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Potential Effect of Migration Strategy on Pollutant Occurrence in Eggs of Arctic Breeding Barnacle Geese (*Branta leucopsis*)

Daniel J. Hitchcock,[†] Tom Andersen,[†] Øystein Varpe,[‡,§] Maarten J. J. E. Loonen,[∥] Nicholas A. Warner,[⊥] Dorte Herzke,[⊥] Ingunn M. Tombre,[#] Larry R. Griffin,[○] Paul Shimmings,[■] and Katrine Borgå*[,†]

[†]Department of Biosciences, University of Oslo, 0316 Oslo, Norway

[‡]Department of Arctic Biology, University Centre in Svalbard, 9171 Longyearbyen, Norway

[§]Akvaplan-niva, Fram Centre, 9296 Tromsø, Norway

[∥]Arctic Centre, University of Groningen, 9718 CW Groningen, The Netherlands

[⊥]Norwegian Institute for Air Research, Fram Centre, 9296 Tromsø, Norway

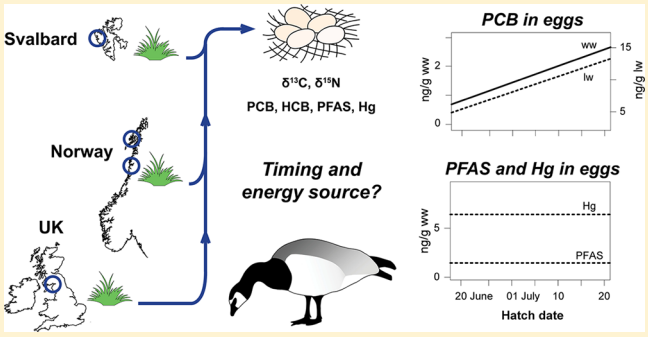
[#]Department of Arctic Ecology, Norwegian Institute for Nature Research, Fram Centre, 9296 Tromsø, Norway

[○]Wildfowl & Wetlands Trust, Caerlaverock Wetland Centre, Dumfriesshire DG1 4RS, United Kingdom

[■]BirdLife Norway, 7012 Trondheim, Norway

Supporting Information

ABSTRACT: Arctic-breeding geese acquire resources for egg production from overwintering grounds, spring stopover sites and breeding grounds, where pollutant exposure may differ. We investigated the effect of migration strategy on pollutant occurrence of lipophilic polychlorinated biphenyls (PCBs) and protein-associated poly- and perfluoroalkyl substances (PFASs) and mercury (Hg) in eggs of herbivorous barnacle geese (*Branta leucopsis*) from an island colony on Svalbard. Stable isotopes (δ^{13}C and δ^{15}N) in eggs and vegetation collected along the migration route were similar. Pollutant concentrations in eggs were low, reflecting their terrestrial diet (∑PCB = 1.23 ± 0.80 ng/g ww; ∑PFAS = 1.21 ± 2.97 ng/g ww; Hg = 20.17 ± 7.52 ng/g dw). PCB concentrations in eggs increased with later hatch date, independent of lipid content which also increased over time. Some females may remobilize and transfer more PCBs to their eggs, by delaying migration several weeks, relying on more polluted and stored resources, or being in poor body condition when arriving at the breeding grounds. PFAS and Hg occurrence in eggs did not change throughout the breeding season, suggesting migration has a greater effect on lipophilic pollutants. Pollutant exposure during offspring production in arctic-breeding migrants may result in different profiles, with effects becoming more apparent with increasing trophic levels.



INTRODUCTION

Migratory birds utilize resources from multiple locations to fuel energetic costs associated with reproduction.[1,2] However, resources can also be geographically isolated, particularly for terrestrial bird species that fly overseas. Individuals may therefore be limited by where they acquire energy for both flight and reproduction.[3] In highly seasonal environments such as the Arctic, terrestrial birds often follow a "green wave" of spring resources,[4] where individuals optimize timing between high quality resources and reproductive success.[5,6] An individual's timing depends on many factors including body condition and resource availability and conditions along the flyway and at the breeding grounds.[7,8]

In female birds, reproduction includes egg production. Given that feeding sites are geographically isolated, energy directed toward egg production will range from exclusive reliance on distant wintering ground resources, to energy obtained during migration, or to reliance on local breeding resources, but it is typically a mix.[3,9] Energy often represents nutrients available to an individual in the form of lipids and protein, with lipids being energetically richer and less costly to transport over long distances than protein.[10−12]

Avian eggs reveal how females both acquire and utilize energy[13] and are useful in the biomonitoring of environmental pollutants.[14] During egg production, females maternally transfer various lipophilic pollutants including polychlorinated biphenyls (PCBs) and hexachlorobenzene (HCB), and

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protein-associated pollutants such as per- and polyfluoroalkyl substances (PFASs) and mercury (Hg).[15−17] These contaminants are known for their persistent, bioaccumulative and toxic properties.[18−20]

In migratory birds such as geese, the consumption of vegetation contaminated via atmospheric deposition represents a source of exposure to certain pollutants.[21,22] Several studies in migratory birds have identified a spatial relationship between latitudinal position and pollutant exposure.[23,24] With increasing latitude, atmospheric and soil deposition of lighter chlorinated PCBs and HCB increases, whereas heavier chlorinated PCBs decreases.[25−27] The exposure profile of many bird species is dominated by heavier, more persistent PCBs,[28] and this profile should also reflect spatial trends in migratory birds that feed at different sites during egg formation.

Ecological tracers such as stable isotopes have been used in large part to identify energy sources utilized during egg production.[29,30] Stable isotopes of carbon (^{13}C and ^{12}C) and nitrogen (^{15}N and ^{14}N) can be used to determine the contribution of different resources acquired during migration.[13] Thus, the combination of ecological and chemical tracers as stable isotopes and pollutants serves as a powerful tool when inferring energy source in ecotoxicological studies.

The purpose of this study was to investigate how migration strategy, both in terms of timing and spatial dietary energy source, affects pollutant occurrence in eggs of Svalbard-breeding barnacle geese (*Branta leucopsis*). Geese acquire and utilize terrestrial resources along their migration route relative to their breeding grounds including: resources from distant overwintering grounds (United Kingdom), staging areas (northern Norway), and local bird cliff and island tundra (Svalbard, Norway).[13,31] Stable isotopes and observational data indicate that early arriving females utilize distant resources for egg production before local breeding ground resources reach peak availability,[13] while late arriving females are better suited at utilizing local resources before laying eggs.[32] To our knowledge, no attempt has been made to combine stable isotopes and pollutants as ecological and chemical tracers in this migratory species. Additionally, storage and transport of lipids are also less costly than proteins, meaning migration strategies may have a greater effect on pollutants associated with lipids than proteins. Given that latitudinal differences exist in the PCB and HCB profiles in air and soil, then geese serve as a model species to track the movement of environmental pollutants.

To determine where geese acquire their energy for egg production and whether this reflects pollutant exposure, we collected vegetation along the flyway of the goose and eggs at the Svalbard breeding grounds. We also quantified nest hatch date for the breeding population as a proxy for migration timing and energy source. We hypothesized that (1) early egg laying females fuel reproduction using either stored body reserves or distant wintering ground resources (UK and/or northern Norway), leading to pollutant remobilization or higher exposure in females and maternal transfer to eggs; (2) late egg laying females feed on local breeding ground resources (Svalbard) and are exposed to lower concentrations of pollutants than individuals relying on distant resources; and (3) migration strategy has a greater effect on concentrations of lipophilic pollutants (PCBs and HCB) in eggs than protein-associated pollutants (PFASs and Hg).

MATERIALS AND METHODS

Barnacle Goose Biology. The barnacle goose population in the present study overwinter on the Solway Firth (UK) and migrate to the high Arctic archipelago of Svalbard, Norway (Figure S1, Supporting Information). Most individuals stopover in spring staging areas along the coast of northern Norway for several weeks,[33] but a small number of birds skip these sites during their northward migration.[34,35] Geese typically depart from the Solway Firth between late April and early May, spending several weeks in mainland Norway before arriving at the Svalbard breeding grounds in late May.[36] The geese also utilize additional prebreeding sites on Bjørnøya and along the west coast of Svalbard, which include tundra vegetation fertilized by marine birds at cliff-breeding colonies.[31] When female geese arrive at the breeding grounds, they commence egg laying in as little as 3 days.[37] Females typically lay a clutch of four eggs and only lay once per breeding season.[38,39] The egg laying period for the breeding colony typically spans approximately 2 weeks, and eggs of a clutch hatch synchronously.[39,40]

Study Sites and Sampling Effort. In 2016, our study included three main areas along the migration route of the Svalbard-breeding population of the barnacle goose, including: UK (Solway Firth); northern Norway (Helgeland and Vesterålen); and Svalbard (Kongsfjorden). Barnacle geese breed on several islands in the fjord,[39] and our study population represented the Storholmen Island colony (78°56′ N, 12°14′ E).

Sighting and Nest Data. Intensive sightings of ringed barnacle geese were carried out in northern Norway from 29 April to 21 May 2016 in Vesterålen (municipalities of Andøy, Hadsel, Sortland, and Øksnes) and from 22 April to 21 May 2016 in Helgeland (municipalities of Herøy and Træna). On Svalbard, we registered all nests on Storholmen Island and recorded ring codes of nesting individuals. At least one member of each nesting pair from our sampling effort was ringed, and we assumed any unringed individuals in nesting pairs represented the partner. For each registered nest, we also recorded the hatching date of the clutch, defined as the first day when an egg in each clutch hatched.

Vegetation and Egg Sampling. Vegetation was collected on the Solway Firth and Vesterålen in May 2016 and on Svalbard June−July 2016. Sites on Svalbard included both island colony and marine bird cliff tundra, referred to as island tundra and cliff tundra, respectively. Vegetation represented a mix of graminoid and forb species, reflecting the diet of the geese (see Table S1, Supporting Information). Diet was sampled in areas where geese had been observed grazing and where fresh droppings were present. Only the top layers of vegetation were used for subsequent analysis, as geese predominantly graze at this level.[36]

For eggs, an intensive sampling effort took place during the main incubation period on Storholmen Island from 9 to 20 June. We had originally planned to sample from early and late arriving females, however almost all individuals had commenced egg laying prior to our sampling period. Instead, we sampled a single egg at random from 61 nests, to reduce the potential effects of intraclutch variation. Although egg laying sequence may affect pollutant concentration in avian species,[41] several studies have demonstrated that mother-egg or interclutch variation is greater than intraclutch variation.[15,42]

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Thus, we assumed that each egg sampled was representative of a female's entire clutch.

We prioritized sampling from nesting pairs where at least one parent was ringed and observed at the staging areas in northern Norway. We attempted to sample eggs from females utilizing early or late migration strategies based on sighting data from northern Norway as well as egg incubation stage.[43] Eggs were stored overnight at 4 °C. Embryonic age (defined as incubation stage) varied greatly across all eggs, so samples were homogenized to obtain a signal representing whole egg content. Homogenates were aliquoted to polypropylene tubes and stored at −20 °C. Samples were analyzed for protein content and stable isotopes of carbon ($\delta^{13}C$) and nitrogen ($\delta^{15}N$), the details of which are described in the Supporting Information.

Pollutant Analysis. Egg homogenates were analyzed for PCBs, HCB, and PFASs at the Norwegian Institute for Air Research (NILU) at the Fram Centre in Tromsø, Norway. Mercury in eggs was analyzed at the University of Oslo, Norway. PCBs and HCB were measured in vegetation from the Solway Firth, Vesterålen, and Svalbard, and PFASs, from one site on the Solway Firth and bird cliff tundra from Svalbard. A total of 43 compounds were analyzed, including 19 PCB congeners, HCB, 22 PFAS compounds, and mercury.

PCBs and HCB Analysis. For eggs, approximately 1.5 g of preweighed homogenate was freeze-dried for moisture content removal in approximately 1:5 weight/weight (w/w) of anhydrous sodium sulfate (burnt at 600 °C). For vegetation, approximately 10 g of preweighed material was pulverized with liquid nitrogen and freeze-dried in 1:3 (w/w) sodium sulfate. Samples were spiked with 2.7 ng/μL of ^{13}C-labeled internal standards: PCB-28, -31, -52, -47, -37, -74, -66, -101, -99, -149, -118, -153, -105, -138, -187, -183, -180, -170, -194, and -209 and HCB. Sample homogenate was extracted three times with cyclohexane/acetone (3:1) (40/30/30 mL) in an ultrasonic bath. Supernatant from each step was combined, and then 10% of the combined supernatant was aliquoted into a preweighed vial for gravimetric lipid determination. The remaining supernatant was evaporated to dryness and reconstituted in 0.5 mL of isooctane and transferred to EZ-POP NP cartridges (Supelco) for cleanup purposes. PCBs and HCB were eluted from the cartridges with 3 × 5 mL of acetonitrile and the eluent was evaporated and reconstituted in 0.5 mL of isooctane. An additional cleanup step was performed using automated solid phase extraction where extract was eluted with 1 g of activated Florisil (burnt at 450 °C) with 12 mL of 1:10 dichloromethane/hexane. The collected extract was evaporated to approximately 0.1 mL and quantitatively transferred to a GC vial, evaporated to 100 μL, and spiked with ^{13}C-labeled PCB-159 volume correction standard. See the Supporting Information for details on instrument analysis.

PFAS Analysis. A 1−1.5 g portion of preweighed homogenized egg material was extracted using 8 mL acetonitrile, while 30 g of vegetation was extracted using ca. 40 mL of methanol following methods described previously.[17] Egg and vegetation extracts were evaporated to 2 and 1.5 mL respectively. Prior to extraction, all samples were spiked with 0.5 ng/μL of ^{13}C-labeled internal standards: PFBA, PFPA, PFHxA, PFHpA, PFOA, PFNA, PFDcA, PFUnDA, PFDoDA, PFTeDA, PFBS, PFHxS, PFOS, PFOSA, 6:2 FTS, and 8:2 FTS. Prior to quantification, each 0.5 mL of solution was spiked with 2 ng of 3,7-brPFDcA recovery standard and 0.1 mL was transferred to an autoinjector vial containing 0.1 mL of 2 mM NH_4OAc in HLB-water. Full details of the instrumental analysis are described elsewhere.[44] A 10 μL portion of extract was used to separate and analyses PFASs by ultrahigh pressure liquid chromatography triple-quadrupole mass-spectrometry (UHPLC-MS/MS). Data quantification was conducted with LCQuan software (Thermo Scientific). Unless specified, all PFASs refer to linear isomers.

Hg Analysis. Total mercury was analyzed by atomic absorption spectrometry using a Direct Mercury Analyzer (DMA-80, Milestone). Approximately 0.03 g of freeze-dried egg homogenate was analyzed. Samples were analyzed in parallel with sample blanks and certified reference material (DORM-4 fish protein; DOLT-5 dogfish liver, National Research Council Canada). Samples were analyzed in at least duplicate to ensure precision of measurements. Average recoveries of the certified reference materials were within 10% of the reported values. The detection limit of the instrument was 0.05 ng mercury.

Quality Assurance/Control. Concentrations reported for PCBs, HCB, and PFASs were blank corrected based on the average concentration detected within blank samples. Limits of detection (LOD) and quantification were calculated as three and ten times the standard variation within blank samples, respectively. LOD for PCBs ranged from 0.001 to 0.012 ng/g wet weight (ww); HCB was 0.026 ng/g ww; and PFASs from 0.015 to 0.100 ng/g ww (Table 1). PCB and HCB concentrations were only reported for analytes that had a quantification/qualifier ion ratio within 20% of the ratio determined within the quantification standard. Reference material for PCBs and HCBs (contaminated fish reference material, EDF-2525) and PFASs (Pike-perch, QM03-2) were also extracted in conjunction with sample material to assess method performance. Internal standard recoveries for PCBs in eggs ranged between 40% and 60% and, for PFASs, between 50% and 73% in eggs and 16% and 165% in vegetation (Table S8, Supporting Information).

Data Treatment and Statistical Analyses. *Pollutant Data Sets.* We used two data sets for statistical analyses, including: (1) lipophilic compounds with 19 PCB congeners and HCB and (2) protein-associated compounds with six PFAS compounds and mercury. Individual pollutants were included in data sets if they were detected in 60% or more of our egg samples, to maximize statistical information and reduce random noise from nondetect samples (see Table S7, Supporting Information for pollutants excluded). When individual concentrations of each pollutant across all samples fell below the LOD, we imputed left-censored data by replacing missing values (53 values for PCB; 71 values for PFAS) with a random number between 0 and the LOD assuming a beta distribution ($\alpha = 5, \beta = 1$). We also calculated pattern or relative contribution of PCBs and PFASs, expressed as the proportion of each PCB congener or PFAS family to the sum total (e.g. $[PCB_i]/\sum PCB$ or $[PFAS_i]/\sum PFAS$). For PCBs, we also summed concentrations according to the number of chlorine atoms as well as metabolic group (Tables S9−10, Supporting Information).

Statistical Analyses. We analyzed pollutant concentrations and patterns in R v. 3.4.1.[45] Multivariate analysis and visualization of data was conducted by principal component analysis (PCA) within the *vegan* package v. 2.4-4.[46] We transformed pollutant concentrations ($\log_{10} x$) to normalize distributions and reduce heterogeneity and/or skewness. We explored absolute concentrations of PCBs, HCB, PFAS, and

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Table 1. Biological and Pollutant Information (PCBs, HCB, PFASs, and Hg) in Barnacle Goose Eggs Sampled on Svalbard in 2016[a]

biological variable		min−max	N	mean ± SD
mass (g)	whole egg	82.0−113.3	61	98.4 ± 7.1
	content	71.0−101.6		87.8 ± 6.6
whole egg size (mm)	length	67.6−92.5	61	76.2 ± 4.2
	width	47.2−55.2		50.3 ± 1.6
embryo age (d)		0−23	61	13.3 ± 5.7
nest hatch date		18 June−20 July	61	28 June ± 5.6 days
lipid (%)		10.6−26.0	59	17.0 ± 2.4
water content (%)		60.2−72.7	61	68.3 ± 1.6
protein (%)		2.8−8.7	50	4.9 ± 1.0

pollutant	LOD	% detected[b]	min−max	median[c]	mean ± SD
		PCBs (ng/g ww, N = 58)			
PCB-28/31	0.003	96	<LOD−0.025	0.009	0.010 ± 0.003
PCB-52	0.005	93	<LOD−0.044	0.008	0.010 ± 0.006
PCB-47	0.003	72	<LOD−0.008	0.004	0.005 ± 0.001
PCB-37	0.001	98	<LOD−0.401	0.013	0.023 ± 0.054
PCB-74	0.002	100	0.010−0.262	0.023	0.031 ± 0.035
PCB-66	0.003	98	<LOD−0.037	0.013	0.014 ± 0.006
PCB-101	0.004	70	<LOD−0.031	0.005	0.008 ± 0.006
PCB-99	0.001	100	0.005−0.101	0.022	0.028 ± 0.019
PCB-149	0.004	98	<LOD−0.040	0.010	0.011 ± 0.006
PCB-118	0.003	70	<LOD−1.104	0.127	0.197 ± 0.176
PCB-153	0.012	100	0.139−1.559	0.335	0.402 ± 0.244
PCB-105	0.002	91	<LOD−0.338	0.044	0.068 ± 0.058
PCB-138	0.010	100	0.056−0.422	0.126	0.150 ± 0.087
PCB-187	0.003[d]	100	0.029−0.156	0.058	0.066 ± 0.025
PCB-183	0.003[a]	100	0.009−0.076	0.022	0.025 ± 0.013
PCB-180	0.002	100	0.041−0.362	0.113	0.129 ± 0.064
PCB-170	0.007[a]	100	0.025−0.199	0.054	0.060 ± 0.033
PCB-194	0.007[a]	100	0.008−0.055	0.016	0.018 ± 0.008
PCB-209	0.007[d]	65	<LOD−0.017	0.010	0.010 ± 0.003
ΣPCB			0.462−4.418	1.006	1.227 ± 0.800
HCB	0.026	100	0.987−5.647	2.368	2.364 ± 0.697
		PFASs (ng/g ww, N = 59)			
PFHpS	0.035	3	<LOD−0.289	0.268	0.268 ± 0.030
branched-PFOS	0.070	7	<LOD−4.247	2.114	2.195 ± 2.089
linear-PFOS	0.070	63	<LOD−11.304	0.314	0.930 ± 2.319
PFNS	0.065	5	<LOD−0.509	0.436	0.456 ± 0.046
PFNA	0.015	81	<LOD−0.326	0.062	0.080 ± 0.060
PFDcA	0.015	81	<LOD−0.367	0.058	0.078 ± 0.067
PFUnDA	0.015	98	<LOD−0.954	0.127	0.167 ± 0.153
PFDoDA	0.015	81	<LOD−0.230	0.056	0.066 ± 0.040
PFTriDA	0.020	75	<LOD−0.261	0.098	0.109 ± 0.055
PFTeDA	0.020	32	<LOD−0.110	0.054	0.053 ± 0.022
∑PFAS			0.054−17.690	0.539	1.209 ± 2.972
Hg (ng/g dw, N = 61)	0.050	100	9.760−40.990	18.520	20.170 ± 7.520

[a]Unless specified, estimates refer to the egg contents. Min = minimum; Max = maximum; N = sample size; SD = standard deviation; LOD = limit of detection; ww = wet weight; dw = dry weight. [b]Percentage of eggs quantified above the LOD. [c]Calculated using values above LOD. [d]Values represent limits of quantification (LOQ).

Hg, as well as relative concentrations (i.e. patterns) of PCBs and PFASs by PCA. Biological variables, which included hatch date, egg size (length), embryonic age, and values of $\delta^{13}C$ and $\delta^{15}N$, were projected on the ordination space as passive variables. We conducted a redundancy analysis (RDA) on both data sets in order to summarize the explanatory power of relevant explanatory or biological variables and quantified the percentage of variation explained by each variable. Biological variables in our RDA included hatch date, egg size (length), embryonic age, values of $\delta^{13}C$ and $\delta^{15}N$ and lipid and protein content. Hatch date was positively correlated with lipid content (Pearson's $R = 0.29$, $P = 0.02$), and PCB concentrations also increased with later hatch date, independent of lipid content (see Results and Discussion). This prompted us to conduct partial RDA (pRDA) by treating PCB and HCB concentrations on wet weight basis and lipid content as a covariable. A pRDA fits the biological variables to the residual variation that is not attributable to the covariables.[47] The relationship between significant biological variables, and pollutant concentrations are depicted using linear regressions.

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Unless specified, PCB, HCB, and PFAS concentrations are reported on a wet weight (ww) basis, and mercury, on a dry weight (dw) basis.

RESULTS AND DISCUSSION

Breeding Population of Storholmen. In 2016, a total of 272 breeding pairs were registered on the Storholmen island breeding colony. Nest hatching commenced 10 June and concluded 20 July, with a peak hatch date between 24 and 25 June (Figure 1). Hatching dates of the subsampled population (N = 61 pairs) were similar to the colony as a whole, with a peak hatch date of 25 June (range 18 June to 20 July; Figure 1; Table 1).

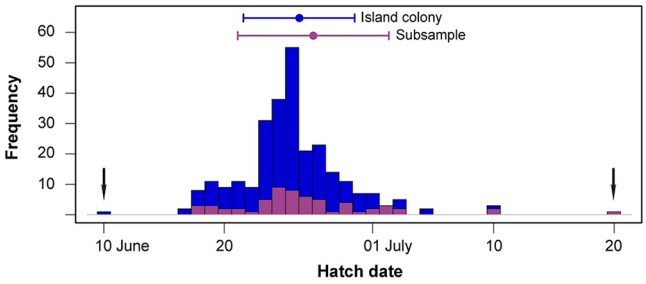

Figure 1. Histogram of nest hatching dates of barnacle geese breeding on Storholmen Island in 2016 (N = 272) and the subsampled population in the present study (N = 61). Arrows indicate the earliest and latest hatching dates. Mean ± SD above the plots.

The spread in hatch dates is twice as large as in 1993 and 1994 (range = 15 days),[48] as well as in 2006 and 2007 (range = 15 days).[13] This new time frame suggests that geese are responding to a warmer climate, due to increased availability of resources at the staging areas in northern Norway and Svalbard breeding grounds and has resulted in a broadening of the time window for reproduction. The mean hatch date for the Svalbard population has also advanced by approximately 1 week since the 1990s,[40,48] and 2016 represented the earliest hatch date on record for the island population.

From the 61 nesting pairs which eggs were sampled, at least one individual from 23 nesting pairs was resighted at the staging areas in northern Norway prior to the same breeding season (Vesterålen N = 18; Helgeland N = 5), meaning that we could not account for the migratory behavior of the remaining geese. It is likely that several nonsighted geese utilized staging areas in northern Norway before arriving in Svalbard but were either not observed during the sighting period or were feeding outside sighting areas. Lipid content in eggs was 17.0 ± 2.4% and was 2−5 times greater than protein content (4.9 ± 1.0%; Table 1). Lipid content in eggs also increased with hatch date, which was contrary to expectation. We expected that earlier arriving females would utilize stored body reserves, resulting in increased lipid availability during egg production. Instead, later arriving females were remobilizing a greater proportion of lipids, which could be due to differences in foraging behavior for geese that migrate late to the Svalbard breeding grounds[7] or energetic differences in vegetation along the migration route.[49] We found no relationships between all other biological variables measured (Tables S2−4, Supporting Information).

Spatial Contribution of Resources for Egg Production. Stable isotope signatures in vegetation overlapped between the wintering, staging, and island colony sites (Figure 2). Vegetation sampled from cliff tundra contained lower δ^{13}C and higher δ^{15}N values compared to all other sites (δ^{13}C: t test t_{13} = −2.75, P = 0.02; δ^{15}N: t test t_{13} = 4.26, P < 0.01; Figure 2). We expected to find a unique isotopic composition along the flyway of the goose following a previous study on goose droppings collected from each site.[13] However, stable isotope signatures between vegetation and droppings may not be comparable given fractionation between diet and droppings takes place during digestion.[50,51]

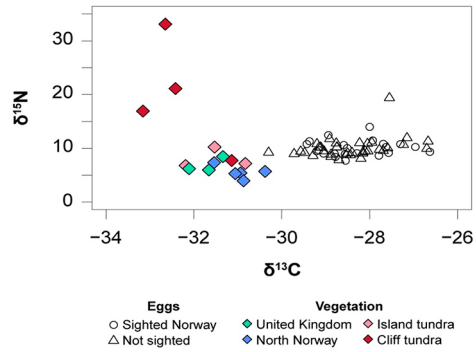

Figure 2. Stable isotope composition of δ^{13}C and δ^{15}N in eggs of barnacle geese sampled on Svalbard (N = 59) in 2016, as well as vegetation collected along the flyway including United Kingdom, northern Norway, and Svalbard island and cliff tundra (N = 15) in the same year. Circles represent eggs of geese sighted in Norway; triangles, not sighted. Vegetation is denoted by diamonds.

Egg stable isotope signatures (δ^{13}C = −28.4 ± 0.8 ‰, range − 30.3, − 26.6; δ^{15}N = 10.1 ± 1.7 ‰, range 7.7, 19.4; Figure 2) were unrelated to lipid and protein content or sighting of individuals in northern Norway (Tables S4−6, Supporting Information). Values of δ^{13}C in eggs increased with later hatch date (Pearson's R = 0.30, P = 0.02; Figure 3b), but δ^{15}N values did not. δ^{13}C and δ^{15}N values were higher in eggs compared to vegetation from all sites (t test δ^{13}C t_{72} = −2.75, P < 0.001; δ^{15}N t_{68} = 6.15, P < 0.001), except for cliff tundra where δ^{15}N was higher than in eggs (t test: t_{61}= −6.54, P < 0.001; Figure 2).

Carbon and nitrogen isotope signatures in the eggs of barnacle geese from Storholmen Island were similar to a neighboring island colony in 2006 and 2007.[13] The high δ^{13}C values in eggs compared to vegetation suggest that geese also utilize stored body reserves for egg production such as breast muscle and abdominal fat, which is often enriched in ^{13}C.[11,29] A previous study on Greater Snow Geese (*Chen caerulescens atlantica*) found a strong positive relationship between δ^{13}C values in maternal storage tissues and eggs,[29] suggesting that an increasing reliance on stored body reserves corresponds to an enriched ^{13}C signal in eggs.

δ^{15}N values in eggs did not change throughout the breeding season, suggesting that most females either did not utilize local Svalbard resources from bird cliff in 2016, or utilized this resource in similar proportions. Due to an overlapping δ^{13}C signal across most sites, we could not calculate the contribution of resources toward egg production under a stable isotope mixing model.[30] A previous model has shown that the Svalbard goose population can allocate 50% of resources from vegetation in the UK and northern Norway for egg production, assuming a limited number of sites along the flyway.[13] However, reliance of resources from UK and northern Norway decreases with later egg laying date; and

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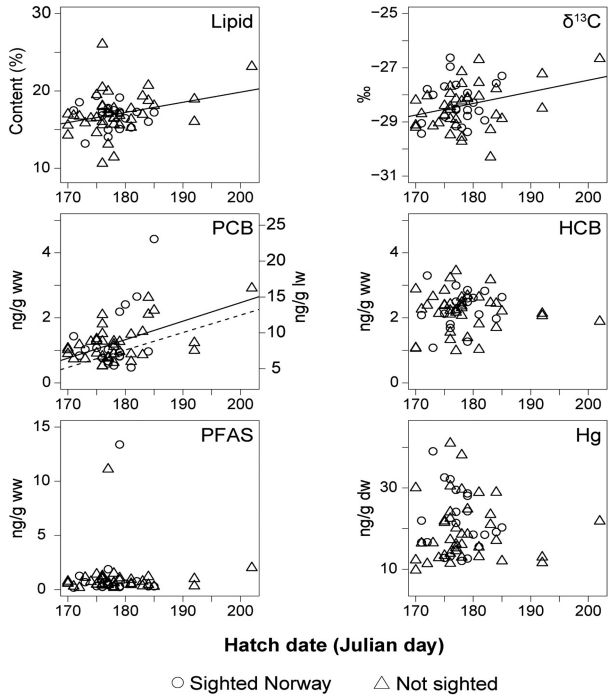

Figure 3. Relationship between nest hatch date and lipid content (%) (R^2 = 0.07, P = 0.02); δ^{13}C (R^2 = 0.09, P = 0.02); ∑PCB concentration (points and solid line on wet weight, R^2 = 0.18, P < 0.01); dashed line on lipid weight; R^2 = 0.11, P < 0.01); HCB concentration; ∑PFAS concentration; and mercury concentration in eggs of barnacle geese sampled on Svalbard in 2016. Circles represent eggs of geese sighted in Norway; triangles, not sighted. Linear regressions presented when relationships are significant.

this relationship has only been observed in the lipid-free yolk component of eggs.[13] Even though we measured stable isotopes in whole eggs, the positive relationship between δ^{13}C signal in eggs and nest hatch date remained, suggesting that egg energy source varies throughout the breeding season.

Low Levels of Pollutants in Vegetation. Low concentrations of HCBs were detected for vegetation at all sites, but PCBs were not (Solway Firth 0.02 ± 0.01 ng/g ww, N = 2; Vesterålen 0.05 ± 0.03 ng/g ww, N = 3; Svalbard cliff tundra 0.09 ± 0.04 ng/g ww, N = 4; Svalbard island tundra 0.03 ± 0.02 ng/g ww, N = 2). PFASs were detected at cliff tundra (0.03 ng/g ww, N = 1), but not on the Solway Firth (N = 1). We could not sample a larger quantity of vegetation across all sites due to intensive goose grazing activity, meaning these values should be treated with caution.

Low Levels of Lipophilic Pollutants in Eggs. Total PCB concentrations in eggs ranged between 0.46 and 4.42 ng/g ww (Table 1). PCB-153 accounted on average for 32% of the total PCB concentration in eggs, followed by PCB-118 (16%), PCB-138 (12%), and PCB-180 (10%). HCB was the dominating chemical in all eggs, where concentrations ranged between 0.99 and 5.65 ng/g ww (Table 1).

Average concentrations of PCBs and HCB in barnacle goose eggs indicate low levels of exposure in adult female geese. Pollutant concentrations are several orders of magnitude lower than in eggs of piscivorous and predatory Arctic seabird species.[52,53] The low concentrations in goose eggs reflects a terrestrial diet and levels are similar to other Arctic terrestrial species occupying low trophic levels including caribou (*Rangifer tarandus*) and hare (*Lepus arctica*).[54,55] Average lipid normalized concentrations of PCBs and HCB in eggs from this study ($\sum_{12}$PCB = 7.2 ng/g lipid weight; HCB = 14.4 ng/g lw) are lower than in eggs from a neighboring Svalbard barnacle goose colony sampled in 2006 ($\sum_{12}$PCB = 53.5 ng/g lw; HCB = 27.4 ng/g lw; n = 6).[56] The temporal decrease in PCB and HCB concentrations in biota is also consistent with decreasing trends in air and monitoring data.[57,58]

Effect of Migration on PCB and HCB in Eggs. With later hatching date, both lipid content and wet weight concentrations of PCB in eggs increased (Figure 3a and c). Hatch date contributed to 11% of the total variation in wet weight pollutant concentrations ($RDA_{Hatch\ date}$ $F_{1,54}$ = 6.62, P = 0.001) and 7% when lipid content was treated as a covariable ($pRDA_{Hatch\ date}$ $F_{1,53}$ = 4.37, P = 0.01; Figure S3, Supporting Information). When compared to a full RDA model containing all relevant explanatory variables (RDA variation = 20%, $F_{7,48}$ = 1.71, P = 0.04), hatch date contributed to 55% of the constrained variation, and 35% with lipid content as a covariable. HCB contributed little to pollutant variation across eggs (Figure 3d). When exploring differences in PCB patterns across eggs, hatch date explained 4% of the total variation in PCB patterns ($RDA_{Hatch\ date}$ $F_{1,54}$ = 2.26, P = 0.05). The relative contribution of tri- and tetra-chlorinated PCBs to the total PCB load was higher in late hatching eggs (75th percentile = 8.3 ± 4.3%) than in early hatching eggs (25th percentile = 6.8 ± 1.5%; $RDA_{Hatch\ date}$ % variation = 6.7; $F_{1,54}$ = 3.86, P = 0.02; Figure S4, Supporting Information). The percentile difference for tri- and tetra-chlorinated PCBs (1.5%) was higher than for penta- (0.6%), hexa- (1.4%), hepta- (0.7%), octo- (0.02%), and deca-chlorinated (0.08%) PCBs. We also found a weak relationship between the enrichment of ^{13}C and increasing concentrations of tri- and tetra-chlorinated PCBs in eggs ($RDA_{\delta 13C}$ % variation = 4.5; $F_{1,54}$ = 2.54, P = 0.07). Hatch date was unrelated to substitution patterns of PCBs when arranged by metabolic group.[59]

The finding that absolute PCB concentrations were higher in late hatching eggs (75th percentile = 1.74 ± 0.66 ng/g ww) than in early hatching eggs (25th percentile = 1.06 ± 0.15 ng/g ww) was contrary to our expectations. We expected the earliest hatching eggs to contain the highest concentrations of PCBs, as these represent females that arrive at the Svalbard breeding grounds prior to snowmelt,[60] thereby relying on resources from wintering grounds, staging areas, cliff tundra, and/or stored body reserves for egg production. However, HCB concentrations in eggs did not change throughout the breeding season, suggesting that consumption of Svalbard resources was similar across females, assuming that HCB concentration in vegetation increases at higher latitudes.[61,62]

Late hatching eggs may instead represent a small number of females that delay their departure from the wintering grounds by several weeks, skip or have a very brief stopover at staging areas in northern Norway. The exact proportion of individuals that utilize this strategy is unclear, but these females arrive later or around the same time as individuals that utilize staging areas in northern Norway.[34−36] In addition, the prenesting period between arrival at the breeding grounds and egg laying may be shorter for late arriving females than early ones.[32] Thus, late arriving females may rely more on overwintering ground resources instead of breeding ground resources. While the migration strategies quantified in this study only represents a small proportion of the total variation in pollutant occurrence across eggs, we expect several unexplored factors may contribute, including timing of departure from the over-

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wintering grounds, duration spent at staging areas, timing of arrival at the breeding grounds, and proportion of resources utilized at different sites.

When breeding females utilize stored body reserves for egg production, PCBs becomes remobilized and translocated within the body. The rate of diffusion depends on chlorine atom placement and degree of the chlorination for a given PCB congener. For example, less chlorinated PCBs translocate more quickly from stored body reserves than more chlorinated PCBs due to their lower lipophilicity (i.e. lower K_{ow}).[63−65] Indeed, we observed the latest hatching eggs to contain a significantly higher relative contribution (1.5% greater) of tri- and tetra-chlorinated PCBs compared to the total PCB load when compared to the earliest hatching eggs. The substitution pattern of PCBs should also affect their diffusion rates,[66] however this pattern was similar across all eggs.

The body condition of females offers an alternative explanation for the higher lipid content and PCB concentrations in late hatching eggs. Females that arrive late at the breeding grounds may be in poorer body condition and thus will depend more on stored body reserves (e.g. lipids) to maintain body condition.[7] A remobilization of lipids will thus lead to increased circulating levels of pollutants in blood,[67] thereby increasing the potential for pollutants to be transferred during egg production. Additionally, a greater reliance on distant resources may result in exposure to higher concentrations of PCBs, as these areas are closer to potential point sources of pollution compared to remote polar regions.[23,24] The high lipid content and PCB concentration in late hatching eggs is likely due to a combination of factors, including females foraging predominantly at distant overwintering grounds, followed by the direct flight to the Svalbard breeding grounds resulting in a greater reliance on stored body reserves and/or poorer body condition. However, we were unable to assess the exact contribution of each of these factors to the overall pollutant profile measured in eggs, and this uncertainty warrants future research. This could include the use of tracking devices to determine each individual's migration schedule.[68]

Similar PFASs and Hg Occurrence Across Eggs. Total detectable PFAS concentrations in eggs ranged between 0.05 and 17.7 ng/g ww (Table 1). When detectable, linear-PFOS on average accounted for 29% of the total PFAS concentration in eggs, followed by PFUnDA (25%), PFNA (13%), PFTriDA (11%), PFDcA (9%), and PFDoDA (8%). We detected mostly long-chained perfluorinated carboxylates (PFCAs) in eggs, which are also common in other bird species and the marine ecosystem in general.[69] Total mercury concentrations in eggs ranged between 9.76 and 40.99 ng/g dw (Table 1).

Occurrence of PFAS and Hg in relation to the protein content of eggs did not change throughout the breeding season (Figures 3e−f), supporting our expectation that migration strategy has a greater effect on pollutants associated with lipids than proteins. Proteins may serve as a limiting resource during egg formation,[29,70] and energetic costs of transporting stored protein during migration may be greater than for lipids.[11] Thus, the acquisition and allocation of PFASs and Hg toward egg production should be limited by similar mechanisms. Alternatively, a similar PFAS or Hg signal across eggs may be due to similar exposure profiles at each site along the flyway. For example, fractionation of PFASs generally does not occur along latitudinal gradients,[71] as the chemicals are mainly transported through oceanic currents.[72] This could be validated by future or increased sampling efforts of vegetation at each site along the migration route.

The present study reveals differences in exposure profiles of eggs of herbivorous geese, which may be a consequence of different migration strategies. Eggs laid later in the breeding season contained higher concentrations of PCBs. Barnacle geese are also responding to a warming climate by arriving earlier at the breeding grounds, which can affect the optimal timing between departure from overwintering grounds, arrival at the breeding grounds, and peak food quality.[68] A shift in timing may also lead to changes in migration strategies of Arctic-breeding goose populations,[37] which may lead to further changes in the exposure profile of eggs. Recent evidence shows some polar bears (*Ursus maritimus*) have shifted their summer diet, which includes increased consumption of goose eggs.[73] This will not only impact the reproductive success of the barnacle goose populations but may cause changes in the distribution pollutants across Arctic food webs. The study of pollutants as chemical tracers in Arctic migrants yields insights into potential energy sources utilized during offspring production. Our study concerned an herbivorous migrant, and we expect stronger relationships for organisms that feed at higher trophic levels, where the effects of migration or reproductive strategies may become more apparent.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b00014.

Schematic of migration timing and route of the barnacle goose (Figure S1); description of vegetation sampled (Table S1); supporting materials and methods; summary statistics of relationships between measured biological variables (Tables S2−S6); summary of pollutant data sets (Tables S7); pollutant recoveries (Table S8); classification of PCBs according to chlorination and metabolic group (Tables S9−S10 and Figure S2); summary statistics of multivariate analyses (Tables S11−S14 and Figures S3−S6); supporting references (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: katrine.borga@ibv.uio.no.

ORCID

Daniel J. Hitchcock: 0000-0001-7683-6128

Katrine Borgå: 0000-0002-8103-3263

Notes

The authors declare no competing financial interest.

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