Guideline for sampling and analysis of seafood suitable for human health risk assessments of PFAS contamination

Introduction

This guide outlines the approach recommended by Queensland Health for sampling and analysis of marine and freshwater biota for per- and poly-fluoroalkyl substances (PFAS) with the intention of assessing public health risk and informing any human health risk assessment (HHRA).

The aim is to assist in standardising sampling methodologies and risk assessment parameters, and aid in the provision of analytical results that can be used by Queensland Health to assess public health risk and reliably inform human health risk assessments. The guide provides minimum requirements that should be considered when investigating PFAS contaminated sites.

If marine and/or freshwater biota samples are taken as part of an ecological risk or broader environmental impact assessment, observing the guidelines below will help ensure the data obtained is suitable for HHRA.

NOTE: This guideline is not intended to address ecological risk assessment nor fully address assessment of actual and potential impacts on environmental values under the *Environmental Protection Act 1994* (Queensland). These assessments require consideration of broader areas, additional samples and potentially additional PFAS and analyses.

Sampling

The requirements below should be considered when collecting samples to inform a Human Health Risk Assessment:

- Biota samples should be legally caught only in recognised fishing areas (excluding green zones, drains etc.) and should be legal and commercial size for take (see Fishing Requirements below for more information).
- 2. Only edible species that are typically consumed from the area of interest must be used. Refer to Table 1 for suitable estuarine and inshore species, and Table 2 for freshwater species.
- Consideration should be given to whether any species need to be harvested for testing that are likely to form a significant proportion of the diet of any sub-populations at risk of higher exposure than the general population.
- 4. Ideally a range of species should be sampled including fish, crustaceans and molluscs. Preference should be given to targeting species that may have higher exposure to PFAS from the contamination source under investigation, considering migratory movements of some species may reduce their exposure. Predatory fish and benthic dwelling species should be included where possible.
- 5. Only edible portions should be analysed. The following portions are recommended as they are likely to represent the most typical parts consumed by the general population in Queensland:
 - a. Fish fillet, skin on with scales removed
 - b. Prawns and yabbies head, tail and shell removed



- c. Crabs and lobsters extracted meat
- d. Molluscs shell and/or non-edible parts removed.
- 6. A sufficient number of specimens should be obtained to account for variability between specimens. Composite samples of a single species from a set area are preferred to help overcome and average differences between individual specimens. Composite samples may be necessary when edible portions sizes are insufficient for analysis. Compositing of samples across broad areas and along pollution gradients must be avoided.
- 7. If the concentration of PFAS is required in the whole organism to assist with any ecological risk assessment, which is generally conducted alongside the HHRA, the portions of seafood which are not consumed by humans, e.g. fish carcass excluding edible portion, can be weighed and analysed separately. This enables the total PFAS concentration in the whole organism to be calculated by adding a weight averaged concentration of the edible and inedible portions once testing is completed.
- 8. Contamination of samples with PFAS during harvesting and the handling of samples should be avoided. PFAS may be found in some water and oil repellent clothing, footwear and fabrics, such as Gore-Tex[™] products. Teflon® containing or coated fishing equipment, knives, sample bottles, et cetera should not be used. Potential contamination from bait should also be excluded. Table 3 outlines known and suspected contamination risks that should be avoided.
- 9. The location of harvested species should be recorded. The GPS location should be considered where relevant, e.g. in the open ocean and larger water courses.
- 10. Where possible, samples should be prepared (e.g. scaled, gutted, filleted, shelled) in a laboratory or suitable facility to minimise the potential for environmental contamination and cross contamination.
- 11. Samples should be placed into sample containers provided or recommended by the laboratory. If not known, new, clean snap lock sample bags should be used.
- 12. Sample data should be recorded, e.g. sample identification number, date, species/ sample description, specimen size when caught and location taken. Samples should be appropriately labelled for the laboratory. Consideration may need to be given to photographing whole specimens to later aid correct identification of the species.
- 13. Samples should be chilled or frozen and packaged to minimise degradation and contamination until received by the laboratory.
- 14. It is advisable when preparing a sampling and analysis plan to separate requirements for seafood sampling for human health risk assessment from ecological risk assessment to help ensure a sufficient number of specimens appropriate for human health risk assessment are sampled.

Analysis

- 1. Analysis of samples to be used for Human Health Risk Assessment should be undertaken using the following methodology: LTM-ORG-2100 Per- and Polyfluorinated Alkyl Substances by LC-MS/MS. PFAS species reported must include PFOA, PFOS and PFHxS.
- 2. TOPA and TOF results are not required by Queensland Health for assessing public health risks or for human health risk assessment. TOPA and or TOF analyses target additional PFAS not detected by the LTM-ORG-2100 analysis method and may be used to more reliably characterise the totality of PFAS contamination present in sources, pathways and exposures under the *Environmental Protection Act 1994* (Queensland), the PFAS National Environmental Management Plan and the *National Environmental Protection (Assessment of Site Contamination) Measure 1999*. Their use

should be discussed with the Queensland Department of Environment and Science prior to commencing testing.

Risk Assessment

- Assessment of the likelihood of consumption should be based on the location from which samples
 are collected (e.g. commercial fishing ground vs drain on an airport site) consider relevant
 consumers (e.g. recreational fishers).
- 2. Consumption figures should be standardised for example using a consumption figure of 90% is not realistic for fish taken from a single site.
- 3. Any assessment of PFAS concentrations in seafood biota (e.g. in a sampling analysis and quality plan and HHRA) should be based on the latest health based guidance values for PFAS published by the Australian Government Department of Health. Key documents (as of April 2018) are:
 - a. Health Based Guidance Values for PFAS for use in site investigations in Australia, Australian Government Department of Health (available at http://www.health.gov.au/internet/main/publishing.nsf/Content/ohp-pfas-hbgv.htm#FSANZ)
 - b. Consolidated Report Perfluorinated Chemicals in Food, Food Standards Australia New Zealand (available at http://www.health.gov.au/internet/main/publishing.nsf/Content/2200FE086D480353CA2580C900817CDC/\$File/Consoldiated-report-perflourianted-chemicals-food.pdf)
 - c. Supporting Document 2, Assessment of potential dietary exposure to perfluorooctane sulfonate (PFOS), perfluorooctanoic acid (PFOA) and perfluorohexane sulfonate (PFHxS) occurring in foods sampled from contaminated sites, Food Standards Australia New Zealand (available at http://www.health.gov.au/internet/main/publishing.nsf/Content/2200FE086D480353CA2580C900817CDC/\$File/Dietary-Exposure-Assesment.pdf)
- 4. When making conclusions about fish consumption, if results indicate that consuming fish at higher than the Food Standards Australia New Zealand recommendation for consumption of fish due to mercury is acceptable in relation to PFAS levels then the default advice should be that for consumption of fish due to mercury, as it would not be advisable to recommend a higher consumption. Consumption advice for mercury in fish may be found at http://www.foodstandards.gov.au/consumer/chemicals/mercury/Pages/default.aspx.
- 5. Risk assessment should only include PFAS for which there is a recognised Tolerable Daily Intake (TDI), e.g. PFOS + PFHxS, and PFOA. TDIs should not be applied as surrogates to other PFAS.

Fishing requirements

Harvest of fisheries resources in Queensland is managed by the Department of Agriculture and Fisheries (DAF). A General Fisheries Permit issued under the *Fisheries Act 1994* will be required to conduct any sampling program where;

- non-prescribed fishing apparatus will be used (e.g. nets, trawlers, electrofishing),
- more than the permitted number of prescribed apparatus will be deployed (e.g. more than four crab pots per person)
- take will exceed any species specific size and/or possession limits
- sampling will occur within closed waters

- sampling will occur during closed seasons
- · pest fish species may be encountered
- other fisheries regulations may be breached.

Details of the rules and regulations for fishing in Queensland may be viewed at https://www.daf.qld.gov.au/fisheries. However, contractors should seek specific advice from Fisheries Queensland prior to commencing any PFAS related aquatic biota sampling program. This will ensure that a properly conditioned, current permit is in place to conduct the sampling activities. Fisheries technical officers may also be able to provide additional advice on appropriate sampling methods and locations. Initial enquiries can be made via the DAF Customer Service Centre on 13 25 23.

Tables 1 & 2 describe preferred target species for sampling programs designed to assess potential for uptake of PFAS by consumption of local seafood in Queensland. Suitable target species will vary according to the location of the investigation area. The tables include estuarine/marine and freshwater species commonly targeted for human consumption in Queensland. Species that predominantly occur in offshore waters have not been included.

Sampling programs designed to assess potential ecological risks should also include small-bodied fish likely to be consumed by higher order predators. There are a large number of such species and as such, no specific list has been developed. Small bodied fish are commonly targeted using seine nets, cast nets, dip nets, funnel traps or electrofishing (in freshwater). Use of such apparatus is regulated and size and possession limits also apply to small-bodied species. Contractors should seek specific advice from DAF prior to commencing any sampling program designed to assess ecological risks from PFAS contamination.

Acronyms used

- HHRA Human health risk assessment
- PFAS Per- and poly-fluoroalkyl substances
- PFOA Perfluorooctanoic acid
- PFHxS Perfluorohexane sulfonic acid
- PFOS Perfluorooctane sulfonate
- TDI Tolerable Daily Intake
- TOPA Total oxidisable precursor assay
- TOF Total organic fluorine

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Table 1 Common edible estuarine and inshore marine species for PFAS sampling programs in Queensland

Common name	Best habitat to sample	Common distribution in Qld	Sample type	Best sampling methods
Bream (Yellowfin, Pikey, Tarwhine)	Estuaries, beaches, inshore waters	Entire coastline	Fillet	Net/Line
Whiting (Sand, Trumpeter, Goldenline)	Estuaries, beaches, inshore waters	Entire coastline	Fillet	Net/Line
Flathead (Dusky, Bar-tailed, Yellow-tailed)	Estuaries, beaches, inshore waters	Entire coastline	Fillet	Net/Line
Barramundi	Estuaries, inshore waters, freshwater rivers & dams	Maryborough & north	Fillet	Net/Line/Electrofishing (f/w)
Threadfin salmon (Blue or King)	Estuaries, beaches, inshore waters	Brisbane & north	Fillet	Net/Line
Blue swimmer (sand) crab	Estuaries	Entire coastline	Claw / leg	Crab pot
Mud crab	Estuaries	Entire coastline	Claw / leg	Crab pot
Prawns (multiple species)	Estuaries, inshore waters	Entire coastline	Whole animal	Net / Trawl
Javelin (Barred or Silver)	Estuaries, beaches, inshore waters	Entire coastline	Fillet	Net/Line
Mullet (Sea, Freshwater, Diamond scale)	Estuaries, beaches, freshwater rivers	Entire coastline	Fillet	Net / Electrofishing (f/w)
Tailor	Estuaries, beaches, inshore waters	Fraser Island & south	Fillet	Net/Line
Garfish (River, Snub-nose, Three-by-two)	Estuaries, freshwater			Net / line / Electrofishing (f/w)
Trevally (multiple species)	Estuaries, beaches, inshore waters	Entire coastline	Fillet	Net/Line
Jewfish (multiple species)	Lower estuaries, beaches	Entire coastline	Fillet	Net/Line
Luderick	Estuaries	Noosa Heads & south	Fillet	Net/Line
Estuary cod	Estuaries, inshore waters	Entire coastline	Fillet	Net/Line
Mangrove jack	Estuaries	Entire coastline	Fillet	Net/Line
Fingermark	Estuaries	Townsville & north	Fillet	Net/Line
Fork-tail catfish (multiple species)	Estuaries, inshore waters, freshwater rivers & dams	Entire coastline	Fillet	Net/Line
Sharks & rays (multiple species)	Estuaries, beaches, inshore waters	Entire coastline	Fillet	Net/Line

Table 2. Common edible freshwater species for PFAS sampling programs in Queensland

Common name	Best habitat to sample	Common distribution in Qld	Sample type	Best sampling methods
Golden perch	Rivers and dams	Murray-Darling Basin, Lake Eyre Basin & coastal rivers Rockhampton & south	Fillet	Electrofishing / gill net / line
Australian bass	Rivers and dams	Coastal rivers Bundaberg & south	Fillet	
Silver perch	Rivers and dams	Murray-Darling Basin & coastal rivers Bundaberg & south		
Murray cod	Rivers and dams	Murray-Darling Basin	Fillet	
Eel-tailed catfish (multiple species)	Rivers and dams	Murray-Darling Basin & all coastal rivers	Fillet	
Fork-tailed catfish (multiple species)	Rivers and dams	All coastal rivers	Fillet	
Garfish	Rivers and dams	All coastal rivers	Fillet	
Sooty grunter	Rivers and dams	Coastal rivers Bundaberg & north	Fillet	
Sleepy cod	Rivers and dams	Coastal rivers Bundaberg & north	Fillet	
Freshwater eels (Long-finned & Short finned)	Rivers and dams	All coastal rivers	Fillet	
Barcoo grunter	Rivers	Inland rivers of Lake Eyre Basin & Cooper Ck.	Fillet	
Welch's grunter	Rivers	Lake Eyre Basin, Bulloo River	Fillet	
Khaki grunter	Rivers	Gulf of Carpentaria, Burdekin River & north	Fillet	
Redclaw crayfish	Rivers and dams	All coastal rivers, Lake Eyre Basin	Claw / leg	Funnel trap
Other freshwater crayfish (multiple species)	Rivers and dams	All coastal and inland river systems	Claw / leg	Funnel trap

Table 3 Known or commonly-suspected sources of environmental sample contamination during PFAS investigations, and recommended mitigation practices and alternatives

(Interim Guideline on the Assessment and Management of Perfluoroalkyl and Polyfluoroalkyl Substances (PFAS) 2016, Department of Environmental Regulation, Western Australia (https://www.der.wa.gov.au/component/k2/item/6439-interim-guideline-on-the-assessment-and-management-of-perfluoroalkyl-and-polyfluoroalkyl-substances-pfas)).

Product	Mitigation Practice	Alternative Product or Practice When PFAS Sampling is to be Undertaken			
Clothing and food					
New clothing		All field clothing to be washed a minimum of six times after purchase before using at the site			
Clothing with stain-resistant, rain-resistant, or waterproof coatings/treated fabric (e.g. GORE-TEX [®])		Avoid sampling during rain if possible; polyethylene rain gear (e.g. disposable LDPE), vinyl, or polyvinyl chloride (PVC) clothing are acceptable			
Tyvek® clothing	Prohibited for sampling personnel ¹	None			
Fast food wrappers and containers		Use rigid plastic containers or bags or stainless steel containers for all food brought to site			
Pre-wrapped foods and snacks (e.g. chocolate bars, energy bars, granola bars, potato chips etc.)		Food brought to the site must be contained in plastic (rigid containers or bags) or stainless steel containers			
Sampling equipment and containers					
Teflon [®] -containing or -coated field equipment (tubing, bailers, tape, plumbing paste, etc.)	Prohibited at site ²	High Density Polyethylene (HDPE) or silicone tubing, and HDPE or polypropylene field equipment recommended			
Teflon [®] -lined lids on containers (e.g. sample containers, rinsate water storage containers)	Prohibited at site ²	Polypropylene lids ³ for sample containers and polypropylene or HDPE containers for rinsate			
Glass sample containers with lined lids	Contact with samples prohibited	Use polypropylene or HDPE for sample containers ³ ; glass jars are acceptable provided lids are unlined or are lined with HDPE			

Other products				
Aluminium foil	Prohibited at site	Thin HDPE sheeting (commonly used as drop cloths for painting or home improvement) can be used		
Self-sticking notes and similar office products (e.g. 3M Post-it notes)	Prohibited at site ²	Avoid the use of these products at the site		
Waterproof paper, notebooks, and labels	Prohibited at site	Standard paper and paper labels		
Drilling fluid containing PFAS	Prohibited for use at site ²	PFAS-free drilling fluids		
Detergents and decontamination solutions (e.g. Decon 90 [®] Decontamination Solution)	Prohibited for all equipment	Follow water-only decontamination approach		
Reusable chemical or gel ice packs (e.g. Bluelce®)	Prohibited for sample storage and transport	Ice contained in plastic (polyethylene) bags (double bagged)		

¹Sampling personnel includes all personnel who:

- are directly involved in the collection, handling, and/or processing of samples prior to the samples leaving the site;
- handle any part of well development equipment that directly contacts bore water being sampled;
- handle any part of equipment that directly contacts surface water or aquatic sediment;
- are within 2-3m of the borehole during soil sampling; or
- are within 2–3m of the collection and processing area on aquatic vessels during sediment or surface water sampling.

Personnel are not included as sampling personnel if they remain at least 2–3m away from sample collection areas prior to and during sampling.

²Entire sample collection and processing area, including vehicles used by sampling personnel.

³USEPA and ASTM method for the analysis of PFAS in solid and liquids specify polypropylene or HDPE with polypropylene lids. Check with the laboratory in regards to preference for polypropylene or HPDE.