Science of the Total Environment 581–582 (2017) 258–267

Contents lists available at ScienceDirect

Science of the Total Environment

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

Depuration of perfluoroalkyl substances from the edible tissues of wild-caught invertebrate species

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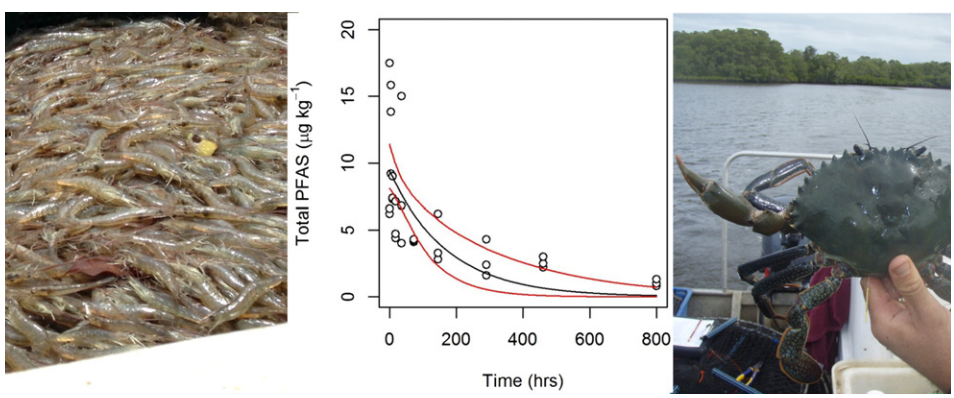
HIGHLIGHTS

- Perfluorooctanoic acid was rapidly depurated from both School Prawn and Mud Crab.
- Perfluorhexane sulfonate completely depurated from School Prawn within 50 h.
- Perfluorooctane sulfonate had a depuration half-life of 158.5 h in School Prawn.
- Depuration of long-chain perfluorosulfonates in Mud Crab requires further investigation

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 14 November 2016
Received in revised form 17 December 2016
Accepted 17 December 2016
Available online 2 January 2017

Editor: D. Barcelo

Keywords:
Penaeidae
Fisheries
Elimination
Exposure
PFASs
PFOS

ABSTRACT

Detection and quantification of poly- and perfluoroalkyl substances (PFASs) in aquatic organisms is increasing, particularly for saltwater species. Depuration can remove PFASs from the tissues of some species once they are removed from the contaminant source, but it is not known if this process occurs for saltwater crustaceans. Such information is important for managing human health risks for exploited migratory species following exposure. We present the results of a depuration trial for School Prawn (*Metapenaeus macleayi*) and Mud Crab (*Scylla serrata*), two commercially important crustaceans in Australia. Perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHxS), and perfluorooctanoic acid (PFOA) were present in samples of both species collected following exposure under natural conditions in contaminated estuaries. Depuration was tested in uncontaminated water for 33 days. PFOA was present at levels close to LOR in both species, and was not detected after 4.5 h and 72 h in School Prawn and Mud Crab respectively. PFHxS was rapidly depurated by School Prawn, and had a depuration half-life of 5.7 h. PFOS was also depurated by School Prawn, with a depuration half-life of 158.5 h. PFHxS and PFOS concentrations were highly variable in Mud Crab both at the start, and during the depuration experiment, and a depuration model could not be fitted to the data. For School Prawn, depuration of total PFASs to the relevant screening value for protection of human health (9.1 µg kg^{-1}) occurred within 7.1 h. Rapid depuration of PFASs in School Prawn indicates that human health risks associated with consumption may decrease as this species migrates away from the contamination source. Further research is required to better

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http://dx.doi.org/10.1016/j.scitotenv.2016.12.116

understand the relationships between contaminant load and life-history characteristics (such as growth, reproduction, and moult cycle) in Mud Crab, and future work should target broader time frames for depuration in this species.

1. Introduction

Poly- and perfluorinated alkyl substances (PFASs) are a group of chemicals that are composed of a fluorinated carbon chain with a hydrophilic end-group (Buck et al., 2011). The fluorinated chain is both hydrophobic and lipophobic, which confers unique properties on these chemicals (Krafft and Riess, 2015). Consequently, they have a broad number of industrial applications and have seen widespread use in consumer goods. There is concern over potential adverse health effects of these compounds, which are also extremely resistant to environmental degradation and thus persist in the environment for extended periods of time (Inoue et al., 2012; Lindstrom et al., 2011). These concerns and improvements in analytical technology have seen an increase in the detection and quantification of contamination by PFASs across a diverse range of terrestrial and aquatic ecosystems during the last 10 years (Houde et al., 2011). Much of the aquatic research to date has focused on freshwater ecosystems in the northern hemisphere (e.g. Murray et al., 2010), however, more recent studies have seen increasing focus on estuarine and marine systems and a broader range of aquatic taxa (Hong et al., 2015; Naile et al., 2013).

In Australia, the investigation of contamination of aquatic ecosystems with PFASs has a relatively recent history (Baduel et al., 2014; Gallen et al., 2014; Thompson et al., 2011a; Thompson et al., 2011b). The long-term use of products containing PFASs across airports and industrial facilities has contributed to an expanding number of contaminated sites being identified (Department of Defence, 2016). The high water solubility of certain PFASs such as perfluorooctane sulfonate (PFOS), perfluorohexane sulfonate (PFHxS), and perfluorooctanoic acid (PFOA), means that transport of these compounds from contaminated sites is thought to occur primarily through the movement of surface water/run-off and groundwater (AECOM, 2016). These facilities are often located at or near estuaries in Australia, and consequently these terrestrial primary pollutant sources can act as ongoing sources of contamination into adjacent saltwater systems.

Accumulation and depuration (or elimination) are two key processes which control the bioaccumulation of contaminants within an organism exposed through water or other media. Quantifying these processes is important for predicting the exposure levels in aquatic environments and understanding temporal variation in organism contaminant loads. Ankley et al. (2005) and Martin et al. (2003a) studied toxicokinetics of PFASs in the freshwater species Fathead Minnow (*Pimephales promelas*) and Rainbow Trout (*Oncorhynchus mykiss*) respectively. Martin et al. (2003a) demonstrated a short half-life of 15 days (for PFOS) and 5 days (for PFOA). These results are comparable to published half-lives as low as 7 days for organochlorine contaminants in Rainbow Trout (Fisk et al., 1998), and suggest that organisms can rapidly eliminate these contaminants from their system once exposure ceases. Jeon et al. (2010) studied uptake and elimination in the marine teleost Blackrock Fish (*Sebastes schlegelii*), and indicated relatively little elimination over the 30 day study period. In this study, however, fish were initially exposed to higher concentrations of PFASs (approximately 8 $\mu g\ L^{-1}$) than the concentrations typically detected (<0.025 $\mu g\ L^{-1}$) in most estuarine or marine systems (Ahrens et al., 2010; Gallen et al., 2014; Naile et al., 2010; Thompson et al., 2011b). To date there are no published studies that examine depuration or elimination of PFASs in crustaceans, despite these species displaying elevated concentrations in contaminated estuaries (Taylor and Johnson, 2016).

While studies on the toxicokinetics of contaminants provides useful information for understanding exposure levels in contaminated aquatic ecosystems, knowledge of depuration rates is also important for determining and managing human health risks in exploited species that undertake migrations throughout their life-history, or where the introduction of PFASs into aquatic systems may temporally vary. Furthermore, it is currently not clear whether water or food represent the dominant uptake route for aquatic organisms with gills, or whether differing uptake routes influence the distribution of PFASs throughout an animal's body, therefore it is useful to study depuration after exposure under "natural" conditions in the field.

PFASs have been detected in soil, surface water and groundwater within and around Newcastle airport and the Royal Australian Airforce (RAAF) base at Williamtown, New SouthWales, Australia (AECOM, 2016; URS Australia, 2015). Williamtown and the surrounding area is bordered by the Hunter River to the south, and Port Stephens to the north, and surface water from the base drains into these systems through Fullerton Cove and Tilligerry Creek respectively (Fig. 1). Preliminary investigations revealed that commercially exploited fish and crustaceans in both these areas contained PFOS, PFOA and PFHxS (Taylor and Johnson, 2016). A preliminary assessment of the human health risk associated with consumption of seafood from the area was conducted (Williamtown Contamination Expert Panel, 2015), and recommended that these areas be temporarily closed to commercial and recreational fishing while further investigations were carried out. School Prawn (*Metapenaeus macleayi*) and Giant Mud Crab (*Scylla serrata*) are two of the most economically important exploited species in Fullerton Cove and Tilligerry Creek, respectively. School Prawn undertake rapid migrations from estuarine habitats to inshore coastal areas both to spawn and also in response to flood events (Ruello, 1973; Taylor et al., 2016), and experience substantial fishing pressure during this period (Glaister, 1978). Mud Crab also leave estuarine nursery habitats, and gradually emigrate to sea as they mature to spawn (Fielder and Heasman, 1978). Consequently, both of these species contribute to commercial harvest in areas outside of the fishery closure areas, but depuration may act to mitigate any associated human health risks. To better understand potential human health risks from species that have migrated outside of the fishery closure areas, this study describes an experiment which examined the rate of depuration of PFASs from animals that were exposed to contaminants under natural conditions, once they were removed from the exposure source.

2. Materials and methods

2.1. Source of animals and experimental design

For each species, animals were collected from a contaminated source area; Fullerton Cove for School Prawn, and Tilligerry Creek for Mud Crab (Fig. 1). Animals collected from a known uncontaminated source area; Wallis Lake for both School Prawn and Mud Crab (Fig. 1) were also held under the same test conditions, to control for any potential uptake of contaminant from unknown sources in the holding aquarium over the course of the experiment. The experiment was conducted over late April and May 2016 at the Port Stephens Fisheries Institute, using 12 independent 5000 L tanks. Each species (School Prawn and Mud Crab) from each source area (Contaminated and Uncontaminated), were held in three separate, replicate tanks. Following introduction to the holding facility, animals were held for up to 33 days (following Martin et al., 2003a), and sampled at intervals within this period. School Prawn ($n = 20$ per tank per time point, to generate sufficient material