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Integrated exposure assessment of northern goshawk (*Accipiter gentilis*) nestlings to legacy and emerging organic pollutants using non-destructive samples

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ABSTRACT

In the present study, concentrations of legacy and emerging contaminants were determined in three non-destructive matrices (plasma, preen oil and body feathers) of northern goshawk (*Accipiter gentilis*) nestlings. Persistent organic pollutants (POPs), including polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs) and polybrominated diphenyl ethers (PBDEs), together with emerging pollutants, including per- and polyfluorinated alkyl substances (PFASs), novel brominated flame retardants (NBFRs), phosphorus flame retardants (PFRs) and Dechlorane Plus isomers (DPs) were targeted. Plasma, preen oil and feather samples were collected from 61 goshawk nestlings in Norway (Trøndelag and Troms) in 2015 and 2016, and pollutant concentrations were compared between the three matrices. In plasma, PFASs were detected in the highest concentrations, ranging between 1.37 and 36.0 ng/mL, which suggests that the nestlings were recently and continuously exposed to these emerging contaminants, likely through dietary input. In preen oil, OCPs (169–3560 ng/g) showed the highest concentrations among the investigated compounds, consistent with their high lipophilicity. PFRs (2.60–314 ng/g) were the dominant compounds in feathers and are thought to originate mainly from external deposition, as they were not detected in the other two matrices. NBFRs and DPs were generally not detected in the nestlings, suggesting low presence of these emerging contaminants in their environment and/or low absorption. Strong and significant correlations between matrices were found for all POPs (r_s = 0.46–0.95, $p < 0.001$), except for hexachlorobenzene (HCB, r_s = 0.20, p = 0.13). Correlations for PFASs were less conclusive: linear perfluorooctane sulfonate (PFOS), perfluoroundecanoate (PFUnA), perfluorododecanoate (PFDoA) and perfluorotetradecanoate (PFTeA) showed strong and significant correlations between plasma and feathers (r_s = 0.42–0.72, $p < 0.02$), however no correlation was found for perfluorohexane sulfonate (PFHxS), perfluorononanoate (PFNA) and perfluorotridecanoate (PFTriA) (r_s = 0.05–0.33, p = 0.09–0.85). A lack of consistency between the PFAS compounds (contrary to POPs), and between studies, prevents concluding on the suitability of the investigated matrices for PFAS biomonitoring.

1. Introduction

Despite the phaseouts and restrictions imposed on persistent organic pollutants (POPs) such as polychlorinated biphenyls (PCBs), organochlorine pesticides (OCPs), polybrominated diphenyl ethers (PBDEs) and perfluorooctane sulfonate (PFOS), these pollutants are still prominent in the environment. Due to their high persistence and slow degradation, they are found in e.g. sediment, air, water and biota (AMAP, 2017; Braune et al., 2019; Luek et al., 2017). Their bioaccumulative and toxic properties can also affect living organisms (Guigueno and Fernie,

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2017; Letcher et al., 2010), underlining the need for continued environmental monitoring.

In addition, further challenges are arising due to the development of new chemicals and the re-introduction or repurposing of previously used compounds to replace the legislated POPs. Many of these substitutes have similar chemical structures and applications as their precursors, but their occurrence and fate in the environment are still relatively unknown (Covaci et al., 2011; Wang et al., 2017). Phosphorus flame retardants (PFRs), for example, have been produced for decades and are now, alongside novel brominated flame retardants (NBFRs) and Dechlorane Plus (DP), used as substitutes for PBDEs (Covaci et al., 2011; Dodson et al., 2012; van der Veen and de Boer, 2012). Similarly, thousands of per- and polyfluorinated alkyl substances (PFASs) are on the global market today and are produced in high volumes, including several short-chain and other fluorinated alternatives to restricted long-chain PFASs (Wang et al., 2013). Despite the large knowledge gaps, some of these compounds, such as certain PFRs, are thought to have a relatively high persistence (Kawagoshi et al., 2002) and undergo long-range atmospheric transport (AMAP, 2017; Möller et al., 2012; Vorkamp and Rigét, 2014). Consequently, a number of these alternatives has been detected in the environment (Greaves and Letcher, 2017; Möller et al., 2011; Sverko et al., 2011; Vorkamp et al., 2015), including birds (e.g. Eulaers et al., 2014; Gauthier et al., 2007; Gómez-Ramírez et al., 2017).

For several decades, birds of prey have been used successfully in environmental pollution monitoring (García-Fernández et al., 2008; Gómez-Ramírez et al., 2014; Helander et al., 2008). Because of their high trophic position, birds of prey accumulate high levels of organic contaminants, enabling studies of both geographical and temporal differences in contaminant concentrations (Dolan et al., 2017; Gómez-Ramírez et al., 2014; Holmström et al., 2010). For ethical, practical and legal reasons, non-destructive sampling methods are increasingly used to sample nestling birds, and have shown great potential for biomonitoring studies (Espín et al., 2016; Eulaers et al., 2011a; Gómez-Ramírez et al., 2014). Additionally, the sampling of nestlings has many advantages (Furness, 1993). The northern goshawk (*Accipiter gentilis*), hereafter called goshawk, is a terrestrial bird of prey that has previously been successfully used for non-destructive biomonitoring. A wide range of pollutants have been detected in goshawk eggs (Herzke et al., 2005, 2002; Mañosa et al., 2003; Martínez-López et al., 2007), feathers (Dolan et al., 2017; Eulaers et al., 2011a) and plasma (Bustnes et al., 2013; Dolan et al., 2017; Gómez-Ramírez et al., 2017). To our knowledge, no biomonitoring studies have been published using goshawk preen oil.

Due to the restricted production and use of POPs, and the increased use of emerging contaminants such as PFASs, PFRs, NBFRs and DPs, goshawks are expected to be exposed to a mixture of legacy and emerging contaminants. Currently, there is limited knowledge about the exposure to and accumulation of emerging contaminants in goshawks. Therefore, this study aims to investigate the quantitative importance of emerging contaminants, relative to POPs, in northern goshawk nestlings from two regions in Norway. The contaminant loads and exposure patterns of POPs and emerging contaminants in three non-destructive matrices, i.e. plasma, preen oil and feathers, are compared and integrated to elucidate potential differences in exposure routes of these compounds. Furthermore, the potential suitability of plasma, preen oil and feathers for biomonitoring of the different classes of compounds are discussed. The feathers of nestlings are connected to the bloodstream during growth (Burger, 1993), preen oil is applied onto the feather surface during preening (Moreno-Rueda, 2017) and the preen gland producing preen oil is well-vascularized (Aslan et al., 2000). Therefore, strong correlations between these matrices are expected.

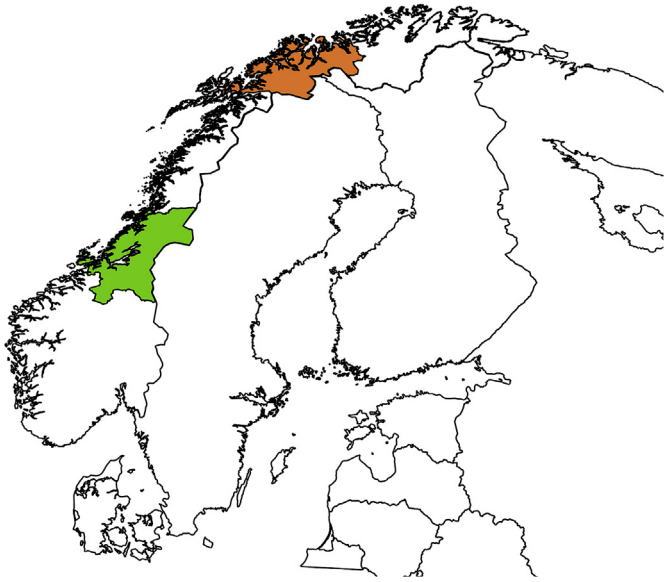

Fig. 1. A map of Scandinavia, showing the Norwegian counties of Trøndelag and Troms in green and orange, respectively, where northern goshawk nestlings from this study were sampled. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

2. Materials and methods

2.1. Sampling

The sampling was approved by the Norwegian Food Safety Authority (Mattilsynet; ID 6432, 8709, 7366) and handling of the birds was conducted in accordance with the Norwegian Animal Welfare Act. The goshawk nestlings were sampled in two Norwegian counties, Trøndelag and Troms (Fig. 1) in 2015 (June–July) and 2016 (June), during the breeding season of the goshawks. Nests in Trøndelag were located between 62.9 and 64.5 °N and 9.5–12.5 °E, while nests in Troms were located between 69.4 and 70.0 °N and 18.3–20.3 °E (Fig. S1). Troms county is located in northern Norway, above the Arctic circle, with approximately 164 330 inhabitants (in 2016) and a population density of 6/km^2 (Statistisk sentralbyrå, 2016). Trøndelag county is located in central Norway, consisting of approximately 449 769 inhabitants (in 2016) and a population density of 11/km^2 (Statistisk sentralbyrå, 2016) and has a higher urbanization and agricultural development compared to Troms (Dolan et al., 2017; EU Copernicus Programme, 2019).

In total, samples from 61 goshawk nestlings (Trøndelag, 2015: $n = 20$ and 2016: $n = 20$; Troms, 2015: $n = 9$ and 2016: $n = 12$) were used in this study. Blood, feather and preen oil samples were collected from one nestling per nest. However, not enough sample amount was available for every analysis. A detailed overview of the samples available for each analysis is given in Table S1. Samples were analyzed for each nestling individually, except for PFAS analyses in 2016, for which feathers were collected from all nestlings in the nest (ranging from one to four nestlings) and pooled to ensure enough sample amount. Nestling age was determined following Kenward (2006) and nestlings were accordingly aged to be between 23 and 37 days old at the time of sampling. The average nestling age in each year and location can be found in Table S1. A maximum of 5 mL blood was sampled from the brachial vein using a heparinized syringe and a 23 G disposable needle (0.6 × 25 mm; BD Microlance™ 3, Spain). Blood was then transferred into heparinized cryogenic tubes (1.8 mL; Nalgene™, Thermo Scientific). Feathers were gently pulled from the nestling's back and stored, per individual, in a polyethylene zipper bag (VWR, USA). Preen oil is produced by the preen (or uropygial) gland located at the base of the

tail feathers and could, therefore, be obtained by gently pressing the preen gland with a pre-cleaned glass rod. The oil-covered feather tuft surrounding the preen gland was then cut using stainless steel scissors and stored in 1.5 mL Eppendorf® tubes (VWR, USA). All samples were kept refrigerated in a cooling bag until arrival in the lab (usually within 6 h after sampling). Upon arrival in the lab, whole blood samples were centrifuged (10 min, 1000 *g*), separating the plasma from the red blood cells. The plasma was then transferred to new cryogenic tubes (Nalgene®, USA). All samples were frozen at −20 °C until analysis.

2.2. Chemical analysis

2.2.1. POPs and alternative flame retardants

Targeted POPs included twenty-five PCB congeners (IUPAC numbers: 28, 49, 52, 74, 95, 99, 101, 105, 118, 138, 149, 153, 156, 170, 171, 177, 180, 183, 187, 194, 196/203, 199, 206, and 209), ten OCPs (dichlorodiphenyltrichloroethane (*p,p'*-DDT) and its metabolites dichlorodiphenyldichloroethylene (*p,p'*-DDE) and dichlorodiphenyldichloroethane (*p,p'*-DDD), three hexachlorocyclohexane isomers (*α*-, *β*-, and γ-HCH), three chlordanes (oxychlordane (OxC), *cis*-nonachlor (CN) and *trans*-nonachlor (TN)), hexachlorobenzene (HCB), and seven PBDE congeners (IUPAC numbers: 28, 47, 99, 100, 153, 154 and 183). Targeted alternative flame retardants included DP (*anti*- and *syn*-isomers, *a*-DP and *s*-DP), three NBFRs (1,2-bis(2,4,6-tribromophenoxy) ethane (BTBPE), 2-ethylhexyl-2,3,4,5-tetrabromobenzoate (TBB) and bis(2-ethylhexyl)-3,4,5,6-tetrabromo-phthalate (TBPH)) and six PFRs (tris(2-chloroethyl) phosphate (TCEP), tris(2-butoxyethyl) phosphate (TBEP), triphenyl phosphate (TPhP), 2-ethylhexyldiphenyl phosphate (EHDPHP), tris(1-chloroisopropyl) phosphate (TCIPP, two isomers) and tris(1,3-dichloro-isopropyl) phosphate (TDCIPP)).

2.2.1.1. Plasma extraction. This procedure was performed as described by Løseth et al. (2019b) and a detailed description can be found in the Supplementary Information (SI). In brief, individual plasma samples (1 mL) were spiked with internal standards (IS). Ultrapure water and formic acid (98%) were then added, followed by the liquid/liquid extraction using *n*-hexane:dichloromethane (DCM; 4:1, *v/v*). Extracts were concentrated to near dryness and reconstituted in *n*-hexane prior to clean-up.

2.2.1.2. Feather extraction. Feathers for POP analyses were analyzed for each individual nestling. Prior to extraction, feather samples were washed with distilled water, and cut as described in detail by Løseth et al. (2019b) and in the SI. Washed and cut feather samples were weighed (median (range): 164 (28–415) mg), spiked with IS and kept overnight at 45 °C in a mixture of hydrochloric acid (HCl) and *n*-hexane:DCM (4:1, *v/v*). The next day, analytes were solid/liquid extracted from the incubated mixture with *n*-hexane:DCM. Extracts were concentrated to near dryness and reconstituted with *n*-hexane prior to clean-up.

2.2.1.3. Preen oil extraction. This procedure is described in detail in the SI. In brief, preen oil on the preen gland feather tuft was solid/liquid extracted from the feathers with DCM. The extract was transferred into a pre-weighed clean-glass tube and the DCM was evaporated, leaving only the lipids in the tube. The tubes were then weighed again after the evaporation to determine the lipid weight (i.e. sample weight, expressed in grams of oil). The lipids were reconstituted in *n*-hexane and spiked with IS prior to clean-up.

2.2.1.4. Clean-up, fractionation and instrumental analyses. Clean-up and fractionation of the extracts were the same for all matrices and, together with the instrumental analyses, are described in detail in the SI. Higher chlorinated PCBs, PBDEs, chlordanes, HCB, HCHs, DPs and NBFRs were analyzed according to Eulaers et al. (2014), using an Agilent 6890 gas chromatograph coupled to an Agilent 5973 mass spectrometer system (GC-MS), equipped with a DB-5ms column (30 m × 0.25 mm, 0.25 μm; J&W Scientific, Folsom, USA) operated in the electron-capture ionization mode (ECNI). Lower chlorinated PCBs, DDT and its metabolites and PFRs were analyzed according to Eulaers et al. (2014) and Poma et al. (2017). The GC system was equipped with a HT-8 column (25 m × 0.22 mm, 0.25 μm; SGE, Zulte, Belgium) and the MS was operated in electron ionization (EI) mode.

2.2.2. PFASs

Targeted PFASs compounds included twelve perfluoroalkyl carboxylates (perfluorobutanoate (PFBA), perfluoropentanoate (PFPA), perfluorohexanoate (PFHxA), perfluoroheptanoate (PFHpA), perfluorooctanoate (PFOA), perfluorononanoate (PFNA), perfluorodecanoate (PFDcA), perfluoroundecanoate (PFUnA), perfluorododecanoate (PFDoA), perfluorotridecanoate (PFTriA), perfluorotetradecanoate (PFTeA) and perfluorohexadecanoate (PFHxDcA)), eight perfluoroalkyl sulfonates (perfluorobutane sulfonate (PFBS), perfluoropentane sulfonate (PFPS), perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), linear (linPFOS) and branched perfluorooctane sulfonate (brPFOS), perfluorodecane sulfonate (PFDcS)) and perfluorooctane sulfonamide (PFOSA). Additionally, in 2016, two fluorotelomersulfonates (6:2 and 8:2 FTS) and one chlorinated polyfluoroalkyl ether sulfonate (6:2 Cl-PFESA or F-53B) were analyzed. Due to the limited amount of sample, PFASs could not be investigated in feathers from 2015, or in any of the preen oil samples. Until now, PFOS is the only PFAS compound to be regulated as POP by the Stockholm Convention and it will therefore be included in the PFAS group throughout the text.

2.2.2.1. Plasma extraction. Plasma samples were extracted following the method described by Hanssen et al. (2013). In brief, individual plasma samples (200 μL) were spiked with IS, and methanol (MeOH) was added for liquid/liquid extraction. A detailed description of the plasma extraction for PFASs can be found in the SI.

2.2.2.2. Feather extraction. Feather samples were extracted based on the analytical method by Powley et al. (2005), modified for feathers as described by Jaspers et al. (2013a). Washed (distilled water) and cut feather samples (as described in SI) were pooled per nest to gain sufficient mass before they were weighed accurately (median (range): 144 (71–338) mg) in a polypropylene tube. In order to remove the preen oil, a second washing procedure was performed in the tube by incubating the feathers for 10 min in *n*-hexane. After removal of the *n*-hexane, feather samples were spiked with IS and extracted with MeOH. A detailed description of the feather extraction can be found in the SI.

2.2.2.3. Clean-up and instrumental analyses. For clean-up, plasma and feather extracts were transferred into an Eppendorf tube containing ENVI-Carb graphitized carbon adsorbent, spiked with glacial acetic acid. The tube was thoroughly vortexed, centrifuged and an aliquot of the extract was then transferred into the injection vial, to which the recovery standard was added. Quantification of PFASs in plasma and feathers was performed as described in Hanssen et al. (2013), using ultra-high pressure liquid chromatography triple–quadrupole mass-spectrometry (UHPLC-MS/MS). Analysis was performed on a Thermo Scientific quaternary Accela 1250 pump (Thermo Fisher Scientific Inc., Waltham, MA, USA) with a PAL Sample Manager (Thermo Fisher Scientific Inc., Waltham, MA, USA) coupled to a Thermo Scientific Vantage MS/MS (Vantage TSQ; Thermo Fisher Scientific Inc., Waltham, MA, USA). Detailed information about the clean-up and instrumental analysis can be found in the SI.

2.2.3. Quality assurance/quality control

Procedural blanks were used to check for interferences or contamination from solvent and glassware and were analyzed simultaneously with every batch of ten samples. Procedural blanks were

consistent (relative standard deviation < 30%) and, therefore, the mean value was calculated for each compound and subtracted from the values in the samples. For POPs and alternative flame retardants, the limits of quantification (LOQs) were calculated as three times the standard deviation of the blank measurements. For PFASs, LOQs were calculated as three times the limit of detection (LOD), which was calculated as the sum of the average of the procedural blanks and three times the signal-to-noise (S/N) ratio. For analytes that were not detected in procedural blanks, LOQs were calculated for an S/N ratio equal to 10. An overview of the LOQs for each compound can be found in Løseth et al. (2019b). LOQs for PFRs in goshawk preen oil are additionally given in Table S2. The analytical procedures for POPs in plasma were validated through the analysis of human plasma from the Arctic Monitoring and Assessment Program (AMAP) interlaboratory exercise, for which deviations from certified values are usually less than 10%. For PFASs, commercially available human serum (NIST SRM, 1957; USA) was used. For preen oil, whale blubber (NIST SRM, 1945; USA) was used, and the obtained values deviated from the consensus values by less than 20%. Standard reference materials (SRM) were analyzed with every tenth sample. The recoveries of the broad spectra of IS were also used to verify the quality of the methods, and were calculated for each sample, as well as for the blanks. Mean ± SD (%) recoveries of the individual internal standards can be found in Table S3. Acceptable recoveries (> 50% for POPs and alternative flame retardants, > 35% for PFASs) were obtained for the majority of the pollutants, except for ^{13}C-TBPH, for which the low recoveries are due to its partial degradation on acid silica.

2.3. Statistical analyses

Statistical analyses were performed in R (version 3.2.2) applying a level of significance of $\alpha = 0.05$. Contaminants were included in the statistical analyses if they were detected in more than 50% of the samples within each matrix from each year and location. Values below the LOQ were substituted with LOQ × detection frequency (DF) (James et al., 2002). Data were tested for normality by Shapiro-Wilk tests and quantile-quantile (Q-Q) plots. Differences in concentrations of the contaminant groups (Σ) between locations and years were investigated by non-parametric Wilcoxon rank sum test (with continuity correction) on untransformed variables as the assumptions of heteroscedasticity and normally distributed residuals were not met. Non-parametric Spearman rank correlations were used on untransformed variables to investigate the relationships of all contaminant groups between matrices. Correlations of PFASs could only be investigated between plasma and feather samples from 2016 since these compounds were not analyzed in preen oil, and feathers were only available for PFAS analysis in 2016.

One nestling sampled in Troms in 2016 had unusually high concentrations for all pollutant groups and matrices, potentially due to siblicide (based on observations at the nest site during sampling). Therefore, this nestling was considered as an outlier and was not included in statistical analyses. However, the outlier was included in the correlation analysis because of its consistently high contaminant levels in all matrices. Concentrations detected in this nestling for the different contaminant groups and matrices, in comparison to the median and range of goshawks from Troms in 2016, can be found in Table S4.

3. Results

3.1. Pollutant concentrations and profiles

The median and range of concentrations in plasma (ng/mL), preen oil (ng/g oil) and feathers (ng/g ww) per location and year can be found in Fig. 2 and Tables S5–10 (also showing DF and the geometric mean). The compounds that could be quantified in more than 50% of the samples within each matrix from each year and location consisted of 10 PCBs (Σ_{10}PCBs: CB99, 105, 118, 138, 153, 170, 177, 180, 183 and 187), four OCPs (Σ_4OCPs: *p,p'*-DDE, OxC, *β*-HCH and HCB), three PBDEs (Σ_3PBDEs: BDE47, 99 and 100) and three PFASs (Σ_3PFASs: linPFOS, PFUnA and PFTriA). Compounds which were not detected in any of the matrices are listed in Table S11.

3.1.1. POPs

The POPs detected in the highest concentrations in plasma were PCBs and OCPs. In general, the two chlorinated contaminant groups were similar in concentrations, with median PCB concentrations per location and year ranging between 2.76 and 6.03 ng/mL and median OCP concentrations between 4.00 and 4.08 ng/mL (Fig. 2). In Troms in 2016, the median PCB concentration in plasma (11.8 ng/mL) exceeded that of OCPs (5.28 ng/mL). In preen oil and feathers, OCPs were the dominant POPs and median OCP concentrations were higher than PCBs in all years and locations (Fig. 2). In all matrices, *p,p'*-DDE was the dominant OCP, and CB153 was the dominant PCB congener (Figs. S2 and S3). PBDEs were found to have the lowest concentrations of all detected (DF > 50%) contaminants in all matrices.

A PCB profile, dominated by the higher chlorinated congeners CB153, 180 and 138, was observed in the goshawk plasma and preen oil. In feathers, however, the lower chlorinated CB99 was one of the three most dominant PCB congeners along with CB153 and CB138 (Fig. S2). In general, feathers had a higher proportion of penta-CBs (CB99, 101, 105 and 118) and a lower proportion of hepta-CBs (CB170, 177, 180, 183 and 187) than plasma and preen oil.

3.1.2. Alternative flame retardants

DPs and NBFRs showed low detection frequencies in samples of goshawk nestlings (Table S8). Detection frequencies of DPs ranged from undetected in feathers to 65% detected in preen oil, while the three investigated NBFRs were detected in less than 50% of all the samples (DF: 0–44%).

PFRs were only detected in a few plasma (DF: 5–11%) and preen oil (DF: 5–20%) samples in 2015 and were, therefore, not targeted for analysis in these matrices in 2016. However, PFRs were the dominant compound group (of all targeted compounds) in feathers, with median concentrations ranging between 22.2 and 206 ng/g (Fig. 2). Among the six targeted PFRs, ΣTCIPP, TCEP, TPhP (in decreasing order of dominance; Fig. S5) were the only compounds which were detected in more than 50% of the feather samples in both locations and years. Median ΣTCIPP concentrations in feathers from Troms, sampled in 2015 (190 ng/g), were approximately ten times higher than the ΣTCIPP concentrations in Trøndelag (2015: 26.9 ng/g) and those in Troms in 2016 (17.9 ng/g), which is also reflected in the ΣPFR concentrations shown in Fig. 2.

3.1.3. PFASs

PFASs dominated in the plasma samples, with median concentrations ranging between 4.69 and 17.5 ng/mL. Two sulfonates (PFHxS and linPFOS) and six carboxylates (PFOA, PFNA, PFDcA, PFUnA, PFDoA, PFTriA) were detected in more than 50% of the plasma samples, and linPFOS was the most abundant compound. In contrast to plasma, PFAS concentrations in feathers were low, relative to PCBs, OCPs and PFRs, with a median concentration of 6.19 and 1.76 ng/g in Trøndelag and Troms, respectively. Only one sulfonate (linPFOS) and three carboxylates (PFUnA, PFTriA and PFTeA) were detected in more than 50% of the feather samples. LinPFOS and PFTriA were equally dominant in feathers (Fig. S6).

3.2. Differences between locations and years

Differences between locations and/or years were detected for Σ_{10}PCBs, Σ_4OCPs, Σ_3PFRs and Σ_3PFASs (Fig. 2). Out of all locations and years, nestlings from Troms, sampled in 2016, had the widest range of PCB concentrations and the highest median PCB concentration in each

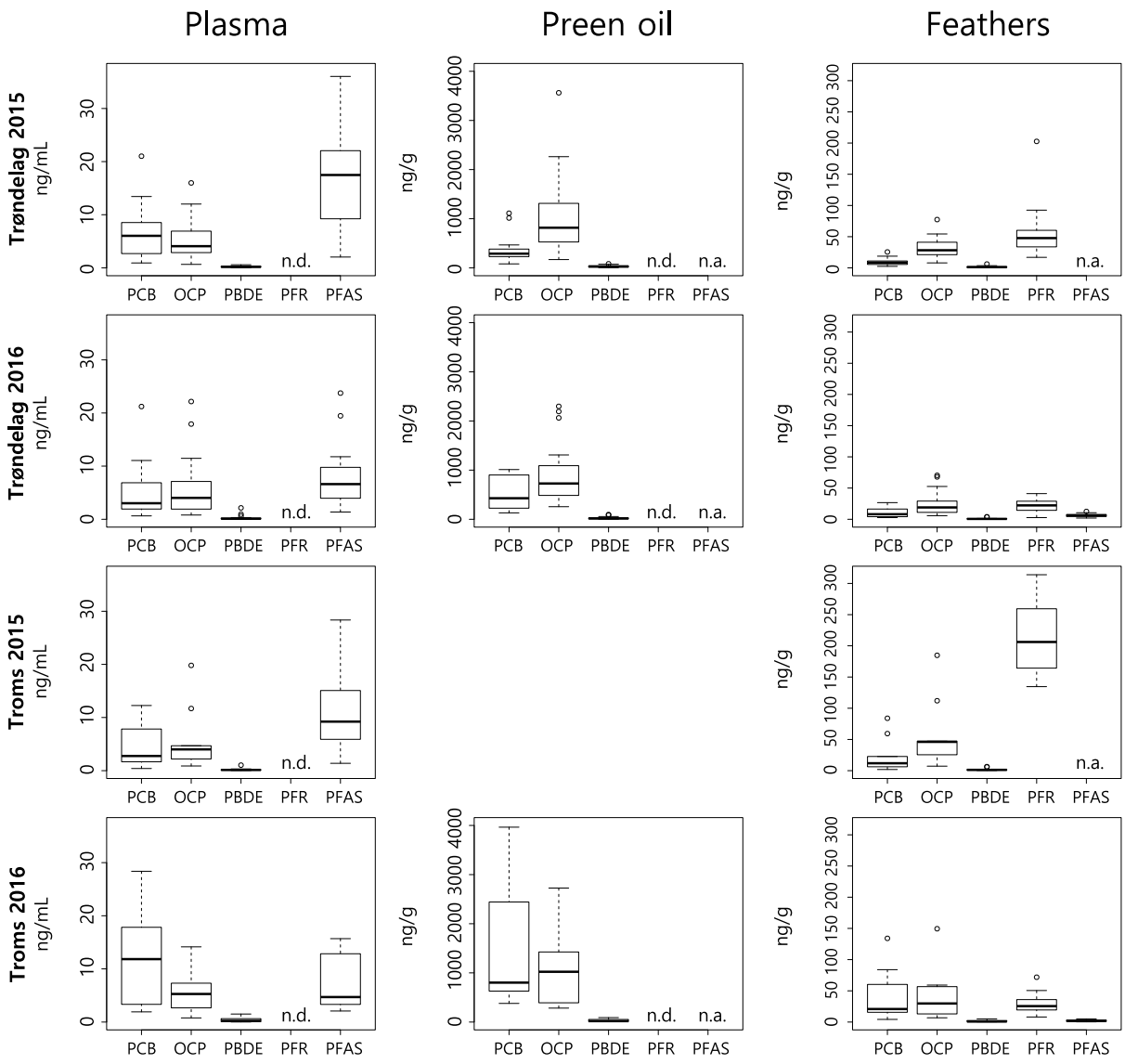

Fig. 2. Boxplots of summed plasma (ng/mL), preen oil (ng/g oil) and feather (ng/g ww) concentrations of PCBs, OCPs, PBDEs, PFRs and PFASs in northern goshawk nestlings, shown per location and year. The sum of PCBs (Σ_{10}PCB) consists of CB99, 105, 118, 138, 153, 170, 177, 180, 183, 187; the sum of OCPs (Σ_4OCP) of *p,p'*-DDE, OxC, *β*-HCH and HCB; the sum of PBDEs (Σ_3PBDE) of BDE47, 99 and 100; the sum of PFRs (Σ_3PFR) of TCEP, TPhP and TCIPP; and the sum of PFAS (Σ_3PFAS) of linPFOS, PFUnA and PFTriA. One nestling from Troms, sampled in 2016, was considered as an outlier and was excluded here. Preen oil samples were not available for nestlings from Troms in 2015. N.d.: not detected; n.a.: not analyzed.

matrix (plasma: 11.8 ng/mL, preen oil: 801 ng/g, feather: 20.8 ng/g). These nestlings showed significantly higher median PCB concentrations compared to nestlings from Trøndelag in the same year ($0.005 < p < 0.03$) and a significantly higher median plasma PCB concentration ($p = 0.05$) compared to nestlings from Troms in 2015.

In Trøndelag, OCP concentrations in feathers were significantly higher in 2015 compared to 2016 (2015: 28.2 ng/g, 2016: 18.9 ng/g, $p = 0.04$).

PFR concentrations in feathers were highest in nestlings from Troms in 2015 (206 ng/g) and were significantly higher compared to nestlings from the same year in Trøndelag (47.7 ng/g, $p < 0.001$). In addition, PFR concentrations were significantly lower in 2016 (Troms: 25.5 ng/g, Trøndelag: 22.2 ng/g, both $p < 0.001$) compared to 2015. However, the difference between years in Troms was much more pronounced than in Trøndelag.

Within Trøndelag, the median PFAS concentration in plasma was significantly higher in 2015 (17.5 ng/mL) compared to 2016 (6.62 ng/mL, $p < 0.001$). In 2016, feathers (pooled per nest) showed significantly higher PFAS concentrations in Trøndelag (6.19 ng/g) compared to Troms (1.76 ng/g, $p < 0.001$).

3.3. Correlations between matrices

The correlations between pollutants concentrations in plasma, feathers and preen oil of the nestlings from both years and locations combined can be found in Table 1. Correlation plots of CB153, BDE47, linPFOS, PFUnA and PFTriA are shown in Fig. 3 and Fig. 4.

3.3.1. POPs and alternative flame retardants

Strong and significant correlations between plasma, feathers and preen oil were found for PCBs, OCPs and PBDEs (Table 1, Fig. 3). Overall, correlation coefficients (r_s) of these contaminants ranged between 0.46 and 0.95 with all *p*-values below 0.001. Only the correlation of HCB between plasma and feathers was both weak and insignificant ($r_s = 0.20$, $p = 0.13$) despite good correlations between plasma - preen oil ($r_s = 0.66$, $p < 0.001$) and feathers - preen oil ($r_s = 0.58$, $p < 0.001$). Correlations of alternative flame retardants could not be investigated due to the low detection frequencies of these contaminants

Table 1
Spearman's rank correlation coefficients (r_s) for POP and PFAS concentrations between plasma, feathers and preen oil from northern goshawk nestlings, with respective *p*-values and sample size (*n*). Significant correlations are marked in bold. "NA" indicates when a correlation could not be determined.

	plasma - feathers			plasma - preen oil			feathers - preen oil		
	n	r_s	*p*	*n*	r_s	*p*	*n*	r_s	*p*
CB99	60	0.80	< 0.001	50	0.66	< 0.001	49	0.83	< 0.001
CB105	60	0.82	< 0.001	50	0.86	< 0.001	49	0.94	< 0.001
CB118	60	0.86	< 0.001	50	0.89	< 0.001	49	0.94	< 0.001
CB138	60	0.70	< 0.001	50	0.72	< 0.001	49	0.93	< 0.001
CB153	60	0.79	< 0.001	50	0.77	< 0.001	49	0.93	< 0.001
CB170	60	0.62	< 0.001	50	0.62	< 0.001	49	0.95	< 0.001
CB177	60	0.64	< 0.001	50	0.70	< 0.001	49	0.93	< 0.001
CB180	60	0.67	< 0.001	50	0.61	< 0.001	49	0.94	< 0.001
CB183	60	0.70	< 0.001	50	0.68	< 0.001	49	0.93	< 0.001
CB187	60	0.62	< 0.001	50	0.54	< 0.001	49	0.93	< 0.001
p,p'-DDE	60	0.77	< 0.001	50	0.88	< 0.001	49	0.91	< 0.001
OxC	60	0.46	< 0.001	50	0.72	< 0.001	49	0.66	< 0.001
HCB	60	0.20	0.13	50	0.66	< 0.001	49	0.58	< 0.001
β-HCH	60	0.52	< 0.001	50	0.89	< 0.001	49	0.57	< 0.001
BDE47	60	0.90	< 0.001	50	0.92	< 0.001	49	0.94	< 0.001
BDE99	60	0.76	< 0.001	50	0.79	< 0.001	49	0.93	< 0.001
BDE100	60	0.78	< 0.001	50	0.83	< 0.001	49	0.90	< 0.001
linPFOS	29	0.72	< 0.001	NA	NA	NA	NA	NA	NA
PFUnA	29	0.42	0.02	NA	NA	NA	NA	NA	NA
PFTriA	29	0.33	0.09	NA	NA	NA	NA	NA	NA
PFHxS	19	0.12	0.62	NA	NA	NA	NA	NA	NA
PFNA	19	0.05	0.85	NA	NA	NA	NA	NA	NA
PFDoA	19	0.71	< 0.001	NA	NA	NA	NA	NA	NA
PFTeA	19	0.68	0.001	NA	NA	NA	NA	NA	NA

among matrices.

3.3.2. PFASs

Correlations of PFAS concentrations between matrices were only investigated for plasma and feathers sampled in 2016 because no preen oil was available for PFAS analyses (Table 1, Fig. 4). Based on these samples, linear PFOS showed a highly significant and strong correlation between plasma and feathers ($r_s = 0.72$, $p = 0.001$) and a weaker but significant correlation was found for PFUnA ($r_s = 0.42$, $p = 0.02$; Fig. 4). Moreover, a significant relationship was found for PFTriA in Trøndelag ($r_s = 0.51$, $p = 0.03$) and Troms ($r_s = 0.71$, $p = 0.03$) separately, but not when all samples were combined ($r_s = 0.33$, $p = 0.09$; Fig. 4). Additionally, four more PFAS correlations were investigated for compounds that were only detected in Trøndelag in 2016, and a strong and significant correlation was found for PFDoA ($r_s = 0.71$, $p < 0.001$) and PFTeA ($r_s = 0.68$, $p = 0.001$). No significant correlations between plasma and feathers were found for PFHxS ($r_s = 0.12$, $p = 0.62$) and PFNA ($r_s = 0.05$, $p = 0.85$; Table 1).

4. Discussion

4.1. Pollutant concentrations and profiles

4.1.1. POPs

PCBs and OCPs were the dominant POPs in all matrices of the northern goshawk nestlings, while PBDEs showed the lowest concentrations. This profile is consistent with previous, recent studies on Norwegian birds of prey and concentrations were in the same range, or lower, compared to previous studies on Norwegian goshawk and other bird of prey nestlings (Eulaers et al., 2011a; Løseth et al., 2019b; Sletten et al., 2016; Sonne et al., 2012). The profile observed in goshawk nestlings also corresponded to the general profile in bird of prey nestlings from North America and Spain, including Cooper's hawk (*Accipiter*

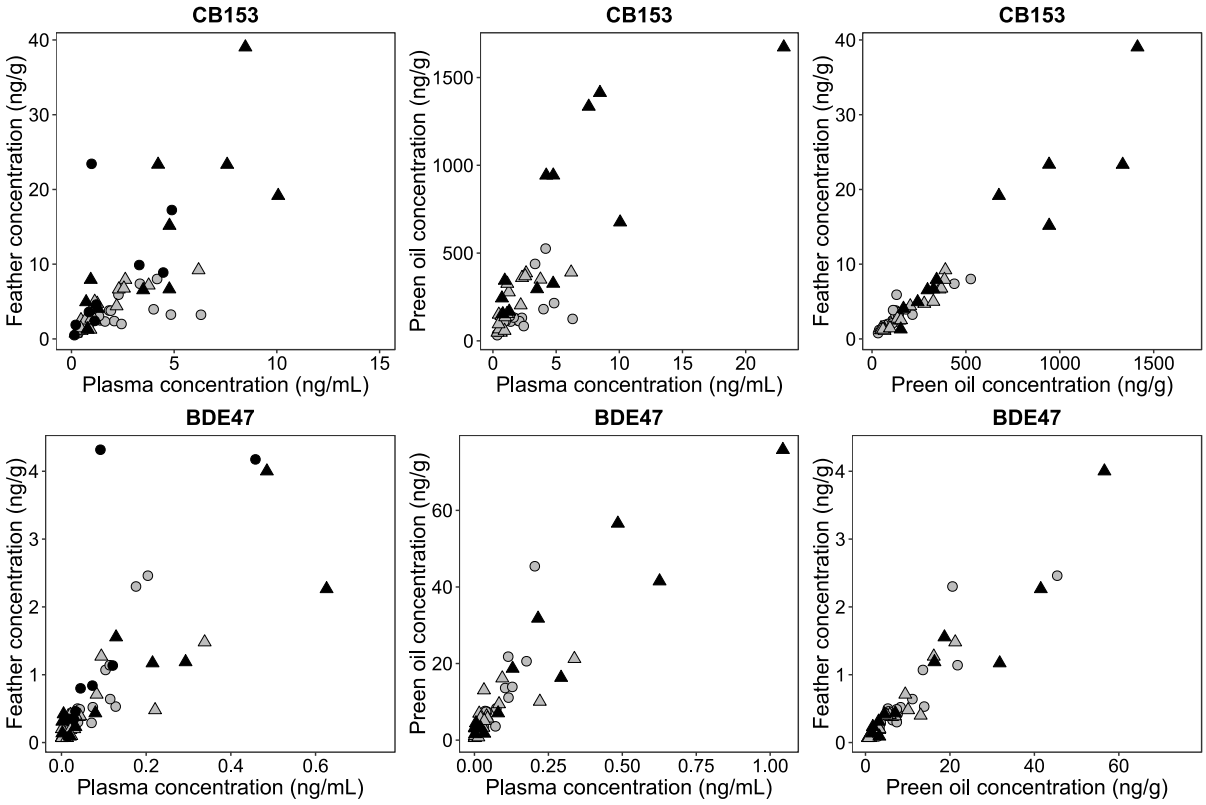

Fig. 3. Correlation (Spearman's rank) plots of CB153 and BDE47 between plasma, preen oil and feathers of northern goshawk nestlings. Black symbols (●▲) represent samples from Troms, grey (●▲) samples from Trøndelag. Circles (●●) represent samples from 2015, triangles (▲▲) samples from 2016.

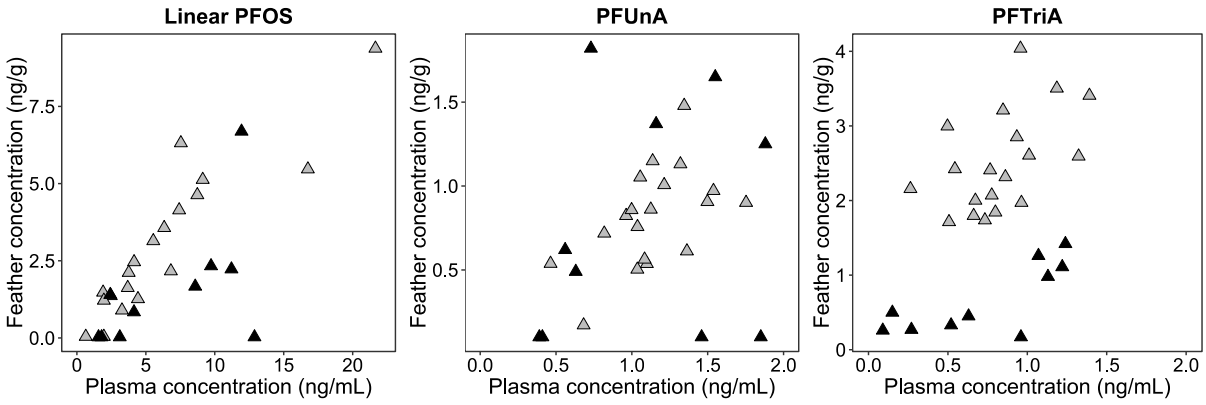

Fig. 4. Correlation (Spearman's rank) plots of linear PFOS, PFUnA and PFTriA between plasma and feathers of northern goshawk nestlings. Black triangles (▲) represent samples from Troms, grey triangles (▲) represent samples from Trøndelag, both sampled in 2016.

cooperii), bald eagle (*Haliaeetus leucocephalus*) and cinereous vulture (*Aegypius monachus*) (Brogan et al., 2017; Monclús et al., 2018; Venier et al., 2010). The low concentrations of PBDEs compared to other POPs is a general pattern seen in the Norwegian environment (Eulaers et al., 2011a; Herzke et al., 2017; Løseth et al., 2019b), which indicates low exposure of goshawk nestlings to PBDEs.

Due to the current strict regulations on the production and use of POPs, no point sources near the sampling locations of this study were expected. POPs detected in the Norwegian environment are, therefore, assumed to originate mainly from long-range transport from more industrialized and urbanized world regions, as well as from historical contamination and subsequent bioaccumulation (Heimstad et al., 2018).

A large proportion of higher chlorinated congeners, such as hexa- and hepta-CBs, was observed in plasma and preen oil. In contrast, a larger proportion of lower chlorinated PCBs was observed in feathers. Lower chlorinated PCBs have been previously found to contribute more to the total PCB burden in feathers than in internal tissues (Dauwe et al., 2005; Jaspers et al., 2007). While higher chlorinated congeners are more hydrophobic and harder to metabolize, leading to their high persistence and bioaccumulation potential (Drouillard et al., 2001; Michielsen et al., 2018), low chlorinated congeners have a lower vapor pressure and subsequent higher abundance in air (Vorhees et al., 1997). Therefore, atmospheric contamination, such as volatilization into the gas phase and wet and/or dry deposition, can be a possible exposure route for CB99 and other lower chlorinated PCBs in feathers.

The high concentrations of POPs in preen oil, compared to plasma and feathers, reflect the high hydrophobicity of POPs and the high lipid content of the preen oil (Jacob, 1976; Solheim et al., 2016). Despite differences in lipid content, the POP profile in plasma and preen oil was very similar, and is in accordance with earlier studies on shearwaters (*Puffinus* sp., Yamashita et al., 2007) and white-tailed eagles (Eulaers et al., 2011b; Jaspers et al., 2013b). Both matrices represent the internal concentration of pollutants in the nestling and similar pathways of exposure are, therefore, expected.

4.1.2. Alternative flame retardants

Even though DPs and NBFRs showed low detection frequencies in all matrices of northern goshawk nestlings, the present study indicates that the terrestrial goshawks are, in fact, exposed to these compounds of emerging concern in the environment. Recently, Løseth et al. (2019b) reported similar results on DPs in plasma (nd - 0.06 ng/mL), feathers (nd - 0.76 ng/g) and preen oil (nd - 0.45 ng/g) of Norwegian white-tailed eagle nestlings sampled in the same period (2015–2016) as the goshawks of the present study.

The low detection and concentrations of targeted NBFRs in plasma, feathers and preen oil of goshawk nestlings are in accordance with earlier studies on birds of prey (Eulaers et al., 2014; Fernie et al., 2017; Løseth et al., 2019b; Verreault et al., 2007). Gastrointestinal absorption and metabolism of BTBPE and TBPH were shown to be very low in mammals (Hakk et al., 2004; Knudsen et al., 2017; Nomeir et al., 1993), while absorption and metabolism of TBB was high (Knudsen et al., 2016; Roberts et al., 2012). Low assimilation efficiency and/or high metabolism could, therefore, potentially explain the absence of these compounds in goshawks. Additionally, as a result of the lower production and usage of these compounds compared to PBDEs (Covaci et al., 2011), levels of these compounds can be low in goshawks and the Norwegian environment in general.

PFRs in plasma of northern goshawk nestlings could generally not be detected, while they were dominant in feathers. In accordance with the present study, PFRs were not detectable (DF $<$ 25%) in plasma of North American herring gulls (*Larus argentatus*) (Greaves and Letcher, 2014), and PFRs were also infrequently detected in plasma of Norwegian white-tailed eagle nestlings (Eulaers et al., 2014; Løseth et al., 2019b). In feathers of white-tailed eagle nestlings from the same sampling period (2015–2016), the same profile as in goshawk feathers from the present study was detected and ΣTCIPP was also observed as the dominant PFR (Løseth et al., 2019b). TCIPP is the main PFR produced and used in Europe (reviewed by van der Veen and de Boer, 2012), and its usage in Norway has increased from 63 tonnes in 2014 to 354 tonnes in 2016 (SPIN, 2019). Despite their hydrophobic nature, PFRs may not be associated with lipids, in contrast to PCBs and BFRs (Malarvannan et al., 2015), explaining their absence in the lipid-rich preen oil of the goshawks. PFRs are also known to be easily metabolized once taken up in the body (Briels et al., 2018; Farhat et al., 2013; Van den Eede et al., 2013), resulting in a rapid excretion and thus low detections in plasma. The detected PFRs in feathers may therefore originate from an external source, such as atmospheric deposition onto the feathers, as TCIPP was globally found to be one of the dominant PFRs in the atmosphere (Rauert et al., 2018).

The unusually high concentrations of ΣTCIPP in feathers from Troms in 2015 are difficult to explain and the possibility of external contamination after sampling cannot be excluded. Potential causes are discussed in section 4.2.

4.1.3. PFASs

PFASs were the dominant contaminant group detected in plasma and linear PFOS was the dominant compound. PFOS and structurally similar compounds have shown to have a high binding affinity to plasma proteins, such as albumin (Jones et al., 2003), which can explain their abundance in plasma. The plasma concentrations of the goshawks reflect the more recent exposure due to the high turnover and blood flow to organs with high metabolic activity (Espín et al., 2016). In addition, previous studies observed increasing PFAS concentrations

with sampling age in Norwegian white-tailed eagle nestlings, suggesting continuous input of PFASs through the diet (Bustnes et al., 2013; Løseth et al., 2019a).

In contrast to plasma, PFASs in feathers of goshawk nestlings showed low concentrations. Higher PFAS concentrations in the plasma compared to the feathers were also found in previous studies on Norwegian white-tailed eagle nestlings (Gómez-Ramírez et al., 2017; Løseth et al., 2019b). In 2016, PFAS concentrations in Norwegian air were reported to be very low, with most PFASs below detection limits (Bohlin-Nizzetto et al., 2017). This observation suggests that external contamination of PFASs on the feathers, originating from air, is rather limited. The PFASs detected in the feathers could also originate from the plasma, because nestling feathers are connected to the bloodstream during feather growth where they can accumulate (Burger, 1993). Even though several studies have confirmed the presence of PFASs in keratinous tissue (Gao et al., 2015; Li et al., 2013; Wang et al., 2018), the binding affinity of PFASs for keratin is, to our knowledge, still uninvestigated. Based on the low concentrations in feathers compared to plasma in the present study, accumulation of PFAS from the plasma into the feathers is thought to be limited.

In the present study, PFASs were not analyzed in preen oil because not enough sample was available. To our knowledge, there are only two studies so far that have investigated PFAS in preen oil (Herzke et al., 2011; Jaspers et al., 2013a). Despite its association with proteins, these studies have detected PFOS in the preen oil of Belgian barn owls (*Tyto alba*) and white-tailed eagles from Greenland.

Overall, PFAS concentrations of goshawk nestlings were in the same range, or lower, compared to similar, recent studies on bird of prey nestlings in Norway (Gómez-Ramírez et al., 2017; Løseth et al., 2019b; Sletten et al., 2016; Sonne et al., 2010). When compared to passerine nestlings living in the vicinity of a 3M fluorochemical plant in Europe and North America, PFAS concentrations in the plasma of northern goshawk nestlings were several orders of magnitude lower (Custer et al., 2017; Lopez-Antia et al., 2019; Route et al., 2014), indicating that their exposure is relatively low, which is expected for a (sub)arctic region. Nonetheless, potential local sources of exposure to PFASs in the Norwegian environment could include the extensive use of ski waxes on ski tracks in winter, as well as the historical use of PFAS-containing fire-fighting foams at fire training sites, which are often in the vicinity of airports (Kärrman et al., 2011; Plassmann and Berger, 2013).

4.2. Differences between locations and years

High PFR concentrations in Troms in 2015, dominated by TCIPP, were unexpected and a fluctuation in PFR concentrations in the same year has not been reported for Troms or adjacent regions (Løseth et al., 2019b). Precipitation in June 2015 was higher compared to June 2016 (Kristiansen et al., 2016, 2015), possibly explaining the higher PFR concentration on the feathers in nestlings from 2015. These aberrantly high values are, nevertheless, thought to originate from a contamination source. Potentially, contamination of the feathers has occurred while using a new car during sample transport. TCIPP is used increasingly as a FR in polyurethane foams and has been detected in indoor air of cars (Hartmann et al., 2004). However, neither high environmental PFR concentrations, nor external contamination can be excluded. Chemical analysis of the feather washings and the use of field blanks is, therefore, recommended for future monitoring of PFRs.

Differences in pollutant concentrations and profiles between Troms and Trøndelag could be attributed to the differences in geography and local pollution sources. A higher degree of urbanization and agriculture close to the nest areas in Trøndelag compared to Troms could cause a difference in pollution load between nestlings from these locations (Dolan et al., 2017). Differences between years could be potentially caused by meteorological differences. The annual precipitation in Norway exceeded normal levels (with 125%) in 2015 and both annual precipitation and temperature were higher in 2015 compared to 2016 (Gangstø et al., 2016; Heiberg et al., 2017). Differences in annual precipitation (rain and snow) between the years could affect the availability of prey (e.g. woodland grouse) (Spidsø et al., 1997; Tornberg et al., 2013) and cause a shift in prey items, potentially changing the pollutant status of the goshawks (Mañosa et al., 2003).

The dominant PCB concentrations in 2016 in nestlings from Troms could also be explained by a prey shift. Goshawks are highly dependent on grouse species, which constitute a large portion of the goshawk diet, especially at higher latitudes such as Troms (Tornberg et al., 2006). When grouse population densities are low, possibly due to cyclicity and/or high predation in the previous year, goshawks might switch to a higher proportion of alternative prey (i.e. corvids, fieldfare, woodcock, squirrel), potentially leading to a different contaminant profile. Unfortunately, contaminant or abundance data for these goshawk prey from Trøndelag and Troms are, to our knowledge, not available to confirm this hypothesis. However, preliminary stable isotope data from the goshawk nestlings indicate that there may have been a dietary shift in Troms between years. Additional stable isotope analyses and chemical analyses of prey items collected at the nest site are necessary to elucidate the contaminant input from the diet and dietary shifts. In conclusion, differences between locations and years can occur because of several possible reasons and are therefore difficult to assign to one specific factor.

4.3. Correlations between matrices

4.3.1. POPs and alternative flame retardants

The strong and significant correlations between plasma, feathers and preen oil found for PCBs, *p,p'*-DDE and PBDEs confirm the findings from previous studies in birds of prey (Eulaers et al., 2011b; Løseth et al., 2019b). In general, during the nestling stage, the plasma of birds reflects pollutants transferred from the mother to the nestling during egg laying (i.e. maternal transfer) and pollutants taken up through the diet (Bourgeon et al., 2013; Bustnes et al., 2013; Løseth et al., 2019a).

The connection of the feather with the bloodstream during feather growth can lead to distribution and deposition of pollutants from the plasma into the feathers. Therefore, a strong correlation between plasma and feather concentrations in nestlings was expected. However, for HCB, a lack of correlation between the plasma and feathers of goshawk nestlings was found, which was already previously observed in the goshawk populations of Trøndelag (sampled in 2014, Randulff, 2015) and Troms (Eulaers et al., 2011a), as well as in other bird of prey species (Eulaers et al., 2014, 2011a; 2011b). In Antarctic cape petrels (*Daption capense*), a significant correlation for HCB was found between blood and preen oil, but compared to PCBs and DDTs, HCB correlated weakly between blood and other internal tissues (Van den Brink, 1997). The weak correlation for HCB could be explained by the relative high volatility of this compound compared to other POPs (Calamari et al., 1991; Domínguez-Morueco et al., 2018), which could lead to evaporation from the feather surface after preening and consequent lack of correlation with internal concentrations.

From the blood, lipophilic compounds such as PCBs, OCPs and PBDEs can be transported to and accumulate in the preen oil due to its high lipid content (Jacob, 1976; Solheim et al., 2016). Preen oil concentrations of POPs, therefore, correlate well with plasma concentrations, which was previously found in studies on different bird species (Van den Brink, 1997; Yamashita et al., 2007). Goshawks practice preening motions from two weeks of age and preening begins at three weeks of age (Boal, 1994), resulting in a thin layer of preen oil coating their feathers. Lipophilic compounds can thereby end up on the feather surface while preening, providing yet another avian-specific pathway for excretion of environmental pollutants (Gutiérrez et al., 1998; Solheim et al., 2016). Even though the feathers were washed with distilled water prior to POP analysis, this procedure is not able to remove the preen oil layer (Kucharska et al., 2015). A strong correlation between the concentrations of POPs in feathers and preen oil was,

therefore, expected (Jaspers et al., 2008).

When discussing any correlation with feather concentrations, it should be considered that contaminants detected in feather samples could originate from 1) the plasma, by internal deposition, 2) the preen oil applied on the feathers during preening activities, and 3) externally deposited particles trapped in the preen oil layer. In addition, it should be taken into account that feather concentrations reflect accumulation over a larger time span (i.e. the growth period of the feather) compared to concentrations in plasma. All of these factors together could influence the correlation between plasma and feathers (García-Fernández et al., 2013).

The strong and significant correlations of POPs between plasma, preen oil and feathers in the present study indicate the suitability of these matrices for further non-destructive biomonitoring. In contrast, because of the low detection frequencies of NBFRs and DP in all the matrices, the correlations (and hence suitability) could not be investigated for these compounds. Nonetheless, feathers could be considered as a potentially suitable matrix to investigate atmospheric PFR exposure, given that external contamination originating from sample storage and handling can be controlled.

4.3.2. PFASs

In contrast to POPs, correlations of PFASs between plasma and feathers were not as strong and significant for every compound. This inconsistency has been observed in previous studies. Gómez-Ramírez et al. (2017) investigated plasma and feather correlations in white-tailed eagle nestlings and found, similar to the present study, a strong correlation for PFDoA and no correlation for PFNA. In contrast to the present study, however, they found a significant correlation for PFHxS and PFTriA, while none was found for linPFOS or PFUnA. Interestingly, in nestlings from the same white-tailed eagle population, Løseth et al. (2019b) found a significant correlation for PFUnA between plasma and feathers for 2015 and 2016 separately, but not when years were combined. This finding was caused by an interannual difference in concentrations detected in plasma and feathers. Therefore, concentration range and sample size might be important factors affecting correlations of PFASs.

Due to limited and ambiguous reports on PFAS correlations between plasma and feathers, the suitability of feathers for PFAS monitoring is unclear. There are several factors that could influence the correlations between plasma and feathers for PFASs. In the present study, feather samples were washed with hexane to remove preen oil remnants prior to PFAS analysis. Preen oil on the feathers is, therefore, not expected to highly influence the correlations between plasma and feathers. More important could be the fact that, in the present study, PFAS concentrations in plasma of individual nestlings were correlated with the average feather concentration of all nestlings in the nest. This may have affected the strength of the correlation. Further (experimental) research is required to elucidate the suitability of feathers for PFAS monitoring.

5. Conclusions

The present study shows that Norwegian northern goshawk nestlings are exposed to a variety of anthropogenic compounds. PCBs and OCPs were the dominant POPs in all matrices, while PBDEs showed the lowest concentrations. Their abundance in all matrices, especially in the lipid-rich preen oil, suggests that they should remain a priority in the future biomonitoring of these birds. Alternative flame retardants were, in general, not detected or in low concentrations in goshawks, which can be explained by rapid biotransformation of these compounds in the body after uptake. Nonetheless, PFRs were dominant in feathers. The absence of PFRs in plasma and preen oil suggests that the exposure of feathers might be solely external, either through environmental contamination or through accidental contamination after sampling. Therefore, we recommend that a strict quality assurance protocol is established for current-use flame retardants to control for any external contamination during sample storage or transport. PFASs were the dominant compounds in plasma (on a wet weight basis) of goshawk nestlings. This suggests that nestlings were recently and continuously exposed to these compounds, potentially through dietary uptake. Correlations between matrices were strong and significant for most POPs, confirming the use of feathers and preen oil as good alternative non-destructive matrices for biomonitoring of POPs in goshawks. In the present study, only some PFAS compounds showed strong correlations between plasma and feathers. Correlations for PFASs between different matrices have shown variable results and the suitability of feathers as a non-destructive matrix for biomonitoring of PFASs can, therefore, not yet be established, in contrast to POPs.

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Appendix A. Supplementary data

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