Quality Assurance Project Plan

PBT Monitoring: Measuring Perfluorinated Compounds in Washington Rivers and Lakes

by

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May 2008

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SWFAP – Solid Waste and Financial Assistance Program
EAP - Environmental Assessment Program
EIM - Environmental Information Management system

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Abstract

This Quality Assurance (QA) Project Plan is provided for analyzing perfluorinated compounds (PFCs) in selected rivers and lakes in Washington State. PFCs are an emerging contaminant used as a processing aid in the manufacture of fluoropolymers which have many useful properties such as the ability to repel oil, water, and grease.

The goal of the study is to evaluate the spatial distribution of PFCs in Washington State and to determine concentrations at which these contaminants are found. The data will be used in the preparation of a future Chemical Action Plan that will identify steps the state may take to further reduce the threat of PFCs in the environment.

During the spring and fall, PFC concentrations in water will be determined at 14 freshwater locations and from effluent at 4 wastewater treatment plants. Fish muscle, livers, and eggs will be analyzed at 8 of the freshwater locations. Additionally, PFC concentrations in osprey eggs will be determined from nests along the lower Columbia River. Sampling will be conducted from May - November 2008.

Each study conducted by the Washington State Department of Ecology must have an approved QA Project Plan. The plan describes the objectives of the study and the procedures to be followed to achieve those objectives. After completion of the study, a final report describing the study results will be posted to the Internet.

Background

Perfluorinated compounds (PFCs) are relatively contemporary chemicals used in hundreds of industrial and consumer applications for their surfactant[1] properties. These applications include stain resistant coatings for clothing and carpet, fire-fighting foams, paints, adhesives, waxes, and polishes (Renner, 2001).

The Washington State Department of Ecology (Ecology) has identified and listed the PFC compound Perfluorooctane-sulfonate (PFOS) as a persistent, bioaccumulative, toxic chemical (PBT). PFOS meets the PBT criteria specified in Section 320 of Chapter 173-333 WAC (Persistent Bioaccumulative Toxins Regulation) and is listed on the PBT List in this regulation. Ecology and the Washington State Department of Health are planning to prepare a Chemical Action Plan in the future which will identify steps the state may take to reduce the threat of PFCs such as PFOS in the environment.

"PFCs" is a generic term for a family of perfluoroalkyl acids (PFAAs) that contain a carbon backbone and a charged functional group (typically carboxylate or sulfonate). The two most widely known PFAAs are perfluorooctanoic acid (PFOA) and perfluorooctane sulfate (PFOS). The carbon-fluorine bonds, from which these compounds are constructed, are among the strongest in organic chemistry and render the acids practically non-biodegradable (Lau et al., 2007).

PFCs have been produced for over 50 years, primarily through electrochemical fluorination and telomerization techniques (Giesy and Kannan, 2002). Historically, PFOS was produced in much greater quantities than PFOA, but since the primary manufacturer of PFOS, 3M Company, phased out production in 2002, PFOA is now the most common PFC in commerce. In 2006, the U.S. Environmental Protection Agency (EPA) began a PFOA stewardship program in which 8 major PFOA producers have committed to reducing the manufacture of PFOA by 95% no later than 2010 (EPA, 2006a). It is unknown if other PFAAs will be produced to fill the commercial void.

PFCs are widespread and found in virtually all media (human serum, surface waters, rain, air, soils, sediments, ice caps, animal tissue) around the globe (Giesy and Kannan, 2001; Kannan et al., 2004). Currently, two major sources have been suggested to account for the widespread distribution of PFCs in the environment: (1) direct discharge from consumer products and industrial processes and (2) degradation of fluorotelomer alcohols (FTAs) to PFCs in the environment (Kim and Kannan, 2007). FTAs are major raw materials used in fluorosurfactant production (Ellis et al., 2004).

The surfactant properties of PFAAs impart unique physical characteristics controlled by a hydrophilic anionic head group and a hydrophobic perfluorinated tail, with overall lipophobic characteristics. The K_{ow} value, measuring the equilibrium concentration of a compound between octanol and water, is a problematic parameter to measure due to the chemical's tendency to concentrate at a liquid-liquid interface (Martin et al., 2003).

[1] Substances that reduce the surface tension of a liquid. Detergents and emulsifiers are surfactants.

The low Henry's law constant, used to predict equilibrium concentrations in a gas/liquid system, suggests the concentrations will preferentially accumulate in aquatic environments (Martin et al., 2003). Subsequently, environmental monitoring of PFCs has largely surrounded aquatic environments (Gannon et al., 2006; Kannan et al., 2005). In general, the highest levels of PFCs have been found in the livers of fish-eating animals (Lau et al., 2007).

Despite the recent advances in analytical techniques measuring PFCs in the environment, the exposure pathways and toxicokinetics of the compounds are poorly understood. Recently the EPA has labeled PFOA and its salts "likely to be carcinogenic" (EPA, 2006b). Epidemiological studies conducted by 3M have not shown PFOA to affect human health. However, PFOA animal tests have shown the chemical to be toxic at high concentrations (Kudo and Kawashima, 2003).

Currently, the only data describing PFC contamination in Washington State are from a national study of concentrations in otter and mink livers. River otters were collected from 4 Puget Sound locations and the Soleduck River. PFOS concentrations were found to be higher in otters from the more urbanized sites (Kannan et al., 2002).

In view of the lack of data and potential carcinogenic effects, Ecology's Environmental Assessment (EA) Program will conduct a statewide survey of PFCs to characterize the current levels of these contaminants. The survey will be conducted during 2008 and will study fish, surface water, wastewater treatment plant (WWTP) effluent, and osprey egg samples.

Project Description

The EA Program will conduct a one-time statewide study during 2008 to measure selected PFC concentrations in resident fish (livers, muscle, and eggs), surface waters, WWTP effluents, and osprey eggs. The goal of the study will be to establish baseline conditions in a variety of matrices (sample types) statewide.

The primary goals of the study are to:

- Determine current levels of PFCs in selected freshwater areas of Washington.
- Evaluate spatial and seasonal concentration patterns.
- Provide data to aid in designing a Chemical Action Plan for controlling PFCs within the state.

Sampling for PFCs will include:

- 14 surface waters (rivers and lakes) during the spring and fall.
- 4 WWTP effluents during the spring and fall.
- Fish livers of 2 species from a subset of 8 waterbodies.
- Fish muscle of 1 species from the 8-waterbody subset.
- Fish eggs of 1 species from the 8-waterbody subset.
- Approximately 4-6 osprey eggs along the lower Columbia River.

Field work will be conducted during May – November 2008. The EPA Office of Research and Development (ORD) will provide the analytical work measuring the PFCs listed in Table 1.

Results from the study will be used to assess seasonal changes and to apply relative contamination rank among waterbodies.

Table 1. PFC compound list.

Name	Acronym	Structure
Perfluorobutane sulfonate	PFBS	$C_4F_9SO_3^-$
Perfluorohexane sulfonate	PFHxS	$C_6F_{13}SO_3^-$
Perfluorooctane sulfonate	PFOS	$C_8F_{17}SO_3^-$
Perfluorohexanoic acid	PFHxA	$C_5F_{11}COOH$
Perfluoroheptanoic acid	PFHpA	$C_6F_{13}COOH$
Perfluorooctanoic acid	PFOA	$C_7F_{15}COOH$
Perfluorononanoic acid	PFNA	$C_8F_{17}COOH$
Perfluorodecanoic acid	PFDA	$C_9F_{19}COOH$
Perfluorundecanoic acid	PFUnA	$C_{10}F_{21}COOH$
Perfluorododecanoic acid	PFDoA	$C_{11}F_{23}COOH$

Organization and Schedule

The responsibilities of various staff and the project schedule are shown in Tables 2 and 3.

Table 2. Organization of project staff and responsibilities.

Staff (EAP unless noted otherwise)	Title	Responsibilities
Chad Furl Toxics Studies Unit (360) 407-6060	Project Manager/ Principal Investigator	Writes the QAPP, oversees field sampling and transportation of samples to the laboratory, conducts QA review of data, analyzes and interprets data, and writes the draft report and final report.
Callie Meredith Toxics Studies Unit (360) 407-6965	Field Lead/ EIM Data Engineer	Leads sample collection and enters data into EIM.
Dale Norton Toxics Studies Unit (360) 407-6765	Unit Supervisor	Provides internal review of the QAPP, approves the budget, and approves the final QAPP.
Will Kendra Statewide Coordination Section (360) 407-6698	Section Manager	Reviews the project scope and budget, tracks progress, reviews the draft QAPP, and approves the final QAPP.
Mike Gallagher Industrial Section, SWFAP (360) 407-6868	EAP Client	Clarifies scope of the project, provides internal review of the QAPP, and approves the final QAPP.
Carol Kraege Industrial Section, SWFAP (360) 407-6906	Section Manager	Clarifies scope of the project, provides internal review of the QAPP, and approves the final QAPP.
Stuart Magoon Manchester Environmental Laboratory (360) 871-8801	Director	Approves the final QAPP.
John Weakland Manchester Environmental Laboratory (360) 871-8820	Unit Supervisor	Provides QA review of data provided by EPA.
Mark Strynar EPA ORD (919) 541-3706	Lead Chemist	Oversees sample analysis.
William R. Kammin (360) 407-6964	Ecology Quality Assurance Officer	Reviews the draft QAPP and approves the final QAPP.

EAP – Environmental Assessment Program
EIM – Environmental Information Management system
QAPP – Quality Assurance Project Plan
SWFAP – Solid Waste and Financial Assistance Program
EPA ORD – Environmental Protection Agency Office of Research and Development

Table 3. Proposed schedule for completing field and laboratory work, data entry into EIM, and reports.

Field and laboratory work	
Field work completed	November 2008
Laboratory analyses completed	February 2009
Environmental Information System (EIM) system	
EIM data engineer	Callie Meredith
EIM user study ID	cfur0003
EIM study name	PBT monitoring: Measuring PFC Levels in Washington
Data due in EIM	June 2009
Final report	
Author lead	Chad Furl
Schedule Draft due to supervisor Draft due to client/peer reviewer Draft due to external reviewer Final report due on web	 March 2009 April 2009 May 2009 June 2009

Quality Objectives

The EPA ORD staff is expected to meet all quality control (QC) requirements of the analytical methods being used for this project. Table 4 displays the measurement quality objectives (MQOs) that will be used to assess the data quality. Based on available literature, the lowest concentrations of interest should be sufficient to detect the majority of PFCs at waterbodies influenced by urban activity.

Table 4. Measurement quality objectives.

Analysis	Lab Control Samples (% recov.)	Laboratory Duplicates (RPD[a])	Method Blanks	Matrix Spike (% recov.)	Field Replicates (RPD %)	Lowest Concentrations of Interest
PFCs	50-150%	± 50%	< LOQ[b]	50-150%	± 50%	1 ng/L in water 0.2 ng/g in tissue[c]

[a] Relative percent difference
[b] Limit of quantitation (lowest quantifiable amount for the method)
[c] Tissue LOQs for PFOS, PFHxA, and PFHpA are 0.2 - 1.0 ng/g

Study Design

Due to the increased potential for PFC contamination in urban areas, water and fish sampling will primarily focus on freshwater areas located near urban settings. Background concentrations will also be characterized through sampling of remote, relatively undisturbed watersheds. Sites proposed for PFC sampling are listed in Table 5, and their locations are shown in Figure 1.

Table 5. Proposed sampling plan.

Name	Water Samples	Fish Samples	WRIA	County	Contamination Potential
Surface Waters					
Duwamish/ Green River	SP, F	F	9	King	High
Lake Washington	SP, F	F	8	King	High
Lower Columbia River	SP, F	F	25	Wahkiakum	High
Puyallup River	SP, F	---	10	Pierce	High
Snohomish River	SP, F	F	7	Snohomish	High
Spokane River at Nine Mile	SP, F	F	54	Spokane	High
South Fork Palouse River	SP, F	---	34	Whitman	High
Columbia River at McNary Dam	SP, F	---	31	Benton	Medium
Franklin D. Roosevelt Lake	SP, F	---	53	Lincoln	Medium
Upper Columbia River	SP, F	---	61	Stevens	Medium
Nooksack River	SP, F	---	1	Whatcom	Medium
West Medical Lake	SP, F	F	43	Spokane	Medium
Entiat River	SP, F	F	46	Chelan	Low
Quinault River	SP, F	F	21	Jefferson	Low
Wastewater Treatment Plants					
Marine Park	SP, F	NA	28	Clark	---
Sumner Municipality	SP, F	NA	7	Pierce	---
Spokane Municipality	SP, F	NA	54	Spokane	---
Medical Lake Municipality	SP, F	NA	43	Spokane	---
Osprey Collection Area					
Columbia River from RM 28 through RM 236	SP	NA	25 - 31	Wahkiakum, Cowlitz, Clark, Skamania, Klickitat, Benton	---

SP = Spring; F = Fall
WRIA = Water Resources Inventory Area
RM = River Mile
NA = Not applicable

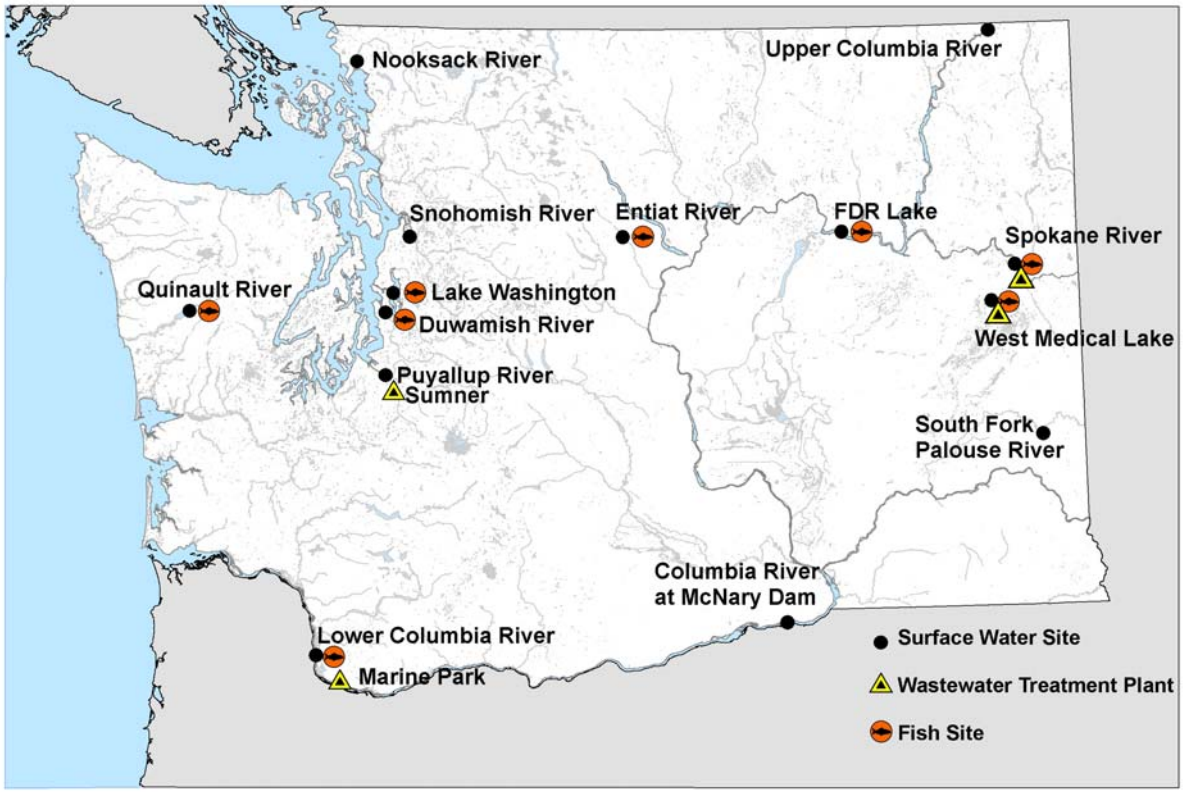

Figure 1. Proposed locations for PFC sampling.

The 14 surface water sites will be sampled during May and October to assess the seasonality of PFC levels. Sampling during these periods will capture spring runoff and summer low-flow conditions (Johnson, 2007). Other Washington State studies have found the highest levels of chlorinated pesticides, PCBs, and PBDEs occurring during these time periods (Coots and Era-Miller, 2005; Joy and Patterson, 1997; Johnson et al., 2004). Flow data from the nearest USGS gaging station will be reported on for each waterbody.

Sampling at the 4 WWTPs will occur concurrently with surface water sampling. WWTPs have been identified as pathways for PFCs into surface waters (Sinclair and Kannan, 2006). The selected WWTPs discharge into surface waters being sampled by this study and represent a range of flow capacities and sources (domestic and domestic/industrial).

During August – October 2008, two species of fish will be collected from 8 of the surface water sites for analysis of muscle, liver, and eggs. Fall spawning species will be targeted in an attempt to acquire eggs. Livers will be tested in both species while only one species will be analyzed for muscle and eggs. Where possible, the species will be from different trophic levels to assess biomagnification. Fish samples will consist of a composite of 3-5 individual fish.

Conductivity, pH, and temperature measurements will be recorded in the field at all surface water, WWTP, and fish collection sites.

During May 2008, osprey eggs will be collected from the lower Columbia River in conjunction with U.S. Geological Survey (USGS) osprey monitoring (Henny et al., 2008). Osprey feed almost exclusively on fish near their nests, making them a useful biomonitoring species. Additionally, little data are available describing PFC concentrations in osprey eggs (Rattner et al., 2004; Toschik et al., 2005) Eggs will be tested from approximately 4 - 6 sites located between McNary Dam and the mouth of the Columbia (river miles 28-286). The number of eggs analyzed will largely depend on the success of the USGS collection effort.

All project samples will be analyzed for the 10 PFCs listed in Table 1.

Sampling and Preparation Procedures

Fish

The collection, handling, and processing of fish tissue samples are guided by methods described in the EPA's *Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories* (EPA, 2000) and the EA Program's *Standard Operating Procedures for Resecting Finfish Whole Body, Body Parts or Tissue Samples* (Sandvik, 2006). Fish will be collected using boat electrofishing, netting (gill and/or fyke nets), or hook and line.

Fish will be inspected to ensure that they are acceptable for further processing (e.g., no obvious damage to tissues, skin intact). Acceptable fish are euthanized by a blow to the head with a dull object, rinsed in ambient water to remove foreign material from their exterior, weighed to the nearest gram, and their total lengths measured to the nearest millimeter. Individual fish are double-wrapped in foil and placed in a plastic zip-lock bag along with a sample identification tag. The bagged specimens will be placed on ice in the field. Fish will remain on ice until frozen at –20° C at Ecology facilities in Lacey, Washington for processing at a later date.

For processing, fish will be removed from the freezer, partially thawed, processed for slime and scales removal, and rinsed in tap water, followed by a rinse in deionized water. Livers and eggs will be removed before the fish are filleted, skin-off. Three to five individual fish will be used for each composite sample when available. To the extent possible, the length of the smallest fish in a composite will be no less than 75% of the length of the largest fish (EPA, 2000).

The composites will be prepared using equal weights from each fish. Muscle samples will be passed three times through a Kitchen-Aid food grinder and stirred to a consistent texture and color. Egg and liver samples will be ground using a sonicator homogenizing device designed for preparation of small samples (< 5g). Subsamples from the homogenate will be placed into pre-cleaned containers provided by the laboratory. Sample jars will be assigned a laboratory identification number and shipped to the laboratory for analyses. Excess homogenate will be labeled and archived frozen at –20° C.

After all desired tissue is removed, the sex of the fish will be determined, when possible, and recorded. Otoliths and scales will be removed from fish to be analyzed and sent to Washington Department of Fish and Wildlife biologists to determine age.

All utensils used for processing tissue samples will be cleaned to prevent contamination of the sample. Utensils include stainless steel bowls and knives as well as tissue grinding appliances having plastic, wood, bronze, and stainless steel parts. All utensils for fish tissue sampling will be cleaned with the following procedure: hand washed with soap (Liquinox) and hot water, hot tap water rinse, and 100% methanol rinse. Utensils will be air-dried and wrapped in aluminum foil until used. Fish will be filleted and tissues processed on the dull side of heavy-duty aluminum foil covering a nylon cutting board laid on the workbench. Each fish will be processed on a new/clean sheet of aluminum foil with clean utensils to prevent contamination from one sample to the next.

Water

Water samples will be collected in pre-cleaned (methanol-rinsed), high-density polypropylene (HDPP) containers provided by the EPA ORD. Teflon bottles and teflon-lined caps along with other fluoropolymer materials will not be used throughout sampling to reduce sample contamination. Glass will also be avoided as PFCs have been shown to bind to glass surfaces in aqueous solutions (Hansen et al., 2002).

Samples will be collected as near-surface grabs (15-30cm below water) from as close to the thalweg as possible for streams. The thalweg is the deepest and fastest moving portion of the stream. Lakes will be sampled using the same near-surface grab technique from an area as far away as possible from surface water inputs and the shoreline. Samples will be retrieved with a stainless steel Kemmerer or a homemade hand dipper consisting of a sample bottle attached to a polyethylene pole. The Kemmerer will be decontaminated between sampling locations with a tap water rinse and a 100% methanol wash.

Multi-point, depth integrated composite samples were considered, but the majority of historical studies characterizing PFCs in surface waters were sampled in the manner described above (Taniyasu et al., 2003; Seung-Kyu and Kannan, 2007; Nakayama et al., 2007; Sinclair et al., 2006).

WWTP effluents will be sampled from final dechlorinated effluent. Samples will consist of composites of a morning and afternoon grab. Grabs will be taken with a methanol-rinsed HDPP bottle and composited in a new clean 1000 mL HDPP bottle.

The latitude and longitude of the WWTP sampling locations and other sampling locations will be located by GPS and recorded in field logs. Flow data will be obtained from WWTPs for loading calculations (concentration x flow). Water samples will be returned to Ecology headquarters and stored at room temperature until shipment to the laboratory. Conductivity, pH, and temperature measurements will be made at all 14 surface water and 4 WWTPs using an Orion multimeter and recorded in field logs.

Osprey Eggs

Partially incubated osprey eggs will be collected during the spring of 2008 in conjunction with USGS long-term monitoring along the Columbia River. Eggs will be collected from accessible nests (generally channel markers) along the river. Egg contents will be homogenized by USGS staff, avoiding contact with fluoropolymers, and placed in the proper pre-cleaned jars. Sample material will be frozen until analysis.

Measurement Procedures

Chemical Analyses

Analytical methods used to quantify PFCs in various environmental matrices are still research methods under continuous development. Water and fish tissue samples will be prepared and analyzed using a modification of a method described by Taniyasu et al. (2003). A description of measurement procedures from the EPA ORD laboratory can be found in Nakayama et al. (2007) and Xibiao et al. (2008 article in press).

Briefly, PFCs will be analyzed using an Agilent 1100 high-performance liquid chromatograph (HPLC) coupled with a PE Sciex API 3000 triple quadrupole mass spectrometer (LC/MS/MS). Six to 8 point quantitation curves will be produced for each matrix through spiking deionization (or reference tissue) with various amounts of target PFCs along with 2 internal standards (18O-PFOS and 13C-PFOA) to produce a quantifiable range of 1 – 500 (ng/L and ng/g). All extracts will be prepared by the laboratory using either Oasis HLB Plus or WAX cartridges.

Low levels of background contamination are unavoidable due to fluoropolymer fittings and parts on the analytical instrumentation. To keep contamination to a minimum, the entire system is flushed with 100% methanol prior to analysis. Additionally, no more than 1 ng/g of any PFC is injected on column at any time.

Issues surrounding holding times for water samples are uncertain. Therefore, water samples will be collected and analyzed as quickly as possible. The project manager will strive to have the analysis completed within 14 days of collection. Holding times for frozen tissue samples are not an issue.

Table 6 contains the expected range of PFOA and PFOS concentrations for the different matrices, based on review of the literature

Table 6. Expected PFOA and PFOS range.

Sample Type	Expected Range
Fish muscle	LOQ - 50 ng/g ww
Fish livers	LOQ - 100 ng/g ww
Fish eggs	LOQ - 200 ng/g ww
Water	LOQ - 50 ng/L
Effluent	25 - 1000 ng/L
Osprey eggs	25 - 500 ng/g ww

LOQ – limit of quantitation
ww – wet weight

Quality Control

Field

Field QC for water samples will consist of blanks and replicates. A replicate sample will consist of a separate sample taken immediately after the first sample using the same sampling technique. Replicate surface water samples will be taken at 1 or 2 study sites. Replicates will be divided equally between spring and fall sampling. One WWTP site will include replicate sampling.

Field blanks will be provided by the laboratory. Blank water will be shipped to the project manager, transported to the field, and be treated as a normal sample. A portion of the blanks will be passed through the Kemmerer to determine contamination introduced from this sampling method. The number of samples tested in this manner will correspond with the percentage of sites sampled with the Kemmerer. All field blanks will be returned to the laboratory and treated as normal samples.

No field QC samples will be analyzed in conjunction with the fish sampling or osprey egg collection. Field variability is being addressed in fish sampling by analyzing composite samples. Collection of more than one egg from an osprey nest is not permitted due to the effects on nest productivity.

Collection, measurement, and equipment calibration for pH samples will be conducted according to EA Program's *Standard Operating Procedures for Collection and Analysis of pH Samples* (Ward, 2007).

Laboratory

Analytical accuracy and precision for water and fish tissue samples will be assessed using matrix spikes and duplicate analyses. For water samples, a low and a high level QC sample will be prepared by spiking deionized water with a known amount of PFC mixture (approximately 5 and 50 ng/L, respectively). Tissue matrix spikes will be prepared from fish tissues previously determined to contain negligible amounts of PFCs. Low and high samples will be prepared containing 2 and 10 ng/g, respectively.

Accuracy will be assessed by recovery of PFCs, and precision will be determined by duplicate analysis of the spiked samples. A low and a high matrix spike sample will be analyzed and duplicated for approximately 10% of each sample matrix.

Blank samples consisting of deionized water or tissue determined to contain < LOQ will be used to determine laboratory contamination. Blank samples will be analyzed for approximately 10% of samples.

Data Management

Data recorded by staff in the field will be written on waterproof paper. Before leaving site locations, data will be checked for legibility and completeness. Field notes will be stored with the project manager. Pertinent field data will be transferred from field notes to electronic format using Microsoft Office programs. Data will be independently reviewed to ensure accuracy.

Analytical data from EPA staff will be provided to Manchester Environmental Laboratory (MEL) in an electronic format. After the data are verified and validated by MEL staff, they will be provided to the project manager as case narratives (as discussed below). Once EPA, MEL, and the project manager have reviewed the analytical data and addressed any issues, the completed data will be entered into Ecology's EIM system. Data entry into EIM is conducted under formal guidelines. EIM data are reviewed by the project manager, staff entering the data, and an independent reviewer.

Audits and Reports

Oversight of project components will occur through established practices within Ecology. The EPA laboratory participates in audits that include review of laboratory facilities, capabilities, and analytical performance.

A draft technical report will be prepared for the client and other interested parties in May 2009. The final report is anticipated in June 2009. A complete project timeline is available under *Organization and Schedule* in this QA Project Plan.

Data Verification and Validation

MEL will conduct a review of all analytical data provided by EPA and summarize findings in a case narrative. MEL staff will verify that all laboratory procedures outlined in the QA Project Plan were conducted and documented. Parameters verified by MEL include but are not limited to: acceptability of holding times, instrument calibration, procedural blanks, spike samples, precision data, laboratory control samples, and appropriateness of assigned qualifiers.

The project officer along with MEL staff will examine the complete data record and determine whether results are acceptable as outlined by the project plan.

Quality control limits outlined in the project plan will be used to determine if the laboratory met MQOs. Estimates of accuracy and precision will be based on laboratory QC, and their acceptability will be based on whether they meet outlined MQOs. At the discretion of the project officer, data will be accepted, accepted with qualifiers, or rejected.

Data Quality (Usability) Assessment

Data quality assessment is the determination of whether the verified and validated data can be used for project objectives. This assessment will require the project officer to analyze the entire data package to determine if the information provided is adequate to assess statewide PFC contamination. The final report will discuss quality, usability, and limitations.

References

Coots, R. and B. Era-Miller, 2005. Lake Chelan DDT and PCBs in Fish, Total Maximum Daily Load Study. Washington State Department of Ecology, Olympia, WA. Publication No. 05-03-014. www.ecy.wa.gov/biblio/0503014.html

Ellis, D.A., J.W. Martin, A.O. De Silva, S.A. Mabury, M.D. Hurley, M.P. Sulbaek Andersen, and T.J. Wallington, 2004. Degradation of Fluorotelomer Alcohols: A Likely Atmospheric Source of Perfluorinated Carboxylic Acids. Environmental Science and Technology, Vol. 38 (12): 3316-3321.

EPA, 2000. Guidance for Assessing Chemical Contaminant Data for Use in Fish Advisories - Volume 1: Field Sampling and Analysis, Third Edition. U.S. Environmental Protection Agency, Office of Water, Washington, D.C. EPA Publication No. EPA-823-B-00-007. www.epa.gov/ost/fishadvice/volume1/

EPA, 2006a. Announcement of Stewardship Program by Administrator Stephen L. Johnson. U.S. Environmental Protection Agency. Available at: www.epa.gov/oppt/pfoa/pubs/pfoastewardship.htm

EPA, 2006b. SAB Review of EPA's Draft Risk Assessment of Potential Human Health Effects Associated with PFOA and Its Salts. U.S. Environmental Protection Agency. EPA Publication No. EPA-SAB-06-006.

Gannon, J.T., R.A., Hoke, M.A. Kaiser, and T. Mueller, 2006. Review II: Perfluorooctanoic acid (PFOA) in the environment. White paper by DuPont Wilmington, DE. DuPont-19567.

Giesy, J.P. and K. Kannan, 2001. Global Distribution of Perfluorooctane Sulfonate in Wildlife. Environmental Science and Technology, Vol. 35 (7): 1339-1342.

Giesy, J.P. and K. Kannan, 2002. Perfluorochemical Surfactants in the Environment. Environmental Science and Technology, Vol. 36: 147-152.

Hansen, K.J., H.O. Johnson, J.S. Eldridge, J.L. Butenhoff, and L.A. Dick, 2002. Quantitative Characterization of Trace Levels of PFOS and PFOA in the Tennessee River. Environmental Science and Technology, Vol. 36: 1681-1685.

Henny, C.J., R.A. Grove, and J.L. Kaiser, 2008. Osprey Distribution, Abundance, Reproductive Success and Contaminant Burdens Along Lower Columbia River, 1997/1998 Versus 2004. Archives of Environmental Contamination and Toxicology 54: 252-534.

Johnson, A., B. Era-Miller, R. Coots, and S. Golding, 2004. A Total Maximum Daily Load Evaluation for Chlorinated Pesticides and PCBs in the Walla Walla River. Washington State Department of Ecology, Olympia, WA. Publication No. 04-03-032. www.ecy.wa.gov/biblio/0403032.html

Johnson, A., 2007. Quality Assurance Project Plan: A Trend Monitoring Component for Organic PBTs in the Washington State Toxics Monitoring Program. Washington State Department of Ecology, Olympia, WA. Publication No. 07-03-104. www.ecy.wa.gov/pubs/0703104.pdf

Joy, J. and B. Patterson, 1997. A Suspended Sediment and DDT Total Maximum Daily Load Evaluation Report for the Yakima River. Washington State Department of Ecology, Olympia, WA. Publication No. 97-321. www.ecy.wa.gov/biblio/97321.html

Kannan, K., J.L. Newsted, R.S. Holbrook, and J.P. Giesy, 2002. Perfluorooctanesulfonate and Related Fluorinated Hydrocarbons in Mink and River Otters from the United States. Environmental Science and Technology, Vol. 36: 2566-2571.

Kannan, K., S. Corsolini, J. Falandysz, G. Fillmann, K.S. Kumar, B.G. Loganathan, M.A. Mohd, J. Olivero, N.V. Wouwe, J.H. Yang, and K.M. Aldous, 2004. Perfluorooctanesulfonate and Related Fluorochemicals in Human Blood from Several Countries. Environmental Science and Technology, Vol. 38 (17): 4489-4495.

Kannan, K., L. Tao, E. Sinclair, S.D. Pastva, D.J. Jude, and J.P. Giesy, 2005. Perfluorinated Compounds in Aquatic Organisms at Various Trophic Levels in a Great Lakes Food Chain. Archives of Environmental Contamination and Toxicology, Vol. 48: 559-566.

Kim, S.K. and K. Kannan, 2007. Perfluorinated Acids in Air, Rain, Snow, Surface Runoff, and Lakes: Relative Importance of Pathways to Contamination of Urban Lakes. Environmental Science and Technology, Vol. 41 (24): 8328-8334.

Kudo, N. and Y. Kawashima, 2003. Toxicity and Toxicokinetics of Perfluorooctanoic Acid in Humans and Animals. The Journal of Toxicological Sciences, Vol. 28 (2): 49-57.

Lau, C., K. Anitole, C. Hodes, D. Lai, A. Pfahles-Hutchens, and J. Seed, 2007. Perfluoroalkyl Acids: A Review of Monitoring and Toxicological Findings. Toxicological Sciences, Vol. 99 (2): 366-394.

Martin, J.W., S.A. Macbury, K.R. Solomon, and D. Muir, 2003. Dietary Accumulation of Perfluorinated Acids in Juvenile Rainbow Trout (*Oncorhynchus mykiss*). Environmental Toxicology and Chemistry, Vol. 22 (1): 189-195.

Nakayama, S., M.J. Strynar, L. Helfant, P. Egeghy, X. Ye, and A.B. Lindstrom, 2007. Perfluorinated Compounds in the Cape Fear Drainage Basin in North Carolina. Environmental Science and Technology, Vol. 41 (15): 5271-5276.

Rattner, B.A., P.C. McGowan, N.H. Golder, J.S. Hatfield, P.C. Toschik, R.F. Lukei, R.C. Hale, I. Schmitz-Afonso, and C.P. Rice, 2004. Contaminant Exposure and Reproductive Success of Ospreys (Pandion haliaetus) Nesting in Chesapeake Bay Regions of Concern. Archives of Environmental Contamination and Toxicology, 47:126-140.

Renner, R., 2001. Growing Concern over Perfluorinated Chemicals. Environmental Science and Technology, 35: 154A-160A.

Sandvik, P., 2006. Standard Operating Procedures for Resecting Finfish Whole Body, Body Parts or Tissue Samples. Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/programs/eap/qa/docs/ECY_EAP_SOP_007ResectingFinfishWholeBodyPartsTissueSamples.pdf

Seung-Kyu, K. and K. Kannan, 2007. Perfluorinated Acids in Air, Rain, Snow, Surface Runoff, and Lakes: Relative Importance of Pathways to Contamination of Urban Lakes. Environmental Science and Technology, Vol. 41: 8328-8334.

Sinclair, E. and K. Kannan, 2006. Mass Loading and Fate of Perfluoroalkyl Surfactants in Wastewater Treatment Plants. Environmental Science and Technology, Vol 40(5): 1408-1414.

Sinclair, E., D.T. Mayack, K. Roblee, N. Yamashita, and K. Kannan, 2006. Occurrence of Perfluoroalkyl Surfactants in Water, Fish, and Birds from New York State. Archives of Environmental Contamination and Toxicology, Vol. 50: 398-410.

Taniyasu, S., K. Kannan, Y. Horii, N. Hanari, and N. Yamashita, 2003. A Survey of Perfluorooctane Sulfonate and Related Perfluorinated Organic Compounds in Water, Fish, Birds, and Humans from Japan. Environmental Science and Technology, Vol. 37 (12): 2634-2639.

Toschik, P.C., B.A. Rattner, P.C. McGowan, M.C. Christman, D.B. Carter, R.C. Hale, C.W. Matson, and M.A. Ottinger, 2005. Effects of Contaminant Exposure on Reproductive Success of Ospreys (Pandion haliaetus) Nesting in Delaware River and Bay, USA. Environmental Toxicology and Chemistry, 24 (3): 617-628.

Ward, W., 2007. Standard Operating Procedure for Collection and Analysis of pH Samples. Washington State Department of Ecology, Olympia, WA. www.ecy.wa.gov/programs/eap/qa/docs/ECY_EAP_SOP_031pHCollectionAnalysis.pdf

Xibiao, Ye, L.S. Heiko, J.D. Nathan, A.D. Delinsky, M.J. Strynar, J. Varns, S Nakayama, L. Helfant, and A.B. Lindstrom (2008 in press). Perfluorinated Compounds in Common Carp (Cyprinus carpio) Fillets from the Upper Mississippi River. Submission to: Environment International.

Appendix. Acronyms and Abbreviations

Following are acronyms and abbreviations used frequently in this document. Those used infrequently are not listed.

EA Program	Environmental Assessment Program
Ecology	Washington State Department of Ecology
EIM	Environmental Information Management system (Ecology)
EPA	U.S. Environmental Protection Agency
LOQ	limit of quantitation
MEL	Manchester Environmental Laboratory (Ecology)
MQO	measurement quality objectives
ORD	Office of Research and Development (EPA)
PBTs	persistent, bioaccumulative, toxic chemicals
PFAA	perfluoroalkyl acid
PFC	perfluorinated compound
PFOA	perfluorooctanoic acid (a PFAA)
PFOS	perfluorooctane sulfate (a PFAA)
QA	quality assurance
QC	quality control
USGS	U.S. Geological Survey
WWTP	wastewater treatment plant