Marine Pollution Bulletin 127 (2018) 207–210

Contents lists available at ScienceDirect

Marine Pollution Bulletin

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

Note

First observations of perfluorooctane sulfonate occurrence and depuration from Sydney Rock Oysters, *Saccostrea glomerata*, in Port Stephens NSW Australia

Wayne A. O'Connor[a,*], Anthony Zammit[b], Michael C. Dove[a], Gavin Stevenson[c], Matthew D. Taylor[a]

[a] Department of Primary Industries – Fisheries, Port Stephens Fisheries Institute, Research Rd, Taylors Beach, NSW 2316, Australia
[b] Department of Primary Industries – Food Authority, 6 Avenue of the Americas, Newington, NSW 2127, Australia
[c] National Measurement Institute, Department of Industry and Science, PO Box 138, North Ryde, NSW 1670, Australia

ARTICLE INFO

Keywords:
Perfluoroalkyl substances
PFOS
Saccostrea glomerata
Depuration

ABSTRACT

Following the discovery of potential chronic perfluoroalkyl substances (PFAS) contamination of Tilligerry Creek, Port Stephens (New South Wales Australia), sampling was undertaken to confirm the presence, extent and levels of contamination in commercial oyster crops of Sydney Rock Oyster (*Saccostrea glomerata*) and Pacific Oyster (*Crassostrea gigas*) grown within the estuary. Among a range of PFAS tested, only perfluorooctane sulfonate (PFOS) was detected. Concentrations of PFOS in oyster tissues for *S. glomerata* ranged from 1.6 μg kg^{-1} ww (wet weight) to below the limit of reporting of 0.3 μg kg^{-1} ww, with concentrations generally decreasing toward the lower reaches of the estuary. The sample of *C. gigas* tested had a PFOS concentration of 0.71 μg kg^{-1} ww that was consistent with concentrations observed in nearby *S. glomerata*. For harvest size (50–60 g) *S. glomerata*, both holding contaminated oysters in a depuration system, and relocation to a non-contaminated area, saw significant reductions in the tissue PFOS concentrations. For oysters held in a depuration system, PFOS depurated at a rate of 0.008 h^{-1} (0.004–0.019 h^{-1}; 90% CI), which corresponded with a depuration half-life of 87 h (35–155 h; 90%). A more conservative model (fitted to data that assumed concentrations < LOR were equal 0.5·LOR) predicted a depuration half-life of 131 h. PFOS concentrations had fallen to below detectable limits within 162 h. Similar decreases were observed in relocated oysters.

1. Introduction

Perfluoroalkyl substances (PFAS) are persistent environmental pollutants that have seen use in a broad range of industrial applications and consumer goods (Lindstrom et al., 2011). These compounds are being increasingly detected across a range of aquatic ecosystems, and are now of worldwide concern both for their persistence and potential adverse effects on human health (Lindstrom et al., 2011). Perfluorooctane sulfonate (PFOS) has attracted particular attention, and in 2010 was added to the Stockholm Convention on Persistent Organic Pollutants (United Nations, 2009). Although there are no records of PFAS manufacture in Australia (Thompson et al., 2011), these compounds have been detected locally in a range of aquatic species (Munksgaard et al., 2016), including wild Sydney Rock Oysters, *Saccostrea glomerata* (Thompson et al., 2011).

PFAS are highly stable compounds that have unique chemical properties, including being both hydrophobic and lipophobic (Conder et al., 2008). These properties make PFAS compounds important components of Aqueous Film Forming Foam (AFFF) (Kannan et al., 2002). Persistent use of AFFF at Williamtown Royal Australian Air Force (RAAF) Base is thought to have led to the contamination of sediments, water and biota in nearby estuaries (AECOM, 2016). Drainage canals from the Williamtown area feed directly into Tilligerry Creek, Port Stephens (Moores Drain, Fig. 1), which is both a popular commercial and recreational fishing area and a major site for the production of *S. glomerata* for human consumption. However, Tilligerry Creek was closed to the direct harvest of oysters for market prior to knowledge of the presence of PFAS under the NSW Shellfish Program for sanitary standards, and quality assurance management practices for the Program mean that any oysters grown in this area must be depurated by either: 1) holding for 36 h in a closed recirculating (depuration) system prior to sale; or 2) transferring to an "open" harvest area for ≥ 14 days prior to sale. PFAS have been shown to depurate from the tissues of Pacific Oyster (*Crassostrea gigas*) with significant reductions in PFOS within

* Corresponding author.
E-mail address: wayne.o'connor@dpi.nsw.gov.au (W.A. O'Connor).

https://doi.org/10.1016/j.marpolbul.2017.11.058
Received 30 July 2017; Received in revised form 21 November 2017; Accepted 24 November 2017

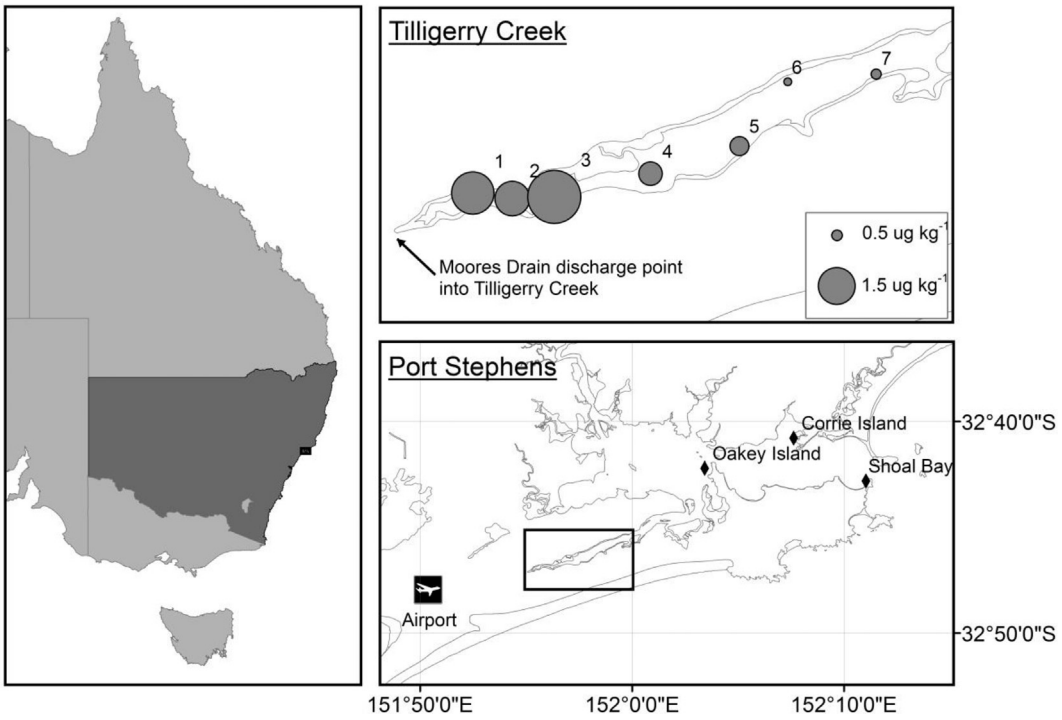

Fig. 1. Map of Port Stephens, NSW, and Tilligerry Creek. Locations referred to in the text are shown in the lower right panel. The upper right panel shows an inset of Tilligerry Creek, showing the 7 sites from which oysters were collected for testing, with symbol size indicating the PFOS concentrations of oysters collected at each site.

days (Jeon et al., 2010). Consequently, if PFAS have accumulated within commercial *S. glomerata* or *C. gigas* stocks grown in Tilligerry Creek, routine application of existing quality assurance management practices may mitigate human health risks associated with consumption of this product.

This initial study forms part of a broader sampling program to monitor potential PFAS contamination across a range of commercial and recreational species (Taylor and Johnson, 2016). Specifically, we aimed to measure the concentrations of PFAS compounds in *S. glomerata* and *C. gigas* from Tilligerry Creek, and ascertain whether the existing quality assurance management practices can eliminate PFAS from oysters prior to sale.

2. Materials and methods

On September 4th 2015, harvest size (50–60 g) oysters (n = 6) were collected from six commercial leases spanning the commercial growing area in upper Tilligerry Creek (Fig. 1). With the exception of one sample of *C. gigas* (Site 5, Fig. 1), all other oysters sampled were adult *S. glomerata*. On September 9th a further 120 harvest size stick-grown *S. glomerata* were obtained from an oyster lease adjacent to the outlet from Moores drain (Site 1, Fig. 1), which drains surface water from the Williamtown area. These oysters had been held at that location for 2.5 years before sampling. The oysters were subsequently divided into two groups. One group was held for 28 days in three, 200 L polythene tanks filled with clean, filtered (5 μm) seawater (collected from Shoal Bay, Fig. 1) at the Port Stephens Fisheries Institute. The water in these tanks was replaced every 2 days, and oysters were fed a mixture of hatchery produced phytoplankton on a daily basis, also grown in clean seawater. Six oysters were sampled from each of three replicate tanks after 36 h (to mimic the existing depuration protocol for Tilligerry Creek oysters), and again after 7, 14, 21 and 28 days. The second group of oysters was concurrently relocated in 3 replicate cages deployed in an open harvest oyster lease off Corrie Island in Port Stephens (Fig. 1), and six oyster samples were collected from each cage at 14 and 31 days. All samples were stored at − 17 °C between collection and analysis.

Samples were sent on ice to the National Measurement Institute (NMI) North Ryde for analysis of PFAS (perfluorohexanoic acid, (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUdA), perfluorododecanoic acid (PFDoA), perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHxS), perfluorooctane sulfonate (PFOS), C_2H_4-perfluorooctane sulfonate (6:2 FTS), C_2H_4-perfluorodecane sulfonate (8:2 FTS) by Solid Phase Extraction and Liquid Chromatography/tandem Mass Spectrometry (LC/MS/MS) using a method based upon USEPA 537 and USEPA 821 draft (see Taylor and Johnson, 2016 for details).

The whole meats (less shell) of the six oysters within each replicate cage/tank were composited for each analysis. The analysis consisted of extraction by overnight tumbling with alkaline methanol, followed by centrifugation and purification by solid phase extraction before Liquid Chromatography/tandem Mass Spectrometry (LC/MS/MS). The Limits of Reporting (LOR) were determined for each compound in each sample based on spiked validation samples, instrumental noise and laboratory blank levels, and varied between samples as a result of instrument performance and the level of sample contamination. The limit of reporting (LOR) for PFOS was 0.3 μg kg^{-1}, and isotopically labelled internal standard recoveries were 59–108%. No other PFAS were detected above LOR in any samples.

To estimate the change in concentrations of PFOS during the laboratory depuration trial, data were analysed using a non-linear least-squares fit of a decay function of the form:

$$[PFOS]_t = a \cdot e^{-k_d \cdot t}$$

where $[PFOS]_t$ is the concentration of the PFOS detected in the sample at time t (h), a is a constant equivalent to the fitted initial concentration (μg kg^{-1}) and k_d (h^{-1}) is the species-specific depuration rate coefficient. All values that were < LOR were considered to equal zero in model simulations. A second, more conservative model was also fitted using the above equation, but assuming values that were < LOR were equal to 0.5·LOR. Modelling was conducted in R v. 3.2.0 (R Development Core Team, 2016) using the nls function (in the package