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RESEARCH ARTICLE

Monitoring of environmental persistent organic pollutants in hair samples collected from wild terrestrial mammals of Primorsky Krai, Russia

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Abstract

Persistent organic pollutants (POPs) constitute a wide range of chemicals. Their release into the environment has raised great concern due to their potentially harmful impact in humans and wildlife species. The aim of this current study was to detect selected POPs in hair samples of wild terrestrial mammals from Primorsky Krai, Russia, so as to assess potential environmental exposure. The tested wild species were leopard cat, musk deer, wolf, amur hedgehog, and raccoon dog. The targeted organochlorines were hexachlorobenzene (HCB) and DDTs (opDDE, ppDDE, and opDDD), polychlorinated biphenyl (PCB) congeners (28, 52, 101, 118, 138, 153, and 180), and polycyclic aromatic hydrocarbons (PAHs) (acenaphylene (ACEN), fluorene (FLU), anthracene (ANTH) phenathrene (PHEN), and pyrene (PYR)). The detection of POPs was conducted in hair samples by a one-step hair extraction method, by using a headspace solid-phase microextraction technique (HS-SPME) and analyzed then by GC-MS. The majority of the wild animal hair samples were found positive in all tested pollutants. More specifically, the percentage of positive hair samples for HCB was 93.3% and for DDTs, PCBs, and PAHs, 20.0 to 100.0%, 6.7 to 100.0%, and 75.0 to 100.0%, respectively. DDT, PCB, and PAH detection ranged from 1.26 to 52.06 pg mg^{-1}, 0.73 to 31.34 pg mg^{-1}, and 2.59 to 35.00 pg mg^{-1}, respectively. The highest mean concentration levels of all tested pollutants were found for musk deer (PCBs 12.41 pg mg^{-1}, DDTs 21.87 pg mg^{-1}, PAHs 22.12 pg mg^{-1}) compared to the other wild species. To the best of our knowledge, this is the first study that provides results regarding contamination in different terrestrial mammals by POP exposure. The use of hair as a matrix is proven to be an effective tool for nondestructive biological monitoring of POP contamination in terrestrial ecosystems.

Keywords Hair · POPs · Wild terrestrial mammals · HS-SPME–GC-MS · Biomonitoring · Russia

Introduction

The global contamination of released amounts of POPs into the environment has raised great concern by the adverse impact in humans and several species of marine and terrestrial ecosystems. Organochlorine pesticides (hexachlorobenzene (HCB), DDTs), polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs) are groups that belong to persistent organic pollutants (POPs) (Cabrerizo et al. 2012; HercegRomanić et al. 2015) and have been found in various environment samples.

Thousands of synthetic chemicals were introduced from mass industry productions especially after World War II. Organic compounds are a group of chemicals with health interest, with categories such as phthalates (additives in

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cosmetics and plasticizers), organophosphorus pesticides (agricultural chemicals), and POPs (Katsikantami et al. 2016; Kavvalakis and Tsatsakis 2012; Tsatsakis et al. 2010; Tsatsakis and Tutudaki 2004). Among POPs, there are many banned compounds that are also classified by the Stockholm Convention on Persistent Organic Pollutants, an international environmental treaty that focuses on restricting the production and use of POPs. HCB and DDT are organochlorine pesticides that had been used until the late 1970s. Another class of synthetic organic compounds is PCBs that were extensively used until the year 2004. PAHs are ubiquitous substances and generally originate from anthropogenic activities. Organochlorine pesticides, PCBs, and PAHs are regarded persistent pollutants due to their physicochemical properties and ability to remain in several environmental matrices (Cabrerizo et al. 2012; Vinceti et al. 2017).

The accumulation of persistent pollutants in terrestrial mammalian food has not been studied extensively. Several persistent pollutants can bioaccumulate within the food chain leading to a potential risk to human or animal health (Sutor et al. 2010; Cabrerizo et al. 2012; Zapletal et al. 2015; Imbert et al. 2016).

In the last two decades, several studies evaluated the presence of persistent pollutants in human hair samples. Indicatively, the median concentrations of PCB congeners were 1.47 pg mg^{-1} and 38.74 pg mg^{-1} in human hair samples collected from inhabitants of the islands of Crete and Peloponnesus, Greece, respectively (Barbounis et al. 2012), while a later study reported that mean concentrations of PCB congeners ranged from 0.6 to 6.7 pg mg^{-1} and for the tested DDTs from 6.3 to 22.4 pg mg^{-1} (Tzatzarakis et al. 2014). Recently, a research conducted in China concluded that the concentrations of sum DDTs ranged from 2.30 to 489 ng g^{-1} (He et al. 2017). Similar studies in Iran and the Philippines dealing with adolescent females reported that mean concentration ranges of PCBs were 4–140 ng g^{-1} (Dahmardeh Behrooz et al. 2012) and 11–72 ng g^{-1} (Malarvannan et al. 2013), respectively. Concerning PCBs, mean concentrations of PCBs in human hair samples from children and adolescents living in Changchun, China, were 21.24–122.45 ng g^{-1} and 72.18–285.31 ng g^{-1} respectively (Liang et al. 2014), while mean concentrations of PCBs ranged from 0.9 to 46 ng g^{-1} in adolescents from Romania (Covaci et al. 2008). As for PAHs, in a recent study for non-smoking and smoking adolescent males, the mean concentrations were 1064.7 pg mg^{-1} and 1389.2 pg mg^{-1}, respectively (Yamamoto et al. 2015).

Choosing the appropriate matrix to conduct exposure estimations is a critical parameter. Hair samples have several advantages over other matrixes as it can be easily collected, stored, and analyzed. Generally, hair analysis is a noninvasive method, making this matrix a useful tool for the biomonitoring of the exposure of wild animals to environmental pollutants (Covaci et al. 2002; Jaspers et al. 2010; Liang et al. 2014).

In particular, there are only a few studies in terrestrial ecosystems species compared to those in aquatic ecosystems. In a recent study, Mamontova et al. (2013) mentioned PCB polluted soil samples in Mongolia and in the surrounding area of Siberia (Russia). The soil samples were from industrial towns and rural areas of Mongolia. The average sum of 37 PCB congeners was 7.4 $ngml^{-1}$ dry weight (DW) (range 0.53–114 ng ml^{-1} DW) wherein the highest PCB levels were from soil samples in towns. The tested PCB congeners belonged to groups of di-CB, tri-CBs, tetra-CBs, penta-CBs, hexa-CBs, and hepta-CBs (Mamontova et al. 2013).

Until now, limited data on the assessment of exposure to persistent pollutants of wildlife animals are available. In particular, there are only a few studies in terrestrial ecosystem species compared to those in aquatic ecosystems. The aim of this current study was to assess the burden of POPs in wild terrestrial mammals. The novelty of the present study is to provide results for accumulation levels of multi-persistent organic pollutants in hair samples of five different wild terrestrial mammals.

Materials and methods

Sampling

A total of 15 hair samples were collected during summer 2016 until winter 2017, from five different species of dead wild animals in the region of Primorsky Krai, Russia. The wild animals were the following: six (6) leopard cats (*Prionailurus bengalensis*), three (3) musk deers (*Moschus moschiferus*), one (1) wolf (*Canis lupus*), one (1) amur hedgehog (*Erinaceus amurensis*), and four (4) raccoon dogs (*Nyctereutes procyonoides*). The specific regional geographic location is known for its rich flora and fauna diversity. Table S1 shows the gender, age, cause of death, and the location of each dead or killed animal. In the current study, all wild animals were found either dead due to traffic accidents (1 amur hedgehog, 4 leopard cats, 4 raccoon dogs) or by hunting (3 musk deers, 2 leopard cats, 1 wolf).

Reagents and materials

The tested organochlorines, HCB and opDDE, ppDDE, and opDDD, were obtained from Chem Service (West Chester, PA, USA). PCB congeners (28, 52, 101, 118, 138, 153, and 180) and sodium chloride (NaCl) were purchased from Fluka Analytical-Sigma Aldrich (St Louis, MO, USA). The PAHs (acenaphylene (ACEN), fluorene (FLU), anthracene (ANTH) phenathrene (PHEN), and pyrene (PYR)) were purchased from Supelco (Bellefonte, USA).The 1,2,3,4-tetrachloronaphtalene (TCN) was used as internal standard (IS) and purchased from Dr. Ehrenstorfer (Augsburg,

Germany). Sodium hydroxide (NaOH) was obtained from Merck, D-6100 (Darmstadt, Germany). All stock solutions of analytes were prepared in hexane and stored at − 20 °C. Mixed solutions were prepared also in hexane and were used for the preparation of spiked hair. Ultrapure water was produced by a Direct-Q 3UV water purification system (Merck, Germany).

Sample pretreatment and headspace solid-phase microextraction procedure

The total amount of each collected hair sample was washed three times with 5 ml of water and twice with 5 ml of hexane, and then all samples were dried in an oven at 50 °C. Afterwards, 200 mg (or 100 mg for PAHs) of hair was placed in 8 ml SPME vials for HCB, DDTs, and PCBs analysis. Specifically, all hair samples (15) were analyzed for HCB, DDTs, and PCBs, while only 8 samples provided enough hair for PAH analysis (1 musk deer, 4 leopard cats, 2 raccoon dogs, 1 wolf). In each vial, 2 ml of NaOH 10 N, 1 ml of ultrapure water, 0.25 g of NaCl and 20 ng of TCN (IS) were added. SPME vials were sealed with PTFE/silicon septum caps and placed in the GC-MS tray. A previously described one-step hair extraction method was applied, by using the headspace SPME technique. Specifically, online extraction followed with a PDMS/DVB type extraction fiber at 90 °C for 30 min and with agitation speed at 250 rpm. After the adsorption of the chosen compounds, the fiber tip was inserted in the injection port of the GC-MS and remained for 3 min until complete releasing of the compounds (Tzatzarakis et al. 2014; Vinceti et al. 2017).

Gas chromatography and mass spectrometry conditions

The validation of the method that followed and the chromatographic and spectrometric conditions have been described in previously published studies (Tzatzarakis et al. 2014; Vinceti et al. 2017). Samples were analyzed with a GC-MS QP-2010 instrument of Shimadzu (Kyoto, Japan) equipped with a split/splitless injection inlet and an AOC-5000 SPME autosampler and was equipped with a syringe 65-μm PDMS/DVB metal alloy fiber from Supelco (Bellefonte, PA, USA). For the GC analysis and separation of the compounds, a Supelco Analytical SLB™-5 ms capillary column (30-m length, 0.25-mm i.d., 0.25-μm film thickness) was used. The conditions applied are the following: the flow rate of helium was constant at 1 ml/min as a carrier gas, the inlet temperature was set at 270 °C, the MS interface temperature at 310 °C, and ion source temperature at 230 °C. For the analysis of HCB, DDTs, and PCBs, the column temperature program was held for 3 min at 60 °C and raised at 15 °C/min to 180 °C and held for 1 min, then raised gradually at a rate 4 °C/min until 250 °C and finally raised at a rate 30 °C/min until 300 °C and held for 5 min (total 36.83 min). For the analysis of PAHs, the column temperature program was held for 3 min at 120 °C and raised at 5 °C/min to 310 °C and held for 1 min, then raised gradually at a rate 10 °C/min until 325 °C and held for 3 min (total 45.50 min). The mass spectrometer detector was operated at the selected ion monitoring mode (SIM) and the qualification *m/z* ions, the target *m/z* ion, and the retention times of each POP were described well in the previous studies (Tzatzarakis et al. 2014; Vinceti et al. 2017).

Spiked hair samples

For blank hair samples, polled human hair with no detected levels or in levels below the LOQ values of tested contaminants were used. The pretreatment of blank hair samples were in accordance with the above-described wash procedure. The human hair samples were spiked at different concentration levels: 0, 5, 10, 20, 60, 80, 100 pg mg^{-1} for HCB and DDTs; 0, 2.5, 5, 10, 20, 40, 60 pg $mg^{-1}$for PCBs; and 0, 10, 25, 50, 100 pg mg^{-1} for PAHs. Then, the spiked hair samples were extracted, analyzed, and used for the preparation of the calibration curves.

Results

Analytical parameters

The ratio of the area of each pollutant to the area of IS was used for the preparation of standard and spiked curves. All standard and spiked curves were linear at the selected concentration range for all POPs. LODs and LOQs were calculated by analyzing the lowest spiked level for each compound and defined as the peaks that gave a signal-to-noise ratio (S/N) > 3 for the LOD and > 10 for the LOQ. It seems that the use of the headspace SPME extraction method coupled with a GC-MS system achieved low detection limits. The range of LOD values were 0.1 pg mg^{-1}, 0.3–2.4 pg mg^{-1}, 0.2–1.5 pg mg^{-1}, and 0.05–0.4 pg mg^{-1} for HCB, DDTs, PCBs, and PAHs, respectively (Table 1).

Monitoring results

The majority of wild animal hair samples were found positive for at least 10 from 16 of the tested pollutants. The percentages of the positive hair samples for HCB, DDTs, PCBs, and PAHs are shown in Table 1.The compounds which appeared more frequently were HCB (93.3%), opDDE (100.0%), and ppDDE (100.0%). In contrast, opDDD was detected only in 3 hair samples collected from the leopard cat (20.0%). Furthermore, for all

Table 1 Mean, median, and range values without and with input values, LODs, LOQs, and frequencies (%) of positive samples for all tested pollutants

Persistent organic pollutants (POPs)	LOD (pg mg^{-1})	LOQ (pg mg^{-1})	N	% positive	Mean (pg mg^{-1})	± SD	Median (pg mg^{-1})	Range (pg mg^{-1})	Mean** (pg mg^{-1})	± SD**	Median** (pg mg^{-1})
Organochlorine pesticides											
HCB	0.1	0.3	15	93.3	0.67	0.41	0.48	0.33–1.55	0.59	0.43	0.48
opDDE	0.3	0.9	15	100.0	10.05	10.66	6.6	1.55–44.03	10.05	10.66	6.60
ppDDE	0.4	1.2	15	100.0	14.66	14.66	7.86	1.26–52.06	13.72	14.59	7.77
opDDD	2.4	8.1	15	20.0	15.33	7.08	13.82	9.12–23.04	4.03	6.43	1.20
Polychlorinated biphenyls											
PCB28	0.3	1.1	15	93.3	2.20	0.2	2.18	1.95–2.62	2.06	0.56	2.16
PCB52	0.2	0.7	15	100.0	6.81	7.51	5.36	0.73–31.34	6.81	7.51	5.36
PCB101	0.4	1.4	15	100.0	4.72	3.66	3.12	1.54–15.91	4.72	3.66	3.12
PCB118	1.5	4.9	15	20.0	8.47	4.78	6.56	4.94–13.91	2.29	3.67	0.75
PCB138	1.2	3.9	15	93.3	11.04	8.63	7.01	4.00–30.17	10.34	8.74	5.94
PCB153	0.5	1.8	15	73.3	7.67	5.34	5.23	2.21–18.09	5.69	5.65	3.61
PCB180	1.1	3.7	15	6.7	5.19*				0.86	1.2	0.55
Polycyclic aromatic hydrocarbons											
ACEN	0.4	1.3	8	87.5	< LOQ	< LOQ	< LOQ	< LOQ	0.59	0.16	0.65
FLU	0.3	1	8	100.0	6.53	2.91	6.17	2.59–11.94	6.53	2.91	6.17
ANTH/PHEN	0.05	0.2	8	100.0	23.56	7.58	24.8	9.28–35.00	23.56	7.58	24.8
PYR	0.3	1.2	8	75.0	< LOQ	< LOQ	< LOQ	< LOQ	0.49	0.21	0.6

*Positive only in one sample

**Input values: in samples not detected = LOD/2 and in samples < LOQ = LOQ/2

POPs, input values LOD/2 and LOQ/2 were obtained in samples that were negative and below LOQ, respectively (Table 1). The mean value of HCB was 0.67 pg mg^{-1} with a range from 0.33 to 1.55 pg mg^{-1} and the mean values of opDDE, ppDDE, and opDDD were 10.05, 14.66, and 15.33 pg mg^{-1}, respectively, with a range from 1.26 to 52.06 pg mg^{-1} (Table 1). The mean concentrations with and without input values of HCB and all DDTs for each species are shown both in Table 1 and in Fig. 1 a and b. The highest concentration of DDTs was detected for ppDDE (52.06 pg mg^{-1}) in a hair sample of leopard cat.

For PCBs, the congeners which appeared more frequently were PCB28, PCB52, PCB101, and PCB138 (from 93.3 to 100.0%). PCB118, PCB153, and PCB180 were detected in the 20.0%, 73.3%, and 6.7% of the samples, respectively. The mean detected levels ranged from 2.20 pg mg^{-1} (for PCB28) to 11.04 pg mg^{-1} (for PCB138). The concentration range of all congeners for all species ranged from 0.73 to 31.34 pg mg^{-1}. The lowest concentration was found for PCB52 in a sample of leopard cat (0.73 pg mg^{-1}) and the highest concentration for the same congener in a sample of musk deer (31.34 pg mg^{-1}). The mean concentrations of all PCBs without and with input values are shown in Table 1 and in Fig. 2 a and b.The contribution of each PCB congener per species is shown in Fig. 3 a and b and Table S2, wherein the highest contribution observed for PCB138 in musk deers (34.38%), leopard cats (26.75%), and raccoon dogs (26.49%). For wolf and amur hedgehog, the dominant congeners were PCB52 and PCB28, with percentages of 26.62% and 40.69%, respectively.

As it is shown in Table 1 and Fig. 4 a and b from the tested PAHs, the FLU and ANTH/PHEN were detected in all samples while ACEN and PYR in 87.5% and 75.0% of them, respectively. However, ACEN and PYR provided levels below the LOQ values. The mean values ranged from 6.53 (for FLU) to 23.56 pg mg^{-1} (for ANTH/PHEN). The highest concentration was found for ANTH/PHEN in the musk deer hair sample (35.00 pg mg^{-1}), and for FLU, the highest concentration was found in one of four leopard cat hair samples (11.94 pg mg^{-1}).

Furthermore, according to the results, it seems that musk deer had the highest mean concentrations levels of all tested pollutants compared to the four species (Table S3, Figs. 1, 2, and 4). For HCB, DDTs, and PCBs, the order of higher to lower mean detected concentrations was musk deer>leopard cat>wolf>raccoon dog>amur hedgehog. The corresponding order for PAHs was also musk deer>wolf>leopard cat>raccoon dog.

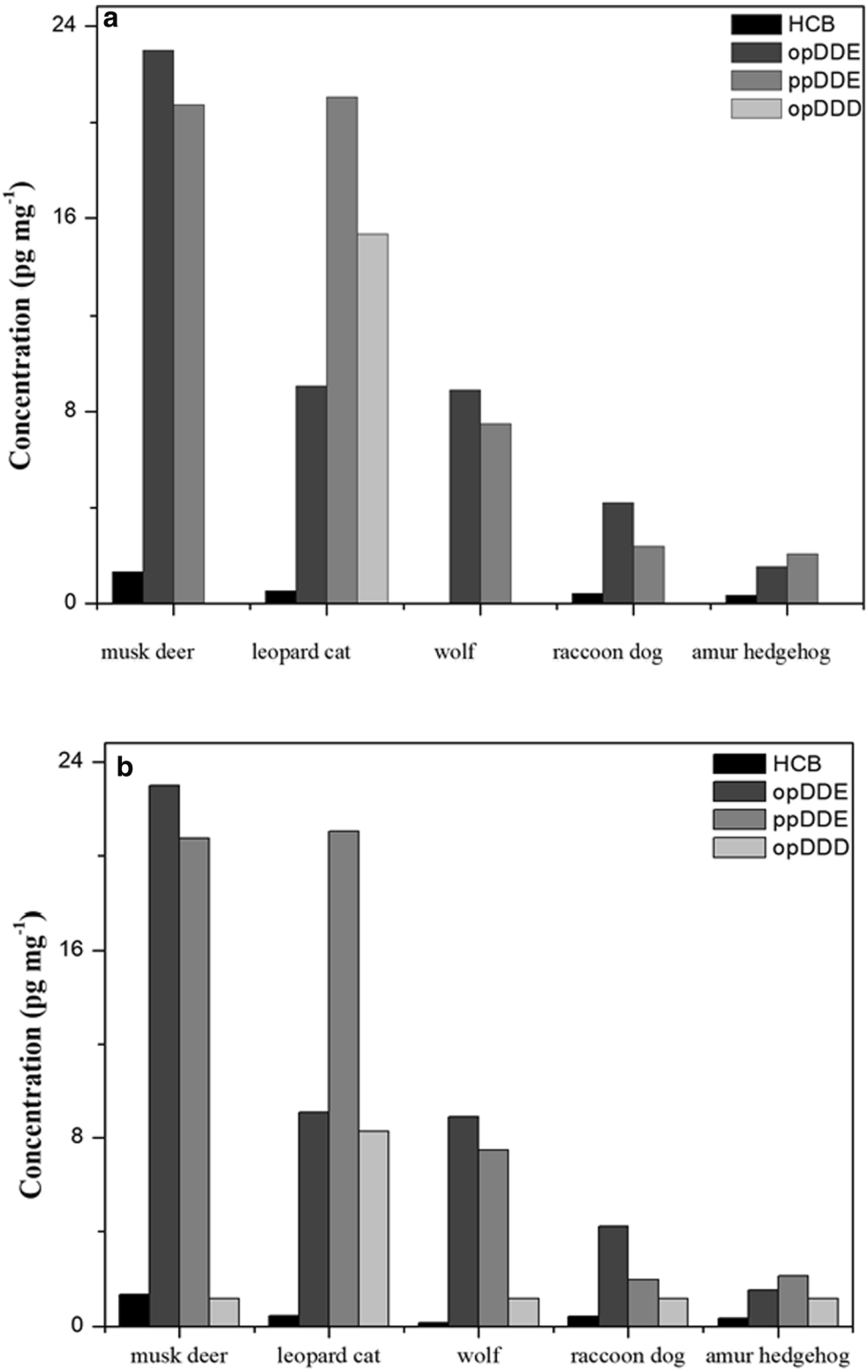

Fig. 1 The mean concentrations (in pg mg^{-1}) of HCB and DDTs in hair samples of the wild animals without (**a**) and with input values (**b**)

Discussion

In Table 2, literature data were depicted concerning the detected levels in various biological samples (hair, adipose tissue, serum, etc.) for different terrestrial mammals. The results of the current study can be directly compared only with the results of the study of D'Havé and co-authors (D'Havé et al. 2006). Specifically, the mean concentrations of DDTs and PCBs were1.82 and 1.68 pg mg^{-1} for amur hedgehog (Table S3) while

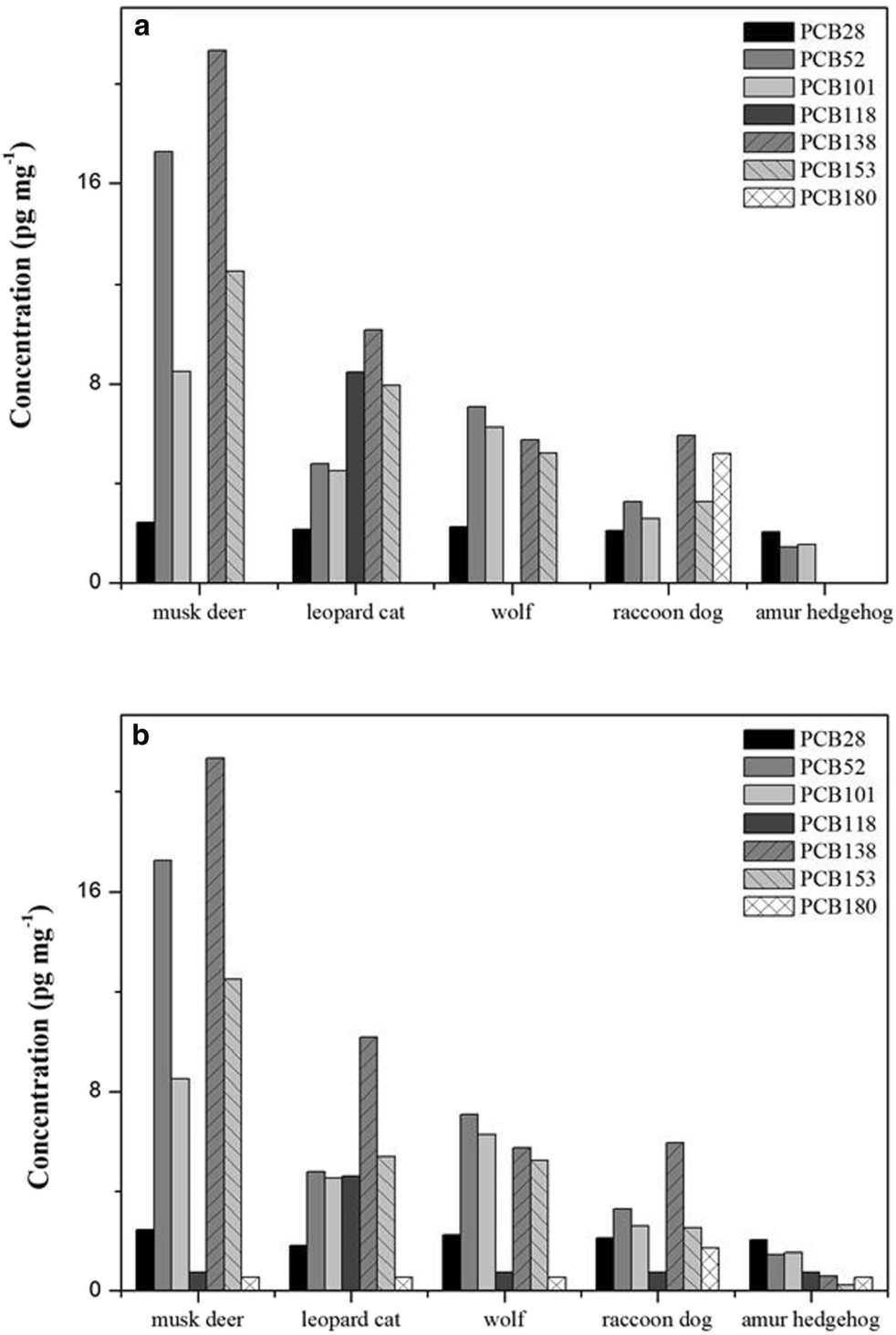

Fig. 2 The mean concentrations (in pg mg^{-1}) of PCBs in hair samples of wild animals without (**a**) and with input values (**b**)

previously reported mean concentrations for European hedgehogs were 23 and 45 pg mg^{-1} (D'Havé et al. 2006) (Table 2). On the other hand, we found higher DDT mean values for all tested hair samples ranging from 10.05 to15.33 pg mg^{-1} (Table 1) compared to those reported for dogs (< 0.1 pg mg^{-1}) and cats (2.4 pg mg^{-1}) (Table 2) (Ali et al. 2013).

Recently, the mean reported concentrations of PCBs and PAHs in dog hair samples were 22 and 329 pg mg^{-1}, respectively (Ali et al. 2013). The PAHs levels were higher from the present study (8.81 pg mg^{-1} (raccoon dog) to 22.12 pg mg^{-1} (musk deer)) (Table S3), possibly attributed by the fact that the hair samples were collected from dogs that lived in houses of smokers (González-Gómez et al.

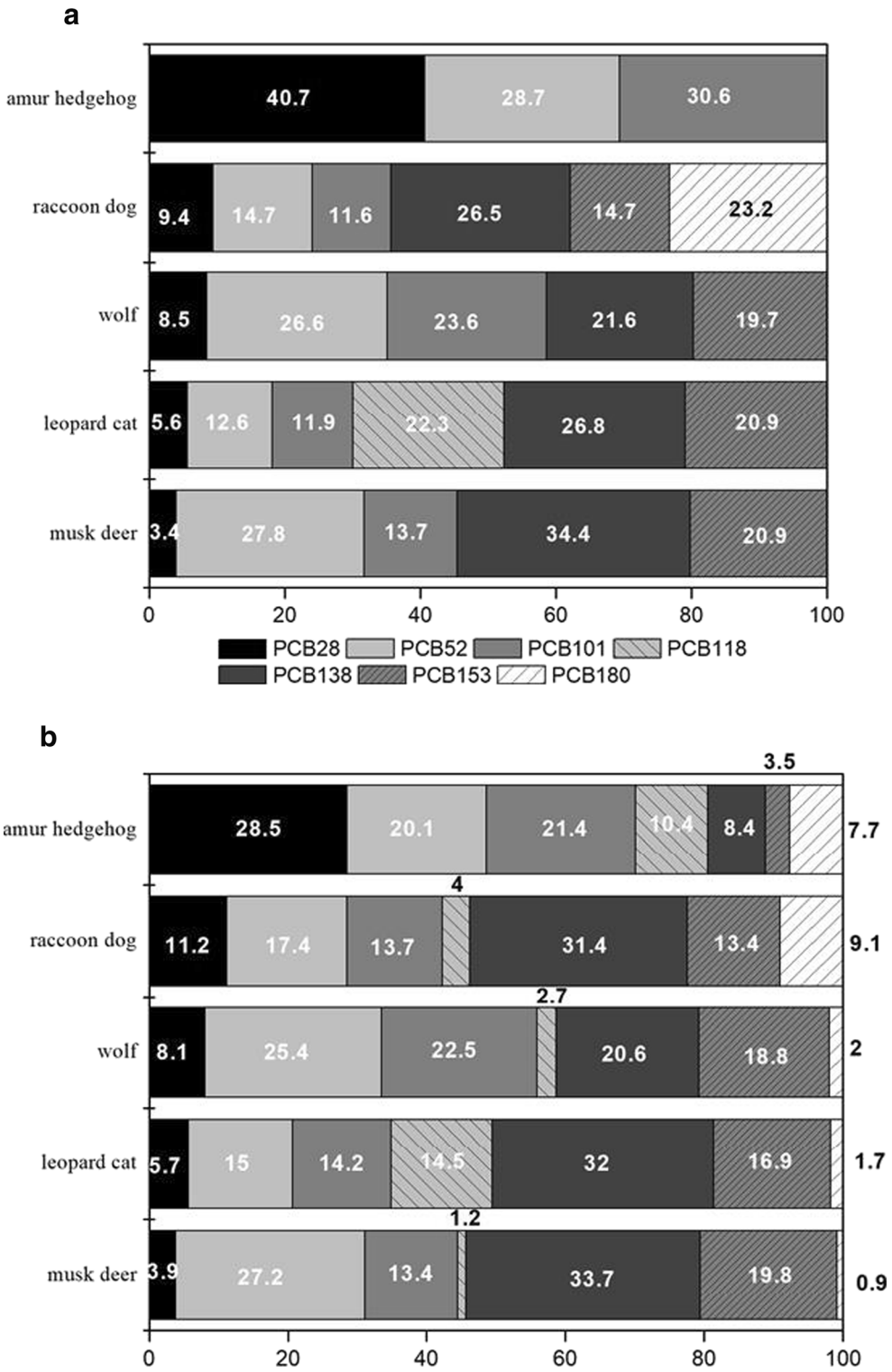

Fig. 3 The contribution (%) of each individual PCB congener to total PCBs burden without (**a**) and with input values (**b**)

2018). Furthermore, in a previous research, the mean concentration of PCBs in the hair of polar bears was found to be 117 ng g^{-1} (Jaspers et al. 2010). This concentration value is much higher than those found in the current study for all wild animals (3.73 pg mg^{-1} (raccoon dog) to 12.41 pg mg^{-1} (musk deer)) (Table S3).

Siberian musk deers are herbivores and they are fed mostly with lichens and mosses (50–90%) (Wang et al. 2015). Several studies indicate that lichens and mosses uptake POPs and toxic pollutants as natural passive air samplers leading to the exposure of musk deers via their diet (Cabrerizo et al. 2012). Available POP concentrations for lichens in

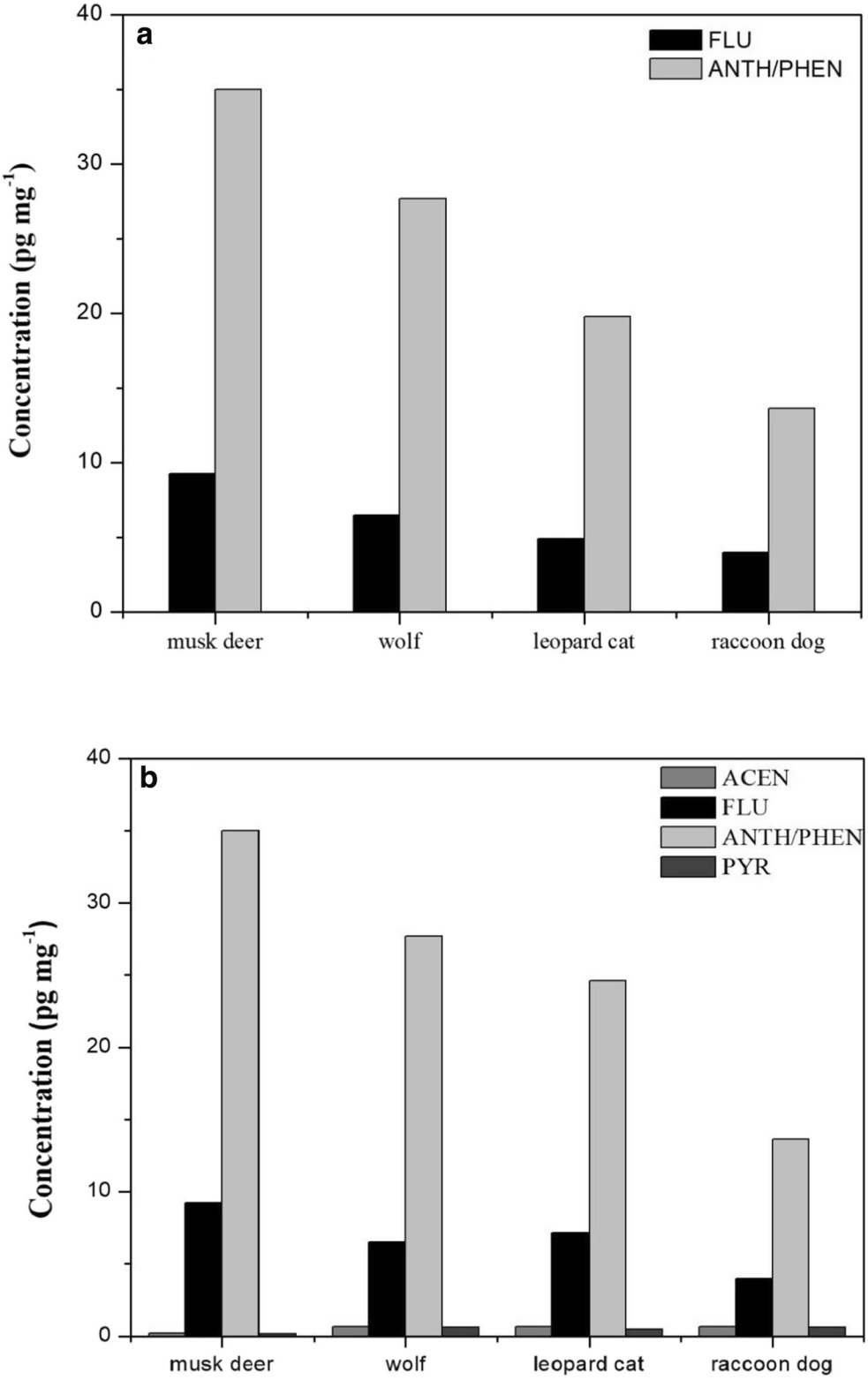

Fig. 4 The mean concentrations (in pg mg^{-1}) of PAHs in hair samples of wild animals without (**a**) and with input values (**b**)

West Antarctica reached a level of 0.0430.61 ng g^{-1} DW, 0.002–0.31 ng g^{-1} DW, 0.003–0.01 ng g^{-1} DW, 15–40 ng g^{-1} DW for PCBs, HCB, ppDDE, and PAHs, respectively (Cabrerizo et al. 2012). Siberian wolves are mainly feed on wild boar and deers (roe, red, musk) and their lives are threatened by hunters (Imbert et al. 2016). The leopard cat has a widespread distribution and its main prey are small mammals, lizards, amphibians, birds, and insects (Grassman

Table 2 Literature data with concentrations of the tested pollutants in different species and various tissues

Species		PCBs	DDTs	PAHs	Reference
Adipose tissue (ng g^{-1} wet wt)					
Raccoon dog $n = 14$	Median	31	111		(Tomza-Marciniak et al. 2014)
	Range	5.0–181.59	2.13–927.74		
Badger $n = 11$	Median	32	380		
	Range	3.04–138.68	69.92–1150.54		
Red deer $n = 8$	Median	13	35		
	Range	2.26–45.09	18.04–123.17		
Roe deer $n = 16$	Median	15	85		
	Range	1.97–34.20	15.08–237.59		
Wild boar $n = 14$	Median	16	237		
	Range	0.72–130.85	3690–1116.64		
Brown bear $n = 19$	Median	2.05	0.232		(HercegRomanić et al. 2015)
	Range	0.797–5.34	0.08–1.19		
Gray wolf $n = 14$	Median	7.12	0.362		
	Range	2.15–34.9	0.221–2.85		
Polar bear $n = 51$	Median	4705			(Tartu et al. 2017)
	Range	1339–67,011			
Serum (ng g^{-1} lipid wt)					
Dog $n = 16$	Median	15	< 1		(Ali et al. 2013)
	Range	9.0–22	< 1		
Cat $n = 20$	Median	36	111		
	Range	16–132	< 1.0–2175		
Hair (pg mg^{-1})					
Dog n = 47^a, 10^b, 48^c	Mean	$22^{a,2}$	$< 0.1^{b,1}$	$329^{c,2}$	[1](Ali et al. 2013)
	Range	0.3–59	< 0.1	8.6–1031	[2](González-Gómez et al. 2018)
Cat $n = 12$	Mean	0.5^1	2.4^1		
	Range	0.05–1.1	< 0.1–7.85		
Polar bear $n = 15$	Mean	117			(Jaspers et al. 2010)
	Range	–			
European hedgehog $n = 45$	Mean	45	23		(D'Havé et al. 2006)
	Range	ND-789	ND-725		
Musk deer $n = 3^a,1^b$	Mean	12.41^a	21.87^a	22.12^b	Current study
	Range	2.44–21.34	20.74–23	9.25–35	
Leopard cat $n = 6^a,4^b$	Mean	6.34^a	15.15^a	12.35^b	
	Range	2.14–10.17	9.08–21.05	4.91–19.79	
Raccoon dog $n = 5^a,2^b$	Mean	3.77^a	3.67^a	8.81^b	
	Range	2.11–5.58	2.74–4.59	3.98–13.64	
Wolf $n = 1$	Mean	5.32	8.19	17.1	
	Range	2.26–7.08	7.49–8.89	6.52–27.68	
Amur hedgehog $n = 1$	Mean	1.68	1.82		
	Range	1.45–2.05	1.55–2.08		
Plasma (ng g^{-1} wet wt)					
Polar bear $n = 62$	Median	2846			(Tartu et al. 2017)
	Range	820–18,567			
Liver (ng g^{-1} wet wt)					
Red deer $n = 18$	Median	1.36			(Warenik-Bany et al. 2016)
	Range	0.36–7.51			
Roe deer $n = 10$	Median	0.42			
	Range	0.40–1.93			
Wild boar $n = 42$	Median	0.46			
	Range	0.07–2.68			

Table 2 (continued)

Species		PCBs	DDTs	PAHs	Reference
European hedgehog $n = 43$	Median	75	1.4		(D'Havé et al. 2006)
	Range	2–5910	ND-750		
Whole blood (pg g^{-1} wet wt)					
Cat $n = 10$	Median	550			(Mizukawa et al. 2013)
	Range	40–16,000			
Raccoon dog $n = 13$	Median	190			
	Range	19–1100			
Dog $n = 10$	Median	91			
	Range	< 7.4–320			
Masked palm civet $n = 8$	Median	4800			
	Range	260–95,000			
Fox $n = 5$	Median	270			
	Range	100–680			
Raccoon $n = 13$	Median	230			
	Range	< 7.4–2600			
Badger $n = 6$	Median	36			
	Range	< 7.4–750			
Mongoose $n = 2$	Median	27,000			
	Range	24,000–29,000			

Superscript letters a,b and c indicate the number of the samples that were analyzed for *PCBs*, *DDTs*, and *PAHs*, respectively

Supersript numbers indicate the corresponding references presented on the right column

2000). Hedgehogs consume a wide variety of insects, snails, frogs, mushrooms, etc. and raccoon dogs feed on insects, rodents, amphibians, birds, fishes, and some fruits, so they can also be used as indicators of environmental pollution in terrestrial ecosystems (D'Havé et al. 2006; Zapletal et al. 2015; Sutor et al. 2010).

The detected concentration levels of POPs in various biological samples (serum, plasma, liver, whole blood, hair, adipose tissue) of mammals can be found in Table 2. Indicatively, for raccoon dog samples, the detected median concentrations of PCBs were 190 pg g^{-1} and 31 ng g^{-1} (Table 2), in whole blood (Mizukawa et al. 2013) and adipose tissue (Tomza-Marciniak et al. 2014), respectively. In liver samples of European hedgehog, the detected median concentrations of PCBs and DDTs were 75 ng g^{-1} and 1.4 ng g^{-1}, respectively (Warenik-Bany et al. 2016).

Conclusion

There are limited data reports on the monitoring of POPs in hair samples from wild terrestrial mammals, and for that reason, there is a need for further research. Among the 16 analyzed pollutants, the most dominant POPs in the majority of all the tested wild animals were HCB, opDDE, ppDDE, PCB28, PCB52, PCB138, PCB153 (positive range from 73.3 to 100%), ANTH, PHEN, FLU (100% positive samples), ACN, and PYR (75–87.5% positive samples). The mean concentrations of all measured pollutants were higher in musk deers compared with the other four species, possibly due to their diet with lichens which can uptake pollutants from the atmosphere.

The current study is the first to provide information about a wide range of POP (HCB, DDTs, PCBs, and PAHs) concentrations in hair samples in different wild animal species (musk deer, leopard cats, wolf, amur hedgehog, and raccoon dogs). Hair analysis is a noninvasive method that can be useful in the biomonitoring of terrestrial wildlife and can be considered a valuable tool for the simultaneous screening of concentration levels of POPs in hair, blood, and urine samples so as to clarify distribution pathways in each species. Finally, the results of the present study provide important data indicating that there is a need to provide risk assessment and biomonitoring studies of emerging organic pollutants in a wide variety of wild terrestrial species.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

References

Ali N, Malik RN, Mehdi T, Eqani SAMAS, Javeed A, Neels H, Covaci A (2013) Organohalogenated contaminants (OHCs) in the serum and hair of pet cats and dogs: biosentinels of indoor pollution. Sci Total Environ 449:29–36. https://doi.org/10.1016/j.scitotenv.2013.01.037

Barbounis EG, Tzatzarakis MN, Alegakis AK, Kokkinaki A, Karamanos N, Tsakalof A, Tsatsakis AM (2012) Assessment of PCBs exposure in human hair using double focusing high resolution mass spectrometry and single quadrupole mass spectrometry. Toxicol Lett 210: 225–231. https://doi.org/10.1016/j.toxlet.2011.07.031

Cabrerizo A, Dachs J, Barceló D, Jones KC (2012) Influence of organic matter content and human activities on the occurrence of organic pollutants in Antarctic soils, lichens, grass, and mosses. Environ Sci Technol 46:1396–1405. https://doi.org/10.1021/es203425b

Covaci A, Tutudaki M, Tsatsakis AM, Schepens P (2002) Hair analysis: another approach for the assessment of human exposure to selected persistent organochlorine pollutants. Chemosphere 46:413–418. https://doi.org/10.1016/S0045-6535(01)00065-0

Covaci A, Hura C, Gheorghe A, Neels H, Dirtu AC (2008) Organochlorine contaminants in hair of adolescents from Iassy, Romania. Chemosphere 72:16–20. https://doi.org/10.1016/j.chemosphere.2008.02.058

D'Havé H, Scheirs J, Covaci A et al (2006) Nondestructive pollution exposure assessment in the european hedgehog (Erinaceuseuropaeus): III. Hair as an indicator of endogenous organochlorine compound concentrations. Environ Toxicol Chem 25: 158–167. https://doi.org/10.1897/05-208R.1

Dahmardeh Behrooz R, Barghi M, Bahramifar N, Esmaili-Sari A (2012) Organochlorine contaminants in the hair of Iranian pregnant women. Chemosphere 86:235–241. https://doi.org/10.1016/j.chemosphere.2011.09.031

González-Gómez X, Cambeiro-Pérez N, Martínez-Carballo E, Simal-Gándara J (2018) Screening of organic pollutants in pet hair samples and the significance of environmental factors. Sci Total Environ 625:311–319. https://doi.org/10.1016/j.scitotenv.2017.12.270

Grassman LI (2000) Movements and diet of the leopard cat Prionailurusbengalensis in a seasonal evergreen forest in south-central Thailand. Acta Theriol 45:421–426. https://doi.org/10.4098/AT.arch.00-41

He C-T, Yan X, Wang M-H, Zheng XB, Chen KH, Guo MN, Zheng J, Chen SJ (2017) Dichloro-diphenyl-trichloroethanes (DDTs) in human hair and serum in rural and urban areas in South China. Environ Res 155:279–286. https://doi.org/10.1016/j.envres.2017.02.011

HercegRomanić S, Klinčić D, Kljaković-Gašpić Z et al (2015) Organochlorine pesticides and polychlorinated biphenyl congeners in wild terrestrial mammals from Croatia: interspecies comparison of residue levels and compositions. Chemosphere 137:52–58. https://doi.org/10.1016/j.chemosphere.2015.05.026

Imbert C, Caniglia R, Fabbri E, Milanesi P, Randi E, Serafini M, Torretta E, Meriggi A (2016) Why do wolves eat livestock?: factors influencing wolf diet in northern Italy. Biol Conserv 195:156–168. https://doi.org/10.1016/j.biocon.2016.01.003

Jaspers VLB, Dietz R, Sonne C, Letcher RJ, Eens M, Neels H, Born EW, Covaci A (2010) A screening of persistent organohalogenated contaminants in hair of East Greenland polar bears. Sci Total Environ 408:5613–5618. https://doi.org/10.1016/j.scitotenv.2010.07.059

Katsikantami I, Sifakis S, Tzatzarakis M et al (2016) A global assessment of phthalates burden and related links to health effects. Environment International 97:212–236. https://doi.org/10.1016/j.envint.2016.09.013

Kavvalakis M, Tsatsakis A (2012) The atlas of dialkylphosphates; assessment of cumulative human organophosphorus pesticides' exposure. Forensic Sci Int 218:111–122. https://doi.org/10.1016/j.forsciint.2011.10.019

Liang B, Liu X, Hou J, Liang G, Gong W, Xu D, Zhang L (2014) PCBs levels and indicator congeners in children's and adolescents' hair. Environ Pollut 185:10–15. https://doi.org/10.1016/j.envpol.2013.10.014

Malarvannan G, Isobe T, Covaci A, Prudente M, Tanabe S (2013) Accumulation of brominated flame retardants and polychlorinated biphenyls in human breast milk and scalp hair from the Philippines: levels, distribution and profiles. Sci Total Environ 442:366–379. https://doi.org/10.1016/j.scitotenv.2012.10.005

Mamontova EA, Mamontov AA, Tarasova EN, Kuzmin MI, Ganchimeg D, Khomutova MY, Gombosuren O, Ganjuurjav E (2013) Polychlorinated biphenyls in surface soil in urban and background areas of Mongolia. Environ Pollut 182:424–429. https://doi.org/10.1016/j.envpol.2013.08.001

Mizukawa H, Nomiyama K, Nakatsu S, Yachimori S, Hayashi T, Tashiro Y, Nagano Y, Tanabe S (2013) Species-specific differences in the accumulation features of organohalogen contaminants and their metabolites in the blood of Japanese terrestrial mammals. Environ Pollut 174:28–37. https://doi.org/10.1016/j.envpol.2012.11.004

Sutor A, Kauhala K, Ansorge H (2010) Diet of the raccoon dog Nyctereutesprocyonoides — a canid with an opportunistic foraging strategy. Acta Theriol 55:165–176. https://doi.org/10.4098/j.at.0001-7051.035.2009

Tartu S, Bourgeon S, Aars J, et al (2017) Sea ice-associated decline in body condition leads to increased concentrations of lipophilic pollutants in polar bears (Ursus maritimus) from Svalbard, Norway. Sci Total Environ 576:409–419. https://doi.org/10.1016/j.scitotenv.2016.10.132

Tomza-Marciniak A, Marciniak A, Pilarczyk B, Prokulewicz A, Bąkowska M (2014) Interspecies comparison of chlorinated contaminant concentrations and profiles in wild terrestrial mammals from Northwest Poland. Arch Environ Contam Toxicol 66:491–503. https://doi.org/10.1007/s00244-013-9989-y

Tsatsakis A, Tutudaki M (2004) Progress in pesticide and POPs hair analysis for the assessment of exposure. Forensic Sci Int 145:195–199. https://doi.org/10.1016/j.forsciint.2004.04.036

Tsatsakis A, Barbounis M, Kavalakis M (2010) Determination of dialkyl phosphates in human hair for the biomonitoring of exposure to organophosphate pesticides. J Chromatogr B – Anal Technol Biomed Life Sci 878:1246–1252. https://doi.org/10.1016/j.jchromb.2010.02.021

Tzatzarakis M, BE G, KM P et al (2014) Rapid method for the simultaneous determination of DDTs and PCBs in hair of children by headspace solid phase microextraction and gas chromatography-mass spectrometry (HSSPME/GC-MS). Drug Test Anal 6:85–92. https://doi.org/10.1002/dta.1631

Vinceti M, Violi F, Tzatzarakis M, Mandrioli J, Malagoli C, Hatch EE, Fini N, Fasano A, Rakitskii VN, Kalantzi OI, Tsatsakis A (2017) Pesticides, polychlorinated biphenyls and polycyclic aromatic hydrocarbons in cerebrospinal fluid of amyotrophic lateral sclerosis patients: a case-control study. Environ Res 155:261–267. https://doi.org/10.1016/j.envres.2017.02.025

Wang W, Zhou R, He L, Liu S, Zhou J, Qi L, Li L, Hu D (2015) The progress in nutrition research of musk deer: implication for conservation. Appl Anim Behav Sci 172:1–8. https://doi.org/10.1016/j.applanim.2015.09.006

Warenik-Bany M, Strucinski P, Piskorska-Pliszczynska J (2016) Dioxins and PCBs in game animals: interspecies comparison and related consumer exposure. Environ Int 89–90:21–29. https://doi.org/10.1016/j.envint.2016.01.007

Yamamoto Y, Ishizaki A, Kataoka H (2015) Biomonitoring method for the determination of polycyclic aromatic hydrocarbons in hair by online in-tube solid-phase microextraction coupled with high performance liquid chromatography and fluorescence detection. J Chromatogr B 1000: 187–191. https://doi.org/10.1016/j.jchromb.2015.07.033

Zapletal M, Sodnompil B, Atwood JL, Murdoch JD, Reading RP (2015) Fine-scale habitat use by Daurian hedgehogs in the Gobi-steppe of Mongolia. J Arid Environ 114:100–103. https://doi.org/10.1016/j.jaridenv.2014.11.010