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Determination of perfluorinated sulfonate and perfluorinated acids in tissues of free-living European beaver (*castor fiber* L.) by d-SPE/ micro-UHPLC-MS/MS

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ABSTRACT

Perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) are the main representatives of an rising class of persistent organic pollutants (POPs), perfluorochemicals (PFCs). In this study, determination of selected PFCs concentration in liver, brain, tail, adipose and peritoneum tissues of free-living European beaver (*Castor fiber* L.) was addressed. Tissue samples, collected from beavers living in Masurian Lakeland (NE Poland), were analyzed by dispersive Solid Phase Extraction (*d*-SPE) with micro-UHPLC-MS/MS system. In a group of ten selected pefrluorinated compounds only two perfluorinated acids (PFOA and PFNA) and one perfluorinated sulfonate (PFOS) were quantified. PFOA was detected in all analysed tissue samples in both female and male beavers in a range from 0.55 to 0.98 ng g^{-1} ww whereas PFOS was identified in all analyzed female beaver tissues and only in liver, subcutaneous adipose and peritoneum tissues of male beavers at the concentration level from 0.86 to 5.08 ng g^{-1} ww. PFNA was only identified in female beaver tissues (liver, subcutaneous adipose and peritoneum) in a range from 1.50 to 6.61 ng g^{-1} ww. This study demonstrated the bioaccumulation of PFCs in tissue samples collected from beavers living in area known as green lungs of Poland. The results provided in this study indicate for the increasing risk of PFCs occurrence in the environment and the level of PFCs in tissue of free-living European beavers may serve as bioindicator of environmental pollution by these compounds.

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1. Introduction

Wild animals are exposed to environmental contaminants of both natural and anthropogenic origin and are suitable bioindicators of environmental pollution (Petkovšek et al., 2014). The beaver (*Castor fiber*), is the second largest amphibious rodent after capybara (*Hydrochoerus hydrochaeris*), and occupy the various temperate zone of Europe, Asia and North America. The genus *Beaver* comprises two species differing in tail proportions, coat color, details of skull structure and karyotype (Korzeniowski et al., 2001). The Eurasian beaver (*Castor fiber* Linneaus 1758) is present in Europe and Asia, and the Canadian beaver (*Castor fiber* canadensis Kuhl 1820) – in North America and Europe, especially in Scandinavia, where the species was introduced. It is currently estimated that 78,000 beavers occur in Poland, and beaver populations continue spreading to new areas, including near human settlements, where they are likely to get exposed to anthropogenic pollutants (Flis, 2013). Beavers are semi-aquatic, territorial herbivorous rodents feeding on the bark, shoots, and leaves of a wide variety of woody plants as well as on non woody terrestrial and aquatic plants (Krojerová-Prokešová et al., 2010). The beaver's population is regulated by the decision of local environment administrative in order to keep the population size in controlled limits. Moreover, tendency of beaver dynamics is growing therefore in the nearest future the specie will be on the list of hunted animals. At present, beavers are partially protected in Poland but this is not the case of other countries through the world.

The average European beaver carcass contains 62.8% meat, 14.5% fat and 22.4% bone (Jankowska et al., 2005). Beavers have high amounts of depot adipose tissue. They maintain energy reserves in the form of adipose tissue beneath the skin (subcutaneous fat). Subcutaneous adipose tissue is deposited unevenly,

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forming the thickest layer around the abdominal region and tail (10–20 mm). Tail fat usually contain over 80% unsaturated fatty acids (Jankowska et al., 2005; Korzeniowski et al., 2000).

Currently, due to the rapid development and wide diversity of human activities, animals are increasingly exposed to harmful effects of toxic compounds (O'Brien et al., 1993). Beavers' catholic diet and sedentary behavior make them suitable bioindicators of environmental pollution.

Perfluorinated compounds (PFCs) are classified as a persistent and biaccumulative substance (Jogsten et al., 2009). Perfluorooctanesulfonate (PFOS) and perfluorooctanoic acid (PFOA) represent a two dominate PFCs in an environment and food chain (Yeung et al., 2009). They are metabolites of several polyfluorinated precursor compounds that are produced and used commercially. PFCs have been detected globally as pollutants in water, plants, foodstuffs, and in animals such as fish, birds, in mammals, as well as in human breast milk and blood in several parts of the world (Giesy and Kannan, 2001; Taniyasu et al., 2003; Higgins et al., 2005; Teng et al., 2009). Moreover, PFCs have been found in wildlife samples from all over the world thus suggesting their bioaccumulation in higher trophic levels in the food chains (Hansen et al., 2001; Kannan et al., 2002; Martin, 2004). Considering of PFCs unique properties as synthetic organic chemicals consisting of fully fluorinated carbon chain and a sulfonate or carboxylic groups, respectively they have been used in numerous industrial and commercial applications including food contact materials, cookware and textile treatments, production of fluoropolimers, cosmetics, insecticide formulation and fire-fighting foams (Dolman and Pelzing, 2011).

At present, there is a lack of information on the possible risk of accumulation of PFOS and PFOA in tissues of European beaver. The superiority of beavers over large animals is due to the fact that beavers are semi-aquatic and territorial animals and therefore as a consequence their use as biomonitor may reflect all changes connected with PFOS and PFOA accumulation in both environments.

The first aim of this study was to developed analytical method, using dispersive Solid Phase Extraction (d-SPE) and micro-UHPLC-MS/MS, applicable for successful determination of perfluorinated compounds in sample of animal origin. The second aim was to determine a selected perfluorinated sulfonates (PFASs) such as perfluorobutane sulfonate (PFBS), perfluorohexane sulfonate (PFHS), perfluorooctane sulfonate (PFOS) and perfluorinated acids (PFCAs) such as perfluorobutanoic acid (PFBA), perfluoropentanoic acid (PFPeA), perfluorohexanoic acid (PFHxA), perfluoroheptanoic acid (PFHpA), perfluorooctanoic acid (PFOA), perfluorononanoic acid (PFNA), perfluorodecanoic acid (PFDA) in tissues of free-living beavers. The subcutaneous adipose tissue, peritoneum tissue, internal organ (liver, brain) and tail tissue samples collected from free-living beavers in Masurian Lakeland (NE Poland), a one of the cleanest tourist region in Europe, were analyzed by the developed method to provide information for the assessment of PFCs pollution in wildlife and the implications for future use of beavers as biomonitors of PFCs environmental pollution.

2. Experimental

2.1. Chemicals and reagents

Reagents in MS grade including acetonitrile (MeCN), methanol (MeOH), formic acid (FA) were purchased from Sigma Chemical Co., St. Louis, MO. Water was purified with a Mili-Q system, Millipore, Bedford, USA. Acetonitrile (for extraction) HPLC grade was purchased from Merck KGaA, Germany. Magnesium sulphate anhydrous p.a. and sodium chloride p.a. were purchased from POCh SA, Poland. The silica: PSA (primary and secondary amine), C_{18} (octadecylsilane), GCB (graphitized carbon black) and polymer based: ENV (styrene-divinylbenzene) SPE Bulk Sorbent derived from Agilent Technologies, USA. PFOA and PFOS were obtained from Sigma-Aldrich Chemie GmbH, Germany. Native PFC Solution/Mixture and 1,2,3,4-^{13}C- labeled PFOA were obtained from Wellington Laboratories, Canada. Stock, intermediate and working standard solutions of PFOS, PFOA and 1,2,3,4-$^{13}C_4$- labeled PFOA (IS – internal standard) were prepared in acetonitrile. Stock, intermediate and working standard solutions of native PFC were prepared in 20% MeOH (v/v) with 1% (v/v) of formic acid.

2.2. Sample collection

The 6 adult beavers (*Castor fiber*) of both sexes (3 females and 3 males) were harvested in their natural environment in northeastern Poland (Masurian Lakeland) in November 2012. Animal captures were allowed due to beaver overpopulation in this area and were conducted by a specialized team from Polish Hunting Association. Beavers were in good physical condition, not exhausted or injured during capture. After animals capture they were transferred to Research Station of Polish Academy of Sciences in Popielno. The animals were between 1.5 and 3.5 years of age and body weight between 7.60 and 22.9 kg (Table 1). Their sex was determined based on the color of anal gland secretions (Schulte et al., 1995) while age was estimated based on body weight (Rosell et al., 2010). Beavers were classified into adults when they were >24 months old. The experimental protocol including euthanasia and decapitation of beavers was approved by the Local Ethical Commission for Experiments on Animals at the University of Warmia and Mazury in Olsztyn, Poland (permit number 33/2009). Beavers were anesthetized in laboratory conditions by intramuscular administration of 60 mg of xylazine (Sedazin, Biowet Pulawy, Poland). After 5 min, they were administrated i.m. of 300 mg of ketamine (VetaKetam, VetAgro, Poland). All possible efforts were made to minimize animal suffering. The experimental materials consisted of liver, subcutaneous adipose, peritoneum, brain and tail tissues. Material was collected by a veterinarian immediately after the beavers had been captured and euthanized. Prior to PFCs extraction the samples were stored at -75 °C.

2.3. Sample preparation

The study implied two steps. The first one was focused on application of the dispersive Solid Phase Extraction followed by micro-UHPLC-MS/MS for determination of selected PFCs in model sample of animal origin (pork liver), based on the modified QuEChERS method (Surma et al., 2014). Within the second part, a developed method was applied for the determination of selected PFCs in tissues of free-living beavers.

For the sample preparation technique development, consisting of selection the appropriate, additional sorbent (ENV, C_{18} or GCB) for clean-up the samples, apart from PSA sorbent a series of experiments were performed. Additionally, the final method of

Table 1
Biometric data and place of capture of Eurasian beavers from northeastern Poland, 2012.

Individual	Sex	Age (years)/class	Body weight [kg]	Place of capture
F1	♀	> 3.5/adult	20.9	Reserve channel
F3	♀	> 3.5/adult	21.1	Onufryjewo
F5	♀	> 1.5/adult	7.60	Popielno port
M2	♂	> 3.5/adult	17.8	Reserve channel
M4	♂	> 3.5/adult	22.9	Popielno port
M6	♂	> 2.5/adult	14.2	Onufryjewo

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