Age dependent accumulation of perfluorinated chemicals in beef cattles

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Introduction

Occurrences of perfluorinated chemicals (FOCs) in the environment recently have brought public concerned as a new group of pollutants. Perfluoroalkylsulfonates and perfluoroalkylacids were found in many environmental compartments including water, sediment and biota. It was reported that FOCs were detected in several species of wild life in various locations including some remote areas.[1] Fish and aquatic animals were to be accumulated greater concentrations of PFOS and PFOA with no clear age- or sex-related differences.[2,3] Consumption of fish and farm animal products were to be the main human exposure route to organohalogen pollutants. It is important to know the human exposure to FOCs, since some of these compounds have high degrees of bioaccumulation and long half-lives in the human body. However, accumulations of FOCs in farm animals are not documented. In this study we examine the age related presence of FOCs in blood plasma collected from 3 beef cattle from Japan.

Methods and Materials

Three male Japanese black beef cattle were randomly selected from a normal raising herd, and blood samples were collected an average age of 9, 13, 17, 23 and 27 months. All the animals were normal during the study period. Plasma were separated by centrifuging and kept –20C until FOCs analysis. Samples were analyzed for 13 FOCs: perfluorobutanesulfonate (PFBS), perfluorohe xanesulfonate (PFHS), perfluorooctanesulfonate (PFOS), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorooctanesulfonylamide (PFOSA) and 1H,1H,2H,2H-perfluorooctanesulfonate (THPFOS). Extraction was carried out by an ion-pairing method, which described elsewhere.[3-4] Briefly, 1 ml of plasma was mixed with 1ml of 0.5M tetrabutylammonium hydrogen sulfate solution and 2ml of buffer (10 pH, 0.25M) in a polypropylene tube. The sample mixture was extracted with three times with methyl tert-butyl ether (MTBE) 5ml after shaking for 20 m followed by centrifugation. The final extract was concentrated under nitrogen after adding 0.5ml of methanol. The sample was passed through a 0.1µm nylon mesh before quantified.[4]

Analysis of FOCs were performed using a high performance liquid chromatograph-tandem mass spectrometer (HPLC-MS/MS), comprising an Agilent HP1100 liquid chromatograph interfaced with a Micromass® (Beverly, MA, USA) Quattro Ultima Pt mass spectrometer operated in the electrospray negative ionization mode. A 10-µL aliquot of the sample extract was injected into a guard column (XDB-C8, 2.1 mm i.d. x 12.5 mm, 5µm; Agilent Technologies, Palo Alto, CA) connected sequentially to a Betasil C18 column (2.1 mm i.d.×50 mm length, 5µm; Termo Hypersil-Keystone, Bellefonte, PA) with 2 mM ammonium acetate/methanol as mobile phase, starting at 10% methanol. At a flow rate of 300 µL/min, the gradient was increased to 30% methanol at 0.1 min, 75% methanol at 7 min, and 100% methanol at 10 min, and was kept there until 12 min before reversion to original conditions, at the 20-min time point. The capillary was held at 1.2 kV. Cone-gas and desolvation-gas flows were kept at 60 and 650 L/h, respectively. Source and desolvation temperatures were kept at 120 and 420°C respectively. MS/MS parameters were optimized so as to transmit the $[M-K]^-$ or $[M-H]^-$ ions as shown in Table 1. Eight calibration curve points bracketing the concentrations in samples were prepared routinely, to check for linearity.The mean procedural blank and recovery of analytics are given in Table 1. Mean blank value was subtracted from the sample data. For the calculation of mean, concentrations below blank were not included.

Table 1. Mass determination of analyte procedural solvent blank and recovery

Analyte	Mass transition	Solvent blank (pg/ml)	Recovery (%)
PFBS	298.7>79.7	3	60
PFHS	398.7 >79.7	3	84
PFOS	498.6 > 79.7	25	70
PFPeA	262.8 > 218.7	3	75
PFHxA	312.8 > 268.8	10	60
PFHpA	362.8 > 318.8	4	95
PFOA	413 > 368.7	90	92
PFNA	462.7 > 418.8	10	86
PFDA	512.8 > 468.8	12	85
PFUnA	563 >519	6	69
PFDoA	612.7 > 568.8	4	60
PFOSA	497.7 > 77.7	2	88
THPFOS	426.7 > 406.7	2	93

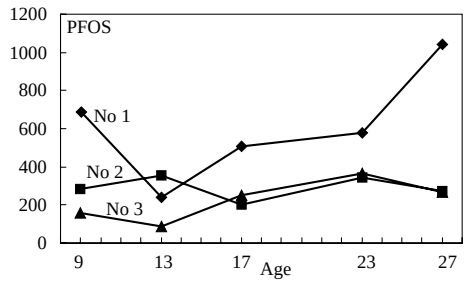

Fig. 1. PFOS accumulation with age in Japanese black beef cattle

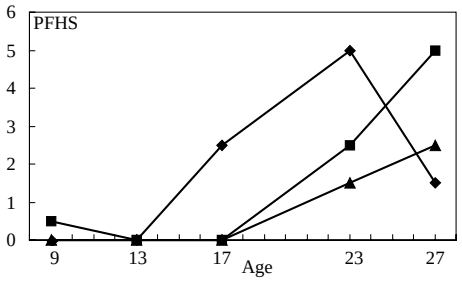

Fig. 2. PFHS accumulation with age in Japanese black beef cattle

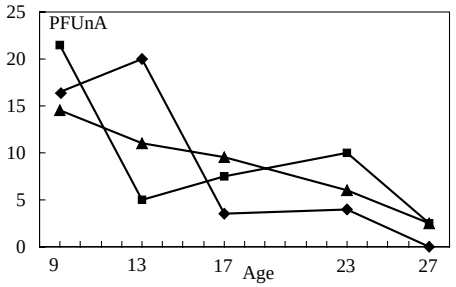

Fig. 3. PFUnA accumulation with age in Japanese black beef cattle

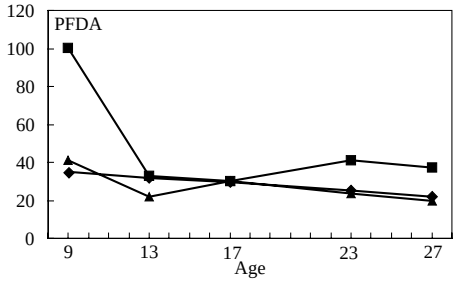

Fig. 4. PFDA accumulation with age in Japanese black beef cattle

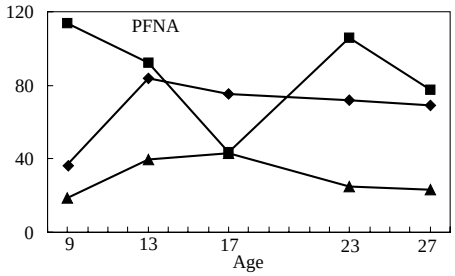

Fig. 5. PFNA accumulation with age in Japanese black beef cattle

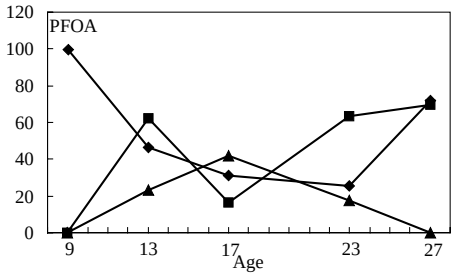

Fig. 6. PFOA accumulation with age in Japanese black beef cattle

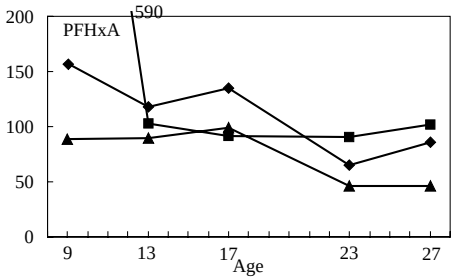

Fig. 7. PFHxA accumulation with age in Japanese black beef cattle

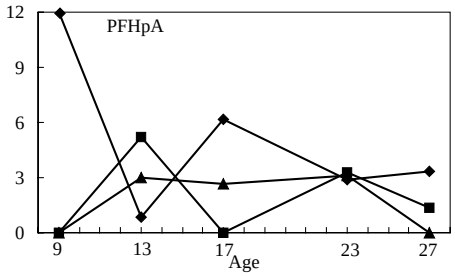

Fig. 8. PFHpA accumulation with age in Japanese black beef cattle

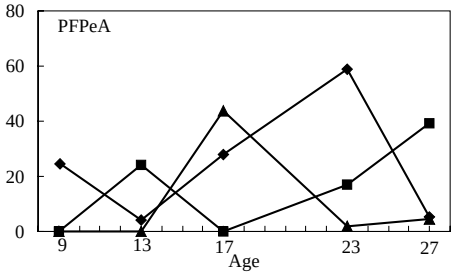

Fig. 9. PFPeA accumulation with age in Japanese black beef cattle

The Age (months) related accmulation of selected fluorinated contaminants (pg/ml) are given in figures 1 to 9. The concentrations of PFBS, PFDoA, PFOSA and THPFOS in bovine plasma were similar or less than those in blank. Hence, those data are not presented. PFOS was the most prominent contaminant detected in few hundred pg/ml levels in bovine plasma (Fig 1). Among the perflourinated acids, PFHxA (Fig 7) concentration was higher than others. The concentrations of PFDA (Fig 4), PFNA (Fig 5), PFOA (Fig 6) and PFPeA (Fig 9) were found at least in few ten pg/ml levels, while others were less than 10 pg/ml. Reports of long chain FOCs contaminants such as PFUnA, PFDA, and PFNA were few in biological matrices.[5]

The mean PFOS concentration in age of 27 months (530 pg/ml) was nearly 1.5 folds greater than the animals were 9 months (370 pg/ml) old. However, the accumulation trend of most perflourinated acids such as PFUnA, PFDA and PFHxA seems to be decreasing with the aging of cattle. Nevertheless, the number of animals was not sufficient to conclude age related accumulation of FOCs in cattle. According to earlier reports, no significant associations were observed between FOCs concentration and age.

In the conclusions, we detected several FOCs in beef cattle blood plasma with greater PFOS concentrations compared to others. The present level of PFOS in beef cattle was to be at least one order of magnitude lower than that in fish from Japan.[4] The current contamination levels of FOCs in beef cattle seems to be not posed any adverse effects to cattle or to human.

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