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Perfluoroalkyl Sulfonates and Carboxylic Acids in Liver, Muscle and Adipose Tissues of Black-Footed Albatross (*Phoebastria nigripes*) from Midway Island, North Pacific Ocean

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Abstract

The Great Pacific Garbage Patch (GPGP) is a gyre of marine plastic debris in the North Pacific Ocean, and nearby is Midway Atoll which is a focal point for ecological damage. This study investigated 13 C₄-C₁₆ perfluorinated carboxylic acids (PFCAs), four (C₄, C₆, C₈ and C₁₀) perfluorinated sulfonates and perfluoro-4-ethylcyclohexane sulfonate [collectively perfluoroalkyl acids (PFAAs)] in black-footed albatross tissues (collected in 2011) from Midway Atoll. Of the 18 PFCAs and PFSAs monitored, most were detectable in the liver, muscle and adipose tissues. The concentrations of PFCAs and PFSAs were higher than those in most seabirds from the arctic environment, but lower than those in most of fish-eating water birds collected in the U.S. mainland. The concentrations of the PFAAs in the albatross livers were 7-fold higher than those in Laysan albatross liver samples from the same location reported in 1994. The concentration ranges of PFOS were 22.91-70.48, 3.01-6.59 and 0.53-8.35 ng g⁻¹ wet weight (ww), respectively, in the liver, muscle and adipose. In the liver samples PFOS was dominant, followed by longer chain PFUDA (8.04-18.70 ng g⁻¹ ww), PFTrDA, and then PFNA, PFDA and PFDoA. Short chain PFBA, PFPeA, PFBS and C₁₆ PFODA were below limit of quantification. C₈-C₁₃ PFCAs showed much higher composition compared to those found in other wildlife where PFOS typically predominated. The concentrations of PFUDA in all 8 individual albatross muscle samples were even higher than those of PFOS. This phenomenon may be attributable to GPGP as a pollution source as well as PFAA physicochemical properties.

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Keywords

perfluoroalkyl acids; perfluorinated carboxylic acids; perfluorinated sulfonates; albatross; Midway Atoll; Great Pacific Garbage Patch

1. Introduction

Perfluoroalkyl acids (PFAAs) and their precursors are a large group of per-/polyfluoroalkyl substances (PFASs) widely used in commercial products, which include water and grease repelling coatings for paper, flame retardant foams, textiles, and prints, because of their excellent surfactant capabilities, stability and amphiphilic properties (Lindstrom et al., 2011; Prevedouros et al., 2006). The high chemical and biological stability of PFAAs is conferred by their strong carbon-fluorine bond. The detection of some PFASs in human blood first raised concerns about their potential toxicity back in the 1970's when the presence of PFASs was reported in human plasma (Singer and Ophaug, 1976). Since then the widespread presence of PFASs, and especially PFAAs, in the environment has been observed in humans and biota including wildlife (Houde et al., 2011; Butt et al., 2010; Gewurtz et al., 2013; Betts, 2007). PFAAs in particular are now considered as a group of globally distributed pollutants.

Several studies have been published on the toxicological effects of PFASs, where they elicit toxicities and effects on exposed mammals and birds (Lau et al., 2007). Due to the stable nature of the carbon-fluorine bond (recalcitrant to chemical, photochemical and biological degradation) and their large-scale production and usage, PFASs and often their precursors are globally distributed in the environment, including remote areas, such as the Arctic and Antarctica (Butt et al., 2010; Gewurtz et al., 2013; Letcher et al., 2010; Kannan et al., 2001; Toa et al., 2006). However, the sources and transport pathway of PFASs in the environment are not well understood (Paul et al., 2009; Wang et al., 2013). The sources of PFASs to the environment include direct manufacturing discharge to air and water and the degradation of their precursors released from commercial products (Lindstrom et al., 2011). Transport of PFASs via atmosphere and ocean water was considered to be the major pathway to reach remote areas (Prevedouros et al., 2006). Unlike legacy persistent organic pollutants (POPs), such as polychlorinated biphenyls (PCBs) and chlorinated pesticides, which accumulate in lipid rich tissues, PFASs bind to proteins and their bioaccumulation tendency differs from the other POPs. Therefore, their environmental behaviour might differ from the other POPs.

Seabirds are exposed to marine contamination and debris and are widely used to monitor marine contamination. As seabirds are globally present and at the top of marine (and to a lesser degree terrestrial) food chain, their contamination level reflects the environments in which they live. PFAAs have been reported in seabird eggs and tissues with relatively high concentrations (Kannan et al., 2001; Gebbink et al., 2011). However, investigations of geographical distribution of PFAAs have mostly focused on avian samples collected from North America and Europe. Very few data of PFASs in seabirds are available for the Southern Hemisphere and Pacific region. Such knowledge gap largely limits understanding of PFAS distribution and evaluation of their global transport processes.

Midway Atoll is a small island, also called Midway Island in the North Pacific Ocean. It is home to millions of seabirds including black-footed albatrosses (*Phoebastria nigripes*). Unfortunately, Midway Atoll is also a focal point for ecological damage impacted by the Great Pacific Garbage Patch (GPGP) that is a gyre of anthropogenic debris in the North Pacific Ocean (Howell et al., 2012; Kaiser, 2010). Seabirds travel thousands of miles over their marine environment in search of food and often concomitantly consume plastic debris. As a result, such plastics have been shown to fill seabird stomachs and cause starvation or rupture organs. Furthermore, the harm is compounded by the fact that plastics both leach out and adsorb harmful pollutants (<http://pacificvoyagers.org/midway-atoll-the-plastic-plight-of-the-albatross>).

The aim of this study was to analyze perfluorinated carboxylic acids (PFCAs) and perfluorinated sulfonates (PFSAs) including perfluoro-4-ethylcyclohexane sulfonate (PFEtCHxS) (collectively PFAAs) in tissues of black-footed albatross from Midway Island, USA. Eighteen PFCAs and PFSAs were determined by liquid chromatography coupled to tandem mass spectrometry and their tissues distributions in live, muscle, and adipose were studied. The purpose of this investigation was to provide advances in understanding environmental behaviour of PFASs in black-footed albatross from the North Pacific Ocean.

2. Experimental section

2.1 Chemicals and standard

The monitored PFAAs in this study were C₄-C₁₆ PFCAs, C₄, C₆, C₈ and C₁₀ PFSAs including PFEtCHxS. Table 1 shows the PFAA full names and acronyms. All analytical standard compounds including the mass-labelled internal standards were purchased from Wellington Laboratories (Guelph, ON, Canada), with exception of PFEtCHxS potassium salt that was purchased from Campro Scientific GmbH (Berlin, Germany). Ammonium hydroxide solution (28-30%) was purchased from Sigma-Aldrich (St. Louis, MO, USA). HPLC grade methanol and acetonitrile were purchased from Fisher Scientific (Pittsburgh, PA, USA). Ultrapure water was obtained from a Milli-Q system. All other reagents were the highest commercial purity and employed as received.

2.2 Sample collection and preparation

A total of 8 black-footed albatross (*Phoebastria nigripes*) were collected on Midway Atoll in the North Pacific Ocean (28°N, 177°W) in 2011. Midway Atoll is a small island and was designated as an overlay National Wildlife Refuge in 1988. The black-footed albatross is a large seabird inhabiting the North Pacific Ocean. Most of the population is found on the Northwestern Hawaiian Islands. Plastic debris and pollutants from the GPGP and impacts on albatross on Midway Atoll is a notorious issue (<http://pacificvoyagers.org/midway-atoll-the-plastic-plight-of-the-albatross>). All of the present albatrosses were found dead on Midway Atoll and collected by the U.S. Fish & Wildlife Service, and then sent to the laboratory in the University of Hawaii at Manoa, where the birds were dissected (Fig. 1), and their tissue samples were kept frozen at -20 °C until analysis.

2.3 Analysis method

PFCAs and PFSAAs in biota samples were analyzed as previously published (Braune and Letcher, 2013) with some modifications and briefly described as follows. About 1 g of liver, muscle, or 0.5 g of adipose tissue sample was weighed in a polypropylene centrifuge tube and spiked with an internal standard solution mixture (Table 1). Three mL of 1 % formic acid acetonitrile solution was added, followed by homogenization for 1 min for extraction. After centrifugation, the supernatant was transferred to a tube. The extraction process was repeated 3 times and the supernatants were combined. Two mL of extract solution was transferred into a 15 mL polypropylene centrifuge tube and diluted by 8 mL of water. The extracts were cleaned up with Oasis WAX SPE cartridges (60 mg $\times$ 3 mL, from Waters, Milford, MA, USA). The cartridge was conditioned with 3 mL methanol and 3 mL water. After the sample solution was loaded on the cartridge, the cartridge was first washed by 1 mL of 2 % formic acid aqueous solution and then by 2 $\times$ 1 mL water. The cartridge was then washed with 2 $\times$ 1 mL methanol. The target PFCAs, PFSAAs and internal standards were eluted by 2 $\times$ 1 mL aqueous ammonium hydroxide solution/methanol (1v/99v) solution. This fraction was collected in a centrifuge tube. The sample solution was concentrated to dryness with a stream of nitrogen and reconstituted in 200 μ L of methanol. The solution was then filtered through a centrifugal filter (modified Nylon 0.2 μ m, 500 μ L from VWR, PA, USA) and transferred to a vial for LC/MS/MS analysis.

PFCAs and PFSAAs were analyzed on a Waters Alliance 2695 high performance liquid chromatograph system coupled to a Micromass Quattro Ultima triple quadrupole mass spectrometer (Waters). The separation was carried out on a Luna C₁₈(2) column (50 mm $\times$ 0.2 mm, 3 μ m particle size) (Phenomenex Co., Torrance, CA, USA). The mobile phases were water (A) and methanol (B) with both containing 2 mM of ammonium acetate. The mobile phase flow rate was 0.2 mL/min. The gradient started at 5% B, increasing to 80% B in 10 min and to 100% B in 20 min and held to 25 min. Thereafter, the mobile phase composition was returned to the initial condition and the column was allowed to equilibrate for 15 min before the next run. A volume of 10 μ L of sample was injected with an auto-injector.

The mass spectrometer was operated in the negative ion ESI mode using multiple reaction monitoring with argon as the collision gas. The capillary voltage was 1.0 kV. The source temperature and probe temperature were 120 and 325 $^{\circ}$ C, respectively. Nitrogen was used as nebulizing gas and dissolvent gas. Cone and desolvation gas flow rates were 100 and 600 L/h, respectively. The MS/MS compound dependent operating parameters were listed in Table 2. The precursor ion for these target compounds was [M-H]⁻. The product ions were [M-COOH]⁻, [SO₃]⁻ and [FSO₃]⁻ for PFCAs, PFSAAs and PF₂EtCH₂S, respectively. The data were processed using Masslynx v 4.0 software (Waters).

2.4. Quality control, quality assurance and data analysis

As a standard procedure, laboratory blanks, method limits of detection (MLODs), limits of quantification (MLOQs), recoveries, and standard reference materials (SRM) were examined. For each batch of samples (n=12), a blank sample and a standard spiked sample were run with real environmental samples to check any possible contamination from the

process, and to check target PFAS recoveries. The MLODs were calculated as 3 times signal-to-noise (peak to peak) for individual compound in samples (S/N=3). MLOQ were defined as 3 times the standard deviation concentration of target compounds in spiked samples. The MLOD and MLOQ values were listed in Table 2. NIST SRM 1947 (Lake Michigan fish homogenate) was analyzed to control the performance of the analytical method and the measured concentrations were within the certification ranges. The analytical quality of the laboratory has been approved in inter-laboratory studies.

GraphPad Prism 5 was used to calculate the data. The significance level was set at $p < 0.05$.

3. Results and discussion

3.1. Overall concentrations

The stomachs of all 8 albatrosses were filled with plastics as exemplified in Fig. 1. For the 18 monitored PFASs, most were detectable in all 8 albatross muscle, liver and adipose (Table 3). The levels of PFASs and PFCAs in samples of black-footed albatross observed in this study were higher than those in most seabird species from the Arctic (Butt et al., 2010; Letcher et al., 2010), but lower than those in most of fish-eating water birds collected in the United States mainland (Kannan et al., 2001; Custer et al., 2013), and from colony sites in urbanized areas of the Laurentian Great Lakes of North America (Gebbink and Letcher, 2012). Kannan et al. (2001) analyzed several PFASs in black-footed albatross and Laysan albatross tissue samples collected back in 1994 from Midway Atoll and found that PFOS concentrations in their liver samples were $<30 \text{ ng g}^{-1} \text{ ww}$. Tao et al. (2006) investigated several PFASs in 8 species of albatrosses from the Southern Ocean and the North Pacific Ocean and in samples collected from 1992-2006. PFOS and PFOA were the only detectable PFASs in the livers of albatrosses from the Southern Ocean, while more PFASs were detectable in serum, and egg samples collected from the North Pacific Ocean. In Laysan albatross liver samples from Indian Ocean, the highest concentrations of PFOS and PFOA were 12.2 ng g^{-1} and $3.66 \text{ ng g}^{-1} \text{ ww}$, respectively. In Laysan albatross liver samples collected on Midway Atoll during 1992-1996, the concentration of PFOS ranged from <0.5 to $16.4 \text{ ng g}^{-1} \text{ ww}$ with a mean value of $5.10 \text{ ng g}^{-1} \text{ ww}$. In the present study, in the black-footed albatross liver samples the concentrations of PFOS ranged from 22.91 to $70.48 \text{ ng g}^{-1} \text{ ww}$ with mean value of $36.05 \text{ ng g}^{-1} \text{ ww}$. By comparison, if we do not consider the species difference (Laysan albatross and black-footed albatross are the two main species of albatross distributed in the northwestern Hawaiian Islands), the PFOS concentration in these birds increased 7-fold during the period from middle of 1990's to 2011.

Although some studies were focused on PFCA and PFSA temporal trends in birds, most monitored contamination trends in eggs (Butt et al., 2010; Braune and Letcher, 2013). Butt et al. (2007) examined PFCA and PFSA temporal trends in northern fulmar (*Fulmarus glacialis*) and thick-billed murre (*Uria lomvia*) liver collected from Lancaster Sound, Canada. The results showed that for PFOS during the period of 1975 to 2003, the doubling times were 10.3 and 9.8 years for thick-billed murre and northern fulmars, respectively (Butt et al., 2007). Holmstrom et al. (2010) studied temporal trends of PFCAs and PFASs in Swedish peregrine falcon eggs (*Falco peregrinus*) and found that PFOS concentration doubling time (1974-2007) was 12 years. The results of the present study suggest that PFOS

contamination in the albatross on Midway Atoll have increased more substantially relative to other exposed seabirds that have been reported. The most reasonable explanation for this is probably due to the impact of the Pacific Garbage Patch, which is a gyre of marine debris particles found in the Central North Pacific Ocean (Day, 1988).

3.2 Distribution of PFAAs in albatross tissues

In the present study, among tissue samples analyzed, the PFOS concentration was the highest in liver (22.91-70.48 ng g⁻¹ ww), followed by muscle (3.01-6.59 ng g⁻¹ ww) and then adipose (0.53-8.35 ng g⁻¹ ww). PFCAs, such as PFOA and PFNA, which were monitored in other environment investigations, showed a similar tissue distribution (liver > muscle > adipose). This tissue distribution is in agreement with available literature in other investigations of fish and wildlife (Rubarth et al., 2011; Holmstrom et al., 2008; Verreault et al., 2005; Greaves and Letcher, 2013; Van de Vijver et al., 2005 and 2007). In the present study, the concentration of PFOS in albatross adipose tissues was about one of tenth of that in liver samples (3.3 ng g⁻¹ ww vs. 36.05 ng g⁻¹ ww). This distribution is consistent with the results found in red-throated divers (*Gavia stellata*) sampled from the Baltic Sea (Rubarth et al., 2011). However, the PFOS ratio of C_{adipose}/C_{liver} found in the present study is much higher than that found in mammal samples, such as polar bear from East Greenland (Greaves and Letcher, 2013).

3.3. PFAA tissue composition profiles

In all 8 albatross liver samples, PFOS was dominant, followed by PFUdA, PFTrDA, and then PFNA, PFDA and PFDoA, and where the latter three were at a similar concentration level. This PFAA composition profile in liver sample was somewhat different from the data reported for birds in the literature, in which the composition of PFOS was much higher than that of other PFASs (Holmstrom and Berger, 2008; Butt et al., 2010). Shorter carbon chain PFASs, such as PFBA, PFPeA and PFBS, were not detectable or below MLOQ in the liver samples. With the improved analysis method, in all 8 albatross liver, muscle and adipose tissue samples, except one of adipose sample, PFHxS was also detectable with a mean concentration of 0.60, 0.28 and 0.12 ng g⁻¹ ww, respectively. PFHxA and PFHpA concentrations were relatively low in the liver samples, which agreed with the literature, as these compounds showed to be low bioaccumulation (Rubarth et al., 2011; Holmstrom and Berger, 2008; Conder et al., 2008).

The concentrations of PFODA and PFEtCHxS were below MLODs in all 8 albatross liver samples. PFEtCHxS was mainly used as an erosion inhibitor in aircraft hydraulic fluids and was detected in fish, snapping turtle and other environmental samples (de Silva et al., 2011; de Solla et al., 2012), especially in the samples collected near airport facilities. In the present study undetectable level of the branched PFEtCHxS in these albatross liver samples is likely due to dietary exposure levels simply being too low. Although the concentration of individual PFAAs in the albatross adipose samples was about one of tenth of that in the liver samples, the composition profile of PFAAs was similar with that found in liver samples with a relative large variation. There were very few data available about composition profile of PFASs in bird adipose samples, because PFAS contamination was monitored with their egg, plasma and liver samples in most studies. In herring gulls (*Larus argentatus*) samples

collected in Great Lakes (one colony site on Chantry Island, Lake Huron), PFSAAs (sum of PFHxS, PFOS and PFDS) were much more highly dominated by PFOS ($171 \pm 83 \text{ ng g}^{-1}$), while only very low concentrations of PFNA and PFUnA were detectable ($0.3 \pm 0.1 \text{ ng g}^{-1}$) in adipose (Gebbink and Letcher, 2012). However, Rubarth et al. (2011) observed a similar composition profile of PFAAs in liver and fatty tissues of red-throated diver (*G. stellata*) collected from the German Baltic Sea.

In the present albatross muscle samples, the profile of PFAAs was different from that in the liver samples. In the muscle sample the concentrations of PFOS, PFUdA and PFTrDA were at a similar concentration level with no significant ($p < 0.05$) difference. This composition profile of PFAAs is very uncommon, especially for birds, and only very few data were reported for such phenomenon in environmental samples (Butt et al., 2007).

In all albatross tissue samples, PFCA composition profiles showed a distinctive “odd even” pattern, in which concentrations of odd chain-length PFCAs were greater than adjacent even chain-length PFCAs. This phenomenon was also found in other environmental biota samples and might be explained as a result of the degradation of fluorotelomer alcohol precursors (Martin et al., 2004; Rubarth et al., 2011; Conder et al., 2008).

3.4. Long chain PFCAs in albatross tissues

There were relatively few reports of longer chain-length PFCAs in seabirds, because it was difficult to determine them in biotic samples (Rubarth et al., 2011). An interesting observation in the present study was that PFCAs with 8 to 13 fluorinated carbons showed much higher composition in the albatross tissues in comparison with those in other wildlife in which PFOS is typically much more dominating in PFAA profiles (Butt et al., 2010; Greaves and Letcher, 2012).

It has been reported that a PFNA commercial product (Surflon S-111) contains significant quantities of PFUdA and PFTrA (Prevedouros et al., 2006) and the environmental presence of longer chain PFCAs may partly be a result of impurities of longer carbon chain compounds in the PFOA and PFNA technical products. However, such high compositions of PFUdA and PFTrA observed in this seabird could not attribute directly to its original commercial product patterns. Although this occurrence was also occasionally observed in other seabird sample (Butt et al., 2010), it was more obvious in the present albatross tissue samples. The concentrations of PFUdA in all 8 individual albatross muscle samples were even higher than those of PFOS. The different composition profiles of PFAAs in these albatross samples and some other wildlife could be attributed to geographical differences in their pollution sources, transportation pathways and physicochemical properties of the compounds themselves. Concentrations of individual compounds in the fish, albatross's main prey, mainly depended on pollution source and their bioaccumulation factors. As a main pollution source is GPGP that is nearby Midway Atoll, which is formed in a gyre of marine debris particles. The composition profile of PFAAs might be very different from their original composition, because long transport pathway in the ocean current and longtime wash process. The PFCAs with low fluorinated carbon chain and PFOS would loss more than long chain PFCAs during the process, because their relative low K_{ow} values (Kelly et al., 2009). For example, the low K_{ow} values of PFNA and PFOS are 4.5 and 4.3,

respectively, while K_{ow} values of PFUdA and PFTrDA are 6.4 and 8.8, respectively. As a result of GPGP, the PFAAs composition profile would be prone to increasing composition of PFCAs with longer chains. On another hand, different from POPs such as PCBs and PBDEs, PFAAs are proteinophilic. In vitro binding assay experiment results showed these compounds strongly bind to albumin and other cytosolic proteins (Han et al., 2003). Long chain PFAAs are more competitive ligands than short chain PFAAs in binding to proteins and they have high bioaccumulation factor values (Jones et al., 2003, Conder et al., 2008). Conder et al. (2008) pointed out that bioconcentration and bioaccumulation factors of PFAAs are directly related to fluorinated carbon chain length, with the highest bioaccumulation potential noted for long perfluorinated acids such as perfluorododecanoic acid (PFDoA, 11 fluorinated carbons) and perfluorotetradecanoic acid (PFTeDA, 13 fluorinated carbons); and also PFSAs are generally more bioaccumulative than PFCAs of the same fluorinated carbon chain length. Although there is still a gap of lack biomagnification (BMF) values of PFASs in food web from fish to albatrosses, it was estimated that BMF_{TL} values (BMF value was normalized by trophic level of PFCAs with 7 to 11 fluorinated carbon chain) ranged from 0.1 to 20 (Conder et al., 2008). Therefore, the composition profile of PFAAs in albatross tissues tends to be long chain perfluorinated compounds, such as PFUdA and PFTrDA. Another reason might be that black-footed albatross has some special behaviour of catching fish and they mistakenly pick up and ingest floating plastics. Although adult albatrosses can regurgitate these ingested plastics, the contamination of PFASs in plastics would be a direct source of exposure and accumulation in their body.

4. Conclusion

This investigation showed that albatrosses from Midway Atoll in the North Pacific Ocean contained notable concentrations of PFCAs and PFSAs. Their PFAA composition profiles differed from most data reported to date in the literature for birds. Long chain PFCAs were dominated and this occurrence might be attributed to their special pollution source of GPGP and the PFAA proteinophilic behaviour. The occurrence of PFAAs in albatrosses suggests the widespread distribution of PFASs in the remote marine locations. The observations warrant further investigation of PFASs in seabirds to understand the impact of GPGP on nearby ocean ecosystems.

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Highlights

Perfluoroalkyl acids (PFAAs) were found in black-footed albatross from Midway Atoll.

PFAA composition profiles in liver differed from most data reported for birds.

PFAA concentrations in the birds were affected by Great Pacific Garbage Patch.

PFAA concentrations in liver were much higher than those reported in the 1990's.

Fig. 1.
Plastic masses within the stomach cavity of a dead Black-footed Albatross, Midway Atoll.
The photo was taken in the laboratory in the University of Hawaii at Manoa.

Table 1

Perfluoroalkyl carboxylates (PFCAs) and perfluoroalkyl sulfonates (PFASs) monitored in this study and their internal stands

	Target compounds	Acronyms
1	Perfluoro-n-butanoic acid	PFBA
2	Perfluoro-n-pentanoic acid	PFPeA
3	Perfluoro-n-hexanoic acid	PFHxA
4	Perfluoro-n-heptanoic acid	PFHpA
5	Perfluoro-n-octanoic acid	PFOA
6	Perfluoro-4-ethylcyclohexane sulfonic acid	PFEtCHxS
7	Perfluoro-n-nonanoic acid	PFNA
8	Perfluoro-n-decanoic acid	PFDA
9	Perfluoro-n-undecanoic acid	PFUdA
10	Perfluoro-n-dodecanoic acid	PFDoA
11	Perfluoro-n-tridecanoic acid	PFTTrDA
12	Perfluoro-n-tetradecanoic acid	PFTeDA
13	Perfluoro-n-hexadecanoic acid	PFHxDA
14	Perfluoro-n-octadecanoic acid	PFODA
15	Perfluoro-perfluoro-1-butanedisulfonate	PFBS
16	Perfluoro-perfluoro-1-hexanedisulfonate	PFHxS
17	Perfluoro-perfluoro-1-octanedisulfonate	PFOS
18	Perfluoro-perfluoro-1-decanedisulfonate	PFDS
Internal standard compounds		
1	Perfluoro-n-[1,2,3,4- ¹³ C ₄]butanoic acid	MPFBA
2	Perfluoro-n-[1,2- ¹³ C ₂]hexanoic acid	MPFHxA
3	Perfluoro-n-[1,2,3,4- ¹³ C ₄]octanoic acid	MPFOA
4	Perfluoro-n-[1,2,3,4,5- ¹³ C ₅]nonanoic acid	MPFNA
5	Perfluoro-n-[1,2- ¹³ C ₂]decanoic acid	MPFDA
6	Perfluoro-n-[1,2- ¹³ C ₂]undecanoic acid	MPFUdA
7	Perfluoro-n-[1,2- ¹³ C ₂]dodecanoic acid	MPFDoA
8	Perfluoro-perfluoro-1-hexane[¹⁸ O ₂]sulfonate	MPFHxS
9	Perfluoro-perfluoro-1-[1,2,3,4- ¹³ C ₄]octanedisulfonate	MPFOS

The compound dependent operating parameters of MS/MS and retention times for perfluoroalkyl sulfonate and carboxylic acid analysis

Table 2

No.	Compound name	Precursor ion (Da)	Product ion (Da)	Cone voltage (V)	Collision Energy (eV)	MLOD (ng g ⁻¹)	MLOQ (ng g ⁻¹)
Target compounds							
1	PFBA	212.9	168.9	40	10	0.04	0.59
2	PFPeA	262.8	218.9	40	10	0.04	0.07
3	PFBS	298.9	80.1	45	35	0.04	0.07
4	PFHxA	312.8	268.9	40	10	0.02	0.04
5	PFHpA	362.9	318.9	40	8	0.01	0.02
6	PFHxS	399.0	80.1	50	45	0.04	0.06
7	PFOA	412.8	368.9	35	8	0.01	0.05
8	PFEtCHxS	460.9	99.0	35	28	0.02	0.05
9	PFNA	462.8	418.9	45	10	0.03	0.04
10	PFOS	499.0	80.1	35	40	0.01	0.31
11	PFDA	512.8	468.9	45	10	0.01	0.05
12	PFUdA	562.8	518.9	35	10	0.01	0.07
13	PFDS	598.9	80.1	35	55	0.04	0.08
14	PFDoA	612.9	568.9	35	10	0.01	0.04
15	PFTeDA	662.9	619.0	35	10	0.01	0.06
16	PFTeDA	713.0	669.0	35	10	0.03	0.08
17	PFHxDA	813.0	769.0	35	10	0.02	0.08
18	PFODA	913.0	869.0	35	10	0.04	0.17
Internal Standards							
19	MPFBA	216.9	172.0	40	10		
20	MPFHxA	314.8	269.9	40	10		
21	MPFHxS	403.0	84.1	35	40		
22	MPFOA	416.9	371.9	35	8		
23	MPFNA	467.9	423.0	45	10		
24	MPFOS	503.0	80.1	35	40		
25	MPFDA	514.8	469.9	45	10		
26	MPFUDa	564.9	519.9	35	10		

No.	Compound name	Precursor ion (Da)	Product ion (Da)	Cone voltage (V)	Collision Energy (eV)	MILOD (ng g ⁻¹)	MILOQ (ng g ⁻¹)
27	MPFD _o A	614.9	570.0	35	10		

See Table 1 for full chemical names.

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Table 3

Concentrations of perfluoroalkyl sulfonates and carboxylic acids in albatross liver, muscle and adipose samples from Midway Atoll (ng g⁻¹ w.w.)

Sample Name	Tissue	1	2	3	4	5	6	7	8	PFEICHS	PFNA	PFOS	PFDA	PFUDA	PFDS	PFDoA	PFTtDA	PFTeDA	PFHxDA	17	18
MLOQ		0.59	0.07	0.07	0.04	0.02	0.06	0.05	0.05		0.04	0.31	0.05	0.07	0.08	0.04	0.06	0.08	0.08	0.08	0.17
MLOD		0.04	0.04	0.04	0.02	0.01	0.04	0.01	0.02		0.03	0.01	0.01	0.01	0.04	0.01	0.01	0.03	0.02	0.02	0.04
B-1-L	Liver	ND	ND	ND	<MLOQ	0.64	0.38	0.38	ND	3.38	26.35	3.16	14.07	14.07	ND	2.55	7.14	0.90	<MLOQ	ND	ND
B-2-L	Liver	ND	ND	ND	0.11	0.32	0.14	0.14	ND	1.52	70.48	1.79	10.37	10.37	ND	1.99	5.97	1.16	<MLOQ	ND	ND
B-3-L	Liver	ND	ND	ND	0.18	0.81	0.42	0.42	ND	4.38	30.56	3.74	17.47	17.47	0.09	3.08	14.18	2.43	0.14	ND	ND
B-4-L	Liver	ND	ND	ND	0.06	0.60	0.77	0.77	ND	4.78	23.40	3.44	13.62	13.62	0.09	2.46	7.36	1.36	0.13	ND	ND
B-6-L	Liver	<MLOQ	ND	ND	0.08	0.52	0.35	0.35	ND	3.53	22.91	3.29	15.49	15.49	0.10	2.67	10.54	1.79	0.04	ND	ND
B-7-L	Liver	ND	ND	ND	0.05	0.03	0.77	0.57	ND	4.15	46.07	3.72	18.70	18.70	0.15	3.36	9.50	1.47	0.13	ND	ND
B-8-L	Liver	ND	ND	ND	0.09	0.54	0.26	0.26	ND	2.17	32.61	1.66	8.04	8.04	ND	1.68	6.73	1.89	0.13	ND	ND
range		-	-	-	<0.04-0.18	0.32-0.81	0.14-0.77	0.14-0.77	-	1.52-4.78	22.91-70.48	1.66-3.74	8.04-18.70	8.04-18.70	ND-0.15	1.68-3.36	5.97-14.18	0.90-2.43	<0.08-0.14	-	-
mean		ND	ND	ND	0.09	0.60	0.41	0.41	ND	3.42	36.05	2.97	13.96	13.96	0.07	2.54	8.77	1.57	0.09	ND	ND
B-1-M	Muscle	ND	ND	ND	ND	0.20	0.14	0.14	ND	0.75	3.01	0.64	4.59	4.59	ND	0.98	4.02	0.80	ND	ND	ND
B-2-M	Muscle	ND	ND	ND	ND	0.33	0.15	0.15	ND	0.96	4.14	0.78	5.73	5.73	ND	1.11	4.04	0.58	<MLOQ	ND	ND
B-3-M	Muscle	ND	ND	ND	<MLOQ	0.44	0.05	0.05	ND	0.82	3.86	0.74	4.00	4.00	ND	0.77	3.83	0.76	ND	ND	ND
B-4-M	Muscle	ND	ND	ND	<MLOQ	0.19	0.20	0.20	ND	0.74	3.49	0.58	3.90	3.90	ND	0.88	3.68	0.75	ND	ND	ND
B-6-M	Muscle	<MLOQ	ND	ND	ND	0.14	0.16	0.16	ND	0.66	3.21	0.70	5.18	5.18	ND	0.96	4.15	0.57	ND	ND	ND
B-7-M	Muscle	ND	ND	ND	0.06	0.35	0.05	0.05	ND	0.96	6.59	1.13	6.93	6.93	ND	1.56	6.02	1.15	ND	ND	ND
B-8-M	Muscle	ND	ND	ND	ND	0.32	0.09	0.09	ND	0.79	3.16	0.53	3.35	3.35	ND	0.65	2.68	0.45	ND	ND	ND
range		-	-	-	-	0.14-0.44	<0.05-0.20	<0.05-0.20	-	0.66-0.96	3.01-6.59	0.53-1.13	3.35-6.93	3.35-6.93	-	0.65-1.56	2.68-6.02	0.45-1.15	-	-	-
mean		ND	ND	ND	ND	0.28	0.12	0.12	ND	0.81	3.92	0.73	4.81	4.81	ND	0.99	4.06	0.72	ND	ND	ND
B-1-F	Adipose	ND	ND	ND	0.05	0.13	0.10	0.10	ND	0.32	1.92	0.41	1.94	1.94	ND	0.31	1.32	0.13	ND	ND	ND
B-2-F	Adipose	ND	ND	ND	ND	0.12	0.34	0.34	ND	0.37	3.64	0.35	2.44	2.44	ND	0.48	1.99	0.18	ND	ND	ND
B-3-F	Adipose	ND	ND	ND	<MLOQ	0.09	0.05	0.05	ND	0.11	1.24	0.17	0.62	0.62	ND	0.10	0.67	<MLOQ	ND	ND	ND
B-4-F	Adipose	ND	ND	ND	ND	ND	ND	ND	ND	ND	0.52	ND	0.30	0.30	ND	<MLOQ	0.25	ND	ND	ND	ND
B-6-F	Adipose	ND	ND	ND	ND	0.18	ND	ND	ND	0.35	5.20	0.39	2.34	2.34	ND	0.45	2.03	0.20	ND	ND	ND
B-7-F	Adipose	ND	ND	<MLOQ	0.05	0.13	0.40	0.40	ND	0.23	2.21	0.32	1.57	1.57	ND	0.44	1.18	0.19	ND	ND	ND
B-8-F	Adipose	ND	ND	ND	<MLOQ	0.17	0.08	0.08	ND	0.28	8.35	0.25	1.03	1.03	ND	0.17	0.68	<MLOQ	ND	ND	ND

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Sample Name	Tissue	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
		PFBA	PFPcA	PFBS	PFHxA	PFHpA	PFHxS	PFOA	PFEtCHxS	PFNA	PFOS	PFDA	PFUdA	PFDS	PFDoA	PFTtDA	PFTeDA	PFHxDA	PFODA
range		-	-	-	-	-	ND-0.18	ND-0.4	ND	ND-0.37	0.52-8.35	ND-0.41	0.3-2.44	ND	<0.04-0.48	0.25-2.03	<0.08-0.20	ND	ND
mean		ND	ND	ND	ND	ND	0.12	0.14	ND	0.24	3.30	0.27	1.46	ND	0.28	1.16	0.11	ND	ND