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POINTING THE FINGER AT A POINT SOURCE: PFASS IN A RURAL TOWN IN AUSTRALIA

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Introduction

Perfluoroalkyl substances (PFASs), including perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), are a group of anthropogenic chemicals used in a variety of commercial and industrial applications since the 1950's [1]. They have, for example, been used in the metal plating industry, in hydraulic fluids, non-stick coatings, textiles and carpets and in aqueous film forming foams (AFFFs) [2]. Their persistence, potential toxicity and bioaccumulation potential indicate both an ecological and human health risk. This risk for potential adverse effects has motivated a progressive phasing out of the use of some PFASs in many applications, including in firefighting foams, and PFOS was added to Annex B of the Stockholm Convention in 2009.

AFFFs were widely used at Australian airports primarily for firefighting training purposes as well as emergency responses. The frequent use and/or spillages of AFFFs has led to PFASs contamination of different environmental media such as soil, groundwater, surface water and biota in the vicinity of firefighting training grounds throughout Australia, and at other sites worldwide [3-6].

The groundwater surrounding an armed forces base and a nearby rural town (approx. 4500 inhabitants) in Southern Queensland, Australia, has been contaminated with PFASs through historical use of AFFFs between 1970 and 2005. Groundwater analysis and hydrogeological mapping conducted by The Department of Defence revealed a groundwater contamination plume of PFOS in an area that stretches from the Army Base southwards across the town [7].

This study aims to investigate how a point source such as a fire-fighting training area at an airport can lead to widespread contamination and result in human exposure at the community level. Specific aims are to identifiy exposure points and characterize exposure routes and draw a site conceptual model.

Materials and methods

Environmental samples (groundwater, soil, grass) and biota samples (cow, sheep, horse and human sera/ blood) were collected from the area known to have elevated concentrations of PFASs in groundwater originating from a nearby fire-fighting training facility (Figure 1). The groundwater in this rural town is mainly used by residents to irrigate crops and gardens and as a water supply for livestock.

Bore water (n = 8), soil (n = 8) and grass (n = 7) samples were taken in private backyards situated in the plume of PFASs contamination. Eggs (n = 7) were sampled from one privately owned chicken coop, while serum samples of cows (n = 5), sheep (n = 4) and horses (n = 9) were taken from animals raised within the boundaries of the plume. All serum samples were taken by trained veterinarians (UQ Ethical Clearance #ANRFA/ENTOX/153/16). Serum samples from residents of the town (n = 11) were collected by a private pathology company, Sullivan Nicolaides Pathology, and analyzed for their PFAS content at our laboratories (UQ Ethical Clearance #2014001211).

Several PFASs of interest, including perfluorooctanoic acid (PFOA) and linear perfluorooctane sulfonate (PFOS) were quantified using isotope dilution tandem mass spectrometry. All samples were extracted according to matrix specific methods adapted in laboratory and validated for each matrix separately. The PFASs of interest were analysed using high-performance liquid chromatography (HPLC, Shimadzu Corp., Kyoto Japan) coupled to a tandem mass spectrometer (QTrap 5500AB-Sciex, Concord, Ontario, Ca). For separation a volume of 5 µl was injected onto a Gemini NX C18 column (50 x 2 mm, 3 µm, Phenomenex, Lane Cove, Australia) held at a constant temperature of 50 °C. PFASs were separated by gradient elution on the HPLC using mobile phase 10% (A) and 90% (B) methanol, respectively, with 5 mM ammonium acetate. Quality control samples were included for quality assurance in each sample batch.

Results and discussion

Environmental samples

Elevated concentrations of PFOS were found in all soil, vegetation and most bore water samples investigated. PFOA was detected in most samples, but concentrations were substantially lower compared to PFOS. Average groundwater concentrations measured were 2.4 µg/L for PFOS and 0.19 µg/L for PFOA and corresponded well with results reported by The Department of Defence [7].

Average soil concentration in resident's backyards were 1.5 µg/kg and 250 µg/kg for PFOA and PFOS, respectively. These values correspond to soil concentrations derived by Kärrman et al. [6] directly from a fire fighting training platform at Flesland, Sweden, where values of 1.4 and 273 µg/kg were measured for PFOA and PFOS, respectively.

Average concentration of PFOA measured in vegetation (mostly grass) was 0.6 µg/kg, while concentrations of PFOS were 23 µg/kg with maximum concentration of 53 µg/kg of PFOS. Residents in this rural town have relied on their bore-water supply to water lawns and garden-beds. Although more than 2 km away from the point source, years of watering with the contaminated water seems to have led to an accumulation of PFOS and to a lower extent PFOA in the soil of their backyards. Results of vegetation analysis indicate that an uptake of PFOS and PFOA from contaminated soils into vegetation has occurred.

Biota

Elevated concentrations of PFOS were found in all domestic animal blood/serum investigated, ranging from 18 – 58 µg/L in horse serum, 62 – 97 µg/L in sheep blood and 94 – 2173 µg/L in cow blood. PFOA was detected in all samples, but concentrations were lower compared to PFOS.

All animals investigated were drinking from contaminated water sources, it is thus likely that uptake of PFOS occurred from the water and potentially from contaminated feed. Differences in animal age, water and food consumption, and the half-life of PFOS may explain observed differences in PFOS concentrations in the animals. In egg yolk an average PFOS concentration of 48 µg/kg yolk was measured.

The PFOS serum levels of the residential group were higher compared to the general population in Australia [8], with an average level of 124 µg/L serum in this study compared to 12 µg/L serum in the general Australian population. A comparison to PFOS concentrations measured in occupationally exposed firefighters revealed a very close average value of PFOS in firefighters (74 µg/L serum) as well as range of serum concentration measured, 3.8 – 303 µg/L in this study and 3.4 – 391 µg/L in fire fighters [9]. Lower average serum levels compared to residents of Oakey were measured in a cohort of women (n = 146) exposed to PFOS through contaminated drinking water in Uppsala, Sweden, where the average value was 13 µg/L [10]. Serum concentrations in 10 people who had drunk from contaminated wells in Cologne, Germany, had a range of 5 – 295 µg/L of PFOS [11], which is comparable to PFOS concentrations found in this study.

The average concentration of PFOA in the residential group was 3 µg/L serum, which was below the average of the general Australian population (4.3 µg/L serum), indicating normal background levels of PFOA. Additionally, the PFOA levels were in the same range as occupationally exposed firefighters, which showed a range of 0.3 – 18 µg/L [9].

A widespread groundwater contamination occurred in a rural town originating from a specific point source. There is evidence that PFOS has bioaccumulated up the food chain, from groundwater to vegetation to livestock and eggs. Residents investigated in this study usually did not drink the groundwater, but rather used an uncontaminated water supply from the nearby town. Their PFOS serum concentrations were nonetheless above the Australian average, and similar to levels seen in other water contamination scenarios, and occupationally-exposed fire fighters. PFOA levels were similar to background Australian population levels. The results presented in this study show that human exposure to PFOS may be the result of consuming food produced within the contaminated area.

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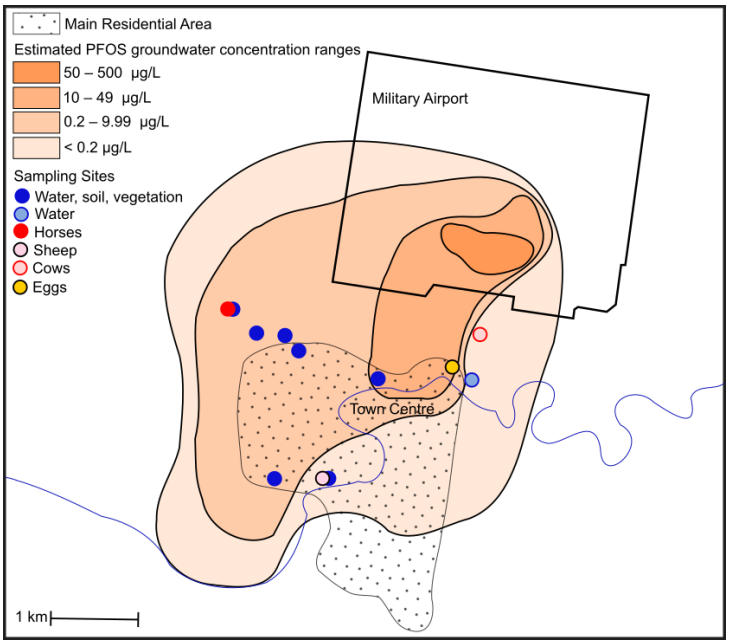
Figure 1: Sampling sites for water, soil, vegetation, eggs, horse, sheep and cow blood. Map and estimated PFOS groundwater concentration ranges redrawn from: http://www.defence.gov.au/id/_Master/docs/ Oakey/0207-AACO-EI2-2015-PFOS-DA-Aug2015.pdf

Table 1: Concentrations of PFOA and PFOS in bore water, vegetation, soil, egg yolk and serum of horses, blood of sheep and cows and serum of humans from a rural town in Australia.



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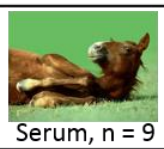
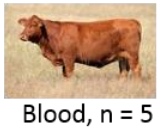
	PFOA Average (Range) Unit	PFOS* Average (Range) Unit
 Bore water, n = 8	0.19 (< 0.08 – 0.4) µg/L	2.44 (< 0.01 – 6.6) µg/L
Vegetation, n = 7 	0.6 (0.2 – 0.8) µg/kg$_{ww}$	22.6 (1.3 – 53.1) µg/kg$_{ww}$
 Soil, n = 8	1.5 (0.07 – 7.3) µg/kg$_{dw}$	250 (4.3 – 1781) µg/kg$_{dw}$
 Serum, n = 9	0.25 (0.09 – 0.48) µg/L	36 (18 – 58) µg/L
 Blood, n = 4	0.13 (0.09 – 0.22) µg/L	72.7 (62 – 98) µg/L
 Blood, n = 5	0.15 (0.08 – 0.24) µg/L	1454 (94 – 2173) µg/L
 Egg yolk, n = 7	0.45 (0.01 – 0.68) µg/kg	47.7 (39 – 60) µg/kg
 Serum, n = 11	4.4 (2 – 9) µg/L	124 (3.8 – 303) µg/L

*linear PFOS