Cod: 8.4016

RELATIONSHIPS BETWEEN PER- AND POLYFLUOROALKYL SUBSTANCES AND STABLE ISOTOPES IN TERRESTRIAL AND MARINE RAPTOR NESTLINGS FROM SPAIN AND NORWAY

M.E. Løseth[1], N. Briels[1], J. Flo[1], I. Eulaers[2], P. Gómez-ramírez[3], T. Nygård[4], D. Herzke[5], B.M. Jenssen[1], V.L.B. Jaspers[1]

[1]*Department of Biology, Norwegian University of Science and Technology (NTNU), Høgskoleringen 5, 7024 Trondheim, Norway*

[2]*Department of Bioscience, Aarhus University (AU), 4000 Roskilde, Denmark*

[3]*Faculty of Veterinary,University of Murcia (UM), Campus de Espinardo, 30100 Murcia, Spain*

[4]*Norwegian Institute for Nature Research (NINA), 7485 Trondheim, Norway*

[5]*Norwegian Institute for Air Research (NILU), 9010 Tromsø, Norway*

Introduction

Raptors occupy high tropic levels and accumulate high concentrations of environmental contaminants. Previous studies have shown that nestling northern goshawks (NG; Accipiter gentilis) and white-tailed eagles (WTE; Haliaeetus albicilla) accumulate a wide range of contaminants (1–4). Concentrations of per- and polyfluoroalkyl substances (PFASs) have recently been shown to exceed those of other legacy persistent organic pollutants (POPs) in these two species (1,3), and accordingly required closer attention. Stable isotopes (SI) of nitrogen (δ15N) and carbon (δ13C) can be applied as proxies to investigate trophic levels and dietary carbon sources, respectively. Bustnes et al. (1) emphasised the importance of feeding ecology when monitoring POPs in raptors, but did not detect any relationship between SIs and perfluorooctane sulfonate (PFOS) in NG and WTE. A possible reason may have been that the authors only investigated intra-population variability and the variation in diet and trophic levels of these birds may thus have been limited.

The aim of the present study was to investigate how the dietary tracers δ13C and δ15N can explain variation in PFASs accumulation in plasma of nestling NG and WTE from several populations. In addition the possible confounding effects of age and body mass were examined.

Materials and methods

Feather and blood samples were obtained from nestling NG from Troms, Trøndelag (Norway) and Murcia (Spain), and from nestling WTE from Steigen and Smøla (Norway) in 2015. For NGs, only the oldest chick in the nest was sampled, while for WTEs all chicks were sampled in the nest. PFASs were analysed in plasma according to Herzke et al. (5) while δ13C and δ15N were analysed in feathers according to Eulaers et al. (4).

For statistical modelling, PFASs detected in over 50 % of the samples were summed (ΣPFAS) as not all compounds were detected at each location. Correlations between ΣPFAS and the explanatory variables; population, age, body mass, δ13C and δ15N, were investigated for WTE and NG separately using Pearson correlation or Spearman's rank correlation. Body mass was mean scaled by sex for each species, due to sexual dimorphism in raptors. Only weight was included in the models, as there was a strong correlation between age and body weight in both species. As only one chick was sampled per nest for NG, we used linear models and ANOVA to investigate variation in ΣPFAS. Due to the structure of the WTE data, with two chicks in some nest, statistical tests from the nlme package (Rstudio) were applied to control for the possible variation between the nests (nest factor). Linear mixed effect models were used to investigate which of the explanatory variables, including the interaction between δ15N and δ13C, that could explain most of the variation in ΣPFAS and the nest was included as a random factor. The nest factor was included in all the models as it explained 28.5 – 37 % of the total variation for WTE. The most parsimonious models were selected based upon Akaikes Information Criterion with a correction for finite sample sizes (AICc) and models with ΔAICc > 2 are discussed. Model selection was performed on models fitted with maximum likelihood (ML), while parameters were estimated using restricted maximum likelihood (REML).

Results and discussion

Northern goshawk

Concentrations of detected PFASs in plasma are presented in Figure 1. The highest mean concentrations in NGs were of linPFOS in Trøndelag and Troms (13.3 ± 1.6 ng/mL and 9.7 ± 1.7 ng/mL); however linPFOS was only detected in four of the 8 samples from Murcia. The pattern of sum PFAS concentrations was Trøndelag > Troms > Murcia (Table 1). The higher concentration in Trøndelag was confirmed by δ15N in Figure 2, indicating that the population was feeding on higher trophic levels compared to those in Troms and Murcia. The δ13C analysis showed that the three populations also had different terrestrial diets, with the Murcia population clearly different. The Murcia region has a subtropical steppe climate and the presence of C4 plants (heat tolerant) is greater than in the rest of Europe (6). C4 plants have a higher δ13C than C3 plants (most plants), and the plant based diets of goshawk prey species explain the SI pattern in Figure 2 (7).

Significant positive relationships were detected between ΣPFAS and age ($r_S = 0.4$, $p = 0.01$) and δ15N ($r_S = 0.7$, $p < 0.001$). But not between ΣPFAS and δ13C ($r_S = -0.2$, $p = 0.24$) or body mass ($r_S = 0.3$, $p = 0.1$). The best model (ΔAICc = 0) explaining ΣPFAS variation included population and δ15N, and explained 58.2 % of the total variation (adj.R2). The second best model (ΔAICc = 1.42) included also δ13C and the third best model (ΔAICc = 1.99) included population, δ15N and body mass. These models indicate that location, trophic level and diet are important in explaining the ΣPFAS variation in NG. The model estimates of the best model show on average a 10.8 ± 4.1 ng/mL significant difference in ΣPFAS between Murcia and Troms ($t = 2.7$, $p = 0.01$) as well an average 10.2 ± 3.6 ng/mL significant difference in ΣPFAS between Murcia and Trøndelag ($t = 2.8$, $p = 0.008$). There was no significant difference between Trom and Trøndelag ($t = -0.2$, $p = 0.87$).

White tailed eagle

The highest mean concentrations detected in WTEs were of linPFOS (Steigen; 17.7 ± 1.3 ng/mL and Smøla; 15.4 ± 1.5 ng/mL), followed by brPFOS in Steigen (5.4 ± 0.6 ng/mL) and PFUnA in Smøla (3.4 ± 0.1 ng/mL). No correlations were detected between ΣPFAS and body mass ($r_P = 0.2$, $p = 0.3$) or age ($r_S = 0.3$, $p = 0.2$) for the WTEs. Neither between ΣPFAS and δ15N ($r_S = 0.2$, $p = 0.3$) or δ13C ($r_P = -0.2$, $p = 0.3$). The best model (ΔAICc = 0) explaining the variation in ΣPFAS in WTEs included population, body mass and δ13C, suggesting that both habitat, increasing body mass and diet are affecting PFAS concentrations. Figure 2 and estimates from the best model shows that the population from Smøla was feeding on a diet more enriched in 13C (+3.6 ± 2.4 ‰) compared to Steigen ($t = 1.5$, $p = 0.2$), however this was not significant. ΣPFAS was, however, significantly different between the two populations ($t = 3.2$, $p = 0.006$) showing that the Steigen population had PFAS concentrations on average 14.9 ± 4.7 ng/ml higher than Smøla. Both populations have marine diets, but δ13C analyses (Figure 2) showed some individuals from Smøla were feeding on a mixed terrestrial and marine diet, indicating a broader dietary niche. This may explain the trend of higher ΣPFAS in Steigen (Table 1). The estimates of the best model also show that ΣPFAS increase on average 58.4 ± 18.8 ng/mL per gram increase in body mass ($t = 3.1$, $p = 0.04$).

The difference in ΣPFAS between the species is very significant ($F = 9.2$, $p = 0.003$) and most likely explained by dietary niches. The diet of WTE consists mainly of fish and seabirds, thus longer food chains and greater potential for biomagnification of PFASs than in the terrestrial diet of NG. For both species it is important to account for variation explained by sampling population, body mass and diet (δ15N and δ13C) as well as variation between nests when investigating PFAS exposure. This study therefore emphasises the importance of ecological and physiological variables when monitoring PFASs in raptors.

Acknowledgements

The Norwegian Research Council and NTNU are acknowledged for funding the project NEWRAPTOR and V.L.B. Jaspers. The authors also acknowledge the help of T.V. Johnsen, J.E Martínez, M. León-Ortega, K. Dolan, M.L. Jacobsen, L. Torgersen, A. Gylseth, S.T. Randulff, G. Stenberg and E.L. Dahl from during the field sampling and in the lab. Dr. P.L. Ambus from Copenhagen University is acknowledged for providing access to stable isotope analyses.

References

1. Bustnes, J.O., Bårdsen, B.J., Herzke, D., Johnsen, T. V., Eulaers, I., Ballesteros, M., Hanssen, S.A., Covaci, A., Jaspers, V.L.B, Eens, M., Sonne, C., Halley, D.J., Moum, T., Nøst, T.H., Erikstad, K.E and Ims, R.A. (2013) Environ Toxicol Chem; 32(11):2520–7.
2. Sonne, C., Bustnes, J.O., Herzke, D., Jaspers, V.L.B, Covaci, A., Halley, D.J., Moum, T., Eulaers, I., Eens, M., Ims, R.A., Hanssen, S.A., Erikstad, K.E., Johnsen, T.V., Schnug, L., Rigét, F.F., and Jensen, A.L. (2010) Ecotoxicol Environ Saf; 73(1):7–17.
3. Sletten, S., Bourgeon, S., Bårdsen, B-J, Herzke, D., Criscuolo, F., Massemin, S., Zahn, S., Johnsen, T.V. and Bustnes, J.O. (2015) Sci Total Environ; 539:337–49.
4. Eulaers, I., Jaspers, V.L.B., Halley, D.J., Lepoint, G., Nygård, T., Pinxten, R., Covaci A. and Eens M. (2014) Sci Total Environ; 478:48–57.
5. Herzke, D., Nygård, T., Berger, U., Huber, S. and Røv, N. (2009) Sci Total Environ; 408(2):340–8.
6. Pyankov, V.I., Ziegler, H., Akhani, H., Deigele, C. and Lüttge, U. (2010) Bot J Linn Soc; 163(3):283–304.
7. Hobbie, E.A. and Werner, R.A. (2004) New Phytol; 161(2):371–85.

Table 1: ΣPFAS concentrations in plasma (ng/mL) from nestling northern goshawk and white-tailed eagles, sampled at different locations.

Species	Location	Area/Country	Number of broods	Sample size	Range	Mean ± SE
NG	Murcia	Southern Spain	8	8	3.6 – 23.3	10.4 ± 2.4
	Troms	Northern Norway	9	9	3.8 – 39.0	17.1 ± 4.2
	Trøndelag	Mid-Norway	20	20	5.7 – 51.5	26.4 ± 2.7
WTE	Smøla	Mid-Norway	10	13	11.1 – 48.1	26.6 ± 2.9
	Steigen	Northern Norway	9	14	18.0 – 53.0	33.3 ± 3.0

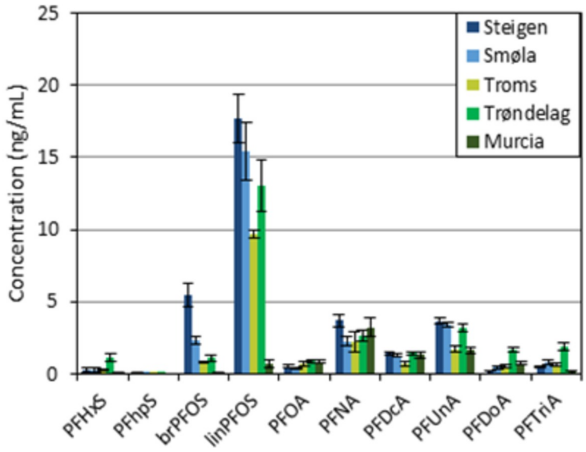

Figure 1: Mean concentrations (±SE) of several PFASs detected in plasma from nestling northern goshawks from Troms, Trøndelag and Murcia and from white-tailed eagles from Steigen and Smøla. Each location has separate colours, NG in shades of green and WTE in shades of blue.

Abbreviations: perfluorohexane sulfonate (PFHxS), perfluoroheptane sulfonate (PFHpS), branched perfluorooctane sulfonate (brPFOS), linear perfluorooctane sulfonate (linPFOS), perfluorooctanoic acid (PFOA), perfluorononaoic acid (PFNA), perfluorodecanoic acid (PFDcA), perfluoroundecanoic acid (PFUnA), perfluorododecanoic acid (PFDoA), perfluorotridecanoic acid (PFTriA).

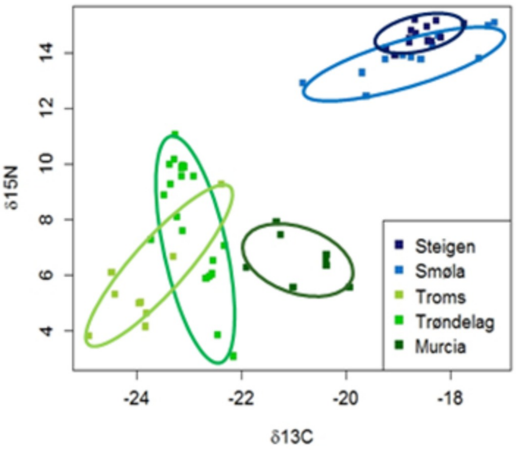

Figure 2: Relationship between stable isotope ratios of $\delta^{15}N$ and $\delta^{13}C$, from northern goshawks from Troms, Trøndelag and Murcia and white-tailed eagles from Steigen and Smøla. Each location has separate colours, NG in shades of green and WTE in shades of blue.