Per- and Polyfluoroalkyl substance (PFAS) testing in sediment and aquatic foods from Darwin Harbour

Prepared for Northern Territory Department of Health

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REPORT BRIEF

Background

Per- and Polyfluoroalkyl Substances (PFAS) are a group of manufactured chemicals that have a wide variety of uses, e.g. it has been used in fire-fighting foams, hydraulic fluids and stain resistant coatings on materials. PFAS can enter the natural environment through run-off from contaminated areas and through the sewerage system. These chemicals have historically been used at airports across Australia, including Darwin Airport.

Previous studies of exposure to PFAS in the general population are inconsistent but suggest a number of potential health effects. Among these are studies showing an association between PFOS (perfluorooctane sulfonate) and PFOA (perfluorooctanoic acid) and a number of adverse health effects. Perfluorohexane sulfonate (PFHxS) which have chemical similarities to PFOS may also be of health concern. However, these data are inconclusive and the associations do not necessarily mean that PFAS caused the observed health effects.

The general community are exposed to low levels of PFAS through many ordinary consumer products and eating food contaminated with low PFAS levels. This means that most people have a baseline level of PFAS in their blood. Other groups may be exposed to higher levels of PFAS through, for example, occupational exposure or eating greater quantities of food that has been exposed to PFAS compared to the general population.

Introduction

The motivation for this study was to address concerns that sediment and aquatic food in Ludmilla and Rapid Creek in Darwin were contaminated by PFAS as these creeks receive runoff from Darwin Airport and surrounding urban areas.

To assess the potential for human and ecosystem health risks from PFAS, traditional aquatic food eating patterns were provided by the Larrakia Nation co-researchers on this study. The Larrakia are traditional owners of the lands in the affected areas, and these data were used to establish rates of intake of aquatic foods from the two creeks. We collected several specimens of each aquatic food to determine the ranges of weights of each food type and the ranges of their PFAS concentrations. The combined information was used to determine the probabilities of different levels of PFAS intake including the most likely (median) and most extreme (maximum) scenarios of PFAS intake and to compare these calculated values to the Australian human health guideline levels for PFAS intake.

It should be noted that this study is not a full assessment of human health risks – for that, all known exposure routes need to be quantified.

PFAS levels in aquatic foods and sediment

The concentrations of thirteen PFAS, including perfluorooctanoic acid (PFOA), perfluorooctane sulfonate (PFOS), and perfluorohexane sulfonate (PFHxS) were measured in aquatic biota and sediment.

Periwinkles, long bums (the two species most thoroughly tested) and sediment from Ludmilla and Rapid Creeks had substantially higher mean concentrations of PFOA, PFOS and PFHxS compared to samples from a remote comparison site at Fright Point (near Gunn Point).

Mean concentrations of PFOA, PFOS and PFHxS in periwinkles and long bums from Ludmilla and Rapid Creeks were from 6 to 22 times higher for PFOA and 48 to 101 times higher for PFOS+PFHxS than in samples from Fright Point.

In Ludmilla and Rapid Creek sediment samples mean concentrations were from 2 to 8 times higher for PFOA and 11 to 85 times higher for PFOS+PFHxS compared to Fright Point samples.

The highest PFOA and PFOS+PFHxS concentrations in aquatic foods were recorded at tidal sites in upper sections of Ludmilla Creek and at tidal sites in lower sections of Rapid Creek. PFAS levels in a small number of samples of red claw yabbies, cockles and oysters were also elevated compared to samples from the comparison site.

Dietary exposure of PFAS chemicals (human health assessment)

A Total Daily Intake (TDI) guideline value is commonly established for chemicals as an estimate of the amount of the chemical in air, food or drinking water, which can be taken in daily over the lifetime of a human without appreciable health risk. The TDI is expressed on a body weight (b.w.) basis and is a conservative intake estimate based on toxicological information to which safety factors are applied. If a TDI is exceeded for short periods no negative effect should be expected. Short-term exposure to chemicals exceeding the TDI is therefore usually not a cause for concern, providing the person's average long-term intake does not exceed this limit.

In June 2016, the Environmental Health Standing Committee of the Australian Government Department of Health (enHealth) released interim TDI guideline values for two PFAS chemicals, PFOS and PFOA, to be applied in Australian site investigations. enHealth also recommended that PFHxS (a third PFAS chemical) should be summed with PFOS and the total compared to the TDI for PFOS. The NT EPA adopted this recommendation. Late in 2016 Food Standards Australian New Zealand (FSANZ) was commissioned by the Australian Government to develop final health-based guidance values for PFOS+PFHxS and PFOA. The final TDI guideline values for PFOS+PFHxS and PFOA have now been released and replace the previous interim guideline values:

Tolerable daily intakes (TDI) - Australian Department of Health (April 2017)

	PFOS+PFHxS	PFOA
TDI	20 ng/kg b.w.	160 ng/kg b.w.

In the present study, the intake of PFAS via consumption of the aquatic foods tested was calculated based on both a maximum intake scenario (using the maximum consumption rate, food weight and PFAS concentrations) and on a median intake – or most likely – scenario (using median consumption rate, food weight and PFAS concentrations) across all sites investigated and compared to the TDI guideline values (refer to summary table below).

Summary of the relationship between the number of molluscs/shell fish consumed, their concentration of PFOS+PFHxS and PFOA, the resulting estimated daily intake of PFOS+PFHxS and PFOA and how this intake compares to Total Daily Intake (TDI) guideline values based on regular consumption over a lifetime

Parameter	PFOS+PFHxS maximum intake	PFOS+PFHxS median intake	PFOA maximum intake	PFOA median intake
Sittings per week	2	1.5	2	1.5
Number of biota consumed per sitting	12 Long Bums 5 Mud Mussels 1 Oyster 10 Periwinkles 1 Red Claw Yabbie	11 Long Bums 5 Mud Mussels 1 Oyster 7.5 Periwinkles 1 Red Claw Yabbie	12 Long Bums 5 Mud Mussels 1 Oyster 10 Periwinkles 1 Red Claw Yabbie	11 Long Bums 5 Mud Mussels 1 Oyster 7.5 Periwinkles 1 Red Claw Yabbie
Weight of individual biota	Maximum individual weight for all species	Median individual weight for all species	Maximum individual weight for all species	Median individual weight for all species
Concentration in consumed molluscs / shell fish	Maximum concentration in each species across all non-reference sites	Median concentration in each species across all non-reference sites	Maximum concentrations in each species across all non-reference sites	Median concentration in each species across all non-reference sites
Estimated daily intake (ng/kg b.w./day)	26	1.4	37	1.5
Dept. of Health TDI guideline value (ng/kg b.w./day)	20		160	
Estimated daily intake as % of TDI	130	7.0	23	0.9

The estimated maximum daily intakes for adults of PFOS+PFHxS is 130% of the TDI and for PFOA it is 23% of the TDI. Modelling of daily intake scenarios suggests that the probability of an individual person reaching the maximum intake of PFOS+PFHxS over a life time is lower than 0.001 (or 1 in 1,000). Under the most likely median scenario, the daily intake for adults drop to 7% of the TDI for PFOS+PFHxS and 1% of TDI for PFOA.

To achieve maximum intakes, and therefore exceed the TDI and be exposed to a health risk, would require an individual to eat the maximum amount of aquatic foods, at the maximum weight and with the maximum PFOS+PFHxS concentration on a regular, on-going basis.

For most people, if they continued to eat 1-2 sittings per week of the tested aquatic seafood over their lifetime, the amount of PFOS+PFHxS and PFOA that they would be exposed to would be less than 7% and 1%, respectively, of the amount that may cause potential health effects. Any additional daily intake of PFAS from, for example, eating of fish or crabs, are not included in this estimate.

There are no defined TDI values for other PFAS chemicals, however, on average PFOS+PFHxS+PFOA accounted for 67% of all PFAS measured in the investigated aquatic foods.

PFAS levels in sediment (ecosystem health assessment)

This assessment is limited to sediment quality only; a full ecological risk assessment requires multiple approaches including sampling of water, sediment and biota. Australian guideline values for maintaining ecosystem health are not available for PFAS in marine sediment. However, a system for classification of environmental quality of marine sediments contaminated with PFOS has been developed in Norway (PFOA guideline levels are not available).

In spite of the elevated levels of PFOS in Ludmilla and Rapid Creek sediment (up to 28 nanogram / gram dry weight) compared to background levels measured at the comparison site (up to 0.1 nanogram / gram dry weight), marine sediment in both creeks are classified as in "good" ecological health when compared to the Norwegian classification system (chronic toxicity effects on bottom dwelling species can be expected above 220 nanogram / gram dry weight).

Both PFOA and PFOS concentrations in the upper freshwater section of Rapid Creek (PFOA and PFOS up to 0.18 and 5.8 nanogram / gram dry weight, respectively) are also well below presently available ecological screening levels applicable to terrestrial soil. These screening levels (3,730 and 373 nanogram / gram dry weight for PFOA and PFOS respectively) were adopted by the Australian Department of Defence in May 2015 on the basis of a draft review of toxicological data undertaken by the Cooperative Research Centre for Contamination Assessment and Remediation of the Environment (CRC CARE).

Further data will assist in assessing ecological risk relating to PFAS concentrations in the aquatic environment. This may include analysis of existing data as well as future measurements of PFAS in surface and ground water, sediment and aquatic organisms.

Sources of PFAS in aquatic foods and sediment

Statistical analysis of PFAS levels across all sites show that the composition of the PFAS group of chemicals in both sediment and fauna at the remote Fright Point comparison site, and in particular a lack of PFOS/PFOA at this site, distinguishes this site from all other sites. This observation suggests that PFOS/PFOA sources are linked to human activities in the catchments of Ludmilla and Rapid Creeks.

Recommendations for further work

The conclusion that PFAS levels in aquatic foods from both Ludmilla and Rapid Creek are elevated compared to similar samples from the remote comparison site, suggests that it would be prudent to assess PFAS levels in higher order species like fish and crabs and to assess the associated human dietary exposure to PFAS. There is a possibility that PFAS levels become biomagnified from lower to higher order biological species.

To further explore the extent of PFAS contamination, as well as explore possible remediation options, a specific tracking study of PFAS sources could be undertaken in the upper catchments of Ludmilla and Rapid Creeks.

PFAS report – talking points (Q&A)

Why and how the study was conducted:

- Why was this study undertaken?
    - To address concerns that sediment and aquatic food sources were contaminated by a group of chemicals called PFAS (Per- and Polyfluoroalkyl substances) which could lead to unacceptable human health risks.
- What were the aims of the study?
    - To measure the amount of PFAS in sediment and aquatic foods and assess human and ecosystem health risks.
- What is PFAS?
    - PFAS is a large group of man-made chemicals similar to hydrocarbon chains but where hydrogen atoms have been replaced by fluorine atoms which provides a range of benefits in both industrial and domestic applications.
    - Three of the chemicals of most health concern in the PFAS group are PFOS (perfluorooctane sulfonate), PFHxS (perfluorohexane sulfonate) and PFOA (perfluorooctanoic acid).
- Where do PFAS come from?
    - PFAS are entirely man-made and have had a wide variety of uses ranging from fire-fighting foams to stain resistant coatings of materials. PFAS can enter the natural environment through runoff from contaminated areas and through the sewerage system.
- What happens to PFAS in the natural environment
    - PFAS are very stable compounds and are highly resistant to break down, consequently they can accumulate in sediment and the food web.
- What are the known or suspected human health risks of PFAS?
    - Studies of the exposure to PFAS in the general population are inconsistent but suggest a number of potential health effects. Among these are studies showing an association between PFOS and PFOA and decreased sperm count, a negative association of PFOS and PFOA with birth weight and size, higher blood levels of PFOS and PFOA being related to thyroid disease and an association between PFOA and elevated cholesterol.
    - Overall these studies are inconclusive and do not necessarily mean that PFAS caused the observed health effects.
- How are people exposed to PFAS?
    - The general community are exposed to low levels of PFAS through many ordinary consumer products and eating food contaminated with low PFAS levels.
    - Other groups may be exposed to higher levels of PFAS through, for example, occupational exposure or eating greater quantities of food that has been exposed to PFAS compared to the general population.
    - The aquatic fauna tested in this study can potentially take up PFAS both from contaminated sediments that they come into contact with and from the water column.

- How was the study designed?
    - PFAS levels in the same type of samples of sediment and aquatic foods were compared at the sites at potential risk with sites remote from urban and industrial influences. The aquatic foods analysed in this study were selected and collected by local indigenous people (Larrakia Nation Aboriginal Corporation).
- What was sampled and why?
    - Sediment from mangrove creeks and flood plains, aquatic foods periwinkles, long bums, cockles, mud mussels, oysters, yabbies. These species are the most commonly consumed aquatic foods along with crabs and fish (to be analysed in stage 2)
- Where did sampling take place and why?
    - The sites at risk are Ludmilla Creek and Rapid Creek as they receive runoff from Darwin Airport and other urban sources. Ludmilla Creek may also be impacted by treated sewage effluent on some occasions. Both creeks have limited flushing in their upstream sections. The remote comparison site was at Fright Point (near Gunn Point).
- What was analysed and why?
    - Thirteen different PFAS chemicals, including PFOA, PFOS and PFHxS which typically account for the majority of PFAS in environmental samples. PFOA, PFOS and PFHxS are also the only PFAS for which human health and ecosystem guidelines exist.
- How were PFAS analysed?
    - Samples were analysed by advanced mass spectrometric methods at the National Centre for Environmental Toxicology (Entox), The University of Queensland.
- How do we know we got the correct data?
    - The analytical methods include many quality control procedures including repetition of analyses and analysis of samples with known amounts of PFAS to check that data is accurate.
- How were human health risks of PFAS assessed?
    - The number and types of aquatic foods consumed on a daily basis was estimated by local indigenous people based on current availability of aquatic species (Larrakia Nation Aboriginal Corporation).
    - The ranges of the weights and the concentrations of PFAS were determined for each food type.
    - The median (most likely) as well as the maximum (extreme) amount of PFOA and PFOS+PFHxS consumed by adults through consumption of the analysed aquatic foods were compared to the 'tolerable daily intake' (TDI) guideline value – a recommended maximum intake level established by the Australian Government following an extensive risk assessment by Food Standards Australian New Zealand (FSANZ)
- How were ecosystem health risks assessed?
    - Levels of PFAS in Ludmilla and Rapid Creek sediment were compared to the levels found at the remote comparison site and to guideline levels and ecosystem quality classification systems for marine sediment and terrestrial soils.

What did the study find?

- How high were PFAS levels in aquatic foods and sediment?
    - The biological species and sediment sampled from Ludmilla and Rapid Creeks had substantially higher (from 6 - 101 times) mean PFOA and PFOS+PFHxS concentrations compared to samples from the Fright Point comparison site. The highest concentrations were measured in samples from the upper tidal sites in Ludmilla Creek and lower tidal sites in Rapid Creek. o There were large variations in PFAS levels in sediment and aquatic foods within each sampling area and over short distances.
- What is the human dietary exposure to PFAS chemicals?
    - The estimated maximum (but highly unlikely) daily intake scenario for adults of PFOS+PFHxS is 130% of the tolerable daily intake (TDI) and of PFOA it is 23% of TDI. These values drop substantially under the most likely median scenario to 7% of TDI for PFOS+PFHxS and 1% of TDI for PFOA.
    - For most people, if they continued to eat 1-2 sittings per week of the tested aquatic seafoods over their lifetime, their exposure to PFOS+PFHxS+PFOA is expected to be insignificant.
    - The probability of an individual person reaching the maximum intake of PFOS+PFHxS over a life time is lower than 1 in 1,000.
    - There are no defined TDI for other PFAS chemicals, however on average PFOS+PFHxS+PFOA accounted for 67% of all PFAS measured in aquatic foods.
    - This study is not a full human health risk assessment – for that, all known exposure routes need to be quantified. This study investigated a specific exposure via ingestion of contaminated aquatic foods by local communities.
- What is the impact on the ecosystem of PFAS contamination?
    - Levels of PFOA and PFOS+PFHxS in Ludmilla and Rapid Creek sediment were up to 8 and 85 times higher, respectively, than at the remote comparison site.
    - Australian ecosystem guidelines are not available for any PFAS concentrations in sediment. However, PFOS levels in marine sediment in the tidal sections of Ludmilla and Rapid Creeks are classified as in "good" ecological health when compared to a Norwegian marine classification system (a PFOA criterion is not available).
    - Both PFOA and PFOS levels in the fresh water section of Rapid Creek are well below ecological screening levels applicable to terrestrial soils adopted by the Australian Department of Defence.
    - Further data will assist in assessing ecological risk relating to PFAS concentrations in the aquatic environment. This may include analysis of existing data as well as future measurements of PFAS in water, sediment and aquatic organisms.
- What are the sources of PFAS in sediment and biota?
    - Analysis of PFAS levels at different sites show that the composition of PFAS in both biota and sediment at the Fright Point comparison site, and in particular a lack of PFOS and PFOA, distinguishes this site from all sites in Ludmilla and Rapid Creeks. This observation suggests that PFOS and PFOA sources are linked to human activities in the catchments of Ludmilla and Rapid Creeks.

- More precise identification of sources and distribution of PFAS in the two creeks require further study.

- What plans are there for further work to assess PFAS contamination and risks?
  - Further assessments of dietary intake against TDI may include measurement of PFAS in crabs and fish. This will enable a more complete assessment of dietary exposure to PFAS chemicals.
  - Further assessment of ecological impact relating to PFAS concentrations in surface water and ground water, and sediment.
  - More detailed sampling and analysis of the creek ecosystems can define the extent of PFAS contamination, track PFAS sources and present options for remediation if necessary.