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First report of perfluoroalkyl substances in South African Odonata

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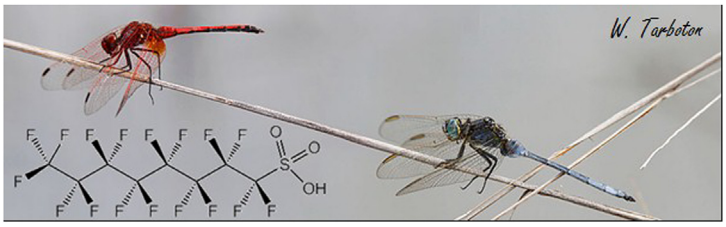
HIGHLIGHTS

- Dragonfly samples collected in South Africa analysed at NIES for PFASs.
- PFOS was quantifiable in all individuals.
- Quantifiable concentrations differ between southern and northern sites.
- Agricultural areas in the northern sites had low concentrations.
- Industrial areas in the southern sites had significantly higher concentrations.

GRAPHICAL ABSTRACT



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ABSTRACT

Perfluorinated substances are global and ubiquitous pollutants. However, very little is known about these substances in invertebrates, and even less in terrestrial invertebrates in particular. We analysed adult male dragonflies from six sites in South Africa for perfluoroalkyl substances (PFASs), including perfluorooctanesulfonic acid (PFOS), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluro-*n*-undecanoic acid (PFUnA), perfluoro-*n*-dodecanoic acid (PFDoA), perfluorohexanoic acid (PFHxA), and perfluorohexane sulfonic acid (PFHxS). PFOS was detected in all individuals, with less quantifiable occurrences of the other substances. The dragonflies from the three northern sites located in farming areas had significantly lower ΣPFASs concentrations than the southern sites located closer to industrial areas (median ΣPFASs of 0.32 ng/g wm (wet mass) for North, and 9.3 ng/g wm for South). All substances except PFOS occurred at similar concentrations at all six sites when quantifiable, but PFOS dominated in the Southern sites. The highest median concentration was from Bloemhof Dam (ΣPFASs = 21 ng/g wm), which is known to be polluted by PFOS. Perfluorinated substances are not known to be manufactured in South Africa, therefore the residues detected are likely to have been derived from imported products. Odonata play a significant role in freshwater ecology. Any impacts on these aquatic and aerial predators are likely to have effects on aquatic and associated ecosystems. Further studies are required over a much larger geographic region and to investigate sources.

1. Introduction

Perfluoroalkyl substances (PFASs) are a group of fluorinated organic compounds that are typically composed of either a straight- or branched perfluoroalkyl chains with a sulfonic or carboxylic acid moiety at one terminal (Newman, 2015). They are man-made only and have been manufactured for over 50 years (Newman, 2015). PFASs are water-soluble surfactants with unique properties of repelling both water and oil with their perfluoroalkyl chains. It is used in either its monomeric form or covalently combined as polymers. PFASs are very stable and resistant to both biotic and

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abiotic degradation, which is why residues are found in the environment. Although they are predominantly used in populated and industrial areas, several studies demonstrated that they are widespread further afield, even in remote areas such as the Arctic and Antarctic (Houde et al., 2011; Kannan et al., 2001).

Perfluorooctanesulfonic acid (PFOS) is volume-wise one of the most produced of the PFASs; their concentrations in both the environment and wildlife therefore tend to be higher than other perfluorinated substances although there are exceptions (Gilljam et al., 2015). PFOS, is used for a wide variety of purposes such as ant-insecticide, refrigerants, acid-mist suppressants for metal plating, floor polishes, aqueous firefighting foams, mining and oil-well surfactants, surfactants in pesticide formulations, and stain resistant treatments for leather, paper, and clothing, to name but a few (Newman, 2015). Environmental monitoring has shown that PFOS can bio-accumulate (Giesy and Kannan, 2001; Houde et al., 2011; Stahl et al., 2011). PFOS, its salts and its precursor, was added to Annex B (Annex B lists compounds for which restricted manufacture and use are allowed) of the Stockholm Convention in 2009 (Stockholm Convention, 2016a), and perfluorooctanoic acid (PFOA), its salts and PFOA-related compounds are nominated as candidate persistent organic pollutants (POPs) under the Convention in 2015 (Stockholm Convention, 2016b).

PFASs, particularly those with carboxylic acid, such as PFOA, are widely detected in the environment, and have adverse effects on human and wildlife (Grandjean and Clapp, 2015; Stahl et al., 2011). In general, the bio-accumulation potential of PFASs increases with longer carbon chains (Newman, 2015). PFOS shows strong retention in the human body with a mean serum half-live of 5.4 years for retired factory workers. For PFOA, it was 3.5 years (Olsen et al., 2007). In fish, PFOS accumulates to higher concentrations than PFOA, and eliminates slower (Falk et al., 2014), probably due to differences in binding to proteins and fatty acids (Ng and Hungerbüler, 2013; Jones et al., 2003). This bio-accumulation of PFASs in organisms could lead to adverse effects such as affecting the properties of the cell membrane (Hu et al., 2003) and disrupting the metabolism of fatty acids and endocrine systems (Stahl et al., 2011; White et al., 2011). PFOS tends to bind to proteins, particularly in the liver and blood, rather than accumulate in lipids like the other POPs (Bossi et al., 2005; Conder et al., 2008; Kannan et al., 2005).

Odonata (dragonflies and damselflies) fossil records date back to the Upper Carboniferous period. Some 300 million years ago, they derived from the Protodonata, and have changed little except in size (Corbet, 1999; Corbet and Brooks, 2008). Dragonflies occur on every continent except Antarctica. The larval stages take place in water, and the adults, that are obligatory aerial predators, are normally found near water. Some species can be found long distances from water in search of prey or when migrating. Especially the larval stages have long been used as bio-indicators of water quality and environmental conditions (Corbet, 1999; Clark and Samways, 1996; Nummelin et al., 2007). Dragonflies are excellent predators in both larval (although there are a few exceptions) and adult stages (Corbet, 1999), thus favouring bio-accumulation of toxicants in these organisms (Yu et al., 2013). All life stages of dragonflies are themselves also prey to a variety of organisms including vertebrates (Knight et al., 2005), facilitating trophic transfer of accumulated pollutants. Any impacts on these aquatic and aerial predators are therefore likely to have effects on ecosystems. Their global distribution and important trophic position potentially makes them well-suited for the testing of PFASs and other POPs.

The aquatic freshwater environment in Japan appears to be an important receiver of various discharged PFASs (Takazawa et al., 2009). Invertebrates commonly found in Japan were analysed for their potential as bio-monitors of PFASs (Yoshikane et al., 2009). Predatory arthropods (such as dragonflies, praying mantises, and spiders) accumulated much higher concentrations of PFASs than herbivorous arthropods. Dragonflies of the genera *Orthetrum, Crocothemis, Pseudothemis*, and *Sympetrum* (Family Libellulidae) caught at the same locations had comparable compositional patterns and concentrations. The apparent bio-accumulation factor, i.e., mean ratio between levels in dragonflies and those in nearby environmental water, was 1300 for PFOS, similar to the experimental bio-concentration factor for rainbow trout (Martin et al., 2003). The aim of this study was to determine and interpret the concentrations and patterns of occurrence of selected PFASs in adult Odonata from different sites in South Africa.

2. Materials and methods

2.1. Chemicals

Native and ^{13}C-labeled PFASs mixture solutions, i.e., PFAC-MXB and MPFAC-MXA, were obtained from Wellington Laboratories. Methanol and acetonitrile were of LCMS grade from Kanto Chemicals Co., Ltd. Water was purified by a Milli-Q water purification system (Millipore Co., Ltd.). Chem Elut cartridges were obtained from Agilent Co., Ltd. The cartridges were pre-cleaned with 5 mL of methanol and air-dried for 1 h with a dry pump, prior to use. Extractions and sample treatments were done in a clean laminar flow cabinet. To further prevent possible PFAS contamination from laboratory air, an additional, pre-cleaned, Chem Elut cartridge was connected on top during the drying process.

OASIS HLB Plus (225 mg) and MCX (60 mg in 3 mL) syringes, obtained from Waters Co, were used after pre-conditioning with 2 mL of methanol and 5 mL of water. A TBA solution (0.5 M) was made from tetrabutylammonium hydrogen sulfate (Wako Pure Chemicals Co., Reagent grade). The sodium carbonate solution (0.25 M; reagent grade) was procured from Kanto Chemicals Co. We distilled methyl *tert*-butyl ether (MTBE) before use. Tetrabutyl ammonium (TBA) and sodium carbonate solutions were pre-cleaned by shacking with MTBE before use. All the other tools and vessels directly contact with samples, such as glass and plastic wares, tweezers, spatulas and mortars and pestles made of agar, were pre-cleaned with methanol and dried before use.

2.2. Sample collection

Adult dragonflies of the Libellulidae family were collected at six sites (Fig. 1 and Table 1) in South Africa, with the necessary permits and permissions. The dragonflies were caught with clean entomological nets (rinsed with water and dried to remove any debris) and placed individually in plastic zip-lock bags, labeled and placed in cold-storage, in darkness. At the laboratory, as soon as possible, the wet mass of the dragonflies were noted to the nearest 0.01 g and stored at −18 °C. The samples were freeze-dried before being shipped to The National Institute of Environmental Studies (NIES) in Japan. A total of 116 individual male dragonflies, *Sympetrum infuscatum*, were caught within NIES, Japan, on 23 Aug 2012, and were weighed, freeze-dried and homogenized together with a clean mortar and a pestle to make a well mixed powder. An aliquot (c.a. 0.3 g dry mass each) of the powder was poured into a 50-mL centrifuge tube made of polypropylene (total 100 bottles), and was used for quality control of the analysis (QC sample).

2.3. Sample preparation and analysis

Each individual sample was placed in a 50-mL centrifuge tube. Two blank samples with 1 mL water and one QC sample were made