

"Trends in Great Lakes Fish Contaminants"

Quality Assurance Project Plan

**Submitted to
U.S. EPA Great Lakes National Program Office
and
U.S. EPA Region V
Chicago, IL**

By

**Deborah L. Swackhamer
University of Minnesota
Environ. Health Sciences, School of Public Health
Mayo Mail Code 807
Minneapolis, MN 55455**

**612-626-0435
dswack@umn.edu**

A1. Approvals

Deborah Swackhamer, Principal Investigator & Project Manager, UMN Date

Elizabeth Murphy, Project Manager, USEPA GLNPO Date

Louis Blume, Quality Assurance Manager, USEPA GLNPO Date

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A3. Distribution List

Louis Blume
U.S.EPA - Great Lakes National Program Office
77 W Jackson Blvd.
Chicago, IL 60604-3590

Elizabeth Murphy
U.S.EPA - Great Lakes National Program Office
77 W Jackson Blvd.
Chicago, IL 60604-3590

Deborah Swackhamer
University of Minnesota, School of Public Health
Environmental Health Sciences
Mayo Mail Code 807
420 Delaware St. S.E.
Minneapolis, MN 55455

A4. Project / Task Organization

Dr. Swackhamer is the Principal Investigator of this project, and as such has the responsibility to oversee all aspects of this project. The PI will review all data generated by her personnel, and review the performance of sample handling and sample analyses by her personnel; she will direct and evaluate any necessary corrective action. She has the overall responsibility to ensure the quality of all data generated by this project. The Data Quality Objectives (DQOs) are spelled out in the EPA Cooperative Agreement of the Great Lakes Fish Monitoring Program (GLFMP). This Quality Assurance Project Plan (QAPP) addresses specific Measurement Quality Objectives (MQOs) that apply to the data for the project.

The US EPA Great Lakes National Program Office (GLNPO) provides for all fish collections, sample handling and processing, and shipping. Ground, homogenous fish tissue composites are shipped to the University of Minnesota Environmental Chemistry Labs (UMN). The responsibility for these samples by the PI begins at the time of receipt.

Dr. Swackhamer reports to the EPA Great Lakes National Program Office (GLNPO) Project Officer, Elizabeth Murphy, or her designate. The QAPP is reviewed and approved by the EPA GLNPO Quality Assurance Officer, Louis Blume.

Dr. Swackhamer will provide interpretation of the data generated by this project in coordination and cooperation with appropriate staff from EPA GLNPO and USGS-BRD.

A5. Problem Definition / Background

We will determine the concentrations of selected organic contaminants in sport fish from the Great Lakes to support the US EPA GLNPO in the GLFMP. Secondly, we will provide scientific expertise and assistance in the analysis of these and previous data to (1) determine time trends in contaminant concentrations, (2) assess impacts of contaminants on the fishery, and (3) to assess potential human and wildlife exposures from consuming contaminated sport fish.

This project addresses two programmatic components of the GLFMP: Element 1 will determine the contaminant concentrations in 600-700 mm lake trout (*Salvelinus namaycush*) whole fish composites (5 fish) from each of the lakes (walleye, *Stizostedion vitreum vitreum*, in Lake Erie). These data are used to assess time trends in organic contaminants in the open waters of the Great Lakes, using fish as biomonitors. These data can also be used to assess the risks of such contaminants on the health of this important fishery, and on wildlife that consume them. Element 2 focuses on assessing human exposures via consumption of popular sport fish. Coho (*Oncorhynchus kisutch*) and chinook salmon (*Oncorhynchus tshawytscha*) from each lake (rainbow trout, *Salmo gairdneri*, in Lake Erie) are collected during the fall spawning run, and composite fillets (5 fish) are analyzed for organic contaminants to assess human exposure. These data also complement those from Element 1. The coho salmon spawn at 3 years of age, and so their body burdens reflect a more focused and consistent exposure time compared to the lake trout which may integrate exposures over 4 to 10 yrs depending on the lake. Chinook salmon

spawn after 4-5 years, and have higher (and thus more detectable) concentrations than the coho salmon and also represent a consistent exposure time. Thus time trends for consistent age fish as well as consistent size fish can be assessed from these data.

Fish monitoring programs of various size efforts have been conducted in the Great Lakes since the 1970's by a number of state, provincial, and federal agencies, but did not have consistent methodologies or aims. The GLFMP was implemented as a coordinated effort that consisted of a Cooperative Agreement between EPA GLNPO and the US Fish & Wildlife Service (the cooperating agency is now the USGS-BRD) and the Great Lakes states (GLNPO 1981). The Department of Fisheries and Oceans of Canada has also monitored organic contaminants in fish since the late 1970s (De Vault et al. 1995). The goals of the GLFMP are to monitor time trends in bioaccumulative organic chemicals in the Great Lakes using top predator fish as biomonitors, and to assess human exposure to organic contaminants found in fall run coho and Chinook salmon.

This highly visible and successful program has provided the Great Lakes community with one of the most useful long-term data sets of organic contaminants on record. No comparable data sets for contaminant concentrations in water exist, and sediment core records of organic contaminants are not available for all compounds of concern in all the lakes. Numerous reports and publications of the interpretation of these data resulted from EPA scientists involved in the GLFMP (De Vault and Weishaar 1983, De Vault 1984, De Vault and Weishaar 1984, De Vault 1985, De Vault et al. 1985, De Vault et al. 1986, De Vault et al. 1988, De Vault et al. 1996), many of which are highly cited. These publications have shown that the concentrations of chemicals that have been banned or whose sources are controlled have declined in a first-order exponential pattern. The classic examples are the trends in PCBs and Σ DDT, both of which were banned in the 1970s. In addition, these data have been used to demonstrate that PCBs have stopped declining in Lake Michigan (Stow et al. 1995, De Vault et al. 1996), not because of new sources but because of changes in the foodweb (De Vault et al. 1996, Madenjian et al. 1998, Madenjian et al. 1999). Other contaminants show different time trends. Toxaphene has shown no decline in Lake Superior fishes but appears to have declined in the other lakes (Glassmeyer et al. 1997).

These data have also served as a valuable resource for other scientists who have used them to corroborate trends from other media such as water and sediment (Rodgers and Swain 1983, Jeremiason et al. 1994, Pearson et al. 1996), to construct or calibrate models of contaminant bioaccumulation (Stow et al. 1994, Stow and Carpenter 1994, Stow 1995, Stow et al. 1995, Jackson and Schindler 1996, Eby et al. 1997, Stow and Qian 1998), or to assess the health of the fishery (Mac and Edsal 1991, Mac et al. 1993, Cook et al. 1997).

A6. Project / Task Description

The overall objective of this project is to provide high quality data of concentrations of organic contaminant residues in Great Lakes fish in support of the GLFMP.

Samples. All fish samples will be supplied to UMN as frozen homogenates, and stored at -20°C . It is understood that the lake trout composites will consist of 5 whole fish between 600-700 mm and the walleye composites will consist of 5 whole fish between 400-500 mm. The fall run coho and Chinook salmon composites will consist of 5 skin-on fillets. Coho salmon stocking is declining in Lake Erie, and thus rainbow trout are being substituted as a monitoring species. We advise GLFMP to sample both coho salmon and rainbow trout in 1999 from Lake Erie, and then rainbow trout in subsequent years. Rainbow trout composites will consist of 5 skin-on fillets. The records of length, weight, and sex of each fish in the composite will be provided by USGS-BRD. A summary of the expected composites to be provided is shown in Table 1.

Table 1. Anticipated fish collections and composite characteristics.

Lake	year	Element 1	#composites	Element 2	#composites
Superior	1999	lake trout	10	Chinook	6
	2000	lake trout	10	coho	6
Huron	1999	lake trout	10	Chinook	6
	2000	lake trout	10	coho	6
Michigan	1999	lake trout	10	Chinook	24
	2000	lake trout	10	coho	24
Erie	1999	walleye	10	rainbow trout	6
	2000	walleye	10	coho*	3
Ontario	1999	lake trout	10	Chinook	6
	2000	lake trout	10	coho	6

*coho are no longer being stocked in L. Erie and thus rainbow trout are the preferred monitoring species.

Data Generation and Interpretation. The samples will be extracted and analyzed by a variety of methods for a specified suite of contaminants. The details of the analytical methods and the contaminants of concern are detailed in section B below.

The data will be used to determine statistically significant changes in concentration over time (time trends), and to assess risk posed by the observed concentrations to the fishery and to consumers of the fishery (wildlife and human health risk assessment). These analyses will be done in consultation and cooperation with GLNPO and USGS-BRD staff.

A7. Quality Objectives and Criteria for Measurement Data

The DQOs for the GLFMP are detailed in the official Cooperative Agreement that established the GLFMP. This project is concerned with the MQOs for the data generated in support of the GLFMP. A summary of the MQOs is found in Table 2.

Table 2. Measurement Quality Objectives for GLFMP samples.

Requirement	Sample Code	Acceptance Criteria	QC Flag
Reporting Units	NA	ng/g, pg/g, or ug/g wet wt. (Surrogate corrected)	NA
Instrument detection limit	IDL	Once per project per analyte; extrapolate from initial calibration curve	IDL
Method detection limit	MDL	Once per project; 40 CFR App B pt 136	MDL*
Continuing calibration frequency criteria	CLS	Set of standards of different concentrations 1 set with each analytical batch See performance standard criteria below	Rerun batch
Routine detectability frequency criteria	RFS	All samples > MDL	MDL*
Blanks: Field blanks Laboratory blanks frequency criteria	LPB	Solvents & reagents 1 per analytical batch (six samples) ≤ MDL	N/A FPB
Performance stds frequency % recovery	LPC	A standard run as check sample One per run batch 70% < % recovery < 130%	FPC
Surrogate stds frequency % recovery	LSS	See Table 3 Every sample, blank & std; 50% < % recovery < 150%	FSS
Reference Samples frequency % recovery	LRS	Lake trout check sample 1 per every 3 sample batches (10/yr) 65% < established value < 135%	FPC; Repeat, work halted until acceptable
Procedural Spikes frequency % recovery	LPS	Analyte cocktail spiked into solvent Beginning of project; if fail check sample 50% < % recovery < 120%	FPS; Repeat, work halted until acceptable
Internal stds frequency criteria	LIS	PCB congener 204 Every sample, blank and std RRF of LIS within factor of 2 in given run	FIS
Completeness	NA	90% valid data; this is a goal and not a requirement	INV
Duplicates Field Duplicate Lab Duplicates frequency criteria	LDn	Duplicate analysis of a composite 1 per every 4 sample batches < 50% RPD	N/A FDL
Confirmation frequency criteria	CON	all samples all peaks within acceptable retention times and m/z ratios	If not confirmed, reported as zero

* Criteria that are homolog specific (PCBs and toxaphene). Individual homologs that are out of control limits will be flagged. Entire sample is flagged if more that 3 toxaphene or 5 PCB homologs are flagged.

Additional QA flags not included in Table 2 include:

- LAC Laboratory accident destroyed sample or rendered it unsuitable for analysis.
- INT Not analyzed due to Interference.
- RIN Re-injection of the sample extract produced the reported value.
- REX Re-prepared sample was used to generate the reported value.
- FBK Found in procedural blank at greater than acceptable criteria and reported value may be an overestimate.
- UND Undetected; no instrument response
- CAN Cancelled; value was not reported because analysis not performed.
- REJ Rejected; reported value was rejected for an unspecified reason by the laboratory based on professional judgement. Value was not utilized in the calculation of any results where a mean was being determined.

Lipid content (wet weight) is done on every sample. It is reported as a percentage (mg lipid/mg wet tissue * 100). Duplicate analyses will be done once per every two batches, and must agree to within 20%. Values not meeting these criteria will be flagged FFD.

A8. Special Training / Certification

The personnel at the University of Minnesota have extensive experience in the trace level analysis of persistent, bioaccumulative toxicants (PBTs) and in the study of the environmental fate and transport of these chemicals. This laboratory has conducted several previous studies of contaminants in Great Lakes foodweb components including the EPA Green Bay Mass Balance Study (GBMBS) and the Lake Michigan Mass Balance Study (LMMBS). Both of these studies included several hundred samples. As part of her effort on the GBMBS, Dr. Swackhamer helped develop the quality assurance and data reporting criteria used by all investigators. She gained familiarity with GLNPO's Data Reporting Standard as part of her work on the LMMBS.

The PI has also had experience identifying unknown compounds in fish tissue, and has had formal training in the interpretation of both EI and ECNI mass spectra. Swackhamer et al. (1988) used GCMS-ECNI full scan to identify a number of chlorinated compounds in fish from Siskiwit Lake on Isle Royale, which confirmed that these compounds were capable of undergoing long-range atmospheric transport and deposition to remote areas.

The personnel working in the UMN Environmental Chemistry Labs undergo expensive training on the analytical, quality assurance, and data management procedures followed for this program. Prior to handling samples, all personnel must demonstrate acceptable quality assurance compliance on a set of 5 procedural spikes. Personnel also take a set of raw data for samples that whose finished data have already been approved and go through all of the quantification procedures to evaluate their ability to reproduce these accepted data. The PI personally oversees all training. Personnel undergo initial training and yearly updates in laboratory safety practices, radioisotope handling, and hazardous waste handling.

A9. Documentation and Records

Project documentation will include lab notebooks, instrument (raw) data files, final processed data (in spreadsheet files), and QA files containing all precision, accuracy and blank data. An electronic inventory of all samples received and their progress in the laboratory is also maintained. These files are available for review on site by the EPA Project Officer or QA Officer.

All concentration and quality assurance data will reported to the GLNPO Project Officer in conformance with the GLNPO “GLENDA” Reporting Standard for the Analysis of Contaminants in Fish Tissue.

The final data reported to GLNPO will include the following:

- External sample ID (xxxxyyyyzzz, where x = year, y = site code, and z = composite number)
- Lab internal sample code (color and date of extraction)
- Sample type (sample, lab blank, matrix blank, lab duplicate etc.)
- Sample information (species, place of collection, composite information)
- Date received by the University
- Date extracted
- Date analyzed on instrument
- Analyte concentration (wet weight)
- % lipid
- Surrogate recovery
- QA remark codes as needed

SECTION B. DATA GENERATION AND ACQUISITION

B1. Sampling Process Design

N/A. All fish samples will be supplied as frozen homogenates.

B2. Sampling Methods

N/A. All fish samples will be supplied as frozen homogenates.

B3. Sample Handling and Custody

Samples will be logged in on receipt and stored in a freezer.

B4. Analytical Methods

B.4.1. Sample Extraction and Interference Removal

Samples are thawed and homogenized. A 2 g subsample (exact weight recorded) is mixed with approximately 14 g anhydrous sodium sulfate to obtain a mealy texture. The mixture is transferred quantitatively to a Soxhlet extractor charged with 150 mL of acetone in a 250 mL roundbottom flask. A set of samples consists of four fish samples, one QA sample (duplicate, spike sample, etc.) and a procedural blank. A procedural blank consists of sodium sulfate without fish carried through the procedure in a manner identical to the samples. An aliquot of surrogate recovery standard solution (see Table 3, below) is added by micropipette. The sample is extracted for 4 hours. The acetone is removed to a Kuderna-Danish (KD) apparatus, and the Soxhlet charged with 150 mL dichloromethane (DCM). The sample is extracted for an additional 18 hrs. This extract is combined with the first Soxhlet extract in the KD apparatus, and reduced in volume and solvent-exchanged to hexane using a Snyder column and steam bath. The extract is brought to exactly 10 mL in hexane, and exactly 1 mL is removed for lipid analysis (see below).

Lipids and other organic compounds must be removed from the extract to accurately detect and quantify the analytes of interest. Lipids are removed by a column (1 x 30 cm) containing 13 g 6% deactivated alumina (60 mesh, w/w) and eluting with 3 x 30 mL hexane. The eluate is collected in a KD and reduced in volume as before to approximately 10 mL. This extract is then placed on a column containing 4.5 g fully activated silica gel over 6 g 2% deactivated neutral alumina (w/w), with anhydrous sodium sulfate above and below each layer. The column is eluted with 3 x 30 mL hexane (Fraction 1). The column is further eluted with 3 x 30 mL 40%/60% DCM/hexane (Fraction 2). Each fraction is solvent exchanged to hexane and reduced to a volume of approximately 1 mL. At this time the extract is stored in a vial with teflon-lined cap and stored in a freezer. Prior to instrumental analysis, the extract is reduced to a few hundred microliters by gentle nitrogen gas stream, and the internal standard is added (PCB #204) to Fraction 1.

B.4.2. Extract Instrumental Analysis

Six separate analyses will be done on a given sample to quantify all the required analytes: (1) PCB congeners; (2) PCB coplanar congeners; (3) individual organochlorine pesticides; (4) toxaphene, chlordanes, and nonachlors; (5) polychlorinated dibenzo-p-dioxins and dibenzofurans (PCDD/Fs); and (6) polychlorinated naphthalenes (PCNs), polybrominated diphenyl ethers (PBDEs), and congener 153 of the polybrominated biphenyl (PBB-153) family. The first two analyses for PCBs are done first on Fraction 1. Once the data have been reviewed and found to be acceptable, then Fraction 1 and 2 are recombined (hence no need for an internal standard in Fraction 2) and the 3rd and 4th analyses are done on the combined extract. This is because of the high potential of interference from other compounds in PCB analyses. The other compounds do not experience interference from the PCBs and our experience has been that recoveries are improved if the two fractions are recombined. The analytes, the instrumental methods used, the surrogate compounds used, and the estimated method detection limits (MDLs) are shown in

Table 3 (below). Note that our estimated MDLs are in general are well-below what is needed for positive detection based on previous data (De Vault et al. 1986, De Vault et al. 1996).

A separate extraction and instrumental analysis is performed to determine mercury concentrations (see below).

B.4.2.1 PCB Congeners

Total PCBs and PCB congeners are analyzed by gas chromatography with electron capture detection (GC-ECD). The method resolves and quantifies 110 congener or congener groups, and is similar to that used for the GLNPO Lake Michigan Mass Balance Study (Swackhamer and Trowbridge 1997) and previous Great Lakes PCB studies (Pearson et al. 1996, Skoglund et al. 1996, Swackhamer 1996). The GC (Hewlett Packard 5988) is equipped with an autosampler, large volume splitless injector, 60 m DB-5 column, Ni-63 ECD, and HP ChemStation data acquisition software. The injection port is kept at 225 °C, the oven is programmed from 100 °C to 280 °C at 1 deg/minute, and the detector is maintained at 325 °C. The carrier gas is hydrogen and the makeup gas is argon-in-methane.

B.4.2.2 PCB Co-Planar Congeners

The above method does not separate all of the toxic co-planar congeners, which preferentially bioaccumulate in fish relative to other PCBs (Trowbridge and Swackhamer 1999) and may be of interest particularly to the Great Lakes states health authorities because of their human health significance (Safe 1994). We use another analysis for the co-planar congeners (Trowbridge and Swackhamer 1999), which is a modification of a method developed by Schmidt and Hesselberg (1992) and uses gas chromatography mass spectrometry (GCMS) in electron capture negative ion mode (ECNI). The method is referred to as GCMS-ECNI#1 in Table 3. This method utilizes the fact that GC/MS in the negative ion mode is very selective and sensitive to highly chlorinated compounds. AHH-inducing PCB congeners often co-elute with other congeners having a different number of chlorine atoms that allows them to be differentiated by GCMS-ECNI. The GC separation is the same, using helium as the carrier gas. The MS (Hewlett Packard 5988) has ChemStation and Aquarius acquisition software. The transfer line is maintained at 270 °C, the source temperature and pressure is 100 °C and 1 torr, the reagent gas is methane.

B.4.2.3. Organochlorine Pesticides

A suite of other chlorinated compounds that are not part of complex families are analyzed by GCMS-ECNI by monitoring selected ions for quantifying and confirming each compound (method #2, Table 3). This group includes hexachlorobenzene, pentachlorobenzene, octachlorostyrene, α -BHC, δ -BHC, dieldrin, aldrin, endrin, p,p- and o,p-DDT, p,p- and o,p-DDE, and p,p- and o,p-DDD. All GCMS conditions are as described above, but a slightly different temperature program is used to optimize resolution.

B.4.2.4 Toxaphene and Chlordane Compounds

Toxaphene, chlordanes and nonachlors are analyzed by GCMS-ECNI (#3, Table 3). This

technique is as sensitive as GC-ECD, but is far more accurate because it affords a means of eliminating interferences and providing confirmation from the resulting mass spectra. One injection and temperature program is used for the toxaphene, chlordanes, and nonachlors, and a second injection and program is used to acquire the data for the remaining organochlorine compounds.

Toxaphene is a complex mixture of hundreds of compounds, and requires a separate analysis. Because of the similarities in mass spectra, cis- and trans-chlordane and cis- and trans-nonachlor are also analyzed in the same run. The method quantifies total toxaphene, and the contributions of each of its homologs (hexa-, hepta-, octa-, nona-, and deca-chlorinated bornanes and bornenes), and was originally developed by this investigator (Swackhamer et al. 1987) and subsequently modified by Glassmeyer (1999). We now use a modification of this method (Symonik and Swackhamer, unpublished) that includes strict confirmation criteria to exclude non-toxaphene interferences. The method monitors selected ions for each of the bornane and bornene homologs, as well as for known interferences so that they can be accounted for. Quantitation and confirmation ions for the 4 chlordane components are also included. All GCMS conditions are similar to those described above, but a slightly different temperature program is used to optimize baseline resolution of the different compounds.

B.4.2.5 Polychlorinated Dibenzo-p-dioxins and Dibenzofurans (PCDD/Fs)

The individual congeners from the PCDD/F family will be reported (Table 4) as requested by GLNPO, as well as homologues and totals (Pearson et al. 1997). The large number of compounds in this family requires that a separate GCMS program be used (method #4, Table 3). The individual congeners can be used to calculate the total toxic equivalency (TEQ) concentrations for public health purposes as well as fish health purposes (Safe 1990, Safe 1994). The typical concentrations of the most toxic PCDD congener, 2,3,7,8-TCDD, are below the detection limit when only 2-3 g of fish are extracted, so this family of compounds is not analyzed for routinely.

B.4.2.6 PCNs, PBDEs, and PBB-153

These new analytes ("emerging contaminants") will be analyzed in 2000 - 2003 fish as per the cooperative agreement with EPA, except for PCNs which are routinely below detection. The MDLs are estimates and may be modified after final method confirmation. When analyzed, total PCNs are determined by summing the individual congeners from the tri- through octa homologs after the method of Kannan et al. (2000) (method #5, Table 3).

The PBDEs will be determined by monitoring m/z 79 and 81 (Br- and its stable isotope) at specific retention times that correspond to the following congeners: 2,2',4,4' (#47); 2,2',4,4',5 (#99); 2,2',4,4',6 (#100); 2,2',4,4',5,5' (#153); 2,2',4,4',5,6' (#154); 2,3,3',4,4',5,6 (#190); and 2,2',3,3',4,4',5,5',6,6' (#209). Three congeners not found in the commercial mixtures are used as surrogate recovery standards, and applied to their appropriate homolog. These include congeners 2,3',4,6 (#71), 2,3',4,4',5 (#118), and 2,3,4,4',5,6 (#166). The GCMS program checks and only includes data that match the retention time, and have the correct ion ratio as confirmation.

PBB-153 will be determined by monitoring m/z 79 and 81 at the appropriate retention time for quantification and confirmation.

B.4.2.7 Mercury

A separate homogenate for fish tissue will be used to determine mercury concentrations. Fish tissue (0.2 to 1.0 g) will be digested in a 5:2 ratio of concentrated nitric (HNO₃) and concentrated sulfuric (H₂SO₄) acids in Teflon digestion bombs in a conventional oven. If samples are not fully digested by this process, we may either add bromine monochloride (BrCl) or heat the samples further in a microwave oven. Total mercury concentrations in the digestate will be determined by cold vapor atomic fluorescence spectrometry (CVAFS) using a slight modification of the method of Bloom and Crecelius (1983) in that we will not add BrCl to the digestate. This method is fairly close to USEPA method 1631. The mercury analyses will be done by Dr. Ed Nater, University of Minnesota.

B.4.2.8 Lipid Analyses

The fraction lipid of each sample will be determined gravimetrically by weighing exactly 1/10 of the extract of a known mass of wet fish tissue and taking to complete dryness and reweighing to constant weight. The residue after evaporation is lipid. The fraction lipid is equal to the mass of remaining lipid divided by the mass of wet weight of fish extract. The percent lipid is the fraction lipid multiplied by 100.

B.4.2.9 Emerging Contaminants

In addition, we will qualitatively report on selected chemicals of emerging concern. These include perfluoro-octane sulfate (PFOS), tetrabromobisphenol A (TBBPA), short chain chlorinated paraffins (SCCPs), alkyl phenol ethoxylates (APEs), and chlorothalonil. The method for PFOS is under development, and involves a separate Soxhlet extraction followed by a cleanup using fluorinated C-18 column chromatography followed by analysis by HPLC-MS (Simcik and Dorweiler, in review). Methods for TBBPA and SCCPs have been developed by Derek Muir and colleagues from NWRI, Ontario, Canada. While TBBPA can be analyzed by GCMS from the extract prepared for the other analytes, the SCCPs require high resolution GCMS-MS, which is not available to us at the UMN. We will arrange for these few analyses through Dr. Muir. We currently analyze APEs using GCMS in electron impact mode. This is a separate instrumental analysis, but can be done on the same extract as the other analytes. Chlorothalonil will be analyzed by GCMS-ECNI from the same extract.

Table 3. List of organic chemicals to be analyzed in fish, their surrogate recovery standards, type of instrumental analysis used, estimated MDL expressed as pg/g wet fish tissue, and quantitation (Q) and confirmation (C) ions.

Analyte	Surrogate	analysis [‡]	MDL, ng/g	Q, C m/z
PCB congeners	PCB- 65, 188	GC-ECD	1 - 10	N/A
PCB co-planars	PCB-65, 188	GCMS-ECNI 1	1 - 10	By homolog
hexachlorobenzene	¹³ C-hexachlorobenzene	GCMS-ECNI 2	1	284/286
Pentachlorobenzene	¹³ C-hexachlorobenzene	GCMS-ECNI 2	5	250/252
Octachlorostyrene	¹³ C-hexachlorobenzene	GCMS-ECNI 2	0.5	380/378
δ-BHC (Lindane)	¹³ C-BHC	GCMS-ECNI 2	1	255/257
α-BHC	¹³ C-BHC	GCMS-ECNI 2	1	255/257
Aldrin	¹³ C-chlordane	GCMS-ECNI 2	5	330/332
Dieldrin	¹³ C-chlordane	GCMS-ECNI 2	5	380/346
Heptachlor epoxide a	¹³ C-chlordane	GCMS-ECNI 2	5	237/239
Heptachlor epoxide b	¹³ C-chlordane	GCMS-ECNI 2	5	237/239
Cis-chlordane	¹³ C-chlordane	GCMS-ECNI 3	0.5	406/408
Trans-chlordane	¹³ C-chlordane	GCMS-ECNI 3	0.5	406/408
Cis-nonachlor	¹³ C-chlordane	GCMS-ECNI 3	0.5	444/442
Trans-nonachlor	¹³ C-chlordane	GCMS-ECNI 3	0.5	444/442
Oxychlordane	¹³ C-chlordane	GCMS-ECNI 2	1	424/422
pp, op-DDT	¹³ C-p,p-DDE	GCMS-ECNI 2	1	281/283; 248/246
pp, op-DDE	¹³ C-p,p-DDE	GCMS-ECNI 2	1	281/283; 246/248
pp, op-DDD	¹³ C-p,p-DDE	GCMS-ECNI 2	1	248/250; 248/246
Endrin	¹³ C-chlordane	GCMS-ECNI 2	5	380/346
Mirex	¹³ C chlordane	GCMS-ECNI 2	1	404/402
Toxaphene&homologs	¹³ C chlordane	GCMS-ECNI 3	10 (total)	Homologs [%]
PCDD/Fs	¹³ C PCDD/Fs	GCMS-ECNI 4	10	Homologs [%]
PBDEs	¹³ C PBDEs	GCMS-ECNI 5	0.3 (congeners)	79/81
PCNs	¹³ C PCNs	GCMS-ECNI 5	1-10 (congeners)	Homologs [%]
Dacthal	¹³ C-p,p-DDE	GCMS-ECNI 2	10	332/330
PBB-153	¹³ C PBDEs	GCMS-ECNI 5	0.3	79/81
Hg	N/A	CVAFS	10	N/A
Fraction lipid	N/A	gravimetrically	0.05%	N/A

[‡]GC-ECD refers to gas chromatography with electron capture detector. GCMS-ECNI 1-5 refer to five different mass spectrometry analyses of the same extract. CVAFS refers to cold vapor atomic fluorescence spectroscopy.

[%] Quantification and confirmation ions are the same within a homolog and differ across homolog

Table 4. PCDD/F congeners to be reported in GLFMP samples.

PCDD and PCDF Congener in Quantitation Standard	Corresponding Homolog
2,3,7,8-	Tetra
1,2,3,7,8-	Penta
1,2,3,4,7,8-	Hexa
1,2,3,4,6,7,8-	Hepta
1,2,3,4,6,7,8,9-	Octa

B.4.3 Data Processing and Quantification Methods

All chromatograms are carefully reviewed by an experienced operator. The ChemStation software automatically integrates all peaks of interest, and to ensure accurate integration, the baselines are also reviewed by an experienced operator for integrity. The peak areas are extracted by a Chemstation macro program and transferred electronically to a PC spreadsheet. These data are then processed through a Basic program that selects only those data that meet confirmation criteria (ie the program checks for the ratio of the quantification ion to the confirmation ion). The filtered data are then transferred to a quantification template spreadsheet that uses the internal standard method to quantify the mass of analyte in each extract. The equation used is as follows:

$$\text{Mass}_{\text{analyte}} = \text{area}_{\text{analyte}} * \text{mass}_{\text{IS}}/\text{area}_{\text{IS}} * \text{RRF}$$

Where RRF = (mass_{qstd}/area_{qstd})/(mass_{IS}/area_{IS})
 IS = internal standard
 qstd = quantitation standard

The internal standard for all analyses is PCB congener #204. The spreadsheet formulas are checked for accuracy with each instrument run using check standards. The mass of analyte in each extract is converted to a concentration by dividing mass of analyte (ng or ug) by the exact mass of fish tissue that was extracted (g wet weight). Concentrations are reported as ng/g or ug/g on a wet weight basis. A master database contains all relevant data such that it can be easily sorted by chemical, by fish species, by lipid content, by year, and by location to perform statistical analyses, graphical results, or tables. This spreadsheet conforms to the GLNPO Reporting Standard for the Analysis of Contaminants in Fish Tissue. All raw data are archived on tape, and all data files and the database have disc backups.

B.4.5. Data Interpretation and Data Reporting

The data will be used to determine statistically significant changes in concentration over time (time trends), and to assess risk posed by the observed concentrations to the fishery and to consumers of the fishery (wildlife and human health risk assessment). These analyses will be done in consultation and cooperation with GLNPO staff. In addition, the Minnesota Department of Health (see attached letter) and statisticians on the faculty of the UMN will advise on the project.

We propose to assess time trends using a first order kinetics models as well as non-linear models such as change point analysis (SPSS and SAS statistical software). Dr. Timothy Church will collaborate on these analyses. Best-fit equations will be determined for each analyte in each species of each lake. Significant changes in the trend slopes can be assessed statistically. Projections of the time trends to the future will provide predictions of concentrations at certain future dates, or for when the concentrations will reach a certain regulatory or advisory level. For certain compounds, we can assess the entire data set (past and current data) for expected first-order declines due to regulatory actions (e.g. DDT, PCBs), and to statistically assess deviations from this due to other factors (e.g. recent PCB increases in Lake Michigan coho due to foodweb changes; (Stow et al. 1995, De Vault et al. 1996, Madenjian et al. 1998)). We will ensure that only appropriate data are used. For example, we will exclude precocious 2-yr old coho salmon from the analyses of trends in constant age fish. We will compare the trends observed in constant age fish (coho and Chinook) to those of constant size (lake trout).

The calculated current concentrations can be used in risk assessment paradigms to determine the potential effects on fish and fish consumers. For example, it has been reported that lake trout reproduction is adversely effected by bluesac syndrome at 60 ppt dioxin toxic equivalents (TEQ) (Cook et al. 1997). Lake trout only naturally reproduce in parts of Lake Superior. Because PCB co-planar congeners comprise a large fraction of the TEQ in lake trout (Williams et al. 1992), the measured concentrations can be converted to TEQ and used to assess reproduction potential or to predict when this potential might occur in the future. Similar assessments can be made for the potential effects to fish consuming birds such as eagle and tern, to mink, etc (Kubiak 1989, Giesy et al. 1994a, Giesy et al. 1994b, Giesy et al. 1995).

The Minnesota Department of Health (MDH) has agreed to cooperate with the calculation of human health consumption advisories using a risk assessment approach agreed upon by the Great Lakes states.

Data will be reported to GLNPO as described in other sections of this QAPP. Data will be reported using the GLNPO Reporting Standard for the Analysis of Contaminants in Fish Tissue. In addition, in cooperation with the GLNPO Project Officer we will disseminate the data and the results of our interpretation in reports, presentations, and peer-reviewed journal articles.

B5. Quality Control Requirements

The Method Quality Objectives are provided in Section A7 and summarized in Table 2. The definitions and equations for assessing attainment of QC objectives are provided below.

B.5.1. Precision

Precision is a quantitative measure of the agreement between two or more measurements of the same parameter. It provides a measure of relative uncertainty about a given measurement. Overall precision of the program is determined by the uncertainty around the mean of the composites for a given lake, site, and year. Laboratory precision will be assessed through analysis of duplicate composite samples (lab duplicates) at a rate of 5%. A replicate lab sample (LDn) is defined as a second analysis of a given composite.

For duplicate measurements, the relative percent difference (RPD) is calculated as follows:

$$\text{RPD} = \frac{| \text{Ca} - \text{Cb} |}{[(\text{Ca} + \text{Cb}) / 2]} * 100\%$$

where

RPD = relative percent difference

Ca = measurement in the sample

Cb = measurement in a duplicate of that sample

Duplicates must agree within 50% analytes for a given analyte. For replicate measurements where $n > 2$, precision is described by the standard deviation or 95% confidence limit.

B.5.2. Accuracy

Accuracy is the degree of agreement between an observed value and an accepted reference or “true” value. It provides a measure of absolute uncertainty about a given measurement. Accuracy will be assessed using check samples, laboratory spikes and surrogate recovery spikes.

Check samples consist of a pooled lake trout sample (provided by USGS-BRD and consisting of 1994 Lake Michigan Sturgeon Bay lake trout) that has been analyzed 10 times prior to the start of the project samples to establish its estimated “true” value. Check samples will be included with at least every 3 sample sets resulting in a minimum of 10 check samples per year. Analytes concentrations must be between 65% - 135% of the initial value. If the check sample recovery exceeds these criteria, all extractions are halted and the procedures are checked by running duplicate laboratory spike samples (see below). Once acceptable laboratory spike recoveries are obtained, the check sample is analyzed until acceptable recoveries are obtained.

Laboratory spike samples consist of the solvent and reagents used to extract the sample that are spiked with representative levels of the analytes, and subsequently treated as a sample through the analytical procedure. Duplicate laboratory spike samples are analyzed at the beginning of the project, and thereafter run only if a check sample recovery fails acceptable criteria. This sample is used to diagnose the poor recovery and then used to check any adjustments made to the analytical procedure.

Surrogate spikes are added to every sample, blank and standard, and consist of compounds having similar structures to the analytes of interest. They are used to monitor any loss of analyte due the sample extraction and analysis. The frequency of inclusion and criteria used to evaluate accuracy are found in Table 2 (Section A.7). The acceptable criteria for spike recoveries are 50% - 120%. If the criteria are exceeded, the sample is flagged but not necessarily considered invalid. The data are examined and expert judgment are used to assess whether the sample needs to be re-extracted or whether the sample data are still considered to be valid.

The percent recovery for the check samples and the surrogate and matrix spikes is calculated according to the following formula:

$$\%R = [\text{Measured} / \text{Actual}] * 100\%$$

where

%R = percent analyte recovery

Measured = mass of analyte measured in the sample

Actual = mass of analyte added to (spikes) or contained in (check samples) the sample

B.5.3. Representativeness

Representativeness expresses the degree to which a sample from a given site is representative of that site or area, and the matrix from which it was taken and to what degree the sample accounts for analyte heterogeneity in the matrix.

Representativeness is dependent upon the proper design of the sampling program. Fish samples are collected by other agencies, and thus sampling representativeness is not addressed in this project. Sample representativeness is addressed by collecting large numbers of fish, and compositing 5 similar size/weight individuals. Analytical representativeness will be maximized by thoroughly homogenizing the sample prior to taking a subsample for analysis.

B.5.4. Comparability

Comparability is an expression of the confidence with which one data set can be compared with another either between laboratories or within the same laboratory over time.

The data generated from this project will be used with data generated by other laboratories (USGS-BRD, Food and Drug Administration labs) to assess time trends in fish contaminants. Thus between-lab comparability is essential to the success of the project. Data comparability will be ensured by the analysis of the lake trout check or reference samples. These samples are derived from a large pool of homogenized lake trout tissue (1994 lake trout from Sturgeon Bay, Lake Michigan) that were used as check samples by USGS-BRD. A minimum of 10 check samples will be run at the beginning of the project, and for each years' samples. Data will be considered comparable if the results are within 95% confidence limits of the mean obtained by USGS-BRD (beginning of project) and $\pm 35\%$ of the mean of the initial 10 check fish analyses by UMN (during the project). In addition, fish tissue from previous years' collections is available for analysis by this laboratory.

Within-project data comparability will be ensured in this study because all analyses of a given parameter will be conducted by the same laboratory using consistent personnel and methods. Any data comparisons in this project will be made on surrogate recovery-corrected data. .

B.5.5. Completeness

Completeness is the percentage of acceptable data needed to validate the study. It is calculated as the number of valid samples divided by the number of samples collected to meet the project objectives, multiplied by 100. Our QA objective for completeness is 95%. This is a goal and not a requirement of the program. Samples passing the MQOs in Table 2 would be considered valid. Invalid samples would be those lost during processing or analysis, those containing unacceptable levels of interferences, or failing QA objectives in certain cases. A flagged result would not necessarily indicate that the result was invalid. For instance, samples flagged with MDL would not be considered invalid. Other data failing one MQO may be judged valid after review of the data. For example, a sample with low surrogate recovery may be considered valid if the data are consistent with other data and the low recovery can be attributed to a known cause such incorrect spike amount. Data judged to be invalid by the PI after review will be flagged with the QC identifier INV.

B.5.6. Blanks

Field blanks are blank sample matrices that contact the sampling equipment, are transferred to a sample container and are then treated identically to the test samples. They are used to assess contamination from the matrix, sample containers and field equipment involved in sampling. There are no applicable matrix blanks in this study.

Laboratory procedural blanks consist of all reagents used in the volumes required for the analyses carried through the entire analytical procedure in the same manner as a sample. A laboratory procedural blank is run with each set of sample extractions (a set consists of 6 extractions) and is used to assess contamination resulting from laboratory procedures. Surrogate standards are spiked into the laboratory blanks in the same manner as for samples. All contaminant concentrations should be less than or equal to the method detection limit. Sample results will not be corrected for blank values; analyte concentrations in the samples and blanks will be reported and the blank flagged if greater than the MDL. If a blank value is greater than 15% of the analyte mass in an extract from the same sample set, that sample will be re-analyzed.

B.5.7. Detectability

Sensitivity can be evaluated at three levels: instrument sensitivity, analytical method sensitivity and overall system sensitivity.

The instrument detection limit (IDL) is the minimum response of the instrument above which you have confidence that the analyte response is greater than the background noise of the instrument. It is determined by running a calibration curve and extrapolating back to the y-intercept. This is done once at the beginning of the project using a minimum of four concentrations in duplicate over at least 2 orders of magnitude in concentration. It is not necessary to determine this more frequently as the IDL is orders of magnitude below the MDL and is not used in any quantitative way in data review.

Analytical sensitivity is defined as the method detection limit (MDL) that is the minimum concentration above which you have confidence that the analyte was present or not. The MDL

for 99% confidence is defined as 3 standard deviations of 7 runs of a blank spiked with a very low level of analyte (40 CFR Part 136, Appendix B, Rev.1.11, October 26, 1984).

The target MDLs for all analytes are shown in Table 3 (below). All sample data are examined as to whether the response is below the MDL. For PCBs and toxaphene, homologs that are below the MDL are considered as zero when summing to determine total concentrations. In data aggregation, processing, and interpretation, values below the MDL are considered as zero.

The overall sensitivity includes influences and uncertainties from the sample collection process and from sample matrices and is the minimum concentration above which you have confidence the analyte was present or not. The system detection limit (SDL) for 99% confidence is defined as three standard deviations of 7 field matrix blanks collected over the course of the project. This measure is not applicable to this project as there are no matrix field blanks, and the project does not have responsibility for the sample collection and processing.

B6. Instrument / Equipment Testing, Inspection and Maintenance

The GC-MS performance is evaluated daily by examining the daily tuning performance standard octafluoronaphthalene (OFN) prior to the day's runs and by the evaluation of a performance standard included in the day's runs. The instrument is inspected daily for pressures and temperatures. Any deviation from the set pressures and temperatures would require the termination of any runs and a complete evaluation of the instrument. Routine maintenance of the instrument includes 2-3 source cleanings per year, pump oil changes every 3-4 months and clipping of the front of the column and injection port cleanings every 5-6 months. A maintenance agreement is in place to address any malfunctions and necessary repairs.

Balance performance is evaluated prior to use by calibration. If a balance cannot be calibrated, the balance will be thoroughly evaluated and sent to the manufacturer for repairs if necessary.

B7. Instrument / Equipment Calibration and Frequency

The GC-MS is tuned approximately every 2 - 3 weeks. The decision to re-tune the instrument is based on evaluating a daily injection of the performance standard, OFN. The peak area, shape and electron multiplier setting (sensitivity) are all subjectively evaluated by a trained operator. If re-tuning is judged to be necessary, the instrument is tuned in negative ion mode. If the instrument is shut down for maintenance or repair, it is first tuned in electron impact mode and then tuned in negative ion mode. All tuning observations, runs and maintenance activities are recorded in a dedicated GC-MS logbook. The calibration response factors used for quantitation are determined from a set of no less than 3 standards run at the same time as a given set of samples (see section B.4.3.).

Balances are calibrated using standard calibration weights every time the balance is used. This is standard operating procedure and is not recorded separately from the weighing activity.

Pipets and glassware are not calibrated because either we do not need to know the amounts of reagents to an extreme degree of accuracy (e.g. 150 mL of solvent added to a Soxhlet extractor),

or the amount that is measured must be very precise but not necessarily very accurate. An example of the latter would be the addition of 50 µL of internal standard solution that is added to every extract using a micropipetter. Because the same pipetter is used for every measurement, the volume added is exactly the same. If the pipetter is replaced, it is calibrated to the previous pipetter by replicate amounts of water that are measured both volumetrically and gravimetrically.

B8. Inspection/Acceptance of Supplies and Consumables

Supplies and consumables include solvents, chemicals, paper supplies, computer supplies, and instrument parts. Items where quality lapses would affect the outcome of the project include solvents and chemicals.

Solvents are unpacked on arrival and placed in solvent storage by the lab technician. Neat standards are kept in the freezer after labeling. Other reagents are kept in the chemical storage in the laboratory. Standards are evaluated after dilution to working standards, when they are compared to existing working standards. Concentrations must agree to within 10%. Reagent quality is monitored by the appearance and acceptability of lab procedural blanks.

B9. Non-direct Measurements

There are no data required from non-measurement sources for the implementation of this project.

B10. Data Management

The sample extracts are injected into the GC-MS, and the resulting ion chromatograms are acquired electronically. All chromatograms will be examined visually for quality of baseline resolution and accuracy of the integration by laboratory personnel, and for spurious peaks that may interfere with the desired signal. After baselines have been reviewed and set, samples will be quantified using the peak areas determined by Hewlett-Packard ChemStation software via a macro program compared to those of the analytical standards. The areas are transferred electronically to a spreadsheet that is processed by a Basic program that filters the data to remove those data that do not meet confirmation criteria. These filtered data are electronically transferred to a Microsoft Excel spreadsheet, which is pre-formatted to calculate masses, concentrations, quality assurance parameters (e.g. precision, accuracy, surrogate recoveries), and flag non-compliant data. The use of a pre-formatted spreadsheet reduces the potential for calculation errors in data handling. The result of the performance standard serves to check for mistakes and errors in the use of the macros and spreadsheets. All concentrations will be calculated using the internal standard method relative to the internal standard PCB #204 as follows:

$$\text{mass} = \text{area}_{\text{analyte-ion}} \times \text{RRF} \times [(\text{mass}_{\text{istd}})/(\text{area}_{\text{istd-ion}})]_{\text{sample}}$$

where RRF = relative response factor of the quantitation standard:

$$\text{RRF} = [(\text{mass}_{\text{analyte}})/\text{area}_{\text{analyte-ion}}]/[(\text{mass}_{\text{istd}})/\text{area}_{\text{istd-ion}}]$$

If the internal standard fails QA criteria (Table 2), the sample will be evaluated for errors and flagged.

The analyte concentrations are calculated as:

$$\text{concentration} = (\text{mass of analyte})/(\text{mass of wet fish tissue})$$

The final data are corrected for surrogate recovery as follows:

$$\text{concentration, corrected} = (\text{concentration} * 100) / \% \text{ surrogate recovery}$$

All QA data are reviewed for acceptability, and all flagged data are carefully examined to attempt to understand the specific problem in that sample. Based on professional judgment, some data are still considered acceptable even if the surrogate recovery was not acceptable, and vice versa. The PI examines all final data.

All chromatographic data are backed up on magnetic tape. All Excel files are backed up on CDs. All electronic files are also permanently archived, with the archived files kept off-site. Hard copies of spreadsheets are also generated and kept in notebooks.

SECTION C. ASSESSMENT AND OVERSIGHT

C1. Assessment and Response Actions

Dr. Swackhamer will monitor all project-related laboratory activities. Any irregularities in staff performance or deviations from lab protocols that affect sample data quality will be corrected and noted in the laboratory book. Internal performance and system audits of laboratory activities will be conducted periodically by the PI to verify that analyses are performed in accordance with the procedures established in this QAPP. All corrective actions resulting from internal audits will be recorded in laboratory notebooks, and indicated with appropriate QC codes.

Corrective actions that are analytical in nature include the following: Samples not meeting the MQO for surrogate or procedural spike recoveries will be rerun to rule out artifacts of instrumental analysis. If the samples are still out of compliance, a second batch of those samples will be re-extracted and re-analyzed. Data not meeting QA accuracy criteria will be flagged. Dr. Swackhamer will determine if data should be judged valid.

If the MQOs regarding laboratory and field blanks are exceeded, the samples associated with the set will be evaluated for consistency with previous data sets and the reagents will be checked for purity. If the mass in the blank is <15% of the mass in the associated samples, the sample data will not be flagged. If the data are of questionable quality following these control actions, these samples will be flagged appropriately.

All data validation procedures and corrective actions are listed in the Table 2. Following corrective action, project validity will be determined by calculating completeness as described previously.

The results of this project may be published, and if so will undergo anonymous outside peer review by experts in the field.

C2. Reports to Management

The PI will provide semi-annual progress reports to the EPA Project Officer summarizing all progress to date, results of any performance or internal audits, interim data quality assessments and any notable lapses in quality assurance and plans for addressing these problems. A Final Project Report will be provided to the EPA Project Officer at the end of the project that includes all data and data interpretation.

SECTION D. DATA VALIDATION AND USABILITY

D1. Data Review, Verification and Validation

All data meeting the Measurement Quality Objectives (Table 2) will be considered acceptable and usable by the project. Data having any QA qualifiers will be carefully examined to determine if the qualifier invalidates the data, or whether the data are still judged acceptable despite the QA qualifier based on professional judgment of the PI. For example, if the concentration of an analyte in the blank is greater than the MDL, but less than 15% of the sample masses in the associated samples, the sample data from that set will be accepted without flagging even though the blank for that set will be flagged.

Every sample set will contain a procedural blank so that laboratory conditions and methods are evaluated on a regular and frequent basis. Procedural blanks with the analyte present greater than the MDL will be considered unacceptable. If these criteria are exceeded, all reagents will be checked before proceeding with additional analyses, and the associated sample sets will be checked against previous ones for self-consistency. If the sample data or reagent purity is questionable, samples will be re-extracted or flagged if no further sample is available. If sample data are consistent with previous data, reagent blanks are acceptable, or the mass of the blank is <15% of the sample mass, then the data will be accepted without flagging. The procedural, field or matrix blanks will not be subtracted from the sample concentrations in any case, but will be reported.

D2. Verification and Validation Methods

The PI will review all data generated by her staff, and conduct occasional audits of the systems and procedures used in the project. The use of laboratory spikes, check samples, and performance standards serves to verify that the systems and procedures are working correctly and to validate the results of the project.

D3. Reconciliation with User Requirements

The MQOs have been designed to provide data having a given uncertainty such that the DQOs of the GLFMP will be met.

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