Marine Pollution Bulletin 111 (2016) 509–513

Contents lists available at ScienceDirect

Marine Pollution Bulletin

journal homepage: www.elsevier.com/locate/marpolbul

Baseline

# Preliminary investigation of perfluoroalkyl substances in exploited fishes of two contaminated estuaries

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ARTICLE INFO

*Article history:*
Received 29 March 2016
Received in revised form 1 June 2016
Accepted 4 June 2016
Available online 9 June 2016

*Keywords:*
Perflouro
PFOS
PFOA
Airport
Marine
Fisheries
Prawn
Crab
AFFF

ABSTRACT

Perfluoroalkyl substances (PFASs) are being increasingly detected in a range of aquatic and terrestrial ecosystems, often resulting from the use of legacy fire-fighting foams. This study conducted an initial investigation of the concentrations of PFASs in the commercially and recreationally exploited species Dusky Flathead, Mud Crab, School Prawn, Sea Mullet, Yellowfin Bream, Eastern King Prawn and Sand Whiting, across two contaminated estuaries. All samples contained perfluoro-*n*-octane sulfonate (PFOS) except four Yellowfin Bream samples (two from each estuary). Perfluoro-*n*-octanoic acid (PFOA) was detected only in School Prawn samples from Fullerton Cove, while perfluoro-*n*-hexane sulfonate (PFHxS) was detected in prawn muscle and in fish liver samples from both estuaries. This study presents one of the first surveys of PFAS in a range of edible saltwater fish and crustaceans in Australia, and these baseline levels of contamination will prove useful for informing future surveys of these emerging contaminants.



Perfluorinated chemicals or perfluoroalkyl substances (PFASs) are emerging contaminants of international concern (Murray et al., 2010), and their presence is being increasingly detected in a range of aquatic and terrestrial ecosystems. While some recent reviews suggest that Australia is unlikely to be affected by transport of the contaminants from northern hemisphere sources, local sources for such pollutants still exist (Thompson et al., 2011b). Several unpublished preliminary investigations in Australia have identified these substances in soil, water, and biota, and much of this contamination has arisen from the use of legacy fire-fighting foams. The historic use of these substances, particularly around airports and other fire-fighting training facilities, mean that such facilities represent a potentially significant local source of this persistent pollutant.

Knowledge of baseline perfluorinated contaminant levels in Australia is lacking, especially in commercial fishes and crustaceans. Some exploratory work has detected PFASs in and around major Australian cities (Gallen et al., 2014; Thompson et al., 2011a,b), but to our knowledge there are few published local studies that have detected these contaminants in marine biota (Baduel et al., 2014; Thompson et al., 2011b). Identifying pollutant sources and the passage of pollutants through ecological systems is essential to understanding potential exposure pathways, and managing any ecological and health effects.

A PFAS contamination issue has recently come to light surrounding a regional airport at Williamtown, New South Wales, Australia. This facility is both a domestic airport and a major air force base, and used legacy fire-fighting foams containing PFASs for several decades into the early 2000s. Initial investigations revealed PFAS contamination within the airport itself and subsequent work identified that the contaminant was present in the network of drains surrounding the facility (URS Australia Pty Ltd, 2015). Williamtown and the surrounding area is bordered by two large estuaries, the Hunter River (to the south) and Port Stephens (to the north), and surface and ground water from the airport drain into both estuaries through Tilligerry Creek (Port Stephens) and Fullerton Cove (Hunter River, Fig. 1). This study conducted an initial investigation of the concentrations of PFASs in a number of commercially and recreationally important species of fish and crustaceans in both estuaries. The Hunter River and Port Stephens are two large adjacent estuaries on the mid-north coast of New South Wales, Australia (Fig. 1). The Hunter River is a mature, wave-dominated barrier estuary, with abundant mangrove and saltmarsh habitat, whereas Port Stephens is a tide-dominated drowned valley estuary, containing extensive mangrove, saltmarsh and seagrass habitats. Port Stephens has a smaller catchment (4950 $km^2$) and larger waterway area (126 $km^2$), whereas Hunter River has a much larger catchment (22,000 $km^2$) and smaller waterway area (30 $km^2$) (Roy et al., 2001). The catchments of both estuaries are largely agricultural and forested; however, the lower reaches of the Hunter River have significant industrial areas. Both estuaries support substantial commercial fisheries, and the two point-sources of

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http://dx.doi.org/10.1016/j.marpolbul.2016.06.023
0025-326X/

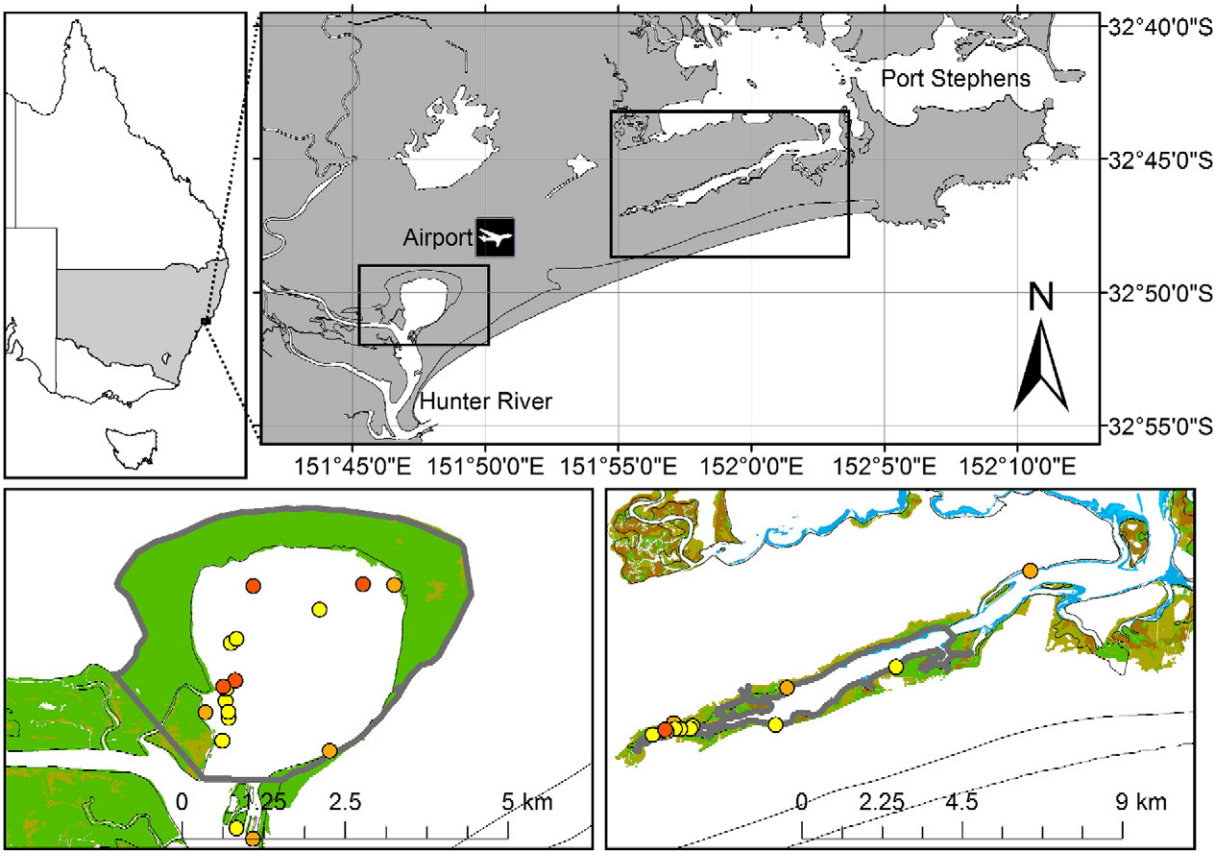


**Fig. 1.** Map of study area indicating the location of Port Stephens and Hunter River, and sampling locations for crabs (yellow circles), prawns (red circles) and fish (orange circles) in Fullerton Cove (lower left panel) and Tilligerry Creek (lower right panel). The dark grey outline in the lower panels indicates the estuarine contamination zone and fishing closure areas. Brown shading indicates saltmarsh habitat, green shading indicates mangrove, and blue shading indicates seagrass. The airport which is the source of the contamination is shown relative to the two estuaries in the upper right panel.

contamination are adjacent to some of the most heavily fished areas in these estuaries, particularly for crustaceans.

Samples were collected in Fullerton Cove and Tilligerry Creek between 10 September 2015 and 1 October 2015. Commercially sized animals were captured from various locations close to the point-source of contamination within each estuary (Fig. 1), using both contracted commercial fishing vessels (with government staff on board) or fishery-independent trapping and trawling. Fish were targeted nocturnally using ≈3 in. mesh nets, whereas prawns were captured using an otter trawl (6 m mouth, 1 in. mesh) and crabs were targeted using baited traps (traps were baited using fish harvested from offshore areas).

Following capture, animals were placed on ice and dissected in the fisheries research laboratory at Port Stephens Fisheries Institute. Whole animals were weighed and total length (TL) or carapace length (CL) was measured. For fish, a ≈ 30 g portion of fish muscle was dissected for analysis from each individual and the skin was removed. Some fish livers were also removed for analysis. For crabs, 30 g of meat was dissected from each individual from the chelipeds and the abdominal segment. For prawns, 9–40 animals captured from the same tow were shelled (but not deveined) and composited to yield a mass of ≈30 g of prawn meat. Following preparation, samples were kept refrigerated and transported directly to National Measurement Institute (NMI) for analysis.

Analysis was conducted using isotopic dilution, based on reference method USEPA 537. Samples were prepared for analysis by homogenisation using a knife mill or hand-held homogeniser and stored in 50 mL Falcon® polypropylene tubes (Corning) at −20 °C. Samples had known amounts of $^{13}C$ isotopically labelled analogues of the target analytes (Wellington Laboratories, Canada) added and were extracted with saponification by tumbling with alkaline Methanol. The extract was centrifuged, and the supernatant concentrated then purified by solid phase extraction. A $^{13}C$ isotopically labelled standard was added to the sample to serve as a recovery standard. Qualitative/quantitative analysis for PFASs was performed using an Agilent 1100 HPLC, ABSciex 4000 Qtrap MS/MS high performance liquid chromatograph/triple quadrupole mass spectrometer/computerised data system (LC/MS/MS). Multiple reaction monitoring (MRM) of two characteristic transitions was performed, with identification confirmed when target ions

**Table 1**
Relative Percent Difference (RPD) from duplicate analyses (of Tilligerry Creek samples), to evaluate reproducibility of analyte concentrations. Only perfluoro-*n*-hexane sulfonate (PFHxS) and perfluoro-*n*-octane sulfonate (PFOS) were detected in these samples.

| Species name | Common name | Analysis 1 | | Analysis 2 | | Relative Percent Difference | |
|---|---|---|---|---|---|---|---|
| | | PFHxS (mg kg$^{-1}$) | PFOS (mg kg$^{-1}$) | PFHxS (mg kg$^{-1}$) | PFOS (mg kg$^{-1}$) | PFHxS (%) | PFOS (%) |
| *Sillago ciliata* | Sand Whiting | <0.00050 | 0.00075 | <0.00050 | 0.00087 | – | 14 |
| *Acanthopagrus australis* | Yellowfin Bream | <0.00050 | 0.00047 | <0.00050 | 0.00036 | – | 23 |
| *Penaeus plebejus* | Eastern King Prawn | 0.00160 | 0.03600 | 0.00140 | 0.03500 | 3 | 3 |