeder
[3] Number of sites where fish were collected and analyzed

SOURCE: AFS, 1980

Pisc. = Piscivorous: Omni. = Omnivorous

TABLE 5-1 (CONT.)

Scientific Name	Common Name	Range [1]	Feeding Strategy [2]	No. of Sites [3]
Micropogonias undulatus	Atlantic Croaker	Both	P	3
Pogonias cromis	Black Drum	M	P	3
Sciaenops ocellatus	Red Drum	Both	P	3
Family - Cichlidae				
Tilapia (species uncertain)		—	B	1
Tilapia zilli	Redbelly Tilapia	F[I]	B	1
Family - Embiotocidae				
Phanerodon furcatus	White Surfperch	M	B	1
Family - Mugilidae				
Mugil cephalus	Striped Mullet	Both	P	3
Family - Scorpaenidae				
Sebastes auriculatus	Brown Rockfish	M	P	1
Sebastes caurinus	Copper Rockfish	M	P	1
Sebastes maliger	Quillback Rockfish	M	P	1
Sebastes paucispinis	Bocaccio	M	P	1
Sebastes proriger	Redstripe Rockfish	M	P	1
Family - Cottidae				
Cottus (species unknown)	Sculpin	—	B	4
Cottus aleuticus	Coastrange Sculpin	Both	B (Plants & Insects)	
Order - Pleuronectiformes				
Family - Bothidae				
Paralichthys dentatus	Summer Flounder	M	P	1
Paralichthys lethostigma	Southern Flounder	Both	P	2
Family - Pleuronectidae				
Hippoglossoides elassodon	Flathead Sole	M	P	2
Hypsopsetta guttulata	Diamond Turbot	M	P	1
Platichthys stellatus	Starry Flounder	Both	P	5
Pleuronichthys verticalis	Hornyhead Turbot	M	P	1
Pseudopleuronectes americanus	Winter Flounder	M	P	4

[1] Estuarine/Marine: M = Marine: F = Freshwater; [I] = Introduced
[2] P = Predator; B = Bottom Feeder
[3] Number of sites where fish were collected and analyzed

SOURCE: AFS. 1980

Pisc. = Piscivorous; Omni. = Omnivorous

PREVALENCE AND AVERAGE CONCENTRATION OF CHEMICALS BY SPECIES

Table 5-2 shows average fish tissue concentrations for each of the dioxin/furan compounds in the 14 most commonly sampled fish species at targeted sites. With the exception of four congeners (1,2,3,4,7,8,9 HpCDF; 1,2,3,4,7,8 HxCDD; 1,2,3,6,7,8, HxCDF; 1,2,3,7,8,9 HxCDF), whole-body samples from bottom-feeding species have higher dioxin/furan concentrations than fillet samples from game fish. Average concentrations were the highest in carp for four of the six dioxins, and three of the nine furans. The highest concentrations of the other congeners were found in spotted and redhorse suckers and channel catfish for the bottom-feeding species. For game fish species, the highest concentrations were found in white crappie for two of the six dioxins, four of nine furans, and TEC. Brown trout had the highest average concentration for one dioxin and two furans. The highest concentrations of the other congeners were found in largemouth bass, white bass, northern pike, and bluefish. The occurrence of pollutants in the most frequently sampled fish species varied by chemical. Some pollutants (i.e., 2,3,7,8 TCDF and 1,2,3,4,6,7,8 HpCDD) were found in the majority of samples (Table 5-3). Two furans, 1,2,3,7,8,9 HxCDF and 1,2,3,4,7,8,9 HpCDF, were not found in quantities above detection in any of the game fish fillets, but were detected in a small number of the bottom feeder whole-body samples.

Table 5-4 shows the average fish tissue concentration of selected xenobiotics for the 14 most commonly sampled species at targeted sites. Average mercury concentrations are higher in game fish analyzed as fillets than bottom feeders analyzed as whole-body samples. As discussed in Chapter 4, this result would be expected because mercury is stored in the muscle tissue rather than the lipid and would, therefore, exhibit higher concentrations in fillets than in whole-body samples. Ten xenobiotics are detected in whole-body samples of bottom feeders and in fillet samples of game fish at roughly the same average concentrations. These compounds are biphenyl, chlorpyrifos, dicofol, dieldrin, endrin, mirex, oxychlordane, PCBs, DDE, and trifluralin. Twelve compounds have higher average concentrations in whole-body samples of bottom feeders than in fillet samples of game fish: alpha and gamma-BHC; heptachlor epoxide; pentachloroanisole; pentachlorobenzene; chlordane; nonachlor; three trichlorobenzenes; 1,2,3,4 tetrachlorobenzene; and hexachlorobenzene. Biphenyl, mercury, PCBs, and DDE were found in a majority of both whole-body and fillet samples with concentrations above detection (Table 5-5). Endrin, 1,3,5 trichlorobenzene and trifluralin were found in quantities above detection in only a few of the game fish fillet samples collected.

HABITAT AND FEEDING STRATEGY OF MOST FREQUENTLY SAMPLED SPECIES

Common Carp

The common carp (Cyprinus carpio) is distributed widely throughout most parts of the country. It prefers the shallows of warm streams, lakes, and ponds containing an abundance of vegetation. It is not normally found in clear, cold waters or streams of high gradients.

The spawning period for this species can last from April to August, but generally spawning occurs in late May and June. Shallow and weedy areas of lakes, ponds, tributaries, streams, swamps, floodplains, and marshes are suitable spawning grounds. The young carp consume zooplankton as

TABLE 5-2
Average Fish Tissue Concentrations of Dioxins and Furans for Major Species

Fish Species	2378 TCDD	12378 PeCDD	123478 HxCDD	123678 HxCDD	123789 HxCDD	1234678 HpCDD	2378 TCDF	12378 PeCDF	23478 PeCDF	123478 HxCDF	123678 HxCDF	123789 HxCDF	234678 HxCDF	1234678 HpCDF	1234789 HpCDF	TEC
Bottom Feeders																
Carp	7.76	3.63	2.16	6.81	1.54	22.29	10.15	1.31	4.01	2.54	1.91	1.16	1.20	2.49	11.22	13.06
White Sucker	8.08	2.05	1.03	1.96	0.88	3.72	22.89	1.10	2.64	2.21	1.29	1.06	1.09	1.23	11.13	12.79
Channel Catfish	11.56	2.37	1.61	5.62	1.29	9.40	2.22	0.52	2.91	2.41	1.41	1.381	1.62	2.55	11.26	14.80
Redhorse Sucker	4.65	1.50	1.40	2.36	0.84	4.94	30.09	0.75	11.28	2.10	1.16	1.191	1.50	1.57	1.361	9.22
Spotted Sucker	1.73	2.34	1.70	12.08	1.14	17.48	7.49	2.12	2.06	2.22	1.79	1.28*	1.78	1.77	11.08	6.23
Game Fish																
Largemouth Bass	1.73	0.59	1.12	1.28	0.64	2.48	2.18	0.37	0.47	1.24	1.23	1.21*	0.88	0.821	1.21*	11.91
Smallmouth Bass	0.72	0.50*	1.13*	0.79	0.64*	0.67	1.93	0.36*	0.51	11.28	1.23	1.26*	0.89*	0.69	1.30*	0.65*
Walleye	0.88	0.54*	0.99*	0.73	0.62*	0.88	1.83	0.351	0.38	1.04	1.09*	1.07*	0.75	0.74	11.21*	0.79*
Brown Trout	2.52	1.01	1.07*	0.98	0.68*	1.18	3.74	0.60	1.36	1.47	1.12*	1.09*	0.94*	0.67*	1.16*	3.31
White Bass	3.00	0.66	1.05*	0.78	0.61*	1.01	5.07	0.40	0.49	1.04	1.16*	1.13*	0.81*	0.63	1.17*	3.44
Northern Pike	0.77	0.46*	1.23*	0.91	0.69*	0.73	1.01	0.44	0.66	1.41*	1.42*	1.381	0.98*	0.56	1.30*	0.66
Flathead Catfish	0.78	0.43	0.90	1.06	0.50	1.67	1.63	0.40	0.56	1.05	1.20*	1.17*	0.61*	0.56	1.10*	0.99
White Crappie	2.13	0.60	1.29*	1.03*	0.83*	1.33	10.46	0.54	0.67	1.33*	1.33*	1.30*	0.95*	0.961	1.34*	3.80
Bluefish	0.85	0.56	1.23*	0.98*	0.69*	0.65	2.11	0.41	0.59	1.42*	1.42*	1.391	0.98*	0.72*	1.31*	1.41

Values calculated using whole body samples for bottom feeding species and fillet samples for Game Fish (predators).
Values below detection have been replaced by one-half detection limit for the given sample. Asterisk indicates all values below detection.
Units = pg/g.

TABLE 5-3
Detailed Summary of Occurrence of Prevalent Dioxins/Furans by Fish Species

Fish Species	2378 TCDD	12378 PeCDD	123478 HxCDD	123678 HxCDD	123789 HxCDD	1234678 HpCDD	2378 TCDF	12378 PeCDF	23478 PeCDF	123478 HxCDF	123678 HxCDF	123789 HxCDF	234678 HxCDF	1234678 HpCDF	1234789 HpCDF
Bottom Feeders															
Carp	106/135	89/133	73/125	102/125	71/125	103/108	124/135	83/134	96/134	79/126	45/126	2/126	63/126	84/109	6/109
White Sucker	28/37	20/36	7/ 34	20/34	7/ 34	28/31	35/37	19/37	27/37	14/34	4/ 34	1/ 34	8/ 34	16/31	2/ 31
Channel Catfish	12 / 19	13 / 17	6 / 18	16 / 18	12 / 18	18 / 18	16 / 19	9 / 19	15 / 19	9 / 18	5 / 18	0 / 18	8 / 18	10 / 18	1 / 18
Redhorse Sucker	9 / 15	7 / 15	1 / 14	9 / 14	3 / 14	12 / 13	14 / 15	6 / 15	11 / 15	5 / 15	1 / 15	0 / 15	3 / 15	5 / 13	0 / 13
Spotted Sucker	6 / 10	5 / 10	4 / 10	7 / 10	6 / 10	10 / 10	9 / 10	2 / 10	6 / 10	2 / 10	1 / 10	0 / 10	1 / 10	5 / 10	1 / 10
Game Fish															
Largemouth Bass	34 / 75	10 / 73	2 / 72	18 / 72	5 / 72	37 / 67	42 / 75	6 / 74	12 / 74	10 / 73	2 / 73	0 / 73	6 / 73	13 / 67	0 / 67
Smallmouth Bass	9 / 22	0 / 21	0 / 20	2 / 19	0 / 20	10 / 18	16 / 22	0 / 22	5 / 22	1 / 20	1 / 20	0 / 20	0 / 20	1 / 18	0 / 18
Walleye	5 / 18	0/18	0/16	1/16	0/16	9/16	12/18	0/18	3/18	1/16	0/16	0/16	1/16	2/16	0/16
Brown Trout	2 / 8	3 / 7	0 / 7	1 / 7	0 / 7	2 / 6	6 / 8	2 / 8	4 / 8	2 / 7	0 / 7	0 / 7	0 / 7	0 / 6	0 / 6
White Bass	5 / 10	2 / 10	0 / 10	2 / 10	0 / 10	8 / 9	10 / 10	4 / 10	4 / 10	1 / 10	0 / 10	0 / 10	0 / 10	1 / 9	0 / 9
Northern Pike	4 / 7	0 / 6	0 / 7	6 / 7	0 / 7	2 / 7	4 / 6	1 / 7	1 / 7	0 / 7	0 / 7	0 / 7	0 / 7	1 / 7	0 /7
Flathead Catfish	3 / 6	3/6	1 / 6	4/6	1/6	5/6	2/6	1/6	2/6	2/ 6	0/6	0/6	2/6	3/6	0/6
White Crappie	1 / 8	1 / 8	0 / 7	0 / 7	0 / 7	2 / 7	3 / 8	1 / 8	1 / 8	0 / 6	0 / 7	0 / 7	0 / 7	0 / 7	0 / 7
Bluefish	3 / 4	1 / 4	0 / 4	0 / 4	0 / 4	1 / 4	4 / 4	1 / 4	4 / 4	0 / 4	0 / 4	0 / 4	0 / 4	0 / 4	0 / 4

Values were determined using whole body samples for bottom-feeding species and fillet samples for game species.
First number indicates number of samples where detected; second number indicates total number of samples at different sites for given species analyzed.
If more than one fillet or whole body sample of the same species at a site was analyzed, only the highest value was used.

TABLE 5-4
Average Fish Tissue Concentrations of Xenobiotics for Major Species

Fish Species	Alpha-BHC	Gamma-BHC	Biphenyl	Chlorpyrifos	Dicofol	Dieldrin	Endrin	Heptachlor Epoxide	Mercury (µg/g)	Mirex	Oxychlordane	PCBs
Bottom Feeders												
Carp	3.10	4.34	4.38	8.23	0.88	44.75	1.40	4 00	0 11	3.20	8 20	2941.13
White Sucker	3.31	1.66	1.28	1.75	0.48	22.75	0 24	1 09	0.11	4 35	3.10	1697 81
Channel Cat	2.87	3.17	1.24	6 97	0 59	15.44	9.07	0 50	0 09	14.59	6 41	1300 52
Redhorse Sucker	0.82	0.41	1.25	0.35	ND	5.35	0 97	ND	0.27	0 57	2 37	487.72
Spotted Sucker	1.45	2.63	3.35	0.56	0.05	5.52	ND	ND	0.12	1 79	0 05	133 90
Game Fish												
Largemouth Bass	0.15	0.07	0.38	0 23	0.20	5.01	ND	0.30	0.46	0.21	0 47	232 26
Smallmouth Bass	0.36	0.15	0.33	0 08	ND	2.34	ND	0.07	0.34	1.99	0 54	496 22
Walleye	ND	ND	0.40	0.04	ND	3.73	ND	0.21	0.51	0 08	1.11	368.65
Brown Trout	1.59	ND	0.81	ND	0.94	20.13	ND	2.08	0 14	43 98	5 38	2434.07
White Bass	0.34	0.79	0.62	1.32	ND	9.35	ND	1 40	0.35	0.21	0 84	288 35
Northern Pike	0.55	ND	0.59	11.43	0.31	9.04	ND	ND	0.34	2.39	4 00	788.40
Flathead Cat	0.92	0.58	0.60	22 57	1.28	37.38	3.45	0.57	0 27	ND	0 63	521.19
White Crappie	0.23	ND	0.21	ND	ND	ND	ND	ND	0.22	ND	ND	22 34
Bluefish	0.38	0.12	0.20	ND	ND	2.87	ND	ND	0.22	0.13	ND	3682.06

Fish Species	Pentachloro-anisole	Pentachloro-benzene	DDE	Total Chlordane	Total Nonachlor	123 TCB	124 TCB	135 TCB	1234 TECB	Trifluralin	Hexachloro-benzene
Bottom Feeders											
Carp	16.50	1.04	415.43	67.15	63.15	1.54	4.77	0 08	0.30	12.55	3.58
White Sucker	9.06	0.39	78.39	18 42	20.83	0.16	0 30	0.14	0.15	ND	3.62
Channel Cat	39.60	1.32	627.77	54.39	66.28	0.14	0.37	ND	0.88	1.00	2.36
Redhorse Sucker	2.87	0.02	87.25	16.48	30.73	0.55	6.48	0 08	0.09	ND	0.58
Spotted Sucker	17.68	0.02	75.31	12.33	15.00	3 34	12.00	1.00	0.09	ND	0.02
Game Fish											
Largemouth Bass	0.57	0.02	55.72	2.89	4.21	0.22	0.19	0.03	0.01	ND	0.20
Smallmouth Bass	0.23	0.02	33.63	4.01	7.82	0.70	0.59	0.04	0.04	ND	0.36
Walleye	0.76	ND	34.00	3.62	8.04	0.29	0 38	ND	0.004	ND	0.11
Brown Trout	0.09	0.60	158.90	7.25	32.60	1.10	0.98	ND	0.09	ND	3.06
White Bass	0.93	ND	17.44	10.87	16.00	0.21	0.10	ND	0.01	ND	0.83
Northern Pike	1.51	0.09	59.50	5.45	13.88	0.30	0.23	ND	0.01	ND	0.20
Flathead Cat	0.31	ND	755.18	16.07	14.04	0.10	0.18	ND	ND	44.37	0 85
White Crappie	0.33	ND	10.04	0.34	0.28	0.08	0.08	ND	ND	ND	ND
Bluefish	0.05	ND	29.23	7.74	7.56	6.25	4 66	0 57	ND	ND	ND

Values calculated using whole body samples for bottom feeding species and fillet samples for Game Fish (predators). Values below detection have been set at zero.

Units = ng/g, unless noted.

TABLE 5-5
Detailed Summary of Occurrence of Prevalent Xenobiotics by Fish Species

Fish Species	Alpha-BHC	Gamma-BHC	Biphenyl	Chlorpyrifos	Dicofol	Dieldrin	Endrin	Heptachlor Epoxide	Mercury	Mirex	Oxychlordane	PCBs
Bottom Feeders												
Carp	77/128	57/128	124/128	46/128	12/128	91/128	16/128	33/128	111/133	55/128	36/128	122/128
White Sucker	24/35	18/35	33/35	7 / 35	7 / 35	24/35	3 / 35	2 / 35	29/34	9 / 35	9 / 35	32/35
Channel Cat	7/16	7/16	16/16	9/16	4/16	11/16	2/16	2/16	16/17	7/16	6/16	15/16
Redhorse Sucker	6/14	4/14	14/14	3/14	0/14	8/14	2/14	0/14	14/15	6/14	5/14	14/14
Spotted Sucker	3/10	2/10	10/10	1/10	1/10	5/10	0/10	0/10	9/10	6/10	1/10	9/10
Game Fish												
Largemouth Bass	5/31	3/31	29/31	4 / 31	7 / 31	9 / 31	0/31	2 / 31	65/66	6 / 31	4 / 31	26/31
Smallmouth Bass	4/15	2/15	15/15	1/15	0/15	8/15	0/15	1/15	20/20	6/15	3/15	14/15
Walleye	0/8	0/8	8/8	1/8	0/8	3/8	0/8	2/8	19/19	2/8	2/8	8/8
Brown Trout	1/3	0/3	3/3	0/3	1/3	2/3	0/3	2/3	7/8	2/3	2/3	3/3
White Bass	3/5	4/5	5/5	3/5	0/5	5/5	1/5	2/5	6/6	3/5	2/5	5/5
Northern Pike	1/6	0/6	6/6	3/6	2/6	3/6	0/6	0/6	7/7	3/6	1/6	5/6
Flathead Cat	2/4	1/4	4/4	3/4	1/4	4/4	1/4	1/4	6/6	0/4	1/4	4/4
White Crappie	1/4	0/4	4/4	0/4	0/4	0/4	0/4	0/4	5/7	0/4	0/4	3/4
Bluefish	1/3	1/3	2/3	0/3	0/3	2/3	0/3	0/3	3/3	1/3	0/2	3/3

Fish Species	Pentachloro-anisole	Pentachloro-benzene	DDE	Total Chlordane	Total Nonachlor	123 TCB	124 TCB	135 TCB	1234 TECB	Trifluralin	Hexachloro-benzene
Bottom Feeders											
Carp	103/128	42/128	126/128	109/128	114/128	35/128	60/128	14/128	16/128	31/128	72/128
White Sucker	25/35	7 / 35	34/35	24/35	24/35	9 / 35	18/35	2 / 35	5 / 35	0/35	16/35
Channel Cat	11/16	4/16	16/16	12/16	14/16	3/16	7/16	0/16	2/16	1/16	6/16
Redhorse Sucker	11/14	1/14	14/14	7/14	10/14	6/14	6/14	2/14	2/14	0/14	4/14
Spotted Sucker	7/10	1/10	9/10	7/10	8/10	7/10	8/10	2/10	1/10	0/10	2/10
Game Fish											
Largemouth Bass	6 / 31	1/31	31/31	12/31	18/31	17/31	17/31	3/31	1/31	0/31	6 / 31
Smallmouth Bass	4/15	1/15	15/15	8/15	9/15	9/15	8/15	1/15	3/15	0/15	5/14
Walleye	6/8	0/8	8/8	4/8	3/8	3/8	3/8	0/8	1/8	0/8	2/8
Brown Trout	1/3	2/3	3/3	2/3	2/3	3/3	3/3	0/3	1/3	0/3	2/3
White Bass	5/5	0/5	5/5	4/5	5/5	4/5	3/5	0/5	1/5	1/5	3/5
Northern Pike	2/6	1/6	6/6	3/6	4/6	3/6	2/6	0/6	1/6	0/6	1/6
Flathead Cat	2/4	0/4	4/4	3/4	4/4	1/4	2/4	0/4	0/4	3/4	2/4
White Crappie	1/4	0/4	4/4	1/4	1/4	1/4	2/4	0/4	0/4	0/4	0/4
Bluefish	1/3	0/3	2/3	3/3	3/3	3/3	3/3	1/3	0/3	0/3	0/3

Values were determined using whole body samples for bottom-feeding species and fillet samples for predator species.
First number indicates number of samples where detected; second number indicates total number of samples at different sites for given species analyzedX
If more than one fillet or whole body sample of the same species at a site was analyzed, only the highest value was used.

their major food source. Adults consume fish, snails, plants, bottom ooze, insect larvae, insects, crustaceans, mollusks, and fish eggs.

White Sucker

The white sucker (Catostomuscommersoni) is found in the northeastern, central, and eastern regions of the country. It is a common inhabitant of the most highly polluted and turbid waters. It tolerates a wide range of environments and stream gradients. However, it is found most often in lakes or reservoirs with clear to slightly turbid waters and a bottom consisting of gravel or sand with sparse vegetation.

Spawning generally occurs in mid-April to early May in swift water or rapids over gravel bottoms. The young feed on algae, zooplankton, and blood worms, and the adults consume fish, fish eggs, mud, plants, algae, insects, mollusks, and zooplankton.

Channel Catfish

The channel catfish (Ictalurus punctatus) is found throughout the central part of the country and into parts of the western and eastern United States. It prefers clear, rocky, well-oxygenated streams, lakes, and reservoirs, but can adapt to slow-moving, silty streams.

The spawning period generally occurs from May to July in inlet streams or tributaries. The spawning nest is located in a crevice, under a bank, rock, or log, and can be constructed on several types of bottom substrate. The young consume aquatic insects and zooplankton, while the adults take any food available to them. This can include fish, plants, frogs, crayfish, clams, worms, algae, and decaying or dead matter.

Spotted Sucker

The spotted sucker (Minytrema melanops) is found in the central and southeastern regions of the United States. It prefers large rivers and their sloughs and reservoirs that are slow moving with a soft bottom of muck or sand with vegetation. It is intolerant of turbid waters, various industrial pollutants, and bottoms covered with flocculent clay silts.

Spawning occurs throughout the month of May in pool-like areas near riffle over a rubble bottom. The young and adult spotted suckers both feed on zooplankton, insect larvae, crustaceans, algae, and higher plant material.

Redhorse Sucker

Redhorse suckers are most commonly found in the central and eastern parts of the country. Redhorse suckers generally prefer swiftly flowing sections of small to medium-sized streams with clear water and a gravel, bedrock, or sand bottom. They are intolerant of siltation and pollution in their habitat.

Spawning generally occurs during the month of April in shallower areas with a proper bottom substrate. Redhorse suckers are highly selective when it comes to choosing a spawning area. The water depth (0.5-2.0 ft) and the bottom substrate (approximately 70 percent fine rubble, 10 percent coarse rubble, and 20 percent sand and gravel) are the most important factors for a proper spawn. The young feed principally on phytoplankton, and the adults feed primarily on aquatic insects. For the data analyses in this report, all species of redhorse sampled were grouped under the name redhorse sucker.

Largemouth Bass

The largemouth bass (Micropterussalmoides) is found in most parts of the country. It prefers medium to large rivers, lakes, sloughs, ponds, and backwaters with clear to slightly turbid waters. It is usually found in shallower areas with dense to sparse vegetation.

The spawning period generally occurs from late April to early June. They tend to spawn a little earlier than the smallmouth bass. The fish spawn in quiet bays with emergent vegetation on a sand, gravel, or, occasionally, mud bottom. The young feed on algae, zooplankton, and insect larvae, while the adults feed on fish, crayfish, mammals, large insects, and amphibians.

Smallmouth Bass

The smallmouth bass (Micropterus dolomieui) is found mostly in the northeastern and central parts of the country, but can be found in limited areas of other parts of the country. It prefers medium to large streams, rivers ,and lakes with clear water, rocky or sandy bottoms, aquatic vegetation, and clean gravel shores.

Spawning generally occurs during late May and throughout June. The spawning nest is built on a gravel bottom beside a large boulder, log, stump, or foreign object in the shallows. The young consume insect larvae, zooplankton, and small insects, and the adults consume mostly fish but will also eat crayfish, insects, mammals, and amphibians.

Walleye

The walleye (Stizostedion vitreum vitreum) is found in most parts of the country except for the most western and southern areas. It prefers large clearwater rivers and lakes with sand and gravel bottoms. It is usually found in quiet backwaters and sloughs of these rivers and lakes.

Spawning generally occurs between mid-April and early May in wave-washed shallows or up inlet streams with gravel bottoms. This species prepares no spawning nest so the eggs are scattered over the gravel bottom of the area. The young consume zooplankton, insect larvae, and fry of other fish species, and the adults consume mostly fish, but will also eat insects, crayfish, and lamprey eels.

White Bass

The white bass (Morone chrysops) is found throughout the country, but is most heavily concentrated in the central United States. It prefers large, open rivers and lakes with clear to turbid waters and moderate currents.

The spawning period runs from late April into early June over most of its range. The spawning grounds consist of a firm bottom of sand, gravel, rubble, or rock in the shallows. This species builds no spawning nest, so the eggs are scattered over the bottom of the spawning area. The young white bass consume algae and zooplankton, and the adults consume fish, insect larvae, insects, and zooplankton.

Brown Trout

The brown trout (Salmo trutta) is most heavily concentrated in the northeastern and western parts of the country. It prefers coldwater streams and lakes, but can tolerate warmer water than other species of trout. In streams, it can be found in deeper and slower moving pools, and in the Great Lakes, it is found close to the shore.

The spawning period generally occurs from October to December in waters ranging in size from large streams to small spring-fed tributaries. The spawning nest is made on a gravel bottom in the shallower sections of the stream. The young feed primarily on zooplankton and insect larvae, and the adults eat mostly fish but will also consume larval insects, insects, leeches, snails, crayfish, freshwater shrimp, and worms. The brown trout is known to eat more fish than the other species of trout.

Flathead Catfish

The flathead catfish (Pylodictis olivaris) is generally found in the central parts of the country. It prefers large, rocky rivers with deep pools, plenty of cover, and swiftly moving waters.

The spawning period generally occurs in the months of June and July. The spawning nest is built in a secluded dark shelter over a gravel bottom. The young consume aquatic insect larvae, and the adults consume mostly fish but will occasionally feed on crayfish.

Northern Pike

The northern pike (Esox lucius) is found in the northeastern and north central parts of the country. It prefers cool to moderately warm weedy lakes, ponds, and slow-moving rivers. It can be found in areas of light to dense aquatic vegetation with clear to slightly turbid waters.

The spawning period generally occurs in late March or early April in shallow flooded marshes or inlet streams. Grasses, sedges, or rushes with fine leaves are most suitable for egg deposition. The young feed on phytoplankton, zooplankton, and insects, and the adults consume mainly fish but will also consume crayfish, mammals, and frogs.

White Crappie

The white crappie (Pomoxis annularis) is found mostly in the central part of the country, but can be found in limited areas in other regions. It prefers sloughs, backwaters, landlocked pools and lakes, and pools in moderate-sized to large streams with slightly turbid to turbid waters. It is found in the shallow and warm areas with sparse vegetation over a variety of substrates.

The spawning period generally occurs in the months of May and June. The spawning nests are made in colonies near vegetation over a hard clay or gravel bottom in the shallows. The young consume zooplankton and small insects, and the adults consume mostly fish but will occasionally feed on insects.

Blue Fish

The bluefish (Pomatomus saltatrix) is an ocean predator found in the tropical and temperate waters of the world with the exception of the central and eastern Pacific. It lives around large shoals in open water and moves in toward coastal waters to feed. This movement inward, as well as other migrations, is correlated with the movement of prey species of fish. It will attack fish almost as long as itself and will kill prey that it does not eat. The bluefish is the only ocean fish included in the 14 most frequently sampled species for this study.

Shellfish

There were 17 shellfish samples analyzed in the study. These included 4 dungeness crabs, 2 hepatopancreas organs of crabs, 3 crayfish, 3 soft shell clams, 2 pacific oysters, 1 unidentified oyster, 1 unidentified mussel, and 1 unidentified shellfish. The different species of shellfish exhibited a wide range of chemical concentrations. This could be attributed to differences in habitat and food sources between species. Varying chemical concentrations within each type of species are most likely related to the location of capture.

The dungeness crabs, on average, were found to have the highest chemical concentrations of all the shellfish analyzed. The chemicals accumulate in the hepatopancreas organ of the crab in very high concentrations. The high concentrations of chemicals in these crabs may relate to the large amount of fish consumed as part of their diet. The crayfish consumes a smaller proportion of fish in its diet than the dungeness crabs. It also consumes other types of food including some plant material. This may account for the differences in chemical concentrations between the two species.

The oysters, mussels, and clams analyzed for some of the study sites are filter feeders and consume similar types of food. The soft shell clams show higher chemical concentrations than the other species of filter feeders. This may be explained by differences in habitat among these species. The clams prefer a muddy or sandy bottom, and the oysters and mussels prefer a rocky bottom. A muddy and soft bottom will tend to accumulate more contaminants than a rocky bottom, so this would most likely have a direct effect on the clams. Overall, the filter feeders showed lower chemical concentrations than the crabs and crayfish.

Chapter 6 - Estimate of Potential Human Health Risks

This chapter presents risk estimates to human health based on fillet concentration data shown in Appendix D. Most of the fillets were from game fish, but a few were from bottom feeders likely to be consumed by humans. Carcinogenic risks were estimated for 14 of the xenobiotic compounds for which cancer potency factors were available. Noncarcinogenic risks were estimated for the 21 compounds for which risk values (i.e., reference doses) were available. Human health risks were not calculated for dioxins/furans due to the current review of the potency of these chemicals. The estimated risks presented in the report are intended as a screening assessment. A detailed site-specific risk assessment would require additional samples and would incorporate local consumption rates and patterns, and the actual number of people exposed. Information on the specific health effects of the study compounds and aquatic or wildlife effects, where available, are included in the chemical profiles, Appendix C.

Potential upper-bound human cancer risks from consumption of fish were estimated using fillet samples for selected analytes. Fillet data were available at 182 sites for mercury and 106 sites for the xenobiotic compounds, excluding dioxins and furans. Risks were calculated using the average fillet concentration at each site for the few places where more than one fillet concentration sample was available. The calculations were based on standard EPA risk assessment procedures for lifetime exposure with upper-bound cancer potency factors and three fish consumption rates of 6.5, 30, and 140 g/day. The reasons for setting these rates are discussed in the section on Exposure Assessment.

The compounds evaluated were those for which cancer potency factors and/or reference doses have been established. These compounds are listed below:

- Biphenyl
- alpha-BHC
- gamma-BHC (Lindane)
- Chlordane
- Chlorpyrifos
- p,p′-DDE
- Dicofol
- Dieldrin
- Endrin
- Heptachlor
- Heptachlor epoxide
- Hexachlorobenzene
- Hexachlorobutadiene
- Isopropalin
- Mercury
- Mirex
- Pentachloroanisole
- Pentachlorobenzene
- Pentachloronitrobenzene
- Polychlorinated biphenyls (PCBs)
- 1,2,4,5 Tetrachlorobenzene
- 1,2,4 Trichlorobenzene
- Trifluralin

METHOD OF ESTIMATING RISKS

Dose-Response Assessment

In developing risk assessment methods, EPA has recognized that fundamental differences exist between carcinogenic dose-response variables and noncarcinogenic dose-response variables that could be used to estimate risks. Because of these differences, human health risk characterization is conducted separately for potential carcinogenic and noncarcinogenic effects. However, carcinogenic chemicals may also cause noncarcinogenic effects (i.e., a variety of toxic endpoints other than cancer may be associated with exposure to carcinogens). Consequently, reference dose (RfD) values have been established for many carcinogens and are used in the evaluation of potential noncarcinogenic effects.

Key dose-response variables used in quantitative risk estimates are cancer potency factors (CPFs) for carcinogens and RfD values for noncarcinogens. The carcinogenic potency factor (expressed in units of $(mg/kg/day)^{-1}$) is typically determined by the upper 95 percent confidence limit of the slope of the linearized multistage model that expresses excess cancer risk as a function of dose. The RfD (expressed in units of mg/kg/day) is an estimated single daily chemical intake rate that appears to be without risk if ingested over a lifetime.

Available dose-response information for quantitative risk assessment is summarized in Table 6-1 for the chemicals investigated. Potency factors and reference dose values were collated primarily from the Integrated Risk Information System database (IRIS, 1989), and supplemented where necessary by information from other sources such as the Public Health Risk Evaluation Database (PHRED, 1988). As shown in Table 6-1, substances with the highest carcinogenic potency (i.e., those with the highest carcinogenic potency factors) are dieldrin, heptachlor epoxide, and PCBs. Substances with the highest noncarcinogenic potency toxicity (i.e., those with the lowest RfD values) are mirex, heptachlor epoxide, and dieldrin.

Human health risks due to PCBs were estimated based on the total of all the congeners present. EPA has developed a CPF only for total PCBs. While recent research (Smith et al., 1990) indicates that toxicity varies depending on the number of chlorines present and their position, EPA has not adopted this type of approach. Smith's research also indicates that certain PCBs can induce similar changes in enzymatic activity as dioxins and furans. At present the approved EPA approach is to estimate risks due to PCBs and dioxins/furans separately. The specific PCBs thought to induce enzyme changes (coplanar PCBs and mono-ortho analogues) were not quantified separately in this study. The risks due to chlordane were estimated using the CPF for chlordane and the sum of the concentrations of cis- and trans- chlordane, cis- and trans-nonachlor, and oxychlordane measured in the same fillet sample. This sum is referred to as combined chlordane. Heptachlor and heptachlor epoxide have separate CPF and RfD values that are different from chlordane.

Exposure Assessment

The exposure assessment for consumption of chemically contaminated fish and shellfish consisted of:

TABLE 6-1
Dose-Response Variables Used in Risk Assessment

Analyte	Cancer Potency Factor (CPF) (mg/kg/day)$^{-1}$	EPA Cancer Evidence Rating[a]	Reference (RfD) (mg/kg/day)
Biphenyl	—	NA	5.00x10^{-2}[b]
Chlordane	1.30x10^{0}[c]	B2	6.00x10^{-5}[c]
Chlorpyrifos	—	NA	3.00x10^{-3}[c]
DDE (p,p-)	3.40x10^{-1}[c,d]	B2	5.00x10^{-4}[c,d]
Dicofol (Kelthane)	4.40x10^{-1}[b]	C	—
Dieldrin	1.60x10^{1}[c]	B2	5.00x10^{-5}[c]
Endrin	—	D	3.00x10^{-4}[c]
Heptachlor	4.50x10^{0}[c]	B2	5.00x10^{-4}[c]
Heptachlor epoxide	9.10x10^{0}[c]	B2	1.30x10^{-5}[c]
Hexachlorobenzene	1.70x10^{0}[f]	B2	8.00x10^{-4}[c]
Hexachlorobutadiene	7.8x10^{-2}[c]	C	2.00x10^{-3}[c]
Isopropalin	—	NA	1.50x10^{-2}[c]
α-Hexachlorocyclohexane	6.30x10^{0}[c]	B2	—
γ-Hexachlorocyclohexane	1.30x10^{0}[f]	B2	3.00x10^{-4}[e]
Mercury	—	D	3.00x10^{-4}[e]
Mirex	1.80x10^{0}[f]	R	2.00x10^{-6}[c]
Pentachloroanisole	1.60x10^{-2}[g]	D,R	3.00x10^{-2}[e,f]
Pentachlorobenzene	—	D	8.00x10^{-4}[c]
Pentachloronitrobenzene	—	pending	3.00x10^{-3}[c]
Polychlorinated biphenyls	7.70x10^{0}[c]	B2	1.00x10^{-4}[h]
1,2,4,5 Tetrachlorobenzene	—	D	3.00x10^{-4}[c]
1,2,4 Trichlorobenzene	—	D	2.00x10^{-2}[c]
Trifluralin	7.70x10^{-3}[c]	C	7.50x10^{-3}[c]

a Designations are (IRIS, 1989): NA = not evaluated, B2 = probable human carcinogen, C = possible human carcinogen, D = not classified, R = under review by EPA.
b Value from PHRED (1988).
c Value from IRIS 1989 (data current as of 9/89).
d Value is for DDT. DDE is assumed to have similar toxic properties.
e Value from ATSDR (1987).
f Value from HEAST (U.S. EPA, 1989c).
g Value from EPA Region X toxicologist
h RfD for Arochlor 1016.

- Defining chemical concentrations to be used,
- Selecting consumption rates for various segments of the population, and
- Estimating chemical doses.

The detected fillet concentration at each site was used to estimate risks. If more than one fillet sample, excluding duplicates, was available, the average concentration was used, even if the fish species were different. Multiple fillets were available at four sites that represented 4 percent of the sites with xenobiotic data. Fillet composite samples consisting of fewer than three fish were not used for the risk assessment. Three consumption rates were used to estimate exposure:

- 6.5 g/day, which is the average fish consumption rate of freshwater and estuarine fish across the United States (U.S. EPA, 1980a);
- 30 g/day, which is representative of the average fish consumption rate by average sport fishermen (U.S. EPA, 1989b); and
- 140 g/day, which is representative of the consumption rate for the 95th percentile of sport fishermen and is appropriate for subsistence consumers (U.S. EPA, 1989b).

Risks for consumption rates of 6.5 g/day, 30 g/day, and 140 g/day can be read directly from the nomographs in Appendix B. The nomographs can be used to estimate risks at consumption rates between 1 and 1000 g/day.

The consumption rate was combined with the chemical concentration data to estimate a range of daily doses over a lifetime associated with each chemical and location. For xenobiotics, a concentration of zero was used for individual samples in which the analyte was not detected. (Specific sample detection limits for xenobiotics were not available.)

Standard EPA methods were used to estimate exposure and risk due to ingestion of fish (U.S. EPA, 1986b, 1989d). Exposure doses were determined using an equation that assumes a constant daily fish ingestion rate over a lifetime (70 years).

$$D_{ij} = (C_i \times I_j) / W$$

where:

D_{ij}	=	estimated dose (mg/kg/day) for chemical i at ingestion rate j
C_i	=	concentration of chemical i in fish or shellfish
I_j	=	ingestion rate for the jth percentile of the population
W	=	assumed human body weight (70 kg).

Risk Characterization

Potential upper-bound risks associated with each carcinogen were estimated as the probability of excess cancer using the equation:

$$R_{ij} = 1 - \exp(-D_{ij} \times P_i)$$

where:

R_{ij}	=	Risk associated with chemical i at consumption rate j
P_i	=	Carcinogenic potency factor for chemical i $(mg/kg/day)^{-1}$
D_{ij}	=	Dose of chemical i at consumption rate j (mg/kg/day).

The carcinogenic potency factors used and methods of dose estimation are as described above (see Dose Response Assessment and Exposure Assessment sections).

Potential hazards associated with noncarcinogenic toxic effects of the various chemicals were expressed as a ratio:

$$H_{ij} = D_{ij}/RfD_i$$

where:

H_{ij}	=	Hazard index of chemical i at consumption rate j
D_{ij}	=	Dose of chemical i at consumption rate j (mg/kg/day)
RfD_j	=	Reference dose for chemical i (mg/kg/day).

The hazard index is a ratio of a dose of a chemical to the level at which noncarcinogenic effects are not expected to occur (i.e., reference dose, RfD). If the value of the hazard index is less than 1.0, it follows that toxic effects are not expected to occur. The methods of dose estimation are as described above.

CARCINOGENIC RISK ESTIMATES

Potential upper-bound human carcinogenic risks were estimated for targeted and background sites using the maximum, mean, and median concentrations for all chemicals with CPF values (Tables 6-2 and 6-3). The fish tissue concentrations associated with these estimated cancer risks are given in Table 6-4. Table 6-5 presents a summary of the fish samples that exceed risk levels of 10^{-6} to 10^{-3} for each of the chemicals with CPF values. The highest lifetime risk levels are associated with total PCBs. The cancer risk exceeded 10^{-4} at 42 of 106 sites for total PCBs, for a fish consumption rate of 6.5 g/day. PCBs also exceeded 10^{-3} risks at 10 sites. A complete list of sites is presented in Appendix D-10.

Risks for chlordane were estimated for the sum of the cis- and trans-chlordane isomers, cis- and trans-nonachlor isomers, and oxychlordane (referred to as combined chlordane). The CPF factor for chlordane is used since separate cancer potency factors are not available for nonachlor and oxychlordane. This method is consistent with the EPA's Office of Pesticide Programs, which also combines the concentrations of the cis- and trans- isomers of chlordane and nonachlor with oxychlordane and the four chlordene isomers (referred to as TTR-Total Toxic Residue). The four chlordene isomers were not measured for this study. Heptachlor and heptachlor epoxide have different CPF and RfD values from those for chlordane, so were not added.

TABLE 6-2
Estimates of Potential Upper-Bound Cancer Risks at Targeted Sites Based on Fillet Samples[a,b,g]

Chemical	Maximum[c]	Mean[d]	Median[e]	No. of Sites with Fillet Data
PCBs	3.7×10^{-3}	3.4×10^{-4}	6.0×10^{-5}	106
DDE	8.9×10^{-5}	4.8×10^{-6}	4.6×10^{-7}	106
Combined Chlordane[f]	9.3×10^{-5}	3.6×10^{-6}	5.5×10^{-7}	106
Dieldrin	6.0×10^{-4}	2.2×10^{-5}	1.2×10^{-6}	106
α-Hexachlorocyclohexane	1.0×10^{-5}	4.4×10^{-7}	—	106
γ-Hexachlorocyclohexane	8.1×10^{-6}	3.6×10^{-8}	—	106
Hexachlorobenzene	8.0×10^{-6}	2.5×10^{-7}	—	106
Heptachlor	1.2×10^{-7}	1.1×10^{-7}	—	106
Heptachlor Epoxide	3.4×10^{-5}	8.7×10^{-6}	—	106
Mirex	3.8×10^{-5}	7.4×10^{-7}	—	106
Trifluralin	8.3×10^{-8}	1.7×10^{-9}	—	106
Dicofol	6.1×10^{-7}	2.8×10^{-8}	—	106
Hexachlorobutadiene	6.4×10^{-7}	7.1×10^{-9}	—	106
Pentachloroanisole	7.2×10^{-8}	2.0×10^{-9}	—	106

[a]Consumption rate of fish set at 6.5 g/day.
[b]Cancer Potency Factors used are given in Table 6-1n
[c,d,e] Risk shown is associated with maximum, mean, and median fillet concentration at targeted sites. Values below quantification set at zero.
[f]Combined chlordane is the sum of cis- and trans-chlordane isomers, cis- and trans-nonchlor isomers, and oxychlordane.
[g]Dash indicates median fillet concentration was below detection.

TABLE 6-3
Estimates of Potential Upper-Bound Cancer Risks at Background[d] Sites Based on Fillet Samples

Chemical	Maximum[a]	Mean[b]	Median[c]	No. of Sites with Fillet Data
PCBs	3.2×10^{-5}	8.0×10^{-6}	—	4
DDE	1.4×10^{-6}	4.1×10^{-7}	1.4×10^{-7}	4

Consumption rate of fish set at 6.5 g/day.
CPF values used are given in Table 6-1.
Dash indicates median fillet concentration was below detection.
[a, b,c] Risk shown is associated with maximum, mean, and median fillet concentration at background sites. Values below quantification were set at zero.
[d] It is important to note that background risks are estimated from a small number of samples. Also, as indicated in Chapter 2, the background samples were, in some cases, selected for purposes of comparison and do not necessarily represent areas completely free from point and nonpoint sources of pollution.

Note:
All fillet concentrations at background sites were below detection for dieldrin, chlordane, alpha-BHC, gamma-BHC, hexachlorobenzene, heptachlor, heptachlor epoxide, mirex, trifluralin, dicofol, hexachlorobutadiene, and pentachloroanisole.

TABLE 6-4
Fish Tissue Concentrations Used to Estimate Cancer Risks

TARGETED SITES

Chemical	Maximum	Mean	Median	No. of Sites with Fillet Data
PCBs	5148.1	477.4	84.5	106
DDE	2820	130.6	14.6	106
Combined Chlordane	770	29.6	4.6	106
Dieldrin	405	15.1	0.8	106
α-Hexachlorocyclohexane	17.5	0.75	ND	106
γ-Hexachlorocyclohexane	6.68	0.30	ND	106
Hexachlorobenzene	50.7	1.6	ND	106
Heptachlor	0.28	0.003	ND	106
Heptachlor Epoxide	40.7	1.0	ND	106
Mirex	225	4.42	ND	106
Trifluralin	116.0	2.35	ND	106
Dicofol	14.9	0.68	ND	106
Hexachlorobutadiene	88.3	0.98	ND	106
Pentachloroanisole	48.6	1.3	ND	106

Units are ng/g unless noted.

BACKGROUND SITES

Chemical	Maximum	Mean	Median	No. of Sites with Fillet Data
PCBs	44.8	11.2	ND	4
DDE	43.0	13.0	4.4	4

All fillet concentrations at background sites were below detection for dieldrin, chlordane, alpha-BHC, gamma-BHC, Hexachlorobenzene, heptachlor, heptachlor epoxide, mirex, trifluralin, dicofol, hexachlorobutadiene, and pentachloranisole.

Combined chlordane is the sum of cis- and trans-chlordane isomers, cis- and trans-nonachlor isomers, and oxychlordane.

TABLE 6-5
Number of Sites with Estimated Upper-Bound Risks

TARGETED SITES

Chemical	No. of Sites with Fillet Data	RISK LEVEL (Cumulative) $>10^{-6}$ (>1 in 1,000,000)	$>10^{-5}$ (>1 in 100,00)	$>10^{-4}$ (>1 in 10,000)	10^{-3} (>1 in 1,000)
PCBs	106	89	79	42	10
Dieldrin	106	53	31	6	0
Combined Chlordane	106	44	10	0	0
DDE	106	40	10	0	0
Heptachlor Epoxide	106	9	2	0	0
Alpha-BHC	106	11	1	0	0
Mirex	106	8	2	0	0
HCB	106	5	0	0	0
Gamma-BHC	106	0	0	0	0
Heptachlor	106	0	0	0	0
Dicofol	106	0	0	0	0
Hexachlorobutadiene	106	0	0	0	0
Pentachloroanisole	106	0	0	0	0
Trifluralin	106	0	0	0	0

BACKGROUND SITES

Chemical	No. of Sites with Fillet Data	RISK LEVEL (Cumulative) $>10^{-6}$ (>1 in 1,000,000)	$>10^{-5}$ (>1 in 100,000)	$>10^{-4}$ (>1 in 10,000)	(>1 in 1,000)
PCBs	4	1	1	0	0
DDE	4	1	0	0	0

Basis: 1) Used EPA (i.e., upper bound) cancer potency factors.
2) Used consumption rate of 6.5 grams/day.
3) Used average fillet concentrations at the few sites with multiple samples.

Combined chlordane is the sum of cis- and trans-chlordane isomers, cis- and trans-nonachlor isomers, and oxychlordane.

The mean, median, and maximum risks using 30 g/day and 140 g/day are compared to the risks using 6.5 g/day in Table 6-6. For the median fillet concentrations at targeted sites, estimated risks equal or exceed 10^{-5} for PCBs at 6.5 g/day and 30 g/day. At the higher consumption rate of 140 g/day, estimated risks due to combined chlordane and dieldrin were also above 10^{-5}.

As a final step in the risk characterization, a graphical tool was developed for estimating potential health risks at consumption rates from 1 to 1,000 g/day for all chemicals that exceeded a 10^{-6} risk level. These nomographs are included in Appendix B. As an example, the graph for estimating the carcinogenic risks from p,p'-DDE is shown in Figure 6-1. In each graph, the methods and assumptions outlined above were used to plot potential health risks for three consumption rates (i.e., 6.5 g/day, 30 g/day, and 140 g/day). In addition to the consumption rates shown, a scale is provided on each graph so that health risks can be estimated for any consumption rate in the range of 1 to 1,000 g/day. This is an important feature because potential health risks may vary with regional, cultural, or ethnic differences in species of fish eaten and consumption rates. Hence, using the nomographs provided herein, it is possible to evaluate potential health risks associated with specific consumption rates at a given site.

NONCARCINOGENIC RISKS

Noncarcinogenic hazard indices were summarized for targeted and background sites for the chemicals with reference dose values available (Table 6-7). Based on a fish consumption rate of 6.5 g/day, the hazard index, defined previously, exceeded 1 (meaning adverse effects may occur) at only a few targeted sites for PCBs, mirex, and combined chlordane. The hazard indices associated with the mean and median concentrations for these same chemicals were less than 1.0. The hazard indices for all chemicals at background sites were also less than 1.0.

Graphs for estimating noncarcinogenic hazard index values at various consumption rates were prepared for most of the compounds evaluated. Using these graphs, one can determine whether the hazard index would exceed a value of 1 at consumption rates between 1 and 1, 000 g/day. For example, using the maximum DDE concentration at targeted sites (2,819 ng/g), a hazard index value of 0.52 was estimated for a 6.5-g/day consumption rate, while for a 30-g/day rate it was about 2 (Figure 6-2). The graphs for the other compounds are included in Appendix B following those for estimating carcinogenic risks.

TABLE 6-6
Estimated Upper-Bound Risks at Three Fish Consumption Rates Based on Fillet Samples

	Maximum				Mean				Median		
Background	**6.5**	**30**	**140**	**Background**	**6.5**	**30**	**140**	**Background**	**6.5**	**30**	**140**
PCBs	3.2×10^{-5}	1.5×10^{-4}	6.9×10^{-4}	PCBs	8.0×10^{-6}	3.7×10^{-5}	1.7×10^{-4}	PCBs	-	-	-
DDE	1.4×10^{-6}	6.4×10^{-6}	3.0×10^{-5}	DDE	4.1×10^{-7}	1.9×10^{-6}	8.8×10^{-6}	DDE	1.4×10^{-7}	6.4×10^{-7}	3.0×10^{-6}
Targeted	**6.5**	**30**	**140**	**Targeted**	**6.5**	**30**	**140**	**Targeted**	**6.5**	**30**	**140**
PCBs	3.7×10^{-3}	1.7×10^{-2}	7.6×10^{-2}	PCBs	3.4×10^{-4}	1.6×10^{-3}	7.3×10^{-3}	PCBs	6.0×10^{-5}	2.8×10^{-4}	1.3×10^{-3}
DDE	8.9×10^{-5}	4.1×10^{-4}	1.9×10^{-3}	DDE	4.1×10^{-6}	1.9×10^{-5}	8.9×10^{-5}	DDE	4.6×10^{-7}	2.1×10^{-6}	9.9×10^{-6}
Combined Chlordane	9.3×10^{-5}	4.3×10^{-4}	2.0×10^{-3}	Combined Chlordane	3.6×10^{-6}	1.6×10^{-5}	7.7×10^{-5}	Combined Chlordane	5.6×10^{-7}	2.6×10^{-6}	1.2×10^{-5}
Dicofol	6.1×10^{-7}	2.8×10^{-6}	1.3×10^{-5}	Dicofol	2.8×10^{-8}	1.3×10^{-7}	6.0×10^{-7}	Dicofol	-	-	-
Dieldrin	6.0×10^{-4}	2.8×10^{-3}	1.3×10^{-2}	Dieldrin	2.2×10^{-5}	1.0×10^{-4}	4.8×10^{-4}	Dieldrin	1.2×10^{-6}	5.5×10^{-6}	2.6×10^{-5}
α-Hexachloro-cyclohexane	1.0×10^{-5}	4.6×10^{-5}	2.2×10^{-4}	α-Hexachloro-cyclohexane	4.4×10^{-7}	2.0×10^{-6}	9.4×10^{-6}	α-Hexachloro-cyclohexane	-	-	-
γ-Hexachloro-cyclohexane	8.1×10^{-7}	3.7×10^{-6}	1.7×10^{-5}	γ-Hexachloro-cyclohexane	3.6×10^{-8}	1.7×10^{-7}	7.8×10^{-6}	γ-Hexachloro-cyclohexane	-	-	-
Hexachloro-benzene	8.0×10^{-6}	3.7×10^{-5}	1.7×10^{-4}	Hexachloro-benzene	2.5×10^{-7}	1.2×10^{-6}	5.4×10^{-6}	Hexachloro-benzene	-	-	-
Hexachloro-butadiene	6.4×10^{-7}	3.0×10^{-6}	1.4×10^{-5}	Hexachloro-butadiene	7.1×10^{-9}	3.3×10^{-8}	1.5×10^{-7}	Hexachloro-butadiene	-	-	-
Heptachlor	1.2×10^{-7}	5.4×10^{-6}	2.5×10^{-5}	Heptachlor	*	*	*	Heptachlor	-	-	-
Heptachlor Epoxide	3.4×10^{-5}	1.6×10^{-4}	7.3×10^{-4}	Heptachlor Epoxide	8.4×10^{-7}	3.9×10^{-6}	1.8×10^{-5}	Heptachlor Epoxide	-	-	-
Mirex	3.8×10^{-5}	1.8×10^{-4}	8.2×10^{-4}	Mirex	7.4×10^{-7}	3.4×10^{-6}	1.6×10^{-5}	Mirex	-	-	-
Pentachloro-anisole	7.2×10^{-8}	3.3×10^{-7}	1.6×10^{-6}	Pentachloro anisole	1.9×10^{-9}	8.9×10^{-8}	4.2×10^{-8}	Pentachloro–anisole	-	-	-
Trifluralin	8.3×10^{-8}	3.8×10^{-7}	1.8×10^{-6}	Trifluralin	1.7×10^{-9}	7.8×10^{-9}	3.6×10^{-8}	Trifluralin	-	-	-

Basis: Used upper-bound CPFs (Table 6-2) fish consumption rates of 6.5, 30, and 140 g/day.
Dash indicates concentration was reported as not detected.
*Only one value was above detection, so risk not computed.
Combined chlordane is the sum of cis- and trans-chlordane isomers, cis- and trans-nonachlor isomers, and oxychlordane.

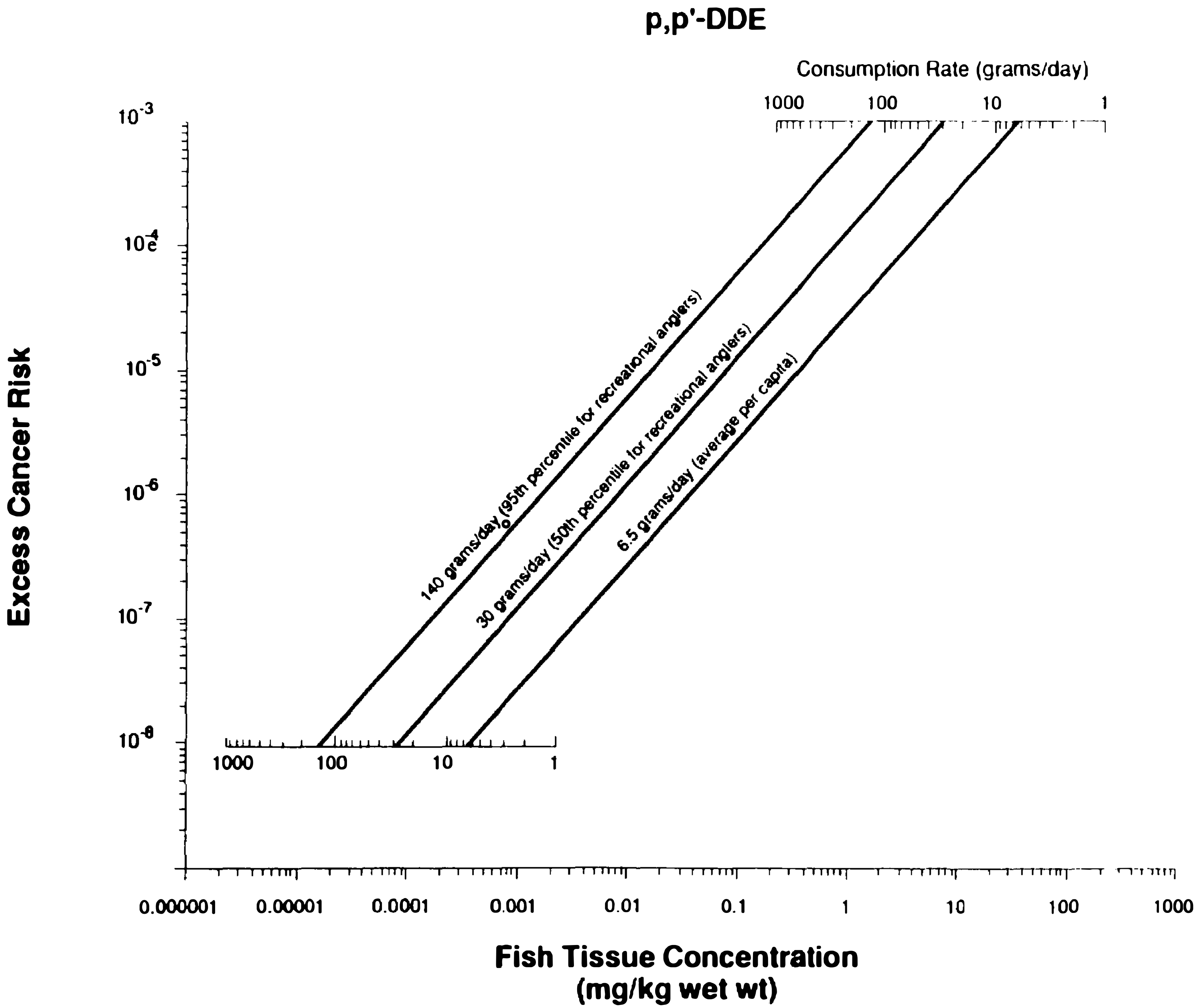


Figure 6-1. Graphical tool for estimating upper-bound cancer risk of p,p'-DDE or equivalents for different fish consumption rates.

TABLE 6-7
Noncarcinogenic Hazard Index Values at Targeted and Background Sites Based on Fillet Samples

TARGETED

Chemical	Maximum	Mean	Median	No. of Sites with Fillet Data
Biphenyl	9.8×10^{-5}	2.0×10^{-6}	3.5×10^{-7} [a]	106
Combined Chlordane	1.2	4.6×10^{-2}	7.1×10^{-3}	106
Chloropyrifos	2.4×10^{-3}	6.4×10^{-5}	ND	106
DDE	5.2×10^{-1}	2.4×10^{-2}	2.7×10^{-3}	106
Dieldrin	7.5×10^{-1}	2.8×10^{-2}	1.5×10^{-3}	106
Endrin	4.3×10^{-3}	9.6×10^{-5}	ND	106
γ-Hexachlorocyclohexane	2.1×10^{-3}	9.3×10^{-5}	ND	106
Hexachlorobenzene	5.9×10^{-3}	1.9×10^{-4}	ND	106
Heptachlor	5.2×10^{-5}	5.6×10^{-7} [a]	ND	106
Heptachlor Epoxide	2.9×10^{-1}	7.1×10^{-3}	ND	106
Hexachlorobutadiene	4.1×10^{-3}	4.6×10^{-5}	ND	106
Isopropalin	ND	ND	ND	106
Mercury	5.1×10^{-1}	9.0×10^{-2}	7.1×10^{-2}	182
Mirex	10.45 [a]	2.1×10^{-1}	ND	106
Pentachloronitrobenzene	2.7×10^{-5}	2.5×10^{-7}	ND	106
Pentachlorobenzene	6.0×10^{-3}	1.3×10^{-4}	ND	106
Pentachloroanisole	1.5×10^{-4}	4.0×10^{-6}	ND	106
PCBs	4.78	4.4×10^{-1}	7.8×10^{-2}	106
1,2,4,5 Tetrachlorobenzene	8.8×10^{-3}	1.2×10^{-4}	ND [a]	106
1,2,4 Trichlorobenzene	4.8×10^{-4}	7.2×10^{-6}	6.5×10^{-7}	106
Trifluralin	1.4×10^{-3}	2.9×10^{-5}	ND	106

BACKGROUND

Chemical	Maximum	Mean	Median	No. of Sites with Fillet Data
Biphenyl	3.7×10^{-7} [a]	2.2×10^{-7}	2.5×10^{-7}	4
Combined Chlordane	5.0×10^{-3}	1.0×10^{-3}	ND	4
Mercury	5.5×10^{-1} [a]	1.5×10^{-1}	1.2×10^{-1}	1
1,2,4 Trichlorobenzene	3.3×10^{-6}	1.6×10^{-6}	1.5×10^{-6}	4
PCBs	4.2×10^{-2}	1.0×10^{-2}	ND	4
p,p′-DDE	8.0×10^{-3}	2.0×10^{-3}	1.0×10^{-3}	4

(All other chemicals were not detected in background samples)

Consumption rate of fish at at 6.5 g/day. RfD values used are given in Table 6-2.
ND, not detected.
Combined chlordane is the sum of cis- and trans-chlordane isomers, cis- and trans-nonachlor isomers, and oxychlordane.

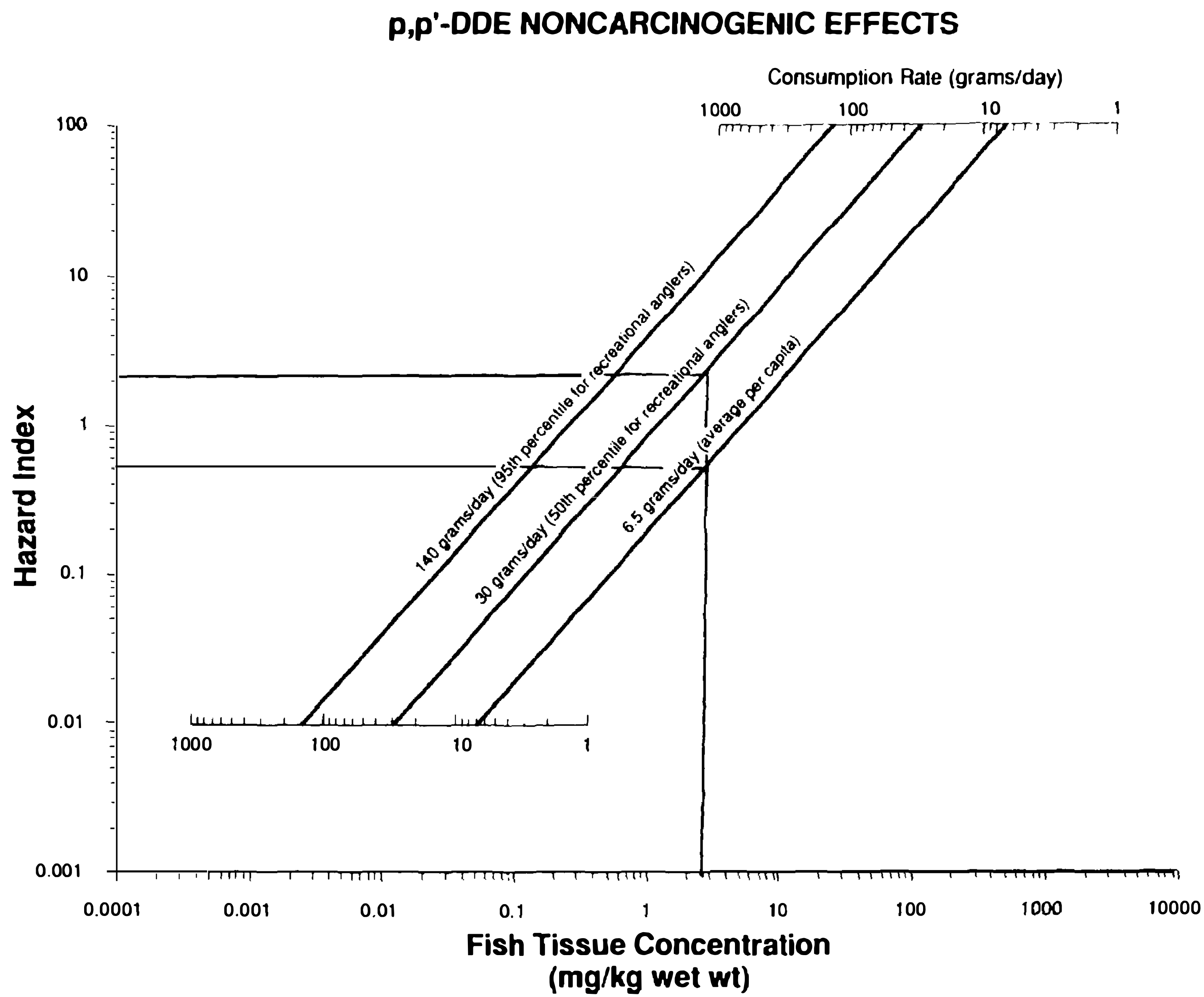


Figure 6-2. Graphical tool for estimating upper-bound noncarcinogenic hazard index of p,p'-DDE for different fish consumption rates.

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Additional specific references for the study compounds are included in the chemical profiles, Appendix C. These references include physical/chemical properties, standards and criteria, major compound uses, health effects, aquatic life effects where available, and factors used to estimate risks (e.g., CPF, RfD, BCF).

Glossary

Bioaccumulation — The net accumulation of a chemical from combined exposure to water, food, and sediment by an organism. This may be further defined as accumulation under a non-steady-state or equilibrium condition of exposure.

BCF — The bioconcentration factor (BCF) is the partition coefficient for the distribution of chemical between water and an organism exposed only through water. BCF = C_t/C_w, where C_t = concentration of a chemical in wet tissue (either whole organism or specified tissue) and C_w = concentration of a chemcial in water. The higher the BCF value, the greater the potential for high concentrations of a chemical to occur in fish tissue samples. BCF values given in the chemical profiles in Volume II are based on water and fish tissue concentrations.

CPF — Cancer potency factor expressed in units of $(mg/kg/day)^{-1}$ based on experiments to determine whether a chemical causes cancer. The method used by EPA to derive this value is to set the CPF equal to the upper 95 percentile of the slope of the linearized multistage model for extrapolation of cancer from high to low doses. Cancer risks derived using this approach are referred to as upper-bound risks.

Combined Chlordane — Combined chlordane is the sum of cis- and trans-chlordane isomers, cis- and trans-nonchlor isomers, and oxychlordane.

Congeners — Related chemical compounds with same basic structure but different number of substitutions (e.g., chlorine). Examples of congeners investigated in this project include the chlorinated dibenzo-p-dioxins (e.g., 2,3,7,8 TCDD with four chlorines and 1,2,3,7,8 PeCDD with five chlorines). Such congeners are sometimes referred to as homologs.

GC/MS — Gas chromatography/mass spectrometry, a laboratory analytical method used in this study for PCDDs, PCDFs, and other xenobiotic compounds.

Hazard Index — Ratio of dose of a chemical to the level at which noncarcinogenic effects are not expected to occur (reference dose or RfD). If the value of the hazard index is less than 1, no toxic effects should occur from the dose tested (e.g., ingestion of fish at a given consumption rate with a specified contaminant concentration).

Isomers	Related chemical compounds that have the same molecular formula but are structurally different. An example of isomers investigated during this study include cis- and trans-chlordane.
NPL	Waste disposal sites included on the National Priority List for clean-up under CERCLA/SARA, also referred to as Superfund sites.
PCDDs	Polychlorinated dibenzodioxins
PCDFs	Polychlorinated dibenzofurans
RfD	Reference dose expressed in units of mg/kg/day. The RFD is the estimated single daily chemical intake rate that appears to be without toxic effects if ingested over a lifetime.
TEC	Toxicity equivalency concentration for dioxins and furans. This represents a toxicity-weighted total concentration of all individual congeners using 2,3,7,8 TCDD as the reference compound. The 1989 interim method advocated by EPA was used for this study (Barnes et al., 1989).
TEF	Toxicity equivalency factors for dioxins and furans. These factors express the relative toxicity of the 2,3,7,8-substituted congeners. The values used in this study were from the 1989 interim method (Barnes et al., 1989).
TEQ	Toxicity equivalents for dioxins and furans (Barnes et al., 1989). This term has the same meaning as TEC.
Total Chlordane	Total chlordane refers to the sum of the measured concentration of cis- and trans-isomers of chlordane measured in the same sample.
TTR	Total toxic residue equals the combined concentration of cis- and trans-chlordane, cis- and trans-nonachlor, oxychlordane, and the four chlordene isomers. This combined concentration is used by EPA's Office of Pesticide Programs.
Xenobiotic	Compounds that do not naturally occur in living organisms.

APPENDIX A

Laboratory QA/QC Procedures and Results

APPENDIX A-1

Analysis of Laboratory QA/QC Data

Appendix A-1 - Analysis of Laboratory QA/QC Data

The QA/QC procedures, as mentioned in Chapter 2 and listed in Table A-1, included analysis of reference fish spiked with the chemicals being studied, analysis of method blanks and duplicate tissue samples, and confirmation sampling using a second GC column. The total number of QA/QC samples of each type is listed below:

	Number of Analyses
Reference Fish	142
Method Blanks	135
Duplicate Samples	117
Confirmation Samples	41

These data were used by the EPA Duluth laboratory to estimate analytical precision and bias.

BIAS

Bias is a systematic error resulting in values that are too high or too low. It can be measured using spiked samples and is defined as follows:

$$B = (100\,(C_a - C_b)/T) - 100$$

where:

B	=	percent bias
C_a	=	measured concentration of analyte after spiking
C_b	=	original concentration in sample
T	=	amount of spike added to sample.

Reference fish, not containing dioxin/furan, were used in this study to determine bias. The QA/QC criteria, listed in Table A-2, specify that the bias be ± 50 percent for tetra- and penta-dioxin/furan congeners, ± 100 percent for hexa- and hepta-dioxins and hexa-furans, and ± 200 percent for hepta-furans. Method bias achieved is reported in Table A-3 for PCDD/PCDF analysis. The reported values are for standard solutions in tridecane solvent and represent the three spiking levels indicated in the Analytical Procedures and Quality Assurance Plan for the Determination of Mercury in Fish (U.S. EPA, 1989a). Method bias prior to the use of the tridecane solvent was, in general, lower. Mean recovery for the dioxins/furans ranged from 94 percent to 109 percent. The percent bias ranged from +9 percent to -6 percent. Thus, the above criteria for bias were met.

The bias QA/QC criteria for xenobiotics were defined in terms of individual analyte recovery and total analyte recovery. The bias for specific analytes must be between +50 percent and +130 percent, except for the following compounds:

TABLE A-1
Laboratory Quality Assurance Procedures

1. All instrument maintenance schedules maintained according to the manufacturer's recommendations
2. Gas Chromatography (GC) performance
   a) Xenobiotics
      1. Column resolution (number of theoretical plates of resolution must not decrease by more than 20%)
      2. Relative retention times (3%) of internal standards
   b) PCDD/PCDF
      1. Resolution of 1,2,3,4 TCDD from 2,3,7,8 TCDD must be 0.75
      2. The R^2 value of the regression of the relative retention time of all biosignificant PCDD/PCDF to the library relative retention should not be <0.995
      3. Elution of all PCDD/PCDF during analysis from a GC window defining solutions of select PCDD/PCDF congener groups (first eluted/last eluted)
3. Mass Spectrometry (MS) performance
   a) Xenobiotics
      1. Sensitivity (signal-to-noise ratio, 3.0 for m/z 198 from injection of 10.0 ng decafluorotriphenylphosphine [DFTPP])
      2. Spectral quality (intensity of ions in the spectrum of DFTPP must meet specified criteria)
   b) PCDD/PCDF
      1. Sensitivity and linearity were evaluated using calibration standards (in pg/µl tridecane) which varied in concentration
      2. Mass resolution was a minimum of 5,000 (10% valley definition)
      3. Percent relative standard deviations for the mean response factors were <20%
4. Gel Permeation Chromatography (GPC) performance
   a) Xenobiotics
      1. Column flow rate (not vary by more than 0.2 ml/min)
      2. Column resolution (daily injection of performance solution)
      3. Collection cycle (start and end of the collect cycle must not deviate by more than 2 ml)
5. Silica Gel Chromatography performance
   a) Xenobiotics
      1. Evaluated by its ability to resolve cholesterol from a select model target analyte, dieldrin

TABLE A-2
Quality Assurance Parameters for Dioxins and Furans

	Ion Ratio	Method[a] Efficiency	Accuracy[a] at 10 pg/g	Precision[b] at 10 pg/g	S/N Minimum
TCDD	0.76±15%	>40%,<120%	±50%	±50%	3.0
PCDD	0.61±15%	>40%,<120%	±50%	±50%	3.0
HxCDD	1.23±15%	>40%,<120%	±100%	±100%	3.0
HpCDD	1.02±15%	>40%,<120%	±100%	±100%	3.0
TCDF	0.76±15%	>40%,<120%	±50%	±50%	3.0
PCDF	1.53±15%	>40%,<120%	±50%	±50%	3.0
HxCDF	1.23±15%	>40%,<120%	±100%	±100%	3.0
HpCDF	1.02±15%	>40%,<120%	200%	200%	3.0

[a] Variance of measured value from actual.
[b] Variance of difference of duplicates from mean.

TABLE A-3
Bias Analysis for PCDDs/PCDFs

Chemical	Mean Recovery	Stan. Dev.	% Bias
2,3,7,8 TCDF	109	16	9
2,3,7,8 TCDD	102	13	2
1,2,3,7,8 PeCDF	104	14	4
2,3,4,7,8 PeCDF	104	12	4
1,2,3,7,8 PeCDD	100	13	0
1,2,3,4,7,8 HxCDF	95	10	-5
1,2,3,6,7,8 HxCDF	104	17	4
2,3,4,6,7,8 HxCDF	96	11	-4
1,2,3,7,8,9 HxCDF	94	12	-6
1,2,3,4,7,8 HxCDD	99	24	-1
1,2,3,6,7,8 HxCDD	108	13	8
1,2,3,7,8,9 HxCDD	96	11	-4
1,2,3,4,6,7,8 HpCDF	99	11	-1
1,2,3,4,7,8,9 HpCDF	104	14	4
1,2,3,4,6,7,8 HpCDD	103	12	3

- Trichlorobenzenes (1,3,5-; 1,2,4-; and 1,2,3-);
- Tetrachlorobenzenes (1,2,4,5-; 1,2,3,5-; and 1,2,3,4-);
- Pentachlorobenzene; and
- Biphenyl.

The recovery for these analytes is low due to some losses during the evaporation steps. The average analyte recovery for the spiked analytes was then determined for these analytes. The QA/QC criteria specified that this value be greater than 35 percent and less than 130 percent (Table A-4).

The bias results are shown in Table A-5 for PCBs and Table A-6 for the remaining xenobiotics, excluding mercury. Mean recoveries for PCBs were estimated using data for PCBs with 3 to 7 chlorines with the recoveries ranging between 58 and 101 percent. The recoveries were higher for the more heavily chlorinated compounds. Bias for the above PCBs ranged between +8 and -37 percent and thus met the criteria.

Method bias values for xenobiotics were determined from two spiking levels (Analytical Procedures and Quality Assurance Plan, U.S. EPA, 1989a). Method bias for xenobiotic analytes varies considerably compared to PCDD/PCDF analysis. As expected, low recoveries are exhibited by the chlorinated benzenes and other semivolatile compounds due to the concentration steps in the analytical procedure. The percent bias for the analytes other than chlorinated benzenes and biphenyl ranged from -45 to +14. The average analyte recovery was 73.8, well within the overall QA/QC criteria.

The QA/QC criteria for mercury are listed in Table A-7. The amount of tissue analyzed decreased from 1.0 g to 0.2 g in 1990 to obtain results within the instrument calibration range established at a lower detection limit. The detection limit for samples analyzed in 1990 was 0.0013 µg/g tissue. Analysis and EPA reference fish (mean value 2.52 µg/g, standard deviation (s) = 0.64) throughout the study gave a mean mercury value of 2.87 µg/g (s = 0.08). This gives a bias of a +14 percent for mercury.

PRECISION

Precision (P) measures the reproducibility of the analyses. It can be determined as follows:

$$P = \frac{\text{difference between duplicate samples}}{\text{mean of duplicate}} \times 100$$

The precision criteria for dioxin/furan congeners are the same as those listed earlier for method bias. Specific precision criteria for the individual xenobiotics were not listed in the Analytical Procedures and Quality Assurance Plan (U.S. EPA, 1989a). The original Work Plan for the study (U.S. EPA, 1986a) listed a general criterion for precision of ± 50 percent.

Estimates of intralaboratory precision expressed as the standard deviation for replicate pairs are presented in Table A-8 for dioxins/furans and in Table A-9 for selected xenobiotics. The

TABLEA-4
QA/QC Criteria for Xenobiotics Analyses

1. GC relative retention time for the target analytes could not deviate by more than + 3% from calibration curve values.

2. Analyte identification criteria - reverse search identification of an analyte must have an FIT value of 800.

3. Signal-to-noise ratio - quantification ion must have a ratio of 3.0.

4. Relative response factor for each analyte quantification ion relative to the appropriate internal standard quantification ion must not deviate by 20% from the previous day's value, and must be within 50% of the mean value from the calibration curve.

5. Percent recovery of each surrogate standard must be determined and must be within 25 and 130 percent for iodonaphthalene and 50 and 130 percent for 4,4'-diiodobiphenyl.

6. Average analyte recovery for all target analytes must be greater than 35% but less than 130%, and for the fortified analytes (except several chlorobenzenes, biphenyl, and hexachlorobutadiene) recovery must be within a range of 50 to 130 percent.

TABLE A-5
Bias Analysis for Polychlorinated Biphenyls

Chemical	Mean Recovery	Stan. Dev.	% Bias
Tetrachlorobiphenyl	63	16.5	-37
Pentachlorobiphenyl	90	12	-10
Hexachlorobiphenyl	108	11	8
Heptachlorobiphenyl	99	23	-1

TABLE A-6
Bias Analysis for Xenobiotics

Chemical	Mean Recovery	Stan. Dev.	% Bias
1,3,5 Trichlorobenzene	25	7	-75
1,2,4 Trichlorobenzene	25	11	75
1,2,3 Trichlorobenzene	21	11	-79
1,2,4,5 Tetrachlorobenzene	32	16	-68
1,2,3,5 Tetrachlorobenzene	39	12	-61
Biphenyl	27	10	-73
1&2,3,4 Tetrachlorobenzene	33	15	-67
Pentachlorobenzene	43	16	-57
Trifluralin	86	25	-14
alpha-BHC	67	18	-33
Hexachlorobenzene	58	16	-42
Pentachloroanisole	67	18	-33
gamma-BHC (Lindane)	64	16	-36
Pentachloronitrobenzene	71	19	-29
Diphenyl disulfide	82	26	-18
Heptachlor	68	18	-22
Chlorpyrifos	106	16	6
Isopropalin	84	49	-16
Octachlorostyrene	96	24	-4
Heptachlor epoxide	88	11	-12
Oxychlordane	76	14	-24
Chlordane, trans	92	15	-8
Chlordane, cis	97	24	-3
Nonachlor, trans	96	22	-4
p,p'-DDE	95	23	-5
Dieldrin	100	14	0
Nitrofen	114	20	14
Endrin	102	14	2
Perthane	78	32	-22
Nonachlor, cis	99	22	-1
Methoxychlor	55	27	-45
Dicofol	96	27	-4
Mirex	90	20	-10

TABLE A-7
QA/QC Criteria for Mercury Analyses

1. Samples are analyzed in batches of 20 to 25, with at least 20% additional reagent blank and duplicate samples per batch.
2. The detection limit for a batch analysis is not to exceed 50% above the detection limit of 0.050 μg/g tissue, or samples are reanalyzed.
3. Complete reagent blanks are to produce a mercury signal equivalent to less than 0.15 μg/g tissue.
4. Signal response to the standards is not to drop below 50% of the optimum value. The instrument is reoptimized if this criterion is not met.
5. The standard deviation for batch duplicates is not to exceed two times the standard deviation for the optimum determined value. Samples outside this range are reanalyzed.
6. Analysis of EPA reference samples for mercury in fish is used to assess accuracy.

TABLE A-8
Intralaboratory Precision Measurements for Replicate Pairs for PCDD/PCDF Analysis

Chemical	# of Observations	Precision[a] (pg/g)	Concentration Range (pg/g)
2,3,7,8 TCDF	51	s=0.07X	1 to 100
2,3,6,7 TCDF	13	s=0.08X	1 to 30
2,3,7,8 TCDD	41	s=0.08X	1 to 120
1,2,3,7,8 PeCDF	14	s=0.21	1 to 10
2,3,4,7,8 PeCDF	29	s=0.09X	1 to 50
1,2,3,7,8 PeCDD	25	s=0.91	1 to 30
1,2,3,4,7,8 HxCDF	18	s=1.37	1 to 50
1,2,3,6,7,8 HxCDF	9	s=0.11X	1 to 30
2,3,4,6,7,8 HxCDF	11	s=0.17X	1 to 5
1,2,3,4,7,8 HxCDD	11	s=0.13X	1 to 10
1,2,3,6,7,8 HxCDD	29	s=0.11X	1 to 35
1,2,3,7,8,9 HxCDD	8	s=0.11X	1 to 10
1,2,3,4,6,7,8 HpCDF	11	s=0.77	1 to 15
1,2,3,4,6,7,8 HpCDD	33	s=0.08X	2 to 150

[a]X = concentration
s = standard deviation

TABLE A-9
Intralaboratory Precision Measurements for Replicate Pairs for Xenobiotic Analysis

Chemical	Number of Observations	Concentration Precision[a] (ng/g)	Range (ng/g)
1,3,5 Trichlorobenzene	5	s=13.05	40 to 100
1,2,4 Trichlorobenzene	5	s=0.28X	8 to 120
1,2,3 Trichlorobenzene	5	s=5.39	15 to 120
Hexachlorobutadene	6	s=0.39X	30 to 150
Biphenyl	5	s=0.19X	4 to 110
la2,3,4 Tetrachlorobenzene	6	s=0.35X	30 to 150
Pentachlorobenzene	5	s=0.04X+5.04	50 to 200
Trifluralin	6	s=0.19X	2.5 to 150
alpha-BHC	7	s=0.05X+1.70	2.5 to 250
Pentachloroanisole	10	s=0.25X	2.5 to 240
gamma-BHC (Lindane)	8	s=0.12X	3 to 240
Pentachloronitrobenzene	5	s=38.81	70 to 280
Heptachlor	6	s=7.44	50 to 250
Chlorpyrifos	8	s=0.05X+8.09	4 to 300
Isopropalin	7	s=38.43	10 to 500
Heptachlor epoxide	6	s=0.13X	15 to 260
Oxychlordane	11	s=0.12X	4 to 300
Chlordane, trans	14	s=0.10X	3 to 300
Chlordane, cis	13	s=0.10X	3 to 200
Nonachlor, trans	21	s=0.16X	4 to 400
p,p'-DDE	29	s=0.17X	10 to 400
Dieldrin	17	s=0.10X	3 to 400
Endrin	5	s=0.10X	100 to 500
Nonachlor, cis	13	s=0.13X	5 to 300
Dicofol	5	s=0.03X+5.66	20 to 300
Mirex	5	s=0.07X	4 to 300
Tetrachlorobiphenyl	14	s=0.17X	10 to 280
Pentachlorobiphenyl	26	s=0.16X	7 to 1000
Hexachlorobiphenyl	28	s=0.14X	8 to 1000
Heptachlorobiphenyl	21	s=8.33	7 to 120
Octachlorobiphenyl	6	s=0.15X+1.41	6 to 100
Hexachlorobenzene	4	N/A	2 to 36

[a]X= concentration
s = standard deviation

standard deviation, s, and coefficient of variation (CV) for each duplicate pair were determined and then plotted against the mean concentration. For most analytes, s increased as the mean increased and CV appeared constant. For these analytes the average CV was used as the precision summary. The precision is reported as s = (average CV)X, where X is the mean concentration of the duplicate pair. The pooled standard deviation value was used as the precision summary for 1,2,3,7,8 PeCDF; 1,2,3,4,7,8 PeCDD; 1,2,3,4,7,8 HxCDF; 1,2,3,4,6,7,8 HpCDF; 1,3,5 and 1,2,3 trichlorobenzene; pentachloronitrobenzene; and isopropalin.

CV decreased with increasing concentration, and s appeared constant over the concentration range for these analytes. For pentachlorobenzene, alpha-BHC, chlorpyrifos, dicofol, and octachlorostyrene, precision was determined by a least-squares linear regression since s increased with concentration and CV decreased with concentration. Precision is not reported for some analytes since not enough data were collected to make any conclusions.

Mercury precision for replicate pairs was estimated as s = 0.047 µg/g in the concentration range of 0.08 µg/g to 1.79 µg/g for 20 samples.

DATA COMPLETENESS

The original work plan (U.S. EPA, 1986a) specified a target for data completeness of 80 percent. This was to be based on verified data as a percentage of all reported data. For the dioxins and furans, 4 percent of all values did not meet the QA/QC criteria and are reported as "QR" in the data base. The xenobiotic data were tested throughout the study and if a run did not meet the 80 percent completeness criteria, the set of samples was rerun. No "QR" values were reported for xenobiotics. Thus, the criterion of 80 percent valid data was met.

APPENDIX A-2

Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish

United States
Environmental Protection
Agency

Environmental Research
Laboratory
Duluth MN 55804

EPA/600/3-90/022
March 1990

Research and Development

EPA

Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish

EPA/600/3-90/022
March 1990

U.S. Environmental Protection Agency

National Dioxin Study - Phase II

Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish

Environmental Research Laboratory
Office of Research and Development
U.S. Environmental Protection Agency
Duluth, MN 55804

NOTICE

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency. It has been reviewed technically and administratively. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ACKNOWLEDGEMENTS

Technical contributions to this research were made by:

<u>U.S. Environmental Protection Agency</u>

Brian C. Butterworth
Douglas W. Kuehl

<u>ASci Corporation</u>

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FOREWORD

Directed by Congressional mandate, the U.S. Environmental Protection Agency during 1983 initiated the National Dioxin Study, a survey of environmental contamination by 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in the United States. Results of this study are published in the National Dioxin Study: Tiers 3,5,6, and 7, EPA 400/4-82-003. This laboratory, the Environmental Research Laboratory- Duluth, was responsible for one part of the Study, the analysis of fish samples. The most significant findings of these analyses was the observation that fish contamination was more widespread than previously thought, and that a primary source of TCDD was discharge from pulp and paper production using chlorine.

A second more detailed characterization of anthropogenic organic chemical contaminants in fish was conducted in subsequent analyses during what is now called Phase II of the National Dioxin Study. This document describes the analytical methods used for the determination of the level of contamination of fifteen biosignificant polychlorinated dibenzo-p-dioxins and dibenzofurans in fish. A companion document (EPA /600/3-90/023) describes the analytical methods used for the determination of levels of contamination of polychlorinated biphenyls, pesticides, and industrial compounds in those same fish.

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TABLES

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1. Introduction

This document, "Analytical Procedures and Quality Assurance Plan for the Determination of PCDD/PCDF in Fish" has been drafted in response to the need for the Environmental Research Laboratory of Duluth (ERL-D) to perform analysis for tetrachloro- to octachloro- congeners/isomers of polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/PCDF), Table 1.

Table 1. Biosignificant PCDDs/PCDFs

Analyte	CASRN
2378-TCDF	51207-3129
2367-TCDF	
3467-TCDF	
2378-TCDD	1746-01-6
12378-PeCDF	57117-41-6
23478-PeCDF	57127-3126
23467-PeCDF	70648-29-9
12378-PeCDD	40321276-4
123467-HxCDF	
123478-HxCDF	70648-26-9
123678-HxCDF	57127-44-9
234678-HxCDF	60851-34-5
123789-HxCDF	72918-2129
123478-HxCDD	32598-23-3
123678-HxCDD	57753-85-7
123789-HxCDD	19408-74-3
1234678-HpCDF	67562-39-4
1234789-HpCDF	55673-89-2
1234678-HpCDD	37871200-4

These analyses are limited by lack of analytical standards; however isomer specificity may be determined using specially developed standards. Analytical results will, therefore, be reported as concentration (pg/g) for each gas chromatography (GC) peak in a congener class by making the assumption that the response for the molecular ion of all isomers in that class is equal to the response observed for the isomer for which ERL-D does have a standard. The target minimum level of detection (MLD) for specific PCDD/PCDF isomers is given in Table 2 below. This document is meant to be only a guideline for analyses and may be modified as needed to satisfactorily analyze any sample.

Table 2. Minimum Level of Detection Values

PCDD/PCDF	Target Minimum Level of Detection
TCDD, TCDF	1 pg/g
PeCDD, PeCDF	2 pg/g
HxCDD, HxCDF	4 pg/g
HpCDD, HpCDF	10 pg/g

II. Sample Preparation

A. Grinding: Frozen fish wrapped in aluminum foil are sent to the ERL-Duluth laboratory. How the fish is ground, (whole body or fillet), is dependent on the species. Bottom feeders are ground whole and predators are filleted with the skin off. Fish tissue is ground frozen inta stainless steel power meat grinder. Each sample is processed through the grinder three times which homogenizes it thoroughly. The ground tissue is stored at -20° C in solvent rinsed glass jars with aluminum lined plastic lids.

B. Extraction: Tissue (20 g) is blended with enough anhydrous sodium sulfate to dry the tissue (100 g). Two-thirds of the sample is placed inta glass Soxhlet thimble, spiked with 100 ul of each Standard Solution A and B (Table 3) and then the remainder of the sample is added to the thimble. The sample is extracted at least twelve hours with a 1:1 mixture of hexane and methylene chloride in a Soxhlet extractor. The sample is quantitatively transferred to a 500 ml Kuderna-Danish apparatus and prewashed boiling chips are added.

C. Percent Lipid Determination: The sample extracted in section I.B. of sample preparation is used to determine percent lipid. After sample concentration, the KD lower tube is placed in a 60° C water bath underta gentle stream of dry carbon filtered air. After any remaining solvent has been evaporated, the lower tube and contents are weighed. The lipid is then quantitatively transferred to the macro column as described in Section I.D. of sample preparation. After transfer, the empty lower tube and boiling chips are weighed. The percent lipid is calculated from the weight differences.

Table 3. Internal Standard Solutions.

Compound	Concentration in solution (pg/µL)	Concentration in tissue (pg/g*)
Internal Standard Solution A. (100 µL)		
$^{37}Cl_4$ 2,3,7,8-TCDD	2.0	10.0
$^{13}C_{12}$ 2,3,7,8-TCDD	5.0	25.0
$^{13}C_{12}$ 2,3,7,8-TCDF	5.0	25.0
$^{13}C_{12}$ 1,2,3,7,8-PeCDD	5.0	25.0
$^{13}C_{12}$ 1,2,3,7,8-PeCDF	5.0	25.0
$^{13}C_{12}$ 1,2,3,4,7,8-HxCDD	12.5	62.5
$^{13}C_{12}$ 1,2,3,4,7,8-HxCDF	12.5	62.5
$^{13}C_{12}$ 1,2,3,4,6,7,8-HpCDD	12.5	62.5
$^{13}C_{12}$ 1,2,3,4,6,7,8-HpCDF	12.5	62.5
$^{13}C_{12}$ OCDD	25.0	125.0
$^{37}Cl_4$ 2,3,7,8-TCDF	2.0	10.0
Internal Standard Solution B.		
1,2,3,4-TCDD	1.0	5.0
1,2,4,7,8-PeCDD	1.0	5.0
1,2,3,4-TCDF	1.0	5.0
1,2,3,6,7-PeCDF	1.0	5.0
Internal Standard Solution C.		
$^{13}C_{12}$ 1,2,3,4-TCDD	50.0	50.0

* Assumes a 20 g sample.

D. Anthropogenic Chemical Isolation: The sample extract is quantitatively transferred to a 30 cm x 2.5 cm glass chromatography column (MACRO-columns) fitted with a 300 mL reservoir on top. The column has been packed with a plug of glass wool (bottom to top), 2 g silica gel, 2 g potassium silicate, 2 g sodium sulfate 10 g celite/sulfuric acid and 2 g sodium sulfate, and previously washed with 100 mL hexane. The column is eluted with 100 mL benzene/hexane (5%) and the eluent is collected in a Kuderna-Danish (KD) apparatus (Caution: benzene is a known carcinogen). Isooctane (1.0 mL) is added, the volume is reduced and then transferred to the florisil column.

E. Florisil Chromatography: A 1.0 cm x 20.0 cm glass chromatogrsphy column fitted with a 100 mL reservoir is packed with a plug of glass wool (bottom to top), 5.0 cm (1.5 g) activated florisil and 1.0 cm sodium sulfate. The florisil is activated at 120t^{o} C for 24 hours. The column is washed with 20 mL methylene chloride followed by 10 ml hexane. Sample and two 1 ml hexane rinses are quantitatively applied in small "plugs". The column is eluted with 20 mL 2% methylene chloride/hexane and the eluate discarded. This wash is followed by 50 mL methylana chloride which flows directly onto the micro carbon/silce gel column for PCDD/PCDF isolation.

F. PCDD/PCDF Isolation: Effluent from the florisil column is passed onto a 4 mm x 200 mm column (micro-column) containing 300 mg silica gal/carbon (see sec. III.A.6) which was previously rinsed with 10 ml toluene followed by 10 ml methylene chloride. The column is fitted with a solvent reservoir. After the sample has almost completely eluted from the micro-column, the reservoir is washed twice with 2 mL 25% benzene/methylene chloride and the column is finally eluted with an additional 11 mL 25% benzene/methylene chloride. The column is inverted on the reservoir and the PCDD/PCDF are eluted with toluene (25 mL). The toluene fraction is collected in a pear shaped flask (25 ml) and reduced in volume to 0.1 mL in a 60°C water bath under a gentle stream of dry carbon filtered air. The sample is transferred to a microvial using toluene to rinse the flask. Prior to GC/MS analysis, the sample is allowed to evaporate to dryness and is spiked with 20 ul of Standard Solution C (Table 3).

III. Reagents and Standards:

A. Reagents:

1. Solvents: Only pesticide grade distilled in glass solvents are used. They are: hexane, isooctane, methylene chloride, benzene, toluene, acetone, and methanol (Burdick and Jackson, Fischer Scientific).

2. Sodium Sulfate: Sodium sulfate (Baker Chemical Company reagent grade anhydrous) is baked at 650°C in a furnace for 24 hours, cooled, and stored in an empty hexane solvent bottle.

3. Silica Gel: Silica-Gel-60 (Merck-Darmstadt), is Soxhlet extracted eight hours with methanol, placed on solvent rinsed foil, air dried for 12 hours, and vacuum oven dried (125°C) for 24 hours. It is stored in an empty hexane solvent bottle. Prior to use it is activated at 105°C for 24 hours.

4. Sulfuric Acid/Celite: Sulfuric acid (Baker Chemical Company, Ultrex) (5 mL) is blended in a 250 mL beaker with Celite 545 (Baker) (10 g).

5. Potassium Silicate: High purity potassium hydroxide (Aldridge Chemical Company) (56 g) is dissolved in methanol (300 mL). Silica-gel (100 g) is added to the mixture and stirred (1 hour, 60° C). The mixture is cooled and the solvent is removed using a Buchner funnel. The potassium silicate is rinsed twice with 100 ml of methanol and once with 100 ml of methylene chloride. The solids are placed on aluminum foil in a fume hood and allowed to dry for approximately 2 hours. The solids are placed in a vacuum oven and dried overnight at 105°C. The reagent is placed in a rinsed beaker and stored (activated) at 120°C until use.

6. Silica Gel/Carbon: Silica Gel-60 (100 g) (Merck-Darmstadt) is Soxhlet extracted with methanol (200 mL) for 24 hours, air dried in a hood, and further dried in vacuum oven for 24 hours. AMOCO PX-21 Carbon (5 g) is added and then blended until uniform in color. The Silica Gel/Carbon is stored in a closed jar at room temperature until use.

7. Florisil: Florisil 60-100 mesh (Baker Analyzed) is soxhlet extracted with methanol for 24 hours, placed on solvent rinsed foil, air dried and stored in an empty hexane bottle. Prior to use it is activated at 120°C for 24 hours.

8. Standards:

1. Analytical Standard Spiking Solution.

Table 3 provides details of the spiking solutions. The surrogate analytes are used by the data reviewer to insure that calculated MLD values are reasonable.

2. Quantification Standards: Quantification standards were prepared by Wright State University. The concentration of 2,3,7,8-TCDD was

checked against a primary standard obtained from the U.S. National Bureau of Standards. A table of the concentrations of each isomer in each standard is given in Table 4.

3. Qualitative Standards: ERL-D has developed two qualitative analytical standards, one containing all 75 PCDD's and all 138 PCDF's was developed from an extraction of municipal incinerator fly ash (Tables 5 and 6) and the other containing only the biosignificant isomers was developed by exposure of fish to an extract of municipal incinerator fly ash and processing the exposed fish for PCDD/PCDF. These standards will be used to assign structures for isomer specific analyses.

   Standard solutions are sonicated for 5 to 10 minutes before use.

4. Mass Spectrometer Mass Calibration Compounds: Perfluorokerosene (PFK) is used for the initial mass calibration of the mass spectrometer. Perfluorodecalin (PFD) is used daily for determining mass resolution on m/z 392.9761.

Table 4: Calibration Standards

Calibration Standard	Concentrations in Calibration Solutions in pg/ul Tridecane							
	V1	V2	V3	V4	V5	V6	V7	V8
2,3,7,8-TCDD	200	100	50	25	10	5	2.5	1
2,3,7,8-TCDF	200	100	50	25	10	5	2.5	1
1,2,3,7,8-PeCDD	200	100	50	25	10	5	2.5	1
1,2,3,7,8-PeCDF	200	100	50	25	10	5	2.5	1
2,3,4,7,8-PeCDF	200	100	50	25	10	5	2.5	1
1,2,3,4,7,8-HxCDD	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,6,7,8-HxCDD	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,7,8,9-HxCDD	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,4,7,8-HxCDF	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,6,7,8-HxCDF	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,7,8,9-HxCDF	500	250	125	62.5	25	12.5	6.25	2.5
2,3,4,6,7,8-HxCDF	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,4,6,7,8-HpCDD	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,4,6,7,8-HpCDF	500	250	125	62.5	25	12.5	6.25	2.5
1,2,3,4,7,8,9-HpCDF	500	250	125	62.5	25	12.5	6.25	2.5
OCDD	1000	500	250	125	50	25	12.5	5
OCDF	1000	500	250	125	50	25	12.5	5
$^{13}C_{12}$ 2,3,7,8-TCDD	50	50	50	50	50	50	50	50
$^{13}C_{12}$ 2,3,7,8-TCDF	50	50	50	50	50	50	50	50
$^{13}C_{12}$ 1,2,3,7,8-PeCDD	50	50	50	50	50	50	50	50
$^{13}C_{12}$ 1,2,3,7,8-PeCDF	50	50	50	50	50	50	50	50
$^{13}C_{12}$ 1,2,3,6,7,8-HxCDD	125	125	125	125	125	125	125	125
$^{13}C_{12}$ 1,2,3,4,7,8-HxCDF	125	125	125	125	125	125	125	125
$^{13}C_{12}$ 1,2,3,4,6,7,8-HpCDD	125	125	125	125	125	125	125	125
$^{13}C_{12}$ 1,2,3,4,6,7,8-HpCDF	125	125	125	1.25	125	125	125	125
$^{13}C_{12}$ OCDD	250	250	250	250	250	250	250	250
$^{37}Cl_4$ 2,3,7,8-TCDD	20	20	20	20	20	20	20	20
$^{37}Cl_4$ 2,3,7,8-TCDF	20	20	20	20	20	20	20	20
$^{13}C_{12}$ 1,2,3,4-TCDD	50	50	50	50	50	50	50	50

Table 5: Relative Retention Times for 4-8 PCDD Isomers

Compound	RRT DB5	RRT SP2330
1368	0.814	0.826
1379	0.838	0.871
1369	0.861	0.948
1378	0.912	0.916
1469	0.912	1.072
1247	0.912	0.948
1248	0.912	0.948
1246	0.921	1.014
1249	0.921	1.014
1268	0.934	0.972
1478	0.940	0.990
1279	0.960	1.027
1234	0.985	1.014
1236	0.985	1.027
1269	0.985	1.105
1237	0.993	1.014
1238	0.993	1.014
2378	1.000	1.000
1239	1.009	1.088
1278	1.028	1.072
1267	1.048	1.130
1289	1.079	1.216
12468	1.224	1.111
12479	1.224	1.111
12469	1.265	1.268
12368	1.293	1.148
12478	1.308	1.188
12379	1.320	1.209
12369	1.348	1.307
12467	1.348	1.321
12489	1.348	1.321
12347	1.368	1.268
12346	1.368	1.352
12378	1.400	1.288
12367	1.415	1.363
12389	1.443	1.463
124679	1.620	1.473
124689	1.620	1.473
123468	1.673	1.473
123679	1.700	1.546
123689	1.700	1.546
123469	1.700	1.681
123478	1.764	1.604
123678	1.775	1.618
123467	1.802	1.789
123789	1.802	1.721
1234679	1.976	2.135
1234678	2.023	2.297
12346789	2.234	3.225

Table 6: Relative Retention Times for 4-8 PCDF Isomers

Compound	RRT DB5	RRT SP2330	Compound	RRT DB5	RRT SP2330
1368	0.730	0.777	13678	1.202	1.083
1468	0.752	0.875	13479	1.217	1.103
2468	0.763	0.989	23469	1.217	1.173
1247	0.782	0.885	12479	1.233	1.142
1347	0.782	0.865	13469	1.253	1.204
1378	0.782	0.853	23468	1.253	1.278
1346	0.782	0.919	12469	1.253	1.278
2368	0.782	1.071	12347	1.253	1.173
1367	0.801	0.881	12346	1.253	1.231
1348	0.801	0.900	12348	1.280	1.216
1379	0.801	0.853	12378	1.280	1.216
1268	0.835	0.943	12367	1.295	1.252
1248	0.835	0.919	23489	1.309	1.388
1467	0.853	0.989	12379	1.309	1.237
1478	0.853	0.943	23478	1.359	1.557
1369	0.863	0.943	12489	1.359	1.446
1237	0.863	0.943	13489	1.359	1.350
2467	0.863	1.109	12369	1.359	1.373
1234	0.880	0.977	23467	1.371	1.612
2349	0.880	0.977	12349	1.392	1.420
1236	0.880	0.989	12389	1.446	1.590
1469	0.880	1.061			
1238	0.880	0.989	123468	1.556	1.336
1278	0.902	1.017	134678	1.570	1.370
1349	0.920	1.013	124678	1.570	1.348
1267	0.920	1.049	134679	1.570	1.348
2378	0.939	1.169	124679	1.602	1.428
2348	0.939	1.175	124689	1.621	1.521
2347	0.939	1.140	123467	1.663	1.533
2346	0.939	1.193	123478	1.663	1.489
1246	0.939	0.940	123678	1.676	1.502
1249	0.939	1.071	123479	1.676	1.489
1279	0.939	1.049	123469	1.712	1.668
2367	0.973	1.206	123679	1.730	1.562
1239	0.988	1.140	123689	1.744	1.668
1269	0.988	1.162	234678	1.744	2.012
3467	0.988	1.264	123789	1.827	1.871
1289	1.071	1.341	123489	1.827	1.940
13468	1.180	1.008	1234678	1.954	1.936
12468	1.920	1.028	1234679	1.979	2.001
23479	1.190	1.065	1234689	2.026	2.161
12368	1.202	1.103	1234789	2.043	2.463
12478	1.202	1.121			
13467	1.202	1.142	12346789	2.240	3.165
12467	1.202	1.160			

IV. Instrumental Parameters:

All gas chromatography/mass spectrometry analyses (GC/MS) will be done on a Finnigan-MAT 8230 high resolution GC/high resolution MS (HRGC/HRMS) system. Instrumental parameters are given in Table 7.

Table 7: HRGC/HRMS Operating Parameters

Data Acquisition: Multiple Ion Selection Electric Sector Scan.

Compound	Mass Window	m/z value Quant.	Confir.*
TCDF	1	305.8986	303.9016
$^{37}Cl_4$-TCDF	1	311.8898	
$^{13}C_{12}$-TCDF	1	317.9389	315.9419
TCDD	1	321.8936	319.8965
$^{37}Cl_4$-TCDD	1	327.8847	
$^{13}C_{12}$-TCDD	1	333.9338	331.9368
PeCDF	2	339.8597	341.8567
$^{13}C_{12}$-PeCDF	2	351.9000	349.9029
PeCDD	2	355.8546	353.8576
$^{13}C_{12}$-PeCDD	2	367.8949	369.8919
HxCDF	3	373.8207	375.8178
$^{13}C_{12}$-HxCDF	3	385.8610	387.8580
HxCDD	3	389.8156	391.8127
$^{13}C_{12}$-HxCDD	3	401.8559	403.8530
HpCDF	4	407.7817	409.7788
$^{13}C_{12}$-HpCDF	4	419.8220	421.8191
HpCDD	4	423.7766	425.7737
$^{13}C_{12}$-HpCDD	4	435.8169	437.8140
OCDF	5	443.7498	445.7369
$^{13}C_{12}$-OCDF	5	455.7801	453.7831
OCDD	5	459.7348	457.7377
$^{13}C_{12}$-OCDD	5	471.7750	473.7721

Sample Introduction:	Capillary Column, Splitless Injection.
Ionization:	Electron Impact, 70eV, 1mA Emission Current.
Source Pressure:	1×10^{-5} torr.
Ionizer Temperature:	250° C.
Mass Resolution:	5000, 10% valley.
Scan Rate:	1 MIS cycle per second.
GC Column:	30 m DB-5, 60 m SP2330
Linear Velocity:	35 cm/sec Helium.
Temperature Program:	180° C (hold 1 min); 13°/min to 200°; 3°/min to 270°; 270° hold 4 min.

Mass windows are monitored sequentially during the temperature programs, with the windows definded by the elution of standards.

* Quant. = Quantifcation ion; Confir. = Confirmation ion.

V. Quality Assurance/Quality Control (QA/QC)

A. General Procedures of Operation

1. Analysis of Samples: Samples are analyzed in sets of twelve consisting of:

   a. Blank: Method Blank (extraction apparatus) is prepared in the laboratory and subjected to the same sample preparation procedures as environmental samples. The Method Blank is used in every sample set.

   b. Fortified Matrix: Native analytes (100 uL) (Table 8) are added to a blank sample matrix. The levels of fortification of native analytes in the matrix spike will be above the target detection limit to provide an estimate of the method's sensitivity, and for determination of percent accuracy of quantification. This sample may be substituted with a reference sample that has been analyzed at least three times and a mean value of contamination has been established.

   c. Detection Limit Verification Sample: An environmental sample with nondetectable amounts of native analyte (determined from a previous analysis) will be spiked with native analytes (Table 8) and analyzed with the next sample set. The addition of the QA/QC sample will be done for only the first three sample sets of any matrix type to establish that the calculated MLD is achievable. If analytical results show difficulty in obtaining the MLD, then this QA/QC sample must be in each set. If no problem is experienced, then this QA/QC sample may be dropped.

Table 8: Native PCDD/PCDF spiking solution (100 uL)

Compound	Concentration (pg/uL Tridecane) Solution A	Solution B	Solution C
2,3,7,8-TCDD	0.50	1.00	1.50
2,3,7,8-TCDF	0.50	1.00	1.50
1,2,3,7,8-PeCDD	0.50	1.00	1.50
1,2,3,7,8-PeCDF	0.50	1.00	1.50
2,3,4,7,8-PeCDF	0.50	1.00	1.50
1,2,3,4,7,8-HxCDD	1.25	2.50	3.75
1,2,3,6,7,8-HxCDD	1.25	2.50	3.75
1,2,3,7,8,9-HxCDD	1.25	2.50	3.75
1,2,3,4,7,8-HxCDF	1.25	2.50	3.75
1,2,3,6,7,8-HxCDF	1.25	2.50	3.75
2,3,4,6,7,8-HxCDF	1.25	2.50	3.75
1,2,3,7,8,9-HxCDF	1.25	2.50	3.75
1,2,3,4,6,7,8-HpCDD	1.25	2.50	3.75
1,2,3,4,6,7,8-HpCDF	1.25	2.50	3.75
OCDD	2.50	5.00	7.50
OCDF	2.50	5.00	7.50

d. Duplicate Sample: Two separate portions of the same environmental sample are processed and analyzed.

e. Environmental Samples: The total number of environmental samples analyzed is eight if the Detection Limit Verification sample is used; otherwise nine samples are analyzed.

2. Sample Tracking and Labeling of Samples:

a. Logging Incoming Samples: ERL-D completes the chain of custody forms and informs the Sample Control Center (SCC) that samples arrived safely or informs SCC of any problems with the samples. Each sample received by ERL-D had previously been assigned two numbers by the Sample Control Center, the Sample Control Center number (SCC#) and an Episode number. The SCC# number is unique for each sample and provides a means for tracking a given sample throughout its analysis and its permanent storage at the locker plant. The samples are placed into freezer A upon arrival at ERL-Duluth, homogenized, (see II.A.), and an aliquot (100-500 g) is placed into freezer B. After the samples are extracted they are put into freezer C. If all the data meets QA requirements after mass spectral analysis and quantification, the samples are transferred to a locker plant for permenent storage (-20° C).

b. Logging and Labeling Samples During Preparation: A laboratory identification code (lab ID) is randomly assigned to each sample in a set of twelve at the start of sample preparation. The code consists of a letter, A through L, date of extraction, and two initials of the sample preparation chemist, (e.g. A091587ML). This code is used to identify the sample throughout the analysis period. The SCC#, lab ID, sample description, weight of sample, and amount of analytical standards added to each sample are recorded in the sample preparation log book at the start of extraction. The lab ID is written on labeling tape which is transferred from beaker to flask during sample preparation. The lab ID is written into the MS log book along with the mass spectra analysis number.

3. Data System Sample Tracking: ERL-D has developed the National Dioxin Study (NDS) Phase II, Bioaccumulative Pollutants in Fish: Sample Tracking Database to facilitate record keeping and summary report generation for each sample on the DEC-VAX 11/785 (Digital Equipment Corporation). For each sample, including QA samples, information pertinent to each sample is entered into the

database. Quantification data (final concentration, ion ratios, percent recovery, MLDs, and signal to noise) are automatically uploaded to the database once all QA criteria have been met. Figure 1 is an example of the NDS database.

The first two letters of the SCC number indicate whether the sample is an Environmental, Method or Matrix Blank, Duplicate Sample or a mass spectral confirmation analysis of an environmental sample. All environmental samples begin with the letter D, or S if it is a mass spectral confirmation analysis of a previously analyzed environmental sample. The Blank and Duplicate samples begin with the letter Q followed by a D or an R for duplicate or reference fish sample, respectively. Table 9 lists the possible codes for the SCC number, and matrix type. Episode numbers for Blanks and Fortified Matrix samples are entered as 0000.

Figure 1: Database Format for Sample Information.

NDS Phase II: BioaccumulatXve PolXutants in Fish:
Sample Tracking System ERL-D loc:25

EPISODE #: 0000 SCC #: QR071486
Sampling Information:
SamplXng Office:
State & City:
Sampling Contact:
Date Sampled: 0/ 0/ 0
Site Location:
LatiXude: N 0 0' 0" Longitude: W 0 0' 0"
Analysis Lab: 0 Date Received: 0/ 0/ 0
Matrix Type: R Rerun: 0

Analytical:	PCDD/PCDF	PesticideX & Industrial Chemicals
Extraction Date:	7/14/86	0/ 0/ 0
GC/MS ID:	MAT86824	
LAB ID:	K071486LH	
Weight:	20.00	0.00
% Lipid:	5.2	0.0
Mass Lipid on GPC:		0.00

Comments: Reference fish 86

Figure 1. cont: Database format for Sample Information

NDS Phase II: Bioaccumulative Pollutants in Fish

EPISODE #: 0000 SCC #: QR071486 ERL-D Loc: 25

DATA FOR BIOSIGNIFICANT POLYCHLORINATED DIBENZODIOXINS AND FURANS:

Analyte	CAS NO.	I/R	S/N	%REC	DL	Amount(pg/g)
2,3,7,8-TCDF	51207-31-9	0.74	55.75	62	0.0000	5.26
2,3,6,7-TCDF		1.00	8.28	62	0.9726	ND
3,4,6,7-TCDF		1.71	16.56	62	0.4863	ND
2,3,7,8-TCDD	1746-01-6	0.78	40.75	73	0.0000	15.63
1,2,3,7,8-PeCDF	57167-41-6	1.33	16.72	56	1.0892	ND
2,3,4,7,8-PeCDF	57167-3166	1.10	11.15	56	1.6357	ND
2,3,4,6,7-PeCDF	70648-29-9	0.00	8.36	56	2.1786	ND
1,2,3,7,8-PeCDD	40321676-4	0.25	4.24	57	4.0729	ND
1,2,3,4,6,7-HxCDF *						
1,2,3,4,7,8-HxCDF	70648-26-9	0.00	57.03	47	0.7327	ND
1,2,3,6,7,8-HxCDF	57117-44-9	0.67	28.52	47	16.4656	ND
2,3,4,6,7,8-HxCDF	60851-34-5	1.25	57.03	47	0.7327	ND
1,2,3,7,8,9-HxCDF	72918-21-9	0.00	57.03	47	0.7327	ND
1,2,3,4,7,8-HxCDD	32598-13-3	0.00	29.08	49	1.3863	ND
1,2,3,6,7,8-HxCDD	57753-85-7	1.31	4.67	49	0.0000	3.23
1,2,3,7,8,9-HxCDD	19408-74-3	0.00	29.08	49	16.3863	ND
1,2,3,4,6,7,8-HpCDF	67562-39-4	0.62	18.97	39	0.0000	ND
1,2,3,4,7,8,9-HpCDF	55673-89-7	0.00	37.96	39	0.0000	ND
1,2,3,4,6,7,8-HpCDD	37871-00-4	1.13	10.50	39	0.0000	5.93

* Coelutes with 1,2,3,4,6,7-HxCDF on a DB5.

I/R = Ion Ratio; S/N = Signal to Noise; DL = Detection Limit

Table 9: Codes for the SCC Number and Matrix Type

SCC number first letter options:

- D -- Environmental samples
- Q -- QA samples
- S -- MS confirmation analysis

Second letter options for Environmental Samples

A - Region 1	G - Region 7
B - Region 2	H - Region 8
C - Region 3	Y - Region 9
D - Region 4	J - Region 10
E - Region 5	T - All regional data
F - Region 6	

Second letter options for QA samples:

- B - Method or matrix blank
- D - Labrotory duplicate
- R - Reference fish or fortified matrix

Matrix Type:

- PF - Predator Fillet
- WB - Whole Bottom
- WP - Whole Predator
- BF - Bottom Fillet
- R - Reference
- Y - Blank
- L - Laboratory Duplicate

B. Instrumental Quality Control

1- Gas Chromatograph

a. Operation and Maintenance: Operation and maintenance of the gas chromatograph will be done according to manufacturer's recommendations.

b. Column Performance: GC column performance will be evaluated by:

i. Resolution of 1,2,3,4-TCDD from 2,3,7,8-TCDD (Table 10).

ii. The R^2 value of the regression of the sample relative retention time of all biosignificant PCDD/PCDF, to the library relative retention should not be less than 0.995.

iii. Elution of all PCDD/PCDF during analysis from a GC window defining solution of select PCDD/PCDF (Table 11).

Table 10: GC Column Performance Quality Control

Resolution of 1,2,3,4-TCDD from 2,3,7,8-TCDD will be used to evaluate general column performance. Resolution (R) must be 0.75 or greater.

$$R = \frac{2d}{W_1 + W_2}$$

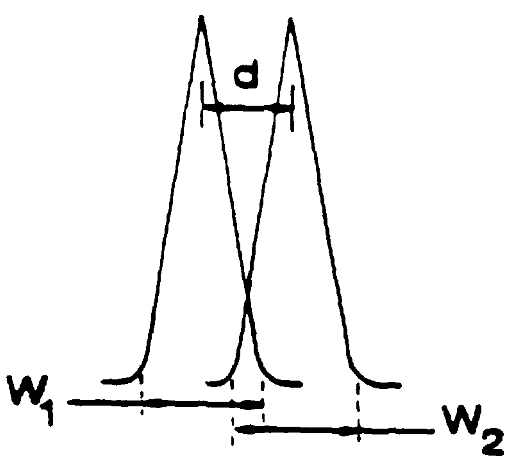


Table 11: GC Eluting Window Defining Solutions for DB-5 Column

Congener Group	First Eluting	Last Eluting
TCDD	1,3,6,8	1,2,8,9
TCDF	1,3,6,8	1,2,8,9
PeCDD	1,2,4,7,9 / 1,2,4,6,8	1,2,3,8,9
PeCDF	1,3,4,6,8	1,2,7,8,9
HxCDD	1,2,4,6,7,9 / 1,2,4,6,8,9	1,2,3,4,6,7
HxCDF	1,2,3,4,6,8	1,2,3,4,8,9
HpCDD	1,2,3,4,6,7,9	1,2,3,4,6,7,8
HpCDF	1,2,3,4,6,7,8	1,2,3,4,7,8,9

2. Mass Spectral Performance: The performance of the mass spectrometer is evaluated for resolution, sensitivity and linearity. The mass resolution used for these analyses is set at a minimum of 5000 (10% valley definition). The mass spectrometer is tuned each day to the required resolution according to the procadures established by the instrument manufacturer. Sensitivity and linearity is evaluated by the use of calibration standards varying in concentration (Table 4). A calibration curve is established for each standard. The curve must be linear over the range of concentrations used in the calibration standards. The percent relative standard deviations for the mean response factors must be less than 20 percent.

C. Evaluation of Data:

1. Accuracy: Accuracy, the degree to which the analytical measurement reflects the true level present, will be evaluated in two ways for each sample set. These are: the difference of measurement of a PCDD/PCDF isomer added to a blank matrix, or difference of measurement of a PCDD/PCDF from the level in an established reference material; and the efficiency for recovery

of the internal standard added for each congener group. The QA requirements for accuracy and method efficiency are provided in Table 12. Percent Accuracy and Percent Method Efficiency are defined as follows:

$$\% \text{ accuracy} = \frac{\text{measured value}}{\text{amount native isomer added to blank matrix}} \times 100$$

$$\% \text{ Method efficiency} = \frac{\text{measured value}}{\text{amount internal standard added to each sample}} \times 100$$

Table 12: Quality Assurance Parameters

	Ion Ratio	Method Efficiency*	Accuracy* at 10 pg/g	Precision** at 10 pg/g	S/N Minimum
TCDD	0.76± 15%	>40%, <120%	±50%	±50%	3.0
PCDD	0.61± 15%	>40%, <120%	±50%	±50%	3.0
HxCDD	1.23± 15%	>40%, <120%	±100%	±100%	3.0
HpCDD	1.02± 15%	>40%, <120%	±100%	±100%	3.0
OCDD	0.88± 15%	>40%, <120%	±200%	±100%	3.0
TCDF	0.76± 15%	>40%, <120%	±50%	±50%	3.0
PCDF	1.53± 15%	>40%, <120%	±50%	±50%	3.0
HxCDF	1.23± 15%	>40%, <120%	±100%	±100%	3.0
HpCDF	1.02± 15%	>40%, <120%	±200%	±200%	3.0
OCDF	1.53± 15%	>40%, <120%	±200%	±200%	3.0

* Variance of measured value from actual.

** Variance of difference of duplicates from mean.

2. __Precision__: Precision, a measure of mutual agreement among individual measurements of the same pollutant in replicate samples, is evaluated for each sample set by the ratio of the difference of duplicate values to their mean value. Table 12 provides QA requirements for precision. Precision is determined only when both values are above the detection limit.

Precision is defined as follows:

$$\text{Precision} = \frac{\text{difference between duplicate samples}}{\text{mean value for the duplicates}} \times 100$$

3. __Signal Quality:__ The quality of the mass spectral signals used for qualitative and quantitative analysis is evaluated using two parameters: the ion intensity ratio for the two ions monitored in each congener group, and the signal to noise (S/N) ratio. Table 12 provides QA requirements for signal quality. In addition, qualitative identification will be based on coelution with the stable isotope labeled compound, or relative retention time correlation (Tables 5 and 6).

4. __Polar Gas Chromatographic Confirmation Analysis__: Ten percent of the sample extracts analyzed are salaceted for GC/MS confirmation analysis on the more polar SP2330 column, (Supelco, Belafonte, PA). Samples which were positive for 2,3,7,8-TCDD were selected for analyais.

D. Quality Assurance Problems and Corrective Actions:

Problem	Corrective Action
MS performance outside QA	Adjust MS parameters for resolution, rerun initial curve and reanalyze sample(s).
GC column performance outside QA.	Reanalyze standards and samples on modified or alternate column.
Method efficiency outside of QA.	If 2378-TCDD method efficiency <40%, reanalyze sample set. If method efficiency <40% for analytes other than 2378-TCDD, flag and report data.
Accuracy outside of QA for spiked matrix. Precision of duplicates outside QA.	If more than 20% of the analytes are outside of QA for accuracy and precision, reanalyze the sample set.
Detection of analyte in blank for 2,3,7,8-TCDD, 2,3,7,8-TCDF and 1,2,3,7,8-PCDD	Reextract and reanalyze all samples for which the level of contamination, or MLD, is < 2.5 x blank levelt
For other analytes in blank	Record blank concentration in comment field of samples.
Analyte exceeds calibration standard range.	Measure method efficiency. Dilute sample 100:1 respike with each standard solution (A and B), adjust volume and reanalyze.
Method efficiency for blank outside of QA or blank lost	Reextract and reanalyze all positives in set.

Because of the complexity of these analyses types, it is not expected that all analytes will meet all QA criteria. Therefore, a complete review of the data by a chemist is essential. Responsibility for the evaluation of data is that of the sample preparation chemist and the mass spectrometer operator. Review of the data, including QA, and resolution of data quality problems is the responsibility of the Principal Investigator/Program Manager Resolution of data questions may require reanalysis of samples to include the addition of confirmatory ions or analysis on different types of GC columns.

VI. Quantification Procedures

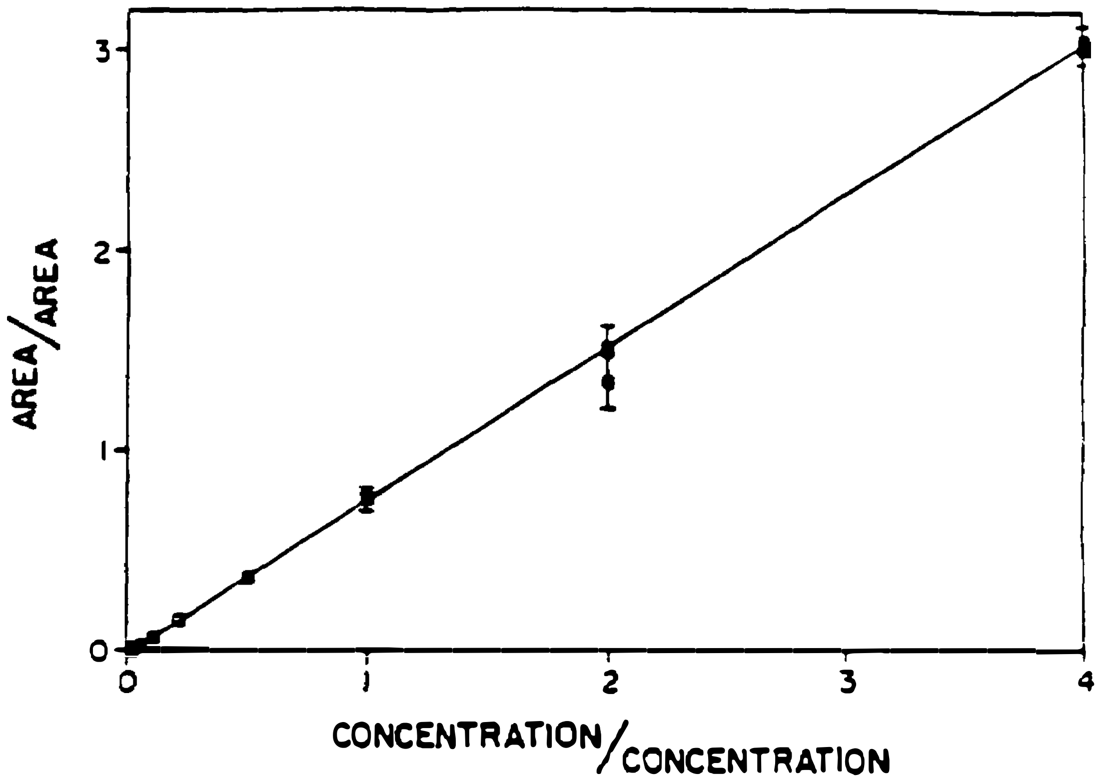
Quantification of analytes is accomplished by assigning isomer identification, integrating the area of mass specific GC peaks, and calculating an analyte concentration based upon an ion relative response factor between the analyte and standard.

A. Initial and Daily Calibration of the HRMS: An initial calibration of the instrument will be performed as needed. This will include making three replicate injections of each calibration standard (Table 4). Weighted least-squares linear regression is used to generate a calibration curve for each analyte. The weighting factor is inversely proportional to the variance among the replicate injections of each calibration standard. The slope of the regression line is the response factor used to quantify the analyte. At least two calibration standards are injected daily to insure that any response factors used for quantification and recovery calculations do not deviate from the initial calibration by more than 20 percent. If the daily calibration generates values outside this margin, and less drastic corrective action does not solve the problem, a new set of initial calibration curves is generated and the old response factor libraries discarded. An example of a typical calibration curve, using 2,3,7,8-TCDD as an example, is shown in Figure 2.

Figure 2

2,3,7,8-TCDD

WEIGHTED CALIBRATION CURVE



SLOPE = RESPONSE FACTOR

B. Signal Quality

1. Minimum Level of Detection (MLD): Minimum Level of Detection is defined as the concentration predicted from the ratio of baseline noise area to labeled standard area, plus three times the standard error of the estimate derived from the initial calibration curve for the analyte of interest.

Initial Calibration Based Method of MLD: MLD is estimated from the ratio of the noise area to the isotopically labeled internal standard area, plus three times the standard error of the estimate (SE) for the arsa ratio, or Y-sxis, of the initial calibration curve. The Y-intercept (INT) is subtracted from this quantity, in keeping with the normal formalism for "inverse prediction" of a point on the X, or concentration ratio axis, from a point on the Y, or signal ratio axis. The SE term is derived from an analysis of variance (ANOVA) performed during the weighted least squares fit of the initial calibration curve. This term represents the random error in the replicate injections used to generate the calibration curve, the error not accounted for by the lineer model. The weighting is necessary because of the relation often observed in instrumental analysis, of increasing variance with increasing concentration. MLD, according to this scheme, is defined below:

$$MLD = \frac{[(N_A/I334) + (3 \times SE) - INT] \times C334}{RF(N/I334) \times K}$$

where: N_A = noise area in the window for the major ion of the native analyte,

I334 = labeled internal standard peak area in the sample,

INT = the Y-axis intercept on the initial calibration curve,

C334 = labeled internal standard concentration,

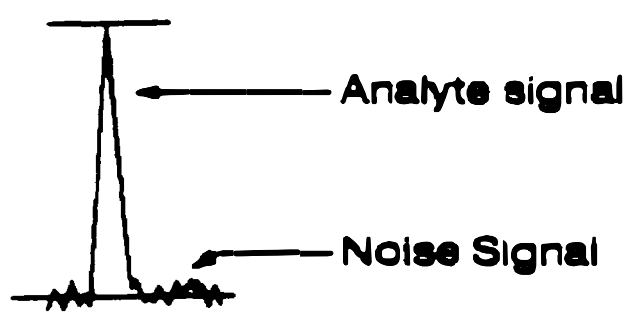
K = constant to adjust for sample size and final volume,

RF(N/I334) = response factor for major native ion to $^{13}C_{12}$ 1,2,3,4-TCDD ion, the slope of the initial calibration curve,

SE = standard error of the estimate of the initial calibration curve.

In addition, fish tissue is spiked with surrogate analytes (see Internal Standard Solution B, Table 3) prior to extraction. The surrogate analytes serve as an added check to insure that MLD values calculated from the initial calibration curve, as discussed above, are reasonable.

2. <u>Signal to Noise (S/N)</u>: The method of determining the signal to noise ratio is shown below.



$$S/N = \frac{\text{Analyte Signal Peak Area}}{\text{Noise Signal Peak Area}}$$

$$S/N = \frac{\text{Analyte Signal Peak Area}}{\text{Noise Signal Peak Area}}$$

The noise area is calculated by integrating over a peak width equivalent to the analyte signal, typically about 10 seconds.

C. Quantification of PCDD/PCDF: The concentration of a natural PCDD/PCDF is determined by calculating a response factor between PCDD/PCDF and the stable isotope labeled PCDD/PCDF for the congener group. Calculations are performed as follows:

Standard:

$$RF(N/L) = \frac{A_N \times C_L}{A_L \times C_N}$$

Sample:

$$V_N = \frac{A_N \times S_L}{A_L \times RF(N/L)}$$

where: $RF(N/L)$ = response factor native to labeled,

A_N = peak area native,

A_L = peak area labeled,

C_N = concentration of native standard,

C_L = concentration of labeled standard,

S_L = labeled spiking level in sample,

V_N = level of native analyte in sample.

D. <u>Method Efficiency</u>: The method efficiency for the recovery of stable isotope labeled compounds is determined by calculating the amount of stable isotope labeled compound in the final extract and dividing by the amount spiked into the sample at the start of the cleanup procedure. This is done by determining the relative response factor between the Internal Standard Solution C, $^{13}C_{12}$ 1,2,3,4-TCDD and the stable isotope labeled internal standard (Solution A).

Determine Response Factor:

$$RF = \frac{A_L \times C_{IS}}{A_{IS} \times C_L}$$

where: RF = response factor,

A_L = area of stable isotope labeled internal standard, (solution A),

A_{IS} = area of 13C12 1,2,3,4-TCDD,

C_L = concentration of stable isotope labeled internal standard, (solution A),

C_{IS} = concentration of 13C12 1,2,3,4-TCDD.

The response factor is then used in calculating the concentration of the internal standard in the final solution,

$$C_L = \frac{A_L \times C_{IS}}{A_{IS} \times RF}$$

where: C_L = concentration of stable isotope labeled internal standard, (solution A).

The concentration in the final solution times the final volume equals the total amount present. The method efficiency is then calculated by:

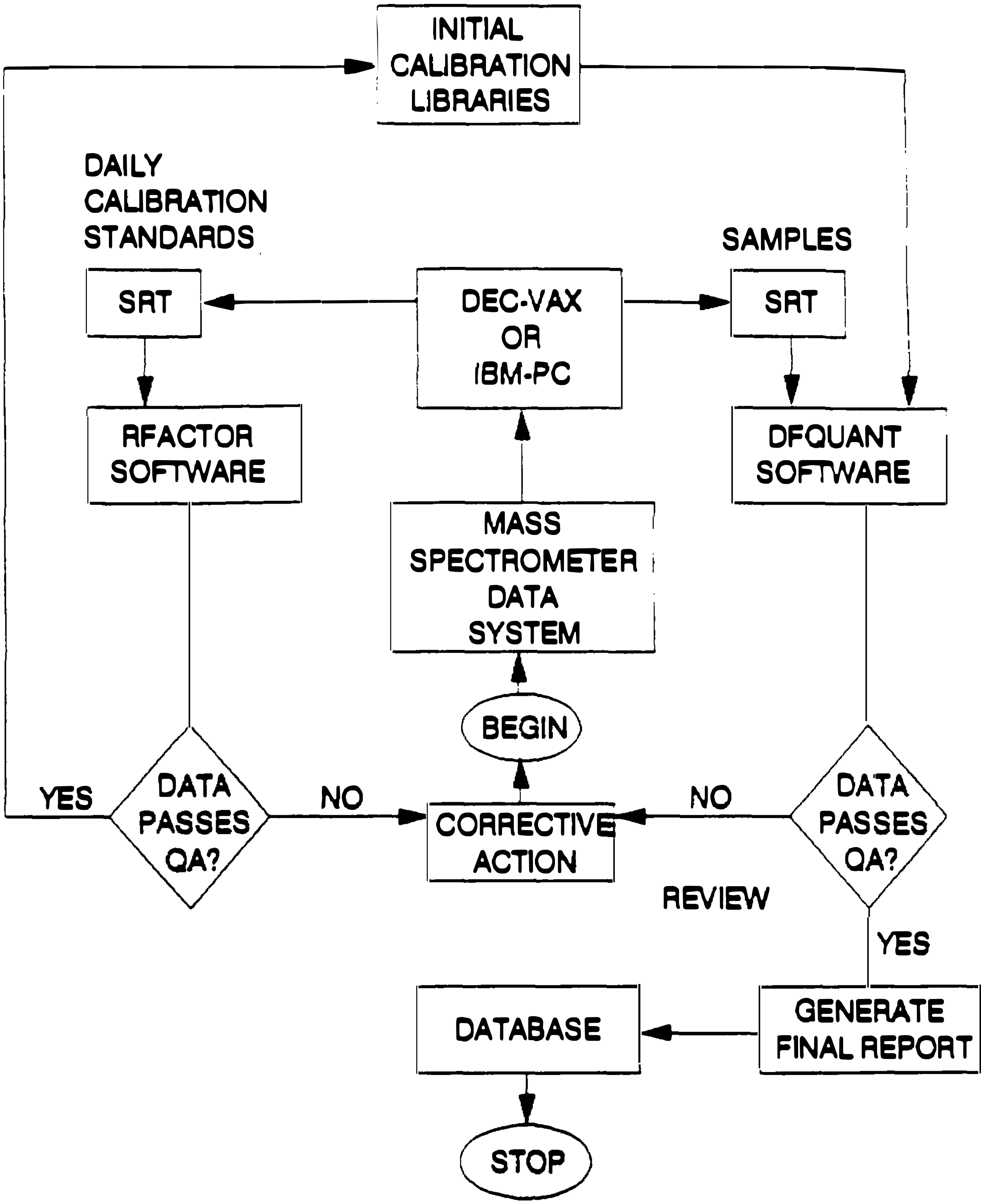
$$\% \text{ Recovery} = \frac{\text{CL found}}{\text{CL spiked}} \times 100$$

E. <u>Integration of Automated Data Processing and Quality Assurance</u>:

QA parameters for method efficiency, ion ratios, retention time correlations, signal/noise ratio, accuracy and precision are monitored with the aid of software either developed in-house, or modified from existing programs included with the HRMS data system. Raw data is sorted and edited using the mass spectrometer's dedicated data system, transferred to the DEC-VAX system and processed using software programs RFACTOR and DFQUANT (Figure 3.). Data is reviewed by the Project Director before entering into the NDS data base.

Figure 3

DATA REDUCTION FOR PCDD/PCDF
NATIONAL DIOXIN STUDY



U.S. GOVERNMENT PRINTING OFFICE 1990/748-159/00433

APPENDIX A-3

Analytical Procedures and Quality Assurance Plan for the Determination of Xenobiotic Chemical Contaminants in Fish

United States
Environmental Protection
Agency

Environmental Research
Laboratory
Duluth MN 55804

EPA 600 3-90 023
March 1990

Research and Development

Analytical Procedures and Quality Assurance Plan for the Determination of Xenobiotic Chemical Contaminants in Fish

EPA/600/3-90/023
March 1990

U.S. ENVIRONMENTAL PROTECTION AGENCY

NATIONAL DIOXIN STUDY
PHASE II

Analytical Procedures and Quality Assurance Plan for the Determination of Xenobiotic Chemical Contaminants in Fish.

December 1989

Environmental Research Laboratory-Duluth
6201 Congdon Blvd.
Duluth, MN 55804

NOTICE

The information in this document has been funded wholly or in part by the U.S. Environmental Protection Agency. It has been reviewed technically and administratively. Mention of trade names of commercial products does not constitute endorsement or recommendation for use.

ACKNOWLEDGEMENTS

Technical contributions to this research were made by:

U.S. Environmental Protection Agency

Brian C. Butterworth
Douglas W. Kuehl

ASci Corporation

Phillip J. Marquis
Marie L. Larsen
Larry G. Holland
Christine E. Soderberg
Jennifer A. Johnson
Kevin L. Hogfeldt
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University of Wisconsin-Superior

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Wright State University

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FOREWORD

Directed by Congressional mandate, the U.S. Environmentel Protection Agency during 1983 initiated the National Dioxin Study, a survey of environmental contamination by 2,3,7,8-tetrachlorodibenzo-p-dioxin (TCDD) in the United States. Results of this study ere published in the National Dioxin Study: Tiers 3,5,6, and 7, EPA 400/4-82-003. This laboratory, the Environmental Research Laboratory - Duluth, was responsible for one part of the Study, the analysis of fish samples. The most significant findinga of these analyses was the observation that fish contamination was more widespread than previously thought, and that a primary source of TCDD waa discharge from pulp and paper production using chlorine.

A second more detailed characterization of anthropogenic organic chemical contaminants in fish was conducted in subsequent analyaes during what is now called Phase II of the Nationel Dioxin Study. Thia document describes the analytical methods used for the determination of the level of contamination of polychlorinated biphenyls, pesticides, and industrial compounds in fish. A companion document (EPA /600/3-90/022) describes the anelytical methods used for the determination of levels of contamination of fitfteen biosignificant polychlorinated dibenzo-p-dioxins and dibenzofurana in thoae same fish.

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I. INTRODUCTION

This document, developed for Phase II of the U.S. EPA National Dioxin Study, describes the analytical procedures and quality assurance plan for the determination of xenobiotic chemical contaminants in fish. The analytical approach includes:

- a simple sample preparation methodology that produces a single extract which minimizes analyte losses,
- a procedure that is cost effective in terms of man power, chemical reagents, and instrumentation,
- a characterization and quantification of a certain set of chemical contaminants,
- an identification of unknown contaminants by screening the data.

The set of analytes quantified was derived through considerations that included, but were not limited to, history (data from previous monitoring efforts), toxicology, persistence, bioavailability potential, total yearly production, and feasibility of analyses. A list of target analytes is presented in Table 1. Limits of quantitation for the Target Analytes are as follows:

Target Analytes (except for PCBs)		2.5 ppb
Polychlorinated Biphenyls		
Level of Chlorination:	1-3	1.25 ppb
	4-6	2.50 ppb
	7-8	3.75 ppb
	9-10	6.25 ppb

Fish were provided by the U.S. EPA Regional labs working with state environmental agencies.

Table 1. LIST OF TARGET ANALYTES, INTERNAL STANDARDS, AND SURROGATE COMPOUNDS AND THEIR QUANTITATION IONS

ANALYTE	CAS NUMBER	QUANT ION	RRT
Biphenyl-d_{10} (Internal Standard)		164	1.000
Iodobenzene (Surrogate)		204	0.309
1,3,5-Trichlorobenzene	108703	180	0.461
1,2,4-Trichlorobenzene	120821	180	0.548
1,2,3-Trichlorobenzene	87616	180	0.625
Hexachlorobutadiene	87683	225	0.629
1,2,4,5-Tetrachlorobenzene	95954	216	0.891
1,2,3,5-Tetrachlorobenzene	634902	216	0.891
Biphenyl	92524	154	1.010
1,2,3,4-Tetrachlorobenzene	634662	216	1.015
Pentachlorobenzene	608935	266	1.378
Phenanthrene-d_{10} (Internal Standard)		188	1.000
1-Iodonaphthalene (Surrogate)		127	0.763
Trifluralin	1582098	306	0.855
Alpha-BHC	319846	219	0.890
Hexachlorobenzene	118741	284	0.912
Pentachloroanisole	1825214	280	0.924
Gamma-BHC (Lindane)	58899	219	0.979
Pentachloronitrobenzene	82688	295	0.994
Diphenyl disulfide	882337	218	1.076
Heptachlor	76448	272	1.185
Chlorpyrifos	2921882	197	1.308
Isopropalin	33820530	280	1.382
Octachlorostyrene	29082744	380	1.395
Heptachlor Epoxide	1024573	353	1.406
Oxychlordane	27304138	185	1.410
Chlordane, Trans-	5103742	373	1.477
Chlordane, Cis-	5103719	373	1.526
Chrysene-d_{12} (Internal Standard)		240	1.000
Nonachlor, Trans-	39765805	409	0.779
DDE, p,p'-	72559	246	0.805
Dieldrin	60571	277	0.807
Nitrofen	1836755	283	0.836
Endrin	72208	317	0.840
Perthane	72560	223	0.844
Nonachlor, Cis	5103731	409	0.875
4,4'-Diiodobiphenyl (Surrogate)		406	0.876
Methoxychlor	72435	227	1.017
Dicofol (Kelthane)	115322	139	1.017
Mirex	2385855	272	1.079

Table 1. LIST OF TARGET ANALYTES, INTERNAL STANDARDS, AND SURROGATE COMPOUNDS AND THEIR QUANTITATION IONS

ANALYTE	CAS NUMBER	QUANT ION	RRT
Chrysene-d_{12} (Internal Standard)		240	1.000
Polychlorinated Biphenyls, Cl 1-10			
Monochlorobiphenyls	27323188	188	0.318
Dichlorobiphenyls	25512429	222	0.452
Trichlorobiphenyls	25323686	256	0.556
Tetrachlorobiphenyls	26914330	292	0.575
Pentachlorobiphenyls	25429292	326	0.801
Hexachlorobiphenyls	26601644	360	0.818
Heptachlorobiphenyls	28655712	394	0.881
Octachlorobiphenyls	31472830	430	1.022
Nonachlorobiphenyls	53742077	464	1.250
Decachlorobiphenyls	2051243	498	1.288

II. PREPARATION OF SAMPLE EXTRACT

A. Sample Handling Methodology

1. Shipment of Samples to ERL-Duluth: The EPA Regional Offices are responsible for the collection of the fish samples. Frozen fish wrapped in aluminum foil are sent to the ERL-Duluth laboratory.

2. Sample Logging and Coding Procedures: The Sample Control Center (SCC) or EPA Regional Offices notify ERL-Duluth when samples have been shipped. Upon arrival, the samples are checked to make sure they are in good condition and the Shipment Records are complete. ERL-Duluth personnel complete the chain of custody forms and then notifies SCC that samples arrived safely or if there were any problems with the samples (example: a mislabeled sampled, no species identification).

   Samples are initially placed in a large walk-in freezer. Aliquots(100-500 g) of ground fish tissue samples (sec. I.A.3.) are transferred to laboratory freezer A. Extracted samples are stored in laboratory freezer B. Completed samples are taken to a locker plant for long term storage. A locker plant log is kept according to Episode and SCC numbers.

   A computerized data base was developed for sample tracking and data storage. The episode number, SCC number, date sample was received, matrix type, latitude, longitude, description of sampling site, and state from which the sample came are entered into the data base. Figure 1 is a sample output of the data base.

   The first two letters of the SCC number indicate whether the sample is an Environmental, Method or Matrix Blank, or Duplicate Sample. All Environmental samples begin with the letter D. The Blank and Duplicate samples begin with the letter Q followed by a D or an R for duplicate or reference fish sample, respectively. Table 2 lists the possible codes for the SCC number, and matrix type. Episode numbers for Blanks and Fortified Matrix samples are entered as 0000.

3. Tissue preparation and storage procedures: Fish tissue is ground frozen at ERL-Duluth in a stainless steel meat grinder. Each sample is processed through the grinder three times which homogenizes it thoroughly. For whole fish samples, the entire fish including organs and fillets are ground. The ground tissue is stored at -20°C in solvent rinsed glass jars with aluminum lined plastic lids.

Figure 1. Bioaccumulative Pollutants in Fish Database Output

NOS PHASE II: BIOACCUMULATIVE POLLUTANTS IN FISH

Sample Tracking System ERL-D Loc.: 1234

EPISODE #: 4444 SCC#: DP022030

Sampling Information:

Sampling Office: ERL-Duluth

State & City: MN Duluth

Sampling Contact: Regional Coordinator

Date Sampled: 8/23/87

Site Location: MN Lester River @ Lake Superior, Duluth

Latitude: N 46 24' 34'' Longitude: W 94 24' 53''

Analysis Lab: D Date Received: 8/31/87

Matrix Type: F PF Steelhead Species Code: A2

Sample Composite: 5

Analyticals	PCDD/PCDF	Pesticide & Industrial Chemicals
Extraction Date:	0/ 0/ 0	11/ 3/87
GC/MS ID:		DR871213
LAB ID:		8110387JJ
Weight:		20.00
%Lipid:		3.2
DPE Indication:	Mass lipid on GPC:	0.68

Comments:

Xenobiotic Definitions:

QA Flags:

E - exceeds highest calibration standard

D - below limit of quantitation

Limits of Quantitation:

Pesticides - 2.50 ppb

PCBs: 1-3 chloro - 11.25 ppb

4-6 chloro - 2.50 ppb

7-8 chloro - 3.75 ppb

9-10 chloro - 6.25 ppb

Figure 1. Bioaccumulative Pollutants in Fish Database Output

EPISODE #: 4444 SCC #: DP022030 ERL-D Loc.: 1234

Target Analyte	CASRN	QA Flag	CONCN (ng/g)	
1,3,5-Trichlorobenzene	108-70-3		ND	
1,2,4-Trichlorobenzene	120-82-1		ND	
1,2,3-Trichlorobenzene	87-61-6		ND	
Hexachlorobutadiene	87-68-3		ND	
1,2,4,5-Tetrachlorobenzene	95-95-4		ND	
1,2,3,5-Tetrachlorobenzene	634-90-2		ND	
Biphenyl	92-52-4	D		0.25
1,2,3,4-Tetrachlorobenzene	634-66-2		ND	
Pentachlorobenzene	608-93-5		ND	
Trifluralin	1582-09-8	D		2.34
Alpha-BHC	319-84-6		ND	
Hexachlorobenzene	118-74-1			13.2
Pentachloroanisole	1825-21-4			23.4
Gamma-BHC (Lindane)	58-89-9	D		1.23
Pentachloronitrobenzene	82-68-8		ND	
Diphenyl disulfide	882-33-7		ND	
Heptachlor	76-44-8		ND	
Chlorpyrifos	2921-88-2		ND	
Isopropalin	33820-53-0		ND	
Octachlorostyrene	29082-74-4		ND	
Heptachlor Epoxide	1024-57-3		ND	
Oxychlordane	26880-44-8		ND	
Chlordane, Trans-	5103-74-2			17.2
Chlordane, Cis-	5103-71-9			33.1
Nonachlor, Trans-	39765-80-5			45.2
DDE, p,p'-	72-55-9	E		1234
Dieldrin	60-57-1			21.2
Nitrofen	1836-75-5		ND	
Endrin	72-20-8		ND	
Perthane	72-56-0		ND	
Nonachlor, Cis	3734-49-4			18.4
Methoxychlor	72-43-5		ND	
Dicofol (Kelthane)	115-32-2		ND	
Mirex	2385-85-5	E		118
Total Monochlorobiphenyl	27323-18-8		ND	
Total Dichlorobiphenyl	25512-42-9		ND	
Total Trichlorobiphenyl	25323-68-6		ND	
Total Tetrachlorobiphenyl	26914-33-0			11.4
Total Pentachlorobiphenyl	25429-29-2	E		60.6
Total Hexachlorobiphenyl	26601-64-4	E		265
Total Heptachlorobiphenyl	28655-71-2	E		187
Total Octachlorobiphenyl	31472-83-0			39.8
Total Nonachlorobiphenyl	53742-07-7		ND	
Total Decachlorobiphenyl	2051-24-3		ND	
Total Polychlorinated Biphenyls				564
Mercury (AA analysis)	7439-97-6	0.36	ug/g	

SURROGATE RECOVERY:

Iodobenzene	12
Iodonaphthalene	48
4,4'-Diiodobiphenyl	93

Table 2. Codes for SCC Numbers and matrix type.

	Environmental sample	QA sample
First Letter:	D	Q
Second Letter:	A -- Region 1	B -- Method blank
	B -- Region 2	D -- Laboratory duplicate
	C -- Region 3	R -- Reference fish or fortified matrix
	D -- Region 4	
	E -- Region 5	
	F -- Region 6	
	G -- Region 7	
	H -- Region 8	
	Y -- Region 9	
	J -- Region 10	

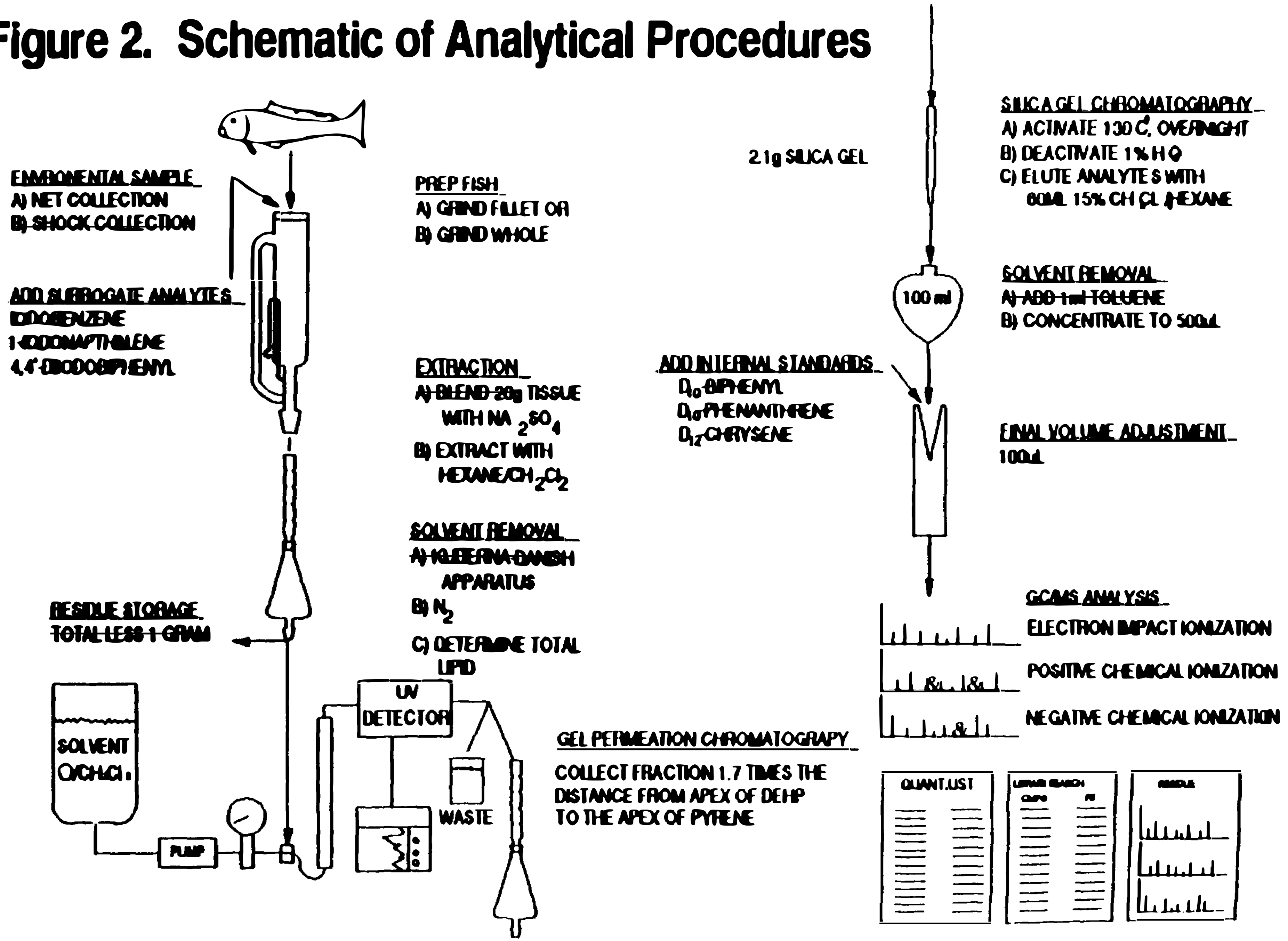
Matrix Code	Matrix Type
F -- Fish	WB -- Whole bottom
L -- Lab duplicate	BF -- Bottom fillet
R -- Reference fish	PF -- Predator fillet
Y -- Method Blank	WP -- Whole predator

B. Extraction of Tissue Samples.

Figure 2 is a schematic of the analytical procedures.

1. Soxhlet Extraction: Groundfish tissue (20 g) is blended with anhydrous sodium sulfate (100 g) inaa 250 mL beaker to completely dry the sample. Two-thirds of the mixture is transferred to a coarse fritted soxhlet extraction thimble and spiked with Surrogate Standard Solution A (25 uL), Table 3. Also, at this time the Fortified Matrix Sample and the Fortified Duplicate Sample, if used, are spiked with 25 ul of Target Analyte Solution (one of eight Target Analyte Fortification Solutions, Table 4). The remaining sample is added to the thimble and the sample is extracted for at least 12 hours with hexane/methylene chloride (1:1, v:v). The extract is then quantitatively transferred to a Kuderna-Danish (KD) apparatus fitted with a 3-ball Snyder column and reduced in volume to less than 5 mL onaa steam bath. The extracts are further reduced under carbon filtered air to remove all solvent. The KD sample tubes with lipid are weighed. Two 0.60 g aliquots are prepered for Gel Permeation Chromatography (GPC) by weighing into 5 ml tubes. The empty sample tube is dried and reweighed to determine the percent lipid.

Figure 2. Schematic of Analytical Procedures



2. Fortification with Surrogate Standards: Each sample is fortified with Surrogate Standard Solution A (25 uL) prior to soxhlet extraction. The standards in this solution have been selected to represent various types of chemicals found in the list of target analytes, and are used to evaluate the recovery of target analytes in cleaned-up environmental samples.

Table 3. Surrogate Standard and Internal Standard Solutions

Surrogate Standard Solution A (25 uL)

Compound	Concentration (ug/ml)
Iodobenzene	125
1-Iodonaphthalene	125
4,4'-Diiodobiphenyl	125

Internal Standard Solution (10 uL)

Compound	Concentration (ug/ml)
Biphenyl-D_{10}	50
Phenanthrene-D_{10}	75
Chrysene-D_{12}	75

3. Fortification with Target Analytes: A blank matrix sample is fortified with one of eight Target Analyte Fortification Solutions (25 uL), Table 4, to evaluate the overall accuracy of a subset of the target analytes. Two blank matrix samples will be fortified with the same solution once in every five (20%) sample sets to evaluate precision.

Table 6. Target Analyte Fortification Solutions (25 uL)

Solution A: Aroclor 1254 at 500 ug/ml (A-1) and 1000 ug/ml (A-2) in toluene.

Solutions B,C and D: Each have Target Analytes at 125 ug/ml (B-1, C-1, D-1) and 250 ug/ml (B-2, C-2, D-2).

Solution B	Solution C
1,2,3-Trichlorobenzene	1,2,4-Trichlorobenzene
1,2,4,5-Tetrachlorobenzene	1,2,3,4-Tetrachlorobenzene
Biphenyl	Gamma-BHC (Lindane)
Alpha-BHC	Chlordane, trans-
Chlordane, cis	DDE, p,p'
Dicofol	Nitrofen
Endrin	Heptachlor
Diphenyl disulfide	Isopropalin
Hexachlorobenzene	Nonachlor, cis
Mirex	Oxychlordane
Octachlorostyrene	Pentachloronitrobenzene
Pentachlorobenzene	Trifluralin
Perthane	Hexachlorobutadiene

Solution D
1,3,5-Trichlorobenzene
1,2,3,5-Tetrachlorobenzene
Methoxychlor
Chlorpyrifos
Dieldrin
Heptachlor Epoxide
Nonachlor, trans-
Pentachloroanisole

C. Isolation of Xenobiotic Chemical Contaminants.

1. Gel Permeation Chromatography: A GPC system is used to isolate xenobiotic chemical conteminents from biological molecules (fish lipid). The GPC column (2.5 X 50 cm) (ACE Glass Company) is packed with previously swelled Biobead SX-3. The GPC injection port velve is fitted with a 0.075 mm stainless steel screen filter to remove particulates. The solvent is pumped at 5 mL/min. The absorbance of the effluent is monitored with a 254 nm UV detector (Varien Aerogreph). Each aliquot of extract is diluted with 2 mL of elution solvent. The supernatant is quantitatively transferred into a sample loop of a 24 port auto-sampler with three additional 1 mL washes of the sample vial. The loops of the auto-sampler are loaded sequentially onto the GPC column under computer control. A GPC performance standard solution (sec. IV.B.1) is run to determine the collection period. This sample is run prior to each sample set. Xenobiotic chemical contaminants which elute 4 minutes after the elution apex of Di-2-ethylhexylphthalate, DEHP, and 1.7 times the elution volume between the epex of DEHP and Pyrene are collected in a KD. Each sample (two loops) are collected in a single KD. Hexane (10 mL) is added to the KD and the sample is reduced in volume (5 mL) on a steam bath using a 3-ball Snyder column. The sample is further reduced in volume to 0.5 mL with a stream of dry filtered air at 40º C prior to silica gel chrometogrepny.

2. Silica Gel Chromatography: A Kontes column packed with freshly prepared, partially deactivated silica gel is used to remove naturally occurring cholesterol and fatty acids. The column (9 mm X 19 cm plus a 50 ml reservoir) is packed with glass wool, anhydrous sodium sulfate (0.5 cm), silica gel (2.1 g about 7 cm), and anhydrous sodium sulfate (0.5 cm). The column is pre-eluted with 50 mL of hexane and the sample is quantitatively transferred to the column with three 0.5 mL methylene chloride/hexane (15%, v:v) washes. The column is then eluted with an additional 58.5 mL of the same solvent. Toluene (1 ml) is added to the collection vial as a "keeper". The sample is reduced in volume (0.5 mL) with a stream of dry filtered air, 40º C, and quantitatively transferred with toluene to a tapered vial (1 mL).

3. Fortification with Internal Standards. The samples are reduced to 90 uL and fortified with 10 uL of Internal Standard solution (Table 3) and stored in a microvial for GC/MS analysis.

III. Standards and Reagents

A. Reagents

1. Solvents: Only pesticide grade distilled in glass solvents are used. They are: hexane, methylene chloride, toluene, acetone, and cylcopentane (Burdick and Jackson and Fischer Scientific).

2. Sodium Sulfate: Sodium sulfate (Baker Chemical Company reagent grade anhydrous) is baked at 650°C in a furnace for 24 hours, cooled, and stored in an empty hexane solvent bottle.

3. GPC Packing: Biobeed SX-3 (BIORAD Corporation) are swollen in the elution solvent, cyclopentane/methylene chloride (1:1, v:v).

4. Silica Gel: Silica-Gel-60 (Merck-Darmstadt) is activated overnight at 225°C. It is then deactivated by adding distilled water (1% w:w) and shaken at high speed for four hours to disperse the water. The mixture is allowed to equilibrate for eight hours.

B. Standards

All pesticide standards are made from pure standard materials.

1. GPC Performance Check Solution: Prepare a solution of 5 mg/ml Dacthal, 4 mg/ml DEHP, and 0.2 mg/ml Pyrene.

2. MS Performance Check Solution: Prepare a 5 ng/ul solution of decafluorotriphenylphosphine (DFTPP) in toluene.

3. Silica-Gel Performance Check Solution: Prepare a solution containing 2 mg/ml Dieldrin and 10 mg/ml cholesterol in an appropriate solvent.

4. Internal Standards: Chrysene-d_{12}, phenanthrene-d_{10}, and biphenyl-d_{10} are used as internal standards. Table 1 indicates which internal standard the target analytes are referenced to in quantitation. Table 6 indicates the concentration of the internal standards in the calibration solutions and in the solution used to add the internal standards to the samples just prior to MS analysis.

5. Surrogate Compounds: Iodobenzene, 1-Iodonaphthalene, and 4,4'-diiodobiphenyl are used as surrogate compounds. Each are present at 125 ug/ml (Table 3) in the sample spiking solution. Table 6 indicates the concentration present in the five calibration solutions.

6. Pesticides and PCB Standards: A stock solution is made containing the pesticides listed in Table 1 and the PCB congeners listed in Table 6. Five calibration solutions are made at the concentrations listed in Table 6.

7. Fortification Solutions: The pesticides are divided into three fortification solutions at two different concentrations (Table 4). Aroclor 1254 is used as the PCB fortification solution at the concentrations listed in Table 4.

IV. Analysis of Extracts

Samples are analyzed on a Finnigan-MAT Model 4500 GC/MS with SUPERINCOS software and supplemental public domain software (1,2) provided by the U.S. EPA laboratories in Cincinnati, OH. All Target Analytes will be quantified individually and the results reported as unique values, except for PCBs, which will be reported by total congener at each degree of chlorination. An analysis set includes an analysis of a mass spectrometer performance check solution (sec. III.B.2), an analytical standard, an unfortified solvent (instrument blank), and twelve prepared samples. The GC/MS operator reviews the MS performance solution, analytical standard, and instrument blank data before starting the analysis of samples.

A. Gas Chromatographic Operating Parameters: A Finnigan-MAT Model 9610 GC is fitted with a 60 m X 0.32 mm ID DB-5 fused silica capillary column (J & W Scientific) and operated in a temperature programmed mode. The capillary column is interfaced directly with the ionizer. Injections are made in splitless mode. Specific operating parameters are provided in Table 5.

B. Mass Spectrometric Operating Parameters: A Finnigan-MAT Model 4500 mass spectrometer is used in the electron impact mode. Specific operating parameters are provided in Table 5. The positive identification of target analytes is based upon a reverse library search threshold value and relative retention time (RRT). Quantification of the target analytes is based on the response factors (RF) relative to one of the three internal standards listed in Table 1. Table 1 is formatted so that the target analytes follow the internal standard used in quantification. RRTs and RFs are initially determined using data from triplicate analysis of each of five target analyte quantification solutions (Table 6).

Table 5. Gas Chromatography/Mass Spectrometry Operating Parameters

GC Parameters:	
Injector Temp.:	250° C
Initial Temp.:	100° C held for 1 min.
First Ramp:	5° C/min to 175° C
Second Ramp:	3° C/min to 280° C hold for 20 min
MS Parameters:	
Cycle time:	1.0 second
Acquisition time:	0.95 second
Scan Rate:	1.0 second
Scan Range:	95 - 550 amu
Electron Voltage:	70 eV
Emission Current:	0.30 mA
Manifold Temp.:	95° C
Ionizer Temp.:	150° C
Transfer Line Temp.:	280° C

V. Quality Assurance/Quality Control (QA/QC).

A. General Procedures of Operation.

1. Sample Analysis Set: Analysis of samples is done in sets of twelve consisting of:

   a. Blank: A METHOD BLANK (blank extraction apparatus) is analyzed with each set.

   b. Fortified Matrix: A blank matrix sample is fortified with one of eight different mixtures of Target Analytes (Table 4) and analyzed with each set.

   c. Duplicate: Each analysis set contains one duplicate sample. In four of five (80%) of the sample sets the duplicate is an environmental sample previously chosen for analysis in that set. In one of five (20%) of the sample sets the duplicate is a blank matrix sample that has been fortified with the same target analyte subset as the Fortified Matrix Sample. This additional type of duplicate insures that sufficient data is available at the end of the study to evaluate precision on all target analytes.

Table 6. Composition and Approximate Concentrations of Calibration Solutions for Full-Range Data Acquisition

Analyte/Int. Std./ Surrogate Compound	Concentration (ng/uL) CAL 1	CAL 2	CAL 3	CAL 4	CAL 5
PCB Cal. Congeners					
Cl_1 2-	0.25	0.50	1.25	2.50	5.00
Cl_2 2,3-	0.25	0.50	1.25	2.50	5.00
Cl_3 2,4,5-	0.25	0.50	1.25	2.50	5.00
Cl_4 2,2',4,6-	0.50	1.00	2.50	5.00	10.00
Cl_5 2,2',3,4,5'-	0.50	1.00	2.50	5.00	10.00
Cl_6 2,2',4,4',5,6'-	0.50	1.00	2.50	5.00	10.00
Cl_7 2,2',3,4,5,6,6-	0.75	1.50	3.75	7.50	15.00
Cl_8 2,2',3,3',4,5,6'-	0.75	1.50	3.75	7.50	15.00
Cl_{10}	1.25	2.50	6.25	12.50	25.00
All Target Analytes other than PCBs listed in Table 1	0.50	1.00	2.50	5.00	10.00
Internal Standards					
Chrysene-d_{12}	7.50	7.50	7.50	7.50	7.50
Phenanthrene-d_{10}	7.50	7.50	7.50	7.50	7.50
Biphenyl-d_{10}	5.00	5.00	5.00	5.00	5.00
Surrogate Compounds					
Iodobenzene	0.50	1.00	2.50	5.00	10.00
1-Iodonaphthalene	0.50	1.00	2.50	5.00	10.00
4,4'-Diiodobiphenyl	0.50	1.00	2.50	5.00	10.00

d. Environmental Samples: Nine Environmental Samples are analyzed wigh each setg

2. Sample Tracking: A sample tracking and logging system is used to assure that no samples are lost (see section I-A).

3. Data Storage: Data folders consisting of all hard copy output is maintained for each sample. In addition, all raw GC/MS data is stored on megnetic tape.

4. Data Review: GC/MS data is initially reviewed during sample set acquisition by the GC/MS operator to assure that all instrumental QA parameters are being met. Final review and release of the data is the responsibility of the Project Manager. Once the qualgty assurance criteria have been met, the quantification information is entered into the database. Quality assured data is then transferred to BIOACC/STORET for availability to the EPA Regions. Before release to the public, all transferred data is verified for completeness by the database manager.

B. General Procedures of Analytical Quality Assurance:

1. Gas Chromatography-Mass Spectrometry System:

a. Instrument Maintenance: The GC/MS system is maintained according to the manufacturer's suggested schedule. The maintenance schedule is indicated on a calendar located near each instrument. Log books will be kept for: Daily instrument settings; Samples analyzed; Maintenance; and Data Storage. Instrumental problems resulting in more than two days of down time are to be reported to tha EPA Mass Spectrometry Fecility Supervisor to discuas solutions to the problems.

b. Gas Chromatography: The performance of the GC is evaluated by determination of the number of theoretical plates of resolution, and by relative retention of the Surrogate Standards.

1e. Column Resolution: The number of theoretical plates of resolution, N, is determined at the time the calibration curve is generated using Chrysene-d_{10} and monitored with each sample set. The value of N shall not decrease by more than 20%. The equation for N is givenas follows:

$$N = 16 \, (RT / W)^2$$

where, RT = Retention Time of Chrysene-d_{10} in seconds
W = Peak width of Chrysene-d_{10} in seconds.

2. Relative Retention Time: Relative retention times of the internal standards shall not deviate by more than +/- 3 % from the values calculated at the time the calibration curve was generated.

c. Mass Spectrometry: The performance of tha mass spectrometer will be evaluated for both sensitivity and spectral quality.

1. Sensitivity: The signal to noise value must be at least 3.0 or greater for m/z 198 from an injection of 10.0 ng decafluorotri-phenylphosphine (DFTPP).

2. Spectral Quality: The intensity of ions in the spectrum of DFTPP must meet the criteria listed below:

m/z	criteria
127	30-60% mass 198
197	< 1% mass 198
198	base peak
199	5-9% mass 198
442	>40% mass 198
443	17-23% mass 442

2. Gel Permeation Chromatography: The GPC is maintained when needed as determined by visual inspection (column discoloration, leaks, cracks, etc) measurement of flow rate, and routine measurement of contamination of instrument blanks.

a. GPC Column Flow Rate: The flow rate of the GPC is measured three times during an analysis: 1) before the GPC resolution solution, 2) after all samples are loaded but before analysis and 3) after all samples have been analyzed. Flow rate should not vary by more than +/- 0.2 mL/min.

b. GPC Column Resolution: A 350 ul injection of a performance solution containing Dacthal (5 mg/mL), DEHP (4 mg/ml), and Pyrene (0.2 mg/mL) must be run daily to evaluate column resolution, and to determine analyte starting and ending collection volume.

c. Collection Cycle: Proper operation of the GPC will also be evaluated by recording the time during an analysis cycle that the collection/waste valve is in the collect position. This is accomplished most easily by recording the valve position on the second pen of a dual pen recorder. The start and end of the collect cycle must not deviate by more than +/- 2 mL.

3. Silica Gel Chromatography: The silica gel column will be evaluated by its ability to resolve cholesterol from a select model target analyte, Dieldrin. A solution (1.0 mL) containing Dieldrin (2.5 mg/mL) and cholesterol (10 mg/mL) is spiked onto a silica gel column and eluted with methylene chloride/hexane (15%, v:v, 60 mL). The eluant, analyzed by flame ionization detector/gas chromatography (FID/GC) must not contain more than 10% of the cholesterol while at least 90% of the Dieldrin must be recovered.

C. Criteria for Quantitative Analysis: All of the following quality assurance criteria must be met before a quantitative value may be reported for an analyte.

1. Gas Chromatographic Relative Retention Time: Relative retention times of the target analytes shall not deviate by more than +/- 3 % from the values established during the generation of the calibration curve (see Table 1 for RRT data).

2. Analyte Identification Criteria: Reverse search identification of an analyte (SEAR) must have an FIT value of 800 or greater.

3. Signal to Noise: The quantification ion must have a signal to noise value of at least 3.0.

4. Relative Response Factor: The relative response factor for each analyte quantification ion relative to the appropriate internal standard quantification ion must not deviate by more than 20% from the value determined on the previous day (within a 24 hour period) and within 50% of the mean value from the calibration curve. The target analytes Endrin, Dicofol, and Decachlorobiphenyl must not deviate by more than 50% from the previous day.

A control chart is maintained on the daily response factors for each target analyte.

5. Surrogate Standard Recovery: The percent recovery (%R) of each surrogate standard will be determined for all samples, as shown below:

$$\%Rs = 100[Co/Ca]$$

where %Rs = surrogate percent recovery
Co = observed concentration of surrogate
Ca = actual concentration of surrogate added to the sample.

The percent recovery must be within 25 and 130 percent for iodonaphthalene and 50 and 130 percent for 4,4'-diiodobiphenyl. The recovery of iodobenzene qualitatively indicates the extent of evaporative losses that the analytes listed in Table 7 may experience.

6. Total Analyte Recovery: The overall accuracy of quantification of all target analytes is evaluated by the analysis of a subset of target analytes fortified into a matrix blank. Recovery of the fortified analytes must fall within the range of 50 to 130% except for those listed in Table 7. The analytes

Table 7. Target Analytes with low recoveries for this method.

1,3,5-Trichlorobenzene
1,2,4-Trichlorobenzene
1,2,3-Trichlorobenzene
1,2,4,5-Tetrachlorobenzene
1,2,3,5-Tetrachlorobenzene
1,2,3,4-Tetrachlorobenzene
Pentachlorobenzene
Hexachlorobutadiene

listed in Table 7 show recoveries that fall in the range of 20 to 30% for this method. An average analyte recovery (%AR) for all target analytes will be calculated and must be greater than 35% but less than 130%.
A control chart for total analyte recovery and analyte recovery is maintained for each spiking solution.
To determine total analyte recovery first calculate the percent recovery (%R) for each fortification analyte using,

%Ra = 100((Ai-Bi)/Ti)

where %Ra = analyte percent recovery
Ai = measured analyte concentration in fortification sample after analysis.
Bi = natural analyte concentration in sample before fortification.
Ti = known true concentration of analyte fortification level.

Then calculate %AR by,

%AR = (Summation of %Ra) /N

where N = number of fortification analytes in spiking solution.

D. Quality Control: Quality control charts displaying quantitative bias (%B) and precision (%P) are maintained for each analyte using LOTUS 123 software, Lotus Development Corporation. Percent bias and percent precision will be recorded and the control chart will be updated after each analysis set. Complete statistics may be done for bias and precision at the completion of the project.

1. Continual Bias Assessment:

$$\%B = (100(Ca - Cb)/T) - 100$$

where Ca = determined concentration after analysis
Ca = concentration present before spike added,
T = known value of the spike.

2. Continual Precision Assessment:

Precision of quantification of each target analyte will be assessed separately for duplicate environmental samples and duplicate fortified matrix samples.

$$\%P = 100[(C1 - C2)/Ct]$$

where C1 = concentration of analyte in spike sample 1.
C2 = concentration of analyte in spike sample 2.
Ct = Actual concentration of analyte for fortified matrix sample or mean of duplicate environmental samples.

3. Quality Control Chart:

QA factor outside of criteria	Corrective Action
DFTPP sensitivity and/or ion ratios	retune MS clean MS
Relative Retention Time	adjust GC parameters flush GC column replace GC column
Relative Response factors	retune MS recalibrate
Recovery of Surrogate Standards	verify MS data repeat sample extraction
Total Analyte Recovery (%AR)	If %R for at least 80% of target analytes not listed in Table 1 meets criteria proceed with calculations, else reextract all samples

VIII. Quantification of Target Analytes:

A. Quantification Procedures

Response factors are determined for each target analyte and surrogate compound relative to one of the three internal standards. The response factors are determined by:

$$RF = A_X C_{IS} / A_{IS} C_X$$

where A_X = peak area of quantitation ion for a target analyte or a surrogate compound,

A_{IS} = peak area of quantitation ion for either Biphenyl-d_{10}, Phenanthrene-d_{10}, or Chrysene-d_{12},

C_{IS} = injected quantity of the internal standard,

C_X = injected quantity of the target analyte or surrogate compound.

Public domain software was provided by the EPA Office of Research and Development, Environmental Monitoring and Support Laboratory for the automated identification and quantification of the target analytes. The data reduction software uses the following formula to calculate target analyte concentrations:

CONC = ((QA * NUM * QRV) * FESV) / (VIA * SIZE)

where QA = concentration as calculated using the response factor from the daily standard,
NUM = factor to convert to number of ug/ml,
QRV = Quan Report Volume (0.100 ml),
VIA = Volume Internal Standard added to (0.100 ml),
FESV = Final Effective Sample Volume,
SIZE = sample size (g).

The FESV term accounts for the total lipid present in the sample and the amount injected on the GPC. The FESV is calculated by:

FESV = Final Volume (ml) * (Total Lipid (g) / Lipid on GPC (g))

Calculations for determining surrogate spikes and fortified amounts use the following equation:

CONC = (SA * FESV) / (FSRV * SIZE)

where SA = spike amount,
FSRV = Final Effective Surrogate Volume,
FESV, SIZE = same as above.

The FSRV term is equal to the FESV term. The concentration of a target analyte is denoted in the final report if it exceeds the calibration range, ('E' flag), or is below the quantitation limit, ('D' flag).

8. Determination of Minimum Level of Quantification

The calculated method detection limits (MDLs) for the analytes, (determined according the Federal Register 1988, Vol. 40, Appendix B, Part 136, Definition and Procedure for the Determination of the Method Detection Limit, Rev. 1.11), are unrealistically low in comparison to the analysis of the xenobiotic calibration solutions over a two month period. Based on the analysis of the calibration solutions a minimum level of quantification was determined for each analyte, as given in the Introduction, which accurately reflects the instrumental detection limits.

U.S. GOVERNMENT PRINTING OFFICE 1990/760-159/00430

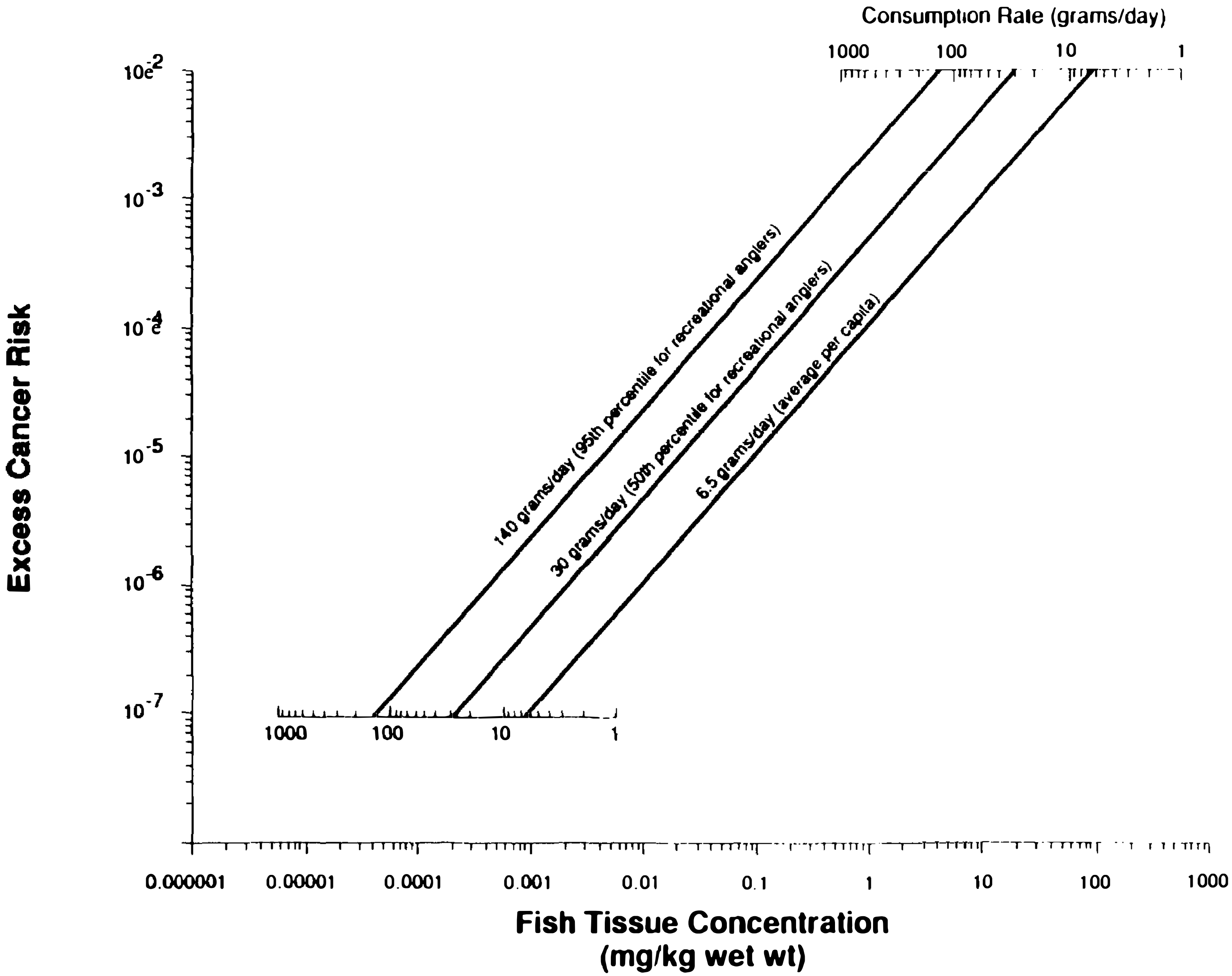
APPENDIX B

ADDITIONAL DATA ANALYSES

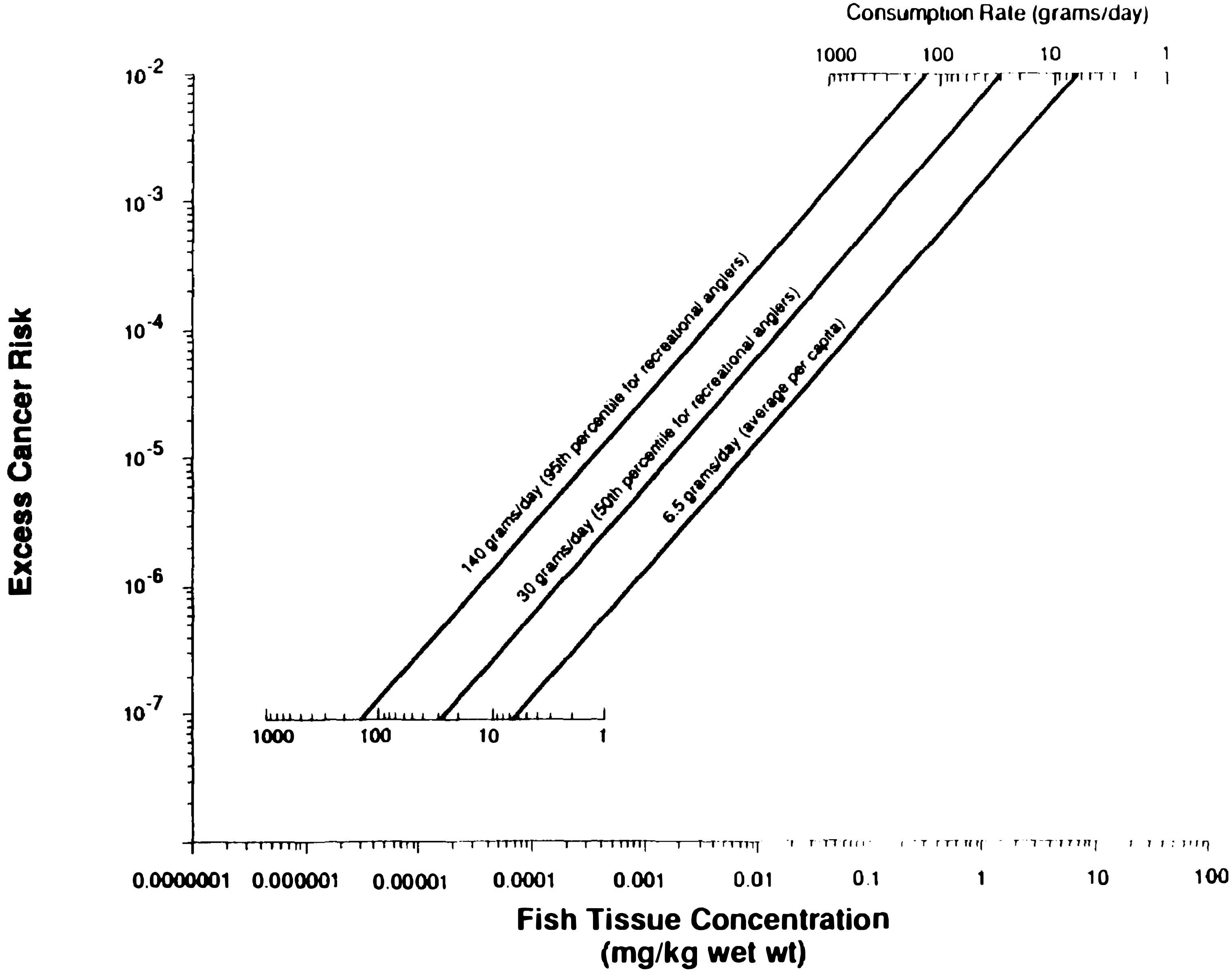
APPENDIX B-1

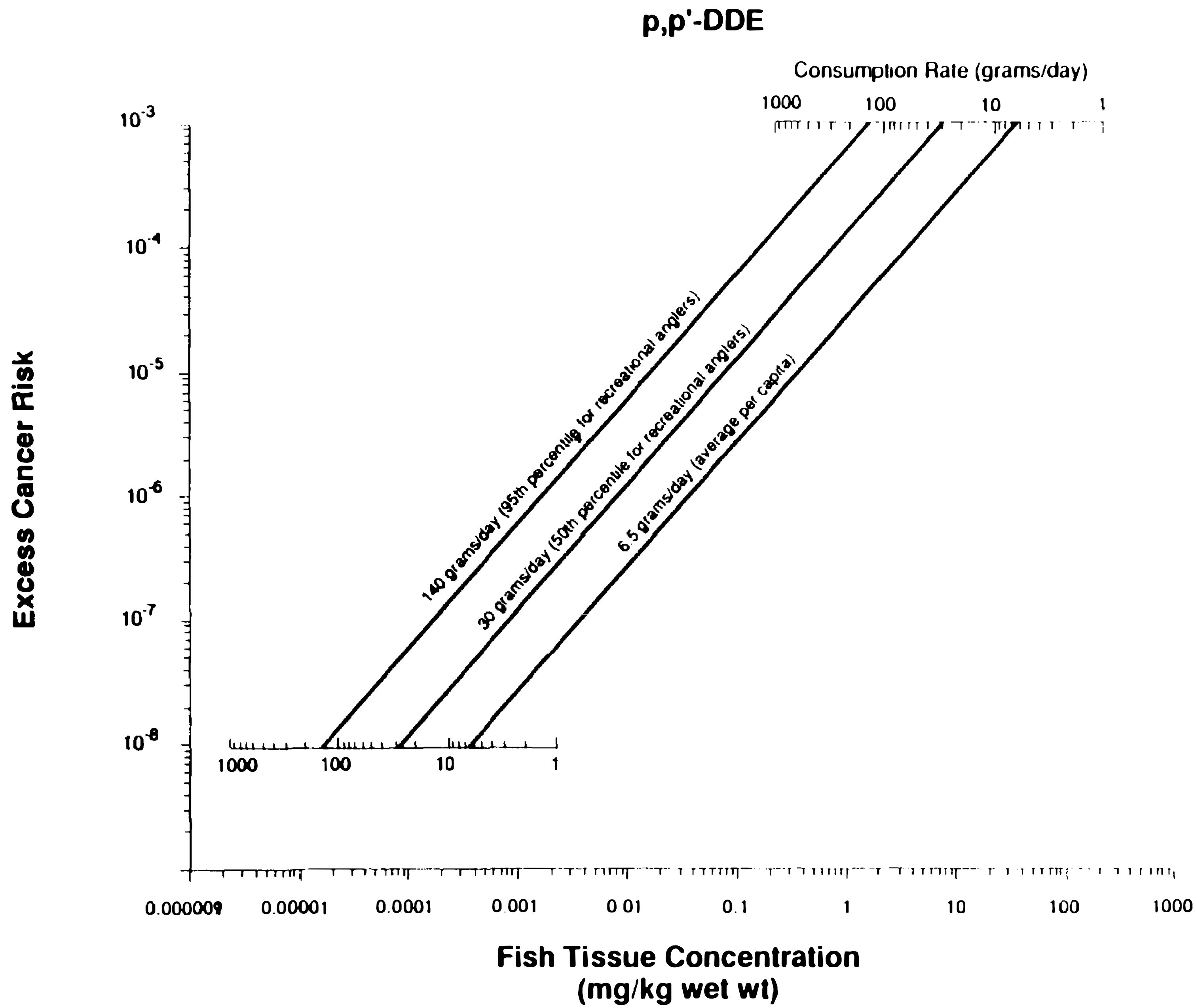
Nomographs for Estimating Cancer Risks

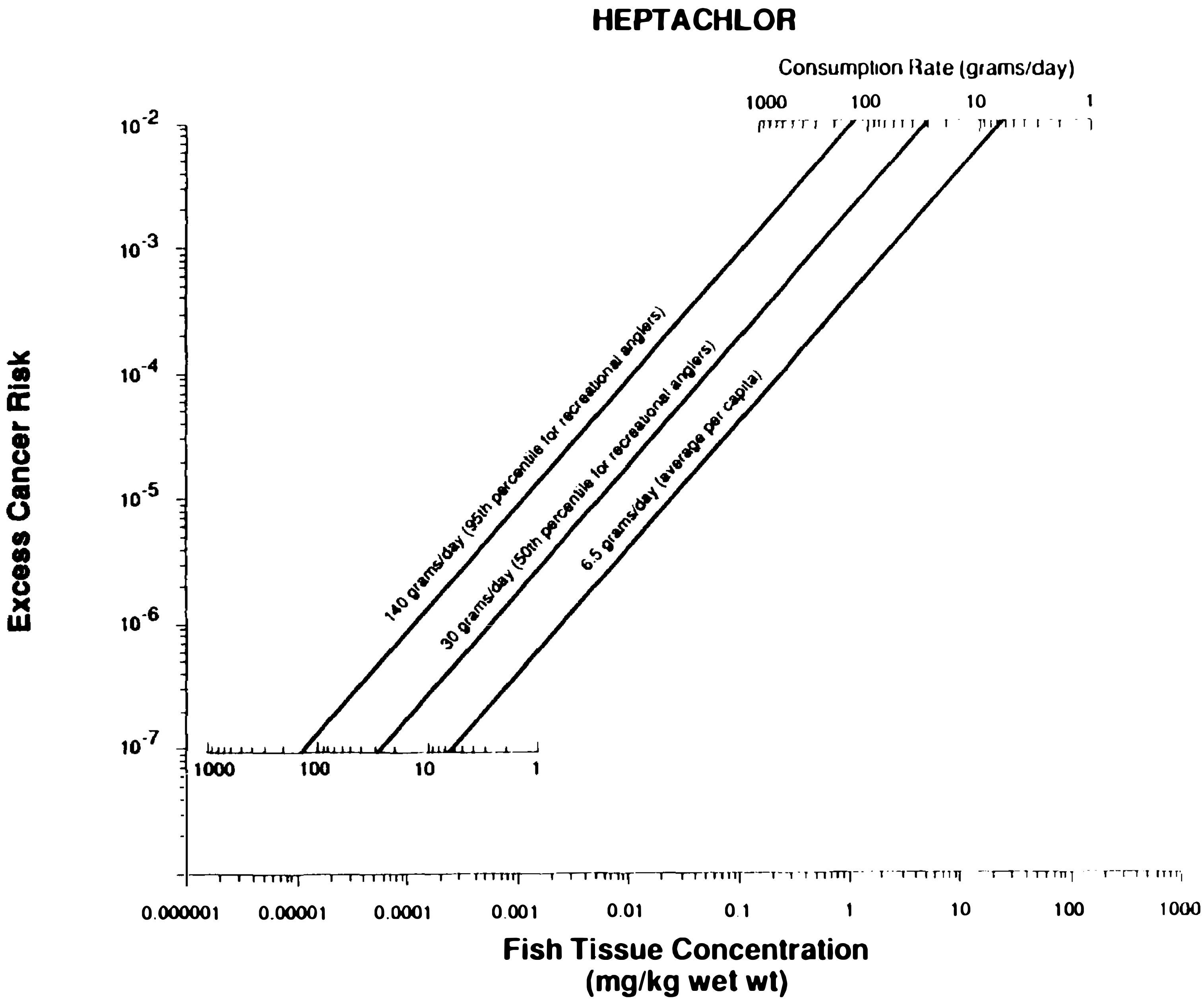
CHLORDANE


Consumption Rate (grams/day)
1000
100
10
1
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
Excess Cancer Risk
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
0.000001
0.00001
0.0001
0.001
0.01
0.1
1
10
100
1000
Fish Tissue Concentration
(mg/kg wet wt)

DIELDRIN

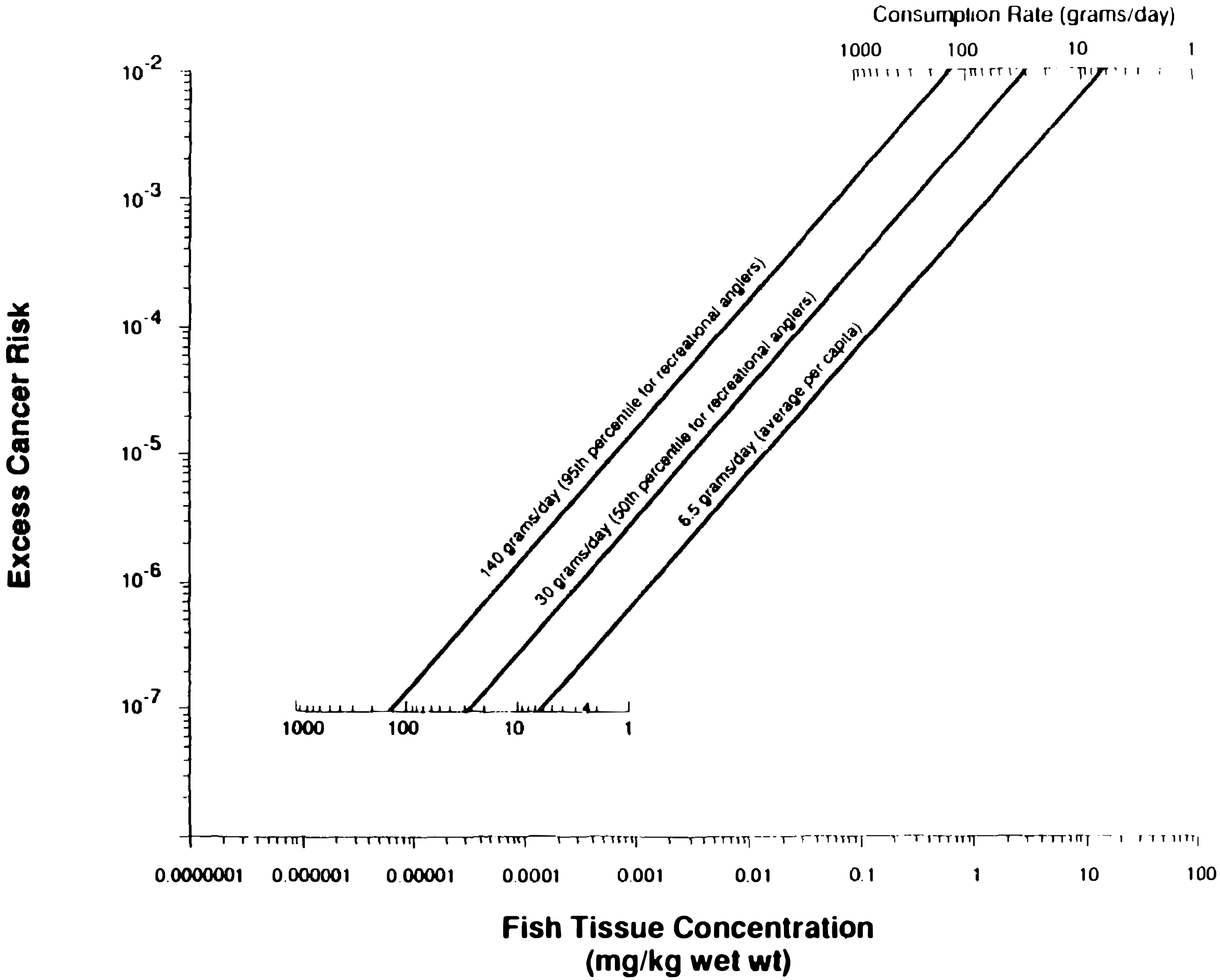

Consumption Rate (grams/day)
1000
100
10
1
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
Excess Cancer Risk
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
0.0000001
0.000001
0.00001
0.0001
0.001
0.01
0.1
1
10
100
Fish Tissue Concentration
(mg/kg wet wt)

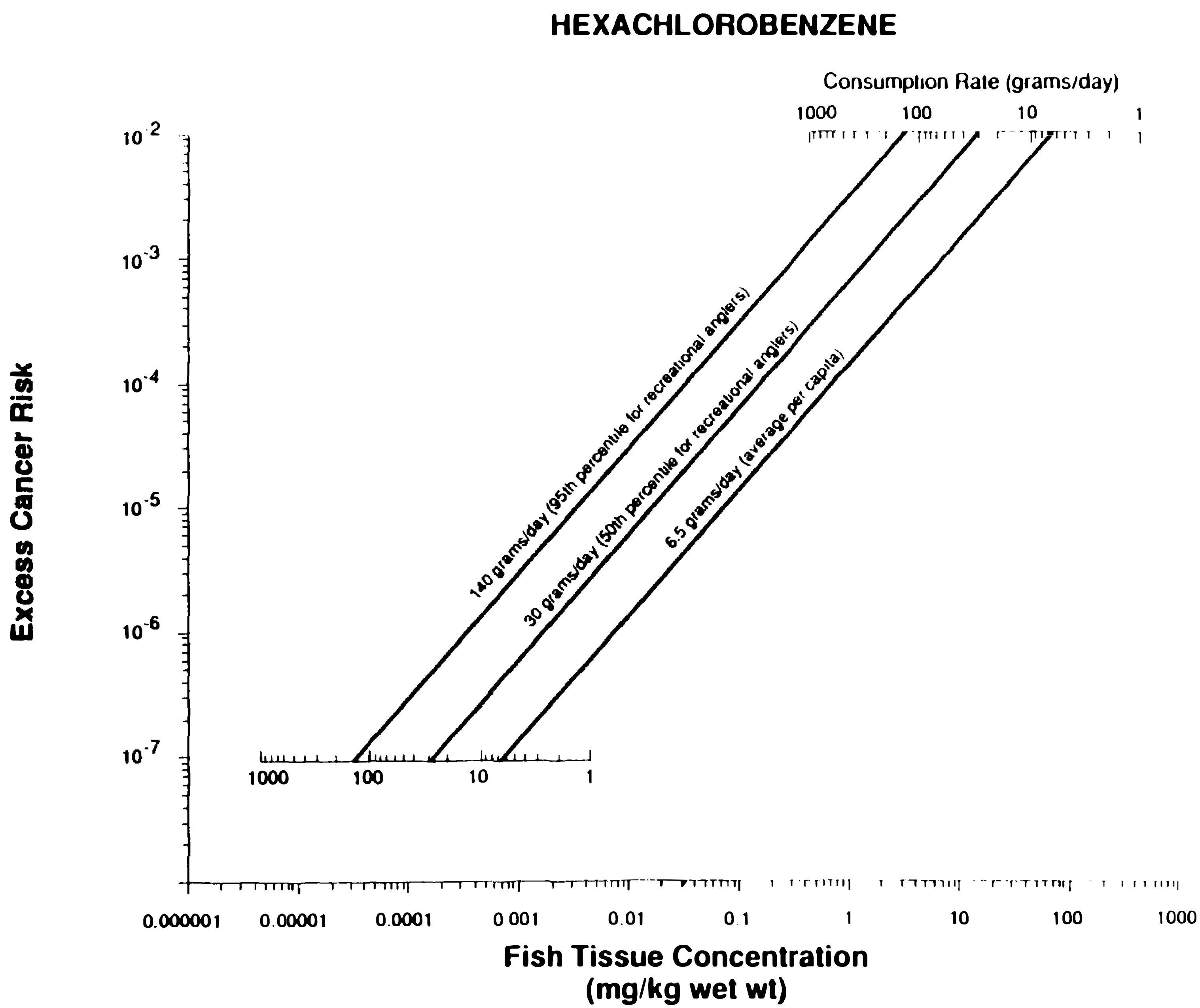

p,p'-DDE
Consumption Rate (grams/day)
1000
100
10
1
10^-3
10^-4
10^-5
10^-6
10^-7
10^-8
Excess Cancer Risk
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
0.000001
0.00001
0.0001
0.001
0.01
0.1
1
10
100
1000
Fish Tissue Concentration
(mg/kg wet wt)



HEPTACHLOR
Consumption Rate (grams/day)
1000
100
10
1
Excess Cancer Risk
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
0.000001
0.00001
0.0001
0.001
0.01
0.1
1
10
100
1000
Fish Tissue Concentration
(mg/kg wet wt)

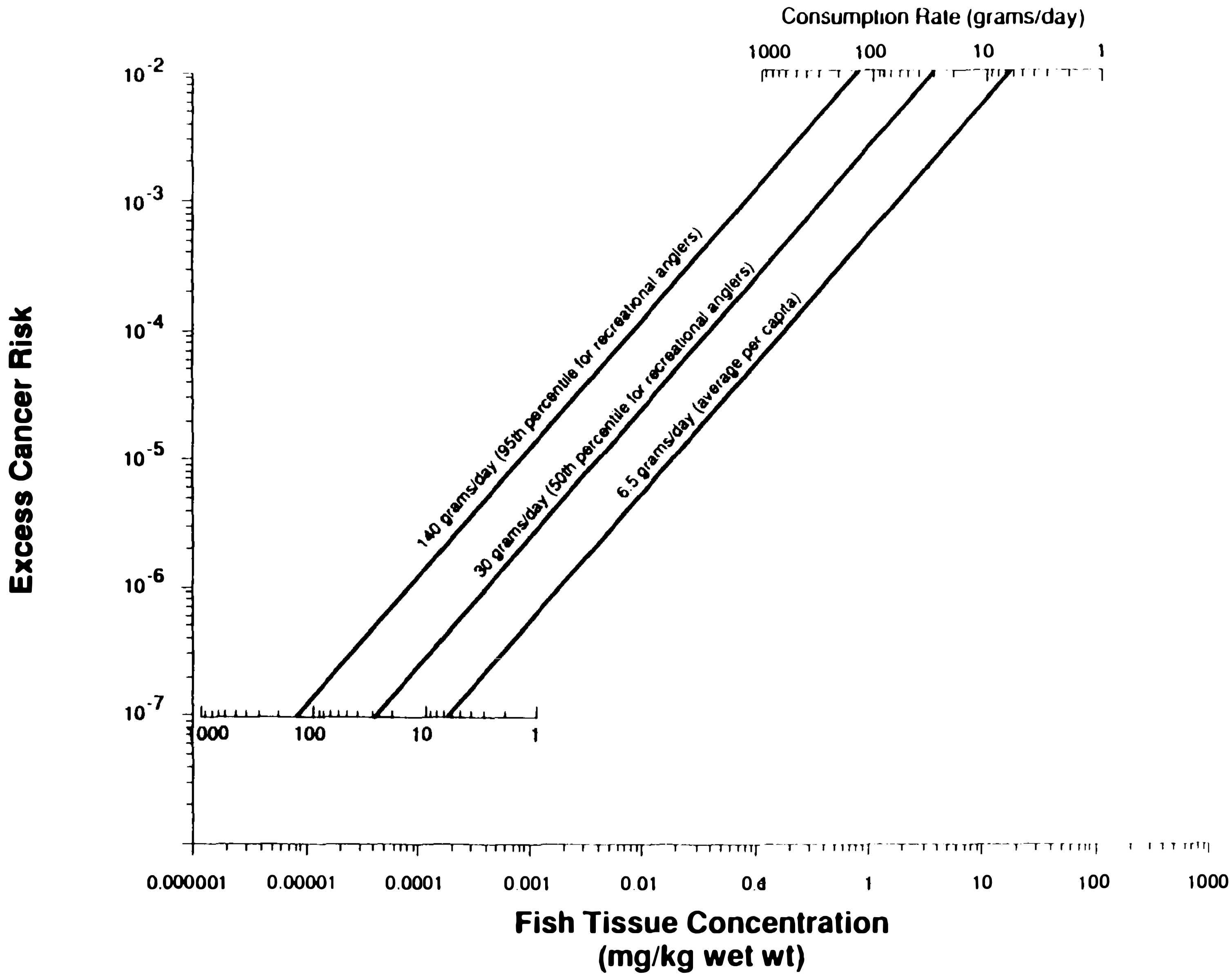
HEPTACHLOR EPOXIDE

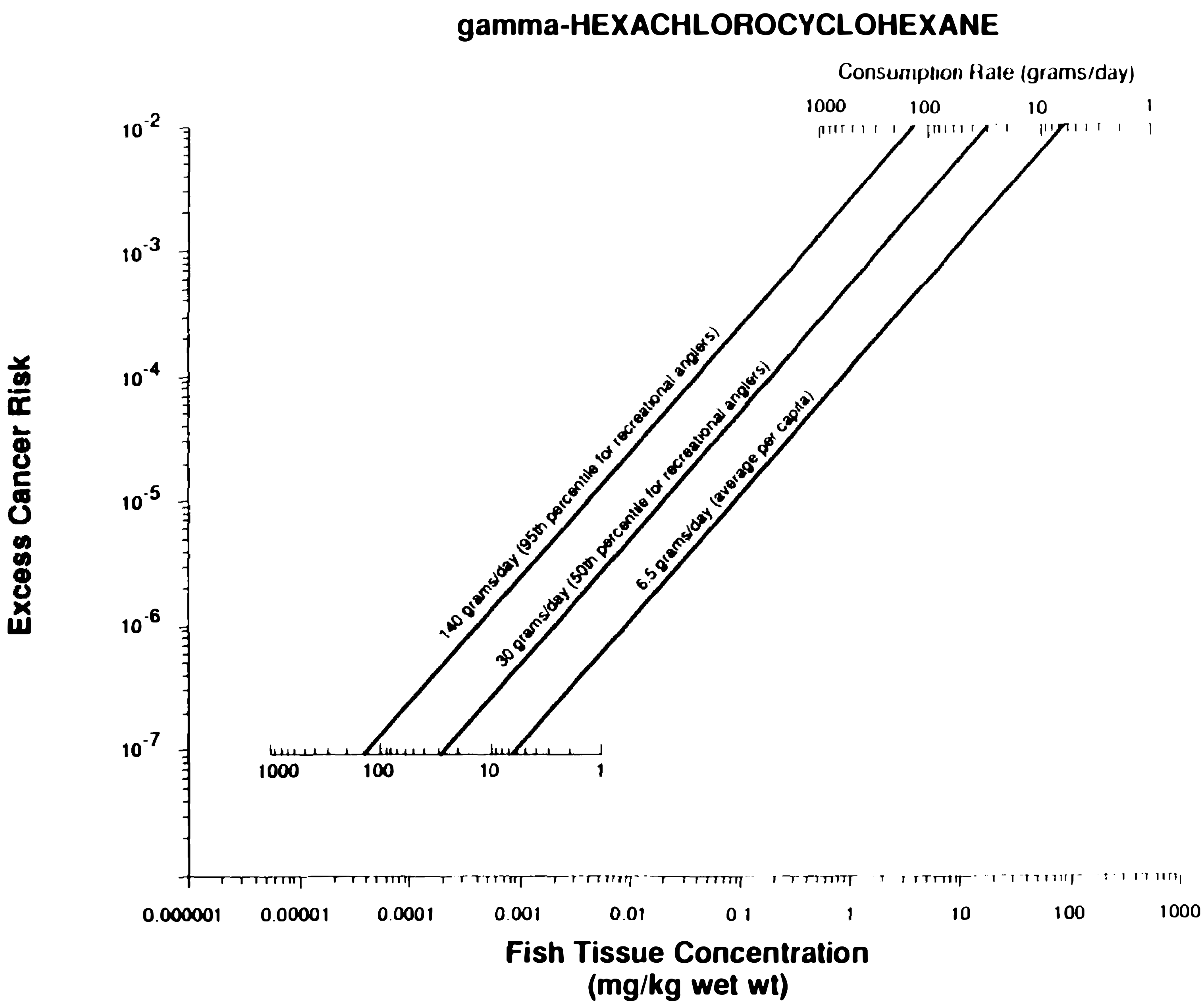


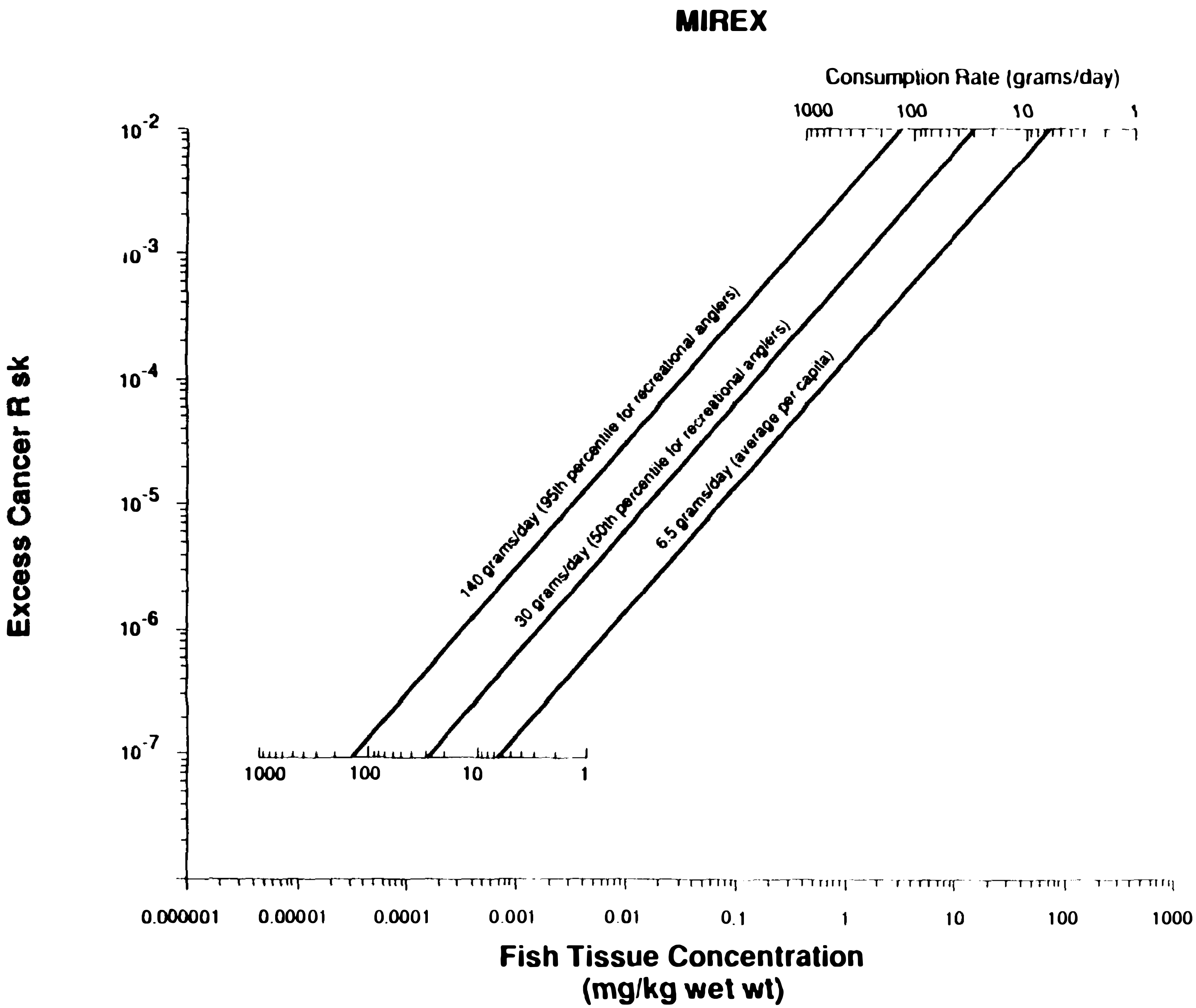


HEXACHLOROBENZENE
Consumption Rate (grams/day)
1000
100
10
1
10^-2
10^-3
10^-4
10^-5
10^-6
10^-7
Excess Cancer Risk
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
0.000001
0.00001
0.0001
0.001
0.01
0.1
1
10
100
1000
Fish Tissue Concentration
(mg/kg wet wt)

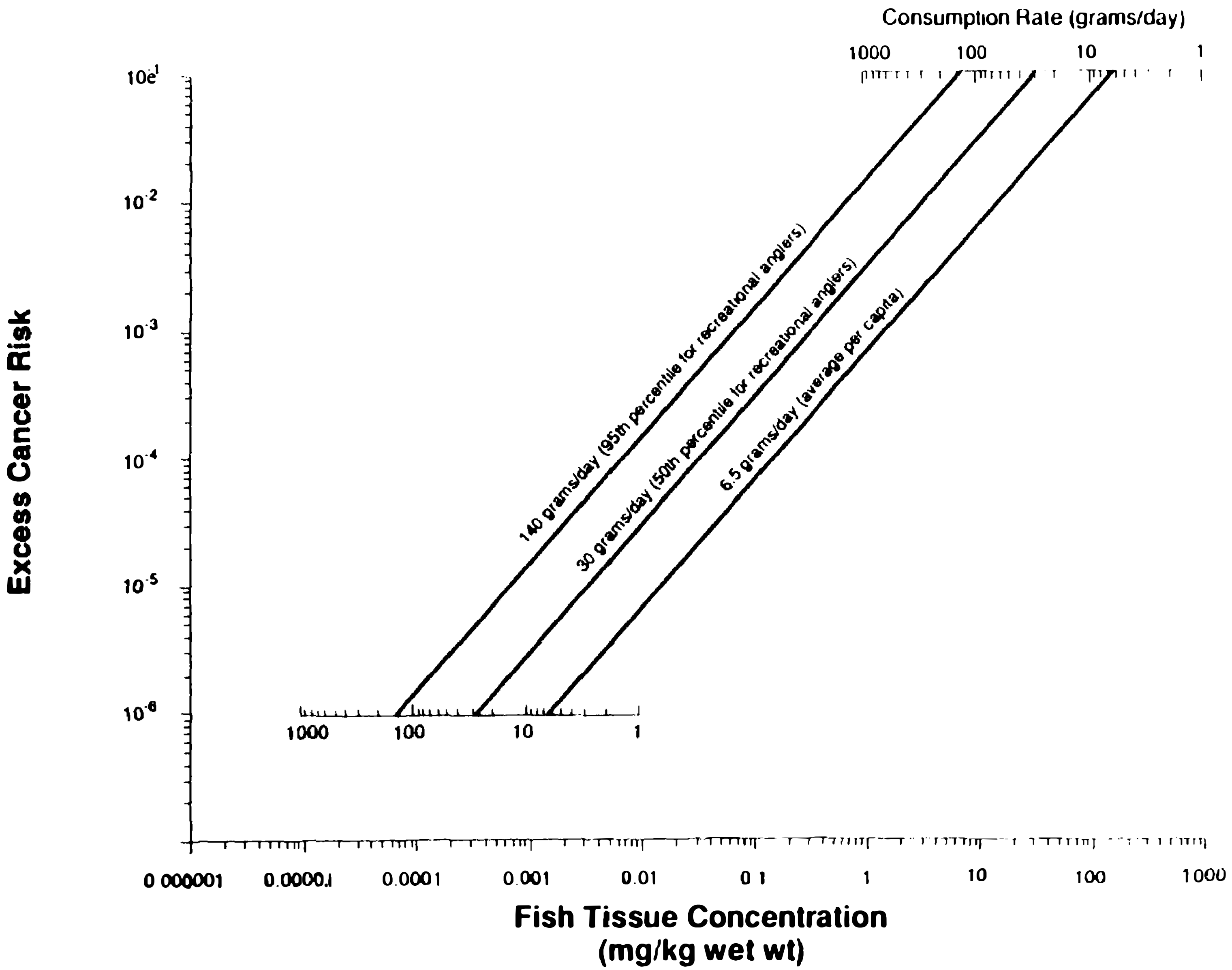
alpha-HEXACHLOROCYCLOHEXANE



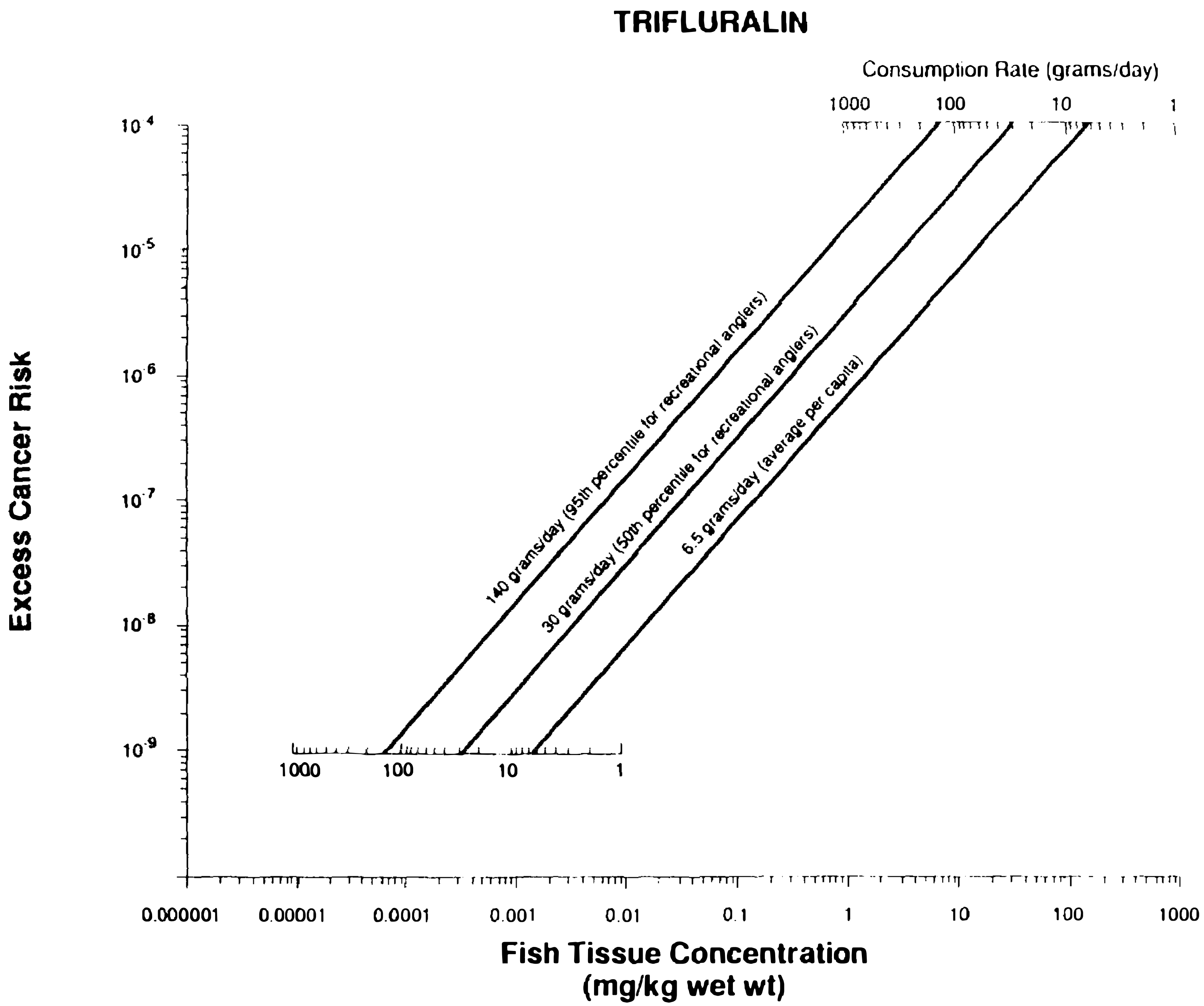

gamma-HEXACHLOROCYCLOHEXANE
Consumption Rate (grams/day)
1000
100
10
1
Excess Cancer Risk
10^{-2}
10^{-3}
10^{-4}
10^{-5}
10^{-6}
10^{-7}
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
0.000001
0.00001
0.0001
0.001
0.01
0.1
1
10
100
1000
Fish Tissue Concentration
(mg/kg wet wt)


MIREX
Consumption Rate (grams/day)
1000
100
10
1
Excess Cancer Risk
10^-2
10^-3
10^-4
10^-5
10^-6
10^-7
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
0.000001
0.00001
0.0001
0.001
0.01
0.1
1
10
100
1000
Fish Tissue Concentration
(mg/kg wet wt)

PCBs



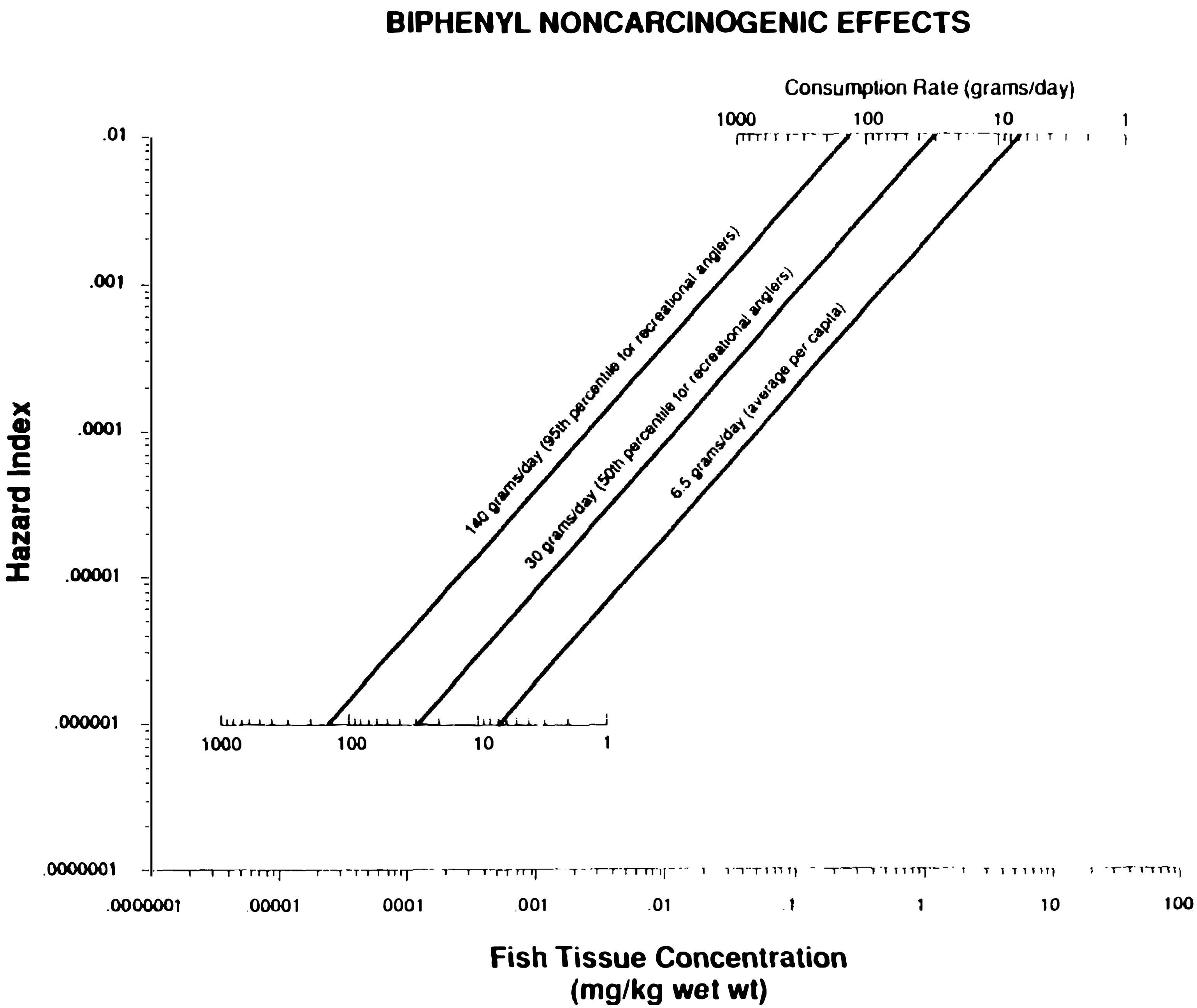
Consumption Rate (grams/day)
1000
100
10
1
Excess Cancer Risk
10e¹
10⁻²
10⁻³
10⁻⁴
10⁻⁵
10⁻⁶
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
0.000001
0.00001
0.0001
0.001
0.01
0.1
1
10
100
1000
Fish Tissue Concentration
(mg/kg wet wt)



TRIFLURALIN
Consumption Rate (grams/day)
1000
100
10
1
Excess Cancer Risk
10^-4
10^-5
10^-6
10^-7
10^-8
10^-9
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
0.000001
0.00001
0.0001
0.001
0.01
0.1
1
10
100
1000
Fish Tissue Concentration
(mg/kg wet wt)

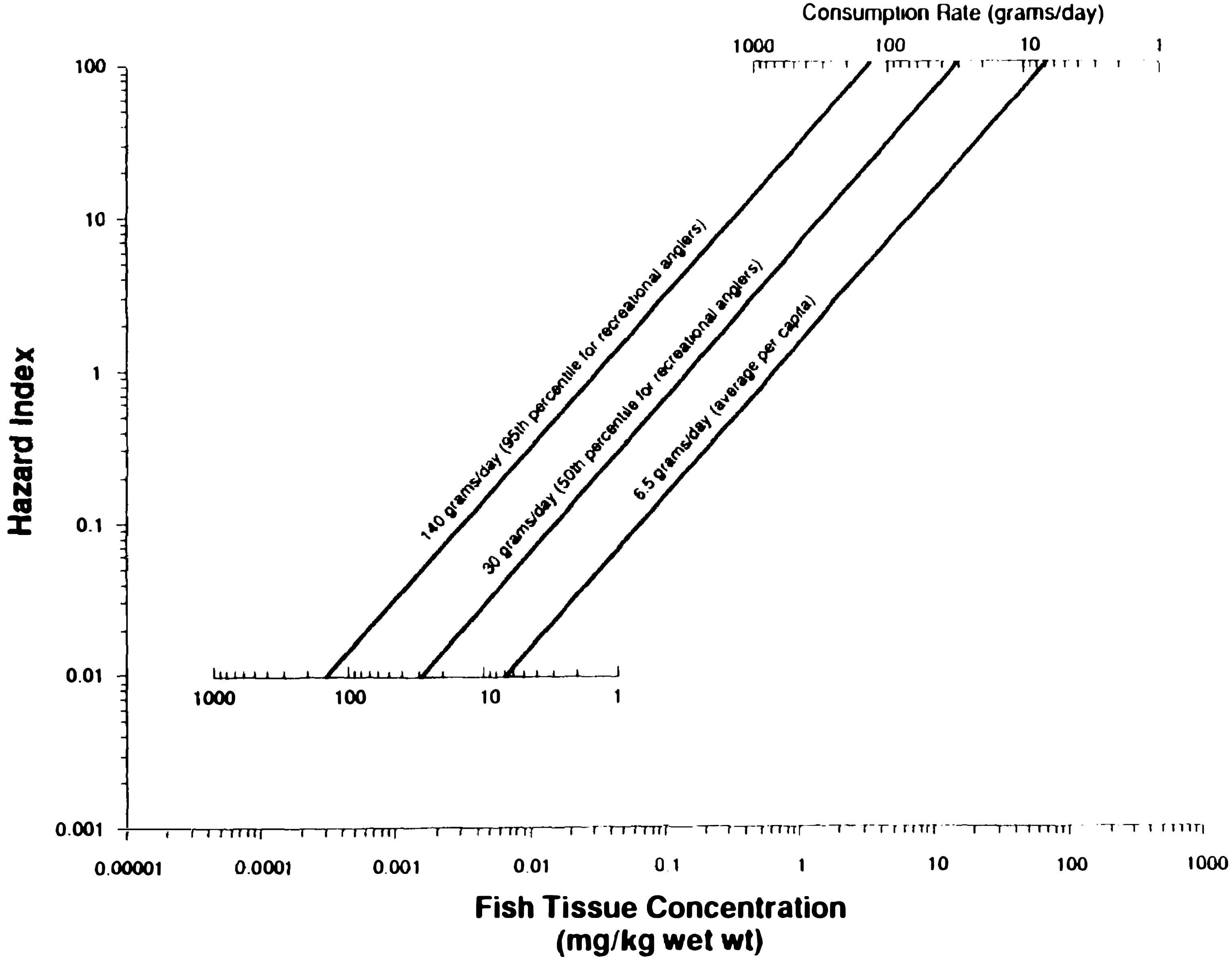
APPENDIX B-2

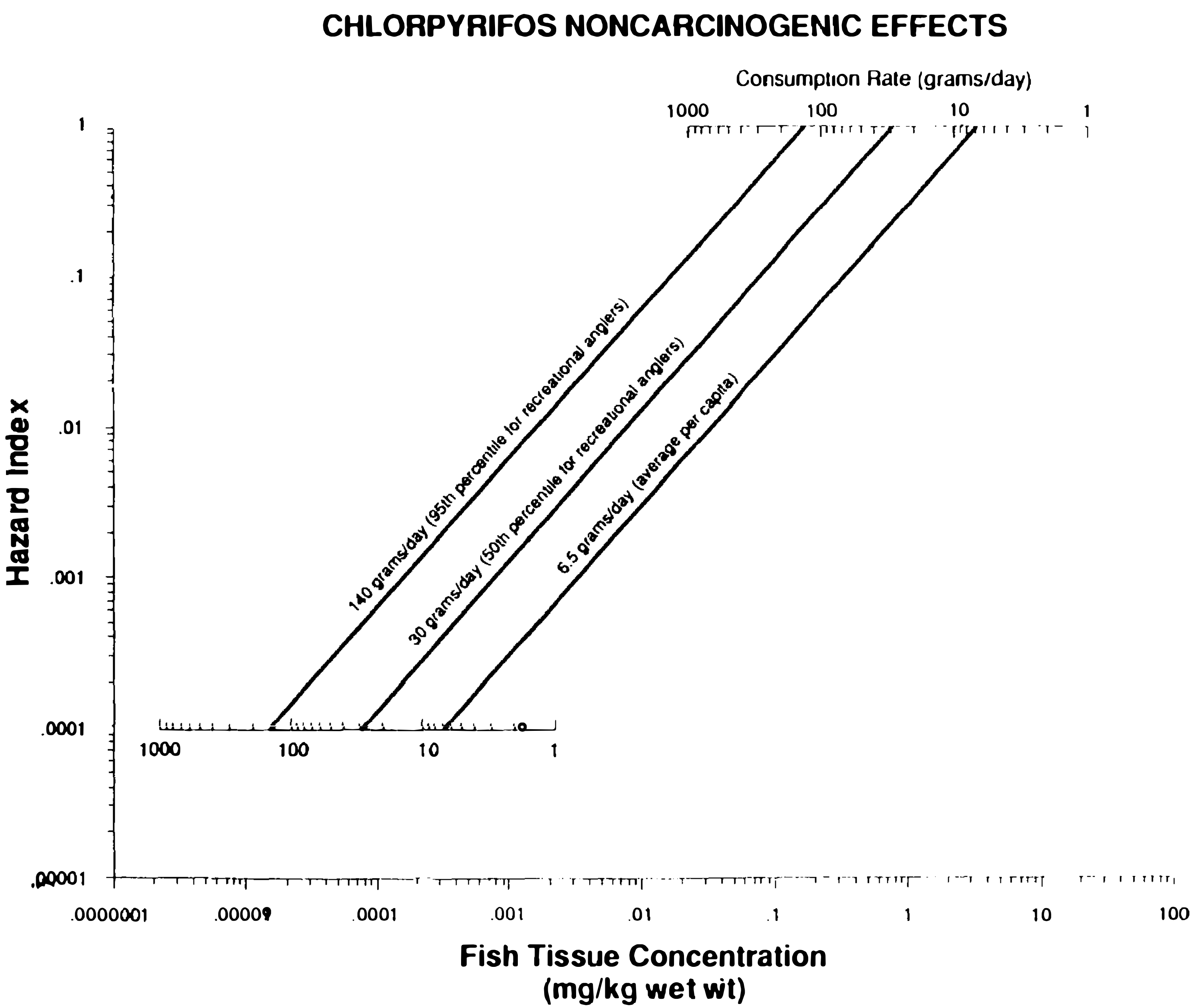
Nomographs for Estimating Noncarcinogenic Hazard Indices



BIPHENYL NONCARCINOGENIC EFFECTS
Consumption Rate (grams/day)
1000
100
10
1
.01
.001
.0001
.00001
.000001
.0000001
Hazard Index
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
.0000001
.00001
.0001
.001
.01
.1
1
10
100
Fish Tissue Concentration
(mg/kg wet wt)

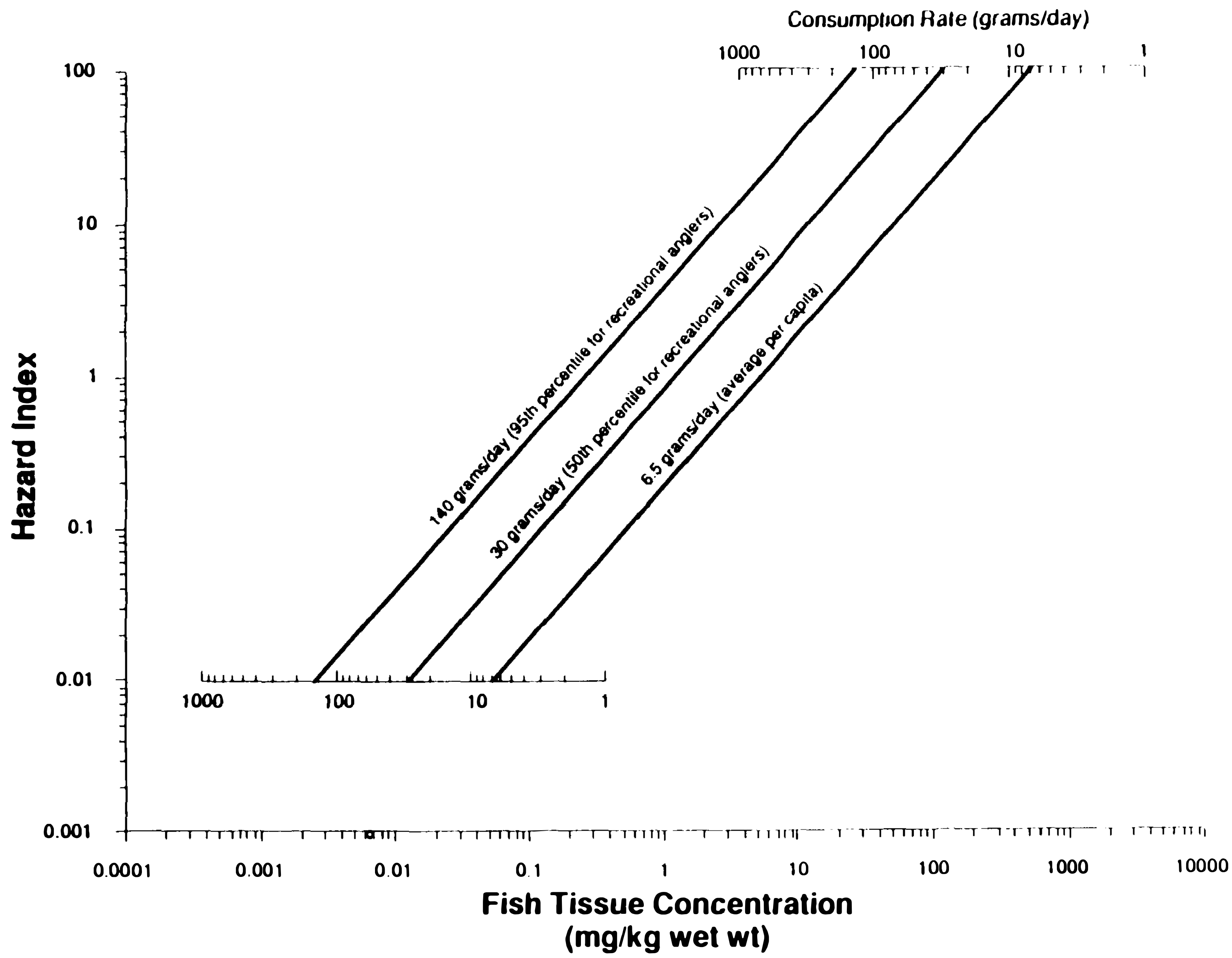
CHLORDANE NONCARCINOGENIC EFFECTS



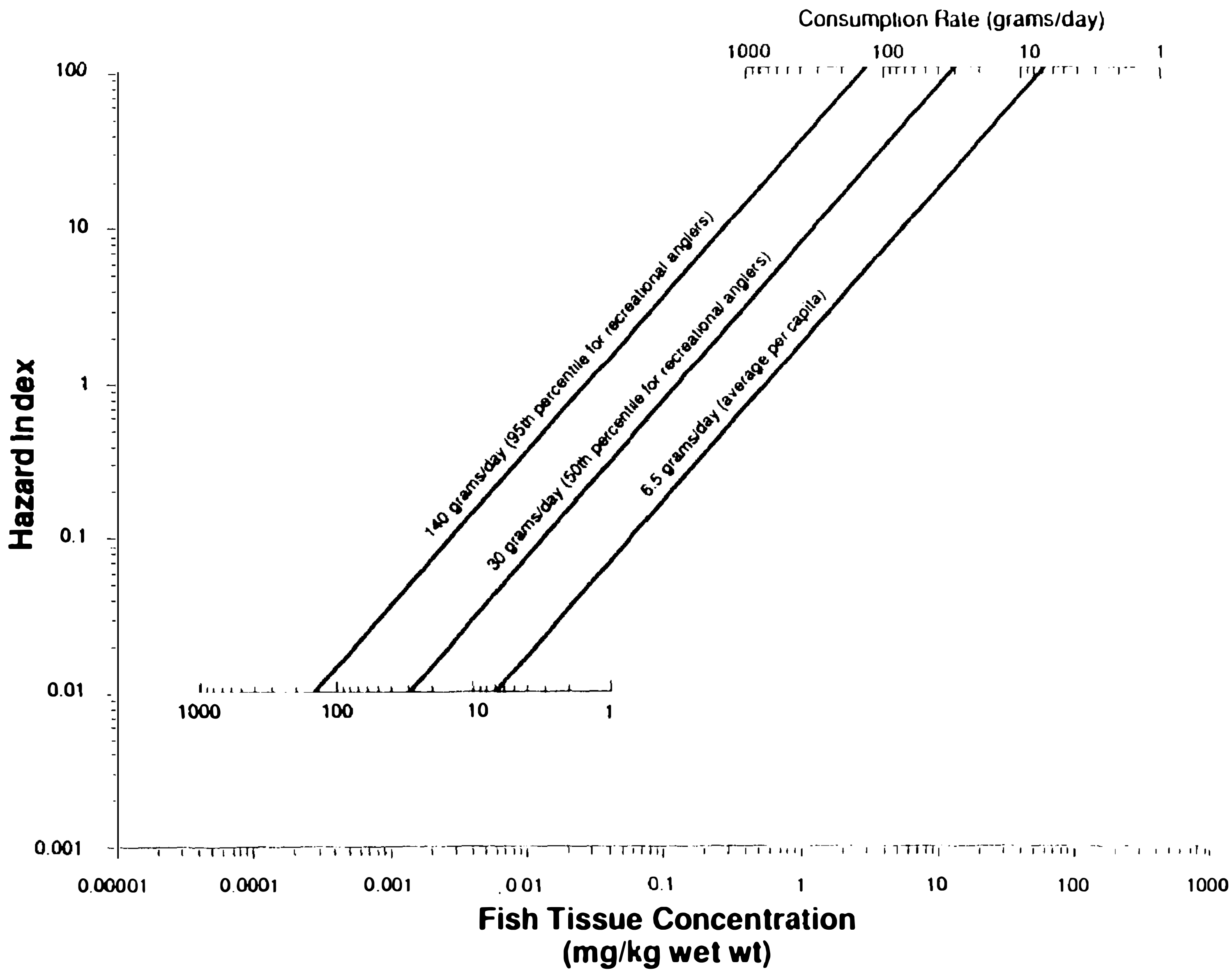


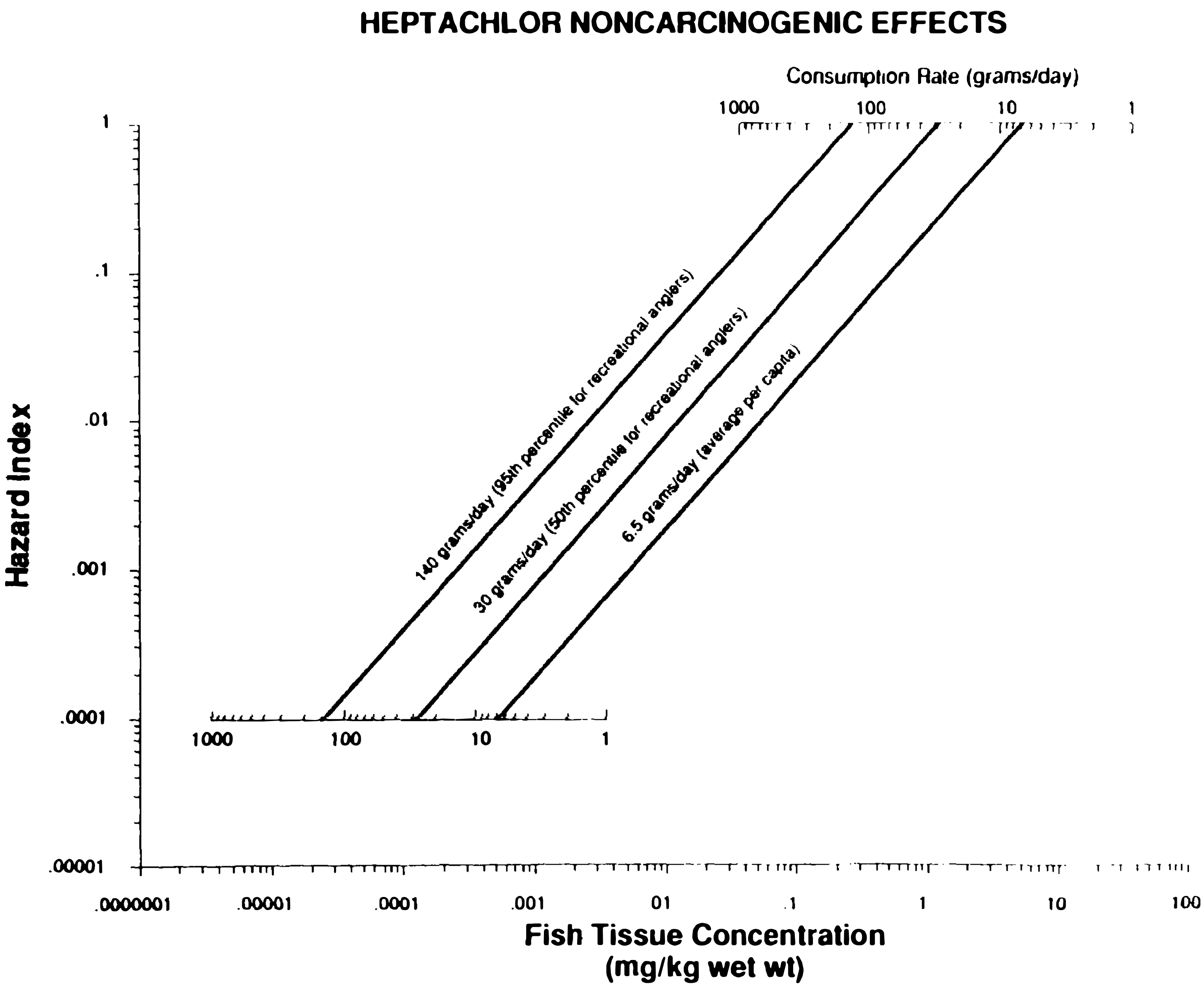
CHLORPYRIFOS NONCARCINOGENIC EFFECTS
Consumption Rate (grams/day)
1000
100
10
1
1
.1
.01
.001
.0001
.00001
Hazard Index
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
.0000001
.000001
.0001
.001
.01
.1
1
10
100
Fish Tissue Concentration
(mg/kg wet wt)

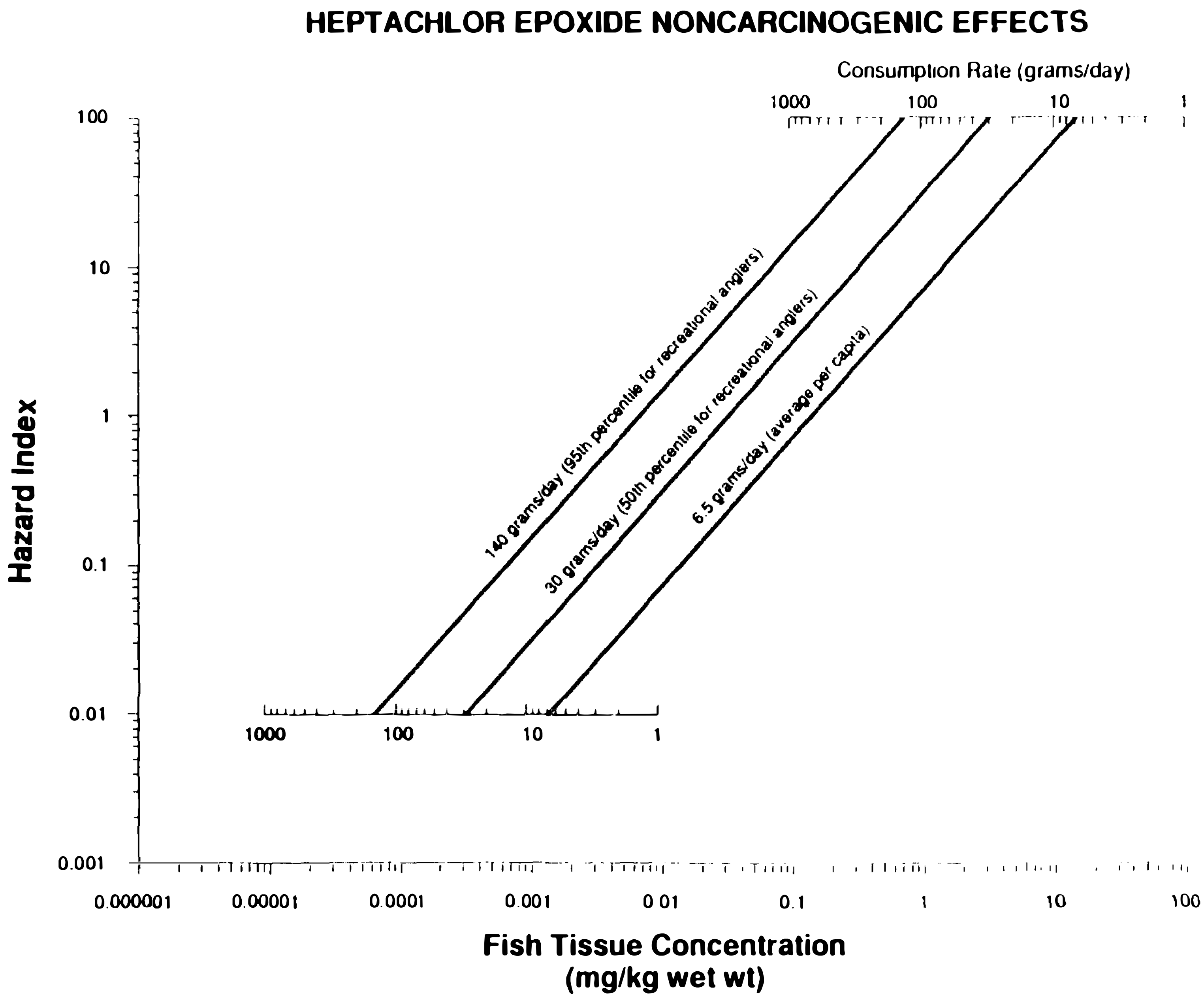
p,p'-DDE NONCARCINOGENIC EFFECTS



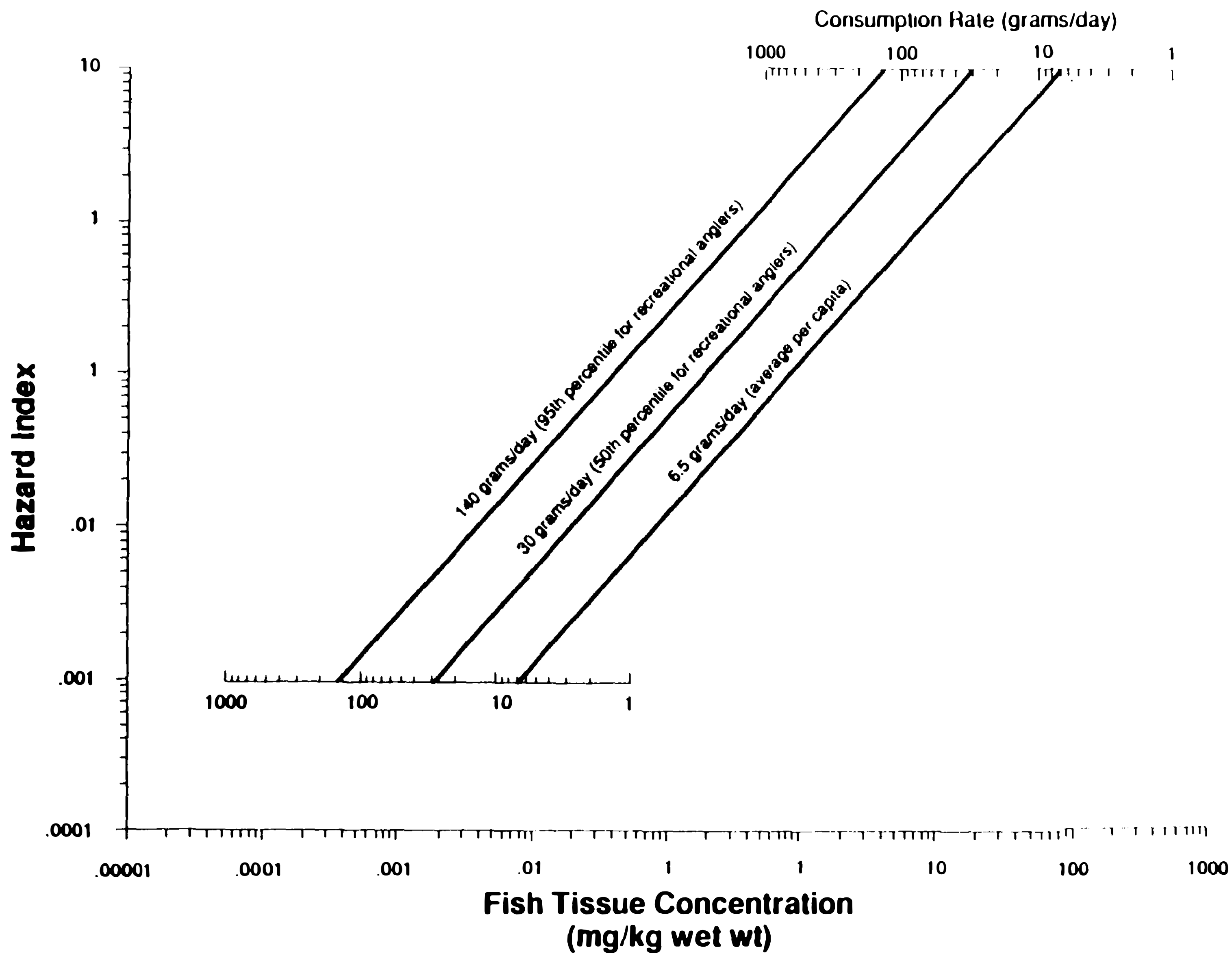
DIELDRIN NONCARCINOGENIC EFFECTS

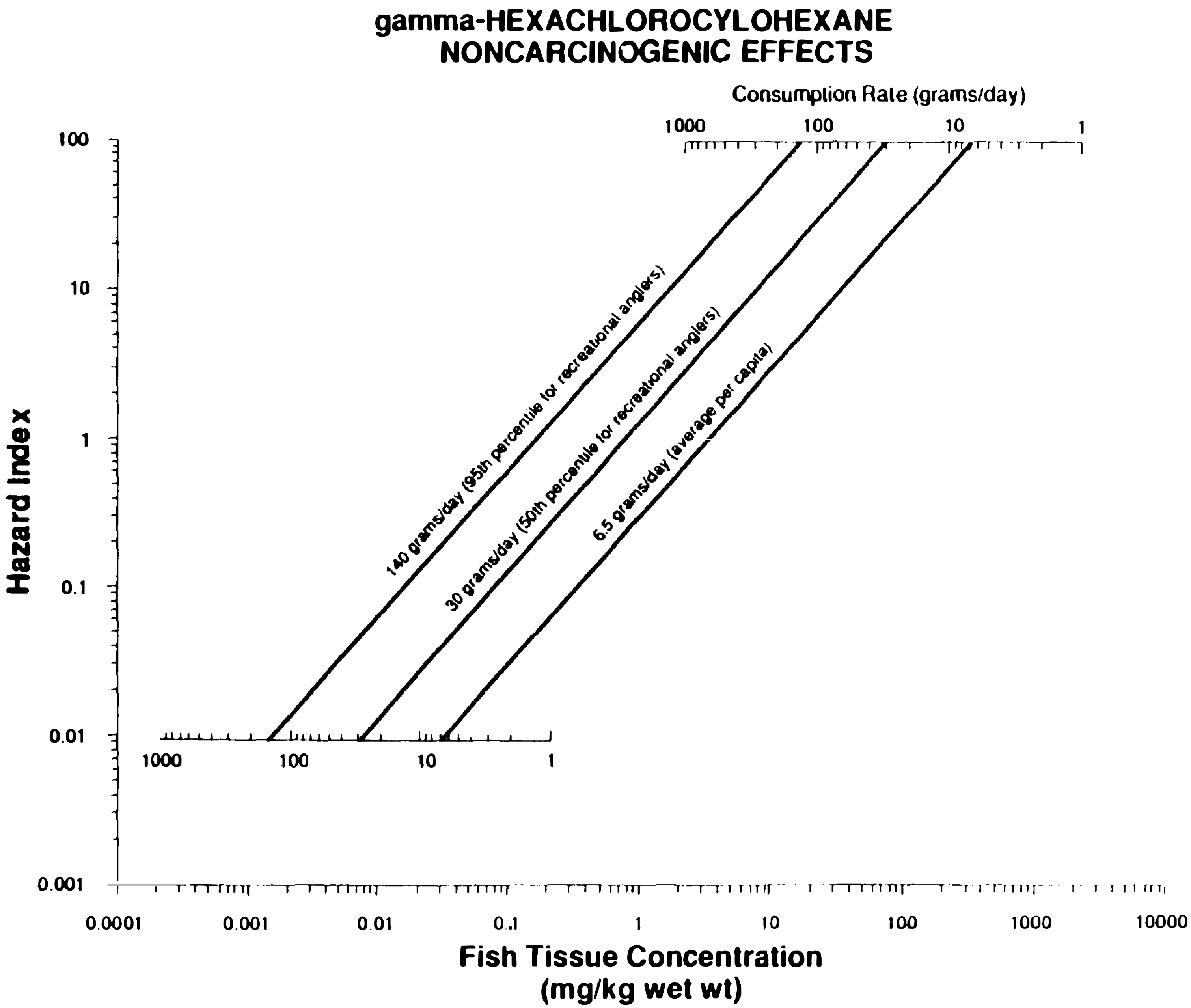



HEPTACHLOR NONCARCINOGENIC EFFECTS
Consumption Rate (grams/day)
1000
100
10
1
Hazard Index
1
.1
.01
.001
.0001
.00001
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
.0000001
.00001
.0001
.001
01
.1
1
10
100
Fish Tissue Concentration
(mg/kg wet wt)

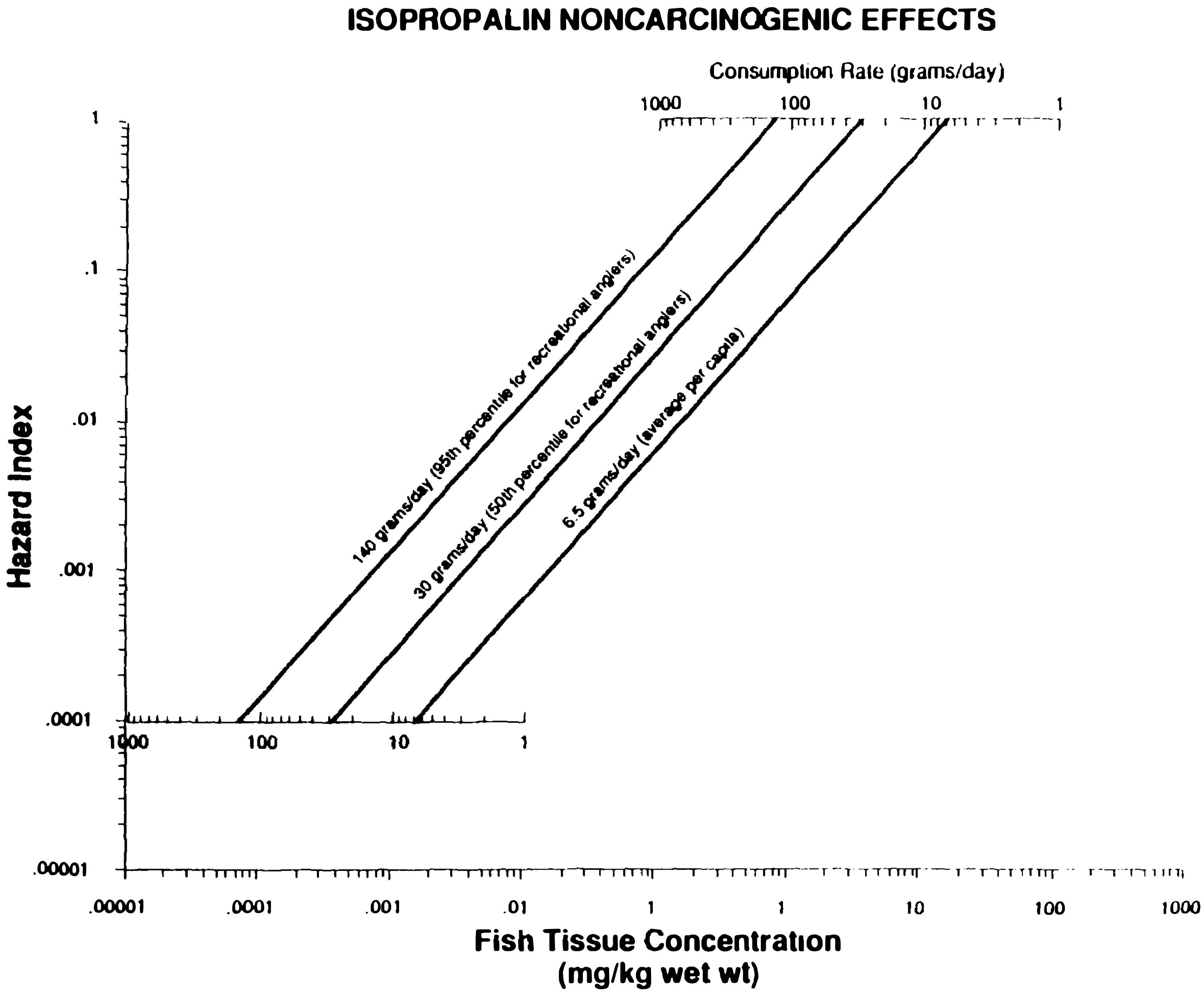

HEPTACHLOR EPOXIDE NONCARCINOGENIC EFFECTS
Consumption Rate (grams/day)
1000
100
10
1
Hazard Index
100
10
1
0.1
0.01
0.001
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
0.000001
0.00001
0.0001
0.001
0.01
0.1
1
10
100
Fish Tissue Concentration
(mg/kg wet wt)

HEXACHLOROBENZENE NONCARCINOGENIC EFFECTS

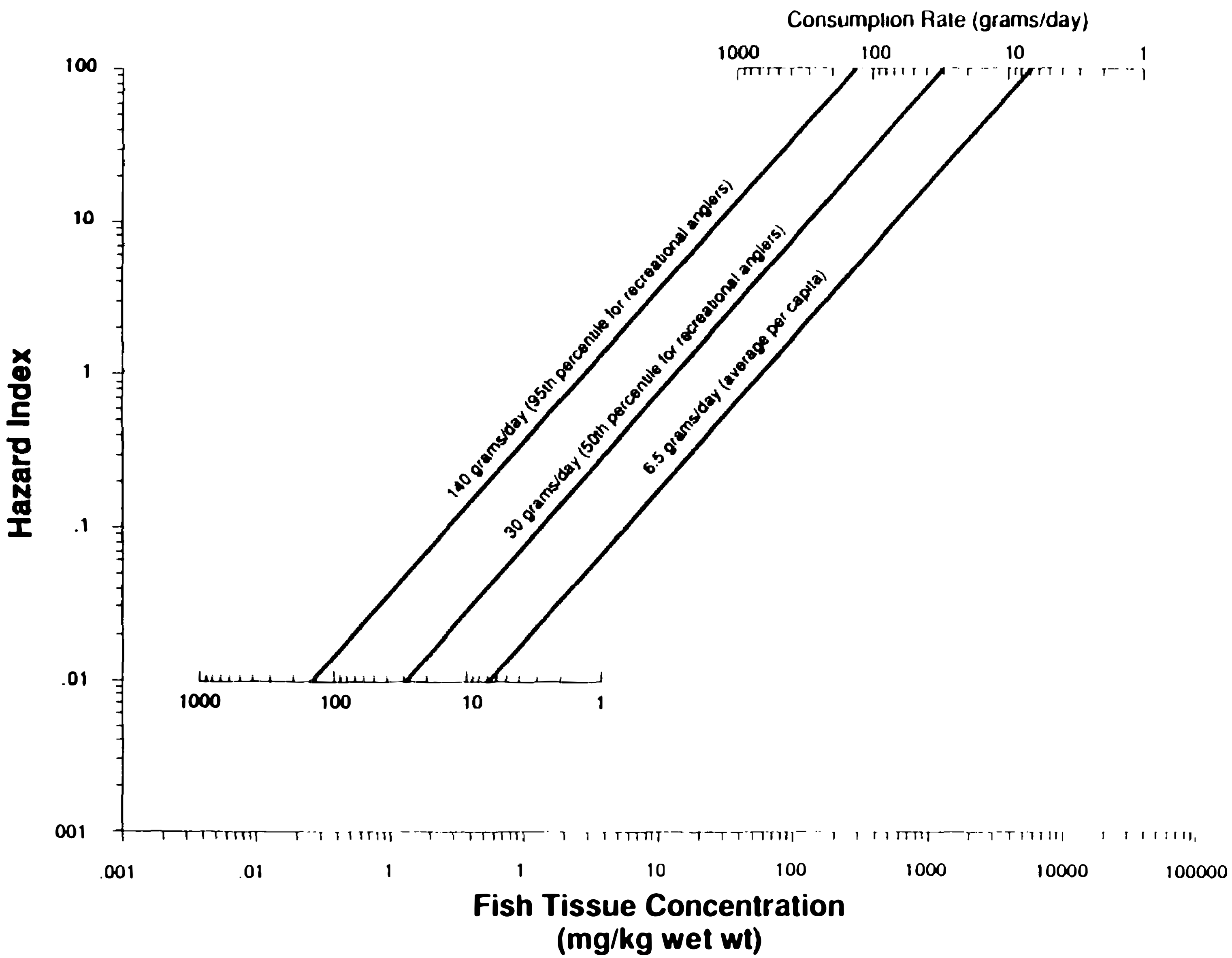




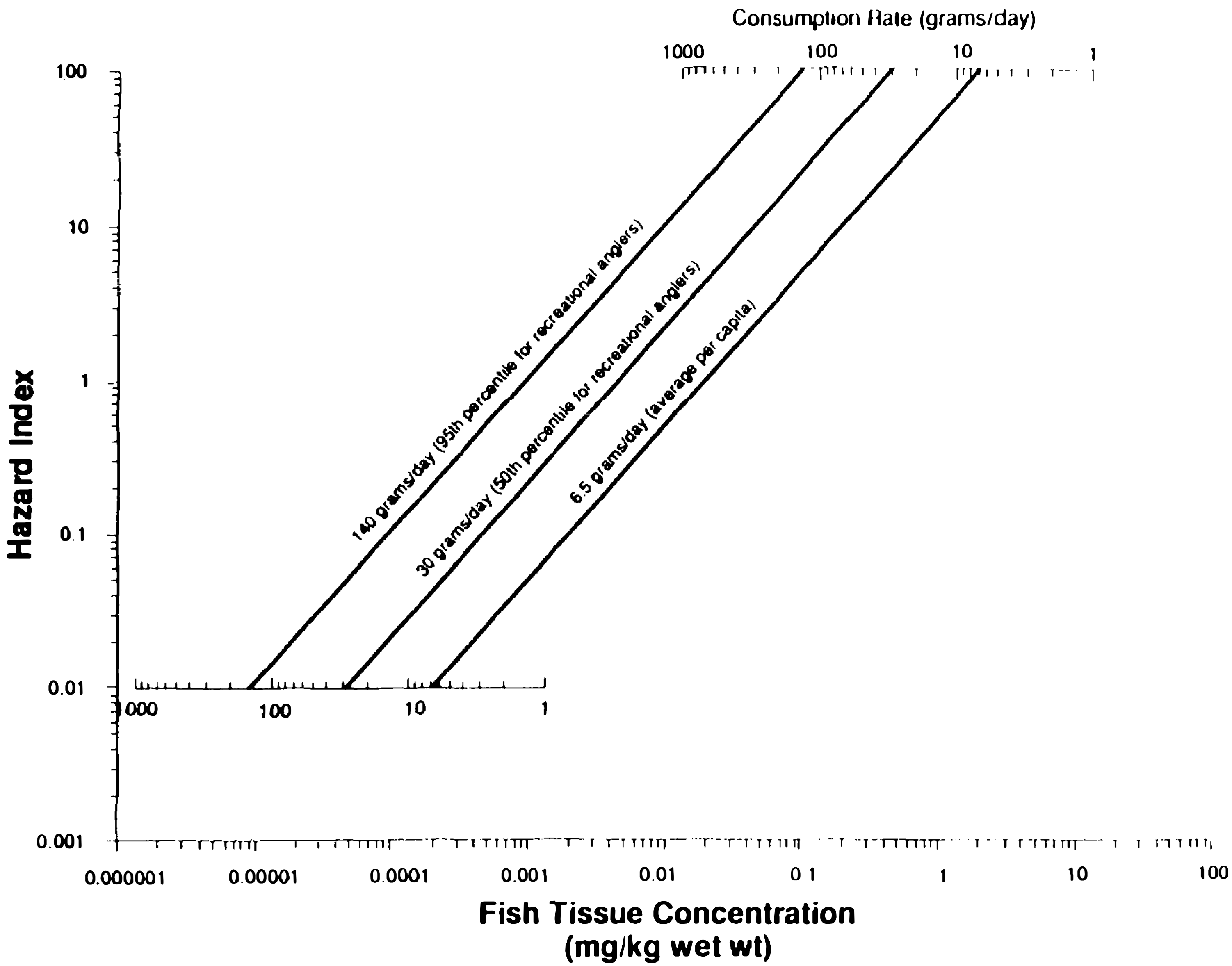
gamma-HEXACHLOROCYLOHEXANE
NONCARCINOGENIC EFFECTS
Consumption Rate (grams/day)
1000
100
10
1
100
10
1
0.1
0.01
0.001
Hazard Index
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
0.0001
0.001
0.01
0.1
1
10
100
1000
10000
Fish Tissue Concentration
(mg/kg wet wt)

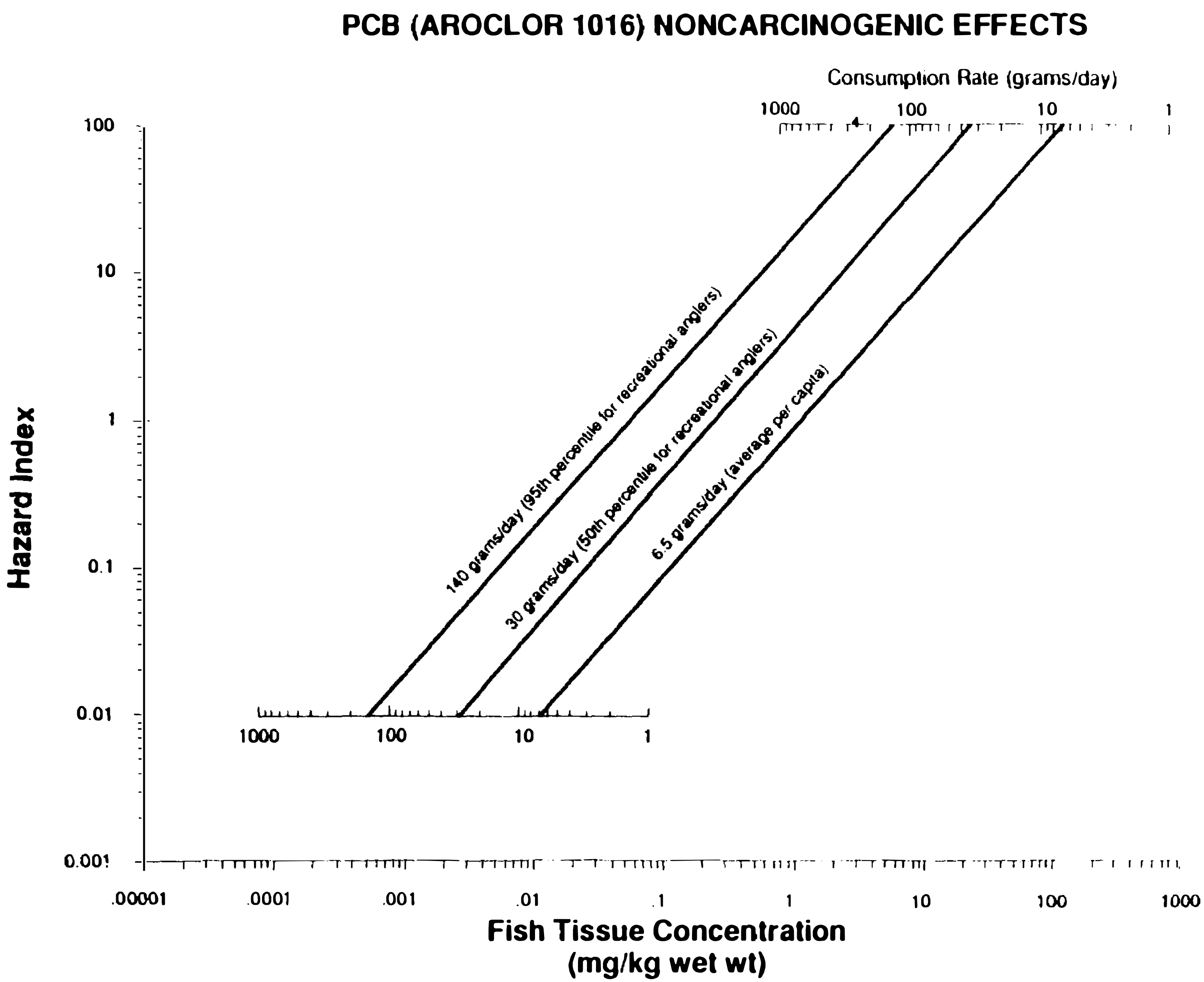

ISOPROPALIN NONCARCINOGENIC EFFECTS
Consumption Rate (grams/day)
1000
100
10
1
Hazard Index
1
.1
.01
.001
.0001
.00001
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
.00001
.0001
.001
.01
1
1
10
100
1000
Fish Tissue Concentration
(mg/kg wet wt)

MERCURY NONCARCINOGENIC EFFECTS

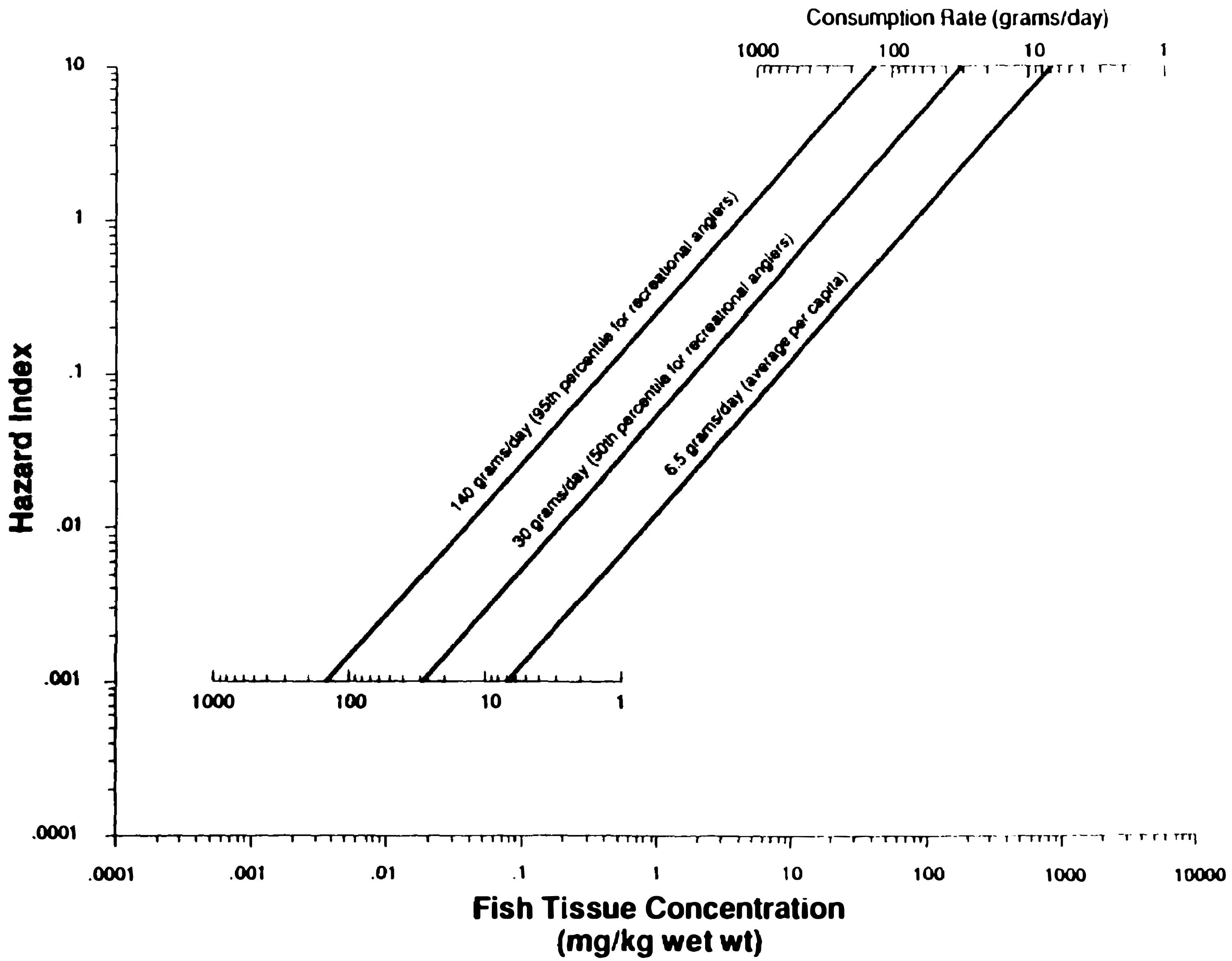


MIREX NONCARCINOGENIC EFFECTS




PCB (AROCLOR 1016) NONCARCINOGENIC EFFECTS
Consumption Rate (grams/day)
1000
100
10
1
Hazard Index
100
10
1
0.1
0.01
0.001
140 grams/day (95th percentile for recreational anglers)
30 grams/day (50th percentile for recreational anglers)
6.5 grams/day (average per capita)
1000
100
10
1
.00001
.0001
.001
.01
.1
1
10
100
1000
Fish Tissue Concentration
(mg/kg wet wt)

TRIFLURALIN NONCARCINOGENIC EFFECTS



APPENDIX B-3

Site Description Matrix

Key to Table B-3
Matrix of Episodes and Site Descriptions

COLUMN HEADING		DESCRIPTION
1.	EPA REGION	The U.S. Environmental Protection Agency Region which includes the sample location.
2.	EPISODE	The EPA Episode Number which is specific to each sampling location.
3.	LATITUDE	The latitude of the sample site in degrees, minutes and seconds.
4.	LONGITUDE	The longitude of the sample site in degrees, minutes and seconds.
5.	STATE	The state where the sample was collected.
6.	WATERBODY	Name of the water body where the sample was collected.
7.	LOCATION	The nearest town, road or county to the sample location.
8.	NSQ	Sample site from the USGS NASQAN monitoring network.
9.	B	Background site as selected for study.
	POINT SOURCES:	**Point sources include the following six categories:**
10.	PPC	Site near paper and pulp mill using chlorine for bleaching (includes mills using the sulfite process).
11.	PPNC	Site near paper and pulp mill not using chlorine for bleaching.
12.	REFINERY	Site near refinery using the catalytic reforming process.
13.	NPLSITE	Site near an EPA National Priority List Site (Superfund site).
14.	OTHER INDUSTRY	Site near industrial facility other than a paper mill, refinery, or wood preserver.
15.	POTW	Site near discharge of a Publicly Owned Treatment Works (POTW).
16.	WP	Site near active or former wood preserving activity.
	NONPOINT:	**Nonpoint sources include the following two categories:**
17.	URBAN	Site near urban runoff.
18.	AGRICULTURE	Site near agricultural area.

TABLE B-3

Matrix of Episodes and Site Descriptions

EPA Reg	Episode #	Latitude	Longitude	State	Waterbody	Location	NSQ	B	POINT SOURCES PPC	PPNC	WP	Rfny	NPL Site	Other Ind	POTW	NONPOINT Urban	Agri	Additional Site Description (Facilities in the vicinity of the sampling site)
I	2376	41:22:00N	072:52:40W	CT	Quinipiac River	North Haven							X	X	X			Industry: chemical & pesticides; electronics; plastics; metals; Superfund site (solvents)
I	2375	41:36:47N	071:58:26W	CT	Quinnebaug River	Jewett City							X	X	X			Ind.: organic chem. & pest., textiles; Superfund site (Furans)
I	2369	42:37:25N	071:23:10W	MA	Merrimack River	Tyngs Island							X	X	X			Ind.: chem. & pest., industrial WWTP; P&P mill on Nashua R. (trib.); Superfund site (solvents)
I	3151	42:35:22N	072:21:08W	MA	Millers River	Erving			X									Erving Paper Mills; wooded area; Ag.: croplands and grazing fields
I	3150	42:35:46N	072:03:27W	MA	Otter River	Baldwinville			X								X	Erving Paper Mills; wooded area; Ag.: croplands and grazing fields
I	2356	44:06:10N	070:13:58W	ME	Androscoggin R.	Lewiston			X					X	X	X		International Paper, Boise Cascade, James River; Ind.: textiles
I	2721	44:15:20N	070:10:50W	ME	Androscoggin R.	Turner Falls			X									International Paper Co. in Jay
I	2725	44:30:09N	070:15:00W	ME	Androscoggin R.	Riley Dam			X									Boise Cascade in Rumford; rural;wooded area
I	3026	44:10:20N	070:20:25W	ME	Androscoggin R.	Auburn			X	X				X		X		Ind.: textiles; downstream of paper mills
I	3028	45:04:48N	067:19:25W	ME	Bearce Lake	Barring		X										
I	2358	44:36:30N	067:55:30W	ME	Narraguagus R.	Cherryfield	X										X	Two blueberry processing plants; blueberry fields (pesticides)
I	3022	44:32:30N	070:07:15W	ME	North Pond	Chesterville		X										No industry; wooded and swampy area
I	2355	44:49:20N	068:42:30W	ME	Penobscot R.	Eddington			X						X	X		James River Corporation on Old Town
I	2722	43:34:35N	070:33:45W	ME	Saco River	Union Falls		X							X			Same as 3027; POTW on upstream trib. yet is Background site
I	3027	43:34:25N	070:33:55W	ME	Saco River	Union Falls		X							X			Same as 2722; POTW on upstream trib. yet is Background site
I	3023	44:54:30N	069:55:05W	ME	Sandy Pond	North Anson		X										
I	3024	44:54:00N	069:15:15W	ME	Sebasticook E. Br.	Newport								X	X			Industrial WWTP
I	3025	44:49:40N	069:24:00W	ME	Sebasticook W. Br.	West Palmyra								X	X		X	Industrial WWTP
I	3152	44:24:42N	071:11:29W	NH	Androscoggin R.	Berlin			X									James River Corporation
II	3426	40:35:45N	074:12:20W	NJ	Arthur Kill	Carteret								X				GAF Corp. (chem. manufacturing)
II	3429	39:34:30N	075:31:00W	NJ	Delaware River	Salem						X	X	X		X	X	Superfund site (several sites; metals & org. chemicals)
II	3430	39:18:00N	074:37:30W	NJ	Great Egg Harbor			X							X		X	Background even though has agricultural area and POTW nearby
II	2651	39:36:00N	074:35:00W	NJ	Mullica River	Green Bank		X										Wooded area
II	3427	40:39:15N	074:09:16W	NJ	Newark Bay	Elizabeth							X	X		X		Landfill
II	2653	40:54:30N	074:12:00W	NJ	Passaic River	Paterson				X			X	X	X	X		Marcal Paper and P&P mill on trib.; Ind.: metals, chem. & pest.; Superfund site (solvents)
II	3428	40:43:15N	074:07:15W	NJ	Passaic River	Newark								X		X		80 Lister Ave.: chem. manufacturing
II	3433	40:28:24N	074:03:40W	NJ	Raritan Bay							X	X	X	X			P&P mill effluent into bay; Exxon Co.; Ind.: chem.; Superfund site (several sites; metals & org. chem.)
II	3434	40:27:00N	074:03:00W	NJ	Sandy Hook							X		X	X	X		Exxon Co.
II	2654	39:57:30N	074:12:30W	NJ	Toms River								X	X	X		X	Ind.: chemical; Superfund site (chlorobenzene; Hg)
II	3304	43:59:30N	076:04:30W	NY	Black River Delta	Dexter				X				X	X		X	Five paper mills (PPNC); Air Brake Co.; hydro-power; dairy fields
II	3296	42:51:45N	078:52:00W	NY	Buffalo Harbor	Buffalo								X		X		Ind.: chemical, steel, petrochemical; landfills
II	3298	42:52:00N	078:52:30W	NY	Buffalo River	Buffalo								X		X		Allied Chemical (manufacturer of HCB); landfills
II	3301	43:20:20N	078:43:00W	NY	Eighteen Mile Creek	Olcott								X			X	Ind.: Harrison Radiator; chem. (HCB); Ag.: orchards and croplands
II	2326	42:13:00N	078:01:00W	NY	Genessee River	Belmont		X							X			Same as 3309. Sampled below Belmont Dam. Superfund site is approximately 10 miles upstream (heavy metals, hydrocarbons)
II	3309	42:13:30N	078:02:00W	NY	Genessee River	Belmont		X							X			Same as 2326

TABLE B-3 (cont.)

EPA Reg	Episode #	Latitude	Longitude	State	Waterbody	Location	NSQ	B	POINT SOURCES PPC	PPNC	WP	Rfny	NPL Site	Other Ind	POTW	NONPOINT Urban	Agri	Additional Site Description (Facilities in the vicinity of the sampling site)
II	3306	44:57:30N	074:49:00W	NY	Grass River	Massena								X				Sampled below ALCOA'S outfall (PCB concern); GM & Reynolds (2 miles below mouth of river)
II	3319	40:40:00N	073:20:00W	NY	Great South Bay	Babylon		X							X		X	Same as 3320
II	3320	40:40:45N	073:19:00W	NY	Great South Bay	Babylon		X							X		X	Same as 3319
II	2709	41:16:30N	073:57:00W	NY	Hudson River	Peekskill							X	X	X			Same as 3409; Ind.: chem.; P&P mill 150 river miles upstream; Superfund site (PCB)
II	3259	43:08:00N	073:36:30W	NY	Hudson River	Fort Miller			X					X				Fort Miller Pulp and Paper (Finch, Pyruyn & Co.)
II	3409	41:20:00N	073:57:30W	NY	Hudson River	Peekskill							X	X	X			Same as 2709; Ind.: chem.; P&P mill 150 river miles upstream; Superfund site (PCB)
II	3321	40:38:40N	073:50:40W	NY	Jamaica Bay	New York								X	X	X		Ind.: chem.; airport; landfill
II	3322	40:37:45N	073:47:00W	NY	Jamaica Bay	New York								X	X	X		Ind.: chem.; airport; landfill
II	3260	43:51:30N	073:22:00W	NY	Lake Champlain	Ticonderoga			X									International Paper Co.
II	2328	43:20:25N	078:43:14W	NY	Lake Ontario	Olcott								X			X	Ag.: apple orchards and croplands
II	2329	43:14:05N	077:32:03W	NY	Lake Ontario	Rochester								X			X	Ind.: chem (Kodak); Site at the mouth of Genesee River
II	3323	40:48:00N	073:45:00W	NY	Little Neck Bay	Long Is. Sound								X	X	X	X	Same as 3324
II	3324	40:47:00N	073:45:00W	NY	Little Neck Bay	Long Is. Sound								X	X	X	X	Same as 3323
II	3325	40:49:00N	073:40:00W	NY	Manhassett Bay	Long Is. Sound								X	X	X	X	Same as 3326
II	3326	40:50:10N	073:40:15W	NY	Manhassett Bay	Long Is. Sound								X	X	X	X	Same as 3325
II	3300	43:15:30N	079:03:45W	NY	Niagara R. Delta	Porter								X	X	X	X	Ind.: chem.; Olin, Dupont, Oxidental (HCB); Ag.: orchards; landfill
II	3297	43:03:00N	078:58:55W	NY	Niagara River	Niagara Falls								X	X	X		Ind.: chem.; Olin, Dupont, Oxidental Chem. (HCB), (companies downstream of site)
II	3299	43:02:00N	078:53:45W	NY	Niagara River	N. Tonawanda								X	X	X		Ind.: chemical
II	3302	43:10:30N	079:03:40W	NY	Niagara River	Lewiston								X	X	X	X	Ind.: chem.; Olin, Dupont, Oxidental (HCB); Ag.: orchards
II	3303	44:12:30N	075:00:00W	NY	Oswegatchie River	Newton Falls			X									Newton Falls Paper Mill (defunct since October 1984)
II	3412	43:28:00N	076:31:00W	NY	Oswego Harbor	Oswego								X				Ind.: Chemical
II	3305	44:58:30N	074:44:00W	NY	Raquette River	Massena				X				X	X			Potsdam Paper and Norfolk Paper (PPNC); ALCOA, GM, Reynolds (upstream of mouth)
II	2322	44:59:00N	073:21:00W	NY	Richelieu River	Rouses Pt.	X								X			
II	3308	45:00:00N	073:21:00W	NY	Richelieu River	Rouses Pt.	X								X			
II	3411	43:11:18N	077:31:30W	NY	Rochester Embay.	Rochester								X				Ind.: chemical
II	3307	44:42:30N	075:28:30W	NY	St. Lawrence River	Ogdensburg								X				Ponderosa Fibers (out of business more than 4 years); Dow chemical in Canada
II	3327	40:38:20N	074:02:15W	NY	Upper Bay	New York								X	X	X		Sampled at 69th Street Pier
II	3432	17:59:40N	066:46:25W	PR	Guayanilla Bay									X	X			
II	3431	18:26:40N	066:06:30W	PR	San Juan Harbor	San Juan						X		X	X			Caribbean Gulf Refining Corp.; landfill
III	2210	38:52:20N	077:02:15W	DC	E. Potomac River	DC								X	X	X	X	
III	3147	38:52:30N	077:02:30W	DC	Potomac River Park	N. of Wilson Br.								X	X	X	X	
III	3099	38:35:00N	075:12:00W	DE	Indian River	Rosedale Beach											X	Estuary
III	3098	39:48:08N	075:39:44W	DE	Red Clay Creek	Ashland							X	X			X	Ind.: metal plating, mining; illegal dump (landfill); Ag.: mushroom farming
III	3097	39:35:40N	075:37:50W	DE	Red Lion Creek	Tybouts Corner							X					Chemical spill (HCB concern); Superfund site (HCB)
III	3149	39:43:58N	075:45:37W	DE	White Clay Creek	Thompson								X				
III	3100	39:15:36N	076:31:30W	MD	Baltimore Harbor	Baltimore								X	X	X		
III	3317	39:28:00N	079:01:00W	MD	Potomac R.N. Br.	Westernport			X						X			Westvaco (indirect); rural

TABLE B-3 (cont.)

EPA Reg	Episode #	Latitude	Longitude	State	Waterbody	Location	NBQ	B	POINT SOURCES PPC	PPNC	WP	Rfny	NPL Site	Other Ind	POTW	NONPOINT Urban	Agri	Additional Site Description (Facilities in the vicinity of the sampling site)
III	2231	39:39:31N	076:10:28W	MD	Susquehanna River	Conowingo								X	X			Same as 3103
III	3103	39:38:00N	076:10:00W	MD	Susquehanna River	Conowingo								X	X			Same as 2231
III	3316	41:25:20N	078:44:10W	PA	Clarion River	Ridgeway			X									Pentech Papers in Johnsonburg; rural; acid mine drainage
III	3161	39:56:30N	075:14:35W	PA	Cobbs Creek	Philadelphia							X	X		X		Old PCP plant (defunct for more than 5 years); landfill
III	3420	39:53:42N	076:49:09W	PA	Codorus Creek	Spring Grove			X									P.H. Gladtfelder in Spring Grove
III	3094	40:02:24N	074:59:20W	PA	Delaware River	Torresdale								X	X	X		
III	3095	39:53:00N	075:11:46W	PA	Delaware River	Schuylkill Jnct.						X		X	X	X		Coastal Eagle Point Oil Co. in NJ; Inorganic chem.
III	3096	39:51:36N	075:18:40W	PA	Delaware River	Eddystone						X		X	X	X	X	Mobil Oil in NJ; Ind.: chem; multiple sources; Ag.: croplands (trucking of vegetables)
III	3318	40:23:20N	078:24:20W	PA	Frankstown Branch	Kladder Station			X									Appleton Paper on the Juniata River (Holter Creek)
III	3419	42:09:25N	080:02:57W	PA	Lake Erie	Erie			X					X	X	X		Hammermill Paper (indirect); railyard; food processing plant
III	3310	40:39:40N	075:14:35W	PA	Lehigh River	Easton								X	X	X		Steel industry
III	3101	40:03:40N	075:28:23W	PA	Little Valley Creek	Paoli								X			X	Paoli Railyard (historic PCB problems)
III	2215	40:17:30N	079:52:33W	PA	Monongahela River	Clairton								X	X	X		Ind.: inorganic chem. and pest.
III	2212	39:58:00N	075:11:20W	PA	Schuylkill River	Philadelphia	X					X	X	X	X	X		Same as 3104; two refineries; Ind.: org. chem. & pest.; P&P mill; Superfund site (PCP)
III	3104	39:58:22N	075:11:33W	PA	Schuylkill River	Philadelphia	X					X	X	X	X	X		Same as 2212; two refineries; Ind.: org. chem. & pest.; P&P mill; Superfund site (PCP)
III	3415	41:23:30N	075:48:00W	PA	Susquehanna N.Br.	Ransom							X					Superfund site (heavy metals)
III	2211	40:03:00N	076:30:00W	PA	Susquehanna River	Columbia			X					X	X			Gladtfelder (bleachkraft) 20 miles upstream on tributary
III	3414	41:18:50N	075:48:45W	PA	Susquehanna River	Pittston							X					Superfund site (heavy metals); acid mine drainage
III	3315	40:21:00N	076:23:00W	PA	Union Canal	Lebanon								X				Pesticide concern
III	2216	41:33:22N	077:41:28W	PA	Young Womens Cr.	Renovo		X										
III	3422	36:33:10N	076:54:57W	VA	Blackwater River	Riverdale			X									Union Camp Corporation in Franklin
III	3421	37:47:15N	080:00:06W	VA	Jackson River	Covington			X									Westvaco Corporation
III	2225	37:35:00N	079:25:00W	VA	James River	Glasgow								X	X		X	Light agriculture; rural
III	2228	37:40:15N	078:05:10W	VA	James River	Cartersville	X		X	X					X		X	Westvaco (PPC); Virginia Fibers and Nekoosa Edwards (PPNC)
III	2227	36:46:13N	077:09:59W	VA	Nottoway River	Sebrell								X	X			Union Camp is 20 miles downstream of sampling site
III	2220	37:46:03N	077:19:57W	VA	Pamunkey River	Hanover	X							X	X			Upstream from the Cheasepeake Corporation
III	3423	37:31:55N	076:48:40W	VA	Pamunkey River	West Point			X									Cheasepeake Corporation (upstream of site)
III	3424	37:32:01N	076:50:38W	VA	Pamunkey River	West Point			X									Cheasepeake Corporation (downstream of site)
III	3193	37:01:45N	078:55:40W	VA	Roanoke River	Brookneal											X	Rural
III	3258	36:49:48N	076:17:30W	VA	S.Br.Elizabeth R.	Norfolk								X		X		
III	2500	38:27:00N	081:49:00W	WV	Kanawha River	Nitro								X	X	X	X	Ind.: pesticides, trichlorophenol, and organic chemicals (Dow and Monsanto); rural
III	3314	38:31:30N	081:54:37W	WV	Kanawha River	Winfield								X	X	X	X	Ind.: pesticides (Monsanto); rural
III	3311	39:40:00N	080:51:52W	WV	Ohio River	Nw. Martinsvle								X	X	X		
III	3312	40:09:10N	080:42:25W	WV	Ohio River	Wheeling						X		X	X	X		Quaker State Oil Refining; steel industries; urban runoff
III	3313	39:31:10N	077:52:30W	WV	Opequon Creek	Bedington								X		X	X	Ag.: orchards; rural
IV	2304	31:32:48N	089:30:45W	AL	Alabama River	Claiborne			X						X			Alabama River Pulp Company
IV	2309	32:24:41N	086:24:30W	AL	Alabama River	Montgomery	X							X	X	X	X	Ind.: organic chem. & pest.; Fence-post company; Ag.: croplands

TABLE B-3 (cont.)

EPA Reg	Episode #	Latitude	Longitude	State	Waterbody	Location	NSO	B	POINT SOURCES PPC	PPNC	WP	Rfny	NPL Site	Other Ind	POTW	NONPOINT Urban	Agri	Additional Site Description (Facilities in the vicinity of the sampling site)
IV	3360	32:07:55N	085:03:43W	AL	Chattahoochee	Cottonton				X								Alabama Kraft in AL (goes into GA water but on AL side)
IV	3170	31:29:40N	085:22:06W	AL	Choctawhatchee R.	Henry:Co.											X	
IV	2302	31:04:01N	087:02:40W	AL	Conecuh River	E. Brewton			X									Container Corporation
IV	3172	31:25:07N	088:26:45W	AL	Coosa River	AL/GA State L								X				
IV	3328	33:17:24N	086:21:42W	AL	Coosa River	Coosa Pines			X								X	Kimberly Clark; wooded area; Ag.: croplands and grazing fields
IV	3171	31:01:02N	085:13:24W	AL	Cowarts Creek	Houston:Co.											X	
IV	3169	33:50:15N	086:31:46W	AL	Inland Lake	Blount Co.		X										
IV	3168	30:52:30N	087:57:48W	AL	Mobile River	near Cold Cr.								X	X	X	X	Several chem. & pest. plants; Hydro-power
IV	3331	30:30:00N	087:20:15W	FL	11 Mile Creek	Cantonment			X								X	Champion International Corp. in Cantonment; rural; swampland; Ag.: croplands
IV	3332	30:38:52N	081:29:28W	FL	Amelia River	Fernandina Bch			X									ITT Rayonier, Inc.
IV	2151	30:23:04N	085:33:24W	FL	Econfina Creek	Panama City	X											
IV	3329	30:01:00N	083:46:00W	FL	Fenholloway River	Perry			X								X	Buckeye Cellulose; rural; swampland; Ag.: grazing fields
IV	3334	29:50:31N	085:17:59W	FL	Gulf Co. Canal	St. Joe			X						X	X		St. Joe Paper *(indirect)*
IV	3174	27:12:18N	080:47:28W	FL	Lake Okeechobee	Okeechobee								X				
IV	2148	27:38:54N	080:24:10W	FL	Main Canal	Vero:Beach	X									X		Collected below salinity structure
IV	3333	30:07:38N	085:39:25W	FL	St. Andrew Bay	Panama:City			X						X			Southwest Forest Ind., Inc. (indirect) (Stone Container Corp.)
IV	2142	29:38:48N	081:37:32W	FL	St. Johns River	Palatka			X						X		X	Georgia Pacific Corporation
IV	3173	30:00:00N	081:40:00W	FL	St. Johns River	Green Cv. Spr					X					X		Wood treatment plant
IV	2152	30:21:30N	082:04:54W	FL	St. Mary's River	Macclenny	X								X			
IV	3330	30:28:00N	083:15:00W	FL	Withlacoochee River	Blue Spring				X								
IV	3337	31:39:10N	081:49:00W	GA	Altamaha River	Jesup			X								X	ITT Rayonier, Inc.: swampland; Ag.: croplands
IV	3177	34:26:00N	083:40:30W	GA	Chattahoochee R.	Gainesville		X						X	X		X	Town of Schoville: heavy metals, wood products; Ag.: chicken farms and orchards
IV	3375	33:39:24N	084:40:25W	GA	Chattahoochee R.	Austell				X					X			Box Board on Hwy 92
IV	3376	33:28:37N	084:54:04W	GA	Chattahoochee R.	Whitesburg				X								
IV	3377	33:16:45N	085:06:00W	GA	Chattahoochee R.	Franklin				X								
IV	3378	31:08:00N	085:04:00W	GA	Chattahoochee R.	Donaldsonville				X					X			Great Southern Pacific Paper Company
IV	3178	34:55:00N	083:10:00W	GA	Chattooga River	Clayton		X										
IV	3179	34:27:00N	083:57:30W	GA	Chestatee River	above:L.:Lanier		X							X		X	Mining: gold, sand, and gravel; Ag.: orchards, dairy farms & chicken houses
IV	2294	32:01:20N	083:56:30W	GA	Flint River	L. Blackshear			X									Procter & Gamble (Buckeye Cellulose)
IV	3176	30:52:00N	084:36:00W	GA	Lake Seminole					X				X			X	Great Southern Pacific Paper Company
IV	3336	30:43:37N	081:32:00W	GA	North River (mouth)	St. Marys			X									Gilman Paper Company
IV	2290	33:22:25N	081:56:35W	GA	Savannah River	Augusta			X					X		X		Federal Paperboard in Pond, Georgia Pacific; Ind.: pest.
IV	3175	32:10:30N	081:08:50W	GA	Savannah River	Savannah			X			X		X	X	X		Fort Howard Paper (PPC), Union Camp and Stone Container Corp. (PPNC); Nuclear power
IV	3338	33:22:00N	081:56:00W	GA	Savannah River	Augusta				X				X	X	X		Ponderosa Fibers (indirect)
IV	3180	31:18:00N	084:45:00W	GA	Spring Creek	Early County											X	
IV	3335	31:08:15N	081:31:35W	GA	Turtle R. (mouth)	S. Brunswick R.			X									Brunswick Paper & Pulp on the Turtle R.; marshland; wooded area; Ag.: grazing fields

TABLE B-3 (cont.)

EPA Reg	Episode #	Latitude	Longitude	State	Waterbody	Location	NSQ	B	POINT SOURCES PPC	PPNC	WP	Rfny	NPL Site	Other Ind	POTW	NONPOINT Urban	Agri	Additional Site Description (Facilities in the vicinity of the sampling site)
IV	3183	38:24:22N	082:35:52W	KY	Big Sandy R.	Cattletsburg						X		X	X			Ashland Oil Inc.; Ind.: chem,. iron and steel; coal mining, timber
IV	3339	36:55:41N	089:05:52W	KY	Mississippi River	Wickliffe			X								X	Westvaco Corporation; Ag.: croplands
IV	3182	36:55:27N	086:52:47W	KY	Mud River	Russellville								X	X		X	Ind.: metal plating; rendering plant; Ag.: croplands
IV	2056	38:00:30N	085:56:30W	KY	Ohio River	West Point							X	X	X	X	X	Same as 3181; Ind.: chem. & pest., refinery; Ag.: crops; Superfund site (PCB's; solvents; dioxins & furans)
IV	2341	38:46:29N	084:57:52W	KY	Ohio River	Markland			X						X	X	X	Williamette Industries; multiple sources; rural
IV	3181	38:00:30N	085:56:30W	KY	Ohio River	Westpoint							X	X	X	X	X	Same as 2056; Ind.: chem. & pest., refinery; Ag.: crops; Superfund site (PCB's; solvents; dioxins & furans)
IV	3446	38:24:22N	082:35:52W	KY	Big Sandy R.	Catlettsburg						X	X	X				Ashland Oil refinery; coal mining
IV	3185	30:25:00N	089:04:00W	MS	Bernard Bayou	Gulfport							X	X		X		Ind.: chem.; wood treatment; (gas recovery) refinery; rural; Superfund site (solvents)
IV	2126	32:20:41N	090:51:48W	MS	Big Black River	Bovina	X								X		X	Ag.: soybeans and cotton
IV	3445	30:19:32N	088:31:00W	MS	Chevron Effluent	Pascagoula			X			X		X		X		Chevron refinery; International Paper; shipyard; fertilizer company
IV	3341	30:25:20N	088:31:10W	MS	Escatawpa River	Moss Point			X									International Paper Company
IV	3340	31:13:28N	089:02:50W	MS	Leaf River	New Augusta			X									Leaf River Forest Products
IV	3435	31:25:00N	091:30:00W	MS	Mississippi River	Natchez			X									International Paper Company
IV	2133	32:29:14N	090:49:02W	MS	Yazoo River	Redwood				X							X	Same as 3184; Ind.: paper; fertilizer plant
IV	3184	32:28:00N	090:49:00W	MS	Yazoo River	Redwood				X							X	Same as 2133; Ind.: paper; fertilizer plant
IV	3344	34:23:50N	078:10:30W	NC	Cape Fear River	Riegelwood			X						X		X	Federal Paper Board; rural; swampland; wooded area; Ag.: croplands
IV	2139	35:40:02N	093:04:23W	NC	Cattaloochee Creek	Cattaloochee		X										Champion Paper (PPC-indirect source); wooded area
IV	3165	34:43:50N	079:39:24W	NC	Deep River	Ramseur Dam								X		X	X	
IV	3345	35:X5:06N	082:40:45W	NC	French Broad River	Pisgah Forest			X						X		X	Ecusta (sulfite mill using chlorine); rural; wooded area; Ag.: croplands
IV	3164	35:56:45N	079:19:20W	NC	Haw River	Saxapahaw								X	X		X	Ind.: textiles; rural; Ag.: croplands
IV	3342	34:36:30N	078:59:00W	NC	Lumber River	Lumberton			X									Alpha Cellulose (sulfite mill using chlorine)
IV	3167	35:50:35N	078:50:20W	NC	Medlins Pond	Morrisville					X							Koppers Company (wood treat.); Superfund site X wood treat. (PCP)
IV	3166	35:08:00N	083:38:15W	NC	Nanthalia River	Macon Co.		X										
IV	2138	35:15:29N	077:35:09W	NC	Neuse River	Kinston			X									Weyerhaeuser Company
IV	3395	35:11:56N	077:06:45W	NC	Neuse River	New Bern			X									Weyerhaeuser Company
IV	3343	35:32:05N	082:54:40W	NC	Pigeon River	Clyde			X						X		X	Champion International in Canton; rural; wooded area; Ag.: croplands
IV	3346	35:51:55N	076:45:40W	NC	Roanoke River	Plymouth			X								X	Weyerhaeuser Company on Welch Creek; rural; wooded area; Ag.: croplands
IV	3385	35:59:25N	081:31:32W	NC	Yadkin River	Patterson				X				X				Sealed Air Corporation (makes absorbant paper for meat trays)
IV	3347	34:42:30N	080:51:50W	SC	Catawba River	Catawba			X								X	Bowater Carolina; rural; wooded area; Ag.: croplands
IV	3186	32:45:50N	079:53:10W	SC	Charleston Harbor	Charleston			X	X				X		X		Westvaco Paper and Pulp; Amoco chemical plant
IV	3348	33:21:24N	079:18:34W	SC	Sampit River	Georgetown			X									International Paper Company; rural; wooded area; Ag.: croplands
IV	3187	32:29:46N	080:31:33W	SC	St. Helena Sound			X									X	
IV	3349	33:51:08N	080:37:32W	SC	Wateree River	Eastover			X								X	Union Camp Corporation; rural; wooded area; Ag.: croplands
IV	2301	35:29:45N	087:49:58W	TN	Buffalo River	Flatwoods		X									X	
IV	3189	35:55:37N	084:58:18W	TN	Ft. Loudon Res.									X		X		Ind.: aluminum
IV	2298	35:X6:31N	088:58:36W	TN	Hatchie River	Bolivar	X											
IV	3350	35:19:08N	084:48:X3W	TN	Hiwasee River	Calhoun			X								X	Bowater South Paper Company; rural; wooded area; Ag.; croplands
IV	2297	36:00:56N	083:49:54W	TN	Holston River	Knoxville			X					X	X			Industry: metals

TABLE B-3 (Cont.)

EPA Reg	Episode #	Latitude	Longitude	State	Waterbody	Location	NSO	B	POINT SOURCES PPC	PPNC	WP	Rfny	NPL Site	Other Ind	POTW	NONPOINT Urban	Agri	Additional Site Description (Facilities in the vicinity of the sampling site)
IV	3403	36:33:02N	082:35:00W	TN	Holston R., S. Fork	Kingsport			X									Mead Corporation (Chlorine Dioxide process)
IV	3444	35:05:15N	090:05:30W	TN	Mississippi River	Nonconnah Cr.						X		X	X	X		Mapco, Exxon, Union refineries; cement factory; soybean processing
IV	3188	35:03:54N	085:20:28W	TN	Nickajack Reservoir									X	X	X		Ind., chem.; coke; rendering; railyards; landfill
IV	3404	36:01:20N	083:12:00W	TN	Pigeon River	Newport			X								X	Champion International in North Carolina
IV	3351	35:56:24N	083:10:52W	TN	Pigeon River	Newport			X								X	Champion International in North Carolina
IV	3190	35:50:15N	084:04:13W	TN	Tennessee River	Knoxville								X		X		
IV	3401	35:03:54N	086:16:39W	TN	Tennessee River	Hardin Co.				X								Tennessee River Pulp and Paper in Counce, TN
V	2379	37:37:31N	089:25:42W	IL	Big Muddy River	Grand Tower		X							X		X	
V	2383	41:35:47N	088:04:07W	IL	Des Plaines River	Lockport						X		X	X	X		Ind.; organic chem. & pest.; Refineries (downstream); steel; incinerator
V	3113	41:52:13N	088:18:31W	IL	Fox River	Geneva								X	X	X	X	
V	2380	41:19:40N	088:45:10W	IL	Illinois River	Marseilles						X		X	X	X	X	Ind.; chem. & pest.; Union oil, Texaco, Mobil; Ammunition plant
V	3114	39:43:00N	091:31:04W	IL	Mississippi River	Quincy				X					X		X	Celotex Corporation (deinking)
V	3115	38:32:30N	090:15:00W	IL	Monsanto Effluent	East St. Louis								X	X			Six chemical/pharmaceutical plants (paradichlorobenzene)
V	3117	42:21:10N	087:49:40W	IL	Lake Michigan	Waukegan							X	X		X		Open lake sample; Superfund site (PCB) at Waukegan Harbor
V	2059	41:37:10N	087:29:15W	IN	Indiana Harbor Can.	East Chicago						X	X	X	X	X		Same as 3356; Amoco Oil; Ind.: primarily steel; wastewater; Superfund site (PCB)
V	3356	41:37:10N	087:29:15W	IN	Indiana Harbor Can.	East Chicago						X	X	X	X	X		Same as 2059; Amoco Oil; Ind.: primarily steel; wastewater; Superfund site (PCB)
V	2060	38:07:50N	087:56:20W	IN	Wabash River	New Harmony								X	X		X	Ind.: chem. & pest.; coal mining; (site at the mouth of the Wabash R.)
V	2057	38:30:45N	087:17:30W	IN	White River	Petersburg								X	X	X	X	Hydro-power; coal mining
V	3119	42:33:00N	085:54:00W	MI	Allegan Lake	Allegan				X			X					Historical PCB contamination from paper deinking; Superfund site (PCB)
V	3118	45:50:00N	087:05:00W	MI	Escanaba River	Escanaba			X									Mead Corporation (historical PCB contamination)
V	1994	43:03:00N	083:48:45W	MI	Flint River	Flushing								X	X	X		Automobile manufacturing (heavy metals and oils)
V	3120	42:39:00N	082:10:00W	MI	Kalamazoo River	Saugatuck								X				Historical PCB contamination site is downstream of Kalamazoo
V	3122	45:47:00N	087:59:00W	MI	Menominee River	Quinnesec			X									Champion International Corporation
V	1998	43:15:05N	086:14:55W	MI	Muskegon Lake	Muskegon			X				X	X	X		X	Scott Paper (indirect); Power & chem. plant; Ag.: orch.; same as 3148; Superfund site (PCB)
V	3148	43:15:05N	086:14:55W	MI	Muskegon Lake	Muskegon			X				X	X	X		X	Scott Paper (indirect); Power & chem. plant; Ag.: orch.; same as 1998; Superfund site (PCB)
V	2432	43:19:57N	086:08:42W	MI	Muskegon River	Bridgton	X								X			Far upstream of bleachkraft (Scott Paper Company)
V	2410	42:16:45N	083:07:20W	MI	Rouge River	River Rouge								X	X	X		Ind.: heavy steel; chem.; automobile (PCB's in effluent)
V	2431	46:29:45N	084:22:25W	MI	St Marys River	Sault St. Marie	X			X				X	X			St Mary's Paper; Algoma Steel; dredging
V	2430	46:34:30N	085:15:10W	MI	Tahquamenon R.	Paradise	X											
V	2435	47:55:23N	089:08:42W	MI	Washington Creek	Isle Royale		X										Canadian Bleach Kraft P&P mill about 30 miles upwind in Thunder Bay, Ont.
V	2387	44:16:08N	093:21:05W	MN	Cannon Lake	Fairbault		X							X		X	
V	2437	44:41:33N	093:38:35W	MN	Minnesota River	Jordan	X								X		X	
V	3112	45:58:17N	094:22:05W	MN	Mississippi River	Little Falls				X								Hennepin Paper
V	3125	44:33:34N	092:25:47W	MN	Mississippi River	Red Wing						X		X	X	X	X	Ashland Oil/Koch Refining; urban runoff; historical PCB contamination
V	2385	48:36:29N	093:24:13W	MN	Rainy River	Intern'l Falls			X						X	X		Boise Cascade on both sides of the river
V	3001	48:35:29N	092:53:34W	MN	Rainy River	Intern'l Falls		X							X			Site is above the dam. Boise Cascade outfall is below dam.
V	2416	41:29:50N	081:42:10W	OH	Cuyahoga River	Cleveland								X	X	X		Ind.: chem.; oil.
V	2394	39:33:44N	084:18:19W	OH	Great Miami River	Franklin				X				X	X			Appleton Papers and Miami Papers (deinking); Ind.: metals and others
V	2439	39:15:53N	084:40:30W	OH	Great Miami River	Nw. Baltimore	X			X			X		X		X	Sorg P&P mill (deinking); Proctor and Gamble; Ag. runoff; Superfund site

TABLE B-3 (cont.)

EPA Reg	Episode #	Latitude	Longitude	State	Waterbody	Location	NSQ	B	POINT SOURCES: PPC	PPNC	WP	Rfnry	NPL Site	Other Ind	POTW	NONPOINT: Urban	Agri	Additional Site Description (Facilities in the vicinity of the sampling site)
V	2618	39:24:40N	084:33:14W	OH	Hamilton Canal	Hamilton				X			X				X	Canal off G. Miami R.; Appleton Paper; Aviation plant; steel; hydro-power; Superfund site
V	3132	39:17:36N	082:55:48W	OH	Scioto River	Chillicothe			X				X	X				Mead Corporation on Paint Creek; Ind.: inorg. chem. & pest.; Superfund site
V	3135	44:49:39N	091:30:38W	WI	Chippewa River	Eau Claire				X								Pope and Talbot (deinking)
V	3136	45:24:05N	091:13:18W	WI	Flambeau River	E.lLadysmith				X								Pope and Talbot (deinking)
V	3137	45:55:00N	090:26:41W	WI	Flambeau River	Park Falls				X					X		X	Flambeau Paper; Ag.: croplands and grazing fields
V	2429	44:27:39N	088:03:30W	WI	Fox River	DePere Dam			X					X	X	X		Fort Howard, James River, Green Bay Pkg., Nicolet Paper, Champion
V	3138	44:16:10N	088:22:18W	WI	Fox River	Appleton				X					X			Kerwin Paper Company (deinking), Gladtfelder, WI Tissue, Kimberly Clark
V	3140	44:13:24N	088:27:34W	WI	Fox River	Lk ButteD.Morts				X								Gladtfelder, WI Tissue Mills, Kerwin Paper (historical PCB contamination)
V	3143	44:00:43N	088:31:00W	WI	Fox River	Oshkosh				X								Ponderosa (deinking)
V	3144	43:32:17N	089:27:36W	WI	Fox River, upper	Portage								X	X		X	Historical PCB contamination
V	2422	46:36:21N	090:52:30W	WI	Lake Superior	Ashland			X									James River-Dixie Northern (deinking); rural
V	3134	44:01:58N	088:08:45W	WI	ManitowocRiver	Chilton								X	X		X	Incinerator; H2O softener plant; Ag.: croplands
V	3141	43:03:26N	087:53:54W	WI	Milwaukee River	Milwaukee								X	X	X		Ind.: metals (historical PCB contamination); 300-400 Industrial discharges
V	2427	45:03:16N	087:44:50W	WI	Peshtigo R. Harbor	Peshtigo			X						X			Badger Paper Mills, (indirect)
V	3142	43:43:51N	087:47:04W	WI	Sheboygan River	Kohler							X	X				Superfund site (historical PCB contamination)
V	3110	44:58:00N	092:46:00W	WI	St Croix River	Hudson												Anderson Windows; wood treatment plant
V	2397	45:37:27N	089:25:14W	WI	Wisc. R/Boom Lake	Rhinelander		X										Upstream of paper mills
V	2608	44:16:00N	089:53:00W	WI	Wisconsin River	U. Pentenwell Fl			X					X	X		X	Nekoosa, Fort Edwards, Consolidated Kraft; Vulcan mat. (rubber & plastic); same as 3106
V	3106	44:16:00N	089:53:00W	WI	Wisconsin River	U. Pentenwell Fl			X					X	X		X	Nekoosa, Fort Edwards, Consolidated Kraft; Vulcan mat. (rubber & plastic); same as 2608
V	3107	45:01:20N	089:39:09W	WI	Wisconsin River	Brokaw			X									Wausau Paper (sulfite mill)
V	3108	45:10:31N	089:40:00W	WI	Wisconsin River	Merrill				X								Ward Paper (deinking)
V	3109	44:56:57N	089:37:45W	WI	Wisconsin River	Wausau								X				Wood treatment plant site is between paper mills.
V	3145	45:26:17N	089:43:56W	WI	Wisconsin River	Mohawskin				X								Rhinelander Paper Company
V	3146	44:52:57N	089:38:17W	WI	Wisconsin River	Rothschild			X								X	Weyerhaeuser, half dozen small mills; Ag.: croplands
VI	2023	35:20:56N	094:17:54W	AR	Arkansas River	Van Buren	X							X	X			
VI	3060	34:26:41N	092:06:38W	AR	Arkansas River	Little Rock								X	X		X	
VI	3062	34:10:09N	091:43:56W	AR	Arkansas River	Pine Bluff			X						X		X	International Paper Company; wooded area; Ag.: croplands
VI	3061	33:10:18N	092:39:00W	AR	Bayou DeLoutre	El Dorado						X		X		X		Lion Oil Company
VI	3078	34:50:39N	092:07:20W	AR	Bayou Meto	Jacksonville							X					Superfund site (dioxins); rural; wooded area
VI	3443	34:09:00N	091:31:00W	AR	Bayou Meto	Reydell								X	X		X	Downstream about 30 miles of the Jacksonville site (3078)
VI	2015	33:33:27N	091:14:15W	AR	Mississippi River	Arkansas City	X		X								X	Potlatch Corporation; Ag.: croplands
VI	2018	35:59:43N	092:12:45W	AR	N. Sylamore Creek	Fifty Six		X										Same as 3073
VI	3073	35:56:33N	092:07:05W	AR	N. Sylamore Creek	Fifty Six		X										Same as 2018
VI	2016	33:33:07N	094:02:28W	AR	Red River	Index	X		X						X		X	Nekoosa Edwards Paper Company
VI	3452	33:34:15N	094:06:00W	AR	Red River	Index			X					X			X	Nekoosa Paper; lime and gravel mines; Ag.: crop and grazing lands
VI	3077	33:57:17N	094:21:49W	AR	Rolling Fork River	De Queen											X	Wood treatment plant on Bear Creek
VI	2017	33:14:32N	093:59:58W	AR	Sulphur River	Texarkana	X		X									International Paper Company in Texas
VI	3088	30:53:00N	093:25:00W	LA	Anacoco Bayou	Deridder			X								X	Boise Southern Co. (Boise Cascade); rural; Ag.: cropland
VI	3083	32:40:00N	091:43:00W	LA	Bayou Bonne Idee	Oak Ridge											X	HCB use in agriculture

TABLE B-3 (cont.)

EPA Reg	Episode #	Latitude	Longitude	State	Waterbody	Location	NSQ	B	PPC	PPNC	WP	R/M	NPL Site	Other Ind	POTW	Urban	Agri	Additional Site Description (Facilities in the vicinity of the sampling site)
									POINT SOURCES							NONPOINT		
VI	3086	30:12:00N	093:17:00W	LA	Bayou D'Inde	Sulfur						X					X	Citgo Petroleum Corporation; Ind.: chem.
VI	3442	30:02:36N	090:22:27W	LA	Bayou Labarche	Norco						X		X				Shell and Norco Refineries; Shell chemical plant
VI	3353	32:31:00N	091:54:00W	LA	Bayou LaFourche	Bastrop			X						X		X	International Paper Company; rural
VI	3063	30:06:00N	093:20:00W	LA	Calcasieu River	Moss Lake						X		X	X	X		Conoco, Inc.; Ind.: chem.
VI	3092	32:05:00N	092:47:00W	LA	Dugdemona River	Hodge				X							X	
VI	3352	32:33:00N	091:51:00W	LA	Lakedrwin	Start											X	Above Bayou LaFourche. This dammed water feeds Wham Brake.
VI	3064	30:02:00N	090:02:00W	LA	Lake Pontchartrian	New Orleans								X	X	X		
VI	3082	32:48:00N	091:11:00W	LA	Lake Providence												X	HCB use in agriculture
VI	2532	30:45:30N	091:23:45W	LA	Mississippi River	St. Francisville			X									Crown Zellerbach
VI	3065	30:27:00N	091:13:00W	LA	Mississippi River	Baton Rouge			X			X		X		X		Georgia Pacific Corporation, Crown Zellerbach; two refineries
VI	3066	30:06:00N	091:01:00W	LA	Mississippi River	Union								X			X	Ind.: multiple sources; Ag.: cropland and grazing
VI	3418	30:39:00N	091:17:00W	LA	Mississippi River	Zachary			X									Georgia Pacific and James Madison Paper; rural; wooded area
VI	3416	33:00:00N	092:04:00W	LA	Ouachita River	Sterlington			X									Georgia Pacific and International Paper; rural; wooded area
VI	3080	32:27:00N	092:07:00W	LA	Ouachita River	Monroe			X						X	X	X	Georgia Pacific in Arkansas; Ag.: crop and grazing lands
VI	2544	30:30:23N	090:21:42W	LA	Tangipahoe River	Robert	X								X			
VI	3087	32:35:00N	091:56:00W	LA	Wham Brake	Swartz			X									Same as 3425; International Paper Co. (discharges to B. LaFourche)
VI	3425	32:33:00N	091:55:00W	LA	Wham Brake	Swartz			X									Same as 3087; International Paper Co. (discharges to B. LaFourche)
VI	3074	35:46:38N	105:39:27W	NM	Rio Mora	Terrero		X										
VI	3105	35:43:42N	098:31:35W	OK	Fort Cobb Reservoir	Fort Cobb											X	Ag.: croplands; golf course near the site
VI	3090	36:04:00N	095:16:00W	OK	Fort Gibson Res.	Pyrer Creek				X								Robell Tissue Mills
VI	3079	36:52:00N	096:56:00W	OK	Kaw Reservoir									X				Vulcan Plant in Wichita, Kansas (chemical processing plant)
VI	2027	34:38:18N	094:36:45W	OK	Kiamichi River	Big Cedar		X									X	Heavily wooded area; Ag.: cattle
VI	3076	33:57:00N	094:35:00W	OK	Little River	Goodwater					X							Wood treatment: Thompson Lumber, Hoffman Preserver, Nixon Bros. Preserver
VI	3091	33:56:00N	095:07:00W	OK	Red River					X								Weyerhaeuser Company
VI	2026	34:14:03N	096:58:32W	OK	Washita River	Durwood	X					X			X			Kerr McGee Refining Corporation, Total Petroleum, Inc.
VI	3089	35:41:00N	095:14:00W	OK	Webbers Falls	Muskogee				X					X			Fort Howard Paper Company
VI	3084	26:11:42N	097:36:06W	TX	Arroyo Colorado	Harlingen											X	HCB use
VI	3085	28:58:59N	095:23:41W	TX	Brazos River	Freeport								X				At Dow Chemical outfall
VI	3068	29:40:48N	094:58:50W	TX	Houston Ship Chnl	Morgan Point			X			X		X	X	X		Champion International and Simpson Paper; four refineries; Ag.: croplands
VI	3069	27:51:30N	097:30:20W	TX	Inner Harbor	Corpus Christi						X		X	X	X		Four refineries
VI	3081	31:25:58N	094:33:56W	TX	Lake Sam Rayburn	Lufkin			X						X			Champion International Corporation on the Angelina River
VI	2280	28:57:35N	096:41:13W	TX	Lavaca River	Edna	X										X	
VI	3075	28:09:00N	096:52:00W	TX	Mesquite Bay			X										
VI	3093	31:08:00N	094:48:39W	TX	Neches River	Diboll				X					X			Temple-Eastex, Inc. in Diboll and Borden Chemical (resin)
VI	3070	29:59:30N	093:54:00W	TX	Neches River (tidal)	Port Arthur			X			X		X				Temple-Eastex, Inc. in Silsbee, TX; two refineries; Ind.: chem. & pest.
VI	3072	31:05:00N	105:36:00W	TX	Rio Grande River	El Paso						X		X		X		Chevron USA, Inc., El Paso Refining Company
VI	3071	29:14:15N	098:21:43W	TX	San Antonio River	Elmendorf						X		X	X	X	X	Howell Hydrocarbons
VI	2283	30:55:25N	098:02:12W	TX	So. Fork Rocky Cr.	Briggs		X										Background site
VII	3035	42:03:54N	091:47:48W	IA	Cedar River	Palo								X		X	X	About 50 miles downstream of Waterloo
VII	3037	41:40:57N	093:40:08W	IA	Des Moines River	Des Moines		X										Upstream about 10 miles from a POTW
VII	3038	41:33:02N	093:31:29W	IA	Des Moines River	Des Moines								X	X	X		Below POTW (pretreatment plant)
VII	3034	41:34:53N	090:23:23W	IA	Mississippi River	LeClaire								X		X	X	Upstream of lock and dam at Davenport (above dam)

TABLE B-3 (cont.)

EPA Reg	Episode #	Latitude	Longitude	State	Waterbody	Location	NBQ	B	POINT SOURCES PPC	PPNC	WP	Rfny	NPL Site	Other Ind	POTW	NONPOINT Urban	Agri	Additional Sites Description (Facilities in the vicinity of the sampling site)
VII	2191	41:15:32N	095:55:20W	IA	Missouri River	Council Bluffs	X							X	X	X		Ind.: chem. and pest.; metals; hydro-power; same as 3042-opposite sides of river
VII	2190	40:36:07N	095:38:44W	IA	Nishnabotna River	Hamburg	X								X		X	Same as 3036
VII	3036	40:36:07N	095:38:44W	IA	Nishnabotna River	Hamburg	X								X		X	Same as 2190
VII	2194	37:32:34N	097:16:29W	KS	Arkansas River	Derby								X	X	X		Same as 3039. Below Wichita
VII	3039	37:32:35N	097:16:29W	KS	Arkansas River	Derby								X	X	X		Same as 2194. Below Wichita
VII	2201	36:02:30N	090:07:30W	MO	Little River Ditch 81	Hornersville								X	X		X	Same as 3040. Rice growing region
VII	3040	36:02:30N	090:07:30W	MO	Little River Ditch 81	Hornersville								X	X		X	Same as 2201. Rice growing region; heavy pesticide use
VII	3047	39:42:36N	091:21:06W	MO	Mississippi River	Hannibal								X	X	X	X	Fish collected near downtown area.
VII	3048	38:52:33N	090:10:26W	MO	Mississippi River	West Alton								X	X	X		Ind.: chem.; heavy metals; heavy shipping traffic
VII	3049	37:17:46N	089:30:56W	MO	Mississippi River	Cape Giradeau								X	X	X	X	Collected at POTW outfall. Proctor & Gamble paper products, Ag croplands
VII	3045	39:07:52N	094:27:58W	MO	Missouri River	Kansas City								X		X		
VII	2199	39:11:14N	093:53:45W	MO	Missouri River	Lexington								X	X	X	X	Same as 3046
VII	3044	39:44:32N	094:51:36W	MO	Missouri River	St Joseph								X				
VII	3046	39:11:14N	093:53:45W	MO	Missouri River	Lexington								X	X	X	X	Same as 2199
VII	3050	37:59:15N	093:48:45W	MO	Osage River	Roscoe	X										X	Ag.: croplands
VII	3042	41:15:32N	095:55:20W	NE	Missouri River	Omaha	X							X	X	X		Ind.: chem. and pest.; metals; hydro power; same as 2191 - opposite sides of river
VII	3043	41:08:18N	095:52:40W	NE	Missouri River	Bellevue								X		X		
VII	3041	41:45:42N	103:25:02W	NE	North Platte River	Mcgrew	X								X		X	
VII	2205	40:59:48N	096:01:18W	NE	Platte River	Louisville	X								X		X	
VIII	3197	38:33:00N	106:01:00W	CO	Arkansas River	Salida												Defunct wood treatment plant
VIII	3198	39:48:10N	104:57:30W	CO	South Platte River	Denver								X	X	X		
VIII	3200	40:10:30N	104:59:00W	CO	St. Vrian River	Longmont		X										
VIII	3236	46:10:00N	112:46:26W	MT	Clark Fork River	Warm Springs								X				
VIII	3237	47:01:05N	114:21:20W	MT	Clark Fork River	Huson			X									Stone Container Corporation
VIII	3235	45:45:35N	111:05:04W	MT	East Gallatin River	Bozeman								X				
VIII	3234	47:56:14N	114:11:04W	MT	Goose Bay	Lakeside								X				
VIII	2122	45:47:48N	108:28:12W	MT	Yellowstone River	Billings	X								X			
VIII	2105	47:35:25N	103:15:05W	ND	Little Missouri R.	Watford City	X											
VIII	2100	49:00:00N	097:13:45W	ND	Red River	Pembina								X	X		X	Sugar beet processing plant; croplands; Same as 3111
VIII	3111	49:00:00N	097:13:45W	ND	Red River	Pembina								X	X		X	Sugar beet processing plant; croplands; Same as 2100
VIII	2109	42:49:42N	096:33:45W	SD	Big Sioux River	Akron								X	X	X	X	Same as 3199
VIII	3199	42:49:45N	096:33:15W	SD	Big Sioux River	Akron	X							X	X	X	X	Same as 2109
VIII	2110	44:00:49N	103:49:48W	SD	Castle Creek	Hill City		X										
VIII	3195	40:45:10N	111:55:15W	UT	Jordan River	Salt Lake City							X	X		X	X	Ind.: pesticides; Superfund site (chlorobenzenes)
VIII	3196	41:20:40N	105:35:45W	WY	Laramie River	Laramie												Railroad tie treating plant (defunct)
VIII	2098	42:34:27N	106:41:31W	WY	North Platte River	Alcova	X											
IX	3266	33:05:00N	113:02:00W	AZ	Gila River	Gila Bend								X	X	X	X	Cotton growing region (Near Phoenix)
IX	3282	33:12:00N	115:37:00W	CA	Alamo River	Calipatria											X	HCB use in agriculture
IX	3288	36:41:00N	121:44:00W	CA	Blanco Drain	Salinas								X			X	Multiple sources
IX	3285	33:46:00N	118:08:00W	CA	Colorado Lagoon	Long Beach								X		X		Multiple sources

TABLE B-3 (cont.)

EPA Reg	Episode #	Latitude	Longitude	State	Waterbody	Location	NSQ	B	POINT SOURCES PPC	PPNC	WP	Rfny	NPL Site	Other Ind	POTW	NONPOINT Urban	Agri	Additional Site Description (Facilities in the vicinity of the sampling site)
IX	3273	41:45:00N	124:11:00W	CA	Elk Creek	Crescent City					X							McNamara & Peepe (historical PCP site)
IX	3286	33:47:15N	118:17:33W	CA	Harbor Park Lake	Harbor City								X		X		Multiple sources
IX	3271	40:34:00N	123:11:00W	CA	Hayfork Creek	Hayfork					X							Sierra Pacific (historical PCP site)
IX	3272	37:55:00N	122:21:00W	CA	Lauritzen Canal	Richmond							X					United Heckathorn: pesticide packaging plant in 60's (PCB's, DDT, Pb)
IX	3275	40:54:00N	124:00:00W	CA	Mad River	Arcata								X				Mollala-Arcata
IX	3276	40:52:00N	124:00:00W	CA	Mad River Slough	Arcata								X				Sierra Pacific
IX	3289	36:48:00N	121:46:00W	CA	Moss Landing Drn.	Moss Landing								X				Multiple sources
IX	3451	34:01:45N	118:40:45W	CA	Mouth of Malibu Cr.	Malibu									X			POTW: Tapia Creek; grazing land (horses)
IX	3354	37:57:00N	121:18:00W	CA	New Mormon Slgh	Stockton							X	X		X	X	McCormick and Baxter (wood preservers); Superfund site (solvents)
IX	3283	33:06:00N	115:40:00W	CA	New River	Westmoreland								X				Multiple sources (HCB use)
IX	3355	37:56:00N	121:19:00W	CA	Old Mormon Slough	Stockton							X	X		X	X	McCormick & Baxter (wood preservers); Ag.: croplands & orch.; Superfund site (solvents)
IX	3290	37:57:00N	121:20:00W	CA	Port of Stockton	Stockton							X	X				McCormick & Baxter (wood preservers); Superfund site (solvents)
IX	3274	41:55:00N	124:07:00W	CA	Rowdy Creek	Smith River					X							Arcata Lumber Company (historical PCP site)
IX	3357	38:05:00N	121:44:00W	CA	Sacramento Delta	Antioch			X					X			X	Gaylord Container Corp.; Ind.: chem.; refinery; power plant; Ag.: orchards and croplands
IX	3267	40:27:00N	122:11:00W	CA	Sacramento River	Anderson			X									Simpson Paper Company; wooded area
IX	3270	40:09:00N	122:11:00W	CA	Sacramento River	Red Bluff				X							X	Diamond International (recycled paper); Ag.: croplands and grazing
IX	3287	33:46:00N	118:06:00W	CA	San Gabriel River	Long Beach				X								Simpson Paper Company, Pacific Coast Paper
IX	2748	34:24:00N	119:30:00W	CA	Santa Clara River	Santa Paula	X											Same as 3281
IX	3281	34:20:00N	119:04:00W	CA	Santa Clara River	Santa Paula	X											Same as 2748
IX	3264	33:54:27N	118:31:28W	CA	Santa Monica Bay	Los Angeles						X		X	X	X		El Segundo Refinery; Hyperion POTW outfall; multiple sources
IX	3450	33:55:00N	118:28:00W	CA	Short Bank (Pac. O.)	Los Angeles									X			POTW: Hyperion outfall
IX	3269	37:43:00N	121:09:00W	CA	Stanislaus River	Ripon								X				Multiple sources
IX	3278	39:24:00N	123:06:00W	CA	Upper Eel River	Potter Valley					X							Louisiana Pacific (historical PCP site)
IX	2037	19:46:15N	155:05:33W	HI	Honolii Stream	Hilo		X									X	Ag.: sugar cane growing (pesticides)
IX	3261	21:18:00N	157:59:00W	HI	Pearl Harbor	Middle Loch							X					Combustion sources; Superfund site (solvents)
IX	3262	22:04:30N	159:22:30W	HI	Wailua Paelekaa St.	Kauai												Agent Orange test site (not a designated superfund site)
IX	2776	35:40:00N	114:40:00W	NV	Colorado River	Blw Hoover Dm	X											
X	3238	60:58:30N	149:27:35W	AK	Bird Creek	Bird		X										
X	3241	61:13:20N	149:51:21W	AK	Ship Creek	Anchorage							X	X		X		Salvage yard with runoff of PCB; Superfund site; landfill
X	3246	57:03:00N	133:14:00W	AK	Silver Bay	Sitka			X									Alaska Pulp Company
X	2070	61:32:42N	151:30:45W	AK	Susitna River	Susitna	X											
X	3244	58:41:00N	134:03:00W	AK	Vanderbilt Creek	Juneau								X		X		
X	3245	55:23:45N	131:44:20W	AK	Ward Cove	Ketchikan			X									Louisiana Pacific Corp. (sulfite mill); Ketchikan Pulp and Paper
X	3252	43:48:29N	117:00:15W	ID	Boise River	Parma								X		X	X	
X	3250	47:38:05N	116:43:15W	ID	Coeur d'Alene Lake	Coeur d'Alene								X			X	Ind.: silver mining
X	3249	47:33:07N	116:22:06W	ID	Coeur d'Alene River	Coeur d'Alene								X			X	Mining
X	3158	42:37:25N	114:31:58W	ID	Rock Creek	Twin Falls											X	
X	2478	43:00:08N	115:12:06W	ID	Snake River	Kings Hill	X										X	
X	3256	46:25:45N	117:02:04W	ID	Snake River	Lewiston			X								X	Potlatch Corporation
X	3248	47:19:08N	116:33:35W	ID	St. Joe River	St. Marie		X										
X	3203	45:37:19N	122:45:20W	OR	Columbia River	Portland								X		X		

TABLE B-3 (Cont.)

EPA Reg	Episode #	Latitude	Longitude	State	Waterbody	Location	NSQ	B	POINT SOURCES PPC	PPNC	WP	Rfny	NPL Site	Other Ind	POTW	NONPOINT Urban	Agri	Additional Site Description (Facilities in the vicinity of the sampling site)
X	3216	45:51:53N	122:47:39W	OR	Columbia River	St. Helens			X					X	X	X	X	Boise Cascade (indirect)
X	3218	46:09:21N	123:24:00W	OR	Columbia River	Wauna			X								X	James River Corporation in Clatskanie
X	3219	45:39:10N	120:56:00W	OR	Columbia River	Dalles								X	X		X	Hydro-power (PCB's generated); food processing plant; Ag.: orch. & croplands
X	3201	45:36:06N	122:43:57W	OR	Columbia Slough	Portland			X					X		X		Five paper mills using Cl bleach, two paper mills not using Cl bleach; shipyard
X	3208	44:03:30N	116:57:00W	OR	Malheur River	Ontario											X	
X	3212	43:46:59N	117:03:09W	OR	Owyhee River	Owyhee											X	
X	3205	45:26:33N	123:14:07W	OR	Tualatin River	Cherry Grove		X										
X	3215	45:23:40N	122:45:30W	OR	Tualatin River	Cook Park								X	X		X	Minor industries; Ag.: croplands
X	3206	45:34:53N	122:44:39W	OR	Willamette River	Portland								X	X	X	X	Ind.: chem.; smelters; shipyards; timber
X	3217	44:23:16N	123:14:03W	OR	Willamette River	Hallsey			X								X	Hallsey Pulp Company (Pope and Talbot); Ag.: croplands
X	3213	45:17:47N	122:58:03W	OR	Willamette River	Newburgh Pool			X						X		X	Deinking plant; other pulp mills upstream; Ag.: croplands
X	3437	45:17:38N	122:46:08W	OR	Willamette River	Wilsonville											X	
X	3226	47:23:30N	122:37:38W	WA	Burley Lagoon	Purdy							X					Below transformer and scrap metal salvage yard; below Superfund site (PCB)
X	3438	46:45:36N	123:57:57W	WA	Columbia R. (lower)	Estuary								X				
X	3220	46:07:50N	122:59:27W	WA	Columbia River	Longview			X								X	Weyerhaeuser and Longview Fiber Company; Ag.: croplands & grazing fields
X	3224	46:06:00N	118:55:00W	WA	Columbia River	Tri Cities			X								X	Boise Cascade; Ag.: croplands & grazing fields
X	3222	45:34:08N	122:24:42W	WA	Columbia River	Camas			X									Crown Zellerbach (James River Corporation)
X	3439	46:15:06N	123:33:32W	WA	Columbia River	Woody Island			X					X		X		Boise Cascade and Weyerhaeuser, Longview Fiber downstream
X	3440	46:00:33N	122:51:04W	WA	Columbia River	Kalama			X					X		X		Boise Cascade and Weyerhaeuser, Longview Fiber downstream
X	3441	45:58:05N	122:49:19W	WA	Columbia River	Deer Island			X					X		X		Boise Cascade and Weyerhaeuser, Longview Fiber downstream
X	3163	47:16:12N	122:25:50W	WA	Commencement Bay	Tacoma			X			X	X	X	X	X	X	Simpson Tacoma Kraft, US Oil and Refining; heavily industrialized; Superfund site (Commencement Bay)
X	3191	46:58:00N	123:53:00W	WA	Grays Harbor	Hoquiam				X								ITT Rayonier, Inc. (sulfite mill, nonchlorine)
X	3192	46:57:13N	123:51:15W	WA	Grays Harbor	Cosmopolis			X									Weyerhaeuser Company (sulfite mill, chlorine)
X	31624	47:17:05N	122:24:28W	WA	Hylebos Waterway	Tacoma			X				X	X		X		Champion Paper Company; heavily industrialized; Superfund site
X	3227	47:14:20N	123:02:40W	WA	Oakland Bay	Shelton								X			X	Simpson Pulp Mill (wood overlay products)
X	3295	48:08:00N	123:24:45W	WA	Port Angeles Harbor	Port Angeles			X					X				ITT Rayonier, Inc.
X	3294	48:06:30N	122:45:30W	WA	Port Townsend	Port Townsend				X								
X	2247	47:12:52N	122:20:25W	WA	Puyallup River	Puyallup	X								X		X	Simpson Paper Company (downstream)
X	2246	47:49:52N	122:02:50W	WA	Snohomish	Monroe	X								X		X	Light agriculture; timber
X	3223	48:01:52N	122:13:00W	WA	Steamboat Slough	Everett			X				X					Wey. .aeuser Company and Scott Paper Company; Superfund site (solvents)
X	3224	48:45:01N	122:29:02W	WA	Whatcom Waterway	Bellingham			X									Georgia Pacific (sulfite process)
X	3231	46:22:42N	119:25:29W	WA	Yakima River	Richland								X		X	X	
X	3230	47:11:10N	120:02:30W	WA	Yakima River	Cle Elum		X										

APPENDIX B-4

Dioxins/Furans: Episode Numbers Used in Statistical Tests (By Category)

TABLE B-4
Dioxins/Furans: Episode Numbers Used in Statistical Tests (By Category)

NASQAN (NSQ)

Episode	State
2015	AR
2016	AR
2017	AR
2023	AR
2026	OK
2070	AK
2098	WY
2105	ND
2122	MT
2126	MS
2148	FL
2151	FL
2152	FL
2191	IA
2205	NE
2220	VA
2228	VA
2246	WA
2247	WA
2280	TX
2298	TN
2309	AL
2322	NY
2358	ME
2430	MI
2431	MI
2432	MI
2437	MN
2439	OH
2478	ID
2544	LA
2776	NV
3036	IA
3041	NE
3042	NE
3050	MO
3104	PA
3199	SD
3281	CA
3308	NY
Total	**40**

AGRICULTURE (AG)

Episode	State
2280	TX
2358	ME
2478	ID
3050	MO
3082	LA
3083	LA
3084	TX
3099*	DE
3105	OK
3158*	ID
3170	AL
3171	AL
3180	GA
3193	VA
3208	OR
3212	OR
3282	CA
3352	LA
3437	OR
Total	**19**

SUPERFUND (NPL)

Episode	State
3078	AR
3097	DE
3226	WA
3261	HI
3272	CA
3414	PA
3415	PA
Total	7

POTW

Episode	State
2122	MT
2152	FL
2322	NY
2432	MI
2544	LA
3308	NY
3450	CA
3451	CA
Total	**8**

BACKGROUND (B)

Episode	State
2027	OK
2037	HI
2110	SD
2139	NC
2216	PA
2283	TX
2301	TN
2379	IL
2387	MN
2397	WI
2435	MI
2651	NJ
3001	MN
3022	ME
3023	ME
3027	ME

No data available for dioxins/furans. Number of data values varies by chemical.

TABLE B-4 (Cont.)

Episode	State
3028	ME
3037	IA
3073	AR
3074	NM
3075	TX
3166	NC
3169	AL
3178	GA
3179	GA
3187	SC
3200	CO
3205	OR
3238	AK
3248	ID
3309	NY
3320	NY
3430	NJ
Total	**33**

PULP & PAPER (Chlorine) (PPC)

Episode	State
2015	AR
2016	AR
2017	AR
2138	NC
2142	FL
2294	GA
2302	AL
2304	AL
2355	ME
2385	MN
2422	WI
2427	WI
2532	LA
2721	ME
2725	ME
3062	AR
3080	LA
3081	TX
3088	LA
3107	WI
3118	MI
3122	MI
3146	WI
3150	MA
3151	MA
3152	NH
3192	WA
3217	OR
3218	OR
3220	WA
3221	WA
3222	WA
3224	WA
3237	MT
3245	AK
3246	AK
3256	ID
3260	NY
3267	CA
3303	NY
3316	PA
3317	MD
3318	PA
3328	AL
3329	FL
3331	FL
3332	FL
3333	FL
3335	GA
3336	GA
3337	GA
3339	KY
3340	MS
3341	MS
3342	NC
3343	NC
3344	NC
3345	NC
3346	NC
3347	SC
3348	SC
3349	SC
3350	TN
3351	TN
3353	LA
3395	NC
3403	TN
3404	TN
3416	LA
3418	LA
3420	PA
3421	VA
3422	VA
3423	VA
3424	VA
3425	LA
3435	MS
3452	AR
Total	**78**

INDUSTRY/URBAN (IND/URB)

Episode	State
1994	MI
2023	AR
2057	IN
2060	IN
2191	IA
2210	DC
2215	PA
2220	VA

No data available for dioxins/furans. Number of data values varies by chemical.

TABLE B-4 (Cont.)

2220	VA	3134	WI	3297	NY
2225	VA	3141	WI	3298	NY
2227	VA	3144	WI	3299	NY
2309	AL	3147	DC	3300	NY
2328	NY	3149	DE	3301	NY
2329	NY	3164	NC	3302	NY
2410	MI	3165	NC	3306	NY
2416	OH	3168	AL	3307	NY
2500	WV	3172	AL	3310	PA
3024	ME	3174	FL	3311	WV
3025	ME	3182	KY	3313	WV
3034	IA	3188	TN	3314	WV
3035	IA	3189	TN	3315	PA
3038	IA	3190	TN	3321	NY
3039	KS	3198	CO	3322	NY
3040	MO	3199	SD	3324	NY
3042	NE	3203	OR	3326	NY
3043	NE	3206	OR	3327	NY
3044	MO	3219	OR	3411	NY
3045	MO	3227	WA	3412	NY
3046	MO	3231	WA	3426	NJ
3047	MO	3234	MT	3428	NJ
3048	MO	3235	MT	3432	PR
3049	MO	3236	MT	3438	WA
3060	AR	3244	AK	3443*	AR
3064	LA	3249	ID	**Total**	**106**
3066	LA	3250	ID		
3079	OK	3252	ID	**PULP & PAPER (No Chlorine) (PPNC)**	
3085	TX	3258	VA		
3094	PA	3269	CA	**Episode**	**State**
3100	MD	3275	CA	3089	OK
3101	PA	3276	CA	3090	OK
3103	MD	3283	CA	3091	OK
3111	ND	3285	CA	3092	LA
3113	IL	3286	CA	3093	TX
3115	IL	3289	CA	3108	WI
3120	MI	3296	NY	3112	MN
				3114	IL

* No data available for dioxins/furans. Number of data values varies by chemical.

TABLE B-4 (Cont.)

3135	WI
3136	WI
3137	WI
3138	WI
3140	WI
3143	WI
3145	WI
3184	MS
3191	WA
3270	CA
3287	CA
3294	WA
3330	FL
3360	AL
3375	GA
3376	GA
3377	GA
3378	GA
3401	TN
Total	**27**

WOOD PRESERVERS (WP)

Episode	State
3076	OK
3077	AR
3110	WI
3167	NC
3173	FL
3196	WY
3197	CO
3271	CA
3273	CA
3274	CA
3278	CA
Total	**11**

REFINERY/OTHER INDUSTRY (R/I)

Episode	State
2026	OK
2380	IL
2383	IL
3061	AR
3063	LA
3069	TX
3071	TX
3072	TX
3086	LA
3095	PA
3096	PA
3125	MN
3183	KY
3264	CA
3312	WV
3431	PR
3434	NJ
3442	LA
3444	TN
3446	KY
Total	**20**

* No data available for dioxins/furans. Number of data values varies by chemical.

APPENDIX B-5

Xenobiotics: Episode Numbers Used in Statistical Tests (By Category)

TABLE B-5
Other Xenobiotics: Episode Numbers Used in Statistical Tests (By Category)

NASQAN (NSQ)

Episode	State
2015	AR
2016	AR
2017	AR
2023	AR
2026	OK
2070	AK
2098	WY
2105	ND
2122	MT
2126	MS
2148	FL
2151	FL
2152	FL
2191	IA
2205	NE
2220	VA
2228	VA
2246	WA
2247	WA
2280	TX
2298	TN
2309	AL
2322	NY
2358*	ME
2430	MI
2431	MI
2432	MI
2437	MN
2439	OH
2478	ID
2544	LA
2776	NV
3036	IA
3041	NE
3042	NE
3050	MO
3104	PA
3199	SD
3281	CA
3308	NY
Total	**40**

AGRICULTURE (AG)

Episode	State
2280	TX
2358*	ME
2478	ID
3050	MO
3082	LA
3083	LA
3084	TX
3099	DE
3105	OK
3158	ID
3170	AL
3171	AL
3180	GA
3193	VA
3208	OR
3212	OR
3282	CA
3352	LA
3437*	OR
Total	**19**

SUPERFUND (NPL)

Episode	State
3097	DE
3226	WA
3261	HI
3272	CA
3414	PA
3415	PA
Total	**6**

POTW

Episode	State
2122	MT
2152	FL
2322	NY
2432	MI
2544	LA
3308	NY
3450*	CA
3451*	CA
Total	**8**

BACKGROUND (B)

Episode	State
2110	SD
2139	NC
2216	PA
2283	TX
2397	WI
2435	MI
2651	NJ
3022	ME
3023	ME
3028	ME
3037	IA
3073	AR
3074	NM
3075**	TX
3166	NC
3169	AL

* No data available for other xenobiotics. Number of data values varies by chemical.

** Data available for mercury only.

TABLE B-5 (Cont.)

3178	GA
3200	CO
3205	OR
3238	AK
3248	ID
Total	**21**

PULP & PAPER (Chlorine) (PPC)

Episode	State
2017	AR
2138**	NC
2294	GA
2302	AL
2422	WI
2532	LA
2721	ME
2725	ME
3107	WI
3118	MI
3122	MI
3151	MA
3152	NH
3192	WA
3222	WA
3224	WA
3237	MT
3245	AK
3246	AK
3260	NY
3267	CA
3303	NY
3316	PA
3318	PA
3332	FL
3335	GA
3336	GA
3340	MS
3341	MS
3342	NC
3348	SC
3395	NC
3403	TN
3416*	LA
3418*	LA
3420	PA
3421	VA
3422	VA
3423	VA
3424	VA
3425	LA
3435	MS
Total	**42**

INDUSTRY/URBAN (IND/URB)

Episode	State
3043	NE
3044	MO
3045	MO
3079	OK
3085	TX
3101	PA
3120	MI
3149	DE
3172	AL
3174	FL
3189	TN
3190	TN
3203	OR
3234	MT
3235	MT
3236	MT
3244**	AK
3258	VA
3269*	CA
3275**	CA
3276	CA
3283	CA
3285	CA
3286	CA
3289	CA
3296	NY
3298	NY
3306	NY
3307	NY
3315	PA
3411	NY
3412	NY
3426	NJ
3428	NJ
3438*	WA
Total	**35**

PULP& PAPER (No Chlorine) (PPNC)

Episode	State
3090	OK
3091	OK
3108	WI
3112	MN
3135	WI
3136	WI
3140	WI
3143	WI
3145	WI
3191	WA
3287	CA
3294	WA
3330	FL
3360	AL

* No data available for other xenobiotics. Number of data values varies by chemical.

** Data available for mercury only.

TABLE B-5 (Cont.)

3360	AL
3376	GA
3377	GA
3401	TN
Total	**17**

WOOD PRESERVERS (WP)

Episode	State
3076	OK
3077	AR
3110	WI
3167	NC
3173	FL
3196	WY
3197*ã	CO
3271	CA
3273	CA
3274	CA
3278	CA
Total	**11**

REFINERY/OTHER INDUSTRY (R/I)

Episode	State
3061	AR
3063	LA
3072	TX
3095	PA
3446	KY
Total	**5**

* No data available for other xenobiotics. Number of data values varies by chemical.

** Data available for mercury only.

EPA

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