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Bioaccumulation potential of bisphenols and benzophenone UV filters: A multiresidue approach in raptor tissues

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HIGHLIGHTS

- Occurrence of eight bisphenols and five benzophenone UV filters in raptor tissues.
- Bisphenol A, bisphenol F, benzophenone-8 and 4-hydroxybenzophenone were predominant.
- Potential bioaccumulation of contaminants in specific raptor tissues was indicated.
- The potential role of the preen gland as a major excretory organ was suggested.

GRAPHICAL ABSTRACT

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ABSTRACT

Environmental exposure to bisphenols and benzophenone UV filters has received considerable attention due to the ubiquitous occurrence of these contaminants in the environment and their potential adverse health effects. The occurrence of bisphenols and benzophenone UV filters is well established in human populations, but data is scarce for wildlife, and especially for raptors (birds of prey, falcons and owls). In this study, concentrations of eight bisphenols and five benzophenone UV filters were determined in six raptor tissues, including muscle, kidney, liver, brain, preen gland (uropygial gland) and adipose. The tissue samples (n = 44) were taken from dead raptor species (1997–2011), including Eurasian sparrowhawks (*Accipiter nisus*, n = 2) and long-eared owls (*Asio otus*, n = 2), both from France, and white-tailed eagles (*Haliaeetus albicilla*, n = 16) from Greenland. Overall, six bisphenols and four benzophenone UV filters were found in the samples. Bisphenol A (BPA), bisphenol F (BPF), benzophenone-8 (BzP-8) and 4-hydroxybenzophenone (4-OH-BzP) were the most abundant contaminants, accounting for median concentrations of 67.5, 3.01, 27.1 and 9.70 ng/g wet weight (w.w.), respectively. The potential role of the preen gland as a major excretory organ for bisphenols and benzophenone UV filters was suggested since the median sum concentration of the two contaminant classes in the white-tailed eagle tissues showed higher bioaccumulation potential in the preen gland (5.86 ng/g w.w.) than the liver (2.92) and kidney (0.71). The concentrations of these contaminants in the tissues of the three raptor species indicated a pattern of increasing detection rates and median concentrations with an increase of the species size and their expected trophic

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position. To the best of our knowledge, this is the first peer-reviewed study to document multiresidues of both contaminant classes in raptor tissues.

1. Introduction

Emerging contaminants (ECs) are currently found widespread throughout the different environmental compartments and have impacted the natural ecosystems worldwide (Thomaidis et al., 2012). Bisphenols (BPs) and benzophenone UV filters (BzPs) are high-volume produced ECs that are used in a multitude of consumer products, including packaging materials (e.g., foodstuffs), personal care products, and pharmaceuticals (Asimakopoulos et al., 2016a; Caballero-Casero et al., 2016; Karthikraj and Kannan, 2018; Lu et al., 2018), while both chemical classes are documented as co-occuring in plastic products (Asimakopoulos et al., 2016a). They exhibit endocrine-disrupting properties and are associated to adverse health effects in humans such as obesity, thyroid related diseases, diabetes, and reproductive dysfunction among others (Joensen et al., 2018; Magueresse-Battistoni et al., 2017; Philips et al., 2020). BPs and BzPs have recently attracted increased scientific attention through biomonitoring studies published on humans, aquatic and marine ecosystems (Asimakopoulos et al., 2014, 2016b; Rocha et al., 2018; Romera-García et al., 2019; Vela-Soria et al., 2014; Yu and Wu, 2014). BPs are a class of chemicals with two phenolic functional groups in their structure, which include several analogues mainly used in the production of polycarbonate plastics and epoxy resins (Asimakopoulos et al., 2016a). Until recently, bisphenol A (BPA) was the most used and studied BP, but due to increased concerns of its toxicity, several BP analogues are nowadays introduced into the global markets as substitutes, e.g., bisphenol F (BPF) and bisphenol S (BPS) (Chen et al., 2016; Qui et al., 2019). However, these chemical substitutes are also currently raising concerns of toxicity and widespread environmental occurrence (Lehmler et al., 2018; Xue et al., 2017). BzPs are another class of chemicals that obtain a diarylketone scaffold molecular structure in which different substitute groups are attached (Asimakopoulos et al., 2014, 2016a). They are frequently used as UV filters in sunscreen products and personal care products (Asimakopoulos et al., 2014, 2016a; Karthikraj and Kannan, 2018), while benzophenone-3 (BzP-3) is the most represented BzP analogue (Asimakopoulos et al., 2014; Li and Kannan, 2018).

Among the wildlife species, raptors [*Accipitriformes* (hawks, eagles, ospreys) and *Strigiformes* (owls)] are important sentinels of environmental contamination and exposures (Espín et al., 2016). They are particularly suitable for monitoring persistent, bioaccumulative and toxic (PBT) contaminants because: (a) they are apex predators, and therefore particularly sensitive "biotracers" of environmental contaminants (Helander et al., 2008; Kovács et al., 2008); (b) they are found widespread in the ecosystems and are relatively long-lived organisms, thus allowing the assessment of spatial and temporal trends of contaminant concentrations (Furness, 1993; Sun et al., 2019, 2020); and (c) specific biological samples, e.g., eggs, feathers and preen oil, can be collected non-invasively without sacrificing or harming the raptors (Eulaers et al., 2011). Numerous studies are published on the determination of contaminants in raptors (Ahrens et al., 2011; Barón et al., 2014; Bustnes et al., 2015; Jaspers et al., 2011, 2013). However, so far most of them are focused on persistent organic pollutants (POPs), while data on the bioaccumulation of ECs in raptors is limited (Briels et al., 2019; Løseth et al., 2019). With this background, the present study aims to investigate the occurrence profiles of BPs and BzPs in selected raptor tissues and assess their bioaccumulation potential. To our knowledge, this is the first peer-reviewed study on the occurrence of eight BPs and five BzPs in raptor tissues.

2. Experimental section

2.1. Chemicals and materials

Methanol of LC-MS grade was purchased from VWR Chemicals (Trondheim, Norway). Ethylacetate, hydrochloric acid (HCl), ammonium hydroxide and ammonium acetate were purchased from Sigma-Aldrich (Steinheim, Germany). Water was purified with a Milli-Q grade water purification system (Q-option, Elga Labwater, Veolia WaterSystems LTD, U.K.). β-Glucuronidase from *Helix pomatia* (type HP-2, aqueous solution, ≥100,000 units/mL) was purchased from Sigma-Aldrich (Steinheim, Germany). Standards of BPA (≥99%), bisphenol AF (BPAF, ≥99%), bisphenol AP (BPAP, ≥99%), bisphenol B (BPB, ≥98%), BPF (≥98%), bisphenol M (BPM, ≥99%), bisphenol P (BPP, ≥99%), BPS (≥98%), bisphenol Z (BPZ, ≥99%), benzophenone-1 (BzP-1, ≥99%), benzophenone-2 (BzP-2, ≥97%), benzophenone-3 (BzP-3, ≥98%), benzophenone-8 (BzP-8, ≥98%) and 4-hydroxybenzophenone (4-OH BzP, ≥98%) were purchased from Sigma-Aldrich (Steinheim, Germany). Internal standards (ISs) were purchased from Cambridge Isotope Laboratories (Andover MA, USA): ^{13}C-isotope of BPA (BPA-$^{13}C_{12}$; ≥99%), BPAF (BPAF-$^{13}C_{12}$; ≥99%), BPB (BPB-$^{13}C_{12}$; ≥99%), BPF (BPF-$^{13}C_{12}$; ≥99%), and BPS (BPS-$^{13}C_{12}$; ≥98%).

A Branson Model 3510-DTH Ultrasonic Cleaner (Branson, Danbury CT, U.S.) was used for the ultrasonication of samples. A Biotage TurboVap Classic LV Concentration Evaporator Workstation (Biotage, Charlotte, NC, U.S.) was utilized for concentrating the extracts using a heated water bath under a nitrogen gas stream. An Innova 44 Incubator Shaker (J&M Scientific, Woburn, Massachusetts, U.S.) was used for the incubation of samples, and a mechanical shaker (KS501 digital, IKA, U.K.) was used for shaking the samples.

2.2. Study population and sample collection

Three different species, including white-tailed eagles (*Haliaeetus albicilla*), long-eared owls (*Asio otus*) and Eurasian sparrowhawks (*Accipiter nisus*), were sampled during 1997–2011 in Greenland and France. Depending on sample availability, a selection was performed from the tissues of muscle, kidney, liver, brain, preen gland (uropygial gland) and adipose. The white-tailed eagles (n = 16) were found dead or dying in West Greenland between March 1997 and January 2009. The Eurasian sparrowhawks (n = 2) and long-eared owls (n = 2) were found dead by the Association of CHENE (Centre d'Hébergement et d'Etudes sur la Nature et l'Environnement) in Normandy, France, between 2009 and 2011. Relevant information on raptors analyzed in this study (Raptor ID, sampling area and year of collection) is provided in Table S1. Further details on the white-tailed eagles (i.e., date and place found, estimated age, plumage, sex, cause of death, weight, etc.) can be found in Jaspers et al. (2013), and for the Eurasian sparrowhawks and long-eared owls in Table S2. Tissues were carefully dissected using stainless steel tools rinsed thoroughly between tissues and individuals. All samples were properly labelled and stored in the darkness at −80 °C.

2.3. Sample preparation

Tissue samples of 0.1–0.2 g were weighted into 15 mL polypropylene (PP) tubes. The sample preparation protocol was adapted from Asimakopoulos et al. (2016b) with minor modifications. Briefly, 1 mL of 1.0 M ammonium acetate aqueous buffer was added to the samples and ultrasonication followed for 45 min. Another 1 mL of 1.0 M ammonium acetate (aqueous buffer) that contained 44 units of β-glucuronidase (prepared by spiking 100 μL of β-glucuronidase into 100 mL of 1.0 M

ammonium acetate solution) was added to the samples, and were incubated at 37 °C for 12 h to establish total concentrations (free and conjugated chemical species). Thereafter, the samples were extracted 3 consecutive times with 4 mL ethyl acetate (3 × 4). For each extraction, the mixture was shaken for 60 min and then centrifuged at 4500*g* for 10 min. The supernatants were combined, and 2 mL of Milli-Q water were added. The derived mixtures were further shaken for 5 min, centrifuged at 4500*g* for 10 min, and the collected supernatants were eventually transferred into a PP tube and concentrated to ~250 μL using the water bath set at 30 °C under a gentle nitrogen stream. Finally, methanol was added up to a total volume of 1 mL, vortex mixed, and transferred for UPLC–MS/MS analysis.

2.4. UPLC-MS/MS analysis

The chromatographic separation was carried out using an Acquity UPLC I-Class system (Waters, Milford, U.S.) coupled to a triple quadrupole mass analyser (QqQ; Xevo TQ-S) with a ZSpray ESI ion source (Waters, Milford, U.S.). The LC column used was a Kinetex C18 (50 × 2.1 mm, 1.3 μm) connected to a Phenomenex C18 guard column (2.0 × 2.1 mm). The column temperature was set at 30 °C. The mobile phase consisted of solvent (A) 0.1% v/v ammonium hydroxide in Milli-Q water and (B) methanol. The flow rate was 300 μL min^{-1} and the injection volume was 4 μL. The gradient elution initiated with 75% A, held for 10 s, decreased to 25% A within 3.4 min, then further decreased to 1% A, held for 30 s, and reverted to 75% A that was held for 20 s, for a total time run of 4 min. The mass spectrometer was operated in multiple reaction monitoring (MRM) mode. Electrospray ionization was performed under negative ionization mode (ESI−). Optimal source settings were the following: source gas temperature 150 °C, capillary voltage −1500 V and nebulizer gas pressure 7.0 bar. Precursor and product ions and relevant detection MS/MS parameters of each target analyte are shown in Table S3. Quantification of the target analytes was accomplished based on the internal standard method and with matrix-matched calibration standards (Asimakopoulos et al., 2014, 2016b).

2.5. Method performance characteristics

The analytical method was validated by analyzing non-spiked, pre-extraction spiked and post-extraction spiked triplicates in pool samples of liver (n = 6) and preen gland (n = 13). The isomers, BPM and BPP, were quantified in samples as a single 1:1 mixture. Contamination during sample preparation was evaluated by analyzing reagent blanks that followed the whole procedure as actual samples. The performance of the developed method was described based on correlation coefficients, relative recoveries, precision, method detection (MDLs) and method quantification (MQLs) limits, ion ratios (IRs%; when applicable), retention and relative retention times (RTs, RRTs), and matrix effects (MEs %). The MDLs and MQLs were estimated and presented here for a typical sample weight of 0.2 g as 3 and 10 times the signal-to-noise ratio in 0.5 mL solvent matrix, respectively. Estimation of MEs (%) during analysis was performed for each target analyte using Eq. (1):

$$\mathrm{ME}\ (\%) = (\mathrm{MF} - 1) \times 100 \quad (1)$$

where MF is the matrix factor, which is estimated by the ratio of the peak area of the target analyte in the post-extraction fortified matrix to that in standard solvent (both at the amount of 20 ng). The IR (%) for a target analyte relates the area of the peak of the qualifier with that of the quantifier ion.

2.6. Data analysis and statistical treatment

UPLC-MS/MS data was acquired with the MassLynx v4.1 software, while quantification processing was performed with TargetLynx (Waters, Milford, U.S.). Excel (Microsoft, 2018) was used for general descriptive statistics. Data analysis, including descriptive statistics, did not include data <MQLs. A substitution or a non-parametric method (e.g., Kaplan-Meier) was not applied for the censored values (<MQLs) due to their large proportion in the concentration data set (Asimakopoulos et al., 2016b). Concentrations were reported as ng/g wet weight (w.w.).

3. Results and discussion

3.1. UPLC-MS/MS bioanalytical method performance

Correlation coefficients were assessed by running internal calibration curves prepared in methanol (fortified with target BPs and BzPs at 0.1, 0.2, 0.5, 1, 2, 5, 10, 20 and 50 ng/mL and ISs at 20 ng/mL). The correlation coefficients in all cases were above 0.991. The IS used, IR (%), RT and RRT for each target analyte are presented in Table S4. The MDLs and MQLs were in the range from 0.004 to 2.00 and from 0.01 to 6.50 ng/g w.w., respectively (Table S5). The MQLs allowed for the quantification of BPs and BzPs with optimal precision at the low concentrations that were present in the actual biological samples. The precision of the UPLC-MS/MS method was evaluated in terms of repeatability (n = 3 for each matrix, liver and preen gland; the fortified amounts of the target analytes and ISs were 20 and 10 ng, respectively) using the internal standard method and expressed as relative standard deviation (RSD%) (Table S6). The precision for most target analytes was <15% and overall ranged from 3.22 (BzP-8) to 26.3 (BPM/BPP)% and from 3.12 (4-OH-BzP) to 24.1 (BPB)% in preen gland and liver matrix, respectively. Trueness of the method was assessed through relative recoveries (adjusted by ISs) in preen gland and liver matrix by fortification of the target analytes (n = 3 for each matrix; the fortified amounts of target analytes and ISs were 20 and 10 ng, respectively); the mean recoveries for BPs and BzPs are presented in Table 1. The recoveries for most target analytes were found to be ≥70%. However, in liver, BP-3 and BP-1 presented recoveries <60%, while BPA and BPB presented recoveries >120%, and both findings were attributed to the higher metabolic activity of the specific matrix; the liver contains excess concentrations of endogenous enzymes responsible for biotransformation reactions of contaminants, e.g., cytochrome P450 (Ashrap et al., 2017; Dudda and Kürzel, 2006).

The MFs and MEs (%) for the target analytes are shown in Tables S7-S8. All target analytes demonstrated ionization suppression with the highest observed for BzP-3, BPZ and BPAP. The bioanalytical method protocol involved a deconjugation step with β-glucuronidase to account for the glucuronide and sulfate conjugated species of contaminants since their occurrence is documented in other instances [e.g., for polycyclic aromatic hydrocarbons (PAHs)] in raptor tissues (Watanabe et al., 2010).

3.2. Bioaccumulation in raptor tissues

A total of 44 biological samples were analyzed (Tables 2–4); and most BPs and BzPs were detected, except for BPAF, BPZ and BzP-2. The DRs rank order for BPs was: BPM/BPP (10/44; 10 out of 44) > BPF (8/

Table 1
Mean relative recoveries (%; n = 3 for each matrix) for the target analytes.

Contaminants	BPA	BPF	BPB	BPS	BPZ	BPAP	BPAF
Preen gland	85.6	117	98.5	111	70.0	97	104
Liver	125	109	137	107	70.0	101	103

Contaminants	BPM/BPP	BzP-8	BzP-3	BzP-2	BzP-1	4-OH-BzP
Preen gland	86.8	107	92.3	78.1	98.0	115
Liver	116	77.4	29.8	71.0	57.6	70.0

Table 2
BPs and BzPs in different tissues from white-tailed eagles (*Haliaeetus albicilla*); concentrations expressed in ng/g w.w.

Matrix	Raptor ID	BPA	BPAP	BPB	BPF	BPM/BPP	BPS	ΣBPs	BzP-1	BzP-3	BzP-8	4-OH-BzP	ΣBzPs	ΣAll
Preen gland	39640	64.1	–	–	–	–	–	64.1	–	–	–	–	–	64.1
(n = 8)	39644	–	–	–	–	–	–	–	–	–	7.42	–	7.42	7.42
	39645	–	–	–	–	–	–	–	0.89	–	–	–	0.89	0.89
	39649	–	–	–	–	0.49	–	0.49	–	–	–	–	–	0.49
	39651	70.9	–	–	–	–	–	70.9	–	–	–	–	–	70.9
	39652	–	–	–	–	–	–	–	4.30	–	–	–	4.30	4.30
	39653	149	–	1.81	1.22	–	–	152	–	–	–	–	–	152
	39654	–	–	–	–	–	–	–	–	0.31	–	–	0.31	0.31
Liver	39652	–	–	–	2.53	0.05	–	2.58	–	–	–	–	–	2.58
(n = 4)	39653	–	–	0.72	2.21	0.12	0.21	3.26	–	–	–	–	–	3.26
	39654	–	–	–	–	0.11	–	0.11	1.43	–	–	9.70	11.1	11.2
	39657	–	–	–	–	–	–	–	0.95	–	–	–	0.95	0.95
Kidney	39652	–	–	–	–	0.05	–	0.05	–	–	–	–	–	0.05
(n = 3)	39653	–	–	–	–	–	–	–	0.71	–	–	–	0.71	0.71
	39654	–	0.81	–	–	0.02	–	0.83	–	–	–	8.21	8.21	9.04
Muscle	39652	–	–	–	3.50	–	–	3.50	–	–	–	–	–	3.50
(n = 3)	39653	–	–	–	–	–	–	–	–	–	–	–	–	–
	39654	–	–	–	–	–	–	–	–	–	–	–	–	–
Adipose	39652	–	–	–	–	–	–	–	–	–	–	–	–	–
(n = 2)	39653	–	–	–	–	–	–	–	–	–	–	–	–	–
Detection rate		3/20	1/20	2/20	4/20	6/20	1/20	10/20	5/20	1/20	1/20	2/20	8/20	16/20
Median		70.9	0.81	1.26	2.37	0.08	0.21	2.92	0.95	0.31	7.42	8.95	2.62	3.38
Mean		94.6	0.81	1.26	2.36	0.14	0.21	29.7	1.65	0.31	7.42	8.95	4.24	20.7
Min.		64.1	0.81	0.72	1.22	0.02	0.21	0.05	0.71	0.31	7.42	8.21	0.31	0.05
Max.		149	0.81	1.81	3.50	0.49	0.21	152	4.30	0.31	7.42	9.70	11.1	152

Table 3
BPs and BzPs in different tissues from long-eared owls (*Asio otus*); concentrations expressed in ng/g w.w.

Matrix	Raptor ID	BPA	BPAP	BPB	BPF	BPM/BPP	BPS	ΣBPs	BzP-1	BzP-3	BzP-8	4-OH-BzP	ΣBzPs	ΣAll
Preen gland	117R2010	–	–	–	–	–	–	–	–	0.47	–	–	0.47	0.47
(n = 2)	76R2011	6.23	–	–	–	–	–	6.23	–	0.68	–	–	0.68	6.91
Liver	117R2010	–	0.76	–	–	–	1.10	1.86	–	–	–	–	–	1.86
(n = 2)	76R2011	–	–	–	–	0.05	–	0.05	–	–	–	–	–	0.05
Kidney	117R2010	–	0.96	0.42	7.32	0.03	0.20	8.93	–	–	–	–	–	8.93
(n = 2)	76R2011	–	–	–	–	–	–	–	–	–	–	–	–	–
Muscle	117R2010	–	–	–	–	0.13	2.06	2.19	–	8.21	46.9	–	55.1	57.3
(n = 2)	76R2011	–	–	1.84	–	–	–	1.84	–	0.32	–	–	0.32	2.16
Adipose	117R2010	–	–	–	6.24	–	–	6.24	–	–	–	–	–	6.24
(n = 2)	76R2011	–	–	–	–	–	–	–	–	–	–	–	–	–
Brain	117R2010	–	–	–	–	–	–	–	–	–	–	–	–	–
(n = 2)	76R2011	–	–	–	2.48	–	–	2.48	–	–	–	–	–	2.48
Detection rate		1/12	2/12	2/12	3/12	3/12	3/12	8/12	0/12	3/12	1/12	0/12	4/12	9/12
Median		6.23	0.86	1.13	6.24	0.05	1.10	2.33	–	0.57	46.9	–	0.57	2.48
Mean		6.23	0.86	1.13	5.35	0.07	1.12	3.72	–	2.42	46.9	–	14.1	9.60
Min.		6.23	0.76	0.42	2.48	0.03	0.20	0.05	–	0.32	46.9	–	0.32	0.05
Max.		6.23	0.96	1.84	7.32	0.13	2.06	8.93	–	8.21	46.9	–	55.1	57.3

Table 4
BPs and BzPs in different tissues from Eurasian sparrowhawks (*Accipiter nisus*); concentrations expressed in ng/g w.w.

Matrix	Raptor ID	BPA	BPAP	BPB	BPF	BPM/BPP	BPS	ΣBPs	BzP-1	BzP-3	BzP-8	4-OH-BzP	ΣBzPs	ΣAll
Preen gland	113R2009	–	–	–	–	0.17	–	0.17	–	–	–	–	–	0.17
(n = 2)	143R2010	–	–	0.74	6.02	–	0.21	6.97	–	–	–	–	–	6.97
Liver	113R2009	–	–	–	–	–	–	–	–	–	–	–	–	
(n = 2)	143R2010	–	–	–	–	–	5.23	5.23	–	–	–	44.3	44.3	49.5
Kidney	113R2009	–	–	–	–	–	–	–	–	–	–	–	–	–
(n = 2)	143R2010	–	–	1.60	–	–	–	1.60	–	–	–	–	–	1.60
Muscle	113R2009	–	–	–	–	–	–	–	–	–	–	–	–	–
(n = 2)	143R2010	–	–	–	–	–	–	–	–	–	–	–	–	–
Adipose	113R2009	–	–	–	–	–	–	–	–	–	–	–	–	–
(n = 2)	143R2010	–	–	–	–	–	–	–	–	–	–	–	–	–
Brain	113R2009	–	–	–	–	–	–	–	–	–	–	–	–	–
(n = 2)	143R2010	–	–	1.69	–	–	–	1.69	–	–	–	–	–	1.69
Detection rate		0/12	0/12	3/12	1/12	1/12	2/12	5/12	0/12	0/12	0/12	1/12	1/12	5/12
Median		–	–	1.60	6.02	0.17	2.72	1.69	–	–	–	44.3	44.3	1.69
Mean		–	–	1.34	6.02	0.17	2.72	3.13	–	–	–	44.3	44.3	11.9
Min.		–	–	0.74	6.02	0.17	0.21	0.17	–	–	–	44.3	44.3	0.17
Max.		–	–	1.69	6.02	0.17	5.23	6.97	–	–	–	44.3	44.3	49.5

44) > BPB (7/44) > BPS (6/44) > BPA (4/44) > BPAP (3/44), while that for BzPs was: BzP-1 (5/44) > BzP-3 (4/44) > 4-OH-BzP (3/44) > BzP-8 (2/44). The maximum DR was 22.7% (10/44) for BPM/BPP, while most of the analogues demonstrated similar DRs that ranged <15% (Table S9).

The DRs rank order for ΣBPs among the raptor species decreased as: long-eared owl [66.6% (8/12)] > white-tailed eagle [50% (10/20)] > Eurasian sparrowhawk samples [41.6% (5/12)]. The median ΣBPs concentrations were found 2.92, 2.33 and 1.69 ng/g w.w. for white-tailed eagle, long-eared owl and Eurasian sparrowhawk samples, respectively. The DRs rank order for ΣBzPs among the three species was: white-tailed eagle [40% (8/20)] > long-eared owl [33.3% (4/12)] > Eurasian sparrowhawk samples [8.33% (1/12)]. The median ΣBzPs concentrations were 2.62 and 0.57 ng/g w.w. for white-tailed eagle and long-eared owl samples, respectively, while only 4-OH-BzP was detected in a single liver sample from a Eurasian sparrowhawk at 44.3 ng/g w.w. In comparison to the Eurasian sparrowhawk, which is a small bird of prey (mean weight male/female: 144/264 g) that feeds on passerine birds, the white-tailed eagle is a very large species of sea eagle (mean weight male/female: 4.0/5.6 kg) feeding on the highest trophic position (including fish and seabirds), while the long-eared owl is a medium-sized owl (mean weight male/female: 256/308 g) feeding on small mammals (Bell et al., 2010; Cramp and Simmons, 1980; Cramp, 1985; Ivanovsky, 2010; Olsen and Marks, 2019; Seibold and Helbig, 1996; Sulkava et al., 1997). The occurrence data of ΣBPs and ΣBzPs in the three studied raptor species showed a pattern of increasing DRs and median concentrations of the contaminants with the increase of the raptor species size. Further studies with larger sample sizes should be conducted to confirm this pattern. It is noteworthy that interspecies differences in contaminant metabolism exist even among raptor species (Watanabe et al., 2010). Moreover, the white-tailed eagle, having a considerably longer life-expectancy, has also higher bioaccumulation potential.

The rank order of [ΣAll] (total load of the selected contaminants; [ΣBPs] + [ΣBzPs]) medians in the white-tailed eagle matrices decreased as: preen gland (5.86 ng/g w.w.) > liver (2.92) > kidney (0.71). The muscle matrix demonstrated low DR (1/3), while no target analyte was detected in adipose tissue of the white-tailed eagle. The non detection of these contaminants in adipose tissue indicated that high concentrations were less likely to occur in this matrix of the white-tailed eagle compared to the preen gland and liver matrix. The number of samples per matrix was limited to draw any further conclusions, especially for the long-eared owl and Eurasian sparrowhawk species. However, in both of these species, all preen gland samples demonstrated [ΣAll] that ranged from 0.17 to 6.97 ng/g w.w. Overall, the significant concentrations determined in preen gland indicated that it is a potential excretory organ for BPs and BzPs. This finding is in accordance to previous studies on POPs. It is well-documented that preen gland contains relatively high concentrations of POPs (Jaspers et al., 2013; Solheim et al., 2016), but to our knowledge, this is the first documentation on BPs and BzPs, which are plastic and personal care product related ECs. Further association of BPs and BzPs concentrations with features such as age and sex were tempered in this study by the small sample size and low DRs.

In contrast to the raptor species studied here, the DRs of some BPs and BzPs analogues in human biological media, e.g., adipose tissue and urine, especially for BPA and BP-3, can reach up to 100% (Rocha et al., 2018; Wang et al., 2015). Nonetheless, the concentrations demonstrated similarities between raptors and humans on the order of magnitude. The rank order of median concentrations for BPs found here for raptors was: BPA (67.5 ng/g w.w.) > BPF (3.01) > BPB (1.60) > BPAP (0.81) > BPS (0.65) > BPM/BPP (0.08) > BPAF, BPZ (not detected) (Fig. 1). The typical rank order of BPs median concentrations in human urine is: BPA (1.65 ng/mL) > BPF (0.58) > BPS (0.35) > BPAP (0.25) > BPZ ~ BPB (0.17) > BPP (0.16)) > BPAF (not detected) (Philips et al., 2020). In both raptors and humans, the highest concentrations were found for BPA and BPF. For the BzPs class, which additionally demonstrates interrelationships between BP-3, as a precursor analogue, with its documented metabolites (BzP-8, 4-OH-BzP, BzP-1 and BzP-2), the rank order of median concentrations found here for raptors was: BzP-8 (27.1 ng/g w.w.) > 4-OH-BzP (9.70) > BzP-1 (0.95) > BzP-3 (0.47) > BzP-2 (not detected) (Fig. 1). Consequently, the rank order for BzPs in raptors was found to be reversed when compared to that of the typical median concentrations excreted in human urine: BzP-3 (1.02 ng/mL) > BzP-2 (0.56) > BzP-1 (0.46) > 4-OH-BzP (0.30) > BzP-8 (0.06) (Asimakopoulos et al., 2016b). By comparison, BzP-3 and BzP-1 were found in similar concentrations between raptor matrices and human urine, BzP-8 and 4-OH-BzP were found ~2 orders of magnitude

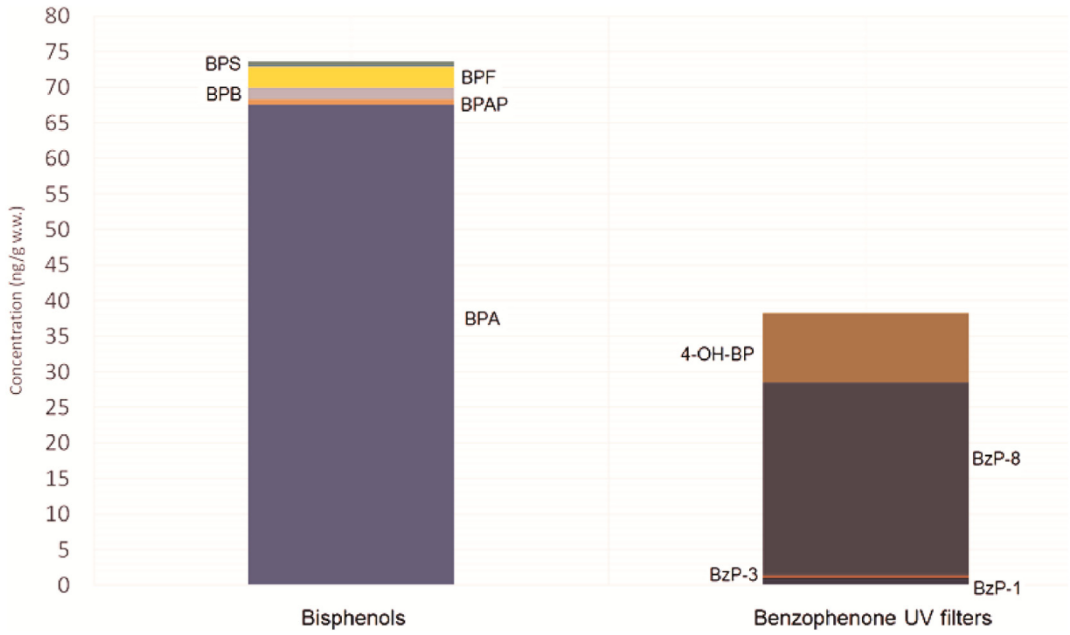

Fig. 1. Concentration profiles of the sum concentrations of bisphenols (ΣBPs) and benzophenone UV filters (ΣBzPs) in raptor tissues; the median concentration values (based on values > MQLs) were used to generate the chart [note: BPM/BPP was not shown due to the low median concentration (0.08 ng/g w.w.)].

higher in raptor matrices, while BzP-2 was not detected in these three raptor species.

From the BPs class, BPF was found in an adipose tissue (6.24 ng/g w.w.) and a brain sample (2.48 ng/g w.w.) from the long-eared owls, BPB was found in a brain sample (1.69 ng/g w.w.) from the Eurasian sparrowhawks, while similarly to BPs, BzPs were not found in either adipose tissue or brain matrix. On the contrary, in human adipose tissue, BPA and BP-3 are documented in significant concentrations, similar to those found in human urine (that is established as the main excretory pathway), which could even reach the order of a few tens and thousands of nanograms per gram (ng/g), respectively (Rocha et al., 2018; Wang et al., 2015). This contradiction on the occurrence profile of the target analytes between humans and raptors suggests differences in contaminant metabolism, toxicokinetics and bioaccumulation potential between the species. Further comparison to other human tissues, e.g., brain and liver, was tempered due to the limited human data availability for only some BPs and BzPs (Geens et al., 2012).

3.3. Comparison to relevant wildlife studies

To the best of our knowledge, this is the first peer-reviewed study to document multiresidues of both contaminant classes, BPs and BzPs, in raptor tissues. From the BPs class, only BPA was studied extensively so far in raptors. Elliott et al. (2019) reported a median BPA concentration of 1.05 ng/mL in bald eagle (*Haliaeetus leucocephalus*) nestling (eaglet) plasma samples (n = 381) from the U.S. Furthermore, BPA concentrations in feathers from the herring gull (*Larus argentatus*; which is a large seabird) were reported ranging on average from 132 to 153 ng/g dry weight (d.w.) (Nehring et al., 2017). It is noteworthy that the excretion of several contaminants in raptors is documented also through feathers (epidermal excretory organ) (Jaspers et al., 2019; Solheim et al., 2016), and similarities were indicated when comparing the BPA concentrations in feathers (from the herring gull; Nehring et al., 2017) with those found in our study in preen gland (from the white-tailed eagles; 64.1–149 ng/g w.w.). Mean concentrations of BPA in the muscle (n = 10), liver (n = 10) and guano (n = 7) from herring gulls (*Larus argentatus*) were reported 62.9, 111 and 996 ng/g d.w., respectively (Staniszewska et al., 2014). In addition, BPA concentrations in the muscle (n = 1) and liver (n = 1) of a great black-backed gull (*Larus marinus*) were reported 39.8 and 324 ng/g d.w., respectively (Staniszewska et al., 2014). However, in our study, BPA was neither detected in muscle nor liver samples. This difference can be attributed to the different feeding patterns and habits, but also to the elimination capacity of specific contaminants among species. Staniszewska et al. (2014) noted that herring gulls gather for feeding purposes on landfill sites, which are highly contaminated areas. This feeding behavior of the gulls on industrial and urban wastes is also well-documented in other studies (Barón et al., 2014; Tongue et al., 2019).

Concentrations of BzP-1, BzP-3, 4-OH-BzP, and 4,4′-dihydroxybenzophenone (which is an isomer of BzP-1) were reported by Molins-Delgado et al. (2017) in 39 unhatched raptor eggs of 7 wild living species [western marsh harrier (*Circus aeruginosus*), common kestrel (*Falco tinnunculus*), white stork (*Ciconia ciconia*), slender-billed gull (*Chroicocephalus genei*), black headed gull (*Chrococephalus ridibundus*), gull-billed tern (*Gelochelidon nilotica*), and gadwall (*Anas strepera*)]. Mean concentrations of BP-3, BP-1, 4-OH-BzP and 4,4′-dihydroxybenzophenone were ranging between species from 22.1 to 46.7 ng/g d.w., 38.1 to 433, 88.4 to 895, and 29.0 to 132, respectively, while the DRs in eggs ranged from 95 to 100% for all analogues indicating bioaccumulation. This was reflected in the egg concentrations, in which the rank order of mean BzPs concentrations found in those (for the majority of the assessed species) decreased as: 4-OH-BzP > BP1 > BP-3 (Molins-Delgado et al., 2017). This agreed to the rank order found in the raptor tissues in our study. Similar bioaccumulation and biomagnification potential of BzPs along the foodchain was also recently suggested for marine organisms (Cocci et al., 2020).

4. Conclusions

In this study, the occurrence and concentrations of BPs and BzPs were determined in raptor tissues. It was shown that the liver, kidney and preen gland tissues are suitable for the biomonitoring of these contaminants. The occurrence data in the tissues of the three raptor species suggested a pattern of increasing DRs and median concentrations with the increase of the raptor species size and expected trophic position, although this needs to be further confirmed with larger sample sizes. The potential role of the preen gland as a major excretory organ for BPs and BzPs was suggested. BPA, BPF, BzP-8 and 4-OH-BzP were the dominant contaminant analogues based on the concentrations found in the tissues. The results provided in this study indicate that BPs and BzPs have bioaccumulation potential in specific raptor tissues.

CRediT authorship contribution statement

Soledad González-Rubio: Data curation, Formal analysis, Investigation, Methodology, Resources, Software, Validation, Visualization, Writing - original draft. **Kristine Vike-Jonas:** Methodology, Resources, Software, Writing - review & editing. **Susana V. Gonzalez:** Methodology, Resources, Writing - review & editing. **Ana Ballesteros-Gómez:** Investigation, Methodology, Resources, Supervision, Writing - review & editing. **Christian Sonne:** Resources, Writing - review & editing. **Rune Dietz:** Resources. **David Boertmann:** Resources, Writing - review & editing. **Lars Maltha Rasmussen:** Resources, Writing - review & editing. **Veerle L.B. Jaspers:** Conceptualization, Funding acquisition, Investigation, Project administration, Resources, Supervision, Validation, Writing - review & editing. **Alexandros G. Asimakopoulos:** Conceptualization, Data curation, Formal analysis, Funding acquisition, Investigation, Methodology, Project administration, Resources, Software, Supervision, Validation, Visualization, Writing - review & editing.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2020.140330.

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